GRAIN SIZE, NUTRIENTS AND HEAVY METALS ANALYSIS TO EVALUATE NATURAL *VS* ANTHROPOGENIC SOURCES IN THE SEA ENVIRONMENT (NAPLES BAY, EASTERN TYRRHENIAN SEA)

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Abstract – The study area is located in the Naples Bay offshore the Sarno River plain, this latter is affected by metals contamination as a result of the geogenic nature and the outflow of industrial waste and the high demographic pressure. Grain size distribution coupled with organic matter, nutrients and metals content were analysed through a statistical approach in order to explore how the onshore documented contamination affect the offshore counterpart. The individuation of areas with different contamination pattern has been performed using statistical techniques recognize the potential independent factors governing specific metal trends. Aiming at assessing the natural vs anthropogenic origin of the contaminant a comparison with the published data analysis conducted onshore in the Sarno Plain was carried out. Results showed that the submarine area could be divided in four zones: the first zone offshore Torre Annunziata, with physical and geochemical association mainly linked to the volcanic rocks thus with metal pattern of natural origin; the second and third zones, which contaminant association from the Sarno Plain are anthropogenic in origin, whereas the fourth zone, characterized by low rate of contamination, is mainly influenced by sediment from Sorrento Peninsula. The results show that the river should account as one of the main contribution sources of anthropogenic contaminants.

Introduction

Over the past century, the rapid industrialization has been responsible of the discharge of heavy metals into coastal environments through river input in this way the offshore areas in front of high populated coast have been affected by both natural and anthropogenic inputs.

Grain-size parameters can intensively reflect local sedimentary environments, such as hydrodynamic conditions, sediment transport, subsidence, and redistribution processes. Whereas the natural geogenic contaminants are linked to the outcropping rocks in the onshore and offshore source areas, on the contrary the contaminants from the human activities are generated onshore and transported and deposited in the sea together the clastic sediments. Sediments are multi-phase solids containing silicates, carbonates, hydroxides/oxides, sulfates and organic substances as major components [25] that for their mineralogic features can influence the distribution of metals. The sea floor sediments are the result of the interaction

Referee List (DOI 10.36253/fup_referee_list)
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between mineral particles and organic matter during the transport of the suspended material/sediment from the catchment area to the bottom-sea, where sediment accumulate [7]. The Sarno river plain is affected by an extreme environmental pollution as a result of the outflow of industrial waste [3 and bibliography therein]. Consequently, the area of the Naples Bay is subjected to the influence by sediment loads derived from the Sarno River. In the in the present study, the distribution of nine metals (Hg, Cd, As, Cr, Ni, Cu, Zn, Pb, Fe and Mn) is investigated coupled with organic matter, nutrient content and granulometry features, aiming to assess metal contamination influence of the Sarno river in the submarine area. A dataset of the sampling campaign referring to 91 sites located in the receiving basin of the Sarno River in the Gulf of Naples, was exploited. The study gets through the following steps *i)* investigation of the current grain size, nutrients (TOC, TN, TP) and heavy metal; *ii)* statistical analysis to extract information on sediment transport path following the TOC and grain-size trend; *iii)* distinguishing pollution sources and recognizing their origin (natural vs anthropogenic) by coupling metals pattern with the spatial grain size and organic matter distribution.

Geological framework

The Southeast Naples Bay is characterized by a relatively wide continental shelf environment with sediment supply from the Vesuvian slope, the Sarno river and Sorrento Peninsula relief (Fig. 1).

