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Baseline

Distribution and enrichment of trace metals in surface marine sediments in the Gulf of Pozzuoli and off the coast of the brownfield metallurgical site of Ilva of Bagnoli (Campania, Italy)

Marco Trifuoggi[a], Carlo Donadio[b], Olga Mangoni[c], Luciano Ferrara[a], Francesco Bolinesi[c], Rosa Anna Nastro[d], Corrado Stanislao[b], Maria Toscanesi[a], Gabriella Di Natale[a], Michele Arienzo[b],*

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Complesso Universitario di Monte Sant'Angelo, via Cintia 26, 80126 Naples, Italy*
[b] *Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università degli Studi di Napoli Federico II, Largo San Marcellino 10, 80138 Naples, Italy*
[c] *Dipartimento di Biologia, Università degli Studi di Napoli Federico II, Complesso Universitario di Monte Sant'Angelo, Via Cintia 26, 80126 Naples, Italy*
[d] *Dipartimento di Ingegneria, Università degli Studi di Napoli Parthenope, Centro Drezionale, Isola C4, 80143 Napoli, Italy*

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ABSTRACT

The distribution of metals in surface sediments of Gulf of Pozzuoli (GoP), embedding the former second Italian largest integrated steelworks of Bagnoli, was studied based on sediment dispersal, quality guidelines (SQGs) and quantitative pollution indices of the respective metals. As, Cd, Hg, Pb, Zn largely exceeded the limits. Hg had a mean of 5.8 mg/kg, twentyfold higher the rule, accumulating primarily near Bagnoli site. The mean effective range quotient, m-ERM-Q, revealed a high potential for negative biological effects especially in the area nearby the Bagnoli site. The enrichment factor (EF) values were outstandingly high, > 1.5 with values which were often ≥ 100. The geoaccumulation index, Igeo, was very critical for Cr, Cu, Hg and Ni, showing an Igeo in the range of strongly polluted ($4 < \text{Igeo} < 5$) and very strongly polluted ($\text{Igeo} > 5$). The principal component analysis (PCA) and Pearson's correlation matrix (CM), excluded significant contribution from weathering products.

Heavy metal pollution is a serious threat to marine environment due to their high toxicity, non-degradability, bioaccumulation and biomagnification (Bryan and Langston, 1992; Wong et al., 2002; Diagomanolin et al., 2004; Luoma and Rainbow, 2008). To date, 12 species of heavy metals have been classified as priority pollutants, including As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Ti, and Zn (Protano et al., 2014; Li et al., 2015a, 2015b). Marine sediment is a large reservoir for heavy metals, monitoring heavy metals in sediment is considered as an approbatory approach for environmental quality assessment (Bellucci et al., 2002; Ianni et al., 2010; Collier et al., 2012). Sediment plays a role in accumulating and transporting contaminants within the geographic area. There are many human activities worked, or still working, along the Italian coastal areas, which determined an high pollution of the marine environment, like as chemical and/or petrochemical industries, harbor or military areas, urban, agricultural or mining settlement, etc. Some national laws identified them as National Relevance Contaminated Sites (Parlamento Italiano, 1998, 2000, 2002) and Ministry of Environment defined specific processes for their remediation (Ministero dell'Ambiente e della Tutela del Territorio, 2001) and 25 of them include a potential polluted marine area. In the urban outskirt of Naples, Italy, there is an industrially contaminated site, Bagnoli, formerly the second largest integrated steelworks in Italy, now closed and subject to a government remediation project, located on the Bagnoli–Fuorigrotta plain (BFP), part of the Campi Flegrei (CF) volcanic caldera. The remediation project, funded by the Italian government, started in 1996 and was extended to the coastal area sea sediments facing the brownfield site in 2001.

The coastal zone of the disused industrial site of Bagnoli has been studied since 1999 in order to highlight chemical and ecological features of pollution, mainly due to a steel plant. Studies carried out in marine sediments sampled just offshore from the Bagnoli area have highlighted that the coastal area is strongly contaminated by metals, PAHs and PCBs (De Vivo and Lima, 2008; Albanese et al., 2010; Arienzo et al., 2017). Romano et al. (2009, 2017), reported high concentrations of heavy metals like as Cu, Fe, Hg, Mn, Ni, Pb, Zn on seabed and in sediment cores. Damiani et al. (1987), Sharp and Nardi (1987), De Vivo and Lima (2008), evidenced the natural origin of heavy metal anomalies in addition to an anthropogenic source (industrial pollution).

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* Corresponding author.
E-mail address: michele.arienzo@unina.it (M. Arienzo).

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Because all these studies investigated nearly exclusively the marine area under the direct influence of the industrial site, it was considered of relevance to extend the area of research to all the Gulf of Pozzuoli (GoP) to evaluate the environmental effects of the presence of the industrial site of Bagnoli and the consequences of its past activity, investigating particularly the chemical and sedimentological aspects, and the correlated ecological features. A stepwise research started in 2016 and is still in progress analyzing levels, spatial distribution, sources and eco-toxicological features of major pollutants (Arienzo et al., 2017) along the entire GoP in sectors never investigated before. As the eco-toxicological data are not yet available, an assessment of contamination status was based on sediment quality guidelines (SQGs) and quantitative pollution indices of the respective metals (Ho et al., 2010). Therefore, this study attempts to determine the distribution of trace metal contamination in the surface sediments of GoP by using different types of pollution indices and ecological risk assessment based on SQGs. For this scope, various parameters were considered such as enrichment factor (EF), contamination factor (CF), pollution load index (PLI), and geo-accumulation index (Igeo). Correlation analysis (CA) and principal component analysis (PCA) were also used to define the possible sources of the heavy metals.

GoP is a large bay of about 8 × 5.5 km representing the northern sector of the wider Gulf of Naples (GoN), Fig. 1, sited along the Campanian Margin of the Tyrrhenian Sea, which originated from the rotation of the Italian Peninsula during Pliocene extensional phases (Patacca et al., 1990; Sgrosso, 1998). GoP extends between Cape Miseno, to the southwest, which is the northern limit of GoN, and Nisida Island to the southeast, facing south to the open sea. The lithological map of the GoP is shown in Fig. 2. Some 50 craters have been recognized both inland and offshore. Actually, GoP is located between two main active volcanic districts, Phlegrean Fields (PF) and Mt. Somma-Vesuvius, developed along the coastland. The GoP represents the submerged sector of PF and is featured by a central plain, with epiplastic sedimentation, delimited to the south by several underwater banks, which are relict of submerged volcanoes. Tectonics of PF is still very dynamic: historical records of bradyseismic vertical movements date back to Greek colonization, over 2000 years bp. Explosive volcanic activity with emission of ignimbrites started over 200,000 years BP (De Vivo et al., 2001) and ended in 1538, when a new mountain (Mt. Nuovo) beside the town of Pozzuoli was formed by a week-long pyroclastic eruption (Di Vito et al., 1987).

