The Old and New Persistent Organic Pollutants

Sources, Risks, Regulations, and Remediation



Edited by **Ravi Naidu**

CRC Press
Taylor & Francis Group

The Old and New Persistent Organic Pollutants

Our understanding of persistent organic pollutants (POPs), their exposure pathways, and their impact on the environment and human health is constantly evolving and the list of new and emerging POPs is constantly changing. This book provides a comprehensive coverage of new and old hazardous chemicals, their physical and chemical properties, their breakdown products, their fate in the environment, and the environmental and human risk impact. It discusses global policies based on the United Nations' FAO frameworks, explains the severity of contamination, and raises awareness on the assessment and remediation of contaminated sites in developed and developing countries.

Features:

- Provides a broad temporal perspective on POPs with contributions from a global team of experts.
- Covers chemistry, toxicology, remediation, regulation, and conventions related to POPs.
- Explains systematically the fate and behavior of POPs and their effect on the environment and ultimately the impact on human health.
- Brings together for the first time information on global policies on POPs.
- Includes case studies that detail assessment criteria of old and new POPs as well as remediation technologies.

This book is an excellent resource for professionals, researchers, academics, and students who work in or study environmental risk assessment and remediation.


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CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

Designed cover image: Shutterstock

First edition published 2026
by CRC Press
2385 NW Executive Center Drive, Suite 320, Boca Raton FL 33431

and by CRC Press
4 Park Square, Milton Park, Abingdon, Oxon, OX14 4RN

CRC Press is an imprint of Taylor & Francis Group, LLC

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Funding for OA publication provided by crcCARE.

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ISBN: 978-1-032-87014-4 (hbk)
ISBN: 978-1-032-87015-1 (pbk)
ISBN: 978-1-003-53046-6 (ebk)

DOI: 10.1201/9781003530466

Typeset in Times
by Apex CoVantage, LLC

To head and neck surgeon Dr Roneal Naidu – 1979–2009

So here's to you, Roneal, our son so bright:

In shadows and echoes, you're our eternal light.

Though the pages turn and life moves along,

Your spirit sings, and in our hearts, you belong.



FIGURE 0.1 Dedication Page


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Foreword

There are few places left on Earth that remain free from harmful chemicals. Historically, we have adopted chemicals for their beneficial properties, often without fully understanding the associated risks. However, we are gradually learning more about their effects on human health and the environment, as well as the mechanisms through which they can cause harm.

Many hazardous chemicals that people recognise tend to cause immediate harm; while they may not persist in the environment long term, their effects can be acute and potentially deadly. In contrast, persistent organic pollutants (POPs) are often less well-known, but their long-lasting presence allows them to continue causing harm well beyond their intended use. Recent media coverage of substances such as PFAS has increased awareness of POPs and emphasised the need for improved regulation of chemicals to protect future generations.

The New South Wales Environment Protection Authority (NSW EPA) and other government agencies worldwide are heavily invested in understanding the risks posed by persistent organic chemicals and in finding ways to mitigate these hazards. At the EPA, we utilise a chemical prioritisation software tool called HazEL to identify which chemicals pose the greatest risk to New South Wales. We have partnered with industry to train the software's AI, enabling it to analyse vast amounts of scientific data and pinpoint chemicals that could pose risks in specific environments.

To better mitigate the risks to human and environmental health, it's essential to adopt a stewardship approach that fosters collaboration among academia, public and private sector organisations, and regulatory bodies. This collaborative approach will raise awareness, develop solutions to existing chemicals in the environment, and prevent further chemicals from entering the environment. The book "The Old and New Persistent Organic Pollutants: Sources, Risks, Regulations, and Remediation" offers an informative contribution to this critical collaborative effort in understanding POPs. It explores the complexities of both legacy and emerging POPs, exploring their interactions with the environment and human health, and critically reviewing the evolving global regulatory landscape, with a particular focus on the Stockholm Convention.

The NSW EPA recognises the urgent need for enhanced regulatory frameworks and innovative remediation techniques to address the impact of these toxic chemicals. By working with Industry, conducting our own research and partnering with universities and academics, such as those who have contributed to this volume, the NSW EPA aims to play its part in protecting tomorrow together. I believe publications such as this book will serve as a valuable resource for researchers, policymakers, industry professionals, and the public alike, fostering a deeper understanding of the challenges and opportunities in managing POPs for a healthier future.

Tony Chappel
Chief Executive Officer NSW Environment Protection Authority


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Preface

In an era marked by rapid industrialization and increasing environmental awareness, the issue of persistent organic pollutants (POPs) looms large. These toxic chemicals, both old and new, continue to pose significant threats to human health and the environment. As UNEP's Executive Director Erik Solheim poignantly stated, "The fight against pollution and climate change is not just about protecting the environment, it's about protecting human health, and it's about creating sustainable development that benefits future generations." This profound insight underscores the urgency of our collective mission to understand, regulate, and remediate POPs.

This book aims to provide a comprehensive overview of old and new persistent organic pollutants, dissecting their sources, risks, regulations, and remediation strategies. We begin with an introduction to POPs and explore the intricacies involved in their persistent nature and the multifaceted challenges they present in our environment and our lives.

The subsequent chapters probe into specific chemicals, practices, and environmental concerns associated with POPs. We delve into the 'Dirty Dozen' lurking within our homes, examining their impacts on our health and well-being. Our exploration of the legacy of chemicals such as hexachlorobenzene and pentachlorobenzene reveals the long-term consequences of past industrial practices and pesticide use while emphasizing the environmental contamination from organochlorines and halogenated compounds.

Throughout the book, we confront the paradoxical nature of industrial chemicals, recognizing their benefits while grappling with their associated risks. We also scrutinize the dangers posed by chlorinated solvents, brominated flame retardants, and per- and polyfluoroalkyl substances (PFAS), investigating their sources, potential health effects, and the complex challenges of remediation.

Given the global scale of these contaminants, our discussions extend beyond localized effects. We analyze pollution levels, mapping the origins of polychlorinated naphthalenes and addressing the implications of glyphosate in our ecosystems. Additionally, we inspect short-chain chlorinated paraffins and petroleum hydrocarbons, recognizing their enduring presence in soil and groundwater.

The contributions of researchers, practitioners, and policymakers are essential in navigating the complexities of persistent organic pollutants. Through collaborative efforts, we can foster innovative strategies for remediation and prevention, ultimately paving the way for sustainable solutions that safeguard our planet and future generations.

This book serves as a call to action for all stakeholders – scientists, environmentalists, policymakers, and the public – to engage in dialogue and take measures that prioritize health and ecological integrity. Together, we have the knowledge and tools at our disposal to confront the challenges posed by POPs and to work towards a healthier, more sustainable world.

As you embark on this exploration of POPs, we hope you find this book both enlightening and empowering. Let's commit to a future in which we protect not only our environment but also the well-being of humanity.

This book was made possible through the leadership and contributions of the lead and associate authors, as well as the many anonymous reviewers whose insights greatly enhanced the final work.

I would also like to acknowledge my wife, Shamila, for her patience and support in allowing me the time and space to dedicate myself fully to this initiative.

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Distinguished Laureate Professor Ravi Naidu is a globally recognized environmental scientist. He has authored over 950 journal papers and edited 16 books on environmental contaminants. He was awarded the prestigious Glinka Award, known as the World Soil Prize, by the United Nations. He has also been elected as a fellow by numerous societies and the science academies of Australia, New Zealand, and India. He chairs the United Nations' Food and Agriculture Organizations' International Network on Soil Pollution (INSOP), which brings together scientists, engineers and environmental practitioners from all over the world.


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1 The Old and New Persistent Organic Pollutants
Sources, Risks, Regulations, and Remediation

Ravi Naidu

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'Persistent organic pollutants pose a threat to human health, the environment, and the economy, and require a multi-faceted approach that involves scientific research, regulatory actions, and public awareness to prevent, mitigate, and remediate their effects.'

1.1 INTRODUCTION

Over the past hundred years, we have witnessed an increasing dependence on synthetic chemicals to sustain industrial and societal requirements. Today, we are confronted with more than 350,000 chemicals that are registered for production and for industrial and consumer use (Wang et al. 2020; Bengtson Nash et al. 2023). Among these chemicals, thousands of synthetic organic chemicals along with natural organic chemicals (for example present in crude oil), once used or released, can enter the environment because of anthropogenic activities. These organic contaminants can be categorised into various classes depending on their physicochemical properties (Table 1.1). They may be sourced from spills and leaks of liquid chemicals and products that might be produced and stored in large volumes (e.g., fuel terminals), via use of chemicals for food production (e.g., in agriculture), manufacturing (e.g., plastics), or protection (e.g., in protective clothing or use in firefighting), or might leach from solids or waste materials (e.g., tyres or e-waste).

Most, if not all, of these groups of organic contaminants are probably present in soil because of human activity. Environmental contamination is classified as either a point source or a diffuse source based on how the pollutants are introduced. Point source pollution involves identifiable releases from specific locations, such as leaky storage tanks, concentrated and waste chemical releases (Franzmann et al. 2000), landfills, or industrial spills (Davis et al. 2009), creating localised hot spots. Worldwide, underground storage systems have been significant point sources, releasing contaminants such as benzene, toluene, ethyl benzene, and xylene (BTEX) and fuel components (Table 1.1), with threats from vapour intrusion into buildings posing inhalation risks to human health (Davis et al. 2021) and from dissolution into groundwater creating plumes that might migrate

DOI: 10.1201/9781003530466-1

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TABLE 1.1
Organic Contaminants Commonly Found in the Environment

Contaminant Class*	Compounds
Non-halogenated volatile compounds	Acetone, acrylonitrile, aminobenzene (aniline), butanol, cyclohexanone, ethanol, ethyl acetate, ethyl ether, isobutanol, methanol, methyl ethyl ketone, styrene, vinyl acetate
Halogenated volatile compounds	Mono-, di-, tri-, tetra-, pentachloroethane, bromoform, bromomethane, chloroform, carbon tetrachloride, chloromethane, dibromomethane, dichloroethane, dichloromethane, ethylene dibromide, Freon (refers to various chlorofluorocarbons, hydrochlorofluorocarbons, and related compounds used as refrigerants), hexachlorobutadiene, hexachloroethane, neoprene, perchloroethylene, tetrachloroethylene, trichloroethylene, vinyl chloride, vinyl trichloride
Non-halogenated semi-volatile compounds	Benzidine, benzoic acid, benzyl alcohol, dibenzofuran, diethyl phthalate, polycyclic aromatic hydrocarbons known as PAHs (acenaphthene, acenaphthylene, anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenz[*a,h*]anthracene, fluorene, fluoranthene, phenanthrene, pyrene)
Halogenated semi-volatile compounds	Mono-, di-, tri-, penta-, hexachlorobenzene, mono-, di-, tri-, tetrachlorophenol, chloronaphthalene, dichlorobenzidine, bromophenyl phenyl ether, chloroaniline, chloroethoxy ethane, chloroethoxy methane, chloroethoxy phthalate, chlorobenzilate, chlorophenothane (DDT – dichlorodiphenyltrichloroethane), hexachlorobutadiene, hyxachlorocyclopentadiene, chlorocresol, pentachlorophenol, polychlorinated biphenyls
Pesticides and herbicides	Aldrin, atrazine, BHC, chlordane, DDD, DDE, DDT, dieldrin, endosulfan, endosulfan sulfate, endrin, endrin aldehyde, ethion, ethyl parathion, fenamiphos, glyphosate, heptachlor, heptachlor epoxide, malathion, methyl parathion, parathion, toxaphene
Explosives	Di-, trinitrotoluene (DNT, TNT), cyclo trimethylene trinitramine (RDX), methyl tetranitrobenzeneamine (tetryl), tetranitro tetraazocyclooctane (HMX), nitroaromatics, picrates, di-, trinitrobenzene (DNB, TNB), nitroglycerine, nitrocellulose, ammonium perchlorate
Crude oil and fuels	Tri-, tetramethylbenzene, trimethylethylbenzene, pentene, methyl pentene, mono-, di-, trimethylheptane, mono-, di-, trimethylpentane, trimethylhexane, dimethylbutane, mono-, dimethylphenol, methyl butadiene, mono-, dimethyl butene, methylnaphthalene, ethyl pentane, BTEX, PAHs, creosols, cyclohexane, cyclopentane, diethylmethylbenzene, butane, isobutane, isopentane, methylcyclohexane, methylcyclopentane, phenol, propane, vinylbenzene, n-alkanes
PFAS	A family of more than 10,000 chemical constituents with the structure including tail made up of C-F bond and carboxylate or sulphonates

* Note: Some chemicals are common among the categories since these are the groups of names depending on the commercial usage.

significant distances (Davis et al. 1999). Non-point source pollution, in contrast, stems from multiple unidentifiable locations (a.k.a. non-point sources). Examples include atmospheric emissions, urban runoff, sewage sludge application, and agricultural activities such as fertiliser use and irrigation. The latter is also called ‘broadacre contamination’ (Naidu, Megharaj et al. 2020).

Once in the soil environment, several physical, chemical, and biological processes may influence the transport and the fate of contaminants. These processes include adsorption to soil surfaces, diffusion into pores, partitioning into the organic materials, volatilisation, and biotic and abiotic degradation. The transformative physical and chemical processes can lead to increased risks to the environment and human receptors (Devi 2020). One of the major concerns has been for those

persistent (recalcitrant) organic contaminants that do not degrade, and persist in the environment. Often, they are referred to as persistent organic pollutants (POP).

We note that often crude oil and petroleum fuels are not designated as POPs; however, petroleum hydrocarbons remain high priority pollutants because (i) they contain carcinogenic compounds such as benzene; (ii) weathering of crude oil and fuels creates new unassessed chemicals with unknown risk profiles, and highly weathered hydrocarbons still contain thousands of compounds that are difficult to quantify (Lang et al. 2009; CRC CARE 2017); and (iii) they can persist as light non-aqueous phase liquids (LNAPLs) in the environment for decades to centuries, and whilst they can biodegrade they can also emit significant fluxes of greenhouse gases (i.e., methane and carbon dioxide) as products from biodegradation process (Sookhak Lari et al. 2024).

Depending on the chemical candidate and ageing in soils, these POP compounds resist degradation through chemical, biological, and photolytic processes and can be easily transported via wind and water, hence being deposited a long distance from the source (Ritter et al. 1995; Reid et al. 2000). Given that some of these are easily transported, their presence has been reported in deep oceans, in the Arctic, and in the pristine parts of Mt. Everest, and thus can affect humans and wildlife far away from where they were first released or generated.

It is well recognised that POPs, whether or not they are freshly emitted, reside in the soil and the earth's critical zone, or migrate from one environmental medium (e.g. soil) to another (e.g. air), are toxic chemicals that adversely affect human health. Most of humankind alive today has been exposed to POPs at some stage in their lives, including pesticides and insecticides, solvents, and pharmaceutical and industrial chemicals. The primary focus of this book is on these highly recalcitrant human-made POP chemicals, which the Stockholm Convention on Persistent Organic Pollutants has recognised. Rather than delving into the extensive array of other organic contaminants, this book explores the mobile and toxic nature of POPs since their presence and behaviour in the environment are far more enduring. As indicated, an additional chapter on petroleum hydrocarbons is included in recognition of their risk profile and prevalence in the environment.

1.2 THE STOCKHOLM CONVENTION: INITIAL AND NEW POPS

The Stockholm Convention was recognised and adopted by the United Nations Environment Program (UNEP) on 22 May 2001. It was concluded at the May 2001 meeting that regulations on POPs are needed globally 'to protect human health and the environment from persistent organic pollutions.' The convention was ratified in 2004 and recognised the initial POPs, termed the 'dirty dozen' (Figure 1.1). This list has grown to 34 POPs, with now 185 countries ratifying the convention. Although the initial POPs, such as DDT and polychlorinated biphenyls (PCBs), are no longer in production, traces of these pollutants are still found in the environment, including soils. The POPs listed under the convention is dynamic; for example, in 2022, perfluorohexane sulfonic acid (PFHxS), its salts, and PFHxS-related compounds were added to the industrial category of chemicals (UNEP 2014). The Stockholm Convention has been incorporated well into other mandates and principles. For example, the third session of the United Nations Environmental Assembly, known as UNEA-3, fully adopted the convention for enhanced measures that address and manage soil pollution (UNEP 2017).

1.3 EXPOSURE TO POPS AND PETROLEUM AND CONSEQUENCES

Whilst POPs and petroleum persistence in the environment and their effects on human health and the environment have been investigated for decades, the Stockholm Convention was the first to formally acknowledge that certain POPs are persistent and that exposure to them has harmful effects. However, our understanding of the toxicity of POPs and petroleum hydrocarbons has significantly improved since the convention and due to the scientific studies and collaboration between different parties (Vallack et al. 1998). Further, the exposure and health effects of POPs and petroleum

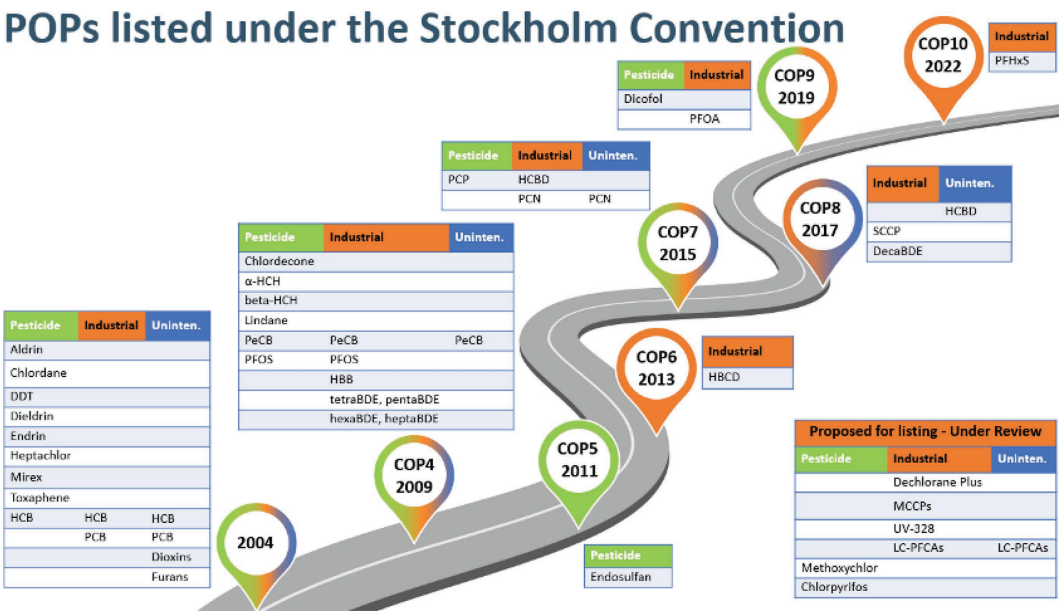


FIGURE 1.1 Conventional and newly adopted POPs in the Stockholm Convention (adopted from UNEP 2014).

compounds continue to be unveiled, particularly from specific sites or environmental media. For petroleum hydrocarbons the strong role of biodegradation has led to greater acceptance that risks at release sites might be mitigated once vapour risks and groundwater movement are addressed (CRC CARE 2013, 2020; Davis et al. 2021). For POPS, Weber et al. (2019) raised concerns about the lack of regulatory limits on soil POPs when food safety is at stake. POPs have been shown to bioaccumulate, especially in fatty tissues, leading to many adverse health effects over time, including developmental defects, chronic illnesses, and in some cases death (Schecter 2012; Haffner and Schecter 2014; Rokni et al. 2023). Recently, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), as well as other per- and polyfluorinated substances (PFAS), were included in a new updated list of POPs. The emergence of these contaminants has resulted in many challenges, including but not limited to health risks from exposure to low concentration levels and limitation of remediation technologies (Naidu et al. 2020). Although there is still much controversy surrounding the health effects of PFAS, numerous reports have claimed that PFOS, PFOA, and PFAS have a significant impact on human health (Brown et al. 2020; van Gerwen et al. 2023). Several recent reports have established a connection between PFAS exposure and various adverse health effects (Figure 1.2). The most recent report, published in Lyon, France, in November 2023 by a working group of 30 scientists from 11 countries, was conducted by the International Agency for Research on Cancer (IARC) (Zahm et al. 2024). This evaluation focused explicitly on the carcinogenicity of PFOA and PFOS and their related isomers and salts. Although PFOA was deemed carcinogenic, there is limited evidence regarding the carcinogenicity of PFOS. However, it is advisable to take a precautionary approach, since PFAS in general may have potential negative impacts on human health.

1.4 REMEDIATION AND MANAGEMENT OF POP- AND PETROLEUM-CONTAMINATED SITES

Article 6 of the Stockholm Convention outlines that POPs should be identified at potential risk sites and those sites remediated if possible (Working-Groups 2022). Likewise petroleum impacted sites

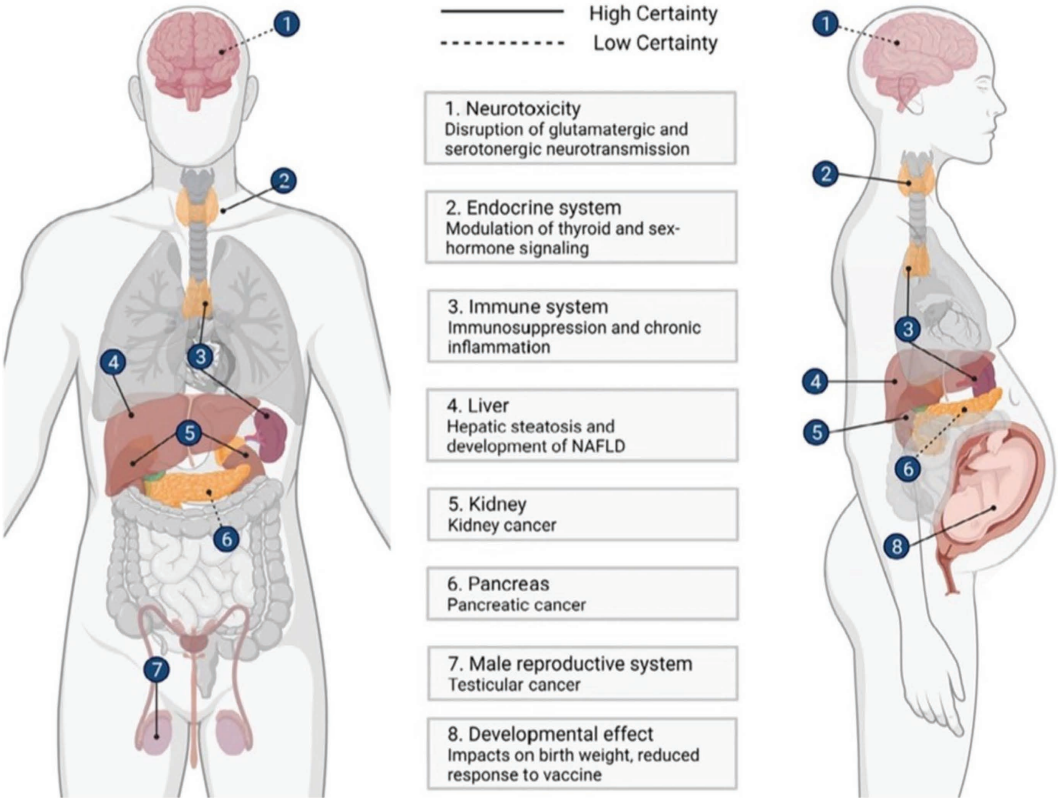


FIGURE 1.2 Human health effects from exposure to PFAS (schematic adopted from Lein 2023).

are regulated as potential risks sites that require active managment. However, despite investments and attempts by practitioners, the remediation of POP- and petroleum-contaminated sites to an acceptable limit remains challenging. A range of technologies and 'natural' approaches have been researched and implemented to remove contaminant mass (Johnston and Trefry 2009), and to add enhancements/amendments to transform (Patterson et al. 2005), biodegrade (Davis 2023), or bind (Das et al. 2013; Navarro et al. 2023) contaminants. Working groups developing guidance on the remediation of POP- and petroleum-contaminated sites have emphasised a risk-based approach. Even though strategic and cost-effective approaches to managing POP-contaminated sites are yet to be adopted, the use of multi-criteria analysis (MCA) is a key consideration for achieving sustainable remediation end points (Working-Groups 2022). More importantly, a significant constraint in financial investment to support detailed scientific studies has hampered research progress over the long term. For petroleum hydrocrabons some longer term efforts have become apparent and have involved regulatory interaction (Davis et al. 2022; CRC CARE 2020). Without increased partnering between researchers, industry, and regulatory involvement, particularly in terms of scaled funding and research efforts, it is likely that sites contaminated with POPs will endure as an issue for future generations to address.

Given the extent and severity of soil and associated groundwater contamination and the risk that these chemicals pose to environmental and human health, the UNEA-3 appealed for enhanced measures that address and manage soil pollution (UNEP 2017). Over 170 countries adopted this resolution. Following the adoption of the UNEA-3 resolution, globally, there has been a significant move towards the enhanced assessment and management of pollution, especially of soils. As an example, in April 2022, the Food and Agriculture Organization of the United Nations (FAO) introduced the

International Network on Soil Pollution (INSOP) to facilitate cooperative efforts in mitigating soil pollution risks and rehabilitating contaminated sites, including those contaminated with POPs.

1.5 CONCLUSION

Although our understanding of POPs along with petroleum hydrocarbons, their exposure pathways, and their impact on the environment and human health continues to evolve, it became necessary to compile a book that covers these topics comprehensively. The collection of articles in this book brings together most, if not all, POPs, their sources, regulatory policies, risks, and strategies for remediation. The book also includes a chapter on petroleum hydrocarbons, because of its risk profile, prevalence, and longevity in the environment.

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2 The 'Dirty Dozen' Hanging Out in Your Home

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2.1 INTRODUCTION

Most household cleaning solutions include a poisonous concoction that can severely worsen or 'destroy' the health of human beings. According to the Environmental Working Group (USA), there are no safety guidelines for household cleaners that specialize in hazardous substance investigations and campaigns. Manufacturers are under no obligation to publish safety data sheets, meaning that customers do not know what the safety parameters are. These manufacturers can use very persuasive marketing to claim that frequent application of such hazardous household cleaners is required to keep premises continually disinfected, scrubbed, and washed to safeguard a family's health. The toxic ingredients included in these items cannot be ignored. Unknown to the consumer, every household cleaning product may include 62 or even more harmful chemical compounds, and their existence in domestic cleansers is 'essential' for keeping people clean and free of dangerous bacteria, even though their ingredients are made from several lethal chemicals.

It is said that the chemical components, although typically quite poisonous, are introduced in minimal doses, ensuring their safety. However, the bioaccumulative impacts of the frequent use of these products have not been clarified. Bioaccumulation is the process by which compounds, such as poisons found in home cleansers, build up in a person or a living thing faster than they are

DOI: 10.1201/9781003530466-2
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eliminated by excrement. Additionally, there is the combinatorial impact, which is a consequence that results of the elements associated with household cleaners and is bigger than the sum of each of their dangerous effects.

On the other hand, there are adverse consequences that produce very harmful results. The severity of risks associated with ordinary household cleaners containing hazardous substances can range from acute (immediate) risks like skin or breathing issues, allergic reactions, and burns caused by chemical substances to chronic (long-term) risks. Examples of these are cancer, infertility problems, cardiovascular diseases, attention-deficit disorders, and weakened immune systems.

The major hazardous compounds used as active ingredients in household cleaning materials belong to the following groups: butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), coal tar dyes (phenylenediamine), diethanolamine (DEA), dibutyl phthalate (DBP), formaldehyde-releasing preservatives, parabens, parfum, polyethylene glycol (PEG) compounds, petroleum (petroleum jelly or Vaseline), siloxanes, sodium lauryl sulphate, and triclosan (Figure 2.1). Since it is a highly exhaustive topic, the primary emphasis of this chapter will be on 'The Dirty Dozen Cleaning Products at Home': air fresheners, ammonia, bleach, carpet and upholstery shampoos, dishwasher detergents, drain cleaners, furniture polish, mold and mildew cleaners, oven cleaners, antibacterial cleaners, laundry room products, and toilet bowl cleaners (Alofe et al., 2019).

2.2 THE HOUSEHOLD DIRTY DOZEN

2.2.1 Butylated Hydroxyanisole (BHA) and Butylated Hydroxytoluene (BHT)

2.2.1.1 General Description of BHA and BHT

Often used in lipsticks and moisturizers, and sometimes as a food preservative, these chemicals have been shown to cause cancer and affect male and female reproduction. BHA and BHT are two synthetic antioxidants widely used as food preservatives, packaging, and animal feeds due to their low cost, widespread availability, and excellent performance. They are also commonly used in a variety of personal care products as preservatives. These chemicals are associated with health concerns such as endocrine disruption and organ-system toxicity-related issues (UNEP and OECD, 2002, 2003; Alofe et al., 2019).

2.2.1.2 Chemical Structures and Properties of BHA and BHT

These are the molecular formulas of BHA and BHT:

$$\text{BHT: } \left(\left(CH_3\right)_3 C\right)_2 CH_3C_6H_2OH\left(C_{15}H_{24}O\right)$$

$$\text{BHA: } \left(CH_3\right)_3 C - C_6H_3 - \left(OCH_3\right)\left(OH\right)\left(C_{11}H_{16}O_2\right)$$

BHA and BHT are thermoplastic polymers with a high molecular weight and polymer chains linking through intermolecular forces. They possess choleretics which means that they can become pliable or moldable above specific temperatures and return to a solid state after cooling down.

2.2.1.3 Usages and Chemical Actions of BHA and BHT

As a food preservative, these chemicals can be found in food items containing lipids (fat-containing products), oils, and margarine. They are stable at high temperatures so that they can retain their superior antioxidant capabilities even during food processing, notably baking and frying (Husøy et al., 2019). They also function as a preservative and antioxidant in various pharmaceutical and cosmetic products containing oils and fats, such as lipsticks, moisturizers, and other cosmetics (sunscreen, fragrance, creams, etc.). BHT is a toluene-based ingredient used as a preservative in food and personal care products (Environmental Working Group). In contrast, BHA is an antioxidant used in cosmetics, especially lipsticks and eye shadow products (IARC, 1986).

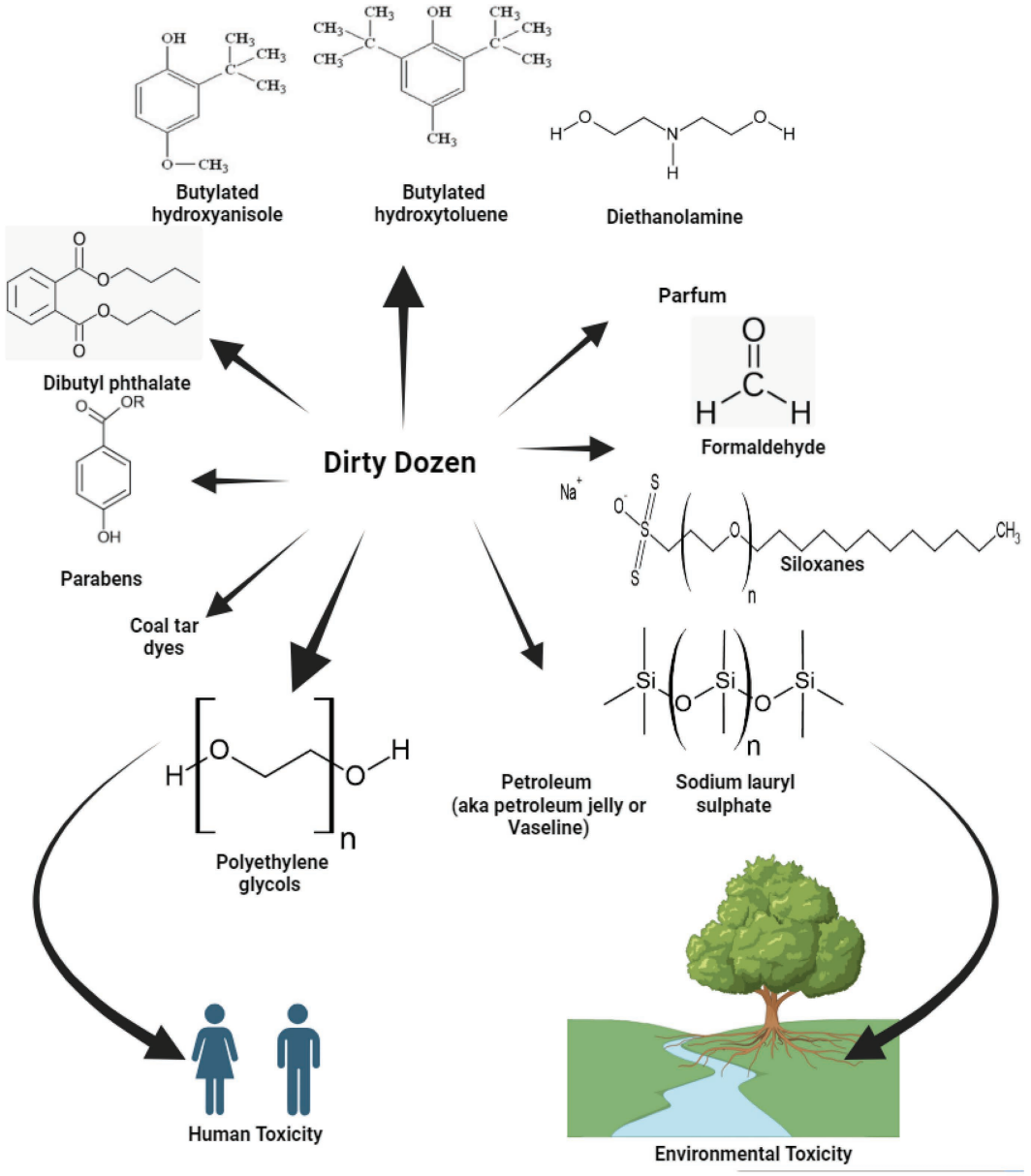


FIGURE 2.1 The indoor Dirty Dozen and their impact on human and environment.

2.2.1.4 Health and Ecological Impacts of BHA and BHT

2.2.1.4.1 Effects on Animal

Exposing BHT to animal (mice and rats) under high doses and prolonged periods would harm lung function and blood coagulation. This will generate problems in the liver, thyroid, and kidney (OECD, 2002). In addition to serving as a tumour promoter in sensitive mice (Bauer et al., 2001), indicated here is that BHT might intervene in the workings of female (Wada et al., 2004) and male (Schrader and Cooke, 2000) hormones, compromising the reproductive functions.

2.2.1.5 Effects on Human Health

It is well noted that both compounds are skin allergens (Occupational Exposure to Hazardous Agents, 2010). The European Commission on Endocrine Disruption listed BHA as a Category 1 priority substance and this was based on solid evidence (Hecker and Hollert, 2011); the International Agency for Research on Cancer listed it as a possible human carcinogen (International Agency for Research on Cancer, 2004).

2.2.1.6 Effects on Environmental Indices

BHA is toxic to aquatic organisms and can bioaccumulate (OSPAR, 2002) and perhaps become biomagnified in the food chain, based on the assessment of UNEP and OECD (2003). It is listed as a chemical of potential concern in the Convention for the Protection of the Marine Environment of the North-East Atlantic.

2.2.1.7 Existing Regulations on BHA and BHT

BHA and BHT are used as food antioxidants in the EU, USA, Australia, New Zealand, and other countries. However, using BHA as a fragrance ingredient in cosmetics is prohibited in the EU. Products using BHA should contain warning labels notifying consumers that it is carcinogenic. BHA is classified as a 'high human health priority', based on its carcinogenicity, while BHT is classified as a 'moderate human health priority' by the Health Department, Canada. Nevertheless, the usage of both chemical compounds is not yet restricted in Canada (Occupational Exposure to Hazardous Agents, 2010).

2.2.2 Coal Tar Dyes: Phenylenediamine and Colors Listed as 'CI' Followed by a Five-Digit Number

2.2.2.1 General Description of Coal Tar Dyes: Phenylenediamine and Colors

Coal tar dyes, a group of synthetic colorants derived from coal tar, play a significant role in a range of industries, including textiles, cosmetics, and food. Colors obtained from coal tar have been commonly used in cosmetics, usually identified by a five-digit color index (CI) number. One of the most critical coal tar dyes is p-phenylenediamine which is used in most hair dyes (Sampathkumar and Yesudas, 2009). Two commonly used coal tar dyes are phenylenediamine and identified by the prefix CI followed by a five-digit number.

2.2.2.2 Usages of Coal Tar Dyes: Phenylenediamine and Colors

Phenylenediamine, often found in hair dyes and certain textiles, has been associated with adverse health conditions. Prolonged exposure to this dye is linked to skin irritation and allergies and, in extreme cases, may lead to more severe dermatological conditions. Moreover, research suggests potential connections between phenylenediamine and respiratory issues, emphasizing the need for cautious use in products that come into close contact with the skin or are inhaled. The colors labeled with CI followed by a five-digit number represent a class of coal tar dyes extensively used in the textile and food industries. The specific numbers denote different shades within this category. However, concerns arise regarding these dyes' impact on human health and the environment.

It was reported that prolonged exposure to CL-dyed products may lead to allergic reactions, particularly in individuals with sensitivities to synthetic dyes. Moreover, certain CL dyes have been associated with carcinogenic properties, raising alarms about their long-term effects on human health. Since these dyes are widely used in the food industry to enhance various products' visual appeal, carefully considering their potential health risks is crucial (Rollison et al., 2006).

2.2.2.3 Health and Ecological Impacts

The manufacturing and disposal of products containing these dyes contribute to environmental pollution. Contaminated wastewater from dyeing processes can harm aquatic ecosystems, affecting

fish and other aquatic life. Additionally, the persistence of these synthetic dyes in the environment poses challenges for waste management and environmental sustainability.

While coal tar dyes contribute significantly to the visual appeal of various products, the potential risks they pose to human health and the environment cannot be ignored. Increased awareness, stringent regulations, and a shift toward sustainable alternatives are crucial steps in addressing the concerns associated with these dyes. When consumers, industry stakeholders, and policymakers collaborate meaningfully, a balance between aesthetics and safety can be achieved, paving the way for a healthier and more ecologically sustainable future (Zhang, 2008).

2.2.2.4 Existing Regulations

In the United States, the Food and Drug Administration (FDA) regulates color additives, including some coal tar dyes, in food, drugs, cosmetics, and medical devices except Coal Tar Dyes. In the European Union, coal tar dyes used in food are subject to strict regulations by the European Food Safety Authority (EFSA). These regulations include permissible limits and specifications for the use of such dyes.

2.2.3 Diethanolamine (DEA)

2.2.3.1 General Description of DEA

Diethanolamine is utilized extensively in producing diethanolamides and diethanolamine salts of long-chain fatty acids. These chemicals are integral to the production of soaps and cleansers in commercial washing, beauty, shampoo, and hair conditioners. Diethanolamine is also utilized extensively for the manufacture of soaps and surfactants. Additionally, diethanolamine is used in manufacturing lubricants in the textiles sector, in the purification of industrial gases to remove acid gases, as an emulsifier and dispersion agent in manufacturing farming substances, and in commercial gas refinement to eliminate acidic gases. As a corrosion inhibitor, diethanolamine can be found in the fluids used in metallurgical processes such as pruning, pressing, and die-casting. Acid neutralization and soil deposition are two of the many applications for diethanolamine in manufacturing cleaning products, metalworking fluids, fabric solvents, and detergents. Numerous medications that are given intravenously are typically dissolved in diethanolamine aqueous solutions, which are then employed as solvents.

According to Zeisel (2007), shampoos and hair dyes may contain free diethanolamine as a component or a contaminant of fatty acid alkanolamides. The diethanolamine detected in these products is typically between 0.2% and 10%. As part of the sulfinol production process, diethanolamine and sulfolane are combined with absorbing carbon dioxide and hydrogen sulphide gases (NTP, 1999; Edens and Lochary, 2004; OECD, 2007, 2008).

2.2.3.2 Chemical Structures and Properties of DEA

Diethanolamine is a type of ethanolamine that belongs to the class of ethanolamines and has an N-hydroxyethyl group in its chemical structure. Its function in the human body forms as foreign substances. It shares some of the same capabilities as an ethanolamine. Its chemical formula is $\left(CH_2CH_2OH\right)_2$ NH with a 105.14 g/mol molecular weight. The physical appearance of DEA is a solid white crystal or a viscous colorless liquid, with a slight whiff of spoiled seafood or ammonia in the air.

2.2.3.3 Use and Chemical Functions of DEA

It is used as an absorbent for acidic gases, as an intermediate for the production of emulsifiers, detergents, and lubricants, as an ingredient in cosmetics and pharmaceuticals, in cutting fluids, and as a textile finishing agent (Knaak et al., 1997).

2.2.3.4 Health and Ecological Impacts of DEA

There is a lack of data concerning the implications that diethanolamine may have on the well-being of individuals. In human, irritation of the throat and nasal passages can occur from acute exposure to inhaled diethanolamine. In contrast, skin irritation may come from acute (short-term) exposure absorbed through the skin (Anderson and Meade, 2014). Currently, not enough information has been published concerning the persistent (long-term), reproductive, growth-related, or oncogenic consequences of diethanolamine in human (New Jersey Department of Health, 1989).

2.2.3.5 Effects of DEA on Animal

Prolonged oral consumption of diethanolamine in animal experiments has been shown to seriously affect the kidneys, liver, blood, and central nervous system (CNS). The National Toxicology Programme (NTP), USA, found that cutaneous contact with diethanolamine led to a higher prevalence of both kidney and liver tumors in mice (Melnick, 1992).

2.2.3.6 Impact of DEA on Environmental Indices

The ecotoxicological inspection of DEA on various marine organisms such as algae, mussels, oysters, and crustaceans was investigated. It has been shown that DEA possesses low levels of acute toxicity. Combined with the fact that it is biodegradable, it may increase the likelihood of possible long-lasting problems for marine life. However, more studies are required to investigate the eventual effects of mixtures, and these studies should concentrate on generating important findings for the potential harmful effects of their contaminants on marine organisms.

2.2.3.7 Existing Regulations of DEA

Several regulatory authorities like the US Environmental Protection Agency (EPA) have regulated DEA under the Clean Air Act (CAA) and listed the national emission standards for DEA. Under the Federal Insecticide, Fungicide, and Rodenticide Act and the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, the EPA mandates a reportable quantity of 45.4 kg. It also lists pesticide tolerances for DEA in several crops. According to the Superfund Amendments and Reauthorization Act (SARA) of 1986, the EPA sets out the requirements for submitting information relating to releasing toxic chemicals. The US Food and Drug Administration (FDA) regulates DEA under the Federal Food, Drug, and Cosmetic Act.

The FDA allows DEA to be used in several indirect food additives. DEA may be used in some adhesives, coating components, and paper and paperboard components. The American Conference of Governmental Industrial Hygienists (ACGIH, 1999) has established a threshold limit value (TLV) for DEA of 0.46 ppm (1.99 mg/m^3) in air and 2 mg/m^3 for dermal exposure.

2.2.4 Dibutyl Phthalate (DBP)

2.2.4.1 General Description

Dibutyl phthalate (DBP) is a chemical compound classified as a phthalate ester. It is derived from phthalic acid and is characterized by its molecular structure, consisting of two butyl groups attached to a phthalic acid backbone. This clear and colorless liquid exhibits a faint, sweetish odor.

2.2.4.2 Chemical Structures and Properties

The chemical formula for dibutyl phthalate (DBP) is $C_{16}H_{22}O_4$. The chemical structure of DBP is $C_6H_4(CO_2C_4H_9)_2$. DBP is typically found as a colorless and oily liquid at room temperature. It possesses a mild and sweetish odor, although the scent is generally not strong. While DBP is soluble in various organic solvents, its solubility in water is limited. The boiling point of DBP is around 340°C, indicating that it remains stable under normal conditions. The density of DBP is approximately 1.05 g/cm^3.

2.2.4.3 Usages

Dibutyl phthalate is widely employed in industrial applications, and some of its primary uses include plasticizer, adhesives and sealants, inks and coatings, and cosmetics. DBP is extensively utilized as a plasticizer, particularly in producing polyvinyl chloride (PVC) products. It enhances plastics' flexibility, durability, and workability, making them more adaptable for various applications such as vinyl flooring, cables, and synthetic leather. Due to its plasticizing properties, DBP is incorporated into the formulation of adhesives and sealants to improve their performance and flexibility (Barlow et al., 2004). The chemical is employed in manufacturing inks and coatings to impart flexibility and enhance the overall characteristics of these materials. In certain cosmetic products, such as nail polishes, DBP functions to improve texture and durability.

2.2.4.4 Health and Ecological Impacts

While dibutyl phthalate has various industrial applications, health, and environmental considerations are associated with its use. Prolonged exposure through inhalation or skin contact may lead to irritation, and there are potential environmental ramifications, particularly damage done to aquatic life (Barlow et al., 2004).

2.2.4.5 Effects on Human Health

Prolonged exposure to dibutyl phthalate (DBP) vapors may lead to respiratory irritation. Individuals working in industries in which DBP is used has raised concerns regarding its potential health impacts, primarily stemming from its pervasive use as a plasticizer in various consumer products (Hasan et al., 2024).

Additionally, direct skin contact with DBP may lead to skin irritation, and repeated exposure could result in dermatitis. Of particular concern are the potential reproductive and developmental effects of DBP, since some studies suggest a link between phthalate exposure and adverse impacts on the endocrine system. Pregnant women and individuals planning to conceive are advised to be cautious about exposure to DBP (Stahlhut, 2007). Furthermore, the cumulative effects of long-term exposure to DBP are under scrutiny, prompting the need for preventive measures in occupational settings. Regulatory bodies have imposed guidelines to limit exposure to DBP, emphasizing the importance of compliance in industrial practices. As research on DBP's health impacts continues, ongoing vigilance and adherence to safety measures are crucial in order to resolve the potential risks associated with this commonly used chemical compound.

2.2.4.6 Effects on Environmental Indices

DBP is widely employed as a plasticizer, posing potential environmental concerns that impact various ecological indices. One notable concern is its effect on aquatic ecosystems. DBP is toxic to aquatic organisms, potentially leading to disruptions in aquatic biodiversity. The compound's chemical properties can contribute to its persistence in water bodies, raising the risk of bioaccumulation in aquatic organisms, which may further magnify the environmental impact of the food chain.

Moreover, the release of DBP into soil has the potential to affect soil-dwelling organisms and disrupt soil ecology adversely. The chemical's mobility in soil may contribute to contamination, potentially affecting plant life and organisms inhabiting terrestrial ecosystems. Understanding the long-term effects on soil health and fertility is critical in assessing the overall ecological impact of DBP.

In the air, DBP may undergo volatilization, leading to atmospheric dispersion. While the direct atmospheric impact is not as pronounced as in water or soil, the potential for long-range transport and deposition raises concerns about widespread environmental contamination. Monitoring and assessing the presence of DBP in different ecological compartments is essential to understand its overall impact on environmental indices. Given these environmental concerns, regulatory bodies have implemented guidelines and restrictions on using DBP in various products. Strategies

to minimize environmental exposure include proper disposal methods, waste management practices, and the development of alternative, less harmful plasticizers. Sustainable and eco-friendly approaches in industrial processes are crucial to mitigating the environmental effects of DBP and preserving ecological balance.

2.2.4.7 Existing Regulations

Due to its possible health and environmental effects, dibutyl phthalate is subject to regulations and restrictions in many jurisdictions. Regulations often include permissible concentration limits in consumer products such as toys and cosmetics, to minimize exposure (Nowshad et al., 2018). Users and manufacturers are advised to adhere to existing regulations, conduct proper risk assessments, and employ safety measures while handling and disposing of products containing DBP. Regular updates to regulations should be monitored to ensure compliance with the latest standards and guidelines.

2.2.5 Formaldehyde-Releasing Preservatives

2.2.5.1 General Description

Formaldehyde-releasing preservatives constitute a class of chemical compounds used in various cosmetic and personal care products, as well as in some pharmaceuticals and industrial applications. These preservatives are designed to inhibit the growth of bacteria, mold, and fungi, thereby extending the shelf life of the products to which they are added. The unique feature of formaldehyde-releasing preservatives is their ability to release formaldehyde over time slowly. Formaldehyde itself is a well-known antimicrobial agent with strong preservative properties. However, due to concerns about its direct use in consumer products, formaldehyde-releasing preservatives offer a controlled and gradual release of formaldehyde when it is applied or stored (Guo et al., 2013). Formaldehyde is employed in various other industrial uses, such as creating resins that are utilized in the production of wooden goods, vinyl flooring and other plastics, permanent-press cloth, and toilet bowl cleansers. Although only trace amounts of formaldehyde are found in the environment, the annual industrial production of formaldehyde has reached 21 million tons worldwide (IARC, 2006). Some common formaldehyde-releasing preservative compounds are diazolidinyl urea, imidazolidinyl urea, DMDM hydantoin, and quaternium-15.

2.2.5.2 Chemical Structures and Properties

The chemical structure of diazolidinyl urea is written as:

$$\left(CH_2CONHC\left(NH_2\right)NHCONHCH_2\right)_2\left(CH_2CONHC\left(NH_2\right)NHCONHCH_2\right)_2$$

Diazolidinyl urea is a white, crystalline solid. It is sparingly soluble in water. Diazolidinyl urea decomposes slowly to release formaldehyde over time when incorporated into cosmetic and personal care formulations.

2.2.5.3 Usages

Formaldehyde-releasing preservatives play a crucial role in formulating a wide range of cosmetic, personal care, and pharmaceutical products. These preservatives are strategically employed to extend the shelf life of these products by inhibiting the growth of bacteria, mold, and fungi. Commonly found in items such as shampoos, lotions, creams, and various other skincare and haircare products, formaldehyde-releasing preservatives contribute to the prevention of microbial contamination, ensuring the safety and stability of the formulations. Their antimicrobial properties are precious in water-based formulations with higher microbial growth risk. While formaldehyde-releasing preservatives are effective, the industry continues to explore alternative preservative systems to

address consumer concerns about potential health risks associated with formaldehyde exposure. As a result, formulators are increasingly exploring new formulations and preservative strategies that balance product safety, regulatory compliance, and consumer preferences (Islam et al., 2017).

2.2.5.4 Health and Ecological Impacts

The use of formaldehyde-releasing preservatives raises concerns regarding potential health and implications for the environment. Formaldehyde, a known antimicrobial agent released by these preservatives, has been associated with health conditions, including skin irritation and allergic reactions in some individuals. Prolonged or repeated exposure may pose a greater risk, particularly for those with sensitivities. Additionally, formaldehyde-releasing preservatives can contribute to indoor air pollution when released into the environment during product usage. In ecological terms, the gradual release of formaldehyde may seriously poison aquatic ecosystems when washed off during activities like bathing, potentially affecting aquatic organisms and biodiversity. Regulatory bodies globally have established guidelines to limit the concentration of formaldehyde and formaldehyde-releasing preservatives in consumer products to mitigate potential health risks.

2.2.5.5 Effects on Human Health

Using formaldehyde-releasing preservatives in various consumer products has raised concerns about their potential effects on human health. Formaldehyde, a well-known preservative released by these compounds, has been associated with skin irritation and allergic reactions in sensitive individuals. Prolonged exposure may lead to elevated risks, primarily through repeated use of personal care products containing formaldehyde-releasing preservatives. Some people may be more susceptible to these adverse effects, necessitating caution in selecting products (Guo et al., 2013; Islam et al., 2017).

The release of formaldehyde can also contribute to indoor air pollution, affecting individuals exposed to the vapors in enclosed spaces. Regulatory agencies worldwide have established guidelines to limit formaldehyde concentration in consumer products to safeguard public health. As a result, there is an increasing emphasis on developing and adopting alternative preservatives that maintain product safety while minimizing potential health risks associated with formaldehyde exposure. Formaldehyde is a chemical that the International Agency for Research on Cancer identifies as a recognized potential carcinogenic (IARC, 2006). It is possible to breathe in formaldehyde that has been released through makeup that includes these elements (the majority of the study on formaldehyde-linked cancer has concentrated on the hazards associated with inhaling). The gassing of formaldehyde from building goods is already a concern for the quality of indoor air. Health Canada recommends the reduction or elimination of as many probable sources of formaldehyde as possible (Health Canada, 2009). Research conducted in laboratories has shown that formaldehyde found in beauty products can be retained via the skin (Bartnik et al., 1985; De Groot et al., 2010).

2.2.5.6 Effects on Environmental Indices

Formaldehyde-releasing preservatives, while effective in extending the shelf life of various consumer products, have been linked with potential environmental impacts that affect key ecological indices. One significant concern lies in the release of formaldehyde into aquatic ecosystems. Runoff from products containing formaldehyde-releasing preservatives, such as shampoos and body washes, can find its way into water bodies, posing a risk to aquatic organisms (Tang et al., 2009).

Formaldehyde is known for its toxicity to marine life, and its presence in water systems can adversely affect aquatic biodiversity and ecosystem health. Moreover, the atmospheric release of formaldehyde during the application and use of products containing these preservatives contributes to air pollution. Formaldehyde can undergo photochemical reactions in the air, leading to the formation of secondary pollutants. This atmospheric dispersion raises concerns about its potential long-range transport and deposition, impacting air quality and ecosystems beyond the immediate vicinity of product use (Nowshad et al., 2018). The soil can also be affected when formaldehyde-releasing

preservatives are washed off during bathing. Introducing formaldehyde into soil may disrupt microbial communities and potentially harm soil-dwelling organisms. The overall ecological impact of formaldehyde-releasing preservatives necessitates a comprehensive understanding of their fate and transport in different environmental compartments. There is an ongoing push within the industry to explore alternative preservatives that are more environmentally friendly while maintaining the efficacy of product preservation to address these concerns. Regulatory bodies continue to monitor and assess the environmental impact of formaldehyde and its releasers, influencing guidelines to strike a balance between product safety and ecological sustainability.

2.2.5.7 Existing Regulations

Formaldehyde-releasing preservatives are subject to existing regulations that aim to ensure the safety of consumer products while mitigating potential health and environmental risks associated with formaldehyde exposure. Regulatory bodies, such as the US Food and Drug Administration (FDA), the European Union's Scientific Committee on Consumer Safety (SCCS), and similar agencies worldwide, have established guidelines and permissible concentration limits for formaldehyde and formaldehyde-releasing preservatives in various consumer goods (EFSA et al., 2017; Health Canada, 2009). In the European Union, for instance, the use of formaldehyde and formaldehyde-releasing agents in cosmetic products is regulated by the Cosmetic Regulation (EC) No. 1223/2009. The regulation sets maximum allowable concentrations and requires clear labeling of formaldehyde-releasing preservatives in cosmetic formulations. In the United States, the FDA monitors using formaldehyde and formaldehyde-releasing preservatives in cosmetics and personal care products. The agency collaborates with the Cosmetic Ingredient Review (CIR) Expert Panel, an independent body, to assess the safety of cosmetic ingredients, including formaldehyde and its releasers.

Regulations often evolve to incorporate new scientific findings and address emerging concerns. Implementing regulations ensures that products on the market meet established safety standards and helps protect consumers from potential health risks. Manufacturers and formulators must adhere to these regulations, conducting safety assessments and labeling products accurately to comply with the stipulated guidelines. As scientific understanding advances, regulatory bodies may adjust standards to reflect the latest knowledge on formaldehyde-releasing preservatives' safety and environmental impact.

2.2.6 Parabens

2.2.6.1 General Description

According to Juliano and Magrini (2017), parabens are a category of antimicrobial preservatives that are typically utilized in producing beauty products, bathroom amenities, medicines, and food goods. Frequently employed parabens are chemical esters of para-hydroxybenzoic acid containing seven particular substitutes. These substitutes include benzyl, butyl, ethyl, isobutyl, isopropyl, methyl, and propyl. The main common types of parabens found in makeup are methyl and propylparaben, which are frequently combined in formulations to maximize their impact as additives (Brausch and Rand, 2011).

Most personal care products (PCPs), including powdered substances, bases, mascaras, eye shadows, lipsticks, lip sparkles, lotions, nail polishes, deodorants, sunscreens, shampoos, toothpaste, and so on (Karpuzoglu et al., 2013), contain parabens that are used as an antimicrobial agent. This is because parabens are relatively inexpensive and have many stability-related features. Most chemicals that go into cosmetics are employed as additives (preservatives) and scents (Zulaikha et al., 2015). This is done so the product can be used for an extended period of time. The user can then enjoy a pleasant aroma that adds to an attractive look. As a result of the widespread usage of these compounds in PCPs, human beings are subjected to high levels of paraben exposure. With this mind, it is essential to have a clear understanding of the consequences of these parabens to ensure the protection of both human and the natural surroundings.

2.2.6.2 Effects of Parabens on Animal

Research conducted on animal has revealed that parabens are toxic, such as endangering reproduction in Wistar rats (Guerra et al., 2023). There is also embryonal toxicity in fish and amphibians (Medkova et al., 2023), lung toxicity in albino rats (Shalaby and Mahmoud, 2023), and genotoxicity (Martín et al., 2023) as well as polycystic ovary syndrome and endocrine toxicity (Srnovršnik et al., 2023) and developmental toxicity in zebra fish (Lite et al., 2022).

2.2.6.3 Effects of Paraben on Human Health

The hormone system in our bodies is critical to development, growth, and reproduction. The presence of endocrine disruptors may lead to alterations in regular hormone activity, which may result in significant repercussions for the well-being of an individual. Even in minimal amounts, a paraben can compromise the growth hormone system, particularly relevant at critical phases. Researchers have identified a link connecting parabens and alterations in the thyroid gland, a higher likelihood of hormone-related malignancies, overweight and obesity, and modifications in both female and male reproduction. Parabens possess the possibility to work in a way similar to estrogen, which plays a vital role in the reproductive processes of both men and women.

2.2.6.4 Effects of Parabens on the Environment

They are commonly found in water sources all around the globe, parabens are now one of the contaminants of increasing relevance, and garnering the most attention. This is due to the widespread consumption of parabens in many consumer goods, including pharmaceuticals, beauty products, and food, all of which produce remnants that are then discharged into aquatic habitats. The regulation of the usage of parabens differs throughout various parts of the world, resulting in different levels being seen globally. It has been discovered that treatment facilities for wastewater and surface waters contain paraben levels that are higher than 100 g/L. However, drinking water sources usually include values lower than 6 g/L.

Though in low quantities found in drinking water, a paraben is a potential route of exposure for human and raises concerns not just for human health but also for the microbiota. Although a few research studies have revealed modifications in the functions and features of communities of bacteria because they make contact with novel pollutants, the effect of the administration of paraben by microbial populations, especially biofilm colonizers, continues to be relatively understudied. This is because only a few investigations have shown variations in the roles and characteristics of microbial communities following exposure to emerging contaminants. Information on the interactions of parabens with microbial communities is limited. However, generating new findings on the interactions of parabens with microbial communities could help us understand the consequences of paraben exposure on microbial ecosystems and their effects on disinfection tolerance and antimicrobial resistance, which may have potential repercussions for public health.

2.2.6.5 Existing Regulations to Control Parabens

Parabens check the growth and development of bacteria, yeasts, and molds in various meals, including baked items, beverages, fruit products, salad dressings, syrups, and olives (Davidson, 2020). Several agencies, including the US FDA, have established that the level should not exceed 12 ppm in a wide variety of fermented malt beverages, non-carbonated soft drinks, and fruit-mediated dietary things. Methyl and propyl parabens being reduced to concentrations of up to 0.1% are used in packaging materials (Fransway et al., 2019). In addition, the FDA has reduced the amount of methyl-, propyl-, and butyl-type paraben in various foods to below 0.1% (Soni et al., 2002). According to the Joint FAO/WHO Expert Committee on Food Additives (JECFA, 1974), the suggested daily consumption of different parabens such as methyl-, ethyl-, and propyl-esters of p-hydroxybenzoic acid should not exceed 0–10 mg/kg body weight/day. The European Food Safety Authority (EFSA, 2004) stated that a daily intake of parabens of the methyl and ethyl types of up to 0–10 mg/kg/day is safe for human.

2.2.7 Perfume

2.2.7.1 General Description

On an ingredient list for a beauty product, the term 'fragrance' or 'parfum' usually refers to a complex blend of various substances. Around 3,000 different compounds serve to create scents (IFRA, 2011; Steinemann, 2016). Scent is a component that is readily apparent in cosmetics such as fragrances, cologne, and deodorant products; however, it is also deployed in almost all other types of personal grooming items. Even products promoted as 'fragrance-free' or 'unscented' can in fact, include smell in addition to a hiding ingredient that inhibits the human brain from sensing smell (Health Canada, 2009). This is because masking agents are used in fragrances. Apart from its usage in beauty products, perfumes can exist in a wide variety of additional consumer items, the most notable of which are softening agents, cleansers for washing, and household cleaners.

2.2.7.2 Human Toxicity

The vast majority of the tens of thousands of chemicals utilized to make perfumes have not been studied for their toxic effects, individually or in combinations. Several of these undeclared substances are irritating, which means they can potentially bring on signs of toxicity such as allergic reactions, attacks of migraines, and asthmatic symptoms (Thyssen et al., 2009). According to the findings of an investigation conducted on people who suffer from asthma, perfumes and colognes are responsible for inciting episodes in about three out of every four sufferers (Shim and Williams, 1986). There is also data suggesting that being exposed to fragrance can worsen symptoms of asthma and possibly even contribute to its development in children (Bridges, 2002). Fragrances have been related to the development of multiple chemical sensitivities (MCS) and the onset of symptoms associated with the disorder. Those already affected by MCS or illnesses linked to the environment are more at risk (Sears, 2007).

Any person, however, has the potential to feel irritated skin as well as watery eyes and runny nose. According to research published by scientists in the United Kingdom, 'perfume' is the subsequent leading explanation for allergies among individuals seeking treatment at dermatological medical centers (Betton, 2005). Furthermore, particular scent compounds have been scientifically linked, through the use of tests in laboratories, to a variety of problems in the health of individuals, including but not limited to malignancy and neurotoxicity (U.S. National Toxicology Program, 2003).

2.2.7.3 Existing Regulation

In terms of their impact on the environment, synthetic musks that are included in fragrances are of special concern. Many of the odor constituents can last in the natural world and develop in the fat deposits of aquatic species through a process known as bioaccumulation. It has been determined that fish from the Great Lakes have measurable amounts of synthetic musks, and the levels of these musks in the sediment are rising. Environment Canada has classified several synthetic musks as being long-lasting, bioaccumulative, and/or poisonous, while additional artificial musks have been designated as being human health concerns (U.S. Environmental Protection Agency, 2009). Fragrance ingredients in synthetic masks must meet the same requirement for safety as other cosmetic ingredients. The law does not require FDA approval before they go on the market, but they must be safe for consumers when they are used according to labeled directions, or as people customarily use them. However, fragrance and flavor ingredients can be listed simply as 'fragrance' or 'flavor.'

2.2.8 Polyethylene Glycols Compounds (PEG)

2.2.8.1 General Description

Polyethylene glycols are a family of linear polymers that can be produced through a process called condensation, and it is stimulated by a base and involves the addition of several molecules of ethylene oxide to ethylene. The formula for the molecule is $\left(C_2H_4O\right)n\,H_2O$, in which n represents a

typical amount of oxyethylene groups. The molecular weight of a compound may vary anywhere from two hundred to multiple millions, corresponding to the number of oxyethylene groups present. The typical molecular weight of any particular polyethylene glycol item found lies in a range only around 5% wider than its maximum.

Polyethylene glycols are liquid if their molecular mass is less than 600, but they are solids if their molecular mass is 1,000 or more. The elements mentioned earlier do not give off any unpleasant odor or flavor, do not evaporate, and are water-soluble. The compounds are not miscible with alkanes, paraffins, waxes, or ethers. However, they are soluble in water, alcohols, esters, ketones, aromatic chemicals, and hydrocarbons with chlorination. As well, they are miscible with chlorinated hydrocarbons.

2.2.8.2 Usage of PEG

PEG is used in various industries like pharmaceuticals, skin creams (Jang et al., 2015), personal lubricants, toothpastes (Fruijtier-Pölloth, 2005), fibers, foam cushions, and excipient chemical uses like a stationary phase for gas chromatography, as well as a heat transfer fluid in electronic testers, preserve waterlogged wood-mass spectrometry experiments, with its characteristic fragmentation pattern allowing accurate and reproducible tuning. Biological uses include recreating vascular environments by encapsulating endothelial cells and macrophages and crowding agents in *in vitro* assays to mimic highly crowded cellular conditions (European Parliament and Council Directive, 1995). Industrial uses include Trident II submarine-launched ballistic missile solid rocket fuel (Spinardi, 1994) and as a binder in preparing technical ceramics (Schneider, 1991).

2.2.8.3 Effects of PEG on Animals

The effects of polyethylene glycol (PEG) on gastric function and lesion formation, evoked by topical applications of absolute ethanol to an *ex-vivo* stomach chamber preparation, have been examined. Although PEG is generally recognized as safe at regulated concentrations, when propylene glycol is ingested at toxic doses it can cause central nervous system depression, neurodegeneration, and lactic acidosis (Fowles et al., 2013). PEG is an approved food additive for dog and sugar glider food under the category of animal feed and is generally recognized as safe for dogs, with an LD50 of 9 mL/kg. The LD50 is higher for most laboratory animals (20 mL/kg). However, it is prohibited for use in food for cats due to links with Heinz body anemia (Elitok, 2018).

2.2.8.4 Effects of PEG on Human Health

Apart from its needed therapeutic qualities, a medicine may cause some unwanted outcomes. Although not all these side effects may occur, if and when they do, people may need medical attention. It is important to check with one's doctor immediately if any of the following side effects occur: bloated feeling, pain in the upper stomach, pressure in the stomach, stomach pain, swelling of the stomach area; vomiting; burning, itching, or pain around the anus; difficulty with sleeping; feeling unusually cold; general feeling of discomfort or illness; hunger; and shivering.

2.2.8.5 Effects of PEG on Environmental Indices

According to the findings of the experiments conducted with fish, aquatic invertebrates, and algae, PEGs do not pose a threat of poisoning to living things in water. Because PEGs with molecular weights between 200 and 20,000 degrade so easily, it is quite unlikely that they will remain in nature for an extended period of time. PEGs do not become more concentrated in the food source chain as time passes.

2.2.9 Petroleum (Petroleum Jelly or Vaseline)

2.2.9.1 General Description

Petroleum jelly, commonly known as Vaseline, is a semi-solid mixture derived from petroleum, a naturally occurring fossil fuel. It is a versatile, translucent substance with a smooth and gel-like texture, known for its exceptional moisturizing and protective properties. Petroleum jelly is

produced by refining of crude oil, during which impurities are removed, resulting in a purified mixture primarily composed of hydrocarbons. Its chemical structure consists mainly of long chains of carbon and hydrogen atoms.

2.2.9.2 Chemical and Physical Properties

Vaseline is a mixture of hydrocarbons derived from petroleum refining. Its chemical composition primarily consists of long-chain saturated hydrocarbons, predominantly paraffin, and microcrystalline waxes. The exact molecular structure can vary, but it generally involves linear and branched arrangements of carbon and hydrogen atoms. The absence of reactive functional groups contributes to its inert nature and lack of chemical reactivity. It is typically colorless or has a faint yellow tint. While it appears opaque in its container, thin layers become transparent when applied to the skin. Vaseline is characterized by its neutral and odorless nature, making it suitable for various cosmetic and medical applications. It has a low melting point, enabling it to transform into a more fluid state upon contact with the skin or when exposed to heat (International Agency for Research on Cancer, 2015).

2.2.9.3 Usage

One of its primary uses is in skin care, serving as an effective moisturizer and protective barrier. Individuals often apply Vaseline to soothe and hydrate dry or chapped skin, especially in areas prone to roughness, such as elbows and knees. Its occlusive nature helps prevent moisture loss, making it a go-to remedy for alleviating skin dryness and discomfort. Beyond skincare, Vaseline is widely employed in the cosmetics industry. It is a crucial ingredient in lip balms, lotions, and creams, contributing to formulations designed to moisturize and soften the skin. In the medical field, Vaseline is employed for wound care, providing a protective layer over minor cuts and abrasions to support the healing process. Its versatility also extends to industrial applications, in which it is utilized as a lubricant, rust inhibitor, and sealant. The widespread use of Vaseline reflects its reputation as a reliable and accessible product with many practical uses in personal care, healthcare, and industrial domains.

2.2.9.4 Health and Ecological Impacts

Petroleum jelly, commonly used for its moisturizing and protective properties, generally has minimal direct health impacts when used as intended. It is considered safe for topical application and is often recommended for alleviating dry skin conditions. However, concerns may arise for individuals with sensitivities or allergies, and there have been occasional reports of skin reactions. Users should conduct patch tests, especially if prone to skin sensitivities. Regarding ecological impact, the production and refining processes associated with petroleum-based products, including petroleum jelly, raise environmental concerns. Extracting and processing crude oil, the source of petroleum, contributes to carbon emissions and environmental degradation. Additionally, the disposal of petroleum-based products may pose challenges, since they are not readily biodegradable. While the direct impact of petroleum jelly on the environment is limited, the broader ecological considerations emphasize the importance of exploring and adopting sustainable alternatives to minimize the overall environmental footprint associated with petroleum-derived products.

2.2.9.5 Effects on Environmental Indices

The environmental impact of petroleum jelly, commonly known as Vaseline, extends to various environmental indices. One notable concern lies in its petroleum-based origin. The production of petroleum involves extraction and refining processes that contribute to environmental degradation, including habitat disruption, soil pollution, and carbon emissions. The extraction of crude oil, the primary petroleum source, threatens ecosystems and biodiversity. Additionally, the refining process may release pollutants and greenhouse gases, further contributing to air and water pollution. While petroleum jelly is inert and does not readily break down, the environmental impact arises from the life cycle of its raw material. Disposing of petroleum-based products also presents challenges,

because they do not biodegrade quickly, potentially leading to long-term environmental persistence. As awareness of sustainable and eco-friendly alternatives grows, there is an increasing emphasis on utilizing products with reduced environmental impacts, prompting the exploration of options to replace petroleum-derived substances.

2.2.9.6 Existing Regulations

Existing regulations related to Vaseline, or petroleum jelly, are typically governed by regulatory bodies overseeing cosmetics and personal care products. In the United States, the Food and Drug Administration (FDA) sets guidelines and standards for cosmetics, including those containing petroleum jelly. The FDA regulates the allowable concentration of ingredients, ensures product labeling compliance, and monitors safety. In the European Union, cosmetic products, including those with petroleum jelly, adhere to the Cosmetic Regulation (EC) No. 1223/2009 (Nowshad et al., 2018). As part of responsible product stewardship, industry operators are encouraged to stay informed about regulation updates, conduct safety assessments, and explore sustainable practices, aligning their formulations with evolving consumer expectations and environmental considerations.

2.2.10 Siloxanes

2.2.10.1 General Description

Siloxanes, often known as silicones, constitute a class of low-molecular-weight chemicals that include organosilicon oligomers and polymers. These chemicals are vitally significant to human beings and serve in several crucial roles. More than 150,000 different practical uses have been registered because of the rapid growth of silicone technologies over the past decade (CES – Silicones Europe, 2008; Tran et al., 2015; Xu et al., 2015). These uses include manufacturing medicinal, medical, beauty, and food-related products (CES – Silicones Europe, 2008; Tran et al., 2015; Xu et al., 2015). It is noted that the entire world's capacity for manufacturing siloxanes was 2,000,000 tons in 2002. However, it jumped to more than 8,000,000 tons more than a decade later (Tran et al., 2015).

Since 2002, the yearly production of solely cyclic methylsiloxanes in the United States was 470,000 tons, while the amount produced in China was 800,000 tons (Tran et al., 2015; Xu et al., 2015). China, Western Europe, and North America have the highest per capita consumption rates of silicones. It was anticipated that the global market for siloxanes (silicones) would exceed 19 billion dollars by the year 2017 (Krenczkowska et al., 2015). According to these statistics, this sector of the financial system in numerous nations is given a great deal of importance. Because siloxanes are so widely used, not just by adults and children, but by young children and newborns, studying them has become an important topic. Schalau and Ulman (2009) showed that over half of all newly developed skin care products on the market comprise a minimum of one variety of silicone.

2.2.10.2 Usage of Siloxanes

There are a wide variety of ways in which siloxane polymers can be used in medical areas (Li et al., 2023; González Calderón et al., 2020). The polysiloxanes' inertness, stability, and flexibility are used in various applications such as prostheses, artificial body parts, face rebuilding, and catheters. Their highly permeable nature is utilized in a variety of applications as well, including skin substitutes, lens implants, and pharmaceutical delivery devices. Aside from medical uses, these polymers can be turned into high-performance elastomers, membranes, insulation materials, water repellents, anti-foaming agents, mold-release agents, adhesives and related products, barrier materials, discharge control substances for chemicals used in agriculture, etc. (Chitrakar et al., 2022).

2.2.10.3 Effects of Siloxanes on Animals

Several investigations reveal that volatile SLS causes acute and chronic toxicity in animal models (Meeks et al., 2007). It has been reported that long-term exposure to SLS also created reproductive abnormalities, respiratory as well as hepatic complications (Burns-Naas et al., 2002; Dekant et al.,

2017), lung interstitial inflammation (Jean et al., 2017), endometrial adenoma (Franzen et al., 2017), cystic hyperplasia (Jean et al., 2017), and ovarian atrophy in rats.

2.2.11 Sodium Lauryl Sulphate (SLS)

2.2.11.1 General Description

In addition to its other name, sodium dodecyl sulphate, sodium lauryl sulphate (SLS) is a detergent with widespread application in the production of cleaning solutions, beauty products, and other items for personal use (Asio et al., 2023). The chemical description for sodium lauryl sulphate is an anionic surfactant, which means it is quite successful in removing greasy stains and residues. It exists in elevated levels in industrial goods, such as engine degreasers, floor cleaners, and vehicle washing solutions. In addition, SLS is frequently found in home items and personal care products, such as toothpaste, shampoo, conditioner, shaving foam, and cleaning products with lower amounts.

2.2.11.2 Effects of SLS on Animal

According to studies conducted on rabbit, 10% SLS on animal that had not been washed would cause stippling and opacity. According to research that has been published, between 28.2% and 30% of SLS was utilized without being washed, and it exhibited mild to moderate illogical behavior in the eyes (Asio et al., 2023).

2.2.11.3 Effects of SLS on Human Health

There is no direct evidence linking SLS to cancer or other development difficulties in humans. However, there are several possible outcomes of exposure to SLS. Long-term usage of these compounds may cause a steady build-up in the body, but the amounts present in products are still very low. When a person uses products containing SLS, there is the most significant risk of irritating one's eyes, skin, mouth, and lungs.

2.2.11.4 Effects of SLS on the Environment

Based on the findings of the reviewed SLS toxicity profiles, it has been determined that SLS is a suitable surfactant for producing household cleaning products, both from a toxicological and a sustainability point of view. However, the fundamental worry that SLS tends to irritate the eyes and skin may be readily solved by the manufacturers of the item through suitable formula development and irritation testing carried out on consumers. Because it is biodegradable, has minimal potential for bioaccumulation, and is made entirely from bio-based components, SLS is regarded as a sustainable substance.

The use of SLS in cleaning solutions has been found to be safe in toxicological studies, despite the skin irritation that can occur. It has been determined that SLS in the formulation of cleaning products does not present an unwarranted risk to end users or the natural environment, so it is unlikely to present as a threat to human health and safety. As a result, the idea that SLS poses a risk to people's well-being is not backed by scientific literature, and any statements to the contrary ought to be considered dishonest and fraudulent (Bari et al., 2023).

2.2.12 Triclosan

2.2.12.1 General Description

Triclosan is a synthetic chemical with broad-spectrum antibacterial and antifungal properties. It belongs to a class of compounds known as chlorophenols and is chemically classified as a polychloro phenoxy phenol. Initially developed as a surgical scrub in the 1960s, triclosan found its way into various consumer products due to its effective antimicrobial characteristics. The chemical structure of triclosan consists of a phenyl ring attached to two chlorinated phenol rings, which confer its antimicrobial activity. Triclosan has been commonly used in personal care products such

as soaps, toothpaste, and deodorants, as well as in household items like cutting boards and textiles, to prevent the growth of bacteria and fungi. However, its extensive use has raised concerns about potential environmental and health consequences, leading to regulatory scrutiny in various regions. The compound has been the subject of ongoing research and discussion, prompting some manufacturers to explore alternative antimicrobial agents.

2.2.12.2 Chemical Structure and Physical Properties

Chemically designated as 5-chloro-2- (2,4-dichlorophenoxy) phenol, triclosan possesses distinctive chemical and physical properties. It is a white crystalline solid at room temperature, exhibiting a crystalline powder or needle-like appearance. With a molecular formula of $C_{12}H_7Cl_3O_2$, triclosan is characterized by its aromatic structure, consisting of a chlorinated phenyl ring linked to a chlorinated phenoxy ring. This chemical configuration contributes to its potent antimicrobial activity. Triclosan is sparingly soluble in water but dissolves readily in organic solvents, making possible its incorporation into various formulations. Its melting point typically ranges between 55°C and 57°C. Beyond its chemical properties, triclosan's physical characteristics make it suitable for integration into a wide array of consumer products. However, its extensive use has led to concerns about potential environmental persistence and effects on health, prompting regulatory scrutiny and a shift toward alternative antimicrobial agents in specific applications.

2.2.12.3 Usage

Triclosan has been widely used for its potent antimicrobial properties, leading to its incorporation into various consumer and industrial products. Initially developed for surgical scrubs and healthcare settings, triclosan found its way into everyday items due to its effectiveness in preventing the growth of bacteria and fungi. Commonly employed in personal care products such as antibacterial soaps, toothpaste, and deodorants, triclosan aims to enhance hygiene by inhibiting the proliferation of microorganisms. Its use also extends to household items like cutting boards, textiles, and plastics, in which its antimicrobial qualities contribute to product longevity.

Triclosan's versatility has made it a popular choice in formulations designed to combat bacteria, but its extensive use has raised environmental concerns and prompted regulatory scrutiny. Consequently, there is a growing shift to prefer alternative antimicrobial agents and an increased emphasis on sustainable and environmentally friendly formulations in the wake of evolving consumer expectations and regulatory guidelines.

2.2.12.4 Health and Ecological Impacts

The usage of triclosan has sparked concerns regarding potential health and ecological impacts. Regarding human health, studies have raised questions about the compound's role in antibiotic resistance and its potential disruption of endocrine systems. Triclosan has been detected in human tissues and has prompted investigations into its long-term effects on human health. Additionally, concerns exist about its environmental impact. Triclosan can persist in water systems, accumulating in aquatic environments where it may pose risks to aquatic organisms (Delbes et al., 2022). Evidence of triclosan's potential toxicity to algae and other aquatic life raises ecological concerns about its effects on freshwater ecosystems. Due to these concerns, regulatory bodies in various regions have taken steps to limit or ban the use of triclosan in certain products, leading to a shift to incorporate alternative antimicrobial agents in consumer goods. These regulatory actions highlight the importance of balancing the benefits of antimicrobial properties with potential risks to both human health and the environment (Delbes et al., 2022; Jurewicz et al., 2018).

2.2.12.5 Effects on Environmental Indices

The presence of triclosan in various consumer products has raised concerns about its potential effects on environmental indices. As a commonly used antimicrobial agent, triclosan has been detected in water bodies, soil, and sediment, indicating its widespread environmental distribution.

One significant environmental concern is its impact on aquatic ecosystems. When released into water systems, triclosan can be toxic to aquatic organisms, mainly algae and certain bacteria. The compound's persistence in the environment raises the risk of bioaccumulation in aquatic organisms, potentially leading to disruptions in food chains and overall ecosystem health. Additionally, there are concerns about triclosan contributing to antibiotic resistance in bacteria, which can affect both environmental and human health. Consequently, regulatory measures have been implemented in various parts of the world to restrict or ban the use of triclosan in certain consumer products, underscoring the need for sustainable alternatives (Zhu et al., 2022).

2.2.12.6 Existing Regulations

Existing regulations related to triclosan vary from country to country and are implemented by government agencies overseeing public health and environmental safety. In the United States, the US Food and Drug Administration (FDA) and the Environmental Protection Agency (EPA) play key roles in regulating triclosan. The FDA has issued regulations regarding its usage in over-the-counter antiseptic products, and the EPA regulates its presence in pesticides. Meanwhile in the European Union, triclosan is subject to the Biocidal Products Regulation (BPR), which governs the use of biocidal products, including those containing triclosan. Over the years, several countries and regions, such as Canada and the European Union, have restricted or banned triclosan in certain consumer products due to environmental and health problems. These regulations often aim to limit concentrations of triclosan in products, restrict its use in specific applications, or encourage the development of alternative antimicrobial agents. The evolving regulatory landscape underscores the importance of ongoing assessment and management of triclosan to ensure its safe and responsible use.

2.3 CONCLUSION

The 'Dirty Dozen' is a series of compounds used as a classic antimicrobial preservative in foods, drugs, and cosmetics for the past 60 years. These substances can enter human bodies through dermal absorption and oral intake and be excreted through urine. Despite the fact that there is no evidence of build-up and toxicity, research on animals strongly suggests that certain types of the Dirty Dozen are almost non-toxic when administered orally or parenterally. In contrast, some recent literature shows that the mechanism of cytotoxic action of the Dirty Dozen might be linked to various health complications. The Dirty Dozen were reported as causing contact dermatitis reactions in some individuals on cutaneous exposure. The consumption of these contaminated chemicals has been linked to several incidents involving contact sensitivity following cutaneous exposure, as well as cases of endocrine disruption and marine animal deaths. Nevertheless, the mechanism that underlies this sensitivity is a mystery. Thus, it can be concluded that the studies currently being conducted and published previously have pointed out the direction of the efficacy and the potentially harmful consequences of the Dirty Dozen.

ACKNOWLEDGMENT

Authors acknowledge the support of the Ministry of Science and Higher Education of the Russian Federation (no. FENW-2023-0008) and the Strategic Academic Leadership Program of the Southern Federal University ('Priority 2030').

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3 Persistent Organic Pollutant Pesticides in the Soil Environment

Ross Sadler and Des Connell

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DOI: 10.1201/9781003530466-3
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3.1 INTRODUCTION

Following the publication of Rachel Carson's classic book *Silent Spring* (Carson, 1962), the soil environment was quickly identified as a major environmental sink for persistent organic pollutants. The enumeration of a number of (then) commonly used pesticides by the Stockholm Convention (Wang et al., 2022) provided a major focus for research into these pesticides – a focus that continues until this day. This chapter aims to present as wide-ranging a perspective as possible of what is currently known regarding these pesticides in soil and to identify as much relevant literature for future reading as possible. Readers are also directed to Chapter 7 that provides further details relating to numerous other persistent organo chlorine pesticides including their degradation products.

3.2 PESTICIDES INCLUDED IN THE STOCKHOLM LIST OF CONTAMINANTS

Persistent organic pollutants (POPs) are a class of pesticide and industrial chemicals characterized by their persistence in the environment, their tendency to bioaccumulate in organisms, their toxicity to human health and the environment, and their ability to be transported over long distances. These properties have led to severe global environmental and health concerns, prompting the adoption of the Stockholm Convention in 2001, which entered into force in 2004.

The Stockholm Convention, a global treaty aimed at mitigating the adverse effects of POPs, has garnered significant international support. As of the current time, a total of 152 countries have ratified the Convention. The full list of signatories, along with associated declarations, provides further insight into the Convention's scope and implications.

This chapter focuses specifically on the pesticide POPs listed in the Stockholm Convention, a detailed account of which is provided in Table 3.1.

The structures of these compounds are shown in Figure 3.1.

TABLE 3.1
Pesticides Listed as POPs by the Stockholm Convention

Pesticide	Listing
Aldrin	Annex A (Elimination)[1]
Chlordane	Annex A (Elimination)[1]
Dicofol	Annex A (Elimination)[1]
Dieldrin	Annex A (Elimination)[1]
Endrin	Annex A (Elimination)[1]
Heptachlor	Annex A (Elimination)[1]
Lindane	Annex A (Elimination)[1]
Mirex	Annex A (Elimination)[1]
Toxaphene	Annex A (Elimination)[1]
DDT	Annex B (Restriction)[2]

[1] Parties must take measures to eliminate the production and use of the chemicals listed under Annex A.

[2] Parties must take measures to restrict the production and use of the chemicals listed under Annex B in light of any applicable acceptable purposes and/or specific exemptions.

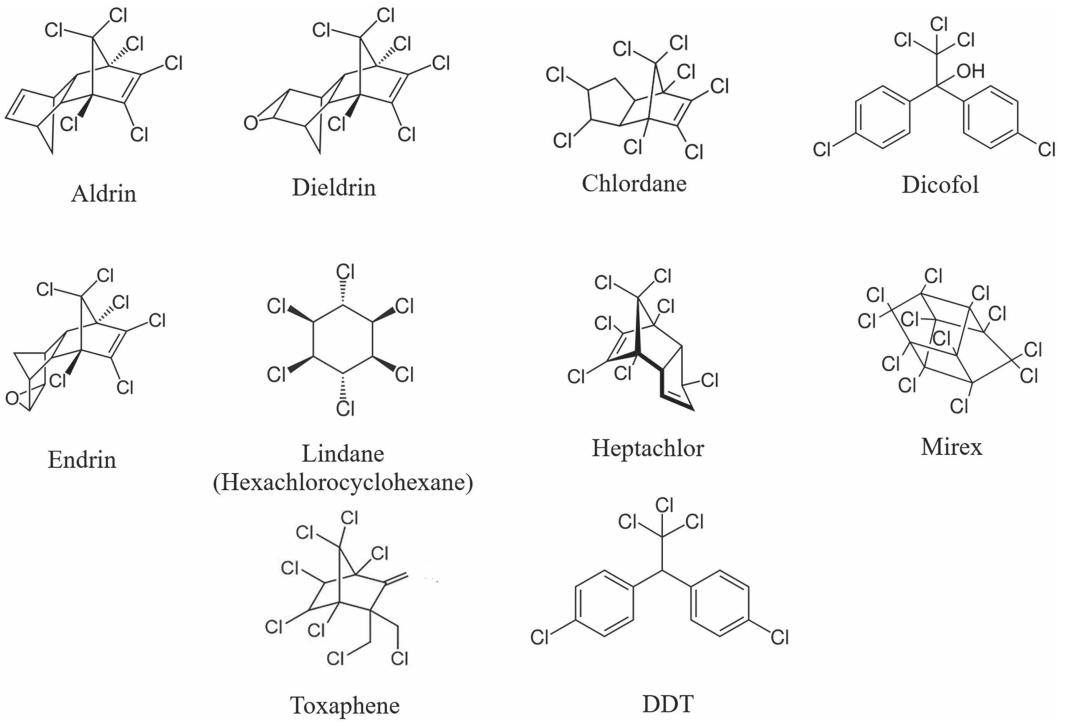


FIGURE 3.1 Structures of persistent organic pollutant pesticides.

Of particular interest in the light of the effects of climate change is the reintroduction of DDT to control mosquitoes which carry the malaria parasite (Biscoe et al., 2005; WHO, 2011). This is the subject of ongoing appraisal by the Expert Group Meeting on DDT, which held its ninth meeting in Geneva in November 2022 (Expert Committee on DDT, 2023).

Table 3.2 gives a range of physical and chemical properties of the POP pesticides.

3.3 BY WHAT CRITERIA IS A SOIL REGARDED AS CONTAMINATED?

The criteria which are used to denote a soil as being contaminated vary from country to country and it is not possible to provide a completely exhaustive list of such criteria in a review of this length. Moreover, the approaches of various countries also differ, with some specifying actual levels above which soils are considered contaminated. But many others, such as Australia, specify investigation levels, above which a site-specific health risk assessment needs to be carried out (cf. NEPC, 2011). This type of risk assessment is generally based upon human health considerations, although some countries also have protocols for ecological risk assessment (cf. UK Environmental Agency, 2017). These human health investigation levels can be subdivided further, according to the end use of the site (e.g. residential in terms of a normal, single-occupier dwelling, where the occupants grow <10% of their own produce vs. an apartment block, with fully paved surrounds). It is important to understand that these criteria are intended *only as trigger levels for a full site-specific health risk assessment and are not (in themselves) outright criteria for declaring a site to be contaminated or cleanup criteria.*

Table 3.3 gives a summary of such criteria in respect of the POP pesticide pollutants in soil.

TABLE 3.2
Physical and Chemical Properties of POP Pesticides[a]

Pesticide	Properties							
	Molecular Weight	Melting Point	Boiling Point	Vapour Pressure	Water Solubility	Octanol Water Partition Coefficient (Log K_{OW})	Henry's Law Coefficient (kPa m^3/mol)	First Order Connectivity Index ($^1\chi$)
Aldrin	364.9	104°C	Decomposes	1.20×10^{-4} mm Hg at 25°C	0.027 mg/L at 27°C	6.5	$2.8 \pm 1.4\times10^{-3}$[b]	8.276[g]
Chlordane	409.8	106–107°C (cis-isomer); 104–105°C (trans-isomer)	Decomposes	9.75×10^{-6} mm Hg at 25°C	0.056 mg/L at 25°C	6.16	$4.91–8.40\times10^{-3}$[c]	8.114[g]
Dicofol	370.5	173.3–175.1°C	225°C	3.98×10^{-7} mm Hg at 25°C[1]	0.8 mg/L at 25°C	5.02	2.4×10^{-5}	11.35–11.73[f]
Dieldrin	380.9	175.5°C	Decomposes	5.89×10^{-6} mm Hg at 25 °C	Insoluble	5.40	$1.1 \pm 2\times10^{-3}$[b]	8.776[g]
Endrin	380.9	226–230°C	Decomposes	3×10^{-6} mm Hg at 20°C	0.25 mg/L at 25°C	5.20	6.44×10^{-4}	8.776[g]
Heptachlor	373.3	95–96°C	Decomposes	4.0×10^{-4} mm Hg at 25°C	0.18 mg/L at 25 °C	6.10	2.98×10^{-2}	7.703[g]
Lindane	290.8	112.5°C	311°C	4.5×10^{-5} mm Hg at 25°C	7.3 mg/L at 25 °C	3.72	5.20×10^{-4}	5.464[d]
Mirex	545.5	485°C	Sublimes and decomposes	8×10^{-7} mm Hg at 25°C	0.085 mg/L at 25°C	6.89	8.2×10^{-2}	9.500[e]
Toxaphene	411.8	65–90°C	Decomposes	6.69×10^{-6} mm Hg at 20°C	Insoluble	5.90	6.07×10^{-4}	7.843[d]
DDT	354.5	108.5°C	260°C Decomposes	1.6×10^{-7} mm Hg at 20°C	5.50×10^{-3} mg/L at 25°C	6.91	$5.32 \pm 3.9\times10^{-3}$ [b]	8.876[d]

[a] All data from PubChem (National Center for Biotechnology Information, 2023) unless otherwise stated.
[b] Mackay and Shiu (1981)
[c] CDCP (2023)
[d] Shabaan and Elprince (1989)
[e] Sabljic et al. (1995)
[f] Stenzel et al. (2012)
[g] Cañas (2002)
Data for technical grade

TABLE 3.3
POP Pesticide Pollutant Criteria for Soil

Pesticide	Pesticide Concentration in Soil (mg/kg)											
	Finland[1]		France[1]		Germany[1]				Australia[2]			
	Lower Guideline Value	Upper Guideline Value	Sensitive Use	Non-Sensitive Use	Residential	Playing Grounds	Parks/ Recreation	Industrial	Residential (<10% home-grown produce)	Residential (fully paved)	Parks/Play Grounds	Industrial
Aldrin	–	–	4	–	4	2	10	–	7**	10**	9**	50**
Chlordane	–	–	–	–	–	–	–	–	50	100	80	560
Dicofol	–	–	–	–	–	–	–	–	–	–	–	–
Dieldrin	1	2	6	6	–	–	–	–	7**	10**	9**	50**
Endrin	–	–	–	–	–	–	–	–	10	20	20	100
Heptachlor	0.2	1	–	–	–	–	–	–	7	10	9	50
Lindane	0.2	2	0.5	470	10+	5+	25+	400+	10+	20+	15+	85+
Mirex	–	–	–	–	–	–	–	–	10	20	20	100
Toxaphene	–	–	–	–	–	–	–		20	35	30	170
DDT	1	2	4*	20*	80	40	200	–	260*	700*	400*	4000*

[1] European Commission (2007)
[2] NEPC (2011)
* ΣDDT (DDT+DDD+DDE)
** Aldrin + Dieldrin
+ Total HCH

3.4 BY-PRODUCTS OF POP PESTICIDES

Considering the range of compounds listed in the foregoing sections, it is clear that there exists a wide scope for by-product formation. Whilst this review cannot deal with the complete spectrum of known chemical reactions for every POP pesticide, it is nevertheless important to recognize by-products that can be expected to form under conditions that would be relevant to soil under environmental conditions. This would therefore include:

- Biotransformation
- Chemical processes that might occur through misadventure (spills, improper disposal, chemical fires, etc.)

Information pertaining to some of the more significant contaminants only will be presented.

3.4.1 Aldrin and Dieldrin

The metabolism of aldrin and dieldrin in soils has been recently reviewed (Pang et al., 2022). A range of organisms is known to be capable of carrying out degradation of these pesticides including the following bacteria*: Pseudomonas fluorescens*; *Burkholderia* sp.; *Cupriavidus* sp.*; Enterobacter* sp.; *Pseudonocardia* sp.; and the following fungi: *Trichoderma viride*; *Mucor alternans*; *Phanerochaete chrysosporium*; *Trametes versicolor*; *Mucor racemosus*; *Phlebiaacanthocystis*; *Phlebia brevispora*; *Phlebia aurea*; *Pleurotus ostreatus*; and *Penicillium miczynskii*. Biodegradation of aldrin and dieldrin by mixed microbial communities has also been reported (Pang et al., 2022).

Aldrin can be degraded by three microbial pathways (Bandala et al., 2006; Sakakibara et al., 2011; Xiao et al., 2011):

- Oxidation to dieldrin or dihydrochlordenecarboxlic acid
- Hydroxylation to 9-hydroxyaldrin
- Reduction to monochlorodieldrin

A joint hydroxylation-oxidation pathway has also been reported, leading to the production of a variety of carboxylic acid compounds usually containing a single hydroxyl group (-OH) and a dihydrochloride group (Xiao et al., 2011).

Relatively little is known of the degradation and environmental fate of any of the aforementioned compounds, with the exception of dieldrin itself. The pathways of degradation for dieldrin are discussed in the next section (Bandala et al., 2006; Sakakibara et al., 2011; Xiao et al., 2011).

3.5 OXIDATION TO KETO-ALDRIN

- Hydroxylation to 9-hydroxydieldrin, which can be further hydroxylated to dihydroxydieldrin
- Hydrolysis and hydroxylation to monohydoxy-6,7-dihydroxydihydroaldrin

Again, little is known of the environmental fate of significance any of these by-products and this is an important area for future research if the potential for use of these microbes in bioremediation of contaminated soil is to be realized. It must be emphasized that complete mineralization of aldrin and dieldrin to carbon dioxide has yet to be demonstrated. A review of conditions that stimulate microbial degradation of these pesticides has been presented by Purnomo (2017).

In terms of the use of chemical reagents for destruction of aldrin and dieldrin, the pathway which has received most attention is oxidation (Tollefsrud and Schreier, 2002). Potential oxidants include Fenton's reagent, hydrogen peroxide, and potassium permanganate. More recently, activated

persulfate oxidation has been advocated as a means for removing aldrin from contaminated soil (Kurakalva, 2022).

3.5.1 Endrin

Fungal degradation of endrin has also been reported with *Phlebia acanthocystis* and *Phlebia brevispora* both being particularly effective in the process. Several hydroxylated products such as 8-hydroxyendrin and 2-monohydroxyendrin were detected, indicating that endrin was initially converted to different monohydroxylated products in fungal degradation. In addition, a carboxylic acid product was obtained from *P. acanthocystis* culture, suggesting that the carboxylation reaction occurred in bioconversion of endrin (Xiao and Kondo, 2019).

3.5.2 Chlordane

Several authors have noted the ability of actinomycetes to remove chlordane from contaminated soils (Fuentes et al., 2010; Cuozzo et al., 2012), with *Streptomyces* strains being particularly active in the process. To date, the degradation products have not been identified.

The wood rotting fungi *Phlebia lindtneri*, *Phlebia brevispora*, and *Phlebia aurea* have also been shown to be capable of degrading chlordane, at least in axenic culture. The authors believed that hydroxylation reactions play an important part in the fungal metabolism of chlordane. These fungi transformed trans-chlordane to at least eleven metabolites including a large number of hydroxylated products such as 3-hydroxychlordane, chlordene chlorohydrin, heptachlor diol, monohydroxychlordene, and dihydroxychlordene. *P. lindtneri* particularly can metabolize oxychlordane, a recalcitrant epoxide product of chlordane, into a hydroxylated product through substitution of chlorine atom by hydroxyl group.

There are several chemical methods for destruction of chlordane in contaminated soil. Hazardous decomposition products of chlordane, which appear when the pesticide is boiled, include toxic gases and vapours, such as hydrogen chloride, chlorine, phosgene, and carbon monoxide. Treatment of chlordane with strong alkalis results in dichlorination (National Center for Biotechnology Information. Pubchem, 2023).

3.5.3 Dicofol

Dicofol has been reported as an intermediate in the microbial breakdown of DDT. Less attention has been paid to the pesticide itself, but a 2020 study showed the turkey tail fungus *Trametes versicolor* to be capable of degrading dicofol. The end product of degradation was found to be benzaldehyde and the authors speculated that the degradation pathway proceeded via dichlorination, resulting in the formation of 2,2-dichloro-1,1-bis-(4-chlorophenyl)-ethanol. This then underwent reductive dechlorinations and oxidative cleavage to form 4,4'-dichlorobenzophenone. Subsequent ring cleavage produced benzaldehyde (Hu et al., 2020).

In terms of chemical breakdown, heating dicofol to decomposition is known to result in evolution of hydrogen chloride fumes (National Center for Biotechnology Information. Pubchem, 2023).

3.5.4 Heptachlor

Heptachlor is known in the environment, both as a result of application of the pesticide itself and also as a result of the use of technical grade chlordane, which contains about 10% heptachlor. Photolysis reactions and conversions of the pesticide have been reported, but are not likely to be of much significance to soils. In soils, heptachlor is known to be metabolized to heptachlor epoxide, with subsequent hydrolysis to the less-persistent 1-hydroxychlordene. Both the endo- and exo-epoxides of heptachlor are known, but the exo form (sometimes referred to as HEPX) is more stable and is

found almost exclusively in the environment. These soil interconversions, followed by subsequent volatilization are thought to be the main source of heptachlor epoxide in air (Bidleman et al., 1998).

As with other chlorohydrocarbon pesticides, white rot fungi such as *Pleurotus ostreatus* have been shown to be capable of effecting degradation of heptachlor and heptachlor epoxide. Degradation of heptachlor produced heptachlor epoxide, which was detected as the main metabolite, along with chlordene and 1-hydoxychlordene. This fungus was also capable to effecting some degradation of heptachlor epoxide, although the amount of degradation over 14 days did not exceed 31% and was highly dependent upon the culture medium employed. The major metabolite observed was 2,3-dihydroxyheptachlor (Purnomo et al., 2013).

Thermal decomposition of heptachlor results in the evolution of carbon monoxide and hydrogen chloride (National Center for Biotechnology Information. Pubchem, 2023).

3.5.5 Lindane

The biodegradation of lindane has been recently reviewed (Zhang et al., 2020). A variety of microbes, particularly Gram-negative bacteria, can transform lindane into non-toxic and environmentally safe metabolites. Fungal biodegradation is also considered an environment-friendly approach for the detoxification of POPs in comparison with the traditional physical and chemical methods and as with other POP pesticides, wood rotting fungi show an excellent capability for degradation of lindane.

The main reactions that occur during aerobic microbial degradation of lindane include dehydrogenation, dechlorination, hydroxylation, dehydrochlorination, and mineralization through ring openings to form acetyl-CoA and succinyl-CoA. These can of course be fed into the Krebs cycle and some organisms have consequently been shown to be capable of using lindane as a sole carbon source.

Anaerobic microbial degradation of lindane has also been demonstrated. Complete mineralization is not achieved and the end products are various chlorinated benzenes. In addition, the metabolic pathways involved are less understood than those associated with aerobic degradation.

When heated to decomposition, lindane emits highly toxic fumes of phosgene and hydrogen chloride gas (National Center for Biotechnology Information. Pubchem, 2023).

3.5.6 Mirex

Less is known regarding the ability of micro-organisms to degrade murex than other POP pesticides. Several pseudomonads are able to live on mirex as a sole carbon source, but the resulting end products have not been specifically identified (George and Claxton, 1988). Given that the organisms can use mirex as a sole carbon source, one would have to assume some similarity to the breakdown outlined for lindane. Early work showed mirex metabolites to also include mono- and di-hydro mirex (Carlson et al., 1976). The closely related compound chlordecone can also act as a sole carbon source for the same pseudomonads as mirex. Based on HPLC co-elution only, hydrochlordecone and dihydrochlordecone were reported as breakdown products (George and Claxton, 1988).

Mirex decomposes above 500°C to give hexachlorobenzene; hexachloropentadiene was found in small amounts in the thermal residue; the products identified from the vapour phase were carbon monoxide, carbon dioxide, hydrogen chloride, chlorine, carbon tetrachloride, and phosgene (National Center for Biotechnology Information. Pubchem, 2023).

3.5.7 Toxaphene

The subject of toxaphene metabolism is complicated by the fact that the technical product consists of several hundred bicyclic components having an average composition of $C_{10}H_{10}Cl_8$. However, studies have shown that the Gram-negative bacterium *Dehalospirillum multivorans* (an obligate

anaerobe) has been shown to rapidly and selectively transform the components of technical grade toxaphene (Ruppe et al., 2004). The degradation was found to proceed through $Cl \rightarrow H$ substitution, particularly at geminal Cls attached to secondary carbons. The resulting products are a number of complex chlorinated bornanes and the spectrum of compounds is quite similar, irrespective of whether the incubation takes place in soil, sediment, or sewage sludge.

As regards abiotic transformations, toxaphene dehydrochlorinates in presence of alkali, under prolonged exposure to sunlight, and at temperatures about 155°C (National Center for Biotechnology Information. Pubchem, 2023).

3.5.8 DDT

The early literature on biotransformation of DDT has been reviewed by Aislabie et al. (1997). The major transformation products found in soils are 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE) and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD). DDD is formed from DDT through reductive dechlorination, while DDE is formed from DDT through photochemical reactions in the presence of sunlight and through dehydrochlorination in bacteria. Further metabolism of these compounds can take place, either by bacteria or wood rotting fungi. End products of metabolism by bacteria are generally chlorinated aromatics such as 4,4'-dichlorobenzhydrol and 4,4' dichlorobenzophenone, whereas metabolism by wood rotting fungi proceed further through ring cleavage and ultimate mineralization. However, it should be noted that the spectrum of end products observed with these fungi can also include a number of intermediates, the mineralization generally being limited to about 10% of the original DDT (Bumpus et al., 1987). In conclusion, it should be noted that the metabolic pathways involved have not been completely elucidated and it is quite possible that more than one pathway may be involved (Xiao et al., 2011). If microbial metabolism is to be successfully employed for the remediation of contaminated sites, a proper understanding of all the physiological and biochemical aspects involved in pollutant transformation is required.

The use of co-cultures of the brown rot fungus *Fomitopsis pinicola* and *Bacillus subtilis* in achieving enhanced DDT degradation has also been advocated (Sariwati et al., 2017). The co-cultures could achieve an 86% loss of DDT, but the incubation period was quite short (7 days), which meant that there was not sufficient opportunity for mineralization to occur and the main products were DDD, DDE, and DDMU (1-chloro-2,2-bis(4-chlorophenyl)ethylene).

DDT can also be degraded by chemical means. The early knowledge of DDT chemistry and chemical degradation is summarized by Gunther (1945). As with other persistent organic pollutants, the residues observed following release, notably with chemical incidents, may be a result of these processes. For example, DDE can be formed by alkaline reflux of DDT. In a chemical fire in southeast Queensland in 1985, only DDE residues were observed in the runoff, even though considerable quantities of DDT were stored on the premises. The fire had been fought with water, and bags of lime were stored above the DDT, so that conditions of alkaline reflux virtually prevailed during the fire.

The spectrum of persistent organic pollutant pesticides observed in the environment following release will not necessarily remain static. Figure 3.2 illustrates the changes in pesticide composition of sediment following another chemical fire in Queensland in 1983 (Craswell et al., 1985). Numerous processes such as fluvial transport of colloids, secondary release and adsorption, etc., will be operative and influence the observed pattern of pesticide distribution. In the example shown in Figure 3.2, the period of observation was one week following the fire.

3.6 INTERACTION OF PERSISTENT ORGANIC POLLUTANT PESTICIDES WITH SOIL

The persistent organic pollutant pesticides are highly lipophilic compounds with generally low biodegradability. General properties of such compounds are fully discussed by Connell and Miller (2022). Over the past 60 years, there have been numerous attempts to investigate the mechanism

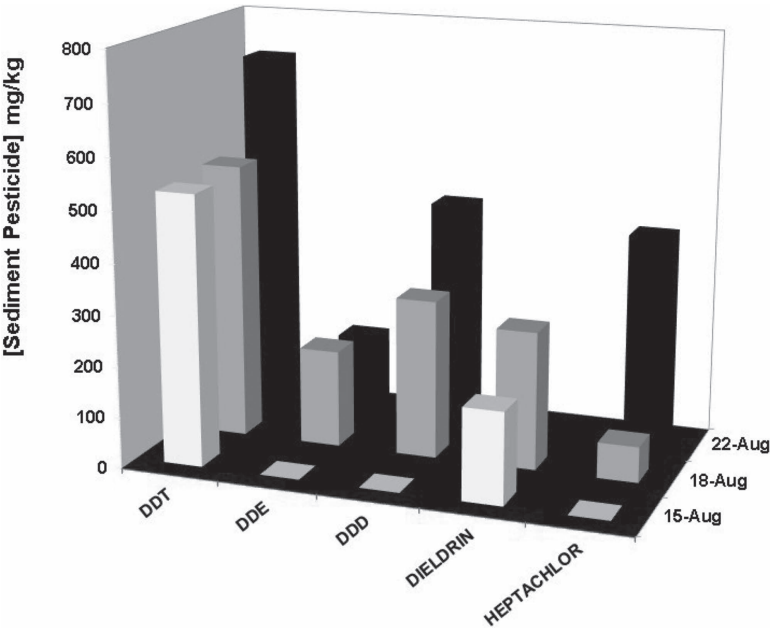


FIGURE 3.2 Changes in persistent organic pollutant pesticide composition at monitoring station following input of runoff from a pesticide warehouse fire.

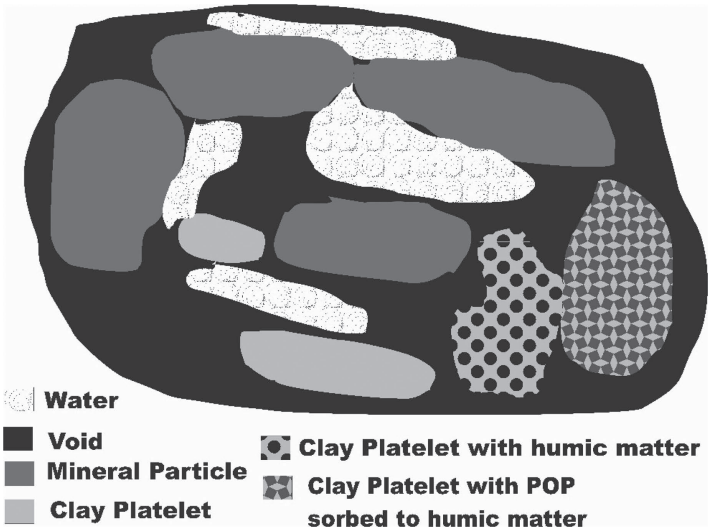


FIGURE 3.3 Schematic representation of sorption of POP pesticide by soil.

of sorption of persistent organic pollutants to soil. Earlier studies were concerned principally with maximizing the efficacy of the pesticide, whereas more recent studies have concentrated upon methodology for potential cleanup of contaminated soils. The general picture presented is that the persistent organic pollutant pesticides are sorbed by organic matter attached to soil particles. This is illustrated in Figure 3.3.

In practice, the actual sorption process is probably more complex. Nam and Kim (2002) reviewed the then-available literature on soil sorption of organics. They described soil sorption of persistent

organic pollutants as a multi-stage process, involving an initial, rapid labile sorption process which they considered to be at least partly reversible. This first sorption phase was followed by a much slower, so-called 'non-labile sorption', which produced a form of the pesticide that was less available to extraction and presumably less bioavailable. Such a model would fit the familiar phenomenon of lower extractable POPs in aged soils. A number of hypotheses are available to explain this observation, including the transfer of sorbed POPs to organic matter-lined micropores in soil.

The nature of interaction between soil organic matter, minerals, and persistent organic matter has been reviewed by Ren et al. (2018). Structure (aromaticity and aliphaticity), polarity, spatial arrangement, and physical conformation of soil organic matter (SOM) are interactive parameters on sorption of POPs. Sorption by minerals only becomes significant in oils of low organic matter content. A complete consideration of the topic in respect of all persistent organic pollutant pesticides is beyond the scope of the present review, but some examples of the findings of studies with DDT are given in the following. The general use of the term 'sorption' has generally been taken to refer to a long-term process. As identified by Nam and Kim (2002), more than one process is probably in operation. For example, in a study of DDT sorption by a number of Indian and African soils, Bami (1961) noted that there were significant differences between the amount of pesticide initially sorbed onto soil surfaces within half an hour of application and the amount remaining after several weeks. These differences could not be simply explained by organic matter content. In a more recent investigation, Cheng et al. (2014) employed selective extraction procedures to examine the sorption of DDT by farmland soils from northeast China. Smaller soil particles exhibited a greater sorption capacity for DDT. Both silica and an illite-montmorillorite mixed layer were capable of only low sorption of the pesticide, although iron oxide could sorb DDT, and manganese was inhibitory to the process. Organic matter however was by far the most efficient sorbent and amongst organic matter, that derived from plant material exhibited the highest sorption capability, followed by aromatic substances and products of microbial degradation. Wolcott et al. (1970) used a variety of extractants, including hydrogen peroxide, mineral acids, alcohol, and ether to study sorption of DDT by a range of US soils, that differed significantly in clay and organic matter content. While it is tacitly assumed that sorption of such pesticides is directly related to organic matter content, these authors identified a number of anomalies that might prevent a simple relationship from being established. For example, they noted that structural effects and water repellency of lipoidal materials may restrict the accessibility of adsorptive surfaces. They went on to point out that the field situation may be very different and it is also noteworthy that a great number of studies have been carried out using pure pesticides, rather than the formulations that are actually employed in the field situation.

Although the majority of POP pesticide soil sorption studies have been carried out with DDT, some investigations have also been carried out with other pesticides from this group. Luchini et al. (1981) studied sorption of four organochlorine pesticides by Brazilian soils. Soils richest in organic matter sorbed all substances except aldrin more strongly than the other soils. DDT was the most and aldrin the least sorbed organochlorine pesticide; dieldrin being sorbed 2- to 4-fold more strongly than aldrin. Sorption of lindane varied in different soils. In a further study of lindane sorption by soils, Wang et al. (2011) concluded that nonspecific interactions govern sorption of phenanthrene and lindane by humic substances. Their sorption is dependent on surface and bulk alkyl carbon contents of the sorbents, rather than aromatic carbon. The few studies that have been conducted with mirex show it to be strongly sorbed by soils with appreciable content of organic matter (Ali and Baugh, 2003).

Although most studies with POP pesticides other than DDT have concentrated on their sorption to organic matter, some investigations have also been carried out with clays. In an investigation of the sorption of endrin by montmorillonite and kaolinite, Peng et al. (2009) concluded the sorption is a combination of hydrophobic interaction and charge–dipole interaction. The sorption on both montmorillonite and kaolinite has obvious troughs at pH about 7.2 and 5.4, respectively, and these were attributed to the proton shift reaction of the broken bonds at the clay edges.

3.7 FATE AND DYNAMICS OF POP PESTICIDES IN THE ENVIRONMENT

From the foregoing sections and also advanced standard environmental chemistry texts, it is clear that the present group of pesticides and probably at least some of their metabolites will have extended environmental half-lives (cf. Connell and Miller, 2022; Manahan, 2022). Sorption of POP pesticides in soil can be satisfactorily described by the Langmuir, Freundlich, and Henry models, with most authors finding Freundlich to be the best fitted model (Cheng et al., 2014).

The significance of half-lives is rather clouded, because of the various processes which may contribute to the decrease of pesticide levels in environmental media. These processes include volatilization, fluvial transport, biodegradation, photolysis, and loss through runoff at the time of application. Very often, the initial application rate is unknown and estimates are made through an assumption that the overall process will follow first order kinetics (Boul et al., 1994; Blaylock, 2005). In general, for soils with low organic matter content and in tropical regions half-lives will generally be at the shorter end of the scale and at the longer end of the scale for soils in warmer regions, with high organic matter content. Some estimates of extremely low environmental half-lives in tropical areas are probably skewed by volatilization loss at the time of application. Of equal significance is the form in which the pesticide was initially applied. Pesticides may be applied as emulsions, wettable powders, granules, etc., and residues from granular formulations persist longer than those resulting from all other application methods (Boul, 1995).

It should also be noted that although the following section refers principally to pesticides that have been introduced by agricultural or other commercial use, there are also consistent reports of POP pesticide contamination in areas that have no history of such practices (Zhang et al., 2012; Tsiantis et al., 2022). Such depositions are taken to result from global distillation phenomena.

With these considerations in mind, Table 3.4 gives some stated half-lives for POP pesticides in soil. The data should be taken as indicative only and further discussion of specific situations follows.

Because of the low biodegradability of POPs in soil, transport processes assume a greater significance than with other types of pollutants. Transport of POPs in a dissolved state is unlikely to occur because of the relative water insolubility of these compounds. The pathway for transportation is via soil pores – the void spaces depicted in Figure 3.3. The contaminants may move through these spaces, either as microparticles of the pollutant molecule itself or as pollutant bound to colloidal material. The

TABLE 3.4
Stated Half-Lives for POP Pesticides in Soil (Indicative Data Only)

Pesticide	Stated Half-Life	Author
Aldrin	53 days	CDCP (Mackay and Shiu, 1981)
Chlordane	2.6–4 years	CDCP (Mackay and Shiu, 1981)
Dicofol	2–4 months	Pubchem (National Center for Biotechnology Information. Pubchem, 2023)
Dieldrin	2.5–5 years	CDCP (CDCP, 2023) Honeycutt and Shirley (2014)
Endrin	4–12 years	Pubchem (National Center for Biotechnology Information. Pubchem, 2023) HERO (1992)
Heptachlor	40 days–5.5 years	Pubchem (National Center for Biotechnology Information. Pubchem, 2023)
Lindane	15–23 months	Pubchem (National Center for Biotechnology Information. Pubchem, 2023) (Usmani et al., 2021)
Mirex	Up to 10–12 years	Deshmukh and Meshram (2015)
Toxaphene	1–14 years	CDCP (Mackay and Shiu, 1981)
DDT	2–15 years	(Blaylock, 2005)

principles of colloid mediated transport have been reviewed by McGechan and Lewis (2002). These authors also point to the significance of transport through macropores, which include worm holes, channels created by plant roots which have since died and withered away, cracks in dry clay soil, etc. The colloids responsible for this transport can include small soil particles to which the POPs have been sorbed by the processes described earlier and also suspended microparticles of humic matter.

The transport of colloid-sorbed POPs through soil pores is facilitated when water fills these spaces, as in during periods of rainfall or artificial irrigation. Naturally, the colloids will only move a certain distance through the soil profile, before being stopped by colloid capture processes, such as soil straining.

Before embarking upon a detailed consideration of processes involving individual POP pesticides in soil, it should be noted that a considerable amount of the research which has been undertaken has been performed with pure pesticide active ingredients, whereas the pesticides observed in field studies are generally formulated. These formulated pesticides contain not only the active ingredient, but also numerous other compounds, such as surface active agents, adjuvants, etc., all of which can be expected to modify the environmental behaviour of the pesticide in question (Jaquess et al., 1989).

3.7.1 Aldrin and Dieldrin

Aldrin and dieldrin are frequently encountered soil contaminants, because of their historical use as termiticides in soil (Bess et al., 1966). Since the application was to the A horizon of soils (where termites would be most likely to be found) the initial source of these pesticides was not simple deposition on the soil surface. Of the two pesticides, application of aldrin was more common, but the epoxidation process, referred to previously, resulted in the formation of dieldrin.

The electricity industry were major users of these pesticides for the preservation of wooden power poles. It was common practice to apply a mixture of aldrin, dieldrin, and creosote to soils as a wood preservative (Sadler et al., 1997). Although this application ceased around 1984 in Australia, aldrin residues between 36 mg/kg and 86 mg/kg and dieldrin residues between 16 mg/kg and 36 mg/kg could still be detected in surface soil samples taken from around the power poles, some 13 years later. Lateral movement downhill from the power poles resulted in levels of both pesticides, near the limit of detection 2 m away from the poles. The soils in question were typical Australian clay loam soils with an organic matter content <1%. Because conversion of aldrin to dieldrin is an aerobic process, it is restricted to the upper soil layers.

In terms of vertical movement of the pesticides through soil, in a dry soil (average annual rainfall 796 mm) both pesticides moved to only a limited extent through the soil and the aldrin:dieldrin ratio remained relatively constant. However, a parallel study at a swampy location (where the soil would have been around field capacity for most of the year), both pesticides were considerably more mobile. Although a significant portion of the aldrin was able to penetrate the subsurface layers, conversion to dieldrin could only take place in the aerobic layer of the soil. This was reflected in the aldrin:dieldrin ratios, as shown in Figure 3.4.

Aldrin and dieldrin also found extensive use in rice paddies for control of mosquitoes (Whitehead, 1951) and were also a popular treatment for the control of insect pests. Thus, elevated levels of these pesticides are frequently reported in soils from rice growing areas (Kim and Smith, 2001; Chaiyarat et al., 2015).

The processes of degradation of aldrin and dieldrin in soils have been outlined in a previous section and will be further considered in the section on bioremediation. Studies under controlled conditions have pointed to the importance of maintaining a soil moisture level above 10% and of constant temperatures of 30°C and above (as compared to variable temperatures experienced in then natural environment). Endosulfan appeared to inhibit the natural biodegradation of aldrin and dieldrin in soils (Ghadiri et al., 1995).

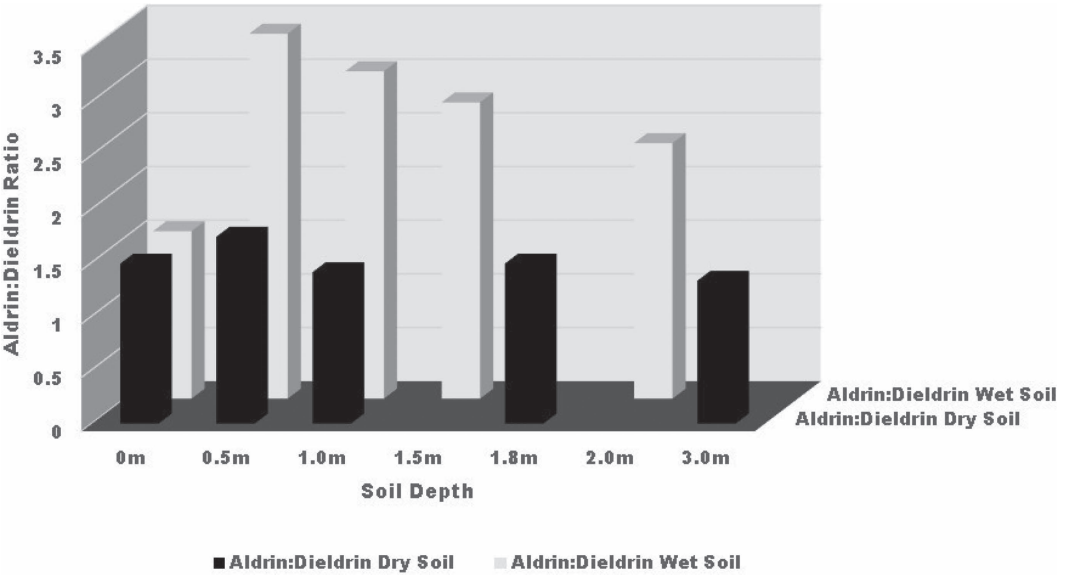


FIGURE 3.4 Variation in the aldrin:dieldrin ratio with depth in soils where there had been historical use of these pesticides for termite control.

3.7.2 Chlordane

Like the previous pesticides, chlordane also has a history of use to control soil-borne pests such as termites and hence its residues do not always result from simple surface application. Moreover, like DDT, which is discussed later, technical chlordane is a mixture of isomers – the most abundant of which are γ-(trans-)chlordane, α-(cis-)chlordane, and trans-nonachlor. Additionally, the old technical chlordane used for over 35 years contained less than 60% of the α and γ-chlordanes, but could contain about 10% heptachlor (Tafuri et al., 1977). In studies with a trial plot of alfalfa, these workers concluded that the γ-chlordane is more stable in soil than the α-isomer.

As has been mentioned before, many studies of POP pesticide pollution in soil are bedevilled by the fact that the original application rate is unknown. However, Mattina et al. (1999) were able to obtain original application data for a lawn on the New Haven campus of the Connecticut Agricultural Experiment Station in the USA that had been treated with technical chlordane in the spring of 1960 as part of a crabgrass control experiment. This site provided a unique opportunity for study of the weathering profile and the vertical and horizontal movement of technical chlordane during the 38 years since its application. It was calculated that 1,818 g of technical chlordane was applied in 1960. The chlordanes exhibited a biphasic decrease at the site, with the first phase from year 0 to year 8 and the second phase beyond that. This second phase was much slower and the authors pointed out that these complex kinetics (which are to be expected for a multi-component mixture such as technical chlordane) mean that the half-life of this pesticide has probably frequently been under-estimated. The value of 2.6–4 years given in Table 3.4 would pertain to the first phase only and the overall half-life could be of the order of 20 years.

The complexity of the chlordane mixtures applied may also reflect the results of a 2007 study of some 31 soil samples from the northern Indo-Gangetic alluvial plain. Although the mean concentration of γ-chlordane was higher than that of α-chlordane in all the soil samples, the detection frequency of the α-chlordane was higher in the soil samples than γ-chlordane (Singh et al., 2007).

3.7.3 Dicofol

This pesticide has received less attention than other POP pesticides as regards its movement and overall behaviour in soils. Nevertheless, there are periodic reports of dicofol residues and their mobility in soil. For instance, in vertisols of the Lower Namoi Valley in New South Wales, residues of dicofol were shown to have moved to an appreciable depth in soil, the dicofol having been applied in the past to control early season insect pests in cotton crops (Weaver et al., 2012). Similarly, at the site of former dicofol production in Vietnam (the factory had closed five years prior to the study), dicofol residues could be detected at up to 5 m depth in the silty clay layer underlying the former factory. Significant quantities of DDE were also found in the soil, DDE being an intermediate in the dicofol production process employed at the factory (Liu et al., 2015).

Colloidal transport is a likely candidate for a transport mechanism with this pesticide. Brunninger et al. (1999) showed that a strain of *Pseudomonas fluorescens* could bioaccumulate ^{14}C-dicofol with a bioconcentration factor of 279 within 30 minutes. In soil column experiments, in which bacteria with a prehistory of dicofol accumulation were used, it was shown that the bacteria could provide a mechanism of colloid transport for the pesticide through soil. The authors noted that soil organic matter has a higher affinity for the pesticide than does the *Pseudomonas* strain employed and much of the applied label was sorbed in the upper soil layer. They speculated that bacterial-mediated colloid transport through the soil profile could be particularly significant at heavily contaminated sites. The former production facility investigated by Liu et al. (2015) could be an example of this.

3.7.4 Endrin

Endrin residues have been frequently encountered in soil and the pesticide shows considerable persistence. In the previously mentioned study (Weaver et al., 2012) of soils in the cotton growing area within the Namoi Valley in New South Wales, endrin residues could be detected up to 1.2 m deep in soil. Of the pesticide residues studied, it ranked behind DDE and endosulfan sulfate as the third most prominent residue. Endrin has also been found as a significant soil pollutant in the land around Bahía Blanca, Argentina, being found at the highest concentrations in the land of the oldest farms. These workers also conducted principal component analysis to identify associations with soil organic matter, and endrin (along with DDT, dieldrin, and heptachlor epoxide) was part of a group associated with higher soil organic matter and clay contents (Andrade et al., 2005).

In a study of endrin of organochlorine insecticides in Palakkad soil in India, endrin was the predominant pesticide and its presence showed a significant positive correlation between sand and proteins, and strongly correlated to lipid content in the soil. The authors underlined the importance of speciating soil organic matter, in order to correctly predict sorption of xenobiotics (Gopalan and Chenicherry, 2018).

A large amount of early work concerns the persistence of endrin in soils and this is summarized in HERO (1992). Endrin can be retained, transported, or degraded in soil, depending on a number of factors. The greatest retention occurs in soils with a high content of organic matter. The persistence of endrin is highly dependent upon local conditions; its half-life in soil can range up to 12 years. Volatilization and photodecomposition are the primary factors in the disappearance of endrin from soil surfaces. Under the influence of sunlight (ultraviolet light), the isomer delta-ketoendrin is formed. In the intense summer sun, about 50% of endrin was isomerized to this ketoendrin within 7 days. Microbial transformation (in fungi and bacteria) takes place, especially under anaerobic conditions, to give the same product.

3.7.5 Heptachlor

A large body of earlier literature pertains to the behaviour of heptachlor in various soils. One of the more detailed studies was reported by Wingo (1966). The study reported on the disappearance of

heptachlor from a typical Missouri soil. Heptachlor was applied in abnormal amounts (11.2 kg/ha), and the effect on these soils was conducted over an eight-year period from 1957 to 1965. The greatest loss (50% or more) occurred during the first two years. Heptachlor had disappeared or occurred only as heptachlor epoxide by the end of the seventh year. The maximum amount of heptachlor epoxide appeared during the fifth year following application and then declined slowly. The rate of disappearance was quite variable but, in general, heptachlor and heptachlor epoxide declined more slowly in soils to which high concentrations were applied initially. In a comparative part of the study, it was found that dieldrin was lost from the soil more slowly than heptachlor.

In a more recent study, Miglioranza et al. (2003) investigated heptachlor and heptachlor epoxide levels from three types of sites in the south eastern region of Buenos Aires Province, Argentina. These sites comprised highland hills (designated 'natural sites'), which had never received any applications of heptachlor; recreational areas on the margin of Los Padres Lake (designated 'recreational areas'), which had also never received any applications of heptachlor; and an agricultural belt on the northwest area of the lagoon. These latter areas (designated as 'agricultural soils') had been continuously farmed for the preceding 25 years, during which time, heptachlor application would have taken place (use of the pesticide was banned in Argentina in 1994). At all sites, the soil concentrations of heptachlor and heptachlor epoxide were measured at three soil depths viz. 0–15 cm, 15–30 cm, and 30–45 cm. The results are shown in Figure 3.5 and clearly demonstrate the movement of pesticides away from the area where they had actually been applied.

There are several comments which could be made regarding these results. Firstly, of particular surprise are the observed levels of heptachlor and particularly heptachlor epoxide from the mountain sites. The paper does not mention the actual mountains or their altitude, but at least some of this deposition may result from the reported cold trapping of POPs by high mountains (Wania and Westgate, 2008).

The relatively low levels of residues observed in agricultural soils could reflect both transport and loss of pesticides from these sites by volatilization and also the fact that, over a lengthy period of pesticide application, an efficient microbial flora in terms of the degradation of these residues may have evolved. The evolution of suitable microbes would undoubtedly have been aided by the ongoing supplementation of the soil through fertilizers etc. as part of normal agricultural practice (cf. Doolotkeldieva et al., 2021).

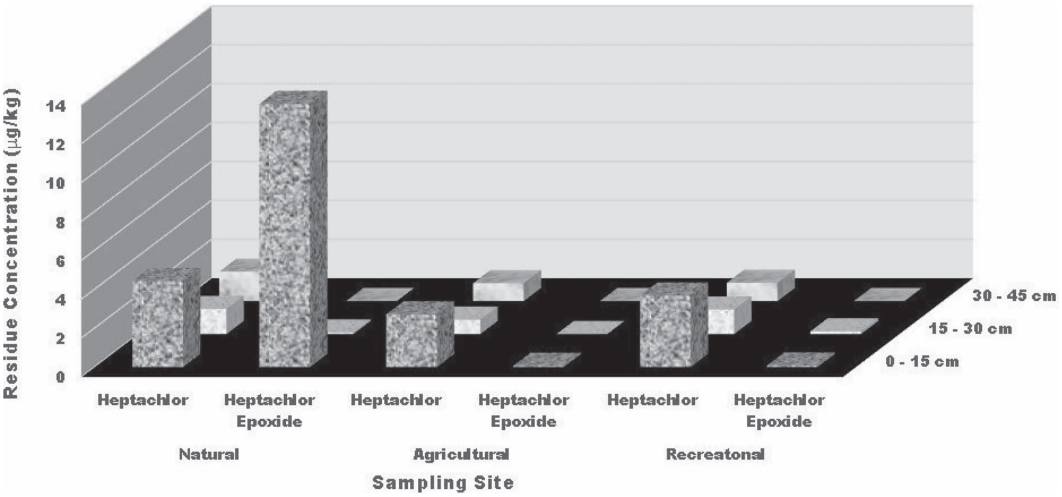


FIGURE 3.5 Heptachlor residues from sites in southeastern Argentina (data from Miglioranza et al., 2003).

