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A statistical approach for the use of environmental quality standards (EQS) in marine sediments in the environmental quality assessment of harbor areas

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Abstract

Purpose The environmental quality standards (EQSs) were defined by the Water Framework Directive (2000/60/EC) and daughter directives for hindering the chemical pollution of surface water bodies. For substances with poor solubility in water and/or the tendency to bioaccumulate along the food chain, member states could choose to define the EQSs on sediments and marine organisms if they guarantee the same level of protection of the EQSs derived for water. Also, Italy defined them on sediments without considering harbors because of their role as pressure sources. Considering the available environmental information, this study focused on verifying the applicability and possible limits of the EQSs in sediments from different Italian harbors.

Materials and methods A dataset with concentrations of metals and trace elements (MTEs) and organic compounds (OCs) from the sediments of 34 Italian harbors was assessed. Grain size parameters were also included for complete information on sediment characteristics. Data were processed through univariate statistics to identify the position of the EQSs within the whole distribution of concentration values. Moreover, a logistic model was applied to verify the probability of exceeding the EQSs for at least one parameter (susceptibility) in the harbor areas.

Results and discussion The EQSs of all MTEs were found close to the overall medians, demonstrating that they are suitable values for highlighting widespread metal contamination, also recognizable in the output of the logistic model, where wide areas with a homogeneous susceptibility were highlighted. The EQSs of most OCs resulted considerably higher than the overall medians, but a minor part of the data exceeded them by far, demonstrating that the contamination was characterized by patchy distribution, as also shown by the susceptibility maps.

Conclusions Applying a statistical approach, this study tried to compare the distribution of concentration data with the EQSs of sediments based on a specific dataset containing many records from many Italian harbors. The logistic model applied in this study, based on the excess of the EQSs for at least one parameter, represented a robust tool to define areas at high susceptibility in the harbors and confirmed their adaptability also in these highly impacted areas.

Keywords Environmental quality standards · Marine sediments · Harbors · Metals and trace elements · Organic contaminants

1 Introduction

The Water Framework Directive (2000/60/EC) defined the strategy for hindering the chemical pollution of surface water bodies with the obligation to prevent any deterioration and achieve a “good” status, which means surface water bodies meet all environmental quality standards. The environmental quality standards (EQSs) established by Directive 2008/105/EC and the subsequent Directive 2013/39/EC

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are the selected tools for assessing their chemical status. The EQSs established for the water column concern various priority and dangerous-priority substances, while for some "specific pollutants," each member state establishes them autonomously, and they contribute, together with the other substances, to the classification of the ecological status of the surface water bodies. For substances with poor solubility in water and/or the tendency to bioaccumulate along the food chain, member states can choose to define the EQSs on sediments and marine organisms if they guarantee the same level of protection of the EQSs derived for

In transposing the European directives, Italy also determined and periodically updated the EQSs for marine coastal and transitional sediments (Ministerial decrees 367/2003, 56/2009, 260/2010, and legislative decree 172/2015) (Table 1). These values were defined based on a chemical–physical and ecotoxicological approach, considering threshold effect level 9TEL), which is the threshold value below which adverse effects for benthic organisms are negligible; in addition, the chemical and ecotoxicological data were also correlated with concentrations determined in mussels' tissues to assess potential bioaccumulation (Romano et al. 2018, 2022). The data were collected along the Italian coasts, characterized by different geomorphological, sedimentological, and geochemical features and varying degrees of anthropogenic impact, during the "National Coastal Marine Monitoring Program," coordinated by the Ministry of the Environment and carried out between 2001 and 2008.

In identifying marine coastal waters, the Italian legislation (Ministerial decree 131/2008) does not consider harbor waters as they do not fall within the definition of a water body according to Annex II of WFD, instead considering them pressure sources. In Italian harbor areas, industrial and maritime activities, commonly considered sources of pressure, often coexist with tourist recreational or fish/mussels farming activities, which instead require greater attention concerning the environmental quality of the sediments. In these contexts, using EQSs defined through a chemical–ecotoxicological approach with data from coastal marine monitoring areas could be more suitable, as they consider the physical and geochemical variability of the Italian coasts.

For this reason, this study aims to verify the applicability and possible limits of the EQSs also in sediments from different Italian harbors, considering the available environmental information, in particular (a) checking through a univariate statistical approach the suitability of the EQS for each chemical parameter and (b) demonstrating that, on the whole, the EQSs can be used for studying the pollutant distribution also in the harbors, applying a multivariate

Table 1 EQSs related to metals and trace elements, polycyclic aromatic hydrocarbons, and polychlorobiphenyls in sediments adopted by national legislation (ministerial decree, D.M., and legislative decree, D.lgs)

Substances	DM 367/2003	DM 56/2009	DM 260/2010	D.lgs. 172/2015
Metals and trace elements	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Arsenic	12	12	12	12
Cadmium	0.3	0.3	0.3	0.3
Chromium	50	50	50	50
Chromium VI	5	2	2	2
Lead	30	30	30	30
Mercury	0.3	0.3	0.3	0.3
Nickel	30	30	30	-
Polycyclic aromatic hydrocarbons (PAHs)	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Anthracene	0.045	0.045	0.045	0.024
Benzo[a]pyrene	0.03	0.03	0.03	0.03
Benzo[b]fluoranthene	0.04	0.04	0.04	0.04
Benzo[g,h,i]perylene	0.055	0.055	0.055	0.055
Benzo[k]fluoranthene	0.02	0.02	0.02	0.02
Fluoranthene	0.11	0.11	0.11	0.11
Naphthalene	0.035	0.035	0.035	0.035
Indeno[1,2,3-c,d]pyrene	0.07	0.07	0.07	0.07
Σ PAHs *	0.2**	0.8	0.8	-
Polychlorobiphenyls (PCBs)	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Σ PCBs ***	0.004	0.008	0.008	0.008

*acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-c,d]pyrene, naphthalene, phenanthrene, pyrene; **benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, indeno[1, 2, 3-c, d]pyrene; ***PCB 28, 52, 77, 81, 101, 118, 126, 128, 138, 153, 156, 169, 180 approach. This study was carried out on a dataset formed of metals and trace elements (As, Cd, Cr, Hg, Ni, Pb) and organic compounds (polycyclic aromatic hydrocarbons (PAHs), and polychlorobiphenyls (PCBs)) derived from 34 Italian harbors distributed along the whole coast analyzing the statistical distribution of their concentrations. The considered harbors are generally different in dimensions and shapes, textural and geochemical characteristics of sediments, and types and degrees of contamination (Fig. 1).

2 Material and methods

2.1 Dataset

The dataset originated from the results of the characterizations carried out between 2001 and 2013 was mainly aimed at defining the environmental assessment of the marine sediments for their subsequent management (i.e., dredging, nourishment) or verifying the need for reclamation actions. The Regional Delegate Commissioners for Environmental Emergency (Calabria, Campania, Puglia, and Sicilia), Port Authorities (Bari, Napoli, Gaeta, Genova, La Spezia, Livorno, Massa Carrara, Palermo, Piombino, Taranto, and Trieste), Regions (Sardinia and Marche), and Provinces mainly carried out the activities (Table 2).

All the investigations followed different in-force legislation based on similar strategies and integrated chemical–physical and ecotoxicological approaches. The main investigated parameters were grain size, metal and trace elements (Al, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, and Zn), and organic compounds (PAHs, PCBs, total hydrocarbons, dioxins, and organochlorine pesticides). The sampling strategy was usually organized in grids of variable size (from 50 × 50 m to 450 × 450 m) according to the complexity of the harbor (i.e., the presence of

Fig. 1 Italian harbors considered

Table 2 Environmental surveys in the Italian harbors. Details about the period of investigations and the number of available samples are reported

#	Harbor	Label	Year	Station number	Sample number
1	Ancona	AN	2009–	62	62
2	Bari	BA	2011	60	60
3	Barletta	BT	2011	31	31
4	Brindisi	BR	2003–	353	739
5	Buggerru	BU	2007	45	90
6	Castellammare di Stabia	CdS	2007–	13	26
7	Civitanova Marche	CM	2009	12	12
8	Crotone	CR	2005–	88	197
9	Fano	FA	2009	22	22
10	Fiumicino	FIU	2007	38	38
11	Gaeta	GA	2013	34	34
12	Gela	GL	2009	9	18
13	Genova	GE	2005	336	336
14	La Spezia	SP	2001–	454	875
15	Livorno	LI	2005	126	252
16	Marina di Stabia	MdS	2008	8	16
17	Massa Carrara	MS	2005	27	54
18	Monopoli	MO	2011	15	15
19	Napoli	NA	2002	191	382
20	Numana	NU	2009	12	12
21	Palermo	PA	2008	8	8
22	Perd'e Sali	PeS	2007	10	20
23	Piombino	PI	2002, 2004	123	238
24	Portoscuso	PS	2012	9	17
25	Portovesme	PV	2006	44	87
26	Porto Torres	PT	2005, 2006	68	107
27	Rada Augusta	AU	2005	288	862
28	Sant'Antioco	SA	2007	44	87
29	Senigallia	SE	2009	14	14
30	Siracusa	SI	2006	46	92
31	Taranto	TA	2004–	1517	3614
32	Torre Annunziata	TrA	2007–	16	32
33	Torre del Greco	TrG	2008	4	8
34	Trieste	TS	2004–	163	234
	Total			**3187**	**7036**

petrochemical, metallurgical, and thermoelectric plants or military arsenals, shipyards, and high maritime traffic) and the closeness to the docks; in each grid, a sediment core of variable length with standardized sampled levels was collected (Dastoli et al. 2012; Ausili et al. 2020).

In this work, only data relating to chemical substances having EQS, obtained from superficial sediment samples, indicatively associated with the first 50 cm, were considered. The dataset included:

- Grain size as a percentage of gravel, sand silt, and clay
- Metals and trace elements (As, Cd, Cr, Hg, Ni, and Pb)
- Polycyclic aromatic hydrocarbons (anthracene (AN); benzo(a)pyrene (BaP); indeno(1,2,3-c,d)pyrene (IND); benzo[b]fluoranthene (BBF); benzo[k]fluoranthene (BkF); fluorene (FL); benzo[g,h,i]perylene (BghiP); naphthalene (NAP)
- ΣPAHs (acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene, pyrene)
- ΣPCBs (PCB 28, PCB 52, PCB 77, PCB 81, PCB 101, PCB 118, PCB 126, PCB 128, PCB 138, PCB 153, PCB 156, PCB 169, PCB 180)

All the activities were carried out under the supervision and with the validation of the National control bodies, which provided technical indications and guidelines for the execution of the different characterization phases; the chemical–physical analyses were carried out in agreement with the official and standardized methods.