From a geological point of view, the area is a large caldera of a supervolcano, currently unrest (Kilburn et al., 2017), with a diameter of 12–15 km, whose limits are the Posillipo hill to the east, the Camaldoli hill and Quarto crater to the north, the Sanseverino hill, the promontories of Cuma and Monte di Procida to the west. Two recent bradyseismic crises in 1970–72 and 1982–84 occurred (Dvorak and Mastrolorenzo, 1991), the last following the Naples earthquake of 23th November 1980, during which the ground uplifted with a rate of 3 mm per day due to positive vertical movement (Damiani et al., 1987). Gas emissions (fumaroles), both on land (Solfatara Volcano) and underwater (Pozzuoli Bay), are also associated with volcanic activity. Underwater gas emission caused a yellow coloration due to colloidal sulphur and iron hydroxides in suspension as sedimentary particles (Colantoni, 1972). The Pozzuoli Bay has a narrow continental shelf with shelf break at about 40 m depth down to 80 m deep, an average depth of ca 60 m, a maximum depth of 110 m (Somma et al., 2016) a surface area of 33 km^2 and a volume of about 2 km^3. Water exchange

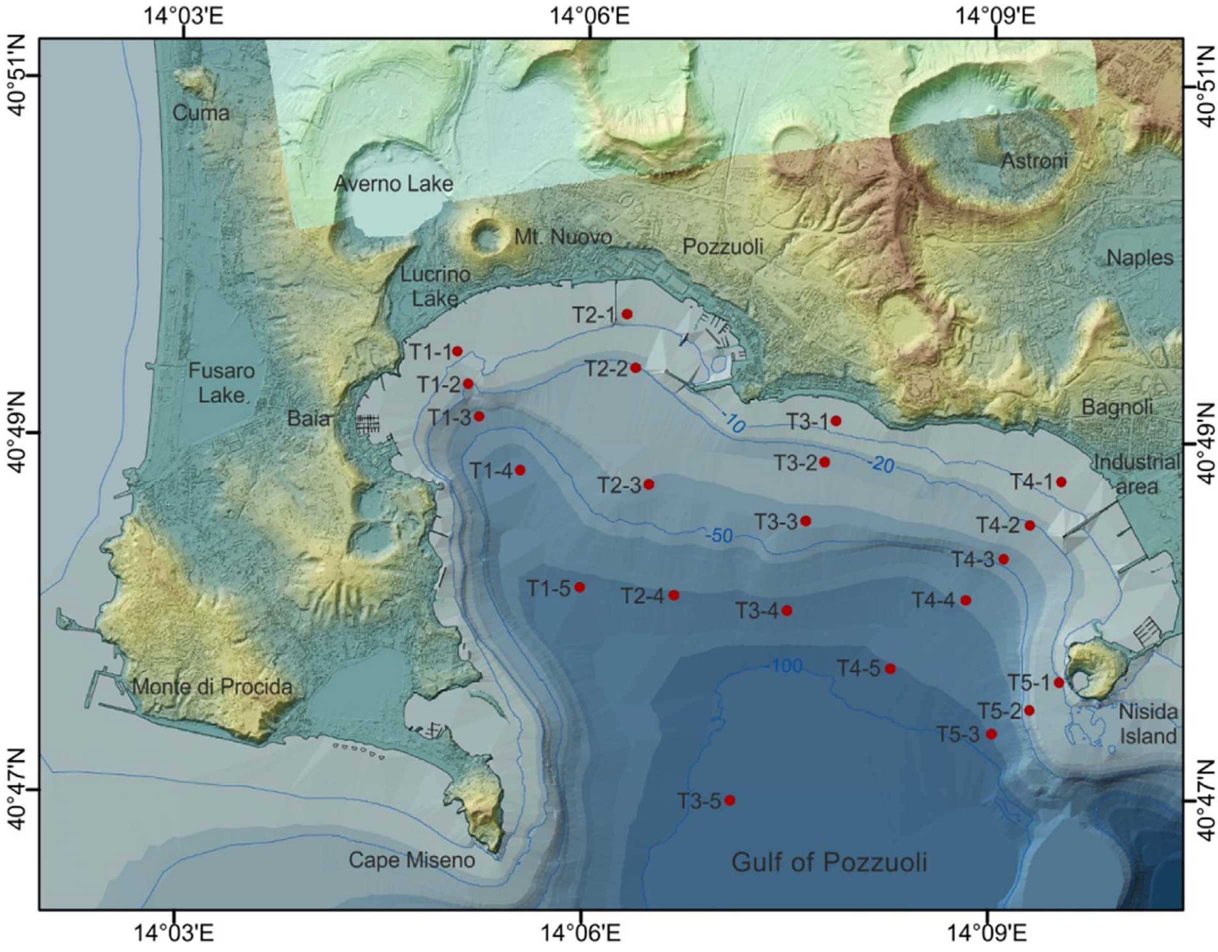

Fig. 1. Map of the sediment sampling in the GoP; DTM Lidar basemap by MATTM - Environmental Remote Sensing Plan (PT-A). Depth is in meters b.s.l., geographic coordinate system is WGS84.

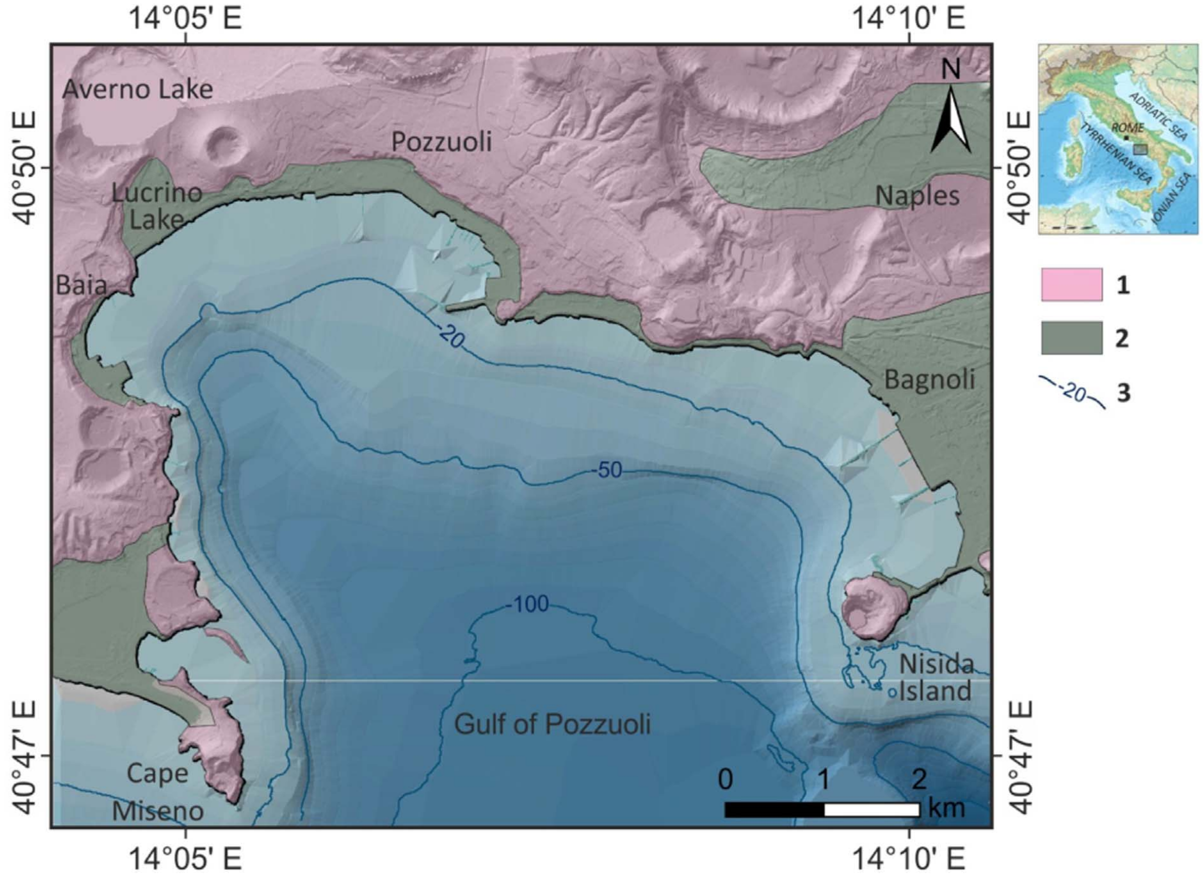

Fig. 2. Lithological map of the GoP: 1, pyroclastic products of Phlegrean Fields (late Pleistocene-Holocene); 2, marine and alluvial deposits (Holocene); 3, isobath (m bsl); geographic coordinate system is EPSG Projection 4326 - WGS84.