3.7.6 Lindane

The term 'lindane' strictly refers to γ-HCH, but technical lindane is a mixture of HCH isomers, which contains 60–70% of α-HCH, 5–12% of β-HCH, 10–12% of γ-HCH, 6–10% of δ-HCH, and 3–4% of ε-HCH (ATSDR, 2023). Both pure lindane and technical lindane have been used as pesticides (Chakraborty et al., 2017), although most experimental studies have concentrated on pure γ-HCH. Early column leaching studies showed γ-HCH to be more mobile in soils than DDT and to be lost more readily when soils were subjected to wetting and drying cycles (Guenzi and Beard, 1967). Several authors have noted γ-HCH to be more mobile in sandy soils than in clay soils. Similarly, in a 2008 study of pesticide sorption to various Indian soils, Krishna and Philip (2008) observed that more than 70% of lindane was adsorbed on compost and clayey soil within 1 hour whereas the adsorption of lindane on sandy soil was only 35%. These workers noted that γ-HCH sorption data fitted better with Freundlich isotherm model ($r^2 > 0.97$) than Langmuir model ($r^2 > 0.88$). There was a direct correlation between the soil K_{OM} and the sorption capacity of the soil. Lindane was more strongly sorbed than the organophosphate and carbamate pesticides with which it was compared in the study, until the pH was decreased below 4.0.

In another study with two Indian soils, Singh et al. (2013) also found the pesticide γ-HCH to be quite mobile in soils, the observed mobility being a product of both the soil type and organic matter content. Sorption in these soils was best described by the Freundlich equation and the authors considered breakthrough into an underlying aquifer to be a distinct possibility.

It is clear from the foregoing publications that most authors have conducted their studies using high purity γ-HCH, although field soils have been contaminated by technical 'lindane', whose composition has been given above. In a study of soils from Poznań, Poland, Waliszewski (1993) concluded that the spectrum of HCH isomers in soils reflected the nature of the chemical applied and was not the result of bioisomerization. Chakraborty et al. (2017) summarized a number of extensive studies pertaining HCH isomers in soil from different areas of India. Isomeric composition of soilborne HCH isomers showed elevated δ-HCH for sites in New Delhi close to the Uttar Pradesh border as well as in all the sites of Agra located within Uttar Pradesh. This contamination may have reflected the proximity to HCH manufacturing sites. In Haryana, a north Indian state in the western part of New Delhi, agricultural soil from paddy-wheat, cotton-wheat, and sugarcane fields were detected predominantly with γ-HCH. In most locations of Kolkata (formerly Calcutta), a major metropolitan city in eastern India, α-HCH was found to be one- to two-fold higher than γ-HCH, indicating ongoing use of technical HCH apart from lindane. Agricultural soil in Thiruvallur district of Tamil Nadu (southern India) showed elevated concentrations of γ-HCH, with residual levels of α- and δ-HCH that were lower than those of γ- and β-HCH. In Bangalore γ-HCH was predominant, but a fair amount of α- and β-isomers were also present. It was pointed out that urban healthcare programs (viz. eradication of malaria-carrying mosquitoes, head lice treatment, etc., could account for the elevated lindane levels in such urban areas). Soilborne β-HCH dominated the concentrations of HCH isomers in Mumbai and Goa possibly due to the ongoing usage of technical HCH mainly for cotton cultivation practiced in the western and central parts of India. Examples of these data are shown in Figure 3.6.

Production wastes from lindane plants can be quite complex mixtures, representing everything from routine wastes to improper disposal of failed batches. Lorenzo et al. (2020) identified 28 chlorinated organic compounds in a liquid waste from a lindane production facility. The waste had been placed in a landfill in Sabiñanigo (Spain). This liquid waste migrated by density through the subsurface to greater depths, being trapped or adsorbed into the soil in this movement posing a significant risk to the groundwater. It was shown that the concentration of chlorinated organic compounds in the aqueous phase depends linearly on its mole fraction in the liquid waste. Furthermore, the partitioning of liquid waste components into water was similar, whether the partitioning took place from free liquid waste or liquid waste sorbed to soil.

Considerable attention is being placed on β-HCH, because of the relatively high levels that have been detected both in the environment and human tissue. Evidence for migration and relocation of

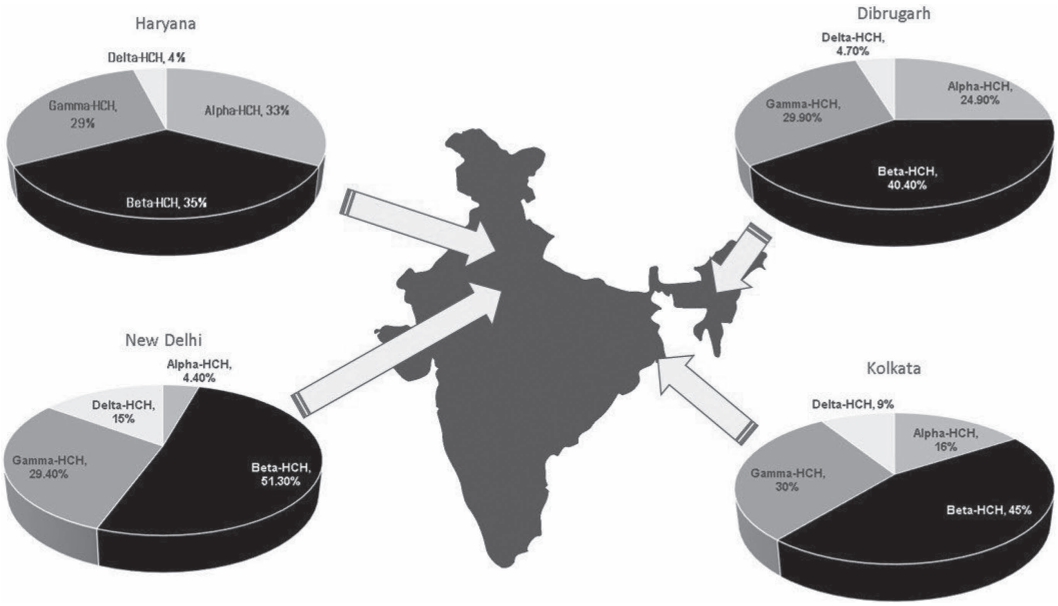


FIGURE 3.6 Differing distributions of HCH isomers at locations in India (data from Chakraborty et al., 2017, and Mishra et al., 2012).

this pesticide from Chinese soils has been obtained, with movement both through global distillation and cold trapping on the Tibetan Plateau (Xu et al., 2012).

3.7.7 Mirex

Most of the environmental fate data pertaining to mirex comes from early work. Furthermore, because the pesticide was generally applied as soil surface baits, it had less opportunity in comparison to other POP pesticides to enter the soil environment. In a study involving application of mirex-containing baits, Jones and Hodges (1974) concluded the pesticide moved only sparingly into soil. They could find no evidence of degradation by soil micro-organisms over a six-month period. Similarly, in Hawaii, where surface baits were employed to control a symbiont of the pineapple mealybug, Johnson et al. (1976) could only demonstrate 4.5% of the mirex in baits made its way into soil.

The pathways by which mirex made it way into biota and became an environmental concern are fully described by Kaiser (1978), but they do not involve the soil environment to any significant degree.

3.7.8 Toxaphene

Toxaphene was a broad-spectrum insecticide with a range of application across virtually all areas of agriculture. The commercial product is known to comprise a mixture of some 177 compounds, of which some 26 occur at concentrations greater than 1%. Toxaphene is known to have an extended half-life in soil and to be capable of being rapidly lost to the air through evaporation, although cultivation of the soil largely eliminates the evaporation pathway (Korte et al., 1979).

Some reports suggest that toxaphene can exhibit relatively rapid mobility in soils. A 1973 study in which toxaphene was applied to Dunbar topsoil in a field plot in the South Carolina Coastal Plain found the pesticide to be lost from the surface layer in a biphasic process – a brief initial phase and a much

more significant second phase which was crudely linear on a log residue vs. log time plot. The overall half-life of toxaphene in the surface layer was of the order of 100 days. Toxaphene could be detected in the underlying groundwater within two months of surface application (LaFleur et al., 1973).

Although the normal processes responsible for movement of POP pesticides through soil would be operative in the case of toxaphene, some special soils may offer additional pathways. Gallagher et al. (1979) noted that in anaerobic salt marsh soils, toxaphene, applied subsurface, could be taken up by the tissue of the marsh plant *Spartina alterniflora*, where it underwent bidirectional translocation – both upward into the stems and downward into the roots. The authors observed this effect in sandy and silty clay loam marshes. They suggested that the downward movement followed by eventual decay of the roots represented a novel means of moving toxaphene downward through the soil profile.

Equally however, there have also been reports that toxaphene is relatively immobile in soils, with the bulk of the applied pesticide remaining in the upper 10 cm of the soil. Very likely, these disparate findings can be rationalized by the fact that the studies which reported high toxaphene mobility employed the commercial formulated product. This product contains many other chemicals (adjuvants, surface active agents, etc.) that can drastically affect the environmental behaviour of a chemical. Studies showing only limited mobility employed the pure pesticide include that of Jaquess et al. (1989). Similarly, Morrison and Newell (1999) concluded that the reason toxaphene could be detected at depths exceeding 30 feet (9.1 m) below a former pesticide formulation facility was that the pesticide had been transported there through solvation in xylene, which was also used at the facility.

3.7.9 DDT

DDT has been a major focus of investigations of the fate of POP pollutants in soil. The studies that have been conducted include specific investigations involving applied p,p′-DDT (e.g. Boul, 1996) as well as field investigations of the situation prevailing in areas where DDT was applied as an insecticide. The DDT applied in these cases would have been technical grade DDT, whose most common formulation used as insecticide contains 85% p,p′-DDT, 15% o,p′-DDT and traces of o,o′-DDT and other compounds.

Despite this, few authors have considered isomer-specific data (cf. Ricking and Schwarzbauer, 2012), the authors finding only about 2.5% of the papers surveyed presented isomeric data. Capillary column gas chromatography, which is required to obtain the relevant data, has been available for many years. The distinction between the two isomers is not merely of academic interest, because differences in physiological effects have been reported (Wetterauer et al., 2012). In their review of the data that were available, Ricking and Schwarzbauer (2012) concluded that the o,p′-/p,p′-ratios of DDT and DDD have been detected more or less on the same level, whereas the isomers of DDE were definitely depleted by the o,p′-isomer in all environmental compartments. Differences in half-life between o,p′- and p,p′-DDT ranged between 14 and 12 years for o,p′-DDT and 11.8 and 10.5 years for p,p′-DDT in control soils and sludged soils, respectively.

Studies in which ^{14}C labelled DDT was applied to soil media have demonstrated that particle mediated vertical transport can occur. When the DDT was applied with sewage effluent, particles to which the pesticide was absorbed were able to transport 18% of the radiolabel to a depth greater than 9 cm in a sandy loam soil (Vinten et al., 1983). This type of study however underlines a major problem as regards attempts to perform controlled experiments with POP pesticide pollutants – viz. that because of the environmental persistence of the compounds, potential studies would have to continue for a very lengthy period.

Particularly in tropical countries, volatilization of DDT from the soil surface at the point of application represents a major pathway of environmental dissipation (cf. (Adetunji et al., 1999). But because there are few applications of DDT today worldwide and because the present review is concerned with soil processes only, this pathway will not be pursued further.

Dalla Villa et al. (2006) investigated the movement of DDT residues into soil over a period of seven months at a site in Mato Grosso State, Brazil, where improper storage of pesticides had taken place. They study concentrated on two soil horizons (0–15 cm and 90–100 cm), the organic carbon contents of the two layers being 4.6% and 0.5% respectively. Even over this limited period, it was concluded that vertical migration of DDT was taking place and posed a threat to groundwater.

It is axiomatic that DDT sorbed in soil, whilst an unfortunate consequence of previous agricultural practices, is also sequestered away from the biosphere. However, so long as the pesticide remains in the soil environment, it constitutes an ever-present threat of re-release and mobilization. Over the past decade, emphasis has moved away from a simple consideration of levels in soil to processes that could lead to re-mobilization from a contaminated soil. The active ingredient of an applied pesticide is only a small proportion of the overall chemical applied. The remainder of the formulation consists of so-called 'inert ingredients'. On average, they constitute 86% (by mass) of the preparation. This group includes solvents, carriers, adjuvants, etc. But because they are added to aid application of the pesticide, they can also alter the environmental properties of the substance. The US EPA estimates that there are around 3,000 'inert ingredients' in pesticide formulations and that about 50% can cause significant harm to the environment or public health (Moore, 2023).

And whilst POP pesticides may be banned in most parts of the world, agricultural lands see ongoing application of other pesticides, which contain inert ingredients. Therefore, the possibility exists that these may alter the environmental status of historically applied pesticides, such as sorbed DDT in the soil. Thus, in field studies, Neitsch et al. (2016) were able to demonstrate an increased release of DDT and its metabolites (collectively referred to as 'DDX') following routine application of modern pesticides to a soil with historical chlorohydrocarbon contamination. The effect was attributed to the presence of surfactants in the modern formulation, with those formulations employing Tween polysorbates being particularly effective in the release of DDX.

Other processes that could occur in a field situation can also lead to mobilization of DDX. These include treatment with oxalate or root exudates (Luo et al., 2006) and increasing concentrations of humic (but not fulvic) acid when the pH was decreased to 5.5 (Haarstad and Fresvig, 2000).

The subject of biodegradation of DDT in soils has received an enormous amount of attention, because of the potential for use as a remediation tool. Organisms active in this process have already been described in an earlier section. The topic will be further considered in the section on remediation of soils contaminated by POP pesticides, but a few basic facts can be given here. In earlier studies, Boul et al. (1994) noted that DDT loss in soil could be enhanced by agricultural practices such as irrigation and addition of superphosphate and the authors correctly attributed the loss to biodegradation. The results of subsequent early field studies were reviewed by Foght et al. (2001). DDT biodegradation has been observed in tropical and temperate soils, with higher levels of degradation being observed in the former soils. Both aerobic and anerobic processes may be involved, with sorption to soil organic matter generally being viewed as a competitive process with biodegradation. Biodegradation of the pesticide is generally reduced at acid pH values and the process shows maximal activity above pH 7. DDT biodegradation may be stimulated by natural inducers such as lignins and terpenes but is inhibited by free radicals produced from naturally occurring humic and fulvic acids.

Bioremediation processes for DDT in contaminated soils are generally based upon means of enhancing the aforementioned naturally occurring processes, which occur at only a slow rate, particularly in temperate soils.

3.8 TOXICITY, EXPOSURE, AND POTENTIAL RISKS TO THE ENVIRONMENT AND HUMAN HEALTH

The fact that the POP pesticides have been included in the Stockholm Convention list of POPs clearly attests to the perceived threat they pose to both the environment and public health. This is detailed more fully elsewhere than could be achieved in the space of the present review (e.g. Connell and Miller, 2022; Adeola, 2004; Alharbi et al., 2018).

In considering the environmental effects of these substances, it is important to note that their effects are not mediated through the formation or breakage of any covalent bonds. Because of their lipophilic nature, the POP pesticides accumulate in adipose tissue and secretions, with generally little metabolism and very slow rates of depuration. Organisms can thus bioconcentrate these pesticides from environmental media and biomagnification can also occur within the food chain Connell and Miller (2022).

Table 3.5 summarizes the reported ecological and human health effects of the POP pesticides.

Because this chapter is primarily concerned with POP pesticides in the soil environment, it is obvious that, leaving aside the consumption of unwashed root crops, exposure to soil-borne pesticides will largely be indirect, via the food chain. It therefore follows that risk of human ingestion

TABLE 3.5
Reported Human and Ecological Health Effects of POP Pesticides[7],[9]

Pesticide	Human Health Effects	Ecological Health Effects
Aldrin	• Because of facile conversion to dieldrin, difficult to determine individual effects and usually considered jointly with dieldrin	• Because of facile conversion to dieldrin, difficult to determine individual effects and usually considered jointly with dieldrin
Chlordane	• Possible human carcinogen • Induces liver enzymes and enhances metabolism of steroid hormones, including oral contraceptives • Can cause permanent alterations of nervous system function, including problems with memory, learning, etc.	• Many marine and freshwater organisms are adversely affected by chlordane at sub ppb levels • Very toxic to some species of birds • Produces liver cancer in laboratory strains of mice
Dicofol	• Listed by the US EPA as a possible human carcinogen • Based upon rat models, may also exert reproductive effects	• Endocrine disrupter • Interferes with ion channels in neurons, so that excessive sodium accumulates, causing abnormal stimulation of the poisoned animal • Several confirmed environmental degradation products also very toxic to wildlife
Dieldrin	• More recent review of 1987 US EPA data does not support the contention that dieldrin is a human carcinogen • Neurotoxic effects in the central nervous system • Implicated by some authors as a causal agent in neurodegenerative diseases	• Very toxic to some bird species, such as meadowlarks, robins, ring-necked pheasants, although others such as house sparrows show a high resistance to dieldrin poisoning • Also very toxic to small mammals, such as ground squirrels, muskrats, and rabbits • Bioaccumulates in organisms • Causes neurotoxic effects in the vertebrate central nervous system • Causes reproductive effects in teleost fish
Endrin	• Acutely toxic to humans with a lethal dose of l0 mg/kg body weight and causes convulsions at a threshold of 0.25 mg/kg body weight	• Toxic to fish and crustacea • Less toxic to amphibians, but some behavioural effects reported with these organisms • Endrin depurates faster than toxaphene • Decreases longevity in some insects but has no effect on oviposition
Heptachlor	• Implicated as a causal agent in breast cancer by some studies • Present in breast milk and has been implicated by some (but not all) studies in early retardation	• Effects on larval epidermis in frogs • Effects on bird populations through accumulation in soil arthropods; particularly significant for ground-dwelling birds

TABLE 3.5 *(Continued)*
Reported Human and Ecological Health Effects of POP Pesticides[7],[9]

Pesticide	Human Health Effects	Ecological Health Effects
Lindane	• Highly immunotoxic and neurotoxic poison • Causes a decrease in lymphocytes • Endocrine disruptor • Possible carcinogen (lindane) • Probable carcinogen (technical grade HCH)	• Highly toxic to aquatic organisms • Moderately toxic to birds • Reports of effects on estrogenic activity for a number of species • Particular concerns regarding arctic species because of the amount of lindane brought to the arctic environment by global distillation
Mirex	• General lack of data; health effects generally inferred from animal studies	• Particularly lethal to crustacea • Also quite toxic to some algae • Moderately toxic to honeybees • Bioconcentration factors in crustacea and sensitive algae >1000
Toxaphene	• Possible effects on liver, kidneys, and immune system • Rated as a probable human carcinogen	• Toxic to fish and crustacea • Less toxic to amphibians, but some behavioural effects reported with these organisms • Possibly liver cancer in mice and thyroid cancer in rats • Decreases longevity in some insects and also affects oviposition
DDT	• Neuropsychological dysfunction • Endocrine disruption • Reproductive disorders (probably mediated by DDE) • Equivocal results from cancer studies, with pancreatic cancer a possible end point • Increasing evidence as a causative agent in diabetes	• DDE decreases eggshell thickness and causes embryo deaths in birds • DDT affects various systems in aquatic animals including the heart and brain • Highly toxic to fish and moderately toxic to amphibians

will be governed by the ability of food species to uptake and bioaccumulate POP pesticides from soil. Initially, it was tacitly believed that POP pesticides could not pass the root barrier. However, the pioneering studies of Lichtenstein and his collaborators clearly showed this not to be the case as regards several POP pesticides including aldrin and heptachlor (Lichtenstein, 1959, 1960; Lichtenstein and Shulz, 1965).

The downward transport of toxaphene by salt marsh plants (Gallagher et al., 1979) has already been described in previous sections. More recently Mattina et al. (2000) described the accumulation of chlordane from soil into the edible parts of carrots, beets, and potatoes, when grown on chlordane-contaminated soil. In terms of other food plants grown on the same soil, individual plant physiology of the species seemed to govern the translocation. Chlordane was detected in the edible aerial tissue of spinach, lettuce, dandelion, and zucchini, whereas it was not detected in edible aerial tissue of tomatoes, peppers, and corn; trace amounts of chlordane were detected in the edible aerial tissue of bush beans and eggplant. Uptake of DDT from contaminated soil into roots of the pumpkin variety of *Cucurbita pepo* ssp. *pepo* was lowest in soil with high organic matter content (Lunney et al., 2010). In further studies with carrot uptake from soil contaminated with α- and γ- HCH as well as DDT and DDE, Waliszewski et al. (2008) found the majority of the POP pesticides accumulation to be in the root peel, the concentration of pesticides in this tissue being 3–7 times that

in the root flesh. Äslund et al. (2010) studied the phytoextraction of ΣDDT (DDT + DDD + DDE) from a contaminated soil by a pumpkin variety of *Cucurbita pepo* ssp. *pepo*. Soil amendments did not increase uptake, and ΣDDT concentration in leaves and stems decreased exponentially with distance from the roots.

In terms of human exposure, which will ultimately drive most risk assessments, the important consideration to come out of these studies is whether phytoextraction of POP pesticides from the soil can lead to an exceedance of the maximum residue level (MRL) in the relevant food product. Olatunji (2019) found that, when grown in DDT-contaminated soil, spinach, lettuce, celery, parsley, cabbage, dhanial, and kale were all capable of accumulating the pesticide in leafy parts used for human consumption, although the levels were below those of the WHO MRL. The author pointed out however that the uptake of DDT from the soil could be a contributory factor to MRL exceedance, were the plant to be exposed to an additional source of DDT. Ali et al. (2019) reached a similar conclusion regarding a range of leaf and root vegetables, grown in Pakistan soil, which was contaminated with a range of POP pesticides. Not all studies however have shown uptake from the soil to result in levels below the MRL in edible parts of food plants. Tao et al. (2005) grew eight types of vegetables in rhizosphere soils and bulk soils collected from two sites (A and B) in Tianjin, China. The soils had appreciable levels of ΣDDT and HCH isomers. ΣDDT in spinach and cauliflower from site B and lindane (γ-HCH) in cauliflower from both sites and violet from site B exceeded the maximum residual limits. Similarly, in a study of vegetables grown on contaminated soil in Ghana, Bolor et al. (2023) concluded that the contaminants (aldrin, endrin, DDT, heptachlor, and HCH isomers) probably posed a significant health risk to children and a lesser one to adults. Given that other chlorinated organic pesticides (currently not listed in the Stockholm Convention) are known to be phytoextracted into food plants, resulting in MRL level exceedances (Florence et al., 2015), it must be concluded that this pathway can, under favourable conditions, constitute a potential threat to public health.

Waste vegetable matter is frequently used as a source of food for animal species used to provide a human food source. This clearly represents an additional pathway for contaminant uptake into the human diet if the animals were fed lettuce and other accumulator vegetables that had been grown in contaminated soil. Tao et al. (2009) concluded that contaminated food was the major source of ΣDDT and HCH isomers found in chicken products in China. Although the levels in chicken flesh were relatively low, much higher concentrations were found in chicken skin and visceral organs, all of which form an important part of the traditional Chinese diet. The investigators went on to point out that in China, as elsewhere, there are two forms of poultry production – namely intensive rearing in battery facilities and also free range, the latter being promoted as offering a more 'organic' product. But this type of husbandry is also probably more prone to animals coming into contact with leaf vegetables grown on contaminated land. The significance of these findings was underlined by the authors' conclusion that as regards the average diet of Chinese residents, the contributions from chicken and egg consumption to per capita daily intake of HCHs and ΣDDTs were 487% and 88% of those of fish consumption.

It would be of interest to see similar studies carried out with pigs, which are also often fed vegetable waste, but the authors are not aware of any such study having been performed at the time of writing (05/2023). In the case of other animals raised for meat production, however, there exists a more direct pathway for uptake of POP pesticides from the soil and that is direct ingestion. Beef cattle for example have been shown to consume around 1 kg of soil per day (Cullen and Connell, 1994). McEwan (1990) estimated that a 300 kg bullock could reach the MRL for dieldrin in about a week, by consuming contaminated soil.

There have been a few studies with dairy cattle, but these do not give a clear representation of the direct soil uptake term, because ingestion of foliage probably also took place. Paton and Petterson (1997) exposed sheep to dieldrin-contaminated soil. Accumulation of dieldrin in fat of sheep was most efficient when soils of high organic matter content were fed, and was lowest when sandy soils

were fed. Tissue residues of dieldrin fell within 10 days of cessation of feeding of contaminated soil. The half-life of the pesticide in fat was estimated to be between 96 and 116 days, but the workers acknowledged that wool could also act as a sink for the contaminant. Harrison et al. (1970) studied the incorporation of DDT from contaminated soil into ewes and noted that maximum residues in fat occurred about one month after lambing.

None of these studies is particularly relevant to the beef cattle situation. With sheep, the high lipid content of the coat provides an additional excretory pathway for POP pesticides ingested. Therefore, a feeding study was conducted with cattle, using the dieldrin-contaminated soil collected from around wooden power poles, illustrated in Figure 3.7. Uptake of dieldrin (but not other pesticides present in the soil) was rapid and substantial. Uptake from sandy soils was more efficient than that from clay soils. The experiment was terminated after 8 weeks, because of the high levels of dieldrin in the tissues. Depuration of the accumulated pesticides was a slow and complex process, requiring a longer period (averaging approximately 7 months) than accumulation. Attempts to speed depuration by including sub-clinical levels of liquid paraffin in the diet did not produce any significant effect (Sadler et al., 2005).

Figure 3.7 Illustrates the uptake of pesticide and the relative distribution in the tissues.

3.9 REMEDIATION OF SOILS CONTAMINATED WITH POP PESTICIDES

Because of the nature of the POP pesticides, their resistance to normal biodegradation, their ability to bind strongly to soils with high organic matter content, and their general immobility in the environment, it is generally unlikely that residues of these substances will exhibit much attenuation with time. Moreover, their persistence, combined with the data in the previous section, showing that their residues can be accumulated by human food sources, provides a high imperative for the remediation of land contaminated by these substances. The overall subject of remediation of these pesticides has been the subject of a recent extensive review (Aparicio et al., 2022).

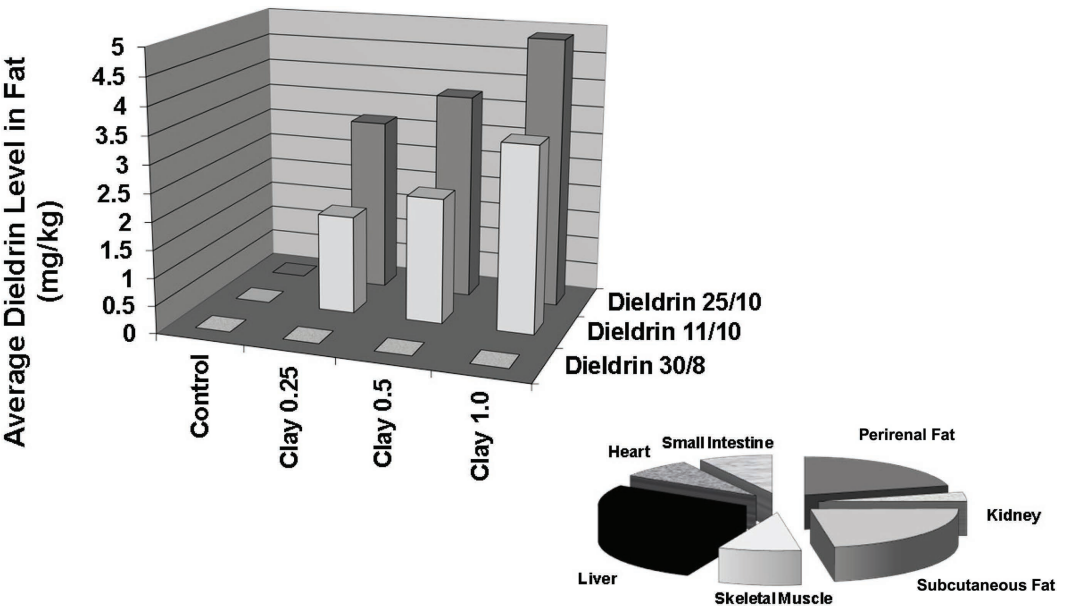


FIGURE 3.7 Uptake of dieldrin from contaminated soil by cattle and relative tissue distribution (data from Sadler et al., 2005).

As with all contaminated land remediation, the most important prerequisite is a set of chemical analyses that will provide a suitably representative picture of the situation at hand and it is advisable that referee samples be sent to more than one laboratory as part of this process. Generally, soil dilution approaches are not a satisfactory means of remediation. The two general approaches which are available are:

- Removal of the soil and treatment of the excavated material with some process which will strip the contaminants from the soil. This does not destroy the contaminants, but does render them in a form that is more amenable to processes such as high temperature incineration, etc., which can then be used to destroy the POP pesticides.
- On-site (*ex-situ*) or *in situ* processes, which may be used to effect degradation of the pesticide.

Both types of remediation will require a final round of analysis before the site can be declared uncontaminated and regulatory bodies will generally insist on referee and analysis as part of this phase. As with development of laboratory methods for extraction of POP pesticides from contaminated soil, the use of spiked soil or sediment is inappropriate for validation of methodology.

In terms of technology that will remove POP pesticides from the soil matrix, many techniques have their origins in scaled-up versions of procedures employed during routine laboratory analysis of soils. Cosolvent washing is a popular method in this regard. For example, Smith et al. (2004) found that the use of cosolvents could release up to 77% of p,p′-DDT from a contaminated soil. Increasing the solution concentration and hydrophobicity of the cosolvent increased the amount of p,p′-DDT desorbed. The amount of p,p′-DDT desorbed increased in the order 5% 1-propanol << 50% ethanol << 50% 1-propanol. Repeated washing of the soil with various cosolvents, in all but two cases, markedly increased the total amount of p,p′-DDT desorbed from the soil. For example, repeated washing of the soil with 50% ethanol increased the amount of p,p′-DDT removed by 42% while repeated washings of the soil with 50% 1-propanol had little effect on the amount of p,p′-DDT desorbed. The authors concluded that that the soil-solution ratio was an important parameter in controlling the amount of p,p′-DDT desorbed. Although the experiments were carried out in batch mode (which would equate to treatment of excavated soil), column studies have also raised the possibility that *in situ* cosolvent washing could prove a viable option (Juhasz et al., 2003). The major drawback of cosolvent extraction is that, although efficient, it requires large volumes of solvent which then require to be regenerated, so they can be re-used.

Other scaled-up versions of laboratory procedures have also offered potential for stripping of POP pesticides from soil. Sonication extraction is a standard laboratory procedure for removing lipophilic organics from the soil matrix, prior to analysis. Thangavadivel et al. (2011) employed high-power low-frequency ultrasound, heated slurries with the anionic surfactant sodium dodecyl sulfate (SDS) to desorb DDT from soils with high clay, silt, and organic matter content over a range of pH values. For a soil slurry (10 wt.%) at pH 6.9 with 0.1% v/v SDS surfactant heated to 40°C for 30 min, desorption was above 80% in 30 s using 20 kHz, 932 W/L ultrasonic intensity without solvent extraction.

Another option for stripping lipophilic contaminants from soil, again based upon analytical laboratory procedures, is supercritical fluid extraction. The potential of the process for this type of work has been reviewed by Sunarso and Ismadji (2009). At the bench scale level, the procedure has demonstrated its effectiveness in removing POPs (particularly polynuclear aromatic hydrocarbons) from the soil matrix. Sahle-Demessie and Richardson 2000 carried out a bench scale study to evaluate the potential for supercritical fluid extraction to remove contaminants from a superfund site soil, which contained high levels of p,p′-DDT, p,p′-DDD, p,p′-DDE, toxaphene, and hexachlorocyclohexane. A 30-minute extraction at 30 MPa and 80°C was able to remove more than 98% of the contaminants and reduce the contaminated volume by a factor of 500. Compared with more conventional procedures, supercritical fluid extraction was equally effective and showed a better

capacity to remove DDE from the soil. Supercritical fluid extraction thus has potential for remediation, although the necessary chemical engineering studies that would make the technique a viable field option have not yet reached the necessary level.

Numerous techniques have been described in an earlier section, that offer potential for at least on-site, if not *in situ* remediation of soils contaminated with POP pesticides. Of these, fungal bioremediation has been seen to offer a very attractive possibility and several very comprehensive reviews have been published on the subject (Foght et al., 2001; Sudharshan et al., 2012; Maqbool et al., 2016; Purnomo et al., 2011).

An in-depth consideration of the various techniques that are available for *in situ* remediation, or batch remediation of excavated soils, is beyond the scope of the present review and the reader is referred to the papers cited earlier. Nevertheless, it is important to understand some of the potential limitations of *in situ* and excavated soil processes, bioremediation in particular.

- Firstly, all processes and particularly bioremediation will be affected by prevailing conditions, such as pH, soil moisture, media composition, presence of other contaminants in the soil, temperature, cultivation status, etc.
- If micro-organisms are being used, they may often be relatively slow-growing and bacteria seem to become more predominant with increasing soil depth.
- Just because the presence of a contaminant can be demonstrated in soil through laboratory analysis does not mean that it will be readily accessible to any *in situ* or excavated soil remediation process. Treatment with surfactants has been shown to improve the efficiency of DDT remediation in soil (Xiao et al., 2015). Equally, the failure of an *in situ* remediation process to access a contaminant does not mean that the contaminant is inaccessible to all biota (cf. Morrison et al., 2000).
- Whatever *in situ* or excavated soil process is employed, there is a clear need to identify the end products and become aware of *their* environmental significance.
- When employing *in situ* or excavated soil processes, there always exists the potential problem of scale-up from laboratory studies. Generally, it would be unwise to proceed directly from laboratory scale to full scale and an intermediary pilot scale process provides the best option for progressing the investigation. Such processes have been employed with chemical treatments (Balawejder et al., 2016; Song et al., 2019), biological treatments (Sun et al., 2015; Qu et al., 2015), and enzymatic technologies (Eibes et al., 2015).

3.10 FUTURE DIRECTIONS

There is no doubt that as a consequence of their properties, the POP pesticides in soil will continue to be a major environmental problem for many years to come. Our ability to better cope with this pesticide problem will depend upon a number of factors:

- Encouraging all countries to become signatories to the Stockholm Convention and putting an end to the use of these pesticides. This will be best achieved through the development of more effective control measures for insect vectors of diseases such as malaria and Lyme disease. Such diseases are expected to become a wider problem as a result of climate change.
- Carrying out realistic studies of the behaviour of formulated as opposed to pure pesticides in the environment.
- Obtaining a better understanding of the factors that govern sorption of POP pesticides in the soil environment and developing the necessary models for their uptake into human food organisms.
- In terms of bioremediation, developing gene probes for enzymes of the POP pesticide degrading pathways (cf. Chakraborty and Das, 2016; Zhang et al., 2023) along with the possible engineering of these genes into endogenous soil bacteria.

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4 Legacy of a Past
The Persistent Presence of Hexachlorobenzene

Ian D. Rae

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4.1 INTRODUCTION

A major review of the environmental chemistry of hexachlorobenzene (HCB) was published by Vladimir Zitko in a 2003 book on persistent organic pollutants. Zitko covered the chemical and physical properties of HCB, its production and dissemination into the environment, its toxicity and the concentrations found in various compartments, and included 173 references.[1] He concluded that "HCB is an environmentally undesirable compound that has no essential uses. All intentional uses have been cancelled. The remaining high priority task is the prevention of unintentional formation and discharges of HCB into the environment. The limiting factors for this task are both technical and economic . . . but . . . steps are underway to eliminate environmental releases of HCB from industrial processes as much as achievable by current technology".

Shortly after, other reviewers wrote that HCB could be regarded as a model persistent organic pollutant. They compiled data on sources, emission, environmental levels and distributions so as to assess the fate and behavior of HCB in the global environment.[2] Taking the degradation half-life of HCB to be 5.7 years, the authors found that although the amount of HCB emitted from contemporary soil had greatly reduced, only a small amount of re-emission from soil to air was required to maintain concentrations in the air. Some of the same authors contributed to a review of HCB – a Science Dossier – the eighth in a series produced under the auspices of Euro Chlor, the association of chloralkali plant operators in Europe.[3] The reported global average concentrations of HCB were 40 pg/m^3 in ambient air, and tens of pg/L or less in water, but higher levels were observed near point sources and in historically contaminated rivers. There were major losses to the environment from contaminated soil and sediment.

By the end of the second decade of this century, reports of HCB concentrations were no longer the most common publications regarding this global pollutant, although research in previously understudied regions and environmental compartments continued to be reported. There were many

DOI: 10.1201/9781003530466-4
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reports from China, for example, the most important of them concerning the Pearl River delta near the south-eastern city of Shenzhen,[4] where the HCB level averaged 81±39 pg/m^3 during the sampling period, and the highest concentration was 138 pg/m^3 during winter in Zhaoqing. It showed a gradually decreasing trend from 2005, most likely because HCB had never been used as a pesticide in China and is mainly unintentionally produced from industrial manufacturing and combustion processes (see a later section). The Chinese authors reported that the levels they observed are lower than those in northern China (~200 pg/m^3) and higher than those in Nam Co in Tibet (9~20 pg/m^3). Compared to other countries, the values are much lower than those reported in Vietnam (~600 pg/m^3), but higher than those reported for Pakistan (~30 pg/m^3) and Spain (~40 pg/m^3), to which references are given.

The decline in releases that Zitko foresaw has indeed taken place, albeit very slowly. New releases have been accompanied by re-releases of HCB, mainly from soils in which organochlorine pollutants (not only, but especially HCB) can persist for long periods, so these reservoirs, together with other contaminated sites and other reservoirs, are likely to become the major source of future pollution problems.[5] Once released from such sources, HCB can migrate from warmer to cooler parts of the world. Some authors have considered how climate change might impact this migration process, and concluded that the indirect consequences of climate change such as shifts in agriculture and changes in resource exploitation will have a more marked impact on contaminant distribution and fate than will direct effects of climate change.[6]

In preparing this review in mid-2023, I have selected papers that show the development over the period since the last major review and presented them, with my comments, under the headings which follow.

4.2 SOURCES OF HCB AND CASE EXAMPLES OF ENVIRONMENTAL CONTAMINATION AND HOW CONCERNED WE SHOULD BE

It is many years since HCB was produced for use as a fungicide to control infections in stored grains. However, HCB has been – and still is – produced inadvertently as a by-product in several industrial processes. Production of chlorinated solvents like tetrachloroethylene (perchloroethylene) and tetrachloromethane (carbon tetrachloride) can generate high volumes of unintentional waste containing HCB and other chlorinated hydrocarbons,[7] and legacy sites where the wastes were stored awaiting destruction posed serious problems for companies and regulatory authorities. As well as these large-scale problems, HCB continues to be released to the environment in low concentrations in the flue gases or waste waters from industrial processes, often those conducted at high temperatures that favour its formation, and it can be produced in the synthesis of other commercial chlorinated compounds in which it remains as an impurity.

4.3 LEGACY SITES

Large quantities of HCB-containing waste were generated during production of carbon tetrachloride and tetrachloroethylene at the Kalush Chemical and Metallurgical Industrial Complex, about 500 km southwest of Kiev and close to the regional city of Lviv. Production ceased in 1973 but a huge stockpile of waste remained, poorly stored and constituting a threat to the environment so long as it was not treated. It was the subject of several presentations to the annual forum held by the International HCH and Pesticides Association, and I take up the story with the report at the 11th Forum of national and international meetings convened to plan for the remediation of the site.[8] A special edition of the journal *Environmental Science and Pollution Research* in 2015 contained selected papers from the 12th Forum as well as selected contemporary case studies on persistent organic pollutants (POPs). In the editorial,[9] three such case studies are summarized, and two of them dealt with HCB. The first of these[10] provided details of how the government of Ukraine

excavated approximately 20,000 tons of HCB waste from a large, poorly engineered landfill in which it had been dumped during thirty years of organochlorine solvent production. The waste followed the common route of being exported for destruction by hazardous waste incineration in Europe, and much of it was accepted by a Polish operator that was, however, found to be incapable of dealing with this quantity of POPs waste in an environmentally safe manner. Thousands of tons of this waste, some in partly torn "big bags" were just piled outside, only approximately 100 m from the Baltic Sea, and as destruction proceeded some of the toxic ash from the incinerator was dumped in a local gravel pit with a high water table but without any engineering or environmental protection measures. The capacity of the incinerator was limited, and the HCB waste was still being processed more than three years after it was received. The report noted that at the time it was written the case was currently being investigated by the state prosecutor and that the company, which is owned by a German investor, needed to build an appropriate storage facility.

Until late in the twentieth century, the standard practice was to keep HCB wastes out of the environment by storing them in landfills of various capacities and effectiveness, but more recent practice involves destruction in hazardous waste incinerators operating at high temperature with effective control of emissions.[11] Large quantities of legacy wastes have been exported to hazardous waste incinerators in France and UK, which were appropriately permitted for the destruction of POPs, but as this practice developed, it became evident that a rigorous monitoring framework was needed in European Union countries when POPs are imported for destruction or when wastes are excavated. This implied the need for specific capacity building so that assessment and management of these sensitive wastes could involve people with appropriate skills and experience, and possible regulation of the storage and treatment processes. There was further need for continuous monitoring of emissions from thermal destruction facilities such as incinerators and (especially) cement kilns.

The second case involved treatment of HCB waste excavated from an organochlorine production site in Austria, which caused widespread contamination of both the environment and of residents through contaminated food. This contamination resulted from the release of HCB during attempts at "destruction" in a nearby cement kiln. The site, known for its extensive manufacture of chlorinated organic chemicals, had accumulated significant quantities of HCB waste over the years. During disposal efforts, the use of the cement kiln for HCB destruction led to incomplete combustion and uncontrolled emissions, dispersing toxic HCB into the surrounding air, soil and water.[12] The HCB waste was fed into the cement kiln at temperatures which were too low, with the result that some was released, unburned, into the atmosphere. By this release, the Görtschitztal valley in Kärnten was contaminated, and HCB was found in fodder, cattle, milk and humans. By March 2015, it was reported that 289 cattle and 800 tons of milk had been destroyed, and approximately 40,000 tons of contaminated fodder (harvested grass) from 332 farms had been removed and stored for further treatment. An investigation concluded that the feeding of the cement kiln with HCB waste that took place over 10–13 months led to releases to the environment because of failures by the cement company and a lack of effective control by the competent authority. The contamination of feed, food, humans and the environment in this case sounded a warning to other companies and other authorities about the need for continuous monitoring and careful supervision of POPs destruction projects including long-term emission monitoring.[13,14]

By way of contrast, a stockpile of HCB waste in Australia that was also shown to include a small proportion of polychlorinated dioxins and furans was destroyed without contaminating the environment, but the case study shows how complex such a project can be. ICI Australia, later Orica Australia, was a producer of chlorinated solvents at their factory in the Sydney suburb of Botany. Carbon tetrachloride, which was their major product, was converted to the chlorofluorocarbons, CFC-11 and CFC-12, by Monsanto (Australia), also in Sydney. Following the entering into force in January 1989 of the Montreal Protocol on substances that deplete the ozone layer, CFC production ceased, and the chlorinated solvents plant was closed down. Throughout its lifetime this plant had produced by-products rich in organochlorines, some of which were reprocessed, but when production ceased there was 15,000 tons of this waste, stored in steel drums,

that required attention. Remediation of the site and destruction of the HCB waste was the subject of a national program that also involved PCBs and unused unwanted organochlorine pesticides.[15] A long drawn-out process followed, and aspects of it are covered by papers in a special issue of the *Journal of Environmental Management*, of which just a few are cited here.[16,17] The drums containing the waste deteriorated due to attack by hydrochloric acid in the waste, and so re-drumming was necessary to prevent escape of the HCB to the environment. The company explored options for destruction of the waste, on site or at another location, but mainly due to opposition by the environment movement in Australia that feared the setting up of a waste-destruction industry that might attract wastes from overseas, no solution could be reached. Microbiological methods were tried, but without success. After a search for a European destruction company that could accept the waste, it has been almost all destroyed in Finland by the Fortum Waste Solutions (previously Ekokem) company.[18] During the search for a suitable technology, and in particular a non-combustion process, with which to destroy the HCB waste, trials were conducted with the Geomelt process.[19] This involved passing a large electric current through a mixture of soil and the organochlorine waste, whereby the molten soil completely destroys the organics. Small-scale trials were successful but the process was not adopted on a large scale.

HCB is reported to be present in organochlorine wastes from a Brazilian facility where ethylene dichloride was produced over at least half a century, and converted to vinyl chloride monomer and ultimately polyvinyl chloride.[20] In the Brazilian waste and in other waste masses listed in this paper, HCB is probably a minor component of the mixture, and polychlorinated dibenzo-dioxins and -furans (PCDDs and PCDFs) are the main toxic concern. Great concern was also expressed about HCB waste from production of the pesticide pentachlorobenzene that had been dumped at the coastal location Baixada Santista in Brazil.[21] A further publication revealed health effects in the local population.[22] Details of the stockpiles are contained in a paper presented at a meeting held under the auspices of the United Nations Environment Programme at Puerta Iguazu, Argentina, in April 1998,[23] but at the time of writing, these legacy stockpiles have not been removed or treated.

4.4 FUGITIVE EMISSIONS

The formation of PCDDs and PCDFs in combustion processes is well known. Less attention has been paid to similar formation of HCB, but the requirement placed on signatories to the Stockholm Convention to compile inventories of their emissions of POPs has raised interest in the detection and measurement of HCB emissions. A toolkit for identification and quantification of releases of dioxins, furans and other unintentional POPs under article 5 of the Stockholm convention on persistent organic pollutants was published by the United Nations Environment Programme (Geneva, Switzerland) in January 2013.[24]

Although not all researchers follow the UNEP protocols, there have been major efforts to measure the concentrations of HCB and other POPs in the environment, especially in developing countries and regions. A good example from the review period is a study of the concentrations arising from biomass burning in countries of the Indo-Chinese peninsula (Thailand to southwest China) that ranged from 46.5±17.8 to 154±150 pg/m^3 with an overall mean of 70.2±47.4 pg/m^3, thus contributing about 105 of the overall mean for organochlorine pesticides of 687±620 pg/m^3.[25]

A report from Poland covered emissions from four selected coal-burning plants.[26] Concentrations in flue gas from which fly ash particles larger than 0.2 μm had been filtered out were 11.5–42.0 ng/m^3, and emission factors 6.19–26.7 mg/ton of fuel, with highest values obtained when waste coal was burned. The role of fly ash in HCB emissions was explored by Chinese researchers, who found that fly ash freed of HCB by baking at high temperature could absorb HCB from the gas phase, and even bring about its partial dechlorination. Montmorillonite was effective in absorbing HCB at a lower temperature (250°C) and it was suggested that it might be a useful absorbent for cleaning flue gas.[27]

The unintentional formation of polychlorinated biphenyls (PCBs) and polychlorinated benzo-dioxins and -furans in reactions involving organic substances and sources of chlorine atoms, and

their inadvertent release to the air, is well known. Less well known are releases of HCB from processes in which organic substances and chlorine are not expected to be present, such as metallurgical operations with metals. Researchers at the State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, have studied a number of such plants in China. They found emissions of HCB in stack gases at concentrations of 448–645 ng Nm^{-3} for copper smelters operating under a range of conditions, 316–396 ng Nm^{-3} for lead smelters, and 92–2398 ng Nm^{-3} for zinc smelters.[28] These concentrations are similar to those they had found for other metallurgical operations involving copper,[29] magnesium[30] and iron ore sintering.[31] Other researchers have concentrated on PCDD/Fs in gas streams from municipal waste incinerators. In the stack gas of municipal waste incinerators in China, the Beijing group have identified HCB as a minor component (11–186 ng/Nm^3) and it was also present in the fly ash (43–48 μg/kg).[32]

HCB along with other POPs is inadvertently produced in many other industrial processes. Flue gases from a magnesium smelter in China contained 820 μg/ton of metal processed, leading to an estimate of 403 g each year for magnesium smelting in that country,[33] while metallurgical operations in Portugal released only 0.013–1.7 mg/year.[34] As described earlier, stockpiles of HCB waste can arise from HCB inadvertently produced in the production of chlorinated methanes and tetrachloromethane (carbon tetrachloride) but it can also remain in the products and be released to air when they are used. Impurity levels in solvents produced in China were 38.8 μg/g,[35] leading to an estimate that emissions of this type would contribute to the high concentrations of HCB found in the atmosphere in China, 10.4–462 pg/m^3, which exceed those in Singapore (9.5–24.5 pg/m^3), Japan (14–95 pg/m^3) and South Korea (26.0–136 pg/m^3).[36]

Ronald A. Hites, who has long been active in this space, recently addressed the question "Have we made any progress in eliminating insecticides from the atmosphere?" and answered it with data that showed that some insecticides, but not HCB, had been virtually eliminated, at least from the Great Lakes region of North America.[37] The continued presence of HCB in the atmosphere he attributes to industrial processes such as the use of hexachloroethane in degassing molten aluminium and the use of carbon electrodes in electrolytic production of magnesium, which could be releasing 13–92 tons/year in the United States.

4.5 HCB AS IMPURITY

Several papers reported HCB contamination of chemicals and consumer goods. For example, HCB was the most common OCP detected in honey samples in Egypt. Concentrations were very low – 6.2–9.7 μg/kg (mean 8.5 μg/kg), well below levels of health concern. The source(s) of the HCB were not identified but may have been historic use(s) of HCB as a pesticide or aerial deposition from other regions.[38] Similar concentrations were found in traditional Chinese medicines – mostly 1–10 μg/kg with a few very high concentrations – and the authors called for the establishment of maximum residue levels (MRL) for HCB and tecnazene (1,2,4,5-tetrachloro-3-nitrobenzene).[39] Pentachlorophenol, mainly used as a wood preservative, is manufactured by the chlorination of phenol at temperatures high enough (~200°C) and in the presence of acidic catalysts, so it is no surprise that the commercial product contains trace amounts of a number of organochlorines, including PCDDs and PCDFs and HCB. Examination of 47 batches of pentachlorophenol revealed HCB concentrations 16.4–27.4 mg/kg (mean 21 mg/kg [ppm]) and details were disclosed of the procedures needed to measure these small concentrations.[40]

Organochlorine pesticides with chemical structures closely related to that of HCB are obvious places to look for impurity levels. The HCB content of five commercial samples of Chinese pentachloronitrobenzene fungicides was 3.7–52 ng/g, and it is estimated that use of these products resulted in the release of 18 to 55 grams/year of HCB.[41] Polychlorinated dibenzo-dioxins and -furans have been detected at low concentrations in a number of commercial pesticides.[42], [43] Because of their pronounced toxicity, their possible presence has been the main driver for the examination of various

commercial pesticides to see if these substances are present. No detections of HCB were reported, but it is not clear whether HCB was not present or that the analytical methods were not appropriate for its detection.

4.6 HCB SEQUESTRATION IN THE ENVIRONMENT

Throughout the review period there was increasing interest in the global threat posed by waste plastics that could absorb pesticides, industrial chemicals and pharmaceuticals from aquatic and marine environments and release them when the contaminated plastic was inadvertently ingested by fish, shellfish and birds, causing harm to these new "hosts". The influence on particle size and plastic identity (polyethylene was most effective as a "carrier") has been explored.[44] An early initiative was the "International Pellet Watch Global Monitoring of POPs" that involved the collection of industrial resin pellets ("nurdles") from beaches by citizen scientists and analysis of the contaminants by a Japanese laboratory.[45] The program concentrated on selected POPs – PCBs, hexachlorocyclohexanes (HCHs) and DDT metabolites.[46]

More detail on this environmental threat has been obtained, for example, by examination of plastic objects in the digestive tracts of eight species of *Procellariiformes* (petrels, shearwaters and albatrosses) collected in southern Brazil that showed the presence of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the ingested plastics pellets and plastic fragments. The concentration of HCB in plastic pellets was 12.4 ng/g, and in plastic fragments, 15.1–17.5 ng/g, much lower than the concentrations of PCBs (491 ng/g) and DDT (68 ng/g), but larger than those of chlordanes (5.22 ng/g).[47]

Laboratory explorations were carried out on the feasibility of transfer of the pollutant from a contaminated plastic to a living organism, in the case of HCB, exposing freshwater fish (*Danio rerio*) to polyethylene carrying the POP at a concentration of 16 μg /g.[48] Transfer of the HCB to the fish was less efficient from the "loaded" microplastic than it was from HCB in water alone, indicating that the plastic route was no more effective than absorption of the pesticides from aqueous solution, which was necessarily very dilute since the solubility of HCB is approximately 5 mg/m^3 at ambient temperatures.[49]

4.7 POLICIES AND REGULATIONS AFFECTING HCB

The production, use and dissemination into the environment of HCB came to the attention of regulatory bodies, notably those in Europe, in the late twentieth century and it is one of the chemical substances covered by the three intergovernmental conventions developed under the aegis of the United Nations Environment Programme (UNEP) and the UN Food and Agriculture Organization (FAO). In order to avoid duplication and to gain synergies, the three chemical conventions have since 2012 had a common secretariat and their annual technical meetings and Conferences of the Parties (COPs) are now held concurrently.[50]

Because it is one of the substances listed in the Stockholm Convention (see the following), HCB is covered (but not specifically mentioned) by the oldest of these chemical control instruments, the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal, that was adopted in March 1989 and entered into force in May 1992.[51] The Rotterdam Convention (formerly the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Materials and Pesticides in International Trade), signed in 1998, came into force in February 2004.[52] It was established jointly by UNEP and the UN Food and Agriculture Organization (FAO) to promote shared responsibility for importation of a wide range of hazardous chemical substances, including hexachlorobenzene.

More attention has been paid to HCB by the third of these conventions: it was one of the first twelve substances to be listed in the Stockholm Convention on Persistent Organic Pollutants (POPs) that was adopted in 2001 and came into force in May 2004. Because of its deliberate production

and use, HCB was among the POPs designated for elimination and therefore listed in Annex A. Because it was an unintentional by-product of a number of industrial processes, HCB was also listed in Annex C and covered by Article 5 of the Convention. Parties to the Convention were required to reduce total releases of these substances, with the goal of continuing minimization and, where feasible, ultimate elimination. Progress on the meeting of this obligation is to be reported at five-year intervals.[53] The UNEP has developed a toolkit to assist countries in their reporting of unintentional emissions of POPs.[54] A significant paper published in 2019 provided data on emissions of unintentionally generated HCB in China and compared them with those reported by other countries. China emissions amounted to 2,146 kg, 60% of this to air with most of the rest remaining in products as an impurity.[55] Release of HCB from production of chemicals and consumer goods (Source Group 7) was 758 kg/year, mostly as HCB impurity retained in products. Also included in this paper were data reported by 31 countries to the UNEP, differentiated by source according to the toolkit methodology. They show a total of 18,586 kg/year released to air, with major contributions by Canada, and by Macedonia, with most from the latter country falling into Source Group 4 (Production of Minerals). In Source Group 7 (production of chemicals and consumer goods) the total from the 31 countries was 132 kg/year, mostly from Canada (116 kg/year), clearly much less than that of China. Most countries signatory to the Stockholm Convention have not established an inventory of unintentionally released hexachlorobenzene, but for those that have, the data reported in Part B, Section IV-5 of the latest round of country reports showed that totals had declined – to approximately 130 kg/year for Japan in 2018; 40 kg/year for United Kingdom; 8 kg/year for Canada; and 22 kg/year for the Netherlands – most of this released to air from waste incineration and ferrous and non-ferrous metal production.[56]

The intergovernmental conventions that address particular aspects of chemicals management are accompanied by a much broader process, also developed under the aegis of the United Nations Environment Programme – the Strategic Approach to International Chemicals Management (SAICM)[57] that was adopted in February 2006. Its overall objective is the achievement of the sound management of chemicals throughout their life cycle so that by the year 2020, chemicals are produced and used in ways that minimize significant adverse impacts on the environment and human health. SAICM's objectives fall into five groups: risk reduction; knowledge and information; governance; capacity-building and technical cooperation; and illegal international traffic. Perhaps because of its breadth and the existence of other conventions, SAICM made little progress towards its ambitious goal and at successive meetings, open to all stakeholders – both those representing governments or organizations, and those expressing interest in seeing progress towards specific objectives – it has recommitted to sound management of chemicals and waste beyond 2020. The situation with HCB has not been addressed specifically by SAICM.

Two regional agreements in North America cover HCB as well as other pollutants. The first concerns contamination of the waters of the Great Lakes.[58] In the second, a task force was established in 1999 to prepare a regional plan for the management of dioxins, furans and HCB by the Commission for Environmental Cooperation of North America, in which Canada, Mexico and the United States participated,[59] and the strategy was published in 2011.[60] Among other matters it covers improved inventories, analytical studies including human biomonitoring, small-scale combustion sources and waste disposal, and micro-contamination in pesticides.

4.8 HCB TOXICITY AND RISKS TO THE ENVIRONMENT AND HUMAN HEALTH

Zitko, in his 2003 review, concluded that while toxicity studies of HCB alone, often using massive doses, are interesting to toxicologists wishing to elucidate the mechanisms of HCB actions, they consume resources that would be better spent on hazard identification and risk assessment of the great variety of currently used pesticides and other chemicals that are released to the environment and have not yet received much publicity.[61] The intervening years have revealed continuing

but declining interest in toxicity as interests have shifted not to the subjects Zitko suggested but instead to global monitoring and the mechanisms of distribution of HCB. Having reliable toxicological data available was important, but perhaps there was no need for new values when the old ones could serve. This was evident, soon after Zitko's pronouncement, when German scientists reported their analysis of the detection frequencies and concentrations for 331 organic compounds measured between 1994 and 2004 in the four largest rivers of north Germany – the Elbe, Weser, Aller and Ems – and assessed the potential risk for aquatic fauna using experimental and predicted acute toxicity data. The detection frequency for most compounds decreased significantly from 1994 to 2004. The maximum concentration found for HCB, 0.03 μg/L, was lower than those of many other contaminants, and well below the EC50 for the green alga *Pseudokirchneriella subcapitata* (222 μg/L), EC50 for the crustacean *Daphnia magna* (5.7 μg/L) and LC50 for the fish *Pimephales promelas* (57 μg/L).[62]

As in the foregoing study, most toxicity threshold and risk assessment studies are based on invertebrates and fish. Data such as "no observed effect concentrations" (NOECs) specific to birds and mammals have been used to derive species sensitivity distributions (SSDs) based on toxicity data pertaining to growth, reproduction and survival or a combination thereof. After estimation of the SSD parameters, a point estimate known as the HC5 (hazardous concentration for 5% of the species) is calculated – the concentration at which fewer than 5% of the species within an ecosystem is expected to be affected. The HC5 value for HCB was 0.49 mg/kg (net weight in food).[63] Interest in the impact of pollutants on the health and reproduction of marine mammals has been strong throughout the review period, and a recent study compares data collected over many years for gray whales on the west coast of North America showed a considerable decline in HCB concentrations. Concentrations in blubber collected during the decade to 2017 averaged 100±7 ng g^{-1}, whereas concentrations 10–100 times greater were found in studies in the 1990s.[64]

Chronic exposure of laboratory animals to HCB elicits a number of toxic effects – neurological, immunological and endocrine – as summarized in the toxicological risk profile compiled by the US Department of Health and Human Services.[65] Laboratory rats gavage-administered a suspension of HCB in water at a rate of 500 mg/kg – far above what might be termed environmental levels – for up to 45 days experienced increased blood pressure and changes to a number of physiological indicators.[66] Much lower concentrations may still produce changes, and the discovery of HCB (concentration ~ 32 pg/mL) and other endocrine-disrupting chemicals in the follicular fluid of women undergoing assisted reproductive technology prompted in vitro studies that revealed cell proliferation that was attributed to insulin-like growth factor.[67] HCB had previously been observed to interfere with steroidogenesis.[68] More significant environmental concentrations were used (25 μg/L) when HCB and pentachlorophenol (PCP) were jointly administered to zebra fish.[69] Assessing the toxicity of mixtures – and organochlorine pesticides recovered from the environment are invariably components of mixtures rather than single compounds – is notoriously difficult, and the possible complexities are exemplified here, because while in this merely binary mixture PCP was mainly responsible for the observed reproduction impairment, HCB exerted a synergistic effect.

Another complication is that toxic effects observed in living organisms can be caused not by the nominated substance but by its metabolites. This observation applies to HCB because of the toxicology of tetrachlorobenzoquinone (TCBQ), a metabolite of HCB and also of pentachlorophenol. Rat cells cultivated on a medium containing bovine serum and 20 μM TCBQ showed morphological changes and changes in iron metabolism that resulted in novel cell death (ferroptosis).[70] Pentachlorophenol is itself a product of the atmospheric oxidation of HCB, a well-known process which must complicate efforts to establish global concentrations of both substances. As a point of chemical interest, the mechanism of oxidation was investigated by theoretical chemists, showing how problems emerging in one scientific discipline attract the interest of those in related spheres of science.[71]

Establishing a connection between HCB body-burdens in humans and health impairment is much more difficult than studies with animals that can be deliberately dosed with the chemical, but a notable case was reported recently. In a subset (n = 1,276) of the adult population participating in

the Korean National Health Survey, HCB was found to be associated with kidney disease, causing reduced glomerular filtration.[72] This same phenomenon has been reported in rodents, and in the most recent paper, the injuries of kidneys due to the presence of HCB included oxidative stress, disturbance of glucose metabolism and damage to enzyme systems.[73]

Two environmental risk assessments of HCB have been published by Euro Chlor. The first of these, in 2002, addressed the risk for the marine environment of the OSPARCOM (fifteen western European countries) Region – North Sea.[74] It found that the presence of HCB in surface water was unlikely to be a risk to aquatic organisms, and that, as a result of declining concentrations in the North Sea, there was little risk to fish-eating birds and mammals, with the possible exception of some highly sensitive species such as mink or ferrets. In 2014 the second aquatic environmental risk assessment dealt with arctic waters and took an approach recommended by REACH, the European regulation that came into force in 2006 for the Regulation, Evaluation, Authorisation, and Restriction of Chemicals, to assess the risk to top predators such as beluga, narwhal, polar bear and glaucus gull.[75] This assessment covered both the risk posed by contamination remaining in the environment from historic use of HCB, and also that posed by only current emissions. There was a significant risk to the top predators, and among fish, and to freshwater species in regions where there is limited potential for dilution into the receiving environment.

4.9 REMEDIATION OF SOIL AND WATER

As recounted in the previous sections, large amounts of HCB-containing waste have been treated by high-temperature incineration, a technique that is also successful in destroying other organochlorines. The technique is not applicable to treatment of contaminated soil or water, in which HCB is, gravimetrically speaking, a minor component, unless a concentrate can be obtained, and the most common way to achieve this is by thermal desorption from contaminated soil, the requirements for which are described in the Technology Guide to Thermal Desorption that is part of the National Remediation Framework published by Australia's Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CARE) in August 2018.[76] The guide contains a list of sites and substances that have been thermally desorbed from them, and selected references. I have taken a formal approach by referring to the desorbed material as a "concentrate", but in fact it is normally passed directly to a thermal oxidizer that destroys the pollutant. Of course, it is not only soil contaminated with organochlorines such as HCB that can be remediated in this way. An example in which the destruction step is made explicit is the "Solve" process used by the Australian company Enviropacific, in which contaminated soil is fed to a thermal desorber, and the resulting vapour is destroyed in a thermal oxidizer.[77] The "Solve" process has been used to remediate soils contaminated with a range of hydrocarbons, organochlorines and PFAS, and it is possible, although not specified, that HCB would have been a component of these industrial wastes. The technique is conducted on a large scale with a kiln similar to that of a cement kiln, which could be erected on site to decontaminate HCB-affected land.

The use of chemical methods, at least for soil remediation, seems feasible, and because HCB is chemically rather unreactive, such processes would need to be carried at high temperatures, probably >1,000°C. Performed with or without additives, such processes could handle large volumes of contaminated soil. Temperatures like this are reached in the impact zones of ball mills, and although no industrial applications have been reported, laboratory scale ball-milling with chemical substances such as calcium carbide[78] or mixtures of calcium oxide and sodium persulfate (PDS)[79] have been successful in destroying HCB. These chemical methods for the destruction of HCB have been explored in the laboratory, but since no industrial applications have been reported they remain in the domain of "interesting chemistry" that has not been adopted in real life, and that applies to other reported destruction procedures, too. Thus, HCB on the surface of alumina in aqueous medium was destroyed by ultraviolet irradiation, probably due to the generation of hydroxyl radicals, and the degradation products were shown to be less toxic,[80] and similar results were experienced when the

solid phase was silica gel (SiO_2).[81] A common laboratory approach for HCB in solution has been to dechlorinate it by reacting in protic media with zero-valent metals such as iron,[82] lead-iron combinations[83] or magnesium/graphite.[84]

Bioremediation of soils contaminated with POPs, using higher plants or micro-organisms to degrade or destroy the toxic substances, has appealed to many researchers (and owners of contaminated land!) as a passive, albeit slow, method for removing POPs from the environment, thus enabling formerly contaminated land to be used safely. Some successful treatments at laboratory scale and under laboratory conditions have been reported but there have been very few successes in the field. In the POPs family of substances, most attention has been paid to polychlorinated biphenyls (PCBs) and to polychlorinated benzo-dioxins and -furans (PCDD/PCDF), with only a few trials devoted to HCB. HCB is toxic to many micro-organisms, and so with a view to bioremediation of soils at the Kalush site in Ukraine, trials have been conducted with the bacterium *Comamonas testosteroni*, which has the capacity to degrade benzene and xylene. Two strains of the organism have been identified that are resistant to even high concentrations of HCB and this has raised the possibility that the organism might be suitable for use in bioremediation.[85] A variant on the usual practice of bioremediation is the use of microbial fuel cells in which bacteria are used to oxidize organic substances at the anode of a cell, and reduction can occur at the cathode. Laboratory experiments with HCB under several conditions destroyed 40–70% of it.[86] Researchers continue to hold out hope that micro-organisms can be found that will completely or near-completely degrade HCB, but nothing in the literature reviewed here suggests that these hopes are near to being achie ved.[87,88,89,90,91] Biological methods have been explored for many of the POPs contaminants, but all suffer from the fact that while high degrees of destruction can be achieved under laboratory conditions, progress is much slower in the field and concentrations of the contaminant are not brought down to regulatory levels.

A 2014 review of electrochemical methods for remediation of pesticides in soils and water[92] hinted at the difficulty of the complete removal of pesticides, by phrasing it as "assisted remediation" and using as a sub-heading "electrokinetic technologies for depletion (sic) of pesticides from soils". An imposed potential can be used to flush water contaminated with pesticide from soil (electrokinetic soil flushing), but in the best literature result cited[93] the extent of removal of HCB from clay was not better than 66%, and the claim that the technology shows good prospects for pesticide removal seems an overstatement. The same optimistic tone was adopted by researchers who reported the use of bacteria, following electrochemical treatment, as a method for destruction of HCB. Germination tests on the post-treatment material showed reduced toxicity, and although this was a laboratory simulation in which HCB (damaged by electrochemical treatment) was the sole carbon source for microbial growth, the authors seemed to be stretching a point by observing that the method could be used *in situ* in areas "contaminated by this recalcitrant compound".[94] Although the results of studies reported in this section could be regarded as "promising", no work of this kind with actual contaminated sites has been reported, and I found no references to the use of electrochemical technologies for the removal of HCB from water.

4.10 CONCLUDING REMARKS

Heidelore Fiedler is a researcher who has long been involved in collaborative work on POPs in the environment and in human body burdens. One of her recent studies show the continuing but declining presence of HCB,[95] but in another, values in Africa increased but those in the Pacific did not, albeit all the values were quite low.[96] Lest we be sanguine about this, other researchers, who found HCB concentrations of the same order as those of DDTs and HCHs, have warned that while the low concentrations were found in their study of air in Tunisia, "we should be careful to claim that some POPs have disappeared globally".[97]

Kevin Jones, who has been prominent in the field of POPs research for many years, reflected on the long-range transport that makes POPs a global and not just a local problem.[98] They are

"endlessly fascinating to scientists", Jones wrote, "and a nightmare to regulators and policy makers". As a type example, he considered HCB and referred to work published in 1991 (not mentioned in Zitko's review) on its global distribution as revealed by its presence in tropical and temperate vegetation.[99] The problem that he and others have identified is that there is no "standard plant" growing everywhere that could be used to monitor the distribution of this and other chemical substances. However, the development of passive air samplers has made something like this possible. Pointing to the properties of HCB – its low air-surface partition coefficient, its atmospheric stability and residence time (longer than those of PCBs, for example), its ready mixing in the atmosphere and the evidence for its cold condensation[100] – he judged that hexachlorobenzene is probably the POP that is furthest along in the transition to "global equilibrium", although the data base for establishing such a conclusion is somewhat shaky because data on unintentional emissions to the environment from industrial, agricultural and combustion-related sources are not well accounted for despite the requirements placed on countries signatory to the Stockholm Convention to provide such data.

Achievement of global equilibrium is a signal that it could be many years before the world is rid of HCB. Legacy concentrations will fall as it is destroyed by natural processes, but continuing inadvertent emissions show that while the Stockholm Convention goal of minimization might be in sight, elimination of this global pollutant is not.

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5 Navigating the Crossroads *Risk Assessment in the World of Industrial Chemicals*

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5.1 INTRODUCTION

Industrial chemicals encompass a vast and diverse array of substances utilized across various industries for a wide range of applications. These chemicals are integral to our daily lives, impacting everything from clothing and electronics to medicines and cleaning products. It is estimated that

DOI: 10.1201/9781003530466-5

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there are more than 350,000 synthetic chemicals and mixtures globally, most of which are relatively recent developments (Naidu et al., 2021; UNEP, 2019; Wang et al., 2020). The annual global production of these synthetic chemicals is ~2.3 billion tons and is expected to double by the year 2030 (Wager & Thompson, 2024). Their intentional or unintentional release into the environment poses potential risks to human health and ecological systems. Exposure to hazardous chemicals can increase the likelihood of adverse health effects, including chronic diseases such as cancer, neurodevelopmental disorders, metabolic diseases, and immune system dysregulation.

Globally, historically contaminated sites resulting from chemical pollution are increasingly being identified. For instance, as of 2018, there were 650,000 formally registered contaminated sites in the EU-28 (Sinnett et al., 2022) with potentially contaminated sites as 2.8 million (European Zero Pollution Dashboard), while the U.S. Department of Defense reported 38,804 contaminated sites in 2014 (Gomez & Office, 2015). Australia is estimated to have over 160,000 contaminated sites (Fergusson, 2017). The global heavy metal contaminated sites are reported to be more than 10 million (Li et al., 2024). Given these statistics, it is critical to regulate chemicals before they are used or released into the environment since currently the progress in remediation of contaminated sites is relatively low.

A multitude of industrial chemicals includes various individual compounds, such as industrial inks, plastics, adhesives, and paints. These substances are prevalent in various aspects of daily life. Commonly identified contaminated sites stemming from industrial chemicals include former industrial locations with inadequate chemical storage, handling, and disposal practices; service stations; dry cleaners; electricity generation facilities; motor vehicle manufacturing and repair workshops; landfill sites; and various manufacturing and storage facilities.

There are numerous policy frameworks currently in place to address industrial chemicals in commerce and pollution. Key features of these frameworks include (1) the delineation of responsibility between industry and government for generating and evaluating data on chemical hazards and risks; (2) the degree to which this data must be made publicly accessible; (3) whether decision-making is based on hazard or risk assessments; and (4) how costs are considered in selecting risk management measures (Woodruff et al., 2023). This chapter will focus on the assessment and regulation of various industrial chemicals on a global scale.

5.2 TYPES OF INDUSTRIAL CHEMICALS

Industrial chemicals are substances produced or used in various industrial processes for manufacturing goods, producing energy, or facilitating other industrial activities, which have an industrial use and cover a broad range of chemicals used in inks, plastics, adhesives, paints, glues, solvents, cosmetics, soaps, and many other products. These chemicals can have diverse applications across numerous sectors, including manufacturing, agriculture, pharmaceuticals, construction, and transportation. They play vital roles in modern industrial processes; however, environmental and health challenges and concern exist for their production, use, and disposal. As a consequence of rapid industrialization, environmental contamination has escalated significantly in the modern world (Tamjidi et al., 2021). Industrial activities produce vast amounts of wastewater and effluents, which, when discharged without proper treatment, can have deleterious effects on water and soil quality (Han et al., 2020).

5.2.1 Industrial Inks

Printing inks are widely used in product packaging, books, newspapers, and various documents (Ramos et al., 2019). However, the wastewater generated from printing processes – including colour matching and equipment cleaning – presents significant challenges. This printing ink wastewater (PIW) typically contains a complex mix of dyes, binders, carriers, and additives (Aquino et al., 2014; Ni et al., 2021). Characterized by its high coloration, PIW is often contaminated with organic

substances, including non-biodegradable compounds and trace heavy metals such as mercury (Hg) and cadmium (Cd) (Zampeta, Mastrantonaki et al., 2022). The deterioration of water quality due to industrial ink discharge is a critical concern, particularly in developing countries like India and China, where inadequate treatment of industrial wastewater poses serious threats to public health and the environment (du Plessis, 2020).

Although industrial-grade inks and actual printing ink wastewater can be treated, conventional methods such as chemical coagulation and biodegradation have their limitations. Chemical coagulation generates substantial sludge, while the effectiveness of biodegradation is influenced by environmental conditions and the characteristics of the effluent, often leading to incomplete waste remediation (Tung et al., 2013).

Innovative technologies, such as hydrodynamic cavitation systems followed by sedimentation (HC/SED), show promise, achieving over 90% decolourization of mixed inks and printing ink wastewater (Zampeta, Bertaki et al., 2022). Advanced oxidation technologies (AOTs) are also effective in treating non-biodegradable organic compounds, significantly reducing organic loads in actual printing ink effluents. Techniques such as the Fenton reaction and electrochemical methods hold potential for efficient treatment (Babuponnusami & Muthukumar, 2014; Vitale et al., 2023).

5.2.2 Plastics

Plastics, encompassing a broad array of man-made polymer substances, have emerged as a ubiquitous problem of human-generated waste and cause adverse effects to the environment (Mushtak et al., 2024). Despite their ubiquitous presence, plastics offer numerous benefits, ranging from facilitating cost-effective packaging for global food and beverage supply, thereby extending food shelf life and reducing waste, to enabling the production of essential electronic devices (Mubin et al., 2023; Zhang et al., 2022).

Polymers and plastics are typically categorized as either thermoplastic or thermosetting. Thermoplastics are linear polymers that soften or melt when heated, allowing them to be reshaped. Examples include acrylic, epoxy, phenol-formaldehyde, polyurethane, aminoplast, and polyester plastics. In contrast, thermosetting polymers form rigid, cross-linked networks upon curing, retaining their final shape. Examples of thermosetting plastics include acrylic, polyvinyl, polystyrene, polyolefin, polyamide, polycarbonate, polyurethane, and polyester plastics (Björkner et al., 2011).

Plastics are categorized based on size, commonly referred to as nano-, micro-, and macroplastics, with size playing a crucial role in ecological interactions and environmental fate (Welden & Lusher, 2020). Industrial wastewater and sewage treatment plants constitute major sources of microplastics, highlighting their significant contribution to environmental contamination (Wong et al., 2020). The extensive use of disposable plastics exacerbates global environmental issues, with microplastics posing considerable threats to natural ecosystems and exacerbating climate change (Molina-Besch & Keszleri, 2023).

Microplastics (MPs), defined as plastic particles measuring below 5 mm or specifically between 1 μm and 5 mm, have emerged as a critical global issue, pervading various ecosystems including air, oceans, rivers, lakes, and soils (Sadia et al., 2024). Global plastic waste, amounting to 275 million tons in 2010, with approximately 8 million tons ending up in the ocean annually, underscores the severity of marine pollution caused by mismanaged plastics (Jambeck et al., 2015). Microplastics have been detected across diverse marine environments, from remote beaches to deep-sea sediments and coral reefs, illustrating the pervasive nature of plastic pollution in marine ecosystems (Besley et al., 2017; Rahman et al., 2023; Van Cauwenberghe et al., 2015). Microplastics in the air pose health risks to humans through inhalation, with sources including urban dust, household items, aerosols from wastewater treatment plants, and agricultural biosolids (Muisa-Zikali & Mpeta, 2022). Agricultural soils are significantly contaminated with microplastics, with studies revealing their presence in soil samples at high concentrations, particularly in floodplain soils (Scheurer & Bigalke, 2018; van den Berg et al., 2020). Given that the vast majority of plastic waste is produced

and disposed of on land, soils could serve as an important long-term repository for MPs (Möller et al., 2020). Quantifying microplastic concentrations in the soil presents challenges due to various soil biotic and abiotic factors, particle interactions with soil components, matrix effects, and extraction complexities (Billings et al., 2023; S. Li et al., 2023; Rillig, 2012). Overcoming microplastic challenges necessitates concerted efforts from all stakeholders, including upstream substitution of plastics and downstream removal strategies. Standardization in the classification, analysis, and quantification of microplastics is imperative to effectively address the multifaceted challenges posed by these pollutants.

5.2.3 Adhesives

Synthetic adhesives play a vital role in various industries, including wood processing, food packaging, construction, and aerospace, with a significant portion designated for engineered wood products (Bakare et al., 2014; Souza et al., 2018). These adhesives, primarily derived from petrochemical sources, consist of prepolymers or polymers (Conner, 2001). Despite their versatility and essential functions across multiple fields, some synthetic adhesives, particularly those sourced from non-sustainable fossil fuels, release volatile organic compounds (VOCs) such as formaldehyde, raising environmental and health concerns (Zhang et al., 2020).

Formaldehyde-based resins, including phenolic resin, urea-formaldehyde resin, and melamine-formaldehyde resin adhesives, are extensively used in the production of wood-based products, such as interior decoration materials and furniture (Souza et al., 2018). Phenolic resin adhesive, created through the polycondensation of phenol and formaldehyde under acidic or basic conditions, has been fundamental to wood adhesives since the nineteenth century (Liu et al., 2016). Known for its remarkable environmental resistance and high bonding strength, phenolic resin adhesive has found applications beyond plywood and wood processing, extending into the automotive, aerospace, and composite materials industries (Xu et al., 2019). Nevertheless, the prevalent use of formaldehyde-based resins raises significant concerns about formaldehyde emissions (Kim, 2010). As a result, there is increasing interest in developing renewable, non-toxic, and biobased alternatives to mitigate the environmental and health issues associated with synthetic adhesives (Li et al., 2022).

Furthermore, glue residues commonly found in the automotive and electronics manufacturing sectors present environmental and health risks if inadequately managed (R. Liu et al., 2018; Y. Liu et al., 2018). Historically significant, glues, including animal glues used in paper manufacturing and restoration, are another category of adhesive materials (Barbabietola et al., 2016). These natural polymers, mainly derived from collagen found in animal tissues, are prone to degradation over time (Singh et al., 2012). Pyrolysis has emerged as a promising technique for recycling waste glue residues, addressing environmental challenges by producing carbon-rich products suitable for sewage treatment (Y. Shi et al., 2020).

The development of sustainable adhesives aims to minimize the use or creation of hazardous substances, reduce environmental impact, and decrease energy consumption throughout the adhesive lifecycle, including design, manufacture, use, and disposal (Rao & Wan, 2023). By prioritizing sustainability in adhesive products and processes, stakeholders can alleviate adverse environmental and health impacts while fostering innovation and moving toward a more sustainable future.

5.2.4 Paints

Interior paints serve the crucial function of protecting, coloring, and texturizing indoor surfaces like walls. However, frequent repainting cycles, typically every 5–7 years, expose both painters and residents to potentially harmful chemicals via inhalation (Huang et al., 2024). Among these chemicals, lead-based paint has historically been a major concern, especially in developing countries, where lead exposure remains a significant public health issue. The World Health Organization (WHO) reports that lead exposure contributed to nearly half a million deaths and over 9 million

disability-adjusted life years (DALYs) in 2016 (WHO, 2019), with a substantial portion occurring in low- and middle-income countries. Notably, a population-based cohort study involving 14,289 US adults revealed that blood lead levels (BLL) were attributable to 18% of all-cause mortality, resulting in an estimated 412,000 deaths annually, placing lead exposure on par with tobacco smoke in terms of mortality risk (Landrigan et al., 2018). The primary sources of lead exposure in children have shifted from leaded gasoline to lead-based paint and contaminated soil in the wake of the US ban on leaded gasoline (Lofgren et al., 2000). Despite this, there remains a lack of consensus on the definition of lead-based paint, underscoring the need for strengthened regulatory oversight, public awareness, and industry acceptance to address this global issue (O'Connor et al., 2018).

Additionally, volatile organic compounds (VOCs) in paints have garnered significant attention in recent decades due to their adverse health effects, including respiratory irritation, organ damage, and carcinogenicity. Common VOCs found in interior paints, such as benzene, toluene, xylene, and formaldehyde, pose health risks, particularly in solvent-based paints (Kim et al., 2011; Månsson et al., 2008). However, the shift towards water-based paints with lower VOC emissions is underway to mitigate these risks (Simion et al., 2015). Despite efforts, air-purifying paints have shown limited effectiveness in reducing indoor air pollutants (Schieweck & Bock, 2015). Thus, addressing VOC emissions remains a critical aspect of promoting indoor air quality and mitigating associated health risks.

5.2.5 Solvents

Organic solvents are vital across various industries for facilitating chemical reactions, extractions, and purification processes, playing a crucial role in achieving product purity (Clarke et al., 2018). However, the life cycle of industrial solvents – from production to disposal – introduces emissions that can adversely impact human health and the environment within affected communities. The annual production of organic solvents on an industrial scale is estimated to be nearly 20 million metric tons (Clark et al., 2015). In response to these environmental concerns, the United States Environmental Protection Agency (USEPA) finalized a Definition of Solid Waste Rule in 2015, promoting the reuse and reprocessing of 18 higher-value hazardous spent industrial solvents across key manufacturing sectors (Vane, 2019). Although these 18 solvents constitute only a small fraction of all organic solvents used, they encompass a variety of categories, including aliphatic hydrocarbons, chlorinated compounds, ethers, ketones, amides, nitriles, and alcohols.

The increasing demand for oils and solvents to meet energy needs has not only spurred economic growth but also led to significant environmental challenges, such as oil spills that adversely affect marine life and ecosystems (Gore et al., 2019). For instance, the Gulf of America (formerly the Gulf of Mexico) oil spill in 2010 posed a severe threat to seabirds and aquatic animals, destroying their breeding grounds and leading to carcinogenic effects and ecological imbalance (Gore et al., 2016). Such oceanic disasters have resulted in substantial losses of marine organisms, further destabilizing the aquatic balance (Bjorndal et al., 2011; Crone & Tolstoy, 2010).

In an effort to mitigate solvent-related pollution and reduce energy consumption, sustainable solvent alternatives have been proposed and developed over the past three decades. While solvents are essential for chemical processes, the excessive use of nonrenewable and toxic solvents is unsustainable. Sustainable solvents, derived from plant biomass, present renewable alternatives for the chemical industry. However, their sustainability is contingent upon the adoption of sound land management practices (Beringer et al., 2011; Berndes et al., 2003; Fischer et al., 2010).

5.2.6 Cosmetics

In recent years, cosmetics have emerged as essential components of daily skincare and beauty regimens, deeply intertwined with individuals' lives (Li et al., 2021). These products encompass a diverse array of functions and characteristics, broadly categorized into cleansing, beautifying,

and nurturing properties. According to the European Council Directive 76/768/EEC, cosmetics are defined as substances or mixtures intended for use in cleansing, enhancing, or modifying the appearance of the skin, hair, lips, nails, or teeth. This classification encompasses a vast spectrum of products catering to both genders, including skincare creams, lotions, powders, perfumes, makeup, hair dyes, deodorants, and sunscreens (Bocca et al., 2014).

In essence, cosmetics represent chemical formulations comprising various raw materials blended in specific proportions (Hu, 2022; Salama, 2016). These products consist of a diverse range of organic and inorganic compounds, incorporating both hydrophilic and hydrophobic substances. For colored cosmetics, mineral pigments are commonly employed, potentially introducing heavy metal contaminants such as copper, nickel, cobalt, lead, chromium, and cadmium (Arshad et al., 2020). Consumers may inadvertently encounter these metals through daily cosmetic use, exposing themselves to potential skin irritations and systemic effects through skin absorption or ingestion.

People can be exposed to metals as trace contaminants in cosmetic products they use daily. While heavy metals are occasionally utilized in cosmetics as coloring agents or preservatives, their toxic nature poses significant health risks, including damage to the nervous system, kidneys, and other organs. Moreover, deliberate addition of heavy metals like lead and mercury by unscrupulous manufacturers to enhance product efficacy can further compromise consumer safety (Perez et al., 2017; Raza-Naqvi et al., 2022). The surge in cosmetic usage over the past decades has coincided with a rise in endocrine disorders such as breast, prostate, and testicular cancers, diabetes, obesity, and reproductive issues (Srinivasulu et al., 2022).

The prevalence of metals in the environment, stemming from natural occurrences in rocks, soil, and water, contributes to their incorporation into cosmetic raw materials (Bocca et al., 2014). Despite this, cosmetic companies are not mandated to disclose such impurities, leaving consumers unaware of potential risks (Tarkeshwar et al., 2023). To address these concerns, initiatives to raise public awareness about the chronic health implications of cosmetics, including health alerts, educational campaigns, and product labeling, are imperative. Regulatory agencies must enforce stringent standards to minimize heavy metal content in cosmetics, while research efforts should focus on assessing contamination sources and associated health hazards, and developing new regulations to safeguard public health and the environment (Abed et al., 2024).

5.2.7 Soaps and Detergents

Soaps and detergents play a vital role in cleaning surfaces such as skin, textiles, and solid materials by dissolving dirt, oils, and stains when mixed with water. Although they share similar functions, they are distinct compounds with differing raw materials, chemistry, manufacturing processes, and applications (Achaw & Danso-Boateng, 2021). Soaps, derived from natural oils and fats through saponification, have been utilized for centuries in religious ceremonies and daily life, serving as essential tools for maintaining hygiene and preventing disease spread (Kirsner & Froelich, 1998). However, their alkaline nature can lead to skin irritation and the formation of insoluble salts in hard or sea water, prompting the development of soap alternatives or synthetic detergents.

Detergents, predominantly synthesized from synthetic compounds, offer advantages over soaps in terms of performance and compatibility with various water conditions. It is classified into four groups based on their hydrophilic qualities and surfactant properties, including anionic, cationic, amphoteric, and non-ionic. The detergents cater for specific uses, levels of irritancy, and toxicity (Kirsner & Froelich, 1998).

While soaps have long been considered essential cosmetics, the modern cosmetic industry has expanded to include a diverse array of personal care products beyond basic cleansing agents, such as shampoo, hair oil, perfume, deodorant, moisturizer, hair color, and hair gel (Srinivasulu et al., 2022). As components of personal care products, soaps undergo disposal through wastewater treatment systems, potentially impacting aquatic environments. The COVID-19 pandemic has led to a surge in soap and detergent consumption, resulting in increased waste generation and wastewater

discharge, posing environmental challenges (Chirani et al., 2021). Direct discharge of untreated wastewater into freshwater bodies can have detrimental effects on both the environment and human health (Lechuga et al., 2016).

Excessive detergent concentrations in freshwater bodies can lead to the formation of foam, inhibiting oxygen penetration and disrupting aquatic ecosystems (Chen et al., 2021). This disruption alters crucial chemical and physical parameters of water, threatening the survival of marine flora and fauna (Bandala et al., 2021). To mitigate the environmental impact of soaps and detergents, efforts should focus on developing biodegradable and herbal alternatives with sustainable and eco-friendly ingredients. Industries should prioritize the use of natural compounds for antimicrobial purposes, employ reusable and recyclable packaging materials, and transition towards producing hygiene products that are non-toxic and environmentally sustainable (Chirani et al., 2021).

5.2.8 Acids and Bases

Acids and bases represent essential chemical categories with widespread utility across diverse industrial sectors. In various industrial settings, acids find multifaceted applications spanning chemical manufacturing, metal processing, food processing, and cleaning products. For instance, in chemical manufacturing, acids serve as catalysts or reagents, facilitating the production of numerous chemicals like fertilizers. A vast array of solid acid-base catalysts, including zeolites, oxides, ion-exchange resins, and phosphates, have found application in over a hundred industrial processes (Tanabe & Hölderich, 1999). Notably, the production of phosphate fertilizers necessitates the intermediate step of phosphoric acid production, a process fraught with challenges such as the release of large volumes of phosphogypsum and the presence of impurities like organic matter and heavy metals sourced from phosphate rocks (Kouzbour et al., 2019).

Bases, also known as alkalis, are indispensable in the production of diverse chemicals such as detergents, soaps, fertilizers, and pharmaceuticals. Soaps, for instance, are water-soluble alkali or ammonium salts of fatty acids (Achaw & Danso-Boateng, 2021). Moreover, bases play crucial roles in water and wastewater treatment processes, with alkali-activation technology emerging as a promising approach in this regard (Luukkonen et al., 2019). Additionally, bases are integral to refining processes aimed at removing acidic impurities from petroleum products and are widely used as food additives, flavor enhancers, leavening agents, and pH regulators. Like inorganic food additives include alkalis, acids, and salts. Although some food preservatives are harmless when used in small quantities (e.g., the authorized amounts), the use of others has risks to human health. Among large numbers of side effects, such as skin rashes and itching, breathing difficulty, sneezing or gastrointestinal upsets, can be found (Silva & Lidon, 2016).

Moreover, acids and bases significantly influence indoor air quality, health risks, and material integrity. Indoor sources such as wood emissions, bleach cleaning, and smoking contribute to elevated concentrations of acids and bases like formic acid, acetic acid, hypochlorous acid, and nicotine (Nazaroff & Weschler, 2020).

5.2.9 Salts

Saline and hypersaline environments are frequently contaminated with organic compounds due to industrial activities, underscoring the pervasive presence of inorganic salts across various industries (Oren et al., 1992; Zhang, 2022). These salts are utilized for multiple purposes in different sectors, ranging from acid-base neutralization, flocculation, scale inhibition, and fungicide application in the coal chemical industry, to mercerization and dyeing/printing processes in the textile industry (Holkar et al., 2016; Katheresan et al., 2018; Liu et al., 2022; J. Shi et al., 2020, 2021; Yaseen & Scholz, 2019). Additionally, they find use in electroplating processes and in chemical reactions and purification steps within the pharmaceutical manufacturing sector (Gadipelly et al., 2014; Scarazzato et al., 2017). Moreover, inorganic salts are essential components of various industrial processes, including

lignin removal in the pulp and paper industry, leachates in landfills and incineration plants, and food preservation and processing (Albarracín et al., 2011; Dereli et al., 2021; Kamali & Khodaparast, 2015; Teng et al., 2021).

However, early policies often lack clear restrictions on the discharge of inorganic salts, leading to limited attention on salt management strategies in wastewater treatment processes compared to other pollutants like chemical oxygen demand, total nitrogen, and total phosphorus. The detrimental effects of inorganic salts on conventional wastewater treatment processes are well documented, including reduced treatment efficiency and decreased degradative activity of microorganisms under high-salinity conditions (Castillo-Carvajal et al., 2014; Zhuang et al., 2010). In biological treatment systems, conventional microorganisms exhibit poor degradative efficacy due to the highly saline environment and exposure to low-level, non-point sources of toxic contaminants.

5.2.10 Petrochemicals

The growth and advancement of petrochemicals remain pivotal concerns for the global industrial economy, given their extensive range of applications across various sectors such as detergents, cosmetics, food, agriculture, and dyes. Petrochemicals, derived from petroleum and other fossil fuels, form a complex industrial sector that profoundly influences nearly every aspect of modern life. The ubiquity of plastics and soaps underscores the indispensable role of petrochemicals in daily activities, linking downstream sectors like pharmaceuticals with the upstream oil and gas industries. Through processes such as steam cracking and catalytic cracking, the petrochemical industry transforms feedstocks like naphtha and natural gas components into essential building blocks such as olefins and aromatics, which are integral to the production of numerous industrial and consumer goods (Tripathy et al., 2017).

The primary application of petrochemicals lies in their utilization as fuel, serving as the predominant energy source for lighting, heating, and transportation, particularly through internal combustion engines (Bankole & Ogunkoya, 1978). With the increasing emissions from transportation due to the widespread use of road and air transport, addressing environmental concerns becomes imperative. Enhancing fuel quality, including the incorporation of biofuels, offers a pathway to mitigate emissions and improve the performance characteristics of automotive fuels (Kubičková & Kubička, 2010). Moreover, the re-evaluation of processes like hydrotreating for diesel fuel production underscores the industry's commitment to meeting stringent environmental regulations and ensuring sustainable practices in petrochemical production (Laredo et al., 2018).

5.2.11 Polymers

Polymers, consisting of repeating monomer units bonded together, form long chains or networks, presenting versatile materials utilized across diverse industries, including automotive, construction, electronics, healthcare, packaging, and textiles (Carothers, 1936). The classification of polymers encompasses various categories based on their structure, properties, and synthesis methods, with conductive polymers (CPs) garnering significant attention due to their superior characteristics compared to conventional materials. CPs nanocomposites exhibit enhanced electrical conductivity, increased surface area, and exceptional electrochemical behavior, broadening their application possibilities (Das & Prusty, 2012; Idumah et al., 2021).

Despite the broad utility of polymers, their production poses challenges in terms of post-use utilization and recycling, leading to significant environmental and social concerns. The slow progress in polymer recycling exacerbates the issue, resulting in the accumulation of millions of tons of discarded polymeric materials annually. Traditional waste disposal methods such as landfill deposition become increasingly unsustainable due to rising costs and diminishing available space (Ignatyev et al., 2014; Zia et al., 2007). Developing fully sustainable plastic materials with alternative chemical structures is a lengthy and expensive process (Hayes et al., 2023). To address these challenges,

efforts are directed towards utilizing renewable resources like lignocellulose, vegetable oils, terpenes, and carbohydrates as feedstocks for synthesizing sustainable polymers, with biomass serving as a source for producing numerous value-added compounds essential for polymer synthesis (Haque et al., 2022; Molina-Gutiérrez et al., 2019).

5.2.12 Surfactants

Surfactants, also known as surface-active agents, are essential compounds that reduce the surface tension between different substances, facilitating processes like detergency, emulsification, dispersion, and foaming crucial for various industrial applications. Industries spanning personal care products, cleaning agents, agriculture, and pharmaceuticals heavily rely on surfactants, highlighting their indispensable role in modern manufacturing (Halliday, 2008). Despite their utility, concerns surrounding surfactant toxicity have spurred global attention and regulatory measures. The synthesis and disposal of surfactants contribute to environmental issues such as global warming, climate change, and ozone layer depletion (Rebello et al., 2014). Efforts to mitigate these concerns include regulations promoting the use of phosphate-free surfactants, wastewater remediation before disposal, and the development of eco-friendly alternatives like green surfactants. Studies suggest that using liquid detergents instead of powder forms can reduce surfactant toxicity, while innovative methods for preparing laundry and liquid detergents for different water types further contribute to toxicity reduction (Goel & Kaur, 2012; Khurana, 2002). Additionally, natural surfactants or biosurfactants, derived from microorganisms and waste materials, offer promising alternatives due to their low toxicity, biodegradability, and stability under various conditions. Despite challenges like high production costs and limited understanding of bioreactor systems, advancements in reactor design and product recovery technology could enhance the ecological and economic viability of biosurfactants, making them favorable alternatives in the future (De et al., 2015).

5.2.13 Agrochemicals

In several developing countries, existing agricultural systems often rely on unsustainable practices that lead to the significant discharge of hazardous effluents into the soil, air, and nearby water bodies (Ez et al., 2002). Currently, numerous agrochemicals are being used without regulation or judicious application. Educating farmers, industry stakeholders, distributors, policymakers, and others about the responsible use of pesticides is crucial to mitigating their harmful effects on both human health and the environment (Meena et al., 2020).

The agricultural industry primarily employs three categories of agrochemicals: fertilizers, plant protection chemicals, and plant growth stimulants. Technological advancements in fertilizer production have resulted in the development of nanofertilizers and improved fertilizer formulations, diversifying the components available to include soil ameliorants, macronutrients, and micronutrients. Moreover, agrochemical application technology has evolved from manual techniques to sophisticated methods, including the use of drones.

Chemical pesticides can be generally categorized into insecticides, bactericides, fungicides, herbicides, and rodenticides, with major chemical groups including triazines, carbamates, organochlorines, dithiocarbamates, and organophosphates. More recent and safer alternatives, such as pyrethrins and neonicotinoids, have emerged as well. The chemical formulations of these substances influence their modes of action and their impacts on the environment and human health. Although herbicides account for most pesticides used worldwide, their prevalence varies by country. For example, whereas herbicides dominate agricultural practices in the United States, insecticides are more widely used in India. This usage disparity is largely influenced by factors such as cropping patterns, climate conditions, and advancements in technology (Devi et al., 2022).

To enhance toxicological and environmental safety, the crop protection industry, along with academic institutions, must adopt innovative research methods to tackle challenges including limited

arable land, increasing extreme weather conditions, and growing resistance among weeds and pests (Lamberth et al., 2013). Furthermore, it is imperative to establish effective mechanisms for evaluating, monitoring, and managing agrochemical usage. The adoption of sustainable green technologies is equally essential to secure the future of agriculture, minimize its environmental impact, and ensure long-term sustainability and resilience.

5.2.14 Catalysts

Catalysts can be categorized into three main types: homogeneous, heterogeneous, and enzymatic, each representing a distinct area of research. Homogeneous catalysts typically operate in the same physical phase as their reactants, commonly in liquid or gaseous states. Examples include metal complexes, organometallic compounds, protons, ions, radicals, and various small molecules. Enzymes, composed of complex three-dimensional structures formed by amino acids, are often viewed as specialized homogeneous catalysts, distinguished by their exceptional chemical complexity and high turnover rates.

In contrast, heterogeneous catalysts operate in a different phase than the reactants. These catalysts can be found on the external or internal surfaces of dense or porous solids, including polymers. Examples of heterogeneous catalysts include metal crystals, porous materials like zeolites and metal-organic frameworks (MOFs), supported nanoparticles, and organometallic or enzymatic compounds chemically bonded to solid surfaces. The advancement of hybrid catalyst systems, which offer increased efficiency and versatility, relies on integrating knowledge from various fields of catalysis (Ye et al., 2018).

Alkali catalysts, for example, are used in biomass gasification to significantly reduce the production of tar and methane. Dolomite is effective in eliminating hydrocarbons generated during this process. Nickel-based reforming catalysts, which are commercially available, can be tailored to adjust gas composition for optimal syngas production (Sutton et al., 2001). Similarly, choosing the right catalyst is essential for biodiesel production through transesterification. While traditional alkaline catalysts such as NaOH and KOH are commonly employed, heterogeneous substitutes, including solid and enzyme-based catalyst systems, can offer substantial advantages in terms of sustainability and efficiency (Atadashi et al., 2013; Sharma et al., 2008).

In recent years, there has been a surge in the development and study of catalysts for the activation of peroxymonosulfate (PMS), each exhibiting unique radical or non-radical degradation pathways. These include metallic and bi-metallic oxides, supported noble and non-noble metals, carbon-based materials, layered double hydroxides, zeolites, metal-organic frameworks, and perovskite systems. By exploring the distinct characteristics and processes of different catalyst types, researchers aim to enhance PMS activation and expand its applications (Kohantorabi et al., 2021).

5.2.15 Specialty Chemicals

Electronic chemicals, surfactants, agrochemicals, adhesives, specialized coatings, sealants, and catalysts are examples of specialty chemicals, each distinguished by its specific application. Electrochemical technologies have demonstrated enhanced efficiency compared to conventional methods, offering promising pathways for the synthesis of new specialized compounds. Addressing current challenges in this domain could represent a significant advancement in sustainable and green chemistry (Y. Li et al., 2023). Additionally, recent findings suggest that fruit and vegetable waste can serve as a valuable resource for producing specialized chemicals (Pradhan et al., 2023).

Despite farmers' reliance on fertilizers, pesticides, and herbicides to boost agricultural productivity, the indiscriminate use of these agrochemicals poses serious risks, including cancer, mutagenicity, and adverse effects on human health and the environment (Guha et al., 2020). Surfactants play a crucial role in modern industrial processes across various sectors, such as personal care, cleaning products, agriculture, and pharmaceuticals (Halliday, 2008). However, their applications are also

linked to significant environmental issues, including ozone depletion and climate change (Rebello et al., 2014). It is essential to address the specific materials responsible for environmental pollution with specially designed chemicals (Karthick et al., 2019). The increasing focus on waste recycling and conversion highlights a growing trend towards more environmentally friendly practices within the industry (Jiao et al., 2024).

5.2.16 Flame Retardants

Flame retardant pollution is closely related to plastic contamination. Plastics, textiles, and electronic circuits are also coated with these compounds to reduce the risk of fire. Brominated organic compounds that are lipophilic, can bioaccumulate, and remain in the environment are commonly used as flame retardants (de Wit, 2002). According to the European Union, plastics are responsible for over 50% of all priority pollutants and toxic substances identified (Rochman et al., 2013), including brominated flame retardants, which are commonly used in consumer products like foams, polymers, electronics, and textiles (Li & Demyanets, 2010; Sharkey et al., 2020). PBDEs, recognized for their environmental durability and ability to bioaccumulate in a variety of species, including humans, are among the most important flame retardants (Sousa-Guedes et al., 2023). To address these issues, PBDE laws must be strengthened and more thorough toxicological studies conducted to determine potential health consequences and preventative regulatory measures (Bartalini et al., 2022).

5.2.17 Corrosion Inhibitors

Using corrosion inhibitors is a widely adopted strategy to prevent or reduce the corrosion rate of metallic copper. This approach is favored for its simplicity, adaptability, and minimal impact on the original copper systems (Berdimurodov et al., 2022; Fateh et al., 2020; Shinato et al., 2020; Verma et al., 2021). Corrosion inhibitors for copper can be broadly categorized as inorganic or organic. While inorganic inhibitors are often less effective and may pose toxicity concerns, organic inhibitors generally offer higher corrosion inhibition efficiency (Ravichandran & Rajendran, 2005). However, many organic inhibitors are also toxic, and their synthesis process can be environmentally harmful, limiting their widespread industrial application. In recent years, carbon dots (CDs) have emerged as promising eco-friendly corrosion inhibitors due to their environmentally friendly nature and excellent water solubility. The use of CDs in aqueous phases represents a green alternative to traditional corrosion inhibitors. With advancements in chemistry, materials science, and nanoscience, research on CDs as effective and sustainable corrosion inhibitors is expected to continue expanding (Liao et al., 2024). This development underscores a growing trend towards environmentally friendly solutions in corrosion prevention, paving the way for greener and more sustainable practices in industry.

5.2.18 Chelating Agents

Ethylenediaminetetraacetic acid (EDTA)'s ability to mobilize heavy metals in polluted soils and facilitate their uptake by plants has made it the most prevalent chelating agent since the 1950s (Wen et al., 2009). Even so, EDTA commonly forces heavy metals into deeper soil layers and groundwater, leading to contamination beyond the treatment area. The slow degradation of it is due to its low biodegradability and high chemical stability, making it a significant environmental pollutant (Beiyuan et al., 2018; Luo et al., 2017; Wu et al., 2013). EDTA has been shown to reduce biomass in shoots and roots by 50% and 43%, respectively, while inhibiting soil respiration, lowering metal absorption, increasing glutathione and phytochelatins (PC) (Guo et al., 2020). Furthermore, its capacity to transport heavy metals into groundwater downstream amplifies environmental hazards, affecting areas beyond the remediation zone (Monti et al., 2019). Heavy metal-EDTA complexes are a major environmental issue, often found in industrial effluents. In place of persistent chelators, biodegradable chelating agents have been developed to address these problems (Yin et al., 2024).

However, they are not widely used in industrial processes. Microbial activity can break down these biodegradable agents into non-toxic and environmentally friendly compounds, resulting in reduced toxicity and ecological consequences (Srivastava et al., 2019).

5.2.19 Refrigerants

Refrigerants are categorized into several types, as well as hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), and other natural alternatives such as ammonia and carbon dioxide. Among these, chlorofluorocarbons (CFCs) have been widely utilized for various applications such as cleaning electric motors, compressors, and aerospace components. However, their use has been linked to the depletion of the stratospheric ozone layer and contributes to global warming, necessitating the exploration of alternative options (Kikuchi et al., 2011). HFCs, which often contain a CF3 group, have emerged as significant substitutes for CFCs and halons due to their lower ozone-depleting potential. Despite being less harmful to the ozone layer, HFCs still contribute to global warming and are subject to regulation (Ravishankara et al., 1994). Consequently, there is a growing imperative to replace CFCs and HCFCs with alternative compounds that not only safeguard the ozone layer but also mitigate their impact on global warming (Kim et al., 2016; Sekiya & Misaki, 2000).

5.3 REGULATION OF INDUSTRIAL CHEMICALS

5.3.1 Regulatory Agencies and Schemes

Regulatory agencies across various countries and organizations are responsible for overseeing specific industries and enforcing regulations that promote public health, safety, and environmental protection. These regulations can differ significantly by country or region, with agencies typically undertaking several key responsibilities: (1) evaluating the safety of both new and existing industrial chemicals; (2) developing and enforcing regulations concerning the use, storage, and transport of these substances; (3) monitoring the environmental impacts of industrial chemicals; and (4) providing information and guidance to industry stakeholders and the public regarding the safe handling of these materials. Table 1 summarizes the key global regulatory frameworks for industrial chemicals.

One of the most comprehensive and ambitious pieces of legislation concerning chemical regulation is the Regulation, Evaluation, Authorization, and Restriction of Chemicals (REACH) implemented by the European Union (EU) (Bergkamp, 2013; Biedenkopf, 2015). The principles and practices established under REACH have far-reaching global implications. The regulation of chemicals under REACH involves four critical steps: registration (companies are required to register chemicals that they produce or import in significant quantities), evaluation (authorities assess submitted information to identify potential risks), authorization (which may be necessary for the specific use of substances classified as very high concern), and restriction (the EU can limit or prohibit the use of certain hazardous substances).

In Australia, the Australian Industrial Chemicals Introduction Scheme (AICIS) governs the management of industrial chemicals and defines industrial use by exclusion. Industrial use covers all applications not classified as agricultural, veterinary (as defined by the AgVet Code), pharmaceutical, or animal feed products according to the Therapeutic Goods Act 1989. Compliance with AICIS or the relevant regulatory agency is mandated based on the intended use of the chemical.

In Canada, the regulation of industrial chemical applications falls under the Canadian Environmental Protection Act (CEPA) 1999. This act requires a thorough assessment of the environmental and health impacts of new chemical substances that were produced or imported into Canada post 1994. The "Guidelines for Notification and Testing of New Substances: Chemicals and Polymers" (2005 version) outline the data requirements for assessing new chemicals. Canada maintains a detailed inventory known as the Domestic Substances List (DSL), while internationally used substances not included on the DSL are classified as the Non-Domestic Substances List (NDSL) (Ji et al., 2017).

TABLE 5.1
Examples of Regulatory Frameworks Globally

No	Scheme	Agency	Country/Region	Description
1	Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH)	European Chemicals Agency (ECHA)	European Union (EU)	REACH is one of the most comprehensive chemical regulations worldwide. It requires manufacturers, importers, and downstream users to register and provide safety data for chemicals placed on the EU market, assess the risks associated with their use, and implement risk management measures. Extensive data submission and safety assessments are required under the scheme. It aims to improve the knowledge and control of chemicals and eventually eliminate the use of the most hazardous ones. The ECHA is established to implement REACH and other chemical regulations in the EU; it provides guidance, support, and enforcement measures to promote the safe use of chemicals and protect human health and the environment. https://echa.europa.eu/regulations/reach/understanding-reach
2	Toxic Substances Control Act (TSCA)	United States Environmental Protection Agency (EPA)	United States of America	TSCA regulates the production, importation, use, and disposal of industrial chemicals in the United States. In 2016, TSCA was amended to strengthen chemical safety standards and facilitate the evaluation and regulation of existing chemicals. It has a pre-market notification requirement for new chemicals and ongoing assessment for existing ones. It focuses on protecting public health and the environment from the unreasonable risks of new and existing chemicals. https://www.epa.gov/tsca-inventory
3	Canadian Environmental Protection Act	Canadian Environmental Protection Agency (CEPA)	Canada	CEPA utilizes a screening process for new chemicals and has specific regulations for existing ones, it includes new substances program and existing substances program. It emphasizes pollution prevention and managing the risks of toxic substances. https://www.canada.ca/en/environment-climate-change.html
4	Australian Industrial Chemicals Introduction Scheme (AICIS)		Australia	AICIS employs a risk-based and tiered approach to assess the risks of chemicals to protect Australians and the environment. The scheme prioritizes chemicals for the risks of industrial chemicals. https://www.industrialchemicals.gov.au/
5	Regulations on Safe Management of Hazardous Chemicals (Decree No. 591), Measures for Environmental Management Registration of New Chemical Substances, etc.	Ministry of Ecology and Environment (MEE), State Administration for Market Regulation (SAMR), National Registration Centre for Chemicals (NRCC), Ministry of Emergency Management (MEM)	China	There are multiple schemes in China under several regulatory agencies for the management of chemicals. The system requires comprehensive management of hazardous chemicals throughout their lifecycle, including production, storage, use, transportation, and disposal. It requires the assessment and management of risks posed by new chemicals.

International agreements and conventions also play a vital role in chemical safety and regulation. The Rotterdam Convention on the Prior Informed Consent (PIC) Procedure for Hazardous Chemicals and Pesticides in International Trade, along with the Stockholm Convention on Persistent Organic Pollutants (POPs), addresses critical aspects of chemical safety. Established in 1970, the Rotterdam Convention aims to ensure equal protection against hazardous substances for countries involved in the export and import of these materials. The PIC procedure mandates that exporters obtain prior consent from the importing country before sending any chemical, thereby facilitating communication between participating nations. This protocol requires exporters to provide detailed information regarding the properties, risks, and proper handling of chemicals, while importing countries retain the authority to permit, conditionally approve, or prohibit such imports.

In contrast, the Stockholm Convention primarily focuses on the management of the production, use, and transportation of persistent organic pollutants (POPs). It allows for the addition of new chemicals and specifies conditions for existing POPs based on scientific evaluations. All member states are required to comply with the convention and its obligations, as outlined in Table 2.

5.3.2 Environmental Management Standards

To reduce the environmental effect of industrial chemicals over the course of their life cycle, environmental management is crucial. There is currently no single or universally accepted standard for environmental management of industrial chemicals, while general principles include seeking and implementing safer alternatives whenever possible; implementing procedures that minimize potential spills, leaks, and releases; implementing procedures for treating and disposing of chemical

TABLE 5.2
The POPs List (2023)

Annex	Initial 12 POPs	New 16 POPs
A (Elimination)	• Aldrin • Chlordane • Dieldrin • Endrin • Heptachlor • Hexachlorobenzene • Mirex • Toxaphene • PCB	• Alpha hexachlorocyclohexane • Beta hexachlorocyclohexane • Chlordecone • Hexabromobiphenyl • Hexabromocyclododecane • Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether) • Hexachlorobutadiene • Lindane • Pentachlorobenzene • Pentachlorophenol and its salts and esters • Polychlorinated naphthalenes • Technical endosulfan and its related isomers • Tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether) • Decabromodiphenyl ether (Commercial mixture, c-DecaBDE) • Short-chain chlorinated paraffins (SCCPs)
B (Restriction)	• DDT	• Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF)
C (Unintentional production)	• Polychlorinated dibenzo-p-dioxins and dibenzofurans • Hexachlorobenzene • PCB	• Hexachlorobutadiene • Pentachlorobenzene • Polychlorinated naphthalenes

waste responsibly to minimize environmental impact; regularly monitoring environmental releases; and reporting any incidents or potential risks to relevant authorities. The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) is one system that promotes consistent hazard communication through classification and labeling even it is not directly related to the management standards. It can contribute to safer handling and disposal, minimizing environmental risks. An international policy framework called the Strategic Approach to International Chemicals Management (SAICM) seeks to manage chemicals responsibly throughout their lifespan in order to safeguard the environment and public health. It provides guidance and promotes the development of national and regional frameworks. Examples for national and regional frameworks include the REACH regulation and Australia's Industrial Chemicals Environmental Management Standard (IChEMS). This Australian standard classifies industrial chemicals based on their environmental risk and establishes guidelines for their safe and sustainable use, storage, and disposal. At the same time, there are industry-specific standards, such as the Responsible Care Global Charter, which is a voluntary initiative that encourages chemical companies to adopt a set of principles for environmental protection, including responsible production, handling, and disposal of chemicals.

The ISO 14001 standard is one of the primary standards for environmental management related to industrial chemicals. It is an internationally recognized framework for environmental management systems (EMS). While it doesn't specifically focus on environmental performance requirements for industrial chemicals, it provides a systematic approach for framework and guidelines for organizations to manage their environmental impacts, including those linked with the manufacturing, use, and removal of chemicals. The key requirements under ISO 140001 as it relates to chemicals of industrial concern for environmental management include:

1) **Environmental Policy**: ISO 14001 requires organizations to establish a clear and documented environmental policy that commits to pollution prevention, compliance with legal requirements, and continual improvement. This policy can include commitments to minimize the environmental impacts of industrial chemical use and disposal.
2) **Legal and Regulatory Compliance**: Organizations must identify and comply with relevant environmental legislation and regulations, including those related to the handling, storage, transportation, and disposal of industrial chemicals.
3) **Environmental Aspects and Impacts Assessment**: ISO 14001 mandates that organizations identify their environmental aspects, which may include the use, storage, and release of industrial chemicals, and assess their associated environmental impacts. This assessment helps prioritize actions to mitigate risks and improve environmental performance.
4) **Operational Controls**: Organizations implement operational controls to manage their environmental aspects, which can include procedures and measures for the safe handling, storage, and use of industrial chemicals, as well as spill prevention and emergency response protocols.
5) **Training and Awareness**: ISO 14001 requires organizations to ensure that employees are trained and aware of their roles and responsibilities in environmental management, including proper handling and disposal practices for industrial chemicals.
6) **Emergency Preparedness and Response**: Organizations develop and implement procedures for responding to environmental emergencies, including spills or releases of industrial chemicals, to reduce their impacts on man and the environment.
7) **Monitoring and Measurement**: ISO 14001 discuss the importance of checking, measuring, and evaluating environmental performance, including indicators related to the management of industrial chemicals, to track progress and identify opportunities for improvement.
8) **Auditing and Management Review**: Organizations conduct internal audits of their environmental management system and regularly review its effectiveness, including the management of industrial chemicals, to ensure compliance with ISO 14001 requirements and drive continual improvement.

While ISO 14001 provides a comprehensive framework for environmental management, organizations may also need to comply with industry-specific standards, regulations, and guidelines related to industrial chemicals, depending on their sector and jurisdiction. Additionally, other standards such as ISO 14031 (environmental performance evaluation) and ISO 14040 series (life cycle assessment) can complement ISO 14001 in assessing and managing the environmental impacts of industrial chemicals throughout their lifecycle.

5.4 ASSESSMENT STRATEGIES

5.4.1 Context for Using Risk Assessment Strategies

Risk is defined as "the probability of an adverse effect of a specific magnitude" (Ricci, 2006). Assessing risks associated with anthropogenic substances is crucial for safeguarding both human health and the environment from the negative effects of exposure. Effective risk management relies on these assessments to inform decision-making processes.

For risk management purposes, it is essential to evaluate the potential impacts of industrial chemicals on people and the environment. The risks posed by pollutants that may enter various environmental sectors (air, water, and land) are assessed using established methodologies and procedures. These standard protocols involve the systematic collection and verification of data, including:

- Environmental concentrations of industrial chemicals in different matrices
- Inventories of environmental emissions and discharges
- Potential environmental exposures for organisms, including humans
- Meteorological data regarding the frequency and intensity of weather events and climate variability

The primary objectives of these assessment strategies are to determine the risks, hazards, and potential effects of industrial chemicals on both the environment and human health. Ultimately, these assessments aim to minimize adverse effects while promoting the safe production, use, and disposal of chemicals.

As illustrated in Figure 5.1, the conventional risk assessment framework follows an iterative process consisting of four essential steps: risk characterization, exposure analysis, hazard identification, and dose-response evaluation.

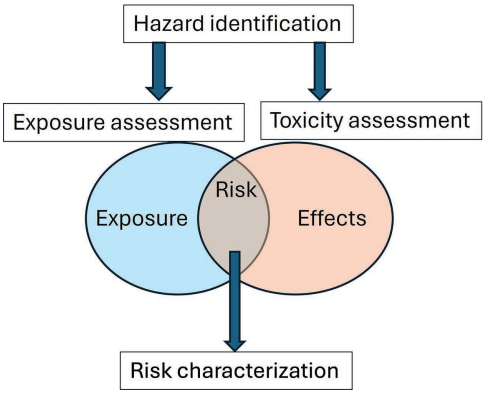


FIGURE 5.1 Chemical risk assessment.

1) **Hazard identification**

This represents the initial step in assessing the risks associated with a hazard. A hazard or risk refers to the likelihood of harm to human health or the environment resulting from exposure to an industrial chemical. Identifying the intrinsic properties of these chemicals – such as toxicity, flammability, corrosiveness, and environmental persistence – is critical for recognizing potential hazards. Original data derived from sample screening, predictive models, and emission inventories are employed to estimate expected contaminant levels in the environment, alongside data collected from screening programs for hazard identification.

Various methods are utilized for identifying chemical hazards (Chartres et al., 2019), including processes to identify substances, formulating relevant questions, conducting reviews, employing systematic reviews, assessing the overall confidence of evidence, and integrating different streams of evidence. The HAZID methodology has been applied for hazard identification and analysis within the manufacturing sector in Mexico (Rivera Domínguez et al., 2021).

In the European Union (EU), the REACH (Registration, Evaluation, Authorisation, and Restriction of Chemicals) framework plays a crucial role in classifying hazardous substances to ensure human health and environmental safety. REACH mandates that information about quantities of substances imported or produced by industries – those exceeding 1 ton per year – be reported (Woutersen et al., 2019). The toxic effects considered in hazard identification include mutagenicity, carcinogenicity, reproductive toxicity, aquatic toxicity, and terrestrial toxicity. The information gathered through this process can subsequently be used for the classification and labeling of chemicals.

In Australia, the Industrial Chemicals Introduction Scheme (AICIS) utilizes standard endpoints to assess risks to workers, the public, living organisms (including air, water, soil, and sediments), and ecosystem impacts that may indirectly affect living organisms. This evaluation considers toxicological, ecotoxicological, and physicochemical effects, as well as acute vs. chronic, local vs. systemic, and reversible vs. irreversible effects on human health. Data from a range of sources – including in vivo, in vitro, ex vivo, and in silico studies, and epidemiological surveys – are employed in hazard identification.

2) **Exposure assessment**

Evaluating potential routes and levels of human and environmental exposure to chemicals involves analyzing occupational exposure in workplaces, consumer exposure from products, and environmental exposure from releases into the air, water, soil, and ecosystems. This process encompasses the scientific assessment and verification of hazardous industrial chemicals in the environment, focusing on both environmental receptors and human populations.

Key steps in this evaluation include identifying the exposed populations and potential exposure pathways. The magnitude, duration, and frequency of exposure to specific chemicals must also be estimated. Various pathways contribute to chemical exposure in humans, including inhalation, dermal absorption, and ingestion. Understanding epidemiological factors – such as daily habits and activities – along with meteorological data is critical for determining the exposure routes and pathways relevant to compounds of concern.

In conducting exposure assessments for environmental contaminants, it is essential to consider the past, current, and future exposure scenarios, as well as the elements of exposure pathways. These elements include the contaminant source, environmental fate and transport, exposure points, exposure routes (dermal, inhalation, ingestion), and the potentially exposed populations. Additionally, site-specific factors and chemical characteristics may influence contaminant transport.

Various tools can facilitate exposure assessments, such as the ATSDR SHOWER model, EPA Science Models and Research Tools (SmaRT), and EPANET, among others. It's important to note that exposure routes may differ significantly between occupational and public settings. For public exposure, indirect exposure through the environment must also be considered. Factors such as type, intensity, frequency, and duration of exposure are critical for accurate assessment. Figure 2 illustrates the key considerations involved in exposure assessment.

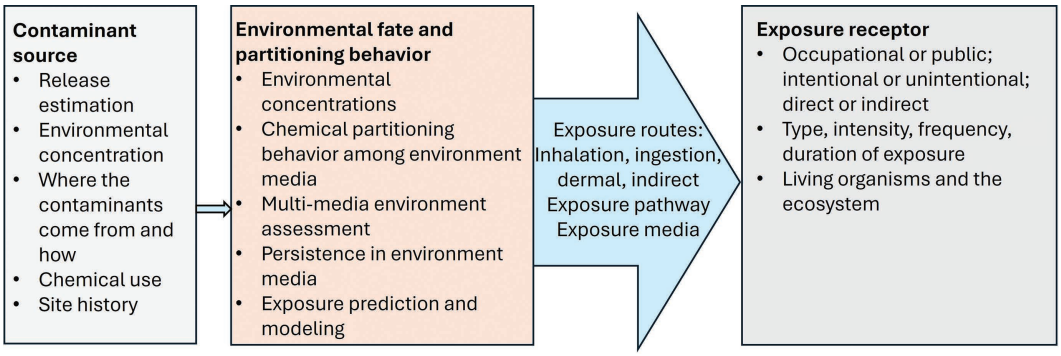


FIGURE 5.2 Considerations for exposure assessment for chemicals.

3) **Toxicity assessment**

The toxicity assessment involves several key components: characterizing the toxicity of a chemical, developing a dose-response relationship, and establishing exposure criteria. To understand the risk posed by chemical exposure, various animal studies and dose-response experiments are conducted. In these studies, organisms are subjected to different concentrations of a chemical, and the resulting effects are meticulously recorded. Toxicological evaluations utilize a range of methodologies, including laboratory tests, animal research, and in vitro assays, to assess the effects of substances on biological systems. These evaluations cover multiple endpoints, including mutagenic, developmental, carcinogenic, and reproductive impacts, as well as both acute and chronic toxicity.

Several metrics are employed to measure the toxicity of a pollutant, notably ED50 (the effective dose for 50% of the population) and LD50 (the lethal dose for 50% of the population). While LD50 indicates the concentration of a chemical that is fatal to half of the test population, ED50 reflects the concentration at which 50% of the population exhibits adverse effects from exposure.

The toxicity assessment will consider both human health and environmental impacts. Toxicity endpoints may encompass acute toxicity (via inhalation or oral routes), chronic toxicity (including carcinogenicity, genotoxicity, reproductive toxicity, neurotoxicity, and endocrine disruption), acute toxicity in terrestrial animals (oral exposure), and both acute and chronic environmental effects. Endocrine disruption specifically refers to a chemical's ability to interfere with the endocrine system, potentially disrupting hormonal functions in both humans and wildlife. Such endocrine disruptors can adversely affect immune system functionality, metabolism, development, and reproductive health.

Ecotoxicity assessments primarily focus on acute and chronic toxicity, the potential for bioaccumulation, and the implications for ecosystems and biodiversity, evaluating how toxins impact both aquatic and terrestrial organisms. Databases such as the US EPA's ECOTOX provide extensive environmental toxicity data across various species, serving as valuable resources in toxicity evaluations. Additionally, a chemical's toxicity and overall risk can be appraised through its persistence, bioaccumulation potential, and toxicity (PBT) properties, which are essential for comprehensive toxicity and risk assessments.

4) **Risk characterization**

According to Dupouy (2023), risk characterization entails offering a qualitative assessment of the probability and seriousness of unfavorable consequences (both known and unknown) within a certain group (Dupouy, 2023). In order to determine the possible dangers that chemicals may cause to human health and the environment, the last stage of risk assessment synthesizes data on hazards,

exposure levels, and toxicity. Environmental risk assessments (ERAs) help to determine the environmental impact of the industrial chemicals. This includes identifying the health and physicochemical hazards. Risk assessment considers factors such as exposure pathways, dose-response relationships, population demographics, environmental fate and transport, and uncertainty analysis. It acknowledges the inherent ambiguities in interpretation brought on by variables like time and data limits, as well as problems with sampling and extrapolation. A chemical's toxicity, physicochemical properties, and emission rates (such as manufacturing volume) all affect the danger it poses. Furthermore, exposure levels are greatly influenced by the way chemicals behave in the environment, including processes like degradation, transformation, bioaccumulation, partitioning, and movement through air, water, soil, and living things.

5.4.2 Strategies for Assessing the Risks of Industrial Chemicals

Developing effective assessment strategies for industrial chemicals is essential for informed decision-making, risk management, and compliance with regulatory frameworks. These strategies play a pivotal role in safeguarding human health and preserving environmental integrity. In the European Union (EU), the precautionary principle is a fundamental aspect of the risk assessment process for industrial chemicals.

To evaluate the risks associated with these chemicals, methods have been established to assess 1) the likelihood of negative public or environmental health consequences, and 2) the occurrence and magnitude of such consequences. Various organizations worldwide have developed tools and methodologies to quantify these risks, which can be leveraged for effective risk management.

Organizations such as the OECD, WHO, ECHA, and ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals) have contributed significantly to this field.

The OECD has created a range of risk assessment toolkits, including the QSAT Toolbox, eChemPortal, the International Uniform Chemical Information Database (IUCLID), and the OECD Product Release and Exposure Data Warehouse. The QSAT Toolbox is designed to assist governments, the chemical industry, and other stakeholders in bridging data gaps related to (eco)toxicity, thereby enhancing chemical risk assessments. eChemPortal offers peer-reviewed data on physicochemical properties, environmental behavior, ecotoxicity, toxicity, and chemical usage and exposure. IUCLID serves as a software platform for recording, storing, and sharing chemical data, making it a valuable resource for regulatory authorities and the chemical sector in ensuring compliance. The OECD Product Release and Exposure Data Warehouse aggregates existing data on emissions and exposures from commercial and consumer products for assessment purposes.

ECETOC provides additional resources, including the hSSD Tool, HEATDB Tool, and TRA (Targeted Risk Assessment) Tool, to aid in the risk assessment of industrial chemicals. The hSSD Tool supports innovative approaches for determining aquatic threshold concentrations based on Scenario-based Species Sensitivity Distributions (SSD). The HEATDB Tool (Human Exposure Assessment Tools Database) is a publicly accessible repository of exposure data and assessment tools organized in a harmonized format, aiding risk assessors in shaping regulatory policies. The TRA Tool evaluates the risk of chemical exposure to humans and the environment.

In the United States, the EPA offers the Exposure Factors Handbook, which compiles information on physiological and behavioral factors used to assess exposure to environmental chemicals. The ECOTOX database catalogs harmful effects of substances on terrestrial and aquatic species, encompassing over 500,000 records related to more than 10,000 chemicals.

Australia has developed its own framework for chemicals risk assessment through the Australian Regulatory Cheminformatics Engine (ARChIE). Initially designed for internal use by chemicals risk assessors at the Department of Climate Change, Energy, the Environment, and Water (DCCEEW), ARChIE features a global knowledgebase and advanced search capabilities that promote a more integrated approach to chemicals risk management. The Industrial Chemicals Environmental Management Standard (IChEMS) represents a national initiative to enhance the

management of environmental risks posed by chemicals in Australia. Additionally, the Australian Industrial Chemicals Introduction Scheme (AICIS) regulates the manufacture and importation of industrial chemicals.

In the EU, the ZeroPM project ("Zero Persistent and Mobile Substances") is a research consortium aimed at developing prevention, prioritization, and removal strategies for persistent and mobile substances. Cheminformatics is integrated into their decision-making frameworks, and the project includes a comprehensive "global inventory" of chemicals.

Together, these initiatives and tools provide a robust framework for assessing and managing the risks associated with industrial chemicals, ensuring protection for both human health and the environment.

5.5 CONCLUDING REMARKS

While the benefits of over 350,000 man-made chemicals are widely recognized and their global use continues to grow, it is crucial to acknowledge that unregulated or poorly managed utilization and release of these chemicals can pose significant threats to human well-being and ecosystem integrity. Therefore, it is essential to rigorously assess the safe use of chemicals through stringent regulations and policies to prevent uncontrolled release into the environment and to address environmental burdens at their source. Local and international regulations are in place to limit exposure to industrial chemicals; however, establishing legal limits for chemical contaminants often requires extensive information and discussions with stakeholders, which can be time-consuming. As a result, not all industrial chemicals have specified regulatory limits.

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6 Halogenated Aromatic Compounds
Impacts, Risks, and Remediation Strategies

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6.1 INTRODUCTION

Halogenated aromatic compounds (HACs) are significant environmental pollutants known for their persistence, potential for bioaccumulation, and detrimental effects on human health and ecosystems (Kodavanti et al., 2023). HACs include polychlorinated dibenzo-p-dioxins (PCDDs), dibenzo-furans (PCDFs), polychlorinated biphenyls (PCBs), and polychlorinated diphenylethers (PCDEs) (Loganathan & Masunaga, 2020; Malisch et al., 2023). Specifically, PCDDs and PCDFs, often collectively called dioxins, are highly toxic persistent organic compounds that represent a major category of soil contaminants. Their high melting and boiling points contribute to their thermal stability, while their low water solubility further enhances their persistence. For instance, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) has a solubility of 1.93×10^{-3} mg/L and octachlorodibenzodioxin (OCDD) is even less soluble at 0.75×10^{-7} mg/L at 25°C (Tran et al., 2024). These compounds' nonpolar,

DOI: 10.1201/9781003530466-6
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hydrophobic nature, coupled with their high octanol-water partition coefficients, enables them to strongly adhere to soil particles, making remediation particularly challenging.

Halogenated aromatic compounds are primarily anthropogenic pollutants produced as byproducts of various industrial processes. For instance, the incomplete combustion of organic materials, particularly chlorinated substances, can generate PCDDs and PCDFs (Solorzano-Ochoa et al., 2012; Wiedinmyer et al., 2014). While PCBs were once widely used in electrical appliances, transformers, and hydraulic fluids, their continued environmental presence poses significant risks despite being banned in many regions. Additionally, the production of certain pesticides and chlorinated organic compounds can unintentionally generate HACs. Industrial activities such as ferrous and nonferrous metal smelting, paper and pulp production, and fuel combustion are common sources of PCDD/F emission (Güzel et al., 2022). For example, PCDD/F emissions from oxygen-rich smelting furnaces have been shown to exceed those from anode furnaces (Li et al., 2021). In industrial biomass boilers, PCDD/F emissions range from 0.0491 to 12.7 ng Nm^{-3} (11% O_2), highlighting the dual role of biomass as a sustainable energy source and a potential contributor to pollutant emissions (Zhang et al., 2022).