2.2 Statistical analysis

The statistical analysis was carried out using univariate and multivariate analysis techniques with different packages of the R 3.6.2 software. The univariate descriptive analysis was applied to grain size and chemical parameters by calculating each harbor's mean and standard deviation. Furthermore, the data distribution associated with each chemical parameter was studied using the SuppDists package (Wheeler 2022). Johnson's (1949) method allowed through the formula:

$$z = \gamma + \delta \, log\left[f(u)\right] \tag{1}$$

where $u = (x\text{-}xi)/\lambda$ and $f()$

The classification of the variable distributions in one of the following four classes of probability functions:

$$SL\, f(u) = u \; log - \text{normal distribution} \tag{2}$$

$$SU\, f(u) = u + sqrt(1 + u^2) \text{ unbounded distribution} \tag{3}$$

$$SB\, f(u) = u/(1 - u) \text{ bounded distribution} \tag{4}$$

$$SN\ F(u) = exp(u)\ normal\ distribution \tag{5}$$

Since the normal distribution results from many small independent effects occurring in a specified order, Johnson's method assumed that the magnitude of an effect is proportional to a function of the variable's value before adding a constant value. Through these transformations, the final variables should be normally distributed. The normality in the distribution of a variable is a fundamental requirement both for applying robust statistical inference techniques and for defining the limits of the confidence intervals calculated on the variables under study. These limits allowed the construction of the control charts of each substance and were useful to define the range of variation and the percentile associated with the EQS and to highlight the upper tail (values above the upper bound (UB), 97.5 percentile) of the distribution. This tail contains 2.5% of the observations, which are the outliers occurring in the distribution of each variable, while some other outliers can be directly eliminated during the logarithmic transformation for the determination of z, as reported in [1].

As regards multivariate analyses, the hierarchical cluster analysis (HCA) using Ward's method was applied to the grain size for identifying groups of harbors with similar sediment texture using the R energy package (Rizzo and Szekely 2022). Moreover, grain size and chemical data (median values for each harbor) were processed together through a coinertia analysis (CA), which plots the results of two distinct principal component analyses, one applied to grain size and the other to chemical parameters, on the same plane (Dray et al. 2003). The Monte Carlo test was applied to the CA to verify the goodness of matching the two analyses using the R ade4 package (Chessel et al. 2004; Dray and Dufour 2007; Dray et al. 2007).

Finally, the logistic regression analysis (Geyer 2003) was applied to highlight the areas within the most representative harbors with a high probability of exceeding the EQSs for at least one parameter and, consequently, to construct "susceptibility" maps using geostatistical techniques. For this purpose, the following dichotomous dependent variable was defined as follows:

$Y = 0$ if the observations do not exceed the EQS.
$Y = 1$ if the observations exceed the EQS for at least one parameter.

ArcGIS Pro 2.7.1 was used to generate the susceptibility maps of selected harbors that, based on the CA results, showed an evident correlation with specific metals and trace elements (MTEs) and organic compounds (OCs), also considering grain size.

3 Results and discussion

3.1 Sediment texture

Overall, the Italian harbors showed a high variability of the sediment texture (Table S1). Considering the mean percentages of grain size classes, sand was the most abundant one, reaching 98% in the Buggerru harbor (western Sardinia), while silt and clay were more abundant at Barletta and Senigallia, in the Adriatic Sea, with the highest mean values of 67.9% and 61.7%, respectively. On the other hand, mean gravel was always scarce, with percentages nearly always lower than 10% and the highest value in the Genova harbor (17.8%). The results of the HCA confirmed a markedly different sediment distribution among the harbors, carried out on 30 of the 34 considered harbors, due to incompleteness of data in four of them. The analysis identified two main clusters, A and B, the first one mostly characterized by coarser sediment, both sand and gravel, and the second one by finer sediment (Fig. 2). A total of 17 harbors were included in cluster A; among these, there were some big harbors, such as Genova on the Ligurian coast, Napoli on the southern Tyrrhenian, and Brindisi on the Adriatic one, as well as smaller harbors like those of the western Sardinia and the Gulf of Naples (Fig. 1). Cluster B was divided into B1 and B2, mostly characterized by clay and silt, respectively. The harbors of Ancona and Senigallia, on the central Adriatic coast, Trieste (northern Adriatic), and Piombino (northern Tyrrhenian) constituted cluster B1, characterized by higher percentages of clay. Cluster B2 was related to the silty fraction and included nine harbors, among which were the big ones of La Spezia, in the Ligurian Sea, Taranto, and Augusta, on the eastern and western Ionian coast, respectively. Harbors of cluster B, particularly those of B1, are potentially exposed to higher contamination due to the adsorption ability of clay minerals owing to a larger surface area and greater cation exchange capacity (Szava-Kovats 2008).