occurs between GoP and GoN through a section 2 km wide and 100 m deep (De Maio et al., 1982). The presence of submarine hydrothermal springs located along a NW–SE axis, in the eastern sector of the GoP (Sharp and Nardi, 1987), is related to secondary volcanic activity of the PF and affects the natural chemistry of coastal marine waters, changing the evaluation of anthropogenic pollution. The fluids from these springs contain heavy and potentially toxic metals such as As, Hg, Cu, Pb, and Cd. In contrast, hydrocarbons (mostly PAHs) are leached by rain fall percolating through soils and landfills contaminated by industrial activities. Mobilization of sediments in GoP is strictly correlated to morphological features, climate and tectonic events. Water circulation in the GoN is strictly related to the general circulation in the Tyrrhenian Sea (Carrada et al., 1980). During winter, a clockwise rotating circulation in the inner part of the gulf and a northward current offshore occur, while during summer the inner circulation shows an anticlockwise direction and the offshore current is towards the south (Pennetta et al., 1998). The contributions from inland determine an eutrophic coastal subsystem, which is conditioned by intense anthropic activity (Pugnetti et al., 2006). In particular, the GoP may be influenced by inputs coming from the Volturno River, which discharges about 35 km to the northwest, and the Naples harbor, 12 km to the east.

Sampling of sediments was performed aboard a boat named Antilia on December 2015 in 22 sites, Fig. 1 and Table 1, by a Van Veen grab along 5 transects, positioned on a coast-offshore alignment, perpendicular to the shoreline and all converging to the site 3–5, Fig. 1. The distribution of samples was designed in order to have a good detail of the entire GoP, covering the highly anthropized area of Pozzuoli and Bacoli, Fig. 1, as well as the brownfield site of Bagnoli. Sea depth was measured by an ecograph and varied between 10 and 20 inshore up to 100 m deep offshore. The position of stations was determined by DGPS (Differential Global Positioning System), Table 1. Sediments were collected in plastic bags, wrapped in aluminum foil and sent in an ice box to the laboratory where they were frozen at − 20 °C.

Sediments were analysed for grain sizes, TOC, and heavy metals (Tables 1, 2). After washing by a vacuum pump, samples were dried in an oven at 80 °C for 72 h, weighed with an analytical balance and subjected to dry sieving through a series of stacked sieves, with 1/4 ϕ class interval up to 63 μm, in a mechanical sieve shaker for 15′. Fractions from 63 to 2 μm were analysed through sedimentation in distilled water with 10% sodium oxalate at specific temperatures, according to Belloni (1969). For each sample, histograms and cumulative curves were plotted (Blott and Pye, 2001), as well as calculated the granulometric fraction percentages (Table 1) and main statistical parameters, according to the graphic method of Folk and Ward (1957).

The dispersal of sediments containing heavy metals along the sea bottom of the Gulf of Pozzuoli, within 100 m depth, was evaluated by a specific software with the aim to identify sedimentary transit axes (Barusseau, 1973; Cortemiglia, 1978a, 1978b, 1978c; De Pippo, 1989). For each sample the frequency curves were analysed and the modal formulas were recognized, the last expressed by mode values and their percentage frequency of appearance (Pauc, 1973; Long, 1975). In particular, the analysis of modal formulas of the 22 samples and their frequency of appearance, allowed to recognize granulometric subpopulations involved in the sedimentary dynamics of the study bay.

In this way, the following modal average expression was obtained:

$$(?)\ 4.54\% + (0.151)\ 9.09\% + (0.302)\ 9.09\% + (0.151)\ 40.90\% + (?)\ 36.36\% \tag{1}$$

For each granulometric fraction the modal average formula (1) was applied by summing the product between modal peaks (in brackets) and their percentage frequency of appearance (%). The formula starts and ends with question marks when undefined modal peaks, due to

Table 1
Sampling locations associated to water depths, TOC and grain size of sediments from Pozzuoli Gulf. Samples MdP1, MdP2 and MdP3 were collected to the southwest of GoP and analyzed as standard reference samples, therefore they are not located in Fig. 1.

Sampling stations	Latitude (N)	Longitude (E)	Depth (m)	TOC[a] %	Gravel %	Sand %	Silt %	Clay %	Mz[b] (ϕ)	Class[c]
1-1	40°49′27.55″	14° 5′2.94″	8.0	1.34	4.68	94.9	0.33	0.05	2.790	Fine sand
1-2	40°49′16.89″	14° 5′8.74″	24.8	1.51	1.59	97.3	0.96	0.16	2.706	Fine sand
1-3	40°49′6.81″	14° 5′15.07″	45.1	3.27	35.3	60.3	4.10	0.29	1.330	Medium sand
1-4	40°48′49.34″	14° 5′31.38″	58.6	1.72	33.7	61.7	4.36	0.19	0.862	Coarse sand
1-5	40°48′10.61″	14° 5′58.29″	80.0	1.59	0.35	84.3	14.4	0.92	3.453	Very fne sand
2-1	40°49′41.34″	14° 6′19.46″	8.0		0.69	99.3	–	–	0.677	Coarse sand
2-2	40°49′23.95″	14° 6′21.93″	25.8	1.84	1.50	97.0	1.4	0.10	3.390	Very fine sand
2-3	40°48′42.91″	14° 6′29.06″	34.0	0.98	6.72	91.8	1.32	0.15	2.500	Fine sand
2-4	40°48′6.96″	14° 6′39.17″	72.5	1.40	4.18	85.9	9.30	0.61	3.358	Very fine sand
3-1	40°49′5.98″	14° 7′50.41″	7.5	0.09	0.67	99.3	–	–	1.777	Medium sand
3-2	40°48′53.02″	14° 7′46.26″	23.8	0.64	5.10	94.9	–	–	2.147	Fine sand
3-3	40°48′33.38″	14° 7′38.47″	38.0	1.17	2.89	96.1	0.88	0.12	2.198	Fine sand
3-4	40°48′2.54″	14° 7′28.73″	75.3	1.66	0.83	89.0	9.71	0.45	0.861	Coarse sand
3-5	40°46′59.22″	14° 7′6.01″	100.0	1.65	2.35	83.9	13.3	0.46	3.441	Very fine sand
4-1	40°48′46.43″	14° 9′30.87″	7.7	9.20	0.06	99.9	–	–	2.691	Fine sand
4-2	40°48′32.74″	14° 9′17.63″	21.5	2.60	0.57	98.9	0.47	0.07	2.528	Fine sand
4-3	40°48′20.83″	14° 9′5.43″	47.8	10.0	6.89	67.1	25.9	0.13	3.477	Very fine sand
4-4	40°48′6.92″	14° 8′49.11″	71.5	4.28	9.42	68.1	21.7	0.75	3.152	Very fine sand
4-5	40°47′33.22″	14° 8′11.91″	98.0	2.17	1.87	93.5	4.29	0.30	2.925	Fine sand
5-1	40°47′33.96″	14° 9′28.91″	22.7	0.34	49.1	50.8	–	–	− 1.152	Very fine gravel
5-2	40°47′29.99″	14° 9′17.74″	47.8	0.12	0.29	99.1	0.52	0.12	2.738	Fine sand
5-3	40°47′24.71″	14° 9′0.89″	91.0	2.44	0.23	88.0	11.4	0.41	3.373	Very fine sand
MdP1	40°47′13.8″	14°03′18.7″	4.1		0.33	98.9	0.73	–		Fine sand
MdP2	40°47′10.9″	14°03′18.7″	5.2		0.21	99.2	0.63	–		Fine sand
MdP3	40°47′05.1″	14°03′12.9″	7.5		0.04	99.7	0.22	–		Fine sand

[a] TOC: total organic carbon.