Halogenated aromatic compounds have been detected globally in soil, sediment, and water samples. In northern Vietnam, for instance, PCDD/Fs were found in soil and sediment samples from secondary copper and aluminum villages, with concentrations of 0.37 ± 0.29 ng TEQ/kg dry weight (d.w.). (Nguyen Xuan et al., 2024). In the Yangtze River Delta, OCDD/F and 1234678-HpCDD/F were identified as dominant congeners in various media (Lei et al., 2024). In Turkey, ambient air and soil samples collected near the IZAYDAS Waste Incineration Plant revealed PCDD/F and dl-PCB levels ranging from 0.00841 to 0.05881 pg I-TEQ/m^3 and concentrations from 0.01 to 520.43 pg g^{-1} d.w., respectively (Güzel et al., 2020). Similarly, studies in Colombia and Spain reported varying concentrations of PCDD/F and dl-PCB in soil samples, with higher levels noted in industrial and urban areas, primarily due to anthropogenic activities such as chemical manufacturing and waste incineration (Lacomba et al., 2025; Tran et al., 2024).

Globally, HACs are pervasive, attributed to their persistence and ability to transport long distances through air and water. Notably, these compounds have even been detected in remote regions like the Arctic, demonstrating their extensive environmental impact (Kannan et al., 2022). In fjord sediments, higher chlorinated congeners constitute over 80% of the total PCDD/Fs, indicating long-range atmospheric transport processes (Güzel et al., 2024).

The persistence and physicochemical properties of HACs contribute to their toxicological effects on human health and ecological systems. PCBs, dioxins (polychlorinated/brominated dibenzo-p-dioxins [PCDDs/PBDDs]), and furans (polychlorinated/brominated dibenzofurans [PCDFs/PBDFs]) exhibit bioaccumulation and biomagnification within food chains, posing toxic risks to both wildlife and humans (Loganathan & Masunaga, 2020). These toxic effects may include liver damage, immune system suppression, reproductive toxicity, and disruptions of nervous and endocrine functions.

This chapter aims to provide a comprehensive overview of the challenges posed by HACs, focusing on their toxicities, associated health and environmental risks, existing regulatory frameworks, and potential remediation strategies for contaminated sites.

6.2 TOXICITIES OF HALOGENATED AROMATIC COMPOUNDS

Halogenated aromatic compounds are a class of organic chemicals characterized by the presence of one or more halogen atoms – such as fluorine, chlorine, bromine, and/or iodine – attached to an aromatic ring structure (Ma et al., 2016; Sun et al., 2013). These compounds have a wide range of applications in industrial, agricultural, and household settings. HACs include polychlorinated biphenyls (PCBs), dioxins, polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-p-dioxins (PCDDs), dibenzo-furans (PCDFs), polychlorinated diphenyl ethers (PCDEs), and various pesticides (Reddy et al., 2019; Schiavone et al., 2010). Due to their widespread use, these chemicals persist in the environment and pose significant health risks, because they are commonly found in household materials and used in fire prevention (Shaw et al., 2010) and pesticide formulations

(Koutros et al., 2009). The toxicity of HACs is linked to their ability to disrupt targeted biological systems and processes (Marino et al., 2024), and their stable structure grants them resistance to biological degradation (Neilson, 1990; Schmidt et al., 1980).

6.2.1 Polychlorinated Dibenzo-p-dioxins (PCDDs)

Polychlorinated dibenzo-p-dioxins (PCDDs), commonly referred to as dioxins, are persistent organic pollutants that pose significant risks to both human health and the environment (Budin et al., 2021; Watanabe et al., 1999). Due to their severe toxicity, PCDDs are classified as organic compounds of health concern and are regulated under the Stockholm Convention (Dembska et al., 2024). These compounds consist of two benzene rings connected by two oxygen atoms, with four to eight chlorine substituents at various positions (Tavakoly Sany et al., 2016). PCDDs are generated as byproducts during the combustion of organic materials and through various chemical processes, including chlorine bleaching in the pulp and paper industry (Stanmore, 2004). Notably, they are also byproducts in the manufacturing of certain pesticides, with significant evidence linking human exposure to PCDDs in these industries, as shown in a study of 48 German workers at a pesticide facility (Flesch-Janys et al., 1996). The biochemical toxicity of PCDDs necessitates stringent regulation and monitoring across a range of matrices, including food, soil, sediment, and human biological materials (Barone et al., 2022).

The toxicity level of PCDDs is influenced by the number of chlorine atoms attached to each benzene ring, with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) identified as the most toxic compound in this category (Kimbrough, 2014). TCDD's lipophilic nature allows for bioaccumulation, leading to human exposure primarily through the food chain, which accounts for approximately 98% of exposure, with an estimated daily intake of 0.05 ng/day (Travis & Hattemer-Frey, 1987). TCDD was first recognized following its use by the U.S. military as a defoliant during the Vietnam War, particularly in Operations Trail Dust and Ranch Hand, exacerbating human exposure and persistence in the environment (Beischlag et al., 2008).

An occupational cohort study investigated the link between cancer mortality and exposure to dioxin- and furan-containing compounds (Becher et al., 1996). This study, consistent with other cohort research, found a significant increase in cancer mortality among individuals exposed to phenoxy herbicides and dioxins over extended periods. Of the 2,479 workers analyzed between 1989 and 1992, approximately 484 deaths were recorded, thus implicating these compounds as carcinogens, adversely affecting biochemical processes and influencing the expression of a range of genes and disrupting tissue formation (Baca et al., 2023). Numerous animal studies affirm TCDD's potency as a carcinogen, prompting increasing interest in its potential effects on human cancer (Mukerjee, 1998).

Polychlorinated dibenzo-p-dioxins exert their toxic effects by binding to the aryl hydrocarbon receptor (AhR), a ligand-activated transcription factor that regulates the expression of various genes (Beischlag et al., 2008; Hankinson, 1995). The toxicity associated with 2,3,7,8-tetrachlorodibenzo-p-dioxin is mediated specifically through the AhR receptor. Once activated, AhR translocates to the nucleus, where it binds with the nuclear translocator protein (ARNT) to form the heterodimeric complex known as the aryl hydrocarbon receptor complex (AhRC) (Hankinson, 1995). This activation subsequently regulates the transcription of genes involved in detoxification, cell cycle control, tumor promotion, immune system modulation, and teratogenesis (Haffner & Schecter, 2014; Verma et al., 2016). Furthermore, PCDDs disrupt endocrine functions and oxidative stress responses, leading to damage to essential cellular structures, including DNA, lipids, and proteins (Becher et al., 1996; Park et al., 1996).

There is also a cross-link between the AhR pathway and the ER pathway, with research investigating the molecular processes that underlie their interaction. Additionally, several adverse effects mediated by the ER have been linked to various disease conditions, including breast and endometrial cancer, thrombosis, central nervous system impacts, and estrogen-independent malignancies

(Ohtake et al., 2003). In general, polychlorinated dibenzodioxins (PCDDs) can impair the immune system, increase susceptibility to infections (Marshall & Kerkvliet, 2010), and disrupt endocrine functions, ultimately leading to reproductive and/or developmental defects (Hess-Wilson & Knudsen, 2006).

6.2.2 Dibenzo-furans (PCDFs)

Like PCDDs, PCDFs exhibit significant toxicological effects. A study of the toxicity and metabolism of PCDDs and PCDFs has revealed complex relationships between the absorption, body distribution, and metabolism of these compounds across species. PCDFs have much preferential retention in tissues such as the liver and fat owing to their limited biotransformation. Some of the most notable PCDD toxicities include developmental effects, neurologic disorders, immunotoxicity, and cancer. According to Safe et al., PCDFs cause endocrine disruption by interfering with hormonal regulation, which affects reproductive health (Safe, 1994). Moreover, chronic exposure to this compound causes neurodevelopmental issues in children (Park et al., 2010). PCDFs also trigger the induction of cytochrome P-450 enzymes. Binding to the PCDF receptor protein (Ah receptor) causes toxic effects; this phenomenon has been demonstrated to have hepatocarcinogenic effects in rodents (Vanden Heuvel & Lucier, 1993). Although intense studies of the toxicity of these compounds in laboratory animals have been conducted, their severity in humans has not been fully characterized. To appreciate the biological response of these compounds to humans, it is vital to investigate the sequence of events triggered by the Ah receptor and their interaction with dioxin-responsive genes. This is especially important given the variability in growth and differentiation processes across tissues, species, sex, and individuals (Vanden Heuvel & Lucier, 1993).

6.2.3 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls are manmade toxic organic contaminants composed of carbon, hydrogen, and chlorine atoms. The number of chlorine atoms in their structure determines their physicochemical properties and associated health risks to humans. Direct contact with these harmful substances occurs primarily through the consumption of contaminated food, including fish, meat, and dairy products (Ngoubeyou et al., 2022). Additionally, occupational exposure in industrial settings represents a significant pathway for human exposure to PCBs. Once ingested, PCBs accumulate in fatty tissues, making their elimination from the body exceedingly challenging (Dodoo et al., 2013).

Like other hazardous air contaminants, PCBs are linked to a range of adverse health effects (Buha Djordjevic et al., 2020). They disrupt the endocrine system, particularly affecting thyroid hormones and reproductive functions, leading to various physiological abnormalities. Children exposed to PCBs during critical developmental periods are at an increased risk of various cancers (Ghosh et al., 2018). Studies have identified PCBs as potential causative agents for skin and liver cancers (Gustavsson & Hogstedt, 1997) and classified them as probable carcinogens by the International Agency for Research on Cancer (IARC).

Moreover, exposure to PCBs can compromise the immune system, heightening susceptibility to diseases and diminishing the effectiveness of vaccinations. At the molecular level, PCBs induce oxidative stress, damaging DNA, proteins, and lipids, and disrupting complex biological processes within cells (Buha et al., 2015). They are also linked to cognitive impairments and behavioral issues (Ngoubeyou et al., 2022).

6.2.4 Polychlorinated Diphenyl Ethers (PCDEs)

Polychlorinated diphenyl ethers are semivolatile organic compounds characterized by an ether functional group situated between two aromatic rings. They belong to the same class of substances as polychlorinated biphenyls (PCBs). Due to their environmental persistence, potential for

bioaccumulation, and negative health impacts, PCDEs have garnered increased research interest in recent years. While often considered less toxic than some other contaminants, emerging evidence underscores their potential effects on human health (Renzelli et al., 2023).

Concerns about PCDEs in the environment stem from their lipophilic nature and resistance to degradation, which facilitate their bioaccumulation within the food chain (Knutsen et al., 2018). The primary route of exposure for most individuals is dietary, particularly through the consumption of fish, meat, and dairy products that may contain PCDEs. Other exposure pathways include occupational contact, living near industrial sites, and working in electronic waste recycling facilities (Kaifie et al., 2020; Shi et al., 2019). Once ingested, PCDEs readily accumulate in body fat, the liver, and other lipid-rich organs, contributing to their persistence in the human body (Knutsen et al., 2018).

PCDEs are known to interfere with various cellular processes and physiological functions. One significant health concern is their disruption of endocrine function, particularly through interference with thyroid hormones. Overall, exposure to PCDEs has been linked to growth and metabolic issues, as well as neurodevelopmental challenges, especially in vulnerable populations such as children (Schreiber et al., 2010).

6.3 RISK ASSESSMENT AND HEALTH IMPLICATIONS

6.3.1 Exposure Pathways

Dietary intake is the primary exposure pathway for hazardous air pollutants (HAPs). Due to their highly lipophilic characteristics, HAPs are not easily degraded and tend to bioaccumulate, entering the human body through the food chain (Knutsen et al., 2018; Kobets et al., 2022). Aquatic ecosystems act as significant repositories for these compounds, facilitating their absorption by aquatic organisms, such as fish (Ngoubeyou et al., 2022). When aquatic animals consume plants grown near industrial sites that release air containing HAPs, they become exposed to these compounds. Over time, HAPs can bioaccumulate in the body, leading to tissue damage and various adverse health conditions. Owing to their hydrophobic nature and high lipophilicity, HAPs are highly soluble in lipids. Prolonged consumption of HAP-contaminated food can result in a significant accumulation of these compounds in body fat (Tebourbi et al., 2006). This accumulated fat does not easily break down, thereby altering physiological functions (Knutsen et al., 2018). Hence, human exposure to HAPs occurs through multiple routes, with dietary intake of contaminated food being the most significant (Ghosh et al., 2010) (see Figure 6.1).

Workers in various industries, including electronics, chemicals, agriculture, and firefighting, are at an elevated risk of exposure to HAPs, known as occupational exposure (Gravel et al., 2019). In such cases, HAPs can be absorbed through inhalation, skin contact, or, less commonly, ingestion via food or drink consumed in the work environment. For instance, firefighters utilize brominated flame retardants to extinguish fires, creating potential routes for occupational exposure to HAPs (Mayer et al., 2021). Additionally, workers who recycle electronic waste are frequently exposed to polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). Without proper protective equipment, these workers are at higher risk of accumulating hazardous concentrations of HAPs in their bodies, which may lead to the development of various health issues over time, including acute or chronic diseases such as cancer, immune system suppression, and endocrine disruption (Buha Djordjevic et al., 2020).

The impact of human activities on health and ecosystems is profound. Industrialization, urbanization, and technological advancements have significantly contributed to the release of HAPs (Patel et al., 2020). Specifically, HAPs enter the environment through industrial waste, agricultural practices, and uncontrolled waste dumping. These compounds can persist in the environment, often being semivolatile, which facilitates their dispersion through air, water, and soil, thereby polluting

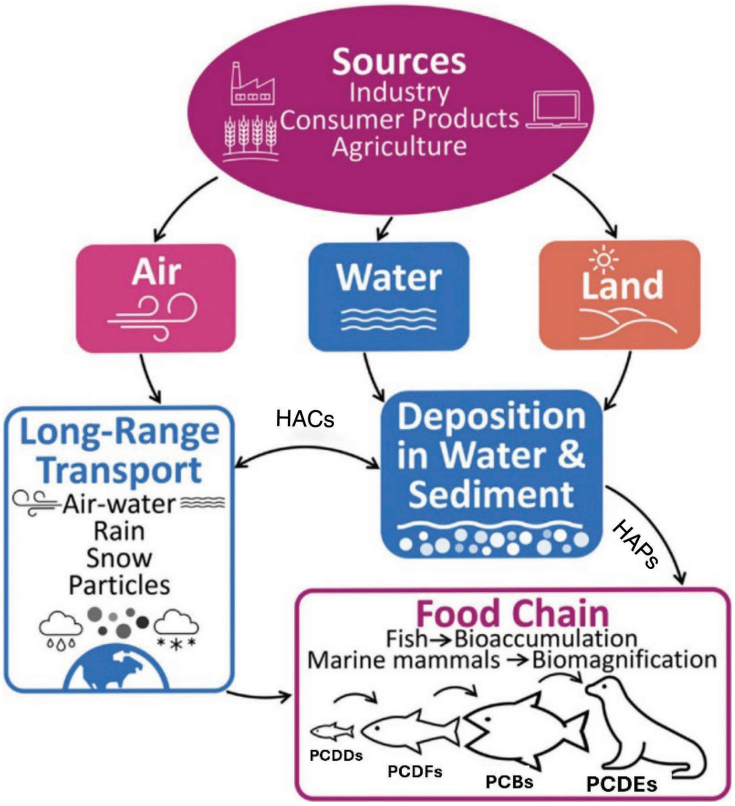


FIGURE 6.1 Schematic diagram showing the distribution of halogenated aromatic compounds and their exposure route to man (modified from Kodavanti et al., 2014).

even the most remote ecosystems (David & Niculescu, 2021). In aquatic environments, sediments contaminated with HAPs can enter the food chain via seafood consumption (see Figure 6.1). Similarly, agricultural activities involving pesticide application, industrial discharge, and landfill leachate contribute to HAP deposition in soil (Dagwar & Dutta, 2024). Crops cultivated in contaminated agricultural soil can absorb HAPs, further compounding dietary intake. Atmospheric deposition represents another significant exposure pathway, because emissions can travel long distances in the air and settle on land or water surfaces (Kodavanti et al., 2023). These characteristics promote the widespread distribution of HAPs and contribute to contamination in remote areas, such as the Arctic, where exposure primarily occurs through the consumption of contaminated fish and marine mammals (Kodavanti et al., 2023).

Indoor environments represent a significant, yet often overlooked, source of hazardous air pollutants. Many common household materials, such as furniture, electronics, and plastics, contain compounds that serve as flame retardants, plasticizers, or insulators (Kodavanti et al., 2014). These compounds gradually release HAPs into indoor air over time, leading to a continuous degradation of air quality. As a result, HAPs accumulate in indoor spaces, contributing to long-term exposure and potential health risks.

Children are particularly vulnerable to indoor HAP exposure due to their hand-to-mouth behaviors and their close proximity to these surfaces and materials (Bridbord et al., 1975; Ohura et al., 2004). Prolonged exposure to indoor HAPs can lead to developmental delays and behavioral issues

in children (Oliveira et al., 2019). Furthermore, pathways of exposure during pregnancy and lactation are critical, because pregnant women can transfer HAPs to the fetus via the placenta (Zhang et al., 2021). Numerous studies have demonstrated the transfer of HAPs from lactating mothers to infants through breastfeeding (Needham et al., 2011; Zhang et al., 2021).

6.3.2 Health Implications

Halogenated aromatic compounds (HACs) are associated with a significantly increased risk of cancer, because they are potential carcinogens capable of inducing mutations and other cellular changes. Prolonged exposure to HACs can result in DNA damage, compromising genetic integrity and heightening an individual's susceptibility to oncogenic transformations (Anzalone et al., 2018; Robertson & Ludewig, 2011). This mechanism elucidates the role of HACs in the progression and development of various cancers, including liver and breast cancer (Robertson & Ludewig, 2011).

An expanding body of research indicates that exposure to these compounds also leads to immune suppression. A compromised immune response may hinder the body's ability to combat infectious diseases, thereby predisposing individuals to additional health issues (Buha Djordjevic et al., 2020). Specifically, the immunotoxicity of HACs can impair immune cell function and increase susceptibility to autoimmune diseases (Patel et al., 2020).

Moreover, HACs can disrupt natural hormone levels, leading to endocrine dysfunction. Such hormonal disturbances pose serious health risks, because they can adversely affect growth, metabolism, and reproduction, potentially resulting in developmental defects such as decreased fertility (Azar et al., 2021; Baldigo et al., 2006).

HAC exposure is also linked to various skin disorders, including chloracne and dermatitis. Additional effects can include weight loss and liver enlargement, stemming from the increased metabolic burden on the liver to process and detoxify these compounds. This situation may ultimately lead to hepatotoxicity or chronic liver disease (Donato et al., 2021). Long-term exposure to HACs has been associated with chronic inflammatory diseases and a heightened risk of metabolic syndrome and degenerative conditions. The reproductive system is particularly vulnerable, with evidence indicating that HACs can diminish sperm quality and cause menstrual irregularities (Donato et al., 2023; Yang et al., 2011).

Furthermore, exposure to HACs is linked to cardiovascular and respiratory issues, including hypertension, asthma, and chronic obstructive pulmonary disease (COPD). These health problems are supported by the pro-inflammatory and oxidative stress-inducing properties of HACs (Hennig et al., 2002; McCann et al., 2021).

6.4 POLICY FRAMEWORKS

Efforts to reduce exposure to hazardous air pollutants (HAPs) rely on a multifaceted approach that combines regulatory measures, technological advancements, public awareness campaigns, and adherence to international agreements such as the Stockholm Convention. This comprehensive strategy has led to significant reductions in environmental pollutants and decreased human exposure levels. Regulatory frameworks and guidelines can operate on both national and international levels, targeting the control of hazardous materials and substances that pose public health risks.

6.4.1 International Regulations

Various international regulatory frameworks have been established to monitor and mitigate the effects of hazardous air pollutants (HAPs). The Stockholm Convention on Persistent Organic Pollutants is a key global treaty aimed at eliminating or restricting the production and use of POPs, which include harmful substances such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) (Malisch et al., 2023). This

convention emphasizes the promotion of safer alternatives and mandates that signatory countries take action to reduce emissions and manage hazardous waste effectively. It also requires that HAP-containing waste be managed in an environmentally sound manner and that their release during industrial activities, incineration, or landfilling be prevented.

Complementing the efforts of the Stockholm Convention is the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal. This treaty serves to bolster the global framework for regulating the trade, handling, and disposal of hazardous materials, including those that contain HAPs. Specifically, the Basel Convention governs the cross-border movement and disposal of hazardous waste, which encompasses electronic waste that may contain harmful substances like PCBs.

Another important treaty is the Minamata Convention on Mercury, which focuses on reducing mercury emissions and use. Mercury is often found alongside HAPs in various industrial processes, thus reinforcing the interconnected nature of these hazardous substances. Collectively, these treaties represent a collaborative international effort aimed at mitigating and monitoring the presence of hazardous materials while promoting the development of non-hazardous alternatives, ultimately striving for a cleaner and safer environment.

Additionally, the Rotterdam Convention plays a pivotal role by facilitating informed decision-making among member countries regarding the importation of hazardous chemicals and pesticides – many of which can contain HAPs. This framework enhances transparency and accountability in the handling of hazardous chemicals, further contributing to global environmental safety efforts.

6.4.2 National Regulations

National regulations serve as the enactments of international treaties, contextualizing these agreements within specific localities. In the United States, the Environmental Protection Agency (EPA) implements various controls through the Toxic Substances Control Act (TSCA) and the Clean Air Act (CAA) to regulate hazardous air pollutants (HAPs). This includes pre-manufacturing reviews of chemicals, emission limits for HAPs from industrial sources, and remediation processes for polluted sites under the Superfund program.

In the European Union, the REACH framework (Registration, Evaluation, Authorization, and Restriction of Chemicals) mandates that manufacturers and importers assess and mitigate any risks posed by HAPs before these substances are marketed within the EU. Additionally, the Industrial Emissions Directive ensures that national facilities comply with the best available practices to minimize the release of hazardous substances into the air, water, and soil.

Developing countries face unique challenges in regulating HAPs due to limited technical expertise and financial resources. However, many are increasingly aligning with international standards by adopting stricter pollution control measures. Notably, India and China are taking significant steps forward in pollution management.

There is also a critical need for public health campaigns and advocacy to raise awareness about the dangers posed by HAPs.

6.5 REMEDIAL STRATEGIES

6.5.1 Bioremediation

The biological breakdown of halogenated aromatics offers ecologically affordable and sustainable method for eliminating these pollutants from the environment (Pimviriyakul et al., 2020). Bioremediation involves the use of microbial species to degrade halogenated aromatic compounds (HACs) in contaminated soil and water. Certain bacteria and fungi can metabolize polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), making this approach a promising strategy for remediation.

The biodegradation process encompasses various metabolic pathways that convert halogenated aromatic compounds into common, non-toxic metabolites within cells. These pathways facilitate energy-generating metabolic processes (Pimviriyakul et al., 2020). PCDD/Fs can be degraded by bacteria through either aerobic or anaerobic pathways (Sebastian & Rao, 2022). Under aerobic conditions, removal efficiencies for these dioxins can reach between 65% and 85%. However, due to their high stability, few studies have demonstrated the capacity of soil microorganisms to aerobically break down highly chlorinated congeners (Tran et al., 2024).

Though highly chlorinated congeners can be significantly decomposed via anaerobic mechanisms, the most common substrate used for the co-metabolism of chlorinated dioxins is the nonhalogenated analogue dibenzo-furan. Bacteria known to contribute to this process include *Sphingomonas* sp. RW16, *Pseudomonas* sp. RW10, and *Burkholderia* sp. JWS, along with members of the *Dehalococcoides* genus. In anaerobic environments, microbial reductive dechlorination has proven to be the predominant metabolic activity (Saibu et al., 2020).

To achieve efficient destruction of PCDD/Fs in environmental matrices, an integrated anaerobic–aerobic biodegradation process is recommended. This approach begins with reductive dehalogenation to convert highly substituted congeners into lightly chlorinated ones, followed by aerobic degradation and assimilation of the aromatic carbon skeleton of the reductive dechlorination products, ultimately leading to the complete mineralization of the compounds (Saibu et al., 2020).

6.5.2 Thermal Treatment

High-temperature incineration is an effective method for destroying PCDDs and PCDFs; however, careful management is essential to prevent the release of dioxins during combustion. The thermal treatment of municipal solid waste incineration fly ash facilitates the solidification of heavy metals, the breakdown of PCDD/Fs, and the production of ecologically stable products (Chen et al., 2020). At elevated temperatures, PCDD/Fs can be completely broken down (over 99%), while lower temperatures can promote their reformation. Treatment of samples at 500°C, 800°C, and 1,100°C in either oxidative or inert conditions has shown that more than 95% of PCDD/Fs in fly ash can be efficiently degraded.

The presence of catalytic metals is a significant factor influencing the reformation of PCDD/Fs. Two distinct mechanisms have been identified to facilitate this process (Themba et al., 2023). The first is the de novo synthesis phase, in which carbon macromolecules or polycyclic aromatic hydrocarbons initiate the synthesis of PCDD/Fs, followed by a condensation reaction. The subsequent rearrangement of the molecular structure of precursor compounds is influenced by various combustion conditions, including temperature, oxygen supply, residence time, fuel processing, and the addition of other fuels (Mukherjee et al., 2016).

To optimize combustion efficiency, it is crucial to establish optimal operating conditions, which may include specialized design features, end-of-pipe treatment, and maintaining higher temperatures (e.g., 850–1,000°C).

6.5.3 Phytoremediation

Phytoextraction is a bioremediation technique that employs plants to absorb and degrade pollutants from soils and water. Certain plant species are theorized to effectively uptake polychlorinated biphenyls (PCBs) and other halogenated compounds. For instance, crops such as zucchini, wheat, and cucumber have demonstrated significant proficiency in dioxin removal through various mechanisms, including transpiration and root uptake (Tran et al., 2024).

Notably, rhamnolipids and sophorolipids – a subclass of biosurfactants – have been utilized in the remediation of dioxin-contaminated soils. These biosurfactants enhance the bioavailability of dioxins and facilitate their interaction with soil microorganisms. The combined application of transgenic plants and associated bacteria represents a promising strategy for cleaning PCB-contaminated soils

(Aken et al., 2010). The mechanisms involved in this process include phytoextraction (uptake from soil), phytotransformation (transformation of PCBs within plants), and rhizoremediation (enhanced biodegradation of PCBs), which occurs through the release of secondary metabolites that stimulate microbial activity in the root zone.

To effectively treat PCBs, bacterial genes, such as biphenyl dioxygenases, can be expressed in target plant species (Munawar et al., 2021). For example, transgenic *Arabidopsis* plants expressing the exogenous genes tfdB (1771 bp) and bphC (900 bp) exhibited a 50% increase in inhibitory concentrations and tolerance indices compared to wild-type *Arabidopsis*. Additionally, enzymatic assays (e.g., POD, CAT, and SOD) showed increased activity in the transgenic plants compared to untreated controls (Ding et al., 2024).

A study comparing various combinations of seven plant species under different soil conditions for the treatment of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-furans (PCDD/Fs) demonstrated that *Festuca arundinacea* achieved a 11–24% reduction in contaminants, indicating a half-life of 2.5–5.8 years (Terzaghi et al., 2020).

6.5.4 Activated Carbon Treatment

Adsorption using activated carbon has proven effective in removing polychlorinated compounds from various water systems, including ultrapure water systems (Schmotzer et al., 2002) and lakes (Patmont et al., 2020). Additionally, activated carbon is employed for the removal and detoxification of PCB-contaminated soils (Vasilyeva et al., 2010). It is suggested that activated carbon facilitates the dichlorination of higher chlorinated congeners, leading to the formation of bounding fractions of PCBs, while also promoting the microbial degradation of less chlorinated congeners. Treatment with activated carbon has been shown to reduce phytotoxicity.

Activated carbon has been used to sequester PCBs from sediment (Werner et al., 2005), with findings indicating that sequestration efficiency improves with increased contact time. The desorption of PCBs was significantly lower (7% after 6 months) following treatment with activated carbon compared to untreated samples (74%). By reducing the concentration of PCBs in pore water, activated carbon decreases their bioavailability and bioaccumulation in aquatic species (Kirtay et al., 2018). The sorbent materials can be directly mixed with the contaminated matrix or applied as a thin layer to create a physical barrier. A full-scale application of activated carbon to a lake yielded 75% and 52% reductions in available PCB concentrations in sediment and surface water, respectively (Patmont et al., 2020). Additionally, lipid-normalized PCBs in fish after 3–5 years of lake treatment reflected the advantages of activated carbon application.

Activated carbon is also effective in removing PCDD/Fs from gas phase emissions, with studies indicating that increasing the dosage of activated carbon enhances adsorption efficiency (Wang et al., 2023). However, some negative effects on aquatic organisms have been reported following exposure to activated carbon; smaller particle sizes generally exhibit greater adsorption efficiency but also higher potential toxicity (Abel et al., 2017). Therefore, amendments are often added to bare activated carbon to improve its efficiency and durability while reducing toxicity.

6.5.5 Legislative Reforms

Continuous updates to policies regulating the manufacture, use, and disposal of hazardous substances are essential. Stricter enforcement of existing regulations, coupled with innovative mitigation strategies, can effectively manage and reduce the prevalence of hazardous air pollutants (HAPs). The Stockholm Convention's Annex C includes polychlorinated dibenzo-p-dioxins and dibenzo-furans (PCDD/Fs), a group of highly toxic compounds that are inadvertently generated as byproducts of various industrial processes, such as waste incineration and the production of certain chemicals and materials. Enforcing stricter laws could significantly diminish the manufacture and release of PCDD/Fs. For example, China's production and release of PCDD/Fs peaked in 2007 and

subsequently declined following the ratification of the Stockholm Convention (Gao et al., 2023). From 2015 onward, the rate of environmental discharge continued to decrease, highlighting the need for more stringent regulations and enhanced management strategies. Implementing tight emission controls for industrial operations could further reduce PCDD/F exposure.

6.6 CONCLUSION

Halogenated aromatic compounds pose significant risks to human health due to their environmental persistence and potential for bioaccumulation. Addressing this global issue necessitates effective policy implementation, continuous monitoring, and innovative remediation strategies. Fostering collaboration among governments, researchers, and communities is essential to mitigate the impact of these hazardous compounds on public health and ecosystems. This article underscores the urgent need for robust response strategies to tackle the dangers posed by halogenated aromatic compounds, especially as ongoing research continues to reveal the challenges they present to human health and the environment.

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7 Environmental Contamination by Organochlorine Persistent Organic Pollutants

A Globally Alarming Detriment from the Past

Helen Karasali and George Pavlidis

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DOI: 10.1201/9781003530466-7
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7.1 INTRODUCTION

Soil is a precious source of life on the planet. Since it is not counted as renewable within the time frame of a human life, soil degradation is a key and presently pressing issue (Lal, 1993). It has been recognized that contamination from anthropogenic activities is a considerable driver in the decrease of environmental value.

Among soil and water contaminants, considerable social concern arises from the use of plant protection products (PPPs). They are widely used in agricultural fields around the world to increase crop production due to their toxicity, which is intended to destroy target organisms (FAO and UNEP, 2021). The use of PPPs has been recognized as a fundamental element contributing to the enhancement of food production in the past decades globally (Silva et al., 2019). On the other hand, PPPs are some of the most notable chemicals in agricultural soils, both for being broadly applied and for their potential harm to different non-target organisms including humans (Sefiloglu et al., 2021; Kalia and Gosal, 2011).

Persistent organic pollutants (POPs) are organic compounds of global concern due to their persistence in the environment, potential bioaccumulation and biomagnification in living organisms, that raise environmental and living organisms' health risks. They can be transported via air, water, or migrant species across global borders, reaching areas where they have never been produced or used. Soil is the final pool for pollutants due to the water cycle. For that reason, intercontinental risk management is necessary because no area can manage the risks posed by these compounds alone (ECHA website, 2024). POPs are resistant to environmental degradation by chemical, biological, or photocatalytic processes (Yi-Fan et al., 2024). They are essentially lipophilic compounds, therefore present remarkable affinity to soil organic matter and lipid membranes of cells; thus, they can be gathered in fatty tissues (Silva et al., 2019).

According to the World Health Organization, the most confronted POPs are organochlorine pesticides (OCPs), industrial chemicals, and polychlorinated biphenyls (PCBs), as well as unintentional by-products of numerous industrial processes, particularly polychlorinated dibenzo-p-dioxins (PCDD) and dibenzo-furans (PCDF), typically known as dioxins. In 2004, the United Nations Environment Program initially listed 12 POPs (the dirty dozen) because they have been identified as causing adverse effects on both human health and the environment; they belong in three different categories: pesticides, industrial chemicals, and by-products. OCPs named aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, and toxaphene were among the 12 POPs that are prohibited worldwide (WHO website, 2024). POPs are regulated worldwide by both the Stockholm Convention and the Aarhus Protocol (UNEP, 2011; UNECE website, 2024). These international agreements are implemented in the European Union by the POPs Regulation (Regulation [EU] 2019/1021 of the European parliament and of the council of 20 June 2019 on persistent organic pollutants). Readers are also directed to Chapter 3 this book noting inclusion of other pesticides in the environment.

Organochlorine pesticides (OCPs) are the earliest organic chemical pesticides manufactured (Li, Qi et al., 2023). OCPs have been significantly used since 1950 in agriculture and the public health sector due to their efficacy, low cost, and wide range of insect-controlling efficiency (Oliveira et al., 2016; Zehra et al., 2015; Zhi et al., 2015). OCPs are chemically stable and for that reason, despite

their benefits of reducing unwanted insects and safeguarding food security, they are grouped as persistent organic pollutants (POPs) (Bergkvist et al., 2012). Soil is a depository of agricultural OCPs because soil absorbs most of them along with their degradation products which ends up placing higher concentrations of these compounds in subsoil than in topsoil (Bhandari et al., 2020). Crops can uptake OCPs from soil which could in turn make the crops potentially toxic for human and livestock consumption (Clostre et al., 2015). Although their fate, behavior, and distribution are significantly affected by soil properties, the persistence, lipophilic properties, and chronic toxicity of OCPs allow their bioaccumulations and biomagnifications in the environment and food chains, posing a threat to humans as well as animals (Bettinetti et al., 2016). Thus, OCPs became a worrying global issue, initiating restrictions in their use in many countries starting in the 1970s and 1980s (Zhi et al., 2015).

7.2 OCPs CLASSIFICATION

OCPs can be classified in five major categories based on their chemical structure: diphenyl aliphatic (DDT and related compounds), cyclohexanes (hexachlorocyclohexane and related compounds), cyclodienes (dieldrin, endosulfan, etc.), polychloroterpenes (toxaphene and related compounds), mirex, and chlordecone structures (Baratzhanova et al., 2024). These categories include also their related compounds such as degradation products and isomers (Blus, 1995).

Organochlorine pesticides include many different compounds with varied chemical structures. DDT is an example of a well-known OCP with many different chemical structures. Chemical analogues of DDT comprise methoxychlor, ethylan, and chlorobenzilate. Furthermore, DDT has two isoforms (o,p′-DDT and p,p′-DDT) and two main metabolites for each isoform (o,p′-DDE and p,p′-DDE) and (o,p′-DDD and p,p-DDD). Hexachlorocyclohexane has eight steric isomers including the γ isomer, which is known as lindane. Cyclodienes include a variety of OCPs such as aldrin, dieldrin, endrin, heptachlor, chlordane, and endosulfan. Toxaphene is used in complex technical mixtures with many different compounds. Mirex has been introduced as a replacement for some cyclodienes as has chlordecone (Gupta, 2004).

7.2.1 Types of Organochlorine Pesticides (OCPs)

Several organochlorine compounds have been used as plant protection products worldwide. OCPs demonstrate some similarities in their chemical structure which involves an aliphatic or aromatic ring with substituted chlorine (Baratzhanova et al., 2024). They differ in their chemical stability and mechanisms of harmfulness to target and non-target species. However, due to their structural similarities, these compounds share specific physicochemical characteristics such as persistence, bioaccumulation, and toxicity.

OCPs enter the environment after PPP applications, polluted waste disposed into landfills, and emissions from industrial units that produce them. Some OCPs can persist in soil and air for several years, leading to high environmental contamination and increasing the risk for chronic exposure for both animals and humans.

7.2.1.1 DDT

DDT is an organochlorine pesticide; it was synthesized in 1874 but its insecticidal properties were revealed in 1939. DDT was first used during World War II to battle malaria and typhus among citizens and troops. Subsequently it was used as an agricultural and household pesticide (Secretariat of the Basel, Rotterdam and Stockholm Conventions, 2024). DDT (1, 1, 1-trichoro-2, 2-bis[p-chlorophenyl]-ethane), was a broad-range organochlorine pesticide that was used in agriculture and public health worldwide, since 1939 (ATSDR, 2022). Its use was banned in the United States and in numerous parts of the world in 1972 (ATSDR, 2022). It has also been recorded in the Stockholm Convention as a persistent organic pollutant (POP) due to its high toxicity and persistence in the

TABLE 7.1
List of Organochlorine Pesticides (Jayaraj et al., 2016)

Compound name	Compound name
1,2,4,5,6-Tetrachlorometa-xylene	Cis-nonachlor
1,2-Dibromo-3-chloropropane (DBCP)	Decachlorobiphenyl
1,4-Dichlorobenzene	DCPA
2,4´-Methoxychlor	Delta-BHC
2,4,5-T	Dieldrin
Chloro propylate	Dicofol
4,4´-Dichlorobenzophenone	Diallate
4,4´-Methoxychlor olefin	Endrin
Alachlor	Endrin aldehyde
Aldrin	Endrin ketone
Alpha-BHC (benzene hexachloride)	Endosulfan sulfate
Alpha-chlordane	Gamma-BHC (lindane)
Alpha-endosulfan	Gamma-chlordane
Beta-endosulfan	Heptachlor
Beta-BHC (benzene hexachloride)	Heptachlor-endo-epoxide
Chlorbenside/chlorobenziate	Heptachlor-exo-epoxide
Chloro propylate	Isodrin
cis-chlordane	Isobenzan
Methoxychlor	Pentachlorophenol
Mirex	Perthane
o,p´-DDD	Quintozene (pentachloronitrobenzene)
o,p´-DDE	Hexachlorobenzene
o,p´-DDT	Hexachlorocyclopentadiene
p,p´-DDD	Tetradifon
p,p´-DDE	Toxaphene
p,p´-DDT	Trans-chlordane
Pentachloroanisole	Trans-nonachlor
Pentachlorothioanisole	

environment (Yu et al., 2020). The Stockholm Convention was adopted in 2004 and for that reason, DDT uses declined (Tyagi et al., 2022).

DDT is manufactured by the reaction of trichloroethanol with chlorobenzene. DDT is a combination of aliphatic and aromatic groups and is an isomer mixture including around 75–85% p,p′-DDT, 10–15% o,p′-DDT, and lesser quantities of o,o′-DDT (ATSDR, 2022). When DDT is mentioned, it is generally indicating the p,p′-DDT, which was manufactured and used for its insecticidal properties. Technical-grade DDT was composed of up to 14 chemical compounds, of which only 65–80% was the active substance, p,p′-DDT. The other compounds contained 15–21% of the nearly inactive o,p′-DDT, up to 4% of p,p′-DDD, and up to 1.5% of 1-(p-chlorophenyl)-2,2,2-trichloroethanol (Mansouri et al., 2017). The most persistent DDT compounds are p,p-DDT and o,p-DDT, with a reported half-life between 2 to 15 years. Because of their toxicity, hydrophobicity, and bioaccumulative properties, DDTs have been classified in the national priority list of environmental pollutants as priority persistent organic pollutants and endocrine-disrupting chemicals.

DDT has two major metabolites, the dichlorodiphenyl-dichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE). It should be noted that DDD was also produced and used as an insecticide to a less significant extent than DDT. DDE is not manufactured commercially

but it is detected in soil more frequently and at higher concentrations than DDT. The long-range transport of DDT has initiated the widespread dispersion of DDT and its metabolites in the world, even in remote areas, such as the Arctic or Antarctic districts. The biodegradation of DDT and its metabolites is slow, and these compounds can bioaccumulate in fatty tissues due to its lipophilic nature. The major route of exposure to DDT and its metabolites is through the consumption of foods such as meat, fish, poultry, and dairy products obtained from places where DDT was used and thus have the potential to contain bioaccumulated residues of DDT and its metabolites (ATSDR, 2022). Different forms of DDT, DDE, and DDD isomers can be found in the environment.

DDT is greatly absorbed into soil, where it is subjected to anaerobic breakdown. DDE is the main metabolite in flooded areas, while DDD is the primary metabolite in unflooded areas. Over 90% of DDT applied remains in the environment as DDT, DDE, and DDD (Barr et al., 2024). Brown-rot fungi and many bacteria can convert DDT into its metabolites, and many of them prosper in anaerobic conditions and alkaline soils (Pan et al., 2016). The effectiveness and rate of decomposition of DDX are related to the type and abundance of bacteria (Pan et al., 2016). Several classes of bacteria, fungi, and animals process DDT in various ways, so there is not a single route for degradation. Nonetheless, in many mechanisms, DDT degrades to DDE, and DDE degrades to DDD (Purnomo et al., 2011). The decomposition rate of DDT into DDE and DDD can be altered by weather and farming methods. Warmer temperatures and a raining environment can increase the degradation rate of DDT (Farmer et al., 1974). Furthermore, irrigation improves DDT degradation and volatilization rate because it establishes an environment that permits specified anaerobic bacteria to flourish (Boul et al., 1994; Spencer et al., 1996). In addition, synthetic phosphate fertilizers and organic fertilizers, like manure and/or compost, have been related to the increase of the degradation rate of DDT (Deng et al., 2016).

7.2.1.2 Lindane

Hexachlorocyclohexane (HCH) was synthesized by Michael Faraday in 1825. In 1912 its isomers δ-HCH and γ-HCH were discovered by Teunis Van der Linden. The γ-HCH is known as lindane and is considered one of the most persistent organic pollutants (IARC, 2018). HCH has many isomers, but only α-, β-, γ-, δ-, and ε-isomers are quite stable. Only γ-HCH has insecticidal properties, and it was used to control herbivorous pests (Brooks, 1977; Shoiful et al., 2016). Its structure is a six-carbon ring with one chlorine and one hydrogen connected to each carbon. The technical grade HCH also contains the other isomers of HCH, which differ only by the chlorine atoms orientation (axial or equatorial positions) around the cyclohexane ring. The five major isomers (α-, β-, γ-, δ-, and ε-isomers) exist in the mixture in the following amounts: alpha-hexachlorocyclohexane (53%–70%) in two enantiomeric forms ((+) α-HCH and (-) α-HCH), β-hexachlorocyclohexane (3%–14%), γ-hexachlorocyclohexane (11%–18%), δ-hexachlorocyclohexane (6%–10%), and ε-hexachlorocyclohexane (3%–5%) (Kutz et al., 1991). The International Organization for Standardization (ISO) common name and the WHO specification use "lindane" to refer to raw material comprising more than 99% γ-HCH. Lindane is manufactured by the technical HCH, which is produced by the photochlorination of benzene, a reaction that can be started by free-radical initiators such as visible or ultraviolet light, X-rays, or γ-rays, and yields to a mixture of five main isomers (ATSDR, 2005). γ-HCH is extracted and purified from this mixture of isomers using fractional crystallization to produce 99% pure lindane.

Both lindane and technical HCH were used as broad-spectrum insecticides, for agricultural and non-agricultural purposes, acting via contact (WHO, 1991). α-HCH, β-HCH, and γ-HCH (lindane) have been included in the Stockholm Convention on Persistent Organic Pollutants for being persistent, bioaccumulative, having harmful effects on human health and on the environment, and having potential for long-range transport. Once released into the environment, lindane can spread to the environmental ecosystem. Lindane and other HCH isomers are commonly more water-soluble and volatile, which explains why they are so omnipresent. Based on the Henry's law constant,

evaporation from water and moist soil is the most notable procedure in the environmental distribution of lindane (Philips et al., 2005). Lindane is stable to light, and does not contain chromophores to absorb light; therefore, direct photolysis either in air, water, or soil is not possible. It also degrades very slowly by microbials with a calculated half-life in soil of 980 days under aerobic conditions. Degradation is considered faster under anaerobic conditions than in the existence of oxygen. Lindane can bioaccumulate undoubtedly in the food chain due to its high lipid solubility and can bioconcentrate in microorganisms, invertebrates, birds, and mammals (Berny et al., 2002).

7.2.1.3 Aldrin and Dieldrin

Aldrin and dieldrin are OCPs which were produced commercially since 1950 and were used up to early 1970s. Both compounds were used as insecticides in agriculture to control many soil pests. Dieldrin was also used in public health to control tsetse flies and other vectors of unbearable tropical diseases. They act as contact and stomach poison for insects. The IUPAC name for aldrin is (1R,4S,4aS,5S,8R,8aR)-1,2,3,4,10,10-hexachloro1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene-HHDN) (WHO, 1989c). The IUPAC name for dieldrin is (1R,4S,4aS,5R,6R,7S,8S,8aR)-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-6,7-epoxy-1,4:5,8-dimethanonaphthalene-HEOD) (WHO, 1989a). The composition of the technical grade aldrin was reported to be as follows: 90.5% hexachlorohexahydrodimethanonaphthalene (HHDN), 3.5% other polychlorohexahydrodimethanonaphthalene (isodrin), 0.5% hexachlorotetrahydromethanoindene (chlordane), 0.2% hexachlorocyclopentadiene (HCCPD), 0.6% hexachlorobutadiene, 0.5% octachlorocyclopentene, <0.1% hexachloroethane, 0.1% HEN diadduct, <0.l% bicycloheptadiene (BCH), 0.3% toluene, and 3.6% other compounds (mainly a complex mixture of compounds formed by polymerization of HCCPD and BCH during the aldrin reaction) (IARC, 1974). Aldrin's impurities include octachlorocyclopentene, hexachlorobutadiene, and their polymerization products, while polychloroepoxyoctahydrodimethano-naphthalenes are dieldrin's impurities. It should be noted that although the use of both OCPs has been strictly restricted and banned in many countries since the early 1970s, they are still used as insecticides in termite control in some countries (Willoughby, 1987; WHO, 2011). In 1997 both OCPs were designated as persistent organic pollutants by the Governing Council of the United Nations Environment Program. Aldrin and dieldrin are basically insoluble in water and moderately to highly soluble in most paraffinic, aromatic, and halogenated hydrocarbons, and in esters, ketones, and alcohols (UNEP, 1997). Since aldrin was mainly used as a soil insecticide, aldrin-treated soil is a significant source of aldrin and its reaction product dieldrin in environmental compartments. Aldrin has a low tendency for movement away from treated areas, through volatilization or by leaching. Aldrin is mainly absorbed very quickly on soils with high organic matter content; however, it is moderately absorbed by clay soils. Most OCPs hardly penetrate more than 20 cm under the top treated layer of soil. Aldrin remains on soil particles and only traces can be removed by water; therefore, groundwater contamination is not reasonable. The loss of aldrin from soil is a first-order reaction. Instantly after usage, there is a quick period of rapid loss mainly due to volatilization and then a second longer exponential period of decrease, mainly due to conversion to dieldrin, which is slower to dissipate. In soil, aldrin is transformed to dieldrin by oxidation. In moderate climates, 75% of aldrin is oxidized in a year after application, while the remaining quantity disappeared from soil slowly since its half-life is around 5 years. However, under hot climates, both oxidation and further loss of dieldrin by volatilization are rapid (WHO, 1989).

7.2.1.4 Endrin

Endrin is the endo, endo stereoisomer of dieldrin. Its chemical name is 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8aoctahydro-1,4-endo, endo-5,8-dimethanonaphthalene (WHO, 1993). It is a foliar insecticide that acts against a large selection of agricultural pests. Additionally, it is used as a rodenticide (IPCS, 1992). Two main mechanisms remove endrin from the environment: photodecomposition and bacterial degradation. Its ketone, δ-ketoendrin, is mainly formed in light. Its microbial degradation depends on the occurrence of suitable microbial species and suitable soil

conditions, such as anaerobic conditions. Biodegradation is driven by fungi and bacteria, and its main transformation product is δ-ketoendrin (IPCS, 1992). Endrin residues are rarely detected in the soil; however, in recent studies conducted in Mexico in 2020 both endrin and endrin ketone were detected in soil samples with the highest concentrations being 60.70 mg/kg dry soil (d.s.) and 2,529 mg/kg d.s., respectively (Sánchez-del Cid et al., 2025).

7.2.1.5 Endosulfan

Endosulfan chemical name is 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9ahexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide. Technical grade endosulfan is a brown crystalline substance composed of α- and β-isomers in the ratio of about 70:30 (WHO, 2004). Endosulfan is a contact and stomach toxic that has been used to control insects such as flea beetle, peach tree borer, and tarnished plant bug, as well as several species of aphids and leafhoppers. In addition, it is used to control pests on fruit, vegetables, and tea, and on non-food crops such as tobacco and cotton. In addition to its agricultural uses it was also a public health insecticide (IPCS, 1984). Endosulfan's key routes of release to soils are direct application to crops, atmospheric deposition from spray drift, volatilized material, or long-range atmospheric transport. Endosulfan, after its release to the soil, undertakes a variety of transformation processes. In soil it is biodegraded to endosulfan sulfate which is its main degradation product from biotic metabolism. Endosulfan sulfate is more persistent in soil than the parent compound. The degradation rate depends on the climate and the type of soil microorganisms (ATSDR, 2000). It is not probable that α-endosulfan, β-endosulfan, and endosulfan sulfate are mobile in soil. Soil erosion, run-off, spray drift, and atmospheric deposition contribute to releases of endosulfan to aquatic ecosystems. Endosulfan residue levels are uppermost and most common in neighboring regions with intense agricultural activity. Since 1976, it has been reported that sixteen species of fungi, fifteen soil bacteria, and three actinomycetes metabolized radiolabeled endosulfan in a laboratory study under aerobic conditions (El Beit et al., 1981; Martens, 1976). Biotransformation appears under both aerobic and anaerobic conditions. Aerobic incubation of soil with endosulfan yielded mainly endosulfan sulfate at a range of 30–60%, some endosulfan diol of 2.6%, and endosulfan lactone of 1.2% (Martens, 1976).

7.2.1.6 Chlordane and Heptachlor

Chlordane and heptachlor are discussed together because of their close structural match and because technical-grade products each have about 10–20% of the other compound (ATSDR, 1989; IARC, 2001). Chlordene is the starting material to produce both chlordane and heptachlor, which is made by Diels-Alder condensation of hexachlorocyclopentadiene with cyclopentadiene. Specifically, chlordane is produced by the Lewis acid-catalyzed addition of chlorine to chlordene, while heptachlor is produced by free-radical chlorination of chlordene (WHO, 1984b; Sittig, 1980). Heptachlor epoxide can be produced from heptachlor in a one-step oxidation, and it is its metabolite and an environmental oxidation product of heptachlor (Anon, 1985).

Chlordane is a versatile, broad-spectrum, contact insecticide and was produced mainly for non-agricultural purposes while it was used as an insecticide since the 1950s (WHO, 1984a). Chlordane is a viscous, light yellow to amber-colored liquid. Technical chlordane is a synthetic organic pesticide composed of 147 separate components, some of which exhibit optical activity, while its main components are trans-chlordane, cis-chlordane, and trans-nonachlor (trans- and cis-chlordane are optically active) which are persistent for decades in the environment (Mattina et al., 2002).

Heptachlor was first introduced in 1952 and was extensively used as a broad-spectrum insecticide on a broad variety of agricultural crops, with major use on corn. It also had non-agricultural uses containing seed treatment, home and garden uses, and termite control. It has also been used to control malaria (WHO, 1988). Heptachlor is transformed into heptachlor epoxide and other degradation products in the environmental compartments including soil. Heptachlor epoxide degrades more slowly and is more persistent than the parent compound heptachlor. Heptachlor is also subject to long-range transport and wet deposition. Heptachlor's log soil organic carbon absorption

coefficient (log Koc=4.34) shows a very high sorption trend, implying that it will adsorb strongly to soil and is not possible to leach into groundwater in most cases (Chapman, 1989). The soil organic matter content is also a soil property that affects heptachlor mobility; therefore the possibility of leaching from soils with high organic matter is less possible. However, volatilization from soil particles to the atmosphere is feasible, and therefore is an essential mechanism of transport from land surfaces (McLean et al., 1988). Heptachlor epoxide is soluble in water at a concentration of 0.275 mg/L (EPA, 1987). The log Koc for heptachlor epoxide was estimated to vary between 3.34 and 4.37, indicating a high sorption tendency; thus this compound is not mobile in soil and has a low potential to leach (Lyman et al., 1982). As with heptachlor, the organic matter content of soil affects the mobility of heptachlor epoxide, and it is less possible to leach from soil with a high organic matter content. Heptachlor epoxide is subject to long-range transport and subsequent removal from the atmosphere by wet deposition (EPA, 2007).

7.2.1.7 Pentachlorophenol and Pentachloroanisole

Pentachlorophenol is a chlorinated aromatic substance which was used widely as a fungicide, while pentachloroanisole is not a registered substance, thus is not released directly into the environment. It is the transformation product of pentachlorophenol and is produced in the environment through the methylation of pentachlorophenol by soil micro-organisms. The formation of pentachloroanisole from pentachlorophenol is not its major route of dissipation, since the main route of its dissipation is the transformation to less chlorinated phenols, such as tetrachlorophenol and trichlorophenols, and the formation of bound residues. It has been verified that pentachlorophenol is not persistent in soil (UNECE, 2009). Pentachloroanisole is sparsely soluble in water, and has a high Koc value implying that it is immobile to slightly mobile in soils.

7.3 TOXICITY

7.3.1 The Silent Spring Trigger

Silent Spring by Rachel Carson, first published in 1962, demonstrates the beginning of public awareness of global pollution (Carson, 1962). Based on FAO statistics, in 2018, the global agricultural use of PPPs has been estimated to go beyond 4 million tons of active ingredients (FAO, 2020). This enormous use has led to global soil contamination, as shown by the widespread pollution of soil in Europe (Silva et al., 2019). The finding of endocrine-disrupting chemicals has also brought serious concerns for public health (Diamanti-Kandarakis et al., 2009).

OCPs accumulate in environmental compartments and living organisms due to their physical properties—such as reactivity and solubility—and their chemical composition. OCPs are persistent in living organisms and in the environment because they are lipid-soluble chemicals; therefore they are considered the most noteworthy environmental pollutants globally (Plaza et al., 2019). OCPs are halogenated hydrocarbons that belong to the group of POPs and exhibit the following properties: decomposition (both biological and chemical), lipophilicity, and absorption in tissues (Olisah et al., 2019). They are dissolved in fat cells of organisms for an extended period. This happens since chlorine substitution and hydrolysis cannot break the strong bond that exists between carbon and chlorine. Semi-volatile OCPs persist in aqueous solution and in the atmosphere and remain there for long periods (Potapowicz et al., 2020). They can be detected in sediments due to their poor solubility in water, therefore can access shrimp in aquatic environments via bioconcentration through direct contact with the aquatic environment and biomagnification. Bioaccumulation and biomagnification are two significant mechanisms. Bioaccumulation defines the insertion of a chemical into a living organism from its environment. Biomagnification defines the enhancing concentration of a chemical used to transfer food energy within the food chain. Since OCPs are harmful, biomagnifying, and semi-volatile, there is a great uncertainty in demonstrating how they impact living organisms (Luo et al., 2019).

Exposure to OCPs causes severe health problems to humans, such as hypertension and other cardiovascular troubles and acute to chronic disorders (Kamalesh et al., 2023). It has also been reported that constant exposure to living organisms drives to numerous undesirable health consequences counting endothelial dysfunction, leukemia, neurological diseases, breathing problems, hormonal imbalances, thyroid disease, inflammatory diseases, diabetes, and obesity (Park et al., 2019).

Epidemiological data demonstrate a connection concerning OCP exposure and Parkinson's disease (Genuis et al., 2016). Other diseases such as hypertension, cancer, Alzheimer's disease, hepatitis, teratogenicity, pulmonary fibrosis, respiratory effects (asthma, cough, and sore throat) and leukemia are related with this persistent detection of OCPs in humans (Peinado et al., 2020). Reduced fertility, instinctive miscarriages, early births, ovarian problems, and hormone dysfunction are the reproductive consequences that have been related to OCPs exposure in women (Hood et al., 2022). Cowie et al. reported that dieldrin relates to the existence of neuroendocrine disorders that impact brain activity. This substance disrupts immune response function, mitochondrial respiration, and proper metabolism (Cowie et al., 2017). Heptachlor epoxide, which is a metabolite of heptachlor, has been associated with the growth of Lewy bodies in the human body (Ross et al., 2019). Chlordane, dieldrin, and lindane have been shown to be appeared in substantial levels in brain samples from Parkinson's disease patients (Ross et al., 2019). Childhood exposure to DDE reduces growth, specifically in height and weight (Balte et al., 2017).

In conclusion, cancer, generative abnormalities, neurological harm, and immune system disruption have all been connected to OCPs (Yahaya et al., 2017). They disrupt the neurological systems of many types of animals and insects, leading to paroxysms, paralysis, and finally death (Thompson et al., 2020).

7.3.2 DDT

DDT is a known neurotoxic, carcinogenic, and endocrine-disrupting OCP that is particularly dangerous when consumed by humans and other animals (Castillo et al., 2021). Furthermore, contact with DDT raises the possibility of developing breast cancer and cancer in other organs (Chang et al., 2018). Additionally, it has been indicated that intake of both DDT and its metabolite DDE has harmful long-term consequences on metabolic, immunological, and neurological systems (Burgos-Aceves et al., 2021). Faggio et al. (2018), reported that DDE is steadily biomagnified by aquatic species such as fish, in which it favorably concentrates in fat stores; thus it can be gathered through the food chain and consequently threaten human and wildlife health (Sun, Sun et al., 2020).

7.3.3 Lindane

Lindane is a neurotoxin which disrupts human hormones. In critical cases, poisoning by lindane can be fatal in humans, but generally it causes respiratory difficulties, disorders, spasm, or extreme salivation (Kumar et al., 2018). As regards the environment, it weakens ecological processes, and detrimentally affects the ecosystem's biodiversity, organism communities, and biological traits. γ-HCH (lindane) has excellent stability and permanence in water; therefore, it is difficult to remove from water. Considering its extensive use, its persistence, and wayward properties in the aquatic ecosystem, lindane is of worldwide interest (Grondona et al. 2019).

7.3.4 Dicofol

Dicofol has been classified as a persistent organic pollutant by the Stockholm Convention and presents endocrine-disrupting properties (Panda et al., 2019). Dicofol can be ingested by inhalation, swallowing, and dermal exposure, and is hazardous to humans and extremely toxic to aquatic

animals (Gulipalli et al., 2021). In mammals, dicofol has been found to cause liver enlargement and induce hepatic microsomal enzymes, while it also presents high toxicity to fish, with effects including reduced growth, altered behavior, and impaired reproduction (Vitcheva et al., 2012). It was the last OCP banned in the EU (2009–2010).

7.4 ALDRIN

Aldrin is believed to be one of the main threats among industrial and ecosystem contaminants (Jhamtani et al., 2018). It is extremely persistent and can be undoubtedly swallowed by living organisms via food sources or direct contact. It undertakes biotransformation in the ecosystem and in living organisms. Although aldrin has long been eliminated, it has been reported that environmental compartments contain dangerous levels of this compound (Wrobel et al., 2015).

7.4.1 Endosulfan

Endosulfan consists of α- and β-endosulfan, which are considered very hazardous because of their bioaccumulation and slow biodegradation in the ecosystem (Preud'homme et al., 2015). Endosulfan and its metabolites can interact with the endocrine system, and negatively impact both humans and wildlife (Reddy et al., 2014). Due to its possibility for biomagnification, high stability, low solubility, and neurotoxicity, it is a challenging agrochemical that requires fast action (Ingaramo et al., 2016).

7.4.2 Chlordane

Chlordane and its metabolites are broadly spread, are persistent, and have a high likelihood for bioavailability in the environment (Wu et al., 2021). Living organisms may be influenced by chlordane primarily via intake of contaminated food, by inhalation, or due to its application (Singh and Singh, 2019). Chlordane presents estrogenic and cytotoxic properties. Based on the results of Singh and Singh's (2019) study, it was proposed that it is initially accumulated in the liver and kidneys before transporting to tissues, where it can be stored for an extended time due to its higher lipophilic activity.

7.4.3 Toxaphene

Toxaphene contains approximately 670 different compounds. It was initially used in the late 1940s and is currently used to control populations of rough fish. Studies on wild aquatic animals have shown that toxaphene constitutes an environmental threat not only because of its persistence in soil and air, but also its frequent use. It has been reported to have endocrine-disrupting properties (Yang et al., 2015).

7.5 OCPS AND AQUATIC SYSTEMS

Marine ecosystems have an essential function in retaining the ecological balance of the earth and provide critical ecosystem services (Barbier, 2017); thus they make up a sink to contaminants resulting from anthropogenic activities on agricultural fields. Therefore, such a contamination is emphasized by the increase of population and the connected coastal development (Mostofa et al, 2013). The processes of bioaccumulation and biomagnification are fundamental in marine ecosystems and have been reported to affect marine mammals and large rough fish classes, since they can store high levels of OCPs primarily via diet (Valente et al., 2025). Hence, knowledge of the contamination levels in marine species is essential for taking actions for recovering these species and whole marine ecosystems (Beausoleil et al., 2018).

Since OCPs are substantially persistent in the ecosystem, they are constituting a menace to nontarget species for extended periods, and for that reason OCPs are known to deteriorate several biological processes and suspend the action of key enzymes in response to xenobiotic-induced stress

(Gonçalves et al., 2021), enhancing oxidative stress and neurotoxicity. Hence, they negatively affect the aquatic ecosystems by deteriorating water quality and unintentionally disturbing non-target species and consequently the ecological balance (Kamalesh et al., 2023). When OCPs are ingested by aquatic organisms they end up on the sediment surface, which assists the insertion of contaminants and other pollutants into organisms and the surrounding habitat. Cruz et al. reported that DDT and dieldrin reduced cholinergic and dopaminergic synapses and decreased heart rate, thus causing tremors in the early stage of zebrafish (Cruz et al., 2017). Once sensitive species are exposed to OCPs, their number is decreased (Wang et al., 2016).

7.6 EXTENT AND SEVERITY OF SOIL CONTAMINATION BY OCPS

OCPs were broadly banned in the 1970s and 1980s, but they are still identified in the ecosystem. OCPs are detected in soil and groundwater, surface water, the atmosphere, oceans, river sediments, lakes, lake sediments, marine sediments, wetlands, snow, and agricultural areas (Sim et al., 2023; Hu and Tao, 2023; Xu et al., 2023; Tang et al., 2023; Alshemmari, 2023; Hao et al., 2023; Wang, Zhang, et al., 2023; Khuman et al., 2023; Zhao et al., 2023; Veludo et al., 2022; Muhammed et al., 2023; Lohmann et al., 2023; Guo et al., 2023; Li, Zhang et al., 2023; Vudamala et al., 2023; Xuan et al., 2023; Wang et al., 2022; Li, et al., 2024; Zheng, Ding et al., 2022; Zhang et al., 2023; Mamontova and Mamontov, 2022). OCPs were also detected in animals and plants numerous times in the past (Munjanja et al., 2024; Capella et al., 2023; Kumah et al., 2023). Detectable levels of OCP in the soil can not only harm terrestrial organisms but also impact aquatic organisms via surface runoff. They also constitute harm to humans via the biological enhancement and growth effect of the food chain of agricultural products (Sasaki et al., 2023; Salimi et al., 2023). Unfortunately, research on soil monitoring regarding OCP residues does not have a widespread record in most countries. Indicative results from all continents are presented in the following subsections.

7.6.1 Europe

Investigation of OCP residues in soil does not have a wide record in Europe (Florence et al., 2015). The latest complete study within Europe regarding the analysis of presently used and illegal pesticides including OCPs has been carried out by Silva et al. (2019). Three hundred seventeen (317) soil samples from 11 different European countries were studied. Twenty-one OCPs encompassing aldrin, α-chlordane, γ-chlordane, chlordecone, o,p′-DDD, p,p′-DDD, o,p′-DDE, p,p′-DDE, o,p′-DDT, p,p′-DDT, dieldrin, α-endosulfan, β-endosulfan, endosulfan sulfate, endrin, α-HCH, β-HCH, γ-HCH, heptachlor, heptachlor epoxide, and pentachlorobenzene were identified. The most frequently detected compound was p,p′-DDE, with detection frequency of 23%, and with the highest content of 310 μg/kg d.s. Next most frequently, o,p′-DDD and p,p′-DDT along with dieldrin were detected at concentrations of 40 μg/kg d.s., 10 μg/kg d.s., and 60 μg/kg d.s. respectively, while their respective detection frequencies were 7%, 7%, and 5%. Then p,p′-DDD and alpha chlordane were rarely detected with respective detection frequencies of 3% and 1%. In all studied soils, γ-chlordane, o,p′-DDE, o,p′-DDT, heptachlor, and HCB detection frequencies were below 1%.

Chengkai Qu et al. conducted a study to systematically explain the contamination status of 24 OCPs (α-, β-, γ-, and δ-HCH, p,p′-DDE, p,p′-DDD, o,p′-DDT, o,p′-DDE, o,p′-DDD, p,p′-DDT, HCB, a-endosulfan, β-endosulfan, endosulfan sulfate, cis- and trans-chlordane, cis- and trans-nonachlor, aldrin, dieldrin, endrin, heptachlor, mirex, and methoxychlor) in the soils from Benevento provincial territory in southern Italy (Qu et al., 2019). Sixty-four surface soil samples (0–5 cm depth) were collected in the entire territory of Benevento Province between December 2014 and February 2015. A countable quantity of OCPs was detected in all samples, with HCB and DDTs being the most frequently detected compounds. Heptachlors were not detected in any of the soil samples. The total concentrations of OCPs in soil ranged from 58 to 16.900 μg/kg d.s., while p,p′-DDE, p,p′-DDD, and HCB dominating among other OCPs contributed 73.5% of the

total concentration of the detected OCPs. Regarding DDTs, their total concentrations varied from not-detected to 16.400 μg/kg d.s., while p,p′-DDT and p,p′-DDE were the dominant compounds. The ratio of p,p′-DDD/p,p′-DDE indicates whether DDT biodegrades to DDE or DDD aerobically or anaerobically. In the examined soil samples, the ratio was found to be higher than 1 in only three of all samples, designating the dominance of the aerobic breakdown of p,p′-DDT. On the other hand, the ratio of p,p′-DDT/p,p′-DDE varied significantly, from 0.0010 to 9.6; therefore it was far below the ratio for fresh application of DDTs, suggesting the occurrence of aged DDT. Concerning HCHs, the highest total concentration was found in central and southern Benevento provincial territory, with concentrations varying from not-detected to 720 μg/kg d.s. Between the HCHs, β-HCH was the most abundant compound, followed by α-HCH, γ-HCH, and δ-HCH. The ratio of α/γ-HCH varied between 0.076 and 1, indicating that HCH residues were most likely from both technical HCH and lindane. The HCB concentrations ranged from not-detected to 4,150 μg/kg d.s. The concentrations of sulfans ranged from not-detected to 1.490 μg/kg d.s.: α-endosulfan was quantified in only 6.25% of all soil samples, while the detection frequencies of β-endosulfan and endosulfan sulfate was only 14.1% and 45.3%, correspondingly, indicating that there is no fresh usage of technical endosulfan. The concentrations of chlordanes in soils of Benevento provincial territory varied from not-detected to 96 μg/kg d.s. In that study, the detection frequencies of chlordane-related compounds were extremely low and followed the order cis-nonachlor (35.9%), cis-chlordane (9.38%), trans-chlordane (6.25%), trans-nonachlor (4.69%), and heptachlor (0%). The concentrations of DRINs varied a little, ranging from not-detected to 370 μg/kg d.s. In soil, aldrin is undoubtedly oxidized to its epoxide metabolite, dieldrin, which is more resistant to chemical degradation and metabolic breakdown (Shegunova et al., 2007). Dieldrin was the most abundant compound, followed by aldrin and endrin.

7.6.2 Asian Countries

In a recent study conducted in the Shouguang City in China, an area with a long history of vegetable cultivation, thirty soil samples were collected from the surface soil horizon of 0–20 cm depth considering soil conditions such as topography and geology, soil physical properties, land uses, and crop types (Li, Qi et al., 2023). BHC, α-HCH, β-HCH, γ-HCH, δ-HCH, p,p′- DDT, p,p′-DDE, p,p′-DDD, o,p′-DDT, methoxy DDT, hexachlorobenzene (HCB), heptachlor, α-chlordane, γ-chlordane, α-endosulfan, β-endosulfan, and endosulfan sulfate were determined in this research, based on the history of OCP usage in the study area. The analysis results indicate a variation in the content of OCPs in the study area. The highest concentration was observed for endosulfan sulfate (128.49 μg/kg d.s.) and DDTs (45.33 μg/kg d.s.). The highest content for HCHs was 18.64 μg/kg d.s., while the maximum content for hexachlorobenzene was 11.54 μg/kg d.s. Among DDTs the highest concentration was observed for p,p′-DDE, followed by p,p′-DDT. The detected content of DDTs was higher than that of HCHs which is mainly ascribed by the authors to the fact that DDTs are more stable than HCHs and the use of DDTs was significantly higher than that of HCHs. Furthermore, HCHs has higher vapor pressure and solubility and thus can migrate easier through air and water flow. As regards HCH isomer contents, their order was β-HCH > γ-HCH > δ-HCH, while α-HCH was not detected. The authors reported that α-HCH and γ-HCH can be transformed into β-HCH, resulting in its accumulation in soil. The content of DDT isomers were in the following order: p,p′-DDE > o,p′-DDT > p,p′-DDT > p,p′-DDD. The authors noted that the detection level of p,p′-DDD was only 10% while the detection rate of p,p′-DDE was 96.67%. The high content of p,p′-DDE in the soil samples of the study area and the low content of p,p′-DDT is attributed by the authors mainly to the fact that the p,p′-DDT was degraded by microorganisms and converted into p,p′-DDD and p,p′-DDE, which were hard to degrade in the natural environment. The transformation and source of DDTs were analyzed. The authors consider the ratio DDT/(p,p′-DDD+p,p′-DDE) to explain if the determined content of DDTs is due to current or historic use. In case that the ratio DDT/(p,p′-DDD+p,p′-DDE) is lower than 1, the determined content is due to past uses, while the opposite is due to current use.

In that study the determined ratio is less than 1 and thus the authors concluded that the determined DDT content is due to past uses.

Another study was conducted in September 2022 in agricultural areas of the black soil region of Shenyang, China. The sampling areas belong to one of the most important agricultural plains in China, where a broad variety of food and cash crops are grown (Lv et al., 2024). A total of 308 soil samples from open-air agricultural fields (286 samples) and greenhouse fields (22 samples) were collected from the soil surface horizon (0–20 cm depth) of the respective agricultural areas for the determination of 23 OCP pesticides including α-HCH, hexachlorobenzene (HCB), β-HCH, γ-HCH, δ-HCH, heptachlor, aldrin, heptachlor epoxide, α-chlordane, γ-chlordane, α-endosulfan, p,p′-DDE, dieldrin, endrin, β-endosulfan, p,p′-DDD, o,p′-DDT, endrin aldehyde, endosulfan sulfate, p,p′-DDT, endrin ketone, methoxychlor, mirex, decachlorobiphenyl, and quintozene. The mean concentrations of OCPs in greenhouse fields and open-air agricultural fields were found to be 20.72 μg/kg d.s. and 16.38 μg/kg d.s., correspondingly, while the detection rates of OCPs were 100% in the greenhouse fields and 72.38% in open-air agricultural fields. Therefore, the detection rate of OCPs and their mean concentration was higher in greenhouse fields. In soils from greenhouse fields the concentration levels of individual OCPs were in the following order p,p′-DDT > p,p′-DDE > p,p′-DDD > γ-HCH > β-endosulfan > HCB, while the total concentration levels ranged from 0.56 μg/kg d.s. to 69.22 μg/kg d.s. The total concentration of OCPs in open-air agricultural fields ranged from 0.50 μg/kg d.s. to 221.72 μg/kg d.s., and the mean concentration was 23.19 μg/kg d.s. The concentration levels of individual OCPs followed this order: endrin ketone > p,p′-DDT > γ-HCH > o,p′-DDT > p,p′-DDE > α-HCH > endosulfan sulfate > p,p′-DDD > HCB > α-chlordane > α-endosulfan. The concentration range for endrin ketone was from non-detected to 216.40 μg/kg d.s., while at high concentrations were also detected p,p′-DDT (not-detected −144.55 μg/kg d.s.), p,p′-DDE (not-detected−117.35 μg/kg d.s.), and α-HCH (not-detected −45.06 μg/kg d.s.). The analysis results suggest that many types of OCPs were used in the black soil region of Shenyang. As regards the concentration levels of p,p-DDT and its degradation products p,p′-DDE and p,p′-DDD, the authors indicated that there might have been a current input of DDT pesticide of p,p′-DDT based on the ratio p,p′-DDT/(p,p′-DDE + p,p′-DDD) which was higher than 1 in most cases. Since o,p′-DDT was also detected, the authors attributed this finding to the presence of triclopyr in the area. As regards the existence of α-HCH and γ-HCH, the ratio of α-HCH/γ-HCH was 3.36 in the present study indicating that HCH residues in agricultural soils are primarily due to substantial use in the past; however a recent input of lindane cannot be excluded. The analysis results of α-chlordane and heptachlor epoxide show that chlordane is still used in the area, since α-chlordane can be degraded to heptachlor which is further degraded to heptachlor epoxide. Moreover, the ratio of α-endosulfan/β-endosulfan of 0.24 in the present study designates past use of endosulfan while the ratio of α-endosulfan/endosulfan sulfate <1, proposing that there may be no infringement of the use of endosulfan after its ban.

Another study was conducted from July to September in 2019 on the national scale of China for the determination of 23 OCPs. A total of 154 surface soil samples were collected from the surface horizon (0–20 cm depth), while the sampling sites enclosed different land use types of soil, included 4 soil samples from background sites (far away from human activities), 35 samples from rural sites (croplands), and 115 samples from urban sites (such as schools and community and city parks) (Wang, Cao et al., 2023). OCPs such as α-HCH, β-HCH, γ-HCH, o,p′-DDT and hexachlorobenzene (HCB) were detected in all soil samples, which undoubtedly designated the environmental persistence of these OCPs. The total concentration of OCPs in surface soil of China ranged from 0.056 to 1.90×10^3 μg/kg d.s., with the mean value of 36.7 μg/kg d.s. The predominant concentration level was detected for DDTs (0.005–1.45×10^3 μg/kg d.s., with the mean concentration of 29.8 μg/kg d.s.), contributing to 73.5% of the total concentration of OCPs. It is well known that DDTs are highly persistent in soil with long half-lives (DT_{50}) of several years (Walker et al., 2004). DDT can potentially be dehydrochlorinated to DDE and dechlorinated to DDD (Kafaei et al., 2020). In

the studied area p,p′-DDE and p,p′-DDT were the most frequently detected OCPs with the mean concentrations of 11.5 μg/kg d.s. and 13.1 μg/kg d.s., respectively. Regarding HCHs, their detected concentration levels were relatively lower compared to the other OCPs. Among HCHs the most abundant isomer was β-HCH contributing to 74.4% to the total HCHs. Considering the usage and degradation perspectives, the order of the four HCHs was as follows: β-HCH > α-HCH > γ-HCH > δ-HCH. α-endosulfan was frequently detected in soil samples with detection frequency approximately 80.5% which indicates the frequent use of technical endosulfan in China. Endrin, aldrin, and dieldrin were never produced in China; however, they were still detected in surface soil with lower detection frequency (approximately 4%). The authors attributed the detection of endrin, aldrin, and dieldrin to the long-range atmospheric transport. The results revealed that the detected levels of OCPs followed the trend of urban-rural-background soils. The authors concluded that in most cases the detected concentrations were due to historical use; however, recent input of DDTs and lindane could not be excluded.

Another study was performed in South Korea for the determination of 22 OCPs in 61 soil samples from the surface horizon (0–10 cm depth) including urban, suburban, agricultural, and industrial sites every year and between the years 2013 and 2016. The determined OCPs included aldrin, dieldrin, endrin, o,p′-DDD, p,p′-DDD, o,p′-DDE, p,p′-DDE, o,p′-DDT, p,p′-DDT, oxychlordane, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor, heptachlor, heptachlor epoxide, mirex, α-HCH, β-HCH, γ-HCH, and α-endosulfan. The concentration of total OCPs varied between not-detected and 66 μg/kg d.s. with a mean concentration of 2.5 μg/kg d.s. in the years between 2013 and 2016. p,p′-DDE and endosulfan sulfate were the most frequently detected compounds and with the highest concentrations. Among all of the hexachlorocyclohexanes (HCHs), β-HCH was the most frequently detected compound. The authors presented that the mean concentration of total OCPs was higher at the urban sites, while the mean concentrations of total DDTs and HCHs varied between 1.23 and 0.69 μg/kg d.s., respectively. In the suburban sites fewer OCPs were detected, and the endosulfan group was the dominant one. p,p′-DDT was only detected in the first year (2013) of the study, while only its metabolites were detected between the years 2014 and 2016. As regards chlordane, the cis-chlordane was the dominant compound between the years 2013 and 2014, while trans-chlordane was dominant in 2015. During the last year of the study no chlordane compounds were detected. In agricultural sites, p,p′-DDT contributed up to 20% to the total DDT detected levels. p,p′-DDE was the major DDT compound between 2013 and 2015; however, in the last year of the study p,p′-DDD was the major detected compound. Based on the ratio p,p′-DDT/(p,p′-DDE + p,p′-DDD) and in urban sites over the years, the recent use of DDT was recognized in some cases; however, there were sampling sites with aged DDT, since the ratio of p,p′-DDT/(p,p′-DDE + p,p′-DDD) was less than 1 indicating aged sources (Qiu and Zhu, 2010). As regards the suburban sites, the p,p′-DDT/(p,p′-DDE + p,p′-DDD) ratio was less than 1 in all sampling years, demonstrating the impact of aged sources. At the agricultural sites, more than 80% of sites showed p,p′-DDT/(p,p′-DDE + p,p′-DDD) ratios less than 1 between 2013 and 2015. In 2016, more than 88% of the agricultural sites showed p,p′-DDT/(p,p′-DDE + p,p′-DDD) ratios of less than 1. In the industrial sites, more than 90% of sites in 2013 and all sites in 2014 showed p,p′-DDT/(p,p′-DDE + p,p′-DDD), with ratios less than 1 indicating past use of DDT. Furthermore, the ratio o,p′-DDT/p,p′-DDT was used to determine if the DDT residues were from technical DDT or dicofol use. The ratio of o,p′-DDT/p,p′-DDT varied from 0 to 0.5 between 2013 and 2016 in all sampling soils indicating that residues of DDT are mainly due to past DDT use. As regards HCH, the ratio of β/(α+γ)-HCH was used for identifying recent or past HCH use. In most sampling sites the ratio β/(α+γ)-HCH was less than 1, suggesting past usage of HCH. The ratio of α/γ-HCH was used as an indicator to identify if the HCH residues come from technical HCH use or lindane use. The α/γ-HCH ratios in that study ranged from 0 to 3 in all soil samples suggesting that HCH residues were more likely from past usage of technical HCH. The ratio of α/β-endosulfan ranged from 0 to 2 over the years, representing historical endosulfan usage. Concerning heptachlor epoxide, it was found that it was the major compound

over heptachlor at all sampling sites. At the urban and industrial sites, only heptachlor epoxide was identified. Heptachlor is metabolized into heptachlor epoxide in soil which has a great affinity to be absorbed in the soil, and it is resistant to biodegradation (Matthiessen et al., 2000). Residues of heptachlor from past usage are possibly metabolizing into heptachlor epoxide, thus enhancing the concentration of heptachlor epoxide in soil.

Many studies have been conducted in India which is one of the main production countries of OCPs in the world (Ashesh et al., 2022). One of the studies reported the residue levels and the distribution pattern of the OCPs including aldrin, dieldrin, endrin, HCB, HCH isomers, DDT metabolites, endosulfan isomers (α- and β-), endosulfan sulfate, heptachlor and its metabolites, α-chlordane, γ-chlordane, and methoxychlor in 31 soil samples collected from the northern Indo-Gangetic alluvial plains (Singh et al., 2007). Based on the study results, the authors iterate that β- and δ-isomers of HCH were the most frequently detected OCPs, whereas methoxychlor was the least detected OCP. The total OCPs level ranged from 0.36–104.50 μg/kg d.s. in soil. Manickam et al. collected soil samples from pesticide factories situated in north, south, and central India. They reported that the maximum concentration of HCH and DDT was detected in south India, and total DDTs, total HCHs, and total endosulfans in soil ranged from not-detected to 244 μg/g d.s., from not-detected to 350 μg/g d.s., and from not-detected to 44 μg/g d.s., in north, south, and central India respectively (Manickam et al., 2010). Mishra et al. (2012) analyzed 175 surface soil samples (0–30 cm depth) which were collected from two districts and various land uses including agricultural fields of paddy and vegetables, tea gardens, fallow land, and urban land for the determination of HCH (α-HCH, β-HCH, γ-HCH, and δ-HCH) and DDT (o,p′-DDE, p,p′-DDE, p,p′-DDD, o,p′-DDT and p,p′-DDT) during the years 2009 and 2010. High residue levels of DDTs were detected in the soils from both the districts. The total DDTs (sum of o,p′-DDE, p,p′-DDE, p,p′-DDD, o,p′-DDT, and p,p′-DDT) varied from 166 to 2,288 mg/kg d.s. and 75 to 2,296 mg/kg d.s. for the districts Nagaon and Dibrugarh, respectively. Between the examined DDT metabolites in soil, p,p′-DDT was the prevalent ranged between 8–1,478 mg/kg d.s. and 8–1,199 mg/kg d.s. for the districts Nagaon and Dibrugarh, respectively, while p,p′-DDE was the second greatest compound which ranged between 11 and 1,159 mg/kg d.s. and from 4 to 1,187 mg/kg d.s. for both districts, respectively. Between DDT metabolites, p,p′-DDT, the parental compound, was found in higher concentrations in tea gardens which had high organic carbon content and the soils were highly acidic, while the p,p′-DDE accounted for higher percentage in paddy soil which had low organic carbon and clay content. The soils under examination confirmed varying concentrations of HCH residues while the total HCH concentration (sum of α-HCH, β-HCH, γ-HCH, and δ-HCH) was between 98–1,945 mg/kg d.s. and 178–1,701 mg/kg d.s. for both districts, respectively. Amongst the four HCH isomers, β-HCH is the predominant isomer, and the next main isomer was γ-HCH. Comparing the three different types of agriculture fields, it was noticed that the percent influence of γ-HCH was more significant in tea garden while the β-HCH was found more important in paddy fields for both the districts.

Kumar et al. determined the health risk associated with OCPs in Korba, India. The total concentration of HCHs and DDTs varied between 0.9 and 20 μg/kg d.s. and from 2 to 315 μg/kg d.s. respectively. It was found that soil samples from the paddy field contain a low level of OCPs due to the degradation of OCP by rice plants (Kumar et al., 2014).

7.6.3 Africa

A few studies in African countries have been devoted to the soil monitoring of OCPs (Iwegbue et al., 2024). A research study conducted in southern Nigeria involved the determination of 13 OCPs, including α-HCH, β-HCH, γ-HCH, δ-HCH, HCB, o,p′-DDD, p,p′-DDD, o,p′-DDE, p,p′-DDE, o,p′-DDT, p,p-DDT, α-chlordane, and γ-chlordane (Udoekpo et al., 2024). The study was conducted in six agricultural zones of Akwa Ibom State, a major cassava-producing area in southern Nigeria covering a total area of 7,081 km². Thirty composited samples were collected from the surface soil horizon (0–5 cm depth) from five commercial farmlands in each cultivated zone. Furthermore, five

grab samples were collected from cultivated areas where farmers stated that they did not apply pesticides, and they were used as control samples. The results prove variable concentrations of OCPs through the monitored agricultural areas. The highest concentration was observed for α-HCH (18.35 μg/kg d.s.) and δ-HCH (9.14 μg/kg d.s.) while the total concentration of OCPs ranged from 3.88 μg/kg d.s. to 21.66 μg/kg d.s. In most cases the ratio of α-HCH/γ-HCH was higher than 3, suggesting that their source is possibly technical HCH and indicating long-range transport because α-HCH is the dominant isomer. In cases where the ratio of α-HCH/γ-HCH is lower than 3 (only one case in this study) designates recent use of lindane, a pesticide dominated by γ-HCH. As regards the β-HCH/γ-HCH ratio, in three out of six agricultural areas it is higher than 1 and that suggests historical input, while in the other three areas it is lower than 1, indicating recent application. Since p,p′-DDT/sum of DDTs ratio was higher than 0.5 only in one case out of six, this suggests historical DDT use.

Another study conducted in the Niger Delta of Nigeria examined the concentrations, sources, and risk associated with OCPs in soils and dusts from a typical urban area (Chukwujindu et al., 2024). Twenty soil samples were collected between January and March 2019 at a soil depth of 0–15 cm, for the determination of 20 OCPs including HCHs (α-HCH, β-HCH, γ-HCH, δ-HCH), DDTs (p,p′-DDE, p,p′-DDD, p,p′-DDT), α-chlordane, γ-chlordane, heptachlor, heptachlor epoxide, chlordanes (cis and trans), methoxychlor, endosulfans (endosulfan I, endosulfan II, endosulfan sulfate), and -drins (aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone). Total OCPs maximum detected levels in soil were 169.8 mg/kg d.s., while the maximum detected levels for HCHs were 28.7 mg/kg d.s., for DDTs were 36.8 mg/kg d.s., for chlordanes were 37.2 mg/kg d.s., for endosulfans were 32.4 mg/kg d.s., and for the -drins were 34.7 mg/kg d.s. The maximum concentrations of the different OCP classes in soil followed the order: chlordanes > dichlorodiphenyltrichloroethane (DDTs) > aldrin + dieldrin + endrin and its isomers (-drins) > endosulfans > hexachlorocyclohexane (HCHs).

Mwevura et al. conducted a study in the Rufiji River Delta in Tanzania which is considered an internationally notable wetland for the determination of pesticide residues in soil samples including 16 OCPs (HCB, α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, ketone endrin, γ-chlordane, p,p′-DDT, o,p′-DDT, p,p′-DDE, p,p′-DDD) (Mwevura et al., 2021). Sixty-six soil samples were gathered during four sampling events in 2003 from six sites. Soil samples were gathered two times during the pesticide application period (February 2003 and April 2003) for a total of 48 soil samples, and two extra gatherings during post-application (June 2003 and August 2003) for a total of 18 soil samples. The authors reported that all four HCH isomers (α-HCH, β-HCH, γ-HCH, δ-HCH) were detected in all soil samples, while γ-HCH (lindane) was detected at higher frequencies. The total concentration of HCHs in soil showed a significant decrease in concentrations between surveys (4.6 mg/kg d.s. to 2.7 mg/kg d.s.). γ-chlordane, endrin, and endrin ketone were not detected in any of the soil samples. The total concentration of DDTs (p,p′-DDT, o,p′-DDT, p,p′-DDE, p,p′-DDD) showed a significant decrease in concentrations between surveys (29 mg/kg d.s. to 8.1 mg/kg d.s.). p,p′-DDE was detected in higher concentration among the other DDT metabolites. Heptachlor, heptachlor epoxide, aldrin, and dieldrin were detected in all soil samples. The concentration of heptachlor, heptachlor epoxide, aldrin, and dieldrin declined obviously between sampling periods.

Ishwar Chandra Yadav et al. determined OCPs including HCHs (α-, β-, γ-, δ-, and ε-HCH), DDTs (o,p′-DDE, p,p′-DDE, o,p′-DDD, p,p′-DDD, o,p′-DDT, and p,p′-DDT), endosulfans (α- and β-endosulfan), heptachlor, chlordane, HCB, aldrin, dieldrin, endrin, isodrin, methoxychlor, and mirex in 72 soil samples from the surface horizon (0–20 cm depth) of 4 regions of Nepal (Yadav et al., 2016). DDT and its metabolites were detected in all study sites. The greatest levels of DDTs were detected in one of the four regions and were in the range of 20.4–250.3 mg/kg d.s. The authors attributed the high content of DDTs to intensive farming and malaria control. The ratio of o,p′-DDT/p,p′-DDT ranged between 0.05 and 0.37, demonstrating the usages of technical DDT. Regarding the ratio of p,p′-DDT/(p,p′-DDD + p,p′-DDE) it should be noted that it varied between 1 and 3,

indicating the fresh usage of technical DDT. The concentration of endosulfan ranged from 2.8 mg/kg d.s. to 8.7 mg/kg d.s., 2.83 mg/kg d.s. to 3.43 mg/kg d.s., 28 mg/kg d.s. to 3.28 mg/kg d.s., and 2.93 mg/kg d.s. to 3.35 mg/kg d.s. in the four regions respectively. The ratio of α-/β-endosulfan was below 2.3 in all studied areas, implying past use of endosulfans. Concerning HCH isomers, all of them were detected in all sampling sites except for β-HCH which was detected only in two samples. The ratio of α-HCH/γ-HCH is used as indicator of HCH sources.

When the ratio of α-/γ-HCH ratio is below 3 it suggests application of lindane, whereas a ratio between 3 and 7 corresponds to application of technical HCHs (Jiang et al., 2009). In that case, the ratio α-/γ-HCH in 50% of total sites was above 3, while in the remaining 50% of sampling sites, the α-/γ-HCH ratio was below 3, representing that HCHs may originate from a mixed source of technical HCH as well as lindane use. In addition, relatively smaller abundance of γ-HCH than α-HCH proves usage of technical HCHs in Nepal. Chlordanes were the least detected. The comparative abundance of cis-chlordane and trans-chlordane presented permanent concentration regardless of sampling sites. The ratio cis-chlordane/trans-chlordane was close to 1, indicating past usage of chlordanes. The detected concentrations of HCB varied between 0.11 and 1.56 mg/kg d.s., 0.02 and 0.81 mg/kg d.s., not-detected and 0.65 mg/kg d.s., and 0.1 and 0.66 mg/kg d.s., in the respective studied four areas.

7.6.4 America

Sánchez-del Cid et al. (2025) performed a study in a crucial agricultural area in the state of Campeche, Mexico in North America for the determination of OCPs in soil samples. The type of climate in this area is warm subhumid, with abundant rains in summer and autumn (June–November) and the dry season between January and April. Soil samples were collected from the surface horizon and from two different depths (0–5 cm and 5–15 cm) from nine plots cultivated with maize, eight plots cultivated with soybeans, and three plots cultivated with pumpkin during the dry season (March 2020) and in the rainy season (August 2020). The determined OCPs were HCHs (α-, β-, γ-, and δ-HCH), endosulfans (endosulfan I, endosulfan II, and endosulfan sulfate), -drins (dieldrin, endrin, and endrin ketone), DDTs (p,p′-DDT, p,p′-DDE, and p,p′-DDD), heptachlors (heptachlor and heptachlor epoxide), chlordanes (cis and trans), and methoxychlor. In the soils from the two crops, heptachlor epoxide had higher residue levels and detection frequency than the parent compound heptachlor. The total concentration of the determined DDTs at soil depth 0–5 cm and endosulfans at soil depth 5–15 cm were higher in maize crop soils than in soybean crop soils. Endosulfan II had the highest concentration in both cultures while endosulfan sulfate was the most frequently detected compound.

7.6.5 The Arctic Region, Where the "Pollution Ignores Boundaries" Theory was Verified

Pollution is not restricted to the site where PPPs are applied; therefore, they are partially transferred to other media, such as water and air, thus subsequently moving to other areas (Mottes et al., 2022). Pesticides are found in inaccessible and theoretically pristine regions of the earth such as Antarctica (Potapowicz et al., 2020). Experts have then recognized that any ecosystem compartment is not closed, so pollutants can be removed from one compartment to another under proper conditions. Consequently, cropped and shepherd soils are of noteworthy concern because these soils are closely connected to aquifers, atmosphere, wildlife, and even saltwater (Mottes et al., 2020).

The arctic zone, including Svalbard, encounters exceptional environmental challenges from the presence and persistence of OCPs, pollutants identified for their long-range atmospheric transport and potential local sources. The primary mode of initiation for POPs into arctic environments is assumed to be through atmospheric transport from sources located in mid- and low-latitude regions

(MacDonald et al., 2000). A study was conducted in this area for the determination of 23 OCPs, including o,p′-DDD, o,p′-DDE, o,p′-DDT, p,p′-DDD, p,p′-DDE, p,p′-DDT, aldrin, α-HCH, β-HCH, cis-chlordane, cis-heptachlor epoxide, cis-nonachlor, δ-HCH, dieldrin, endrin, γ-HCH, HCB, heptachlor, mirex, oxychlordane, trans-chlordane, trans-heptachlor epoxide, and trans-nonachlor in soil samples which were collected from the surface horizon 0–5 cm. Generally, most of the 23 OCPs were detected with 100% detection rate in soil samples from the study area, demonstrating the widespread presence of OCPs in the arctic environment. The total concentration of OCPs ranged from 0.28 μg/kg d.s. to 3.6 μg/kg d.s. (Lin et al., 2025). Between the OCPs, HCB was detected at the highest level, accounting for 19% of the total OCPs, followed by DDTs (particularly p,p′-DDT and p,p′-DDD) and HCHs (11%). Regarding the detection levels of HCHs in the study area, in general, the relative amount of α-HCH was the highest, followed by γ-HCH, β-HCH, and δ-HCH. This composition was different from that of technical HCH mixtures, as well as from that of lindane (>99% γ-HCH). The α/γ-HCH ratios in most samples indicate a combination of two sources, lindane and HCH mixtures. Specifically, in soil samples with ratio of α/γ-HCH lower than 0.2, the primary source is lindane, while soil samples with a ratio of 7 suggest a stronger indicator of technical HCH mixtures. β-HCH is the most resistant isomer to biodegradation among the HCH isomers, while α-HCH and γ-HCH can be converted into β-HCH in the environment. The β-HCH/(α-HCH + γ-HCH) ratio higher than 0.5 indicates historical usage; however, in the present study, the ratio of β-HCH/(α- + γ-HCH) in soils was usually lower than 0.5, demonstrating fresh inputs of HCHs (Chen et al., 2022). Regarding DDTs, in most soils and due to aerobic environment, the dominance of DDD over DDE in soil samples is unusual. The authors attributed this finding to the fact that the DDD detected may not only derive from historical DDT use. The authors noted that the presence of o,p′-DDD strongly suggests current use or a regional contamination source. It is well known that chlordane consists of cis-chlordane and trans-chlordane, with the trans-chlordane being more susceptible to photolysis and transformation. Also, heptachlor can degrade to heptachlor epoxide which is a more stable compound in the environment. Hence, the indicative ratios of trans-chlordane/cis-chlordane and heptachlor/heptachlor epoxide, both of which are used to indicate the origin of chlordane and heptachlor, respectively, revealed that many of the samples had diagnostic ratios of trans-chlordane/cis-chlordane below 1 while the ratios of heptachlor/heptachlor epoxide were above 1. This shows that chlordane originated from a historical source, while heptachlor was recently used.

Zheng, Han et al. (2022) determined the distribution characteristics, sources, and risk levels of OCPs in Ny-Ålesund of the arctic region. In that study 24 surface soil samples had been collected from eight stations. OCPs were detected in the surface soil samples from Ny-Ålesund, containing α-HCH, γ-HCH, p,p′-DDE, o,p′-DDD, p,p′-DDD, and p,p′-DDT. α-HCH and γ-HCH were found in all soil samples; however, β-HCH and δ-HCH were not found in any of the samples. The total OCPs concentration ranged from 0.59 μg/kg d.s. to 3.87 μg/kg d.s.; α-HCH and γ-HCH were detected in soil samples, while their concentration ranged from 0.28 μg/kg d.s. to 1.36 μg/kg d.s. and the content of γ-HCH was higher than that of α-HCH indicating that HCHs underwent obvious transformation in the environment. Considering the low content of HCHs in the soil, the authors attributed their findings to historical pollution. p,p′-DDE, o,p′-DDD, p,p′-DDD, and p,p′-DDT were detected in the topsoil of Ny-Ålesund region, with their content varying from 0.31 μg/kg d.s. to 2.76 μg/kg d.s. The average contents of DDE, DDD, and DDT were 0.04 d.s., 0.96 d.s., and 0.55 μg/kg d.s., respectively, indicating that DDD was the main contaminant. The results confirmed that the ratio of DDD+DDE/DDT in most samples was >1, implying that DDT has been degraded for a long time, indicating historical pollution, but there were also results indicating the existence of new sources of pollution. The authors attributed their findings to atmospheric transport, ocean currents, and biological transport, while atmospheric transportation was considered the main route of OCPs in the arctic region, because semi-volatile OCPs enter the atmosphere at lower latitudes and higher temperatures, and they settle at higher latitudes with lower temperatures through atmospheric flow.

7.6.6 Australia

Weaver et al. (2012) conducted a study to determine the content of OCPs in 211 soil samples from different soil depths: 0–0.3 m, 0.3–0.6 m, and 0.6–0.9 m in 2000 and 2002, and from soil depth 0.9–1.2 m in 2000, 2001, 2002 and 2003 for the same sampling sites, under irrigated cotton farming systems in the lower Namoi Valley of New South Wales in Australia. α-endosulfan, β-endosulfan, endosulfan sulphate, DDD, DDE, DDT, and endrin were detected in all soil samples, while DDE, a breakdown product of DDT, was the most persistent OCP in all depths analyzed. Endosulfan sulphate was the second most persistent followed by endrin > α-endosulfan > β-endosulfan > DDT and DDD. Aldrin, α-HCH, β-HCH, γ-HCH (lindane), trans-chlordane, cis-chlordane, total chlordane, heptachlor, and methoxychlor were not detected in any soil.

Another more recent study was conducted by Conrad et al. (2021) in the Coffs Harbor region in northern New South Wales, Australia, to determine the presence of OCPs, which were not detected in any of the studied soil samples.

7.6.7 New Zealand

The Ministry for the Environment in New Zealand (2024) established an organochlorines monitoring program to carry out research and to assess data about the levels of OCPs in different environmental compartments including soil. Soil samples were gathered from different areas around New Zealand to cover the country's variable range of climates and land uses. The sites sampled involved native forests, grasslands, agricultural soils, city parks, and reserves in regional and resident places. Native forest and grassland soil were taken from national parks and Department of Conservation land, while agricultural soil was taken from hill country and flat land rural farms throughout the whole country. Urban soil was gathered from parks and reserves in the regional centers, including more than 50 parks and reserves. The sampling campaign was from late February to early May 1996. The levels of OCPs in the examined soils were quite low. In native forests, grassland, and urban soils, HCB, dieldrin, and DDT were detected. In addition to dieldrin and DDT being detected in all urban soil samples, however, lindane and chlordane were detected only in a limited number of samples. In urban soils, DDTs ranged from 1.50 to 244.0 μg/kg d.s. Based on the measured levels of OCPs, the Ministry for the Environment concluded that the background levels of OCPs in the New Zealand were commonly very low and were among the lowest levels detected anywhere in the world.

In the report it was also noted that OCP emissions or use in other countries, and their global transportation, correspond to a supplementary and continuing source of OCPs to the New Zealand ecosystems. However, the implication of these inputs comparative to 'local' sources of organochlorines is hard to assess and quantify.

7.6.8 Siberia

The initial theories that OCPs might migrate via air as gases and aerosols concentrating in zones of reduced temperatures evolved in 1974. Later, the belief of worldwide fractionation procedures of OCPs arose. According to that theory, they migrate to polar latitudes, a series of quite short jumps due to seasonal differences in temperatures. The detected levels of OCPs in soils of Siberia ranged from 0.009 to 10.8 μg/kg d.s. for HCB, 0.02 to 1.67 μg/kg d.s. for the sum of HCHs, and 0.01 to 0.60 μg/kg d.s. for the sum of DDTs (Mamontova et al., 2016). The authors reported that the distribution of OCPs varies with the latitudes of sampling sites. The detected levels of HCB in soils are constantly higher to the north than that to the south. The detected levels of α- and γ-HCH rose from south to north, while the ratio of α-HCH/γ-HCH increased from 1.28 in south to 4.75 in the north areas. Concerning DDT, consistent decline was recorded for the levels of p,p′-DDE and

p,p′-DDT along the subarctic areas, as well as for those of p,p′-DDE from the southern boundaries of Mongolia to the coasts of the subarctic areas. The ratio of p,p′DDE/p,p′DDT was also reduced from 10.7 to the south to 0.53 to the north. This might be affected either by a fresh supply of p,p′-DDT and slowing down of metabolism due to low temperatures or by the starting of temporary atmosphere transport of more volatile p,p′-DDE to the southern parts of the considered areas of Mongolia and Russia from the neighboring fields of China where DDT is still applied as a component of dicofol. The authors, based on the results of the study from soils from background areas of Siberia, present an unusual distribution of OCPs from south to north, i.e., from Central Asian regions (Mongolia) to subarctic areas.

This spreading indicates different periods of OCPs migration, which proves the theory of global fractionation of OCPs and additionally presents the significance of long-range atmospheric transport in the northern areas where the climate conditions improve the accumulation of OCPs (Ma et al., 2021). The low temperatures encourage OCPs adsorption on the particles in air, which are then precipitated onto the soil. The reactions of natural OCPs decomposition are slowed down in a cold climate, granting persisting incidence of these compounds in unchanged forms. Even though the polar regions are reached by only a minor part of OCPs, their detected levels are greater compared to tropical and middle latitudes because of the moderately smaller area of the polar regions of the earth.

7.7 FATE AND DYNAMICS OF ORGANOCHLORINE PESTICIDES (OCPs) IN THE ENVIRONMENT

Organochlorine pesticides (OCPs) are a class of synthetic chemicals that have been widely used as pesticides and insecticides since the 1940s. Among all OCPs, DDT was the most rapidly adopted due to its effectiveness against malaria-carrying mosquitoes and agricultural pests, with limited consideration of long-term impacts (Dunlap, 2014). Despite their effectiveness in pest control, OCPs have raised significant environmental and health concerns due to their persistence, bioaccumulation potential, long-range transport potential, and toxicity (Iwata et al., 1994). This chapter explores the fate and dynamics of OCPs in various environmental compartments, including air, water, soil, and biota. Organochlorine compounds are considered very persistent in soil: their residual concentrations may remain in soil even for more than a century, because they tend to accumulate and consequently reach a plateau after a certain period of application (Tsiantas et al., 2023) and, due to their lipophilicity, also enter, bioaccumulate, and bioconcentrate in crops and the food chain (Jeong et al., 2024). Subsequent human exposure to these contaminants can lead to cancer, immune system disorders, and other health issues (Jeong et al., 2024).

The major OCPs along with their main environmental properties are presented in Table 7.2.

7.7.1 Atmospheric Transport, Deposition, and Redistribution

OCPs may enter the atmosphere via various processes, such as volatilization from contaminated soil, wind erosion of contaminated soil particles, and apparently direct application as pesticides. Once found in the atmosphere, they can undergo long-range transport and distribution even in remote areas (Wania and Mackay, 1996).

The main parameters that play a role in the atmospheric transport of OCPs are their physicochemical properties, mainly vapor pressure, Henry's law constant, and water solubility. Compounds with higher vapor pressures, such as hexachlorocyclohexanes (HCHs), tend to be more volatile and therefore prone to long-range transport, as compared to less volatile ones such as DDT (Shen et al., 2005).

Atmospheric OCPs are deposited onto terrestrial and aquatic substrates via dry and wet deposition mechanisms. Atmospheric removal of OCPs through wet deposition (rain and snow) is highly

TABLE 7.2
Environmental Properties of the Major OCPs

Substance	Soil DT50 (days)	Koc (mL/g)	Vapor Pressure (mPa at 25°C)	Log Pow	Water Solubility (mg/L at 25°C)	BCF	References
DDT	6,200	151,000	0.025	6.91	0.006	51,000	Mackay et al., 1997; WHO, 1989b; Ritter et al., 1995; ATSDR, 2002a
DDE	5,500	87,000	0.9	6.51	0.04	12,037	Mackay et al., 1997; Aislabie et al., 1997; ATSDR, 2002a
DDD	7,000	45,800	0.09	6.02	0.09	3,100	Mackay et al., 1997; ATSDR, 2002a; WHO, 1989b
Aldrin	365	17,500	3.0	6.50	0.027	6,000	Mackay et al., 1997; Jorgenson, 2001; WHO, 1989a
Dieldrin	1,000	12,100	0.24	5.40	0.195	12,500	Mackay et al., 1997; Beyer and Biziuk, 2009; US EPA, 2003; WHO, 1989a
Dicofol	80	6,064	0.25	4.3	0.8	10,000	PPDB, 2023b
Chlordane	350	51,310	0.013	6.16	0.056	37,800	Mackay et al., 1997; Dearth and Hites, 1991; ATSDR, 1994
Heptachlor	250	24,000	0.053	5.44	0.056	17,500	Mackay et al., 1997; WHO, 1994; ATSDR, 2007
Heptachlor epoxide	1,460	20,000	0.053	5.40	0.275	14,400	Mackay et al., 1997; ATSDR, 2007; US EPA, 1992
Endosulfan	50	11,500	1.48	4.75	0.32	2,755	Mackay et al., 1997; Weber et al., 2010; ATSDR, 2015
Hexachlorobenzene (HCB)	2,700	54,954	1.45	5.73	0.005	35,000	Mackay et al., 1997; Barber et al., 2005; WHO, 1997
α-HCH	120	1,762	4.2	3.8	2.0	1,100	Mackay et al., 1997; Vijgen et al., 2011; ATSDR, 2005
β-HCH	184	2,139	0.053	3.78	0.24	1,460	Mackay et al., 1997; Vijgen et al., 2011; ATSDR, 2005
γ-HCH (Lindane)	980	1,270	4.4	3.72	8.52	1,300	Mackay et al., 1997; Vijgen et al., 2011; ATSDR, 2005
Mirex	730	38,000	0.07	6.90	0.085	5,100	Mackay et al., 1997; Kaiser, 1978; US EPA, 1978
Toxaphene	360	95,816	0.2	5.50	0.55	76,000	Mackay et al., 1997; de Geus et al., 1999; ATSDR, 2014
Endrin	4,300	10,500	0.036	5.20	0.23	3,970	Mackay et al., 1997; Blus, 2002; ATSDR, 1996
Methoxychlor	120	80,000	0.0013	5.08	0.1	8,100	Mackay et al., 1997; US EPA, 2004; ATSDR, 2002b
Lindane	980	1,270	4.4	3.5	8.52	1,300	PPDB, 2023a
Alachlor	35	1,994	2.9	3.09	240	39	PPDB, 2023c

Note: Water solubility at pH 7.

effective (Lei and Wania, 2004). Once deposited, OCPs can undergo various redistribution processes, including:

1. Re-volatilization: OCPs have the potential to enter the atmosphere from contaminated surfaces, especially during warmer seasons.
2. Runoff: Precipitation events may mobilize OCPs from soil contamination to water bodies.
3. Leaching: OCPs can percolate through soil profiles, potentially reaching groundwater.

These processes play a role in the dynamic patterns of OCP distribution in the environment and may result in secondary pollution of previously uncontaminated regions.

7.7.2 Fate in Environmental Compartments

7.7.2.1 Soil

Soil is a sink and a source of OCPs in the environment. The fate of OCPs in soil depends on numerous factors such as soil properties (e.g., organic matter content, pH), climatic conditions, and the physicochemical properties of the OCP (Arias-Estévez et al., 2008). OCPs are known to strongly adsorb to soil organic matter, thereby impeding their mobility and bioavailability. However, this adsorption also makes OCPs difficult to degrade in soil environment. The soil persistence half-lives of OCPs vary from months to a century, according to the compound and the environmental conditions (Hitch and Day, 1992). Microbial degradation is a key process influencing OCPs fate in soil. Nevertheless, it may remain low, especially for very chlorinated molecules. Certain microorganisms are now able to access OCPs as a carbon source and thereby accelerate their removal in polluted soils (Chaussonnerie et al., 2016).

7.7.2.2 Water

OCPs can enter aquatic environments through various pathways, including atmospheric deposition, runoff from contaminated soils, and direct application. In water, OCPs can partition between the dissolved phase, suspended particulate matter, and sediments. The behavior of OCPs in aquatic systems is influenced by their hydrophobicity, typically expressed as the octanol-water partition coefficient (Kow). Highly hydrophobic OCPs, such as DDT and its metabolites, tend to associate strongly with organic matter in sediments and suspended particles (Zhou et al., 2001). Aquatic organisms can accumulate OCPs from water, suspended particles, and contaminated food sources. This bioaccumulation can lead to biomagnification through aquatic food chains, resulting in higher concentrations in top predators (Borgå et al., 2004).

7.7.2.3 Biota

OCPs can accumulate in living organisms due to their lipophilic nature and resistance to metabolic degradation. Bioaccumulation factors for OCPs can be very high, particularly in aquatic organisms and species with high lipid content (Kelly et al., 2007). The fate of OCPs within organisms depends on various factors, including:

1. Uptake rates from the environment and diet
2. Metabolic capacity to transform OCPs
3. Elimination rates through excretion or biotransformation

Some organisms, particularly certain fish species, have developed enhanced metabolic capabilities to transform OCPs into less toxic metabolites. However, these metabolites can sometimes retain significant toxicity and persistence (Letcher et al., 2010).

7.7.3 Environmental Transformation Processes

OCPs are capable of multiple chemical transformation reactions in the environment, such as hydrolysis, oxidation, and reductive dehalogenation. Rates and products of these reactions are dependent on environmental conditions (pH, redox potential) and on the chemical structure of the OCP. Photochemical reactions have significant influence on the fate transformation of OCPs in the environment especially in the air and surface water. Both direct photolysis and indirect photochemically mediated reactions (e.g., hydroxyl radical) can play a role in OCP decay.

Efficiency of photodegradation among the different OCPs is dependent and can differ based on light intensity, wavelength, or the use of photosensitizers. For instance, DDT in general will be more prone to photolysis than its more chemically resistant analogs such as hexachlorobenzene (HCB) (Konstantinou et al., 2001). Hydrolysis is also a significant degradation pathway of certain OCPs, especially under alkaline conditions. As an example, endosulfan can be hydrolyzed to produce the endosulfan diol that is less toxic and persistent than endosulfan (Weber et al., 2010). Microbial degradation is another significant process affecting the fate of OCPs in soil and aquatic environments. Various bacteria, fungi, and algae have been identified that can partially or completely degrade OCPs. However, the rates of biodegradation can be slow, especially for highly chlorinated compounds (Ortiz-Hernández et al., 2013).

The biodegradation of OCPs often involves complex pathways and can result in the formation of metabolites that may retain significant toxicity and persistence. For example, the anaerobic degradation of DDT can lead to the formation of DDD (dichloro-diphenyl-dichloroethane), which is also a persistent organic pollutant (Boul et al., 1994). It should also be mentioned that dicofol and 4,4'-dichlorobenzophenone may be produced via DDT metabolism nevertheless, since the metabolism scheme in soil is still unclear and most indications propose metabolism of DDT to these compounds in body tissues rather than soil (Tsiantas et al., 2023).

7.7.4 Factors Affecting the Transport and Transformation of OCPs in the Environment

The interactions among the OCPs physicochemical properties such as vapor pressure; pKa; solubility; soil adsorption; soil factors such organic matter, soil microflora, pH, soil moisture, and soil fauna; plant species; and climate conditions are principally responsible for the detrimental effects of OCPs to the environment (Muhammed et al., 2023). Soil properties have a great influence on the transport and transformation of OCPs in soil environment (Liu et al., 2023). In more detail, the main affecting factors are:

a. pH

Soil pH affects the adsorption and degradation of OCPs to a particular level. It has been proved that the adsorption of OCPs in soil reaches its highest level when the pH reaches the value of 6.14 (Sun, Chang et al., 2020). The pH also affects the transformation of OCPs in soil, due to changes in the molecular state of OCPs, which affects the colloidal stability and efficient adsorption sites in soil, though the soil itself has a better buffering effect on pH, and the pH of the reaction system is dynamically modified, which in turn affects the transport performance of OCPs in soil (Shen et al., 2021). It has been observed that some soil microbial groups are able to degrade OCPs in soil, while soil pH affects the activity of microbial groups, which indirectly affects the transformation of OCPs. It has been demonstrated that the higher the soil pH value, the greater the microbial activity, therefore the higher the degradation rate of OCPs (Sun et al., 2019).

Furthermore, some studies have suggested that pH also affects the adsorption of OCPs by soil plants (Chen et al., 2023). The results showed that the residual amount of DDT and HCH reduced

with the increase in soil pH, since some types of crops were able to adsorb OCPs from the soil through their root system and leaves. Therefore, the change of soil pH would affect the adsorption rate of OCPs by their root system and leaves, which affects the migration and transformation of OCPs in the soil. Furthermore, other studies considered the synergistic effect of soil pH value along with the enzyme activity by choosing both acidic and alkaline OCP-contaminated soils (Yao et al., 2009). The results showed that alkaline soils could improve the activity of oxidative enzymes, and the corresponding concentration of OCPs was lower; while acidic soils suppressed the enzyme activity, and the concentration of OCPs was higher in this type of soil.

b. Soil organic matter

Soil organic matter (SOM) is formed from plant remnants such as roots, stems, and leaves, through their decomposition and transformation (Kou et al., 2024). Several studies have confirmed that soil will absorb and degrade OCPs through SOM. It was found that once OCPs were dispersed in the heterogeneous region of SOM, they were able to bind to SOM through hydrophobic interactions, by covalent bonding and diffusion-controlled partitioning, and that the adsorption of OCPs in the carbon structure and micropores of SOM could significantly reduce the bioavailability of pollutants, thus greatly reducing the harm of OCPs to the soil environment. It should be noted that soil microbial groups and enzyme actions can have opposed impacts on SOM degradation of OCPs (Wang et al., 2018).

c. Soil temperature

Another factor that affects the fate and transport of OCPs in soil is the soil temperature (Tian et al., 2024). Recent studies have proven that changes in soil temperature can directly affect the adsorption and/or degradation of OCPs. Considering that adsorption is normally an exothermic reaction, the adsorption of OCPs by the soil environment then declines when the soil temperature is higher, thus altering the transformation of OCPs (Cai et al., 2024). Pan et al. investigated the synergistic effects among microbial communities and soil temperature and identified that soil temperature clearly affects the activity of microbial communities, which ultimately affects microbial degradation of OCPs (Pan et al., 2024).

d. Soil moisture content

Soil moisture content (SMC) is defined as the total amount of water contained in the soil and can be affected by a variety of factors such as rainfall, soil type, and human activities (He et al., 2013). The influence of SMC on the migration and transformation of OCPs in soil has been extensively studied. Wang et al. recently noticed that water particles in soil would compete with OCP compounds for the adsorption sites in soil, decreasing the total amount of OCPs adsorbed by soil particles. Furthermore, they are inhibiting the adsorption and thus the degradation of OCPs in soil (Wang et al., 2024). The degradation rate of OCPs, such as DDT, has been examined under different soil moisture content and proved that OCPs at medium-level soil moisture content (30% and 60% of water-holding capacity) have reduced adsorption rates, while the adsorption is increased under high levels of soil moisture content (90% of water-holding capacity) (Rocci et al., 2023). The authors explained that many micropores and mesopores of soil particles are filled with water atoms thus forming a water layer. When OCPs reach the adsorption sites on these pores, they must pass through the water layer before they can reach the surface of the pore, which will block the OCPs from diffusing into the soil pores or cause water molecules and OCPs to be mixed, which results in a slower degradation rate of OCPs at moderate soil moisture contents. In the case of high soil moisture content, OCPs are more prone to migrate and attach to the pores.

e. Soil oxygen content

Soil oxygen content indicates the quantity of dissolved oxygen in soil and is usually expressed as a volume or mass fraction (Lacroix et al., 2021). It has significant results on soil microbial and enzyme activities and in plant growth and metabolic activities (Turkeltaub et al., 2023). Furthermore, it has been proved that increased soil oxygen content enhances soil aeration, thus boosting soil photosynthesis (Andrade et al., 2018). The authors attributed these results to the combined control of soil plant root uptake, and water and nutrient transfer. Therefore, the adsorption of OCPs improved by the enhancement of soil plant activity. This indicates that soil oxygen content incidentally influences the adsorption of OCPs by affecting the activity of soil plants. The authors concluded that when soil oxygen content is higher the activity of microbial community and enzyme activity will be greater; thus the soil plants are growing quicker and the degradation of OCPs is greater.

f. Soil organic carbon

Soil organic carbon plays a key role because it retains the stability of soil configuration and acts as a nutrient hub. Furthermore, it assists in the persistence and actions of a wide selection of organisms in the soil. It is acquired from the decomposition of soil organic matter by soil microorganisms (Moreno Muñoz et al., 2024). The loading and dynamic forces of soil organic carbon play a critical role in the characteristics and performance of soil ecosystems, such as soil texture, nutrient availability, and biodiversity, all of which change with soil organic carbon content (Stevenson et al., 2024). It has been reported that OCPs behavior in soil depends on soil organic carbon content (Chen et al., 2024). In soil with low organic carbon content a fragment of OCPs can be accumulated on soil particles or combined with minerals; thus the interaction between accumulated OCPs and minerals or soil particles is weaker than that with soils with high organic carbon (Li et al., 2025).

7.7.5 Ecological Impacts of OCPs

Organochlorine pesticides (OCPs) have caused significant and global far-reaching effects on the environment and ecosystems. Their persistence, bioaccumulation, and toxicity characteristics have caused multiple ecological disruptions that are still being observed several decades after their first release. Among the most significant effects of OCPs have been their impact on birds. DDT and DDE metabolites, in particular, DDE, induced thinning of eggshells in birds of prey and contributed to dramatic population declines of species like the bald eagle, peregrine falcon, and osprey (Hickey and Anderson, 1968). This phenomenon was first reported by Ratcliffe in 1967 and has since been extensively documented (Ratcliffe, 1967). The process is characterized by inhibition of calcium ATPase in the shell gland which decreases calcium uptake for shell formation (Lundholm, 1997).

Aquatic ecosystems have been particularly vulnerable to OCPs contamination. These compounds are known to concentrate in sediments and bioaccumulate (i.e., uptake into the food chain) in which top predators are exposed to the highest levels. A study by Borgå et al. (2001) showed biomagnification factors up to 10^7 for some OCPs in arctic marine food webs. This bioaccumulation has caused reproductive failures and population crashes in numerous aquatic species such as fish and marine mammals. For instance, high levels of PCBs and DDT have been linked to immunosuppression and reproductive disorders in Baltic seals (Helle et al., 1976).

Soil ecosystems have also been significantly impacted by OCPs. These substances are persistent in soil for decades, impacting soil microbial community and nutrient cycling. A meta-analysis by Johnsen et al. (2001) demonstrated that OCPs could lower soil microbial biomass and change community composition, perhaps impacting soil fertility and ecosystem processes. In addition, the presence of OCPs in the soil has driven their transport into plants that can bring them to terrestrial food chains. Long-range delivery of OCPs has led to their pervasive distribution in global ecosystems, extending from remote sites away from point of application. Wania and Mackay (1993) defined the

"global distillation" phenomenon in which OCPs volatilize over warmer sites and condense over colder sites resulting in their deposition in polar sites. This effect has led to their high accumulation in the arctic biota, affecting, for example, polar bears and arctic foxes (Letcher et al., 2010).

OCPs have also been linked to endocrine disruption in a range of wildlife species. A comprehensive review by Colborn et al. (1993) showed the broad impact of endocrine-disrupting chemicals, such as OCPs, on wildlife reproductive and development. The following effects such as feminization in male fish, masculinization in female mollusks, and disruption in avian thyroid functions are included. The impact of OCPs on biodiversity has been significant. A global assessment by Geiger et al. (2010) reported that insecticide, and hence OCPs, application correlated with decreased agricultural land biodiversity. This loss of biodiversity can lead to a troubling effect on ecosystem services, for example, pollination and natural pest control. Although many OCPs have been banned or restricted, their legacy is continuing to impact ecosystems. Recent work has identified that these chemicals can have synergistic interactions with other stressors, including climate change, which may lead to its intensification of ecological effects. For example, Noyes et al. (2009) proposed that elevated temperatures may promote toxicity of some OCPs towards aquatic life. In conclusion, the environmental and ecological effects of OCPs have been pervasive and long-lasting, affecting ecosystems from the arctic to the tropics. Their effects on wildlife, biodiversity, and ecosystem functioning highlight the need to take account of longer-term environmental impacts during pesticide regulation and application. Current and future research ongoing is uncovering the intricate relationships among these historic contaminants and contemporary environmental threats, highlighting the continuing necessity for monitoring and mitigation.

7.7.6 Remediation Techniques

When OCPs are applied in agricultural land, their fate is often unpredictable; because their impact is not restricted to the area, they may contaminate larger areas. Their removal or degradation could be possible by using several conventional water treatment processes (Pichel et al., 2019). There are different processes for eliminating or stabilizing the concentration of OCPs in contaminated sites that could be applied as remediation techniques including physical, chemical, and biological processes such as incineration, adsorption, supercritical or electrochemical or molten salt oxidation, chemical reduction, phytoremediation, and bioremediation (Ajiboye et al., 2020). However, these conventional methods have definite drawbacks such as the production of harmful byproducts, ineptitude in terms of cost and efficiency, important energy consumption, and challenging maintenance. Hence, technological innovations should be utilized considering aspects such as cost, energy consumption, and environmental effect.

Bioremediation is a universal, environmentally reliable, and inexpensive technique for removing pollutants from contaminated areas. With the use of microorganisms and plants OCPs could be removed from the contaminated sites by converting them to less harmful compounds such as carbon dioxide and water (Parween et al., 2018). Environmental components, pH, moisture, organic content, micronutrients, microbial function, and OCPs structure have a substantial effect on bioremediation.

Myco-remediation is a bioremediation technique that uses fungi to eliminate contaminants. Fungal strains are extensively used for the degradation of OCPs in both contaminated soil and water. Fungi are extensively allocated and appear in all types of ecosystems such as agricultural lands, oceans, tropical rainforests, aquatic environments, and sediments (Vargas-Gastélum and Riquelme, 2020).

Phytoremediation is an *in situ* remediation technique, which uses plants and bacteria to remove OCPs. The mode of action of this technique is based on the penetration of OCPs into plant membranes thus eliminating them from the ecosystem. This plant-based OCPs removal technique is being encouraged because of its great effectiveness, simplicity, environmental friendliness, and relatively low cost (Mudhoo et al., 2019). Algae has been extensively used to filter wastewater for OCPs (Benemann et al., 2018). Finally, bacterial and microbial remediation techniques are a worthy method for detoxifying sites contaminated by OCPs. The bacterial species remove OCPs and their degradation products in a safe way (Bilal et al., 2019).

7.8 REGULATORY CRITERIA FOR ORGANOCHLORINE PESTICIDES: FROM LAUNCH TO BAN

Organochlorine pesticides (OCPs) played a significant role in agriculture and public health from the 1940s to the 1970s. However, their environmental persistence, bioaccumulation potential, and adverse effects on ecosystems and human health led to increasing regulatory scrutiny and eventual bans in many countries. The key events that raised awareness about OCP impacts were:

- 1962: Publication of Rachel Carson's *Silent Spring* (Carson, 1962)
- 1964: Identification of DDE (a DDT metabolite) in bird eggs, linked to eggshell thinning (Ratcliffe, 1967)
- 1967: Environmental Defense Fund (EDF) formation, leading to legal actions against DDT use (Dunlap, 1978)

This chapter explores the evolving regulatory landscape of OCPs, from their initial approval to their subsequent restrictions and prohibitions. The criteria considered by regulatory agencies to ban or severely restrict OCPs, were:

- Environmental persistence (e.g., soil half-life > 6 months)
- High bioaccumulation factor (e.g., BCF > 5000)
- Potential for long-range transport (e.g., detected in arctic biota)
- Toxicity to non-target organisms (e.g., LC50 for aquatic organisms < 1 mg/L)
- Evidence of carcinogenicity, mutagenicity, or reproductive toxicity in mammals
- Detection in human samples (e.g., breast milk, blood) far from sources
- Endocrine disruption potential
- Market availability of less harmful alternatives
- Cost-benefit analysis considering environmental and health impacts

When OCPs were first introduced, the regulatory framework for pesticides was rudimentary. The primary focus was on efficacy rather than environmental or long-term health impacts. In the United States, the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of 1947 was the first comprehensive law regulating pesticides, but it mainly addressed labeling and registration requirements (US EPA, 2022, 2024). Most European countries lacked specific pesticide legislation until the 1960s, relying instead on general chemical safety laws (Jas, 2007). The majority of developed nations began phasing out OCPs in the 1970s and 1980s, with the Stockholm Convention on Persistent Organic Pollutants in 2001 marking a significant milestone in their global regulation (UNEP, 2019; Jeong et al., 2024). The WHO supported this exemption under the Stockholm Convention (WHO, 2011). This treaty, which came into force in 2004, aimed to eliminate or restrict the production and use of several OCPs, including aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, and toxaphene. Before this convention, the major regulatory actions towards OCPs prohibition were:

- 1969: Sweden bans DDT for agricultural use (Bernes, 1998)
- 1972: United States bans DDT for agricultural use (US EPA, 1972)
- 1979: European Economic Community (now EU) bans several OCPs (Directive 79/117/EEC) (European Council, 1979)
- 1983: Japan bans the production and use of DDT, BHC, and aldrin (Ministry of the Environment, Japan, 2002)
- 1990s: Many developing countries phase out OCPs following the FAO Code of Conduct (FAO of the United Nations, 2010)

Nonetheless, the aforementioned treaty allowed for certain exemptions, most notably the continued use of DDT for malaria vector control in some countries (van den Berg et al., 2017). Despite these international efforts, the complete elimination of OCPs use has been a gradual process, with some countries continuing their application well into the twenty-first century. As of 2020, about 14 countries still use DDT for malaria control (van den Berg et al., 2017). For instance, India only banned the manufacture and use of several OCPs, including aldrin, chlordane, and heptachlor, in 2018 (Sharma et al., 2020). China, another major producer and user of OCPs, has also been slow to phase out certain compounds. The country continued to produce and use lindane (γ-HCH) until 2019, making it one of the last countries to ban this particular OCP (Chinese Ministry of Ecology and Environment, 2019).

In Africa, where malaria remains a significant public health concern, DDT use has persisted longer than in many other parts of the world. Countries such as South Africa, Mozambique, Zambia, and Zimbabwe have continued to use DDT for indoor residual spraying to control malaria vectors well into the 2010s (Bouwman et al., 2011; Choi et al., 2014). The World Health Organization (WHO) still recommends DDT as part of a comprehensive malaria control strategy in certain high-risk areas, although its use is strictly regulated and monitored (WHO, 2021).

Interestingly, some OCPs have found new, limited applications during the last few years. For example, endosulfan, while banned for agricultural use in most countries, is still permitted for specific non-agricultural purposes in some regions (Weber et al., 2010). In the United States, lindane was used in pharmaceutical applications (as a treatment for lice and scabies) until 2006, long after its agricultural use had been prohibited (Humphreys et al., 2008). The continued presence of OCPs in the environment, even decades after their official bans, complicates the notion of a "last use date" and implicates the management of the contaminated areas. Many of these compounds are extremely persistent, with half-lives in soil ranging from months to decades as described earlier, while there are records that small amounts of banned OCPs enter EU member states from developing countries and countries with insufficient regulation and control of pesticides. This persistence means that OCPs can continue to impact ecosystems and human health long after their active use has ceased.

Moreover, the illegal trade and use of OCPs remain ongoing issues in some parts of the world. Developing countries, in particular, may struggle with enforcing bans due to limited resources for monitoring and regulation. There have been reports of banned OCPs being used in countries such as India, Pakistan, and various African nations well into the 2010s, despite official prohibitions (Sharma et al., 2014). In terms of legal use, as of 2024, the most prominent remaining application of OCPs is the use of DDT for malaria control. While many countries have phased out DDT entirely, a handful of nations in Africa and Asia still retain the right to use it under the Stockholm Convention's exemptions (van den Berg et al., 2017). However, even in these cases, the trend is towards finding alternatives and reducing reliance on DDT. As such, today there are some ongoing initiatives to phase-out OCPs, with the major being the UNEP/FAO program for managing and disposing of OCP stockpiles (FAO of the United Nations, 2010), the Global Environment Facility (GEF) funding for POPs reduction projects (GEF, 2024) as well as some regional initiatives (e.g., African Stockpiles Programme) (World Bank, 2013). It's also worth noting that research into the environmental and health impacts of OCPs continues, and the scientific community understanding of their long-term effects is still evolving. This ongoing research may influence future decisions about any remaining uses of these compounds (Loomis et al., 2015).

In conclusion, while the vast majority of OCPs have been officially banned or severely restricted globally, their complete elimination from use remains an ongoing process. The persistence of these compounds in the environment, coupled with limited ongoing legal uses and instances of illegal application, means that the legacy of OCPs continues to be a relevant issue in environmental science and public health. As we move further into the twenty-first century, the focus is increasingly shifting from banning these substances to managing their environmental legacy and addressing the challenges posed by their persistence in ecosystems worldwide (Köhler and Triebskorn, 2013).

Significant efforts are also ongoing both in developed and developing countries to monitor, assess and intervene with decontamination activities (e.g., the Global Monitoring Plan under the Stockholm Convention and US EPA Superfund program for management of contaminated sites), so as to achieve a full compliance with the international treaties and fully eliminate environmental and health impacts occurring from the residual OCP amounts in the environmental compartments (UNEP, 2015; US EPA, 2022).

7.9 CONCLUSIONS AND FUTURE CHALLENGES

The fate and dynamics of OCPs in the environment are complex and influenced by numerous factors, including their physicochemical properties, environmental conditions, and biological processes. Today, OCPs are fully prohibited in the vast majority of the world following decades of their regular use. The regulatory evolution of OCPs from widespread use to global bans reflects the growing understanding of chemical impacts on human health and the environment. The unplanned experience gained has shaped modern pesticide regulation, emphasizing comprehensive safety assessments, long-term environmental monitoring, and a precautionary approach to persistent and bioaccumulative substances. The ongoing challenges of managing legacy OCPs contamination and ensuring the safety of alternative pest control methods underscore the importance of rigorous, science-based regulatory frameworks in chemical management. Despite the global ban or restriction on the use of most OCPs, their environmental persistence and potential for long-range transport continue to make them a concern for environmental and health scientists. Ongoing research into the environmental behavior of OCPs and their degradation products remains essential for addressing the legacy of these persistent organic pollutants.