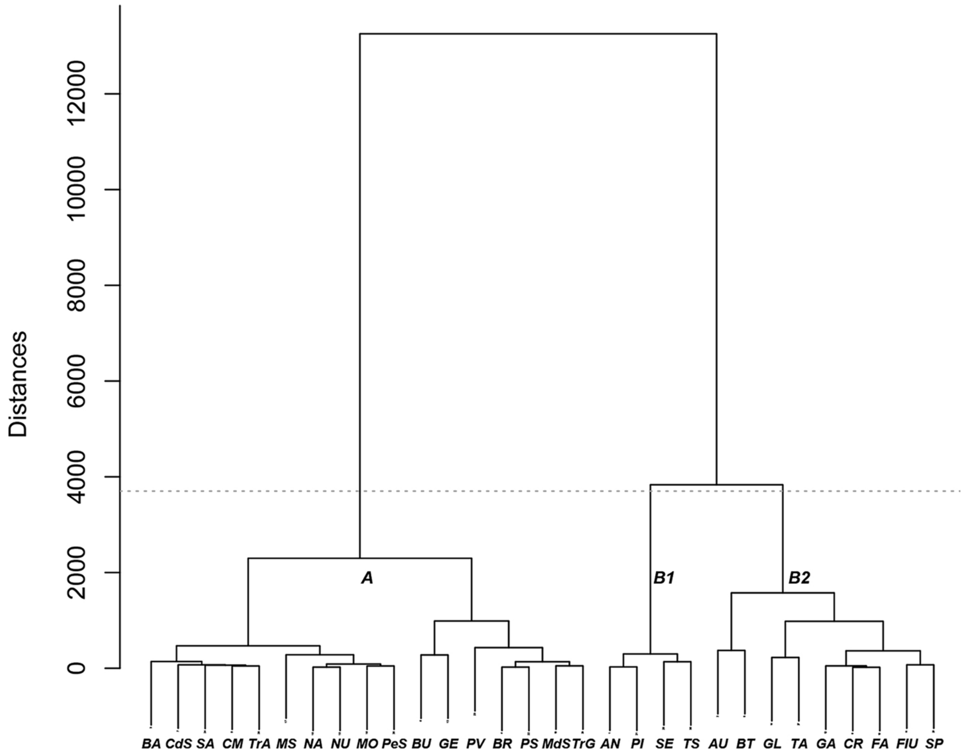
3.2 Chemical substances

The concentrations of MTEs and OCs in each harbor have been synthesized in terms of mean and standard deviation in the supplementary materials (Tables S2 and S3). From the data of MTEs, it resulted that those affected by averages overcoming the EQS for most of the elements were mainly big ports such as Genova, La Spezia, Napoli, and Piombino, with very high concentrations mainly for Cr (173, 90, 144, and 107 mg kg^{-1}, respectively), Hg (0.76, 3.02, 2.49, and 0.82 mg kg^{-1}, respectively), and Pb (148, 306, 203, and 467 mg kg^{-1}, respectively). However, the highest average concentrations were associated with high standard deviations to indicate wide data variability inside each harbor. Other big harbors such as Bari and Trieste, despite average concentrations below the EQS for most elements, showed excesses only for Hg (1.53 and 0.73 mg kg^{-1}, respectively) and Pb (138 and 210 mg kg^{-1}, respectively). On the other hand, the Sardinian small harbors of Buggerru, Portovesme, and Sant'Antioco displayed average concentrations remarkably above the EQS for Cd (47, 4, and 3 mg kg^{-1}, respectively), Hg (0.97, 1.37, and 0.98 mg kg^{-1}, respectively), and Pb (623, 177, and 130 mg kg^{-1}, respectively). Worthy of note is the moderate excess of the As averages common to all the small harbors of the Gulf of Naples (Castellammare di Stabia, Marina di Stabia, Torre Annunziata, and Torre del Greco) with values of 15.7, 19.2, 19.2, and 14.9 mg kg^{-1}, respectively, associated to limited standard deviation.

The overall distribution of all analyzed data for each substance was represented in the normalized curves obtained through Johnson's method (Figs. 3 and S1). The positioning of the EQS on the curve of each element was quantified by the percentile determined on the whole data distribution. Moreover, the comparison of the location of the median of each harbor with the EQS allowed us to evaluate their degree of compliance with the environmental standards.

From the comprehensive observation of the diagrams relating to the MTEs, it was clear that large Italian harbors, such as Bari, Genova, La Spezia, Napoli, and Piombino, were affected by systematic excesses of the EQS mostly

Fig. 2 Dendrogram from hierarchical cluster analysis carried out on grain size data (see Table 1 for the correspondence of the harbor labels)



