



Gathering new knowledge from existing monitoring dataset of Campania marine coastal area (Southern Italy)

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Abstract

In this study we propose, a multi-step strategy of selection and characterization of long-term dataset of contaminant concentrations in different environmental matrices (i.e., water and sediment). Starting from a high quality and homogeneous dataset of chemical parameters, a selection of a usable refined dataset followed by statistical characterization and hazard assessment was performed. The database of chemical contamination data from monitoring activities in the coastal marine water area of the Campania Region (Italy) produced by the Regional Agency for Environmental Protection of Campania (ARPAC) between 2013 and 2019 was utilized. Descriptive and multivariate statistics were applied to the extracted data subset to describe spatial variability and to investigate the relationships between matrices and contaminants. In addition, the impact on the sediment matrix was considered using the contamination factor (Cf), the sediment quality guidelines (SQG), and the probability of exceedance (PoE) of given thresholds for metals and organic compounds. The results highlighted the main anthropogenic pressures between the Gulf of Pozzuoli and the Gulf of Napoli, and the potential hazard posed in particular by metals (i.e., Pb, C, and Hg), TBT, and PAHs. A wide range of As concentration along the Campania coastline and Ni occurrence in the southern part of the region, mainly attributable to geogenic origin, was also evidenced. This approach allows extracting new knowledge from large dataset systematically collected by ARPAC monitoring activity, to support possible actions of contamination control and mitigation.

Keywords Heavy metals · Organic compounds · Hazard evaluation · Chemical dataset · Environmental monitoring

Introduction

The marine environment is experiencing increased anthropogenic pressure deriving from coastal area activities. Coastal land use and development have a direct effect on water quality by creating more impermeable surfaces of urbanized areas and consequently increasing the run-off and transport of pollutants into rivers, estuaries, and coastal waters.

Moreover, the characteristic riverine services and products (e.g., tourism, maritime activities) inevitably can contribute to a deterioration of coastal environmental quality. Rigorous control of the coastal area contamination is therefore needed to guarantee protection and mitigation actions. In particular, datasets of monitoring measurements at relevant spatial and temporal scales are an essential source of information to direct decision making on coastal areas and to optimize experimental activities. Additionally, characterization and assessment of the potential risks posed by contaminants in coastal marine areas is an essential information for managing them in an economically and environmentally sustainable manner. In this work, we present a strategy for data analysis finalized to produce additional knowledge useful for risk characterization in coastal areas, by using the Campania Region long-term monitoring data as case study.

In the case of Campania Region, the coastal system is mainly impacted by domestic and agricultural wastewaters, which, directly or indirectly, reach the sea through canals

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and estuaries. Significant pressures linked to various industrial activities are also reported in the urban coastal areas (Lofrano et al. 2016; Ferraro et al. 2006). Additionally, intense maritime traffic and tourism activities represent, especially in the summer months, a relevant source of sea pollution (Tornero and d'Alcalà 2014).

The Campania Regional Agency for Environmental Protection (ARPAC) develops control and monitoring activities aimed at protecting the coastal seawaters and more in general, the entire territory. Besides, ARPAC provides data to the Italian Institute for Environmental Protection and Research (ISPRA) for the implementation of the Marine Strategy through the integration of the objectives of environmental sustainability and the achievement of the Good Status of the Marine Environment. Therefore, the numerous data produced by ARPAC represent a precious tool for the evaluation of the anthropogenic pressures, the definition of the water quality, and the assessment of the space-temporal variations of chemical contamination. Actually, data relative to water and sediment are available starting from 2013. In the present study ARPAC data, which have the benefit to be homogenous and trustworthy (since they were produced by the same laboratories, according to standard methodologies), were gathered in a single dataset and subjected to a multi-step procedure of data selection and characterization. Advanced data elaboration such as multivariate statistics is useful for interpreting and analyzing complex temporal and spatial trends in environmental quality datasets and for the optimization of regional monitoring networks (Zhou et al. 2007; Bierman et al. 2011; Boye et al. 2019). The analysis allows to identify the main matrices and contaminants of interest to focus the efforts and to assess the impact of chemicals and their mixtures, providing a reference value for areas and periods comparison.

In this study, we apply this strategy to Campania region marine coastal data with the aim to (i) obtain a deeper environmental quality evaluation, (ii) explore spatiotemporal variations of different types of contaminants, (iii) understand the possible contamination pathways in coastal marine areas, and (iv) evaluate the potential ecological risk posed by single chemical contaminant and mixtures.

Materials and methods

Study area

The 512-km coastline of the Campania Region extends along rocky coasts engraved in carbonate, terrigenous and volcanic deposits, and alluvial plains such as those of the Volturno, Sarno, and Sele Rivers. Between the mouth of the river Garigliano (North) and Pozzuoli (South), the coast is low and sandy while the Naples and the Salerno metropolitan

areas are mainly characterized by high and rocky coasts. The Gulf of Salerno starts from Punta Campanella, with high and rocky coasts, up to Salerno where a long alluvial plain starts, ending at Punta Tresino (Agropoli) characterized by rocky shore. The high and rocky coast returns in Punta Licosa, the south limit of the Gulf of Salerno, and extends along the Cilento plateau up to the Gulf of Policastro where sandy and gravelly beaches are also present. The main sedimentary lithology consist of (i) limestone, dolostone, siliceous schist, and terrigenous sediments (clays, siltstone, sandstone, conglomerate), part of the Mesozoic Units, that characterize mostly the external Apennine domains, (ii) the Neogene Units, made up mostly of silico-clastic, carbonatic, and evaporitic sediments, and (iii) quaternary sediments represented by alluvial, lacustrine, and evaporitic sediments and by pyroclastic fall and flow deposits, occurring mainly in the Campania plain (Minolfi et al. 2018).

Natural and protected marine areas (e.g., Regno di Nettuno, Baia, Gaiola, Ischia Island, Punta Campanella, Santa Maria of Castellabate, Infreschi coast, and Masseta coast) areas characterized by high anthropic impacts as site of national interest for the Italian Government (SIN) (i.e., brownfield of Bagnoli-Coroglio in the Gulf of Pozzuoli), and the area of Napoli Orientale (port of Naples and the industrial site of San Giovanni) as well as other sites of regional interests (Litorale Domitio Flegreo, Sarno river basin), are located along Campania coastline (Guida and Valente 2019; Balassone et al. 2016; De Pippo et al. 2008).

Data elaboration

A three steps strategy data elaboration (i.e., collection of homogenous data, exploration and characterization of data, and hazard evaluation) was applied to extract and characterize a subset of usable data form a large set of monitoring ones, and then to evaluate the impacts in the coastal area (Fig. 1). Below is a detailed description of each phase.