The proper selection of remediation techniques for heavily contaminated soil is of the utmost importance and requires due diligence. For example, certain OCPs including DDT are converted to more toxic metabolites than the parent compound: DDT is converted to DDD and DDE, which are equally toxic. This barrier can be eliminated by the proper selection of microorganisms. The degradation mechanism of OCPs by enzymes or bacteria is not currently well known. New bacteria species could be used, but the degradation mechanism, the concentration of OCPs in the ecosystem, the growth, and the isolation of these species could be identified. Considering that all remediation studies are conducted on a lab scale, noteworthy efforts are required in the coming years to create remediation technology on a large scale.

Last but not least, long-term monitoring on all continents of the residual levels of OCPs in the ecosystem, humans, and animals including marine mammals is critical to understanding how these contaminants affect the ecosystem and living organisms, and how contaminant burdens shift over time. Continuous monitoring of OCPs, which are contaminants of emerging concern, can be made more realistic by executing the routine collection of samples. Yearly, long-term monitoring provides a thorough understanding into OCPs movements across time, distance, and species, and can facilitate management decisions.

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8 Chlorinated Solvents

Pu-Fong Liu, Wei-Ting Chen, and Chih-Ming Kao

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8.1 CHLORINATED SOLVENTS

In recent years, organic chlorinated solvents have had a significant impact on the environment. These solvents are commonly used in industrial and commercial applications, such as cleaning agents, degreasers, solvents, and process mediums. However, their volatile and soluble nature allows them to enter the environment during these processes and cause pollution. Organic chlorinated solvents, including trichloroethylene, dichloromethane, and carbon tetrachloride, have been identified as key contributors.

Unfortunately, these solvents are highly toxic and have persistent effects on the environment. Their use can lead to environmental pollution, particularly in the case of accidental spills or emissions, by which they can contaminate soil and groundwater, posing hazards to ecosystems. Additionally, they release compounds with ozone depletion potential, which are widely distributed globally and require international cooperation for management and control. Furthermore, exposure to organic chlorinated solvents can have detrimental effects on human health, including damage to the nervous system, liver, and other organs, as well as an increased risk of cancer. Workers and residents who come into contact with these solvents are particularly susceptible.

To mitigate the impact of organic chlorinated solvents on the environment and health, the international community has taken various measures. Numerous international conventions and national policies have been formulated to regulate the production, use, and emission of organic chlorinated solvents. These measures include:

1. The Montreal Protocol, aimed at protecting the ozone layer, designates several organic chlorinated solvents, such as dichloromethane, carbon tetrachloride, and trichloroethene (TCE), as phased-out substances.

DOI: 10.1201/9781003530466-8

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2. The Stockholm Convention, which aims to prevent the hazards of persistent organic pollutants, identifies specific organic chlorinated solvents as substances subject to reduction.
3. The Basel Convention and Rotterdam Convention regulate many organic chlorinated solvents as hazardous wastes and chemicals subject to restriction.

Moreover, individual countries have implemented regulations and policies to manage organic chlorinated solvents. For instance, the United States has restricted and remediated the use of these solvents through the Superfund Act. The European Union has imposed restrictions on the production and use of many organic chlorinated solvents through the REACH regulation. Canada has established strict standards for some organic chlorinated solvents through the Canadian Environmental Protection Act.

These international and domestic political and regulatory measures have expedited the restriction and substitution of organic chlorinated solvents, thereby reducing their impact on the environment and health. They have made a significant contribution to safeguarding the ecological environment and promoting public health.

8.2 BACKGROUND AND SOURCES OF CHLORINATED SOLVENTS

Chlorinated solvents are organic compounds containing chlorine that are used as industrial solvents. The most common chlorinated solvents include (Ciampi et al., 2022):

1. Trichloroethene (TCE): An effective and low-cost solvent used for removing oils, waxes, and other contaminants from metal surfaces. It is widely used in metal cleaning and degreasing in electronics, automotive, and other heavy industries. TCE is also common in printing, textiles, pharmaceuticals, and chemical formulations. It is typically produced through ethylene chlorination.
2. Tetrachloroethene or perchloroethylene (PCE): Used in dry cleaning processes and metal degreasing in industrial applications. PCE is also common in plastics manufacturing or as a coating. It is produced through ethylene chlorination, similar to TCE.
3. Methyl chloroform or 1,1,1-trichloroethane (TCA): Used industrially as a solvent for dissolving oils, greases, and waxes. TCA is typically produced through the chlorination of ethane. In this reaction, ethane reacts with chlorine gas in the presence of a catalyst to form TCA.
4. Methylene chloride or chloroform: Used as a solvent in various industrial processes. It is produced through methane chlorination.
5. Chloroform: Formerly used as an anesthetic, but now mainly for the production of fluorocarbons. It is produced through methane chlorination.

These chlorinated solvents were once widely used but their use has greatly declined due to environmental and health concerns, particularly their carcinogenicity and hazards to occupational workers. Most of these solvents can release toxic gases and long-term exposure can damage the central nervous system, liver, and kidneys.

Major sources of chlorinated solvents entering the environment include (Hussain et al., 2023; Song et al., 2023; Hyldegaard et al., 2019):

1. Industrial releases: The largest source is emissions and releases from industrial facilities that produce or use these chemicals, including metal degreasing, dry cleaning, and chemical manufacturing processes.
2. Landfills and hazardous waste sites: Chlorinated solvents are often disposed of in landfills and industrial waste sites, where they can leach into the environment.

3. Groundwater and soil contamination: Past industrial releases and spills have resulted in contaminated groundwater and soils. These chemicals act as long-term sources of pollution because they leach into the environment.
4. Consumer products: Some chlorinated solvents are still used in adhesives, chemical intermediates, and other consumer products, and are released during use and disposal.
5. Incineration byproducts: Burning chlorinated wastes and plastics can release these chemicals as byproducts. During incineration, chlorinated solvents may break down and transform, producing harmful gases and particulate matter that pollute air quality and the environment.

Chlorinated organic compounds often exhibit low aqueous solubility due to their physicochemical properties, earning them the designation of dense non-aqueous phase liquids (DNAPLs) with regards to groundwater contamination. As the name implies, DNAPLs are liquids denser than water that can occur in soil and groundwater systems. Chlorinated solvents are a major source of DNAPL contamination due to the relatively high atomic weight of chlorine in organic compounds, which increases their density above that of water. The most frequently detected DNAPL contaminants at hazardous waste sites in the United States are TCE, PCE, chloromethane, trichloroethane (TCA), and dichloroethenes (DCEs) (National Research Council [NRC], 1994). Other common chlorinated DNAPL contaminants include chlorobenzenes, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), creosote, and coal tar (NRC, 2005). Due to their high density and low solubility, DNAPLs can migrate vertically through soil and groundwater until reaching confining layers. Their low solubility allows them to remain in liquid form during downward migration, acting as long-term sources of groundwater contamination (Lucas and Jauzein, 2008). Since DNAPL contamination can extend from the water table down to the bottom of aquifers, it poses much greater characterization and remediation challenges compared to light non-aqueous phase liquid (LNAPL) contamination found near the water table.

8.3 EXTENT AND SEVERITY OF CONTAMINATIONS

Chlorinated organic compounds such as dichloromethane, trichloromethane, TCE, and PCE have high aqueous solubility and volatility, making them highly mobile in the subsurface and prone to forming dissolved plumes in aquifers or vapor phase contamination in the unsaturated zone (Vadillo and Ojeda, 2022). Undissolved and unvolatized dense non-aqueous phase liquids (DNAPLs) can penetrate into aquifers as pure phase liquids. During subsurface migration, DNAPLs are subject to capillary forces and form residual droplets. Once formed, these are barely mobile with groundwater flow, though may slowly dissolve and leach over time. The mobile portion of DNAPLs continues migrating downward due to gravity, penetrating the water table and pooling atop low permeability layers in the saturated zone, accumulating as DNAPL pools. DNAPLs also pool at interfaces where permeability contrasts significantly along the path of least resistance. DNAPL pools and residual droplets in aquifers act as persistent sources of groundwater contamination, potentially causing extensive dissolved plumes. For site assessment, locating the DNAPL source zones is critical, necessitating sampling as close as possible to release areas. Otherwise, only dilute dissolved plumes may be detected, illustrating the challenge of investigating chlorinated solvent sites.

According to a review by Taiwan's EPA (2016) (Figure 8.1), major chlorinated solvents including dichloromethane, trichloromethane, and TCE were imported at average quantities exceeding 4,500 metric tons annually prior to 2000, while PCE imports averaged just over 700 metric tons. Tightening regulations and improved recycling subsequently decreased TCE and PCE imports. Common chlorinated solvents used in Taiwanese industries included dichloromethane, trichloromethane, TCE, PCE, 1,2-dichloroethane, vinyl chloride, chloroform, and chlorobenzene. From 2008–2013, Taiwan EPA assessed 343 facilities, discovering chlorinated solvent contamination at 66% of sites

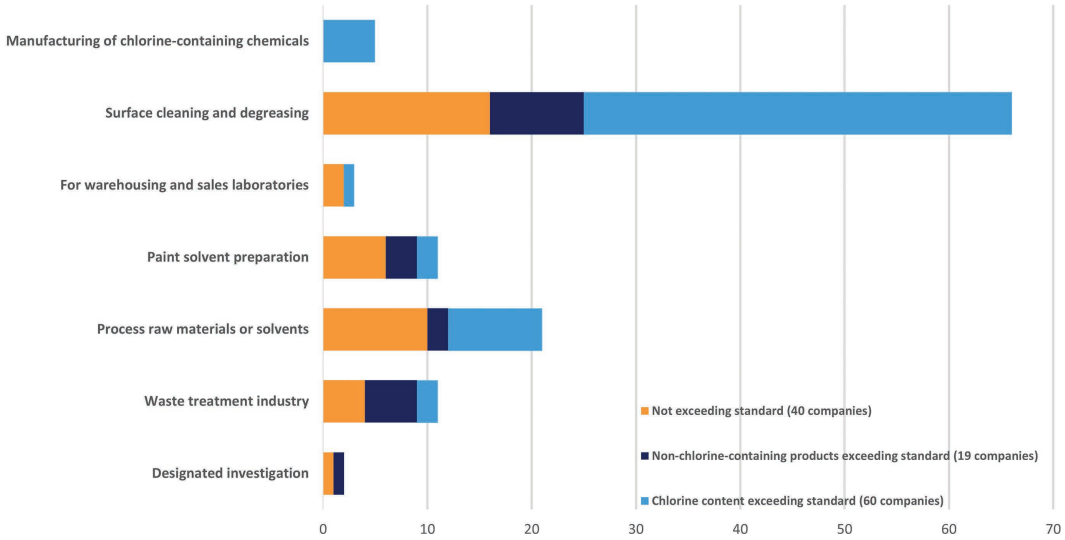


FIGURE 8.1 Taiwan's chlorinated solvent operation factory was found to exceed regulatory standards (EPA, 2016).

investigated. Chemical producers showed 100% contamination rates, while 75.8% of surface treatment plants were contaminated. The most frequent source processes were surface cleaning/degreasing, solvent usage, chemical manufacturing, waste treatment, paint solvent blending, and laboratory chemical storage/sales. Trichloroethene at cleaning facilities showed the highest detection frequency, along with dichloromethane at cleaners and pharmaceutical plants, and trichloromethane and chlorobenzene in drug and pesticide manufacturing, respectively (EPA, 2016).

8.4 TOXICITY

The chlorinated solvent perchloroethylene (PCE), also known as tetrachloroethene, is a dense non-aqueous phase liquid (DNAPL) that is a well-known groundwater contaminant in industrialized societies (You et al., 2020). PCE is often trapped in subsurface source zones and dissolves into groundwater aquifers over time. Under anaerobic conditions, dissolved PCE can undergo successive dechlorination and transform into less chlorinated compounds. The degradation pathway is PCE → TCE → dichloroethylene (DCE) → vinyl chloride (VC) → ethene. While ethene is non-toxic, PCE and its degradation products TCE, DCE, and VC present potential human health risks that require monitoring. PCE, TCE, and DCE are suspected carcinogens, while VC is a confirmed human carcinogen. The contaminant plume thus consists of a mixture of compounds with varying toxicities. To manage risk at PCE-contaminated sites, the spatiotemporal distribution of PCE and its daughter products must be modeled and their cumulative toxicity characterized. PCE's carcinogenicity and the accumulation of its hazardous degradation products create the potential for significant human health impacts from PCE-contaminated groundwater (Lee et al., 2010). Probabilistic risk assessment accounting for uncertainty in aquifer parameters is needed to fully evaluate the overall health risk posed by PCE and its toxic breakdown compounds (Henri et al., 2016).

8.5 REGULATORY CRITERIA

Internationally, management of contaminated sites typically involves several phases including site investigation (hydrogeology, geology, contaminants, water chemistry, biology), risk assessment

(hazard, health, ecological), remediation (technology evaluation, design, implementation), and monitoring (regulatory compliance, performance, long-term).

For example, the Interstate Technology and Regulatory Council (ITRC) in the United States published two editions of Integrated DNAPL Site Strategy (IDSS) guidance in 2011 and 2020 (Interstate Technology & Regulatory Council, 2011, 2020). The IDSS outlines a five-part approach for DNAPL remediation:

1. Conceptual Site Model (CSM): Develop a reliable understanding of contaminant fate and transport, chemical reactions, and distribution in the subsurface environment.
2. Remedial Objectives: Objectives should be Specific, Measurable, Attainable, Relevant, and Time-Bound (SMART).
3. Treatment Technologies: Apply technologies in parallel or sequence to optimize performance and harness synergistic effects.
4. Monitoring and Modeling: Select applicable tools based on interim or final remedial goals, chosen technologies and remedies, and performance.
5. Reevaluating the Strategy: Continuously reassess the strategy and modify approaches if goals are not met or more effective, lower-cost alternatives emerge.

This phased approach allows sites to systematically implement characterization, develop a CSM, identify technologies, establish remedial objectives, execute remediation strategies, and monitor performance. The IDSS provides a framework for iterative decision-making to optimize DNAPL cleanup.

8.6 SOIL AND GROUNDWATER ASSESSMENT AND REMEDIATION

8.6.1 Soil and Groundwater Assessment

When conducting remediation at DNAPL-contaminated sites, site assessment is the critical first step. DNAPLs tend to migrate along paths of least resistance and pool at interfaces with significant permeability contrasts. DNAPL pools in the saturated zone and residual DNAPL are persistent sources of groundwater contamination that can cause extensive dissolved plumes. For site investigations, detecting DNAPL sources by sampling as close as possible to suspected release areas is crucial to avoid missing the presence of contamination. Otherwise, only dilute dissolved plumes may be detected, illustrating the challenge of chlorinated investigations. Site assessment can follow the phased process outlined in ASTM E1527–21 (ASTM, 2021) and E1903–19 (ASTM, 2019), with the following steps guided, and DNAPL site assessment generally involves the following investigation steps: 1) collect site data and history to determine contamination potential, 2) conduct site reconnaissance and develop an investigation plan, 3) implement field investigations like geophysics and intrusive sampling to refine the conceptual site model, 4) interpret data to delineate contamination, and 5) determine next steps for remediation or risk management. The selection of appropriate investigation techniques is crucial for effective Phase II environmental site assessments. Technology choice should balance field logistics, equipment access, analytical expenses, data resolution, and real-time data acquisition. Applying the right suite of characterization tools to fit site conditions and program objectives is crucial to improving the value of subsurface investigations. Optimizing site assessment strategies through informed technology selection represents an essential continuing education goal for environmental drilling and sampling practitioners.

Conventional DNAPL site characterization employs both invasive and non-invasive investigative approaches (EPA, 2010). Invasive methods, like drilling, sampling, and monitoring wells, provide discrete ground-truth data on contamination. However, the scale and density of sampling required to delineate pollution boundaries can be resource-intensive. Non-invasive geophysical tools offer rapid site screening to focus sampling, but direct measurements are still needed for confirmation.

Integrating invasive and non-invasive techniques leverages their complementary strengths for effective site assessments. Careful coordination of field investigations and laboratory analyses is crucial to developing confident conceptual site models within reasonable project budgets.

8.6.2 Application of Geophysical Techniques (Non-Invasive Investigative Approaches)

8.6.2.1 Ground Penetrating Radar (GPR)

GPR profiling applies electromagnetic pulses and signal travel times to image the shallow subsurface (Figure 8.2). It excels at high-resolution mapping of buried objects, structural features, and utility lines. However, the technique is generally limited to depths less than 10 meters depending on site conditions. GPR works best in dry, non-conductive soils. Performance declines in clay-rich or highly conductive geologic media. Due to penetration limits, GPR viability for chlorinated solvent site assessments depends on release history and depth to groundwater. It can delineate sources if spills are recent or vadose zone contamination is shallow. Otherwise, GPR serves better for preliminary screening to guide intrusive sampling locations and depths. Integrated GPR results help refine the 3D conceptual site model (T. EPA, 2017; Ajo-franklin et al., 2006; Wilson et al., 2009).

8.6.2.2 Electro-Magnetic Method (EM)

Electromagnetic induction (EM) methods apply electromagnetic principles by generating a time-varying primary electromagnetic field from a transmitter coil at audio frequencies. Eddy currents are induced in the subsurface due to variations in stratum conductivity. This in turn produces secondary electromagnetic fields that are measured by a receiver coil at the surface, providing a depth distribution of subsurface conductivity. The system operation is illustrated in Figure 8.2. Induced eddy current density depends on layer resistivity, which relates to mineralogy, particle size, porosity, moisture content, and salinity. Contaminants often greatly contrast layer resistivity. Their presence can alter local conductivity.

In practice, EMI detects stratum conductivity differences to categorize materials, averaging effects at a location without depth resolution. Lower frequencies and greater coil spacing provide deeper investigation. EMI is advantageous for rapid, wide-area surveys useful for mapping buried wastes, contaminant plumes, and other subsurface features. Strategically sampling across surface terrain and cultural features provides a rapid contaminant screening tool to focus intrusive sampling.

EM provides a rapid reconnaissance of subsurface conductivity variability indicative of contamination or buried features. It serves as a screening tool for guiding more invasive sampling to areas of

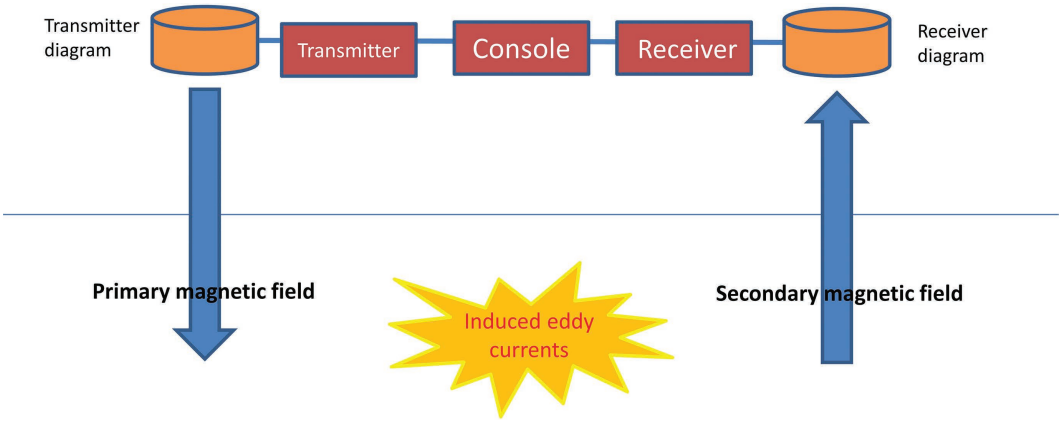


FIGURE 8.2 Schematic diagram of an electromagnetic induction system operation.

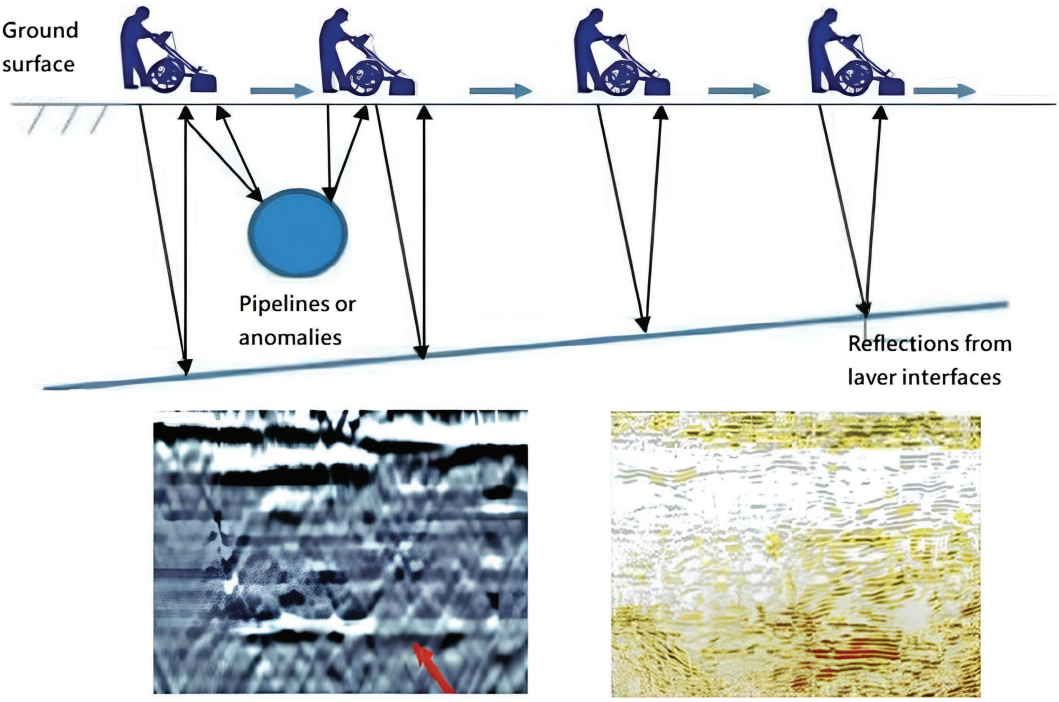


FIGURE 8.3 GPR survey operation schematic.

interest. EM alone lacks the resolution to fully characterize source zones, plumes, or other targets. It is most effective when integrated with intrusive techniques like soil borings and monitoring wells to relate EM anomalies to ground-truth contaminant distributions. Advances in multi-level EM and 3D inversion modeling are improving subsurface resolution (T. EPA, 2017).

8.6.2.3 Electrical Resistivity Tomography (ERT)

ERT can effectively detect and monitor chlorinated solvent DNAPL sources and plumes due to the stark resistivity contrast between contaminants and native materials. It involves installing electrodes at the surface or in wells to induce current flow and measure potential differences related to subsurface resistivity distributions.

For site screening, surface ERT with electrode spacing of 1–3 m provides suitable resolution to delineate contamination in the shallow subsurface. Longer survey lines increase depth penetration up to around 1/4 of the total array length. Data inversion generates 2D profiles or 3D models depicting anomalies indicative of DNAPL presence.

Time-lapse electrical tomography (TLERT) using fixed electrode wells monitors temporal resistivity changes associated with shifting contaminant distributions. This helps evaluate remedial effectiveness and changing conditions over time. TLERT at appropriate frequencies (e.g. quarterly, annually) serves as a performance metric for sites undergoing treatment (Trento et al., 2021).

When combined with intrusive sampling, ERT and TLERT greatly improve spatial delineation and volume estimates of DNAPL extent. They are limited by inversion model resolution constraints and ambiguity. Ground-truth data verifies causes of resistivity anomalies. Integrating ERT with other methods like soil gas surveys and EM profiling provides complementary lines of evidence to strengthen site conceptual models (Power et al., 2014).

GPR provides higher-resolution shallow imaging but is more constrained by site conditions and penetration depth. ERI offers greater depth with more flexible field deployment, but lower

resolution. Integrating the two methods provides complementary subsurface profiling for improved site characterization.

8.6.3 Borehole Sampling or Setting Up Monitoring Wells (Invasive Investigative Approaches)

8.6.3.1 Membrane Interface Probing System (MIP)

The MIP system consists of a thin film probe, carrier gas lines, enclosure chamber, heating system, semi-permeable membrane, and connected analytical instruments. The metallic MIP probe body has a diameter of approximately 3.8 cm and length of 30 cm. It is coated with a semi-permeable metallic/polymer thin film (Figure 8.4).

In operation, the MIP probe is inserted directly into the subsurface using direct push techniques. The probe surface is heated to 100–120°C by the heating system. This volatilizes organic contaminants in soil and groundwater, which permeate through the thin film into the sealed chamber. The carrier gas transfers the vapor phase organics to surface analytical instruments like gas chromatography (GC) for quantification.

Based on the contaminants present, different detectors can be coupled to the MIP to optimize analytical sensitivity. Common detectors include the photoionization detector (PID), flame ionization detector (FID), electron capture detector (ECD), dry electrolytic conductivity detector (DELCD), and halogen specific detector (XSD). PID is suitable for aromatics like BTEX, FID for aliphatics, and ECD, DELCD, and XSD for chlorinated hydrocarbons like TCE.

The direct sensing and continuous profiling capabilities of MIP make it advantageous for delineating the distribution of chlorinated solvent plumes in the subsurface. MIP provides real-time data for rapid site screening and characterization (Interstate Technology & Regulatory Council, 2019).

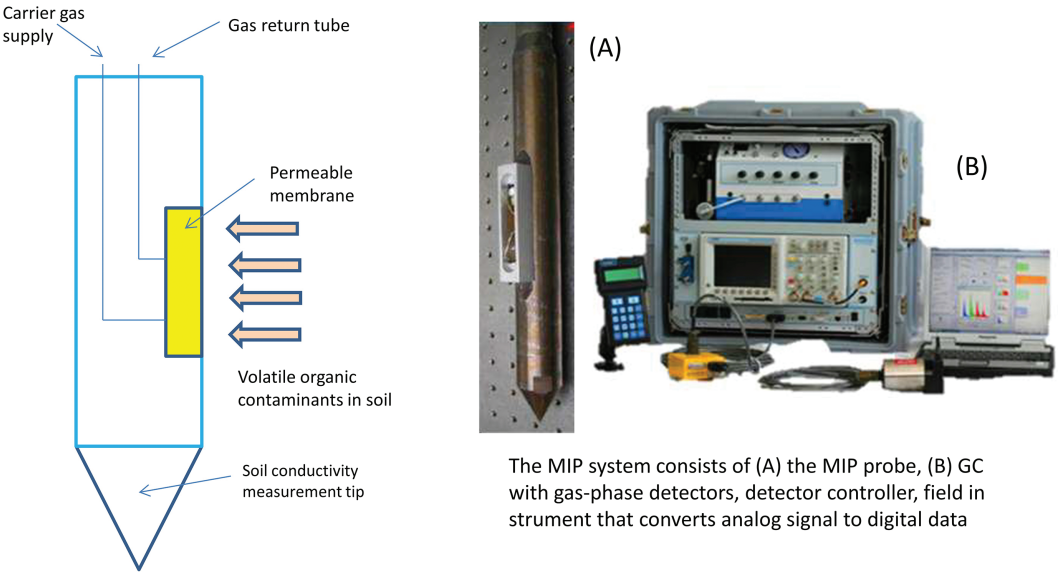


FIGURE 8.4 Components of a typical MIP system (source: Geoprobe Systems®, Interstate Technology & Regulatory Council, 2019).

8.6.3.2 Laser-Induced Fluorescence Detection System (Laser-Induced Fluorescence, LIF)

LIF utilizes laser excitation and fluorescence detection to identify organic contaminants. LIF probes inserted into the subsurface excite target compounds, causing them to fluoresce at characteristic wavelengths measured by the probe. For chlorinated solvents like TCE, proprietary hydrophobic dyes are injected during probing to enhance fluorescence. The dyes partition into the non-aqueous phase liquids (NAPLs), increasing the fluorescent signal. Real-time fluorescence data is continuously recorded as the probe advances, generating high-resolution contaminant profiles. The intensity and spectral fingerprints indicate the presence and depths of chlorinated NAPL zones. LIF provides direct *in situ* detection, overcoming limitations of headspace screening tools like PID which cannot detect low-volatility NAPLs. The method locates residual NAPL source areas that may act as long-term contaminant reservoirs. While LIF effectively delineates the vertical distribution of chlorinated solvent DNAPLs, quantification may be semi-quantitative. LIF screening should be paired with confirmatory soil and groundwater sampling to characterize the full lateral and vertical extent of contamination.

Overall, LIF is advantageous for identifying DNAPL source zones and defining dissolution plume boundaries for chlorinated compounds. The high-resolution optical data accelerates site characterization and remediation design.

8.6.3.3 Soil Gas Detection

Soil gas generally migrates towards relatively high permeability strata, and is often a reference for identifying areas of potential organic pollution at a site. However, during soil gas sampling, collecting samples from multiple depths should be considered to avoid misjudging actual contamination conditions. Chlorinated organic compounds are volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs). For site investigations, soil gas can be collected into suitable sampling bags by manual or mechanical drilling. Although soil interstitial gas analysis can be performed, laboratory analysis takes a long time. Generally, a photoionization detector (PID) and flame ionization detector (FID) are used to detect the concentration of volatile gases in the sampling bags.

The PID uses ultraviolet light with energy of 8.4–11.7 eV to ionize organic gas molecules. By detecting the current produced after ionization and using the specific ionization potential and ionization efficiency of different gases, the PID can quantify results but cannot definitively identify compounds. The PID is more sensitive to aromatic organic compounds. Using a 10.6 eV lamp, the PID can detect benzene, toluene, ethylbenzene, TCE, dichloroethylene, etc. For better selectivity in detecting halogenated alkanes, an 11.7 eV UV lamp can be used to obtain higher detection sensitivity.

The FID ionizes organic gases using a hydrogen flame. By measuring the current produced by the free ions and the proportional relationship between ionization current and volatile compound concentration in the sample, the FID can quantify results. The FID produces distinct responses for most organic gas molecules, and is especially sensitive in detecting aliphatic and straight-chain hydrocarbons. However, detection of chlorinated organics may be interfered by high concentrations of methane and propane.

PID/FID screening of soil gas can only indicate VOC anomalies and cannot confirm pollutant types. Results are also easily interfered by moisture and other gases. Gas detector tubes can be used to supplement real-time on-site qualitative and quantitative analysis. For soil gas measurements with anomalies or maxima, soil gas can be pumped into the detector tubes at a fixed flow rate. After measurement, the length of the colorimetric stain corresponds to the gas concentration, so the concentration can be determined from the stain length.

Detector tubes are simple to operate, highly mobile, provide instant results, and are economical. They do not require electricity, but different tubes must be used for different chemicals. Results rely on visual interpretation so errors may occur.

Passive soil gas samplers like the GORE-SORBER modules can also collect soil vapor samples. These consist of at least 2 permeable 4-foot adsorbent sections, each filled with an equivalent amount of granular resin adsorbent. The protective outer layer is permeable expanded polytetrafluoroethylene (ePTFE). Soil vapors can freely diffuse in and out, and adsorb onto the resin. The GORE-SORBER is installed in 2–3-foot boreholes for 10 days before retrieval and analysis. It adsorbs soil vapors to assess contaminant distribution and vapor intrusion potential.

8.6.3.4 Soil Sampling

To determine organic pollutant concentrations in the subsurface, soil sampling is typically conducted at depths with expected higher concentrations. Direct push tools are recommended for collecting contaminated soil to minimize volatilization losses. Sampling locations can be selected based on soil gas results, choosing points with higher PID/FID readings. These samples would be collected following the procedures in ASTM D1586 and ASTM D1587 to be sent to the laboratory for analysis of volatile organic compounds.

If soil gas screening yields no contamination, samples can be collected above the water table. Manual direct push paired with thin-walled tubing can sample ~2–3 meters depth. Mechanical direct push using a Geoprobe rig with dual tube or piston samplers can match MIP depths up to ~20 meters. However, direct push is limited by gravel or hard layers. While air rotary with split spoon sampling can retrieve soil, the significant disturbance may impact results and rarely exceeds regulatory levels. Sonic drilling is better for sampling while enabling lithologic logging and well installation, although water is needed above the water table for sound propagation, requiring confirmation of minimal sample disturbance.

In summary, the appropriate soil sampling technique depends on the site geology, depth, and expected analyses. Direct push methods are ideal for collecting volatile organics with minimal losses, while sonic drilling provides a versatile platform for detailed characterization and monitoring. The sampling plan should balance disturbance versus retrieval of representative soils for contaminant delineation.

8.6.3.5 Groundwater Sampling

Groundwater sampling in heterogeneous aquifers poses challenges, since contaminant fate and transport are impacted by variations in soil permeability and chlorinated solvent DNAPL distribution. Site conceptual models developed using MIP delineate 3D dissolved plume and DNAPL residual variability. Previous studies have recommended collecting instantaneous grab samples at high concentration areas using direct push techniques with integrated screens and pumps (Engelmann et al., 2019). If depth-discrete sampling is needed to characterize vertical concentration profiles, published guidance suggests installing nests or multi-level wells with short screens, generally 1 to 3 meters (EPA, 2015).

Screen placement is critical – standards recommend opening screens from bottom to top so the denser-than-water chlorinated organics accumulate in the well sump for detection (ASTM D5092, 2022). If seasonal water table fluctuations exceed 2 meters, discrete depth sampling is recommended to account for the vertical smearing of concentrations (Engelmann et al., 2019). The goal should be to provide cost-effective designs optimized for the site geology and contaminant distribution. Representative samples and high-quality data should be collected through strategic screening and sampling to support remedial decisions.

8.6.4 Soil and Groundwater Remediation

When selecting remediation technologies for chlorinated solvent contaminated sites, it is important to consider not just the contaminant and site conditions, but also coordination with regulators, responsible parties, and local communities. Currently, many remediation projects focus on

aggressive technologies that promise rapid cleanup, but without holistic consideration of sustainability, these approaches can consume more resources and cause secondary pollution.

Since 2006, the concept of green and sustainable remediation (GSR) has emerged internationally (Figure 8.5). GSR evaluates the environmental, social, and economic impacts of site investigation, remedial alternative selection, and implementation. By taking a comprehensive approach, GSR aims to reduce environmental footprints while balancing economic, social, and environmental benefits to achieve sustainable site reuse.

Based on the principles of environmental sustainability, it is recommended to incorporate GSR through stakeholder engagement, life cycle assessments, and selection of green and sustainable technologies. This provides long-term value by conserving resources, minimizing air and water pollution, improving community acceptance, and upholding corporate social responsibility.

8.6.4.1 Green and Sustainable Remediation

With the development of international environmental protection and sustainability concepts, green and sustainable remediation (GSR) and reducing carbon emissions during remediation have become trends globally. The US EPA Office of Solid Waste and Emergency Response (OSWER) defines GSR as "the practice of considering all environmental effects of remedy implementation and incorporating options to maximize net environmental benefit of cleanup actions" (EPA, U.S., 2021).

The US EPA identified five core GSR elements related to the environment: (1) reducing energy use and increasing renewable energy; (2) reducing air pollutants and greenhouse gas emissions;

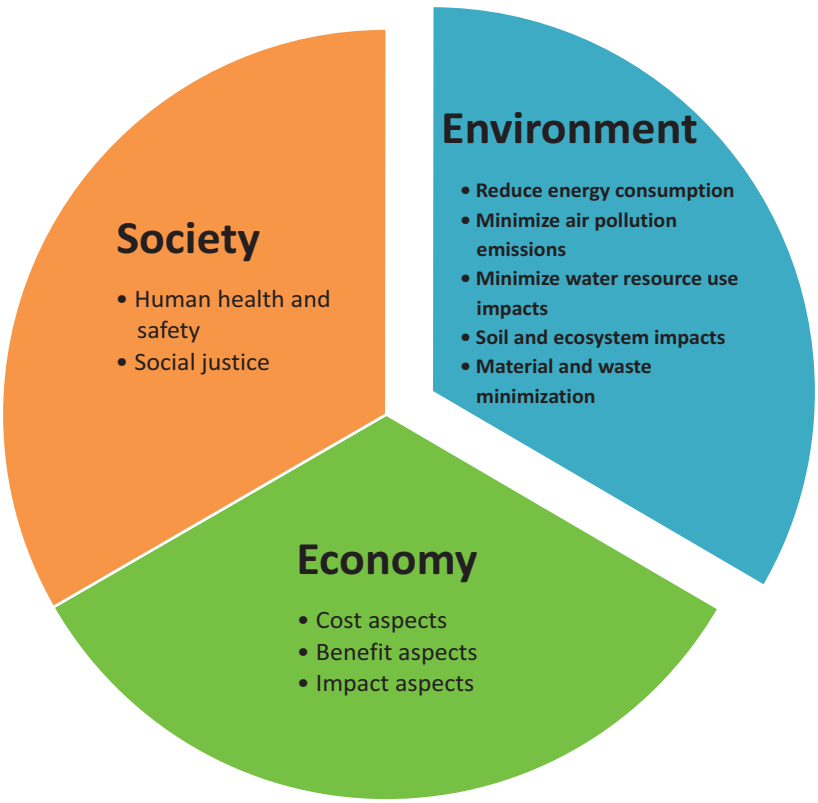


FIGURE 8.5 The concept of green and sustainable remediation (GSR).

(3) conserving water and minimizing impacts on water resources; (4) managing materials and minimizing waste; and (5) reducing impacts to land and ecosystems.

While site investigation and remediation aim to resolve contamination issues, associated activities like transportation, equipment operation, waste handling, water use, and wastewater treatment can have secondary adverse impacts environmentally, socially, and economically. GSR principles can be applied at any stage, even before remedial options are selected, through tools that evaluate potential impacts of different remedies environmentally, economically, and socially. After remedy selection, environmental assessment tools can still identify emissions hotspots from site activities and determine optimized operating strategies using best management practices. Implementing GSR provides an opportunity to holistically improve the sustainability of site investigation and remediation, beyond the core goal of addressing contamination.

8.6.4.2 Pump and Treatment

From 1982 to 1992, pump and treat (P&T) was used at 75% of US Superfund sites to remediate contaminated groundwater. At the time, the remediation goal at most sites was to restore aquifer water quality so treated water could be used as a drinking water source without additional treatment. Although later studies found P&T rarely restores water to drinking water standards by itself, it remains a common initial step in a treatment train approach.

P&T is an *in situ* method to remove dissolved groundwater contaminants from the saturated zone. By extracting contaminated groundwater, it also contains plume migration, so P&T serves as both a remediation and containment technology, similar to hydrodynamic isolation. The two main components are extraction wells that pump contaminated groundwater above ground for treatment (Figure 8.6) (EPA U.S. Office of Solid Waste and Emergency Response, 2012).

The pumping creates a capture zone that intercepts contaminated groundwater flow. P&T achieves two goals: hydraulic control to halt plume migration and treatment to lower dissolved contaminant concentrations. Extracted groundwater is replaced by clean groundwater from outside the capture zone or reinjected treated water. P&T is an established remediation technology for soluble groundwater contaminants that controls hydraulic flow and reduces dissolved phase concentrations.

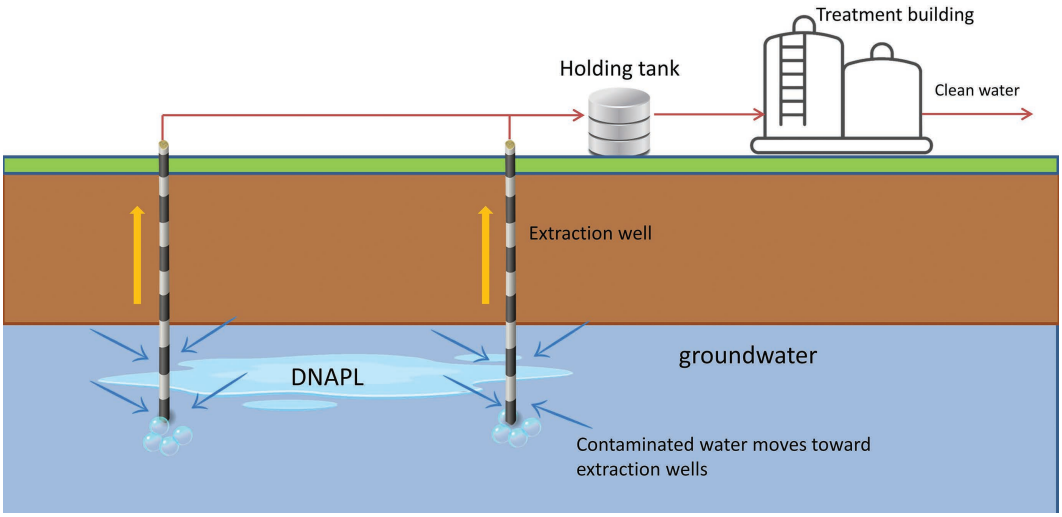


FIGURE 8.6 Example of a pump and treat system with two extraction wells (EPA et al., 2012).

8.6.4.3 Soil Vapor Extraction/Air Sparging/Dual-Phase Extraction

Soil vapor extraction (SVE) is a physical treatment technology that removes volatile contaminants from unsaturated zone soils by reducing soil vapor pressure, causing the contaminants to volatilize from solid and liquid phases into the gas phase where they can be extracted. SVE is a proven and widely used technology in Taiwan for treating soils contaminated by volatile chemicals like PCE and benzene.

Air sparging (AS) is another prevalent *in situ* treatment, but it has been mostly applied at sites with LNAPL contamination like gas stations.

SVE works by using a vacuum pump to extract gases from the vadose zone, causing volatile contaminants in the soil to vaporize. The resulting soil gas is extracted through extraction wells, creating a negative pressure gradient that causes contaminants to migrate towards the wells for removal. The extracted vapors can be treated by methods like granular activated carbon adsorption, catalytic oxidation, or thermal oxidation before discharge.

Dual-phase extraction combines SVE to treat vadose zone contaminants with groundwater extraction and treatment. It can remove contaminants present in different phases by extracting vapors from unsaturated soil and pumping contaminated groundwater (U.S. EPA, 2017).

Air sparging (AS) involves injecting air or oxygen under pressure into the saturated zone to strip and volatilize contaminants into the vapors phase in the vadose zone, where SVE can be applied to extract the vapors (Figure 8.7). Air sparging enhances biodegradation by increasing dissolved oxygen and oxygen levels. Initially, AS removes lighter and more volatile contaminants, while biodegradation becomes more important over time for less volatile compounds (Brusseau, 2019).

8.6.4.4 *In situ* Chemical Oxidation (ISCO)

In situ chemical oxidation (ISCO) is a remediation technology for contaminated soil and groundwater. It works by injecting chemical oxidants directly into the subsurface of contaminated sites, where they react with and destroy or degrade contaminants into less harmful substances or mineralize them. Oxidation and reduction are mirrored processes that transfer electrons to transform contaminants. In oxidation reactions, substances lose electrons and increase in oxidation

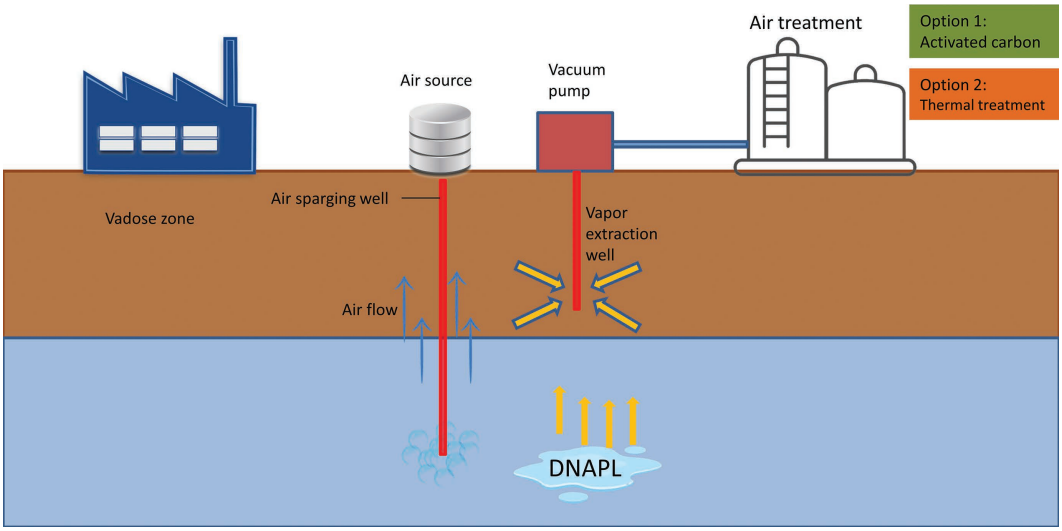


FIGURE 8.7 Air sparging to remove volatile contaminants from the saturated zone. The contaminated air extracted from the system can be treated above ground using a number of different methods (Brusseau, 2019).

number. In reduction reactions, substances gain electrons and decrease in oxidation number. Commonly used ISCO oxidants include hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), sodium persulfate ($Na_2S_2O_8$), and ozone (O_3). When selecting a suitable remediation technology for a contaminated site, the first priority is to establish a conceptual site model (CSM) to understand necessary site conditions and characteristics. Additionally, four aspects should be considered when evaluating ISCO applicability: (1) whether the oxidant can effectively react with contaminants of concern; (2) whether site hydrogeology is suitable; (3) the nature and extent of contamination (e.g. NAPL or low dissolved concentrations); and (4) remediation goals. Detailed screening considerations for ISCO application include selecting appropriate oxidants or activation methods, and delivery of oxidants into the subsurface. Decision tools like those compiled by (Siegrist et al., 2011) can aid in screening by first selecting an oxidant and activation method if needed, then evaluating compatibility with site hydrogeology, and finally choosing suitable oxidant delivery methods for the site conditions.

8.6.4.5 Thermal Treatment

Thermal remediation utilizes the volatility of organic contaminants, which increases with temperature, to achieve accelerated mass removal. It works by heating the subsurface environment first, then combining that with soil vapor extraction to remove volatilized contaminants from the contaminated zone. *In situ* thermal treatment can remove or destroy contaminant sources, address dissolved plumes, and control groundwater pollution. However, it requires energy input, which may lead to carbon emissions.

A key benefit of thermal remediation is that contaminated soils do not need to be excavated for off-site treatment, making it cost-effective. It is suitable for low permeability formations, areas with surface structures, zones below the water table, or where excavation is not feasible. However, soil heterogeneity and variable groundwater flow can make it difficult to effectively control and validate performance.

Common thermal technologies include steam injection (SI), electrical resistive heating (ERH), and thermal conduction heating (TCH). SI and ERH can be applied for temperatures under 100°C, while TCH is suitable for over 100°C. SI is often used at high permeability sites, and ERH and TCH at low permeability sites. The choice of thermal technology should be suited to site conditions and remediation objectives. Careful system design, monitoring, and modeling is crucial to ensure successful treatment while minimizing energy use and emissions.

8.6.4.6 Surfactant and Cosolvent Flushing

Surfactant/cosolvent flushing is a specialized technology that can shorten remediation timeframes. It works by injecting a combination of surfactants and/or cosolvents to remove chlorinated solvent contamination from the subsurface environment. Contaminants have a higher affinity for organic compounds compared to water. As a result, their dissolution, diffusion, and detachment in groundwater is relatively low. Past experience with pump-and-treat remediation of contaminants with low solubility or high adsorption or as non-aqueous phase liquids (NAPLs) found direct pumping inefficient due to their poor affinity for water. Therefore, increasing contaminant solubility is one way to address these difficulties. Adding surfactants enhances solubility through solubilization, improving contaminant dissolution and having the potential to reduce the required flushing fluid volume and shorten remediation timeframes (Liu et al., 2021; Ji et al., 2021).

Surfactants can increase the solubility and diffusion rates of contaminants in water. Cosolvents like alcohols can dissolve contaminants and improve their miscibility in water. Careful design of injection schemes and selection of appropriate surfactant and cosolvent types and concentrations is crucial for achieving good remediation outcomes. Compared to conventional pump-and-treat methods, surfactant/cosolvent flushing can improve contaminant recovery and removal efficiency, and lower risks of secondary pollution.

8.6.4.7 Permeable Reactive Barrier (PRB)

Permeable reactive barriers (PRBs) have emerged in recent years as an effective and economically viable *in situ* remediation technology (Freidman et al., 2017; Castro, 2016). Initial PRB research was conducted at the Borden site in Canada (O'Hannesin and Gillham, 1998), followed by a series of subsequent studies and investigations. PRB design involves installing an impermeable barrier wall downstream of a contaminant plume to divert flow through an adjacent permeable, semi-permeable, or sorptive reactive treatment unit. Within the reactive barrier, target contaminants are treated. After passing through the barrier, the treated groundwater continues flowing along its natural gradient. As the water flows through the barrier via hydraulic gradients, PRBs are also known as passive treatment walls. If the plume is very narrow, a permeable reactive trench equal in width to the plume can be installed instead of using an impermeable barrier wall to direct flow.

PRBs require very little or no mechanical systems, avoiding long-term operation and maintenance costs and significantly reducing overall remediation expenses (Obiri-nyarko et al., 2014).

The permeable medium in the barrier can be designed to target specific contaminants via mechanisms such as sorption, precipitation, biodegradation, or abiotic degradation. PRBs are best suited for contaminant plumes from low to moderate dissolved concentrations. They provide a passive, low-maintenance, and cost-effective remediation option if properly designed and monitored (Budania and Dangayach, 2023).

8.6.4.8 *In situ* Bioremediation

DNAPLs, or dense non-aqueous phase liquids, are common chlorinated organic contaminants such as carbon tetrachloride, PCE, TCE, and 1,1,1-trichloroethane (1,1,1-TCA). These chlorinated compounds contain a double carbon bond and have at least one hydrogen atom substituted by chlorine. Microorganisms possess the ability to degrade these chlorinated organics via aerobic, aerobic cometabolism, anaerobic, and reductive dechlorination pathways.

During microbial degradation of chlorinated organics, the level of halogenation affects the process. Highly halogenated compounds (with more chlorine atoms) tend to be more amenable to degradation under anaerobic conditions.

Anaerobic dechlorination is the primary mechanism for bioremediation of chlorinated ethene DNAPL contaminants. Under anaerobic conditions, all chlorinated organics and their metabolites can be transformed by anaerobic microbes. Their concentration loading limits are higher than aerobic cometabolism, since even relatively high concentrations of chlorinated organics do not inhibit the anaerobic reductive dechlorination reactions.

PCE undergoes stepwise anaerobic reductive dechlorination to TCE, DCE, VC, and finally non-toxic ethene, which can be further reduced to ethane.

For DNAPL treatment via *in situ* bioremediation (ISB), typical goals are increasing removal rates, reducing plume longevity, and lowering source zone mass loading. For anaerobic ISB, two main approaches exist: passive delivery of solid, semi-solid, or non-aqueous phase slow-release electron donors like vegetable oils, slow-release electron donor, and emulsified oils that are directly injected at multiple locations in the source zone; and active delivery via frequent injection of soluble donors like lactate and molasses that can be transported more comprehensively to target zones, enhancing removal of dissolved and adsorbed DNAPLs and stimulating biodegradation.

In practical application, ISB can be conducted via bioaugmentation, biostimulation, or integrated treatment trains combining multiple technologies. The approach is selected based on site conditions and requirements.

Overall, anaerobic processes are considered a primary mechanism for DNAPL removal via ISB (Ciampi et al., 2022). Anaerobic microbes can utilize chlorinated organics as terminal electron acceptors for respiration, reducing them to non-toxic compounds, even in oxygen-limited environments, enabling effective treatment of DNAPLs.

8.6.4.9 Biostimulation

Biostimulation is a bioremediation technique that aims to accelerate the degradation of pollutants by enhancing the activity of indigenous microorganisms in soil or water. Approaches for biostimulation can include:

1. Addition of substrates: Providing supplemental carbon sources and energy to contaminated sites by adding organic matter such as sugars, fats, proteins, or inorganic nutrients including nitrogen, phosphorus, and potassium to stimulate microbial growth and metabolic activity.
2. Modulation of environmental conditions: Altering environmental factors like pH, temperature and oxygen levels to establish conditions optimal for microbial growth and degradation activity. For instance, decreasing oxygen content can promote the activity of anaerobic microbes, while increasing temperature can accelerate microbial metabolic rates.
3. Bioaugmentation: Inoculating specific microbial strains into contaminated areas to augment the capacity for biodegradation of hazardous pollutants. These can be native strains or genetically engineered organisms.
4. Promoting cometabolism: Adding other readily degradable compounds to stimulate cometabolic reactions for pollutants that require it for their degradation.

In summary, biostimulation aims to enhance the native microbial activity and biodegradation potential in soil and aquatic environments through substrate amendment, microbial amendment, and optimization of environmental conditions to achieve rapid removal of hazardous contaminants.

8.6.4.10 Bioaugmentation

Bioaugmentation is a bioremediation technique that introduces specific microbial strains to enhance the biodegradation capacity of natural environments. The strains used can be indigenous or artificially cultivated organisms selected for their ability to effectively degrade the target contaminant. A key step in bioaugmentation is choosing microbial strains capable of surviving and propagating in the prevailing environmental conditions while efficiently mineralizing the pollutant. The selected strains are grown under laboratory conditions to ensure adequate cell numbers before being inoculated into the contaminated site, either by direct injection or immobilization on carriers. Periodic monitoring of the microbial community is necessary after inoculation to evaluate the survival and biodegradation performance of the introduced strains.

The advantages of bioaugmentation include accelerated degradation rates from strains with high catabolic activity, enhanced biodegradation capacity by supplementing microbial communities with specialized degraders, and the adaptability of inoculated strains to propagate in the target habitat. However, there are also challenges such as the potential costs of strain isolation and cultivation, ensuring the survival of non-native strains in the environment, and competition or inhibition of augmented strains by indigenous microbes or environmental factors. Careful strain selection and monitoring is crucial for effective bioaugmentation to boost biodegradation.

8.6.4.11 Applications of Molecular Biotechnology

Recent advances in high-throughput sequencing technologies like Illumina and ABI SOLiD systems can generate hundreds of megabases to terabases of DNA sequences per run, though the individual reads are relatively short (75–300 bp). In contrast, the Roche 454 pyrosequencing platform produces longer reads (250–1000 bp) with fewer total sequences, making it well suited for phylogenetic analyses and environmental microbiota profiling. This advanced sequencing capability has proven valuable for characterizing microbial communities in bioremediation of chlorinated solvent contaminants. Kotik et al. (2013) leveraged Roche 454 to examine the active and total bacterial communities at three chloroethene-contaminated groundwater sites by pyrosequencing of extracted

DNA and RNA, respectively. This sequencing allowed simultaneous profiling of the total microbiome and detection of dechlorinating populations composing less than 0.25% of the community. The longer read lengths facilitated by 454 pyrosequencing permitted phylogenetic identification of even low abundance organohalide-respiring bacteria based on RNA transcripts in the contaminated groundwater samples. Characterizing these dechlorinating populations is key to understanding and enhancing the biodegradation of chlorinated ethenes like TCE and vinyl chloride through reductive dechlorination pathways. High-throughput sequencing provides a powerful molecular tool to comprehensively analyze complex microbial communities driving contaminant bioremediation processes.

8.7 CHALLENGES

The severe situation of current chlorinated solvent contamination has been recognized by many studies. The high toxicity and persistence of chlorinated solvents pose grave threats to the ecological environment and public health, but the widespread contamination sources across various industries make remediation extremely difficult. Despite many measures taken by the government and enterprises, past technologies such as pump-and-treat and soil vapor extraction have had limited effectiveness and high costs. Tailored solutions are needed for different contaminated sites, and the risks of secondary contamination also need early prevention. Research suggests (Padhye et al., 2023) that remediation priority should be determined based on contamination risks and remediation benefits. Technological innovation will be the core development direction of the solution to chlorinated solvent contamination. Some forward-looking reports call for developing new efficient and energy-saving remediation technologies and materials for chlorinated solvents (Lyu et al., 2023), and enhancing adaptability of solutions. Meanwhile, strengthening fundamental research on biogeochemical processes of contamination to predict emerging pollution patterns is important. Additionally, establishing risk assessment systems for dynamic monitoring, and promoting international technology exchange and policy coordination will also play vital roles in advancing chlorinated solvent pollution control.

8.8 CONCLUDING REMARKS

Chlorinated organic solvents have been extensively used in industrial processes, leading to their ubiquitous distribution in the environment. As mentioned earlier, the impacts of chlorinated solvent contamination on ecosystems and human health are severe, and strategies for mitigating this pollution are being actively explored. Despite the strengthening of environmental regulations on chlorinated solvents in recent decades, usage of TCE and PCE has remained high over the past few decades, indicating the need for continued pollution control efforts. Chlorinated solvents can persist in soils and groundwater aquifers, posing toxicity risks through exposures via water ingestion, inhalation, and dermal absorption. Adverse effects include carcinogenicity, liver and kidney damage, impairment of the central nervous system, and reproductive toxicity. To alleviate environmental contamination, legal restrictions have been imposed to reduce chlorinated solvent usage. Additionally, remediation technologies have been developed, including methods harnessing contaminant-degrading bacteria or surfactants. Ongoing research has focused on pollution monitoring, fate and transport modeling, and health risk assessment to support remediation design. Integration of innovative characterization methods with models and risk analysis provides critical information for remediation decision-making. Continued technology development coupled with strengthened regulatory oversight is essential to protect ecosystem and public health from chlorinated solvent releases. This review summarizes key information on chlorinated solvent behavior, toxicity, and control methods useful for supporting environmental management.

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9 Pentachlorobenzene
A Toxic Legacy in the Chemical Landscape

Qi Wang

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9.1 INTRODUCTION

Chlorobenzene, a class of compounds formed by replacing one or more hydrogen atoms on a benzene ring with chlorine atoms, is produced primarily through direct chlorination of benzene. This synthetic organic material, encompassing 12 homologous compounds ranging from monochlorobenzene to hexachlorobenzene, is characterized by the number and positions of chlorine substituents. Its stability, low water solubility, bioaccumulation, and potential for long-distance movement in the atmosphere result in the substance's widespread contamination of the environment, including soil, air, and water. Due to their resistance to degradation, chlorobenzene compounds accumulate in the food chain, especially in apex predators, in which concentrations significantly exceed those in the surrounding environment. This results in notable bioaccumulation and biomagnification in organisms like algae, worms, and fish. Studies strongly suggest that a significant amplification of organochlorine pesticides, including chlorobenzene, occurs through aquatic food chains as far north as arctic seawater.

Pentachlorobenzene (PeCB), a chlorobenzene compound with five chlorine atoms substituting the hydrogen atoms on the benzene ring, has various applications such as dye carrier, herbicide, pesticide, fungicide, flame retardant, components in polychlorinated biphenyls (PCBs), and chemical intermediate in pentachloronitrobenzene production. It exists as white or colorless crystals. At 20°C, PeCB is a solid with very low volatility and solubility, strongly adsorbing to organic matter. In soil, it volatilizes and dissolves very slowly, potentially reaching water tables and diluting in waterways before partially volatilizing. PeCB fragments can settle in waterways, dissolving very slowly. Once the source is removed, the adsorbed phase lingers, releasing contaminants in gaseous or dissolved states, although the subsequent plumes are typically small.

Recognized for its hazards to human health and ecosystems, PeCB was added to the Stockholm Convention as a POP in 2011. The physicochemical properties of PeCB are summarized in detail in Table 9.1. It is important to note that PeCB is moderately toxic to humans but highly toxic to aquatic organisms.

The primary concern with PeCB lies in its extreme resistance to biodegradation and bioaccumulation. Its high degree of lipophilicity facilitates environmental persistence. Although its production

DOI: 10.1201/9781003530466-9
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TABLE 9.1
Physicochemical Properties of Pentachlorobenzene

Property	PeCB (CAS Number 608-93-5)
Molecular Formula	C_6HCl_5
Molar Mass	250.34
Density	1.609 g/mL at 25°C (lit.)
Melting Point	84–87°C (lit.)
Boiling Point	275–277°C (lit.)
Flash Point	131.6°C
Water Solubility	1.332 mg/L (25°C)
Solubility	Very soluble in ether
Vapor Pressure	6×10^{-3} mmHg at 20–30°C

as a pesticide has ceased, large quantities were already produced and dispersed, making it difficult to estimate the total amount produced and how much currently exists due to numerous legal but also undocumented illegal producers. PeCB can be formed during the burning of organic compounds or exposure to high energy in the presence of chlorine, and is released into the environment via waste incineration and the burning of household waste in barrels.

Three main sources [1–5] of PeCB in environment include:

- Release due to chemical transformations of substrates needed for industry (i.e., metallurgy, etc.)
- Elimination from unintentional production
- Residual presence in the environment once it has been utilized

(1) Intentional production of industrial chemicals such as insecticides, flame retardants, and insulating fluids

Historically, PeCB was commonly added to polychlorinated biphenyls (PCBs) in industrial settings to diminish their viscosity, thereby enhancing heat dissipation. Despite the 2010 prohibition on PeCB production and use, substantial quantities remain in outdated electrical equipment, which are now primary contributors for its environmental release. Additionally, PeCB is emitted as a byproduct in various chemical and metallurgical operations. Its presence in the environment is also attributed to its inclusion in certain chlorinated pesticide mixtures. The regional concentration of PeCB varies; post-2000 data indicates average atmospheric levels of approximately 45 pg/m^3 in the United States and Canada, and 33 pg/m^3 in Sweden. Furthermore, the estimated annual PeCB inflow to the Arctic Ocean was approximately 400 kg, and to the Humber estuary around 0.8 kg, up to the end of the twentieth century.

(2) Unintentional production and emissions in industrial manufacturing

In some industrial manufacturing processes, PeCB is unintentionally generated, and this is typically referred to as unintentional POPs. These unintentional pollutants often emerge as byproducts of industrial production, entering the environment through emissions or residues, or as part of industrial products, and have become a recognized serious environmental problem worldwide.

Based on the nature of industrial activities, the primary sources of these unintentional POPs can be categorized as follows: combustion sources, metal smelting sources, chemical production sources, and sources from biological and photochemical processes. Key combustion sources include waste incineration, coal-fired power generation, and heating; metal smelting sources primarily involving iron ore sintering and electric arc furnace steelmaking; and non-ferrous metal smelting. Chemical production sources mainly encompass the production and use of chlorine-containing chemicals and the chlorination bleaching process in pulp and paper manufacturing. As indicated in Table 9.2, the level of unintentional emissions from thermally related industrial processes significantly exceeds that from the production, use, and leakage of chemicals. Highlighted here is that unintentional emissions from thermal processes have become a significant source of PeCB.

(3) Natural degradation of hexachlorobenzene

In aged hexachlorobenzene-contaminated soils, PeCB often appears as a natural degradation product of hexachlorobenzene. Although PeCB also undergoes continuous natural degradation, its persistence over a certain period of time is due to the presence and ongoing degradation of hexachlorobenzene.

9.2 POLICY AND REGULATORY GUIDELINES

PeCB's recognized dangerousness to human health and the biosphere have led to regulatory measures, notably the Stockholm Convention on Persistent Organic Pollutants (referred to as the POPs Convention) signed in 2001. EU countries, which are also members of the United Nations, adhered to the Stockholm Convention and its protocols, including amendments adopted on December 18, 2009 (ECE/EB. AIR/104), regulating or banning substances present in many biocides due to concerns over bioaccumulation and propagations.

In Canada, under the Canadian Environmental Protection Act, 1999, PeCB is listed as a toxic substance and subject to regulations prohibiting its manufacture, import, use, sale, and offer for sale. These regulations aim to prevent its reintroduction into the Canadian natural environment. The regulations amending the Prohibition of Certain Toxic Substances Regulations, 2005, were issued by the end of 2006.

TABLE 9.2
Global Sources and Annual Emission Quantities of Pentachlorobenzene (2001–2009)

No.	Source Category	Emission (kg yr^{-1})
1	Insecticide Production	5,400
2	Production of Chlorinated Solvents	<2
3	Leakage with PCBs	400
4	Chemical Production and Waste Processing	400
5	Aluminum Casting	1,100
6	Waste Incineration	3,600
7	Uncontrolled Waste Incineration	28,000
8	Coal Combustion	11,000
9	Biomass Burning	45,000
10	Degradation of Other Chemicals	26,000
11	Total Emissions	120,902

On May 23, 2001, China signed the POPs Convention. The Convention was ratified by the Tenth Standing Committee of the National People's Congress during its tenth session on June 25, 2004. Following this, the Chinese government submitted the ratification, acceptance, approval, and accession documents to the United Nations on August 13, 2004. According to the provisions of the Convention, it officially came into effect for China (including the Hong Kong Special Administrative Region) 90 days later, on November 11, 2004. On April 14, 2007, the State Council approved the National Implementation Plan for the People's Republic of China on the POPs Convention, establishing the country's compliance objectives, measures, and specific actions. On August 30, 2013, the fourth session of the Twelfth National People's Congress Standing Committee approved amendments to add nine new POPs to the Convention, as well as the amendment concerning the addition of endosulfan. On March 26, 2014 the production and use of substances like PeCB were banned.

Over the past 19 years, China has made significant progress in fulfilling its obligations under the Stockholm Convention. Firstly, a coordination mechanism for compliance was established. With the approval of the State Council, the Ministry of Ecology and Environment led the formation of a national coordination group for implementing the Stockholm Convention (referred to as the coordination group). This group guides and supervises the establishment of provincial-level compliance coordination mechanisms involving relevant functional departments, creating a pattern of horizontal and vertical collaborative compliance. Secondly, the top-level design for compliance was strengthened. The coordination group and its relevant departments jointly formulated the national compliance implementation plan and issued joint announcements regarding the effectiveness of the Stockholm Convention and its amendments, specifying control requirements. Thirdly and equally important was the promotion of 'green' technologies in various industries. Over 40 alternative technology demonstration projects were devised and implemented in more than 10 industries, for instance steel and paper. Mandatory national standards in 15 industries specify emission limits for dioxins and other POPs. Additionally, best available technology guides were issued for 12 industries, aiding the green transformation and upgrading of key technologies in relevant sectors. Fourthly, the issue of being deeply involved in global governance meant that China now actively participates in the negotiations for various decision-making proposals under the Convention, and regional compliance projects. The Chinese government is proposing its own solutions, and sharing its experiences and practices with other nations of the world.

9.3 TOXICITY, EXPOSURE, AND RISKS TO THE ENVIRONMENT AND HUMANS

POPs such as PeCB pose serious health risks, entering organisms through contaminated food or meat. PeCB is particularly toxic to the pancreas and exhibits mild immunotoxicity. Its environmental abundance, despite prohibitions on its production, is attributed to physical properties that facilitate redistribution across ecosystems via processes like adsorption, leaching, and volatilization. Historically used as pesticides, these compounds inadvertently polluted the atmosphere, seas, and oceans, contributing to their circulation in the biosphere. Studies on bioaccumulation indicate their entry into plants primarily via the air-plant route. Despite limitations on application and production bans, these compounds continue to be released as by-products from chemical transformations.

9.4 REMEDIATION: SOIL AND WATER

Due to the persistent, long-distance migratory, and ecotoxicological characteristics of PeCB, relying solely on its natural degradation in soil and water often requires waiting for months or even years. Therefore, developing effective remediation technologies to remove PeCB from environmental media, or implementing control measures to manage the risk of PeCB environmental pollution, is imperative.

Current research on the remediation of PeCB-contaminated soil and water mainly includes physical, chemical, and biological methods. Physical methods separate pollutants from gas, liquid, or solid phases based on their physical properties, using adsorption, stripping, extraction, etc., and include adsorption, stripping, air sparging, and extraction methods. Chemical methods include ultraviolet-ozone oxidation, photocatalytic degradation, electromagnetic wave degradation, electro-Fenton degradation, and degradation catalyzed by metals and complexes. However, physical methods are generally only suitable for treating small concentrations of PeCB, are expensive, and may cause secondary pollution. Chemical strategies are often beset by complex operations, high running costs, harsh reaction conditions, and poor engineering feasibility.

Bioremediation [6], due to its small footprint, simple operation, low investment requirements, no need for special equipment, minimal impact on the surrounding environment, and not causing secondary pollution, has become a major topic in domestic and international soil pollution remediation technology research. Bioremediation refers to the process whereby microorganisms transform and decompose organic pollutants. On one hand, microorganisms can effectively stabilize organic matter by using it as a carbon and energy source. On the other hand, in the process of co-metabolism, by decomposing growth substances to continuously provide carbon sources and energy, the degradation of non-growth substances can proceed. For chlorobenzene organic compounds, bioremediation is divided into aerobic degradation and anaerobic degradation. Low-chlorinated benzenes are easily biodegraded under aerobic conditions, while high-chlorinated benzenes generally undergo anaerobic biodegradation.

PeCB, as a high-chlorinated benzene compound, shows better anaerobic biodegradability due to the lowered electron cloud density on the benzene ring caused by the introduction of chlorine substituents, making the ring electron-deficient. In aerobic conditions, it is difficult for oxidases to obtain electrons from the benzene ring and undergo oxidation reactions, while in anaerobic conditions, the lower redox potential of the environment makes possible the effective anaerobic biodegradation of PeCB. Some studies have shown that in anaerobic environments like digested sludge and sediment, PeCB is prone to dechlorination degradation, transforming into low-chlorinated benzene compounds that are easily degradable under aerobic conditions.

Additionally, risk management is also an effective choice for controlling the environmental pollution risk of PeCB. Risk management involves adopting engineering techniques, institutional measures, and monitoring and evaluation to reduce or eliminate the adverse effects of contaminated sites on human health and the ecological environment, achieving safe land resource utilization and sustainable development. For farmland contaminated with PeCB, risk management involves agricultural control, alternative planting, adjustment of planting structures, and designating specific agricultural product prohibition zones to ensure the safety and quality of agricultural products and the safe use of arable land. For lightly to moderately polluted soils, it is necessary to implement safe use plans for contaminated farmland, adopting agricultural control and alternative planting measures, the objective being to reduce the risk of contamination of agricultural produce.

For heavily polluted soils it is necessary to strictly control their use, legally designate specific agricultural product prohibition zones, strictly prohibit the planting of edible agricultural products, and implement plans for adjusting the planting structure of heavily polluted farmland or to return farmland to forest or grassland. For construction land contaminated with PeCB, risk management involves setting up signs and markers for polluted plots, adopting isolation and interception measures to prevent further pollution spread, designating controlled areas to restrict access and prevent soil disturbance. A great deal of this process requires incorporating soil environment management strategies for land set aside for construction, into urban planning, land supply management, and land development. Proper management practices will avoid risks associated with indiscriminate construction and development.

9.5 CONCLUSIONS

This chapter has demonstrated that, whenever feasible, microbial decomposition should be utilized due to its eco-friendly and cost-effective nature. Pentachlorobenzene (PeCB) has been identified as a persistent organic pollutant (POP), posing significant ecological risks due to its persistence and mobility. Its resistance to biodegradation and tendency for atmospheric transfer enable it to contaminate regions where it has never been used. The high toxicity of PeCB can adversely affect both environmental and human health, leading to a range of issues, including liver damage, infertility, and developmental disabilities in children.

To mitigate these risks, it is essential to limit the consumption of crops that may be contaminated with PeCB. This can be accomplished by raising public awareness about the health and environmental impacts of such crops and encouraging individuals to avoid those grown in known contaminated areas.

Remediation efforts in polluted regions, particularly in agricultural zones, are critical. Strategies may include the use of phytoremediation – planting species capable of extracting POPs from the soil – or selecting crops that are less likely to absorb these contaminants, thereby allowing for the safe utilization of the land for farming. Overall, addressing the challenges posed by PeCB requires a multifaceted approach that prioritizes both public health and environmental integrity.

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10 Burning Issues
The Health and Environmental Concerns of Brominated Flame Retardants

Naga Raju Maddela, Kadiyala Venkateswarlu, Ravi Naidu, and Mallavarapu Megharaj

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10.1 BACKGROUND AND SOURCES OF BROMINATED FLAME RETARDANTS

Brominated flame retardants (BFRs) are organic bromine compounds with anti-combustion properties, which reduce the flammability of a material or compound that contains them (Figure 10.1). For this reason, BFRs have been widely used in textile and plastic products which include, but are not limited to, electronics, clothes, furniture, etc. BFRs are several groups of chemically synthesized compounds. There are five main classes of BFRs and they have specific applications (ESFA, 2023a): (i) polybrominated diphenyl ethers (PBDEs) in plastics, textiles, electronic castings, circuitry; (ii) hexabromocyclododecanes (HBCDDs) for thermal insulation; (iii) tetrabromobisphenol A (TBBPA) and other phenols in printed circuit boards, thermoplastics (mainly in television sets); (iv) polybrominated biphenyls (PBBs) for consumer appliances, textiles, plastic foams; and (v) other BFRs. This diversity in BFR groups has been attributed to their applications and purpose. Of the different polymers, the amount of BFR varies as follows: polystyrene foam (0.80–4% HBCDD), high impact polystyrene (11–15% decaBDE, brominated polystyrene), epoxy resin (0–0.10% TBBPA), polyamides (13.16% decaBDE, brominated polystyrene), polyolefins (5–8% decaBDE, propylene dibromo styrene), polyterephthalate (8–11% brominated polystyrene), unsaturated polyesters (13–28% TBBPA), polycarbonate (4–6 brominated polystyrene), and styrene copolymers (12–15% brominated polystyrene) (Alaee et al., 2003). According to 2019 estimates (https://www.flameretardants-online.com/flame-retardants/market), BFRs account for 17% of global consumption of various FRs. In fact, the global shares of BFRs and non-BFRs are, respectively, 64% and 36% (Leventon et al., 2019). These statistics imply the widespread application of BFRs on a global scale. It is important to note that the global bromine market for 2019–2024 is 4.92% of the compound annual growth rate (GlobeNewswire, 2019) (Figure 10.2). Large amounts of BFRs are consumed in the electronics

DOI: 10.1201/9781003530466-10
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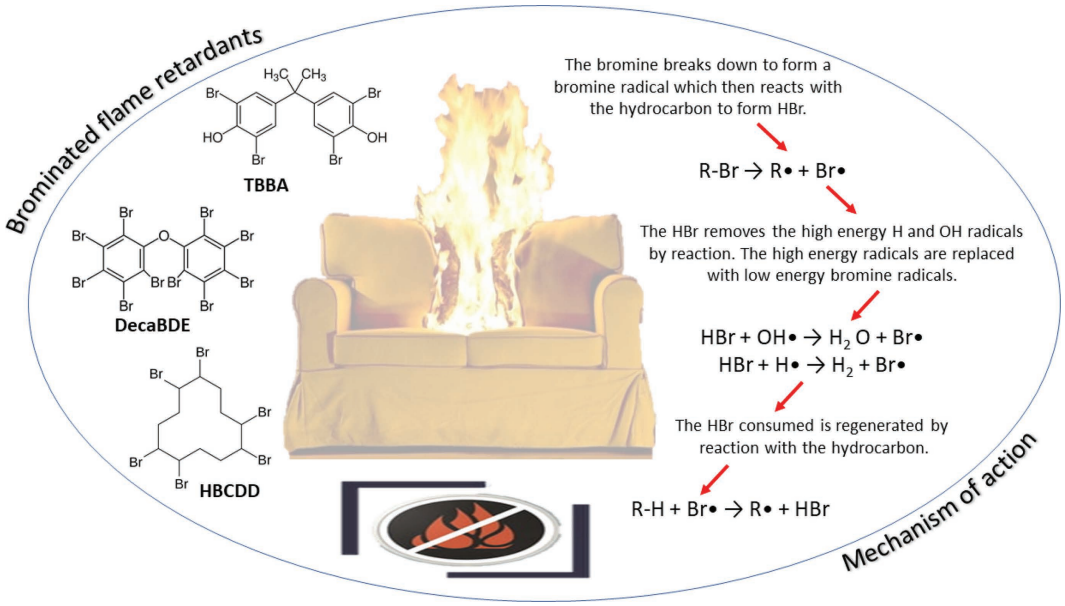


FIGURE 10.1 Selected brominated flame retardants (BFRs) and their mechanism of action (data from Morgan, 2014).

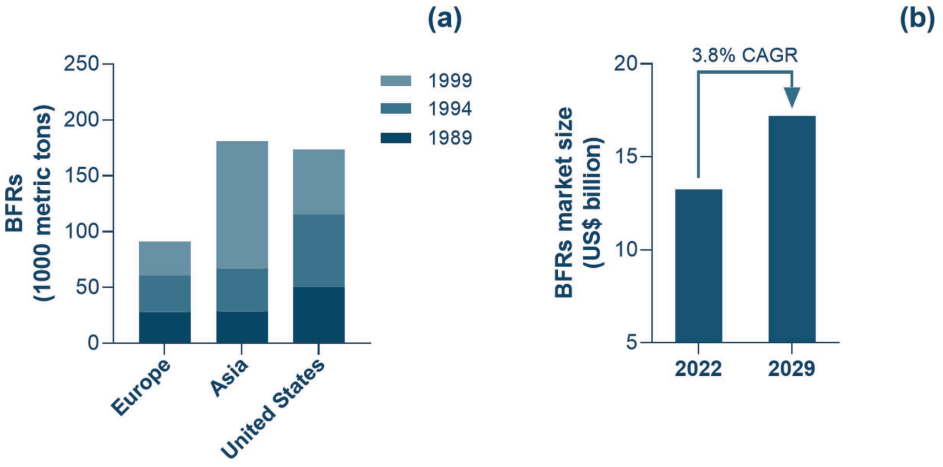


FIGURE 10.2 Global production and use of flame retardants. **(a)** Production of BFRs during the years 1989–1999 in selected regions of the world (data from Alaee et al., 2003), **(b)** Market size of BFRs, with a projected 3.80% increase in compound annual growth rate (CAGR) for the period 2022–2029 (data from MMR, 2023).

industry, including but not limited to printed circuit boards, connectors, electrical cables, plastic covers of TV sets, etc.

PBDEs are recalcitrant chemicals and can resist physicochemical and biological degradation. However, compared to PCBs, PBDEs are somewhat more susceptible to environmental degradation which is attributed to the presence of bromine atoms in PBDEs. Bromine atoms are readily detached from PBDE core components and make PBDE easily degradable (Prasada Rao et al., 2011). There

are about 209 different substances of PBDEs which are called 'congeners'. These PBDEs congeners have different levels of bromination. Typically, PBDEs are produced using three different types of bromination, viz., pentaBDE, octaBDE, and decaBDE; this classification is based on the average amount of bromine they contain. In 1999, global market demand for deca-, penta-, and octaBDE was 54,800, 8,500 and 3,825 tons, respectively. These figures underscore the demand for the three PBDEs congeners as FRs. Conversely, the composition of PBDE congeners in different commercial products greatly vary depending on the manufacturer and the purpose of the product.

DecaBDE [1163-19-5] is a white powder, and its formulation mainly consists of BDE-209 congener (97–98%), and a small amount of nonaBDE (0.30–3%) (Alaee et al., 2003). As an FR, decaBDE is used in a wide range of polymers, such as polycarbonates, polyester resins, polyolefins, ABS, polyamides, polyvinyl chloride, and rubber. The market for decaBDE for 2018 and 2025 amounted to >US$313 and >US$430 million, respectively, which is equal to 5% of the CAGR during this period (Kunal and Sarita, 2019). By 2025, the market value of decaBDE in North America, Asia, and the rest of the world is expected to reach US$180, US$130, and US$120 million respectively. Commercially sold octaBDE (e.g., DE-79 and Bromkal 79-8DE) is a white powder available as a mixture of several congeners and contains 79% bromine (Alaee et al., 2003). Congener types and composition of a commercially available octaBDE are as follows (La Guardia et al., 2006): BDE-153 (0.15–8.70%), BDE-154 (0.04–1.10%), BDE-171 (0.17–1.80%), BDE-180 (n.d. –1.70%), BDE-183 (13–42%), BDE-196 (3.10–10.50%), BDE-197 (11.22%), BDE-203 (4.40–8.10%), BDE-206 (1.40–7.70%), BDE-207 (11–12%), and BDE-209 (1.30–50%). PentaBDE [32534-81-9], which is commercially available in the form of a viscous liquid, is 70% bromine, and is made up of different congeners, i.e., 41–42% of BDE-47, 44–45% of BDE-99 (predominantly) and BDE-100 (minor extent), 6–7% of BDE-153 and BDE-154 (Alaee et al., 2003). In summary, BFRs are chemically diverse compounds with bromine as the major component. Although these compounds do not require specific background structure, the only requirement is for BFR to remain stable during product lifetime and its compatibility with the polymers. Thus, a wide range (>75 types) of chemicals (i.e., aliphatic, aromatic, and cyclo-aliphatic) have emerged as BFRs.

10.2 EXTENT AND SEVERITY OF CONTAMINATIONS

BFRs are very common in the environment and their concentrations have been detected at rates ranging from ng to μg g^{-1} of samples (Yu et al., 2016). There are many ways in which BFRs can enter the environment. The most common sources of entry are urban-based anthropogenic activities and household items. Consequently, BFRs have been detected in sediments, surface waters, soils, outdoor air, indoor dust, plants, fishes, invertebrates, birds, and humans (Yu et al., 2016). Details regarding the presence of BFRs in various household materials in selected countries worldwide are presented in Figure 10.3a and 10.3b.

The pollution caused by BFRs in different human-associated environments is quite alarming. Factories associated with TBBPA and textile works discharge significant levels of TBBPA, PBDEs, and HBCDD into surrounding river bodies; the concentrations of these contaminants are significantly higher in the downstream river sediments than upstream (Sellström and Jansson, 1995; Sellström et al., 1998). US dust samples contained 10 times higher PBDE median levels than German dust samples (Schecter et al., 2009). Similarly, US sewage sludge samples were shown to have 10- to 100-fold higher concentrations of PBDEs than Europe sewage sludge samples (EPA, 1999). The median concentrations of PBDEs in different US food samples in decreasing order are as follows: fish (1,725 pg g^{-1}) > meat (283 pg g^{-1}) > dairy products (31.50 pg g^{-1}) (Schecter et al., 2004). It is also worth noting that indoor air samples contained 15–20 times higher PBDEs than outdoor air samples, which can be attributed to the presence of BFRs in several household materials that are released from the parent materials (Butt et al., 2004). In developing countries, e-waste recycling sites are the important sources of emissions of different PBDEs congeners, such as BDE-47, BDE-99, BDE-209, etc. (Liu et al., 2019). Evidently, PBDEs have been detected at 250–8740 ng g^{-1} of indoor dust in e-waste recycling sites.

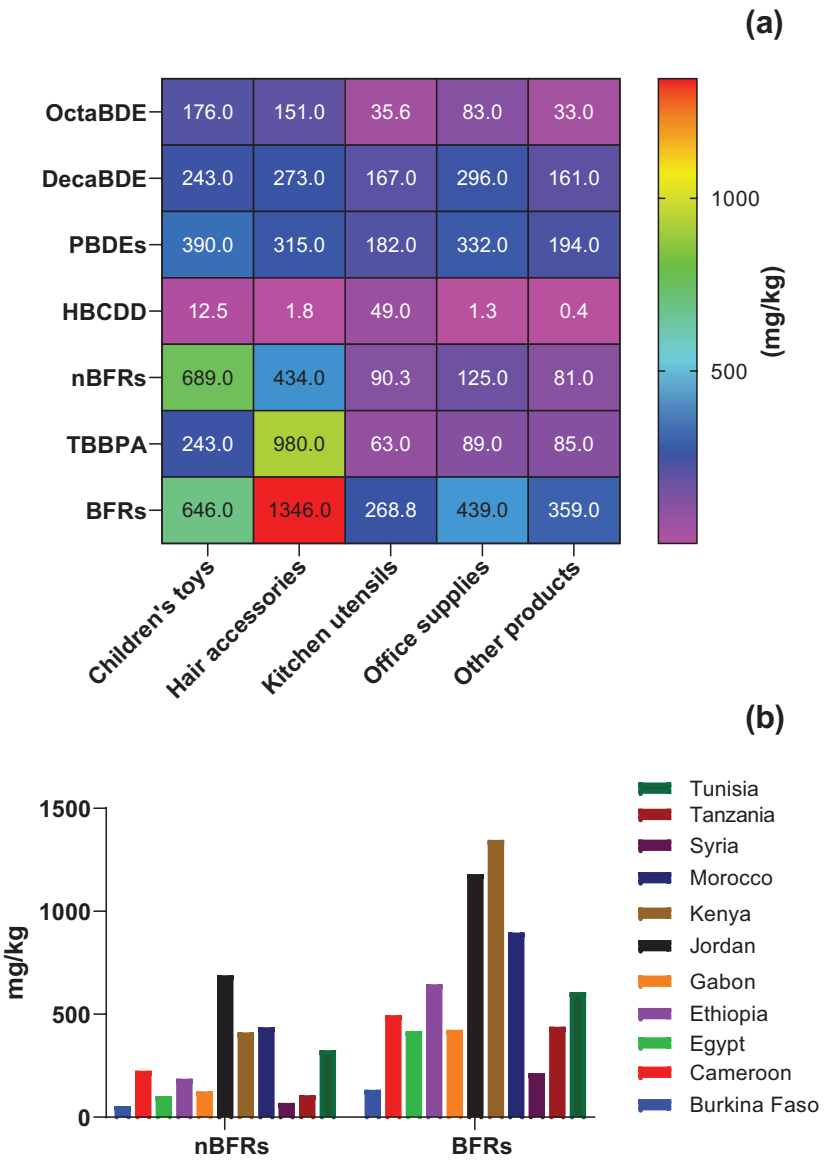


FIGURE 10.3 Environmental occurrence of BFRs in different **(a)** consumer products, and **(b)** African and Arabic countries (data from IPEN, 2022). BDE, bromodiphenyl ether; PBDE, polybrominated diphenyl ethers; HBCDD, hexabromocyclododecane; nBFRs, novel brominated flame retardants; TBBPA, tetrabromobisphenol A; BFRs, brominated flame retardants.

The latest investigations reveal much more important insights over the grave situation of BFRs' environmental burden. The concentrations of ∑PBDEs and ∑NBFRs (new BFRs) in agricultural soils were found to be 283–928 μg kg^{-1} and 54.70–437 μg kg^{-1}, respectively (Luo et al., 2023). Quantitative differences in soil concentrations of these two types of BFRs can be attributed to differences either in their leaching properties or in quantities used. It is also important to note that different parts of a plant have varying bioaccumulation propensities for BFRs. For example, concentrations of BFRs in some parts of rice plants revealed the following order: root > leaf > stem > grain (Luo et al., 2023). Very recently, in the US, 100% of breast milk samples were discovered

to be positive for the presence of BFRs, which strongly suggests the extent to which BRFs occur in the environment (Schreder et al., 2023). Animals are not exempted from exposure to BFRs. For example, concentrations of PBDEs and NBFRs were found to be 4.40–250 and 2.90–22 ng g^{-1} lipid in snakes and 2.90–120 and 7.10–97 ng g^{-1} lipid in frogs, respectively (Sun et al., 2023). These authors also found that PBDEs and NBFRs have the capacity to be transferred from mothers to eggs (Sun et al., 2023), clearly suggesting the material transfer efficiency of BFRs.

The environmental pollution caused by BFRs is now evident in the world's polar regions, because they have been detected in the liver and blubber tissues of young harbor seal pups (<6 months old) from the northwest Atlantic region (Berger et al., 2023). Based on these findings, there is a significant environmental burden of BFRs. Because BFRs are present in every component of the environment and have bioaccumulation propensities, both aquatic and terrestrial food chains are highly vulnerable to these contaminants of emerging concern. Due to the amount of environmental pollution caused by BFRs, human exposure to these pollutants is inevitable, and there are several routes by which this occurs, such as direct exposure to BFR emissions, skin contact, and ingestion of BFR-laden foods and water.

10.3 FATE AND DYNAMICS IN THE ENVIRONMENT

Being halogenated compounds, BFRs are persistent and less degradable, and they accumulate in the environment. However, depending on the environmental conditions they can be affected by both abiotic and biotic factors (Segev et al., 2009). For instance, based on the environmental temperature and pH, BFRs are subjected to different types of physicochemical reactions, such as photodegradation, wet and dry deposition, high temperature-induced degradation, and chemical reactivity with other chemicals or free radicals. Such physicochemical reactions induce significant modifications in the characteristics of BFRs. In a recent investigation, it emerged that BFRs were subjected to progressive debromination in zebrafish and transferred to the next generation (Qiao et al., 2023). BFRs have also been found in the world's remote (e.g., Qinghai-Tibet Plateau) and polar regions, suggesting that these chemicals have long-range transport propensities (Dreyer et al., 2019; Xian et al., 2021). Therefore, studies emphasizing the fate of BFRs are hugely important in the risk assessment and control of these chemicals in the environment.

In urban soils, it has been reported that the volatility of BFRs diminishes over time since they are strongly bound to soil particles (Wong et al., 2012), suggesting the persistent nature of BFRs in soil environments. Furthermore, certain BFRs (e.g., α- and β-TBECH, β-TBCO, DPTE, and BDE-17) were degraded in soil over 360 days but not others (BDE-28, BDE-47, and BDE-99). The photoreactivity of BFRs is largely dictated by the number of Br atoms they contain. In the photochemical transformation of BFRs in tetrahydrofuran solvent at 290 nm, the quantum yield (Φ) of TBBPA (Φ = 0.05) and BDE-209 (Φ = 0.27) were significantly different (Khaled et al., 2018b), suggesting that increased photo-reactivity was due to the increased number of Br atoms in BFRs. In this investigation, BFRs were shown to undergo <2% degradation in dark control experiments, meaning that the fate of certain BFRs is affected by sunlight in the environment.

In addition, the fate of BFRs is influenced by the type of polymer. For instance, BDE-209 exhibited higher photo-reactivity in polystyrene (PS) polymer than polyethylene terephthalate (PET) and cellulose (Khaled et al., 2018a). Thus, BFRs with a high number of Br atoms experience faster photodegradation than those with minimal Br atoms (Staszowska, 2017). With respect to the emissions and partition of PBDEs in different environmental scenarios, both congeners number and Br atoms have significant importance. The emission rates of different PBDEs congeners, BDE-47, BDE-99, and BDE-209 to air, soil, and water were found to be $4.90–92 \times 10^{-3}$, $0.91–17.40 \times 10^{-3}$, and $0.21–4.04 \times 10^{-3}$ kg h^{-1}, respectively (O'Driscoll et al., 2016). PBDEs are readily partitioned in the air as the number of congeners falls. On the other hand, PBDE congeners readily partition into sediments as the number of Br atoms increases. Importantly, during storm events there is a possibility

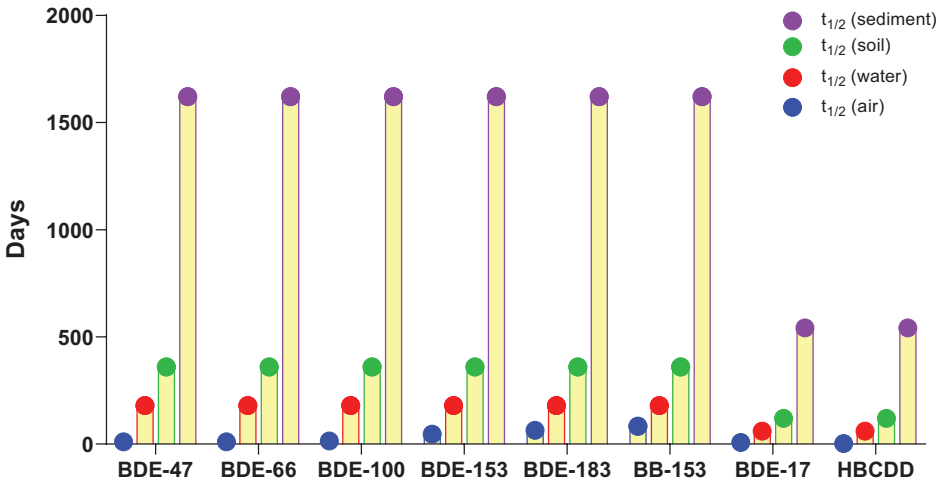


FIGURE 10.4 Half-lives ($t_{½}$), in days, of different BFRs in air, water, soil, and sediments (data from Olaniyan et al., 2023). BDE, bromodiphenyl ether; HBCDD, hexabromocyclododecane.

for PBDEs to be released from sediments to a water column; thus, sediments are a long-term source of PBDEs in the environment (O'Driscoll et al., 2016). Half-lives determined for different PBDE congeners and HBCDD in soil, water, and sediments are depicted in Figure 10.4.

10.4 TOXICITY

Legacy BFRs (PBDEs, HBCDD, etc.) and novel BFRs (DBDPE, BTBPE, etc.) are found to be toxic to several biotic matrices. The principal mechanisms by which BFRs exhibit toxicities are hormone and endocrine disruption, genotoxicity, and behavioral modification (Xiong et al., 2019). BFRs, especially PBDEs, have lipophilic, persistent, and bioaccumulation propensities, and these chemicals are also being considered by the REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) legislation. For certain types of BFRs, such as TBBPA, HBCDD, etc., exposure pathways and toxicity studies in animals and humans have been published (Feiteiro et al., 2021). HBCDD, an additive BFR, is not chemically bound to the polymers, and has high lipophilicity and low water solubility; these properties enable HBCDD to be highly persistent in water with a half-life of 2,025 days with a high bioaccumulation factor of 18.10 in fathead minnows (Lyman et al., 1982).

Certain BFRs have the capacity to undergo trophic transfer in the human aquatic food chain (Ruan et al., 2018) and phytotoxicity as well (Wu et al., 2012). Nevertheless, human exposure to BFRs is the easiest path, since BFRs (for example, PBDEs) can rapidly move into air, water, soil, food, and feed (ESFA, 2023b). A recent literature review reported that health risks and body burden of BFRs, especially household emissions of PBDEs, are much more serious in children who live in urban areas (Maddela et al., 2020). BDE-209, which is a congener of decaBDE debromination, causes serious health problems in humans. It is to be noted that the legacy and emerging FRs even have the capacity to exhibit maternal transfer in utero in certain types of sharks, for instance the blacknose shark, blacktip shark, Atlantic sharpnose shark, and spinner shark (Marler et al., 2018). Figure 10.5 illustrates the intake values of ∑PBDEs, ∑bromophenols, and PBBZ by infants (Figure 10.5a), and bioaccumulation factor (BAF) in earthworms when subjected to some selected

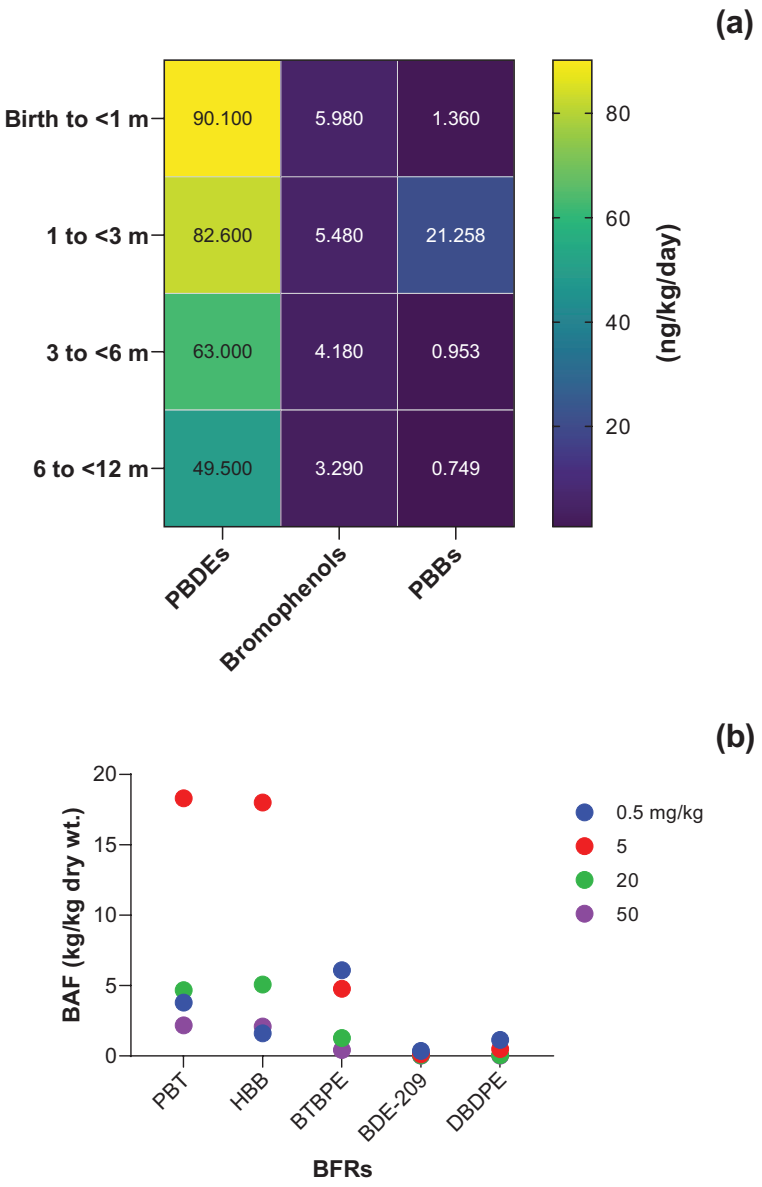


FIGURE 10.5 **(a)** Intake of selected BFRs in children from birth to <12 months (data from Schreder et al., 2023), and **(b)** bioaccumulation factor in earthworms when exposed to the selected BFRs at concentrations of 0.50–50 mg/kg soil (data from Qiao et al., 2022). PBDEs, polybrominated diphenyl ethers; PBBZ, pentabromobenzene; PBT, pentabromotoluene; HBB, hexabromobenzene; BTBPE, 1,2-bis(2,4,6-tribromophenoxy) ethane; BDE, bromodiphenyl ether; DBDEP, decabromodiphenyl ethane.

BFRs at concentrations ranging from 0.50 to 50 mg kg^{-1} soil (Figure 10.5b). Also, the toxicities of major BFRs are shown in Table 10.1.

10.5 REGULATORY CRITERIA

Regarding the protection of human health and the environment, the European Union (EU) has established guidelines on the sales and use of certain BFRs (ESFA, 2023a). The directives 2003/11/

TABLE 10.1
Selected BFRs' Toxicity to Humans and Other Life-Forms

BFR	Host	Impact	Reference
HBCDD	Liver cancer cell line (Hep G2)	Induced cytotoxicity	Zhang et al. (2008)
HBCDD	Neuroblastoma cell line (SH-SY5Y)	Inhibited SERCA (sarcoplasmic-endoplasmic reticulum Ca^{2+}-ATPase), ATP binding and the E2 to E1 transition of SERCA	Al-Mousa and Michelangeli (2014)
HBCDD	Zebrafish embryos	Induced cardiac hypertrophy and arrhythmia (low concentrations)	Wu et al. (2016)
HBCDD	H9C2 cells (cell line of embryonic rat cardiomyocytes)	Induced Ca^{2+} overload from the sarcoplasmic reticulum; increased Ca^{2+}-ATPase activity	Wu et al. (2016)
TBBPA	Zebrafish embryos	Induced toxicity after 96 h of exposure (LC_{50} =1.30 mg L^{-1})	Godfrey et al. (2017)
TBBPA	Fathead minnow	Induced toxicity after 96 h of exposure (LC_{50} =1.30 mg L^{-1})	Pittinger and Pecquet (2018)
TBBPA	Earthworm (*Eisenia fetida*)	Induced toxicity after 14 d of exposure (LC_{50} >500 mg L^{-1})	Chen et al. (2017)
TBBPA	Mouse macrophage cell line (RAW264.7 cell line)	Increased TRAP (tartrate-resistant acid phosphatase) activity and osteoclast differentiation	Park et al. (2019)
TBBPA	Human airway epithelial cells (A549)	Increased caspase-3 activity, ROS generation, and MDA (lipid peroxidation) content	Wu et al. (2018)
TBBPA	Human hepatocellular liver carcinoma cell line (HepG2)	Induced liver cancer disorders	Lyu et al. (2020)
BDE-47	Wistar rat	Decreased testes wt. and sperm number and increased abnormal sperm and altered DNA methylation at 0.20 mg kg^{-1} oral doses	Khalil et al. (2017), Suvorov et al. (2018)
BDE-209	Parkes mice	Decreased testes wt., testosterone, steroid enzymes at 500 and 700 mg kg^{-1} oral doses	Sarkar et al. (2018)

EC and 76/769/EEC entail a ban on the sale of commercial mixtures pentaBDE and octaBDE if the concentration is >0.10% by mass. Directive 2002/95/EC strictly prevents the use of PBBs and PBDEs of any concentrations in new electrical and electronic equipment. The European Court of Justice (ECJ) banned decaBDE in 2008. The European Chemicals Agency (ECHA) has stated that, through the implementation of 'EU-wide restriction', release of aromatic BFRs into the environment can be minimized (ECHA, 2023a). ECHA is also working on whether many aliphatic BFRs and some organophosphorus-based FRs need to be restricted or not; ECHA is expected to reassess the situation of these chemicals by 2025 (ECHA, 2023a). Importantly, according to the latest report of ECHA (March 2023), more than 50% of the registered substances are yet to be either assessed and/or grouped in the list of FRs (ECHA, 2023b) (Figure 10.6).

The other global health agencies are paying attention when they can as several types of BFRs continue to emerge. According to the Stockholm Convention, chemicals listed in Annex A consist of several BFRs, such as decaBDE, HBB, BHCDD, hexaBDE, heptaBDE, HCBD, tetraBDE, and pentaBDE (UNEP, 2019a). Certain BFRs were deemed to be persistent organic pollutants (POPs) and included them in the Annex A by UNEP for the following reasons: (i) they remain intact for exceptionally long periods of time; (ii) they become widely distributed throughout the environment; (iii) they accumulate in the fatty tissues of living organisms; and (iv) they are toxic to both humans and wildlife. Likewise, commercial mixtures of pentaBDE and octaBDE were first listed in the

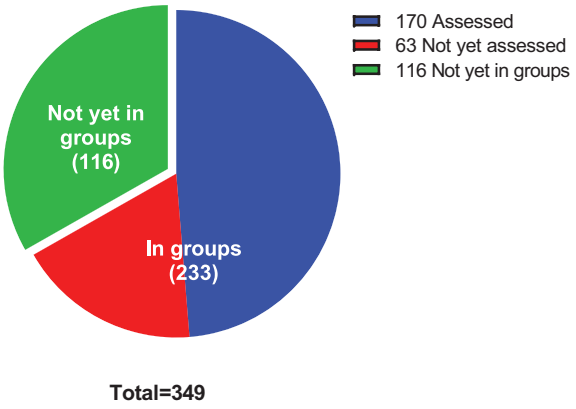


FIGURE 10.6 Number of registered substances and possible regulatory requirements according to the European Chemicals Agency (ECHA) as of 8 June 2022 (data from ECHA, 2023b).

Stockholm Convention in 2004, and subsequently decaBDE emerged as a replacement of former two BFRs (Sharkey et al., 2020). However, due to the POP nature of decaBDE, it was also later listed in the Stockholm Convention in 2019.

According to the Stockholm Convention on POPs, revised text and annexes in 2019 (SC-9/4, SC-9/11, and SC-9/12 of 10 May 2019) (UNEP, 2020), specific exemptions were indicated on the use of BDE-209 in different products, such as vehicles and aircraft spare parts, textiles, plastics, households (heating appliances, irons, fans, and immersion heaters), and PU foam for building insulation. Specific exemptions in the production and use of BFRs are as follows (UNEP, 2020). The production of HBCDD is permitted for the registered listed parties in accordance with the provisions of part VII of Annex A. Specific exemption is applicable on the use of HBCDD in expanded and extruded PS polymers in accordance with the same provisions. Similarly, the use of hexaBDE and heptaBDE is allowed in the articles of the same provision. In this Annex (UNEP, 2020), guidelines were also set on the recycling and final disposal of BFR-containing materials.

Recycling and final disposal of hexaBDE- and heptaBDE-containing materials are permissible under specified conditions, such as a process carried out in an environmentally responsibly way, and that does not focus on the recovery of either of these two BFRs for their reuse. Also, the party needs to avoid the export, import, sale, use, and manufacture of any materials that contain levels or concentrations of hexaBDE and heptaBDE exceeding the accepted values. Nevertheless, the party must notify the Secretariat of its intention to make use of this exemption. In the aim of supporting the transition to safer alternatives, the Stockholm Convention has listed certain alternatives to POP chemicals listed in Annex A (UNEP, 2019b), the details of which are presented in Table 10.2.

10.6 SOIL AND GROUNDWATER ASSESSMENT AND REMEDIATION

Soil samples are assessed for the presence of BFRs by using different analytical techniques. Gas chromatograph-mass spectrometer (GC-MS) has served to assess 55 surface soils (0–20 cm) for the presence of BFRs (Ling et al., 2022). Initially, the samples were freeze-dried and sieved (80-mesh sieves) after manual grinding, and a 3-g soil sample was used for further analysis. Authentic samples of $^{13}C_6$-HBB, and $^{13}C_{12}$-BDE-209 were added to the soil samples before extraction to function as surrogate standards. Sulfur was removed by adding copper powder before extraction. Using 40 mL of acetone and 1:1 (v/v) dichloromethane, samples were extracted in ultrasonic extractor. The extracted samples were concentrated and cleaned utilizing rotary evaporator and alumina/silica columns, respectively. Column eluent consisted of a total of 120 mL n-hexane and dichloromethane

TABLE 10.2
Alternatives to BFRs for Different Plastic Materials

BFR	Alternative Chemicals for Use in Plastics
c-DecaBDE (commercial)	• Decabromodiphenyl ethane • Bisphenol A bis(diphenyl phosphate) • Resorcinol bis(diphenylphosphate) • Ethylene bis(tetrabromophthalimide) • Magnesium dihydroxide • Triphenyl phosphate • Aluminum trihydroxide • Red phosphorus
Hexabromobiphenyl (HBB)	• Tris-chloropropyl-phosphate • Tris-chloroethyl-phosphate • Tris dichloropropyl phosphate
HBCDD in HIPS material	• DecaBDE • Tris(tribromoneopentyl) phosphate/antimony trioxide (ATO) • 2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine/ATO • Ethane-1,2-bis(pentabromophenyl)/ATO • Ethylenebis(tetrabromophtalimide)/ATO
HBCDD in textile back coating material	• DecaBDE • Decabromodiphenyl ethane • Ethylene bis(tetrabromophthalimide) • Chlorinated paraffins • Ammonium polyphosphates
c-OctaBDE in ABS plastic	• Tetrabromobisphenol-A • 1,2-Bis(pentabromophenoxy) ethane • 1,2-Bis(tribromophenoxy) ethane • Triphenyl phosphate • Resourcinol bis(diphenylphosphate) • Brominated polystyrene
c-OctaBDE in synthetic textiles	• Reactive phosphorus constituents • Hexabromocyclododecane
c-OctaBDE in thermoplastic elastomers	• Bis(tribromophenoxy) ethane • Tribromophenyl allyl ether
c-OctaBDE in polyolefins	• Polypropylene-dibromostyrene • Dibromostyrene • Tetrabromobisphenol A (TBBPA)

(v/v = 1:1). A gentle nitrogen flow (99.99%) was used to concentrate the eluates and finally the extracts were redissolved in 1.0 mL of toluene. Samples were analyzed by using GC-MS and concentrations were adjusted using surrogate standards. Likewise, other analytical procedures have also been applied in the assessment of samples for BFRs. For example, LC-MS/MS has been used in the analysis of HBCDDs in mixed engineering plastic materials (Stubbings et al., 2021). Nonetheless, in most investigations, GC, LC, and MS-based analytical procedures have been employed to assess the soils and sediments for different BFRs (Jans, 2016).

For the assessment of water samples (e.g., drinking water, sea water, lake water, river streams, etc.), samples were collected at a depth of 20–50 cm (García-Córcoles et al., 2019). The common criterion in the assessment of water samples for BFRs is as follows. The best volume for assessing samples is 50 mL to 20 L, depending on the analytical method and its sensitivity. Prior to use, collection bottles are rinsed with deionized water and an organic solvent like methanol. Once collected,

samples are subjected to membrane filtration (0.45 µm pore size) and stored at 4°C in brown bottles to prevent the photocatalytic degradation of chemicals which will be analyzed. It is always preferable to examine the samples within 48 h after collection for reliable results (Komolafe et al., 2019).

The analytical techniques applied to assess the water sample were found to be GC coupled with tandem MS (MS/MS), LC coupled with MS/MS, HPLC-UV, HPLC-ICP-MS/MS, etc. (García-Córcoles et al., 2019; Olaniyan et al., 2023). To extract the BFRs from water samples, different types of extraction procedures have been employed, namely liquid-liquid extraction (LLE), solid-phase extraction (SPE), solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), dispersive liquid-liquid microextraction (DLLME), and ultrasound-assisted emulsification microextraction (USAEME) (García-Córcoles et al., 2019). The main advantage in using such extraction procedures is that it is possible to minimize or completely avoid the use of extraction solvent. Figure 10.7 presents the concentrations of BRs determined upon the assessment of surface waters in different countries.

Removal of BFRs from the contaminated site is a challenging issue because of their poorer degradability, persistence, toxicity, and propensity to bioaccumulate. However, available literature suggests that microbial degradation of BFRs is possible (Segev et al., 2007), which gives hope for advocating biodegradation-based approaches either for the removal or the reduction of the toxicity of BFRs in the contaminated environment. Aerobic and anaerobic microbial degradations were found against different BFRs, such as 2,4,6-tribromophenol (TBP) (Arnon et al., 2005), BDE-209 (Gerecke et al., 2006), TBBPA (Welshons et al., 2006), etc. Principal bacteria that were found to degrade BFRs are *Achromobacter piechaudii*, *Desulfovibrio* sp. TBP-1, *Ochrobaceterium* sp. TB01, *Sphingomonas* sp., and *Rhodococcus* sp. 1395. However, according to a recent investigation, even soil macrofauna can remove BFRs from soil (Qiao et al., 2022). Experiments with earthworms and co-exposure to five common BFRs (BDE-209, DBDPE, BTBPE, HBB, and PBT) resulted in different enrichment and removal dynamics. The elimination capacity of earthworms was observed to be much higher for HBB and PBT than other types of BFRs. Added to these approaches, other appropriate methods seem to fit the remediation of BFR-contaminated sites that include biopiles (Lin et al., 2022), biostimulation by suitable organic materials, bioaugmentation, phytoremediation, etc.

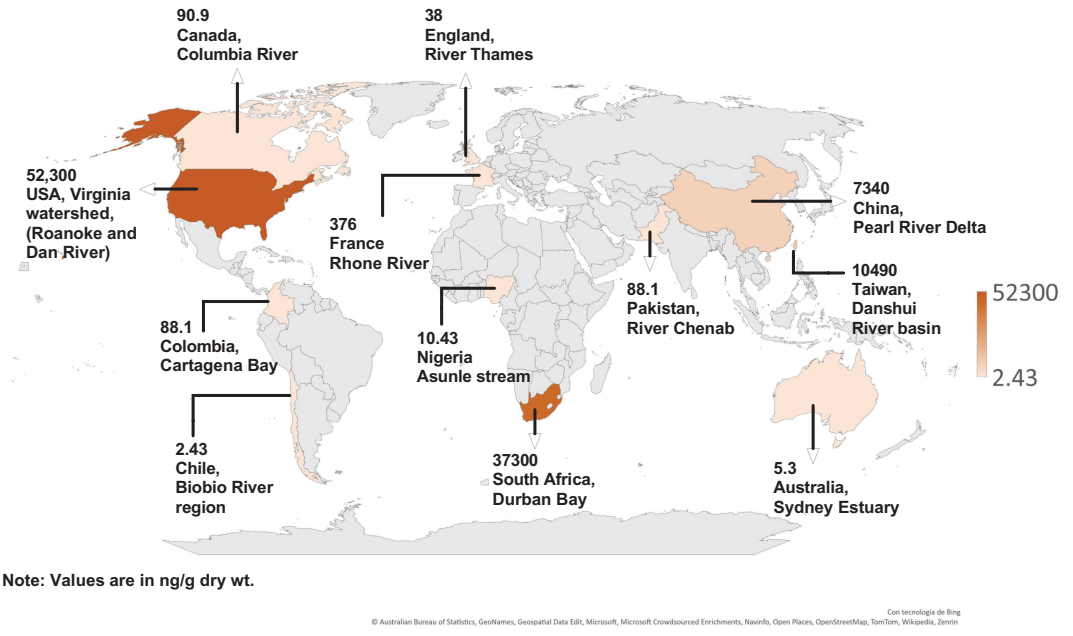


FIGURE 10.7 Occurrence of BFRs in surface water in selected countries (data from Olaniyan et al., 2023).

10.7 CHALLENGES

- One of the challenging issues is finding alternatives to BFRs because substitutes are not 100% equal to BFRs in the applications that BFRs offer (RSCTIG, 2022). In view of what manufacturers claim, BFRs are most favorable in terms of technical, performance, and cost reasons. On the other hand, complete toxicity assessment data are not available for alternatives to the BFRs.
- Mitigation of BFR contamination in certain countries is impossible, especially in developing countries. No guidelines are available for the control of these chemicals in water or sediments of fresh and marine water systems (Olaniyan et al., 2023).
- Assessment of soils and waters for the presence of BFRs is quite complex and generates conflicting results. This situation is attributed to the use and availability of various extraction and analytical procedures for BFRs (García-Córcoles et al., 2019; Olaniyan et al., 2023). Detection limits and sensitivities vary from technique to technique, which makes assessment difficult and leads to discrepancies in the results documented in research studies. Certain types of analytical procedures cannot characterize isomers. For instance, the GC/MS method can only determine total HBCDDs but cannot separate stereoisomers (Schrenk et al., 2021), which causes difficulties in the risk assessment of contaminants. In addition, environmental factors at the contaminated sites have a huge impact on the fate of BFRs (Segev et al., 2009); therefore, results cannot be compared between different studies at the same site either.
- Children are more vulnerable to toxic environmental exposures (Sly and Flack, 2008). There are several unresolved issues related to this area, such as pediatric research, biomarkers, and ethics in children-based research (Peter et al., 2009). Therefore, undertaking biomarker research in vulnerable communities is a challenging issue and for this reason, toxicity assessment in these communities becomes complicated.
- Another challenging issue is improper recycling of BFR-containing waste electrical and electronic equipment (WEEE). For instance, 55% of BFR-containing plastics are not treated by proper WEEE recycling channels in Europe. This situation might be due to consumer failure (i.e., improper sorting of WEEE) and/or implementation of substandard WEEE treatment practices (BSEF, 2020). Therefore, the fate of BFR-containing plastics is of great concern because the pressure on the environment to remove BFRs is great.

10.8 CONCLUDING REMARKS

BFRs compose approximately 20% of the FRs market. BFRs have a wide range of applications in plastics and textile products like electronics, clothes, and furniture. Important BFRs are TBBA, decaBDE, HBCDD, and dechlorane. The content of BFRs in different polymers ranges from 0.1% to 28%; unsaturated polyesters are especially known to contain large amounts of BFRs. They have been reported in different abiotic settings like sediments, surface water, soils, outdoor air, and indoor dust, and biotic environments such as plants, fishes, invertebrates, birds, and humans (Yu et al., 2016). This suggests not only an easy release of BFRs from polymers but also the extent of environmental pollution caused by these chemicals. Since BFRs are easily accessible to the human food chain, they have been detected in food originating from animals, including fish, meat, milk, and others (ESFA, 2023a).

In general, BFRs are not readily degraded; instead they are persistent and subjected to accumulation in the environment. Both abiotic and biotic factors wield a significant impact on the fate of BFRs in the environment (Segev et al., 2009). Certain BFRs like HBCDD and TBBPA have already been linked with different health disorders related to different organs and/or systems – thyroid, neurological, immune, cardiovascular, reproductive, etc. (Feiteiro et al., 2021). In addition, they were found to be oncogenic. Likewise, BFRs are amidst the hashtag of ‘POPs’, and are the main concern

of several global health and environmental organizations such as the WHO, REACH, Stockholm Convention, US EPA, etc. Limited and flexible or ambiguous regulations result in the uncontrolled circulation of BFRs in developing and undeveloped countries. Various analytical methods (e.g., GC, LC and MS, GC coupled with MS/MS, LC coupled with MS/MS, HPLC-UV, HPLC-ICP-MS/MS) have been used in the assessment of BFR-contaminated soils and waters. However, differences in the sensitivities and limits of detection of different analytical procedures led to inconsistent reports on the quantity of BFRs in different environmental samples.

To reduce the risk of BFRs to human health and the environment, future studies are immensely warranted in different fields. More experimental studies are needed with various human cells to confirm the extent of their cytotoxicity. More attention should be paid to searching for suitable alternatives to BFRs. Nanomaterials such as nanohydrogels and nanofluids can be a suitable alternative to hazardous BFRs (Rani et al., 2022). In-depth studies are still required for a better understanding of removal mechanisms of BFRs from soils and sediments.

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11 Per- and Polyfluoroalkyl Substances (PFAS)

Sources, Potential Health Problems, Remediation, and Remediation Challenges

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11.1 INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a family of anthropogenic compounds that are derived from fluorine and have extensive structural diversity and physicochemical characteristics. PFAS are fluorinated aliphatic substances containing at least one carbon atom in their structures on which all hydrogen atoms in the methyl group ($-CH_3$) or methylene group ($-CH_2-$) have been replaced by fluorine atoms (Buck et al., 2011).

PFAS are categorised into polymers such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and non-polymers. The non-polymers are further divided into two individual subclasses, perfluoroalkyl and polyfluoroalkyl substances. A perfluoroalkyl substance is an organofluorine substance with fluorine replacing every possible bonding position on the carbon chain. In contrast, polyfluoroalkyl substances are partially fluorinated, so that all hydrogen atoms are

DOI: 10.1201/9781003530466-11
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TABLE 11.1
List of PFAS Nomenclature and Acronyms

Full Name	Acronym
Ammonium perfluorooctanoate	APFO
Ammonium salt of hexafluoropropylene oxide dimer acid	GenX (HFPO-DA)
Aqueous Film-Forming Foams	AFFFs
Hexafluoropropylene oxide dimer acid	HFPO-DA
Per- and polyfluoroalkyl substance	PFAS
Perfluoroalkyl acid	PFAA
Perfluoroalkyl carboxylic acid	PFCA
Perfluoroalkyl sulfonates	PFSA
Perfluorobutane sulfonic acid	PFBS
Perfluorobutanoic acid	PFBA
Perfluoroether carboxylic acid	PFECA
Perfluoroether sulfonate	PFES
Perfluoroheptanoic acid	PFHpA
Perfluorohexane sulphonic acid	PFHxS
Perfluorohexanoic acid	PFHxA
Perfluorononaoic acid	PFNA
Perfluorooctane sulfonate	PFOS
Perfluorooctane sulphonamide	PFOSA
Perfluorooctanoic acid	PFOA
Polyvinylidene fluoride	PVDF
Polytetrafluoroethylene	PTFE
Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	F-53B
P-perfluorous nonenoxybenzene sulfonate	OBS
6:2 fluorotelomer alcohol	6:2 FTOH
6:2 fluorotelomer sulfonamidoalkyl betaine	6:2 FTAB

TABLE 11.2
List of Acronyms of Additives and Technologies

Full Name	Acronyms
Adsorptive photocatalyst	AP
Advanced oxidation processes	AOPs
Advanced reduction processes	ARPs
Agency for Toxic Substances and Disease Registry	ATSDR
Anion exchange resins	AXRs
Biochar	BC
Biochar – Zero valent iron	BC – ZVI
Boron-doped diamond	BDD
Carbon nanotube	CNT
Centers for Disease Control and Prevention	CDC
Direct electron transfer	DET
Dissolved organic matter	DOM

(*Continued*)

TABLE 11.2 (*Continued*)
List of Acronyms of Additives and Technologies

Full Name	Acronyms
Effluent organic matter	(EfOM)
Electro Fenton – Electrooxidation	EF – EO
Electrochemical advanced oxidation process	EAOP
Electron beam – Persulfate	EB – PS
Granular activated carbon	GAC
Granular activated carbon – Thermolysis	GAC – TM
Hexadecyl trimethyl ammonium bromide	CTAB
Hydrogen peroxide activated by iron modified diatomite	HP – MD
Ion exchange resins	IXRs
Ion-exchange resin – Electrooxidation	IXR – EO
Magnéli phase titanium sub-oxide	Ti_4O_7
Multiwalled carbon nanotubes	MWCNTs
Nanofiltration	NF
Nanofiltration – Electrooxidation	NF – EO
Natural organic matter	NOM
Non-thermal plasma	NTP
Periodate	PI
Permanganate	PM
Persulfate	PS
Powdered activated carbon	PAC
Reactive oxygen species	ROSs
Reverse osmosis	RO
Sodium bicarbonate	$NaHCO_3$
Thermolysis – Photocatalysis	TM – PC
Total oxidisable precursor	TOP
Ultrasound	US
Ultraviolet	UV
The United States Environmental Protection Agency	US EPA
Ultraviolet – Electrooxidation	UV – EO
Wastewater treatment plants	WWTPs

replaced by fluorine on at least one carbon atom (Kemi, 2015; Teymourian, Teymoorian, Kowsari, & Ramakrishna, 2021).

PFAS are water-, oil-, stain-, and soil-repellent, chemically inert, thermally and oxidatively resistant, and amphipathic, and have permittivity, low friction coefficient and refractive index, and low dielectric constant. These features are due to their molecular skeleton containing an inert C-F bond (Ameduri & Fomin, 2020). Consequently, many fields of advanced industrial and consumer technology can benefit from their high-add-value products, such as surfactants and polymers (Améduri, 2022). As a result, these substances have been utilised since the 1950s in many goods and services that improve people's lives (Glüge et al., 2020). For instance, an external surface or a paper product covered by fluorinated tail repels both water and oil, reflecting a developed self-cleaning process (Garg et al., 2020). Subsequently, this feature makes PFAS a potential candidate for extensive usage like paper packaging and textiles (Glenn et al., 2021; Trier, Taxvig, Rosenmai, & Pedersen, 2018). Furthermore, the chemistry of PFAS, especially taking advantage of surface chemistry, echoes their

application in lubricants and mist suppression as well as an emulsifier in fluoropolymer manufacturing (Walkowiak-Kulikowska, 2022).

Widespread exploitation of PFAS, however, may lead to their constant dissemination and ubiquitous presence in the environment, leading to widespread contamination of water supplies, soil, and sediments. For example, training sites for firefighters, wastewater treatment plants (WWTPs), biowastes, and landfill leachate disposal are now deemed potential sources of PFAS. Consequently, this issue poses a risk to the environment, flora, fauna, and most importantly, to humans. Because human and animal bodies are unable to break down strong C-F bonds, PFAS exposure results in their binding to blood proteins and accumulating in organs such as the liver and kidney for a long time (Araújo et al., 2022; Fenton et al., 2021). Unfortunately, according to recent epidemiological assessments, PFAS exposure is directly linked to several adverse health outcomes in both adults and unborn babies, such as thyroid disease, male reproductive system, circumventricular organs, and cholesterol level (Calvert et al., 2022; Kurwadkar et al., 2021; Starnes, Rock, Jackson, & Belcher, 2022; Teymourian et al., 2021).

Thanks to recent advances in analytical chemistry, PFAS quantification is very accurate even in the part-per-trillion (ppt, in mass, or ng/L) scale in the environment. However, global awareness of environmental contamination caused by PFAS has only been evident since the early 2000s, when PFAS was detected in the blood of wildlife in remote zones and in more than 98% of the US population (Sunderland et al., 2019). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most well-known PFAS which have become the most recognisable ones in the environment due to their extensive application and resistance to biodegradation. Both compounds are highly persistent, bioaccumulative, and toxic. In response, some programmes and alternatives for discontinuing these chemicals' so-called PFAS legacy were imposed by the US government and then the European Union (Fujii, Polprasert, Tanaka, Hong Lien, & Qiu, 2007; Sharifan et al., 2021; Sunderland et al., 2019).

To solve the environmental contamination issue, researchers have investigated a variety of remediation techniques to mitigate the damage wrought by PFAS. These techniques include sorption, immobilisation, stabilisation, filtration, coagulation, separation, chemical oxidation/reduction, thermal decomposition, UV/photo-catalytic degradation, etc. As a general classification, all the foregoing approaches can be classified as non-destructive (such as sorption) or destructive (such as degradation, mineralisation) (Kucharzyk, Darlington, Benotti, Deeb, & Hawley, 2017; Ross et al., 2018; Verma, Varma, & Nadagouda, 2021; Wanninayake, 2021).

In this chapter, application of PFAS is investigated in a variety of sectors, including domestic products, commercial exploitation, and industrial and military uses. We also discuss potential sources and contaminated sites associated with PFAS applications directly or indirectly. Additionally, toxicological and epidemiological consequences, especially for humans, of PFAS exposure and distribution in the environment are explained. A summary of guidelines, exceptions, and alternative options announced by relevant organisations is then provided. Our review also focuses on recent developments regarding PFAS remediation technologies, such as categorisation, remediation mediums, advantages and disadvantages, and emerging synergistic technologies. Among them, sonolytic destruction of PFAS is explained in detail, including its advantages and challenges.

11.2 PFAS APPLICATION AND POTENTIAL SOURCES

Figure 11.1 presents a small portion of the widespread usage of PFAS in different sectors, ranging from domestic products to technologically advanced manufacture, including carpets and upholstery, leather, electronics, semiconductors, construction and building, aviation and aerospace, cosmetics, and fire retardants, as well as the automotive industry (Améduri, 2022; Naidu et al., 2020; Walkowiak-Kulikowska, 2022). When PFAS-containing products are no longer useful, they are disposed of in landfills, causing contamination; this not a proper way to handle this material (Gaines, 2022;



FIGURE 11.1 PFAS wide application and some potential sources.

Glüge et al., 2020). Furthermore, PFAS can find a way into the environment at sites where AFFFs are applied, during their disposal at landfills, and in leachate from wastewater treatment plants (WWTPs) (Brase, Mullin, & Spink, 2021; Reinikainen, Perkola, Äystö, & Sorvari, 2022). This issue in turn will contaminate soil/sediments and surface water, then groundwater locally, and ultimately, contamination of remote zones (De Silva et al., 2021; Sunderland et al., 2019).

11.2.1 Manufacturing and Industrial Facilities

As a key component of industry, PFAS are either synthesised as a starting material or used in PFAS-containing products. Industrial activities can release PFAS, mainly fluoropolymers, into the environment by means of atmospheric dissemination, spills, and disposal of manufacturing wastes and wastewater (Shin et al., 2011). As an example, sampling from rivers and streams has been shown to be influenced by nearby fluorochemical manufacturing plants (Boiteux et al., 2017). Also, industrial plants that recycle and incinerate PFAS-containing products, for instance PTFE, are potential sources of these chemicals (Aleksandrov et al., 2019; Björklund, Weidemann, Yeung, & Jansson, 2021). It is worth noting that, as a source point of PFAS, textiles for coating in medical use, etching in producing plastic and rubbers, wiring in electronics, aviation and transportation industry, paper products, cardboard packaging, fluoropolymers, and construction are all suspected (Panieri, Baralic, Djukic-Cosic, Buha Djordjevic, & Saso, 2022). A better way to state this is that those industrial applications of PFAS lead them to being discharged into the environment advertently or inadvertently.

11.2.2 Aqueous Film-Forming Foams (AFFFs)

PFAS is the main component of aqueous film-forming foams (AFFFs) for fire-quenching operations at military sites, airports, and firefighting training activities. The main reasons are due to their low surface tension, considerable spreadability, trace fuel diffusion, and thermal stability to form foam (Brusseau, 2018; Kurwadkar et al., 2021; Vecitis et al., 2010). Through the general mechanism, AFFFs create a vapour-sealing foam surrounding burning fuels to isolate them from atmospheric oxygen and prevent them from re-igniting (Leeson et al., 2021). However, the highest levels of PFAS

contamination are typically associated with AFFF discharges (Reinikainen et al., 2022). In fire extinguishing operations, PFAS can leak in large or trace amounts in the form of a concentrated foam during storage, careless handling during transfer of containers, and calibration and equipment use. A considerable amount of PFAS can also be released into surrounding areas by artificial ponds used to temporarily store water impacted by AFFFs (Bolan et al., 2021). Therefore, surrounding areas including surface water, soils, and sediments, followed by receiving waters and drinking water, are potentially affected by AFFF discharge (Leeson et al., 2021).

11.2.3 Consumer Products

PFAS constitute an inseparable part of household products due to their unique physicochemical properties. They are used in textiles and leather, cosmetic and personal care products, paper and food packaging, non-stick cookware, and electronic devices (Glüge et al., 2020). Much of this usage is due to their simultaneous hydrophobic and hydrophilic properties that repel water, oil, and stains; and their thermal stability makes them able to resist degradation (Kemi, 2015). In cosmetic and personal care products for instance, they are used as emulsion agents, antistatic, stabilising agents, surfactants, film formers, and viscosity controllers leading higher durability and product wear. Furthermore, functionalised textiles containing PFAS with diverse structural composition are used for consumer product applications like leather articles, parasols, carpets, bags, umbrellas, outer garments, etc. (Ahrens, 2011; Herzke, Olsson, & Posner, 2012; Prevedouros, Cousins, Buck, & Korzeniowski, 2006). However, when these products no longer work or are damaged, they are dumped in municipal solid waste management or wastewater facilities, followed by their discharge into the environment.

11.2.4 Solid Waste Management Facilities and Landfill Leachate

Municipal wastes facilities receive huge amounts of solid and liquid wastes from residential, commercial, and industrial sectors (Yalan Liu, Ptacek, Baldwin, Cooper, & Blowes, 2020). Following disposal, a leachate is produced because of permeation of precipitation of solid and liquid waste migrating downward. These wastes typically contain PFAS, mainly polyfluoroalkyl substances such as fluorotelomer-based derivatives known as precursors (Buck et al., 2011; Masoner et al., 2020). Under biotic or abiotic transformation conditions, they may form perfluoroalkyl acids (PFAAs) referred as to terminal PFAS, which can be released into landfills, followed by their accumulation in leachate (Busch, Ahrens, Sturm, & Ebinghaus, 2010; Hamid, Li, & Grace, 2018). The leachate is then directly transferred by waste collection vehicles into WWTPs before their final disposal in surface water supplies (Eggen, Moeder, & Arukwe, 2010). Leachate can, however, be discharged into adjacent groundwater due to inadequate infrastructure and lining of such facilities or during transportation (Brase et al., 2021; Yalan Liu, Robey, et al., 2020). Furthermore, some municipal solid waste facilities are designed to incinerate solid wastes (Solo-Gabriele, Jones, Lindstrom, & Lang, 2020). However, this method produces a considerable amount of ash. Unfortunately, ash is often co-disposed with other unburned wastes in landfills (Yalan Liu et al., 2022). The main causes can be attributed to the capacity restrictions or facility outage, or due to high wetness and vast size of waste materials such as sewage sludge, construction and demolition debris, and furniture. These unburned wastes contain PFAS in landfills (Bečanová, Melymuk, Vojta, Komprdová, & Klánová, 2016; Stoiber, Evans, & Naidenko, 2020).