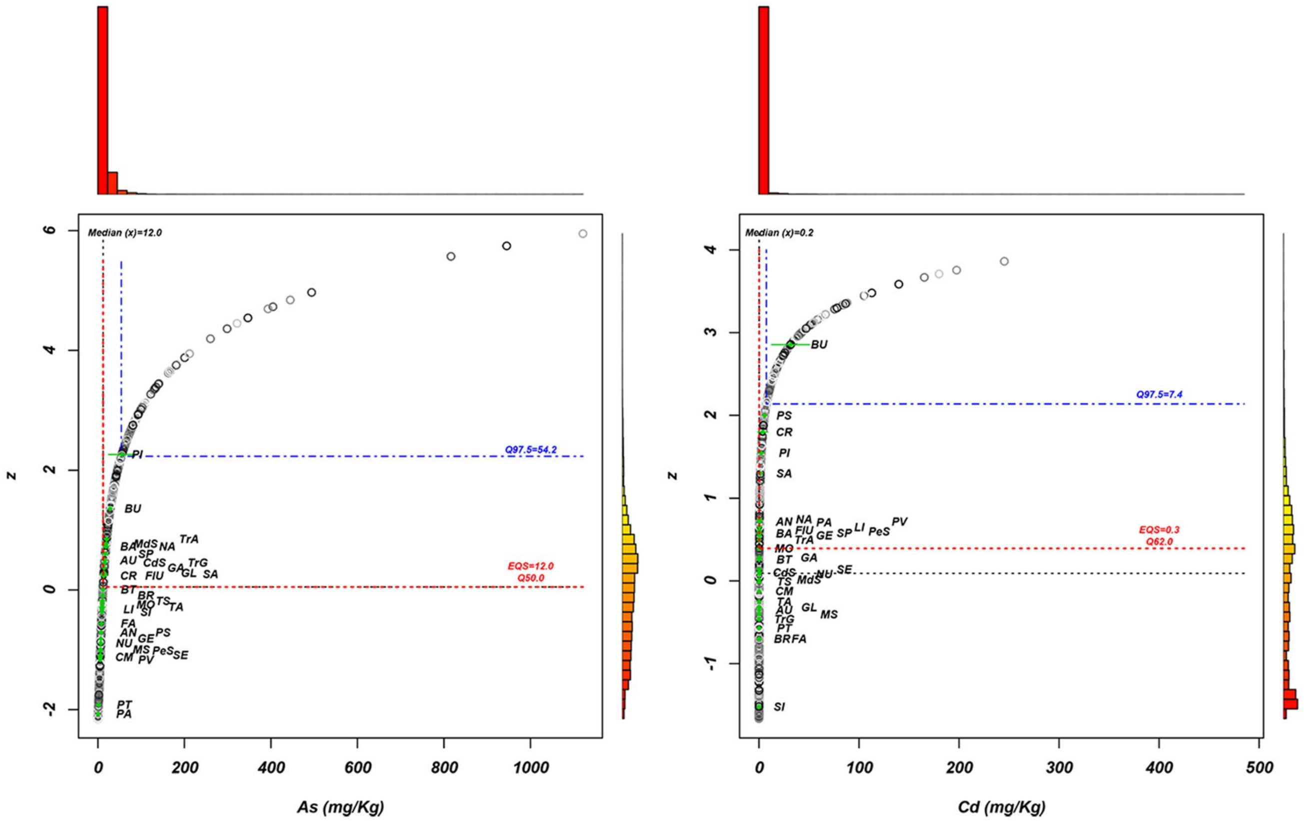


Fig. 3 Two examples of concentration distribution of MTEs processed through Johnson's method. The medians of each harbor were highlighted on the distribution curve. The black dashed line indicates the data distribution's overall median (OM, 50th percentile), the red dashed line indicates the position of the EQS, and the blue dashed line is the upper bound (UB, 97.5th percentile)

for Cd, Cr, Hg, and Pb. Another characteristic of the MTEs is the systematic overcoming of the EQSs of specific elements in well-defined areas in terms of mean and median. In particular, the Ligurian Sea harbors (Genova, La Spezia, and Massa Carrara) and most of those of the central Adriatic Sea (Ancona, Fano, and Senigallia) were characterized by medians above the EQS for Cr and Ni; in the last ones, the metal enrichment was also enhanced by the silty clayey nature of sediments. Similarly, some Sardinian harbors (Buggerru, Portoscuso, Portovesme, and Sant'Antioco) were characterized by an excess of Cd and Pb, while those of the Gulf of Naples (Torre Annunziata, Torre del Greco, Castellammare di Stabia, Marina di Stabia, and Napoli) showed an excess of As (Figs. 1 and 3). These regional enrichments may be attributed, at least partially, to the high geogenic supply due to geochemical anomalies on the mainland (Romano et al. 2022, and references therein).

In Johnson's curves, the EQSs of most MTEs resulted coinciding or very close to the overall median (OM) (50th percentile), in the range between 46.0 and 54.4 percentile, while it was higher for Cd, at the 62.0 percentile (Figs. 3 and S1, Table 3). This result pointed to the EQS adaptability also in highly impacted areas. However, it showed that, in many observations, all MTEs exceeded the EQSs, pointing to the widespread contamination of the Italian harbors. The rate UB/EQS was determined to quantify to what extent, excluding the outliers, each metal exceeded the EQSs. The upper

Table 3 Environmental quality standards (EQSs) of MTEs and main characteristics of Johnson's distribution curve: overall median (OM) and upper bound (UB)

	As	Cd	Cr	Hg	Ni	Pb
EQS (mg kg^{-1})	12.0	0.3	50.0	0.3	30.0	30.0
EQS percentile	50.0	62.0	54.4	51.0	46.1	46.0
OM (mg kg^{-1})	12.0	0.2	46.5	0.29	32.6	34.9
UB (mg kg^{-1})	54.2	7.4	212.5	6.8	95.3	670.0
UB/EQS	4.5	24.6	4.3	22.7	3.2	22.3

concentrations recorded for As, Cr, and Ni were from 3- to fourfold the EQS, while those of Cd, Hg, and Pb exceeded it by 22- to 25-fold, indicating that, in univariate terms, these are the metals that are affected by the widest excesses of the EQSs, mostly contributing to sediment contamination.

As concerns OCs, average concentrations in each harbor indicated that Piombino, Trieste, and, to a lesser extent, Genova were by far the most contaminated by PAHs, showing considerable excess of the EQS for all the eight considered PAHs, and for ΣPAHs, that was 141.849, 92.475, and 15.826 mg kg^{-1}, respectively (Table S3). La Spezia and Taranto harbors showed wide excess of the EQS for all the single PAHs, except NAP, and for ΣPAHs, which was 4.802 and 6.794 mg kg^{-1}, respectively. Several harbors showed average concentrations of ΣPCBs above the EQS, with high values at Taranto, La Spezia, and Piombino (0.746, 0.263, and 0.261 mg kg^{-1}, respectively) and a very high value (26.79 mg kg^{-1}) at Palermo (Table S3). A high standard deviation indicated wide data variability in all the described cases.

Analyzing the normalized curves obtained through Johnson's method, it may be observed that for every PAH, except NAP, Piombino, Genova, Napoli, and, sometimes, Bari showed medians largely exceeding the EQS. At the same time, harbors that mostly contributed to the outliers were Piombino, Taranto, and Trieste. For those with the EQS positioned lower in the curve, such as BaP and BbF, the medians of smaller harbors, such as Torre Annunziata, Castellammare di Stabia, and Monopoli, were clearly above this threshold. On the other hand, only Palermo exceeded the EQS of NAP, being positioned very high on the curve (Figs. 4, S2, and S3), and the harbors of Trieste, Genova, and Piombino mostly contributed to the outliers. The last one showed by far the highest median for ΣPAHs, followed by Genova, Bari, and Napoli, although also Taranto and Trieste displayed very high values in the field of outliers. The distribution of ΣPCBs among the Italian harbors was quite different from that of ΣPAHs, due to the very high number of outliers, with the highest medians recorded at La Spezia, Bari, and Piombino (Fig. 4).