Data collection

ARPAC regularly evaluates the chemical contamination (both inorganic and organic) of the local coastal system through monitoring campaigns on sediments and seawaters in five different “physiographic Units”: The Gulfs of Gaeta, Naples, and Salerno, the Cilento Coast, and the Gulf of Policastro (Fig. 2). The chemical analyses are conducted by ARPAC Laboratories in accordance with standard methodologies reported in 2000/60/EC “Water Framework Directive” (D. Lgs 152/2006 and D. Lgs 190/2010) and in manual guidelines of the Institute for Protection and Research (ISPRA, Italy). ARPAC utilizes these data for the classification of coastal marine water bodies, (D. Lgs. 152/2006) and to guarantee the implementation of the Marine Strategy

Fig. 1 Strategy of analysis of monitoring marine coastal areas dataset

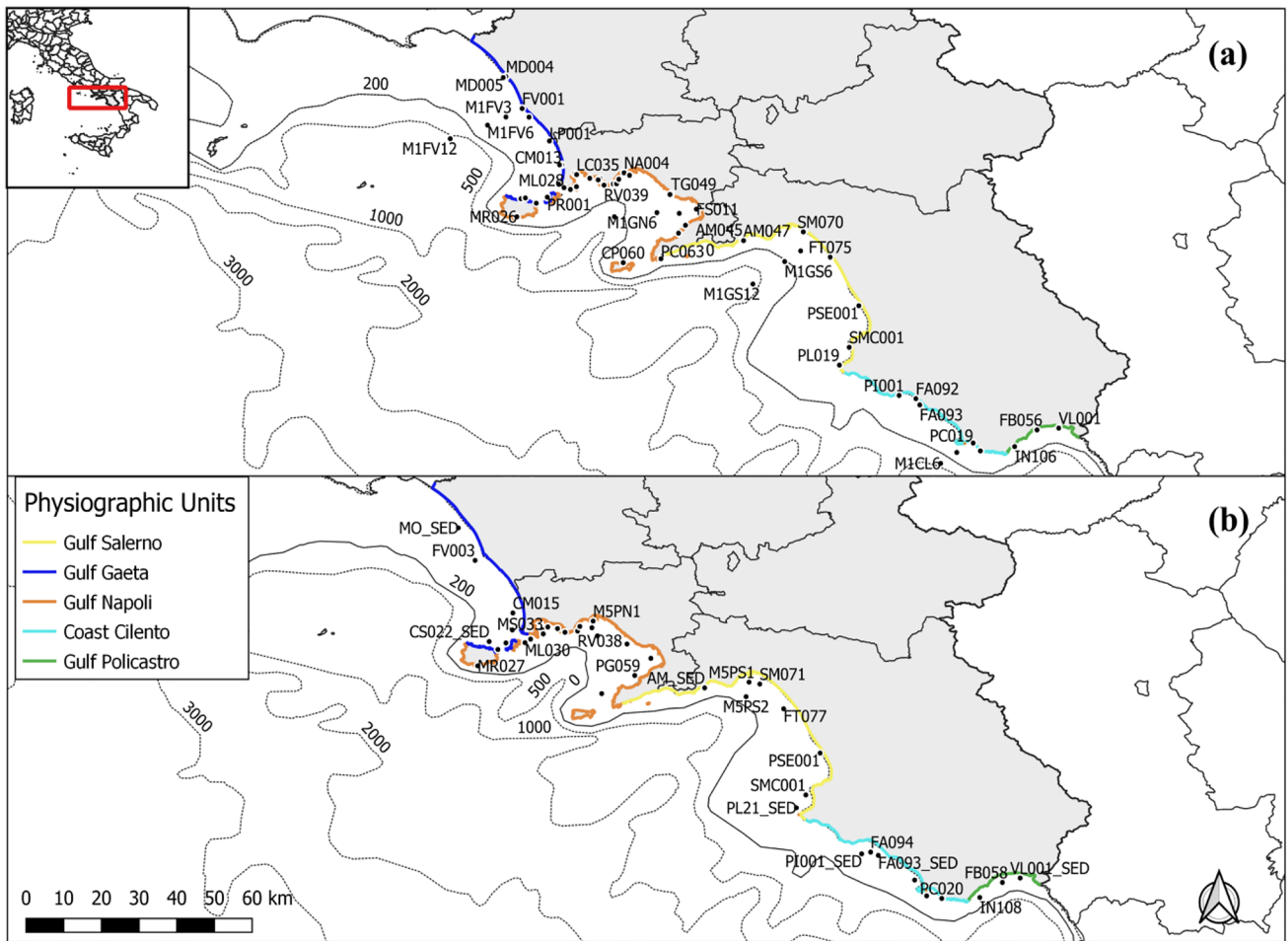
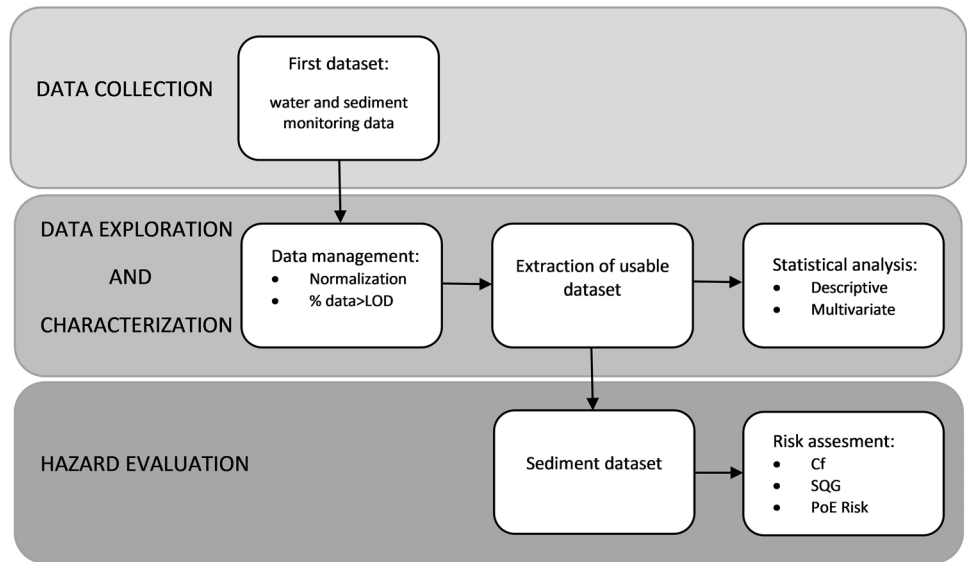


Fig. 2 Maps of Physiographic Units and sampling stations (black dot) of water (a) and sediment (b) matrices along the Campanian coast

(2008/56/EC) for the achievement of the good environmental status of marine water.

In the first collection step, the data available on institutional sites of ARPAC for quality monitoring (<https://dati.arpacampania.it/group/marino-costiero>) and of ISPRA for the Marine Strategy (<http://www.db-strategiamarina.isprambiente.it/app/#/>) were collected and gathered in a single dataset of 8489 records. This includes the following group of contaminants for seawater (i) and surface sediments (ii): (i) metals, organometallic compounds (TBT), polycyclic aromatic hydrocarbons (PAHs), pesticides, semivolatile organic compounds (SVOCs), and volatile organic compounds (VOCs); (ii) metals, TBT, PAHs, pesticides, dioxins, and polychlorinated biphenyl (PCBs) relative to 2013–2019 period.

Data exploration and characterization

In the second step, the initial dataset was normalized to eliminate redundant data and to ensure that data were logically stored. In data storage, we assign to data below the LOD a fixed reference value corresponding to half of the limit of detection (Helsel 2006) and successively, the percentages of data above the limit of detection (LOD) were calculated. Then, we selected the chemical contaminants showing a percentage of actually measured data (> LOD) higher than 10%, so obtaining an available dataset for the following characterization. In particular, descriptive statistical analysis of the data was performed to assess temporal and spatial variation in relevant contaminants. Multivariate statistical analysis using principal component analysis (PCA) was performed to investigate relationships between different types of contaminants in sediments. The data normalization was performed by subtracting the mean from each value and dividing by the standard deviation.

Hazard evaluation

The third step evaluated the environmental impact to surface sediments and considered the final sink of marine coastal areas contamination.

According to Hakanson (1980), we obtained the single metal enrichment of the coastal area by the commonly used contamination factor, calculated as follows: where C_{site} is the mean content of metals in the surface sediment of the

sampling site in the concerned area; and $C_{\text{background}}$ is the natural reference level of metal. Cf calculation was performed by two background reference levels: the average shale concentration (Turekian & Wedepohl 1961) and the regional background levels estimated by Sprovieri et al. (2006). The environmental quality sediments were evaluated by using the Sediment Quality Guidelines (SQG) reported in Table 1: TEL (threshold effects levels), PEL (probability effects levels), ERL (effects range-low), and ERM (effects range-median) (Long et al. 1995; MacDonald et al. 1996).