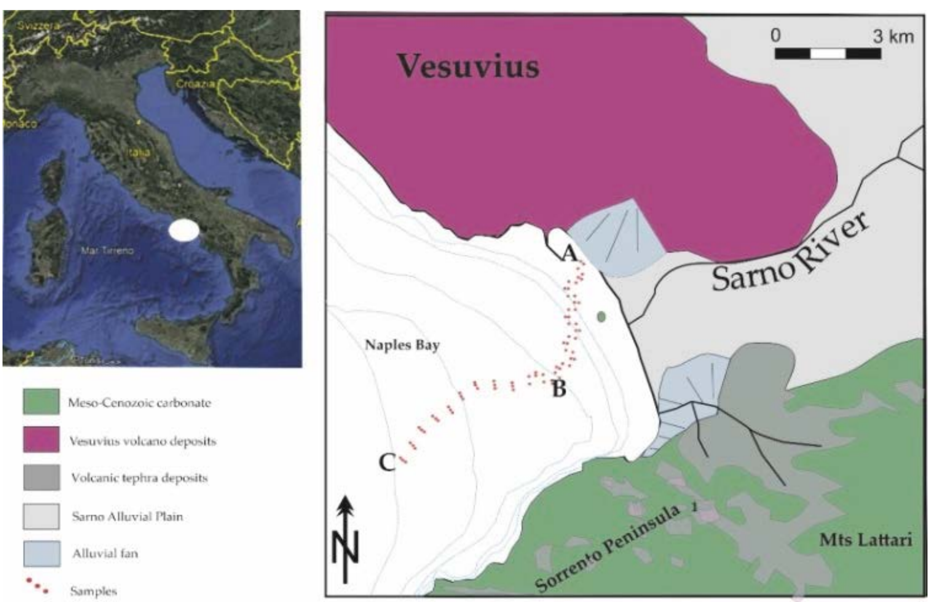

Figure 1 – Location maps of the study area.

The Vesuvius volcano grew up to around 2000 m in height over a time span of ca. 20 ky. The main effusive activity was interrupted around 22 ky BP by the trachytic Pomici di Base Plinian eruption [20], responsible of the formation of the breached crater and the deposition of a large debris avalanche in the submarine counterpart [17, 19]. The deposits of the AD 79 Pompeii Plinian eruption are represented by a widely dispersed pumice fallout and by numerous pyroclastic flow deposits arrived offshore Ercolano [18]. The AD 1631 eruption was followed by the last period of effusive activity (1638–1944). The Sarno river basin is an alluvial plain, that extend for about 440 km^2 (Fig. 1). Much of the coastal zone of the basin and many inland areas are strongly urbanized and industrialized is used for very intensive agriculture, mainly consisting of field horticulture, orchards, vineyards, chestnuts and greenhouse horticulture and floriculture. The upper Sarno valley is largely affected by the presence of numerous leather tanneries, several chemical-pharmaceutical, engineering and manufacturing industries [9]. The Sorrento Peninsula bounding the southern margin of the Naples bay, it is characterized by a thick meso-cenozoic succession of limestone and dolomite covered by clastic sediments. These latter are made up of clastic deposits of Miocenic succession in the western part of the Peninsula and by tephra deposits from Vesuvius and Campi Flegrei that cover the carbonatic relief (Fig.1).

A geochemical prospect was conducted in the Sarno Plain by several authors [e.g. 1, 5, 2, 9, 3]. In particular [3] performed a factor analysis to assess the nature and the extent of contamination sources for the river sediments. The results individuate two main environmental areas: one contaminated mainly by metals of natural origin, corresponding to the hilly and mountain areas; and another moderately to very highly contaminated by metals of anthropogenic sources, corresponding to the economically developed areas in the plain and distinguishing between agricultural, tannery, traffic, and other sources.

Data set and Methodology

A total of 91 sediment samples have been collected by van Veen grab along a transect (long about 9 km) offshore the Sarno Plain coast of (Fig. 1). In particular, surface sediment samples were analyzed for grain size, organic matter, nutrients (TOC, TN, TP) and heavy metals (Hg, Cd, As, Cr, Ni, Cu, Zn, Pb, Fe and Mn). Standardized procedures for sampling, transport and handling sediments were adopted. A first aliquot of sediments sample were stored in clean polyethylene bags and frozen at +4/+6 °C for the physical analyses, whereas a second aliquot was stored in decontaminated HDPE (High-Density Polyethylene) containers at -18°/-25 °C for the chemical analyses.