The position of the EQSs in the whole data distribution was more variable for the OCs with respect to MTEs (Table 4, Fig. 4), always above the OM, in a very wide range of positions on the distribution curves, between the 53.1 and 93.9 percentile of ΣPCBs and NAP, respectively.

For AN, IND, FL, BghiP, NAP, and ΣPAHs the EQSs were considerably higher than the OM; consequently, most concentrations recorded in the Italian harbors were below

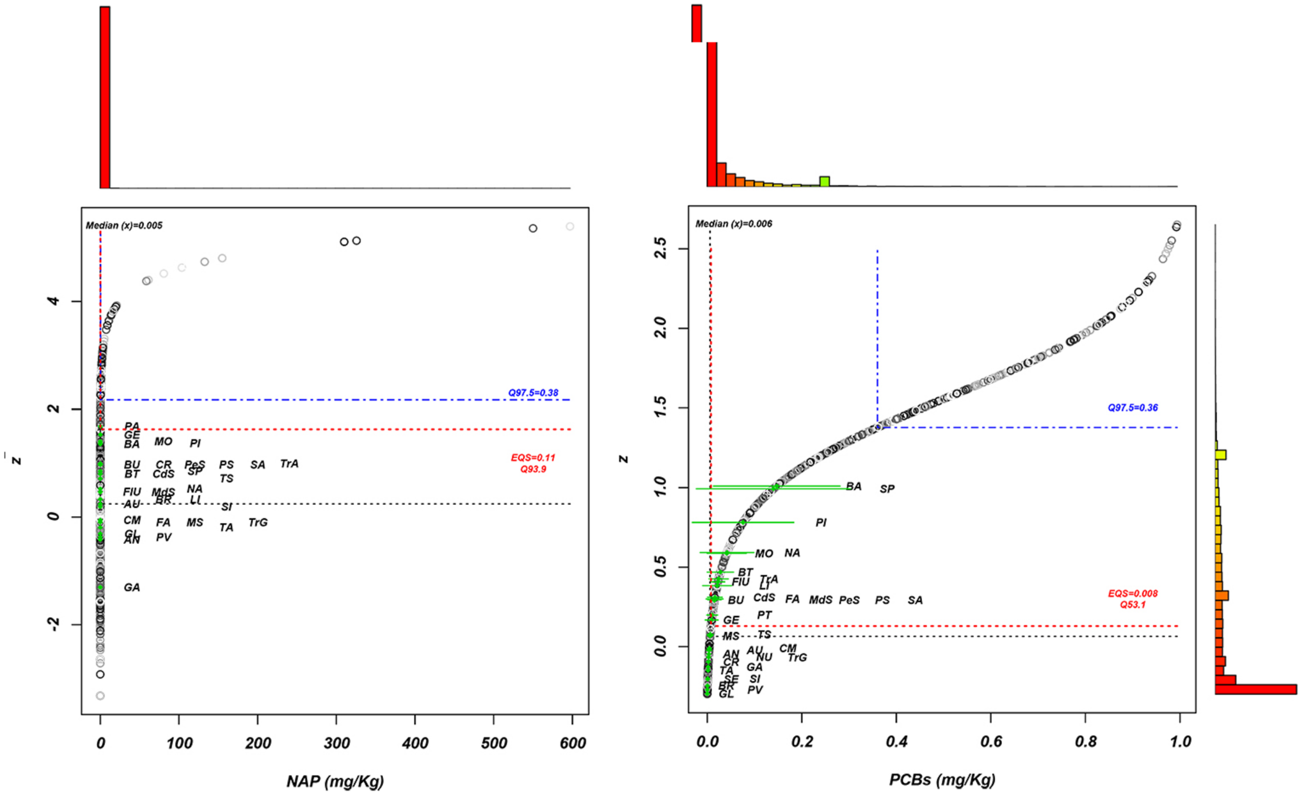


Fig. 4 Two examples of concentration data distribution of organic compounds processed through Johnson's method. The medians of each harbor were highlighted on the distribution curve. The black dashed line indicates the data distribution's overall median (OM, 50th percentile), the red dashed line indicates the position of the EQS, and the blue dashed line is the upper bound (UB, 97.5th percentile)

the EQSs for these parameters. An extreme case was represented by the NAP, whose EQS was close to the UB; therefore, nearly all the recorded data were below this threshold. The UB/EQS (45.0–266.6) testified that the highest concentrations of OCs, excluding the outliers, were far above the EQS. Then, despite most data being below the EQSs, a minor part of the data exceeded by many orders of magnitude the EQSs.

3.3 Comprehensive distribution of grain size and contaminants in the Italian harbors

Data regarding all the environmental parameters have been processed to illustrate what kind of sediments were present in each harbor considering overall grain size and chemical parameters. Some harbors (Buggerru, Crotone, Livorno, Napoli, Numana, Palermo, Porto Torres, and Siracusa) were excluded from the analysis due to missing data for at least one parameter.

Using the CA, it was possible to recognize which were, overall, the most important contaminants, both MTEs and OCs, affecting each of the harbors, also in relation to sediment grain size (Fig. 5). The first two axes explained about 88% of the total variability, and the Monte Carlo test demonstrated that the correlation between the grain size and chemical parameters was significant (RV = 0.22, $p = 0.0025$). In the CA, regarding grain size, clay plotted on the positive side of the first axis and was independent of the other variables, while silt was on the second axis, negatively correlated with sand, and gravel was little significant. Among chemical parameters, Pb and all PAHs, except NAP, mostly loaded on the first axis, correlated with clay; the harbors of Piombino and Genova were strictly associated with all these parameters. Cr and Ni, and to a lesser extent As, were positively correlated among them and negatively correlated with NAP; both were associated with silt and clay. Sediments of the harbors from the Adriatic coast (Senigallia, Ancona, and Fano) and Gaeta on the Tyrrhenian Sea showed these characteristics. PCBs loaded on the positive side of the second axis negatively correlated with Cd, the first associated with silt and the second with sand.