In addition, the mean PEL and ERM quotient (PEL-Q; ERM-Q) method (Long and MacDonald 1998) was applied to determine the possible adverse effects of contaminant complex mixture in marine sediments.

$$ERM \text{ or } PEL - Q = \sum_{i=1}^8 \left(\frac{[Metal_i]}{ERM_i \text{ or } PEL_i} \right) / n$$

Finally, for each Physiographic Units, the potentially ecologically risk due to each chemical contaminant in sediments was determined. The risk, expressed as a probability of exceedance (PoE) (Solomon et al. 1996), was obtained by comparing the exposure concentration distribution calculated using the data from 2013 to 2019 and the corresponding annual mean environmental standard quality (SQA-MA) established by Italian legislation (DM 260/2010, D. Lgs. 172/2015). Therefore, in this work, the SQA-MA are not intended for management purpose but as an effect benchmark level. The results express the probability that the contaminant concentration will exceed the corresponding SQA-MA in the different Physiographic Units and provide reference values able to highlight significant variations of future monitoring datasets respect to the historical dataset.

The statistical analysis and the estimate of PoEs was carried out by using SIGMAPLOT software version 14.5.

Results and discussion

Data exploration

The maps in Figs. 3 and 4 show, for each station, the percentage of observations higher than the corresponding limit of detection (LOD). For all the contaminant classes, about

Table 1 Numerical sediment SQGs for metals (mg/kg) and PAHs (µg/kg)

| | | AS | Cd | Cr | Hg | Ni | Pb | ANT | BaP | FLT | NAP |
|-----|-----|------|------|------|------|------|------|------|------|------|------|
| SQG | TEL | 7.24 | 0.68 | 52.3 | 0.13 | 15.9 | 30.2 | 46.9 | 88.8 | 113 | 34.6 |
| | PEL | 41.6 | 4.21 | 160 | 0.7 | 42.8 | 112 | 245 | 763 | 1494 | 391 |
| | ERL | 8.2 | 1.2 | 81 | 0.15 | 20.9 | 46.7 | 85.3 | 430 | 600 | 160 |
| | ERM | 70 | 9.6 | 370 | 0.71 | 51.6 | 218 | 1100 | 1600 | 5100 | 2100 |

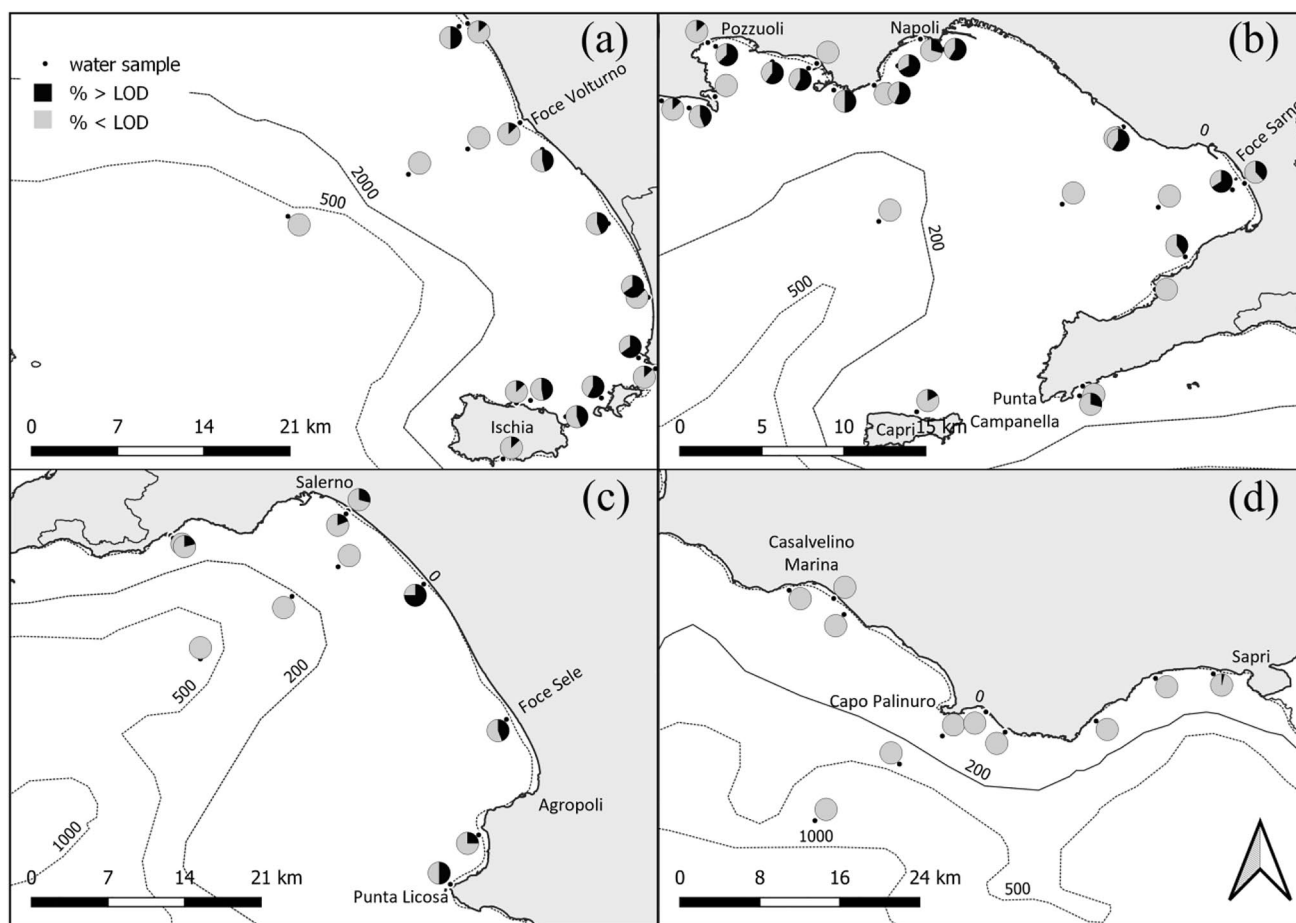


Fig. 3 Percentages of chemical parameter observations above the corresponding LOD values in seawater samples of Gulf of Gaeta (a), Gulf of Napoli (b), Gulf of Salerno (c), and Cilento Coast and Gulf of Policastro (d)

9% of 6.468 measures relative to seawater, exceeded their respective LOD. In particular, 6.4% exceedances are relative to metals and 1.7% to VOCs while the remaining investigated contaminants (i.e., PAHs, TBT, pesticides, and SVOC) showed a percentage < 1%.

Unlike seawater data, the results obtained for the sediments showed that, on 2.021 observations, 49% exceed the LOD values. In particular, 21% exceedances are relative to PAHs, 17% to metals, 6% to pesticides, 3% to TBT, and 3% to dioxin and PCBs.

It is worth noting that, compared with the sediments, a higher number of measurements were not quantified (< LOD) on the water samples. Therefore, these results well evidenced the key role of sediment as a final repository of contaminants in marine systems. However, even if the contaminant amounts in water were below LOD, a potential hazard due to the resulting mixtures cannot be excluded. For this reason, the integration of data relative to water and sediments is a desirable step in properly assessing the chemical quality of coastal areas (Tueros et al. 2009; Tavakoly Sany et al. 2014).

Finally, the dataset usable for the next elaboration include metals data (As, Cd, Cr, Hg, Ni, and Pb) for waters, and metals, TBT and PAHs (anthracene (ANT), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(ghi)perylene (BgP) fluoranthene (FLT) indenopyrene (IND) naphthalene (NAP)) for sediments.