The granulometric features of sediments were determined with Laser diffraction granulometry (Laser Particle-Size Analyzer). Samples for grain size analysis were treated with H_2O_2 solution, aiming at removing organic constituents and support deflocculating, then washed and dried at 40 °C, and analyzed following the ICRAM Manual Procedure [12]. Trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) (EPA Method 6020) after strong acid digestion (HF + HNO3) of sediments in a microwave oven (EPA Method 3052).

TOC and TN were determined according to ICRAM Method [12], whereas TP content was assessed following APAT IRSA-CNR 4110 [4] spectrophotometric method using a Varian Cary 50 spectrometer.

SIMCA 17.01 Program (17, MKS Umetrics AB, Sweden) was used to perform multivariate statistical analyses [10]. The dataset is constituted by 91 sites and 21 variables referring to the absolute values of concentration of As, Cd, Cr_{tot}, Cu, Hg, Ni, Pb, Zn, Fe and Mn, the total organic carbon (TOC), total nitrogen (TN), total phosphorous (TP), including also the percentage of the Wentworth size classes for granulometry. Prior to statistical analysis, log-transformation was performed on variables as well as scaling to unit-variance [24]. On the other hand, STATISTICA 10.0 was used to perform the ANOVA analysis aming to investigate significant differences in metal concentration according to different factors (organic matter and granulometry). The experimental design incorporated independent factor "granulometry" setting up five (5) classes: “silty” class that includes samples with a predominance of the fine fraction (clay+silt) content (more than 55 %); the “sandy” class that includes samples with a predominance of sand fraction (more than 55 %); “mix” class accounting for the remaining cases and other two classes named “silty-coarse” and “sandy-coarse” that include samples in which the “coarse” fraction display content from 2-10 % within the two main classes group ("silty" and "sandy"). As for the independent factor "Organic matter content" expressed in term of TOC, three different range-concentrations were defined: “low TOC”, from 0 to 1 %; “medium TOC”, from 1-3 %; and “high TOC”, more than 3 %.

Finally, regression analyses applying Pearson Correlation were conducted to analyze the correlation between Metal content and the TOC content or granulometry fractions.

Results and Discussion

The study area displays different sediment features in terms of grain size (Fig. 2) with a prevalence of sandy and silty fraction ranging in the intervals of 7÷96 %w and 3÷72 %w respectively.

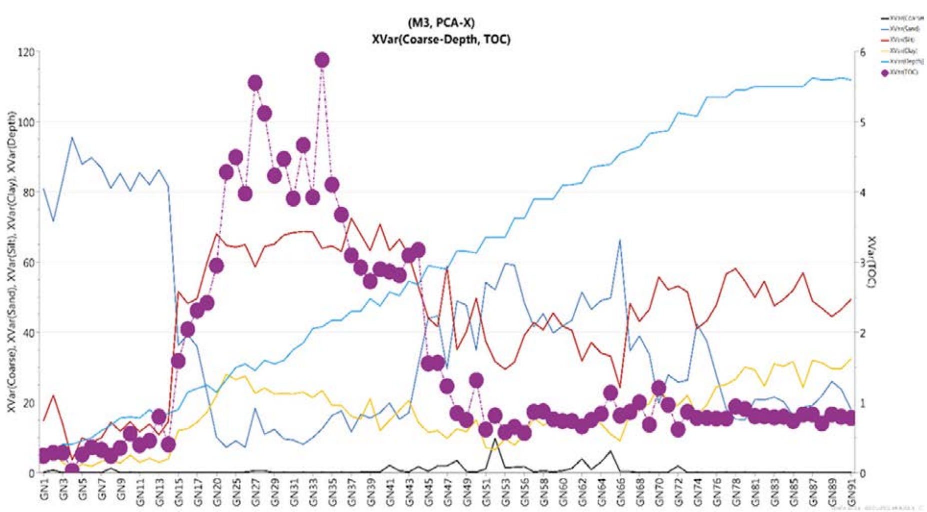

Figure 2 – Comparison between grain size, TOC percentages and water depth in the sediment samples.