Silty sediments with high PCBs concentrations characterized the harbors of La Spezia and Fiumicino, while the Portoscuso, Portovesme, and Perd’e Sali harbors (Sardinia), Torre del Greco, and Brindisi were mainly sandy, with high Cd concentrations. In the plot, Hg negatively correlated with most PAHs and Pb, regardless of grain size, and was associated with several harbors such as Taranto, Barletta, and Massa Carrara. Overall, the analysis revealed the sediment texture’s basic importance in facilitating higher contamination levels due to MTEs and OCs.

3.4 Logistic regression analysis

The logistic regression analysis made it possible to quantify the chance of exceeding the EQSs for at least one parameter both for MTEs (Table 5) and OCs (Table 6), by determining the odds ratio (Exp [cβ]). The significance of the model applied to MTEs (Table 5) was demonstrated by (a) the percentage of variance explained by the model (pseudo $R^2 = 0.796$); (b) the analysis of variance of the regression (Chi-square test $p < 0.001$); (c) the significance of all the MTEs considered in the model contributing to the explanation of the dichotomous dependent variable *Y*, as demonstrated by p values close to 0, except for As which has a higher but still very low value ($p = 0.0451$); (d) the proportion of correctly classified units (95.42%); and (e) the specificity, corresponding to the proportion of 0 correctly classified by the model, equal to 89.76%, and the proportion of 1 correctly classified (sensitivity) equal to 96.92%.

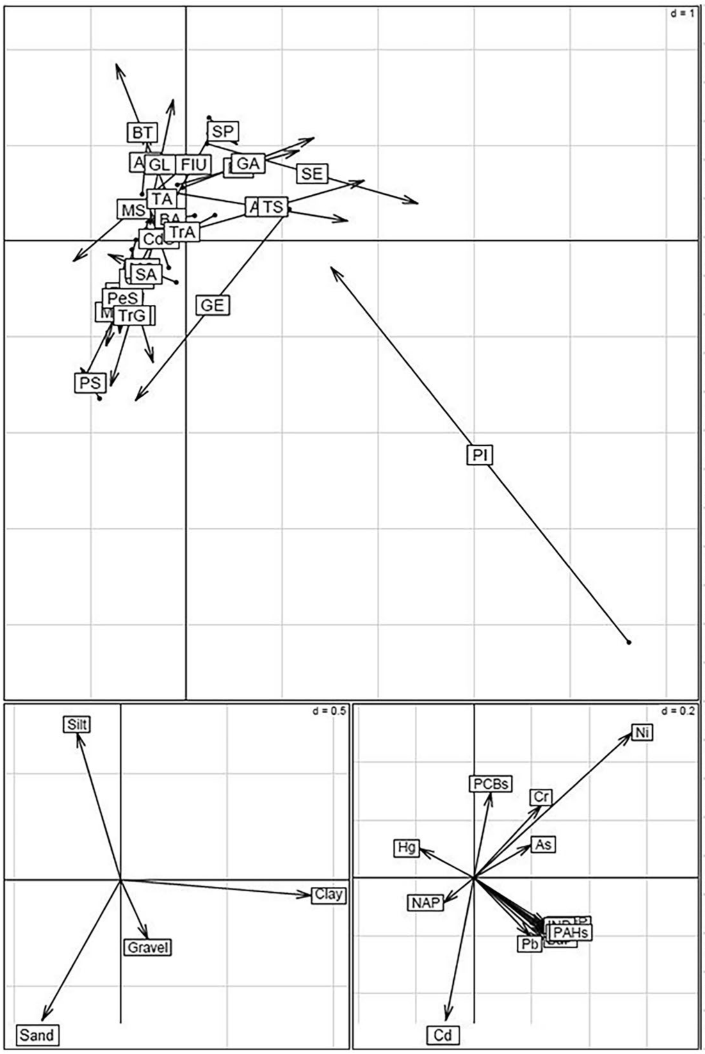
The last column of Table 5 reports for each MTE the Exp (cβ) that corresponded to the increase in the chance of exceeding the EQS when an explanatory variable increased by c units of concentration, coinciding with the 25th percentile of the concentration range. The positive values of the β coefficients indicated that all MTEs contribute to the excess of the EQSs (Table 5). From values of the coefficient β, considering the *p* values, it resulted that all metals contributed in a highly significant way to the explanation of the model in multivariate terms; only As showed a less strong but evident significance ($p = 0.045$).

The logistic model was also applied to the OCs, and its significance was demonstrated by: (a) the percentage of variance explained (pseudo $R^2 = 0.909$); (b) the analysis of variance of the regression (Chi-square test $p < 0.001$); (c) the significance of all the OCs considered in the model, except AN, contributing to the explanation of the dichotomous dependent variable *Y* (see *p* values in Table 6); (d) the

Table 4 Environmental quality standards (EQS) of OCs and main characteristics of their Johnson’s distribution curve: overall median (OM) and upper bound (UB)

	AN	BaP	IND	BbF	BkF	FL	BghiP	NAP	∑ PAHs	∑ PCBs
EQS (mg kg^{-1})	0.024	0.030	0.070	0.040	0.020	0.110	0.055	0.110	0.800	0.008
EQS percentile	68.0	57.1	75.6	58.2	58.0	67.2	71.5	93.9	67.6	53.1
OM (mg kg^{-1})	0.005	0.020	0.010	0.021	0.011	0.028	0.013	0.005	0.284	0.006
UB (mg kg^{-1})	1.429	6.571	4.796	6.352	5.332	9.075	4.136	0.379	59.434	0.360
UB/EQS	59.500	219.000	68.500	158.8	266.6	82.500	75.200	3.400	74.300	45.000