Data characterization

The SQA-MA and descriptive statistical parameters of the dataset, for each chemical parameter, have been reported in Table 2. Furthermore, box plots have been created to describe synthetically the concentration distribution of contaminants for the two matrices (Fig. 5).

Regarding seawater (Fig. 5 a, e, i, m, q), the concentration ranges showed values higher than the SQA-MA only for As (5 µg/l, Table 2). The highest As values have been observed in the Gulf of Gaeta and Napoli (8 µg/l and 10 µg/l respectively), while a value close to environmental standard is recorded in the Gulf of Pozzuoli (4.5 µg/l). Moreover,

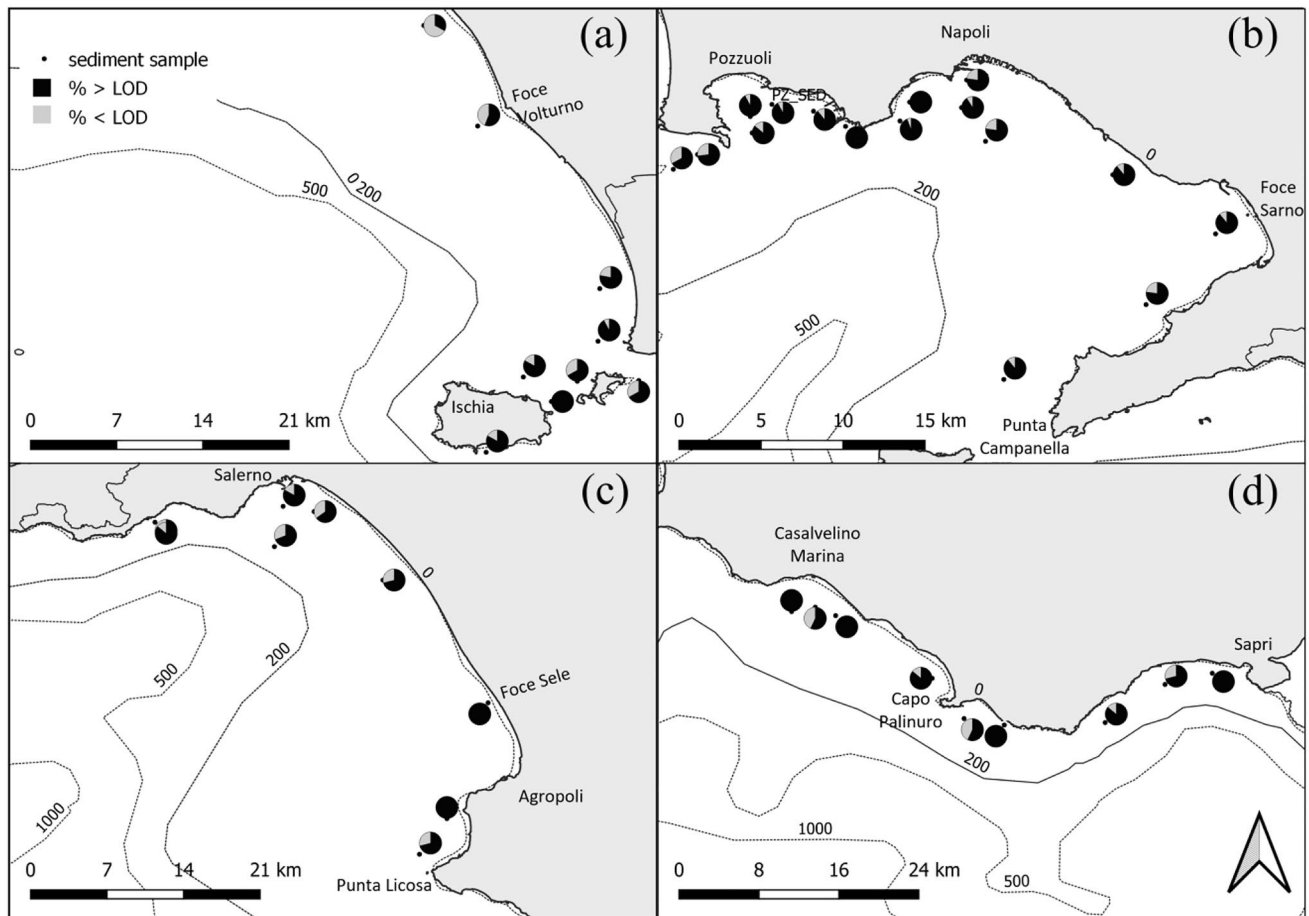


Fig. 4 Percentages of chemical parameter observations above the corresponding LOD values in sediment samples of Gulf of Gaeta (a), Gulf of Napoli (b), Gulf of Salerno (c), and Cilento Coast and Gulf of Policastro (d)

Cd and Hg always showed values lower than the respective detection limits.

In sediments, remarkable concentrations exceeding the SQA-MA values (Table 2) for heavy metals (Fig. 5b, c, f, g, j, k, n, o), organic compounds, and TBT (Fig. 5d, h, l, p, t), in samples from the Gulf of Napoli and Gulf of Pozzuoli were especially detected. Among the investigated areas, the most contaminated site is the Gulf of Pozzuoli, due to the presence of the brownfield of Bagnoli-Coroglio (Armiento et al. 2020). In this area, the highest values of Pb (568 mg/kg), As (32 mg/kg), Hg (1.6 mg/kg), and Cd (0.8 mg/kg) have been observed. Besides, in the Gulf of Naples, Pb (113 mg/kg), As (22 mg/kg), and Hg (1 mg/kg) overcame the corresponding standards and, in absolute terms, the maximum Cr (364 mg/kg) concentration was observed. This last value is most probably attributable to the influence of highly polluted Sarno River (Albanese et al. 2013; Cicchella et al. 2014; Thiombane et al. 2018). The Gulf of Salerno showed critical values for Cr (66 mg/kg) and Pb (86 mg/kg) probably originating from the local commercial port activities (Birch & Taylor 1999; Jahan & Strezov 2018). Also As (24 mg/

kg) showed high value respect to the reference threshold. In the area of Cilento Coast and Gulf of Policastro, only Ni (27 mg/kg) and As (15 mg/kg) concentrations, are higher than the standard quality reference values, while Pb (35 mg/kg) exceeds SQA-MA in the Gulf of Gaeta and the As mean concentration (11.4) is close to its threshold value. The higher Ni measurements in the Southern Campania Region are mainly influenced by marly arenaceous flysch deposition which more than 50% occur in this area (Budetta et al. 2008; Thiombane et al. 2018). The relatively high levels of As (Table 2) reported for water and sediment samples along the Campania coastline originated from both anthropic and geogenic sources. In fact, large portions of the Region (mainly corresponding to the Physiographic Units of the Gulfs of Naples and partly of Gaeta and Salerno) are characterized by the occurrence of arsenic (and other metals) in rocks and fluids ascending through the hydrothermal system associated to the volcanic areas of the Phlegrean Fields and Vesuvius. Accordingly, Sprovieri et al. (2006) estimated, in the Southern Campania shelf area, between the Gulf of Salerno and the Gulf of Policastro, a geochemical background level for