[b] Mz: mean grain size, $\phi = -\log_2 D$ where D is the grain diameter (mm).

[c] Classification of sediment grain size (Folk and Ward, 1957).

Table 2
Summary of heavy metals concentrations in the GoP and other referenced sites surface sediments (mg/kg). For Fe, units were in g/kg.

Locations	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	References
Research area (range)	12.3–100.4	0.0–0.7	0.5–49.5	3.5–86.2	10.5–66.8	0.0–25.3	20–1353	0.0–35.4	11.5–378.4	42.1–869.9	This study
Research area (mean)	35.2	0.04	14.0	25.6	29.1	5.8	419	9.9	105.8	224.5	
GoP background values			0.30	0.20	25.0	0.25	0.70	0.20	60	80	Damiani et al. (1987)
Monte di Procida, Italy	11.0	0.14	10.9	7.2	28.8	0.02	1153	11.0	21.7	54.6	Mangoni et al. (2016)
South China Sea	–	0.40	105	38.1	–	–	–	–	23.6	87.4	Zhu et al. (2011)
South Yellow Sea	–	0.30	–	16.9	–	–	–	–	17.8	93.7	Hu et al. (2013)
Masan Bay, Korea	–	–	67.1	43.4		–		28.8	44.0	206.3	Hyun et al. (2007)
Arabian Gulf			38	9				30	–	22	Basaham and El-Sayed (1998)
Bremen Bay, Germany			131	87				60	122	206	Hamer and Karius (2002)
Florida Bay			162	15				21	8.4	31	Caccia et al. (2003)
MSQ (Italy)	12	0.3	50			0.3		30	30	80	Ministero dell'Ambiente e della Tutela del Territorio (2003)
Mediterranean coastal areas	40–1400	0.02–64		0.5–1890		0.05–0.1			3–3300	1.7–6200	UNEP (1996)

The concentrations of national regulatory guidelines (Ministero dell'Ambiente e della Tutela del Territorio, 2003), the background concentrations for the study area (Damiani et al., 1987), and the ranges recorded by UNEP (1996) for the Mediterranean area are given at the bottom of the table.

equal values of mode, are present. Transit axes are identified considering the value as a gradient: direction of sedimentary drift is from the higher values of modal peak towards the lower ones.

For TOC determination, samples of 0.5 g of ≤ 2 μm dry sediments were weighed in ceramic vessels and analysed by a total organic carbon analyser, Skalar (The Netherlands). The ≤ 2000 μm fraction was used for analyses of the total pool of As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Zn by digesting about 0.5 g of sediment in 12 mL of H_2O_2–HCl-HNO_3, in Teflon vessels in an Ethos Plus Microwave Lab Station (Milestone) for 15 min; the obtained solution was taken to a final volume of 100 mL with 5% HCl and then filtered by 0.45 μm (Cicchella et al., 2008). Samples were analysed by ICP-MS (Aurora M90 Bruker, US). Samples were analysed in triplicate. The percentage of recovery was estimated by analyzing 10 replicates of a fortified matrix, constituted by 8 metals at a known concentration. The detection limit (LOD) and limit of quantification (LOQ) were calculated using the method of blanks variability, for each investigated metal. The calculated average values of LOD and LOQ were 0.06 and 0.16 μg/g, respectively. The quality of the analytical results is assured by participation in ring tests for the determination of metal from sediments and similar matrices. Mean recoveries ranged from a minimum of 85% to a maximum of 97%.

The principal component analysis (PCA) and the Pearson's correlation matrix were conducted in order to investigate the relationship between the heavy metals and to investigate the possible sources. Statistical analysis of data was performed using STATISTICA 5 (StatSoft Inc., Tulsa, OK, USA).

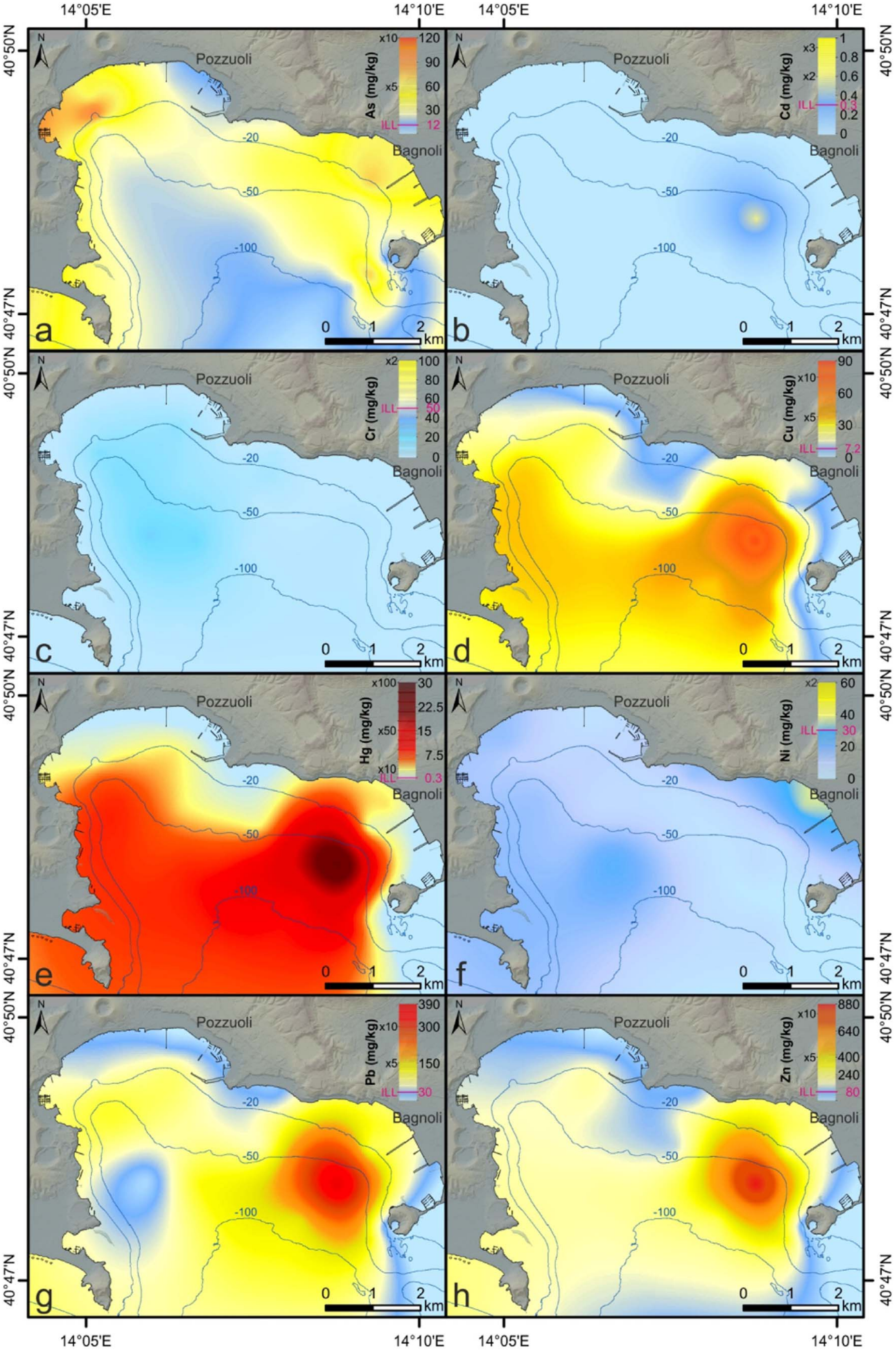

Fig. 3. Spatial distribution of heavy metals in the sediments along the seabed of GoP. ILL: Italian law limit; depth is in meters b.s.l., coordinate system is EPSG Projection 4326 - WGS84.