11.2.5 Wastewater Treatment Plants (WWTPs)

WWTPs receive a large amount of PFAS-containing leachate from industries, solid waste management facilities, and landfill disposal areas (Gallen et al., 2017; Kurwadkar et al., 2021; Robey et al., 2020). Unfortunately, these facilities are not designed to treat PFAS. In WWTPs, conventional

sewage treatment methods or even technologically advanced remediation techniques such as granular activated carbon (GAC), powdered activated carbon (PAC), or reverse osmosis (RO) may not be able to fully remove PFAS (Speth, 2020; Vo et al., 2020). WWTPs also produce PFCAs and perfluoroalkyl sulfonic acids (PFSAs) because of the biodegradation of precursors. Accordingly, PFAS after treatment is released into surface water even with elevated concentrations up to 100 ng/L through point source discharges of effluent, inadvertent leakage from surface impoundments and infrastructure, air emissions via aeration tanks, and disposal of biosolids. Consequently, it is believed that WWTPs are a major source of such compounds in the aquatic environment (Ahrens, 2011; Hamid and Li, 2016).

11.3 FATE, TRANSPORT, AND HUMAN EXPOSURE

PFAS footprints exist everywhere. Manufacturing, utilising, transporting, and disposing and treatment of PFAS-containing materials result in their emission into the environment whether advertently or inadvertently (Brase et al., 2021; Lyu et al., 2022). These compounds are commonly released from industrial waste leachates, AFFFs-utilised organisations, landfills, biosolids, sewage sludge from WWTPs, and consumer products (Berg et al., 2022; Bolan et al., 2021; Masoner et al., 2020; Stoiber et al., 2020). Unfortunately, contamination of different sites caused by PFAS is a cyclical process at the continental scale, with soil and surface water being the primary targets. Groundwater comes next, followed by drinking water which can be contaminated (Figure 11.2).

As stated previously, transformation of PFAS under partial degradation conditions results in formation of PFAAs (Sunderland et al., 2019). These compounds are highly stable and able to be impervious to environmental degradation and amphiphile. Their tendency to accumulate at interfacial regions such as soil-water and air-water interfaces, depending on their chain length, enables them to migrate, affecting all earth systems through oceanic and atmospheric transportation, contributing to global PFAS contamination (Brusseau, 2019; Sharifan et al., 2021).

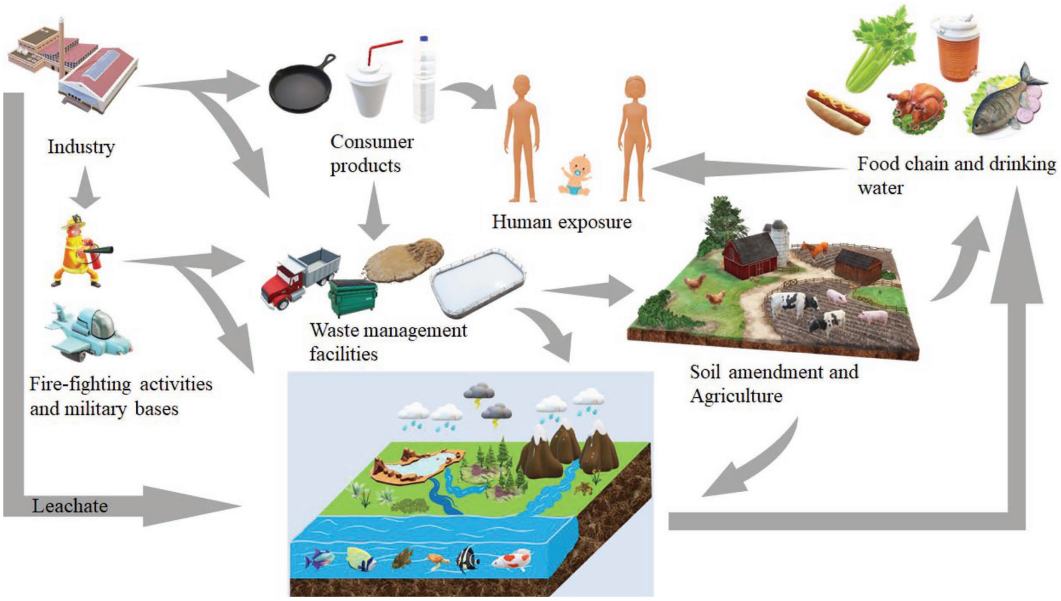


FIGURE 11.2 Conceptual overview of PFAS distribution, environmental contamination, and human exposure.

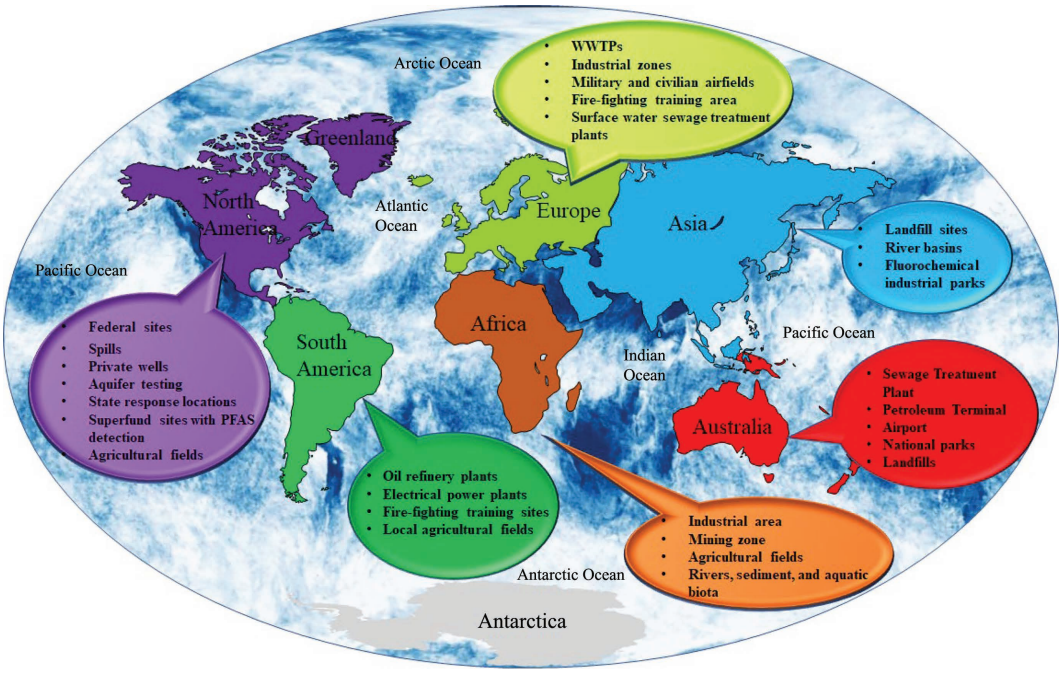


FIGURE 11.3 Schematic of PFAS global contamination with reference to individual continents.

This issue is now very exacerbated in developed countries such as Australia, Germany, Norway, Sweden, the United Kingdom, Canada, and the United States. They have to deal with numerous contaminated sites (Kurwadkar et al., 2021). PFAS contamination and impacted sites on each continent are shown in Figure 11.3 with respect to industrialisation, urbanisation, general observations, and geographical trends. For instance, most of the suspected sites in Australia are relevant to the sewage treatment plants and WWTPs while in Europe and the US, major contaminated sites are those where AFFFs are used or places with direct contact with chemical manufacturing industries (Banzhaf, Filipovic, Lewis, Sparrenbom, & Barthel, 2017; Coggan et al., 2019). Furthermore landfills, recycling, incineration plants, and reusing contaminated sewage sludge plants are other possible contaminated sites mainly located in European countries; these amount to nearly 100,000 sites (Goldenman et al., 2019). Furthermore, on a regional scale, municipal WWTPs are thought to affect streams and rivers in China and Germany (Becker, Gerstmann, & Frank, 2008).

11.4 TOXICITY, EXPOSURE AND RISKS

The ubiquitous presence of PFAS in the environment creates serious problems for ecosystems, animals, and humans. Studies on the toxicology and epidemiology of vegetation and animals exposed to these substances have revealed several intractable issues (DeWitt, 2015). Contaminated soil, for instance, results in diminished seedling size and shoot growth in plants. Furthermore, such chemicals cause earthworms and roundworms to reproduce more slowly and live for shorter periods of time (Kwak et al., 2020).

As for marine and mammal creatures, PFAS can influence their reproductive systems by altering gene and peptide levels, as well as egg production (Kang, Ahn, & Park, 2019). They significantly impact liver, kidney, and spleen functioning in young mice by converting to more stable precursors

that in turn, prevent protein activity (S. Gao et al., 2020; Perera, Miksovska, & O'Shea, 2022). Further, enzyme performance may be affected by hydrogen bonding affinity of PFCAs, as a result of changes in enzyme morphology (H. Guo et al., 2021).

PFAS intake by humans can occur through eating, inhalation, and dermal contact (Teymourian et al., 2021). It is generally the result of consuming contaminated drinking water, food chains (marine food), inhaling indoor air and dust, and being at the mercy of a variety of contaminated settings (Trudel et al., 2008). For instance, PFAS can migrate from paper containing fluorochemicals in food packaging, to food simulants like butter, vinegar, and water/ethanol mixtures, posing a direct human exposure pathway (Begley, Hsu, Noonan, & Diachenko, 2008; Begley et al., 2005; Yuan, Peng, Huang, & Hu, 2016). In addition, PFAS emissions from carpets and furniture designed to repel stains are found in high concentrations in the air and dust in indoor spaces, reflecting inhalation exposure in indoor environments (Fraser et al., 2013; Haug, Huber, Becher, & Thomsen, 2011). Consequently, the intake of such chemicals by humans causes them to accumulate in critical organs where they generally remain for a long time.

It has been demonstrated that PFOA and PFOS, the most commonly detected ones in human bodies, are linked to adverse health conditions, depending on the level of exposure, gender, and duration. It is generally the case that precursors are absorbed by the blood proteins, such as serum albumin and fatty acids, and then accumulate in the tissues after oral ingestion (Kennedy et al., 2004). According to epidemiological studies, exposure to PFAAs has been strongly associated with impaired immune function, thyroid problems, and some life-threatening diseases (Fenton et al., 2021). It is evident that immune system performance is primarily influenced by maternal and childhood factors, resulting in a poorer vaccine response (DeWitt, 2015). As a result of damaged thyroid hormones, chronic kidney cancer, liver toxicity, and systemic effects can result from PFAS exposure (Joensen et al., 2009; Omo-Okoro, Daso, & Okonkwo, 2018; Post, Louis, Cooper, Boros-Russo, & Lippincott, 2009). Cancerous diseases and tumours such as breast cancer can also be worsened by long-term exposure to these chemicals. During exposure, male and female reproductive systems are affected, resulting in altered fertility hormones, poor pregnancy chances, pre-eclampsia in pregnant women, and delayed childhood development (Chohan et al., 2021; Preston et al., 2022; X. Wang et al., 2014). Exposure may affect articulation and memory-related abilities in children aged 4–5 (Carrizosa et al., 2021). Adiposity, neurodevelopmental disorders, and developmental disorders in childhood are also associated with parents' exposure to these substances (Fenton et al., 2021). Similarly, studies on unborn and newborn infants have revealed the same trend. Because PFAAs can cross the placenta and are excreted in breast milk, they pose a dangerous threat to the unborn and nursing infant (Fenton et al., 2021; Gyllenhammar et al., 2018). The reason is that infants have a smaller blood volume and mass, which makes them more susceptible to higher PFAA concentrations (Koponen et al., 2018). Maternal exposure reduces fetal growth, increases hypertension, and affects estrogen balance (H. Wang et al., 2019). Figure 11.4 illustrates a small sample of negative health effects of human exposure to PFAAs (DeWitt, 2015; Dickman & Aga, 2022; Fenton et al., 2021; Teymourian et al., 2021). Accordingly, to minimise this health-related issue, further precautionary measures including administrative regulations and sustainable remediation are needed due to the toxicological and epidemiological effects of these chemicals.

11.5 HISTORICAL GUIDELINES, ADMINISTRATIVE POLICIES, AND LEGISLATIVE BANS

PFAS have been used in many scenarios for more than 8 decades due to their unique features (Glüge et al., 2020). This dates back to the late 1930s with the accidental discovery of polytetrafluoroethylene (PTFE) by Dr. Roy Plunkett who was trying to invent a better coolant gas while working for DuPont (Plunkett, 1986). Later in 1949, the commercial production of PTFE was initiated by DuPont. Around the same time, fluorochemical technology was being developed by 3M, which was

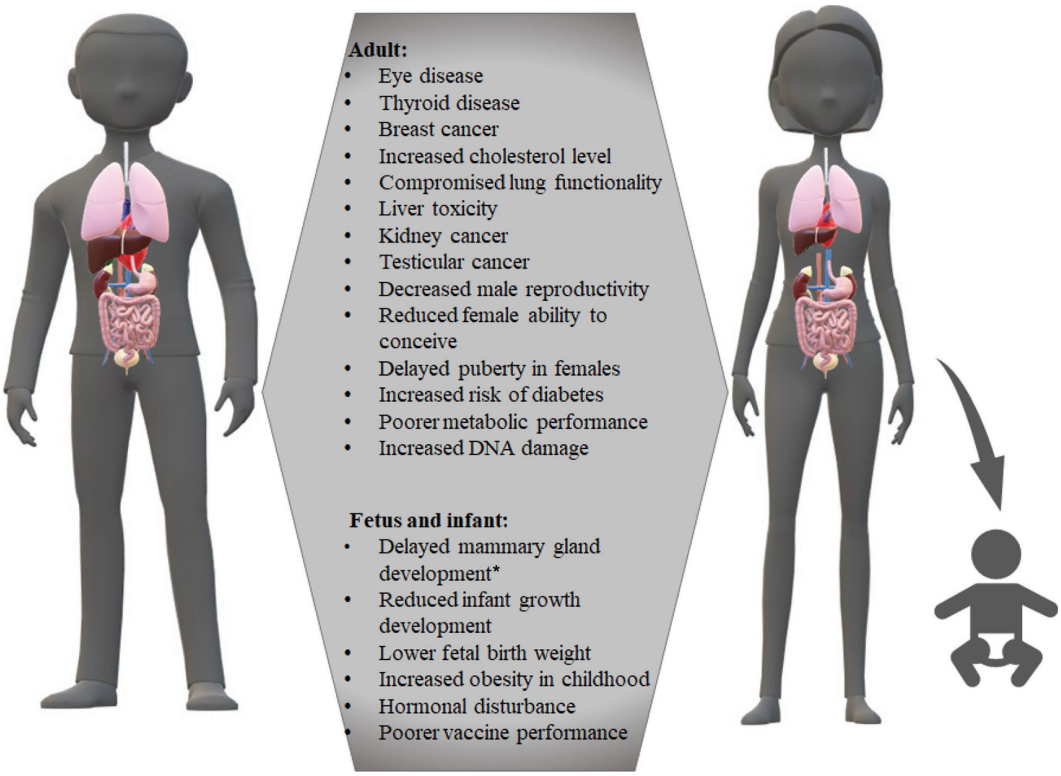


FIGURE 11.4 Adverse health effects when humans are exposed to PFAS.

then known as the principal universal manufacturer of PFAS (Buck et al., 2011). Mass production of these substances continued until the early 2000s when PFOS was detected in arctic wildlife, located far from the source of origin (Giesy & Kannan, 2001). Further investigations revealed that PFOS exposure can occur through the marine food web, and then in 2002, the US Centers for Disease Control and Prevention (CDC) announced officially that these compounds are virtually identifiable in more than 98% of the US population (Calafat, Wong, Kuklenyik, Reidy, & Needham, 2007; Control & Prevention, 2009; Lewis, Johns, & Meeker, 2015). Meanwhile, following negotiations between the EPA and 3M, the company voluntarily discontinued producing the parent compound, perfluorooctane sulfonyl fluoride, which is utilised in manufacturing of PFOS and PFOSA (perfluorooctane sulphonamide). Further measures were taken for some PFAS, replacing them with new alternatives configured with shorter chains such as GenX (ammonium salt of hexafluoropropylene oxide dimer acid [HFPO-DA]), F-53B (potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate), and OBS (p-perfluorous nonenoxybenzene sulfonate) (B. Xu et al., 2021). These new options are regarded as being less toxic and recalcitrant due to their distinct chemical structure and shorter biological elimination half-lives compared to PFOA and PFOS (Gannon et al., 2016; Gannon et al., 2011; Nilsson et al., 2010; Olsen et al., 2009).

A stewardship program was launched in 2006 to eliminate long-chain compounds by 2015. PFOS in 2009 was included in Annex B of the Stockholm Convention (confinements and some certain exemptions) as a persistent organic pollutant (POP) (Sunderland et al., 2019). In a parallel development, 3M suspended PFOA production as did other producers such as Arkema,

Asahi Glass, BASF (Ciba), and DuPont. Then, in 2019, PFOA and several exemptions on PFOS utilisation were introduced in Annex A of the Stockholm Convention to ban their manufacture (USEPA, 2015).

The United States Environmental Protection Agency (US EPA) also considered provisional health-based drinking water legislation and accompanying regulations in 2009. The main cause was the widespread contamination of drinking water throughout the US, affecting more than 6 million people, especially those living close to impacted areas. Drinking water health advisory limits were established by the US EPA at 200 ng/L for PFOS and 400 ng/L for PFOA. The US EPA updated this value in 2016 to 70 ng/L for a mixture or individual concentrations of PFOA and PFOS in drinking water (https://www.epa.gov/sdwa/drinking-water-health-advisories-pfoa-and-pfos), and 300–7000 ng/L for short-chain counterparts (X. C. Hu et al., 2016; Sunderland et al., 2019; Verma et al., 2021). In 2018, the Agency for Toxic Substances and Disease Registry (ATSDR) further reduced these levels to 11 ng/L for PFOA and 7 ng/L for PFOS (ATSDR, 2018). The US EPA (https://www.epa.gov/sdwa/questions-and-answers-drinking-water-health-advisories-pfoa-pfos-genx-chemicals-and-pfbs), however, updated the PFAS health advisory limits to 0.004 ng/L, 0.02 ng/L, 2000 ng/L, and 10 ng/L for PFOA, PFOS, PFBS, and GenX, respectively, in 2022. This was done to protect people from suspected health dangers associated with prolonged exposure to these substances (USEPA, 2022c). Subsequently, in 2023, the US EPA established enforceable maximum contaminant levels (MCLs) for six PFAS, including PFOA and PFOS, at 4 ng/L (4 ppt) each, marking the first federal drinking water standards for PFAS under the Safe Drinking Water Act (USEPA, 2023). It is important to note that drinking water contamination normally follows surface and groundwater contamination. Despite this, only a few states in the US established official surface water criteria in 2022 (USEPA, 2022a, 2022b). The major implication of this is that surface water supplies might take precedence over drinking water sources. As a whole, because reducing PFAS contamination in environmental matrices to below the aforementioned health advisory levels is quite challenging, advanced remediation techniques are urgently required.

11.6 REMEDIATION

In the past few decades, scientists have explored and developed numerous remediation techniques to deal with widespread environmental contamination caused by PFAS. These techniques are generally classified into two categories, non-destructive and destructive methods. Adsorption, immobilisation, stabilisation, filtration, coagulation, and isolation are regarded as non-destructive methods while chemical redox, incineration, UV/photocatalytic degradation, ultrasonication, and electrochemical degradation are considered as destructive ones (Dickman & Aga, 2022; Kucharzyk et al., 2017; Verma et al., 2021; Wanninayake, 2021). Due to the persistent nature, generation of intermediates during remediation, and quantitative detection limit in analytical methods of PFAS, all techniques can still be utilised at the laboratory scale; this method continues to grow (Chropeňová, Karásková, Kallenborn, Gregušková, & Čupr, 2016).

11.6.1 Water Remediation

11.6.1.1 Non-Destructive Technology

All non-destructive water remediation approaches are based on precipitation and phase separation processes designed to transfer high concentrations of PFAS from aquatic media to the solid surface (Ross et al., 2018). The most common and effective techniques are adsorption processes (e.g., granular and powder activated carbon [GAC and PAC], biochar, modified clay sorbent [matCARE™ Composite], and ion exchange resins [IXRs]), filtration methods (e.g., nanofiltration, NF), and reverse osmosis (RO) (Dixit, Dutta, Barbeau, Berube, & Mohseni, 2021; Hassan, Liu, Naidu, Du, & Qi, 2020; T. Lee, Speth, & Nadagouda, 2022; C. Wu, Klemes, Trang, Dichtel, & Helbling,

2020). However, these techniques come with added costs of adsorbent regeneration and operational conditions, creation of waste sludge, and low to moderate efficiency due to the presence of co-contaminants in real water matrix (Kucharzyk et al., 2017; Sörengård, Östblom, Köhler, & Ahrens, 2020). More importantly, these methods are not only unable to destroy PFAS but they might also further enhance the potential risk of secondary contamination if simply disposed of/stored in landfills (Simon et al., 2019). Consequently, destructive methods are favoured although there has been limited success in their development to date (Kazwini et al., 2022; Wanninayake, 2021).

11.6.1.2 Adsorption

A number of commercial and synthetic adsorbents have been investigated for concentrating and eliminating PFAS from aquatic environments. The most common adsorbent used so far is carbonaceous material such as activated carbon (AC), in both granular and powder form (C. J. Liu, Werner, & Bellona, 2019; Murray et al., 2019). Due to its high hydrophobicity and specific surface area, AC can adsorb a considerable amount of PFAS (up to 1,000 mg/g levels), mainly PFOA and PFOS, through hydrophobic interaction (D. Zhang, He, Wang, Zhang, & Liang, 2021). Furthermore, AC – specifically GAC – has been used extensively to remove PFAS from municipal wastewater treatment and domestic point entry systems (Ross et al., 2018). Despite this, GAC is not cost-effective and its utility is limited to long-chain compartments because short chains result in reduced hydrophobicity, compromising GAC removal efficiency (Inyang & Dickenson, 2017). Moreover, the non-selectivity and poor regeneration of GAC in the presence of coexisting species, such as dissolved organic matter (DOM), are other disadvantages of employing such adsorbents (Gagliano, Sgroi, Falciglia, Vagliasindi, & Roccaro, 2020).

When compared to AC, matCARE™ technology proved to be more effective in treating PFAS, particularly PFOS, PFOA, PFHxS, GenX, and other 25 PFAS that could be quantitatively detected by analytical techniques. This composite can remove PFAS even when co-contaminants are present. The matCARE™ Composite (patent number 2009905953) is a modified fibrous clay (palygorskite-based material modified with oleylamine), developed by crc CARE (Cooperative Research Centre for Contamination Assessment and Remediation of Environment, Australia), that is able to trap and immobilise PFAS molecules for remediation of soils, surface water, and groundwater contaminated by PFAS (Das, Arias E, Kambala, Mallavarapu, & Naidu, 2013; Mukhopadhyay et al., 2021). In Australia, a variety of contaminated sites have been treated by matCARE™ technology, including Darwin (Northern Territory), Edinburgh and Adelaide Airport (South Australia), Pearce (Western Australia), and Townsville (Queensland). As an example, AFFF's wastewater treatment plant at the Edinburgh Royal Australian Air Force Base successfully treated >99% of PFAS including 99.7% of PFOS and 98.8% of PFOA, 5 g/L within a 918,000 litre volume (CARE, 2020; Piw, Venkata, Megharaj, & Ravi, 2010). This technology using nano-matCARE™ composite has been applied to contaminated concrete in the form of a slurry and enabled 99.97% of PFAS to be locked up for a short period of time and in total, 99.61% after more than one year. A key point to keep in mind is that matCARE™ is considered the most effective PFAS remediation technology currently on the market. However, due to the limitations of this analytical instrument in detecting PFAS level, at least 2 ng/L concentration in remediated media, it is still not yet 100% effective. Nonetheless investigations are being carried out to achieve 100% effective and permanent remediation (CARE, 2020).

Biochar (BC) has also been reported in much literature as a practical and environmentally friendly adsorbent for remediation of a wide range of organic and inorganic contaminants (Murtaza et al., 2022). BC displays a natural propensity to have alkaline pH, containing a small amount of minerals and volatile organic compounds ranging from 40% to 75% carbon content; it is not degraded by microorganisms (Graber et al., 2010; Tan et al., 2015). This translates into a high chemically and biologically stable structure compared to other legacy carbon sources (Ahmad et al., 2014). The sources of BC are found in plant waste, wood chips, crop residues with remarkable variations in compositions, and animal litter (T. Lee et al., 2022; Mohan, Sarswat, Ok, & Pittman

Jr, 2014; K. Yang, Wang, Zhu, & Xing, 2006). Due to the profusion of biochar in feedstock, its production through biomass pyrolysis in a zero-/low-oxygen setting, for example, is much cheaper than that of AC ($246/ton vs. $1,500/ton) (Ahmad et al., 2012). Taking advantage of its widespread availability, low production costs, and advantageous physicochemical properties, this make biochar a viable option for PFAS removal (Inyang & Dickenson, 2017; Mohan et al., 2014; D. Zhang et al., 2021). In the adsorption process, interaction of biochar with PFAS can be varied from hydrophobic to ionic, depending on number elements including conversion temperature, residence time, type of feedstock, pyrolytic condition, and operational design (Ahmad et al., 2014; W. Guo, Huo, Feng, & Lu, 2017; Lehmann & Joseph, 2015).

For instance, pyrolysis is an influential parameter in determining BC characteristics (Ahmad et al., 2014). High temperature pyrolysed BC has a large surface area with great microporosity and large carbon content, while BC obtained by low temperature has a smaller pore volume containing oxygen-rich functional groups (hydroperoxide, -CO, and, COOH) (Y.-F. Huang, Cheng, Chiueh, & Lo, 2017; X. J. Lee, Lee, Gan, Thangalazhy-Gopakumar, & Ng, 2017; Murtaza et al., 2022; Tomczyk, Sokołowska, & Boguta, 2020). However, it has been widely reported that GAC generally and somehow helps create a higher adsorption capacity and faster kinetics compared with BC. The main reason for this can be explained by larger surface area and bigger pore size in GAC (H. Chen, Chen, Quan, Zhao, & Zhao, 2009; Inyang & Dickenson, 2017; Yu, Zhang, Deng, Huang, & Yu, 2009; D. Zhang et al., 2021). Consequently, biochar might need to be engineered by rectified surface using functionalities such as metal oxides, carbon nanotubes, and graphene, leading to better PFAS decontamination (Hassan et al., 2020; Y. Zhang et al., 2023).

In the adsorption process, the type of interaction between adsorbent/adsorbate plays a key role. It is important to note that, regardless of hydrophobic interaction, the adsorption process may also involve electrostatic interaction, hydrogen bonding, and ligand and ion exchange (Du et al., 2014). In addition to the hydrophobic interaction, the electrostatic one is significant in the adsorption process, mainly occurring between positive charge of the adsorbent molecules and anionic species of PFAS (Hassan et al., 2020). This process is primarily controlled by pH value with acidic regions potentially elevating the adsorption capacity, whereas alkaline regions decrease it (Hussain, Janisse, Heffern, Kinyua, & Velázquez, 2022). Many researchers, however, argue that PFAS adsorption is driven by hydrogen bonds between head groups in PFAS, and oxygen- and nitrogen-containing groups functional groups in adsorbents (X. Gao & Chorover, 2012; Takayose, Nishimoto, & Matsui, 2012). In ligand and ion exchange interactions on the other hand, functional groups of PFAS are most likely adsorbed by functionalities on some adsorbents. Examples here are metal oxides and ion exchange resins through exchange reaction, forming inner sphere and outer sphere complexes (X. Gao & Chorover, 2012). Even so, to achieve maximum adsorption, investigated adsorbents may have to be engineered and functionalised with interactive substitutions incorporating the aforementioned interactions, requiring further research and funding.

11.6.1.3 Filtration and Reverse Osmosis

Filtration is an efficient technique to remove PFAS by forcing pressurised contaminant fluids through a semipermeable membrane (Meegoda, Kewalramani, Li, & Marsh, 2020). NF and RO membrane systems have confirmed that PFAS can be effectively removed while microfiltration and ultrafiltration were greatly inefficient (Appleman et al., 2014; Dickenson & Verdugo, 2018). These approaches can remove a wide range of PFAS regardless of their chain lengths, and this capacity could be reasonably expected to translate to PFAAs and their precursors (Ross et al., 2018). However, there are a number of limitations to these treatment systems which might dictate their performance: subpar efficiency, low throughput flow rates, contaminant rejection, background constituents, pH, charge, and molecular size of the individual PFAS (Tow et al., 2021). The filtering membrane might be blocked by suspended particles and geochemistry of the water which potentially increases the costs when fouling occurs (Horst et al., 2018; Page et al., 2019). In addition to all the foregoing, the most problematic issue remains the obstacles of treating and disposing of concentrated waste streams. It

is therefore necessary to conduct further research on developing used membranes based on recovery strategies, their selectivity for specific PFAS molecules, and their ability to remove PFAS without adsorption on the membrane.

11.6.1.4 Anion Exchange Resins

Anion exchange resins (AXRs) are a promising alternative to AC and can be applied to treating natural water (Dixit, Barbeau, Mostafavi, & Mohseni, 2019; Rahman, Peldszus, & Anderson, 2014). This method is of great interest due to its operational simplicity, considerable effectiveness, small footprint, and regenerative capabilities (Caltran, Heijman, Shorney-Darby, & Rietveld, 2020; Dong, Lin, & SenGupta, 2020). Generally in this process, counter ions with negative charge such as, Cl^-, OH^- and HCO_3^- are exchanged reversibly from a polymeric resin to its surrounding aquatic media (Levchuk, Màrquez, & Sillanpää, 2018). This technique is also efficient in removing background organic and inorganic anions simultaneously (Dixit, Barbeau, & Mohseni, 2018).

Recent studies on PFAS removal have revealed that AXRs can efficiently remove them, particularly short-chain compartments, compared to carbonaceous material which is unable to remove them (Gagliano et al., 2020). For PFAS removal, the most common AXRs that have been used so far are polystyrenic-based skeleton ones, based on the single use-and-dispose mode (Park, Daniels, Wu, Ziska, & Snyder, 2020). PFAS in this system is removed through ion exchange, hydrogen bonding, and hydrophobic and electrostatic interactions. In light of this, a number of contributing elements could impact AXR's performance including polymer composition, pore structure, functional group, pH, and water matrix (Dixit, Barbeau, Mostafavi, & Mohseni, 2021). For example, in real water matrix, there are a number of compounds including natural organic matter, effluent organic matter, and inorganic species which can be captured by AXRs. These compete with the PFAS removal process, affecting the efficiency of AXRs (Appleman et al., 2014; Maimaiti et al., 2018). Despite this, methanol, which is the most commonly used solvent for regeneration of AXRs, is toxic and can cause a highly concentrated contaminant layer to form. It is usually known as a 'still bottom' (S. Liang, Pierce Jr, Lin, Chiang, & Huang, 2018). Thereby, a secondary destructive technique is required to effectively degrade this PFAS-concentrated 'still bottom' such as electrochemical oxidation (Lu, Sha, Luo, Huang, & Jackie, 2020).

11.6.1.5 Destructive Methods

Traditional water treatment techniques have proven to be ineffective in destroying PFAS contamination, leading to new destructive techniques being devised. These techniques to destroy PFAS are not fully understood yet, but most likely occur through free radicals and oxidative mechanisms, known as advanced oxidation processes (AOPs) (Kucharzyk et al., 2017; Wanninayake, 2021). Moreover, these methods not only aim to break down the strong C-F bond, but also mineralise it into non-hazardous and less toxic species such as CO_2, F^-, and others, depending on the structure of PFAS (Lei, Tian, Sobhani, Naidu, & Fang, 2020). Despite this, the AOP requires chemicals or other supports such as UV, serving as a catalysis to generate $\cdot OH$ radicals (Tang et al., 2012).

The most common destructive approaches are heat-activated persulfate, electrochemical advanced oxidation, ultrasonication, advanced reduction processes, plasma-based degradation, and zero valent iron reduction (Nzeribe, Crimi, Mededovic Thagard, & Holsen, 2019; Ross et al., 2018; Stratton et al., 2017). Of these methods, electrochemical advanced oxidation and ultrasonication have garnered much attention because of their durability, non-secondary contaminants, and considerable efficiency in mineralising PFAS skeletons into less hazardous products (Lei et al., 2020; H. Lin et al., 2018). Nevertheless, considering the number of drawbacks like energy consumption, generation of reaction intermediates, and discrepancies in mass balance, further investigation is required of these problems so that they are addressed.

11.6.1.6 Electrochemical Advanced Oxidation Process (EAOP)

Among available destructive remediation techniques, EAOP has revealed promising results for overcoming some drawbacks in AOPs, generating *in situ* reactive oxygen species (ROSs). PFAS can be oxidised electrochemically either through free radical attacks, mainly hydroxyl radicals (•OH), or electron transfer from PFAS to the anode (Fang, Sobhani, Niu, & Naidu, 2018; J. Niu, Li, Shang, Xu, & Liu, 2016; Vecitis, Park, Cheng, Mader, & Hoffmann, 2009). Furthermore, EAOP is promising due to its mild reaction condition, simple operation, chemical-free approach, less production of intermediates, and complete mineralisation (Hwang et al., 2022; M.-K. Kim, Kim, Kim, Joo, & Zoh, 2020; F. Liu, Jiang, You, & Liu, 2023; Saeidi, Kopinke, & Georgi, 2021).

In EAOP approaches, electrode material, applied voltage, supporting electrolyte, and solution pH play a key role in the method's performance (H. Lin et al., 2018; Shi et al., 2019). Of the aforementioned influencing factors, electrode material is critically significant. The main reason for this is that reaction mechanism is dependent on the direct electron transfer (DET) process which is a rate-limiting step of this approach. To make it happen, high anodic potentials are required (Zaky & Chaplin, 2013; Zhuo et al., 2016). Anode material is generally divided into non-active and active types, depending on their oxygen overpotential and strength of interaction between the anode and generated oxidising agents. Non-active anodes are those which show low interaction between anode and oxidising agents and high oxygen overpotential whereas active ones exhibit a reverse trend (Serrano, 2018). Thus, physicochemical characteristics of the electrode such as conductivity, porosity, robustness, and skeletal features should be considered.

So far, boron doped diamond (BDD), Ti/SnO_2-Sb, PbO_2, and Magnéli phase titanium sub-oxide (Ti_4O_7) as anodic electrode (usually > 3.0 V vs. SHE) have indicated promising results in PFAS degradation (Fang, Sobhani, Niu, & Naidu, 2019; Le, Haflich, Shah, & Chaplin, 2019; H. Lin, Niu, Ding, & Zhang, 2012; Uwayezu et al., 2021) (Table 11.1). Nonetheless, these electrodes have a number of drawbacks. BBD anodes for instance, are expensive (~ \$7,000/m^2) and difficult to prepare with specified geometries for large-scale applications (Chaplin, 2019). Furthermore, PbO_2 electrodes can potentially release toxic Pb into the solution during the reaction which potentially produces secondary contamination (Panizza & Cerisola, 2009). Ti_4O_7 anodes in recent years have displayed promising performance compared to the aforementioned anodes due to their high conductivity, proven stability in aggressive solutions, remarkable energy efficiency, cost-effectiveness, and availability (H. Lin et al., 2018). Besides, Ti_4O_7 acts as both an active and non-active electrode for DET and •OH production (L. Wang et al., 2021). Even so, owing to oxygen defects in Ti_4O_7 configuration, its behaviour under anodic oxidation conditions is complicated and challenging, necessitating further investigations and validations.

As noted earlier, applied current density, supportive electrolyte, and solution pH can potentially contribute to the greater efficiency of EAOP. Increasing the current density results in producing more ROSs which in turn, facilitates two things: free radical attack and improved decay rate in PFAS degradation (L.-H. Yang et al., 2022). Supportive electrolyte on the other hand not only contributes to electro-generation of oxidants such as sulphate and chlorin species, but also enables the passage of electrical current in the electrochemical cells (Canizares, Paz, Lobato, Sáez, & Rodrigo, 2006; Titchou et al., 2021). Solution pH can also tune the stability of oxidative factors in the solution, oxygen evolution potential, and lifespan of electrode service (F. Liu et al., 2023). Acidic media for example, might promote •OH formation and affect its redox potential by shifting from the neutral region to the acidic one (1.8–2.8 V) (C. Liang & Su, 2009; W. Wu, Huang, & Lim, 2014). More importantly, conductivity and wettability of the electrode surface could be influenced by solution pH, followed by influencing PFAS degradation (Radjenovic, Duinslaeger, Avval, & Chaplin, 2020).

In addition to EAOP, electro-adsorption and electro-coagulation have been explored for PFAS degradation. Electro-adsorption is an applicable technique which is a Faraday-free process, meaning that electron transfer does not occur during the reaction. Thus, the mechanism is mainly based on the adsorption process, taking advantage of applied voltage (Ma, Huang, Chou, Den, & Hou,

TABLE 11.3
Electrochemical-Based Techniques for PFAS Destruction in Aquatic Settings

Anode Material	Technology	PFAS	Operational Scenario	Results: Removal (%)	Results: Defluorination (%)	Ref
PbO_2	Extracted PbO_2 panel from lead acid battery	PFOA PFOS 6:2 FTS[a]	5 A (10 cm × 10 cm and 1 cm gap), Na_2SO_4 (10 mM), 0.1 g/L NaF + 0.5 g/L Ce $(NO_3)_3$, PFAS (10 μM, 1000 mL), and 6.0 h	> 99	~59 ~60 ~ 0.5	(Fang et al., 2019)
	Tubular PTFE-doped on PbO_2 anode supported over a ceramic (ceramic/PbO_2-PTFE)	PFOA	15 mA/cm^2 (2.0 cm gap), Na_2SO_4 (15 mM), pH ~7, PFAS (20 mg/L, 800 mL), and 6.0 h	90	52.5	(Lou et al., 2022)
	Zr-doped nanocrystalline PbO_2 at 75°C (75-Zr-PbO_2)	PFOA	10 mA/cm^2 (1 cm gap), $NaClO_4$ (10 mM), pH 4.8, PFAS (100 mg/L, 100 ml), and 1.5 h	97	88.1	(Z. Xu, Yu, Liu, & Niu, 2017)
	Ce-doped modified porous nanocrystalline PbO_2 coated on Ti/SnO_2-Sb (Ce-PbO_2)	PFOA PFHpA PFHxA PFPeA PFBA	20 mA/cm^2 (15 cm × 6.5 cm × 1 mm and 1 gap), $NaClO_4$ (10 mM), PFAS (100 mg/L, 100 mL), and 1.5 h	~ 97 ~ 98 ~ 78 ~ 41 ~ 32	~ 82 ~ 86 ~ 62.5 ~ 27.5 ~ 15	(J. Niu, Lin, Xu, Wu, & Li, 2012)
	Hydrophobic polyvinylidene fluoride doped (1.0 wt%) on PbO_2 (PVDF-PbO_2)	PFOA	40 mA/cm^2 (4.2 cm × 4.2 cm and 1 cm gap), $NaClO_4$ (1.4 g/L), pH 3, PFAS (100 mg/L, 200 mL), and 3.0 h	~ 92	31	(Zhuo et al., 2017)
	Layered PbO_2 with TiO_2 and Ag_2O (Ti/TiO_2-NTs/Ag_2O/PbO_2)	PFOS PFHxS PFBS	30 mA/cm^2 (3 cm × 2 cm and 1 cm gap), $NaClO_4$ (1.4 g/L), PFAS (0.0929 mM, 90 mL), and 3.0 h	~ 75 ~ 15 ~ 5	~ 11.5 ~ 2 ~ 0.7	(Zhuo et al., 2016)
BDD	Ultrananocrystaline boron doped diamond coated on niobium, circular mode system (Nb-BDD)	PFOA	200 A/m^2 (8.4 cm × 50 and 0.8 cm gap), flowrate (1.11×10^{-4} m^3/s), $NaClO_4$ (1.4 g/L), PFAS (100 mg/L), and 6.0 h	93	95[b]	(Urtiaga Mendia, Fernández González, Gómez Lavín, & Ortiz Uribe, 2015)
	Facilitated electron transfer using titanium wire (reduction of physical resistance) Si-BDD	PFOA PFHxS PFOS	40 mA/cm^2 (3 cm gap), Ti wire (1 mm) Na_2SO_4 (10 mM) + NaCl (2.0 mM), PFAS (1 mg/L, 350 mL), and 5.0 h	~ 89 ~ 88 94	~ 89 82 82.5	(Sukeesan, Boontanon, & Boontanon, 2021)
	Combined applied current density in designed timeframes (Nb-BDD)	PFOA	50 mA/cm^2 for first 25 mins and 5 mA/cm^2 for the remained 45 mins (3 mm gap), Na_2SO_4 (50 Mm), PFAS (6–6.5 mg/L), and 1.0 h	~ 100	75	(Ensch, Rusinek, Becker, & Schuelke, 2021)

(*Continued*)

TABLE 11.3 (*Continued*)
Electrochemical-Based Techniques for PFAS Destruction in Aquatic Settings

Anode Material	Technology	PFAS	Operational Scenario	Results: Removal (%)	Results: Defluorination (%)	Ref
	Dependence of removal efficiency on enhanced anodic potential (Si-BDD)	PFDeA PFOA PFHxA PFBA PFOS PFHxS PFBS	23.24 mA/cm^2 (25 mm × 34 mm and 30 mm gap), $NaClO_4$ (1.4 g/L), PFAS (0.114 mM), and 2.0 h	~ 97.5[c]	~ 50[d] ~ 60 ~ 70 ~ 80 ~ 70 ~ 68 ~ 50	(Zhuo et al., 2012)
	Flow-through electrooxidation of groundwater amended by AFFFs (Nb-BDD)	AFFFs (3M)	25 mA/cm^2 (10 cm^2 and 4 mm gap), Na_2SO_4 (500 mg/L), AFFFs (0.02 mL in 250 mL groundwater), and 8.0 h	NA	NA	(Schaefer et al., 2018)
	Rotating disk electrode (RDE) or a parallel plate flow-through reactor (p-silicon-BDD)	PFOS	20 mA/cm^2 (12 cm long × 0.3 mm diameter) for RDE and (5 cm × 2.5 cm and 3 mm gap) for flow-through reactor. $NaClO_4$ (7.5 for RDE and 10 mM for flow-through reactor), PFAS (~ 0.4 mA), and 25 h	60[e] ~100[f]	NA	(Carter & Farrell, 2008)
	Boron doped diamond synthesised on p-doped monocrystalline silicon for synthetic solutions and industrial wastewaters (Si-BDD)	PFBA PFHxA PFOA PFBS PFHxS PFOS	100 mA/cm^2 (3 cm^2 and 1 cm gap), Na_2SO_4 (15 mM), PFAS (0.33 μM), and 5.0 h	> 95[g]	> 90	(Nienhauser et al., 2022)
	Electrooxidation of synthetic solutions and groundwater (Nb-BDD)	PFBA PFPeA PFHxA PFHpA PFOA PFBS PFHxS PFOS 6:2 FTS	2.3 mA/cm^2 (35 cm^2 and 2 cm gap) PFAS (0.26 – 34 mg/L), Na_2SO_4 (0.1 M), 48 h for synthetic solution and 120 h for groundwater	45[h] 91 98	66[i]	(Trautmann, Schell, Schmidt, Mangold, & Tiehm, 2015)

Ti_4O_7	Macroporous Magnéli phase ceramic fabricated for electrooxidative mineralisation	PFOA PFOS	5 mA/cm^2 (10 cm × 5 cm), $NaClO_4$ (20 mM), PFOA (0.5 mM) and PFOS (0.1 mM), and 3.0 h	> 99.9 ~ 93	> 95 ~ 81	(H. Lin et al., 2018)
	Flow-through reactive electrochemical membrane (REM) anode	PFOA PFOS	240 LMH j (0.5 cm^2), PFOA (4.14 mg/L) and PFOS (5 mg/L), K_2HOP_4 (100 mM, pH 7) and methanol as a cosolvent (1:100 methanol: water volumetric ratio), 11.3 s residence time	~ 82 ~ 74	~ 75 ~ 69	(Le et al., 2019)
	Electrooxidation of concentrated PFAS in waste streams	PFOA PFOS	10 mA/cm^2 (5 cm × 10 cm and 2.5 cm gap), Na_2SO_4 (100 mM), PFAS (10 mg/L), and 3.0 h	96 ~ 99	NA	(S. Liang et al., 2018)
	Electrooxidation process in the presence of trichloroethylene (TCE) in a gas-tight reactor	PFOS	10 mA/cm^2 (75 cm^2) Na_2SO_4 (100 mM), PFAS (1 mg/L) and TCE (10 mg/L), and 1.0 h	75 53[k]	~ 83 81[k]	(P. Yang, Wang, Lu, Tishchenko, & Huang, 2020)
	Direct electron transfer facilitated employing amorphous Pd cluster loaded on Ti_4O_7	PFOA	10 mA/cm^2, (25 cm^2 and 10 mm gap), Na_2SO_4 (50 mM), PBS (50 mM, pH = 7.2), 1.8 to 2.2 nm average particle size for loaded amorphous Pd, PFAS (0.12 mM), and 1.0 h	~ 87	~ 78	(D. Huang et al., 2020)
	Surface-fluorinated Ti_4O_7 anodes for treatment of chloride containing water	PFOA PFOS 6:2 FTS	5 mA/cm^2 (2.5 cm gap), Na_2SO_4 (100 mM) and NaCl (10 mM), mixture of PFAS (2.0 μM for each), and 8.0 h	> 99	~ 100	(Y. Wang, Li, & Huang, 2022)
	Employing mesh anodes for electrooxidation process using flow-through approach (Magnéli-phase Ti_nO_{2n-1})	PFOS	60 mA/cm^2 (11 cm height × 1 mm thickness + 1 mm × 3 mm diamond-shaped openings, 4 mm gap by a rubber gasket), Na_2SO_4 (500 mg/L) and NaCl (10 mg/L), PFAS, (mg/L), and 74 h	> 99	107	(Fenti et al., 2022)

[a] 1H,1H,2H,2H-perfluorooctanesulfonic acid
[b] Total organic carbon (TOC) has been used as an indication of PFOA mineralisation
[c] Degradation of PFOA
[d] Data was extracted from the figures
[e] Removal efficiency of PFOS using RDE reactor and extracted from the figure
[f] Removal efficiency of PFOS using flow-through reactor and extracted approximately from the figure
[g] Approximate transformation of initial PFASs
[h] Degradation of PFBS, PFHxS, and PFOS from top to bottom
[i] Total maximum defluorination of PFAS (PFBS, PFHxS, and PFOS)
[j] Permeate flux rate in litre per square meter per hour (LMH)
[k] Degradation and defluorination efficiency in the presence of TCE

2016). In this approach, graphene and multiwalled carbon nanotubes are primarily employed as the anode materials due to their electrochemical robustness and conductivity (Z. Niu et al., 2017; S. Wang et al., 2014). To describe the dominant mechanism, negatively charged PFAS move toward the anode orientationally, when the electric current is applied (F. Liu et al., 2023). A major reason for this can be explained by the electrostatic-driven interactions and complexation of PFAS with the anode surface (S.-Y. Huang, Fan, & Hou, 2014). In this way, PFAS is enriched on the anode surface, resulting in a faster removal process. Furthermore, adsorption rate and capacity can be improved by rectifying the surface material in which other types of interaction like hydrophobic, F-F interaction and hydrogen bonding would be possible (L. Liu, Li, Li, Ji, & Tian, 2018; L. Liu, Liu, Che, Gao, & Li, 2021; Quan et al., 2020).

Electro-coagulation, on the other hand, uses a soluble metal in anode material. For example, Al and Fe anodes can produce their respective cations (e.g., Fe^{3+} and Al^{3+}) when an external current is exerted (Si et al., 2021). Through series hydrolysis and complexation reactions, additional amorphous hydroxyl complexes or hydroxide flocs are generated by these cations. As the process proceeds, H_2 and O_2 bubbles may form on the electrode surface. By adsorbing them, flocs eventually take them to the solution surface via electrical floatation, resulting in solid-liquid separation (Brillas & Martínez-Huitle, 2015; He et al., 2021). PFAS can therefore be effectively eliminated by coagulation and adsorption (Y.-F. Li, Hu, Lee, & Lo, 2022; Mu, Park, & Kim, 2021). However, it is important to note that, due to conducting electrochemical reactions in synthetic supporting electrolyte solutions for PFAS degradation, further investigations are needed to expand these methods from the laboratory to industrial context. This is because, in the laboratory, large amounts of initial PFAS concentrations are added to these systems to determine the fluoride ion release which in turn, makes it difficult to draw an accurate conclusion for environmental degradation of PFAS in real water matrices (McKenzie, Siegrist, McCray, & Higgins, 2015; Radjenovic et al., 2020; Y. Wang, Shi, Li, & Huang, 2020).

11.6.1.7 Sonochemical Destruction

Ultrasonication is regarded as a physicochemical treatment method used to destroy recalcitrant organic pollutants such as PFAS (Lei et al., 2020). In this technique, acoustic waves propagate into the solution via a crystal transducer, in which electrical energy is converted into mechanical energy. Sound waves generally oscillate at frequencies ranging between 20 kHz and 1,100 kHz, leading to the microbubbles being generated in aqueous media (Ross et al., 2018). As the ultrasound propagation continues, microbubble nuclei grow to reach their maximal radial expansion. Due to the rarefaction (negative pressure) and quasi-adiabatic compression (positive pressure) consecutive cycles, microbubbles collapse violently, leaving behind shock wave generation, namely cavitation (Figure 11.5). Following this event, microjet plasma (500 m/s) with high localised temperature (4,000–7,000 K) and pressure (several hundred bar) are released which might be energy-wise enough to pyrolyse the PFAS backbone inside the bubble (Garg et al., 2021; Gole, Sierra-Alvarez, et al., 2018; Uriakhil et al., 2021). Moreover, during cavitation, water-splitting molecules, gas ionisation, and dissociation of other potential species inside the bubble occur, which in turn results in generating ROSs. Accordingly, destruction of PFAS under ultrasonication is followed by pyrolytic cleavage (inside the bubble or interfacial region) and free radical attack processes (Figure 11.6) (Sidnell, Wood, Hurst, Lee, & Bussemaker, 2022).

Ultrasonication performance depends on some parameters such as frequency, power input, solution pH, temperature, atmosphere, initial concentration of PFAS, and co-existing contaminants (Cao, Zhang, Wang, & Liang, 2020; Sidnell et al., 2022). Among them, oscillator frequency and power input play a prominent role (Lei et al., 2020). The frequency (υ) in ultrasonication systems can control ROSs generation, lifespan, oscillation rate, symmetry, size distribution, and number of collapsing bubbles (Pflieger, Nikitenko, Cairós, & Mettin, 2019; Shende, Andaluri, & Suri, 2021; Wood, Lee, & Bussemaker, 2017). Studies on the effect of ultrasonic frequency have demonstrated that mid-high frequencies (100–1,100 kHz) are more efficient than low-middling ones (20–100 kHz). The main explanation for this is that higher frequencies produce more cavities in number, stable

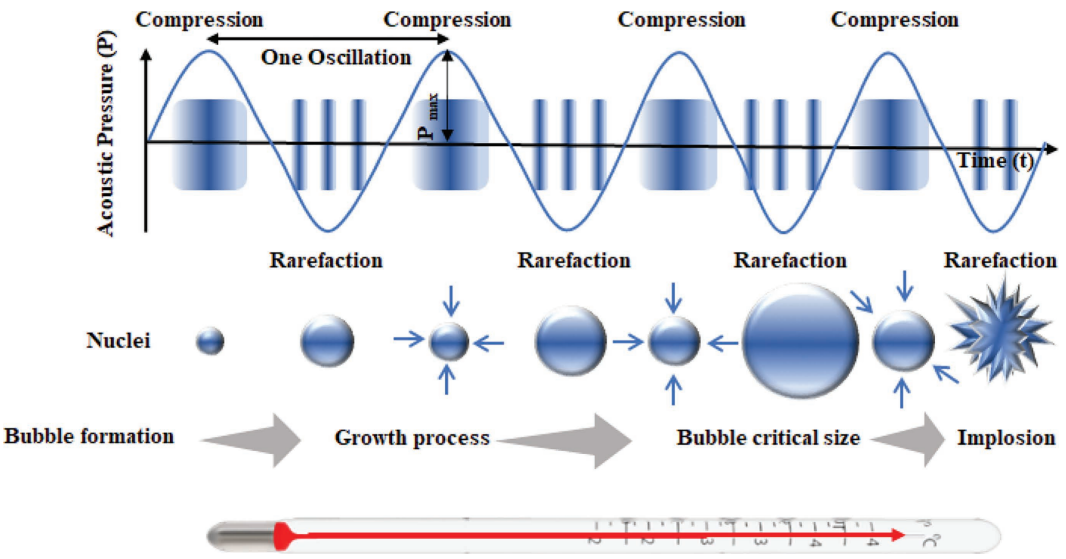


FIGURE 11.5 Schematic of bubble nucleation and cavitation.

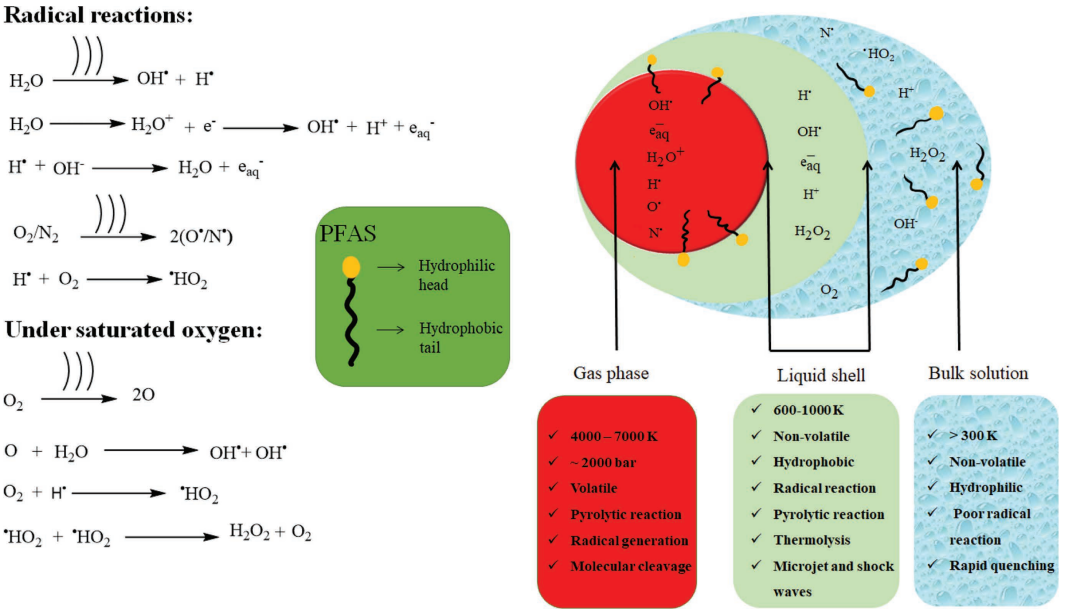


FIGURE 11.6 Schematic of bubble regions, ROSs formation and related reactions (adopted from Adewuyi, 2005; Babu, Ashokkumar, & Neppolian, 2016; Uriakhil et al., 2021; Wanninayake, 2021).

collapse, and smaller cavity size, translating into higher bubble surface area (T. Campbell & Hoffmann, 2015; T. Y. Campbell, Vecitis, Mader, & Hoffmann, 2009). Conversely, lower frequencies result in larger bubble size with unstable collapse, slower degradation rate, and fewer cavities (Cao et al., 2020; Ross et al., 2018; Wanninayake, 2021). Therefore, higher frequencies, ideally 300–500 kHz, are favoured when attempt to reach a convincing PFAS destruction rate (Sidnell et al., 2022). Enhanced power input in the ultrasound system can also increase the population, size, heat, and pressure of active bubbles. In addition, formation of more radicals, higher mixing strength, and the

mass transfer owing to stronger turbulence generation constitute advantages of employing substantial power required for ultrasonication systems (Cao et al., 2020; Kanthale, Ashokkumar, & Grieser, 2008; Lei et al., 2020; Wood et al., 2017; Zhou, Yusof, & Ashokkumar, 2013).

In the meantime, it is worth noting that solution pH and initial concentration of PFAS as documented in many studies have proven to be effective parameters. The pH of solutions influences radical generation, reactivity, and degradation kinetics (Hao, Guo, Wang, Leng, & Li, 2014; Y.-C. Lee, Chen, Huang, Kuo, & Lo, 2016; J.-C. Lin, Lo, Hu, Lee, & Kuo, 2015). The pH range, desirably in the acidic region (3.2–4), has indicated a considerable increase in PFAS degradation rate (Cheng, Vecitis, Park, Mader, & Hoffmann, 2008; Y.-b. Hu et al., 2018). This can be explained by the fact that decreasing the pH is assumed to result in the collapsing microbubbles becoming positively charged. Given that PFAS are acids behaviourally, they can be adsorbed to the bubble-water interface or bubble surface with the opposite charge, facilitating fissional pyrolysis. Most importantly, the radical-driven mechanism becomes significant in acidic pH, particularly for low-frequency systems supported by oxidative agents (Gole, Fishgold, Sierra-Alvarez, Deymier, & Keswani, 2018; Y.-C. Lee et al., 2016; J.-C. Lin et al., 2015). This is because •OH, as the most dominant ROSs in ultrasonication in the aquatic setting, demonstrates a more substantial redox potential at acid pH compared to neutral/alkaline pH (27.8 vs. 1.8 V) (Wei, Spinney, Ke, Yang, & Xiao, 2016). On the other hand, at a fixed frequency and power input, elevated initial concentration of PFAS can somehow trigger a higher degradation rate. This is because with a higher concentration of PFAS, meaning higher hydrophobicity, more of them are exposed to a nearby collapsing bubble (Gole, Fishgold, et al., 2018). Some comparative studies utilising different experimental conditions have been done on the effect of interconnected factors on ultrasonication of PFAS (Table 11.4).

Among the theories devised to explain sonochemistry, the hot spot theory is widely accepted, and it contends that mechanistic reaction of ultrasonication occurs in 3 potential zones: (i) hot core of gas bubble, (ii) water-bubble (supercritical) interface, and (iii) bulk solution (Babu, Ashokkumar, & Neppolian, 2017). Due to the surfactant-like features of PFAS, especially long-chain counterparts with a negligible Henry's constant, they are mainly adsorbed at the water-bubble interface prior to bubble collapse. This means that hydrophobic perfluoroalkyl tail is orientated in the gas phase while the hydrophilic functional group is in the gas-liquid interface (Figure 11.6) (Moriwaki et al., 2005; Vecitis, Park, Cheng, Mader, & Hoffmann, 2008). Consequently, PFAS degradation is thought to commence through pyrolytic fission between the hydrophobic tail and functional group to form an unstable fluoroalkyl radical (Equation 11.1). This is known as truncation (Rodriguez-Freire et al., 2015; Shende et al., 2019).

$$C_nF_{2n+1}X(X = COOH \ \& \ SO_3H) \xrightarrow{)))} \bullet C_nF_{2n+1} + \bullet X \qquad \text{Equation 11.1}$$

To explain this process, pyrolytic cleavage of C-C (348 kJ/mol) in PFCA or C-S (301–355 kJ/mol) in PFSA is more likely than C-F (440–530 kJ/mol), which requires more activation energy (3M, 1999; Franklin & Lumpkin, 1952; Hadad, Rablen, & Wiberg, 1998; O'Hagan, 2008). Furthermore, cavitation phenomena can split water molecules and dissolved gases through *in situ* pyrolytic reactions to generate ROSs such as •OH, superoxide, and hydroperoxyl radicals (OOH•) which are highly reactive. As a result, these radicals can attack PFAS either in the gas phase (short chains, volatile) or in water-bubble (long chains, non-volatile) interface (Cao et al., 2020). It is important to note that some of these radicals are capable of spreading in the bulk solution in the event of a non-spherical collapse (Uriakhil et al., 2021). However, it is still unclear whether pyrolysis and radical attack occur simultaneously or sequentially. Nonetheless they both have a synergistic effect when it comes to degrading PFAS.

Despite considerable efficiency of ultrasonication in degrading PFAS, this method demands a lot of energy, is limited to laboratory analysis, restricted to trace solution volume, and requires supportive oxidising agents such as persulfate $\left(S_2O_8^{2-}\right)$, periodate $\left(IO_4^-\right)$, and permanganate $\left(KMnO_4^-\right)$

TABLE 11.4
Ultrasonication of PFAS under Different Conditions

Technology	PFAS	Frequency and power input	Experimental condition	Results		Ref
				Removal (%)	Defluorination (%)	
US-PS	PFOA PFOS 6:2 FTS	20 @ 550 W and 43 kHz @ 250 W[a]	PFAS (10 μM), PS (1 g/L), 1.0 L working solution, pH = 3.69, 6.0 h	~ 100 > 99 100	~ 100 ~ 47 ~ 87	(Lei et al., 2020)
	PFECAs[b] PFESs	28 kHz @ 200 W	PFAS (50.7 μM), PS (10 mM), 6 L working solution, 15 L/min (circulatory mode), 28°C 24 h	~ 44 - 58	~ 28 - 60	(Hori, Nagano, Murayama, Koike, & Kutsuna, 2012)
	APFO[c]	20 kHz @ 300 W	PFAS (46.4 μM), PS (10 mM), 50 mL working solution, pH = 6, 25°C, 2.0 h	~ 51	11.15	(Hao et al., 2014)
	PFOS	40 kHz @ 100 W	PFAS (100 mg/L, 0.186 mM), PS (5.0 g/L, 18.5 Mm), 100 mL working solution, pH = 7, 20°C, 12 h	NA	~ 5.8	(S. Yang, Cheng, Sun, Hu, & Liang, 2013)
	PFOS PFHxS PFBS	20 kHz @ 100 W	PFAS (20 mM), PS (25 mM), 500 mL working solution, pH = 7, 25°C, 2.0 h	NA	1.7 11 8.9	(Gray, 2018)
US-S[d]	PFOA	40 kHz @ 150 W	PFAS (0.12 mM), Sulfate ion (117 mM), 300 mL working solution, pH = 4.3, 25°C, 1.5 h	~ 100	~ 100	(J.-C. Lin et al., 2015)
US-PI	PFOA	40 kHz @ 150 W	PFAS (170.1 μM), PI (45 mM), 300 mL working solution, N_2 (200 mL/min), pH = 3.9, 25°C, 2.0 h	96.5	~ 96	(Y.-C. Lee et al., 2016)
US-$NaHCO_3$	PFOA	40 kHz @ 150 W	PFAS (50 mg/L), $NaHCO_3$ (30 mM), 1.0 L working solution, N_2 (~ 6.7 mL/min), pH = 8.65, ~ 25°C, 4.0 h	> 98	~ 97	(Thi, Do, & Lo, 2014)
US-PM	PFOA	40 kHz @ 150 W	PFAS (132 μM), PM (6.0 mM), 500 mL working solution, Argon (500 mL/min), pH = 4.0, ~ 30°C, 2.0 h	84.3	~ 63	(Y.-b. Hu et al., 2018)
US-CTAB[e]	PFOA	40 kHz @ 150 W	PFAS (0.12 mM), CTAB (0.12 mM), 300 mL working solution, ~ 25°C, 2.0 h	79	~ 13	(J.-C. Lin, Hu, & Lo, 2016)

(*Continued*)

TABLE 11.4 (*Continued*)
Ultrasonication of PFAS under Different Conditions

Technology	PFAS	Frequency and power input	Experimental condition	Results: Removal (%)	Results: Defluorination (%)	Ref
High frequency induced US	HFPO-DA[f] 6:2 FTAB[g]	700 kHz @ 1040 W	PFAS (900 μM), 2.0 L working solution (deionised water), pH = 4, Argon, 10°C, 4.0 h	99 94	99 98	(Kalra et al., 2021)
	PFOS	1 MHz @ 8 W/cm^2	PFAS (100 μM), 200 mL working solution, Argon, 30°C, 5.5 h	100	100	(Rodriguez-Freire, Balachandran, Sierra-Alvarez, & Keswani, 2015)
	3M Ansul[h]	1 MHz @ 8 W/cm^2	3M (200 × dilution) and Ansul (500 × dilution), 200 mL working solution, Argon for 20 min, 30°C, 3.0 h	~ 16 ~ 39	~ 11 ~ 47	(Rodriguez-Freire et al., 2016)
	PFOA PFOS	575 kHz @ 77 W/L	PFAS (0.1 – 20 mg/L), 200 mL working solution, 21°C, 3.0 h	> 95 > 75	NA	(Shende, Andaluri, & Suri, 2019)
US-multi-transducer (large scale)	3M Ansul	500 + 1000 kHz @ ~ 8 W/cm^2	3M and Ansul (25 × dilution), 91 L, continuous supply of N_2 (5–10 psi), Argon for 30 mins, pH = 4, 13 h	90.5 26.6 38.4[i]	NA	(Gole, Sierra-Alvarez, et al., 2018)
US-$NaClO_4$	PFOA PFOS	612 kHz @ 250 W	PFOS (100 μg/L) and PFOA (200 and 240 nM), $NaClO_4$ (10 mM), Argon for 30 mins, pH = 3, ~ 10°C, 2.0 h	11 47	NA	(Cheng, Vecitis, Park, Mader, & Hoffmann, 2010)
Low-frequency US	PFOA PFOS	20 kHz @ 375 W	PFAS (2000 pM), 100 mL working solution, pH = 2, 20°C, 2.0 h	~ 100	NA	(Panda, Sethu, & Manickam, 2019)
US-TiO_2 (US-photocatalysis)	PFOA	40 kHz @ 500 W	PFAS (120 μM), 2 g TiO_2 (sol-gel) 254 nm UV irradiation continuous mode, oxygen bubbling (140 mL/min), pH = 10, ~ 25°C	64	NA	(Panchangam, Lin, Tsai, & Lin, 2009)

[a] Combined frequencies used in this study: 20 kHz @ 500 W is the low frequency, and 43 kHz @ 250 W is high frequency
[b] In this study five perfluoroether carboxylic acids and two perfluoroether sulfonates were investigated
[c] Ammonium perfluorooctanoate
[d] Implemented technology referring to ultrasound assisted by sulfate ions
[e] Cationic surfactant (Hexadecyl trimethyl ammonium bromide)
[f] Hexafluoropropylene oxide dimer acid
[g] 6:2 fluorotelomer sulfonamidoalkyl betaine
[h] Two types of commercial aqueous film-forming foams (AFFFs)
[i] Reduction of perfluoroalkyl sulfonates (PFSA) and perfluoroalkyl carboxylates (PFCA) in 3M, respectively, and reduction of fluorotelomer sulfonates in Ansul

(Y.-b. Hu et al., 2018; Y.-C. Lee et al., 2016; Lei et al., 2020). As a result, it is desirable to combine ultrasonication with other remedial methods known as treatment train techniques. This will help to minimise energy, chemicals usage, and operating time while developing a strategy for large-scale systems. There are a number of limited hybrid techniques using ultrasound assisted by AOPs such as sono-ozone, sono-ultraviolet, sono-photocatalysis, sono-Fenton, and sono-photo Fenton (Babu et al., 2017; Kucharzyk et al., 2017). However, due to the complexity of the PFAS behaviour, compatibility of emerging methods, reaction pathway, mechanism, and operational requirements require further investigation.

11.6.1.8 Other Destructive Techniques

Despite the aforementioned technologies to destroy PFAS, photocatalysis, bioremediation, plasma, and gamma rays (γ-rays) are the most recently evaluated PFAS remediation technologies (C. Chen et al., 2021; T.-H. Kim, Yu, Choi, Jeong, & Kim, 2018; Mahyar et al., 2019; Turner et al., 2021; Ze Zhang, Chen, Lyu, Yin, & Sheng, 2014; Zhiming Zhang, Sarkar, Biswas, & Datta, 2022). Each technique has some advantages and disadvantages based on its operational conditions, costs, energy, and chemical requirements, effectiveness, and practicability as far as large-scale contexts are concerned (Alalm & Boffito, 2022; Leung et al., 2022; Z. Li, Luo, Huang, Wang, & Ouyang, 2022).

Photodegradation is an effective technique for treatment of contaminants in drinking and wastewater including, PFAS (Dickman & Aga, 2022). This method is mainly categorised into photochemical and photocatalytic types. The photochemical method relies on a high energy light beam in the presence of oxidising/reductive agents, while photocatalytic systems depend on redox capacity and carrier migration of photocatalysts (Z. Li et al., 2022). In the former method, oxidative/reductive additives are deployed under UV illumination to generate highly reactive substances, namely hydrating electron $\left(e_{aq}^{-}\right)$, iodine ion (I^{-}), sulfite radical $\left(SO_3^{2-}\right)$, and $\bullet OH$ as reductive agents. These agents play a key role in controlling the degradation efficiency (Biswas, Yamijala, & Wong, 2022; L. Huang, Dong, & Hou, 2007; C. J. Liu et al., 2021; Trojanowicz, Bojanowska-Czajka, Bartosiewicz, & Kulisa, 2018; Vellanki, Batchelor, & Abdel-Wahab, 2013). Photocatalytic degradation process, on the other hand, usually employs the same light beam (UV) whereas photocatalysts in this system are mainly inorganic semiconductors like TiO_2 and ZnO with a considerable band gap (Dehghani, Naseri, Nadeem, Holl, & Batchelor, 2022; M. Li, Yu, Liu, Sun, & Huang, 2016; D. Wu et al., 2017). Thus, in the presence of energetically adequate light irradiation, an electron-hole pair $\left(e_{CB}^{-}\text{-}h_{VB}^{+}\right)$ is generated. As a result, this photo-induced h_{VB}^{+} has a strong oxidative potential in reacting with H_2O and OH^{-} adsorbed at the surface of the semiconductor, leaving behind producing $OH^{\bullet}$ to destruct PFAS (Z. Li et al., 2022). However, despite the use of a health-threatening UV beam as the main component of photoremediation techniques, they require both energy input (light beam) and additives which add costs and complicate the reaction.

Bioremediation of PFAS is quite challenging due to their persistence in avoiding environmental degradation (Ross et al., 2018). However, dehalogenation is still a thermodynamically desirable reaction since a number of studies have proved that halogenated compounds such as chlorophenols and 1,2-dichloroethane can be degraded using biological additives (Bhatt, Kumar, Mudliar, & Chakrabarti, 2007; Parsons, Sáez, Dolfing, & De Voogt, 2008). A similar trend in dichlorination and defluorination processes taking into account reaction pathways such as haloacid dehalogenation, reductive dehalogenation, and halohydrin dehalogenation, suggests that defluorination might be possible through biological routes (Leung et al., 2022). It is important, however, to state here that highly chlorinated compounds have existed in the natural environment for millennia, whereas PFAS are man-manufactured substances and have been discharged into the environment since the 1950s. This suggests that microbial activities might need much more time to tailor an effective metabolic PFAS degradation strategy (Leung et al., 2022).

In the meantime, bacterial and fungal degradation approaches proved to be effective for PFAS removal. Yi, Chai, Xie, Peng, & Peng (2016) and Kwon et al. (2014), for example, respectively

investigated *Pseudomonas aeruginosa* culture (bacterial species) for PFOA and PFOS removal. It emerged that 32% of PFOA and 67% of PFOS were removed during the treatment within 96 h for the former and 48 h for the latter. Investigations of fungal-based degradation methods for PFAS on the other hand have rarely been reported due to the incomplete degradation and the remediation process taking a long time. For instance, Tseng, Wang, Szostek, & Mahendra (2014) studied 6:2 FTOH (6:2 fluorotelomer alcohol) using the ligninolytic fungi *Phanerochaete chrysosporium* (wood-rotting fungus). The investigated fungus could potentially transform 50% of 6:2 FTOH in 28 d. Therefore, although biodegradation is representative of the 'green chemistry' concept, it has no obvious advantages concerning mineralisation and defluorination, which needs further investigation for microorganisms to be implemented efficiently.

Plasma is the partially or entirely ionised gas as a result of an electrical discharge between two electrodes (Cui, Cheng, Chen, & Yin, 2018; Horikoshi & Serpone, 2017). It contains free radicals, electrons, ions, free neutrons, and atoms with the highest energy state. Taking into account temperature and electron density, plasmatic systems are mainly categorised in two groups, thermal and non-thermal plasma (Attri et al., 2018; Chang, 2009; Foster, 2017; Reddy & Subrahmanyam, 2012). In previous studies, it has been reported that non-thermal plasma (NTP) is more efficient in destroying PFAS at atmospheric pressure compared to thermal plasma. Additionally, NTP is consistent with other gases such as He, Ne, Ar, O_2, and N_2, and contributes to higher excitation selectivity and energy efficiency (Palma, Richard, & Minella, 2022). There are several techniques for generating electrical discharges, such as corona discharges, glow discharges, spark discharges, and dielectric barrier discharges (Meegoda, Bezerra de Souza, Casarini, & Kewalramani, 2022). When an electrical discharge occurs, its energy is transferred to the electrons, which in turn raises their temperature.

In this way, ions, radicals, electrons, and photons are frequently generated when they collide with the gas's atoms (Jovicic et al., 2018; Leung et al., 2022). In the next step, the PFAS moiety is adsorbed onto the water-bubble interface, where the ions with the heightened energy in the plasma state collide with the negatively charged or positively charged moiety of the PFAS. This results in the complete mineralisation of PFAS without the need for any additives (Palma et al., 2022). As an example, in one study by Hayashi, Obo, Takeuchi, & Yasuoka (2015), they investigated DC plasma within oxygen bubbles for PFOA (41.4 ppm) and PFOS (60 ppm) in an aquatic setting. After 3 h for PFOA and 8 h for PFOS operation, complete degradation was achieved. They proposed a 4-step mechanism in which (1) negatively charged PFCAs on the surface of the contaminated water collide with high-energy ions generated by plasma; (2) electrons are stripped from the carboxyl group to form an unstable relevant radical; (3) decarboxylation reaction leads to the formation of CO_2 and fluorocarbon radicals; and (4) fluorocarbon radicals react with water, leaving behind an unzipped CF_2 group, producing shortened PFCAs. Regardless of the convincing effectiveness of the plasmatic technique, it is sensitive to co-contaminants such as nitrate concentration, especially when treating real water matrix and pH range. Moreover, the reaction pathway of PFAS mineralisation by plasma is still poorly understood and requires further research (Meegoda et al., 2022).

In the electromagnetic spectrum, gamma rays (γ-rays) are the shortest, most energetic electromagnetic waves which can result from the disintegration of radioactive atomic nuclei (Bagher, 2014). This technology employs ^{60}Co as a source of emission and can potentially produce numerous radicals simultaneously including $\bullet OH$, $\bullet H$, and hydrated electrons $\left(e_{aq}^{-}\right)$ through radiolysis of the water (Trojanowicz et al., 2020). Furthermore, γ-rays can particularly penetrate deeply into the aquatic setting which contributes to considerable amounts of $\bullet OH$ and e_{aq}^{-} compared to other methods of their generation. As well, this technique does not require any additives to completely mineralise contaminants (Getoff, 1996; Wojnárovits & Takács, 2008). Thus, it has been utilised for disinfection of a wide range of wastewater and sludge as well as persistent organic contaminants including PFAS (Leung et al., 2022). In one study by Ze Zhang et al. (2014), PFOA was completely mineralised at alkaline pH (~13) under N_2 saturated atmosphere into CO_2 and fluorine. They used ^{60}Co as a source of irradiation and the dominant radical species were $\bullet OH$ and e_{aq}^{-} according to

experimental results and quantum chemical calculations. They also ascertained that generated •OH or e^-_{aq} were unable to mineralise PFOA molecules solely, reflecting a synergistic effect of both reactive species. Consequently, this method might be a viable alternative and efficient enough to cleave strong C-F bond and ultimately produce complete mineralisation. Nonetheless, the main disadvantage of γ-rays emitted from isotopic sources is their *permanently declining* intensity over time due to the continuous *radiation* (Trojanowicz et al., 2020). Besides, employing highly energetic γ-rays may raise concerns in personnel who use it for water treatment regarding potential health dangers due to its leakage (Ze Zhang et al., 2014).

11.6.1.9 Hybrid Techniques

Despite extensive investigations of PFAS remediation technologies, it is still a challenge to obliterate these substances effectively due to their recalcitrance. This is because most of these remediation technologies have several disadvantages like high-energy footprints, large-scale limitations, operational complexity, poor efficiency, high costs, and limitations in removing a wide variety of PFAS-impacted media (Ahmed et al., 2020; Lu et al., 2020; Verma, Lee, Sahle-Demessie, Ateia, & Nadagouda, 2022). To overcome these restrictions, synchronising remediation approaches has been found to be effective and applicable, namely treatment train strategies (Lu et al., 2020). These approaches are generally classified into tandem and parallel remediation which are summarised in Table 11.5.

The tandem treatment method uses both ex-situ and *in situ* remedial measures in which PFAS is usually removed from an aquatic medium by adsorption, filtration, and RO. It is followed by degradation of PFAS on the spent adsorbent and/or concentrated retentate using destructive techniques such as electrooxidation and ultrasonication (Kucharzyk et al., 2017). As an example, Soriano, Gorri, & Urtiaga (2017) developed a novel technique aiming to separate and destroy perfluorohexanoic acid (PFHxA) derived from industrial process waters (204 mg/L). They incorporated a nanofiltration (NF) process to separate PFHxA and implement electrochemical degradation of the separated contaminant. The commercially available NF270 (DowFilm) membrane and BDD electrode were supplied for NF and electrochemical degradation, respectively. Under optimised conditions (10 bar pressure gradient and pH 7), ~ 98% of PFHxA was rejected by NF270, representing an enhanced concentration of PFHxA from 204 mg/L in feed water to 870 mg/L in retentate water. The concentrated retentate stream was then electrochemically degraded by feeding it to a cell equipped with BDD. After ~1.5 h electrolysis, 98% of pre-concentrated PFHxA was degraded.

Similarly, an electrochemically degraded mixture of PFOA (100.5 mg/L) and PFOS (68.6 mg/L) in IXR regenerant (still bottom) with high organic carbon content (15,800 mg/L) employing Magnéli phase Ti_4O_7 electrode was investigated by (S. Liang et al., 2018). The total removals of PFOA and PFOS were obtained (77.2% and 96.5%, respectively) with the final concentration of 22.9 mg/L for the former and 2.4 mg/L for the latter after 17 h of continuous treatment. Besides, fluoride concentration increased significantly from 0.84 mg/L to 836 mg/L during this electrolysis timeframe, demonstrating complete mineralisation had occurred.

Parallel treatment methods, on the other hand, employ multiple destructive techniques to treat PFAS concurrently. As stated previously, electrochemical oxidation, ultrasonication, photocatalytic degradation, and plasmatic destruction have generated promising results in PFAS remediation (C. Chen et al., 2021; J.-C. Lin et al., 2016; Stratton et al., 2017; P. Yang et al., 2020). *In situ* generation of ROSs is an inseparable part of these technologies which means that they can be coupled together. Accordingly, it is anticipated that parallel treatment may help improve efficiency, facilitating the operational establishment and/or activation of the process, and reducing the need for additives (Lu et al., 2020). Recently, a novel technology was developed by Luo et al. (2022) which employs electrochemical degradation assisted by acoustic sound waves propagation (EO-US) using Magnéli phase titanium suboxide (Ti_4O_7) as an anode for AFFFs remediation. PFOA was first studied and under optimised conditions (130 kHz @ 100 W for ultrasonication and 50 mA/cm^2, 0.15 M Na_2SO_4, and

TABLE 11.5
List of Investigated Hybrid Techniques (Tandem and Parallel) for PFAS Treatment

Hybrid System	Acronym	PFAS	Experimental Conditions	Removal (%)		Ref
Tandem	NF-EO	PFHxA	NF: DowFilm NF270 membrane, 10 bar, pH 7, 155 cm^2 membrane internal cell area, total volume reduction factor (VRF) of 5 ~ 6 h, 10 L feed volume EO: 50 A/m^2 (1 mm gap), 1 L feed tank of the NF concentrate, 20°C ~ 1.5 h PFAS: 204 mg/L	NF EO	~ 98 91	(Soriano et al., 2017)
	BC-ZVI	PFCAs PFSAs	BC (0.5 – 2.36 mm): 3.5 gr (carbon content of 99.9%) ZVI (0.25 – 1.19 mm): 7 gr PFAS: 20 mg/L, 0.8 mM $NaHCO_3$, 35 mL working solution, 23°C in an anaerobic glove box (3.5% H_2 and 96.5% N_2, 120 d	PFHxA PFHpA PFOA PFBS PFHxS PFHpS PFOS	0 ~ 17 60 20 40 70 94	(YingYing Liu, Ptacek, Baldwin, Cooper, & Blowes, 2020)
	AP	PFOA	Adsorption: Fe/TNTs@AC (1 g/L) PFAS: 0 - 100 mg/L, 40 mL working solution, pH 7, shaking in darkness (100 rpm), ~ 22°C, 24 h Photocatalysis: 10 mL working solution, pH 7, UV irradiation (254 nm, 21 mW/cm^2 and 38 cm gap), 4 h	> 90		(F. Li et al., 2020)
	GAC-TM	PFHxA PFOA PFOS	Adsorption: GAC (1 g), PFOA and PFHxA (1000 mg/L), PFOS (200 mg/L), ~25°C, 24 h GAC-adsorbed PFASs (3 ~ 6 for PFHxA and PFOA, 0.6 ~ 3 for PFOS), NaOH (0.5 mL, 8M) 700°C, 300 mm heat length, dry N_2, 10 min thermal treatment	91[b] 74 90		(Watanabe, Takata, Takemine, & Yamamoto, 2018)

	IXR-EO	PFBA	IXR: fiberglass-reinforced plastic (23 × 122 cm), generation of still bottom samples with NaI 2%, by weight in regeneration of IXR, 200 h EO: Ti_4O_7 (Magnéli phase), 10 mA/cm^2 (10 cm × 5 cm and 2.5 cm gap), PFAS (~ 2.3 mg/L to ~ 18.7 mg/L), 40 h	~ 87	(L. Wang et al., 2021)
		PFBS		~ 100	
		PFPeA		100	
		PFPeS		100	
		PFHxA		100	
		PFHxS		100	
		PFHpA		100	
		PFHpS		100	
		PFOA		~ 99	
		PFOS		96.5	
		6:2 FTS		96	
Parallel	EF-EO	PFOA	BDD (2.85 mA/cm^2) as an anode and Fe10MnC[c] as a cathode (7 cm^2 working area, 2 cm gap), 100 mL working solution, N_2 (100Ml/min), Na_2SO_4, pH 3, PFAS (50 mg/L), 25°C, 4 h	97	(Q. Wang et al., 2019)
	HP-MD	PFOA	HP (15 mol/L), MD (1 g), 60 mL working solution, PFAS (10 mg/L, 0.024 mmol/L), pH 9, 25°C,	83	(da Silva-Rackov et al., 2016)
	TM-PC	PFOA	PFAS (1 mg/L), light intensity (72 ± 10) × 100 μW/cm^2, H_2SO_4 (1 M), 60°C, 12 h	70	(J. Liu, Qu, Wang, Mendoza-Sanchez, & Sharma, 2017)
	EB-PS	PFOS	EB (100 kGy), PS (0.1 mg/L), conveyor belt (10 m/min), PFAS (0.1 mg/L, pH 5.74), 15 mL working solution	~ 80	(T.-H. Kim et al., 2019)
	UV-EO	PFHpA	Pt-Ti as an anode/CNT membrane as cathode (-2V potential, 4 cm gap), medium pressure UV lamp, $NaClO_4$ (50 mM), N_2, PFAS (5 mg/L), pH 11.5, 2 h	22.7	(Rao et al., 2020)
		PFOA		28.5	
		PFNA		32	
		PFBS		0	
		PFHxS		7.8	
		PFOS		19.2	

[a] An adsorptive photocatalyst referring to iron-modified (Fe) titanate nanotubes (TNTs) combined with activated carbon (AC)

[b] Recovery of mineralised fluorine

[c] Fe (II) and Mn (II) doped carbon aerogel with Fe/10Mn weight ratio

[d] Results indicate defluorination efficiency of studied PFAS

10 mm electrode gap for electrooxidation), efficient degradation and defluorination were achieved. The respective percentages were approximately 100% and 63.5%, after 6.0 h operational time. The investigated technology was then extended to three individual AFFFs (2 Ansulite and 1 Orchidee), namely AFFF #1, AFFF #2, and AFFF #3. Due to the complexity of AFFFs containing PFAS and PFAS precursors with a wide range of concentration, total oxidisable percussor (TOP) was assessed, reflecting the amount of fluoride. Thus, defluorination of AFFF #1, #2, and #3 were obtained – 38%, 90%, and 43%, respectively – with the best possible experimental conditions and time required to complete the process.

11.6.2 Soil Remediation

PFAS-affected soil remediation is very challenging and complex to achieve. Once the substances are released into the environment, the terrestrial ecosystems are affected first before the substances end up in bodies of water. The extensive physicochemical characteristics of PFAS allow it to bind with organic and inorganic soil components, subsequently immobilising it. More importantly, the area beneath the soil known as the 'vadose zone' is affected; this zone functions as a protective layer separating shallow soil horizons and groundwater via different interactions such as adsorption, ion exchange, and partitioning (Sharifan et al., 2021). The behaviour of PFAS in soil is therefore more complicated than in an aqueous medium, adding to the intricacy of soil remediation.

To remediate soil contaminated by PFAS, several approaches have been studied including destructive technologies, based on mobilisation and immobilisation strategies (Bolan et al., 2021). Remediation of soil using destructive methods have been proven by a limited number of techniques such as chemical oxidation, incineration, ultrasonication, biodegradation, electron beams, and mechanical degradation (ball milling) (Lei et al., 2020; Mahinroosta & Senevirathna, 2020). To date, only a few reports on these methods have been done, and they investigated issues in the laboratory (Sörengård, Niarchos, Jensen, & Ahrens, 2019). Given the extraordinary stability of the C-F bond from PFAS structure, destruction might completely damage the soil structure and especially if direct destruction is employed on site. While the selective destruction of PFAS from soil has not yet been convincingly demonstrated, the pre-sorption process is a mandatory step to immobilise PFAS as a part of sample preparation prior to using a destructive technique.

In mobilisation, some soil amendments such as surfactants are deployed to desorb PFAS from the soil followed by washing them out using organic solvents to concentrate them into a solution (Guelfo & Higgins, 2013; Pan et al., 2009). Subsequently, PFAS can be removed via efficient removal technologies like adsorption, ion-exchange, and reverse osmosis which are non-hazardous disposal methods. However, the soil's chemical/physical properties dictate if the washing process is practicable or otherwise. In other words, the loading affinity of PFAS onto the soil matrix needs to be strong to resist any washing off; otherwise, even if the organic solvent is used, it will lead to secondary contamination. Moreover, soil washing is most suitable for sandy soils, whereas clay soils require more remediation due to soil desorption components (Mahinroosta & Senevirathna, 2020).

Another option is to immobilise and lock soil-PFAS on site if the loading affinity is big enough to lock PFAS for the long term without leakage occurring. In contrast to mobilisation, in immobilisation, some potential adsorbents like carbonaceous materials (e.g., AC and CNTs) are utilised to redistribute PFAS from solution to solid phase, thereby diminishing their mobility and bioavailability (Ahrens & Bundschuh, 2014; Hale et al., 2017). This might be a cost-effective way to remediate PFAS contaminated soil.

Overall, as stated earlier, due to the complex behaviour of PFAS with soil components, remediation at this stage is extremely challenging and requires much more research and development. Destructive methods can remove PFAS completely, but they may at the same time damage soil during remediation, thereby rendering soil unsuitable for any purpose. Furthermore, for complete removal of PFAS using either mobilisation or immobilisation, additives, massive amounts of solvent,

and extensive and expensive operational installations in several consecutive remediation steps are required. It is therefore necessary to further investigate the possibility of combining remediation techniques, which would minimise the number of steps and enable soil treatment to move from the laboratory to the commercial sector where it is affordable, environmentally friendly, and efficient.

11.7 SUMMARY AND CONCLUDING REMARKS

This chapter presents some indispensable information on PFAS literature, definitions, classifications, encyclopaedic access to an array of findings in various sectors, and potential sources of these substances. The ways in which PFAS are discharged, transported, and transformed into highly recalcitrant and bioaccumulative substances are also discussed. There is also an explanation of the toxicological consequences of human and non-human life-forms' exposure to PFAS. Furthermore, a history of administrative guidelines and remediation techniques in both aquatic and soil environments is presented, especially electrochemical advanced oxidation processes and ultrasonication.

The unrivalled properties of PFAS have made them very useful in a wide range of domestic and commercial contexts and activities. As a result of AFFFs being used in many regions of the world, these substances can leak into the environment, and remediation requires waste management facilities and the proper disposal of consumer products containing PFAS. PFAS exposure endangers the food chain and drinking water supply, which in turn has serious ramifications for all creatures on this planet. Following rising global concerns, administrative rules and guidelines have been devised regarding production, phasing out some PFAS legacies, and desired levels of PFAS concentrations, especially in drinking water. These rules set the stage for PFAS manufacturing to shift from long chains to short chains. Meanwhile, non-destructive as well as destructive remediation techniques have been investigated extensively to reduce PFAS levels so that the health levels are safe.

matCARE™ has been reported as a superior candidate for large-scale PFAS adsorption in non-destructive technologies. Because destructive techniques can destroy PFAS, they have shown promise in reducing its toxicity. It is desirable to use electrochemical advanced oxidation processes and ultrasonication. Both techniques depend on the generation of free radicals for their effective performance. Through ultrasonic chemistry, PFAS skeletons are destroyed by collapsible bubbles formed in aquatic media during sound propagation in aqueous media. Sound frequency and power input are connected parameters that wield a significant effect on bubble dynamics. Although this technology has some limitations concerning energy consumption, operational setups, and confined working operations, further development should lead to larger-scale and successful outcomes.

Although soil is usually contaminated before aquatic media, soil remediation has received less attention. Because soil interacts with PFAS in a complex manner, remediation is extremely challenging. As long as the affinity of PFAS on the spent adsorbent is large enough to lock up PFAS for a long time, destructive technologies are less likely to be needed in soil remediation. The future is promising in the development of more practical, efficient, and large-scale remediation techniques. Additionally, combining remediation techniques can be beneficial in terms of efficiency, time and energy consumption, and research investment, as well as reducing the number of steps required. Ongoing research and investigation as well as investment in this area of environmental remediation must continue.

ACKNOWLEDGMENT

Support by the crc for Contamination Assessment and Remediation of the Environment (crc CARE), Global Centre for Environmental Remediation (GCER), the University of Newcastle, and Australian Research Council [G180200015] are appreciatively acknowledged.

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12 Uncovering the Origins and Pollution Levels of Polychlorinated Naphthalenes
A Comprehensive Analysis

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12.1 BASIC PROPERTIES OF POLYCHLORINATED NAPHTHALENES

Polychlorinated naphthalenes (PCNs) have the molecular formula $C_{10}H_{(0\sim8)}Cl_{(0\sim8)}$. They are a class of compounds comprising 75 congeners, in which the hydrogen atoms on the naphthalene ring are replaced with chlorine atoms. PCNs are insoluble in water but soluble in organic solvents, and with a vapor pressure range of 1.3×10^{-4}~2.1 Pa (25°C), they are semi-volatile and can be transmitted and distributed worldwide. They are characterized by long-range transport and commonly detected in polar atmospheres, sediments, and biological samples (Bidleman, Helm et al., 2010). PCNs are highly lipophilic and thus easily amplified by bioconcentration in the food chain (Falandysz, 2003). PCNs are chemically stable, heat resistant, and persistent in environmental media.

PCNs are coplanar congeners of the most toxic dioxin, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), and thus they can trigger enzymatic reactions such as the ethoxyresorufin *O*-deethylase (EROD) and arylhydrocarbon hydroxylase (AHH) reaction. They have embryonic, hepato-, immuno-, teratogenic, and carcinogenic toxicity, and they also cause skin damage (Blankenship, Kannan et al., 2000, Omura, Masuda et al., 2000, Villeneuve, Kannan et al., 2000, Galoch, Sapota et al., 2006, Kilanowicz, Sitarek et al., 2011). According to tests of fish and mouse liver tumor cells, toxicity is mainly caused by pentachloro, hexachloro, and heptachloro congeners (Villeneuve, Kannan et al., 2000). Among them, hexachloronaphthalene congeners CN-63, CN-66/67, and CN-69

DOI: 10.1201/9781003530466-12
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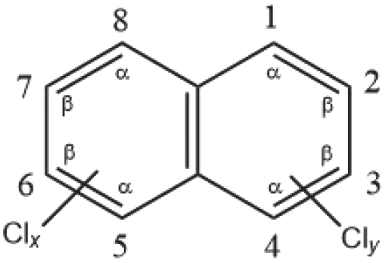


FIGURE 12.1 Chemical structure of polychlorinated naphthalenes (PCNs).

are the main sources of toxicity, and the relative toxicity equivalent factor (REP) of these congeners is 0.002. In general, among the 75 congeners, trichloro or tetrachloro substituted congeners at 2-, 3-, 6-, and 7-positions, namely TeCN-48, PeCN-54, HxCN-66, -67, -68, -69, -70, -71, and HpCN-73, are similar to dioxins in toxicity. PCNs are potentially harmful to human health and can cause symptoms such as chloracne.

12.2 SOURCES OF POLYCHLORINATED NAPHTHALENES

PCNs are mainly found in materials related to the power industry, such as insulating oil in capacitors or transformers, cable insulators, and flame retardants. PCNs are also used to make surface packaging materials, lubricants, adhesives, plasticizers, and other industrial materials. Prior to the 1980s, PCNs were extensively produced and widely used in various fields. Until it ceased production of PCNs in 1977, Koppers, a company in Pennsylvania, USA, was the largest producer of PCNs, namely the Halowax series. In addition to the industrial production of PCNs, PCNs are unintentionally produced in waste incineration, metal smelting, chemical production, and other processes. PCNs are on the waiting list of persistent organic pollutants (POPs) compiled by the United Nations Economic Commission for Europe (UNECE). PCNs have been found in the atmosphere, soil, sediments, water bodies, and organisms worldwide (Harner, Kylin et al., 1998, Jarnberg, Asplund et al., 1999, Kannan, Hilscherova et al., 2001, Lee, Harner et al., 2007, Lin, Zhao et al., 2013, Huang, Li et al., 2016, Li, Jin et al., 2016, Dat, Chang et al., 2019), posing a potential hazard to human health. There are three main sources of PCNs in environmental media: (1) production and use of PCNs as industrial chemicals; (2) production and use of polychlorinated biphenyls (PCBs) producing PCNs as a by-product; and (3) unintentional emissions of PCNs from industrial processes, such as incineration and metallurgy.

PCNs were first synthesized in the 1830s but not commercialized until 1910, and they were widely used in the 1930s–1950s. Industrial production of PCNs is mainly through the chlorination of molten naphthalene catalyzed by metal halides at a certain temperature. The Halowax series, produced by Koppers, USA, was the prominent product name of PCNs, and was discontinued in 1977. Other major product names included Nibren waxes (Bayer, Germany), Seekay waxes (ICI, UK), and Clonacire waxes (Proelec, France), which were also discontinued in the 1980s. The cumulative amount of PCNs produced globally is approximately 150,000 tons, of which 10% is associated with the production of PCBs. Yamashita et al. estimated the amount of PCNs generated as impurities during the production of PCBs in several countries (Yamashita, Kannan, Imagawa, Miyazaki et al., 2000), and they found that the production of Phenoclor and Sovol products in France and the former Soviet Union generated the highest amount of PCNs as impurities, which is approximately 169 tons. Although the production and use of PCNs and PCBs as industrial chemicals have been eliminated, the use of obsolete equipment containing PCBs and PCNs still pose a potential threat to the environment.

Since 1980, the production and use of PCNs have been restricted and the concentration of PCNs in the environment has decreased significantly. However, the proportion of PCNs produced and emitted unintentionally by industrial processes has significantly increased. Waste incineration is an important source of PCNs in the environment. PCNs can be detected in fly ash and flue gas from waste incineration. Unintentional generation and emission from secondary metal smelting, coking, and steelmaking processes are considered the major sources of PCNs.

PCNs have been included in the controlled list of the Stockholm Convention on Persistent Organic Pollutants in 2015, which is a new type of persistent organic pollutant. The main sources of unintentional POPs can be categorized according to the industrial activity, namely combustion, metal smelting, chemical production, and biological and photochemical process. For example, combustion sources are waste incineration, coal-fired power production, and heating, and metal smelting sources mainly include iron ore sintering, electric arc furnace steelmaking, and non-ferrous metal smelting, while chemical production sources mainly include the production and use of chlorinated chemicals.

Waste incineration is the main source of PCNs, identified earlier. The emission levels of PCNs in flue gas from five solid waste incineration plants in Spain are in the concentration range of 1.08–21.36 ng/Nm^3 (mono- to octa-chlorinated) and 0.33–5.72 ng/Nm^3 (tetra- to octa-chlorinated) (Abad, Caixach et al., 1999). The emission levels of PCNs in the flue gas of nine incineration plants with different waste treatment types and scales in China are in the high concentration of 97.6–13,000 ng/Nm^3 (1.74–198 pg TEQ/Nm^3), and the distribution of PCNs is mainly low-chlorinated naphthalene congeners. Moreover, a study found that the concentrations of PCNs in the flue gas of MSW incineration plants without pollution control technologies are high, reaching 939.2–9,986.0 ng/Nm^3 (Oh, Gullett et al., 2007).

The levels of PCNs emitted during iron ore sintering and electric arc furnace steelmaking are in the range of 3–983 ng/Nm^3 and 458–1,099 ng/Nm^3, respectively (Liu, Zheng, Hu et al., 2012; Liu, Zheng, Liu et al., 2012). Investigations of six typical iron and steel plants in northern China revealed that the levels of PCNs emitted during iron ore sintering and converter steelmaking are 24.5 ng TEQ/t and 0.81 ng TEQ/t, respectively (Li, Zheng et al., 2014, Li, Liu et al., 2017).

An investigation of China's four secondary metal smelting industries (secondary copper, secondary aluminum, secondary zinc, and secondary lead) revealed that secondary copper smelting emits the highest level of PCNs, which is 428 ng TEQ/t, followed by secondary aluminum smelting, secondary zinc smelting, and secondary lead smelting, with PCN emission levels of 143 ng TEQ/t, 126 ng TEQ/t, and 20.1 ng TEQ/t, respectively (Ba, Zheng et al., 2010). This result indicates that PCNs are emitted in high concentrations during secondary copper smelting. The emission level of PCNs during China's unique magnesium smelting process, the Pidgeon process, is 3,329 μg/t (Nie, Zheng et al., 2011). Moreover, studies on the unintentional generation and emission of PCNs during various industrial thermal processes concluded that secondary copper smelting is one of the important emission sources of PCNs in China (Liu, Cai et al., 2014, Liu, Cai et al., 2015).

Coking, wire incineration, and cement production are also emission sources of PCNs. The level of PCNs emitted by China's coking industry is 1.0 ng TEQ/t (Liu, Zheng et al., 2010). Wire burning in waste metal dismantling industrial parks is an important emission source of PCNs in China (Nie, Zheng et al., 2012). The results show that incineration of waste motors and waste enameled wires can produce PCNs in high concentrations. The average concentration of PCNs in the flue gas of cement kiln calcination in China is 710 ng/m^3, and the concentration of PCNs in particulate phase samples collected at each calcination stage is 1.1–84.7 ng/g (Liu, Zhan et al., 2016).

12.3 METHODS FOR THE ANALYSIS OF POLYCHLORINATED NAPHTHALENES

PCNs are often present in trace amounts in environmental samples, requiring analytical methods with high sensitivity and selectivity. Typically, PCNs undergo solvent extraction and purification separation prior to determination by gas chromatography and mass spectrometry. However, the

chromatographic outflow curves of PCNs are similar to those of PCBs and other coplanar compounds, and thus complete separation of PCNs is difficult.

Column chromatography is still the most commonly used method to purify and separate PCNs. During the purification of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), multilayer silica gel columns are often used to remove sulfur, fat, and other interfering substances in sediments and biological samples, which are also applicable to PCNs. In addition, copper powder can be added to remove sulfur. Fat in biological samples can be removed using gel permeation chromatography (GPC), which removes fat according to the size of the molecule by volume exclusion, and the addition of concentrated sulfuric acid. PCNs can be further separated from other substances using activated carbon columns and other methods. In a study analyzing the levels of PCNs in soil samples from urban, residential, and industrial areas, samples were subjected to accelerated solvent extraction, purification by alumina-silica gel column and then composite silica gel column, and finally analysis by gas chromatography and mass spectrometry (Krauss and Wilcke, 2003). In another study, atmospheric samples underwent Soxhlet extraction and then separation and purification by composite silica gel column. Components containing PCNs continued to pass through the activated carbon microcolumn to separate the main congeners of PCNs and PCBs, and components containing multi-ortho and some mono-ortho PCBs were eluted by 5 mL of 30% dichloromethane/cyclohexane, while components containing non-ortho and remaining mono-ortho PCBs and PCNs were eluted by 5 mL of toluene (Harner, Shoeib et al., 2006).

At present, there are no internationally recognized standards for the analysis of PCNs. In the absence of standardized methods for the sampling and analysis of PCNs, comparative analysis of data is challenging. Isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) is the most accurate method for PCN analysis. Early studies of PCNs were limited by instrumental setups, most of which used gas chromatography with electron capture detectors, high-performance liquid chromatography (HPLC), and thin-layer chromatography with electrochemical detection to determine certain isomers or industrial mixtures. In recent years, with the rapid development of analytical instruments, methods for the analysis of PCNs have also improved. Since 2002, isotope-labeled reference materials have been developed to support a more efficient method, known as isotope dilution of PCN congeners. PCN congeners without isotope labeling are corrected by an internal standard method. The first study using the ^{13}C-PCN isotope labeling method was published in 2004. Commercially available ^{13}C-PCNs include TeCN-42, -27, PeCN-52, HxCN-67, -64, HpCN-73, and OCN–75.

HRGC/HRMS is the preferred technology for accurate qualitative and quantitative analysis of trace organic pollutants in environmental samples owing to the high resolution of both gas chromatography and mass spectrometry. It is widely used for the analysis of PCNs in atmospheric, soil, sediment, and biological samples. Specifically, ^{13}C-labeled standard substances added before sample extraction can be used to calibrate the loss of target substances during the pretreatment process and ensure accuracy of test results. There is a relative retention time relationship between the recovery standard, purification internal standard, and target compound to facilitate rapid qualitative analysis of complex environmental samples. In addition, HRMS can reach more than 10,000 resolution and has good selectivity for target compounds in complex environmental media. Moreover, matrix interference is reduced in HRGC/HRMS. However, the detection limit of HRGC/HRMS is 2~3 orders of magnitude lower than that of GC coupled with low-resolution mass spectrometry (LRMS), which is more suitable for the analysis of ultra-trace pollutants in complex environmental media. Nevertheless, HRGC/HRMS is an ideal method for the detection of PCNs in samples such as breast milk, which contains low concentrations of PCNs.

Because there is no standard analytical method for PCNs, two international comparative studies have been conducted on the analysis of PCNs in environmental samples to eliminate the bias between the experimental data published by different laboratories using different instruments and quantitative methods. The first international comparison trial was organized in 2003 to evaluate existing PCNs analytical methods. A total of nine laboratories participated in the study. The total

PCN content of the Halowax solution was determined, and some individual congeners were quantified. The experimental results of the total PCN content were consistent, and the relative standard deviation (RSD) was 11%. However, quantitative determination of individual congeners varied greatly, and the RSD value was between 20% and 40%. Because ^{12}C-PCNs and ^{13}C-PCNs standards are limited, the isotope dilution method is not widely used in the analysis of PCNs. Compared with the first comparison experiment, only five laboratories participated in the second international comparison experiment, and the determination results of the Halowax solution and standard reference materials were in good agreement, with RSD values of approximately 10% or lower.

In general, the early detection of PCNs mostly adopt gas chromatography–electron capture detector (GC–ECD). In recent years, with the rapid development of analytical instruments, methods for the analysis of PCNs have greatly improved. Gas chromatography/mass spectrometry (GC/MS) has become common for PCN analysis (Kucklick and Helm, 2006). The application of electron capture negative chemical ionization (ECNI) has also greatly improved instrumental response to high chlorinated congeners, although the response to low chlorinated congeners is relatively low. HRGC/HRMS has become the preferred technology for accurate qualitative and quantitative analysis of trace organic pollutants in environmental samples owing to the high resolution of gas chromatography and mass spectrometry. However, HRGC/HRMS is expensive to maintain and complicated to operate. Therefore, sole reliance on HRGC/HRMS for PCN analysis will greatly limit the progress of PCN-related research. In recent years, gas chromatography/triple quadrupole tandem mass spectrometry (GC-MS/MS) has advanced and has been applied to the analysis of trace POPs in environmental samples.

12.4 ENVIRONMENTAL POLLUTION LEVELS OF POLYCHLORINATED NAPHTHALENES

12.4.1 PCNs in the Atmosphere

At present, there are many studies on the pollution level of PCNs in the atmosphere of different countries and regions. The concentrations of PCNs range from 7.3 to 84.5 pg/m^3 in urban air samples from Toronto, Canada. Harner et al. used passive sampling to monitor PCN levels at 15 sampling sites in St. Lawrence Great Lakes (Harner, Shoeib et al., 2006), discovering significant differences in the levels of PCNs between urban and rural areas. The concentration of PCNs in rural areas is several pg/m^3, which is an order of magnitude higher than that in urban areas, such as Toronto (12–31 pg/m^3) and Chicago (13–52 pg/m^3). The concentration and homologue distribution of PCNs in the polar atmosphere from 1993 to 2005 have been reported, with an average concentration of 0.16–40 pg/m^3 (Bidleman, Helm et al., 2010). The ambient PCN level in the atmosphere of Ghana is 27.4–94.6 pg/m^3 (Hogarh, Seike et al., 2012). The concentrations of ∑63 PCNs in the atmospheres of Japan, China, and South Korea, determined using passive sampling, are 9.5 ± 1.5, 61 ± 6, and 16 ± 2.4 pg/m^3, respectively. Studies on gas–solid phase partitioning of PCNs have shown that PCNs are mainly present in the gas phase. For example, in the atmosphere of Chicago urban areas, low-chlorinated naphthalenes (tri- and tetra-chlorinated naphthalenes) are mainly present in the gas phase, while high-chlorinated naphthalenes (hepta- and octa-chlorinated naphthalenes) are mainly present in the particle phase. Moreover, in the atmosphere of Izmir, Turkey, the proportion of PCNs in the gas phase is 33%–94%, and the proportion of volatile PCNs in the gas phase is higher in summer than in winter (Odabasi, Bayram et al., 2012). Additionally, in atmospheric aerosols from Venice, Italy, PCNs are mainly present in the gas phase, and most of the PCNs in particulate samples are below the detection limit. The gas/particulate (G/P) values of PCNs are 0.91 and 22 in 2009 and 2012, respectively (Gregoris, Argiriadis et al., 2014). As the particle size decreases, the proportion of PCNs in fine particulates increases. In components with kinetic diameters $d_{ae} \leq 1.0$ μm, PCNs account for approximately 63.5% of total particles (Zhu, Zhang et al., 2016).

12.4.2 PCNs in Soil and Sediment

The concentrations of PCNs (from TeCNs to HpCNs) in surface sediments from the northern areas of the Baltic Sea range from 0.27 to 2.8 ng/g (dry weight, dw), and the amount of PCNs deposited in the sediments of the Baltic Sea, estimated using the deposition rate equivalent, is approximately 91 kg/year (Lundgren, Tysklind et al., 2003). This level is similar to the PCN contents in sediment samples from other parts of Europe, North America, and Japan. In addition, the concentrations of PCNs in sediment samples from the Baltic Sea and the west coast of Sweden are 0.6–7.6 ng/g dw and 0.1–1.3 ng/g dw, respectively (Jarnberg, Asplund et al., 1999). Kannan et al. reported a PCN concentration of 0.3–0.8 ng/g dw for sediment samples obtained from Lake Michigan in 2000 (Kannan, Imagawa et al., 2000). In Japan, the concentration of PCNs in surface sediments of Tokyo Bay is 1.8 ng/g dw (Yamashita, Kannan, Imagawa, Villeneuve et al., 2000). In contaminated areas, such as near an industrial area in Germany, the total concentration of PCNs is as high as 2,500 ng/g dw (Brack, Kind et al., 2003). Thus far, sediment samples with the most serious levels of PCNs are from an area polluted by the chlor-alkali industry in the United States, and these samples have PeCN, HxCN, and HpCN contents of 2.6, 7.3, and 9.6 μg/g dw, respectively (Kannan, Imagawa et al., 1998). The level, time trend, and characteristic source of PCNs in soil from two sampling sites in the UK have been investigated (Meijer, Harner et al., 2001). In soil samples collected from Luddington, the total content of PCNs decreased from 6,000 pg/g dw in 1968 to 420 pg/g dw in 1990. In contrast, soil samples collected from an area near a petrochemical plant, urban/residential areas, and assumed uncontaminated areas in Spain have lower levels of PCNs, with the total content of PCNs ranging from 32 ng/kg (uncontaminated samples) to 180 ng/kg (urban/residential areas) (Schuhmacher, Nadal et al., 2004). In soil samples from a German city and village, the total content of 35 PCNs congeners was 100–15,400 ng/kg and 100–820 ng/kg, respectively (Krauss and Wilcke, 2003). A recent study reported that the total content of PCNs in soil from a region of Poland is between 350 and 1,100 pg/g dw, which may be related to the use of industrial PCN commodities in this region (Wyrzykowska, Hanari et al., 2007).

12.5 LEVEL OF POLYCHLORINATED NAPHTHALENE CONTAMINATION IN FOOD

At present, data on PCNs in food are still limited, and there is not enough data to support the global risk assessment of PCNs based on dietary exposure. The following section surveys some studies on PCNs in human food as well as in retail foods.

In 2000, an investigation of animal-derived food samples collected from markets and large supermarkets in seven cities in Catalonia, Spain was conducted (Domingo, Falco et al., 2003, Falandysz, 2003, Fernandes, Mortimer et al., 2010, Fernandes, Rose et al., 2017). According to this study, the concentrations of PCNs in animal-derived foods decrease in the following order: oily foods (447 ng/kg dw), fish and shellfish (39 ng/kg dw), eggs (23 ng/kg dw), and meat and meat products (18 ng/kg dw). In 2006, the concentrations of PCNs in food samples collected from supermarkets in 12 cities in Catalonia, Spain were determined. The highest PCN content is 47.1 ng/kg (wet weight, ww), found in fish and seafood, followed by 21.5 ng/kg ww in oily foods, 11.7 ng/kg ww in dairy products, and 2.8 ng/kg ww in cooked foods.

In 2022, various foods from 24 provinces of China were systematically analyzed (Li, Zhang et al., 2022), revealing that animal-derived foods generally have a higher PCN content than plant-based foods. The PCN content is the highest in meat, in the range of 49.2–174.1 ng/kg ww (mean: 92.0 ng/kg ww), followed by eggs (7.6–159.0 ng/kg ww, mean: 31.4 ng/kg ww) and fish (11.1–138.6 ng/kg ww, mean: 27.2 ng/kg ww), with the lowest PCN content in milk (8.6–51.6. ng/kg ww, mean: 22.2 ng/kg ww). The average detection rates of PCNs in fish, meat, eggs, and milk are 82%, 89%, 90%, and 80%, respectively.

In 2022, the concentrations of PCNs in food crops in the vicinity of two secondary copper smelters were determined. The concentration of PCNs is 20.0–116 ng/kg ww (mean: 50.5 ng/kg ww) in aquatic products and 12.3–38.6 ng/kg ww (mean: 26.1 ng/kg ww) in eggs collected from within 10 km of the copper smelter. In farms 20–30 km from the smelter, the PCN concentration is 20.4–24.5 ng/kg ww (mean: 22.4 ng/kg ww) in aquatic products and 18.6–24.1 pg/g ww (mean: 20.9 ng/kg ww) in eggs. There is no significant difference in the concentrations of PCNs in similar animal-derived food samples surveyed in 24 provinces of China in 2022 (Li, Zhang et al., 2022).

The concentrations of PCNs in plant-based foods obtained from the Catalonia region of Spain in 2000 are as follows: cereals (71 ng/kg dw), fruits (0.7 ng/kg dw), tubers (3 ng/kg dw), and vegetables (4 ng/kg dw). Additionally, the concentrations of PCNs in vegetables, fruits, and cereals obtained from Catalonia in 2006 are 2.3 ng/kg ww, 1.2 ng/kg ww, and 8 ng/kg ww, respectively. The concentration of PCNs in tuber plants is 10.2 ng/kg ww (Domingo, Falco et al., 2003, Falandysz, 2003, Fernandes, Mortimer et al., 2010, Fernandes, Rose et al., 2017).

Analyses of plant-based foods obtained from 24 provinces of China in 2022 show that (Li, Zhang et al., 2022) legumes have the highest PCN concentrations (8.2–29.0 ng/kg ww, mean: 16.8 ng/kg ww), followed by vegetables (2.5–23.6 ng/kg ww, mean: 12.1 ng/kg ww), cereals (2.0–17.9 pg/g ww, mean: 7.6 pg/g ww), and potatoes (1.6–47.2 pg/g ww, mean: 31.4 pg/g ww). The concentrations of PCNs in cereals grown on farms near a secondary copper smelter in the same year are 115 ng/kg ww in cereals within 10 km of the smelter and 75.1 ng/kg ww in cereals within 20–30 km of the smelter. The concentrations of PCNs in grains around the secondary copper smelter are significantly higher than the average concentration of the survey results for food from 24 provinces.

The concentrations of PCNs in plant-based foods are generally one to two orders of magnitude lower than those in animal-derived foods, especially fish and seafood. Compared with plant-based foods, animal-derived foods may have a higher human intake.

The characteristics of congeners of PCNs are of great significance to determine the source and toxicity of PCNs. According to a study of tetra- to octa-chloronaphthalene congeners, tetra-chloronaphthalenes are the dominant congeners in fish and shellfish, meat and meat products, eggs, dairy products, milk, oily foods, and cooked foods, followed by penta- and hexa-chloronaphthalenes (Domingo, 2004). Tetrachloro congeners PCN-28/36 and PCN-42 are the major contributors to total PCN concentration, followed by pentachloro and hexachloro congeners PCN-52, PCN-60, and PCN-66/67 (Domingo, Falco et al., 2003, Falandysz, 2003, Fernandes, Mortimer et al., 2010, Fernandes, Rose et al., 2017).

In plant-based foods, namely wheat, rice, fruits, legumes, vegetables, cereals, and tuber foods, tetra- and penta-chloronaphthalenes are the dominant congeners. Moreover, another study found that hexa-chloronaphthalenes are the dominant congeners in fruits and legumes (Domingo, 2004). However, among PCN congeners, octa-chloronaphthalenes are present with the lowest concentration in both plant- and animal-based foods.

A comparison of dietary PCN contamination levels in different countries is shown in Table 12.1. Owing to differences in the types of dietary samples and the number of PCN congeners involved in different studies, the concentrations of PCNs in diets between different regions are difficult to compare. Therefore, the concentrations of PCN congeners reported in different literatures are further compared (Table 12.2). The concentration of PCNs in foods from China is considerably lower than that in foods from European countries. The concentration of PCNs in fish samples from European countries is 10–15 times higher than that in fish samples from China, while the concentration of PCNs in egg samples from European countries is about half of that in egg samples from China, and the concentration of PCNs in other types of foods from European countries are comparable to those in other types of foods from China. Among the food samples collected from China, meat samples have the highest concentration of PCNs, and among the food samples collected from European countries, fish samples have the highest concentration of PCNs. The reason for these differences in PCN concentrations may lie in the history of generating and using commercial PCNs products in European countries, leading to an accumulation of PCNs in the aquatic food chain over time

TABLE 12.1
Comparison of Dietary Levels of PCNs in Different Countries

Country	Food Category	Number of Mixed Samples (Number of Single Samples)	Sample Time	Number of Homogeneous Objects	Average Concentration (pg/g wet weight)	References
China	Fish	24 (2160)	2016–2020	75, mono-octa	27.2	(Li, Zhang et al., 2022)
	Meat	24 (2160)	2016–2020	75, mono-octa	92.0	
	Eggs	24 (2160)	2016–2020	75, mono-octa	31.4	
	Dairy products	24 (2160)	2016–2020	75, mono-octa	22.2	
	Legumes	24 (2160)	2016–2020	75, mono-octa	16.8	
	Cereals	24 (2160)	2016–2020	75, mono-octa	7.6	
	Vegetables	24 (2160)	2016–2020	75, mono-octa	12.1	
	Potatoes	24 (2160)	2016–2020	75, mono-octa	9.9	
Spain	Meat	30 (300)	2000	WD, tetra-octa	18	(Domingo, Falco et al., 2003)
	Fish	16 (160)	2000	WD, tetra-octa	39	
	Vegetables	16 (160)	2000	WD, tetra-octa	4	
	Tubers	4 (40)	2000	WD, tetra-octa	3	
	Fruits	12 (120)	2000	WD, tetra-octa	0.7	
	Eggs	4 (40)	2000	WD, tetra-octa	23	
	Milk	4 (40)	2000	WD, tetra-octa	0.4	
	Dairy products	4 (40)	2000	WD, tetra-octa	36	
	Cereals	8 (80)	2000	WD, tetra-octa	71	
United Kingdom	Meat	Single sample (9)	2007	12, penta-octa	1.64	(Fernandes, Mortimer et al., 2010)
	Fish	Single sample (13)	2007	12, penta-octa	19.9	
	Poultry meat	Single sample (9)	2007	12, penta-octa	2.38	
	Dairy products	Single sample (9)	2007	12, penta-octa	1.51	
	Vegetables	1 (WD)	2007	12, penta-octa	0.15	
	Bread	1 (WD)	2007	12, penta-octa	0.28	
Ireland	Fish	12 (WD)	2007–2008	12, penta-octa	21.8	(Fernandes, Tlustos et al., 2011)
	Milk	15 (WD)	2007–2008	12, penta-octa	0.22	
	Eggs	15 (WD)	2007–2008	12, penta-octa	0.62	
	Dairy products	6 (WD)	2007–2008	12, penta-octa	1.81	
	Lipid	21 (WD)	2007–2008	12, penta-octa	3.69	
	Vegetables	4 (WD)	2007–2008	12, penta-octa	1.44	
	Potatoes	1 (WD)	2007–2008	12, penta-octa	0.17	
	Bread, corn, oats, etc.	5 (WD)	2007–2008	12, penta-octa	0.44	
	Baked beans	1 (WD)	2007–2008	12, penta-octa	0.19	
Latvia	Fish	Single sample (16)	2019–2020	26, tetra-octa	45.7	(Zacs, Perkons et al., 2021)
	Meat	Single sample (11)	2019–2020	26, tetra-octa	3.13	
	Dairy products	Single sample (10)	2019–2020	26, tetra-octa	5.29	
	Eggs	Single sample (9)	2019–2020	26, tetra-octa	1.14	
	Bread	Single sample (6)	2019–2020	26, tetra-octa	9.49	
	Vegetable oil	Single sample (3)	2019–2020	26, tetra-octa	3.53	
	Fish oil	Single sample (4)	2019–2020	26, tetra-octa	10.5	

Note: WD means no data.

TABLE 12.2
Reported concentrations of commonly measured polychlorinated naphthalene congeners in foods

Country	Number of Homogeneous Objects	Number of Mixed Samples (Number of Single Samples)	Sample Time	Fish	Meat	Eggs	Dairy Products	Legumes	Cereals	Vegetables	Potatoes	References
China	12	192 (17,280)	2016–2020	2.1	2.24	1.45	0.71	0.38	0.3	0.38	0.35	(Li, Zhang et al., 2022)
China	26	192 (17,280)	2016–2020	5.28	5.08	3.12	1.27	0.98	0.65	1.05	1.05	(Li, Zhang et al., 2022)
China	tetra-octa	192 (17,280)	2016–2020	13.32	9.92	5.93	2.34	2.03	1.43	2.18	2.04	(Li, Zhang et al., 2022)
Latvia	12	WD (55)	2019–2020	29.36	0.6	0.29	0.34	WD	0.893	0.98	WD	(Zacs, Perkons et al., 2021)
Latvia	26	WD (55)	2019–2020	45.7	3.13	1.14	5.29	WD	9.49	3.53	WD	(Zacs, Perkons et al., 2021)
United Kingdom	12	WD (43)	2007	19.9	1.64/2.38	WD	1.51	WD	0.28	0.15	WD	(Fernandes, Mortimer et al., 2010)
Ireland	12	88 (WD)	2007–2008	21.8	3.69	0.62	0.22/1.81	0.19	0.44	1.44	0.17	(Fernandes, Tlustos et al., 2011)
Spain	tetra-octa	86 (890)	2000	39	18	23	0.4/36	3	71	4	WD	(Domingo, Falco et al., 2003)

Note: WD indicates no data, and the concentration unit is pg/g wet weight.

(Fernandes, Mortimer et al., 2010). China does not have a history of producing and using commercial PCNs products, and thus the amount of bioaccumulation in the aquatic food chain over time is relatively small.

12.6 LEVEL OF POLYCHLORINATED NAPHTHALENES IN HUMAN SAMPLES

At present, there are very limited studies on human exposure levels of PCNs, and only a small amount of data has been found in various literatures. Breast milk is one of the core media of the Global Monitoring Project (GMP) of the United Nations Environment Programme (UNEP). Breast milk monitoring is of great significance for human health risk assessments. Breast milk is rich in fat and the main food source of newborn infants. It is also an ideal matrix for monitoring human POP levels, reflecting maternal exposure levels, which enables an understanding of the health risks of sensitive populations, such as infants, in addition to dietary exposure levels.

Considering the advantages of breast milk in enhancing the immunity of infants and young children, the World Health Organization (WHO) actively promotes breastfeeding worldwide. The WHO recommends that the vast majority of infants are exclusively breastfed within 6 months of birth, with breastfeeding continuing for the following 2 years or longer. Research on PCNs in breast milk is of great significance for health risk assessment of infants.

Studies on PCNs in breast milk have been conducted in Sweden and Ireland (Lunden and Noren, 1998, Pratt, Anderson et al., 2013), and studies on PCNs in human blood have been conducted in Germany and Korea (Horii, Jiang et al., 2010, Park, Kang et al., 2010, Fromme, Cequier et al., 2015). Studies on PCNs in human adipose tissue have been conducted in Canada, Sweden, Italy, the United Kingdom, and the former Soviet Union (Williams, Kennedy et al., 1993, Weistrand and Noren 1998, Witt and Niessen 2000, Kunisue, Johnson-Restrepo et al., 2009, Schiavone, Kannan et al., 2010), and a study on PCNs in liver tissue has been conducted in Sweden (Weistrand and Noren, 1998). Data from these studies are insufficient to support the assessment of human exposure levels and potential health risks of PCNs. Most of these studies were conducted more than a decade ago or even earlier, and only a few PCN congeners were investigated.

A study of 75 PCN congeners in 4,480 breast milk samples from 100 cities in China was conducted to determine the concentrations of PCNs in the breast milk of the general population of China, the distribution of congeners, the potential health risks of PCN exposure for infants who are predominantly breastfed, the potential sources of PCNs in breast milk, and the differences in the effects of historical residues of PCNs and sustained unintentional release from industrial processes on human exposure to PCNs (Li, Zhang et al., 2020, Li, Li et al., 2021). The concentrations of PCNs in the breast milk of the general population across 24 provinces of China range from 211 to 2,497 pg/g lipid weight, which is a moderately low level. The carcinogenic risk of PCN intake through breast milk for infants is not obvious. The unintentional emission of PCNs during industrial thermal processes may be the main source of PCNs in the breast milk of the general population of China. Historically, the residues of commercial PCN products have a significant effect on human exposure and potential health risks, although this effect shows a significant downward trend over time.

Current studies cover only a few PCN congeners and lack a survey of the contribution of all PCN congeners to the overall TEQ owing to limited available data. Detecting 75 congeners is necessary to determine the source of PCNs in the environment. Data on PCNs in food and dietary intake are also very limited. The amount PCNs ingested through the human diet has not been thoroughly clarified, and thus the long-term effects of PCN intake on humans need to be further studied.

12.7 CONCLUSION AND OUTLOOK

PCNs are listed in the Stockholm Convention on Persistent Organic Pollutants. To meet the requirements of the Convention, global monitoring of PCNs is imperative. However, there is no international consensus on standard methods for the analysis of PCNs in various environmental media,

and the establishment of standard analytical methods is the basis for effective data comparison and research. Therefore, it is necessary to establish standard sampling and analysis methods for detecting PCNs in various environmental and industrial emission media.

There are many sources of PCNs, and there are significant differences in the scale, process technologies, and pollution control technologies at different production facilities within the same source category. Therefore, the generation mechanism and emission characteristics of PCNs still need extensive and in-depth research. From an understanding of the mechanism underlying the generation of PCNs, it is necessary to develop technologies to mitigate PCN emission and pollution. In addition to identifying pollution sources, identifying potential sources and quantifying emission still need to be continued. Concurrently, the levels of PCNs in industrial workers and surrounding populations also need to be determined to assess potential health risks.

ACKNOWLEDGMENTS

We are thankful for the support from the Second Tibetan Plateau Scientific Expedition and Research Program (STEP) (grant No. 2019QZKK0605), National Natural Science Foundation of China (22076201), and the Chinese Academy of Sciences Innovation Team Project (JCTD-2019–03).

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13 Glyphosate in Our Ecosystem
Identifying Sources, Assessing Toxicity, and Exploring Remediation Approaches

Md Nuruzzaman, Sonia Shilpi, Md Abdul Halim, and Ravi Naidu

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ABBREVIATIONS

AMF	arbuscular mycorrhizal fungi
AMPA	aminomethylphosphonic acid
BMI	body mass index
EC	European Commission
EU	European Union
EFSA	the European Food Safety Authority
EPSPS	5-enolpyruvylshikimate-3-phosphate synthase
FIFRA	the Federal Insecticide, Fungicide, and Rodenticide Act
FIGO	the International Federation of Gynecology and Obstetrics
GBH	glyphosate-based herbicide
GE-HT	genetically engineered herbicide-tolerant
GOR	glyphosate oxidoreductase

DOI: 10.1201/9781003530466-13
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GR	glyphosate resistant
IARC	the International Agency for Research on Cancer
ISS	Istituto Superiore di Sanità
NHL	non-Hodgkin's lymphoma
Pi	inorganic phosphorus
POEA	polyethoxylated tallow amine
ROS	reactive oxygen species
SAP	the Scientific Advisory Panel
TIDES	the Infant Development and the Environment Study
US EPA	United States Environmental Protection Agency
WHO	World Health Organization

13.1 INTRODUCTION

The widespread, popular application of pesticides including herbicides is a rising global concern because they may turn into persistent environmental contaminants. As a single entity, application of glyphosate (N-[phosphonomethyl]glycine) has drawn a lot of attention due to its dominance of the worldwide herbicide market during the past few decades. It was apparently first synthesized by Swiss chemist Henri Martin in 1950, and patented as a chemical chelator due to its metal binding capability (Richmond, 2018). Later, herbicidal glyphosate was developed and tested by chemist John E. Franz at Monsanto Chemical Company, USA in the 1970s (Duke and Powles, 2008). The binding ability of glyphosate to manganese inhibits the synthesis of an enzyme which is essential in plants and bacteria for biosynthesis of three amino acids, namely tyrosine, phenylalanine, and tryptophan which are found in all proteins (Richmond, 2018). Because of this characteristic, glyphosate sparked interest in the development and marketing of its formulation as a broad-spectrum herbicide. The first product, Roundup™, was marketed in 1974 by Monsanto (Duke, 2018). Some other glyphosate-based formulations marketed by Monsanto are Roundup Pro®, Roundup PowerMAX™, Roundup WeatherMAX®, RoundupCT, AquaMaster®, etc. The expiration of its patent held by Monsanto in 2000 permitted other companies such as Adama Agricultural Solutions Ltd., DuPont, Syngenta, BASF, Crop Science, Nufarm Limited, and Dow AgroSciences as well as several Chinese companies to introduce different glyphosate-based herbicide (GBH) formulations.

From the chemical perspective, glyphosate is a phosphonomethyl derivative of the amino acid glycine (Peillex and Pelletier, 2020). Generally, it is a white and odorless crystalline solid having one basic amino group and three ionizable acidic sites belonging to the phosphonate and carboxylate groups (Figure 13.1). The formulations contain active ingredients, mostly isopropylammonium

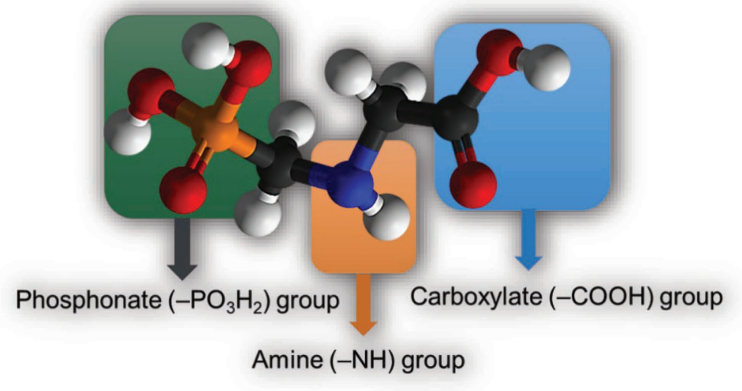


FIGURE 13.1 Chemical structure of glyphosate (adapted and modified from Jayasumana et al., 2014.)

salt of glyphosate. The active ingredients can differ and present in other forms; however, it converts to its acidic form once it is applied. Other forms of active ingredients present in glyphosate formulations are mono-ammonium, dimethyl ammonium, sodium and potassium as the counter ions, or dianionic form paired with one protic cation like diammonium salt or more than one cation including potassium/ammonium salt. Along with active ingredients, glyphosate formulations contain adjuvants such as surfactants, for instance polyethoxylated tallow amine (POEA). POEA present in the formulations facilitates the entry of glyphosate across the cuticle of target plants.