Table 2 SQA-MA and summary statistics for metals in water (µg/l) and metals (mg/kg), TBT (µg/kg), and PAHs (µg/kg) in sediment

| | Water (µg/l) | | | | | | | | | | Sediment (mg/kg) | | | | | | | | | | Sediment (µg/kg) | | | | |
|--------------------------------------|--------------|-------|------|------|--------|------|------|-----|------|-----|------------------|-----|-----|--------|--------|--------|------|--------|--------|--------|------------------|----|--|--|--|
| | As | Cd | Cr | Hg | Ni | Pb | As | Cd | Cr | Hg | Ni | Pb | TBT | ANT | BaP | BbF | BkF | BgP | FLU | IND | NAP | | | | |
| Gulf of Gaeta | SQA-MA | 5 | 0.2 | 4 | 0.01 | 8.6 | 1.3 | 12 | 0.3 | 50 | 0.3 | 30 | 5 | 24 | 30 | 40 | 20 | 55 | 110 | 70 | 35 | | | | |
| | N | 52 | 21 | 52 | 21 | 21 | 21 | 4 | 21 | 4 | 21 | 4 | 21 | 21 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 21 | | | |
| | Min | 1.2 | 0.02 | 0.02 | 0.004 | 0.05 | 0.01 | 7 | 0 | 26 | 0 | 8.5 | 0 | 0.5 | 0.5 | 1.8 | 0.8 | 2.2 | 1.1 | 0.8 | 1.1 | | | | |
| | Max | 8.0 | 0.1 | 2.3 | 0.005 | 1.9 | 0.01 | 11 | 0.1 | 36 | 0.1 | 20 | 35 | 14 | 19 | 103 | 41 | 47 | 105 | 59 | 23 | | | | |
| Gulf of Pozzuoli | Mean | 2.2 | 0.02 | 0.7 | 0.005 | 0.2 | 0.01 | 9.0 | 0.03 | 31 | 0.05 | 15 | 17 | 2.2 | 2.8 | 24 | 14 | 18 | 53 | 22 | 2.3 | | | | |
| | SD | 1.2 | 0.02 | 0.7 | 0.0005 | 0.4 | 0 | 1.9 | 0.04 | 4.5 | 0.04 | 5.3 | 7.5 | 4.0 | 27 | 30 | 12 | 15 | 38 | 20 | 4.8 | | | | |
| | N | 60 | 12 | 60 | 12 | 12 | 12 | 3 | 13 | 3 | 13 | 3 | 13 | 13 | 12 | 12 | 12 | 12 | 12 | 12 | 13 | | | | |
| | Min | 0.005 | 0.02 | 0.02 | 0 | 0.05 | 0.01 | 12 | 0 | 28 | 0.1 | 4.7 | 67 | 0.5 | 13 | 156 | 87 | 106 | 302 | 0.8 | 1.1 | | | | |
| Gulf of Napoli | Max | 4.5 | 0.1 | 3.4 | 0 | 1 | 0.5 | 32 | 0.8 | 39 | 1.6 | 8.3 | 568 | 12,307 | 18,001 | 14,985 | 8323 | 12,840 | 54,795 | 14,454 | 80 | | | | |
| | Mean | 1.9 | 0.03 | 0.5 | 0 | 0.3 | 0.05 | 21 | 0.3 | 34 | 0.5 | 6.8 | 173 | 10 | 2368 | 5912 | 2839 | 5124 | 14,110 | 4582 | 17 | | | | |
| | SD | 1.2 | 0.03 | 0.7 | 0 | 0.3 | 0.1 | 10 | 0.3 | 5.3 | 0.5 | 1.9 | 152 | 17 | 3686 | 6809 | 3271 | 5946 | 18,532 | 6335 | 27 | | | | |
| | N | 155 | 42 | 155 | 46 | 46 | 46 | 15 | 36 | 15 | 36 | 15 | 37 | 36 | 35 | 36 | 35 | 35 | 36 | 35 | 35 | 35 | | | |
| Gulf of Salerno | Min | 0.005 | 0.02 | 0.02 | 0.004 | 0.05 | 0.01 | 7.0 | 0 | 19 | 0 | 0 | 11 | 0.5 | 0.5 | 1.8 | 0.8 | 2.2 | 1 | 0.8 | 1.1 | | | | |
| | Max | 10 | 0.1 | 2.6 | 0.005 | 1.6 | 1.9 | 22 | 0.2 | 364 | 1 | 24 | 113 | 30 | 114 | 390 | 202 | 362 | 787 | 408 | 12 | | | | |
| | Mean | 1.8 | 0.02 | 0.5 | 0.004 | 0.2 | 0.1 | 13 | 0.08 | 75 | 0.3 | 10 | 57 | 5.2 | 21 | 100 | 48 | 86 | 148 | 90.0 | 2.1 | | | | |
| | SD | 1.6 | 0.02 | 0.6 | 0.0003 | 0.3 | 0.3 | 4.0 | 0.07 | 99 | 0.3 | 5.9 | 27 | 6.3 | 30 | 108 | 54 | 94 | 169 | 115 | 2.3 | | | | |
| Cilento Coast and Gulf of Policastro | N | 40 | 12 | 40 | 14 | 14 | 14 | 10 | 13 | 10 | 13 | 8 | 13 | 13 | 12 | 12 | 12 | 12 | 12 | 12 | 13 | | | | |
| | Min | 0.005 | 0.02 | 0.02 | 0.004 | 0.05 | 0.01 | 6.2 | 0 | 10 | 0 | 6.6 | 6.3 | 0.5 | 0.5 | 1.8 | 0.8 | 2.2 | 1.1 | 0.8 | 1.1 | | | | |
| | Max | 3.2 | 0.02 | 1.5 | 0.005 | 0.6 | 0.5 | 24 | 0.2 | 66 | 0.2 | 29 | 86 | 430 | 6.0 | 32 | 65 | 19 | 51 | 17 | 13 | | | | |
| | Mean | 1.2 | 0.02 | 0.2 | 0.004 | 0.09 | 0.05 | 13 | 0.08 | 29 | 0.04 | 16 | 24 | 35 | 1.5 | 12 | 9.1 | 5.5 | 18 | 4.3 | 2.2 | | | | |
| Cilento Coast and Gulf of Policastro | SD | 0.9 | 0 | 0.5 | 0 | 0.2 | 0.1 | 4.9 | 0.06 | 17 | 0.06 | 7.9 | 22 | 119 | 10 | 18 | 5.4 | 15 | 5.2 | 3.3 | | | | | |
| | N | 36 | 14 | 36 | 14 | 14 | 14 | 5 | 10 | 5 | 10 | 5 | 10 | 10 | 6 | 6 | 6 | 6 | 6 | 6 | 10 | | | | |
| | Min | 0 | 0.02 | 0.02 | 0 | 0.05 | 0.01 | 6.4 | 0 | 14 | 0 | 18 | 7.3 | 0.45 | 0.5 | 1.8 | 0.8 | 2.2 | 1.1 | 0.8 | 1.1 | | | | |
| | Max | 0.05 | 0.02 | 0.02 | 0.01 | 0.05 | 0.01 | 15 | 0.2 | 40 | 0.1 | 39 | 30 | 0.45 | 4.0 | 7.9 | 3.9 | 2.2 | 2.5 | 3.5 | 1.1 | | | | |
| Cilento Coast and Gulf of Policastro | Mean | 0.02 | 0.02 | 0.02 | 0 | 0.05 | 0.01 | 11 | 0.08 | 25 | 0.04 | 27 | 16 | 0.45 | 1.0 | 2.8 | 1.3 | 2.2 | 5.2 | 1.3 | 1.1 | | | | |
| | SD | 0.02 | 0 | 0 | 0 | 0 | 0 | 3.3 | 0.06 | 11 | 0.04 | 8.6 | 6.4 | 0 | 1.4 | 2.5 | 1.3 | 0 | 9.7 | 1.1 | 0 | | | | |