Table 3
Classification of sediment quality guidelines (SQGs) and its effects.

SQGs		Effect	References
TEL and PEL guidelines	< TEL	Not associated with adverse biological effects	MacDonald et al. (1996), MacDonald et al. (2000)
	≥ TEL < PEL	Occasionally associated with adverse biological effects	
	≥ PEL	Frequently associated with adverse biological effects	
ERL and ERM guidelines	< ERL	Minimal effects range	Long et al. (1995)
	≥ ERL < ERM	Effects would occasionally occur	
	≥ ERM	Effects would frequently occur	

Table 1 reports the granulometric composition of GoP sediments. Mean grain size (Mz) varied from − 1.152 to 3.477 ϕ, with an average Mz of 2.219 ± 1.351 ϕ whereas the amount of TOC varied from 0.09 to 10.05%, with a mean of 2.38 ± 2.61%. A significant linear correlation was observed between the total TOC and Mz (0.41 ϕ) and thus, Mz has a significant impact on TOC concentration. It is interesting to note how the high values of the TOC were observed in the south eastern part of GoP especially facing the Bagnoli industrial plant, i.e. along all transect 4 with a peak of 10.05% at 4-3, where sediments also show a peak of Mz, 3.477 ϕ, very fine sand. There is also a significant correlation between Fe concentration and Mz (0.54 ϕ) as a result of natural weathering and inputs from the former Bagnoli steel plant, thus Fe concentrations are mainly controlled by grain size.

Table 2 reports the range of variation of the studied heavy metals compared with other referenced sites and marine standard quality outlined by the Italian regulatory guidelines (Ministero dell'Ambiente e della Tutela del Territorio, 2003). Mean data of As, Cd, Hg, Pb, Zn, Table 2, were generally largely above, from two to twenty fold, the national regulatory guidelines, whereas those of Cr and Ni were below the law limits of 50 and 30 mg/kg d.w., respectively. Fig. 3 shows the spatial distribution of the heavy metals in the surface sediments of the GoP. The spatial distribution of the metals was obtained by a dedicated software (ArcMap version 10.2.2). In the case of As, one hotspot was determined in the north western and other two in the eastern side, inshore and offshore, with values above 60 mg/kg d.w. and hence about five fold higher the law limit as well as above the mean level determined at the low anthropized site of Monte di Procida, located just beyond Cape Miseno, Fig. 1. Levels of Cd were in general very low with the exception of site 4-4 where value was twofold the limit, 0.677 vs 0.3 mg/kg. Regarding the spatial distribution of Cr, Fig. 3, it was interesting to note how the metal displayed higher loads in the western part of the GoP, along transect 1, 11.50–49.55, and 2, 4.80–45.50 and from inshore to offshore. In the case of Cu, the law does not establish any quality standard; anyway the determined mean levels of Cu, 25.6 mg/kg, fall inside the range of other sea sites as the Arabian Gulf, 9 mg/kg, and Bremen Bay, 87 mg/kg. However, the average Cu was 125 folds the GoP background value (Damiani et al., 1987). Likewise As and Cd, the distribution of Cu revealed a hotspot along transect 4 with a peak of 86.16 mg/kg at 4-4. Outstanding values of Fe were observed with a mean of 29.1 g/kg, which was higher than the GoP background value of 25.0 g/kg. Once again, there is an extraordinary accumulation of Fe in transect 4, with peaks of 66.8 g/kg at T4-3, which exceeded of more than two folds the GoP background value, 25.0 g/kg. By contrast, mean Mn value, 419 mg/kg, was ~600 folds the GoP background value, 0.70 mg/kg, with higher accumulation in transect 4, up to 1353 mg/kg at T4-1. The range of Hg was 0.0–25.3, with a mean of 5.8 mg/kg, which was twentyfold higher than the law limit of 0.3 mg/kg and of the GoP background value of 0.25 mg/kg (Damiani et al., 1987) and ~300 folds the mean level determined at Monte di Procida. The elevated concentrations of Hg were noticeable dispersed throughout the study area with a stronger accumulation in the sea portion near the brownfield site. Ni mean value, 9.9 mg/kg, was below the limit of the law, 30 mg/kg, and just at one site, T4-1, the concentration, 35.45 mg/kg, exceed the law limit. The level of variation of Pb was 11.5–378.4, with a mean of 105.8 mg/kg, which was more than threefold higher than the law limit of 30 mg/kg and ~twofold the GoP background value of 60 mg/kg (Damiani et al., 1987). With the exception of the Bremen Bay, mean Pb was outstandingly high respect to the referenced sites reported in Table 2, where Pb varied between 8.4 mg/kg in Florida Bay and 44.0 mg/kg in the Arabian Bay. Once again the distribution of Pb was high in proximity of the former industrial site. Zn range of variation was 42.1–869.9 with a mean value of 224.5 mg/kg, which was three times above the rule and the GoP background of 80 mg/kg. This mean value was also very high if compared with referenced sites (Table 2) and up to more than four times the highest referenced values determined in the Masan Bay, Korea, 206.3 mg/kg. Likewise the majority of the above reported metals, Zn occurred primarily near the Bagnoli site.

The sediment quality criteria of the Florida Department of Environmental Protection (FDEP) and the National Oceanic and Atmospheric Administration (NOAA), the TEL and PEL, and the ERL and ERM, respectively, were used to assess the potential toxicity of sediments (Long et al., 2006; MacDonald et al., 2000), Table 3. The 10th percentile values represent the "Effects Range-Low" (ERL) values and the 50th percentile values "Effects Range-Median" (ERM) values. The ERL values indicate concentrations below which adverse effects rarely occur, and the ERM values those above which adverse effects frequently occur. For each metal the ERL and ERM were calculated. Other two indexes were taken from similar studies, the comparable Threshold Effects Levels (TEL) and the Probable Effects Levels (PEL) to reveal if a specific metal present in sediment represents a threat to aquatic ecosystem, Table 3 (MacDonald et al., 1996; MacDonald et al., 2000).

In this study, our results show that the concentrations of Hg were above the corresponding PEL and ERM by 95.5 and 86.4%, respectively. The concentrations of As, Pb and Zn also revealed threatening conditions for aquatic ecosystems falling in the highest ranges for the indexes reported in Table 4, with concentrations above the PEL by 31.8, 22.8 and 13.6% for Pb, As and Zn, respectively and above the ERM by 9.1,

Table 4
Comparison between heavy metal concentrations (mg/kg) and sediment quality guidelines.