On the base of the granulometric distribution, it is possible to recognize four sectors. Sediments, collected between the samples GN1 – GN17 in correspondence of Torre Annunziata (TA) shoreline, are mainly composed of sand (up to 96 W%) and by a minor amount of silty and clay fraction. The second sector, between the samples GN18 - GN42-43, of the track displays a heterogeneous granulometric content with a silty fraction that represents the main component reaching more than 60 %. The third sector, between the samples GN44 – GN71, displays sand and silt that are represented with a similar percentage between 30 % and 60 %, whereas the clay is below the 20%, furthermore, it is important to note the presence of gravel between the 0 and 10 %. Finally, the fourth sector, between the samples GN72-GN91, at a water depth of more than 100 m increase the presence of clay that reach the 30 % and of the silt until the 60 %, whereas decrease the sand around the 20 %.

On the other side, the organic matter (expressed in terms of TOC) spans an unusually large range from 0.01 up to 5.88 %w. The highest concentrations of TOC are displayed offshore the Sarno alluvial plain where TOC reached 5.88 %w. This value is higher respect to that detected in an adjacent area, corresponding offshore Naples, ranging between 0.05 % and 4 % [22]. As can be seen from the plot of TOC content in the plot of the grain size curve (Fig. 2), a "bell" of high TOC area is displayed in the second sector (B). On the other side, the sector A displays low TOC content, whereas the third and fourth sectors (C and D) show a medium TOC content (lower than 3 %).

A positive correlation of the TOC concentration versus the finest grain size fractions (clay and/or silt) is also verified, as can be inferred by the Pearson coefficients TOC *vs* fine grain size (clay and silt) (Table S2). The close association of the two components can be explained by (1) the capacity of the finest particles to hinder the diffusion of the oxygen into the sediments, that induce the preservation of organic matter, and (2) the adsorption of organic particles onto the charged surfaces of the clay minerals [16,11, 8, 15].

The distribution of the heavy metals is represented through the box and whisker plots in Figure 3 reporting a summary of the basic statistics of the concentrations of trace metals analyzed in the study area.

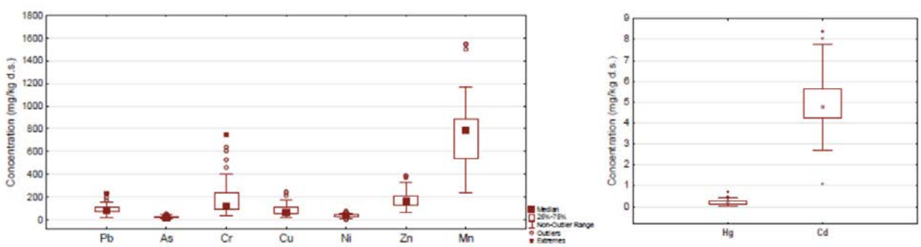

Figure 3 – The box and whisker plot for Pb, As, Cr, Cu, Ni, Zn, Mn and for Hg, Cd.

ANOVA analysis

Aiming at understanding the influence of organic matter content, one-way ANOVA has been performed using as independent factor the TOC content, this approach highlighted the presence of two groups of metals displaying a distinguished trend (Fig. 4): Cr, Cd, Cu, Pb and Zn concentrations increase with increasing of TOC content, while for Fe, Mn, As and Ni a decrease concentration is logged with increasing of TOC content. An irregular trend is displayed by Hg, albeit to a less extent the average concentration of As and Ni within the three classes-groups (low TOC content, high and medium).