Although glyphosate is a highly water-soluble herbicide, it can be adsorbed by soils and persists for a long period of time (average half-life 47 days). On degradation, glyphosate also generates metabolites including aminomethylphosphonic acid (AMPA). Research has revealed that long-term environmental contamination of glyphosate and its metabolite AMPA causes harm to '**One Health**', i.e., the health of all people, animals, and ecosystems. Concerns about health were taken much more seriously after it was declared a possible carcinogen (Group 2A) by IARC (IARC, 2015). However, the world's leading regulatory bodies claimed that it is not a carcinogen and there are no risks to human health when glyphosate is used according to the label (CropLife, 2018). It is also evident that glyphosate in commercial formulations even goes beyond regulatory limits and causes carcinogenic, hepatorenal, teratogenic, and tumorigenic conditions, besides threatening endocrine disruption, metabolic alterations, and oxidative stress. These scenarios depend on dose and exposure time (Mesnage et al., 2015). Even exposure to glyphosate was linked to the formation of non-Hodgkin's lymphoma in humans (IARC, 2015). It has been found that glyphosate existing in formulations is more toxic because of the adjuvants present in glyphosate formulations (Gandhi et al., 2021). For instance, the surfactant POEA was discovered as having a serious effect on aquatic and terrestrial animals (Van Bruggen et al., 2018b). In this context, this chapter outlines the trend of glyphosate use and its ubiquitous growth to focus on its short- and long-term environmental impacts. Concerns about safety of the general environment and ecosystem, waterways, animals, and, ultimately, humans have been highlighted. Considering the risk of GBH formulations, current regulatory guidelines have been discussed as to their effectiveness. This chapter also summarizes the technological developments made to remediate glyphosate- and AMPA-contaminated soil and water. This chapter concludes on the progress that has been made to date and future actions required to achieve the sustainable management of glyphosate contamination and exposure.

13.2 SOURCES OF GLYPHOSATE IN THE ENVIRONMENT

Generally, glyphosate is a broad-spectrum, post-emergent, non-selective, systemic herbicide, which effectively kills or suppresses all plant types, including grasses, perennials, vines, shrubs, and trees (Okada et al., 2020). It also acts as a plant-growth regulator and desiccant when applied at smaller rates. Introduction of glyphosate as a commercial formulation was recognized as a "breakthrough" in the herbicide industry. It was identified as a broad-spectrum herbicide and exhibited low acute toxicity, which means that it is far less toxic than several other broad-spectrum herbicides. The mean lethal acute dose is virtually the same as that of table salt (Fred Fishel et al., 2019). Furthermore, its high-water solubility theoretically indicated its rapid excretion from human and animal bodies on intake. In this context the application of glyphosate is not limited to controlling weeds in the agriculture industry but extends to non-agricultural removal of unwanted plants and weeds. Thus, the intentional application of huge amounts of GBH formulations explains why so much glyphosate ends up in the natural environment. In some cases, accidental spillage or effluents of glyphosate synthesis or some textiles industries due to using glyphosate as raw materials for additives, introduces glyphosate as an active ingredient to the environment.

Globally, glyphosate was applied steadily so that by 1994 the total application reached 56.3 million kg when 43 million kg of the substance as an active ingredient was applied in agriculture; another 13 million kg was applied for non-agricultural purposes. With the rise of genetically engineered herbicide-tolerant (GE-HT) crops in the 1990s, a huge impact was also observed in glyphosate use worldwide. Further, the global use of glyphosate increased dramatically once Monsanto's

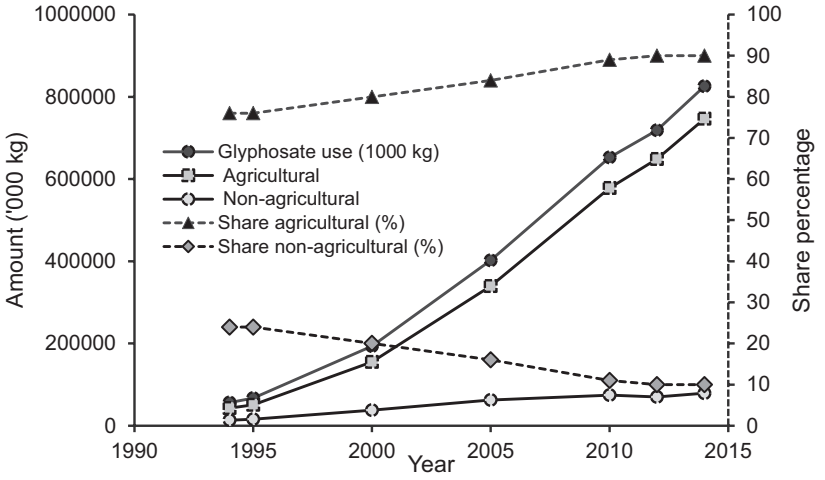


FIGURE 13.2 Global use of glyphosate from 1994–2014 (data adapted from Benbrook, 2016).

glyphosate patent expired in 2000, giving the green light to other companies to produce glyphosate and sell it (Perry et al., 2019). The total global application increased more than 12-fold from 1995 to 2014, specifically from 67 million kg to 826 million kg (Figure 13.2).

13.3 CASE EXAMPLES OF ENVIRONMENTAL CONTAMINATION AND MAJOR CONCERNS

Although glyphosate-based formulations are used to destroy weeds, their application in both agricultural and non-agricultural scenarios is currently a global problem. Previously, it was considered relatively safe for humans; however, in recent years, glyphosate exposure has been the subject of extensive debate regarding its potential toxicity. Along with active ingredients, a pesticide formulation contains additives (e.g., surfactants) that primarily act as wetting agents, assist uniform spreading of the herbicide on the leaf surface, and help in the penetration of glyphosate into the leaf, ultimately improving the effectiveness of the pesticide active ingredient. At the same time, however, it may increase the toxicity to non-target biota (Bradberry et al., 2004, Tsui and Chu, 2003, Edginton et al., 2004). Recently, Maggi et al. (2020) analyzed the global environmental contamination by glyphosate and its primary metabolite, AMPA (Figure 13.3). Worldwide, less than 0.1% of croplands have a high contamination hazard, but approximately 1% of croplands (385,000 km^2) are susceptible to medium to high hazards (Maggi et al., 2020). Widespread glyphosate use in pastures, soybean, and corn was the main contributor to hotspots found in South America, Europe, and East and South Asia. In addition, biodegradation resistance, residue accumulation in the topsoil, leaching below the root zone, and persistence contributed locally to hazards arising these hotspots.

Glyphosate's global ubiquity, increasing spray rates, and evidence of *in vitro* and *in vivo* toxicity raise concerns as to whether it also affects human physiology and health. Humans can be exposed to glyphosate through water, food, the workplace, and domestic habitats near agricultural areas. Indeed, studies analyzing urine samples from occupationally exposed persons find glyphosate levels ranging from 1.54 to 434.73 nM (Gillezeau et al., 2019a, von Osten and Dzul-Caamal, 2017, Lacroix and Kurrasch, 2023). Humans can also be exposed to glyphosate accidentally. For instance, one 42-year-old worker with a history of agricultural work ended up in a hospital emergency department with signs of dizziness, nausea, abdominal pain, and respiratory distress. The patient reported that the symptom developed due to a recent accidental exposure to a GBH after cleaning a logged sprayer containing Roundup inside a small room (US EPA, 2014). The IARC Working Group cited

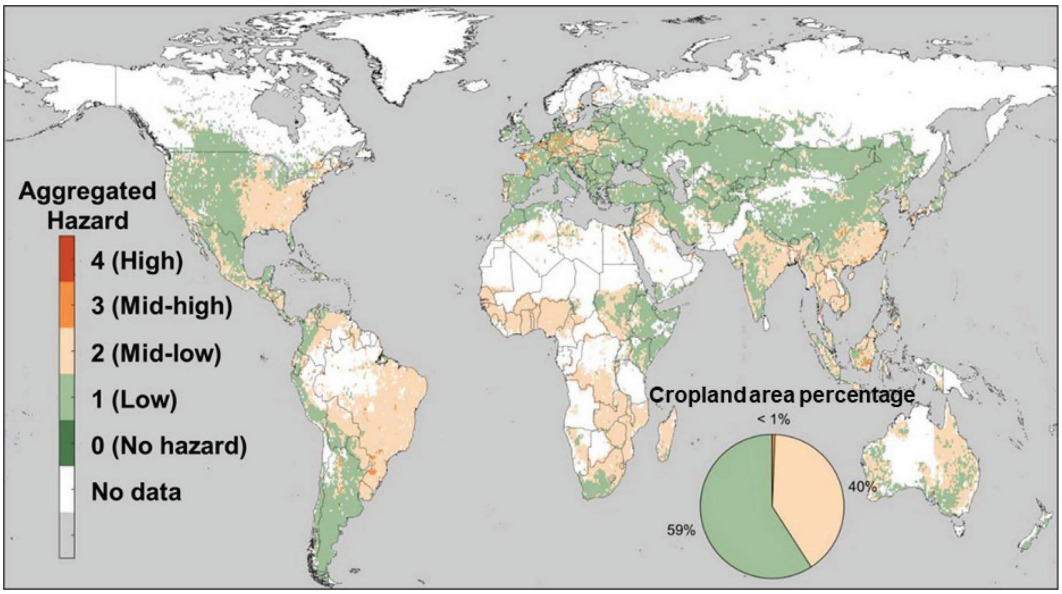


FIGURE 13.3 Aggregated contamination hazards of glyphosate and AMPA resulting from biodegradation recalcitrance, residue accumulation in the topsoil, leaching below the root zone, and persistence (adapted from Maggi et al., 2020).

sufficient evidence for the carcinogenicity of glyphosate in experimental animals, as well as strong evidence that exposure to glyphosate is genotoxic and can induce oxidative stress in experimental animals and humans (IARC, 2015). Hence, IARC has categorized glyphosate as 'probably carcinogenic' under Group 2A (IARC, 2015). Also, limited evidence was reported in humans, noting the increased risk of non-Hodgkin's lymphoma in some epidemiological studies. However, the European Food Safety Authority (EFSA) and US EPA opposed this conclusion on glyphosate. These agencies suggested that glyphosate is not a concern as far as human and animal health are concerned (EFSA, 2015, US EPA, 2019).

Various reviews also suggest that glyphosate exposure occurs at concentrations irrelevant to human and animal health or that any associations are weak. For example, Mink et al. (2011) reported there were no associations in their analysis of non-cancer human health risks based on cohort studies, including those outcomes encompassing respiratory, cardiovascular, neurologic, and reproductive systems. In another study involving 44,932 glyphosate users, 5,779 (approximately 13%) were diagnosed with cancer in the study follow-up period, leading the authors to conclude that no association between glyphosate use and cancer existed given this relatively low percentage (Andreotti et al., 2017). Conversely, a secondary meta-analysis states that there is a compelling link between non-Hodgkin's lymphoma and glyphosate (Zhang et al., 2019). The International Federation of Gynecology and Obstetrics (FIGO) committee recommended with reference to reproductive and environmental health that glyphosate exposure should cease with a full global phase-out (FIGO, 2019).

So far, glyphosate has been categorized as a class action chemical against which thousands of lawsuits have been filed. Most of these cases claimed to have non-Hodgkin's lymphoma due to glyphosate exposure. In May 2018, Dewayne Johnson, a 46-year-old Californian groundskeeper, became the first person to take the global seed and chemical company, Monsanto, to court. Johnson's suit alleges that the company suppressed evidence that its product (Roundup) is responsible for causing non-Hodgkin's lymphoma cancer (Guardian, 2018). Similarly, California couple Alva and Alberta Pilliod claimed Bayer-Monsanto's glyphosate-based weed killer, Roundup, caused their cancer (Firm, 2018). Edwin Hardeman, who sprayed Roundup on his properties, claimed that Roundup caused his cancer. The US jury granted millions of dollars in compensation over

such claims which accused Roundup of causing people's cancer. Bayer agreed to pay in total US$10.9 billion to settle about 95,000 cases claiming Roundup caused cancer (Guardian, 2020).

Similarly, in Australia, Ross Wild, a 67-year-old farmer from New South Wales, is suing Monsanto, claiming long-term exposure to Roundup caused his non-Hodgkin's lymphoma. The first Australian legal case against the agribusiness giant Monsanto was lodged by a Melbourne gardener, Michael Ogliarolo, 54, who claimed his cancer was triggered by the herbicide Roundup after he developed non-Hodgkin's lymphoma (Guardian, 2020). The weed killing chemical glyphosate has been reported in the urine as biomarkers related to the development of cancer and other diseases, such as oxidative stress in the pathogenesis of hematologic cancers, lymphoma, myeloma, and leukemia.

The specific mechanism by which glyphosate exerts its toxicity in humans is not yet fully understood. It is hypothesized that it disrupts the shikimate pathway, which is vital for synthesizing aromatic amino acids in bacteria and plants. Human cells lack this pathway; however, emerging evidence indicates that glyphosate can affect the human gut microbiota, potentially contributing to various health problems. Recent studies show that childhood exposure to glyphosate is linked to liver inflammation and metabolic disorder in early adulthood, which could lead to liver cancer, diabetes, and cardiovascular disease later in life (Eskenazi et al., 2023, Christensen, 2023). Of all concerns to human health, the discourse on carcinogenic effects is the most publicized, receiving significant attention in the media. Reviews on human epidemiological studies regarding the carcinogenicity of glyphosate tend to be inconclusive.

13.4 FATE AND DYNAMICS OF GLYPHOSATE IN SOIL AND WATER ENVIRONMENTS

Once it is applied, glyphosate reaches both target and non-target plants as well as covering the soil surface. It undergoes several processes including onsite and offsite movement through air drift, surface runoff, leaching, volatilization, etc., so apart from soils it can also contaminate the air and nearby groundwater and surface water (Figure 13.4). However, the fate and distribution of glyphosate in the environment vary due to the surrounding climatic factors, e.g., precipitation, temperature, wind speed, etc. Soil, surface water, groundwater, sediments, and the atmosphere are significant sinks for glyphosate where it is applied.

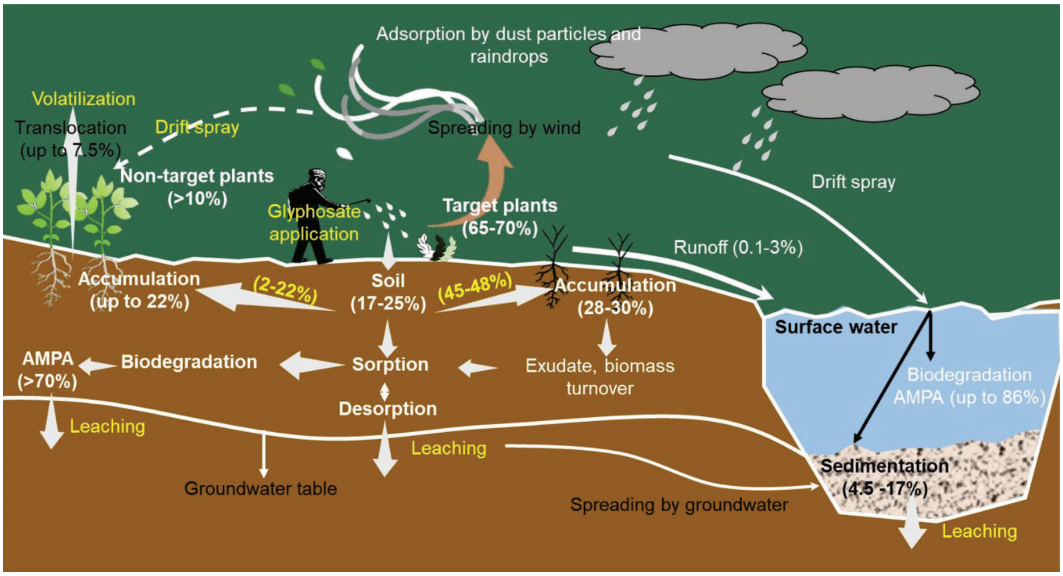


FIGURE 13.4 Environmental fate and behavior of glyphosate (adapted and modified from Villamar-Ayala et al., 2019).

Glyphosate-controlling factors in surface water and soil include adsorption and dispersion, dissociation, volatilization, microbiological degradation, plant uptake and assimilation, rhizome degradation, adsorption complexes in clay and sediments, precipitation, and dissolution. In subsurface soils, at low concentrations it can be degraded through aerobic and anaerobic processes. Conversely, the primary fate mechanisms of water-borne glyphosate include precipitation, metal–glyphosate complexation, photolysis, biological oxidation, biodegradation, and volatilization, etc. Consequently, glyphosate can be volatilized as a gaseous substance mixed with atmospheric droplets, before being precipitated into surface water. It may also be biodegraded into CO_2, ammonia, and nitrate. Accidental spills or continuous application lead to high concentrations of water-soluble glyphosate and AMPA, which is toxic to microorganisms and may leach into groundwater. Phytoavailable glyphosate and AMPA can be taken up by herbivores and insects, then to higher animals. Animal waste (e.g., feces) and the remains of dead animals and plants are processed by soil microorganisms before being taken up by plants. Therefore, glyphosate is recycled through water and soil surfaces and groundwater.

13.4.1 Fate of Glyphosate in Soil

Soil is the biggest sink of applied pesticides including glyphosate which potentially affects various components of the soil environment and ecosystem. Applied glyphosate ends up in different soil pools including direct deposition on soil surface, wash-off from foliage, dead and decaying glyphosate-treated plants, and from root exudates. Once the glyphosate reaches soils after application or the plant-entrapped glyphosate is released to the soil on the decomposition of plant tissues, they rapidly interact with soils. Glyphosate interacts with soil in various ways influenced by the intrinsic properties of the molecule (e.g., sorption sites or functional groups, solubility, persistence, etc.) as well as the physicochemical and biological properties of the soil.

Generally, glyphosate is a small molecule with three different functional groups, i.e., carboxylate, amine, and phosphonate (Figure 13.1); hence, it has high binding affinity with soil through the adsorption process. Various physicochemical properties of soils including organic matter content, clay content, cation exchange capacity, metal oxides, phosphorus content, and pH influence the adsorption of glyphosate (Gómez Ortiz et al., 2017). It has a high affinity to be adsorbed on soils with variable charge compared to permanent charge (Gimsing et al., 2004, Gimsing and Borggaard, 2007). In earlier research, it was observed that glyphosate adsorbed by soil constituents followed similar mechanisms of inorganic phosphorus (phosphate) and shared the same adsorption sites on soil (Sprankle et al., 1975b). As a result, they compete but phosphate bonded more strongly than glyphosate (Gimsing et al., 2007, Hance, 1976). Thus, plant injury increases with a rising amount of inorganic phosphate in a glyphosate-treated soil (Sprankle et al., 1975b). Sorption of phosphate and glyphosate was positively correlated with contents of extractable aluminum and iron including their oxides (Gimsing et al., 2004, Gimsing et al., 2007). In this scenario, the glyphosate is adsorbed by the ligand exchange mechanism in which a –OH group present in Fe/Al-hydration sphere is exchanged by the –OH group of phosphonic moiety (Piccolo et al., 1994). This mechanism explained the reason for glyphosate's high affinity for variable-charge soils since they may contain iron and aluminum oxides, aluminum silicates (allophone and imogolite), and goethite (α-FeOOH) (Duke et al., 2012).

It is noted that the type of clay minerals has little influence on the sorption of glyphosate, whereas the types of exchangeable cations of the clays or Fe-oxide coatings of permanent-charge minerals (e.g., illite, smectite, and vermiculite) can dictate glyphosate sorption. It was observed that glyphosate adsorption on bentonite clays saturated with cations diminished in the following the order: $Al^{3+} > Fe^{3+} > Mg^{2+} > Zn^{2+} > Mg^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+}$ (Sprankle et al., 1975a). This may occur due to the formation of terdenate or tetradenate complex or chelates with metal ions coordinating the metal surface (McBride, 1994). Similarly, chelates or complexes are formed with micronutrient metal ions present in soil solution. Further, adsorption of glyphosate on soil organic matter somehow depends on their degree of humification. It was observed that glyphosate interacts with humic acids (HA) through the formation of multiple hydrogen bonding. This kind of bonding may

occur between the phosphonic group of glyphosate and complementary oxygen-containing functional groups of humic acid such as ketones and qui-ketones (Piccolo and Celano, 1994).

Moreover, metal-humic complexes as well as the cations present on the surface of organic matter positively influence the sorption of glyphosate. Specific interactions among glyphosate and soil can vary due to local environmental and climatic factors including precipitation and temperature. In contrast the pH of the soil solution plays the most important role during adsorption because glyphosate is a polyprotic acid having different dissociation values (Figure 13.5). As such, the system pH controls the ionic or charge structure of glyphosate molecules as well as pH-dependent active sites in soil. In most cases, the adsorption of anions is coupled with a release of OH- ions, so adsorption is favored by lower pH values. At higher pH the sorption of glyphosate declines because of the repulsion forces generated from high negative charge in soil.

In soils, glyphosate undergoes further degradation occurring through the action of both biotic and abiotic factors. Degradation takes place either through the cleavage of a C–N bond or a C–P bond.

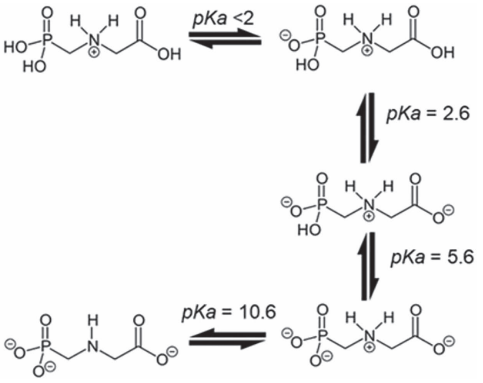


FIGURE 13.5 Chemical speciation of glyphosate.

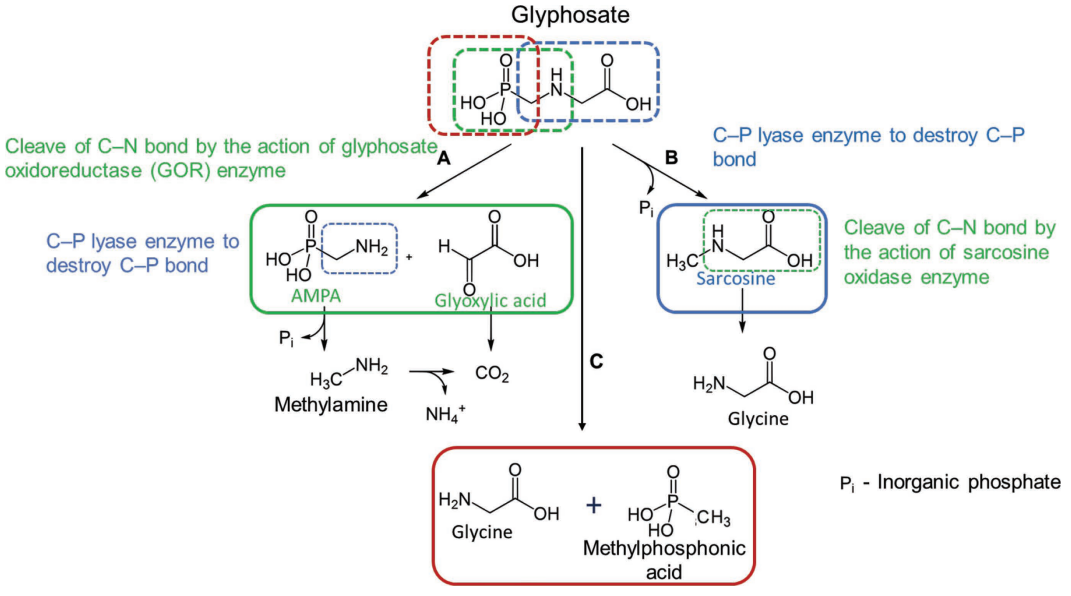


FIGURE 13.6 Biodegradation pathways of glyphosate in bacteria (Zhan et al., 2018).

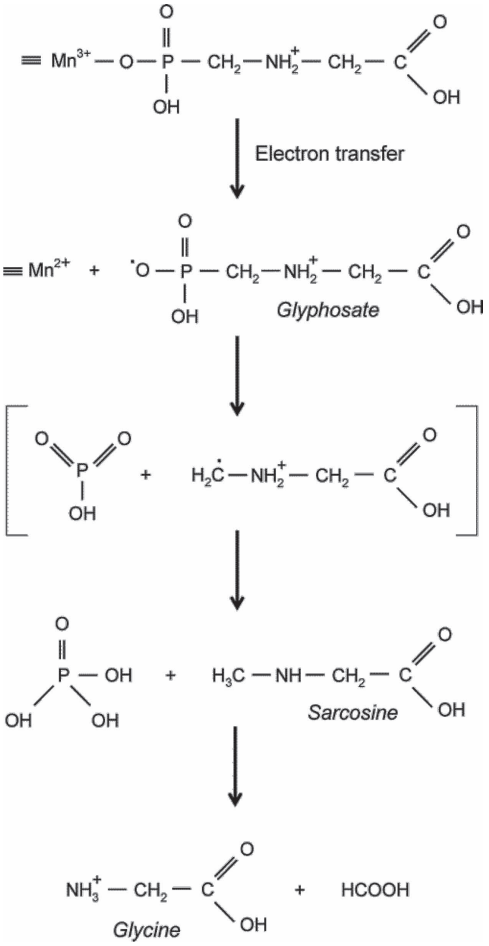


FIGURE 13.7 A possible degradation reaction scheme for glyphosate adsorbed on manganese oxide (adapted from Barrett and McBride, 2005).

The cleavage of a C–N bond generates AMPA and glyoxylic acid (glyoxylate) whereas the cleavage of a C–P bond results in the formation of sarcosine followed by glycine (Figure 13.6). In the biotic process, microorganisms such as bacteria and fungi are the major vectors that cause the degradation of glyphosate because the microbes – especially various bacterial species – utilize glyphosate as a source of nitrogen. They cleave the C–N bond by the action of the glyphosate oxidoreductase (GOR) enzyme and subsequently, equimolar quantities of AMPA and glyoxylic acid are generated. Some bacterial species also utilize glyphosate as a source of phosphorus for which they possess a multienzyme complex known as C–P lyase, which destroys C–P and produces sarcosine and inorganic phosphorus (P_i). It was also reported that a few bacterial strains are able to metabolize the persistent metabolite AMPA by secreting C–P lyase enzyme, yielding methylamine and P_i. Microbial activities in soil are regulated by soil moisture and temperature, organic matter content, pH, and soil texture, consequently affecting glyphosate degradation and AMPA formation (Zhang et al., 2015).

Chemical degradation and photolysis are the two dominant methods of abiotic degradation of glyphosate, and they are driven by soil minerals and the presence of light (Barrett and McBride, 2005). For example, oxidative degradation of glyphosate took place on Mn oxide surface where sarcosine was generated as the degradation product due to the cleavage of the C–P bond (Figure 13.7). In comparison, the degradation of glyphosate was faster than that of AMPA; however, several other factors such as temperature or presence of other cations/anions (e.g., SO_4^{2-}, Cu^{2+}) influences the reaction rate.

13.4.2 Fate of Glyphosate in Water

Glyphosate was not deemed to be a problem for groundwater and surface water in the past because of its relative minimal tendency to move through soil and contaminate aquatic environments (Sihtmäe et al., 2013, Monsanto, 2002, 2014). However, glyphosate and its metabolites, especially AMPA, are highly polar compounds; thus, both the molecules have high affinity to dissolve into water. High water solubility properties give the substances a great leaching ability through the soil macropores that assist their entry into groundwater (Skark et al., 1998). Soil-adsorbed glyphosate and AMPA also dissolve in soil solution following heavy rainfall (Maqueda et al., 2017, Rendón-von Osten and Dzul-Caamal, 2017). Heavy rainfall shortly after glyphosate application also poses a great risk of its transport to groundwater.

Similarly, application timing, agronomic practices, and other weather conditions cause seasonal differences in glyphosate and AMPA in water systems (Carretta et al., 2022). In some cases, root exudation transports glyphosate into a deeper soil layer that facilitates more penetration of glyphosate and AMPA into groundwater. Rain, irrigation, and soil erosion can also transfer glyphosate, as well as soil particles with glyphosate and AMPA, into surface water in the form of surface runoff (Van Bruggen et al., 2018a). During the application of glyphosate formulations, it can directly deposit into nearby water bodies via drift. Once the glyphosate and AMPA reach surface water and groundwater they undergo several processes including degradation. Moreover, dissolved glyphosate and AMPA in surface water can sorb to the underneath sediment. Polluted particles can also settle and become absorbed in the bottom sediment (Aparicio et al., 2013, Maqueda et al., 2017). Glyphosate biodegradation is much slower in sediment than in dissolved water (Wang et al., 2016).

13.5 TOXICITY, EXPOSURE, AND RISKS TO 'ONE HEALTH'

Glyphosate-based formulations (e.g., Roundup, Rodeo, Aquamaster, etc.) are applied to destroy weeds because they are commonly assumed to be safe. Advances in research have revealed their risk to the ecosystem, animals, and human health, designated in the concept known as 'One Health'. This approach was devised by the Italian ISS (Istituto Superiore di Sanità). The aim of this approach is to maintain and improve the health of all people, animals, and ecosystems, emphasizing the strong relationships, sustainability, and dependency between the environment and all living organisms, including humans (Ferrante et al., 2023).

13.5.1 Human and Animal Exposure to Glyphosate

Human exposure to glyphosate happens mainly through skin exposure during mixing and usage of glyphosate or direct contact with treated crops, ingestion of contaminated crops or water, inhalation, eye exposure, and oral exposure as a result of accidental ingestion (Williams et al., 2012). Ingestion for suicidal reasons has also been reported. Exposure through inhalation is likely to be negligible due to its non-volatile nature and this explains why the US EPA ignored the registration requisite for an acute inhalation research study on the effects of glyphosate (US EPA 1993). Exposure through application, handling, and manufacturing of glyphosate are the main work-related exposures which cause direct neighborhood exposure by not directly applying the chemical. Instead, direct contact is due to its application and release in the surrounding areas where agriculture and farmsteads occur.

Likewise, farmers and gardeners in agricultural areas and farms can be exposed to glyphosate through dermal contact and visual contact during glyphosate use; this is referred to as residential exposure (Gandhi et al., 2021). Residents in faraway areas can be exposed to glyphosate-contaminated water and food (WHO, 2017). Due to the long-term use and its high thermal stability, glyphosate can accumulate in crops and be transferred to plant-based foods (Narimani and da Silva, 2020, Gillezeau et al., 2019b). Consumption of these contaminated foods and water by humans and animals is indirect exposure to glyphosate; this is called dietary exposure (Myers et al., 2016, Muñoz et al., 2021). Another type of indirect exposure is environmental exposure which happens due to the presence of residues or metabolites of glyphosate in air, water, and soil (Gandhi et al., 2021).

Glyphosate's main routes of entry into the body are dermal, oral, and pulmonary pathways (Williams et al., 2000). Although the dermal route permits very low absorption (nearly 2%), it is the main reported method of entry in farmers exposed to the substance (Connolly et al., 2019). Glyphosate then moves and accumulates mainly in the kidneys, liver, colon, and small intestine and is removed in feces (90%) and urine in 48 h (Williams et al., 2000). Both glyphosate and AMPA are eliminated in urine along with half-lives ranging from 3 to 15 h without changing their structure (Anadón et al., 2009). In one study, glyphosate residues were reported in urine but not breast milk of lactating mothers (McGuire et al., 2016). Glyphosate has also been detected in human blood (Kwiatkowska et al., 2013, Acquavella et al., 2004, Gillezeau et al., 2019b). For instance, Kongtip et al. (2017) measured glyphosate concentrations in maternal and umbilical cord serum in 82 pregnant women in Thailand. They found that the glyphosate concentrations in the pregnant women's serum at childbirth (median: 17.5, range: 0.2–189.1 ng mL^{-1}) were significantly higher ($P < .007$) than those in the umbilical cord serum (median: 0.2, range: 0.2–94.9 ng mL^{-1}).

13.5.2 Toxicity and Risks to Human and Terrestrial Animal Health

Generally, toxicity is classified into two types: acute toxicity and chronic toxicity. Acute toxicity refers to the hazard associated with exposure to a chemical due to inhalation and dermal and oral exposure during spraying of chemicals (Wallace and Lingenfelter, 2019). Meanwhile chronic toxicity refers to the continuous ingestion of small amounts of chemicals in diets and their associated hazards (Wallace and Lingenfelter, 2019). The absence of the shikimate pathway in animals is the basis for the lack of acute toxicity of glyphosate after a single exposure to relatively high dosages. For example, in glyphosate, in the context of mammalian toxicity, the acute LD_{50} (lethal dose, 50%) is approximately 5,037 mg kg^{-1}, and according to EPA registration, any herbicide having an LD_{50} of more than 5,000 mg kg^{-1} means that it will be in Category IV, so it will have the least acute toxicity. The LD_{50} values of glyphosate are just at the borderline of Category IV chemicals. The literature indicated that exposure to glyphosate has risen in the general population and especially with some occupations such as farming, revealing higher levels of exposure through dermal contact. However, there has been a lack of research on glyphosate exposure levels, particularly in children.

With more systematically collected data, it is easier to establish a clear link between glyphosate exposure and disease. A comprehensive analysis of the nutritional risks associated with glyphosate exposure is necessary to address this knowledge gap. However, to date, there is no evidence linking glyphosate exposure to disruptions in the environment that cause human microbiome-related disorders. We emphasize the need for more comprehensive data on the occurrence of glyphosate in the atmosphere with a proven link to exposure toxicity that affects the environment and human health. Finally, more data needs to be amassed on exposure levels in susceptible groups and high-risk areas of the general population, to accurately document the outcomes for human health based on glyphosate toxicity and environmental exposure. This chapter focuses on glyphosate and AMPA occurrence in the environment as presented earlier, showing they are ubiquitous in ecosystems and frequently occur in several types of food.

While acute toxicity of glyphosate to mammals is minimal, what has been detected is that products with glyphosate formulations are more harmful than glyphosate itself, which has raised concerns about its potential impact on humans as a contributor to many cancers and mental disorders in specific circumstances. For instance, the FAO states that the dietary risk of glyphosate and AMPA is unlikely if the maximum daily intake of 1 mg kg^{-1} body weight (bw) is not exceeded. However, rats exposed to Roundup® at rates between 50 mg kg^{-1} and 450 mg kg^{-1} for 21 days during pregnancy showed no adverse effects. Interestingly, however, male offspring did incur damage to their reproductive organs (Dallegrave et al., 2007).

Research has suggested a lower absorption/resorption and systemic availability in humans than in animals. Additionally, several studies reported glyphosate detection in other biological matrices such as plasma, umbilical cord serum, hair, and breast milk. For example, animal studies reported that glyphosate was poorly metabolized and rapidly excreted from the body, primarily via fecal

elimination and approximately 10–30% via urine. In humans, although information on the kinetics of elimination of glyphosate was minimal, some studies documented that about 1–6% was excreted unchanged in the urine, with a biological half-life ranging from approximately 3 to 33 h.

A recent study done in the French population showed that glyphosate was quantifiable in 99.8% of urine samples with a mean of 1.19 ng mL^{-1} ± 0.84 after adjustment to body mass index (BMI), which requires special attention. Again, the Infant Development and the Environment Study (TIDES), a multi-center US pregnancy cohort, found that vast glyphosate exposure to the general population might affect reproductive health by shortening gestation length. Furthermore, in children, high levels of glyphosate in urine were associated with more kidney injury biomarkers, indicating a potential negative impact on young children's kidney function. These might have happened due to glyphosate contaminating the food chain via rice, fruits, and vegetables, as has been reported in countries such as Germany, Mexico, Slovenia, the USA, Australia, Canada, Japan, and Portugal. This is because glyphosate binds strongly to nutrients in the soil, which could significantly reduce nutrients' availability in the soil. Then, glyphosate and AMPA residues were observed in 25% and 8.3% of analyzed cannabis samples, respectively. Similarly, concentrations ranged from 1,000 to 0.3 mg kg^{-1} in tree foliage sampled within 3 days of glyphosate application. On the issue of glyphosate in water, it is potentially toxic to amphibians and fish at over 400 μg L^{-1}. Farmers' exposure to glyphosate can occur in different ways, including direct handling and indirect contact through spills, sprays, and splashes.

While it is unclear how many people have been occupationally exposed to glyphosate, one study estimated that 11–13% of agricultural workers were exposed in Canada. Until 2015, occupational exposure to glyphosate was reported to range up to 0.01 mg kg^{-1} $BW{\cdot}d^{-1}$. In this chapter, we have reviewed the level of exposure to glyphosate in occupational settings since 2015, with detected concentrations ranging from 0.26 to 292 μg L^{-1} . The studies included horticulturalists in Ireland, farmers in Mexico, Sri Lanka, Thailand, and the state of Wisconsin in the USA, and industrial workers in China. They confirmed previous reports that glyphosate and its metabolite, AMPA, were widely detected in urine samples obtained after work tasks. Overall, these reports confirmed that the highest concentrations were observed in samples taken up to 3 h after completing a work task, while urine samples taken 24 h after applying the herbicides did not show traces of glyphosate, suggesting the possible intake of pesticide and a subsequent renal clearance of the compound in the urine.

High glyphosate values were detected in a study that analyzed the levels of glyphosate in urine samples from manufacturing workers in China. Its results concluded that the geometric median was 262 μg L^{-1} in the 0.020–17.202 mg L^{-1} range. Furthermore, the concentration of glyphosate and AMPA in urine was positively correlated with the concentration of glyphosate found in the air, reflecting the dangerous conditions the workers were exposed to and suggesting an eventual air-mediated intake. For instance, only a few studies investigated the occupational exposure of workers before and after using GBH formulations in their duties. The impact of glyphosate exposure on workers is evident in Latin American countries like Argentina and Brazil, where widespread GBH use remains understudied. Only one study from China assessed glyphosate levels in the employees of GBH factories. Given the potential toxicity of glyphosate and GBHs, the sparse information on occupational exposure is of paramount concern, especially given the extensive and frequent use of glyphosate in global agriculture. Furthermore, the determination of average levels is affected by LOQ variation, which also limits the integration of data from various studies and comprehending the effects of GBHs. For example, studies reported a geometric mean concentration of 0.7 μg L^{-1} in Irish horticulturists and up to 292 μg L^{-1} in Chinese workers who manufacture glyphosate. The IARC stated in 2015 that glyphosate was probably carcinogenic to humans, which adds credence to it being linked to non-Hodgkin's lymphoma.

One mechanism by which glyphosate may cause genotoxicity is producing reactive oxygen species (ROS). Chemically reactive ROS molecules contain oxygen, such as superoxide, hydrogen peroxide, and hydroxyl radicals. Studies have shown that glyphosate can induce the production of ROS in human cells by impairing mitochondrial functioning. In addition, glyphosate has been shown to inhibit catalase and superoxide dismutase, active antioxidant enzymes in living organisms, including humans. Thus, glyphosate-mediated inhibition of these enzymes can accumulate ROS and oxidative stress. Glyphosate can also cause genotoxicity through the chelation of metals

such as manganese, iron, and zinc, which have the ability to disrupt metal homeostasis and help produce ROS. For example, when buccal epithelial cells were exposed to glyphosate and Roundup® at 10 and 20 mg L^{-1} rates, DNA damage was reported. Since then, several scientific groups have evaluated the toxicological profile of glyphosate, and its carcinogenic potential has been reviewed and debated by many researchers and regulatory agencies.

Further, correlation between occupational exposure to glyphosate and the risk of lymphoma subtypes was investigated through case studies. For example, a multicenter case-control study known as the Italian Gene-Environment Interactions in Lymphoma Etiology study inquired into the correlation between occupational exposure to glyphosate and the risk of lymphoma subtypes during the period 2011–2017 in Italy, including 867 incident lymphoma cases and 774 controls (Meloni et al., 2021). The results strongly suggested that the risk of follicular lymphoma rose 7-fold in subjects classified as continually exposed to glyphosate with medium-high confidence, 4.5-fold in association with a medium-high cumulative exposure level, 12-fold with a medium-high exposure intensity, and 6-fold with exposure lasting ten days or more each year (Meloni et al., 2021). In another case-control study, Omidakhsh et al. (2022) investigated the risk of thyroid cancer in relation to environmental factors, specifically pesticides. The case-control study was performed utilizing the thyroid cancer cases from the California Cancer Registry from between 1999 and 2012, involving 2,067 cases and 1,003 controls. In single pollutant models, 10 of 29 selected pesticides were closely linked to thyroid cancer, including glyphosate (Omidakhsh et al., 2022).

Thus, humans can be exposed to glyphosate directly through GBH application or indirectly through contaminated food. For example, some studies showed that the exposure of insects to glyphosate, such as bees and beetles, altered their normal gut microbiota, affecting their efficiency as pollinators and their development. However, no direct evidence has proven there is a link between GBH exposure and microbiome-related diseases in humans. The European Food Safety Authority (EFSA) asserted that glyphosate is unlikely to be carcinogenic since the IARC has yet to consider all the relevant literature and is open to further clarifying its assessment to address all concerns raised by other parties.

13.5.3 Toxicity and Risk to Aquatic Animals

Leaching of glyphosate to the water system affect many aquatic animals and cause serious toxic outcomes in them (Pérez et al., 2011). Similar to the effects on terrestrial organisms, glyphosate as well as the surfactants POEA and MON 0818 (75% POEA) can have adverse impacts on the health of different animals in the aquatic food web such as protozoa, mussels, crustaceans, frogs, and fish (Tsui and Chu, 2003, Bringolf et al., 2007, Durkin, 2017, Zhang et al., 2017, Rissoli et al., 2016, Li et al., 2017, Prosser et al., 2017). There is limited research on the health effects of adjuvants due to the proprietary nature of these chemicals (Diamond and Durkin, 1997; Durkin, 2017). Glyphosate as an acid or salt (LC_{50} or EC_{50} between 1 and 100 mg L^{-1}) was usually considered "slightly or moderately toxic to aquatic organisms." However, some algae and aquatic plants exhibited higher sensitivity to glyphosate exhibiting EC_{50} between 0.1 and 1 mg L^{-1} (Pérez et al., 2011).

Among the commercial formulations, polyoxyethylene amine-15 (POE-15) is one of the most toxic ones for human cells and, at environmental doses between 1 and 3 ppm, exerts negative dose-dependent effects on cellular respiration and membrane integrity. The genotoxicity of the commercial formulation was evident on the European eel species *Anguilla anguilla*. Fish of this species were subjected to equal amounts of glyphosate (17.9, 35.7 μg L^{-1}), POEA (9.3, 18.6 μg L^{-1}), and Roundup (58, 116 μg L^{-1}) for the first and third days. The findings demonstrated Roundup's genotoxicity while also showing the genotoxicity of glyphosate and POEA independently. Roundup's extremely high toxicity to many freshwater invertebrates and fish is now evident.

Commercial formulations with POEA showed higher toxicity than the active ingredient itself for aquatic organisms. Aquatic animals are more sensitive to POEA than terrestrial animals. The high mortality in fish and amphibians was mainly due to the presence of POEA surfactant and not to glyphosate itself (Servizi et al., 1987, Perkins et al., 2000, Folmar et al., 1979). Rodriguez-Gil et al. (2017) reported that formulations with POEA were more toxic to the microcrustacean *Artemia*

salina and young zebrafish *Danio rerio* than formulations without POEA (both at 360 g glyphosate a.i. L^{-1} water). Pérez et al. (2011) reported that Roundup® was evidently more than 7 times more toxic than glyphosate in algae and aquatic plants, up to 42-fold in fish, up to 13-fold in protozoa, up to 70-fold in crustaceans, and up to 130-fold in frogs and toads. Bringolf et al. (2007) also found that several species of freshwater mussels were more sensitive to glyphosate with MON 0818 (EC_{50} = 1 mg a.i. L^{-1}) and Roundup® (EC_{50} = 4 mg a.i. L^{-1}) than to technical grade glyphosate with EC_{50} > 200 mg a.i. L^{-1}. In their research, Sandrini et al. (2013) reported that pure glyphosate had adverse effects on the activity of acetylcholinesterase at low concentrations (1–676 mg L^{-1}) in brown mussels (*Perna perna*) and some fish species.

Exposure of the European eel (*Anguilla anguilla*) to smaller concentrations of Roundup® (3.6 mg L^{-1}) for four hours damaged the DNA in blood, gills, and liver (Guilherme et al., 2009). Moreover, larger concentrations of Roundup® (50 mg L^{-1}) exposed to zebrafish embryos reduced the development of forebrain and midbrain, and caused eye damage (Roy et al., 2016). Also, chronic exposure of gold fish (*Carassius auratus*) to a glyphosate concentration of 34 mg L^{-1} disrupted metabolism in various tissues resulting in the overproduction of reactive oxygen species, oxidative stress, and finally severe renal injury (Li et al., 2017). Szarek et al. (2000) also reported that freshwater carp (*Cyprinus carpio*) exposed to Roundup® (205 mg or 410 mg of glyphosate L^{-1}) triggered changes in liver cells and mitochondria.

The interactions between fish and their pathogens or parasites can also be affected by glyphosate application. Glyphosate concentrations of 0.36 mg a.i. L^{-1} increased infection of the freshwater fish *Galaxias anomalus* by the trematode flatworm parasite *Telogaster opisthorchis* (Kelly et al., 2010). Moreover, exposure to sublethal concentrations of glyphosate (0.73 mg L^{-1}, 10% of the LC_{50} for 96 h) compromised the survival rate of silver catfish (*Rhamdia quelen*) by reducing the number of blood erythrocytes, thrombocytes, lymphocytes, and total leukocytes, decreasing immune cell phagocytosis and increasing susceptibility to the pathogen *Aeromonas hydrophila* (Kreutz et al., 2010, 2011). Even minute levels of glyphosate might disrupt the balance between hosts and pathogens or parasites in surface water resulting in unforeseen changes in aquatic groups (Van Bruggen et al., 2018a).

13.5.4 Toxicity and Risk to Microorganisms

13.5.4.1 Toxicity to Terrestrial Microorganisms

Glyphosate application can affect the microbial composition and enzymatic activity in the rhizosphere, and the surrounding soil and plant endosphere (Arango et al., 2014, Schafer et al., 2014, Druille et al., 2015, Banks et al., 2014). Due to the presence of the shikimate pathway in plants as well as in fungi and bacteria, various taxonomic groups of microorganisms are sensitive to glyphosate (Van Bruggen et al., 2018a). There are two classes of organisms: class I EPSPS that is sensitive to glyphosate and class II EPSPS that is glyphosate tolerant (Funke et al., 2007, Pollegioni et al., 2011). Plant growth-stimulating microorganisms such as *Burkholderia* spp., *Pseudomonas* spp., arbuscular mycorrhizal fungi (AMF), and nitrogen-fixing *Rhizobium* spp. were adversely affected by glyphosate application even at small concentrations (Druille et al., 2015, Schafer et al., 2014, Arango et al., 2014, Zobiole et al., 2011). It exhibited adverse effects on the growth rate of beneficial microorganisms causing reduced nitrogenase activity, lower indole-3-acetic acid and gibberellin production, and lower phosphate and zinc solubilizing activities (Madhaiyan et al., 2006). Zaller et al. (2014) reported that glyphosate also reduced root mycorrhization by decreasing soil AMF spore biomass, propagules, and vesicles formation in *Trifolium repens* L inoculated with arbuscular mycorrhizal fungi. Reduced growth of beneficial rhizospheric communities resulting from diminished profusion of indole acetic acid-producing rhizobacteria, Mn-reducing bacteria, indole acetic acid-producing bacteria, etc., were also reported (Zobiole et al., 2011).

13.5.4.2 Toxicity to Aquatic Microorganisms

Aquatic microorganisms (various species of microalgae, aquatic bacteria, and protozoa) are adversely affected by glyphosate and the surfactant POEA (Rodriguez-Gil et al., 2017, Tsui and Chu, 2003,

Sihtmäe et al., 2013). Glyphosate interrupts the synthesis of aromatic amino acids, chlorophyll production, photosynthesis, and respiration (Mensink and Janssen, 1994). Various eco-toxicological effects on aquatic environments largely depend on the type of glyphosate formulations including glyphosate active ingredients, AMPA, glyphosate and surfactant, concentration, non-target-organism exposure, and exposure time (Tsui and Chu, 2003). Bacteria (*Vibrio fischeri*), microalgae (*Selenastrum capricornutum* and *Skeletonema costatum*), and protozoa (*Tetrahymena pyriformis* and *Euplotes vannus*) are microorganisms exposed to glyphosate (Tsui & Chu, 2003). Sihtmäe et al. (2013) noted that the marine bacteria *Vibrio fischeri* was sensitive to relatively lower doses of glyphosate in water (EC_{50} values ranged from 5.4 to 7.6 mg a.i. L^{-1}) irrespective of the formulation used.

Microalgae commonly showed more sensitivity to glyphosate and Roundup® (1.2–7.8 mg L^{-1}) than heterotrophic bacteria, while some of them are more tolerant than other species (Tsui and Chu, 2003, Mensink and Janssen, 1994, Wang et al., 2016). Rodriguez-Gil et al. (2017) observed that exposure to a typical application rate of glyphosate (0.89 kg a.e. ha^{-1}, resulting in about 1.2 mg glyphosate L^{-1} and 0.21 mg POEA L^{-1} of surface water) reduces photosynthesis, cell densities, and growth rates of three microalgae. In river water, the growth of autotrophic community was hampered by even a minute glyphosate concentration (0.011 mg L^{-1}) for 3 weeks with no chlorophyll reduction (Bricheux et al., 2013). In pondwater, Roundup® application (6 and 12 mg a.i., higher than the 3.5 mg a.i. recommended for weed control) reduced the density of total micro- and nanophytoplankton and increased the abundance of picocyanobacteria and whole primary production. This was due to the direct toxicological impact of glyphosate on other microorganisms, resulting in the release of nutrients from their dead bodies (Pérez et al., 2007). In tap water in mesocosms (left outside for 6 months), application of technical grade glyphosate with a single dose of 2.4 mg L^{-1} increased the total phosphorus concentration 7-fold (to 0.7 mg L^{-1}) while the density of picocyanobacteria doubled after 1–8 days (Pizarro et al., 2016).

13.6 POLICIES, REGULATORY GUIDELINES, AND PUBLIC ACCEPTANCE CHALLENGES

Glyphosate is registered as an herbicide worldwide and continuously reviewed by various regulatory authorities to evaluate and ensure its safety and usage, including registration processes being conducted properly. When glyphosate was first introduced as an herbicide, many regulatory agencies concluded that, as used, glyphosate was not a carcinogen and posed little health danger by assessing risk factors to the general population or to farm/orchard and other field workers. Even the IARC showed little interest in assessing the carcinogenicity of glyphosate in 1994 (Vainio et al., 1994). However, with its increased use and continuous application, negative effects on humans and other living beings emerged, resulting in increasing lawsuits against its application. The major glyphosate users and their corresponding regulatory authorities are very much concerned and have different views on glyphosate application.

In May 2009, the Environmental Lawyers Association of Argentina filed a lawsuit for a ban on glyphosate based on the study carried out by Professor Carrasco's team. Thus, Argentina was the first country that implemented restrictions on glyphosate's implementation. Due to several documented health complaints, the court banned spraying near the suburb Ituzaingo Anexo suburb in the central Argentinean city of Cordoba. The ban still currently applies to all fields within 1,000 m of Cordoba's residential areas. Meanwhile the Ministry of Defense banned the planting of glyphosate-tolerant soybean on land that it rents to farmers (Misculin, 2009). In 2009, the US EPA initiated a review of glyphosate registration and the agency requested additional studies to support updated human health and ecological risk assessments from registrants of glyphosate products. The EPA collaborated with Canada's Pest Management Regulatory Agency to share information for risk assessment.

In 2014, the IARC listed organophosphate pesticides including herbicide among the groups of chemicals that need moderate or high priority for assessment of health dangers. As a consequence, in March 2015, the IARC decided that glyphosate is "probably carcinogenic to man" and classified

as "Category 2A" (IARC, 2015). The decision was made based on a wide review of the published peer-reviewed epidemiological, toxicological, and genetic literature on glyphosate and independent of the pesticide manufacturing industry. It was claimed that their products caused DNA damage and oxidative stress (Kier and Kirkland, 2013). The IARC's assessment also included glyphosate metabolites such as AMPA.

In 2015 the US EPA undertook an in-depth review of the cancer database of glyphosate, including data from epidemiological, animal carcinogenicity, and genotoxicity studies to re-examine the carcinogenic potential of glyphosate. As part of its registration review the US EPA consulted the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Scientific Advisory Panel (SAP) in December 2016. The agency's proposed a classification that glyphosate is "not likely to be carcinogenic to humans" at doses relevant for human health risk assessment (US EPA, 2016). In December 2017, the EPA published the glyphosate human health and ecological risk assessments for public comment while in May 2019, the agency published the proposed interim registration review decision for glyphosate. The EPA published the interim registration review decision for glyphosate in February 2020 after reviewing public comments on the proposed interim decision. In March 2020, the glyphosate ID was challenged in the US Court of Appeals for the Ninth Circuit. The petitioners challenged the EPA's analysis of human health and ecological risk, the weighing of such risks against the benefits of glyphosate, and the interim risk mitigation measures and alleged that the EPA violated the Endangered Species Act (ESA). The agency issued a draft biological evaluation for glyphosate in November 2020 for public comment. On May 2021, the EPA sought partial voluntary remand without vacatur for the ecological portion of the ID so it could revisit aspects of its analysis reflecting the EPA's November 2020 draft biological evaluation for glyphosate and recent court decisions for other herbicides, among other reasons. The EPA released the final biological evaluation in November 2021.

On June 17, 2022, the US Court of Appeals for the Ninth Circuit vacated the human health portion of the glyphosate ID and held that the EPA's registration review decision under FIFRA was an "action" that triggered ESA obligations. The court also granted the agency's request for voluntary remand, without vacatur, of the ecological portion of the ID but imposed an October 1, 2022, deadline for it to issue a new ecological portion. The EPA sought relief from this deadline, which the court denied on August 5, 2022.

Subsequently, the EPA has determined that withdrawal of the glyphosate ID is appropriate in consideration of the Ninth Circuit's June 17, 2022, decision. The agency is unable to finalize a new ecological portion in a registration review decision for glyphosate by the court-imposed October 1, 2022, deadline because of the time needed to address the issues for which the EPA sought remand of the ecological portion and satisfy ESA requirements. The EPA initiated formal ESA consultation with the US Fish and Wildlife Service and the National Marine Fisheries Service (the Services) for glyphosate in November 2021; consultation is ongoing. Moreover, before issuing any decision, the EPA must first prepare a proposed decision, publish for a 60-day public comment period, and consider any statements received. The EPA cannot complete these processes by the court-imposed deadline.

The EPA's underlying scientific findings regarding glyphosate, including its finding that glyphosate is not likely to be carcinogenic to humans, remain the same. In accordance with the court's decision, the agency intends to revisit and better explain its evaluation of the carcinogenic potential of glyphosate and to consider whether to do so for other aspects of its human health analysis. For the ecological portion, the agency intends to address the issues for which it sought remand, including the following: firstly, to consider whether additional or different risk mitigation strategies may be necessary based on the outcome of ESA consultation for glyphosate; secondly, to prepare an analysis of in-field effects of glyphosate on the habitat of monarch butterfly; thirdly, to consider whether there are other aspects of its analysis of ecological risks and costs to revisit; and fourthly, to consider what risk mitigation measures may be necessary to reduce potential risk following completion of analyses left outstanding in the ID. The EPA also intends to complete ESA consultation with the

Services, make a determination under the Endocrine Disruptor Screening Program, and respond to an administrative petition regarding glyphosate before issuing a final registration review decision.

In comparison the pesticide legislation in the European Union (EU) is the most comprehensive and stringent in the world. The EU launched its "Thematic Strategy on the Sustainable Use of Pesticides" in 2010 (Kudsk and Mathiassen, 2020). Glyphosate was accepted in 2002 for the first time at the EU and has been already used in a majority of EU countries and the approval was extended until the end of 2015 (Kudsk and Mathiassen, 2020). However, the glyphosate ban has been an unending discussion in the European Union. In November 2015, the Environmental Food Safety Authority (EFSA) considered glyphosate to be "unlikely to pose a cancer risk for man" based on a glyphosate renewal assessment report (RAR) by the Federal German Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) in January 2014 (EFSA, 2015). The EFSA and RAR review scientists groups hid their names and financial interests and also relied on unpublished, non-peer-reviewed reports generated by the industry (Authority, 2015). Upon its later consideration of low likelihood of being carcinogenic, the European Food Safety Agency (EFSA) initiated the discussion on the use of surfactant polyethoxylated tallow amine (POEA) in glyphosate formulations (Kudsk and Mathiassen, 2020).

The European Chemical Agency (ECHA) agreed with the glyphosate classification by EFSA and stated that glyphosate should not be categorized as carcinogenic in 2017 (Kudsk and Mathiassen, 2020). Lastly, in November 2017, the European Commission continued the authorization for glyphosate application for another 5 years until December 2022. This was opposed by major EU members such as France and Italy, subject to further evaluations (EC, 2017). The use of glyphosate has been further extended by the EU until December 16, 2023.

13.7 REMEDIATION APPROACHES OF RESIDUAL GLYPHOSATE FROM SOIL AND WATER

Care should be taken to eliminate this herbicide rapidly after weed treatment so that its accumulation in soils is minimized. While spillage or leakage occur during their production, storage, shipping, and usage will have to be managed thoroughly so no leakage occurs (Ermakova et al., 2010). As a preventive measure, edge-of-field and riparian buffer strips and vegetated drainage ditches are the mostly applied methods to reduce contamination of water bodies (Reichenberger et al., 2007, Liu et al., 2008, Krutz et al., 2005, Lacas et al., 2005, Dosskey, 2001). Filter strips (the narrow strips of constant vegetation) adjacent to agricultural areas are highly recommended to reduce the contaminants that originate from surface runoff (Schmitt et al., 1999, Otto et al., 2008). The creation of vegetative barriers using a strip of tall, dense and stiff grass produces a permeable wall for temporary pond runoff water that settles down the sediment load, slowly releasing water downslope (Dosskey, 2001).

It is also essential to remove glyphosate and its metabolites from the environment especially from soil and water because of their ubiquitous presence as well as their widespread toxic impact on the environment and people's health including allergic reactions, cardiac and respiratory problems, and endocrine disruption (Dinehart et al., 2009, Souza et al., 2013, Richard et al., 2005). To date, many biotic and abiotic methods have been reported which are broadly divided into the physicochemical and biological approaches. These methods have some advantages and limitations. For this reason, combined methods are also employed such as biotic and abiotic technologies of glyphosate removal.

13.7.1 Physicochemical Methods

Various abiotic approaches are currently being employed for the removal of glyphosate such as adsorption, advanced oxidation process, membrane filtration, chlorination, and ozonation (Assalin et al., 2009, Speth, 1993, Mohanty and Das, 2022, Feng et al., 2020, Espinoza-Montero et al., 2020). All these treatment processes are explained in more detail in the following sections.

13.7.1.1 Adsorption

Adsorption is an effective technology for removing glyphosate from water and effluents with a contaminant concentration of ng L^{-1} to mg L^{-1} (Ding et al., 2018, Jiang et al., 2018). In this process the glyphosate molecules are adsorbed by the adsorbents by establishing physical and/or chemical interaction(s) among them (Pereira et al., 2021). During physical interactions, adsorption is mostly initiated by the molecular forces involving permanent dipole or induced dipole, the van der Waals dispersion forces and hydrogen-bond with acid groups (-OH and -COOH) on the material's surface (Li et al., 2018). Physical adsorption is also initiated by the diffusion of the glyphosate molecules to the porous structure in which total pore volume and type of pores play an important role (Herath et al., 2016). In addition, the electrostatic attraction between the glyphosate molecule and surface of adsorbent causes chemical adsorption which is highly pH-dependent. Glyphosate shows a negative charge in acidic conditions and the materials with positively charged surface are attracted to it (Li et al., 2018, Herath et al., 2016).

Recently, various adsorbents such as biochar, clay substances, activated carbon, industrial residues, resins, etc., have been applied to remove glyphosate and its metabolites from wastewater under various conditions (Feng et al., 2020). Due to the high adsorption capacity and high contaminants elimination rate, their large-scale possibilities to ease glyphosate's harmful effects on the environment are promising. Other materials such as graphene, reduced graphene oxide doped with metals, and double lamellar hydroxides are achieving importance (Pereira et al., 2021). Activated carbon (Jönsson et al., 2013), bio-carbon (Herath et al., 2019), zeolite (Zavareh et al., 2018), goethite (Jönsson et al., 2013), alum sludge (Hu et al., 2011), graphene oxide, and iron-based adsorbing materials (Li et al., 2018) are currently used adsorption materials.

Activated carbon was the earliest adsorbent investigated for glyphosate remediation and it revealed an efficiency range of 12–20% (Jönsson et al., 2013, Speth, 1993). Speth (1993) utilized granular activated carbon as an adsorbent in distilled water to remove glyphosate. He repeated the experiment in river water; the results were stable and better than the inadequate elimination reported in previous work. Organic matter competes with the granular activated carbon in adsorbing glyphosate or AMPA. Kempeneers (2000) used virgin granular activated carbon with a spiked concentration of 1 μgL^{-1} in his experiment and achieved 97% removal of glyphosate and 60% removal of AMPA even though this success only lasted for a few days. He suggested that granular activated carbon is not a good option for practical treatment. Mohsen Nourouzi et al. (2010) used newspaper waste to synthesize activated carbon for glyphosate removal. However, the high cost of activated carbon materials limits its practical applications in industry (Feng et al., 2020).

Another common adsorbent like activated carbon is biochar and it has garnered more attention because of its low cost and highly aromatic and porous structure, which contributes to the high efficiency in removing glyphosate. Herath et al. (2016) employed a synthesized rice husk biochar derived from slow pyrolysis and obtained an adsorption capacity of glyphosate amounting to 123 mg g^{-1}. Mayakaduwa et al. (2016) reported the adsorption capacity of glyphosate of 44 mg g^{-1} after investigating the application of woody biochar obtained from a bioenergy industry plant waste. Wastes from agro-industry are abundant ecological and economical sources of adsorbent materials, having low market value but a great efficiency in removing contaminants from aqueous effluents (Herath et al., 2016, Jiang et al., 2018). Resin presents good adsorption capacity of glyphosate in aqueous media with a maximum amount of 833 mg g^{-1} removed due to its distinctive porous structure and surface chemistry (Chen et al., 2016). Cheap and eco-friendly biopolymers such as chitin and chitosan adsorbents which are applied at low concentration for the removal of this herbicide show lower adsorption than by activated carbons, biochars, and resins (Rissouli et al., 2017). To conclude, adsorption is a very promising removal technique due to its simple design, high separation efficiency, easy use, low cost, flexibility, and non-toxic nature (Bonilla-Petriciolet et al., 2017, Saxena et al., 2020). However, the main drawback of this method is its pH dependence, and no specific adsorbent material is selective for glyphosate. It is evident that further investigations are needed to know how to dispose of the residues generated from the adsorption approach.

13.7.1.2 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) constitute a promising technology to remove non-easily eliminating organic compounds from both water and wastewater (Mahalakshmi et al., 2007, Tran et al., 2013). AOPs have been suggested recently as an option for treating glyphosate-contaminated water (Villamar-Ayala et al., 2019). At or near ambient temperature and pressure conditions, these processes usually generate sufficient powerful oxidizing agents which trigger water purification (Andreozzi et al., 1999). During the oxidation process, hydroxyl radical groups (•OH) act as powerful oxidizing agents which have a short life, high reactivity, non-selectivity, and oxidizing ability of many organic contaminants in aqueous environments (Feng et al., 2020). Hydroxyl radical (•OH) decomposes organic matter into CO_2, H_2O, and its subsequent mineral salt (Andreozzi et al., 1999, Wang and Xu, 2012). It starts to break down the cleavage of the C–N and C–P bonds to generate metabolites of glyphosate such as AMPA and sarcosine or final degradation products consisting of nitrate, ammonium and phosphate ions, carbon dioxide, and water (Espinoza-Montero et al., 2020). The main mechanism in which AOPs remove glyphosate from water is stated here (Espinoza-Montero et al., 2020):

$$C_3H_8NO_5P + {}^{\bullet}OH \rightarrow CO_2 + H_2O + NO_3^- + NH_4^+ + PO_4^{3-}$$

The main advanced oxidation methods are Fenton and photo-Fenton, photolysis through hydrogen peroxide and UV light $\left(H_2O_2\text{-}UV\right)$, electrochemical treatment, photocatalysis, and photoelectrochemical processes (Andreozzi et al., 1999, Wang and Xu, 2012, Sirés et al., 2014, Espinoza-Montero et al., 2020). Fenton and photo-Fenton processes use powerful oxidant species produced in water which decompose toxic organic particles in aqueous media. For example, ferrous ion $\left(Fe^{2+}\right)$ as a catalyst is utilized in this process to decompose hydrogen peroxide (H_2O_2) converting it to •OH radicals (Serra-Clusellas et al., 2019) and the accepted mechanism of the Fenton process is given here (Espinoza-Montero et al., 2020):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

Glyphosate can be removed from polluted water utilizing two UV-based processes, namely photolysis $\left(UV/H_2O_2; UV/O_3\right)$ and heterogeneous photocatalysis (Wang and Xu, 2012). The photocatalytic process is an effective one for glyphosate degradation in which titanium dioxide TiO_2 is the mostly used semiconductor catalyst (Nevárez-Martínez et al., 2017). Chen and Liu (2007) carried out their study with 3.5 h of irradiation with a starting concentration of 0.25 mmol L^{-1} and 6.0 g L^{-1} of TiO_2 as an ideal quantity of photocatalyst, and they reported that 92% of glyphosate was removed. Electrochemical oxidation technology provides sufficient anodic energy for the decomposition of organic pollutants until their total mineralization is achieved, or even less complicated biodegradable elements (Comninellis and Chen, 2010) through direct or indirect anodic oxidation reactions. Lan et al. (2013) utilized RuO_2/TiO_2 coated titanium mesh as both anode and cathode assisted with MnO_2 and reported a significant glyphosate removal. The majority of the released Mn^{2+} ions oxidatively reverted to MnO_2 which enhanced the removal of glyphosate reaching 80% degradation after treatment for 120 min at 10 mA cm^{-2} in 400 mL of solution with sodium sulphate as an electrolyte.

Photo electrocatalysis is a promising technique that combines photocatalysis with anodic oxidation. The electrochemical advanced oxidation process combined with UVC light irradiation (photo-electro-chemical, P-EC) is an exciting opportunity for water treatment (Sánchez-Montes et al., 2020). The performance of DSA and BDD anodes was evaluated in one experiment. Glyphosate completely converted to CO_2 with the DSA® electrode and low-power UVC sources (9 W) after treatment lasting 1 h. Also, energy intake was as low as 1.25 kWh g^{-1} (Sánchez-Montes et al., 2020).

13.7.1.3 Chlorination

Chlorination is a highly effective method in wastewater treatment technology; it involves the reduction of glyphosate and AMPA in presence of chlorine (Jönsson et al., 2013, Assalin et al., 2009, Speth, 1993). The efficiency of this method depends on temperature, pH, and chlorine concentration. However, information related to the impact of these factors on the whole performance is very limited. The application of 0.2–0.6 mg L^{-1} of chlorine degraded between 40% and 100% of AMPA wherein the initial concentrations of 0.2–5 µg L^{-1} and a chlorine dose of 2 mg L^{-1} degraded >98% AMPA; however, the contact times were not stated (Hopman et al., 1995). Hopman et al. (1995) reported that AMPA was not degraded due to oxidation, but did so when chlorine was added to the AMPA solution. Kempeneers (2000) concluded that 1.2 µg L^{-1} glyphosate was completely degraded by 2 mg L^{-1} of chlorine with a contact time of 20 min and 0.56 µg L^{-1} AMPA was degraded in similar circumstances. A chlorine dose amounting to 0.75 mg L^{-1} can degrade 5 µg L^{-1} of glyphosate and 0.42 µg L^{-1} of AMPA with a contact time of 4 hours. After a contact time that lasted 120 seconds, 11.5 µg L^{-1} glyphosate and 0.14 µg L^{-1} AMPA were completely degraded, specifying fast kinetics. Lange and Post (2000) noted that 0.08 mg L^{-1} of chlorine concentration degraded 74% and 80% of glyphosate and AMPA, respectively, from a drinking water spiked at 0.05–0.4 µg L^{-1} with contact time of 5 min. They also found that a dose of 0.40 mg L^{-1} of chlorine attained 94% degradation. Jönsson et al. (2013) stated that chlorination is highly efficient in degrading both glyphosate and AMPA but a decrease in temperature compromises the degradation efficiency.

13.7.1.4 Ozonation

Ozonation is the most common abiotic degradation method observed in the natural environment. On application, ozone reacts with glyphosate very rapidly (Mahalakshmi et al., 2007). Two oxidation processes, i.e. direct and indirect oxidation, are the main pathways for ozonation of glyphosate (Jönsson et al., 2013). The direct method involves oxidation by ozone whereas the indirect method employs the oxidation of the compound by hydroxyl radicals (Mohanty and Das, 2022, Rosal et al., 2009). Unlike other organophosphates, the compounds' highly reactive amino group if not protonated is the targeted site for ozonation (Assalin et al., 2009). Literature indicated that more than 90% degradation of glyphosate and AMPA can be achieved with ozonation (Jönsson et al., 2013). However, the pH can affect the nature of the products formed as well as ozonation efficiency (Assalin et al., 2009).

Ozone concentration and the contact time are the two key factors in defining the glyphosate remediation (Mohanty and Das, 2022). Jönsson et al. (2013) reported that 22 µg L^{-1} of glyphosate can be removed by a dose of 0.8 mg L^{-1} of ozone to below the limit of detection from contaminated effluent (Jönsson et al., 2013). Due to the formation of glyphosate and the intermediate AMPA during the ozonation of water containing methylene phosphonic acid (EDTMP) at pH 5, removal of glyphosate by ozonation of water is still a very debated technique (Jönsson et al., 2013). Process-based industries utilize EDTMP as a chelating agent which occurs in the water bodies adjoining the industrial areas. Indicated here is that a proportion of glyphosate and AMPA found in ozonated water may not be completely herbicide-derived.

13.7.1.5 Membrane Filtration

In many areas of water and wastewater treatment, membrane filtration technologies have been applied over the last few years. Acting as a barrier for material transport of an influent stream and splitting it into two waste streams such as the permeate and the retentate or concentrate are the main pathways of this approach (Liu et al., 2012, Chen et al., 2006). Polymeric membranes filtration is generally an effective way to remediate water by removing pollutants. However, due to no investigations being done in real water there is a limited understanding regarding the operation's procedure (Espinoza-Montero et al., 2020). In order to eliminate color, dissolved organic substances and pesticides from water, the nanofiltration approach has been used in aqueous media (Yuan et al.,

2018, Saitúa et al., 2012). The membrane filtration method does not break down the glyphosate into toxic by-product molecules so it can be more harmful than the original chemical. When the membrane becomes saturated, the contaminant can be recovered by this process (Castrejón-Godínez et al., 2021). The main disadvantage of it is that it is pollutant-specific which make this process less satisfactory (Espinoza-Montero et al., 2020). Also, the removal of glyphosate has not been proved in actual contaminated water in several studies. Consequently, a detailed evaluation on the effect of organic matter on the efficiency of this approach for glyphosate-contaminated water is required for effective membrane filtration (Castrejón-Godínez et al., 2021).

13.7.2 Biological Methods

Biotic technologies break down organic compounds into smaller molecules; this is now known as an effective and eco-friendly method of eliminating organic contaminants from the environment (Feng et al., 2020, Zhao et al., 2015). These processes include enzymatic reactions which generally end with harmless particles. However, these reactions can produce highly toxic metabolites like AMPA without controlled operational conditions (Zhan et al., 2018). Highly efficient mineralization is not possible due to the generation of intermediate metabolites such as AMPA, sarcosine, and acetylglyphosate at the time of degradation (Zhan et al., 2018, Fan et al., 2012, Wijekoon and Yapa, 2018, Fu et al., 2017). The main biotic methods are microbial degradation and phytoremediation.

13.7.2.1 Microbial Degradation

Microorganisms can eliminate this herbicide and its metabolites from soils by biodegradation (Rueppel et al., 1977, Strange-Hansen et al., 2004) and it is the most important mechanism of soil decontamination (Fomsgaard, 1997). However, the key factors affecting herbicide mineralization in soils are its bioavailability and the size and the activity of microbial populations, including indigenous glyphosate-degrading microorganisms (Sørensen et al., 2006). Instead of chemical action, microbial action can cause complete degradation of glyphosate in soil and/or water (Villamar-Ayala et al., 2019). As mentioned earlier, microorganisms including bacterial or fungal species which generally use glyphosate as a source of nitrogen, carbon, and phosphorus are able to transform glyphosate into new compounds through different degradation pathways (Fan et al., 2012, Wijekoon and Yapa, 2018). Of all the glyphosate-degrading microorganisms, bacteria have been more examined than fungi. The reason for this is the presence of C-P lyase enzyme systems which appear widely in bacteria and are known to break down glyphosate (Hove-Jensen et al., 2014).

Heterotrophic aerobic/facultative microbes such as *Pseudomonas* spp., *Arthrobacter* spp., *Enterobacter aerogenes*, *Geobacillus caldoxylosilyticus*, *Flavobacterium* sp., and *Bacillus* spp. identified in soil/sediment (from water) and sludge activated technology are able to biodegrade glyphosate (Solomon and Thompson, 2003, Balthazor and Hallas, 1986, Ermakova et al., 2010, Wijekoon and Yapa, 2018). *Pseudomonas* spp. is a very popular glyphosate-degrading microorganism (Manogaran et al., 2017). Mixed cultures can also be used to degrade glyphosate fully and more effectively compared to the pure cultures. The presence of a wide range of enzymes in mixed culture enhances the degradation of the contaminant (Nourouzi et al., 2012). Thus, mixed cultures are chosen for different industrial remediation techniques (Mohanty and Das, 2022). On the other hand, pure cultures are very expensive in handling and require high maintenance. The main drawback of microbial remediation is that it is a slow process and demands high maintenance of environmental conditions if microorganisms are to be viable (Wang et al., 2016).

13.7.2.2 Phytoremediation

Phytoremediation is the use of native (wild) plants to eliminate glyphosate residues from the environment for reconstitute contaminated soils, sediments, and/or groundwater where plants together with their associated microbiota establish high tolerance levels against herbicides and can degrade chemicals (Santos et al., 2009). Plants can have the capacity to tolerate comparatively highly

concentrated organic xenobiotic chemicals with no toxic effects (Burken and Schnoor, 1998). Moreover, they can readily take up certain chemicals and transform them into less toxic metabolites through various metabolic activities (Schalk et al., 1997, Ohkawa et al., 1999, Newman et al., 1997, Werck-Reichhart et al., 2000, Kolb and Harms, 2000, Laurent et al., 2006). In the rhizosphere, plant root exudates and enzymes stimulate the degradation of organic chemicals (Anderson et al., 1993, Shimp et al., 1993, Burken and Schnoor, 1996). Reduction of contaminants leaching, aeration of soil, phytodegradation or transformation, evapotranspiration, phytovolatilization, and rhizoremediation are the different ways in which plants make remediation possible (Amos and Younger, 2003, Chang et al., 2005, Cunningham et al., 1995, Macek et al., 1998, Newman and Reynolds, 2004). *Canavalia ensiformis* L., *Stizolobium aterrimum*, and *Glycine max* L. from the *Fabaceae* family effectively degrade glyphosate. However, the degradation efficiency varied due to the microbial community closely associated with a plant's roots; as a result, rhizospheric soil cultivated with soybean was more efficient in glyphosate degradation (Santos et al., 2009).

The model plant for phytoremediation can adjust to the contaminated area easily, grow very quickly, build a deep and extensive radical system, yield a high quantity of biomass, produce high levels of enzymes that degrade xenobiotic chemicals, compete with other plants, accumulate large quantities of contaminants, and store them in the above-ground parts of the plants (Del Buono et al., 2020). *Typha* is another plant which is able to reduce the half-life of a number of pesticides from 90 to 5 days on terrestrial soils resulting in pesticides' immobilization rather than degradation (Terry and Banuelos, 2020). The phytoremediation technology removes about 8% of glyphosate in soil medium and 11% in the presence of plants (Dosnon-Olette et al., 2011). Phytoremediation is widely employed due to its aesthetic benefits, cost-effectiveness, versatility, and ongoing applicability (Schnoor et al., 1995).

13.7.3 Combined Treatment Processes

Combined treatment processes use both biological (microorganisms and plants) and physicochemical processes together to treat drinking water and stormwater. For example, biofilter technique involving both adsorption and microbial degradation processes remove glyphosate effectively (Espinoza-Montero et al., 2020). Utilization of different types of vegetation with biofilters or in bio-retention areas that involve a porous soil filter media in shallows basins is effective for removing glyphosate from surface water (Zhang et al., 2015, Yang et al., 2013). A few promising plant species are *Melaleuca ericifolia*, *Eupatorium perfoliatum*, *Tradescantia ohiensis*, *Veronicastrum virginicum*, *Eragrostis spectabilis*, *Sorghastrum nutan*, *Echinacea purpurea*, etc. (Zhang et al., 2015, Yang et al., 2013).

Constructed wetland is another viable option for utilizing adsorption and microbial activity together to remove glyphosate (Liang et al., 2020). In some cases, combinations of other methods are also effective. In their study, Zhang et al. (2011) combined adsorption (over nano-metal/resin) with advanced oxidation (Fenton oxidation) for the degradation of an industrial wastewater sample contaminated with 258 mg L^{-1} of glyphosate. These researchers obtained a glyphosate degradation efficiency amounting to 60%. Since different processes can be used together in combined methods, this is proving to be an exciting glyphosate treatment technology.

13.8 CONCLUDING REMARKS

Glyphosate is the most widely used herbicide throughout the world and continues to increase. It is a unique non-selective herbicide with a mode of action that is ideal for vegetation management in both agricultural and non-agricultural settings, and its use has more than doubled with the introduction of transgenic, glyphosate-resistant (GR) crops. All its phytotoxic effects are the result of inhibition of only 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS), but inhibition of this single enzyme of the shikimate pathway results in many phytotoxicity outcomes, both upstream and downstream

from EPSPS, including loss of plant defenses against pathogens. Although the herbicide is biodegradable and leaves the soil clean, on degradation it produces more persistent metabolites including AMPA. Thus, residual glyphosate and AMPA have been found in both soil and water all over the world. Recently, its serious consequences for human health and the environment are well documented to the point that the IARC concluded that it "probably causes cancer in humans." Various studies also proved that glyphosate formulations containing POEA are more toxic than technical grade glyphosate. The problem is that many regulatory authorities have their own rules and assumptions in place regarding its toxicity and safe exposure levels. Considering that it is a major pollutant, different techniques have proved to be effective in removing this pesticide from the environment including soil and water.

The potential toxicity of glyphosate exposure and the need for caution when handling and using GBH s is evident. Further research is warranted to determine the extent of human health risks associated with glyphosate and its metabolites. To reduce possible dangers to health and to produce consistent data and regulatory/legislative agreements, collaboration should be established between researchers, government officials, and workers in all sectors, not only at the local, national, and regional levels but also at the global level. Enhanced awareness among healthcare professionals is crucial for prompt recognition and appropriate management of glyphosate toxicity. It will be necessary to have shared databases in which new problems are highlighted, to identify possible solutions and solve them collaboratively, and provide the necessary information to link the risks posed by the glyphosate-based formulations.

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14 Endosulfan
Unveiling Sources, Toxicity, Risks, and Remediation Strategies

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14.1 INTRODUCTION

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,3,4-benzo-dioxathiepin-3-oxide, CAS No. 115–29–7), an organochlorine pesticide, is a 70:30 mixture of α- and β-isomers of endosulfan. Endosulfan was extensively used worldwide until it was banned during 6th meeting of Persistent Organic Pollutants Review Committee (POPRC) to the Stockholm Convention (2011) at Geneva (Li, 2018). The decision to ban it was mainly governed by its acute toxicity, potential for bioaccumulation, highly persistent nature, and ability to disrupt the endocrine system (Milesi et al., 2017).

Endosulfan shows significant environmental contamination and adverse effects on human health and wildlife. Accidental and unintentional exposure of endosulfan leads to human fatalities and environmental tragedies throughout the world. The worst cases were reported from the Kasaragod district in Kerala, India; the Borgou province in Benin, West Africa; the western province of Matanzas, Cuba; the Latin American countries Colombia, Ecuador, and Costa Rica; Queensland, Australia; and California, United States. Exposure has been linked to congenital physical disorders,

DOI: 10.1201/9781003530466-14
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mental disabilities, and deaths in exposed communities across the globe. More than 80 countries across the world have banned production and consumption of endosulfan.

Humans become exposed to endosulfan through different ways such as accidental exposure, dietary exposure, and occupational exposure, the major exposure path being accidental exposure. Acute and chronic toxicity results in seizures, gastro-intestinal disorders, neurotoxicity, reproductive disorders, and carcinogenic effects in humans (Nawaz et al., 2014; Syed et al., 2014). Persistence of endosulfan in soil is affected by its physico-chemical characteristics like pH and organic matter content, etc., as well as environmental conditions (Harikumar et al., 2014). Endosulfan isomers (α and β) vary in their persistence and β-endosulfan is easily converted to α-endosulfan (Schmidt et al., 1997). Endosulfan undergoes oxidation resulting in the formation of endosulfan sulphate, which is a persistent metabolite and considered more toxic than the parent endosulfan. Hydrolysis of endosulfan results in the formation of endosulfan diol, endosulfan lactone, endosulfan ether, etc., which are less toxic than the parent molecule (Zaffar et al., 2018). Photo, chemical, and biological degradation are mainly responsible for endosulfan degradation in soil and water.

The persistent nature of endosulfan and endosulfan sulfate results in their frequent detection in water bodies and the environment. The maximum permissible limit of endosulfan in lakes, rivers, and streams is 74 μg L^{-1} (USEPA, 2002). Different techniques for endosulfan/metabolites remediation have been reported. Physico-chemical methods like adsorption, photolysis, membrane filtration, and biological methods involving bacteria, fungi, and plants have been successfully demonstrated for endosulfan removal/degradation (Jesitha et al., 2015; Mukherjee et al., 2020; Zieliński et al., 2022; Kalsoom et al., 2023). This chapter gives an overview of endosulfan contamination, fate, regulatory aspects, exposure, toxicity, risks, and remediation.

14.2 SOURCES OF ENDOSULFAN AND ENVIRONMENTAL CONTAMINATION

Endosulfan, an organochlorine insecticide and acaricide, was widely used in agriculture to control pests on crops. Its acute toxicity, potential for bioaccumulation, and ability to disrupt the endocrine system have made it a highly controversial agrichemical (Forero, 2011). Recognizing the significant risks posed by endosulfan, international efforts have been made to eliminate its use and ban it worldwide. The main sources of endosulfan contamination in the environment are as follows:

a) ***Agricultural use:*** The primary cause of endosulfan contamination is its use in agriculture. It has been extensively utilized in many countries for pest control on crops, particularly in regions with weaker regulations and enforcement.
b) ***Spray drift:*** During the application of endosulfan on crops, spray drift can occur, resulting in the unintended dispersion of the pesticide beyond the targeted area. This drift can contaminate nearby surface waters, soil, and vegetation.
c) ***Soil residues:*** Endosulfan can persist in soil for extended periods due to its high stability. Residual endosulfan from previous applications can remain in the soil and leach into water bodies, leading to long-term contamination.
d) ***Runoff:*** Runoff from endosulfan treated agricultural fields can carry insecticide into surface water bodies such as rivers, lakes, and ponds. Endosulfan is poorly soluble in water and highly sorbed on soil particles and can be easily carried away with running water to contaminate aquatic ecosystems.
e) ***Atmospheric transport:*** Endosulfan can undergo long-range atmospheric transport. It volatilizes from treated fields or evaporates from contaminated water bodies and can be transported over long distances by wind currents.
f) ***Illegal use and dumping:*** Despite being banned or restricted in many countries, illegal use and dumping of endosulfan still occur. Improper disposal of unused or expired endosulfan products can lead to contamination of soil and water.

Widespread use of endosulfan during 1980s and 1990s resulted in widespread contamination in the environment as well as exposure to humans.

Endosulfan poisoning in humans: Most of the reported cases of endosulfan poisoning occurred in the developing countries. Quijano (2000) reported that endosulfan barrels washing in irrigation canals in Sudan in 1988 and drinking of contaminated water led to the death of three people as well as fish. Most pesticide poisoning deaths in 1991 in the Philippines involved endosulfan (Quijano, 2000) and the highest number of human poisoning cases with fatalities following improper usage of endosulfan to kill snails was observed in 1996 (Anonymous, 2002a). During 1990–1993, 32 cases of endosulfan poisoning were documented on the Indonesian island of Sulawesi (Anonymous, 2002b). Similarly, 60 and 155 cases of endosulfan poisoning in Columbia were reported in 1993 and 1994, respectively (Anonymous, 2002b). Endosulfan use increased the number of poisoning deaths in Sri Lanka from 1994–1998 (Roberts et al., 2003). Turkey has also documented cases of poisoning due to eating food tainted with endosulfan (Oktay et al., 2003). Numerous incidents of endosulfan poisoning death have been reported in Guatemala, Costa Rica, and other Central American nations (Anonymous, 2002c). Two South African boys, who lived close to Ntabamhlophe, Kwa-Zulu Natal, died as a result of endosulfan exposure (Anonymous, 2003a). Eighteen cases of endosulfan toxicity, caused by unintentional overexposure during spraying, were reported in northern India between 1995 and 1997 (Chugh et al., 1998). Many people were accidently exposed to endosulfan due to eating contaminated food (Campoy et al., 2001; Dewan et al., 2004).

Contamination in water bodies and fish kills: Endosulfan (30 kg) release into the Rhine River, Federal Republic of Germany, caused a widespread fish kill (Anonymous, 1984; Sang et al., 1999). Similarly, an accidental spill of endosulfan in 1975 caused a major fish kill in a tributary of the Dunk River on Prince Edward Island, and the brook trout population was reduced from 2,227–4,147 to 45–246 (Sang et al., 1999). More than 24,000 fish in a river in Alabama perished as a result of mixing of runoff from endosulfan-treated cotton fields (Quijano, 2000).

Contentious cases of endosulfan poisoning/contamination: The broad environmental pollution brought on by endosulfan use in various agricultural settings is highlighted by these case studies.

(a) ***Kasaragod, India:*** The district of Kasaragod in the Indian state of Kerala saw one of the most well-known and worst pesticide disasters in recorded history involving endosulfan (James and Emmanuel, 2021). The Plantation Corporation of Kerala (PCK) had been recommending endosulfan spray, three times a year, on cashew plantations for the control of tea mosquito bugs since 1980 on roughly 4,696 acres land (Satheesh, 2017; Kumar and Jayakumar, 2019; Melangadi, 2017). Insecticide was used on tea plantations, paddy fields, and fruit orchards using manual pumps or aerial spraying (Gupta, 2021). Stunted growth and malformed limbs were noted in newborn calves as early as 1979 while health issues of a very serious nature, affecting human population, came to light by the 1990s. There have been reports of high rates of congenital abnormalities, physical deformities, mental impairments, cerebral palsy, epilepsy, hydrocephalus, delays in boys' sexual maturation, and other health issues among the locals (Patočka et al., 2016; Melangadi, 2017; Anonymous, 2019). Affected residents were presumed to have either dietary exposure (by eating food sprayed with endosulfan or drinking water tainted with endosulfan), occupational exposure (via topical or inhalation routes during mixing, loading, and/or applying endosulfan or by immediately re-entering the endosulfan-treated areas), or accidental exposure (via topical or inhalation routes as a result of proximity to endosulfan use) (Anonymous, 2011a). Reports suggested that plantation employees were not provided with the necessary safety equipment (Anonymous, 2003b). Extremely high levels of endosulfan residues were detected in human blood, human milk, soil, water, fruits, vegetables, cows' milk, cows' skin tissue, fish, and frogs (Anonymous, 2001). Harikumar et al. (2014) reported that endosulfan residues persisted for 1.5–2 years in soil and it depended on climate conditions and soil physico-chemical properties. The Kerala government banned endosulfan usage

in 2005 (Pradyumna, 2009). Its production and use were banned worldwide in 2011 (Anonymous, 2011c). A Supreme Court-appointed panel recommended phasing out the usage of endosulfan over a 2-year period.

Cuba: Endosulfan poisoning in February 1999 led to the deaths of 15 people in the western province of Matanzas. Authorities in Cuba claim that a total of 63 people fell ill after eating food tainted with endosulfan (Dinham and Malik, 2003).

The Benin Tragedy: During the 1999–2000 cotton season, at least 37 deaths and 36 critically ill patients due to endosulfan poisoning were reported in the Borgou province, Benin, West Africa (Ton et al., 2000).

Queensland, Australia: Endosulfan has long been used to manage pests on a variety of crops, including cotton, in the Lockyer Valley, Queensland, Australia that led to contamination of surrounding creeks, waterways, and surface water (Anonymous, 2002d). Concerns about the potential effects on the ecosystem and public health were raised due to presence of endosulfan residues in fish and other aquatic organisms because endosulfan isomers can have half-life of 30 (aerobic) and 34–47 weeks (submerged) in Australian soils (Ghadiri and Rose, 2001).

California, United States: Due to its previous use on cotton, tomatoes, and melons, endosulfan was detected in surface water, groundwater, and sediment, endangering aquatic ecosystems (May, 2011). Endosulfan concentration in downstream was 28 times greater than the level necessary to kill an average freshwater fish after a normal endosulfan application on tomatoes. The US Fish and Wildlife Service reported that the Wyoming toad, Nashville crayfish, piping plover, wood stork, and other federally protected fish and mussel species were among the numerous endangered species due to risk from endosulfan use (Anonymous, 2012) and advised the EPA to stop using endosulfan in 2002 (Rossi, 2002). Endosulfan poisoning is linked to demise of the mountain yellow-legged frog in the Sierra Nevada, San Joaquin Valley (Jeff, 2004).

Latin America: The Latin American countries Colombia, Ecuador, and Costa Rica widely employed endosulfan on banana farms. Water bodies and soils close by were contaminated as a result of runoff from the plants (Stover and Simmonds, 1987; Mansour, 2018). Endosulfan exposure extended beyond the areas immediately surrounding banana fields (Shunthirasingham et al., 2011) and higher quantities of endosulfan sulfate were detected (Bruehl et al., 2023).

Bangladesh: Joint US-Bangla research reported death of 13 children in Dinajpur in 2012 due to consumption of endosulfan-contaminated litchi (Anonymous, 2018).

14.3 ENDOSULFAN REGULATORY POLICY IN DIFFERENT COUNTRIES

Endosulfan is an isomer combination of α- and β-endosulfan; between them, α-endosulfan is more toxic in nature (Anonymous, 2015). The molecule was first made public in 1956 and 12,800 tons of endosulfan were produced globally each year (Li and Macdonald, 2005) and on a cumulative basis, ~308,000 tons of endosulfan was used during the first 50 years of its introduction. India was thought to be the greatest producer of insecticide with ~5,400 tons annual production (Ayres and Ayres, 2000). The United States consumed ~26,000 tons of endosulfan until 2000 (Li and Macdonald, 2005) while during 1998–2004, China used ~2,800 tons of endosulfan annually (Jia et al., 2009).

At the 6th meeting of the Persistent Organic Pollutants Review Committee (POPRC) to the Stockholm Convention (2011) at Geneva, 24 member countries supported an endosulfan ban. Four members (Germany, Ghana, Nigeria, and China) abstained while India opposed; even then, the committee recommended the ban (Misra, 2010). More than 80 countries including the European Union, Australia (Anonymous, 2009), New Zealand, several West African nations, the United States (Anonymous, 2010a), Brazil (Anonymous, 2010b), and Canada (Anonymous, 2011b) had already banned it or announced phase-outs by the time the Stockholm Convention ban was agreed upon. May 13, 2011, India's Supreme Court prohibited the production and sale of endosulfan in

India (Anonymous, 2011c, 2023). The status of regulatory policies in different countries is as follows:

European Union (EU): The EU banned the use, sale, and production of endosulfan inside the member nations in 2008. Endosulfan is not approved for use under EC 1107/2009 in any of the EU states nor in the European Economic Area (EEA) nations of Iceland and Norway (Lewis et al., 2016).

United States (US): An endosulfan phase-out strategy was announced by the US Environmental Protection Agency (US EPA) in 2010 since it could pose unacceptable health hazards to farmworkers, wildlife, and the environment. Before the complete ban, a phase-out period allowed for a steady decrease in usage (Anonymous, 2010a).

Australia: Endosulfan was phased out and a full ban was enforced in December 2012. All active constituent endosulfan licenses were cancelled by the Australian Pesticides and Veterinary Medicines Authority (APVMA) on October 11, 2010, while endosulfan product registrations were cancelled on October 12, 2010 (Anonymous, 2024).

India: Due to the Kasargod, Kerala tragedy highlighting endosulfan's negative effects on human health and the environment, the Honorable Supreme Court of India passed an ad-interim decision for prohibiting the manufacture, distribution, and use of endosulfan on May 13, 2011. The Joint Expert Committee on endosulfan permitted the export of endosulfan formulation (2698.056 KL) and existing stocks of technical endosulfan (1090.596 MT) produced prior to the endosulfan ban on May 13, 2011 (Anonymous, 2011c).

Brazil: Based on the decision of the Brazilian Institute of Environment (IBAMA), Ministry of Agriculture (MAP), and National Agency for Sanitary Surveillance (ANVISA), import of endosulfan was prohibited on July 31, 2011. Domestic manufacturing was reduced until endosulfan production and use was altogether prohibited in July 2013 (Birkett, 2010).

Canada: Canada banned the majority of uses for endosulfan in 2007. Restricted uses (ornamentals in greenhouses) were permitted and completely phased out by December 31, 2016, when the registrations for all endosulfan pesticide products in Canada expired (Anonymous, 2011b).

South Africa: Endosulfan was banned in 2012 after a phase-out period in accordance with Government Notice No. 853 of the Republic of South Africa's Department of Agriculture, Forestry, and Fisheries on October 26, 2012. (Anonymous, 2017).

New Zealand: The Environmental Risk Management Authority (ERMA), Government of New Zealand, phased out and banned endosulfan use on January 16, 2009 (Anonymous, 2008).

China: Endosulfan registration in China was cancelled on July 1, 2018. All endosulfan products were prohibited to be used on agricultural crops on March 27, 2019 (Anonymous, 2018).

Japan: Japan has added the brominated flame retardant HBCD and "technical endosulfan and its related isomers" to its list of class I specified substances in 2013. Manufacturers and importers of the class I substances must obtain a permit before their manufacture or import (Anonymous, 2013).

Bangladesh: Endosulfan is still listed among the approved pesticides in Bangladesh despite being banned in more than 80 nations. Joint US-Bangla research reported death of 13 children in Dinajpur in 2012 due to endosulfan poisoning from litchi (Hossain, 2018).

Countries that have banned endosulfan: Austria, Australia, Bahrain, Belgium, Belize, Benin, Brazil, Bulgaria, Burkina Faso, Cambodia, Canada, Cape Verde, Chad, China, Colombia, Cote d'Ivoire, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Gambia, Germany, Greece, Guinea-Bissau, Hungary, India, Indonesia, Iran, Ireland, Italy, Japan, Jordan, Korea, Kuwait, Latvia, Lithuania, Luxembourg, Malaysia, Mali, Malta, Mauritania, Mauritius, Netherlands, New Zealand, Niger, Nigeria, Norway, Oman,

Philippines, Poland, Portugal, Qatar, Romania, Saudi Arabia, Senegal, Singapore, Slovakia, Slovenia, Spain, Sri Lanka, St. Lucia, Sweden, Syria, United Arab Emirates, United Kingdom, United States of America

Countries that have restricted endosulfan use: Bangladesh, Honduras, Iceland, Madagascar, Panama, Russia, Thailand

Countries still manufacturing endosulfan: Israel

14.4 EXPOSURE, TOXICITY, AND RISKS TO THE ENVIRONMENT AND HUMANS

14.4.1 Exposure to Endosulfan

Humans become exposed to endosulfan through different ways (EJF, 2009). The different types of exposures are discussed in this section:

(a) **Dietary exposure:** Dietary exposure can result from the ingestion of endosulfan-contaminated food or water. There are reports of the transfer of endosulfan present in soil to the agricultural products (Jung et al., 2023). The rate of transfer and accumulation in different agricultural commodities is different and depend on the nature of the soil, its physicochemical properties, the type of crop, etc. Reports suggested that compared to endosulfan concentration in soil, concentration up to <0.1% in grains, 1.3–4.7% in leafy vegetables, and 0.1–13.6% in fruits and vegetables (Choi et al., 2018, 2018a; Hwang et al., 2018) can be detected. With increase in contact period, absorption by the plant as well as the transfer of endosulfan residues to edible parts increases (Sathishkumar et al., 2021).

(b) **Occupational exposure:** Occupational exposure can occur via skin exposure or inhalation during the mixing, loading, or applying of the pesticides. It can also happen when a person enters a pesticide-treated field. This type of exposure is unavoidable for people engaged in pesticide field applications (farm workers). The exposure is aggravated if adequate protective equipment is not used during the spray operations. The US EPA has stated that "the endosulfan handlers are at short to intermediate risk even with the use of maximum use of personal protective equipments" (US EPA, 2007).

(c) **Accidental exposure:** Accidental exposure is very common and countless incidents can be cited (Menezes et al., 2017). It can occur due to the exposure of skin or due to inhalation of endosulfan. This type of exposure, apart from pesticide handlers, can happen to non-handlers as well as animals. Many individuals have been affected due to the long-range transport of endosulfan (Patočka et al., 2016).

14.4.2 Toxicological Effects

Endosulfan is a highly toxic molecule and it can enter in the body by absorption through skin, mouth, or inhalation. After a pesticide enters in human body, it eventually enters the blood stream and is distributed to all organs. Pesticide poisoning symptoms vary with the type of pesticide and include headaches, dizziness, nausea, vomiting, mental confusion, convulsions, hyperactivity, seizures, coma, and respiratory depression, and even death at severe conditions. The acute symptoms arise due to a single exposure to a high dose of a chemical while the chronic poisoning symptoms can result from repeated intake of low levels of the chemical for a long period of time (EJF, 2009). The toxicological effects of endosulfan on aquatic and terrestrial animals including mammals are reported.

(a) **Acute toxicity:** The primary acute effect of endosulfan is on the nervous system. It can cause hyperexcitation and convulsions, and nervous system-mediated effects on respiration

and heart. Low levels of exposure can also result in death of animals (Annex, 2008). Oral LD_{50} value of endosulfan varies with the species, sex, formulation, and the nutritional status of the test animal. Among the different species, mice appear to be more susceptible to endosulfan toxicity: the males have an LD_{50} value of 7.36 mg kg^{-1} and there were reported deaths of 2 out of 10 male mice after consuming a 7.5 mg technical endosulfan kg^{-1} diet for 7 days (Wilson and LeBlanc, 1998). The oral LD_{50} for rats is reported to be 10–23 mg kg^{-1} (female) and 48–160 mg kg^{-1} (male). However, the dermal LD_{50} values for rats are reported to be 500 mg kg^{-1} (female) and >4,000 mg kg^{-1} (male). The inhalation toxicity values for rats are 0.0126 mg L^{-1} for female and 0.0345 mg L^{-1} for male (Annex, 2008). The α- and β-isomers of endosulfan have different LD_{50} values in rats. Between the two, the α-isomer is more toxic in female rats. Both endosulfan sulfate (oxidative metabolite of endosulfan) and α-endosulfan's lethal doses for mice are comparable (~8 mg kg^{-1}) (ATSDR, 2015).

(b) **Chronic toxicity:** It is reported that the exposure of laboratory mice to endosulfan results in compromised fertility in both sexes (Sharma et al., 2022). The exposure of endosulfan can lead to tenacious higher levels of DNA damage resulting in compromised DNA repair. Researchers have reported an increase in the occurrence of tumor development in the endosulfan-exposed mice in their later life (Sharma et al., 2022). The sub-acute and chronic toxicity of endosulfan targets different organs such as liver, kidneys, immune system, and testes. An oral dose of 10 mg kg^{-1} d^{-1} in rats can cause high rates of mortality within 15 days, but the lower doses (5 mg kg^{-1} d^{-1}) can cause liver enlargement and some other effects within the same time period (EXTOXNET, 1996).

(c) **Reproductive effects:** The effects of endosulfan on the reproductive system in experimental animals depend on species, age at exposure, dose, duration of exposure, and study end points. The experimental studies suggest that the human male reproductive system can be affected by endosulfan and prominent effects are likely to occur if exposure occurs during the developmental phase (Saiyed et al., 2003). Exposure to endosulfan may delay sexual maturity and interfere with hormone synthesis in male children.

(d) **Teratogenic effects:** No conclusive study is available which confirms the role of endosulfan in inducing teratogenic effects (ATSDR, 2015). However, a few studies indicated that transplacental exposure can result in neurochemical alterations in the brains of animals.

(e) **Neurotoxicity:** Endosulfan is reported to have neurotoxic effects in laboratory animals. The expected mechanism of neurotoxicity includes:
- Variation of neurotransmitter levels in brain areas by affecting synthesis, degradation, and/or rates of release and reuptake
- Interfering with the binding of neurotransmitters to their receptors

Alterations in behavioral responses have been recorded when the animals are repeatedly exposed to tolerated doses of endosulfan (Paul and Balasubramaniam, 1997). It is believed that a serotonergic mechanism is involved in endosulfan-induced learning impairment. Gross impairment of visual-motor coordination was also reported (Anonymous, 2011a).

14.4.3 Risk to the Environment and Humans/Mammals

(a) **Risk to humans/mammals:** The exposure concentration and exposure duration determine the possible health effects of endosulfan in humans. Based on monitoring data of endosulfan in the environmental matrices, it is proposed that the environmentally relevant concentrations are much less than the concentrations at which the animal studies are conducted. Higher levels of exposure result in tremors and seizures; only at extreme levels, death happened. In general, endosulfan readily degrades into hydrophilic compounds and is removed with the least absorption in the gastrointestinal tract of mammals. The β-endosulfan was readily removed as compared to α-endosulfan from rabbit blood plasma

with half-life in blood of 6 h and 10 days, respectively. Most of the endosulfan is eliminated from the body within days to weeks (EXTOXNET, 1996).

Some studies indicated the effect of endosulfan on the alteration of thyroid and sex hormones in humans. An Indian study found that exposure to endosulfan was not associated with increased risk of Alzheimer's disease (Singh et al., 2013). A recent study by Sharma et al. (2023) indicated the role of β-endosulfan as an endocrine disruptor for thyroxine II leading to breast cancer. However, the US Department of Health and Human Services (HHS), the US Environmental Protection Agency (EPA), and the International Agency for Research on Cancer (IARC) have not classified endosulfan as carcinogenic (ATSDR, 2015).

(b) **Risk to the environment:** Endosulfan, being hydrophobic in nature, accumulates in the fatty tissues of living organisms. Da Cuña et al. (2020) conducted a study to evaluate the bioaccumulation and organ distribution of waterborne endosulfan in the freshwater fish *Cichlasoma dimerus*. They found that endosulfan is rapidly metabolized into endosulfan sulfate in the tissues. Endosulfan sulfate levels correlated with the tissue fat content in fish. Cerrillo et al. (2005) studied the occurrence of α- and β-endosulfan and their metabolites in fatty and non-fatty tissues and fluids in women in their reproductive age and the children in southern Spain. They found that the maximum concentration of commercial endosulfan isomers was found in adipose tissue (~17.72 ng g^{-1} lipids), followed by human milk (~11.38 ng mL^{-1}). These conclusions support the hydrophobicity of endosulfan and its removal by milk secretion. Botella et al. (2004) studied the levels of 15 organochlorine pesticides in the fat tissue and blood of 200 women in southern Spain. Endosulfan was found both in fat tissue and serum samples. Among the different endosulfan metabolites, the most predominant compound was endosulfan ether both in fat tissue (68%) and serum (86%) samples. Their results suggested that endosulfan exposure to a child via the mother is common, both in utero and via breastfeeding, due to the high rate of exposure to women at reproductive age (Cerrillo et al., 2005; Amizadeh and Saryazdi, 2011).

14.5 FATE AND DYNAMICS IN THE ENVIRONMENT

Once released into the environment, endosulfan undergoes various transfer and transport processes. The fate of endosulfan in the environment is determined by its physico chemical properties. Endosulfan is reported to be present in almost all environmental matrices, even though it is released in the environment during pesticide application on crops. The commercial product of endosulfan is a mixture of two isomers, α and β, in a 2:1 ratio. Between the two isomers, the α-isomer is considered to be more volatile and dissipative, whereas the β-isomer is considered to be more adsorptive and persistent (US EPA, 2007). The volatile nature of the compound enables it to be transported as vapor and spray drift to different environmental media, whereas its adsorptive and persistent nature helps it to stay in the environment for a long period of time. Endosulfan can also be transported via runoff to surface water bodies or via dust dispersion in the atmosphere and redeposition in diverse areas. The overall fate of endosulfan in the environment is depicted in Figure 14.1.

14.5.1 Fate in Soil

Oxidation and hydrolysis are two major pathways of endosulfan degradation in soil. The major degradation product of endosulfan is its oxidation to endosulfan sulfate which is more persistent than its parent isomers (Fan, 2008; Romero-Aguilar et al., 2014; Fang et al., 2016; ATSDR, 2015). Parent (α- and β-isomers) and endosulfan sulfate are not expected to be highly mobile in soil and cause groundwater pollution (US EPA, 2007). Further, they can enter the water bodies through soil erosion, runoff, spray drift, and atmospheric depositions. Endosulfan sulfate further undergoes degradation and results in the formation of endosulfan lactone. The endosulfan molecule is quite stable to photodegradation, but its degradation product endosulfan sulfate is susceptible to photodegradation

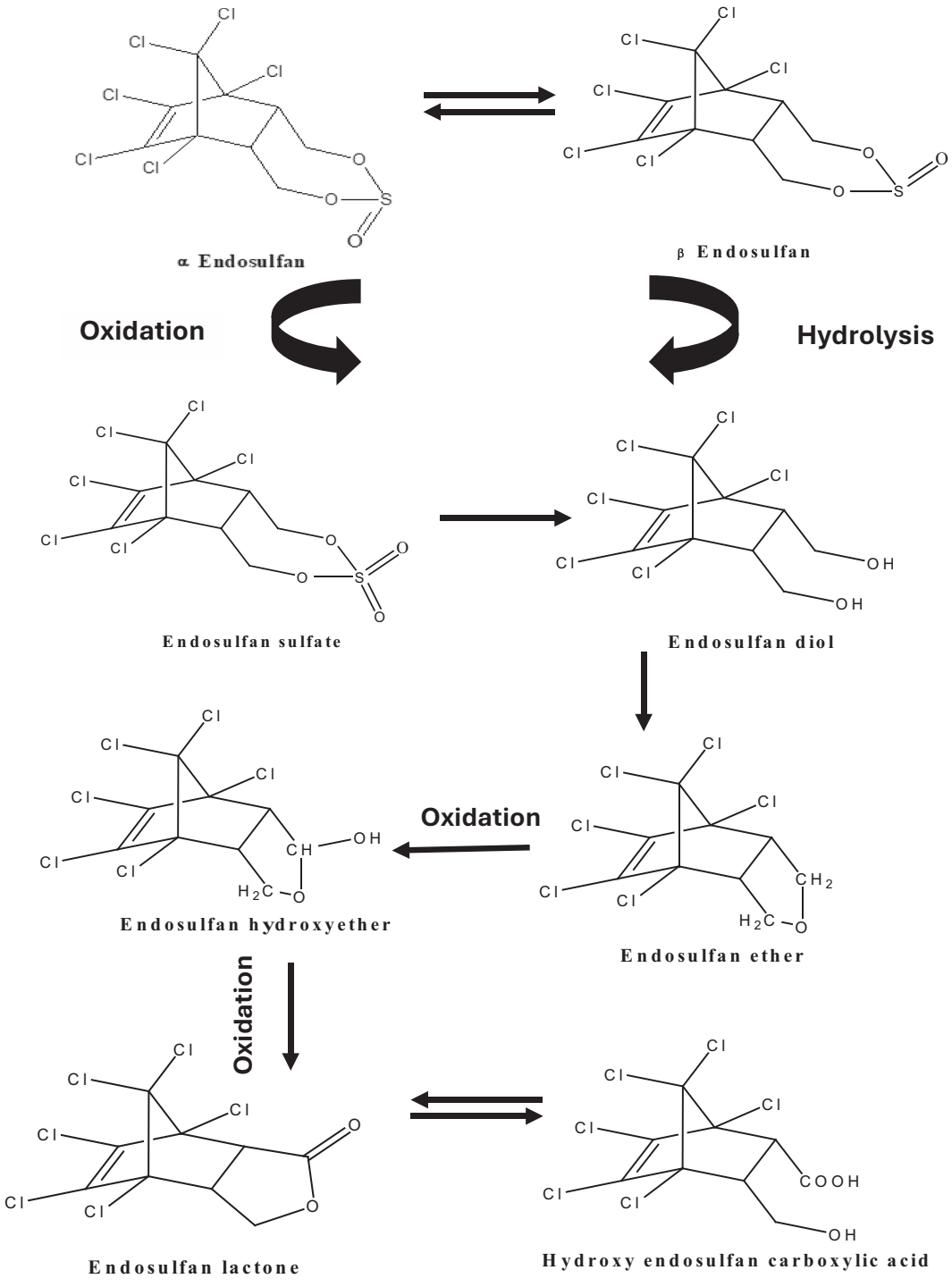


FIGURE 14.1 The fate of endosulfan in the environment.

under favorable conditions. The adsorption of endosulfan to soil particles results in increased persistence of insecticide. Endosulfan adsorbs onto soil colloids when applied in aqueous solution. It exhibits moderate affinity to soil colloids as evidenced from its average adsorption coefficient Koc = 12,000 $cm^3\ g^{-1}$. The mobility of the compound is reduced by its adsorption. However, the adsorbed endosulfan-soil colloid complex can also be transported via runoff to surface water bodies or via dust dispersion to the atmosphere and redeposit to off-target areas. Endosulfan persists in acidic soil for weeks to months after application because of unfavorable conditions for hydrolysis. The US EPA reports that "the potential for endosulfan to reach ground water is limited to acidic to neutral soils and aquifers, where preferential flow may be a prevalent pathway to ground water or where the ground water is shallow and is overlain by highly permeable soils" (US EPA, 2007). The loss of endosulfan from agricultural land via runoff and leaching is affected by many factors, such as soil texture, organic matter content, rainfall intensity, water table level, etc. Endosulfan is degraded in soil by both abiotic and biotic processes. The rate of degradation depends upon the conditions such as soil type, organic carbon content, pH, temperature, moisture content, microbial population and biomass, etc. Abiotic hydrolysis is considered to be the major mechanism of degradation. Half-lives of endosulfan vary with the soil pH.

14.5.2 Fate in Water

The contamination of surface water bodies by endosulfan is mainly due to spray drift and runoff. Spray drift carries both α- and β-isomers of endosulfan and deposits them into water bodies. Horizontal transport of endosulfan is caused by runoff and it can carry both the isomers of endosulfan and its degradation product, endosulfan sulfate. Endosulfan can undergo hydrolysis both by abiotic and biotic processes. The half-lives of endosulfan in natural waters depends on redox potential, pH, microbial population, organic matter content, etc. (Fan, 2008). The major transformation pathway of endosulfan in water is the formation of endosulfan diol, which is a less toxic metabolite of endosulfan (ATSDR, 2015). Endosulfan reactivity towards oxidation in water varies between the two isomers of endosulfan: the α-isomer is readily converted to endosulfan sulfate as opposed to the β-isomer (Landeros et al., 2018). However, the rate of conversion of endosulfan sulfate to endosulfan diol is slower as compared to the direct conversion of α-endosulfan to diol by hydrolysis. Rapid degradation of endosulfan-to-endosulfan sulfate is also reported in seawater because of base-mediated hydrolysis (Landeros et al., 2018). Alkaline pH favors hydrolysis and endosulfan diol is obtained as the major degradation product. The degradation of endosulfan sulfate is considered to be the slowest. Endosulfan volatilization from water to atmosphere is another process which results in a decrease in its concentration; weather conditions affect the volatilization of endosulfan.

14.5.3 Fate in Air

The entry routes for endosulfan into atmosphere are volatilization and vapor transportation. When it is applied on crops, volatilization from the crop surface results in vapor transport. Dust transportation can contribute to atmospheric endosulfan activities besides volatilization and spray drift. Regional weather, geography, and topography conditions, and anthropogenic activities affect the dust transportation. All three forms of endosulfan, α-isomer, β-isomer, and endosulfan sulpfate, are carried away by dust transport (Fan, 2008). A study by Hapeman et al. (2013) suggested that heavy agricultural use of endosulfan led to high atmospheric concentrations of endosulfan, especially the α-isomer. Endosulfan is not liable to atmospheric degradation. Abiotic hydrolysis and photolysis do not contribute significantly to endosulfan degradation in the troposphere. Endosulfan reacts with hydroxyl (OH)-radical in the atmosphere and is considered to be an effective atmospheric removal process for gaseous endosulfan (Fan, 2008).

14.5.4 Fate in Biota

Endosulfan is not found to be persistent in biota. It is metabolized very easily in terrestrial animals and in most aquatic organisms. However, endosulfan is found to be very toxic to some aquatic species, especially fish. Fish exhibit extreme sensitivity to endosulfan. There are reports of the killing of fish due to the discharge of endosulfan into rivers. A study on the acute toxicity of endosulfan on two fish species (*Hyphessobrycon bifasciatus* and *Brachydanio rerio*) indicated behavioral changes including hyperactivity, erratic swimming, and convulsions at the highest exposure levels. The half-life was found to be around 24 hours for both α- and β-isomers of endosulfan (Jonsson and Toledo, 1993). Endosulfan is found to have moderate toxicity for honey bees. Toxicity for birds is high in lab conditions, but no poisonings have been reported under field conditions (Fan, 2008). The bioaccumulation for endosulfan was found to be significant in mussels (*Mytelus edulis*) with 600 times accumulation as compared to the ambient concentration (EXTOXNET, 1996).

14.5.5 Regional Transport

There are reports of the presence of endosulfan all over the world – even in the Arctic. This could be attributed to its long-distance travel. This transportation involves different processes and routes occurring at the same time. The main routes for endosulfan's long-range and regional transportation include volatilization, vapor transportation, and runoff transportation (Fan, 2008).

14.6 REMEDIATION

Degradation of endosulfan in contaminated soil and water samples is highly desirable because endosulfan residues can pose threats to living organisms, especially because insecticide is poorly soluble in water, is highly lipophilic in nature, and can easily be transferred from one tropic level to another with ease and might result in bioconcentration and biomagnification. Remediation of endosulfan-/metabolite-contaminated soil and water can be mediated by physico-chemical and biological methods. Among physico-chemical methods, adsorption, photo-chemical, oxidation/advance oxidation process (AOP), and membrane filtration methods are more common; while in biological methods, microbial degradation mediated by bacteria and fungi and phytoremediation using plants are common methods (Pradeep and Subbaiah, 2012; Mudhoo et al., 2019). Each remediation method has its advantages and disadvantages. Adsorption of contaminants from water using adsorbents is a low-cost process, is nonspecific in nature, and can be used for all types of contaminants. Generally, activated carbon is the most preferred adsorbent, although recently, agricultural biomass, natural and modified clays, clay composites, zeolites, and molecularly imprinted polymers have been used and recommended as adsorbents for pesticide removal from water (De Smedt et al., 2015; Huong et al., 2016; Wen et al., 2016; Zieliński et al., 2022). Although adsorption is the most preferred method for contaminants' removal, this process involves transfer of the contaminant from one matrix to another matrix where contaminants are concentrated; this residual toxic sludge generated poses a threat to the environment, and its incineration is the only option for disposal. Photo-chemical degradation of pesticides also results in removal of pesticides from water, but sometimes, photo-chemically produced degradation products are toxic in nature, so this process might not be applicable to all pesticides. Moreover, the process requires a special setup and the cost of the energy required is relatively high. Similarly, the chlorine-mediated oxidation process is highly effective for microbial contaminants, but its efficiency to remove pesticides not well studied. AOPs are potent oxidizing agents of the hydroxyl group formed by the combination of free radicals and are more effective than single oxidation processes. Therefore, the combination of UV radiation with ozone, hydrogen peroxide, and ferrous and titanium oxide are used for micro-pollutant removal. These systems are used for treating drinking water containing organic pollutants and for wastewater treatment.

14.6.1 Photocatalysis and Oxidation Processes

Photocatalytic process is considered to be a green technology and is used to remove organic pollutants from aqueous solution. Among several catalysts, titanium oxide (TiO_2) is considered to be the best photocatalyst due to its stability, minimal toxicity, and high efficiency in the degradation of pollutants (Sood et al., 2015; Yu et al., 2010). However, inefficient harnessing of visible light, low adsorption capacity, homogeneity of photocatalyst particles, and less recovery after the first treatment are limiting its use at commercial levels. Therefore, approaches like doping and replacement of UV light with solar photocatalysis processes have been used to enhance the efficiency of TiO_2 (Kalsoom et al., 2023). The application of TiO_2 along with a semiconductor in visible range and TiO_2 along with metal/non-metals in UV light showed promising result for degradation of endosulfan. Turkyilmaz and Kucukcongar (2023) demonstrated the removal efficiency of $Ag/TiO_2/Fe_3O_4$ photocatalyst for endosulfan and its metabolites (endosulfan sulfate, endosulfan ether, and endosulfan lactone) that varied from 84.8–94.2% in synthetic, raw, and spring water samples. Further, 77.23% removal efficiency was achieved after five consecutive uses of the catalyst. Similarly, graphitic-carbon nitride/copper/titanium oxide ($g\text{-}C_3N_4/Cu/TiO_2$) removed 60% endosulfan from aqueous solution (Nekooie et al., 2022). Endosulfan removal efficiency of >95% was achieved when the photocatalytic reactor was coated with TiO_2 (Begum and Gautam, 2011). Use of a solar photocatalyst (Ag-doped nano TiO_2 crystal) showed better removal efficacy than TiO_2 and Degussa P25, commercially available photocatalysts. Solar light-driven photocatalytic degradation of endosulfan was achieved by $Cu:Cu_2O$ core-shell based nanoparticles via oxidation, reduction, and hydrolysis reaction (Goel and Arora, 2022). Iron molybdate photocatalyst ($Fe_2(MoO_4)_3$) was also effective in degrading 77% endosulfan (Parveen et al., 2020). Metal ferrite-loaded guar gum nanomaterials ($GG\text{-}CdMgFe_2O_4@TiO_2$) exhibited adsorption as well as photocatalytic degradation of endosulfan and 20 mg adsorbent degraded 94% endosulfan at neutral pH under sunlight (Rani and Shanker, 2023).

Generation of hydroxyl radical and degradation of pollutant in the environment can be achieved by ozonization, although it is very successful technique for microbial contaminants. Mitra and Varshney (2013) reported that endosulfan ozonization resulted into the formation of endosulfan diol that is 1,000 times less toxic than endosulfan. The combined use of electro-fenton/electro-oxidation/ozonization (EF/EO/O3) resulted in 92% degradation of endosulfan in 1 h as compared to the ozonization process alone which removed 62% endosulfan in 2 h (Rodriguez-Peña et al., 2020). The use of 57 mg min^{-1} ozone application resulted in 89% endosulfan degradation (Begum and Gautam, 2011). Yazgan and Kinaci (2004) reported 97% β-endosulfan degradation using a 16 mg min^{-1} ozone dose, pH 4, 60-min ozonization period.

Dechlorination processes and use of metallic/bimetallic compounds can be used for removal of endosulfan. Removal of endosulfan is achieved due to reductive transformation by zero valent magnesium (70% removal at 10 mg L^{-1}) and bimetallic system, Mg^0/Pd^0-carbon (90% removal at 10 mg L^{-1}) after 30 min reaction (Suresh and Thangadurai, 2019). Pillai and Kottekottil (2016) showed the use of nano zero valent iron (1,000 mg kg^{-1}) in soil, which reduced the endosulfan concentration in crops due to hydrogenolysis and reductive dechlorination. More than 99% degradation was observed and use of immobilized palladium was recommended due to the possibility of recovery and reuse of the materials (Thangadurai and Suresh, 2013). Abbas et al. (2019) demonstrated that zero valent iron (Fe^0) and iron oxide removed 85% endosulfan following oxidation and dechlorination in a batch experiment. Hwang and Kim (2021) demonstrated the application of 1% commercial zero valent iron (mZVI) along with 0.01 M ascorbic acid (AA) and 0.1 M hydrogen peroxide (H_2O_2) removed 98–100% endosulfan within 24 h from aqueous solution, 65–73% from soil slurry, and 64–66.2% from soil.

14.6.2 Adsorption Process

Materials with superior specific surface area, highly porous structure, conducive pore size distribution, high variability in surface chemistry, and significant degree of surface reactivity have

exhibited significant adsorption capacity for contaminant removal from contaminated/polluted water. Adsorption, in general, is a non-specific process and can be applicable for different types of contaminants, although capacity of a particular adsorbent will vary with the nature of the contaminant. Researchers have used several adsorbents primarily made from organic and inorganic sources. Zeolite, activated carbon, nano particles, nanocomposites, biopolymers, etc. are mainly used as adsorbents. Carbon slurry-based adsorbent was found to be effective for removal of endosulfan and adsorption capacity of 34.11 and 32.62 mg g^{-1} in batch and column operation, respectively (Gupta and Ali, 2008). Lu et al. (2011) demonstrated that adsorption capacity of chitosan beads was higher (6.7–10 μg) than crab shell powder (0.1–0.15 μg) and more than 99% removal of endosulfan was achieved. Researchers have used oil shale ash (Al-Qodah et al., 2007) and wood charcoal (Sudhakar and Dikshit, 1999) as adsorbents for endosulfan removal. The use of nanocomposites for contaminant removal is increasing due to their high adsorption capacity. Memon et al. (2022) synthesized diallylcalix[4]arene incorporated polystyrene nanofibers (PS-CLX NFs) and reported 22.12 and 20.11 mg g^{-1} α- and β-endosulfan removal at 120 rpm, 60-min incubation period, and 7.5 mg adsorbent. Alkali activated municipal waste fly ash and their polymers showed 1.87–20.01 mg g^{-1} endosufan adsorption and alkylation-enhanced adsorption capacity by ~8–10 times and affinity by ~30 times (Luttah et al., 2023). Carbon-based adsorbent (powdered activated carbon, granular activated carbon, oak charcoal, rice husk charcoal) were more effective (60–100%) than inorganic adsorbent (silica and alumina) for α- and β-endosulfan removal from water (Eun et al., 2021). Biopolymer Ɛ-caprolactone (Mourabit and Boulaid, 2019), sucrose derived activated graphene clay composite (Mathanakeerthi et al., 2021), magnetite diatomite (Alacabey, 2022), and activated carbon and biochar-based adsorbents (Kalsoom et al., 2023) have been successfully employed for adsorption of endosulfan.

14.6.3 Membrane Separation Process

The use of an ion exchange membrane and surface functionalization of the membrane increases retention of pollutants on the membrane. However, foul odor and blocking of pores due to cake formation reduces the retention capacity during prolonged use (Jhaveri and Murthy, 2016). Despite limitations, due to high retention capacity, research using membranes has attracted researchers to work on the different aspects of the process. Banasiak et al. (2011) demonstrated that ion exchange resin works better for endosulfan adsorption at pH 7 than at pH 11, and that the pH of the medium and the molecular weight of the membrane are important factors controlling the retention of the endosulfan on the surface (De Munari et al., 2013). Mukherjee et al. (2020) developed an asymmetric polysulfone-based low-pressure thin film composite membrane that was efficient in rejecting organochlorine pesticides including endosulfan (100%). A hydrogen-based membrane biofilm (H_2-MBfR) reactor effectively removed more than 99% endosulfan from water (Cuci and Taşkın, 2020).

14.6.4 Biological Remediation

Biological methods can be classified into two major categories: (i) microbial degradation and (ii) phytoremediation. Microbial degradation is the phenomenon of biological transformation of organic compounds by living organisms, particularly bacteria and fungi. Phytoremediation is the use of living green plants for risk reduction and/or removal of contaminants from contaminated soil, water, and sediments. There are many advantages of biological degradation: (i) it can be conducted *in situ* as well as *ex situ*; (ii) it is an environmentally friendly technique; (iii) it is low cost and low maintenance. These techniques have some disadvantages like (i) the time required for complete remediation is variable and relatively long; (ii) biological processes are often highly pesticide-specific; and (iii) the presence of metabolically capable microbial populations, suitable environmental growth conditions, and appropriate levels of nutrients required for success.

Biological degradation of endosufan can be mediated by primarily two prominent pathways (i) hydrolysis which leads to the formation of endosulfan diol, endosulfan ether, endosulfan lactone as major degradation metabolites which are non-toxic in nature, (ii) oxidation results in the formation of endosulfan sulphate which is a toxic and persistent metabolite.

14.6.4.1 Bacterial Degradation

Microbial remediation might utilize native microbes for degrading any contaminant, because when exposed to any contaminant, microbes develop enzyme systems to degrade that contaminant. Bacteria from genuses *Pseudomonas*, *Bacillus*, *Klebsiella*, *Mortierella*, *Stenotrophomonas*, and *Achromobacter* have shown endosulfan degradation potential (Seralathan et al., 2015; Singh and Singh, 2014a; Mir et al., 2017; Ozdal et al., 2017; Zaffar et al., 2018). Addition of microbes having capability to degrade a particular contaminant enhances the process of remediation and is known as bioaugmentation. Success of bioaugmentation depends on the survival and proliferation of added microbes. Bioaugmentation can be coupled with biostimulation, a process which involves adding nutrients or introducing oxygen in contaminated soil/water so that microbes' survival and activity can be enhanced. A few studies reported that microbes used endosulfan as their sole source of carbon or sulfur (Castillo et al., 2011; Singh and Singh, 2011; Seralathan et al., 2015).

Pseudomonas sp. is the most studied bacterial species that has been isolated from the contaminated soil or endosulfan-seasoned soil (Harikumar et al., 2013; Zaffar et al., 2018). Degradation of α-endosulfan and its oxidative metabolite endosulfan sulfate followed a hydrolytic pathway and resulted in the formation of endosulfan diol, endosulfan ether, and endosulfan lactone (Bajaj et al., 2010; Mir et al., 2017; Zaffar et al., 2018). Similarly, *Alcaligenes faecalis* strain JBW4, isolated from activated sludge, degraded α- and β-endosulfan following a hydrolytic pathway; endosulfan ether and endosulfan lactone were the major metabolites (Kong et al., 2013, 2014). The bacterium was able to colonize in endosulfan-contaminated soils, confirmed by PCR-DGGE assay.

Bacteria of the genus *Bacillus* have shown endosulfan degradation potential. *Bacillus* sp. KF984414 and *Bacillus* sp. LN849696 isolated from endosulfan-stressed soil showed plant growth promoting effect and could degrade 70–74% endosulfan in medium and 63–67% in soil (Rani and Kumar, 2017). Seralathan et al. (2015) reported that *Bacillus megaterium* converted endosulfan into the toxic metabolite endosulfan sulfate, while *Pseudomonas aeruginosa*, *Ochrobactrum* sp., and *Achromobacter xylosoxidans* followed the hydrolytic pathways with formation of endosulfan diol and their consortium could degrade 94% of endosulfan as their sole source of sulfur. Similarly, *Achromobacter xylosoxidans* strain C8B (Singh and Singh, 2011) and *Azotobacter* sp. (Castillo et al., 2011) utilized endosulfan as their sole source of sulfur. Mostly, bacteria used endosulfan as their source of sulfur; however, Verma et al. (2006, 2011) isolated an endosulfan-degrading bacterial strain from earthworm gut that used endosulfan as its sole carbon source.

Silambarasan and Abraham (2014) reported that *Halophilic* bacterium JAS4 from the *Gossypium herbaceum* rhizosphere had remarkable potential to degrade α-endosulfan (1,000 mg L^{-1}) and endosulfan sulfate in the aqueous medium with a half-life (DT_{50}) of 0.01 d and 1.07 d, respectively. *Klebsiella* sp. M3 could tolerate and degrade 50 mg L^{-1} (medium) and 100 mg L^{-1} (soil) of endosulfan and was more effective in degrading α-endosulfan (Singh and Singh, 2014a). Ozdal et al. (2017) and Zaffar et al. (2018) reported that α-endosulfan-degrading potential of *Stenotrophomonas maltophilia* OG2 was greatly influenced by many factors and optimum (81.53%) degradation was observed at concentration of 100 mg L^{-1}, temperature 30°C, and pH 8.0.

In general, most of the bacteria used for endosulfan degradation were more effective in degrading α-endosulfan. However, Odukkathil and Vasudevan (2015) reported that *Bordetella petrii* I GV 34 and *Bordetella petrii* II GV 36 degraded both endosulfan isomers with equal ease. Contrary to this, Jimenez-Torres et al. (2016) reported that *Enterobacter cloacae* PMM16 was more efficient at degrading β-endosulfan (100%) than α-endosulfan (71.32%).

Most of the studies on microbial breakdown of endosulfan were conducted in an aerobic environment. But, a few researchers have studied anaerobic microbial breakdown of endosulfan (Sutherland et al., 2002; Kwon et al., 2005). Endosulfan degradation under anaerobic conditions can follow a hydrolysis pathway and result in the formation of endosulfan diol (Guerin, 1999), which can be metabolized further to endosulfan lactone, endosulfan hydroxyether, and endosulfan monoaldehyde and dialdehyde by anaerobic bacterial and fungal cultures (Sutherland et al., 2000; Awasthi et al., 2003). Sadiq et al. (2019) reported that *Pleurotus ostreatus*-mediated degradation of α-endosulfan was higher under solid-state fermentation than submerged fermentation, while the inverse was true for β-isomer. The calculated DT_{50} of α- and β-endosulfan under solid-state fermentation was 3.99 and 44 days, respectively, while respective values were 10 and 20 days under submerged fermentation. Rapid reduction in endosulfan sulfate metabolite under submerged fermentation revealed its ascendancy in degradation over solid-state fermentation.

