THE OFFSHORE ENVIRONMENTAL IMPACT BY SARNO RIVER IN NAPLES BAY (SOUTH-WEST ITALY)

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Abstract – The Sarno River Basin (South-west Italy) is one of the most polluted river basins in Europe due to widespread industrialization and intensive agriculture. From the geological point of view, it lies between the Somma-Vesuvius volcanic complex and the limestone formations of the Campania-Apennine Chain. The goal of this work has been to establish the influence of the Sarno river on the present sedimentation in the Naples bay continental shelf by evaluating organic matter contribution and pollution. Sediments samples were collected, by van Veen grab, in 71 stations located offshore the Sarno river between Vesuvian and Sorrento Peninsula coasts. The characteristics of the surface sediments were analysed to highlight spatial trends in the (i) granulometry (grain-size); (ii) total nitrogen, organic carbon and total phosphorus; (iii) metal content (Hg, Cd, Pb, As, Cr, Cu, Ni, Zn, Fe and Mn).

The sediment distribution suggested that sediments from the Sarno River prevailed in the central part of the bay between the sand grained deposits from Vesuvius and coarser grained sediments from Sorrento Peninsula. The Sarno River deposition is characterized by silt/clays rich in organic elements with a high water content. A comparison with a previous study carried out onshore in the Sarno river basin has allowed to interpret the elevated Pb, Zn, Cd, and Hg concentrations most likely related to geological and anthropogenic sources, to underlying volcanic rocks, and contamination from fossil fuel combustion associated with nearby urban centres. In particular, as verified onshore, Ni and Cr contamination is most likely originating from anthropogenic sources as the Solofra tannery industry; the results suggest as these metals have been dispersed offshore. All these elements permit to identify the distribution of the present Sarno prodelta and to identify the influence of the onshore anthropogenic pollution in the adjacent submarine area.

First results from this study highlight the influence of the Sarno prodelta in Naples Bay and represent the first step in the characterization of a marine area strongly influenced by a very high populated and touristic coast. Therefore, the study represents a data base for the offshore environmental impact evaluation.

Introduction

Metal contamination in sediment and water is one of the largest threats to the environment. It is well documented that sediments play a key role in the sorption and transport of trace metals in aquatic environments. More than 97 % of the mass transport of

Di Leo A., Giandomenico S., Spada L., Cardellicchio N., Buonocunto F.P., Esposito E., Ferraro L., Giordano L., Milia A., Violante C., *The offshore environmental impact by Sarno river in Naples bay (South-West Italy),* pp. 392-401, © 2020 Author(s), CC BY 4.0 International, DOI 10.36253/978-88-5518-147-1.39

heavy metals to the oceans is associated with river sediments [Jain and Sharma, 2001]. Trace metals tend to be adsorbed onto the suspended particles after entering into the aquatic systems, whereas > 90 % of trace metals are bound to suspended solids and sediments, leading to their significant accumulation and enrichment in sediment in aquatic systems [Wei et al., 2016]. The metals adsorbed in this way are not stable and unchanging. They can go through a series of physical, chemical, and biological processes and be released as the metals adsorbed of aquatic environments [Gaur et al., 2005]. Under variable hydraulic conditions and through various remobilization processes some sediment bound metals might be released again into the water body [Jahan and Strezov, 2018]. Various studies have demonstrated that marine sediments from industrialized coastal areas are greatly contaminated by heavy metals; therefore, the evaluation of metal distribution in surface sediments is useful to assess pollution in the marine environment.