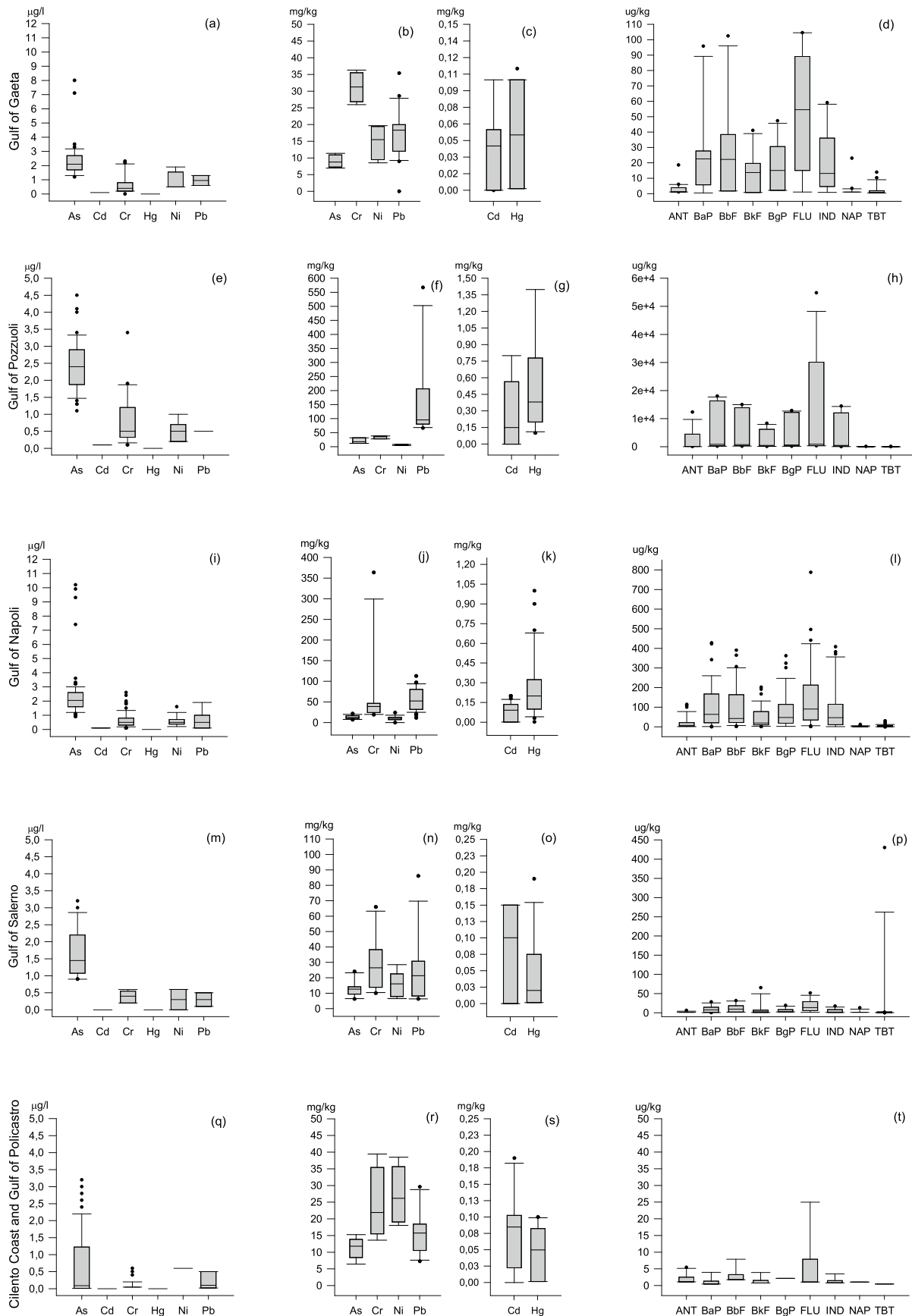


Fig. 5 Box plots of metal distribution in the water (a, e, i, m, q) and metals (b, c, f, g, j, k, n, o, r, s) PAHs, and TBT (d, h, f, p, t) in sediments of five coastal areas of Campania Region (Gulf of Gaeta, Gulf of Pozzuoli, Gulf of Napoli, Gulf of Salerno, Cilento Coast, and Gulf of Policastro). The box represents the 25th and 75th percentiles; the solid line represents the median value; lower and upper whisker are the 10th and 90th percentiles and the dots represent the outlying points

As of 21.49 mg/kg, about twice the reference standard value (SQA-MA = 12).

Finally, TBT contamination and PAH occurrence can be evidenced in several sediment samples. Overall, the PAH highest concentration values are found especially in the Gulf of Pozzuoli (where threefold the SQA-MA values were evidenced), Napoli, and Gaeta. Instead, TBT concentrations with values higher than the corresponding SQA-MA (5 µg/kg, Table 2) were observed in all gulfs except in the area of the Cilento Coast and the Gulf of Policastro.

Since organic compounds were never reported in seawaters, a multi-pollutant PCA elaboration (based both on inorganic and organic pollutants) was possible only on sediments data (Fig. 6). Data strictly related to the brownfield area of Bagnoli represented outliers, due to the sensibly higher values of organic pollutants (especially PAHs) compared to the other samples and therefore were removed from the data processing. The PCA results showed the highest contamination in the Gulf of Napoli and Pozzuoli. All PAHs, excluding Naphthalene, have a very similar orientation in the PCA

graph, suggesting a common source. PAHs have, moreover, a good correlation with organotin compounds and with most heavy metals (As, Pb, Hg). Naphthalene, instead, mostly correlates with Cd and Cr. Ni enrichments affect essentially the Gulf of Policastro and Salerno (these two areas, moreover, are the ones with negligible organic pollution if compared to the others). Ni exhibited a strong negative correlation with the other anthropogenic components, suggesting a different pattern of enrichment in the sediments and therefore a geogenic origin. However, Ni and Cr enrichments influenced by the discharge of the drainage channel collecting water from farmlands and wastewaters were already observed in Cilento coastal areas (Lofrano et al. 2016).

Hazard evaluation

Data relative to sediment contaminants and background levels relative to average shale and Campania shelf were utilized for the hazard evaluation by Cf values (Table 3). The results always show low levels of metals pollution in Gulf of Gaeta, Salerno, and Cilento coast and Gulf of Policastro, unless moderate pollution relatively to Pb in the Gulf of Salerno. Noticeable differences in Cf values obtained with the two background levels (Table 3) can be observed in the Gulf of Pozzuoli and Napoli. In particular, Cf values calculated relatively to Hg show low (0.68) in Napoli and moderate (1.29) in Pozzuoli pollution using the average shale, and considerable (3.90), in Napoli and very high pollution