Sediment quality guidelines	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
TEL	7.2	0.68	52.3	18.7	0.174	15.9	30.2	124
PEL	41.6	4.21	160.4	108.2	0.486	42.8	112.2	271
ERL	8.2	1.2	80	34	0.15	21	47	150
ERM	70	9.6	370	270	0.71	52	218	410
% of sample in each guideline								
Compared with TEL and PEL								
< TEL	0	100.0	100.0	50.0	4.5	90.9	18.2	22.7
≥ TEL < PEL	77.2	0	0	50.0	0	9.1	50	54.5
≥ PEL	22.8	0	0	0	95.5	0	31.8	13.6
	3	0	0	2	4	1	3	3
Compared with ERL and ERM								
< ERL	0	100.0	100.0	77.3	4.5	90.9	22.7	40.9
≥ ERL < ERM	95.4	0	0	22.7	9.1	9.1	68.2	50
≥ ERM	4.6	0	0	0	86.4	0	9.1	9.1

9.1 and 4.6% for Pb, Zn and As, respectively. Only Cd and Cr showed concentrations for the entire set of samples (100%) below the corresponding TEL, PEL, and ERL, ERM.

The hazardous of the contaminated sediments was determined by a sediment Ecological Risk Assessment (ERA) The chosen method was that reported by Long and MacDonald (1998), which considered the mean ERM quotient (m-ERM-Q). This index considers the number of pollutants with concentrations higher than the respective Standard Quality Guidelines (SQGs) and the extent to which the concentrations of metals exceeded the SQGs. Thus, the m-ERM-Q represents the effects of multiple anthropogenic contaminations.

$$\mathrm{m-ERM-Q} = \frac{\sum_{i-1}^{Q}\left(\frac{C_i}{\mathrm{ERM}_i}\right)}{n} \tag{2}$$

where C_i is the concentration of the measured metal I, ERM_i is the ERM value of metal I, and n is the number of metals. Long and MacDonald (1998), defined several classes of toxicity probability for biota depending on the value of m-ERM-Q: m-ERM-Q < 0.1, reveals 9% probability of toxicity, $0.1 \leq$ m-ERM-Q < 0.5 denotes 21% probability of toxicity, $0.5 \leq$ m-ERM-Q < 1.5 denotes 49% probability of toxicity, $1.5 \leq$ m-ERM-Q denotes 76% probability of toxicity. The spatial distribution of the m-ERM-Q in the study area is reported in Fig. 4. The spatial distribution of the metals was obtained by a dedicated software (ArcMap version 10.2.2). The m-ERM-Q values indicate a potential for negative biological effects in all the study area, falling in the range 0.5–1.5 with higher probability of toxicity, m-ERM-Q > 1.5, in the area nearby the metallurgic plant. Thus, these results match quite well with the spatial distribution of the heavy metals.

Table 5
Enrichment factors (EF) in GoP of heavy metals in surface sediments.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
T1-1	9.7	0.0	70.0	140.4	8.3	134.4	1.4	2.4
T1-2	15.3	0.0	79.9	137.8	9.4	88.2	1.6	2.4
T1-3	2.6	0.0	132.0	166.8	24.1	67.7	1.9	2.1
T1-4	2.4	0.0	131.5	183.7	35.5	81.2	2.0	2.2
T1-5	1.5	0.0	153.6	153.7	27.8	71.3	0.2	2.1
T2-1	3.3	0.0	31.2	57.3	0.0	36.2	0.7	1.1
T2-2	2.7	0.0	107.1	145.6	14.2	50.1	1.7	2.6
T2-3	2.7	0.0	88.1	106.7	18.4	42.6	1.6	2.3
T2-4	1.3	0.0	129.1	131.8	27.3	104.0	1.6	2.0
T3-1	1.6	0.0	22.8	17.3	1.6	49.7	0.3	0.8
T3-2	3.4	0.0	50.4	47.5	5.9	17.4	1.2	2.3
T3-3	2.7	0.0	5.6	56.6	10.2	18.9	1.0	1.4
T3-4	1.3	0.0	13.1	151.8	31.9	47.5	1.9	2.5
T3-5	1.4	0.0	17.3	151.2	32.4	38.3	1.6	1.9
T4-1	4.3	0.0	4.8	56.2	10.3	136.6	1.4	2.4
T4-2	4.2	0.0	3.5	34.1	5.4	48.4	1.2	1.9
T4-3	1.2	0.8	6.8	105.5	18.1	7.1	1.6	2.8
T4-4	1.6	3.0	7.2	189.5	44.6	10.6	2.8	4.8
T4-5	1.8	0.0	10.7	142.9	31.6	12.5	1.9	2.7
T5-1	2.7	0.0	4.4	42.0	4.9	0.0	0.8	1.3
T5-2	4.1	0.0	3.4	45.4	7.5	0.0	1.4	2.6
T5-3	1.2	0.0	15.0	141.3	27.8	15.6	1.7	2.5

To determine the sources and extent of metal pollution in sediments the enrichment factor (EF) was calculated using Fe as the reference element (Table 5), (Zhang and Liu, 2002):

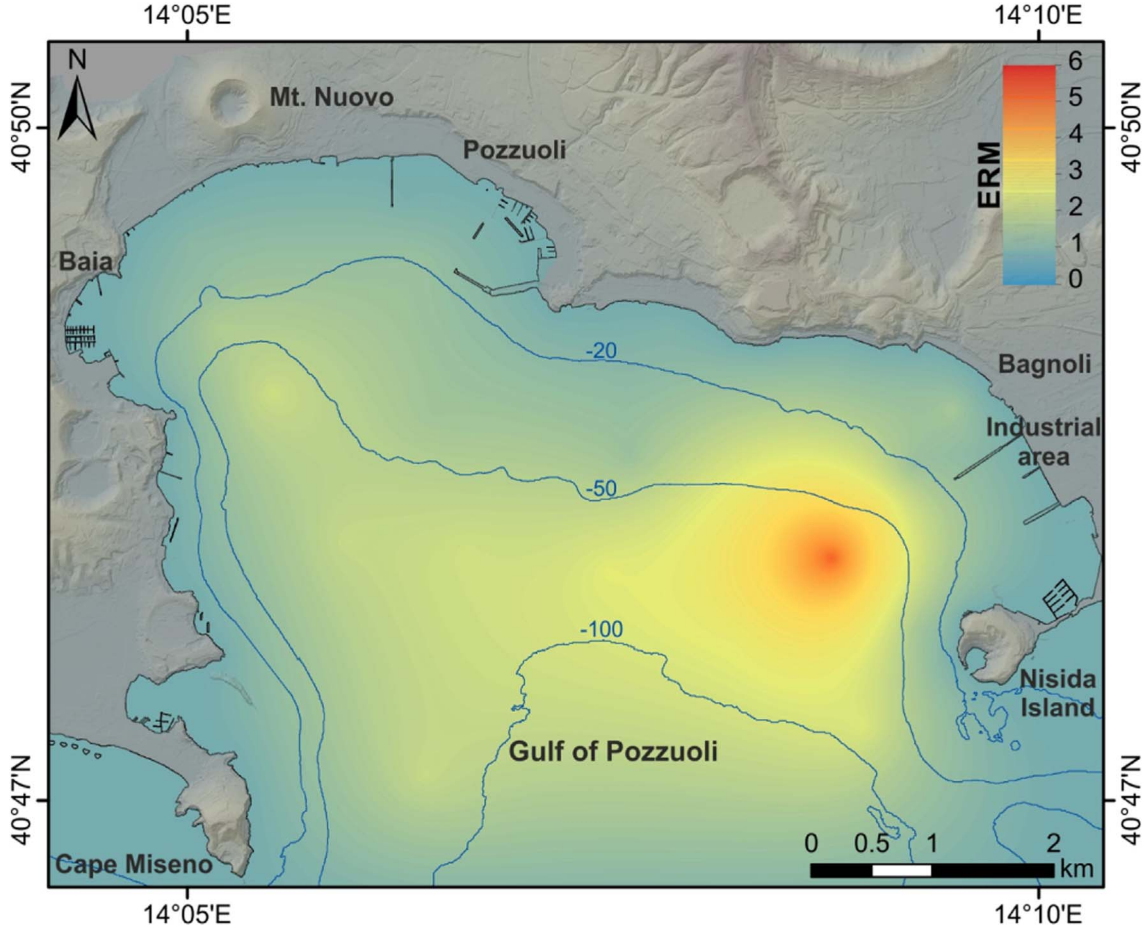

Fig. 4. Spatial distribution of mean-ERM-quotient for the study area. Values along the color ramp are in mg/kg; depth is in meters b.s.l., geographic coordinate system is EPSG Projection 4326 - WGS84.