The Gulf of Naples is an area where sediments have different geochemical composition: metal concentrations vary according to the different geologic substrate and different inputs from the coastal environment. The main geologic features of the Campania Margin are represented by an elongated mountain ridges bounded by normal faults that affected the older Apennine thrust belt [Milia et al., 2017]. The ridges are made up of Meso-Cenosoic calcareous rocks and locally by Miocene clastic deposits. One of this is the Sorrento Peninsula-Capri Island ridge, oriented ENE-WSW, that bound the Bay of Naples southward. Recently, over the last 400 ky, several volcanic eruptions affect the area which deposits as the Pyroclastic deposits of Campania Ignimbrites and the pyroclastic deposits, lavas and fall deposits of the Vesuvius and Campi Flegrei cover largely the Campania Plain and the Naples Bay [Torrente et al. 2010; Milia and Torrente, 2012]. An alluvial plain is present between the Vesuvius and the carbonatic ridge corresponding to the Sarno Plain where a river catchment draining toward the Naples Bay. The Sarno river hydrographic basin cover an area of approximately 500 km^2.

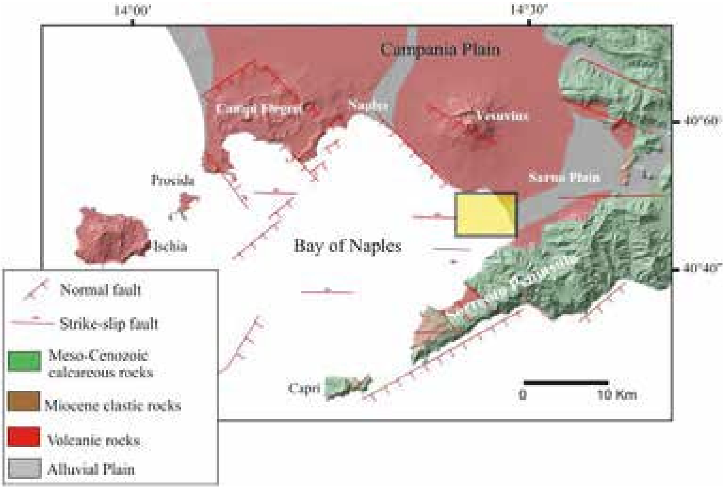


Figure 1 - Geological sketch of the Campania margin. The yellow rectangle corresponds to the study area.

The adjacent Campania Plain is characterized by high density population and in particular the Sarno Plain is one of the most polluted area in Europe due to widespread industrialization and intensive agriculture. The goal of this work has been to establish the influence of the Sarno river on the present sedimentation in the Naples bay continental shelf by evaluating organic matter contribution and pollution. Sediments samples were collected in 71 stations located offshore the Sarno river between Vesuvian and Sorrento Peninsula coasts. The characteristics of the surface sediments were analysed to highlight spatial trends in the (i) granulometry (grain-size); (ii) total nitrogen, total organic carbon and total phosphorus; (iii) metal content (Hg, Cd, Pb, As, Cr, Cu, Ni, Zn, Fe and Mn).

Materials and Methods

Surface sediments samples were collected by Van Veen grab (25 L) in 71 sites located offshore the Sarno river between Vesuvian and Sorrento Peninsula coasts (Figure 1). After sampling, sediments were stored in clean polyethylene bags and frozen at -20 °C until analysis. The sediment stations were distributed from 5 meter to about 100 meter of water depth on the continental shelf. Samples for grain size analysis were treated with H_2O_2 solution, then washed and dried at 40 °C. Grain size analyses were performed following the ICRAM "*Metodologie analitiche di riferimento*" (2003). The coarse fraction (> 63 µm) was sieved using ASTM series sieves, while the fine fraction (< 63 mm) was analysed by means of laser diffraction granulometer (Laser Particle-Size Analyzer). The Wentworth grain size classification was used as reported in Table 1.

Table 1 - Wentworth grain-size scale.