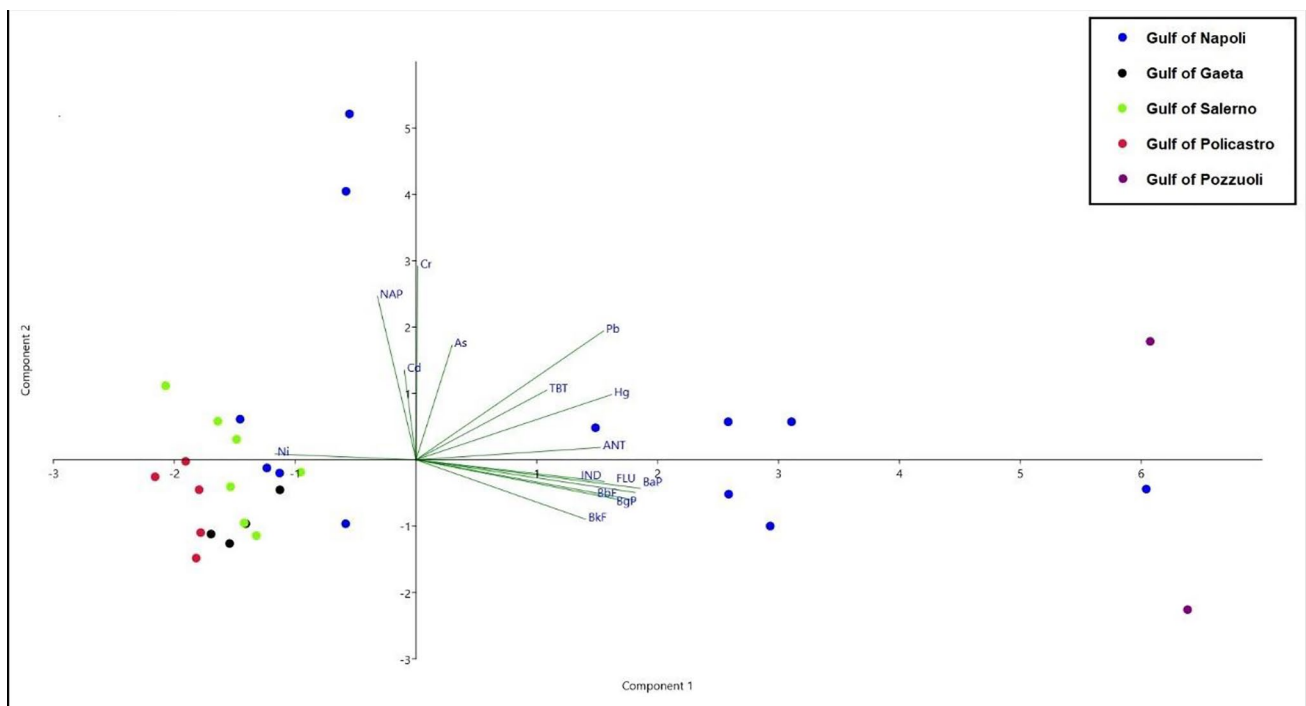


Fig. 6 Surface sediments metals and PAHs distribution on a two-dimensional PCA plot (component 1 and component 2)

Table 3 Contamination factor of five marine coastal areas of Campania Region

| | Average shale* (mg/kg) | Campania shelf** (mg/kg) | Contamination factor (Cf) | | | | |
|----|---------------------------|--------------------------------|---------------------------|-------------|-----------|------------|--|
| | | | G. Gaeta | G. Pozzuoli | G. Napoli | G. Salerno | Cilento Coast and G. Polli- castro |
| As | 13 | 21.5 | 0.69/0.42 | 1.60/0.97 | 1.03/0.62 | 0.98/0.59 | 0.87/0.52 |
| Cd | 0.3 | 0.16 | 0.11/0.21 | 0.90/1.68 | 0.25/0.48 | 0.27/0.50 | 0.25/0.47 |
| Cr | 90 | 51.0 | 0.35/0.61 | 0.38/0.67 | 0.83/1.46 | 0.32/0.56 | 0.28/0.49 |
| Hg | 0.4 | 0.07 | 0.12/0.71 | 1.29/7.37 | 0.68/3.90 | 0.11/0.61 | 0.11/0.62 |
| Ni | 68 | 28.9 | 0.22/0.51 | 0.10/0.24 | 0.14/0.34 | 0.23/0.55 | 0.40/0.94 |
| Pb | 20 | 21.4 | 0.86/0.80 | 8.62/8.05 | 2.86/2.66 | 1.22/1.14 | 0.79/0.74 |

Cf < 1 low pollution; 1 < Cf < 3, moderate pollution; 3 < Cf < 6, considerable pollution; Cf > 6, very high pollution

*From Turekian and Wedepohl (1961)

**From Sprovieri et al. (2006)

(7.37) in Pozzuoli, using the local background Campania shelf. Finally, moderate pollution and very high pollution, in the Gulf of Napoli and Pozzuoli, were respectively observed for the Pb with both background levels. By using the local background levels, the following metal pollution ranking was obtained Pb > Hg > Cr > Ni > As > Cd in the Gulf of Gaeta, Pb > Hg > Cd > As > Cr > Ni in the Gulf of Pozzuoli, Hg > Pb > Cr > As > Cd > Ni in the Gulf of Napoli, Pb > Hg > As > Cr > Ni > Cd in the Gulf of Salerno, and Ni > Pb > Hg > As > Cr > Cd in the Cilento coast and Gulf of Policastro. The comparison of sediment values with SQG (Table 4) showed that only As falls in medium range of possible effects (89% > TEL < PEL and 84% > ERL < ERM). However, since the concentration of organic and inorganic contaminants overcame PEL and ERM thresholds at

maximum in 10% of samples, a clear hazard due to single contaminants cannot be advocated.

Instead, the effects of multiple contamination (i.e., metals and PAHs), evaluated by the mean PEL and ERM quotient, evidenced high hazard at Bagnoli site, in the Gulf of Pozzuoli, while slight hazard was observed in the Gulf of Naples, Salerno and Policastro (Fig. 7).

Finally, the PoE value percentages for each contaminant in the sediment and in each investigated area are reported in Fig. 8.

The results showed that potential ecological risk posed by metals and PAHs is maximum in the central zone of the Campania coastline, between the Gulf of Pozzuoli and the Gulf of Napoli. In this area the probability that exposure concentrations for contaminants will exceed the corresponding

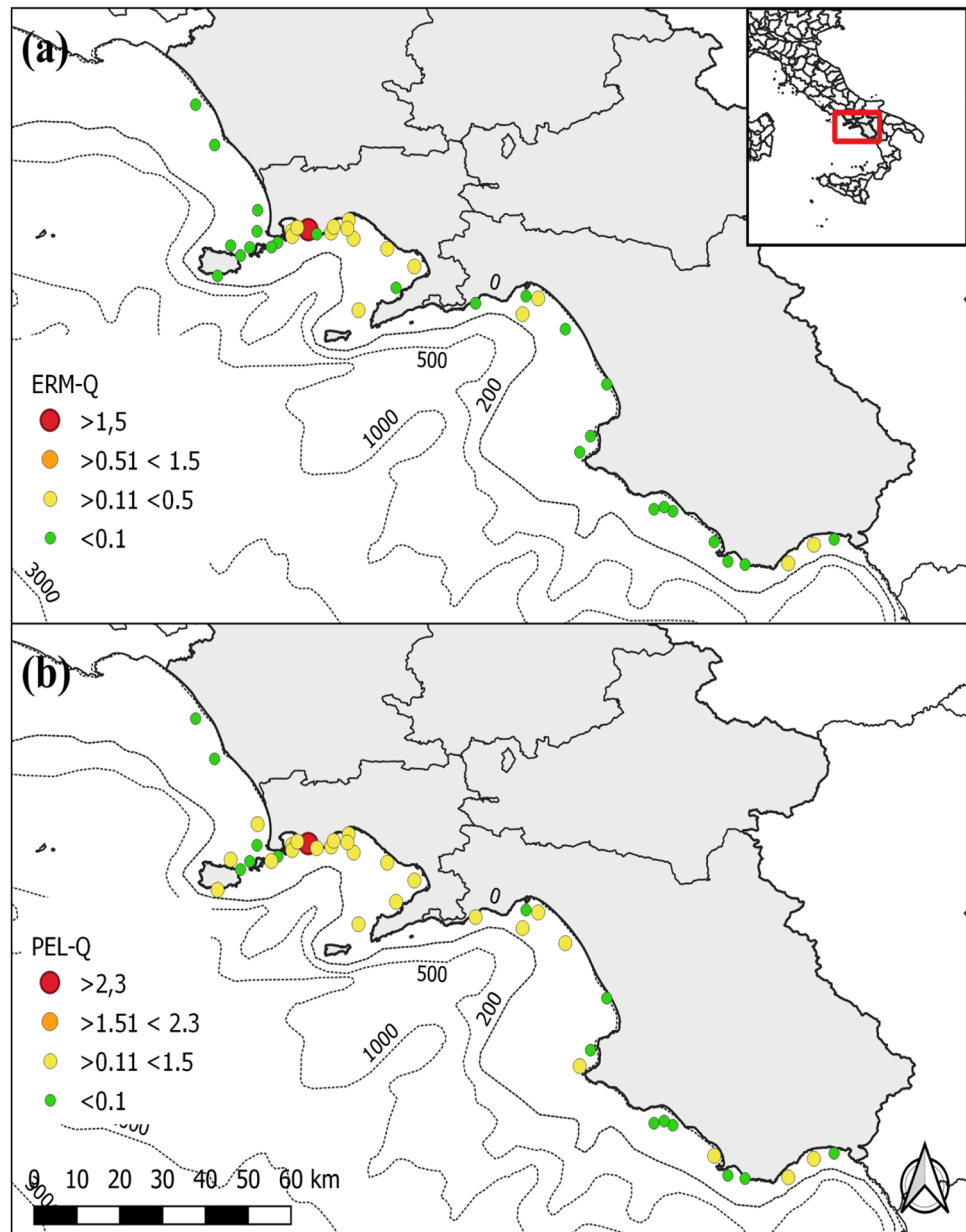
Table 4 SQGs of superficial marine sediment samples of the Campania Region