Immobilization of the pure cultures may help to improve the bioremediation potential, since immobilized cells have prolonged microbial cell viability and improved capacity to tolerate higher concentrations of pollutants and repeated use (Richins et al., 2000; Chen and Georgiou, 2002). Jesitha et al. (2015) compared endosulfan degradation in batch and column reactor using free and immobilized *Pseudomonas fluorescens*. The bacterium was able to utilize both α- and β-endosulfan as its sole source of carbon and energy and tolerated 550 mg L^{-1} concentration. Degradation was relatively faster when the bacterium was immobilized in calcium alginate beads. Degradation was mediated by a hydrolytic pathway and the formation of endosulfan diol, endosulfan ether, and endosulfan lactone metabolites was confirmed. Pradeep and Subbaiah (2016) used Ca-alginate immobilized cells of *Pseudomonas aeruginosa* for endosulfan degradation using a repeated continuous batch. Immobilized bacteria were highly effective in degrading 2% endosulfan solution at 100 mL h^{-1}; endosulfan lactone and endosulfan ether were the products of degradation.

14.6.4.2 Fungal Biodegradation

There are very few reports that fungi have shown an ability to degrade endosulfan. The filamentous nature of fungal growth offers a major advantage over bacteria because it helps fungi to effectively permeate the soil environment. Fungi can degrade a wide variety of pesticides by introducing minor structural changes in the molecule to convert them into a less or nontoxic form; the biotransformed pesticide is then released into the soil, where it is further degraded by bacteria (Kumar and Philip, 2017). Fungal enzymes like laccase, dehydrogenase, peroxidase, hydrolases, lignin peroxidase, and manganese peroxidase have shown an ability to degrade endosulfan by hydrolysis, oxidation, chlorination, dehydrochlorination, and esterification mechanisms (Maqbool et al., 2016). *Aspergillus niger* showed very high capability to degrade endosulfan (95%) (Goswami et al., 2009; Mukherjee and Gopal, 1994). Silambarasan and Abraham (2013) isolated *Botryosphaeria laricina* JAS6 and *Aspergillus tamarii* JAS9 that could degrade endosulfan and endosulfan sulfate from endosulfan-spiked soil. Both strains were able to tolerate elevated levels of endosulfan (1,300 mg L^{-1}) and grew well up to 1,000 mg L^{-1}.

Similarly, white rot fungi *Trametes hirsuta*, *Trametes versicolor*, *Pleurotus ostreatus*, *Bjerkandera adusta*, and *Phanerochaete chrysosporium* harbor lignin degrading enzyme systems which have been reported for endosulfan degradation (Kullman and Matsumura, 1996; Bisht et al., 2019). *Trametes hirsuta* showed complete degradation of both α- and β-endosulfan isomers (Bisht et al., 2019) and endosulfan sulfate was the major degradation product recovered. Wang et al. (2018) suggested that *Pleurotus eryngii* and *Coprinus comatus*, alone or in combination, resulted in endosulfan removal exceeding 87%. There is a need to isolate and identify endosulfan-degrading fungal strains since fungi are more tolerant to environmental stress.

14.6.4.3 Phytoremediation

Plants can be used for removal and degradation of contaminants and have been widely reported for both organic and inorganic contaminants. Plants facilitate remediation of soil and water by different

mechanisms: rhizofiltration is used for contaminated water while rhizodegradation, phytodegradation, phytostabilization, etc. can be used for contaminated soils. Success of phytoremediation is mainly dependent on the ability of plants to survive in contaminated soil (Prasad et al., 2011; Mitton et al., 2016) and efficiency of plant roots and rhizosphere microbes to uptake and degrade contaminants. A robust root system is the key to successful phytoremediation because it helps in better uptake of contaminants from soil and promotes proliferation and habitation of rhizosphere microbes that can degrade contaminants by metabolism (using them as source of energy) or co-metabolism. Efficiency of phytoremediation varies with type of plant, soil type, weather, stage of plant, etc. Mersie et al. (2003) evaluated ability of plant buffer strips to remove endosulfan from runoff water and reported over 98% endosulfan removal. Ramirez-Sandoval et al. (2011) reported that *Ocimum* sp. is a good candidate for endosulfan degradation in contaminated soils; *Ocimum basilicum* was more effective in degrading endosulfan than *Ocimum minimum*. Rose et al. (2006) reported that macrophytes and algae can reduce the persistence of endosulfan in on-farm constructed wetlands water because partitioning onto sediment acted as a sink for the insecticide. Sethunathan et al. (2004) reported that green algae, *Chlorococcum* sp. or *Scenedesmus* sp., enhanced degradation of α-endosulfan; endosulfan sulfate (major) and endosulfan ether (minor) metabolites were detected along with isomerization of α-endosulfan to β-endosulfan. Thus, coupled with a biotransformation ability, especially at a high inoculum density, the biosorption ability of algae makes them effective candidates for remediation of α-endosulfan-polluted environments.

Harikumar et al. (2013) showed that the aquatic plant *Salvinia molesta* was highly efficient in endosulfan removal (97.94 ± 0.33% in 21 days) from water. Among the terrestrial plants, tomato and spinach took 21 and 24 days, respectively, for complete removal of pesticide from soil (140 μg kg^{-1} endosulfan). Mitton et al. (2016) reported that among four plants used for endosulfan degradation, sunflower was the best phytoremediation plant for endosulfan residue uptake from contaminated soils and maximum decrease in its concentration in contaminated soil.

Abaga et al. (2014) reported effectiveness of *Vetiveria zizanioides* in degrading endosulfan because it harbored a greater number of endosulfan-degrading microorganisms. Singh and Singh (2014b) reported similar observations while evaluating uptake and accumulation of the α- and β-endosulfan and endosulfan sulfate from contaminated soil. Out of seven plants used, *V. zizanioides* accumulated 343 ng g^{-1} of endosulfan (α+β) and endosulfan sulfate (21 ng g^{-1}). The variations in the uptake of the endosulfan isomers was attributed to the morphology of the plant, type of root system, number of branches and extent of branching, types and surface area of leaves, and tolerance of the plant to the individual chemical. Singh et al. (2018) reported that out of nine locally available plant species *V. zizanioides* accumulated the highest amount of endosulfan. No significant reduction in lipid peroxidation and chlorophyll content in *V. zizanioides* supports its suitability for phytoremediation.

Earlier, wetland was evaluated for degradation of 8 priority pesticides, including endosulfan (Matamoros et al., 2007) and results suggested that wetland showed maximum degradation of endosulfan. It was attributed to biodegradation and plant uptake since retention in the sediment was negligible. Authors suggested that reductive dehalogenation was the major mechanism of endosulfan degradation. Zhao et al. (2014) evaluated vertical-flow constructed wetlands at the lab scale for bioremediation of endosulfan. After 20 days' experiment, endosulfan isomer removal efficiencies were increased to 89.24–97.62% through bioremediation. Bacteria bioaugmentation and sucrose biostimulation promoted biodegradation while KH_2PO_4 biostimulation promoted plant uptake.

14.7 CONCLUSION

Endosulfan, an organochlorine insecticide, was banned by the Persistent Organic Pollutants Review Committee (POPRC) to the Stockholm Convention in 2011. However, due to its persistent nature and long-distance transport, endosulfan is still detected in environmental components. Although the hydrolytic metabolites of endosulfan, namely endosulfan diol, endosulfan ether, and endosulfan

lactone, are less toxic than the parent molecule, the oxidized metabolite endosulfan sulfate is equally persistent and toxic in nature. Endosulfan is considered to be an endocrine disruptor and adversely affects human health by inducing seizures, cancer development, and reproductive and gastrointestinal disorders. Both physico-chemical and biological methods have been suggested for remediation of endosulfan-contaminated soil and water, but techniques that can be effectively scaled up need more research and standardization.

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15 Short-Chain Chlorinated Paraffins (SCCPs)

Environmental Contamination in Soil and Water and Potential Remediation Strategies

Md Abdul Halim, Md Nuruzzaman, and Ravi Naidu

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15.1 INTRODUCTION

Chlorinated paraffins (CPs) are a class of lipophilic, polychlorinated n-alkanes classified according to their carbon chain lengths into short-chain CPs (SCCPs, C10–13), medium-chain CPs (MCCPs, C14–17), and long-chain CPs (LCCPs, C18–30) (Chen et al., 2024; Jiang et al., 2020; Xie et al., 2024). Among these, SCCPs are of particular concern due to their environmental

DOI: 10.1201/9781003530466-15
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persistence, bioaccumulation, biomagnification, and potential for long-range transport (Du et al., 2020; Zhou et al., 2018; Knobloch et al., 2021; Wu et al., 2021). Characterized by the chemical formula $C_nH_{2n+2-z}Cl_z$, SCCPs contain chlorine in amounts ranging from 30% to 72% by weight. Their pervasive presence in various ecosystems raises significant health risks for living organisms via exposure through air, water, soil, and sediments (Li et al., 2023; Wu et al., 2021). Industrial applications of SCCPs – which include their use in polyvinyl chloride (PVC) processing, lubrication, metal cutting fluids, the rubber industry, paints, and textiles – further contribute to their environmental contamination (Guida et al., 2022; Girones et al., 2023).

Given their unique physical-chemical properties, SCCPs have come under increasing regulatory scrutiny in several countries, including those in Europe, the US, and Canada (Wang et al., 2019). Regulations now impose limitations on their production and use due to their toxic characteristics and environmental persistence. For example, concentrations of SCCPs in surface sediments of the East China Sea have been recorded at levels ranging from 5.8 to 64.8 ng/g dry weight, underscoring their widespread occurrence in marine ecosystems (Ji et al., 2022). Despite regulatory efforts, the industrial sector remains a significant source of SCCP release, with annual production in Europe estimated between 1,000 to 10,000 tons (Chen et al., 2021). Detection of SCCPs has been reported in various environmental media – ambient coniferous leaves, local lettuce, soils, and maize foliage – highlighting the extent of contamination (Guida et al., 2022).

The health and environmental risks associated with SCCPs are exacerbated by their capacity for chemical transformation, which includes processes like hydrochlorination, cyclization, and aromatization, augmenting their persistence and toxicity (Xie et al., 2024). The pyrolysis of waste materials also significantly contributes to the environmental burden of SCCPs. Bioaccumulation studies indicate that these compounds can concentrate in various organisms, including plants like maize, potentially serving as a pathway for human exposure in agricultural contexts (Jiang et al., 2020). Moreover, the volatilization of chlorine and the formation of alkali metal cyanides from SCCPs introduce additional risks to ecosystems and human health (Wang et al., 2019).

Considering these challenges, there is an urgent need to develop sustainable and environmentally sound approaches for managing SCCP contamination. This chapter aims to investigate the volatilization mechanisms of SCCPs, their potential to generate toxic byproducts, and the implications for environmental and human health. We will also evaluate the associated risks in soil and water systems and explore potential remediation strategies to mitigate their impact. By enhancing our understanding of these processes, we can inform more effective policies and practices aimed at reducing the environmental and health risks linked to SCCPs.

15.2 SOURCES OF SHORT-CHAIN CHLORINATED PARAFFINS

The widespread presence of SCCPs is evident across nearly all environmental matrices, including air, water, soil, sediment, and wildlife. They are also found in other mediums such as sewage sludge, e-waste, household dust, and human breast milk (Ma et al., 2020). SCCPs are extensively utilized as flame retardants in textiles and rubbers, as well as in paints, plasticizers, and metalworking fluids (Babayemi et al., 2022; Guida et al., 2022; Mu et al., 2023).

Spatial distribution studies, alongside various geochemical proxies, indicate that the primary sources of SCCPs are river inputs, with significant deposition observed along the inner shelf. However, there is ongoing seaward transport towards more distal areas (Zeng et al., 2013). Recent findings reveal that e-waste contains approximately 30% plastics, contributing to an annual global generation of around 12 million tons of plastic waste from electronic products. Notably, concentrations of SCCPs in PVC cables can reach up to 191 mg g^{-1} (Chen et al., 2021).

By 2020, it is estimated that approximately 5.2 million metric tons of chlorinated paraffins (CPs) had been released into the environment, with the annual emission rate rising to roughly 193,000

tons. SCCPs represent around 30% of these cumulative CP emissions (Chen et al., 2021). Among the sectors affected by these emissions, soils received the largest share at 74%, followed by air at 10% and fresh water at 16% (Chen et al., 2022; Zhang et al., 2023).

Furthermore, wastewater treatment is identified as the principal emission source for CPs, contributing approximately 84% of the total cumulative emissions (Zhang et al., 2023). This predominance arises from the large volumes of wastewater generated from the production and use of CPs, particularly in metalworking fluids. During treatment, CPs can volatilize into the atmosphere, flow into freshwater systems through effluent discharge, and ultimately find their way into the soil via the land application of biosolids (Goldenman et al., 2017). The second largest emission source stems from in-use stock of CPs, accounting for about 9% of the cumulative emissions, while industrial processes related to the production and processing of CP-containing products contribute a relatively minor 4% to the overall cumulative total, as depicted in Figure 15.1.

SCCPs were once produced in numerous countries, including the United States, Canada, Brazil, South Africa, Germany, France, the United Kingdom, Italy, Russia, Spain, Japan, and China (Glüge et al., 2016). However, obtaining precise figures on global SCCP production proves challenging due to limited publicly available production data, the inconsistent use of Chemical Abstracts Service (CAS) numbers across different countries, and varying nomenclature practices that categorize chlorinated paraffins (CPs) by chlorine content rather than carbon chain length in some regions (Yuan et al., 2021). Historical estimates regarding the production, consumption, and emissions of SCCPs can be found in several reviews (Fiedler, 2010; Glüge et al., 2016; Mu et al., 2023).

SCCP production experienced gradual growth from 1935 to 2000, followed by a sharp increase attributed to significant production in China. At its peak, worldwide SCCP production reached approximately 165,000 tons per year, amounting to an estimated total of about 25 million tons produced between 1935 and 2012 (Mu et al., 2023). The dynamic substance flow analysis model and estimated that the cumulative global production of CPs from 1930 to 2020 was around 32.5 million metric tons, with SCCPs composing 28% of this total (Chen et al., 2022).

Following mounting environmental concerns, SCCP production declined sharply and was ultimately banned in Europe and North America when it was added to Annex A of the Stockholm Convention in 2017. Nevertheless, SCCPs continue to be produced and/or used in several developing nations, including China, Brazil, and India (Zhang et al., 2023; Mu et al., 2023). For example, it is estimated that in China, 225.2 and 236.4 kilotons of SCCPs were consumed in 2018 and 2019, respectively, with emissions of approximately 3.9 kilotons and 4.2 kilotons released into the environment during the same years (Chen et al., 2021).

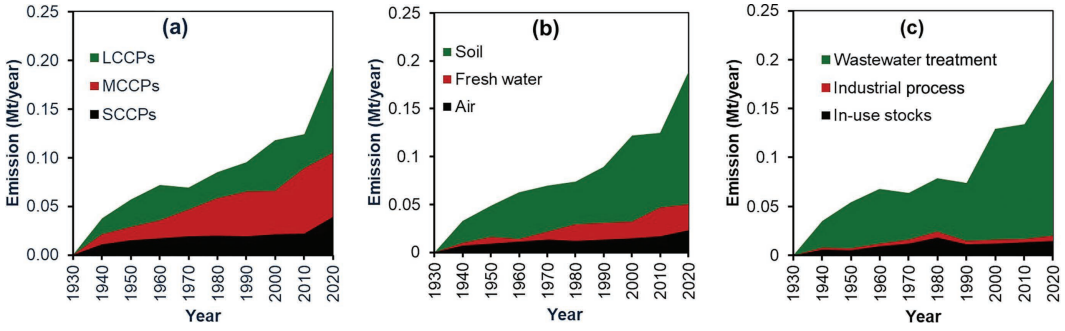


FIGURE 15.1 Spatio-temporal evolutions of global emissions of CPs (a) for SCCPs, MCCPs, and LCCPs; (b) to different receiving environments; and (c) from various emission sources (sourced from the American Chemical Society reference as Jiang et al., 2020).

Information regarding the annual production and consumption of SCCPs in India remains elusive due to a lack of available data (Babayemi et al., 2022). However, SCCPs are listed in the product catalogues of several Indian chlorinated paraffin manufacturers, such as PayalGroup and SevenPH Interchem (Mu et al., 2023). Although Brazil ceased domestic production of CPs in 1994, it continues to rely heavily on imported technical CPs that likely contain SCCPs (Guida et al., 2022; Mu et al., 2023).

15.3 TOXICITY, EXPOSURE, AND POTENTIAL RISKS OF SCCPS TO THE ENVIRONMENT AND HUMANS

SCCPs have been detected in a wide range of environmental media, including air, sediment, surface waters, and wastewater. Figure 15.2 illustrates the various sources of SCCPs and their potential toxicological exposure risks to humans. Additionally, SCCPs have been identified in various biota, encompassing freshwater aquatic species, marine mammals, and both avian and terrestrial wildlife. While SCCPs exhibit low acute toxicity in animals, their carcinogenic potential has been evidenced by a two-year oral exposure study involving F344/N rats and B6C3F1 mice. The highest dose that can be administered without eliciting adverse effects – the no observed adverse effect level (NOAEL) – is established at 10 mg/kg/day for rats (Kale et al., 2022).

Subchronic toxicity studies conducted on laboratory animals reveal that SCCPs can produce harmful effects on the kidneys, liver, thyroid, and parathyroid glands. Research findings from studies involving rats and mice exposed to SCCPs suggest that liver damage is linked to peroxisome proliferation, while thyroid effects are associated with altered thyroid hormone levels and the induction of glucuronyl transferase (Chen et al., 2023).

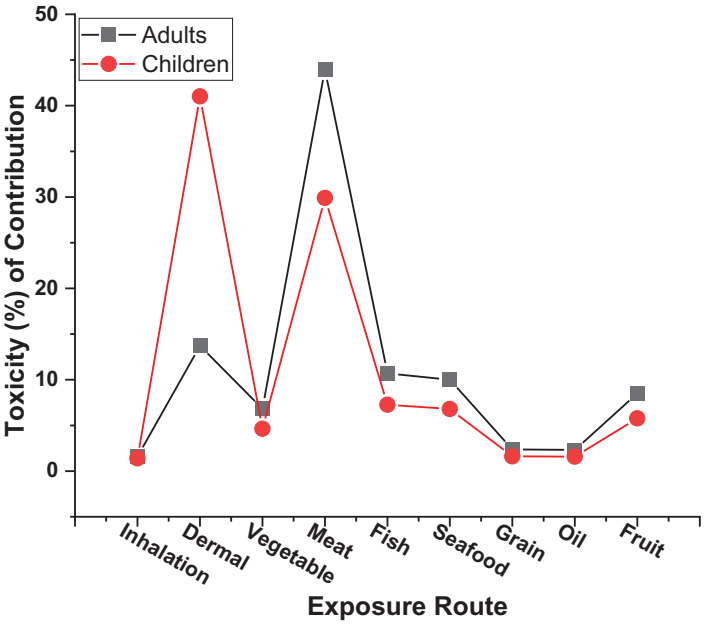


FIGURE 15.2 The different sources and their potential toxicology exposure in humans by SCCPs in adult and children (Chen et al., 2024).

Cell viability decreased significantly with increasing exposure doses of SCCPs. Notably, exposure to C10-CPs for 48 hours caused a marked reduction in cell viability compared to exposure for just 24 hours, even at a concentration of 1 μg L^{-1} (Chen et al., 2024).

The impact of SCCPs on cellular viability is linked to alterations in intracellular redox status, which leads to considerable metabolic disruptions. As peroxisome proliferators, SCCPs notably stimulate the β-oxidation of unsaturated and long-chain fatty acids (Gong et al., 2021). Additionally, SCCP exposure disrupts glycolysis and amino acid metabolism while promoting the upregulation of glutamate metabolism and the urea cycle. The toxic effects associated with SCCPs primarily involve disturbances in energy production, protein biosynthesis, fatty acid metabolism, and ammonia recycling (He et al., 2023).

Furthermore, transcriptional changes induced in zebrafish embryos, which correlate with specific pathways and molecular initiating events – such as the activation of the nicotinic acetylcholine receptor – indicate that SCCPs may interfere with neural development processes (Xia et al., 2021).

15.3.1 Toxicity to Human Beings

No relevant human toxicokinetic studies on SCCPs were identified within the scope of this opinion. However, the presence of SCCPs in human blood and milk samples suggests that they are absorbed by humans to some extent (Li et al., 2020). Furthermore, the detection of SCCPs in umbilical cord blood indicates that they can be transferred to the fetus. To establish elimination half-lives, more comprehensive information is necessary.

Animal studies have provided some insight into the toxicokinetics of SCCPs. For instance, a study in mice found that highly chlorinated SCCPs and medium-chain chlorinated paraffins (MCCPs) are metabolized and excreted primarily through feces, whereas lower chlorinated SCCPs and MCCPs are partially metabolized and exhaled as carbon dioxide. In rats and mice administered with chlorinated paraffins (CPs) orally, the primary route of excretion was through feces, with smaller proportions excreted in urine and expired air (Darnerud and Bergman, 2022).

Repeated dose toxicity studies in rats, mice, and dogs have identified the liver, kidney, and thyroid as target organs for SCCPs (C10–12, 58% chlorination; C12, 60% chlorination) (Chen et al., 2024). For the tested SCCPs, a no observed adverse effect level (NOAEL) of 10 mg/kg body weight per day was established, based on increased kidney weights and histopathological changes in the kidney and thyroid (Chen et al., 2024; Li et al., 2020). Figure 15.3 illustrates the relationship between SCCP concentrations and lipid contents in various food species.

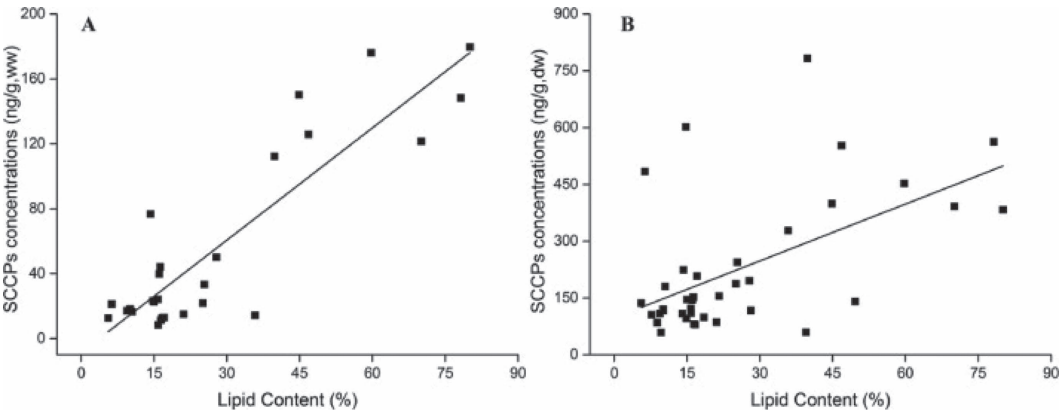


FIGURE 15.3 Relationships between SCCP concentrations and lipid contents in different food species (A: SCCPs ng/g ww = −8.63 + 2.31 × lipid content, $R^2 = 0.773$, $p < 0.01$; B: SCCPs ng/g dw = 97.3 + 5.01 × lipid content, $R^2 = 0.289$, $p < 0.01$) (Copyright: Elsevier, 2020; Li et al., 2020).

An SCCP (carbon chain length unspecified, 58% chlorination) demonstrated teratogenic effects in rats, including digit absence or shortening, at a high dose of 2,000 mg/kg bw per day. This was accompanied by maternal toxicity, evidenced by high mortality rates and reduced weight gain. There is no observed adverse effect level (NOAEL) for developmental toxicity was determined to be 500 mg/kg bw per day, while the NOAEL for maternal toxicity was established at 100 mg/kg bw per day (Catlin et al., 2024).

In a developmental toxicity study involving rabbits treated with the same SCCP, the NOAEL for developmental toxicity was found to be 10 mg/kg bw per day, based on increased resorption rates, with no associated maternal toxicity. Another SCCP tested (C12, 60% chlorination) was linked to increased tumor incidence in rats and mice, notably in the liver (both rats and mice), kidneys (male rats only), and thyroid (female rats and mice) (Schrenk et al., 2020). Notably, the liver tumors observed in rodents due to SCCP exposure, which are associated with constitutive androstane receptor or PPARα transactivation, appear to be irrelevant for human health. These rodent responses could induce toxicity if the energy balance required to sustain this compensatory mechanism is disturbed, thereby compromising cell viability. The kidney tumors induced by SCCPs in male rats seem to be linked to chronic nephropathy (partly due to α2u-microglobulin accumulation), resulting in compensatory regenerative hyperplasia and increased S-phase activity (Gong et al., 2021).

The CONTAM Panel conducted benchmark dose (BMD) modeling using data from various rodent studies. For one tested SCCP (C10–12, 58% chlorination), a $BMDL_{10}$ of 2.3 mg/kg bw per day was identified as the reference point for risk characterization concerning increased incidences of nephritis in male rats (Zhang et al., 2023). At the 95th percentile exposure level, the lower-bound and upper-bound assessments ranged from 4.9 to 87 ng/kg bw per day (Aikins et al., 2023). For SCCPs, estimated exposure levels ranged from 60 to 445 ng/kg bw per day for the average consumption of human milk, rising to 90 to 668 ng/kg bw per day for high consumption of human milk.

Comparisons of these exposure estimates with the $BMDL_{10}$ of 2.3 mg/kg bw per day yielded margins of exposure of approximately 5×10^3 and 3×10^3 or higher for average and high human milk consumption, respectively. Analysis of the highest median exposure values from dust samples collected across four European countries indicated daily exposures of 26 ng/kg bw per day for toddlers and 1.8 ng/kg bw per day for adults relating to SCCP ingestion via dust (Yuan et al., 2021).

15.3.2 Toxicity to Soil Organisms

SCCPs are toxic chemicals and pose significant concerns for both environmental and human health due to their widespread use and contamination. A key finding in evaluating the toxicity of SCCPs is their detrimental impact on soil organisms, particularly earthworms. The earthworm species *Eisenia fetida*, commonly employed as a standard test organism in ecotoxicological studies, has been shown to exhibit high sensitivity to SCCPs in soil. Research indicates that *E. fetida* experiences a statistically significant decrease in reproduction when exposed to SCCP concentrations as low as 900 µg/g dry weight (dw) of soil (Glüge et al., 2018). This result underscores the potential for SCCPs to adversely affect the reproductive capacity of soil-dwelling organisms, which play a crucial role in maintaining soil health and ecosystem functioning.

The predicted no effect concentration (PNEC) for *E. fetida* reproduction in soil has been estimated at 28 µg/g dw. This figure derives from a no observed effect concentration (NOEC) of 280 µg/g dw, wherein an assessment factor of 10 was applied to accommodate potential variability and uncertainties within the data (Gomes et al., 2017). The PNEC represents the threshold concentration below which no adverse effects are anticipated in the environment. Notably, the study's soil organic carbon (OC) content was 4.7%, leading to a corresponding PNEC of 5.9 mg/g OC. This conversion

is essential for understanding the bioavailability and potential toxicity of SCCPs in soils with varying organic carbon levels (Chen et al., 2024).

The composition of SCCPs is variable, influencing their environmental behavior and toxicity. Their high chlorine content is characteristic and contributes to their persistence in the environment, as well as their tendency to bioaccumulate in organisms, including soil fauna like earthworms. Given that significant reproductive impacts have been noted at concentrations as low as 900 μg/g dw of soil, the toxicity of SCCPs to terrestrial ecosystems – especially soil-dwelling organisms – constitutes a critical environmental issue. Establishing PNEC values and elucidating toxicity thresholds offer valuable insights for risk assessment and the regulation of SCCPs in soil environments, thereby aiding in the protection of biodiversity and the maintenance of essential ecosystem services (Wang et al., 2024).

15.3.3 Toxicity to Sediment Organisms

Among the organisms tested, *Hyalella azteca* and *Lumbriculus variegatus* exhibited the highest sensitivity to SCCPs in sediment. *H. azteca* demonstrated a statistically significant reduction in mean weight at a concentration of 270 mg/g dry weight (dw) sediment, while *L. variegatus* showed a statistically significant decrease in the total mean weight of worms per replicate at 410 mg/g dw sediment (Aikins et al., 2022).

The predicted no effect concentration (PNEC) for sediment was estimated to be 13 μg/g dw for both species, derived from a no observed effect concentration (NOEC) of 130 μg/g dw sediment and an assessment factor of 10. The organic carbon content in both studies was approximately 5%, leading to a corresponding PNEC of 260 μg/g organic carbon (OC). Both investigations utilized a C14–17 chlorinated paraffin with 52% chlorine content (El Zokm et al., 2022).

15.3.4 Toxicity to Aquatic Invertebrates

The SCCPs have demonstrated toxicity to *Daphnia magna* in both short- and long-term exposure scenarios. Most available data have been derived from a SCCP mixture containing 52% chlorine. A reported 48-hour EC_{50} value for *D. magna* is 5.9 μg/L; however, other studies indicate that the EC_{50} may be higher (Paylar et al., 2023). Long-term investigations suggest that the 21-day lowest observed effect concentration (LOEC) for SCCPs is approximately 18 μg/L, with a no observed effect concentration (NOEC) around 10 μg/L. Consequently, the predicted no effect concentration (PNEC) for medium-chain chlorinated paraffins (MCCPs) in aquatic environments for invertebrates is estimated to be 1 μg/L, derived from the NOEC of 10 μg/L for *D. magna* and applying an assessment factor of 10 (Chen et al., 2024).

15.3.5 Toxicity to Fish

To date, only one study has investigated the toxicity of SCCPs in fish. The rainbow was exposed trout to various concentrations of SCCPs in their diet, observing behavioral changes as well as alterations in liver and thyroid histology in fish exposed to the SCCP with 55% chlorine at concentrations of 0.22 and 1.3 μg/g wet weight (ww) of whole fish. In contrast, no significant effects were noted for the SCCP containing 48% chlorine at concentrations ranging from 0.02 to 0.11 μg/g ww whole fish (Chen et al., 2024).

Based on these findings, we propose a predicted no effect concentration (PNEC) for SCCP toxicity in rainbow trout of 11 ng/g ww whole fish. This threshold is derived from the no observed effect concentration (NOEC) of 0.11 μg/g ww whole fish, applying an assessment factor of 10. Considering a lipid content of 0.24 g lipid/g ww whole fish, this results in a PNEC of 46 ng/g lipid for rainbow trout (Glüge et al., 2018).

15.4 RESILIENCE OF BY-PRODUCTS/DAUGHTER COMPOUNDS AND WHERE AND UNDER WHAT CONDITIONS THESE ARE NORMALLY FOUND

SCCPs are intricate mixtures of chlorinated alkanes characterized by variable chain lengths and levels of chlorination. Congeners with a specific chain length (n) and chlorine count (m) are categorized as a "congener group" designated as CnClm. Although SCCPs have been subjected to environmental monitoring for several decades, no universally accepted standard quantification method has yet been established. Standards for SCCPs and samples contaminated with chlorinated paraffins (CPs) consist of thousands of compounds, many of which are isomers that cannot be resolved even through tandem chromatography.

Among the various SCCP groups, the C10 homologues are the most frequently detected, composing 93% of the samples from rubber consumer products and toys, followed by C12 (32%), C11 (21%), and C13 (7%). The next most prevalent carbon chain length is C12, averaging 16% ± 30%, with C11 and C13 contributing 4% ± 9% and 1% ± 4%, respectively. Notably, hexachlorinated isomers (Cl6 congener groups) dominate in consumer goods, contrasting with the profiles of industrial CP mixtures analyzed by electrospray ionization and atmospheric pressure chemical ionization techniques.

In formulations produced in Germany (Witaclor 149) and the UK (Cereclor 60L and Cereclor 70L), C13 homologues and C12 groups predominated, with C10 and C11 present in much smaller proportions. The dominance of C13 congener groups among SCCPs was even more pronounced in industrial settings. Yuan et al. (2021) analyzed 11 technical products, including variants of Witaclor, Cereclor, Hüls, and Hordalub tradenames, revealed a diverse range of homologue distributions, with C10 congeners constituting less than 7% of all mixtures.

In industrial mixtures, the most prevalent chlorine groups typically range from Cl6 to Cl9, correlating with the overall chlorine percentage outlined by the manufacturer. In the gas phase, SCCP homologues are predominantly C10 (55.2%) and Cl6 (45.7%), while in the particle phase, C11 (33.5%) and Cl7 (30.6%) are more prevalent. The gas–particle partitioning of SCCPs significantly influences their environmental behavior, including atmospheric transport and deposition. Shorter carbon chains and lower chlorination levels in SCCPs are more likely to partition into the gas phase, facilitating their persistence and long-distance atmospheric transport. In some background areas, as much as 66.1% of C10 SCCPs have been detected, although no similar distribution pattern was observed for the chlorine homologues.

15.5 CASE EXAMPLES OF ENVIRONMENTAL CONTAMINATION AND HOW CONCERNED WE SHOULD BE

Prohibited SCCPs have been widely detected in indoor consumer products despite their ban. In 2017, SCCPs were included in the list for elimination under the Stockholm Convention due to their persistence and toxicity. Canada has prohibited the manufacture, use, and import of SCCPs since 2013; however, our findings reveal their widespread presence in Canadian consumer products. Specifically, SCCPs were detected in 84 out of 96 products purchased after 2013, including electronic devices, clothing, plastics (such as toys), and paints. Alarmingly, newly purchased toys also contained SCCPs, highlighting the potential risk of exposure for children.

These are the first data demonstrating the ubiquitous occurrence of SCCPs in a diverse range of currently marketed products, indicating that indoor exposure to these substances persists despite their prohibition. Furthermore, research by Guida et al. (2022) suggests that medium-chain chlorinated paraffins (MCCPs) and long-chain chlorinated paraffins (LCCPs) may be replacing SCCPs in applications in the short to medium term following SCCPs' inclusion under the Stockholm Convention.

China is reported to be the largest global producer and consumer of SCCPs, with estimates from Chen et al. (2021) indicating there are approximately 100 to 150 chlorinated paraffin (CP) producers in the country. Additionally, in India as the second largest producer of CPs (Guida et al., 2022) According to Chen et al. (2022), India manufactured 150,000 tons of CPs in 2011. However, contemporary supply volumes or specific data on CPs with C14–17 chain lengths remain unavailable.

Within the European Union, registered tonnage of CPs fluctuates between 10,000 and 100,000 tons annually. Glüge et al. (2016) provide historical production figures for several countries: North America produced 17,800 tons in 1998; Russia's production increased from 21,000 tons in 2007 to 27,000 tons in 2011; Thailand's production was at 20,000 tons in 1994. Some of these figures are over 20 years old, suggesting that current supply volumes may have changed.

Additional production volumes reported by Chen et al. (2022) which is 19,500 tons per year from Bangladesh in 2011 and 12,000 tons per year from Jordan between 2011 and 2015. In Australia, total annual introduction volumes were reported to be between 1,000 and 9,999 tons in both 2002 and 2006 which was primarily reflecting local manufacture. New Zealand, while not manufacturing MCCPs, approves products containing these substances (based on three CAS numbers) for import. Based on the data available, the current global production of CPs with C14–17 chain lengths may be approximately 800,000 tons per year (Daniel et al., 2024).

15.6 FATE AND DYNAMICS IN THE ENVIRONMENT

SCCPs are widely distributed across various environmental matrices, including air, soil, water, sediments, and biota. The occurrence of SCCPs in the environment has been extensively reviewed. Atmospheric levels of SCCPs exhibit seasonal variations, influenced by changes in temperature and wind direction, as well as spatial differences resulting from the production and usage of these compounds. For instance, concentrations of atmospheric SCCPs in the highly industrialized areas of the Yangtze River Delta, China, in 2011 ranged from 6.1 to 63 ng/m³ during summer, while in winter, levels ranged from 6.2 to 42 ng/m³. Moreover, SCCP contamination in Asian countries presents a more serious concern compared to that in Europe and North America (Mi, 2024).

Beyond outdoor air pollution, SCCPs have been detected in dust and indoor air, with their distribution influenced by the decor and layout of indoor environments. The spatial distribution of SCCPs in soil and water closely correlates with industrial activities, sewage treatment plants, and other human actions. Generally, SCCP levels are higher in soil samples collected near factories, domestic waste disposal sites, and sewage treatment facilities, as well as in urban settings compared to rural areas. For example, the concentrations of SCCPs in soil samples collected from inside and outside a chlorinated paraffin production plant in Shandong, China, were found to be 28–554 μg/g and 102–441 ng/g, respectively (Wang et al., 2018).

Additionally, concentrations of SCCPs in seawater and sediments tend to decrease with increasing distance from the coast, and sediment core analyses show that SCCP levels decrease exponentially with depth. Notably, SCCPs with shorter carbon chain lengths (C10–11) and lower chlorination levels (Cl6–7) are more likely to migrate over long distances. Environmental SCCPs can bioaccumulate in various organisms, including zooplankton, invertebrates, and fish (Zhang et al., 2022). Evidence suggests that SCCPs are biomagnified within the marine food web, with the trophic magnification factor influenced linearly by carbon chain length and parabolically by chlorine content and the octanol-water partition coefficient (Kow) (Hu et al., 2021).

15.6.1 Chemical Properties

SCCPs are persistent and can be bioaccumulated (PB) in the environment. The Persistent Organic Pollutant Review Committee (POPRC) of the Stockholm Convention has determined that SCCPs meet the persistence and bioaccumulation criteria outlined in the Stockholm Convention on POPs

(Chen et al., 2024). Generally, as the carbon chain length and chlorine content of SCCPs increase, water solubility decreases while Henry's law constant and log Kow increases. Short- and medium-chain chlorinated paraffins exist as liquids, whereas longer-chain, more heavily chlorinated variants are solid. At room temperature and normal pressure, SCCPs are viscous liquids, with vapor pressure declining as molecular weight (a function of the number of chlorine atoms) increases. Although chlorinated paraffins typically exhibit low to negligible water solubility, lower molecular weight variants can be emulsified with an organic cosolvent (Hu et al., 2021).

The octanol-water partition coefficients (log Kow) for chlorinated paraffins range from 4.5 to 12, with SCCPs showing log Kow values between approximately 4.5 and 7.4. Most SCCPs have log Kow values exceeding 5. The European Union has classified SCCPs as PB substances, as well as very persistent and very bioaccumulative substances. Similarly, Canada has confirmed that SCCPs are PB (Ruan et al., 2023).

In the atmosphere, SCCPs are expected to exist in both vapor and particulate phases, influenced by their range of vapor pressures. Vapor-phase SCCPs degrade in air through reactions with hydroxyl radicals, with half-lives ranging from just over one day to slightly more than ten days. A half-life greater than two days is significant for the long-range transport of persistent chemicals. When released into water, SCCPs are likely to adsorb sediment and suspended particulate matter based on log Koc values. They are stable against hydrolysis and photolysis, and while volatilization from water is moderate, adsorption may reduce this rate. No degradation has been observed in sediments under anaerobic conditions, and the presence of SCCPs in sediment cores dating back to the 1940s serves as further evidence of their persistence (Wang et al., 2023).

When released to soil, SCCPs are expected to have low mobility due to their log Koc values. Volatilization from moist soil surfaces is similarly moderate, and adsorption may again mitigate volatilization rates. Data indicate that SCCPs bioaccumulate significantly in biota, with bioconcentration factors ranging from 1,000 to 50,000 across various freshwater and marine organisms (). Field-derived bioaccumulation factors exceeding one million have been recorded in vertebrates from the Great Lakes and arctic marine mammals (Zhang et al., 2022).

Henry's law constant values for SCCPs indicate potential partitioning from water to air or from moist soils to air, influenced by environmental conditions and concentrations in each compartment. This transport is supported by evidence of SCCPs' global dispersion, including their presence in the Arctic. The POPRC has concluded that there is sufficient evidence to suggest that SCCPs meet the screening criterion for potential long-range environmental transport. In December 2009, the Executive Body of the Convention on Long-Range Transboundary Air Pollution will consider the addition of SCCPs to the POPs Protocol (Ruan et al., 2023).

15.6.2 Physicochemical Properties

The environmental behavior of SCCPs is shaped by several critical factors, including the octanol-water partition coefficient (Kow), vapor pressure (VP), and Henry's law constant (HLC). These properties are notably influenced by both the length of the carbon chain and the chlorine content. As the carbon chain length of SCCPs increases, there is a corresponding increase in Kow and lipophilicity, assuming a constant level of chlorination. However, when the chlorine content is below 55%, the degree of chlorination has little effect on Kow and lipophilicity. In contrast, at higher levels of chlorination, Kow values can exhibit a nonlinear increase (Han et al., 2021).

Regarding vapor pressure, the subcooled-liquid VP of chlorinated paraffins generally decreases with longer carbon chain lengths and increased chlorination. For SCCPs, the vapor pressure at 25°C for those containing 45–61% chlorine is approximately 0.00014–0.028 Pa, while for SCCPs with over 70% chlorine content, the VP drops to about 1.34×10^{-5} Pa. Additionally, HLCs tend to decrease as the degree of chlorination increases; reported values for tetrachloro and pentachloro congeners range from 0.68 to 17.7 Pa m³/mol at 23°C (Zhan et al., 2017).

15.6.3 Degradation in the Environment

The degradation of SCCPs in the environment is significantly affected by their degree of chlorination. In the past five years, there has been a noticeable increase in reports of SCCPs across various environmental matrices, a trend that parallels advancements in cleanup procedures and analytical techniques. Research into the thermal degradation of chlorinated compounds, including CP52, CP59, and CP70—which are polychlorododecanes containing 52%, 59%, and 70% chlorine, respectively—has provided significant insights into the decomposition of carbon chains. These findings have been particularly valuable when compared with other commercial chlorinated paraffins (van Mourik et al., 2016).

Research has also documented the uptake and translocation of polychlorinated biphenyls (PCBs) in agricultural crops, with key examples including beans (*Phaseolus vulgaris*), cabbages (*Brassica oleracea* var. *capitata*), carrots (*Daucus carota*), and turnips (*Brassica rapa*) (Olatunji et al., 2020). Interestingly, poplar plants have been shown to not only uptake PCBs but also hydroxylate specific compounds such as 3,3′,4,4′-tetrachlorobiphenyl (PCB 77) and 4-monochlorobiphenyl (PCB 3). Additionally, maize (*Zea mays*) has demonstrated the ability to absorb and metabolize both PCBs and polybrominated diphenyl ethers (PBDEs) in hydroponic exposure studies (Wang et al., 2016).

POPs, such as 2,2-bis(chlorophenyl)-1,1,1-trichloroethane (DDT) and chlordane, are well known for their tendency to bioaccumulate and translocate within vascular plants and crops. The dynamics of chemical translocation can be further illustrated by the behavior of 1,2,5,5,6,9,10-heptachlorodecane in pumpkin plants, in which processes such as bidirectional translocation, phytovolatilization, dechlorination, and chlorine rearrangement are observed (Li et al., 2020).

Among the compounds studied, lower-chlorination variants, including 1,2,5,6,9,10-HexCD (61.0% Cl), 1,1,1,3,10,11-HexCU (58.7% Cl), and 1,1,1,3,12,13-HexCU, reveal distinct behaviors that warrant further investigation into their environmental impact and degradation pathways (Li et al., 2019).

15.6.4 Photochemical Degradation

For the photolysis, the photochemical degradation of chlorinated paraffins (CPs) was investigated by Koh and Thiemann (2001) (see Figure 15.4). Their research primarily focused on the factors influencing the kinetics of CP degradation, including solvents and hydrogen peroxide. Notably, the photosensitization mediated by acetone significantly surpassed the direct photochemical degradation of CPs. Acetone acts as a sensitizer, accelerating the photodegradation of SCCPs through photosensitization. In the absence of UV irradiation, the photochemical degradation of 1-chlorodecane was almost negligible; however, under UV irradiation, it occurred rapidly. The degradation kinetics of 1-chlorodecane adhered closely to pseudo-first-order kinetics, with the rate constant decreasing from 0.028 to 0.006 min^{-1} (Zhang et al., 2019). This reduction indicates that hydroxyl radicals (•OH) contributed to a degradation efficiency of 58.0%, highlighting that the photochemical degradation of 1-chlorodecane was predominantly induced by •OH. Furthermore, the inclusion of triethylamine oxide (TEOA), a scavenger for the triplet excited state, reduced the rate constant to 0.014 min^{-1}, suggesting that 25.8% of the degradation originated from this triplet state (Zhao et al., 2021).

The experiment highlighted the essential role of the triple excitation state in the photodegradation of SCCPs, providing a crucial basis for the photochemical degradation of SCCP homologues. Dissolved organic matter (DOM) is commonly found in natural water environments, where it can generate hydroxyl radicals (•OH), singlet oxygen ($^1O_2$), and triplet states of DOM (3DOM*) under solar irradiation. These reactive species have been demonstrated to significantly contribute to the degradation of halogenated compounds (Zhang et al., 2019). Similarly, both •OH and triple excited states are critical to the photochemical degradation of SCCPs, as indicated by this study's exploration of the charge transfer mechanism, which differs from the findings of Koh and Thiemann (2001).

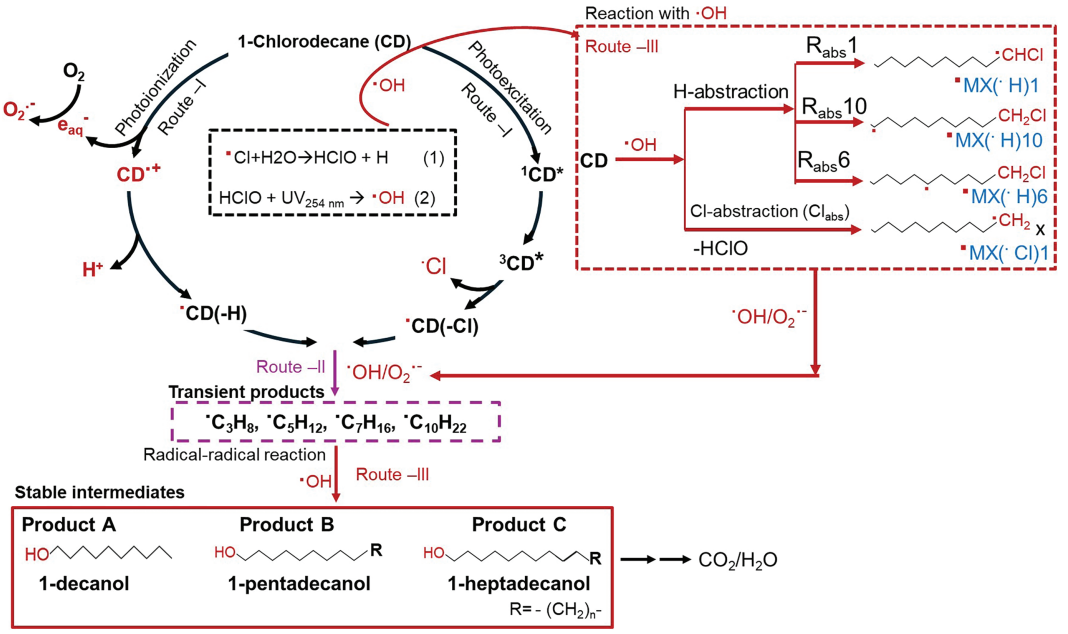


FIGURE 15.4 The proposed photochemical degradation mechanism of 1-chlorodecane (Copyright: Elsevier, 2019; Zhang et al., 2019).

15.6.5 Biodegradation of SCCPs

Various methods have been employed to reduce short-chain chlorinated paraffins (SCCPs), including metal sodium dispersion dechlorination, zero-valent iron treatment, and photocatalytic degradation (Qian et al., 2022). While these physicochemical approaches can be effective, they often entail high costs and harsh operational conditions, which limit their broader applicability (Lepom et al., 2009). In contrast, biological methods are increasingly preferred due to their simplicity, cost-effectiveness, and environmental sustainability, with bacterial degradation emerging as a particularly promising strategy (Ethiraj et al., 2024). *Rhodococcus* sp. S45–1, a Gram-positive bacterium, can utilize SCCPs as its sole carbon and energy source for metabolic degradation. Research indicates that the biodegradability of chlorinated paraffins decreases with increasing chlorine content and carbon chain length, with shorter-chain SCCPs demonstrating greater biodegradation potential (Chen et al., 2024). Furthermore, higher water temperatures in aquatic environments may enhance microbial activity, thereby accelerating SCCP degradation (Xie et al., 2024).

Additionally, several Gram-negative bacteria, such as *Pseudomonas* sp. strain 273 and *Pseudomonas* sp. strain N35, also exhibit the capability to degrade SCCPs. These strains demonstrate significant dechlorination rates, although the process may take up to 30 days (Bhandari, 2024). The introduction of bacteria into sludge has led to SCCP removal rates of up to 73.4%, with optimal degradation occurring at moderate rotational speeds that effectively balance mixing and rotor wear (Periyasamy et al., 2024).

Overall, bacterial degradation offers a viable, sustainable, and environmentally friendly alternative to traditional physicochemical methods for SCCP treatment. These findings underscore the potential of microbially mediated dechlorination in addressing SCCP contamination.

15.6.6 Transformation Pathways and Products

Plentiful studies have documented the extensive occurrences and trophic transfer behaviors (magnification/dilution) of SCCPs in various environments, including polar regions and the Tibetan Plateau. Despite the substantial volumes of SCCPs released into the environment, there is a shortage of research on their transformation behaviors, which are crucial for a comprehensive assessment of the environmental behaviors of POPs. Abiotic transformation by different factors such as root exudates and rhizosphere microorganisms are presented in Figure 15.5. Recent studies have identified

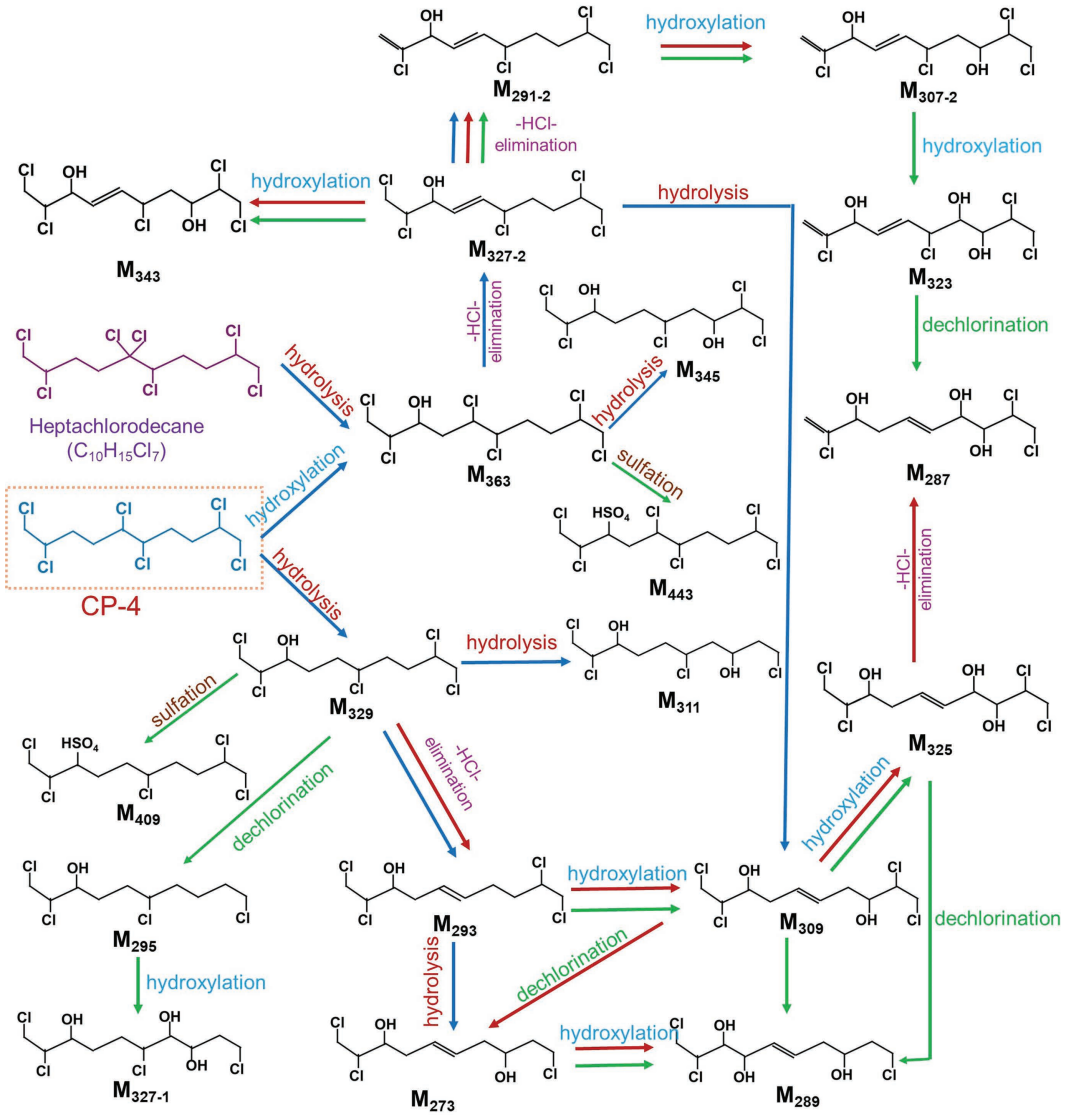


FIGURE 15.5 Proposed pathways of CP-4 through abiotic transformation (orange arrow), transformation under the role of root exudates (dark red arrow), and transformation by rhizosphere microorganisms (bright green arrow). Substitution sites of the functional groups of the products are only one of the possible substitution modes shown as an example (sourced from the American Chemical Society reference as Chen et al., 2022).

that SCCP congeners are transformed into chlorinated olefins and mono/dihydroxylated-SCCPs metabolites through the actions of bacterial enzymes, specifically dehydrohalogenase LinA2 and dehalogenase LinB, from the *Sphingobium* family (Schinkel et al., 2018).

15.7 POLICY: REGULATORY GUIDELINES FOR USING SCCPS

The Stockholm Convention on POPs is a global treaty designed to safeguard human health and the environment from the harmful effects of POPs (Lallas, 2001). POPs are chemicals that persist in the environment, are widely distributed, accumulate in living organisms, and pose significant toxicity risks to both humans and wildlife. The ultimate objective of the Convention is to eliminate both intentionally produced and unintentionally generated POPs (Borgå et al., 2022).

SCCPs have been assessed in accordance with documentation provided by the EU proposal to the 2nd POPs Review Committee (POPRC). Relevant documents include UNEP/POPS/POPRC.2/14; Annex D: Screening – Decision POPRC.2/9; Annex E: Revised Risk Profile – UNEP/POPS/POPRC.4/10/Rev.1; and Annex E: Supporting Document – UNEP/POPS/POPRC.4/IRegulationNF/20 (Fiedler, 2010). According to the EU's proposal, SCCPs (specifically alkanes C10–C13, with over 48% chlorination) were nominated for listing as a POP under the Stockholm Convention (Fiedler, 2010; Girones et al., 2023). Although SCCPs have been listed under the Convention since 2017 due to their long-range transport potential, bioaccumulation, and toxic properties, emissions into indoor and outdoor environments continue, primarily stemming from their historic use as flame retardants and polymer additives (South et al., 2022).

Health guidance values for SCCPs have been derived from animal studies. The International Programme on Chemical Safety (IPCS) established a no observed adverse effect level (NOAEL) for SCCPs at 10 mg/kg body weight per day (bw/day) – associated with increased liver weight – based on repeated oral dose tests in rats (Huang et al., 2023). Recently, the European Food Safety Authority (EFSA) identified the benchmark dose lower limit ($BMDL_{10}$) for SCCPs as 2.3 mg/kg bw/day, based on observed nephrotoxicity in rats. It is important to note that most existing health guidance values are based on hepatotoxicity or nephrotoxicity from oral exposure to chlorinated paraffins (CPs). Further research is needed to establish more comprehensive health guidance values that consider additional exposure pathways and sensitive outcome indicators (Zhang et al., 2023).

Regulatory frameworks for managing SCCPs have evolved over time. SCCPs have been classified as carcinogens by the International Agency for Research on Cancer (IARC) and included in the Stockholm Convention. Within the European Union (EU), SCCPs are listed in the Regulation on POPs, which permits the manufacturing, marketing, and use of substances or mixtures containing SCCPs in concentrations below 1% by weight and articles containing SCCPs in concentrations below 0.15% by weight. In Canada, reporting thresholds for SCCPs are established at 1 kg and 0.5% (w/w) under the Prohibition of Certain Specific Toxic Substances Regulations. Furthermore, China is actively implementing policies to regulate SCCPs, while Minnesota, US, has designated SCCPs as Chemicals of High Concern and Priority Chemicals. Notably, EU Regulation No. 1272/2008 identifies SCCPs as potential carcinogens, and other studies have reported their neurotoxic and endocrine-disrupting properties (Fiedler, 2010).

In assessments of baby foods, the portion-based intake of SCCPs varied from 0.3 to 19.1 ng/kg bw. Among these, the highest intake levels (5.5–19.1 ng/kg bw) were associated with ready-to-eat cereals and porridge. The estimated daily intake (EDI) of CPs from infant formula ranged from 182 to 354 ng/kg bw for SCCPs, while EDI figures from cereals and purees were approximately 46 and 67 ng/kg bw, respectively. In a report it was observed similar EDI estimates for SCCPs in infant formulas, with a mean ranging from 35 to 130 ng/kg bw. In addition, the lactational intake of CPs across Europe to be in the range of 280–810 ng/kg bw/day for SCCPs. The EFSA Panel on Contaminants in the Food Chain has reaffirmed a NOAEL of 10 mg/kg bw/day based on toxicological assessments for SCCPs (Perkons et al., 2022).

The first Brazilian inventory of SCCPs aims to evaluate the applicability of the SCCP inventory guidance and provide technical insights for updating Brazil's National Implementation Plan in accordance with the Stockholm Convention (Guida et al., 2022).

15.8 REMEDIATION OF SHORT-CHAIN CHLORINATED PARAFFINS: SOIL AND WATER

SCCPs have been detected ubiquitously across various environmental matrices, including water, soil, sediment, and air. Concentrations of SCCPs in soils vary widely, ranging from 56.8 to 1,348 ng/g (dry weight) and averaging 434 ng/g in the Tibetan Plateau. In China, SCCP concentrations in agricultural practices have been reported between 38.7 and 1,609 ng/g, while wastewater irrigation shows levels from 160 to 1,450 ng/g. Additionally, background soils in Norway range from not detected to 570 ng/g, in the United Kingdom from not detected to 490 ng/g, and in Switzerland from 3.0 to 35.0 ng/g (Li et al., 2019).

In atmospheric studies, SCCP concentrations in the highly industrialized and developed regions of the Yangtze River Delta, China, were found to range from 6.1 to 63 ng/m³ in summer and from 6.2 to 42 ng/m³ in winter, based on data collected in 2011 (Wang et al., 2019).

To mitigate SCCP contamination in soil and water sources, several remediation techniques are employed. These include thermal transformations, photolytic oxidation, photocatalytic degradation, nanoscale zero-valent iron-assisted remediation, microbial degradation, and phytoremediation, all of which show potential in effectively addressing SCCP contamination. The available remediation Techniques for Cleaning Up the SCCPs from Soil and Water Environments are listed in Table 15.1.

In the pressurized system, a moderate pure oxygen pressurization was found to be more conducive to the removal of SCCPs by bacteria when compared with air pressurization. In particular, a notable increase in SCCP removal was observed when using *E. coli* strain 2 at 0.15 MPa, with an improvement in removal rate from 20 mg/L to a 25% higher value. Moreover, the total amount of extracellular polymeric substance (EPS) increased significantly upon increasing both the SCCP concentration and pressure (up to 0.3 MPa). Notably, the tightly bound EPS content was greater than that of loosely bound EPS in these experiments.

The main degradation products detected by gas chromatography-mass spectrometry (GC–MS) were 2,4-dimethylheptane (C9H20), 2,5-dimethylheptane (C9H20), and 3,3-dimethylhexane (C8H18), regardless of the type of pressurization applied. In relation to thermal processes, SCCPs were found to be gradually released into the gas phase at temperatures lower than 400°C, with considerable amounts of aromatic and chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) formed at higher temperatures. A report demonstrated the synergistic emission of SCCPs and Cl-PAHs during thermal processes, such as incineration, open burning, or accidental fires in a department. While higher temperatures can minimize the formation of SCCPs, they may result in the generation of Cl-PAHs (Xin et al., 2017).

Further studies on the thermal transformations of CCPs were conducted by Xin and co-workers (Xin et al., 2018), who used CP-70 (a LCCP with 70% chlorination) and investigated the thermal transformations at temperatures ranging from 250 to 800°C.

In the context of photocatalytic degradation of SCCPs, the reaction pathway mediated by hydroxyl radicals (•OH) was hypothesized as follows:

$$\mathrm{SCCP} + \bullet\mathrm{OH} \rightarrow \bullet\mathrm{SCCP} + \mathrm{H_2O} \tag{15.1}$$

$$\bullet\mathrm{SCCP} + \bullet\mathrm{OH} \rightarrow \mathrm{HCl} + \mathrm{H_2O} + \mathrm{CO_2} \tag{15.2}$$

TABLE 15.1
Remediation Techniques for Cleaning Up the SCCPs from Soil and Water Environments

Technique/Treatments	Concentrations	Sample Phase	Efficiency	References
Basic anaerobic–anoxic–aerobic processes; biodegradation/biotransformation	184 ± 19 ng/L, 27 ± 6 ng/L, and 15.6 ± 1.4 μg/g dry weight (d.w.)	Sewage sludge	82.2%	(Zeng et al., 2013)
Haloalkane dehalogenase LinB	2 μg/m L	Liquid	ND	(Knobloch et al., 2021)
Wastewater filtration	Wastewater-irrigated soil (159.9–1,450 ng/g)	Solid	83%	(Zeng et al., 2011)
Thermal treatment	63–183 μg/m^3	Solid	99%	(Zhan et al., 2017)
Sorption	Effluent discharge 35 ng/g	Solid	93–97%	(Wang et al., 2019)
Reduced graphene oxide/$CoFe_2O_4$/Ag nanocomposite	5.0 μg/g	Solid	91.9%	(Chen et al., 2016)
Coniferous leaves	(SCCP + MCCP) 4,548.7 ng/g	Solid	-	(Yu et al., 2023)
Phytoremediation	71.1 to 300 ng/g	Solid	-	(Li et al., 2019)
Phytoremediation using pumpkin	99.7, 202, 199, and 199 ng/mL for 1,2,5,6,9,10-HexCD, 1,1,1,3,8,10,10,10-OctaCD, 1,1,1,3,10,11-HexCU, and 1,1,1,3,12,13-HexCT, respectively	Solid	Roots (23.6% to 59.9%) Stems (0.7% to 3.81%)	(Li et al., 2019)
Phytoremediation using soybean	99.7, 202, 199, and 199 ng/mL for 1,2,5,6,9,10-HexCD, 1,1,1,3,8,10,10,10-OctaCD, 1,1,1,3,10,11-HexCU, and 1,1,1,3,12,13-HexCT, respectively	Solid	Roots (1.98% to 54.5%) and Stems (0.50% to 2.54%)	(Li et al., 2019)
Phytoremediation using maize	5.41–381 ng/g	Solid	71%	(Chen et al., 2021)
Phytoremediation using rice	250 ng/mL of 1,2,5,6,9,10-$C_{10}H_{16}Cl_6$	Solid	16%	(Chen et al., 2022)
Aquabacterium and *Hydrogenophaga*; anaerobic organohalide respiration	70.3 μg/L	Liquid	11.2–65.8%	(Wu et al., 2021)
Basic anaerobic–anoxic–aerobic processes; biodegradation/biotransformation	184 ± 19 ng/L, 27 ± 6 ng/L, and 15.6 ± 1.4 μg/g dry weight (d.w.)	Sewage sludge	82.2%	(Zeng et al., 2013)
Thermal degradation	unknown concentrations	Liquid	37–44% after 24 h	(Schinkel et al., 2017)
Escherichia coli strain 2	20, 30, and 50 mg/L	Liquid	85.61%	(Qian et al., 2022)
Biodegradation, biotransformation, and volatilization	3,809 ± 670 ng/L	Liquid	83.5%	(Li et al., 2023)
Thermochemical emission (210–320°C)	100 ng/L	Solid	92%	(Xin et al., 2017)
Thermal treatment (N_2 at 800°C)	10 ng/mL	Liquid	ND	(Xin et al., 2018)

(*Continued*)

TABLE 15.1 (*Continued*)
Remediation Techniques for Cleaning Up the SCCPs from Soil and Water Environments

Technique/Treatments	Concentrations	Sample Phase	Efficiency	References
Hydrochloric acid at 220°C	10 ng/μL	Liquid	ND	(Schinkel et al., 2018)
Combustion and flue gas treatments	330 mg/mL	Solid	99.99%	(Matsukami and Kajiwara, 2019)
Photochemical degradation	5 mg/L	Liquid	99%	(Zhang et al., 2019)
Fenton (Fe^{2+}/H_2O_2/dark) and Fenton-like (Fe^{3+}/H_2O_2/dark) conditions	394 ng/μL	Liquid	61%	(El-Morsi et al., 2002)
Photochemical reaction with 0.1% acetone–water medium	250 μg/L	Liquid	99.5%	(Koh and Thiemann, 2001)
Photodegradation by TiO_2	240 μg/L	Liquid	85%	(El-Morsi et al., 2000)
Fe_2O_3@PDA-Ag hybrids	10 μg/μL	Liquid	91.9 %	(Xiong et al., 2018)
Pseudomonas sp. N35	66.1 mg/kg	Solid	73.4%	(Li et al., 2023)
Low-resolution mass spectrometry	100 ng/g wet weight	Detection method	ND	(Vorkamp et al., 2017)
Degradation by $KMnO_4$	0.10 mg/g	Solid	93.3 %	(Ye et al., 2023)
Sodium persulfate ($Na_2S_2O_8$)	0.10 mg/g	Solid	91.9%	(Ye et al., 2023)
Organohalide-respiring bacteria	8.3 to 9.4 × 10^4 ng/g dw	Sediment	ND	(Guan et al., 2023)

15.9 TRADING SCCPS

The guidance on preparing inventories of SCCPs recommends a foreign trade data assessment based on the Harmonized System (HS) (Guida et al., 2022). The Harmonized System (HS) codes are a standardized numerical method of classifying traded products (the first two digits represent the chapter, the second two digits represent the heading, and the third two digits represent the subheading) in the Comtrade database, from the United Nations (Baumgartner et al., 2023).

For instance, in 2010, the Brazilian Federal Revenue highlighted that the classification of SCCPs is quite complex, with these chemicals having been traded under three generic MERCOSUR Common Nomenclature (NCM) codes and four HS codes. These are listed as:

MERCOSUR Common Nomenclature (NCM) codes:

(i) "Chlorinated paraffin consisting of molecules of a single size and all with the same amount of chlorine atoms, that is, with the defined chemical constitution" was traded under the NCM 29.03.19.90 (Other saturated derivatives of acyclic hydrocarbons).
(ii) "Chlorinated paraffin in solid form (powder, granules, etc.), with characteristics of wax and constituted by the mixture of molecules of various sizes, that is, with 10–13 carbon atoms and 3 to 12 chlorine atoms" was traded under the NCM 34.04.90.19 (Other artificial waxes).
(iii) "Chlorinated paraffin in liquid form and constituted by the mixture of molecules of different sizes, that is, with 10–13 carbon atoms and 3 to 12 chlorine atoms. If it's solid, it can't have wax characteristics" was traded under the NCM 38.24.90.89 (Other products and preparations based on organic compounds, not elsewhere specified or included).

Harmonized System (HS) codes:

Additionally, according to the guidance on preparing inventories of SCCPs, SCCPs may be traded under four different HS codes (Guida et al., 2022):

(i) HS 27.12.20: "Paraffin wax, containing by weight less than 0.75% of oil, obtained by synthesis or by other processes, whether or not coloured";
(ii) HS 27.12.90: "Paraffin wax, containing by weight 0.75% or more of oil, obtained by synthesis or by other processes, whether or not coloured";
(iii) HS 38.12.20: "Plasticizers, compound; for rubber or plastics";
(iv) HS 38.24.90: "Chemical products, preparations and residual products of the chemical or allied industries, n.e.s. or included in heading No. 3824."

The use of multiple nomenclature systems makes classification and inventorying of SCCPs challenging.

15.10 CONCLUDING REMARKS

SCCPs are commonly found in various environmental matrices, human food sources, and biological samples, raising serious health concerns despite their classification as persistent organic pollutants (POPs). Their continued production and use in developing countries like China, India, and Brazil underscore the urgent need for more research and regulatory interventions. Studies from China reveal that estimated daily intakes from food often surpass safety thresholds set by the European Food Safety Authority and the World Health Organization for neoplastic effects of SCCPs. Exposure pathways – for instance, inhalation and dermal absorption from contaminated air – highlight the broader risks of SCCPs, especially among occupational groups such as those involved in e-waste recycling.

Emerging evidence shows that serum SCCP levels correlate with adverse health markers for liver, kidney, and blood systems, indicating a pressing need for further investigation in highly contaminated areas. Several critical research areas warrant further attention. Firstly, the mechanisms of liver toxicity from SCCPs must be examined more thoroughly, especially regarding the role of PPAR-α activation. Secondly, research on the impacts of SCCPs on kidney function and hematologic parameters is crucial, because toxicokinetic studies suggest potential organ impairment.

Additionally, understanding the toxicological effects of synthesized SCCP congeners versus commercial products is vital for accurate risk assessments. The current tolerable daily intake for SCCPs also requires reevaluation, because contemporary findings indicate that adverse effects may occur at lower doses than previously established. Finally, investigating the synergistic effects between SCCPs and other pollutants is essential, since co-exposure studies could elucidate the intricate health implications of SCCP exposure.

Addressing these issues through comprehensive research will enhance our understanding of SCCPs' health impacts and inform regulatory policies and public health measures in light of ongoing exposure challenges.

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16 Navigating the Shadows
An In-Depth Exploration of Polyaromatic Hydrocarbons in Our Environment

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16.1 INTRODUCTION

Polyaromatic hydrocarbons (PAHs), also known as polycyclic aromatic hydrocarbons or polynuclear aromatic hydrocarbons, are a group of persistent organic pollutants characterized by the presence of two or more fused benzene rings. Due to their widespread occurrence, persistence in the environment, and significant impacts on both environmental and human health, PAHs have been

DOI: 10.1201/9781003530466-16

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extensively studied and widely monitored and regulated for decades (Sims and Overcash, 1983, Mersch-Sundermann et al., 1992, Juhasz and Naidu, 2000). Major anthropogenic sources of PAHs include the combustion of fossil fuels and biomass for energy, coking, metal production, oil refining, wood preservation, and the production of manufactured gas (Duan et al., 2015b, Ruby et al., 2016). These contaminants are often released into the environment as byproducts in the form of soot, char, tars, and pitch (Ruby et al., 2016, Yu et al., 2018, Yu et al., 2023).

Incomplete combustion is identified as the predominant source of PAHs, allowing these pollutants to undergo long-range atmospheric transport before being deposited through dry and wet means (Figure 16.1) (Keyte et al., 2013). This process contributes to the ubiquity of PAHs even in remote areas such as the Arctic, Antarctic, and Tibetan Plateau (Drotikova et al., 2021, Wang et al., 2013b, Wei et al., 2024). Although global atmospheric emissions of PAHs peaked in 1995 at approximately 592,000 tons, they have since shown decreasing trends in major emitting countries and regions, including China (Wang et al., 2021), North America (ECCC, 2022), and Europe (Katsoyiannis et al., 2011), in response to international agreements such as the Paris Agreement aimed at reducing fossil fuel usage. However, the ongoing greenhouse effect may counteract these reductions by causing the re-volatilization of PAHs previously retained in sinks like soil and sediment (Yu et al., 2019, Bao et al., 2023).

Various industrial and anthropogenic activities also contribute to localized sources and hotspots of PAH contamination, primarily through disposal and/or leakage, resulting in contaminated sites where soil, surface water, groundwater, and sediment are severely affected (Figure 16.1). By 2015, the United States Environmental Protection Agency (EPA) identified 1,408 sites on the National Priorities List, with at least 600 of these sites containing PAHs (Duan et al., 2015b). The European Environment Agency (EEA) reported that approximately 13% of contaminated soil in Europe contained PAHs (Duan et al., 2015b). While exact estimates for Australia remain unavailable, PAHs and other hydrocarbons are believed to be significant contaminants at around 160,000 identified contaminated sites (Duan et al., 2015b). Moreover, undocumented disposal and leakage, particularly in developing countries, complicate efforts to estimate the actual number of contaminated sites globally. Given the vast number of facilities such as manufactured gas plants, coking plants, steel works, and incineration plants – both historical and operational – the number of contaminated sites is likely substantial.

With the pervasive presence of PAHs in the environment and the multitude of contaminated sites worldwide, modern society, which still heavily relies on fossil fuels for energy and industrial



FIGURE 16.1 Sources of PAHs and pathways to enter the environment, their impacts on and risks to the ecosystem and human health, and the relations between PAH contamination with UNSDGs.

products, must confront the consequences of PAH contamination. Additionally, global warming has the potential to diminish the ability of environmental sinks to retain these contaminants (Figure 16.1). Extensive research conducted by academic institutions, governments, and organizations provides ample evidence that PAH contamination undermines the United Nations' Sustainable Development Goals (SDGs) as of 2023 (Figure 16.1) through a range of socioeconomic impacts.

The FAO has published a comprehensive report outlining the environmental, health, and socioeconomic ramifications of soil pollution, emphasizing that PAHs can lead to soil degradation and a loss of ecosystem services by adversely affecting terrestrial organisms, soil structure, erodibility, and plant growth and yield, as well as impacting higher mammals, including humans (FAO and UNEP, 2021; see citations therein). Human exposure to contaminated soil, water, air, and food through ingestion, inhalation, and dermal contact is linked to cancer, endocrine disruption, and various respiratory, cardiovascular, immunological, and developmental diseases. For instance, it is estimated that 6% of cancer cases in Stockholm annually can be attributed to airborne PAHs, and 8% of lung cancer cases in the UK have been associated with exposure to $PM_{2.5}$ – of which PAHs are the primary organic component (Dreij et al., 2017). Moreover, environmental and bioaccumulation modeling predicts that human respiratory risks from atmospheric PAHs could increase by up to 5.8% in China as a result of global warming (Bao et al., 2023). Vulnerable populations – identified by factors such as age, gender, socioeconomic status, and geographical location – are particularly impacted by PAH contamination, leading to environmental injustice (FAO and UNEP, 2021).

In summary, PAH contamination has severe implications for human health (SDG 3), ecosystems on land (SDG 15), and aquatic environments (SDG 14), while threatening food security and access to clean drinking water (SDGs 2 and 6). The adverse health effects and challenges related to food security and clean water access disproportionately affect vulnerable populations (SDG 1). Furthermore, PAH contamination can negatively influence economic growth in certain contexts (SDG 8). To address these challenges, the international community must seek solutions for clean energy (SDG 7), sustainable cities and communities (SDG 11), and responsible consumption and production (SDG 12). Such efforts must be coordinated with innovation (SDG 9) through global partnerships (SDG 17) in conjunction with actions against climate change and its associated impacts (SDG 13) (see Figure 16.1 and related SDG targets).

16.2 PHYSICO-CHEMICAL PROPERTIES

The physico-chemical properties of PAHs are critical in determining their toxicity, environmental fate, behavior, and bioavailability. These properties are generally associated with the number of rings in the PAH structure. For instance, melting and boiling points, along with hydrophobicity and persistence, tend to increase with molecular weight and the number of fused rings, while volatility, vapor pressure, and water solubility decrease (see Tables 16.1 and 16.2). This relationship

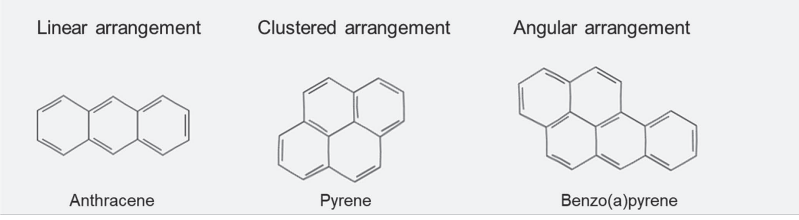


FIGURE 16.2 Examples of linear, clustered, and angular PAHs (WHO, 2021, FAO and UNEP, 2021).

TABLE 16.1
Physical-Chemical Properties of PAHs

PAH	Rings	CAS No.	Formula	M.W. (g/mol)	B.P. (°C)	V.P.(mmHg)	S_W (mol/L)	K_H	Log K_{OW}	Log K_{OA}
Naphthalene [a]	2	91-20-3	$C_{10}H_8$	128.2	218	8.50×10^{-2}	2.43×10^{-4}	4.40×10^{-4}	3.30	5.19
Acenaphthylene [a]	3	208-96-8	$C_{12}H_8$	152.2	280	6.68×10^{-3}	1.08×10^{-4}	1.14×10^{-4}	3.94	6.56*
Acenaphthene [a]	3	83-32-9	$C_{12}H_{10}$	154.2	279	2.15×10^{-3}	2.55×10^{-4}	1.84×10^{-4}	3.92	6.31
Fluorene [a]	3	86-73-7	$C_{13}H_{10}$	166.2	295	6.00×10^{-4}	1.17×10^{-5}	9.62×10^{-5}	4.18	6.79
Phenanthrene [a]	3	85-01-8	$C_{14}H_{10}$	178.2	340	1.21×10^{-4}	6.45×10^{-6}	4.23×10^{-5}	4.46	7.57
Anthracene [a]	3	120-12-7	$C_{14}H_{10}$	178.2	340	6.53×10^{-6}	3.31×10^{-7}	5.56×10^{-5}	4.45	7.55
Fluoranthene [a]	4	206-44-0	$C_{16}H_{10}$	202.3	380	9.22×10^{-6}	1.29×10^{-6}	8.86×10^{-6}	5.16	8.88
Pyrene [a]	4	129-00-0	$C_{16}H_{10}$	202.3	399	4.50×10^{-6}	6.61×10^{-7}	1.19×10^{-5}	4.88	8.80
Benzo[c]fluorene [b]	4	205-12-9	$C_{17}H_{12}$	216.3	385*	1.78×10^{-6}*	1.41×10^{-7}*	1.12×10^{-5}*	5.38*	8.52*
Benzo(a)anthracene [ab]	4	56-55-3	$C_{18}H_{12}$	228.3	438	2.10×10^{-7}	5.17×10^{-8}	1.20×10^{-5}	5.60	9.37*
Chrysene [ab]	4	218-01-9	$C_{18}H_{12}$	228.3	448	6.23×10^{-9}	8.71×10^{-9}	5.23×10^{-6}	5.81	9.37*
Cyclopenta[cd]pyrene [b]	5	27208-37-3	$C_{18}H_{10}$	226.3	437*	2.24×10^{-8}*	9.44×10^{-8}*	5.50×10^{-6}*	5.70*	9.63*
Benzo(b)fluoranthene [ab]	5	205-99-2	$C_{20}H_{12}$	252.3	455*	5.00×10^{-7}	6.03×10^{-9}	6.57×10^{-7}	5.78	8.64*
Benzo[j]fluoranthene [b]	5	205-82-3	$C_{20}H_{12}$	252.3	473*	7.46×10^{-9}*	9.95×10^{-9}	8.51×10^{-7}*	6.21*	10.3*
Benzo(k)fluoranthene [ab]	5	207-08-9	$C_{20}H_{12}$	252.3	480	9.65×10^{-10}	3.20×10^{-9}	5.84×10^{-7}	6.11	9.38*
Benzo(a)pyrene [ab]	5	50-32-8	$C_{20}H_{12}$	252.3	495	5.49×10^{-9}	6.44×10^{-9}	4.57×10^{-7}	6.13	9.61*
Dibenzo(a,h)anthracene [ab]	5	53-70-3	$C_{22}H_{14}$	278.4	524	9.55×10^{-10}	2.19×10^{-9}	9.33×10^{-7}	6.63	11.7*
Indeno(1,2,3-cd)pyrene [ab]	6	193-39-5	$C_{22}H_{12}$	276.3	536	3.23×10^{-10}*	6.90×10^{-10}	3.48×10^{-7}	6.73*	11.7*
Benzo(g,h,i)perylene [ab]	6	191-24-2	$C_{22}H_{12}$	276.3	500	1.00×10^{-10}	9.37×10^{-10}	3.31×10^{-7}	6.63	11.7*
Dibenzo[a,l]pyrene [b]	6	191-30-0	$C_{24}H_{14}$	302.4	540*	3.39×10^{-11}*	8.40×10^{-10}*	1.20×10^{-6}*	7.71	11.7*
Dibenzo[a,e]pyrene [b]	6	192-65-4	$C_{24}H_{14}$	302.4	533*	4.45×10^{-11}*	8.38×10^{-10}*	3.09×10^{-7}*	7.35*	11.8*
Dibenzo[a,i]pyrene [b]	6	189-55-9	$C_{24}H_{14}$	302.4	540*	5.75×10^{-7}*	4.07×10^{-11}*	1.82×10^{-9}	7.41*	11.7*
Dibenzo[a,h]pyrene [b]	6	189-64-0	$C_{24}H_{14}$	302.4	540*	5.75×10^{-7}*	4.07×10^{-11}*	1.37×10^{-9}	7.43*	11.7*

Note: PAHs listed by the US EPA as prior contaminants (EPA 16 PAHs) and by the European Commission (EC) and Joint FAO/WHO Expert Committee on Food Additives (JECFA) (EU 15 + 1 PAHs); 5-methylchrysene (listed by the EC) is included in Table 16.2 as an Alkyl-PAH.

*Physical-chemical properties are acquired from EPA DDSTox (https://comptox.epa.gov/dashboard) with experimental medium values; values marked by * are predicted medium. [a] US EPA prior PAHs. [b] European Commission 15+1 PAHs.

TABLE 16.2
Physical-Chemical Properties of Selected Alkylated PAHs (Alkyl-PAHs), Nitrated PAHs (Nitro-PAHs), Oxygenated PAHs (Oxy-PAHs), and Heterocyclic PAHs (N/S/O-PAHs)

Alkyl-PAHs	Rings	CAS No.	Formula	M.W. (g/mol)	B.P. (°C)	V.P.(mmHg)	S_W (mol/L)	K_H	Log K_{OW}	Log K_{OA}
1-Methylnaphthalene	2	90-12-0	$C_{11}H_{10}$	142.2	242	6.70×10^{-2}	2.00×10^{-4}	5.14×10^{-4}	3.87	5.01*
2-Methylnaphthalene	2	91-57-6	$C_{11}H_{10}$	142.2	242	5.50×10^{-2}	1.73×10^{-4}	5.18×10^{-4}	3.86	5.83*
1-Methylphenanthrene	3	832-69-9	$C_{15}H_{12}$	192.26	341*	1.50×10^{-5}	1.41×10^{-6}	4.93×10^{-5}	5.08	7.55*
3,6-Dimethylphenanthrene	3	1576-67-6	$C_{16}H_{14}$	206.29	357*	7.24×10^{-6}*	6.68×10^{-7}*	3.24×10^{-5}*	5.39*	7.87*
1-Methylpyrene	4	2381-21-7	$C_{17}H_{12}$	216.28	401*	6.17×10^{-7}*	2.23×10^{-7}*	1.12×10^{-5}*	5.47*	9.00*
4-Methylchrysene	4	3351-30-2	$C_{19}H_{14}$	242.32	430*	3.39×10^{-8}*	1.06×10^{-7}*	4.90×10^{-6}*	6.13*	9.43*
5-Methylchrysene [a]	4	3697-24-3	$C_{19}H_{14}$	242.32	447*	1.86×10^{-8}	2.56×10^{-7}	5.89×10^{-6}*	6.13*	9.82*
Nitro-PAHs	**Rings**	**CAS No.**	**Formula**	**M.W. (g/mol)**	**B.P. (°C)**	**V.P.(mmHg)**	**S_W (mol/L)**	**K_H**	**Log K_{OW}**	**Log K_{OA}**
1-Nitronaphthalene	2	86-57-7	$C_{10}H_7NO_2$	173.17	304	4.80×10–4	5.30×10^{-5}	1.76×10^{-6}	3.19	5.77*
5-Nitroacenapthene	3	602-87-9	$C_{12}H_9NO_2$	199.21	339*	1.46×10–5*	4.57×10^{-6}	8.91×10^{-6}*	3.85	7.46*
2-Nitrofluorene	3	607-57-8	$C_{13}H_9NO_2$	211.22	375	2.88×10–6*	1.02×10^{-6}	8.91×10^{-6}*	3.37	7.55*
9-Nitroanthracene	3	602-60-8	$C_{14}H_9NO_2$	223.23	275	2.47×10–6*	5.12×10^{-7}	1.20×10^{-7}*	4.78	7.37*
3-Nitrofluoranthene	4	892-21-7	$C_{16}H_9NO_2$	247.25	427*	8.71×10–8*	7.91×10^{-8}	2.63×10^{-5}*	4.83*	4.61*
1-Nitropyrene	4	5522-43-0	$C_{16}H_9NO_2$	247.25	436*	3.31×10–8	4.78×10^{-8}	8.13×10^{-5}*	5.06	9.32*
6-Nitrochrysene	4	7496-02-8	$C_{18}H_{11}NO_2$	273.29	473*	1.06×10–9*	1.50×10^{-7}*	2.04×10^{-4}*	5.46*	10.6*
Oxy-PAHs	**Rings**	**CAS No.**	**Formula**	**M.W. (g/mol)**	**B.P. (°C)**	**V.P.(mmHg)**	**S_W (mol/L)**	**K_H**	**Log K_{OW}**	**Log K_{OA}**
1-Hydroxynaphthalene	2	90-15-3	$C_{10}H_8O$	144.17	279	2.74×10^{-4}	6.03×10^{-3}	6.00×10^{-8}	2.85	9.44
1,4-Naphthoquinone	2	130-15-4	$C_{10}H_6O_2$	158.16	297*	7.69×10^{-4}*	1.92×10^{-3}*	1.62×10^{-6}*	1.71	5.72*
2-Hydroxyfluorene	3	2443-58-5	$C_{13}H_{10}O$	182.22	321*	1.07×10^{-5}*	2.77×10^{-4}*	1.07×10^{-7}*	3.42*	8.59*
2-Hydroxyphenanthrene	3	605-55-0	$C_{14}H_{10}O$	194.23	356*	5.13×10^{-7}*	7.30×10^{-5}*	5.62×10^{-8}*	3.90*	9.80*
9-Fluorenone	3	486-25-9	$C_{13}H_8O$	180.21	342	8.01×10^{-5}*	4.69×10^{-5}*	6.61×10^{-7}*	3.58	7.51*
Anthraquinone	3	84-65-1	$C_{14}H_8O_2$	208.22	377	1.16×10^{-7}	6.46×10^{-6}	3.02×10^{-7}*	3.39	8.41*
2-Methyl Anthraquinone	3	84-54-8	$C_{15}H_{10}O_2$	222.24	366*	8.13×10^{-8}*	4.43×10^{-6}*	2.82×10^{-7}*	3.81*	8.94*
2-Ethylanthraquinone	3	84-51-5	$C_{16}H_{12}O_2$	236.27	185	4.17×10^{-8}*	1.56×10^{-6}*	6.46×10^{-8}*	4.37	8.63*
2,3-Dimethylanthraquinone	3	6531-35-7	$C_{16}H_{12}O_2$	236.27	375*	6.31×10^{-8}*	1.55×10^{-6}*	2.82×10^{-7}*	4.21*	8.52*
1-Hydroxypyrene	4	5315-79-7	$C_{16}H_{10}O$	218.26	422*	4.83×10^{-9}	6.39×10^{-6}*	5.62×10^{-8}*	4.44*	10.8*
3-Hydroxychrysene	4	63019-39-6	$C_{18}H_{12}O$	244.29	455*	1.10×10^{-9}*	1.86×10^{-6}*	4.17×10^{-8}*	5.11*	11.0*
1-Hydroxybenz[a]anthracene	4	69847-26-3	$C_{18}H_{12}O$	244.29	455*	9.64×10^{-10}*	1.86×10^{-6}*	4.17×10^{-8}*	5.04*	11.0*
Benz[d,e]anthracene-7-one	4	82-05-3	$C_{17}H_{10}O$	230.27	433*	2.04×10^{-8}*	1.15×10^{-6}*	1.86×10^{-8}*	4.81	9.69*
3-Hydroxybenzo[a]pyrene	5	13345-21-6	$C_{20}H_{12}O$	268.32	496*	2.07×10^{-10}*	2.85×10^{-7}*	1.12×10^{-9}*	5.65*	10.7*

(*Continued*)

TABLE 16.2 (*Continued*)
Physical-Chemical Properties of Selected Alkylated PAHs (Alkyl-PAHs), Nitrated PAHs (Nitro-PAHs), Oxygenated PAHs (Oxy-PAHs), and Heterocyclic PAHs (N/S/O-PAHs)

Heterocyclic-PAHs	Rings	CAS No.	Formula	M.W. (g/mol)	B.P. (°C)	V.P.(mmHg)	S_W (mol/L)	K_H	Log K_{OW}	Log K_{OA}
2,3-Benzofuran	2	271-89-6	C_8H_6O	118.14	174	4.40×10^{-1}	6.81×10^{-3}*	8.32×10^{-6}*	2.67	4.47*
2-Methylbenzofuran	2	4265-25-2	C_9H_8O	132.16	198	4.87×10^{-1}	4.34×10^{-3}*	8.71×10^{-6}*	3.32	4.81*
Indole	2	120-72-9	C_8H_7N	117.15	254	1.22×10^{-2}	3.02×10^{-2}	2.51×10^{-6}*	2.14	7.46*
Quinoline	2	91-22-5	C_9H_7N	129.16	237	6.00×10^{-2}	4.79×10^{-2}	8.71×10^{-6}*	2.03	5.21*
8-Methylquinoline	2	611-32-5	$C_{10}H_9N$	143.19	135	2.50×10^{-2}	5.76×10^{-3}*	4.47×10^{-5}*	2.6	5.74*
Benzothiophene	2	95-15-8	C_8H_6S	134.2	221	2.38×10^{-1}	9.73×10^{-4}	6.31×10^{-4}*	3.12	5.00*
Dibenzofuran	3	132-64-9	$C_{12}H_8O$	168.20	288	2.48×10^{-3}	1.86×10^{-5}	1.12×10^{-4}*	4.12	6.90*
Xanthene	3	92-83-1	$C_{13}H_{10}O$	182.22	311	6.73×10^{-4}*	2.05×10^{-5}*	1.23×10^{-4}*	4.23	7.26*
Acridine	3	260-94-6	$C_{13}H_9N$	179.22	346	1.35×10^{-4}	2.14×10^{-4}	1.23×10^{-4}*	3.40	7.37*
Carbazole	3	86-74-8	$C_{12}H_9N$	167.21	355	7.50×10^{-7}	1.07×10^{-5}	1.16×10^{-7}	3.60	9.13*
Benzo[h]quinoline	3	230-27-3	$C_{13}H_9N$	179.22	339	2.18×10^{-4}	4.11×10^{-4}*	1.35×10^{-4}*	3.43	7.37*
1, 10-Phenanthroline	3	66-71-7	$C_{12}H_8N_2$	180.21	330	3.57×10^{-5}*	1.49×10^{-2}	9.77×10^{-5}*	1.78	7.38*
1, 7-Phenanthroline	3	230-46-6	$C_{12}H_8N_2$	180.21	350*	3.42×10^{-5}*	2.09×10^{-3}	9.55×10^{-5}*	2.49*	7.38*
4, 7-Phenanthroline	3	230-07-9	$C_{12}H_8N_2$	180.21	342*	3.38×10^{-5}*	9.89×10^{-4}*	9.55×10^{-5}*	2.05	7.38*
Benz[a]acridine	4	225-11-6	$C_{17}H_{11}N$	229.28	408*	9.76×10^{-8}*	1.55×10^{-6}	1.51×10^{-4}*	4.48	9.16*
Dibenz[a,h]acridine	5	226-36-8	$C_{21}H_{13}N$	279.34	501*	5.35×10^{-10}*	5.27×10^{-7}	1.86×10^{-8}*	5.73	9.88*
8-Methylquinoline	2	611-32-5	$C_{10}H_9N$	143.19	135	2.50×10^{-2}	5.76×10^{-3}*	4.47×10^{-5}*	2.6	5.74*
Benzothiophene	2	95-15-8	C_8H_6S	134.2	221	2.38×10^{-1}	9.73×10^{-4}	6.31×10^{-4}*	3.12	5.00*
Dibenzofuran	3	132-64-9	$C_{12}H_8O$	168.20	288	2.48×10^{-3}	1.86×10^{-5}	1.12×10^{-4}*	4.12	6.90*
Xanthene	3	92-83-1	$C_{13}H_{10}O$	182.22	311	6.73×10^{-4}*	2.05×10^{-5}*	1.23×10^{-4}*	4.23	7.26*

* Physical-chemical properties are acquired from EPA DDSTox (https://comptox.epa.gov/dashboard) with experimental medium values; values marked by * are predicted medium. [a] 5-Methylchrysene is listed in European Commission 15+1 PAH.

significantly influences the environmental behavior of PAHs. Low molecular weight (LMW) PAHs, which typically consist of two to three rings, are generally more bioavailable and biodegradable, whereas high molecular weight (HMW) PAHs, containing four or more rings, tend to be more persistent. In the atmosphere, LMW PAHs are predominantly found in the gaseous phase, while HMW PAHs are primarily associated with particulate matter (Kameda, 2011).

Another significant property of PAHs is the arrangement of their fused benzene rings, which can be linear, angular, or clustered. PAHs with angular ring arrangements feature a concave area known as the "bay region," which has a high electron density and exhibits enhanced chemical and enzymatic activity. As a result, angular PAHs are more metabolically susceptible to forming highly reactive diol epoxides, making them more potent in terms of mutagenicity and carcinogenicity (Jerina et al., 1986).

16.3 TOXICITY

16.3.1 Mechanisms of Toxicity

There are two primary mechanisms underlying the toxicity of PAHs: nonpolar narcosis and aryl hydrocarbon receptor (AhR) activation (Jesus et al., 2022). Nonpolar narcosis plays a crucial role in the toxic effects of PAHs on invertebrates and plants in both aquatic and terrestrial environments (Jesus et al., 2022, Aabbar et al., 2024). This process involves the partitioning of lipophilic PAHs into cell membranes, leading to the disruption of membrane properties. Such disruption interferes with cellular processes and induces physiological depression (Sverdrup et al., 2002c).

Activation of the AhR triggers the expression of cytochrome P450 enzymes (specifically CYP1A1, CYP1A2, and CYP1B1) (Martins et al., 2013, Nebert et al., 2004). This enzymatic activation results in the formation of highly reactive metabolites, such as diol epoxides, quinones, and radical cations, which can form DNA adducts, thereby leading to genotoxicity and potential carcinogenicity (Baird et al., 2005). Additionally, AhR activation elevates the levels of reactive oxygen species (ROS), causing damage to DNA, proteins, and lipids, which can result in adverse outcomes such as cell proliferation, apoptosis, and inflammation (Dasgupta et al., 2014).

Different PAHs exhibit varying capacities for AhR activation, which is not always directly correlated with their carcinogenic potential. For instance, oxy-PAHs have been reported to induce weak AhR activation; nevertheless, these substituted PAHs are highly toxic due to their ability to directly generate hydroxyl radicals that induce oxidative stress on biological molecules (Lui et al., 2017) or trigger alkylation of cellular nucleophiles (Benigni and Bossa, 2011). Some heterocyclic PAHs, particularly N-PAHs, are more potent toxicants than homocyclic PAHs because they can utilize both ring oxidation and nitro reduction pathways to form DNA adducts (Watt et al., 2007). Notably, dinaphthofurans and 2–(2-naphthalenyl) benzothiophene have been identified as significant inducers of CYP1A pathways and possess greater potency than benzo(a)pyrene, a well-known reference PAH (Brack and Schirmer, 2003).

Another critical mechanism through which oxy-PAHs, particularly hydroxyl-PAHs, exert their toxic effects involves endocrine disruption. This occurs due to the structural similarity between hydroxyl-PAHs and 17β-estradiol, which can induce estrogenic or antiestrogenic activities (Honda and Suzuki, 2020).

16.3.2 Human Health Effects

The specific congeners responsible for acute symptoms in humans remain largely unidentified, though naphthalene, anthracene, and benzo(a)pyrene are known direct skin irritants, with anthracene and benzo(a)pyrene identified as skin sensitizers (Kim et al., 2013, IPCS, 1998). It is uncertain whether PAHs at ambient concentrations affect human health. However, symptoms such as eye

and skin irritation, nausea, vomiting, diarrhea, and inflammation have been documented in studies involving occupational exposure to high concentrations of PAH mixtures (Unwin et al., 2006).

Chronic exposure to PAHs may result in hepatic and renal impairment, cataracts, and jaundice (ATSDR, 1995). Additionally, inhalation exposure to naphthalene has been associated with erythrocyte hemolysis (Srogi, 2007). Epidemiological and animal studies have provided compelling evidence that long-term exposure to PAHs at elevated concentrations can cause cancers of the lung, skin, bladder, liver, stomach, colon, and other parts of the digestive system, including the oropharynx and larynx (Diggs et al., 2011, Diggs et al., 2012, Armstrong et al., 2002, Armstrong et al., 2004, Bach et al., 2003, Moolgavkar et al., 1998, Boers et al., 2005, Clapp et al., 2008, Boffetta et al., 1997, Samanta et al., 2002, Latif et al., 2010).

PAH exposure during pregnancy has been linked to various harmful outcomes, including low birth weight, premature delivery, delayed child development, abnormal head circumference in infants, and altered cord blood lymphocyte distribution, which may impair fetal immune development. Additionally, low levels of cord serum estradiol and testosterone have been observed (Perera et al., 2005, Huang et al., 2020a, Herr et al., 2010). Other birth defects associated with prenatal PAH exposure include gastroschisis (Lupo et al., 2012), cleft lip and/or palate (Langlois et al., 2013), congenital heart defects (Kim et al., 2013), and neural tube defects (Ren et al., 2011, Yuan et al., 2013). Furthermore, endocrine disruption has been reported, with effects such as premature ovarian failure (Ye et al., 2020), testicular atrophy, and reduced testosterone levels (Schraplau et al., 2015, Chung et al., 2011), as well as issues with implantation and pregnancy maintenance (Li et al., 2017, Zhao et al., 2014).

Immunotoxicity and neurotoxicity associated with PAHs are also well established. Recent studies have indicated that benzo(a)pyrene significantly inhibits C-X-C motif chemokine ligand 12-induced T lymphocyte chemotaxis and trans-endosomal migration and activates interferon (IFN) signaling pathways (Liamin et al., 2018). This represents the first evidence of benzo(a)pyrene's capability to disrupt and impair normal T lymphocyte function by preventing effective localization and inducing abnormal activation of IFN. Research on occupational exposure has also linked high concentrations of PAHs to impairments in auditory memory, information processing, visual memory, and increased negative emotional states, which are attributed to declines in monoamines, amino acids, and cholinergic neurotransmitters (Wang et al., 2020a, Niu et al., 2010).

The most severe health consequence associated with PAHs is cancer, leading to the classification of several congeners as carcinogens, probable carcinogens, or possible carcinogens by the International Agency for Research on Cancer (IARC) and the US EPA. Benzo(a)pyrene serves as a reference carcinogen and is used to assess the relative carcinogenic potentials of other PAHs through benzo(a)pyrene equivalency factors (BEFs) or toxic equivalency factors (TEFs), thus enabling an evaluation of the risks posed by PAH mixtures. Table 16.3 summarizes the carcinogenic classifications and TEFs of PAHs.

16.3.3 Ecotoxicity

The ecotoxicity of PAHs is primarily evaluated based on their adverse effects on invertebrates, vertebrates, and plants in both aquatic and terrestrial environments. Notably, similar to mammals, PAHs exhibit carcinogenic properties, particularly hepatocarcinogenicity, in wild fish such as English sole (*Parophrys vetulus*) and flounder (*Platichthys stellatus*), with a specific susceptibility observed in juvenile individuals (Varanasi et al., 1987).

Research investigating PAH toxicity in fish often focuses on developmental and metabolic effects, utilizing model species like Japanese medaka (*Oryzias latipes*), zebrafish (*Danio rerio*), and rainbow trout (*Oncorhynchus mykiss*). The impacts of PAHs, particularly through DNA adduction, have been thoroughly documented across various developmental stages, including embryogenesis, the formation of the dorsal-ventral axis, and the development of critical structures such as the heart, eyes, and muscle. Additionally, gene expression related to energy supply and stress-response

TABLE 16.3
Carcinogen Classification of PAHs

PAH Compound	TEF	IARC Classification[a]	US EPA Classification[b]
Benzo(a)pyrene	1	Group 1	Group B2
Dibenzo(a,h)anthracene	1	Group 2A	Group B2
Benzo(b)fluoranthene	0.1	Group 2B	Group B2
Benzo(k)fluoranthene	0.1	Group 2B	Group B2
Indeno(1,2,3-cd)pyrene	0.1	Group 2B	Group B2
Benzo(a)anthracene	0.1	Group 2B	Group B2
Chrysene	0.01	Group 2B	Group B2
Fluoranthene	0.001	Group 3	NA
Phenanthrene	0.001	Group 3	NA
Pyrene	0.001	Group 3	NA
Acenaphthylene	0.001	Group 3	NA
Acenaphthene	0.001	Group 3	NA
Anthracene	0.01	Group 3	NA
Naphthalene	0.001	Group 2B	Group C
Fluorene	0.001	Group 3	NA
1-Methylphenanthrene	0.01	Group 3	NA
2-Methylphenanthrene	0.01	Group 3	NA
3-Methylcholanthrene	0.3	Group 2A	NA
7,12-Dimethylbenz(a)anthracene	1	Group 2A	NA
Benzo(c)phenanthrene	0.1	Group 2B	NA
5-Methylchrysene	0.5	Group 2B	NA
Dibenzothiophene	0.001	Group 3	NA
Carbazole	0.001	Group 3	NA
Benzo(b)naphtho(2,1-d)thiophene	0.1	Group 2B	NA

Note: Includes substituted PAHs and heterocyclic PAHs, by IARC and US EPA and their TEFs.

[a] IARC classification: Group 1: carcinogenic to humans; Group 2A: probably carcinogenic to humans; Group 2B: possibly carcinogenic to humans; Group C: not classifiable.

[b] US EPA classification: Group B2: probable human carcinogen; Group C: possible human carcinogen; NA: not accessible.

proteins has been assessed (Bekki et al., 2009, Incardona and Scholz, 2016, Magnuson et al., 2018, Chen et al., 2017, Honda and Suzuki, 2020).

Adverse effects from PAH exposure include cardiac and ocular dysfunction, disruption of bone development, and metabolic disturbances in liver function in fish administered benzo(a)anthracene. These disturbances often manifest as altered activity and/or levels of various metabolic enzymes (e.g., alkaline phosphatase and lactate dehydrogenase) alongside disruptions in cholesterol and high-density lipoprotein levels (Cai et al., 2019). Endocrine disruption resulting from hydroxylated PAHs, in addition to immune system dysfunctions and inflammation, has been reported in male tilapia exposed to benzo(a)pyrene (Colli-Dula et al., 2018).

When examining benthic organisms, toxicological effects – including alterations in growth, development, mortality, physiology, reproduction, hatching, and immobilization – are well documented (Jesus et al., 2022). A comprehensive review by Jesus et al. (2022) collated data from literature and the US EPA ECOTOX database, focusing on 30 freshwater benthic species and their toxic responses to varying exposure periods and PAH concentrations. The findings revealed that median

lethal concentrations (LD_{50}) for specific PAH congeners, such as benzo(a)anthracene, chrysene, and benzo(a)pyrene, exceed their water solubility, indicating that these PAHs would likely present low lethal toxicity in field conditions unless accompanied by agents like surfactants and microplastics that enhance their solubility and promote uptake (Sun et al., 2021, Jesus et al., 2022). However, employing Species Sensitivity Distribution (SSD) curves to represent community sensitivity to chemicals indicated that much lower hazardous concentrations (HC_5) values for aquatic organisms chronically exposed to more hydrophobic PAHs were observed (Jesus et al., 2022).

Furthermore, PAH contamination significantly alters the structure and composition of soil microbial communities (Song et al., 2023). This shift in microbial community composition can lead to changes in the ecological functioning of contaminated soils, including reductions in metabolic pathways related to carbohydrates, amino acids, and lipids, as well as inhibitions in essential processes like nitrogen fixation and phosphorus solubilization (Song et al., 2023).

In a series of studies, Sverdrup and colleagues examined the toxicity of PAHs and N/S/O-heterocyclic compounds in contaminated soils on various organisms including springtails (*Folsomia fimetaria*), enchytraeids (*Enchytraeus crypticus*), earthworms (*Eisenia veneta*), and plants (*Sinapis alba*, *Trifolium pratense*, and *Lolium perenne*). They evaluated survival and reproduction in soil invertebrates (LC_{50} and no-observable-effect concentrations, NOECs) alongside germination and growth responses in plants over exposure periods ranging from 14 to 28 days (Sverdrup et al., 2002a, 2002b, 2002c, 2003). Among the 16 PAHs prioritized by the US EPA, only those with Log KOW < 5.2 adversely affected the survival and reproduction of springtails (*F. fimetaria*), revealing a positive correlation between hydrophobicity and toxicity. The lack of observed impact from the other PAHs was attributed to their low water solubility and was confirmed to be through narcosis (Sverdrup et al., 2002c). The studies highlighted that *F. fimetaria* was the most sensitive species, while *E. crypticus* displayed the least sensitivity. *E. veneta* was particularly susceptible to acridine, an N-heterocyclic PAH (Sverdrup et al., 2002b). A later investigation by Eom et al. reconfirmed that juvenile *Eisenia fetida* are more sensitive to soil PAHs than adults (Eom et al., 2007). Additionally, Sverdrup et al. proposed that plant growth is more sensitive to PAHs and heterocyclic PAHs compared to germination (Sverdrup et al., 2003).

16.4 REGULATION

Their severe impacts on human health and ecosystems and ubiquitous existence in the environment have led to wide monitoring and regulation on PAHs. A brief summary of guideline values for PAHs in soil, air, drinking water, and food are presented in Table 16.4.

TABLE 16.4
Regulatory Guidelines and Compliance Levels of PAHs for Different Countries and Regions

Medium	Country/Region	Regulatory Status	Compound Regulated	Value
Drinking Water	US	National Primary Drinking Water Regulations	Benzo(a)pyrene	0.2 µg/l
	UK	EU Drinking Water Directive	Sum of 4 PAHs	0.1 µg/l
	EU	EU Drinking Water Directive	Sum of 4 PAHs	0.1 µg/l
	Australia	Australian Drinking Water Guidelines	Benzo(a)pyrene	0.01 µg/l
	China	GB 5749–2006	Benzo(a)pyrene	0.01 µg/l

TABLE 16.4 (*Continued*)
Regulatory Guidelines and Compliance Levels of PAHs for Different Countries and Regions

Medium	Country/Region	Regulatory Status	Compound Regulated	Value
Food	US	No specified limits by FDA		
	UK	Not specified		
	EU	Regulation (EC) No 1881/2006	Benzo(a)pyrene in oils and fats	2 µg/kg
	Australia	Food Standards Australia New Zealand (FSANZ)	Benzo(a)pyrene in oils and fats	5 µg/kg
	China	GB 2762–2017	Benzo(a)pyrene in vegetable oils	10 µg/kg
Soil	US	EPA Regional Screening Levels	Benzo(a)pyrene in residential soil	0.015 mg/kg
	UK	Varies by site and land use		
	EU	Varies by member state		
	Australia	National Environment Protection Measure (NEPM)	Benzo(a)pyrene in residential soil	1 mg/kg
	China	GB 15618–2018	Benzo(a)pyrene in agricultural soil	0.55 mg/kg
Air	US	Not specified		
	UK	National Air Quality Objective	Benzo(a)pyrene in ambient air (annual mean)	0.25 ng/m^3
	EU	EU air quality standards	Benzo(a)pyrene	1 ng/m^3
	Australia	Not specified		
	China	GB 3095–2012	Benzo(a)pyrene (annual mean)	1 ng/ m^3

16.5 SOURCES

16.5.1 Sources and Source Materials

A variety of processes and activities generate PAHs. Anthropogenic sources of PAHs, primarily linked to human activities, are considered the major contributors, while natural processes are deemed minor and insignificant (Abdel-Shafy and Mansour, 2016, Juhasz and Naidu, 2000). Depending on temperature, pressure, and other environmental conditions, PAH sources can be categorized into four main types: pyrogenic, petrogenic, diagenetic, and biogenic (Abdel-Shafy and Mansour, 2016). Unlike other hydrophobic organic contaminants (HOCs), PAHs are released into the environment as highly complex mixtures known as "source materials." These source materials can take the form of non-aqueous phase liquids (NAPLs) such as coal tar, crude oil, and fuel oils, as well as solids like soot and char. They may also exist in multiphase forms, combining solid and NAPL, such as pitch. These materials enter the environment through various pathways, resulting in both point and diffuse contamination (Ruby et al., 2016, Yu et al., 2023, Yu et al., 2018).

The incomplete combustion of fossil fuels and biomass is the most significant pyrogenic source of PAHs (Lima et al., 2005). Activities such as the use of combustion engines, operation of power plants, waste incineration, and the use of domestic fireplaces and stoves, as well as wildfires, all contribute to the generation of pyrogenic PAHs. Moreover, thermal processes involving coal and petroleum, such as the destructive distillation of coal to produce coke, coal tar, coal tar pitch, and manufactured gas, as well as the cracking of crude oil to yield lighter hydrocarbons, also release pyrogenic PAHs (Boehm, 2005, Abdel-Shafy and Mansour, 2016, Yu et al., 2018, Yu et al., 2023). In addition to soot and char from incomplete combustion, byproducts such as tar, pitch, and creosote – which are still widely used today – serve as source materials of PAHs in NAPL form (Yu et al., 2023, Yu et al., 2018, Ruby et al., 2016). Improper handling or disposal of these byproducts,

along with leaks, spills, and releases following their application in wood preservation, road paving, waterproofing, and other uses, allow NAPLs to enter terrestrial and aquatic environments (Yu et al., 2023).

Petrogenic PAHs are generated under moderate temperatures (100–300°C) and elevated pressures during the formation of fossil fuels (Boehm, 2005). Various types of fossil fuels, including coal and petroleum, act as source materials for petrogenic PAHs (Yu et al., 2018, Ruby et al., 2016). Pathways for petrogenic PAHs to enter the environment include seepage from coal and petroleum, erosion of sedimentary rocks rich in petroleum hydrocarbons, and spills or leaks from crude oil, coal, fuel oils, and related products.

Minor amounts of PAHs with simpler profiles are derived from diagenesis and biological synthesis (Boehm, 2005). Diagenetic PAHs form during the aromatization of organic matter freshly deposited in soil and sediment, increasing in abundance and complexity as burial occurs and fossil fuels are generated (Boehm, 2005). Biological synthesis of PAHs can take place through plants, algae, phytoplankton, and various microorganisms (Rocha and Palma, 2019, Mojiri et al., 2019).

Typically, PAH profiles resulting from combustion processes are dominated by 3- to 5-ring congeners, since larger PAH molecules tend to be incorporated into soot or char, which are residues of combustion (Richter and Howard, 2000). In contrast, products like coal tar, coal tar pitch, creosote, and similar materials contain significantly higher concentrations of PAHs – with parent PAHs being orders of magnitude more concentrated compared to those derived from combustion (Xia et al., 2016, Yu et al., 2023, Boehm, 2005). Source materials with petrogenic origins, such as coal, crude oil, and various fuels (including lubricants), are primarily characterized by 2- to 3-ring PAHs and their alkylated derivatives (Achten and Hofmann, 2009, Goto et al., 2021, Boehm, 2005, Xia et al., 2016).

16.5.2 Source Apportionment

The chemical fingerprints of PAHs in source materials of different origins enable source apportionment via approaches such as diagnostic ratios (Lima et al., 2005, Boehm, 2005, Zhang et al., 2021b, Sofowote et al., 2010, Tobiszewski and Namieśnik, 2012, Wang et al., 1999, Yu et al., 2021), receptor models including the chemical mass balance model, principal component analysis, positive matrix factorization model, and the Unmix model (Zheng et al., 2017, Zhang et al., 2021b, Syed et al., 2017, Yang et al., 2021, Yu et al., 2021), as well as compound-specific isotopic analysis for stable carbon ($\delta^{13}C$) and hydrogen ($\delta^{2}H$) and radiocarbon ($\Delta^{14}C$) (Zhang et al., 2020, Yang et al., 2021, Bosch et al., 2015, Ya et al., 2021, Tang et al., 2020), either applied individually, or in combination (Yang et al., 2021, Zheng et al., 2017, Zhang et al., 2021b, Yu et al., 2021).

Diagnostic ratio is the most widely used approach to PAH source apportionment, but it has limits due to the highly varying PAH contents in petrogenic and pyrogenic source materials, and their complex transformation behavior in the environment. It was suggested diagnostic ratios involving high molecular weight PAHs that are more recalcitrant to photochemical and biological degradation should be used (Famiyeh et al., 2021), preferably among multiple ratios and in combination with other source apportionment techniques (Zhang et al., 2021b, Yu et al., 2021).

Receptor models use statistical and mathematical tools to solve the chemical mass balance between measured pollutant concentrations in samples (receptors) and pollutant profiles in known or unknow sources by decomposing the dataset matrix (X) containing **i** pollutants and **j** samples into factor contributions (G) and factor profiles (F):

$$X_{ij} = \sum_{k=1}^{p} G_{ik} F_{kj} + E_{ij} \qquad \text{(Equation 16.1)}$$

in which X_{ij} represents the concentration of *i*th pollutant in *j*th sample, G_{ik} represents the *i*th pollutant concentration from *k*th source, F_{kj} represents the contribution from *k*th source to *j*th sample,

p is the number of sources, and E_{ij} is the residual of the ith pollutant in jth sample (USEPA, 2014, Famiyeh et al., 2021). Principal component analysis (PCA) is widely used and often in combination with multiple linear regression (PCA-MLR) to quantify the contributions of identified sources (Yu et al., 2021). The positive matrix factorization model is an improvement from PCA using a multilinear engine that allows individual weighing of data points and non-negativity constraints, thus providing better performance when several zeros are present in the loading and score matrices (Henry and Christensen, 2010).

Source apportionment using compound-specific isotopic analysis (CSIA) with carbon stable isotope signature ($\delta^{13}C$) expressed as

$$\delta^{13}C = \left[\frac{\left({}^{13}C \div {}^{12}C \right)_{sample}}{\left({}^{13}C \div {}^{12}C \right)_{standard}} - 1 \right] \times 1000‰ \qquad \text{(Equation 16.2)}$$

relies on the so-believed distinct and distinguishable $\delta^{13}C$ of PAHs from different sources (Lima et al., 2005, Ya et al., 2022). It is believed that $\delta^{13}C$ could maintain the isotopic signature of the original precursors from source to sample (Lima et al., 2005, Ya et al., 2022). In addition, compound-specific hydrogen stable isotope $\delta^{2}H$, especially in conjunction with $\delta^{13}C$, could provide enhanced efficiency in differentiating PAHs from fuels and PAHs from different coal conversion processes (Sun et al., 2003). CSIA could avoid the influences from different degrees of PAH transformation in the environment due to their varying inertness, which are not accounted for by diagnostic ratio and receptor models. Compound-specific radiocarbon analysis (CSRA) is an alternative CSIA to provide definite distinctions between PAHs from biomass burning and fossil fuel combustion due to the depletion of ^{14}C during millions of years of fossil fuel formation (Zhang et al., 2021a, Ya et al., 2022).

These techniques are more robust when used in combination so that their respective limitations are compensated by each other. Source apportionment not only provides crucial information of the geochemistry, fate, and behavior of PAHs released to the environment, but also facilitates informed policymaking and judiciary practices regarding the controlling and management of PAH contamination.

16.6 EXTENTS AND SEVERITY OF PAHS CONTAMINATION

PAHs enter the environment via various pathways, constituting their ubiquitous existence. Emission inventories have been estimated by several studies over the past few decades, with more focus directed to the projection of spatiotemporal atmospheric emissions at global, national, and regional scales (especially national and regional China) (Wild and Jones, 1995, Shen et al., 2011, Shen et al., 2013, Li et al., 2021, Li et al., 2022). More specific research was conducted to investigate extents of PAH contaminations from point sources, which are discernible and confined, and nonpoint sources, which are diffusive (USEPA, 2023a).

16.6.1 Global Inventories

16.6.1.1 National and Regional Estimations

16.6.1.1.1 China

An estimation of China's PAH inventory in soil, air, water, and sediment was conducted by Wang and co-workers in 2013, suggested that approximately 530,000 tons of Σ14 PAHs were distributed in the investigated environmental compartments (Wang et al., 2013a). Soil was the main sink of

the PAH inventory (> 60%) according to the authors, while air only contained < 0.5% of the Σ14 PAHs (Wang et al., 2013a). Energy sections were considered the main emitters (Wang et al., 2013a). A decreasing time trend in total emission was obtained from 112,920 tons in 2013 to 100,090 tons in 2018, with the fastest decreases in the industrial (by 17.32%) and commercial/residential (by 10.58%) sectors and in regions of eastern China (by 3.39 kg/km^2) and northern China (by 2.91 kg/km^2) (Wang et al., 2021).

16.6.1.1.2 UK

The first estimation of inventory of 12 PAHs in the UK showed that over 53,000 tons of Σ12 PAHs were in different environmental compartments with soil being the major sink, while > 1,000 tons Σ12 PAHs were estimated to be released to the atmosphere annually via domestic coal combustion, vehicles, and unregulated fires; about 210 and 1,000 tons Σ12 PAHs enter soil via atmospheric deposition waste disposal each year, respectively (Wild and Jones, 1995). The annual emissions of total PAHs reduced from approximately 5,500 tons/year in 1990 to < 1,000 tons/year in 2008, with aluminum production being the major contributor from 1990 to 1997, and residential sources from 1998 to 2008 (Katsoyiannis et al., 2011).

16.6.1.1.3 Europe

Total annual emission for benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene as four indicator PAHs were 907, 1,040, 459, and 700 tons/year, respectively (van der Gon et al., 2007) (also see full details in the cited publication). The technical report from EMEP (European Monitoring and Evaluation Programme) released in 2020 indicated that benzo(a)pyrene emission in the whole of Europe, Caucasus, and Central Asia remained similar, around 500 tons/year in the period of 2000–2018, with residential combustion for heating contributing > 60% of the emission inventory, followed by industrial and agricultural emissions (Gusev and Batrakova, 2020).

16.6.1.1.4 North America

The atmospheric emission inventory of six appreciably semi-volatile PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, and chrysene) in the United States and southern Canada in 2002 was estimated to be 18,273 tons/year, with 90% emission coming from the US, and 73% from sources related metal production, open burning, incineration, and forest fires (Galarneau et al., 2007). Total emissions of four indicator PAHs, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene, in Canada in 2020 was estimated to be 60 tons, decreased by 80% from 1990 at 290 tons (ECCC, 2022). Among the emission sectors, contributions from aluminum and iron and steel industries were almost eliminated from 1990 to 2020, while commercial/residential/institutional emissions became the largest contributor (84%, 54 tons by 2020) (ECCC, 2022).

16.6.1.2 Global Estimations

Global atmospheric emission of sixteen EPA PAHs in 2004 was estimated to be 520,000 tons/year, with China (114,000 tons/year), India (90,000 tons/year), and the US (32,000 tons/year) being the top three emitters (Zhang and Tao, 2009). A global atmospheric emission inventory from 1960 to 2030 was estimated, resulting in the suggestion that global emission of PAHs was highest in 1995 (592,000 tons) and declined to 499,000 tons in 2008; by 2030, the contribution of airborne PAHs will decrease by 46–71% and 48–64% in developed and developing countries, respectively (Shen et al., 2013).

16.6.2 Examples of Point Source Contamination

Point source emissions of PAHs could be from (a) industrial sites such as manufactured gas plants, coking plants, oil refineries, aluminum works, steel works, waste incinerators, fire plants, etc., and (b) incidents such as oil spills and leaks (Juhasz and Naidu, 2000, Torbeyns, 2005, Abdel-Shafy and Mansour, 2016, Ruby et al., 2016, Yu et al., 2018, USEPA, 2023b). Hot spots contain high levels of PAHs, especially in aquatic and terrestrial environments.

16.6.2.1 Industrial Sites and Facilities

16.6.2.1.1 Manufactured Gas Plants

Even after decades of phase-out of manufactured gas, Σ16 PAHs concentrations in soil of former MGP sites could still be up to 23,370 mg/kg (mean and median ranges were 119–8,633 and 57–5,299 mg/kg, respectively), whereas Σ21 alkyl-PAHs ranged from 8 to 6,867 mg/kg (Williams-Clayson et al., 2023). Total 16 PAHs in groundwater of an MGP site in Austria was determined to be up to 1,692 µg/L (Wirthensohn et al., 2009). MGP impacted sediments collected from different locations in the US were tested to contain Σ34 PAHs (including 16 EPA PAHs, benzo(e)pyrene, perylene, and 17 alkyl-PAHs) in the range of 10–11,400 mg/kg d.w. (Hawthorne et al., 2006).

It was estimated that more than 50,000 MGPs operated in the US over a time span of 150 years (USEPA, 2002), 2,149 in the UK, 1,700 in Germany, 1,087 in France, and 6,677 in the whole of Europe (Thomas and Brinckerhoff, 2014). In southern hemisphere, the Environmental Protection Authority of New South Wales, Australia is now tracking over 60 former gasworks (Department of Environment and Conservation NSW, 2005). It is also noteworthy that coal tar, a primary product of coal gasification, is still being produced with a global annual production of 2,994,065 tons in 2021, according to the United Nations Statistics Division database record for 18 countries (UNSD, 2023).

16.6.2.1.2 Coking Plants and Metal Works

Concentrations of 16 PAHs in soils around an operating coking plant in Tangshan, China were up to 16,600 µg/kg d.w. in surface soil and 22,800 µg/kg d.w. in subsurface soil (Zhang et al., 2021b). Levels of 18 parent PAHs, 8 alkyl-PAHs, 20 heterocyclic PAHs, 9 nitro-PAHs, 24 halogenated PAHs, and 7 oxy-PAHs in soils collected from a coking plant in the Shanxi Province of China were significantly higher than those obtained from an impacted residential area nearby and background area (Zhang et al., 2023c). Wastewater samples collected from two coking facilities in Guangdong, China were found to contain PAHs (16 EPA PAHs and 2 alkyl-naphthalene) ranging from 345 ± 45.8 to 8,710 ± 950 µg/L (Zhang et al., 2013).

The highest levels of 16 PAHs in road and roof dust samples as well as $PM_{2.5}$ collected around a steel work in northern China was measured to be 6.97 µg/g, 17.14 µg/g, and 3.01 µg/m^3, respectively (Wei et al., 2021). Concentrations of Σ16 PAHs ranged from 33.8–18,800 µg/kg in soils from a secondary copper smelter and 20.7–557 µg/kg in soils from a secondary aluminum smelter in China, with a negative dependence on the distance from the smelter sites (Hu et al., 2017). Concentrations of 12 out of 16 EPA PAHs in tree leaves sampled from areas around a large aluminum smelter in Argentina were identified with a steep gradient related to distance from the smelter site, ranging from 8.48–3283.2 µg/kg d.w. for *E. rostrata*, 7.58–2271.57 µg/kg d.w. for *P. radiata*, and 7.69–917.5 µg/kg for *P. hybridus* (Rodriguez et al., 2012).

The annual production of coke in China reached 438.2 million tons by 2018, accounting for 67% of world production (Yang, 2019). Along with coke is the continuing high demand for steel and metals required for production and construction, especially in developing countries. PAH contamination from these industrial facilities would remain significant for the foreseeable future.

16.6.2.1.3 Power Plants and Waste Incinerators

Concentrations of 15 PAHs in soils collected from areas surrounding a coal fire power plant in South Africa was determined to be in the range of 9.73–61.24 mg/kg (Okedeyi et al., 2013). PAHs were found to be enriched in soils (Σ16 EPA PAHs ranging from 55.2 to 495 μg/kg) in the vicinity (area stretching 100 km long and 15 km wide) of a lignite power plant in West Macedonia of Greece, (Stalikas et al., 1997). Ashes collected from a heating station and power plant stacks in the Liaoning Province of China were analyzed for PAHs which were at levels of 620.14 ± 120.30 mg/kg for the heating station and 708.66 ± 239.32 mg/kg for the power plant (Kong et al., 2011).

Parent and halogenated PAHs in soils from e-waste open burning sites from Vietnam, Philippines, and Ghana were investigated by Nishimura et al. (2017). The authors obtained Σ15 PAHs at 7,200 and 6,500 μg/kg, 2,900 and 4,000 μg/kg, 390 and 710 μg/kg for Vietnam, Philippines, and Ghana sites (two for each country), respectively, whereas total halogenated PAHs in the study areas ranged from 5.8 to 2,800 μg/kg (Nishimura et al., 2017).

16.6.2.1.4 Oil Refineries

Soils from sludge deposit sites of three oil refineries in India was characterized with high levels of 13 of 16 PAHs at 67.02–95.21 mg/kg (Tarafdar and Sinha, 2018). Total levels of 19 PAHs (16 EPA PAHs and benzo(e)pyrene, perylene, and coronene) in 84 total suspended particles samples collected at different distances from an oil refinery site in South Korea presented 0.42–13.1 ng/m^3 for all seasons in the three sampling sites (Thang et al., 2019).

16.6.2.2 Spill and Leak Incidents

Anthropogenic activities related to exploitation, refining, and storage of crude and fuel oils are also important point sources that might create point source contamination of PAHs contamination via incidents of spills and leaks.

Soils collected from three oil drilling/gas flaring sites and three farmlands impacted by crude oil contamination in Nigeria was found to contain high concentrations of Σ18 PAHs (16 EPA PAHs, benzo(e)pyrene, perylene), ranging from 248.7 to 421.1 mg/kg and 5.66 to 54.5 mg/kg for farmland soils and drilling site soils, respectively (Anyanwu and Semple, 2022). Levels of five alkylated PAHs were up to 1,284.6 mg/kg for farmland soils, while N-heterocyclic-PAHs were in the range of 3.30–3.51 mg/kg for farmland (Anyanwu and Semple, 2022). The abundance of alkyl-PAHs in farmland soils indicated a petrogenic source of PAHs from oil spills (Anyanwu and Semple, 2022).

A pipeline leak incident in the Dayao Bay of Dalian, China in July 2010 resulted in 1,500 tons of crude oil beaning spilled which in turn caused severe contamination in the Yellow Sea of China (Liu et al., 2013b). Concentrations of 18 parent PAHs (16 EPA PAHs, benzo(e)pyrene, perylene) and derivatives in seawater collected from 20 locations along the coast of Dalian 50 days after the incident were 9.87–81.7 ng/L and 6.10–61.7 ng/L, respectively (Liu et al., 2013b). Sediment collected in the same area demonstrated elevated levels of parent PAHs (64.1–1,824 μg/kg d.w.) and derivatives (7.84–59.3 μg/kg d.w.), respectively. Negative relations between PAH levels in seawater and distance from spill site, as well as similar chemical fingerprints, indicated the impacts from the spill (Liu et al., 2013b).

Concentrations of 16 PAHs in soils collected from storage tanks of an abandoned gas station operated for more than 50 years in Beijing, China were tested to be up to 35.67 mg/kg d.w. (Geng et al., 2022). Two- and three-ring PAHs were found to dominate parent PAHs, whereas alkyl-PAHs also contributed large portions of total PAHs (Geng et al., 2022). The strong signature of petrogenic sources and result of positive matrix factorization source apportionment indicated long-term leakage (Cao et al., 2020, Geng et al., 2022).

16.6.2.3 Municipal Wastewater Treatment, Dumpsites, and Landfills

Fifteen parent PAHs, five Cl-PAHs, seven Br-PAHs, and three oxy-PAHs at ranges of 8.99–88.38, not detected–5.70, not detected–13.11, and 15.47–106.92 ng/L, respectively, were

obtained from five WWTP effluents collected from Beijing, China (Liu et al., 2021). Halogenated and alkylated PAHs might be generated during the chlorination disinfection process of wastewater treatment (Liu et al., 2021). Seventy-five sewage sludge samples collected from WWTPs in different locations of China demonstrated Σ16 EPA PAHs from 0.57 to 280 mg/kg d.w. (Sun et al., 2019).

Total concentrations of 16 EPA PAHs in soil in vicinity to a municipal solid waste landfill site in Poland were determined to be in the range of 892–3,514 μg/kg (Melnyk et al., 2015). Soil and sediment impacted by a poorly managed dumpsite in southwest Nigeria through draining by an adjacent river was found to contain high levels of 15 PAHs at 489–5,616 μg/kg and 642–2,159 μg/kg for soil and sediment, respectively (Parra et al., 2020).

16.6.3 Global Occurrence of PAHs in Different Environmental Compartments

Leaching, runoff, and other forms of fugitive releases of PAHs from disposed source materials (Jiang et al., 2022, Wang et al., 2009), contaminated soils (Yun et al., 2017), drains (Hoffman et al., 1984), and source materials applied in road pavement, roofing, and waterproofing (Boehm, 1964, Mahler et al., 2005, Ahrens and Depree, 2010), as well as the diffusion of airborne and waterborne PAHs are nonpoint sources that create diffusive contamination even in remote areas owing to their potentials for long-range atmospheric or oceanic transportation (Zhang et al., 2023a, Qi et al., 2023, Keyte et al., 2013).

Backgrounds of 15 parent PAHs in global soils were estimated to be in the range of < 1 to 7,840 ng/kg d.w. (mean 328 ng/kg) and followed the continental order of Europe > North America > Asia > Oceania > Africa > South America (Nam et al., 2009).