Gravel > 2 mm
Sand 2 mm > x > 0.063 mm
Silt 0.063 mm > x > 0.004 mm
Clay < 0.004 mm

Total organic carbon (TOC) and total nitrogen in samples sediment were determined using the technical reported in "*Metodologie Analitiche di Riferimento*" [ICRAM, 2001]. Total phosphorus content was determined following APAT IRSA-CNR 4110 (2003) method. For metal analysis the sediment samples were digested using a microwave assisted acid digestion procedure. Briefly, three replicates of 0.25 g dried sediment sample were digested with 9 mL of nitric acid, 2 mL of hydrochloric acid and 3 mL of hydrofluoric acid [SW-846 EPA Method 3052, 1996] using a MARSX microwave oven (CEM Corporation, Matthews, NC). For each digestion program, a blank sample was prepared with the same amount of acids. After digestion, 20 mL of saturated solution of boric acid was added to samples in order to delete excess of hydrofluoric acid. Each sample was diluted to 50 mL with ultra pure water (conductivity <0.1 µS, obtained from a MILLI-QR system, Millipore, Bedford, MA, USA) and analyzed. All reagents were of analytical grade and contained very low concentrations of trace metals. Normal precautions for trace metal analysis were observed throughout. Nitric acid (70 % w/w), hydrochloric acid (37 % w/w), hydrofluoric acid (48 % w/w) and boric acid were ULTREXR II Ultra-pure Reagent (J.T. Baker, Phillipsburg, USA). Metal concentrations (Hg, Cd, Pb, As, Cr, Cu, Ni, Zn, Fe and Mn) were determined by ICP-MS, using a Perkin Elmer-model Elan 6100 DRC Plus (PerkinElmer, Norwalk, CT, USA). Each sample was analyzed for three replicates (RSD <5 %). Accuracy was verified using the certified reference marine sediment IAEA-356. The recovery percentage for IAEA-356 was in the range between 95 % (Pb^{208}) and 105 % (Zn^{66}).

Results

The spatial distribution of total organic carbon (TOC) in sediment samples (Fig. 2) was very different and depending on the sampling area.In particular, a high TOC value is present in correspondence of the Sarno prodelta (between stations 15 and 45). As regards total nitrogen and total phosphorus values are in most cases below the detection limit. The grain size of the sediments (Fig. 3) remains almost constant and they are constituted from: medium/fine to very fine sand, to silty up to the isobaths of 17 meters; weakly clayey silt to silty with clayey sand between the isobaths of 17 and 25 meters. Moreover, the sediment is mainly represented by sandy coarse silt to clayey with delimited areas where the sandy component prevails on the silty part. The sands consist mostly of volcano-clasts, litoclasts and bioclasts. The metal concentrations of the surface sediments exhibited clear spatial variations (Fig. 4). The Cd, As, Ni, Fe and Mn concentrations decreased gradually with distance from the shore, while Pb, Cr, Cu and Zn increased in correspondence with the Sarno prodelta (between stations 15 and 45).

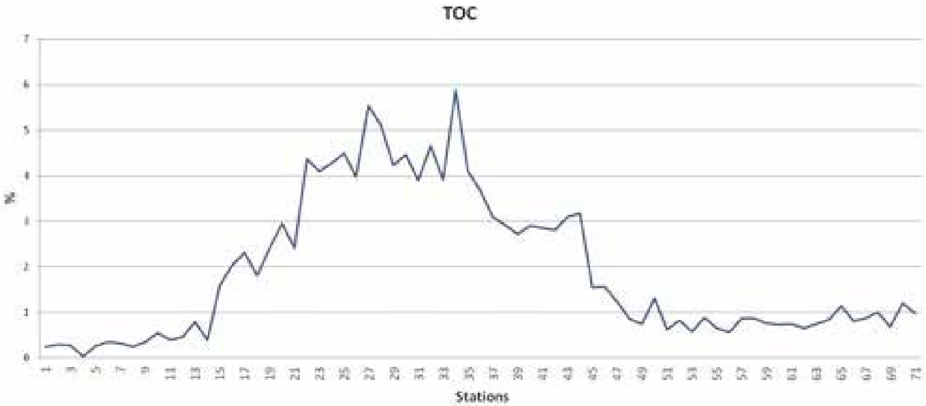


Figure 2 - Distribution of TOC in sediments.