| Substance | N samples | Percentage of sample compared to each guideline (%) | | | | | |
|--------------------|-----------|---|-------------|-------|-------|-------------|-------|
| | | ≤ TEL | > TEL < PEL | ≥ PEL | ≤ ERL | > ERL < ERM | ≥ ERM |
| As | 37 | 11 | 89 | 0 | 16 | 84 | 0 |
| Cd | 92 | 98 | 2 | 0 | 100 | 0 | 0 |
| Cr | 37 | 89 | 5 | 5 | 92 | 8 | 0 |
| Hg | 93 | 62 | 33 | 6 | 65 | 30 | 5 |
| Ni | 34 | 62 | 38 | 0 | 82 | 18 | 0 |
| Pb | 94 | 51 | 41 | 7 | 62 | 35 | 3 |
| Anthracene | 92 | 84 | 11 | 5 | 86 | 9 | 5 |
| Benzo(a) pyrene | 77 | 66 | 25 | 9 | 91 | 3 | 6 |
| Fluoranthene | 76 | 67 | 26 | 7 | 88 | 5 | 7 |
| Naphthalene | 92 | 97 | 3 | 0 | 100 | 0 | 0 |

Effects range: ≤ TEL minimal; > TEL < PEL possible; ≥ PEL probable

Effects range: ≤ ERL rarely; > ERL < ERM occasionally; ≥ ERM frequently

Fig. 7 Maps of the priority sample site based on ERM_q values and PEL_q values. Priority site: highest ERM-Q > 1,5 or PEL-Q > 2,3; medium 0,51 < ERM-Q < 1,5 or 1,51 < PEL-Q < 2,3; medium low 0,11 < ERM-Q < 0,5 or 0,11 < PEL-Q < 1,5; lowest eRM-Q < 0,1 or PEL-Q < 0,1



SQA-MA is between 8 and 60%, except for Ni. This probability is lower in the Gulf of Gaeta, Salerno, in the Cilento Coast and Policastro. The evidenced probability of Ni excess in the Gulf of Policastro, a low anthropogenic pressures area, strongly suggest its geogenic origin as discussed above.

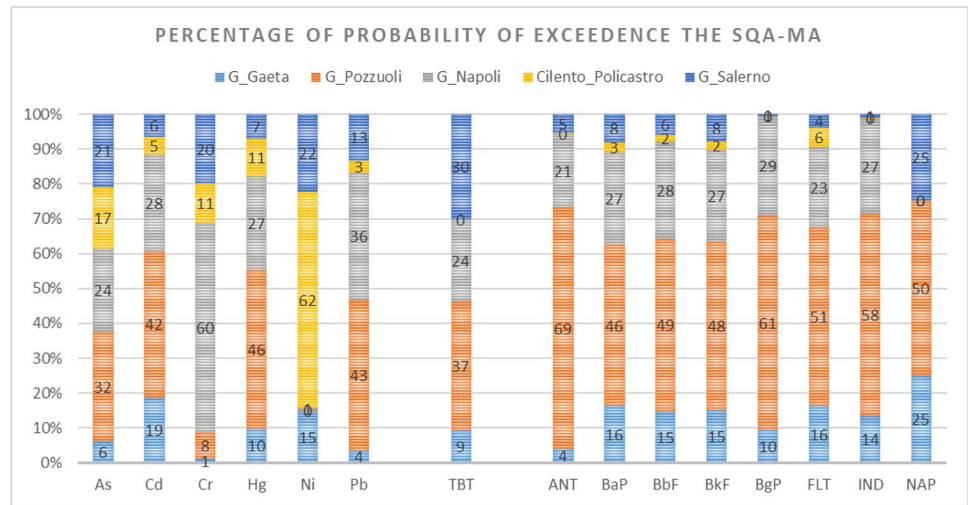
Conclusions

Numerous chemical monitoring activities are being carried out on regional and national scales worldwide.

The large dataset on the chemical contamination of the marine coastal systems of the Campania Region, provided by the constant monitoring activity of the ARPAC, represents a precious scientific experience useful as a reference point for the entire scientific community and interested stakeholders. A better coordinated, integrated approach to management and assessment of the existing data would contribute to an improved assessment of relevant legislation and protection of citizens and the environment.

The proposed strategy of data analysis allowed us to evaluate the main anthropogenic pressures and optimize the

Fig. 8 Percentage of probability of exceedance of the SQA-MA for each contaminant in the 5 marine coastal zones of the Campania region



needed information for the proper protection and management of coastal systems.

In this study, the chemical dataset useful for a more in-depth assessment of environmental quality was determined, highlighting the need to use both the information on the aqueous matrix and those coming from the sediment one. The dataset allowed highlighting peculiar situations not evidenced by water analyses alone, such as the large distribution of As amount in the sediment and the relevant presence of Ni in the southern part of the region. Actually, by using a strategy of data analyses that considered not only the chemical measurements but also the hazard evaluation, that takes into account site-specific background levels and therefore the local lithology, the source (geogenic and/or anthropogenic) and the degree of contamination can be more properly determined.

However, it is worth noting that in the case of the Campania Region, the current monitoring programs show some weak points suggesting further steps for the future. Firstly, the chemical analysis of the waters, based on discrete observations, should be complemented with integrated measurements, e.g., by passive sampling that allows the measurement of very low concentrations of contaminants, to overcome the frequent occurrence of data under LOD. Secondly, the hazard evaluation should be tailored to the site-specific conditions and the local natural background, and specific benchmarks should be defined and adopted as reference thresholds. Lastly, the combined action due to the co-occurrence of different contaminants is not predictable solely on the base of chemical analyses and needs to be evaluated by effect-based monitoring.

Author contribution Conceptualization and methodology were performed by Sonia Manzo and Luisa Parrella. Data collection was performed by Simona Schiavo, Stefano Capone, and Anna Valeria

Siciliano. Visualization was done by Carlo Tebano. Formal analysis was performed by Luisa Parrella, Fabio Spaziani, and Salvatore Chiavarini. The first draft of the manuscript was written by Sonia Manzo. Lucio De Maio and Giovanna Armiento revised previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The data analyzed during this study are available on institutional sites of ARPAC (<https://dati.arpacampania.it/group/marino-costiero>) and ISPRA (<http://www.db-strategiamarina.isprambiente.it/app/#/>).

Declarations

Ethical approval and consent to participate. Not applicable.

Consent to publish Not applicable.

Conflict of interest The authors declare no competing interests.

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