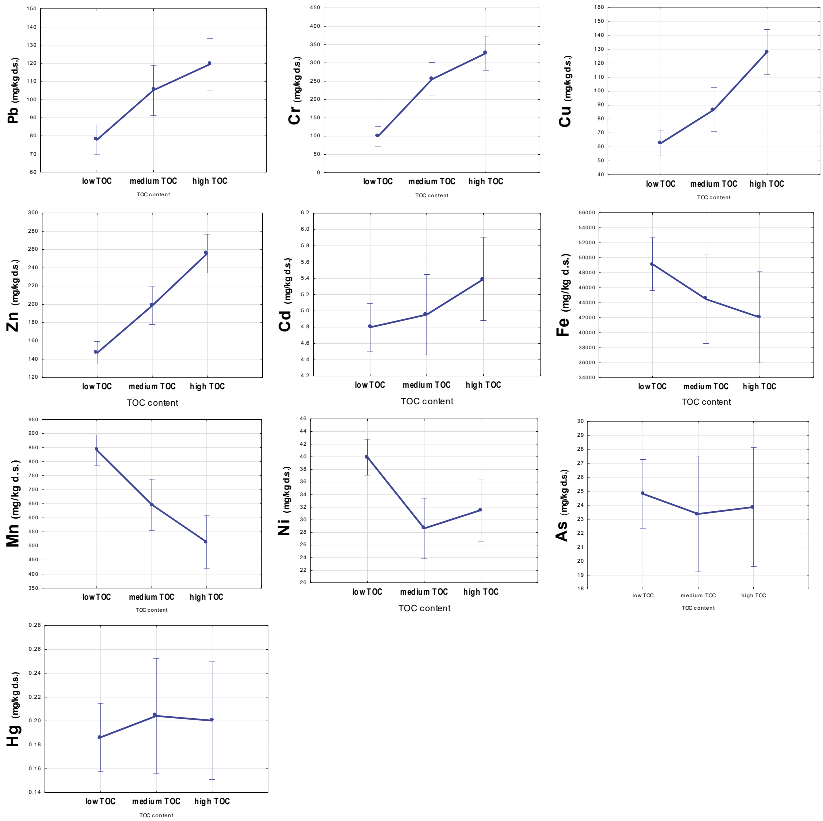

Figure 4 – One-way ANOVA representing variability of the concentration of Pb, Cr, Cu, Zn, Cd, Fe, Mn, Ni, As and Hg within the different TOC content classes defined. The vertical bars denote 0.95 confidence intervals. Wilks lambda=.26442, F(20, 158)=7.4632, p=.00000.

Similarly, the average concentration of metals according to the fixed classes of granulometry were also investigated.

Nevertheless, high variability is detected for same metals when coarser fraction appears. Some studies have indicated that coarser particles show a higher heavy metal concentration than finer ones and the presence of coarser particles are possibly responsible for higher metal content in the coarser size fractions [23, 21]. In our case, this trend is confirmed noticeably for almost all metals (Fig. 5). We can suppose that the heterogeneity of the behaviors of metals with granulometry can be related to the different affinity of these metal for different mineralogical phases (ion-exchangeable, carbonate, organic, iron-oxy-hydroxide, sulphides etc.) of sediments [6, 13, 14].