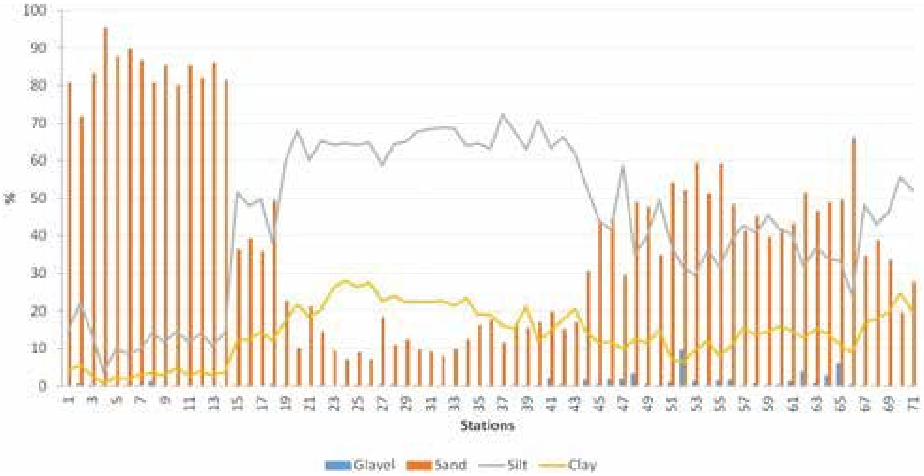


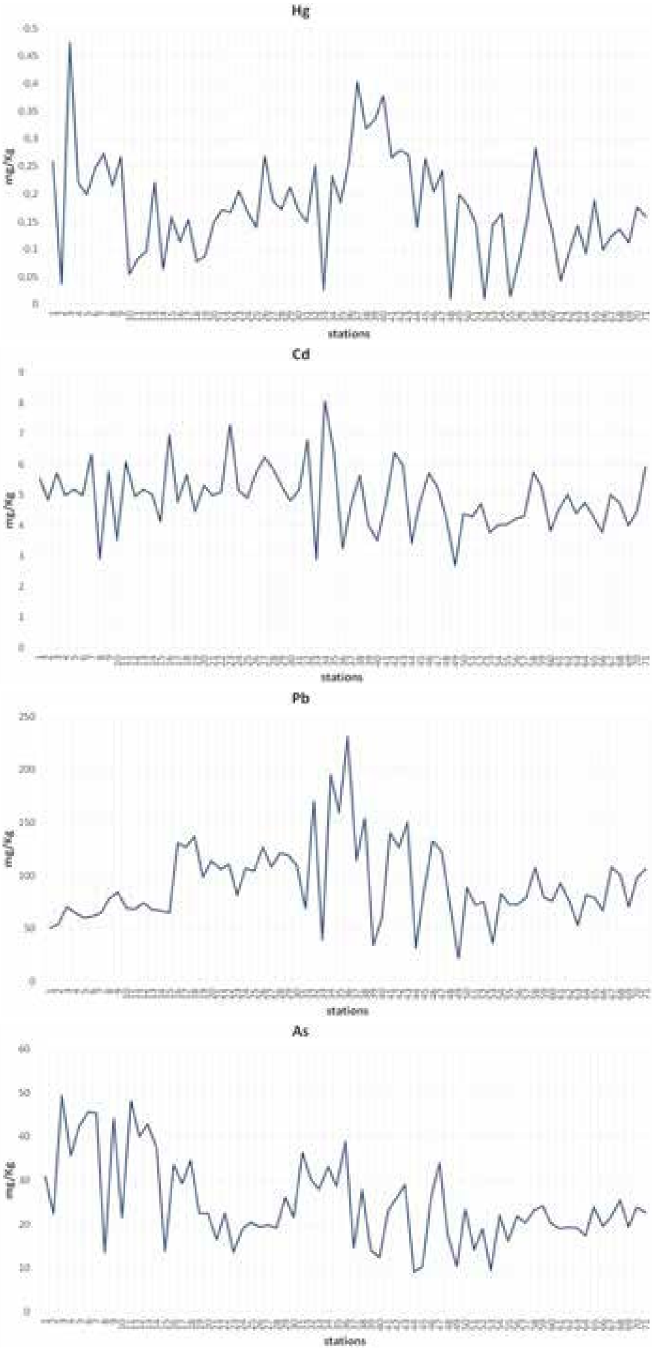
Figure 3 - Distribution of grain size in sediments.