16.6.3.1 Soil

Soil is a major sink for PAHs in the environment. Distribution of PAHs in global soil is diverse, ranging up to five orders of magnitude (Table 16.5) (Nam et al., 2009). Levels of PAHs in urban soil are generally higher than those in rural soils (Yuan et al., 2014), whereas soils from remote areas, such as mountainous and forest soils, have the lowest ranges of concentrations (Choi et al., 2009, Abdul Hussain et al., 2019, Wei et al., 2024). Soil from industrialized regions, especially those with a longer history of industrialization, are more contaminated by PAHs. For example, a national survey by the Department of Environment, Food, and Rural Affairs (DEFRA) of the UK obtained highest concentration of 16 PAHs in soil from Wales at 186 mg/kg (Creaser et al., 2007), while up to 18 mg/kg of 16 PAHs were obtained from Chinese cities (Zhang et al., 2023b) (Table 16.5). Investigations conducted on urban and rural soils from five Asian countries found the highest PAH concentration in China (7,310 μg/kg), followed by India (2,160 μg/kg), Japan (1,420 μg/kg), Vietnam (1,290 μg/kg), and South Korea (259 μg/kg) (Table 16.5) (Hong et al., 2020), indicating that both industrialization and population are determining factors for PAH levels in soil. Given that sources of soil PAHs are mostly related to fossil fuel or biomass combustion (Nam et al., 2009) (also see literature cited in Table 16.5), countries and regions with higher population and longer histories and intensity of industrialization have higher soil PAHs. Moreover, decreasing trends in soil PAHs as well as diversified sources have also been identified in soils, which reflects the lessening contribution from fuel combustion as a result of global effort to reduce reliance on fossil fuels (Table 16.5) (Cui et al., 2020).

16.6.3.2 Sediment

Sediment serves as a significant sink for PAHs in the environment. A literature analysis by Xia et al. (2023) revealed that PAH concentrations in lake sediments varied widely: from 38 to 49,392 μg/kg dry weight (d.w.) in North America, 73 to 17,272 μg/kg d.w. in Europe, and 11 to 5,279 μg/kg d.w. in Asia. Notably high total PAH levels were reported in Lake Hamilton (134 mg/kg d.w.) and the Detroit River (132 mg/kg d.w.) in North America (Marvin et al., 2021), as well as the River Tyne (43.5 mg/kg) in the UK (Woodhead et al., 1999) (see Table 16.6). These regional differences

TABLE 16.5
Concentrations of PAHs in Global Soils with No Emission Sources in Adjacent Areas from Selected Literature

Location							Concentration (ug/kg d.w.)					
Region	**Detailed Location**	**Country**	**Type**	**Depth**	**Target**	**Sample time**	**Min**	**Max**	**Med**	**Mean**	**SD**	**Reference**
North America	Orlando	Florida, USA	Urban	Surface	16 PAHs	2016	43	30428	1640	3227	4676	(Liu et al., 2019)
	Tampa						59	58640	1020	4562	10031	
	Milwaukee	Wisconsin, USA	Urban	Surface	16 PAHs + 2 alkyl-PAHs	2017	597	63793	5492	7946	8156	(Siemering and Thiboldeaux, 2021)
				Subsurface			668	8023	1908	2408	8110	
	Various parks	Delaware, USA	Rural	Surface	12 of 16 PAHs (3- to 6-ring)	2011	NA	NA	NA	78.7–497	NA	(Yuan et al., 2014)
			Suburban				NA	NA	NA	70.0–448	NA	
			Urban				NA	NA	NA	362–16462	NA	
	Revelstoke	Rocky Mountains, Canada	Remote (mountain)	Surface	16 PAHs	2003–04	20.5	50.4	27.8	30	NA	(Choi et al., 2009)
	Yoho						5.51	789	12.2	167	NA	
	Observation						2.03	16.4	7.27	7.94	NA	
	Mt. Anderson	Canada	Remote (mountain)	Surface	8 PAHs	2007	21.8	72.2	33.2	37	17.8	(Abdul Hussain et al., 2019)
	Grouse Mt.						708	1147	910	916	178	
	Four Brothers Mt.						83.2	297	131	144	75.1	
	Blue Grouse Mt.						3.64	51.5	22.3	25.9	17.9	
	Chilkoot Trail						2.96	97.4	14.1	20	25.3	
South America	Transect from Pampas to Patagonian Steppe	Argentina	Remote (mountain)	Not specified	21 parent PAHs	2010	0.84	57.6	4.13	6.34	7.56	(Wilcke et al., 2014)
					7 alkyl-PAHs		0.11	2.33	0.38	0.54	0.61	
					15 oxy-PAHs		0	7.21	1.20	20.6	43.9	
					4 N-PAHs		0	2.86	0	0.24	0.69	
	Amazon basin	Brazil	Remote (forest)	Surface	20 PAHs	1998	15	397	NA	38–101	NA	(Wilcke et al., 2003)
	Pantanal						29	142	NA	68	NA	
	Cerrado						4.8	107	NA	17–75	NA	
	Mata Atlantica						62	143	NA	115	NA	
	Caatinga						7.1	64	NA	23	NA	
Europe	Scotland	UK	Rural	Surface	16 PAHs	1990	414	2270.5	15690	3659	3131	(Cui et al., 2020)
						1999	196	1362	5283	1644	1247	
						2007–09	83.7	523	3295	727	654	

	National	UK	Rural	Surface	20 PAHs + 2 alkyl-phenanthrene	2001–02	12.4	185835	746	2446	10480	(Creaser et al., 2007)
	England						435	22018	1009	2079	3182	
	Northern Ireland						206	3056	559	802	820	
	Scotland						47.8	24883	502	1405	3070	
	Wales						96.9	185767	665	9734	32894	
	Greater London	UK	Urban	Surface	16 PAHs	2009	4217	62931	16285	22110	14931	(Vane et al., 2014)
					50 PAHs		7067	86387	23712	30847	20205	
			Suburban		16 PAHs		3730	65551	8084	11884	11537	
					50 PAHs		6013	87884	12047	16927	15357	
	National	Germany	Remote (forest)	Surface	16 PAHs	Not specified	20	9038	551	NA	NA	(Aichner et al., 2015)
				Subsurface			7	4423	174	NA	NA	
	Kosetice	Czech Republic	Rural	Surface	27 PAHs	2010–17	18.6	390	103	142	128	(Wietzoreck et al., 2022)
					13 Oxy-PAHs + O-PAHs		0.71	10.0	2.81	4.03	3.03	
	Mokra		Suburban		27 PAHs	2006–15	57.5	417	216	223	85.3	
					13 Oxy-PAHs + O-PAHs		2.51	10.8	5.83	5.91	2.30	
Asia	National	China	Urban and rural	Surface	16 PAHs	2017	74.0	17700	200	NA	NA	(Zhang et al., 2023b)
	East						96.7	2920	220	NA	NA	
	North						93.9	8070	180	NA	NA	
	Northeast						74.0	10200	1960	NA	NA	
	Northwest						92.2	10200	204	NA	NA	
	South Central						100	5620	187	NA	NA	
	Southwest						96.5	17700	139	NA	NA	
	National	China	Remote (forest)	O-horizon	16 PAHs	2012–13	40.4	870	229	275	201	(Syed et al., 2017)
				A-horizon			24.5	721	159	217	176	
	National	China	Urban, rural, and remote	Surface	47 PAHs including 18 parent PAHs, 26 alkyl-PAHs, and 2 heterocyclic PAHs	2012	13.1	7310	NA	1060	1300	(Hong et al., 2020)
	National	Japan					72.9	1420	NA	512	406	
	National	South Korea					23	259	NA	108	71.2	
	National	Vietnam					71.9	1290	NA	288	348	
	National	India					32.1	2160	NA	447	613	
Other	Tibetan Plateau		Remote	Surface	15 parent PAHs, 7 oxy-PAHs, 10 nitro-PAHs	2014–16	1.49	610.83	15.71	66.54	NA	(Wei et al., 2024)
	Arctic						3.57	574.93	45.43	109.51	NA	
	Antarctic						17.69	94.88	40.15	46.62	NA	

TABLE 16.6
Concentrations of PAHs in Sediments from Selected Literature

Region/ Country	Type	Location	Target	Sample period/time	Concentration (μg/kg d.w.)					Reference
					Min	Max	Median	Mean	SD	
North America	Lake sediment	Lake Superior	17 parent PAHs	2016	38.7	3872	NA	558	NA	(Marvin et al., 2021)
		Lake Huron		2017	1.43	721		272		
		Lake Erie		2014	41.3	29190		1601		
		Lake Hamilton		2011	5496	134010		44201		
		Lake Toronto		2018	2120	84248		11239		
	River sediment	Saint Mary		2017	71.3	23474		3661		
		St. Clair River		2014	29	8360		1209		
		Lake St. Clair		2013	57.8	386		207		
		Detroit River		2013	54.6	132129		24478		
	Lake sediment	Lake Michigan	14 parent PAHs	2011	212	1291	502	567	286	(Huang et al., 2014)
			11 nitro-PAHs		2.87	18.4	6.73	7.86	3.85	
	Lake sediment	10 Lakes in NA	Not specified	Not specified	38	49392	NA	5518	6572	(Xia et al., 2023)
China	Lake sediment	28 Lakes	Not specified	Not specified	11	5279	NA	478	812	(Xia et al., 2023)
	Coastal and estuary sediment	Beibu Gulf	16 PAHs	2017	2.36	359	50.6	110	112	(Han et al., 2022)
	Intertidal sediment	National	15 PAHs	2015	2.3	2890	6.1–283	5.8–321	NA	(Lv et al., 2020)
	Coastal and sea sediment	Bohai Sea	16 PAHs and 2 Alkyl-Naphthalene	2017	25	308	204	184	135	(Wang et al., 2020b)
		Yellow Sea			43	659	85.3	138	133	
UK	Estuary sediment	Mersey Estuary	15 PAHs	2000–02	626	3766	2570	2316	1018	(Vane et al., 2007)
	River sediment	River Tyne	15 PAHs	1993–96	260	43470	23853	21343	16165	(Woodhead et al., 1999)
		River Humber			132	7041	1906	2428	2695	
		River Thames			0	6519	771	2426	2792	
	River and estuary sediment	River Thames	19 parent, 3 alkyl-PAHs	2017	18	1871	NA	312	NA	(Vane et al., 2020)

Europe	Coastal and sea sediment	Baltic Sea	16 PAHs, 2 alkyl-Naphthalene	2017	0.91	5361	135	549	1124	(Wang et al., 2020b)
		North Sea			0.46	227	30.2	30.2	57.2	
	Coastal and sea sediment	River Elbe	16 PAHs	2001–04	NA	NA	NA	9566	2003	(Li et al., 2019a)
				2005–08	NA	NA	NA	7865	2174	
				2009–12	NA	NA	NA	6842	2231	
				2013–16	NA	NA	NA	5994	2201	
	Coastal sediment	Atlantic Spanish Coast	22 parent, 13 alkyl-PAHs	2011–12	9.65	1853	132	358	472	(Pérez-Fernández et al., 2019)
Brazilian Amazon	Coastal sediment	Santana	24 parent PAHs, 13 alkyl-, 3 N-PAHs	2007	101	554	219	300	168	(Lima et al., 2021)
		Belém			141	566	263	312	147	
		Barcarena			390	2412677	1004	245774	761447	
	Coastal and estuary sediment	Santana to Macapá	16 PAHs	2017	22.2	159	42.2	49.4	33.1	(dos Santos Rodrigues et al., 2018)
	Coastal sediment	Oyapock Estuary	19 parent alkyl-PAHs	2018	99.7	1224	305	328	161	(Pichler et al., 2021)
Australia	River sediment	Brisbane River	15 PAHs	2012–15	148	3079	670	849	646	(Duodu et al., 2017)
	River sediment	Kogarah Bay	15 PAHs	2012–13	490	5190	NA	1760	NA	(Nguyen et al., 2014)
Arctic	Coastal and sea sediment	Bering Sea	16 PAHs and 2 Alkyl-Naphthalene	2010	26.2	51.2	40.4	39.5	11.3	(Ma et al., 2017)
		Bering Strait			8.5	25.8	16.5	16.8	7.1	
		Chukchi Sea			8.8	78.3	47.0	49.7	21.2	
		Canada Basin			58.9	75.5	70.5	68.3	8.5	
		Central Arctic			5.8	33.9	9.7	13.1	9.6	
Antarctic	Coastal sediment	Prydz Bay	14 PAHs	2013	12.6	30.9	NA	18	NA	(Xue et al., 2016)

are closely linked to historical industrial activities and population dynamics, as discussed in the previous section.

Sediment cores also reveal important temporal trends in PAH release. For instance, lakes in southeastern China exhibited a declining trend in PAH concentrations from 2001 to 2015, which occurred later than the trends observed in the Western world. In the West, PAH levels in sediments began to rise in the 1930s, peaked in the 1950s, and have been on the decline since then (Vane et al., 2022). These temporal variations are primarily attributed to differences in industrial and economic structures across regions in China. Key influencing factors include regional GDP, population density, the usage of pesticides and fertilizers, and the consumption of coal and gasoline (Xia et al., 2023). This observation is further supported by data from surface intertidal zone sediments throughout China, where urbanization, economic development, and population dynamics explained regional variations in the concentrations of 16 PAHs (ranging from 2.3 to 2,890 μg/kg d.w.) across different sampling locations (Lv et al., 2020).

Source apportionment studies indicate that the primary contributors to PAHs in rivers and lakes include the combustion of fossil fuels, biomass burning, and industrial processes (Vane et al., 2022). In contrast, marine sediments exhibit a more diverse array of PAH sources, including oil spills, seepage, and natural diagenetic transformations (Han et al., 2022; Lima et al., 2021; Ma et al., 2017; Xue et al., 2016) (for further details, refer to the citations in Table 16.6).

16.6.3.3 Freshwater and Seawater

Unlike the general continental trends in soil and sediment, which typically follow the order of Europe > North America > Asia, PAHs in the dissolved phase of lakes and rivers are found at much higher levels in Chinese water bodies. For instance, the Songhua River Basin recorded concentrations as high as 92.9 μg/L (Yu et al., 2021), and the Taihu Lake Basin measured 4.94 μg/L (Huang et al., 2020b). In contrast, PAH levels in Lake Erie and Lake Ontario were significantly lower, with concentrations of 10.1 ± 7.80 ng/l and 6.09 ± 3.17 ng/l, respectively (McDonough et al., 2014) (Table 16.7). European rivers also exhibit low aqueous PAH concentrations, ranging from 13.0 to 81.0 ng/l in the River Seine Basin and 23.9 to 72.0 ng/l in the River Tiber (Uher et al., 2016, Patrolecco et al., 2010).

Three- and four-ring PAHs, such as phenanthrene, fluoranthene, and pyrene, are typically more dominant in river and lake waters (McDonough et al., 2014, Sharma et al., 2018). Spatial variations in PAH levels across river and lake basins can be attributed to factors such as energy consumption, the proportion of heavy industries, population density, and economic development. This observation is supported by Yu et al. (2021), who analyzed seven major river basins in China. Furthermore, low concentrations of PAHs were recorded in lakes and reservoirs located in remote areas of China, such as Bosten and Tianchi Lakes in Xinjiang (with a sum of 15 parent PAHs and 9 alkyl-PAHs ranging from 1.3 ± 0.9 to 16.4 ± 5.9 ng/l) and Namco and Palgon Lakes in Tibet (ranging from 0.79 ± 0.15 to 0.28 ± 0.16 ng/l) (Yao et al., 2017).

Similarly, three- and four-ring PAHs are predominant in seawater, including samples collected from the coastal and central Mediterranean Sea (Vecchiato et al., 2018), surface waters of the North Atlantic Ocean and Arctic Ocean (Lohmann et al., 2009), and during a cruise from the West Pacific to the East Indian Ocean and Southern Ocean (Cai et al., 2016). The proximity to populated areas significantly influences PAH concentrations in seawater (Cai et al., 2016), while oil spills present a critical source in these environments (Zhang et al., 2021c).

16.6.3.4 Atmosphere

Compared to soil, sediment, and water bodies, the occurrence, distribution, and levels of PAHs in the atmosphere are also consequences of the dynamics in climate and meteorological events, in addition to industrial and economic development and population density. In a selection of literature, the highest concentration of PAHs in $PM_{2.5}$ were found in city of Taiyuan, China, at 580 ng/m^3 in $PM_{2.5}$ (Liu et al., 2017b), whereas the highest concentration of gaseous PAHs was found in city of

TABLE 16.7
Concentrations of PAHs in global waterbodies from selected literature.

Region/Country	Location	Water Body	Target	Sample Period/ Time	Concentration (ng/l) Min	Max	Median	Mean	SD	Reference
North America	Lake Erie	Lake	16 Parent, 2 alkyl-PAHs	2011	2.40	30.4	7.30	10.1	7.80	(McDonough et al., 2014)
	Lake Ontario				2.70	12.3	5.45	6.09	3.17	
Europe	River Seine Basin	River	12 PAHs	2008–09	13.0	81.0	29.4	33.9	16.4	(Uher et al., 2016)
	River Tiber	River	6 PAHs	2007	23.9	72.00	30.5	43.4	21.9	(Patrolecco et al., 2010)
China	Songhua River Basin	River	16 PAHs	2000–18	33.9	92899	2055	1970	NA	(Yu et al., 2021)
	Yangtze River Basin				1.68	2095	210	216	NA	
	Yellow River Basin				2.16	18662	1708	884	NA	
	Pearl River Basin				9.19	20032	1315	838	NA	
	Huai River Basin				84.5	21400	268	559	NA	
	Hai River Basin				98.4	14196	117	262	NA	
	Liao River Basin				55.7	5610	1295	1156	NA	
	Taihu Lake Basin	Lake and river	16 PAHs	Not specified	5.4	4940	206	292	NA	(Huang et al., 2020b)
	Taihu Lake Basin	River	9 PAHs	2009	1290	2166	1842	1742	345	(Zhang et al., 2011)
India	Ganges River Basin	River	16 PAHs	2013	3.60	61.5	33.9	31.9	16.0	(Sharma et al., 2018)
Mediterranean Sea		Sea/ocean	16 parent, 1 alkyl-PAHs	2016	1.6	43	5.6	8.94	8.81	(Vecchiato et al., 2018)
North Atlantic and Arctic Ocean										
West Pacific		Sea/ocean	9 PAHs	2004	43.6	416	83.7	104	75.5	(Lohmann et al., 2009)
East Indian										
Southern Ocean		Sea/ocean	9 PAHs	2010–11	0.1	8.2	3.9	3.87	2.11	(Cai et al., 2016)
Prydz Bay					1.5	21	4.75	6.81	5.01	
South China Sea					0.3	4.2	1.5	1.93	1.26	
					0.2	6.3	2	2.16	1.77	
		Sea/ocean	15 PAHs	2015	14.6	746	198	252.00	235.00	(Zhang et al., 2021c)

TABLE 16.8
Concentrations of PAHs in Gaseous and Particulate Phases of Global Atmosphere from Selected Literature

Region/ Country	Location	Site type	Phase	Target	Year	Sampling regime	Levels (ng/m^3)				Reference
							Min	Max	Mean	SD	
Nepal	4 major cities	Urban, suburban	Gas	16 PAHs	2014	Summer	4.3	131	45.1	32.8	(Yadav et al., 2018)
Pakistan	8 major cities	Urban, suburban, rural	Gas	16 PAHs	2014	Summer, 24h	NA	NA	0.15–2.02	NA	(Ishtiaq et al., 2021)
			PM2.5				NA	NA	0.04–0.37	NA	
Sri Lanka	Kandy City	Urban	PM10	12 PAHs	2017	Daytime	NA	NA	3.06–36.9	NA	(Abayalath et al., 2022)
Japan	Kamihaya	Background	TSP	17 PAHs	2013–14	Weekly, 24h	0.08	6.51	1.63		(Jadoon and Sakugawa, 2016)
	Hiki	Rural					0.09	4.74	1.18		
	Higashi-Hiroshima	Urban					0.21	6.53	2.43		
China	Tuoji Island	Background	PM2.5	15 PAHs	2011–13	4 seasons	4.24	40.62	15.34	8.87	(Wang et al., 2018)
	Ningbo	Background	TSP	15 PAHs	2012–15	4 seasons, fortnight, 24h	0.01	38.6	5.84	7.82	(Mao et al., 2018)
	9 major cities	Urban	PM2.5	16 parent PAHs	2013–14	4 seasons, monthly, 24h	3	580	65	120	(Liu et al., 2017b)
				12 nitro-PAHs			0.37	6.5	1.1	0.9	
Australia	Brisbane	Urban background	Gas	13 PAHs	2013–14	720 h	1.3	3.0	NA	NA	(Wang et al., 2016)
			TSP				0.06	0.35	NA	NA	
		Urban traffic area	Gas				3.1	5.8	NA	NA	
			TSP				0.35	1.3	NA	NA	
USA	National	Urban	Gas+TSP	15 PAHs	1990–2014	every 6–12 days	NA	NA	56.2	140	(Liu et al., 2017a)
		Rural	TSP				NA	NA	38.1	72.1	
UK	Birminham	Not specified	PM10	16 PAHs	2010	Winter, 24 h for 5 days	NA	NA	9	NA	(Delgado-Saborit et al., 2013)
			Gas				NA	NA	78.6	NA	

France	Grenoble	Urban	Gas	16 Parent and 5 alkyl-PAHs	2013–14	Four seasons, every 3 days, 24 h	0	105	18.15	NA	(Tomaz et al., 2016)
			PM10				0.28	36.2	4.96	NA	
			Gas	27 oxy-PAHs			0.009	41.9	5.47	NA	
			PM10				0.13	141	5.01	NA	
			Gas	32 nitro-PAHs			0	0.37	0.11	NA	
			PM10				0.002	0.86	0.12	NA	
Portugal	Monte Velho	Rural	PM10	7 carcinogenic PAHs	2014–14	Winter, monthly, 24h	0	3.39	0.66	0.85	(Matos et al., 2021)
						Spring, monthly, 24h	0	0.25	0.074	0.07	
						Summer, monthly, 24h	0	0.34	0.1	0.1	
						Autumn, monthly, 24h	0	3.02	0.47	0.71	
Croatia	Delnice	Rural industrial	PM10	10 PAHs	2010	Winter, daily, 24 h	0.8	429	48.5	75.1	(Godec et al., 2016)
	Zagreb	Urban background				Winter, daily, 24 h	3.9	72.2	21.7	16.6	
	Delnice	Rural industrial				Summer, daily, 24 h	0.1	4.5	0.8	0.8	
	Zagreb	Urban background				Summer, daily, 24 h	0.1	1.3	0.1	0.2	
The Arctic	Canadian Arctic	Background	Gas+TSP	8 parent, 1 alkyl-PAH, 1 heterocyclic PAH	1992–2015	Cold and warm seasons, 7-day	0.003	14.6	0.34	NA	(Yu et al., 2019)
	Norwegian Arctic				1994–2015	Cold and warm seasons, every 2 days	0.008	21.6	0.65	NA	
	Finnish Arctic				1996–2015	Cold and warm seasons, 7- and 30-day	0.028	4.89	0.71	NA	

Birgunj, Nepal, at 131 ng/m^3 (Yadav et al., 2018) (Table 16.8). Cities with higher population and extensive energy demand presented higher levels of atmospheric levels of PAHs in both gas and particle phases, which are particularly prominent in winter (Liu et al., 2017b, Ma et al., 2018).

Higher concentrations of PAHs in particulate matter in winter were also observed in background sites of northern and eastern China (Mao et al., 2018, Wang et al., 2018) (Table 16.8), which reflects the atmospheric transportation of PAHs from more populated areas (Zhang et al., 2022, Matos et al., 2021). Such transportation of PAHs with air trajectories also results in the monsoon seasonal variation of PAHs in the air (Nargis et al., 2022).

For parent PAHs, three- and four-ring congeners are dominant in the gaseous phase, while five- to six-ring congeners tend to distribute in the particulate phase (Abayalath et al., 2022, Ishtiaq et al., 2021, Ma et al., 2018, Nargis et al., 2022). Long-term monitoring of airborne PAHs indicated declining trends of both gaseous and particulate PAHs since 1994–1995 in Brisbane, Australia, with estimated $t_{1/2}$ of 6.2 years (Wang et al., 2016), while decreases in atmospheric PAHs were only observed in urban sites (6–9% annually) in the US (Liu et al., 2017a).

It is noteworthy that PAHs in arctic air did not show declines as expected due to reduction of emissions, as a result of re-volatilization of PAHs caused by global warming (Yu et al., 2019). Although nitro- and oxy-PAHs only had minor contributions to total atmospheric PAHs, the higher toxicity and potentially distinct source, such as secondary formation, should raise more attention (Liu et al., 2017b, Matos et al., 2021).

16.7 ENVIRONMENTAL FATE AND BEHAVIOR OF PAHS

16.7.1 Atmospheric Environment

The partitioning of PAHs between gaseous and particulate phases is primarily influenced by their molecular weight. Under ambient conditions, naphthalene predominantly exists in the gas phase, while PAHs with five or more rings tend to partition almost exclusively into particulate matter (Kameda, 2011). PAHs with three to five rings exhibit a dynamic partitioning between vapor and particle phases, which is significantly affected by temperature, leading to seasonal variations (Keyte et al., 2013, Ma et al., 2019, Liu et al., 2013a, Wilson et al., 2021). Upon release into the atmosphere, PAHs are mainly found in ultrafine particles and accumulation modes with aerodynamic diameters ranging from 0.01 to 1 μm. Subsequently, semi-volatile congeners may undergo redistribution through gas-particle partitioning (Keyte et al., 2013).

The chemical reactions of PAHs with hydroxyl (OH), nitrate (NO_3), and ozone (O_3) radicals have been extensively studied (Figure 16.3). Reactions with OH radicals result in the formation of hydroxyl-PAHs, which can further react with nitrogen dioxide (NO_2) or ozone to produce nitro-PAHs and quinones, while also potentially forming phthalic acid, phthalaldehyde, and phthalic anhydride through ring-opening reactions, as evidenced by field observations (Qu et al., 2006a, Bunce et al., 1997, Kautzman et al., 2010, Keyte et al., 2013). For reactions involving nitrate radicals, the addition of NO_3 to PAHs is typically followed by reactions with NO_2 that yield nitro-PAHs (Atkinson and Arey, 2007, Phousongphouang and Arey, 2003, Qu et al., 2006b), with the kinetics of these reactions being influenced by NO_2 concentration (Keyte et al., 2013). During the daytime, reactions with OH radicals are predominant, presenting rate constants five orders of magnitude greater than those involving NO_3 radicals; conversely, NO_3 reactions become more significant at night (Keyte et al., 2013).

Heterogeneous reactions involving PAHs adsorbed onto particulate matter occur with OH, N_2O_5/NO_3, and O_3 radicals. The rates of these heterogeneous reactions are influenced by both the radicals and particle matrices, including carbonaceous particles like soot and graphite, as well as mineral particles such as silica and magnesium oxide (Keyte et al., 2013). For reactions involving OH

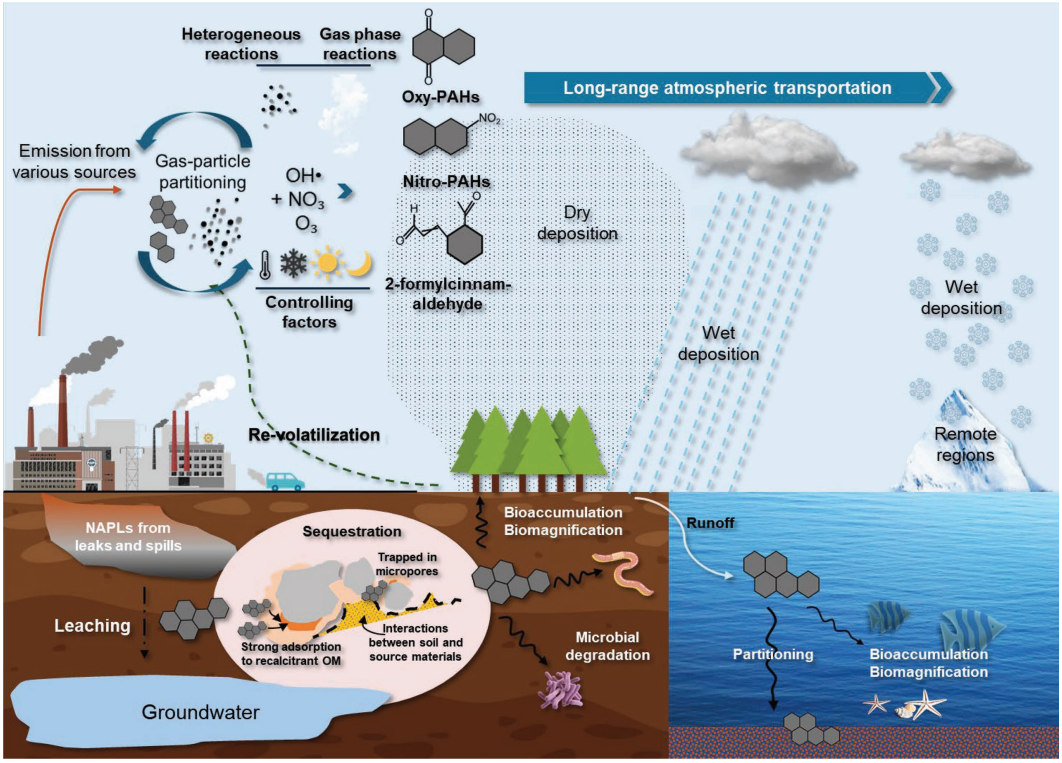


FIGURE 16.3 A schematic summary of the fate and behavior of PAHs in different environmental compartments.

radicals, the rates on particulate matter are typically one to three orders of magnitude lower than those in the gas phase (Esteve et al., 2004, Esteve et al., 2006), with the rate-limiting factor being the availability of particle-bound PAHs (Pöschl et al., 2001, Zhou et al., 2012). In contrast, reactions with O_3 radicals on graphite and silica particulate matter occur at rates two orders of magnitude faster than in the gas phase (Keyte et al., 2013). Overall, reactions with OH radicals in the gas phase are considered the dominant mechanism for PAH transformation in the atmosphere, followed by heterogeneous reactions of particle-bound PAHs with NO_3 and O_3 radicals (Keyte et al., 2013). The incorporation of PAHs into particle matrices serves a protective function that reduces the accessibility of PAHs to atmospheric radicals, thereby enhancing their persistence, as demonstrated by laboratory simulations and field observations.

Dry and wet deposition are key scavenging mechanisms for airborne PAHs. Wet deposition tends to be less effective for PAHs that are not bound to particles (Bidleman, 1988). Dry scavenging is believed to be predominantly driven by particle deposition (Bidleman, 1988, Gocht et al., 2007), with three-ring PAHs exhibiting higher deposition velocities compared to four- and five-ring congeners, attributed to the size distribution of semi- and non-volatile PAHs (Demircioglu et al., 2011, Ligocki et al., 1985). In general, dry deposition involving particle-bound PAHs is more effective than gaseous or wet deposition (Škrdlíková et al., 2011, Balasubramanian and He, 2010), while semi-volatile PAHs are scavenged more efficiently than their non-volatile counterparts (Ligocki et al., 1985). Deposited or condensed three- to four-ring PAHs on surfaces of water bodies, soil, and vegetation are also subject to re-volatilization (Figure 16.3) (Keyte et al., 2013).

16.7.2 Terrestrial Environment

After entering soil, PAHs and their metabolites may undergo various processes including volatilization, leaching, bioaccumulation by soil organisms, microbial degradation, and sequestration (Figure 16.3). The relative importance of these processes in determining the fate of PAHs is dependent on environmental conditions (e.g. precipitation and temperature), physico-chemical properties of PAHs, and soil characteristics (Semple et al., 2001). Under stable environmental conditions, the fate and behavior of PAHs in the same soil is controlled by their properties.

Volatilization and leaching are more likely to take place for LMW PAHs given their vapor pressure and water solubility. These processes are negligible for HMW PAHs. Ambient temperature was found to be influential on volatilization of LMW PAHs, since two- to three-ring PAHs were substantially lost after incubation at 10–30°C for 240 days, while five- and six-ring PAHs remained stable irrelative to temperature changes (COOVER and SIMS, 1987). Leaching of dissolved PAHs in soil was also considered negligible (Stroo et al., 2000) Only a minor proportion of total PAHs (<2%) was observed to leach from a contaminated soil after 2 years of landfarming (Saison et al., 2004). Limited information is available on the colloid-assisted migration of PAHs to groundwater, but enhancement on hydrophobic pollutant mobility in porous media has been recorded (Jones et al., 1989, Maxin and Kögel-Knabner, 1995).

Bioaccumulation and biomagnification are results of the uptake of PAHs by soil-dwelling organisms such as earthworms and plants and subsequent entrance to the related food web. Living in direct contact with contaminated soil, earthworms are able to uptake PAHs via passive diffusion from soil porewater to lipids of outer membranes, as well as ingestion of soil (Lanno et al., 2004, Cachada et al., 2014). It was suggested that soil porewater is the primary route for uptake of PAHs with Log $K_{OW} < 5$, while ingestion of soil is important for more hydrophobic congeners (Ma et al., 1998). Root uptake of PAHs in soil by plants is also a passive diffusion process, especially to the lipid contents of plant roots, from soil porewater (Cachada et al., 2014). Root concentration factor and bioconcentration factor are both functions of freely dissolved PAHs in porewater, and are linearly correlated with hydrophobicity of PAHs expressed as Log K_{OW} for plants (Gao and Collins, 2009). Notably, root exudates like low molecular weight acids are able to disrupt soil bound PAHs and promote the dissolution of these compounds, thus enhancing accumulation by plants (Ling et al., 2009).

Biodegradation of PAHs in soil by microbial and fungal communities has been widely investigated (Juhasz and Naidu, 2000, Thavamani et al., 2011, Thavamani et al., 2012). Soil microbes are able to utilize PAHs such as naphthalene, phenanthrene, and pyrene as their sole carbon sources, or decompose more hydrophobic congeners, such as benzo(a)pyrene, through co-metabolism (Juhasz and Naidu, 2000). The freely dissolved fraction of soil PAHs are also key to the extent of biodegradation, although direct absorption via contact between microorganisms with sorbents of PAHs was also proposed (Duan et al., 2015b). Extracellular enzymes and biosurfactants excreted by microorganisms were found to enhance the degradation of PAHs in soil (Duan et al., 2015b). Moreover, the biodegradation of PAHs in soil is characterized by a bi-phasic feature: a fast initial phase is followed by a slower phase when the readily available fraction is depleted (Cornelissen et al., 1998, Reid et al., 2000).

Sequestration is arguably the most important process for the fate of soil PAHs. It is a time-dependent process, leading to declined chemical extractability and toxicity (also termed "ageing") (Alexander, 2000). It is the consequence of the interactions between soil matrices and PAHs, in which soil organic matter (SOM) plays a crucial role. The underlying mechanisms of such interactions could be described by the widely adopted dual-mode sorption model that includes the reversible, fast, non-specific, and linear partitioning of PAHs in the labile fraction of SOM, as well as the largely irreversible, slow, site-specific, and nonlinear adsorption of PAHs to the recalcitrant fraction of SOM (Xing and Pignatello, 1997). The dual-mode model consists of a linear partition domain and a site-specific adsorption domain expressed by the sum of a series of Langmuir model:

$$C_S = K_P \times C_W + \sum_{i=1}^{n} \frac{C_{S,MAX,i} \times K_{L,i} \times C_W}{1 + K_{L,i} \times C_W} \quad \text{(Equation 16.3)}$$

The forces driving the adsorption of PAHs to recalcitrant soil organic matter include dipole-dipole interactions, π-π interactions, hydrogen bonding, and steric hindrance (Zhu et al., 2004). While the sorption of PAHs to soil mineral content is generally regarded as minimal, some studies have nevertheless observed influences from clay minerals on the partitioning behavior of phenanthrene, leading to the proposal of a capillary condensation mechanism (Hundal et al., 2001, Ghosh and Keinath, 1994, Hwang and Cutright, 2003, Doick et al., 2005). Another potential binding mechanism for PAHs on soil minerals involves cation bridging with π electron donor congeners (Zhang et al., 2010). Additionally, steric hindrance within the pore structures of SOM plays a significant role in the sequestration of PAHs in soil (Semple et al., 2013).

16.8 RISK-BASED MANAGEMENT OF CONTAMINATED LAND WITH PAHS

Contaminated land with PAHs poses significant challenges for stakeholders and researchers, necessitating robust management strategies. Traditionally, the assessment of receptor exposure to hydrophobic organic compounds (HOCs) in contaminated soil has relied on total extractable concentrations, assuming that all detectable HOCs can induce adverse effects. However, as discussed in the previous section, ageing effects, which lead to the sequestration of PAHs in soil, reduce the risks associated with these compounds over time (Alexander, 1995, Hatzinger and Alexander, 1995, Alexander, 2000). Consequently, the total extractable fraction of soil PAHs can lead to an overestimation of risk; this has prompted the introduction of the concept of bioavailability.

In recent years, exposure assessments of contaminated land have shifted towards practices based on bioavailability and bioaccessibility, accounting for the reduced risks associated with ageing (Duan et al., 2014, Duan et al., 2015b, Naidu et al., 2015, Semple et al., 2004, Semple et al., 2007). Contamination scientists have made significant strides in integrating risk-based management of contaminated land into regulatory frameworks, thereby expanding the body of knowledge related to ageing, bioavailability, and bioaccessibility, as well as developing a diverse array of measurement techniques (Riding et al., 2013).

16.8.1 Bioavailability and Bioaccessibility

The mass body of knowledge and measuring techniques for bioavailability and bioaccessibility also created confusions It was suggested that definition and measurement of bioavailability/bioaccessibility are the two fundamental problems to be addressed before a comprehensive inclusion of bioavailability in regulation can take place (Ortega-Calvo et al., 2015).

16.8.1.1 Definition

The term "bioavailability" and related terms have been used in many disciplines and led to numerous definitions (Ehlers and Luthy, 2003, NRC, 2003, Semple et al., 2004) and there is no single harmonized method for estimating bioavailable fractions. In a way, bioavailability is a method-defined concept, since it is dependent on the receptor or toxicological endpoints being investigated (Kelsey et al., 1997, White et al., 1997, Semple et al., 2003, Semple et al., 2004, Naidu et al., 2008, Rostami and Juhasz, 2011). In general, bioavailability and bioaccessibility of organic contaminants can be categorized in two contexts based on the receptors concerned: ecological risk assessment (ERA) and human health risk assessment (HHRA) (Figure 16.4).

For ERA, receptors are soil-inhabiting organisms such as microorganisms, terrestrial invertebrates, and plants. In this case, it has been proposed that the bioavailable fraction is the fraction of the total quantity of a contaminant that is readily dissolved in the soil aqueous phase and available to cross membranes of specified receptors, while the bioaccessible fraction is the total amount of a

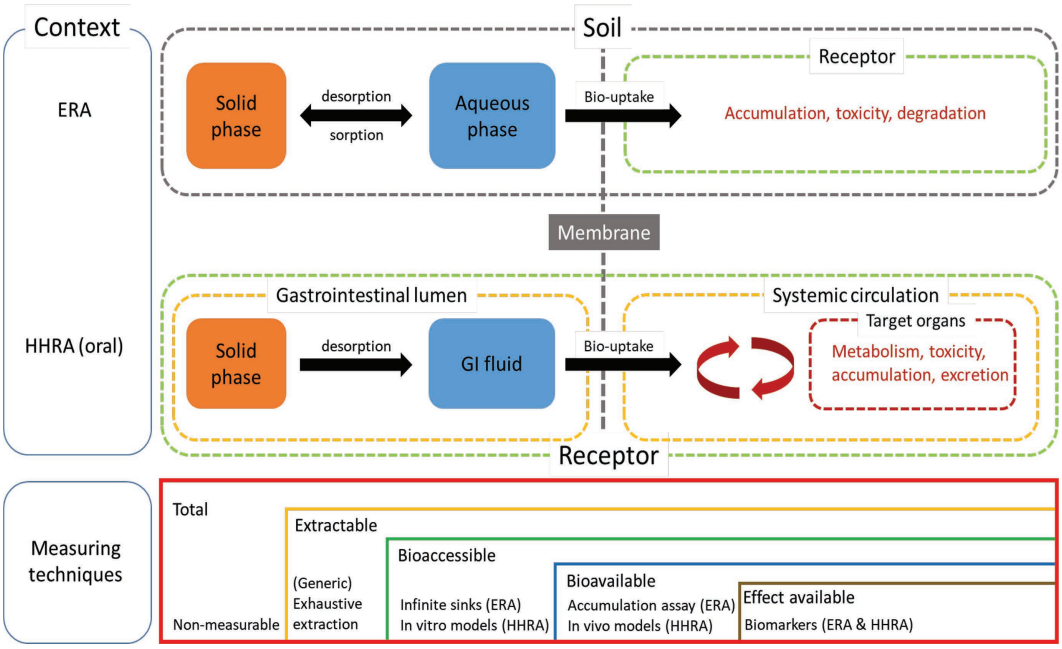


FIGURE 16.4 A schematic of bioaccessibility, bioavailability, and toxicity exertion of organic contaminants in soils to both ERA and HHRA receptors and their implications in measurement and evaluation of risks. Desorption of contaminants from soil to either soil pore water or GI fluid is emphasized.

contaminant that is desorbable from the soil solid phase to the aqueous phase (Semple et al., 2004). Thus, the bioavailable fraction may be seen as a subset of the bioaccessible fraction (Figure 16.4).

For HHRA, incidental oral ingestion of contaminated soil has been extensively studied as the most important exposure route, especially for young children (Cave et al., 2010, Rostami and Juhasz, 2011, Ruby and Lowney, 2012). In oral exposure of HHRA, the amount of soil contaminant dissolved in a solution that simulates the gastrointestinal (GI) tract in a given time was defined as oral bioaccessibility, while the amount of contaminant that enters the systemic circulation system from GI lumen was defined as oral bioavailability, or absolute bioavailability (Ruby et al., 1999) (Figure 16.4). Relative bioavailability was defined as the comparative bioavailabilities of different forms of contaminants or contaminants in different exposure media (Ruby et al., 1999).

From a risk-based standpoint, the role of desorption in conceptualizing and measuring bioavailability has been emphasized (Ortega-Calvo et al., 2015). This is because contaminants have to be taken up by receptors to exert toxic effects, and biological uptake of contaminants mainly takes place from the dissolved phase (Cerniglia, 1992, Vasiluk et al., 2007, EFSA, 2009). Therefore, desorption of PAHs from soil solid phase to either soil aqueous phase or GI fluid is of importance for bioavailability (Figure 16.4).

16.8.1.2 Measurement

Measurement techniques for the bioavailability and bioaccessibility of PAHs and other HOCs in soils, for both ERA and HHRA, have been extensively reviewed (MacLeod et al., 2001, Semple et al., 2003, Lanno et al., 2004, Semple et al., 2007, Rostami and Juhasz, 2011, Peijnenburg et al., 2012, Cui et al., 2013, Riding et al., 2013, Cachada et al., 2014, Lal et al., 2015, Cui et al., 2016, Ruby et al., 2016).

Biological assays can directly reflect the risks associated with soil PAHs. An array of bioassays using living organisms and biological endpoints have been developed, many of which have been

standardized by organizations such as the OECD and ISO (Duan et al., 2015b, Ortega-Calvo et al., 2015).

For ERA, biodegradation assays using PAH-degrading microorganisms, and bioaccumulation assays using earthworms and plants, have been widely adopted by researchers investigating bioavailability of soil PAHs. The use of a slurry system for biodegradation assays with microorganisms overcomes temporal and spatial constraints in soils (Bosma et al., 1997, Reid et al., 2001, Semple et al., 2004). The bioavailable concentrations are reflected by the differences in contaminant concentrations before and after degradation assays. However, this approach is intrinsically limited by the degradability of the target PAH. For relatively inert PAHs such as benzo(a)pyrene, the application of biodegradation assays is limited. Accumulation of PAHs by earthworms and plants is through passive diffusion processes across membranes and tend to take up more recalcitrant PAHs (Gomez-Eyles et al., 2010). But slurry systems cannot be used in accumulation assays. Test organisms are therefore spatially and temporally constrained when accessing contaminants in soil (Semple et al., 2004).

Animal surrogates are used to assess oral bioavailability for HHRA. A range of biological endpoints can be employed to evaluate oral bioavailability (Ruby et al., 2016, Duan et al., 2015b). Metabolism related biomarkers such as urinary metabolites, DNA-adducts, and enzyme induction indicate the specific availability of PAHs to certain organs and metabolic processes in test animals (i.e., effect availability), while endpoints such as blood and fecal concentration reflect the total absorption of target PAHs (Pu et al., 2004, Juhasz et al., 2014) (i.e., bioavailability). An issue associated with these in vivo methods is that they are affected by physiological differences among test individuals. One solution is to measure relative bioavailability which is able to normalize differences in doses and physiological variations among test individuals (Ruby et al., 2016). A prerequisite for assessment of relative bioavailability is that the dose administrated to the animals must be within the range of linear dose-responses (Ruby et al., 2016).

In both cases of ERA and HHRA, bioavailability measured with bioassays is species- and endpoint-specific. For example, the bioavailabilities of the same PAH in the same soil to microorganisms and earthworms were different (Kelsey et al., 1997), while the orally bioavailable fractions measured with blood concentrations also differed from that measured with fecal residues (Van Schooten et al., 1997). Moreover, bioassays are also more financially demanding and are associated with ethical issues.

Chemical assays have long been used to estimate bioavailability and bioaccessibility of PAHs in soils with greater time- and cost-efficiency than biological assays.

Numerous chemical methods have been developed for ERA receptors based on mild organic solvents (e.g. n-butanol and water/methanol), desorption reagents with infinite sinks (e.g. hydroxypropyl-β-cyclodextrin (HPCD), Tenax, and XAD2), chemical reactivity (persulfate oxidation), or partitioning into a third phase (passive sampling) (Cachada et al., 2014). In brief, desorption reagents such as HPCD and Tenax, and SPME are considered better techniques to measure bioaccessibility of soil PAHs (Brand et al., 2009). This is because infinite sinks like HPCD and Tenax are able to drive the mass transfer of contaminants from solid phases to the aqueous phase, thus reflecting bioaccessibility, while passive sampling is able to mimic the diffusive uptake of organic compounds by soil organisms from the aqueous phase (Cachada et al., 2014).

For HHRA, some in vitro models were developed and applied to investigate oral bioaccessibility of PAHs in soils, such as Simulator of the Human Intestinal Microbial Ecosystem (SHIME), Fed ORganic Estimation human Simulation Test (FOREhST), Physiologically Based Extraction Test (PBET) and Colon Extended PBET (CE-PBET), and Unified BARGE Method (UBM) (Lal et al., 2015). These models simulate the internal environments and processes in organs involved in ingestion of contaminated soils such as mouth, stomach, small intestine, and colon. A stream of development in Europe focused on mimicking human digestive systems as closely as possible, while another stream in North America and Australia focused on the correlation between in vivo and in vitro results (Ruby et al., 2016). A disadvantage of these in vitro methods is that they are relatively less time- and cost-effective than simple extraction assays. Simplification may be achieved after the

key components in these models are identified so that routine methods that are more reliable, rapid, and cost-effective can be established.

Chemical measurements of bioavailability and bioaccessibility of soil HOCs are also method-specific but are more controllable compared to biological methods. A challenge faced by these techniques is the correlation with bioassays. In published literature, there are relatively fewer correlations found between in vivo and in vitro assays for HHRA, but with increasing input of researching efforts correlations can be anticipated (Ruby et al., 2016).

16.8.2 Factors Controlling Bioavailability and Bioaccessibility of PAHs in Soil

From the standpoint of risk, both ERA and HHRA (oral) emphasize the importance of sorptive and desorptive behavior of PAHs from contaminated soil, either to soil pore water or to GI fluid. To identify factors controlling bioavailability and bioaccessibility of PAHs, soils of different properties could be selected or artificially constructed; model solids could also surrogate certain soil contents (Yu et al., 2018). Spiking strategies using single PAH, contaminant mixtures, or source materials at different levels could be adopted, followed by bioassays, chemical assays, equilibrium, or kinetic studies that are linked to bioavailability or bioaccessibility (Yu et al., 2018). By comparing results of assays or parameters of equilibrium or kinetic models, key influential factors are obtained.

Soil organic matter is widely accepted as the most important soil component to determining PAH sequestration and release in soil, i.e., their bioavailability and bioaccessibility (Xing et al., 1996). Total organic carbon (TOC) was found to dominate bioavailability and bioaccessibility of PAHs to an array of receptors (Nam et al., 1998, Alexander and Alexander, 2000, Bogan and Sullivan, 2003, Tao et al., 2006, Rhodes et al., 2010b, Pu et al., 2004, Chung and Alexander, 2002). Quality of SOM has also been extensively studied due to the dual-mode sorption of HOCs in soil (Xing and Pignatello, 1996, Xing et al., 1996, Xing and Pignatello, 1997, Huang et al., 1997). Several strategies have been adopted to distinguish SOM of different qualities, such as extraction of humic substances under different pH (Lehmann and Kleber, 2015), thermal/oxidative fractionation of SOM (Cornelissen et al., 2005), size fractionation of soil (Doick et al., 2005, Amellal et al., 2001, Pernot et al., 2013, Siciliano et al., 2010), quantification of pore size (Luo et al., 2012, Duan et al., 2014, Duan et al., 2015a), and investigation directly on structural characteristics of SOM (Xu et al., 2006, Chen et al., 2007, Cornelissen et al., 2005, Semple et al., 2013).

Humic acid and humin were suggested to dominate site-specific adsorption of PAHs (Kang and Xing, 2005, Pan et al., 2006, Chen et al., 2007, Chiou et al., 2000). Negative relationships were obtained between soil contents after thermal and chemical oxidation and rate constants of slow desorption of phenanthrene, pyrene, and benzo(a)pyrene (Luo et al., 2012). Predominant distribution of aged PAHs was found to associate with fine silt and clay fractions of soil (Doick et al., 2005, Amellal et al., 2001, Pernot et al., 2013, Siciliano et al., 2010), whereas a negative correlation was found between relative oral bioavailability of benzo(a)pyrene tested by a swine model and the fine particle associated carbon (FPAC) (Duan et al., 2014) given by

FPAC = (silt + clay)/TOC (Equation 16.4)

Duan and co-workers also found the negative effects of volumes of pore with diameter < 6 nm (PF_{6nm}) on relative oral bioavailability of benzo(a)pyrene (Duan et al., 2014, Duan et al., 2015a), which was supported by the findings of Luo who linked PF_{6nm} with slow desorption of phenanthrene, pyrene, and benzo(a)pyrene (Luo et al., 2012). Aromatic structures were found to dominate humic substances (Xu et al., 2006, Chen et al., 2007), black carbon (Cornelissen et al., 2005, Semple et al., 2013), and soil fine fractions (Krauss and Wilcke, 2002, Kiem et al., 2002). Namely, aromaticity was associated with non-linear adsorption of PAHs in soil, and aliphaticity with linear absorption. Formation of soil pores was also linked to aliphatic and aromatic structures (Han et al., 2014).

Most published literature did not distinguish natural organic matter (NOM) and xenobiotic organic matter (XOM). There has been an evolving prospective on NOM in recent years, which considers NOM a consortium of biological residues at different stages of carbon turnover facilitated

by biodegradation rather than a binary split of labile and recalcitrant SOM (Lehmann and Kleber, 2015). It is also noteworthy that XOM, often being carbonaceous sorbents like soot, char, pitch, and tar, are also source materials of PAHs but not given particular attention in majority of related research (Yu et al., 2018, Yu et al., 2023, Ruby et al., 2016, Xia et al., 2016, Roberts et al., 2016).

Source materials, which were introduced in Section 5.1, are carbonaceous materials with high affinity to PAHs in soil. As such, they are considered to be sinks for PAHs in general by researchers (Boyd and Sun, 1990, Luthy et al., 1997, Luthy et al., 1993). Even low levels of source materials are able to dominate PAH sorption in soil (Jonker and Koelmans, 2002, Cornelissen et al., 2005, Khalil et al., 2006), while in hotspots of PAH contamination, source materials such as XOM could make up most of the SOM (Bayard et al., 2000).

Solid-liquid partition coefficients (K_d) for PAHs in soot and charcoal was found to be 1,000 times higher than those in NOM (Jonker and Koelmans, 2002), whereas release of PAHs from these materials was highly inhibited, hence significantly reduced their bioavailability (Rust et al., 2004, Thorsen et al., 2004, Jonker et al., 2005). For source materials in the form of NAPLs or semi-solids, high partition coefficients of PAHs were found for coal tar pitch (Khalil et al., 2006, Ghosh and Hawthorne, 2010, Xia et al., 2016), those for fuel oil were obtained up to 10^9, even higher than soot (Jonker et al., 2003, Jonker and Barendregt, 2006, Xia et al., 2016). Consequently, slow desorption was also characterized for contaminated soil with coal tar and pitch (Yeom et al., 1996, Williamson et al., 1998, Stroo et al., 2000, Benhabib et al., 2006, Eberhardt and Grathwohl, 2002, Yu et al., 2023). However, bioavailability tests found that benzo(a)pyrene was more available in fuel oil-amended soil than soil spiked by benzo(a)pyrene in solvent (Roberts et al., 2016), despite higher K_d (Xia et al., 2016). Slow kinetics of benzo(a)pyrene and six other carcinogenics were obtained from soils amended with coal tar and coal tar pitch compared to solvent spiked soils (Yu et al., 2023). Importantly, after initial incubation up to 48 days, rapidly desorbing fractions (F_{rap}), which is linked to bioaccessibility of soil PAHs (Rhodes et al., 2010b, Cornelissen et al., 1998), presented increasing trend in coal tar-amended soils, i.e., no ageing was observed for up to 48 days (Yu et al., 2023). It was suggested that coal tar continuously migrated into soil pore structures. With stretched and larger surfaces in contact with soil particles, release of PAHs from coal tar was enhanced and led to increased F_{rap} and thus higher bioaccessibility and associated risks (Yu et al., 2023). An important implication of these findings is that source materials, especially those similar to coal tar and coal tar pitch, act as reservoirs, rather than sinks, of PAHs soil and should be considered carefully during risk assessment (Yu et al., 2023).

Concentration and co-contaminants are other factors influencing bioavailability and bioaccessibility of PAH. With high concentrations of PAHs or high levels of other HOCs, higher rates of sorption and desorption were obtained due to steeper concentration gradients (Huang and Weber, 1998, Braida et al., 2001, Braida et al., 2002, Li et al., 2013). Large quantities of HOC molecules could soften and swell soil pores, causing larger pore volumes or pore collapse and induce conditioning effects (Braida et al., 2002). Competitive sorption by organic co-contaminants also leads to higher bioavailability of PAHs (White and Pignatello, 1999, White et al., 1999a, White et al., 1999b, van den Heuvel and van Noort, 2003, Stroud et al., 2009, Wang et al., 2014). Co-existing heavy metals might lead to decreases in bioavailability of PAHs due to reduced dissolved organic matter, changed SOM composition, and cation-π bridging (Zhang et al., 2010, Liang et al., 2016). It should be noted that in case of soils contaminated by coal tar, large quantities of PAHs and other HOCs released from this NAPL source materials would saturate non-linear adsorption cites in SOM, rendering the quality of SOM unimportant. In this scenario, only the quantity of SOM determines the release of PAHs from contaminated soil (Yu et al., 2023).

16.8.3 Risks of Non-Extractable Residues of PAHs in Soil

An inevitable challenge for risk-based management of contaminated land with PAHs is associated with the non-extractable residues (NERs). Formation of NERs is the result of long-term

sequestration of PAHs in soil (Umeh et al., 2017) (Figure 16.3). The remaining fraction of PAHs in soil after sequential exhaustive solvent extractions was defined as NERs and demonstrated via isotopic tracers (Kästner et al., 2016, Kästner et al., 2014). There are three types of NERs: the fraction entrapped in pore structures and strongly adsorbed in soil (Type I), the fraction covalently bound in soil (Type II), and the fraction degraded to non-toxic products and incorporated into NOM (Type III) (Kästner et al., 2014, Barriuso et al., 2008, Macleod and Semple, 2003). As such, Types I and II are of different stability while Type III NER bears no environmental risks (Umeh et al., 2018a).

From a risk-based standpoint, Types I and II NERs could be remobilized and pose hazardous effects on receptors. Based on sequential mild (butanol) and exhaustive (dichloromethane/acetone, DCM/Ace) extractions followed by methanolic saponification (Umeh et al., 2018a), readily available fraction, total extractable fraction, and NER of benzo(a)pyrene spiked to soils of different properties and incubated for up to 200 days were assessed by Umeh et al. (2018b). Umeh et al. (2018b) further assessed the remobilization of benzo(a)pyrene by re-equilibrating soils after the removal of butanol and DCM/Ace extractable fractions (Umeh et al., 2018b). It was suggested that remobilization occurred via slow intercompartmental partitioning of the target PAH from a highly sequestrated domain to a less sequestrated domain due to re-existing concentration gradients (Umeh et al., 2018b). The extent of benzo(a)pyrene remobilization decreased with increasing ageing time, and was largely controlled by recalcitrant SOM fraction (Umeh et al., 2018b). Such findings were further confirmed by extensive ageing of benzo(a)pyrene-spiked soils for 4 years with <5% sequestrated benzo(a)pyrene remobilized by butanol and DCM/Ace (Umeh et al., 2019b). As such, risks of NERs of PAHs from a desorptive point of view are minimal. This is further supported by the results of DNA damage assessment on earthworms (*Eisenia fetida*) which demonstrated no significant difference between exposure to benzo(a)pyrene NERs in soils aged for 350 days and to unspiked soils (Umeh et al., 2019c), as well as the incremental lifetime cancer risks (ILCRs) of benzo(a)pyrene NERs in spiked soils aged for 500 days and carcinogenic PAHs in MGP soils tested by a Si-Org-PBET in vitro model, in which remobilized PAHs did not pose ILCRs above target levels (10^{-5}) except one MGP soil (Umeh et al., 2019a).

16.8.4 Remediation Techniques

Traditional strategies for cleaning up highly contaminated sites typically involve methods such as soil washing, excavation followed by landfill or incineration, and removal of contamination plumes (e.g., non-aqueous phase liquids, NAPLs) from source zones (Duan et al., 2015b). These strategies may also include implementing impermeable barriers to prevent the migration of contaminants to the air, groundwater, or uncontaminated soil. Chemical methods that promote the oxidation of PAHs can also be employed for remediating contaminated soils (Medina et al., 2018). However, excavation and thermal or chemical treatment of contaminated soil often require ex situ interventions and can impose significant costs on remediation practitioners and stakeholders (Duan et al., 2015b). From a risk-based management perspective, focusing on the removal of only the bioavailable and bioaccessible fractions of PAHs is a more feasible approach, both financially and operationally, considering that the NERs of PAHs pose no significant risks, as discussed in Section 8.3.

Microbial degradation plays a crucial role in many risk-based remediation strategies for PAH-contaminated land by targeting the bioavailable and bioaccessible fractions. However, *in situ* bioremediation methods, such as landfarming and bioaugmentation, face challenges due to the limited solubility of PAHs and the resistance of high molecular weight PAHs to degradation by single strains of bacteria (Juhasz and Naidu, 2000, Thavamani et al., 2013, Duan et al., 2015b). Bioreactors that enhance control over microorganism growth and maintain optimal levels of nutrients, oxygen, moisture, and temperature present more viable solutions (Duan et al., 2015b).

Research has successfully isolated strains of microorganisms from contaminated soils that demonstrate the ability to survive and degrade PAHs, even in soils contaminated with both PAHs and heavy metals. Notable work by Thavamani and colleagues involved a consortium of bacteria,

including *Alcaligenes* sp., *Pseudomonas* sp., *Pandorea* sp., and *Paenibacillus* sp. (Thavamani et al., 2012). The addition of surfactants, such as cyclodextrin, has been shown to enhance the biodegradability of soil-bound PAHs (Allan et al., 2007). Additionally, the rhizosphere effect has been found to promote microbial growth, desorption, and degradation of PAHs in soil (Li et al., 2019b).

The amendment of sorbents is another effective strategy, leveraging the high affinity of materials like biochar and activated charcoal for PAHs. These sorbents can capture and bind the bioavailable and bioaccessible fractions, thereby reducing associated risks (Bielská et al., 2017, Rhodes et al., 2010a, 2012). Notably, biochar has been shown to enhance the degradative capabilities of soil microbial communities, particularly in soils with high soil organic matter content (Song et al., 2017). Given the degradative potential and growth of PAH-degrading microbial communities, alongside the benefits provided by the rhizosphere and biochar amendments, hybrid approaches appear to be more cost-effective and time-efficient for achieving risk-based remediation goals in PAH-contaminated soils.

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17 Understanding and Managing the Risks of Petroleum Hydrocarbons in Soil and Groundwater

Greg B. Davis, John L. Rayner and Trevor P. Bastow

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17.1 INTRODUCTION

17.1.1 Background

Petroleum hydrocarbons occur naturally (Dembicki, 2017), are extracted from petroleum reservoirs and are altered via refining and other means to create fuels, lubricants, solvents, chemicals and feedstock for industries such as plastics manufacturing (Bazzanella and Ausfelder, 2017). Unfortunately, vast tankage and storage volumes of petroleum and inventory throughput over the last 50 years has led to substantial spillage and leakage from above ground and underground storage tanks, pipelines

DOI: 10.1201/9781003530466-17
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and ancillary pipes and service lines. This has been common at crude oil rigs, refineries, fuel depots and transfer stations, re-fuelling service stations, airports and the like (Kuppusamy et al., 2020).

Whilst marine incidents and releases such as the Exxon Valdes tanker in 1989 (Barley, 2012) and the Deepwater Horizon oil platform in the Gulf of Mexico in 2010 (US EPA, 2022) have significant impact, land-based releases are more numerous and are also of significant concern, often with releases being subsurface and hence less visible (Ivshina et al., 2015). Petroleum hydrocarbon releases and spills are some of the most common globally (Kuppusamy et al., 2020). Of all contaminated sites in the US half were deemed to be petroleum-contaminated sites (US EPA, 2023). It is recognised, too, that atmospheric air pollution by volatile hydrocarbons occurs and can be of concern. Recently, a methodology for quantifying the scale of global emissions from petroleum hydrocarbon contaminated land was published (Sookhak Lari et al., 2024a). Here, we focus on the land-based contamination caused by petroleum releases that lead to contamination of soil and groundwater. Research on petroleum hydrocarbons as contaminants has been undertaken for over 50 years (Raymond, 1974), yet many challenges remain.

17.1.2 Petroleum, Crude Oils and Fuels: An Overview of Types

Here we are not seeking to be exhaustive in our descriptions of petroleum (crude oil and fuels) components and fuel types. Kuppusamy et al. (2020) provided details of petroleum hydrocarbon types and chemical components. Here our focus is on characterisation, fate and behaviour, and remediation options for petroleum hydrocarbons in subsurface environments. To do so, we provide an overview of fuel types, components and weathering profiles.

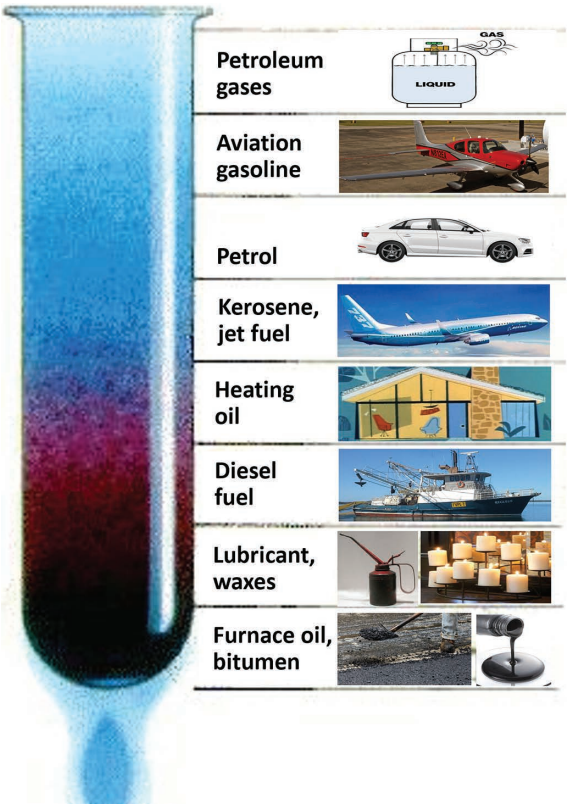


FIGURE 17.1 Schematic of products produced by distillation and further refining of crude oil (used with permission of the Australian Institute of Petroleum). Light end products are petroleum gases, aviation gasoline and petrol for cars, with heavier end products being heating oil, diesel fuel, lubricants and bitumen.

Crude oils have a high level of variability in their compositions and refining generally carried out via distillation, cracking, reforming, alkylation, polymerisation and isomerisation produces fuels and other products (e.g., gasoline, diesel, aviation fuels, heating oils, lubricants – Figure 17.1). Petroleum refining can enrich and fractionate components present in the crude oil as well as transform components through chemical reactions to produce chemicals that were not in the source crude oil (Speight, 1997).

Crude oils and refined petroleum products can contain thousands of compounds depending on the petroleum product type. As light non-aqueous phase liquids (LNAPLs), petroleum fuels and oils have variable properties (e.g., density, viscosity, interfacial tension), and these change when LNAPL enters the subsurface and undergoes weathering processes (losses to volatilisation, water washing and degradation). Components of petroleum also have variable solubilities, volatilities and other properties, with partitioning of these components to air and water phases in the subsurface based on the molar fraction of components present in the LNAPL which evolves with weathering.

Crude oils can be termed light or heavy, generally meaning they have a higher portion of compounds with lower or higher molecular weights respectively. The carbon range profiles of crude oils can be highly variable and mainly comprising hydrocarbons containing four (C4) to forty (C40) carbon atoms. For diesel the carbon range would generally be much narrower from C8 to C28, and for unleaded gasoline generally C4 to C12. Importantly, gasoline contains a higher mole fraction of volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene, and the xylene isomers (BTEX). Such compounds are also deemed sparingly soluble with benzene having a solubility of 1,750 mg/L (or approximately 20–40 mg/L when in equilibrium with a fresh gasoline NAPL – Lekmine et al., 2017); however, regulatory criteria for benzene dissolved in drinking water is typically 1–10 µg/L (e.g., US EPA, 2021).

In Figures 17.2 and 17.3 examples of the gas chromatography (GC) analyses of fresh and weathered crude oil and diesel are shown. When released into the subsurface, petroleum changes its composition due to water washing (dissolution processes), evaporation or volatilisation of components and via degradation and transformation (abiotic and biotic). The changes are apparent in Figures 17.2 and 17.3.

In Figures 17.2 and 17.3 significant weathering of the crude oil and diesel have resulted in the removal of n-alkanes and the depletion of methylalkanes and some aromatics. The underlying unresolved complex mixture (UCM) profile and profile of the abundant, more resistant biomarkers (isoprenoids such as IP15, IP16, norpristane, pristane and phytane) match between the fresh and weathered products. Such fingerprinting and resistant biomarkers can be used, for example, to estimate mass losses, which in this case suggests a 38% and 63% mass loss since the initial release of the crude oil and diesel, respectively. This has likely happened over a period of at least 20 years due to the complete removal of *n*-alkanes (based on Christensen and Larsen, 1993). The weathered crude oil and diesel fuel are examples of changes that can occur due to weathering in the subsurface over a multi-decadal time period.

17.2 CONCEPTUALISATION AND POTENTIAL RISKS

17.2.1 Conceptualisation

As an example, Figure 17.4b illustrates a petroleum release for an underground storage tank. Given a large enough volume or rate of release, LNAPL migrates downward through the soil vadose zone until meeting a hydraulic barrier or the capillary fringe. The LNAPL will move in response to pressure differentials and hydraulic head gradients within the LNAPL, usually in the direction of groundwater flow. Petroleum components of the LNAPL partition into the vapour phase moving vertically upwards and into groundwater moving laterally away from the LNAPL (Figure 17.4a). Here some of the exposure pathways and risks are discussed. The fate and behaviour of the LNAPL, the vapour phase and dissolved plumes are described in greater detail in Section 17.3.

Risks posed by petroleum fuels and crude oils have largely focused on benzene (a known carcinogen) and polycyclic aromatic hydrocarbons (PAH), e.g., benzo-a-pyrene, with increasing interest

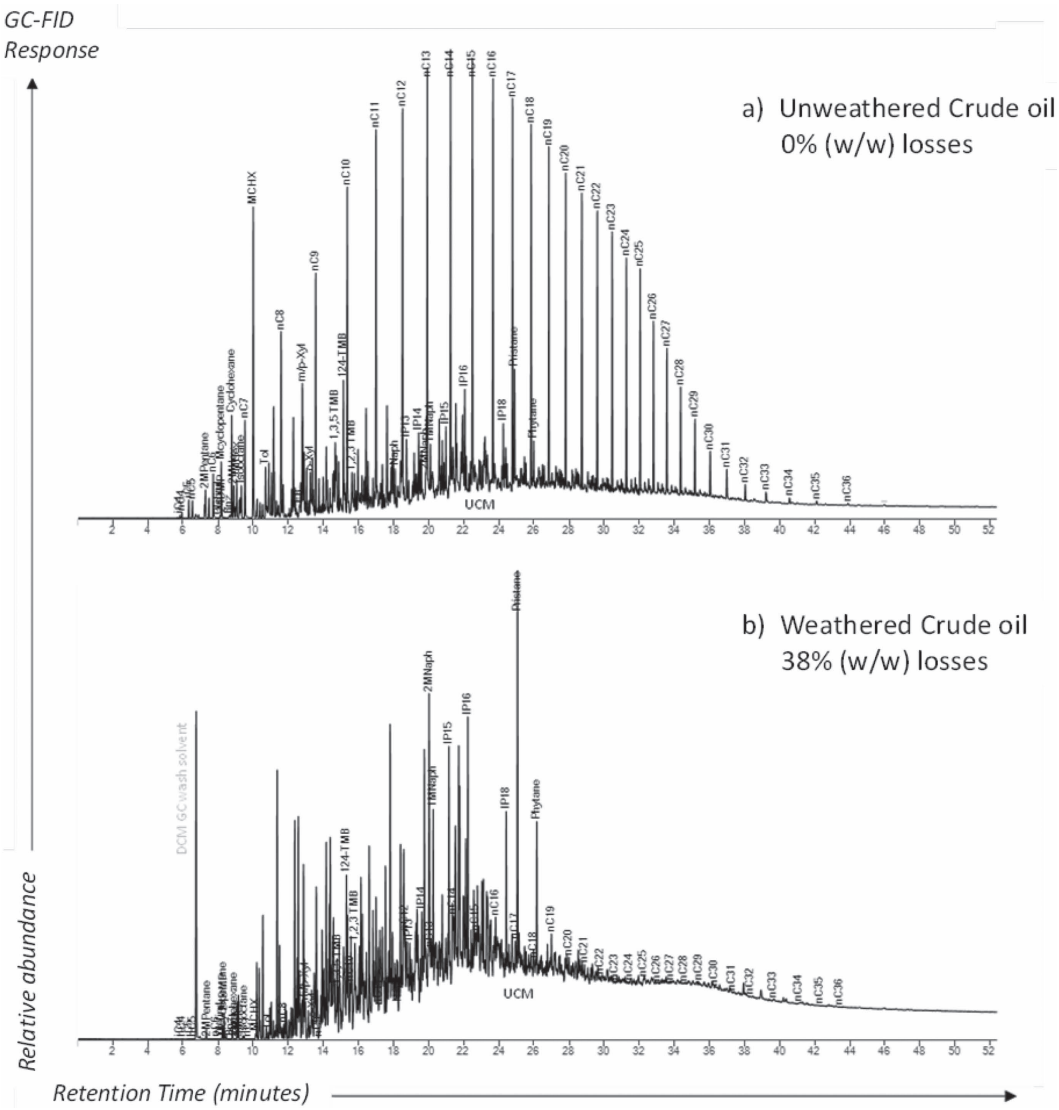


FIGURE 17.2 GC-FID analysis shown as chromatograms of a) unweathered crude oil and b) weathered crude oil. Benz: benzene, CHX: cyclohexane, Cx: straight or branched alkane containing x carbons, D: di, DCM: dichloromethane E: ethyl, i: iso, IP: isoprenoid, M: methyl, n: normal, Naph: naphthalene, P: pentane, TMB: trimethylbenzene, Tol: toluene, Xyl: xylene. (Bastow – unpublished data). The unweathered crude oil chromatogram has prominent peaks of individual components and a lower concentration and mass of unresolved complex mixture (UCM) whilst the weathered crude oil has much less prominent peaks and a much-increased concentration and mass in its UCM. Analysis of relative peaks indicates that perhaps 38% of the mass has been removed due to weathering compared to the unweathered crude sample.

in new compounds formed during weathering and performance-enhancing fuel additives such as methyl tertiary-butyl ether (MTBE) and 1,2 dichloroethane (1,2 DCA). The total petroleum hydrocarbon (TPH) concentration as a measure does not define risk, since it is a consolidated concentration across all hydrocarbon components in a sample. The TPH Criteria Working Group (TPHCWG, 1997) defined representative fractions of TPH carbon ranges that might be clustered based on effects and fate and transport properties. Much has been advanced since (e.g., ITRC, 2018), but largely based on this seminal TPHCWG work.

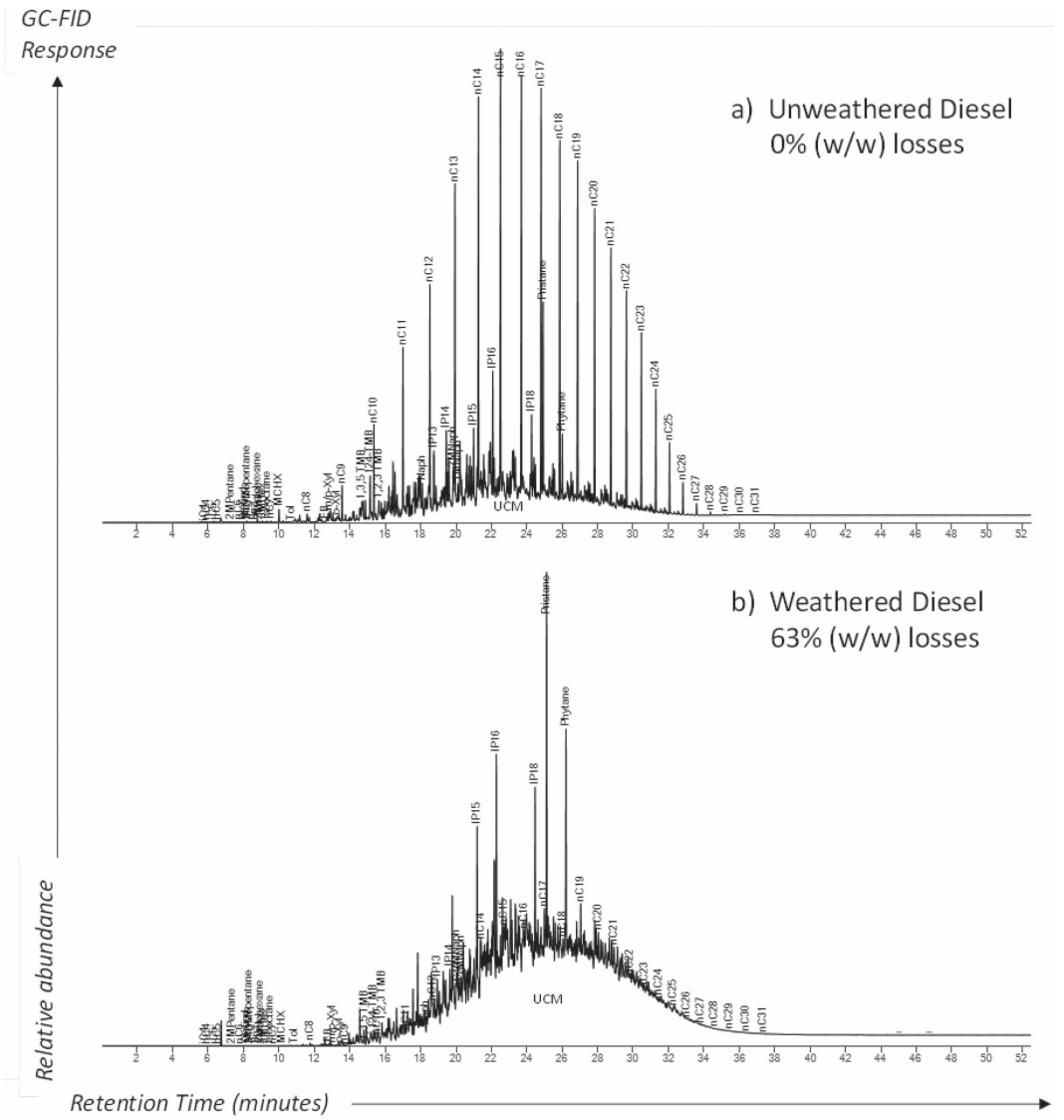


FIGURE 17.3 GC-FID analysis of a) unweathered diesel and b) weathered diesel. Benz: benzene, CHX: cyclohexane, Cx: straight or branched alkane containing x carbons, D: di, E: ethyl, i: iso, IP: isoprenoid, M: methyl, n: normal, Naph: naphthalene, P: pentane, TMB: trimethylbenzene, Tol: toluene, Xyl: xylene. (Bastow – unpublished data). Similarly to Figure 17.2 for crude oil, the unweathered diesel chromatogram has prominent peaks of individual components and a lower concentration and mass of unresolved complex mixture (UCM) whilst the weathered diesel has much less prominent peaks and a much-increased concentration and mass in its UCM. Analysis of relative peaks indicates that perhaps 63% of the mass of diesel has been removed due to weathering compared to the unweathered diesel sample.

17.2.2 Exposure Pathways

Figure 17.4 illustrates some key exposure pathways for human health and the environment for petroleum hydrocarbons which include (i) direct and indirect exposure to the hydrocarbons in contaminated soil in and around the point of release including for example dermal contact, ingestion of soil and plant uptake where release impacts are shallow or where soil has been excavated or reworked in some way (Pinedo et al., 2014); (ii) exposure or ingestion of dissolved hydrocarbons

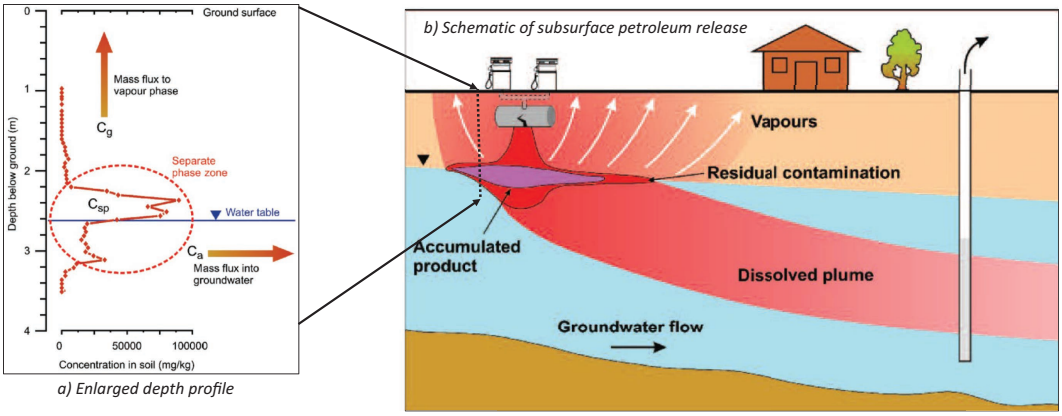


FIGURE 17.4 a) A depth profile from ground surface to below the water table showing a typical LNAPL soil concentration (here denoted C_{sp} in mg/kg). C_g represents hydrocarbons in the soil gas phase moving upwards in the soil profile above the LNAPL and C_a represents hydrocarbons dissolving into the groundwater aqueous phase. b) Schematic of a subsurface petroleum release showing some of the potential exposure pathways and the vertical dotted line denoting the effective equivalent position of the depth profile in a) from immediately below the water table and LNAPL up to ground surface. The 'accumulated product' and 'residual contamination' as labelled in b) and the 'separate phase zone' in a) are all LNAPL. (modified from Davis et al. 2006).

in a groundwater plume for example via pumping of contaminated groundwater for use (Wu et al., 2021) or via discharge of a plume to receiving waters such as rivers lakes and the ocean (Westbrook et al., 2005); and (iii) exposure to volatile hydrocarbons that might move through the vadose zone and potentially enter buildings at the ground surface (Luo, 2009; Patterson and Davis, 2009) or where structures are constructed into the subsurface such as underground carparks or basements.

For soils, direct dermal and ingestion exposures are seen to be less impacting than via soluble water pathways such as pumping contaminated groundwater for drinking purposes. Risk assessment is complicated by the definition of the pathway of exposure, likely exposure times, ingested volumes or concentrations, the age of persons or the type of ecological receptor being exposed. Additionally, the many compounds in petroleum and the soil condition such as its organic carbon content can also affect ecotoxicological measures for animals such as soil invertebrates (Gainer et al., 2019). Much has been done to incorporate standard parameters into risk evaluations (Pinedo et al., 2014) but overall, the risk from soil exposure is deemed low to moderate unless exposure is prolonged or the exposure is to pure selected components that might absorb into the skin (e.g., aromatic hydrocarbons) (Jakasa et al., 2015). The presence of petroleum hydrocarbons in soils can also adversely affect aesthetics including the release of odours, or visible impacts of oil/fuel staining of soils/plants or infrastructure.

For groundwater, near the LNAPL source, plume concentrations may be very high especially for a fresh release of gasoline that can contain a range of more soluble BTEX and other fractions compared to a fresh release of diesel for example (Guard et al., 1983; Lekmine et al., 2014). Also, in the direction of groundwater flow, plume concentrations would be expected to reduce via attenuation mechanisms (to be discussed later). The concentration in drinking water or a production well in the path of the plume (that may pose a risk) (e.g., Figure 17.4b) or upon discharge of a groundwater plume to a surface water body will depend strongly on the distance from such sources and the LNAPL age and type. For older weathered fuels or where fuels have less soluble components (e.g., diesel) dissolved plume concentrations will be lower (Vasudevan et al., 2016). Additionally, for a production well, the concentration in produced water will be volume- or flux-averaged from across the screened interval of the well and will depend on the volume and rate of groundwater pumped (Einarson, 2005). Likewise, the concentration in a receiving water body may be reduced due to mixing at the interface of the surface water body and groundwater discharge (Trefry et al., 2007).

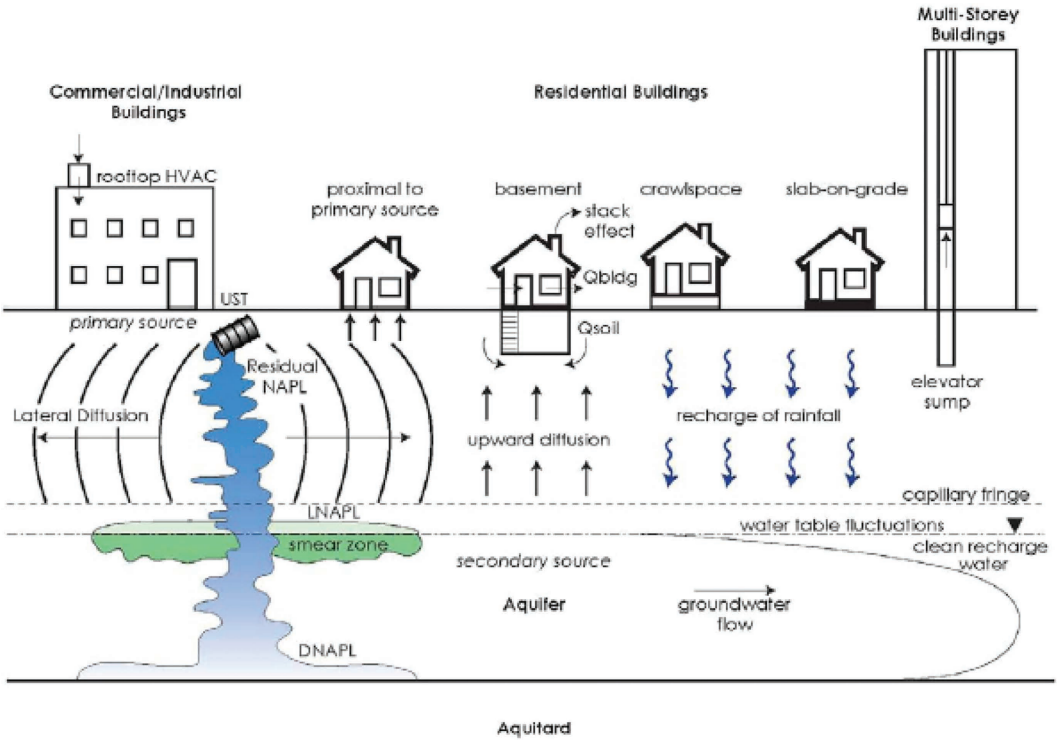


FIGURE 17.5 Conceptualisation of vapour interactions with a range of built structures (after Abreu and Ettinger, 2009). Vapours migrate in the soil away from a release of LNAPL in the soil or close to the water table. Vapours may migrate into different types of nearby buildings that have basements, are slab on ground, or have crawl spaces or into multistorey buildings that have lift shafts, or commercial buildings that have negative or positive pressures due to air conditioning or air movement controls.

The vapour exposure pathway is strongly focused on human health risks posed by inhalation of vapours that might migrate into a building's indoor air. For many years conservative (non-degrading) assessment of vapour behaviour was the default (e.g., Johnson and Ettinger, 1991) while the potential for biodegradation of petroleum vapours (compared to, say, chlorinated solvent vapours such as trichloroethene) was being investigated and quantified (Davis et al., 2005; DeVaull, 2007; Lahvis et al., 2013). A wide variety of built structures as in Figure 17.5 may have different risk profiles. Turczynowicz and Robinson (2001) developed a model of benzene vapour transport from a subsurface source into a building with a crawl space. They found that the dominant influencing parameter on the cumulative indoor dose was the air exchange within the crawl space rather than soil properties. Risk factors and vapour attenuation where buildings have basements have also been assessed (Abreu and Johnson, 2006). The most common assessments have been for slab-on-ground buildings (Knight and Davis, 2013). Petroleum vapour exposures are now seen as lower risk or less frequent, due to the very high potential for aerobic biodegradation due to oxygen availability (Davis et al., 2021), compared to chlorinated solvent sites (US EPA, 2012), although some chlorinated compounds such as vinyl chloride and 1,2 DCA have also been shown to degrade under aerobic conditions (Patterson et al., 2013).

17.2.3 Complexity that Challenges Risk Assessment

Whilst petroleum hydrocarbons degrade and attenuate, the many thousands of compounds that can be present in fuels and crude oils and the formation of new compounds due to weathering and biodegradation make a complete risk assessment challenging. For example, Figures 17.2 and 17.3 show that the UCM becomes enriched upon weathering with less distinguishable individual

hydrocarbons, but a growing proportion of compounds with complex and biodegradation resistant carbon skeletons that can form even more biodegradation-resistant metabolites or polar compounds (Lang et al., 2009). Interestingly, for weathered diesel, new compounds (often described as, e.g., partially oxidised chemicals, non-volatile organic compounds or polar compounds) are seen and produced over the period of weathering since the original diesel likely contained no polar compounds (Lang et al., 2009), and there is much interest in understanding the risk profile and persistence of such compounds. In contrast, the occurrence of polar compounds associated with crude oil releases can be difficult to assess because the polar compounds may be present in the parent crude oil or be generated during the weathering of crude oil, and in some cases can be due to entrained natural organic matter. These can present in GC analyses as a polar UCM and difficult to distinguish from petroleum-derived polar UCMs (Lang et al., 2009). Some studies have tried to quantify their presence, formation (Lang et al., 2009; Podgorski et al., 2021) and biodegradability (Bruckberger et al., 2018, 2019) and ultimately to understand their inherent risk (CRC CARE, 2017). The resilience and toxicological effects of some of these by-products/daughter compounds and where and under what conditions these are normally found remain to be fully resolved.

17.3 FATE AND DYNAMICS IN THE ENVIRONMENT

A focus here is the fate and behaviour of the LNAPL, groundwater and vapour phases.

17.3.1 LNAPL Behaviour

As described earlier (see Figure 17.4), LNAPL can migrate through the vadose zone and reside across the zone of water table fluctuation. LNAPL behaviour was well described by Tomlinson et al. (2017) who illustrated LNAPL transport and fate. A measure of the mobility of LNAPL in the subsurface is its transmissivity, which is assessed from the disturbance of the LNAPL thickness in a well (e.g., by bailing or pumping) and measuring the recovery rate back to the pre-disturbance LNAPL thickness (Gatsios et al., 2018). It is not only a measure of how fast an LNAPL plume might be migrating, but it is also a measure of how recoverable LNAPL is from the subsurface. Lenhard et al. (2017, 2018) reported a simple model to estimate what fraction of the LNAPL in the subsurface might be (i) mobile (perhaps recoverable), (ii) entrapped below the water table and (iii) at residual levels above the water level. The fraction of each is largely dictated by the aquifer and LNAPL properties, the water table variability and the thicknesses of NAPL observed in wells. Estimates of NAPL transmissivity were also an outcome from the model.

This links to the key risks posed by LNAPL in the subsurface, as to how much of the LNAPL mass is distributed above and below the water table, because this dictates how much of the LNAPL is exposed to the soil gas phase of the vadose zone and how much is in contact with groundwater flowing past (as in Figure 17.4a). Depending on the composition of the LNAPL this will then determine which compounds might partition to groundwater and create dissolved plumes and which might volatilise into the soil gas phase and create vapour plumes. Such partitioning also leads over time to potentially significant mass loss of the LNAPL, reducing its risk profile and mobility. For example, for gasoline, approximately 90% of the total mass might be soluble or volatile in the long term, compared to diesel which might have 50–70% that is soluble or volatile. Long-term time scales may be greater than 50 years, since many compounds are only very sparingly soluble.

The LNAPL mass resident above and below the liquid saturated zone will vary with water table fluctuations. LNAPL may move into and out of wells screened across the water table seasonally as water tables rise and fall – showing variable thicknesses in the absence of remediation or additional product releases (Steffy et al., 1995). This variability complicates the management of LNAPL in the subsurface; however, given enough data over time, relationships between LNAPL thicknesses in wells and water table elevations (so called diagnostic gauge plots) will show a consistent pattern. Deviations from the correlation can be used as an indicator of potential addition or removal of LNAPL in the subsurface (Atteia et al., 2019).

17.3.2 Groundwater Plumes

The longevity and extent of groundwater hydrocarbon plumes depend initially on the 'strength' of the source of the plume (Huntley and Beckett, 2002) – i.e., both the hydrocarbon contaminant concentration in the LNAPL or soil source and the net flux of dissolved components at the source entering the plume. Apart from the primary plume LNAPL source, secondary sources may occur due to back-diffusion from tight, low-conductivity or less mobile parts of aquifers and soils which can continue to feed groundwater plumes over long periods (Borden and Cha, 2021). Within a plume, hydrocarbon compounds migrate and dissipate due to advective groundwater flow, dispersion (due to variations in groundwater velocities), adsorption to the aquifer sediment (and possibly desorption), diffusion and degradation processes. Examples across all processes were investigated by Davis et al. (1999) with links to dissolution feeding the plume from the LNAPL gasoline residing across the water table. The *in situ* deuterated hydrocarbon tracer injection investigation of Thierrin et al. (1995) differentiated sorption processes from degradation. Ham et al. (2004) showed that for a bimolecular reaction of two chemical species dissolved in groundwater (e.g., benzene and sulfate) that the dispersion coefficient transverse to the groundwater flow direction largely controlled the length of the benzene plume in groundwater.

Mace et al. (1997) reviewed data from 605 hydrocarbon plume sites in Texas to estimate typical plume lengths. They found that three quarters of benzene plumes were less than 76 m (250 feet) long based on a 0.01 mg/L plume contour limit. Recently, O'Reilly et al. (2021) undertook a similar assessment across 529 sites, to estimate plume lengths (and other statistics) for dissolved gasoline, diesel, benzene and MTBE plumes. They showed that the median length of plumes was shorter and in the range 27–32 m (assuming screening concentrations of 0.10 mg/L for gasoline and diesel, and 0.005 mg/L for benzene and MTBE). In the upper 90th percentile, benzene plume lengths were 71 m and gasoline was 90 m. Whilst largely in agreement with the earlier study, these plume lengths are short compared to some plumes reported. For example, Davis et al. (1999) reported a benzene plume more than 420 m long when monitored intensively across several years (1991–1996). Over a more prolonged period, depletion of soluble materials in such LNAPL releases would likely lead to shorter plumes, as seen with shrinking plumes in groundwater.

17.3.3 Vapours

Individual petroleum compounds will partition from an LNAPL in soil into the soil gas phase based on the vapour pressure of each LNAPL component but also based on the molar fractions of the volatile compounds in the petroleum LNAPL. Additionally, methane vapours and carbon dioxide might be produced within the subsurface due to bioreactions (Garg et al., 2017). Transport of gases and vapours is most often dominated by diffusion in soil gas; however, if gas consumption and/or production or the rate of volatilisation from the LNAPL is high, advective or convective gas flows may eventuate (Amos and Mayer, 2006; Yao et al., 2015; Sookhak Lari et al., 2024b). This might also be induced via heat production from biodegradation reactions at depth, or via barometric or temperature effects at shallow depths near the ground surface. Since they are transported through the vadose zone, the vapours will partition into soil moisture and will also adsorb onto sorption sites on the soil matrix. These may be transient processes, during an initial phase of release, but would be expected to largely be in equilibrium after days to months depending on the depth of the vadose zone. For VOCs such as the BTEX, adsorption is commonly to organic carbon in the vadose zone (Breus and Mishchenko, 2006). Layering and soil moisture can influence movement. Davis et al. (2005) showed this for the effects of seasonal wetting and drying of a shallow finer-textured zone above a gasoline LNAPL (details are in Section 17.3.4).

Based on a review of data across field studies, four general categories of soil depth distributions of petroleum hydrocarbon vapours and associated gases were described by Roggemans et al. (2001). All implied that biodegradation played a role. DeVaull (2007) reviewed data across

petroleum vapour sites and created a model of their biodegradation by accommodating the role of natural organic matter in consuming oxygen that might otherwise have been available to consume hydrocarbon vapours. Davis et al. (2009a) proposed that an approximate instantaneous model of vapour and oxygen biodegradation was supported by available data across six sites. Based on these observations and as discussed in Section 17.2.2, a range of studies have sought to describe vapour risks in and around buildings. Knight and Davis (2013) and Davis et al. (2021) showed mathematically how vapour risks might be 'extinguished' based on the availability of oxygen to migrate under buildings with different building footprint sizes. Verginelli et al. (2016) additionally considered the diffusion of oxygen through the slab foundation and showed even greater reductions in risks from vapours due to enhanced biodegradation, if such an assumption was made. Despite apparently high biodegradation rates that mitigate risks, movement of vapours along preferential channels such as conduits, gas and water mains and drains can short-circuit the migration of vapours into buildings and as such may complicate assessments (Yao et al., 2017).

17.3.4 Transients

Figure 17.4 essentially depicts a scenario in which the LNAPL has traversed the vadose zone and been distributed across the water table zone, whereby groundwater and vapour plumes have become established and somewhat stable. Several different time scales of transient occurrences can alter this depiction.

- The initial stage of spill and release is quite dynamic (dependent on the volume released) with LNAPL imbibing into the pore space of the vadose zone, at the same time with vapours being emitted from the migrating LNAPL, with compounds dissolving into the soil moisture in the vadose zone and with potential sorption of compounds onto organic carbon in the vadose zone soil, all before reaching the water table. Sookhak Lari et al. (2016) modelled such a transient release phase for gasoline and depending on the duration of the release (20, 200 or 500 days) and the location of the release (at ground surface or deeper in the vadose zone) they showed strong depletion of volatile organic compounds over the initial period of release, and with a somewhat stable composition and resulting distribution after about 7 years. Over this same period the initiation of biodegradation of the petroleum components occurs.
- Seasonal transients due to changing rainfall can cause water table fluctuations, groundwater flow direction changes, and wetting and drying of the vadose zone that alter the fate and behaviour of petroleum LNAPL, groundwater plumes and vapours in soil gas.
  - LNAPL: As referenced earlier, water table fluctuations expose more or less LNAPL if the LNAPL is at non-mobile saturations across the zone of fluctuation. Steffy et al. (1995, 1998) explained some of these features of LNAPL movement, and Davis et al. (1993) showed the effects of such seasonal variations on the changed vertical depth of the LNAPL in contact with groundwater that acted as a source of soluble compounds to an extensive groundwater plume. For example (Figure 17.6), this altered the net flux of soluble LNAPL components into the resultant groundwater plume seasonally, with the integrated vertical mass of benzene more than doubling with a water table rise of 0.7 m over less than a month, at a location adjacent to the initial release of gasoline at the site (increasing from 12 g/m^2 on 10 June to 25 g/m^2 on 15 July – see MP10 on Figure 17.6).
  - Plumes: By monitoring a BTEX and naphthalene plume over 5 years Davis et al. (1993, 1999) showed strong changes in the plume flow direction induced by seasonal rainfall and groundwater influences. In multi-depth sampling wells placed in depth cross-sections across the plume, benzene concentrations varied seasonally from >1,000 µg/L reducing to zero everywhere over the aquifer depth at certain times of the year and

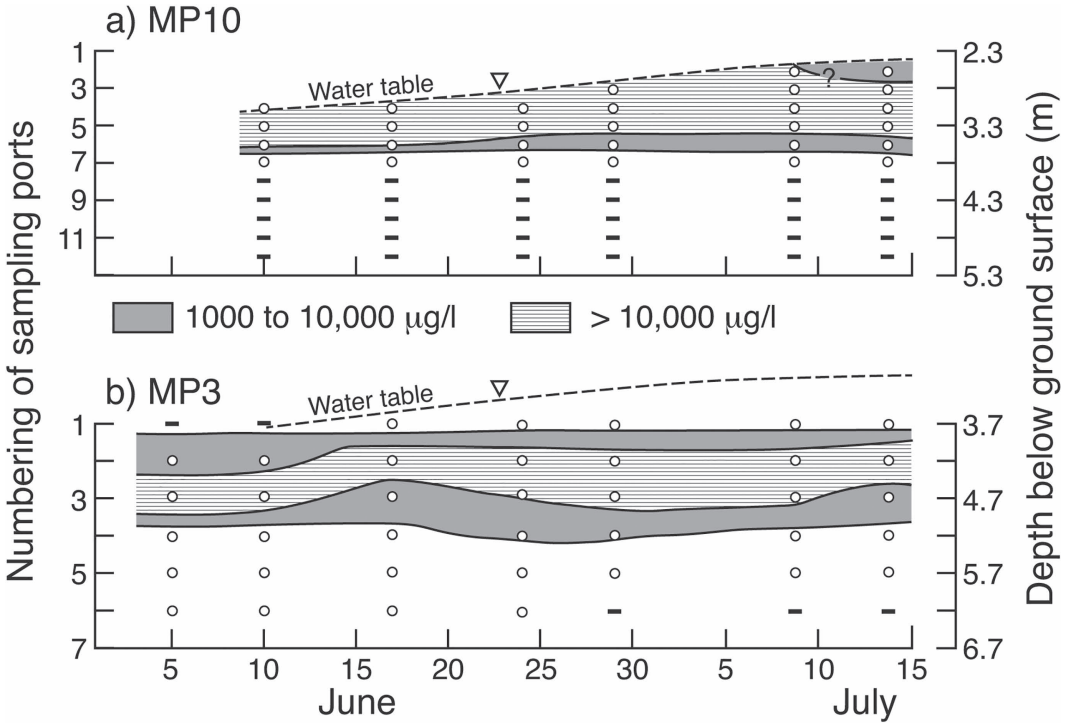


FIGURE 17.6 Changes in dissolved benzene concentrations over a period of water table increase in June-July for two multi-depth sampling boreholes MP10 and MP3. The dots indicate the depth of sampling ports where a sample was recovered. The dashes indicate a sample was not recovered. Whilst MP3 (60 m downgradient of the gasoline release point) showed little change over the period of water table rise, the shallowest ports available to be sampled at MP10 (adjacent to the gasoline release point) showed ever increasing thicknesses of the dissolved plume, reflecting increased total loadings to groundwater near to this source of the groundwater plume (after Davis et al., 1993).

returning to >1,000 μg/L at later times. Thierrin et al. (1995) confirmed such variations with short-term bromide and deuterated tracer injection experiments. To further quantify the linkages between such transients and plume behaviour Prommer et al. (2002) found that despite the changes of groundwater flow directions this did not significantly enhance plume dispersion (dilution) nor natural attenuation rates of the groundwater plume in the sand aquifer investigated. Such flow direction changes, however, mean that even long-term monitoring of a plume might be confused if the number of monitoring points is sparse.

- Vapours: Increased soil moisture in a vadose zone reduces the air-filled fraction of the pore space and as such decreases diffusion coefficients, leading to altered transport rates for soil gases and vapours. This was shown by Davis et al. (2005) to be the case for oxygen and gasoline vapours that were being consumed by biodegradation. At the end of winter, with high soil moisture in a shallow (<0.5 m deep) layer of the depth profile, gasoline vapours travelled up to the base of that shallow layer, and oxygen only penetrated down to that layer to be consumed. At the same site at the end of summer that same year, the soil profile was drier over the whole depth interval, and oxygen penetrated an additional 1.5 m into the vadose zone where vapours were biodegraded and were not transported to the shallow zone of the profile. Such dynamics might lead to intermittent access of vapours into buildings on such sites.

- Longer-term transients might be decades or longer, which can lead to (i) significant LNAPL compositional changes over time (as in Figures 17.2 and 17.3), (ii) lower LNAPL saturations because of mass loss over time or via spreading of NAPL mass leading to more immobile LNAPL, (iii) possibly stable or shrinking plumes in groundwater because of reduced soluble components in source LNAPL and (iv) probably leading to a LNAPL strongly depleted in volatile compounds and hence vapour plumes dissipating. Davis et al. (2022) reported data over 15–26 years for diesel and gasoline which show some of these features.

It is recognised too that even shorter-term transients might occur due to extreme, or daily events, tides or management actions, and these might require consideration of near continuous monitoring and sensing of processes (Davis et al., 2023) when risks or remedial tracking deem it necessary.

17.4 POLICY AND REGULATORY GUIDELINES

A range of organisation undertake research on TPH, as well as the development of guidance, standards, policy and regulation for assessment of TPH in the environment and defining risk. In Europe CONCAWE was formed in 1963 by oil companies to carry out research on environmental issues relevant to the oil industry. In the United States (US) of America the American Petroleum Institute (API) has a similar ambit. Guidance in each country is usually enacted by national and state or county environmental regulatory agencies (e.g., US EPA, UK EA). In Australia, absent of a national EPA, all state environmental regulatory agencies collaborated and agreed to establish and adopt national regulation, called the Assessment of Site Contamination National Environment Protection Measure (NEPM, 2013) which contains guidance on methods for characterisation of soil and groundwater and regulatory criteria specific to hydrocarbons in soils and groundwater and as vapours. In the US, a broader collective across regulators, industry and researchers, the Interstate Technology and Regulatory Council (ITRC), have collaborated to develop extensive training and research outputs applicable to petroleum hydrocarbons and their risks and management (ITRC, 2023).

Because of the multiple risk pathways and phases of petroleum hydrocarbons (LNAPL, soil, groundwater, vapours), investigation and measurement guidance are extensive and broad. Searches of web sites curated by the US EPA, and other countries' environmental agencies as well as organisations such as ITRC and CRC CARE reveal an extensive list. Numerous compendiums exist (Nielsen, 2005). Most countries have national standards for soil sampling (e.g., AS, 2005) for example – and most consider volatile and non-volatile compounds in soils. Davis et al. (2006) provided an overview of protocols and techniques for characterising sites with petroleum contamination, and subsequently provided guidance on the field assessment of vapours (Davis et al., 2009b). Davis et al. (2023) provided an overview of the history of site investigation approaches, and in that case looked ahead towards autonomous sensing of contaminants in soils and groundwater. They provided a case study example of a petroleum-contaminated site on which automated sensing of subsurface processes was undertaken.

Whilst many investigative approaches are now well established, some are still being developed for more rapid and improved quantification of subsurface processes. One example is laser-induced fluorescence (LIF) geo-probing that seeks to assess TPH/LNAPL depth profiles more rapidly across a petroleum-contaminated site, in place of more laborious coring and laboratory analysis of selected samples (García-Rincón et al., 2020). An example is in Figure 17.7 for diesel, crude oil and aviation gasoline locations in a sandy soil profile. Correlations between the cored and LIF depth profiles are reasonable, but a perfect overlay is not achieved. Potential loss of core and calibration of the LIF response to cored TPH/LNAPL profiles for different types of soil and petroleum hydrocarbons is an advancement being explored.

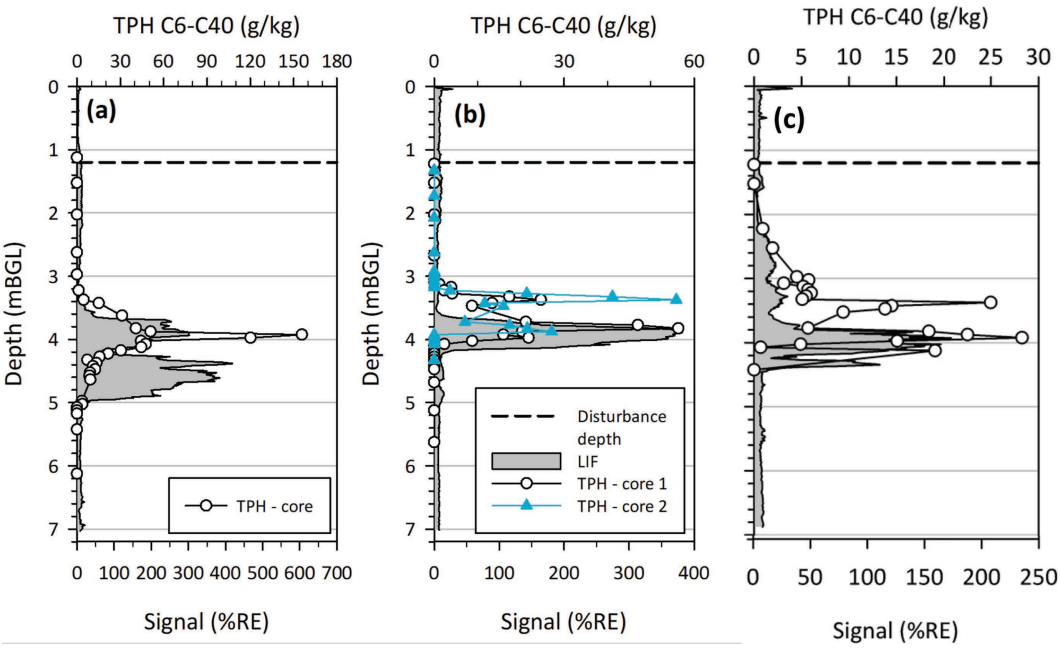


FIGURE 17.7 Laser induced fluorescence (LIF) depth profiles, along with LNAPL total petroleum hydrocarbon (TPH) determined from soil cores for (a) diesel with a TPH peak of about 150 g/kg at 4.2 m below ground and TPH over a vertical thickness of ~1.8 m, (b) two crude oil cores with a TPH peak of about 60 g/kg at 3.2 m and 3.8 m below ground and TPH over a vertical thickness of ~1.0 m, and (c) aviation gasoline with a TPH peak of about 27 g/kg at 3.8 m below ground and TPH over a vertical thickness of ~3 m (after Rayner et al., 2023).

For petroleum products and crude oil, the occurrence of biodegradation is well recognised. Biodegradation processes and rates have been investigated for decades (Atlas, 1981) and for groundwater plumes (Chapelle, 1999; Thierrin et al., 1993) outcomes from groundwater investigations are now formalised in national guidelines in the USA, Australia, and the United Kingdom – most often termed monitored natural attenuation (MNA) (ASTM, 1998; CRC CARE, 2019; UK EA, 2000). Criteria for acceptance of MNA for petroleum hydrocarbons in groundwater are (i) the need to demonstrate stable or shrinking plumes that are not crossing jurisdictional boundaries; (ii) that risks to human health and the environment are acceptable, e.g., from compounds such as benzene, and (iii) that data and information are of such a quality to enable an MNA assessment. Often MNA approval for management of a petroleum hydrocarbon plume also requires removal of the source of the plume, which is usually a LNAPL in the vadose zone or within the depth interval of the zone of water table fluctuation. Natural source zone depletion (NSZD) is increasingly being used to manage LNAPL in the subsurface where NSZD rates are deemed high enough compared to active source removal techniques (Smith et al., 2022). NSZD guidance has been developed in Australia over the last 3–5 years (CRC CARE, 2018; CRC CARE, 2020; Rayner et al., 2020). NSZD is revisited later when considering biodegradation in the context of holistic approaches to plume management.

17.5 REMEDIATION OPTIONS

Here we describe some remedial options for petroleum as LNAPL, and as a contaminant in soil and groundwater. A recent review by Ossai et al. (2020) compiled descriptions of a range of remedial options for soil and water. Not all options are described here. Some overarching principles and common factors are described initially.

17.5.1 Remediation Principles and Common Factors

Selection of remediation options and their appropriate design requires a good conceptual site model (CSM) which embodies data and understanding of site conditions, contaminant distributions in all phases and likely exposure pathways (Suthersan et al., 2017). Options can be assessed and evaluated in laboratory-based proof of concept experimentation and/or via modelling that can evaluate design options (Prommer et al., 2000) and potentially assist in optimising remedial engineering configurations and practice (Sookhak Lari et al., 2019a; Verardo et al., 2021).

Depending on risk drivers, remediation might be weighted to removal or truncation of the vapour intrusion pathways (e.g., Figure 17.4) where petroleum sources are shallow or close to the base of a building or might tackle the leading edge of a groundwater plume where it threatens to discharge to a surface water body or enter a pumping water supply well. In some circumstances the benefits of removal of the LNAPL source might be weighted highest. The remedial method and target might also be driven by the presence of known hazardous compounds such as benzene. All are factors in selection and design of remediation options.

Generic to many remediation strategies is bioremediation. Bioremediation is possible across each of the phases in which hydrocarbons can exist – including LNAPL, groundwater, soil and vapour. Some bioengineering approaches are described in this section. Much has been done to determine the appropriate conditions for biodegradation to occur and to be enhanced (Wiedemeier et al., 1999). Fundamental studies of the biodegradation of hydrocarbons under different electron acceptor conditions were conducted in the 1970–1990s. For example, Edwards and Grbić-Galić (1992) showed complete mineralisation of benzene in anaerobic groundwater, Patterson et al. (1993) showed biodegradation of benzene under aerobic conditions with limited biodegradation under nitrate-reducing conditions and Davis et al. (1999) showed soluble hydrocarbons such as toluene, ethylbenzene and xylenes degraded under sulfate-reducing conditions, but that benzene seemed to persist. Prommer et al. (1999a, 1999b) were one among the first to embed the range of electron acceptor–donor biodegradation processes into a reactive transport model of groundwater plume natural attenuation to assess the fate of petroleum components. The potential bioremediation of groundwater contaminants and lessons learnt over the last 40 years has been reviewed and reported recently (Davis, 2023). Additionally, much research has investigated the microbial communities responsible for biodegradation. Bruckberger et al. (2021) identified the variety of microbial communities associated with jet fuel, diesel and crude oil sites and for extremely weathered crude oil in Kuwait (Bruckberger et al., 2020). Murphy et al. (2022) also identified taxa that may be chemotactic toward petroleum compounds. These all play a role in natural biodegradation processes and may be targets for enhanced bioremediation of petroleum hydrocarbon contamination. Additionally, a number of other factors influence biodegradation, for example temperature changes (Ferguson et al., 2003).

17.5.2 LNAPL Recovery

Mobile LNAPL can be measured in wells but effective removal from the subsurface can be problematic. Recovery methods might include skimming of LNAPL, skimming combined with drawdown of the water table to enhance the hydraulic gradient and flow of LNAPL to pumping wells, and some combinations of skimming, water table drawdown and vacuum extraction. When done through one ‘straw’ inserted into a well this is termed multiphase extraction (Johnston and Trefry, 2009; Sookhak Lari et al., 2018a).

Some have questioned the value of LNAPL recovery at least in the short term. Huntley and Beckett (2002) reported that product recovery had little effect on plume size, except over many decades whereby plumes might shrink based on LNAPL mass removal. Sookhak Lari et al. (2018b) showed the potential end points of LNAPL recovery across a range of five aquifer property types, four remedial approaches, and two starting specific mass values for two LNAPL lateral dimensions (finite and

effectively infinite LNAPL plumes). They showed that the time to effectively achieve a technology endpoint (i.e., for product recovery to asymptote to a minimum) varied from 2 to 6 years and recovered LNAPL in the liquid phase varied from 5% to 53% of the initial mass. To assess risks further, they also quantified LNAPL mass extracted as vapour. Sookhak Lari et al. (2020) summarised the learnings on LNAPL recoverability across a program of modelling and field investigations. Sookhak Lari et al. (2021) also showed the value of a rapid response (compared to a delay) and the importance of the proximity of the location of LNAPL product recovery wells for an acute release of LNAPL product. For example, immediate remediation with a recovery well located at the centre of the LNAPL plume was estimated to recover 190 times more LNAPL mass than a one-month delay through a well 15 m away from the centre of the LNAPL plume.

17.5.3 Soil Remediation

Remediation of soil might focus on what's achievable *in situ* verses excavated or ex-situ soils. Additionally, the risks posed by hydrocarbon contaminated soils might be due to deeper LNAPL resident in the soil that is feeding a groundwater plume, in which case remediation may treat or partially treat both soil and groundwater – for example using air injection strategies such as bioventing, sparging, biosparging or other techniques, recognising that air sparging would normally be applied to groundwater plumes.

17.5.3.1 Ex-Situ Remediation Approaches

Kuppusamy et al. (2017) provided a review of remediation approaches for PAHs in soil and technological constraints. They considered thermal treatments, soil/solvent washing, chemical oxidation, biotreatment and other options. PAHs in soil can be particularly recalcitrant and difficult to remediate. PAHs are in most petroleum products; however, the predominant point source of PAHs in the environment comes from heavy products (coal tars, bunker oils) and from dispersed sources resulting from fuel combustion (heating and vehicle exhaust). However, the remediation approaches considered may also be more generally relevant beyond PAHs and have been applied to petroleum hydrocarbons in soils. For example, for thermal techniques, Gimžauskaitė et al. (2023) assessed the potential of thermal water vapour and air plasmas to remediate soil contaminated with diesel. They demonstrated that 99.9% contaminant removal was achieved but after significant energy input and with changes to soil natural organic carbon. A more passive and perhaps sustainable example is the use of organic amendments such as waste and other organic materials (e.g., crop residues, biosolids) to mitigate petroleum hydrocarbons in soils (Hoang et al., 2021). Competing processes and factors such as sorption-inducing reduced bioavailability, desorption due to enzymatic bioprocesses in organic material and sequestration and biodegradation all play a role. Complications might also arise during extraction and chemical analysis when additional organic phases are present.

A key to choosing a remedial method is how cost-effective technologies can be. For example, Lukatelich (1999) showed that landfarming, biopiling and composting were all cost-effective treatment techniques for the treatment of oily sludges and hydrocarbon-impacted soils compared to engineered alternatives such as thermal desorption, fixation or stabilisation. In particular, he compared the use of biopiles, land farming and composting as methods for the aerobic biodegradation of petroleum hydrocarbons contained in oily sludges and soils. He determined average degradation rates to be 42 mg/kg/day for landfarming, 20 mg/kg/day for biopiling and 450 mg/kg/day for composting. Depletion of PAHs in biopiles was very effective with some PAHs reduced to non-detectable levels within 300 days, while most showed at least 50% depletion.

Biopiles as an example of soil biotreatment is described here with associated data in Figure 17.8. Biopile remediation of petroleum-impacted soils has been developed and deployed for some time (Huesemann and Truex, 1996). Biopiles consist of hydrocarbon-impacted soil engineered as 1–2 m high soil piles onto a reusable pad containing pipes for aerating the soil piles, and usually with a water and/or nutrient reticulation system applied from the top surface. Figure 17.8 depicts

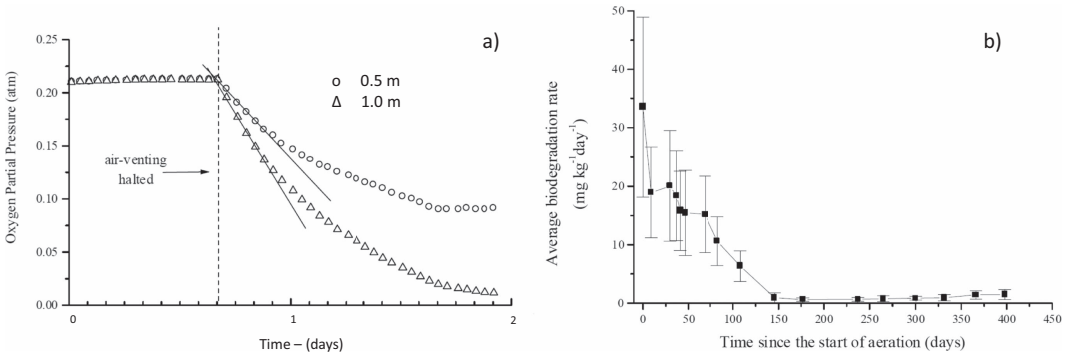


FIGURE 17.8 Data from hydrocarbon contaminated soil biopile remediation. a) Shows oxygen concentrations as measured on oxygen probes (Patterson and Davis, 2008) buried in a biopile at depths of 0.5 m and 1.0 m below the top of the pile, showing an aeration phase from 0 to 16 hrs, and the decrease in oxygen concentration over the following 32 hrs due to oxygen consumption by biodegradation once aeration had ceased at 16 hrs. The lines are linear fits to the initial oxygen depletion stage to calculate zero-order consumption rates. b) Biodegradation rates determined in the biopile from the periodic halting of aeration as shown in a), over approximately 400 days. Biodegradation rate estimates are shown to decrease from 20–50 mg/kg/day to 1–2 mg/kg/day after approximately 150 days of periodic aeration.

biodegradation data from one such biopile, which can be used to assess when active aeration might be halted. Using a 'respirometry' method as in Figure 17.8a (see Davis et al., 1998) to calculate the hydrocarbon biodegradation rate from oxygen consumption, rates can be determined periodically over the implementation. Figure 17.8b shows that degradation rates decreased from high initial average rates of approximately 33 mg/kg/day to a low (< 1 mg/kg/day) asymptotic rate after about 180 days. It indicates that readily degradable hydrocarbons are depleted within 150–180 days and that operationally a new biopile of hydrocarbon-impacted soil might be established on the pad for remediation beyond this time.

17.5.3.2 *In Situ* Remediation Approaches

Soil vapour extraction (SVE) can be used to remove volatile hydrocarbons from the vadose zone. SVE is implemented by extraction of soil gas from wells installed with screens above or within the hydrocarbon-impacted zone (Suthersan, 1999). Readily volatile hydrocarbons will partition to the air phase and move with the air when a vacuum is applied. SVE can have a reasonably large radius of influence and can also enhance biodegradation by inducing the movement into the soil vadose zone of atmospheric air containing oxygen. The extraction efficiency is influenced by a range of factors (Albergaria et al., 2012). Often the hydrocarbon mass removed in extracted air will asymptote to lower mass removal rates once a significant mass of volatile compounds is depleted from the soil/LNAPL.

Air sparging (injection of air below the water table) can augment the removal of LNAPL jointly with SVE. Johnston et al. (2002) reported on a trial for gasoline LNAPL, in which they sparged 2.9 m below the LNAPL zone resident across the water table and showed initially 3–4 times greater recovery of LNAPL mass than SVE alone with a decrease to 1.9 times after a month of sparging that removed nearly 700 kg of LNAPL. It also led to significant depletion of volatile hydrocarbon components from the LNAPL local to the sparging well. Some of the volatiles such as benzene, can be dominant risk drivers.

Bioventing is similar to SVE, except commonly air is injected into or extracted from the soil vadose zone (above the water table) to stimulate biodegradation rather than volatilisation (Lee and Swindoll, 1993). Davis et al. (2013) undertook the bioventing remediation of a highly weathered diesel NAPL residing across the water table and used the oxygen consumption technique as shown in

Figure 17.8a to quantify *in situ* biodegradation rates. Volatile mass loss was expected to be minimal given the lack of volatiles in diesel and its weathered status. They showed, with nutrient addition and induced water table drawdown, bioventing degradation rates could be as high as 100 mg/kg/day; with aeration only, rates were 20–30 mg/kg/day. Over a 14-month field trial, in some locations, soil core petroleum concentrations reduced from peak concentrations of 150,000 mg/kg to below 1,000 mg/kg which is often recommended as a soil clean-up criterion (also see Davis, 2023).

Biosparging is another variant of air sparging (below the water table) using periodic gas sparging compared to continuous or high-pressure flows to maximise biodegradation of petroleum compounds in the soil vadose zone, even for LNAPL with high volatile fractions. For example, Johnston et al. (2011) reported on the biosparging of gasoline, successfully showing enhanced biodegradation in the soil above the LNAPL zone while limiting fugitive volatile emissions from the subsurface, despite VOC concentrations up to 160,000 µg/L being generated from the gasoline LNAPL. Johnston et al. (2008) conducted a similar trial for diesel showing induced changes to LNAPL compositions for a distance of 5 m from one biosparging well, whilst biodegrading all VOC emissions in the vadose zone.

Vidonish et al. (2016) undertook a review of thermal treatment options for petroleum hydrocarbon-impacted soils, with a view to sustainability. As mentioned earlier, a range of thermal treatments can be effective for ex-situ and *in situ* soils especially given the nature of petroleum compounds, for example hot air injection, steam injection, electrical resistance heating and other electrochemical techniques. Hot air injection increases the phase-change and diffusion rates of organic contaminants, enhancing volatilisation allowing SVE; steam stripping induces the flow and mobilisation of contaminant liquids ahead of the steam condensation front; and electrical resistance heating can be effective for low-permeability soils such as clays so otherwise trapped water and contaminants are mobilised and sometimes vaporised to allow extraction. Streche et al. (2018) determined the cost effectiveness of an electrochemical technique; direct current technologies to decontaminate petroleum contaminated soils, which can enhance several processes including transport, mobilisation, concentration and electro-oxidation according to relevant redox reactions. *In situ* smouldering and combustion has also been proposed, offering self-sustaining destruction of petroleum in *in situ* soils (Switzer et al., 2009). It can achieve a high degree of mass destruction (e.g., > 90%) *in situ* and very high temperatures (>500°C) that enhances complete treatment. Uptake of the technology has not been rapid, but application to material contaminated with per- and poly-fluoroalkyl substances has additionally been investigated (Duchesne et al., 2020).

17.5.4 Groundwater Remediation

Groundwater remediation is often focused on MNA (see earlier discussion); however a range of other strategies can be applied and may be warranted. These include enhanced bioremediation, air sparging, injection of liquid or solid oxidants or permeable reactive barriers.

The bioremediation of dissolved petroleum plumes is well researched and applied (Chapelle, 1999). Based on fundamental understanding of the biodegradation of petroleum compounds as described earlier (e.g., Edwards and Grbić-Galić, 1992), the requisite redox conditions and electron acceptors needed for biodegradation have been well defined (Davis, 2023; Wiedemeier et al., 1999). Microorganisms typically utilise oxygen first if available, then nitrate, then manganese and iron oxides resident on aquifer sediments within the groundwater plume, then sulfate, and then methanogenesis might be induced. Some can be concurrent where aquifer variability and micro-niches allow. If groundwater or the aquifer sediments are depleted in these electron acceptors, enhanced bioremediation can be induced by adding such acceptors. Delivery of such amendments into groundwater is not always straightforward given the laminar nature of groundwater flow (Davis, 2023). In part to address this, addition of dissolved electron acceptors (nitrate, oxygenated water, sulphate) and/or nutrients have been injected in pulses (Devlin and Barker, 1996; Roberts et al., 1991) leading to successful enhanced biodegradation. Pulsed injection avoids undue displacement of the plume

away from the injection location but also creates a greater contact surface area of the injectant and the dissolved hydrocarbon within the plume, compared to continuous injection of amendments.

As previously mentioned, air sparging of groundwater has been widely researched and adopted. The key to successful deployment is the radius of influence of air injection below the water table, and the relative fractions that are volatilised vs biodegraded. If the radius of influence is small and there is a large mass of volatile hydrocarbons to capture (e.g., via SVE) and treat, then air sparging becomes less cost-effective. Johnston et al. (1998) investigated these key attributes for a dissolved gasoline plume in a sand aquifer. They found that most organics were removed in 3 days of sparging thereby remediating the groundwater local to air injection. The majority of the mass volatilised, with the mass biodegraded being at least an order of magnitude lower. Observations also suggested that the injected air moved laterally 1 m but not 2 m, indicating for the sand aquifer that air injection induced largely upward movement of air local to the sparge point, implying that close spacing between air injection wells would be warranted to treat all areas of a dissolved plume.

Permeable reactive barriers (PRBs) can be quite effective in remediating groundwater (Davis and Patterson, 2003; Singh et al., 2023) but are restricted to zones of an aquifer where feasible (e.g., not too deep to the base of the aquifer), where a plume might threaten to move offsite or discharge to an ecosystem (Westbrook et al., 2005), or perhaps close to the source of a plume to cut off the source from a dissolved plume. A number of researchers trialed the addition of electron acceptors into PRBs. Bianchi-Mosquera et al. (1994) sought to enhance the degradation of dissolved benzene and toluene using solid oxygen-releasing compounds whilst Kao and Borden (1997) reported on the effectiveness of a dual barrier system – the first adding nitrate as an electron acceptor to degrade toluene, ethylbenzene and xylene (TEX) and the second being a peat layer to denitrify residual nitrate and sorb any residual TEX. They found in preliminary tests that benzene was not readily biodegraded under nitrate-reducing conditions. Mumford et al. (2015) evaluated the need for three PRB gates for treating diesel located in the Antarctic under freeze/thaw cycles of release. The first gate focused on controlled nutrient release to enhance biodegradation, the second focused on hydrocarbon and nutrient sorption and hydrocarbon degradation (including use of granular activated carbon and zeolite), and the third focused on the capture of excess nutrients. Whilst hydrocarbon mass removal was observed, the outcomes were variable across five options deployed at field scale. Sorption to organic substrates emplaced in PRBs has also been trialed especially for PAHs and semi-volatile hydrocarbons in groundwater that may emanate from manufactured gas plant sites (Birke et al., 2003). Patterson et al. (2002) also explored sorption and stripping of VOCs and PAHs from groundwater using woven polymer mats.

17.5.5 Natural Source Zone Depletion (NSZD)

NSZD refers to all processes across the soil profile and groundwater acting on a petroleum LNAPL source that leads to mass depletion and is being increasingly used and accepted as a holistic management option (CRC CARE, 2020). It is strongly focused on the vadose zone since biodegradation rates in that zone were estimated to be many times that observed in groundwater where MNA investigations had occurred (Garg et al., 2017; Johnson et al., 2006). Rates are commonly estimated either by measuring carbon dioxide and methane production, oxygen and methane consumption, temperature increases, LNAPL compositional changes and/or LNAPL mass reductions (Smith et al., 2022). A range of techniques have been described in CRC CARE (2018). Recently, Rayner et al. (2024) reported on side-by-side comparison of NSZD rate estimation methods for four fuel types (gasoline, diesel, crude oil and aviation gasoline) and showed the importance of fuel composition and weathering in influencing overall LNAPL–NSZD rates. Applicability of the technique in managing sites with remaining LNAPL relies on risks being assessed and remediated, and that NSZD rates might be deemed adequate and perhaps larger than rates achievable via conventional engineered recovery of LNAPL via well extraction. This was shown to be the case by Rayner et al. (2020) for six sites in Australia. Additionally, of interest to industry and regulators is the longevity of NSZD rates and

how they might change over decades-long periods of mass depletion when LNAPL compositions may change like in Figures 17.2 and 17.3. Davis et al. (2022) showed reductions in NSZD rates for gasoline and diesel over 15–26 years. For longer periods modelling platforms are being established to enable NSZD rates to be estimated over many decades (Sookhak Lari et al., 2019b, 2022). The challenge for such models is to mimic, for example, the weathering seen in Figures 17.2 and 17.3 whereby fingerprinting of the hydrocarbon changes suggests as much as 63% of the original mass of diesel has been depleted. Future challenges for NSZD were recently articulated along with research needs (Sookhak Lari et al., 2025). Research is continuing to tie actual mass losses measured from core analyses to such NSZD rates over time. Additionally, research is needed to determine the point at which engineered recovery might cease relative to NSZD rates, given NSZD effectively commences as soon as a fuel or crude oil release occurs.

17.6 CONCLUDING REMARKS

Much is known regarding petroleum hydrocarbons based on over 50 years of research and investigations. The complexity of many thousands of compounds that are present in some petroleum, different petroleum fuel types, and with ongoing changes from weathering and the formation of new compounds over time such as polar compounds, make petroleum releases to the environment a challenge for the future. Investigation and analytical techniques have become somewhat standardised, yet there are still issues characterising and distinguishing the UCMs left from weathered petroleum products from UCMs derived from natural organic matter in GC analyses as well as adequate measurement and sensing in appropriate phases (LNAPL, soil, groundwater, soil gas) and at appropriate time intervals. Site investigations rarely have rapid turnaround times in data and interpretation, let alone capacity for real-time decision making for managing petroleum-impacted sites. Advances have been made (Davis, 2023, Davis et al., 2023) but more research and development is required to optimise resource use in treating legacy sites and in tackling the prevention of contamination of subsurface environments from occurring in the first place.

ACKNOWLEDGEMENTS

Current and former colleagues at BP, Dr Rod Lukatelich and Andrew King are thanked for supporting long-term research undertaken by the authors. Additionally, Colin Johnston and Bradley Patterson are acknowledged for their contributions to petroleum hydrocarbon research discussion and activities over many years.

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