$$\mathrm{EF} = \frac{\left(\mathrm{metal}/\mathrm{Fe}\right)_{\mathrm{sample}}}{\left(\mathrm{metal}/\mathrm{Fe}\right)_{\mathrm{background}}} \tag{3}$$

The index was made employing as background values for metals those reported by Damiani et al. (1987) for GoP. When the index is > 1.5, the source of the metal is due to anthropic pollution and not to crustal materials or natural weathering processes (Zhang and Liu, 2002). With the exception of Cd, the values of EF were outstandingly high, > 1.5, over the entire GoP, with values which were often ≥ 100, especially in the case of Cr, Cu and Ni. As already observed for the distribution of metals and of m-ERM-Q, the EF highest values were determined in the sea facing the industrial site, Cu 189.5, Hg 44.6, Pb 2.8 and Zn 4.8 at T4-4.

Similarly, the geoaccumulation index, Igeo, can give an idea of the degree of the metals contamination:

$$I_{\mathrm{geo}} = \log_2\left(C_i/kB_i\right) \tag{4}$$

where C_i is the concentration of element I, B_i is the geochemical background value of the element, and coefficient k is used to correct possible variations in regional background values for the given elements. A very critical situation was assessed for Cr, Cu, Hg and Ni which showed an Igeo mostly in the range of strongly polluted (4 < Igeo < 5) and very strongly polluted (Igeo > 5) (Table 6), as outlined by classification proposed by Müller (1981). Likewise the EF, Igeo was calculated using the regional background values (Damiani et al., 1987).

The output of the principal component analysis (PCA) was shown in Table 7. PCA serves to transform a complex dataset creating new variables or factors whereas Pearson's CM to find out the correlation among the metals and confirm the PCA. Three principal components were determined accounting for 78% of total variance. The first principal component explained 46.9% of total variance and loaded heavily on Cd, Cu, Fe, Hg, Pb and Zn. The second principal component, PC2, also heavily loaded Mn, Ni and TOC, whereas the third principal component PC3 correlated with As (moderate positive load) and very strongly with Cr (high negative load).

These results were confirmed by Pearson's correlation matrix (CM), applied to the data (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn, TOC, Mz), which showed significant positive correlations, with an r range of 0.45–0.98 (significant at the 0.05 level), between Cd, Cu, Fe, Hg, Pb and Zn which also grouped in the first principal component PC1. As and Cr did not show any significant correlation, revealing a different source. No significant correlation was found between As, Cd, Cr, Cu, Hg, Ni, Pb and Zn with Mz, likely excluding terrigenous sediments and weathering products as their sources.

Table 6
Geoaccumulation indexes (Igeo) of the heavy metals in the surface sediments.

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
T1-1	1.84		4.69	5.69	− 1.44	1.60	5.63	− 0.98	− 0.16
T1-2	2.61		4.99	5.77	− 1.33	1.90	5.13	− 0.69	− 0.07
T1-3	0.64		6.28	6.62	− 0.76	3.82	5.32	0.12	0.29
T1-4	0.54		6.32	6.80	− 0.72	4.43	5.63	0.26	0.41
T1-5	0.09		6.78	6.78	− 0.48	4.32	5.68	− 2.97	0.60
T2-1	0.19		3.42	4.29	− 1.55		3.63	− 2.15	− 1.36
T2-2	0.62		5.91	6.36	− 0.83	3.00	4.82	− 0.06	0.58
T2-3	0.45		5.45	5.73	− 1.01	3.20	4.41	− 0.30	0.18
T2-4	0.08		6.66	6.69	− 0.35	4.42	6.35	0.34	0.67
T3-1	0.66		4.51	4.10	− 0.01	0.65	5.63	− 1.59	− 0.31
T3-2	1.22		5.11	5.02	− 0.55	2.02	3.57	− 0.26	0.64
T3-3	1.10		2.14	5.47	− 0.35	3.00	3.89	− 0.34	0.14
T3-4	0.14		3.47	7.00	− 0.24	4.75	5.33	0.66	1.06
T3-5	− 0.19		3.45	6.59	− 0.66	4.36	4.60	0.06	0.27
T4-1	1.89		2.04	5.60	− 0.21	3.16	6.88	0.30	1.05
T4-2	2.06		1.82	5.09	0.00	2.42	5.60	0.26	0.95
T4-3	1.06	0.55	3.60	7.56	0.83	5.01	3.66	1.51	2.31
T4-4	1.31	2.17	3.46	8.17	0.60	6.08	4.01	2.07	2.86
T4-5	0.64		3.22	6.96	− 0.20	4.78	3.45	0.74	1.24
T5-1	− 0.42		0.29	3.56	− 1.84	0.44		− 2.13	− 1.51
T5-2	2.07		1.79	5.55	0.05	2.96		0.58	1.42
T5-3	0.19		3.78	7.02	− 0.12	4.68	3.84	0.67	1.19

Table 7
Factor loading and accumulated variance of the heavy metals in the surface sediments.

	PC1	PC2	PC3
As	− 0.101	0.289	0.527
Cd	0.822	− 0.164	0.029
Cr	− 0.108	0.153	− 0.911
Cu	0.943	0.117	− 0.209
Fe	0.766	0.357	0.253
Hg	0.957	0.045	− 0.185
Mn	0.129	0.836	0.372
Ni	− 0.237	0.746	− 0.325
Pb	0.946	0.154	0.179
Zn	0.951	0.189	0.186
TOC	0.397	0.804	0.264
Mz	0.376	0.452	− 0.162
Initial eigenvalue	5.633	2.191	1.532
% of total variance	46.943	18.261	12.770
% of cumulative variance	46.943	65.205	77.975

Table 8 and average modal formula (1) show that granulometric subpopulations which effectively contribute to sedimentary dynamics of study area are the fine sand, secondly the medium and coarse sand. In order to recognize features of drift of marine sandy sediments along the coast and seaward, maps of transit axes of the recognized subpopulations (Fig. 5) were drawn, including those of finer sands to which some heavy metals could combine. Particularly, transit axes of very fine sand, which shows not evident or equal modal peaks but high frequency of appearance, were constructed also considering the increasing percentages of granulometric fraction from inshore dispersal zones towards offshore accumulation areas related to sea-bottom morphology.