Discussion

Metals through human activities such as industrial wastewater processing and discharge fossil fuel use, pesticide and fertilizer application, and household waste disposal enter water bodies and accumulate in sediment [Han et al., 2016]. Besides, also the erosion and weathering of rock minerals contribute to metal levels in water bodies [Sun et al., 2018]. In particular, the Sarno Plain is one of the most polluted area in Europe due to widespread industrialization and intensive agriculture. Water from the Sarno River is heavily contaminated by the discharge of human and industrial wastes [Albanese et al., 2010; Arienzo et al., 2017]. The Gulf of Naples are the receiving environment for persistent toxic substances from the Campania Plain. The variations of metal concentrations in sediments can result from differences in the grain size, the mineralogy, organic matter and the redox of the sediment [Nabavi et al., 2013]. Metal concentrations obtained in this study were further comparable to or higher than that reported from other polluted harbours of the Mediterranean area. In particular, Cd, Cu, Mn, Pb and Zn levels were higher to those reported in the Taranto Gulf, Italy [Cardellicchio et al., 2009]. In relation to the spatial distribution the Cd, As, Ni, Fe and Mn concentrations decreased gradually with distance from the shore, while Pb, Cr, Cu and Zn increased in correspondence with the Sarno prodelta (between stations 15 and 45). A similar spatial distribution was observed for the TOC, silt and clay.

There were two areas of higher concentration: the area proximal to the coast (area between stations 1 and 14) and the area of the Sarno prodelta. This could be probably due to high concentration of industrial and urban wastes in the onshore counterpart of the study area.

However, the major factors controlling heavy metal distribution are their source, hydrodynamic conditions, sediment properties, adsorption and flocculation by fine particulate matter, and adsorption and desorption characteristics [Hosono et al., 2011].



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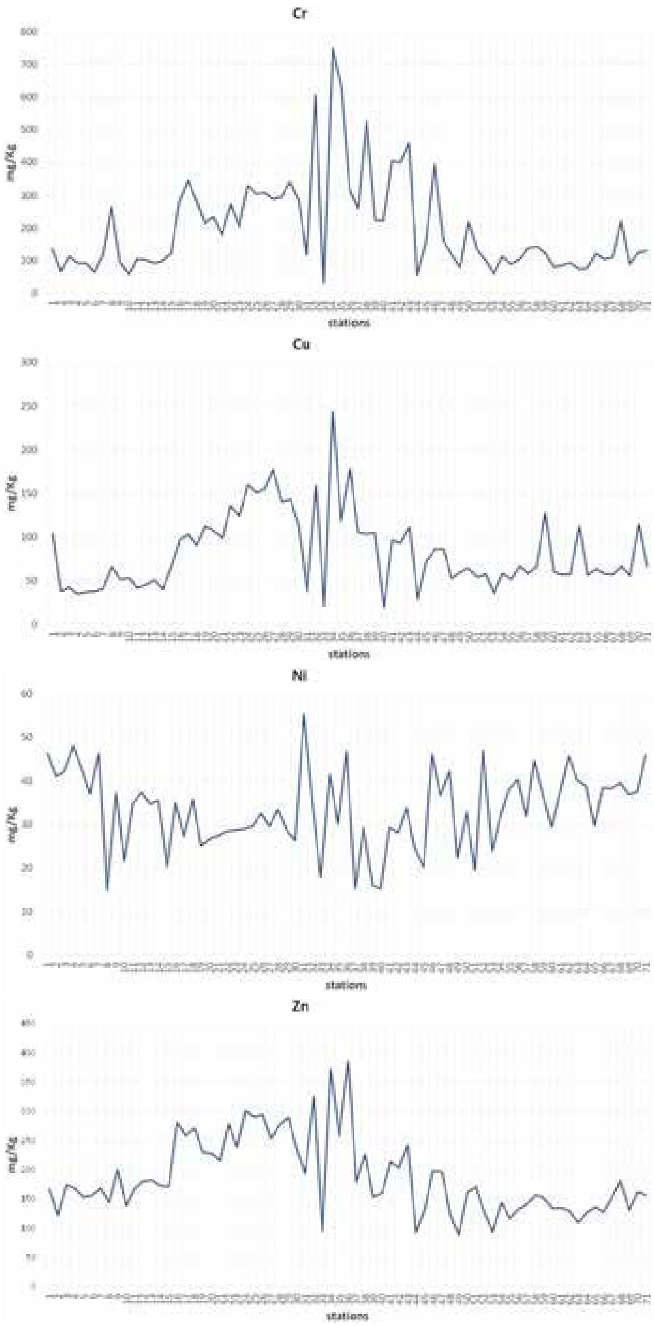