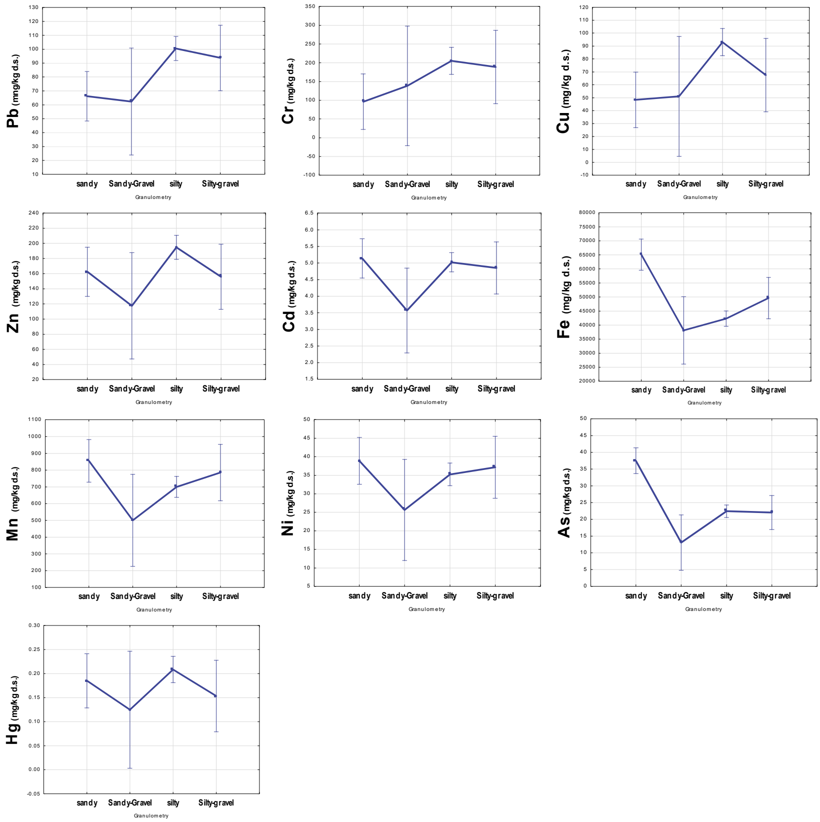

Figure 5 – One-way ANOVA representing variability of the concentration of Pb, Cr, Cu, Zn, Cd, Fe, Mn, Ni, As and Hg within the different Granulometry classes defined. The vertical bars denote 0.95 confidence intervals. Wilks lambda=.24876, F(30, 209.08)=4.2261, p=.00000.

Natural *vs* anthropogenic sources

Tacking in account the heterogeneous lithological substrate of the area that include volcanoclastic sediments reach in heavy metals, to further evaluate whether the metals in this study were influenced by natural or anthropogenic sources the results of this study has been compared with the published data collected onshore. The comparison permitted us to evaluate anthropogenic sources and to bound the area of the influence of the Sarno Plain sediments in the Naples Bay. Among other, the paper of [3] identified metal associations that has been linked to natural or anthropogenic origin. The authors recognize four metals association: F1 (As, La, Al, Mn, U, Fe) associated to the pyroclastics volcanic soils; F2 (Sr, K, P, V, Cu, Co, U) typical of agricultural areas; F3 (Zn, Pb, Cd, Sb, Hg) due to the human activities; and F4 (Ni, Cr, Fe) associated to the tannery district.

Statistical analysis reveals a positive correlation between Fe, As and Mn with the coarse grained sediments and Low TOC percentage. Tacking in account the position of tsamples offshore Vesuvio slope, we can interpret a natural origin for these contaminants mostly controlled by the presence of pyroclastics and volcanic deposits covering hilly and mountain areas surrounding the Naples Bay. Relatively high values of As also characterize sediments collected onshore at the slopes of Vesuvio. Furthermore, this interpretation is in accord with the F1 association of [3]. Some metals as Zn, Cu, Cr and Pb are correlated to the high percentage of silt and high percentage of TOC. These metals are included in the F2, F3 and F4 metal associations of [3] and result linked to the contamination of anthropogenic origin. In addition, the correlation between Zn, Cu, Cr and Pb silt and high percentage of TOC is characteristic of the samples located offshore the Sarno river suggesting that these deposits are the result of the river discharges reflecting the anthropogenic pressure of the receiving Sarno Plain. Between them it is not possible to discriminate from agricultural, human activities and that from tannery district because all are collected in the river and discharged in the sea in correspondence to the Sarno delta. Hg and Cd that are more widely distributed suggesting a mixed origin. Both elements might reflect influence of both human induced discharges (traffic ships, wastewater discharges, etc.) as well as natural phenomena related to the phosphorous (of anthropogenic origin) absorption to the clay fractions that act as carrier for these metals.

The distribution of the contaminant along the tract permit to define a boundary to the major influence of the Sarno delta in the marine environment until the water depth of 60 m.

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