Fig. 5 shows the 3D–model of marine sediments mobilization along the seabed of GoP, obtained by modal analysis. Regarding coarse sand, transit axes within 10 m depth due to westward longshore currents were identified. Locally, to these littoral currents a seaward drift joins, NE-SW oriented, due to rip currents inside underwater incisions or interbar channels transversal to the coast. Sediments mainly originate from the erosion of Lucrino beach, to the west. Transit vectors of medium sand highlighted mobilization within 10–15 m depth, mainly due to longshore currents from east to west in the central sector of gulf. Even in such a case, transverse currents move from northeast to southwest along underwater channels close to the coastline, contributing to the morphoevolution of discontinuous system of submerged bars. These sediments mostly originate from the erosion of Bagnoli beach, to the east.

Transit vectors of fine sand show a prevailing littoral drift westward due to longshore currents, within 10 m depth in the central sector of the gulf. An aliquot of sediment moves towards the southwest and south, according to an anticlockwise cell circulation, depositing 30–40 m depth along a wide marine terrace. Instead, part of sediment not far

Table 8
Range of mode values, modal peaks and frequency percentage of appearance of the five granulometric subpopulations identified in the 22 samples of the seafloor of Gulf of Pozzuoli, from about 5 to 95 m depth. [a] Question marks indicate undefined modal peaks due to mode equal values (for details see formula (1)).

Subpopulation	Mode (mm)	Modal peak (mm)[a]	Appearance (%)
Very coarse sand	0.853–0.853	?	4.54
Coarse sand	0.0755–0.603	0.151	9.09
Medium sand	0.0755–0.302	0.302	9.09
Fine sand	0.0755–0.213	0.151	40.90
Very fine sand	0.0755–0.0755	?	36.36

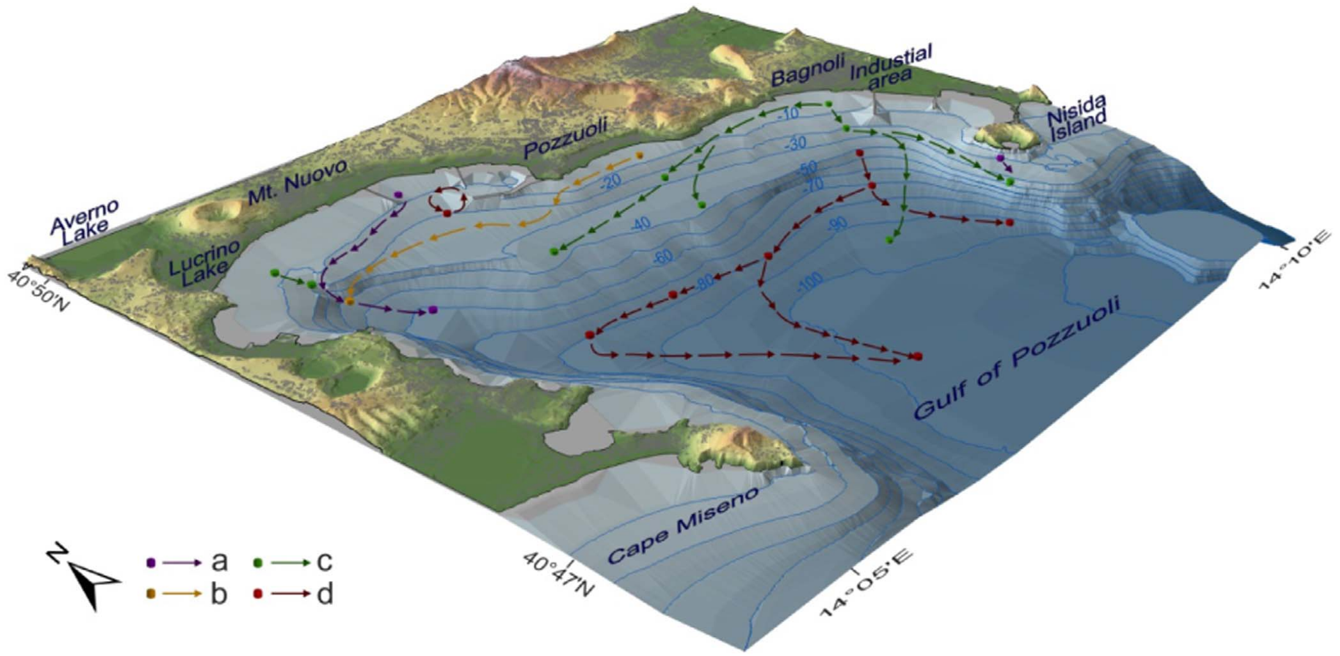

Fig. 5. 3D-model of marine sediments mobilization along the seabed of GoP, based on modal analysis: transit axes of (a) coarse, (b) medium, (c) fine and (d) very fine sands. TIN (Triangulated Irregular Network) basemap by technical maps of Campania region, scale 1:5000. Depth is in meters b.s.l., geographic coordinate system is EPSG Projection 4326 - WGS84.

from the northern pier of former steel industry at Bagnoli, moves in NE-SW direction along an underwater transverse incision, between 20 and 80 m depth, then accumulates to about 90 m depth. A smaller amount of sediment drifts towards southeast, parallel to the shoreline, depositing at 30 m depth along a marine terrace to the southeast of Nisida Island.

Transit axes of very fine sand highlight that sediment dispersal is strictly related to offshore currents. From the shelf, these sediments move transversely along an underwater incision crossing the slope, with head to about 40 m depth. These sediments shift to the west along the base of slope at 80 m depth, due to contour currents, and deposit to the south at about 90 m depth, at the end of a westernmost underwater incision. An aliquot of sediments drifts towards southeast, depositing down to 90 m depth close to Nisida Island.

Dispersal and concentration of eight heavy metals, higher than Italian law limits (see Fig. 3), along the sea bottom (Fig. 5) highlight that two main sources are identified in the gulf: the Bagnoli industrial area, to the east, and the Baia-Pozzuoli industrial and port areas, to the west. Moreover, starting from these sources, two significant directions of sedimentary dispersion, strictly related to morphologic features of the seabed, are identified: one to the west, the other to the east, both converging to the depocenter of gulf.

Particularly, arsenic (Fig. 3a) is uniformly spread throughout with a higher concentration close to the port of Baia, around 15 m depth, very likely as it is a geogenic element of the pyroclastics outcropping in the Phlegrean Fields.

Cadmium, copper, mercury, lead and zinc (Fig. 3b, d, e, g, h) especially accumulated at 50–70 m depth in front of the Bagnoli industrial area, to the east. Instead, nickel (Fig. 3f) is deposited in the same zone within 10 m deep, close to the littoral. Finally, the chromium (Fig. 3c) is mostly concentrated as well as widely distributed to the west, in front of the industrial and port areas of Baia and Pozzuoli, from about 15 down to 90 m depth.

Summarizing, marine sediments within 15 m depth show a littoral drift activated by a clockwise cell circulation, already inferred from analysis of their distribution, due to E-W longshore currents and rip currents towards southwest, according to De Pippo et al. (2002). Sediments over 20 m deep move along two main underwater transversal incisions located at the margins of gulf, NW-SE oriented and 4 km length the western one, while NE-SW direction and 2 km long the eastern one. Finally, these fine sediments accumulate to about 90 m depth. Both paleo-channels are characterized by large paleo-alluvial fans at their base. These narrow valleys were modeled on the mainland by streams in the Late Quaternary and gradually submerged during postglacial sea-level rise interacting with volcano-tectonics. Currently, the underwater channels play still a significant morphological control on offshore dispersal of marine sediments (De Pippo et al., 2004): actually, they capture sands containing heavy metals, which drift longshore within 15 m depth, gradually carrying them through the channel outlet, where these sediments are deposited at the base down to about 95 m deep.

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