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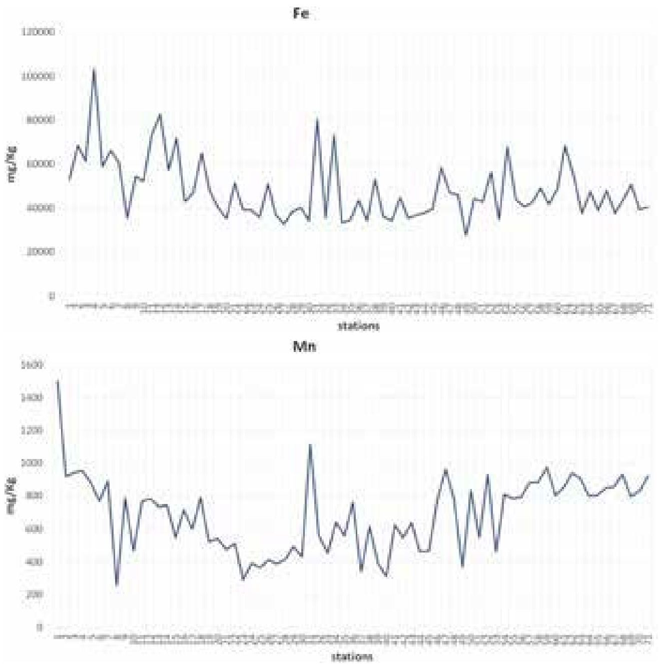

Figure 4 - Distribution of Hg, Cd, Pb, As, Cr, Cu, Ni, Zn, Fe and Mn in sediments.

Inshore, where pH and salinity were appropriate, organic flocculants and iron (Fe) and manganese (Mn) oxides coagulated the fastest, which expedited the deposition of metals in sediments. Similarly, under oxidized conditions, metals in oxidizable fraction can also be re-released during the oxygenation of organic substances and/or sulphides, and retained by Fe/Mn oxides.

Principal component analysis allowed us to clearly discriminate three areas mainly affected by heavy metals contamination and influenced by different sources related to industrial, commercial and/or urban activities. Especially the stations 1-14 near coast, characterized by sandy sediment with a pollution pattern dominated by Fe, Mn, As and Ni, while the stations 15-45 are characterized by silty sediment with a high severe pollution pattern dominated by Cu, Pb, Cr and Zn. These sites last are controlled by high level of TOC. Lastly the stations 46-71 are characterized by coarse sediment with a pollution patterns mainly dominated by Cd and Hg.

Conclusion

This study allowed us to determine the spatial distribution of metals and TOC in sediments located offshore the Sarno river between Vesuvian and Sorrento Peninsula coasts. In addition, it was possible to assess how organic matter and grain size could influence the distribution of metals in sediments. In general, distribution show accumulation areas especially close to the coasts and in correspondence with the Sarno prodelta.

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