Fig. 5 Output of the Coinertia analysis. The PCA of grain size (bottom left) and chemical data (bottom right) have been plotted on the same coinertia plane, like the harbor scores (top, main plot). The first and second coinertia axes explain 54.9% and 33.19% of the total variability, respectively. The Monte Carlo test was significant (RV = 0.226, $p = 0.001$). The scores of the centroids of the harbor vectors in the main plot are provided in the table on the right



	CAX1	CAX2
AN	0.780	0.356
AU	-0.428	0.821
BA	-0.167	0.232
BR	-0.679	-0.538
BT	-0.455	1.137
CdS	-0.286	0.026
CM	-0.514	-0.394
FA	0.539	0.765
FIU	0.078	0.796
GA	0.645	0.816
GE	0.273	-0.663
GL	-0.278	0.798
MdS	-0.721	-0.737
MO	-0.476	-0.284
MS	-0.548	0.329
PeS	-0.664	-0.601
PI	3.061	-2.229
PS	-1.001	-1.483
PV	-0.492	-0.769
SA	-0.419	-0.349
SE	1.312	0.704
SP	0.382	1.146
TA	-0.254	0.441
TrA	-0.044	0.093
TrG	-0.567	-0.769
TS	0.906	0.359

proportion of correctly classified units (97.34%); and (e) the specificity, corresponding to the proportion of 0 correctly classified by the model, equal to 97.33, and the proportion of 1 of correctly classified (sensitivity) equal to 96.92%.

The results of the logistic model of the OCs are reported in Table 6. Among the considered parameters, only AN did not significantly contribute to the definition of the model ($z = 0.525$; $p = 0.5$). The negative coefficient β of IND indicated that it had an inhibitory effect on the increased risk of exceeding the EQS. In multivariate terms, the risk of exceeding the EQSs increases with the decrease in IND concentrations. From the values of coefficient β, considering the p values, ΣPAHs, ΣPCBs, BkF, and BbF were the parameters with the highest chance of exceeding their EQSs.

Using the estimated β coefficients (Tables 5 and 6), it was possible to define the probability of observing an EQS excess

Table 5 Logistic regression on MTEs: estimated coefficients (β); standard error (SE); Wald's test (z); significance (p), concentration increase to exceed the EQS (c); the chance to exceed the EQS (Exp[cβ]). Significance codes: 0***, 0.001**, 0.01*

	EQS (mg kg^{-1})	***β***	***SE***	*z*	*p*	***c*** (mg kg^{-1})	**Exp (cβ)**
Intercept		−7.856	0.277	−28.388	< 2e-16***		
As	12.0	0.014	0.006	2.004	0.0451*	7.12	1.104
Cd	0.30	8.011	0.657	12.193	< 2e-16***	0.09	2.056
Cr	50.0	0.033	0.004	7.626	< 2e-16***	24.90	2.274
Hg	0.30	9.499	0.498	19.072	< 2e-16***	0.065	1.854
Ni	30.0	0.125	0.007	18.070	< 2e-16***	16.98	8.352
Pb	30.0	0.091	0.006	15.505	< 2e-16***	13.90	3.543

Table 6 Logistic regression on OC parameters: estimated coefficients (β); standard error (SE); Wald's test (z); significance (*p*); concentration increase to exceed the EQS (*c*); chance to exceed the EQS (Exp[cβ]). Significance codes: 0***,0.001**, 0.01*

	EQS (mg kg^{-1})	**β**	***SE***	*z*	***p***	***c*** (mg kg^{-1})	**Exp(cβ)**
Intercept		−7.158	0.327	−21.883	< 2e-16***		
AN	0.024	−1.157	2.203	−0.525	0.599	5e-04	0.994
BaP	0.030	43.595	13.518	3.225	0.00126**	0.0025	1.115
IND	0.070	−49.117	19.050	−2.578	0.00993**	0.0015	0.929
BbF	0.040	34.275	4.708	7.279	3.35e-13***	0.0026	1.092
BkF	0.020	133.838	17.538	7.631	2.32e-14***	0.0017	1.253
BghiP	0.110	40.595	15.038	2.700	0.00694**	0.0020	1.085
FL	0.055	11.515	4.003	2.876	0.00402**	0.0050	1.059
NAP	0.110	18.061	5.699	3.169	0.00153**	0.0010	1.018
∑ PAHs	0.800	5.548	0.796	6.970	3.17e-12***	0.0473	1.299
∑ PCBs	0.008	589.614	32.129	18.352	< 2e-16***	5e-04	1.343

for each chemical parameter from the dataset entered in the two models. These probabilities have been georeferenced and displayed on the maps of different harbors characterized by different contamination and sediment texture. Brindisi and Taranto were the selected harbors for drawing the related susceptibility maps.

The harbor of Brindisi was characterized by very limited areas in the inner sector with a high probability of excess of the EQSs for at least one MTE (Fig. 6a), while somewhat larger areas at a high probability of excess for at least one OC were in both the inner and outer sectors (Fig. 6b).

Both maps represented all the probability classes between 0 and 1, from the lowest to the highest excess risk. The overall low risk of excess highlighted in this harbor is partially due to the sandy texture of sediment recognized by HCA and CA, which does not favor the accumulation of contaminants. The CA associated this harbor with Cd and NAP, and both parameters were highly significant in the logistic model (Tables 5 and 6).

The harbor area of Taranto was characterized by the highest risk of excess of the EQSs for MTEs in the whole eastern

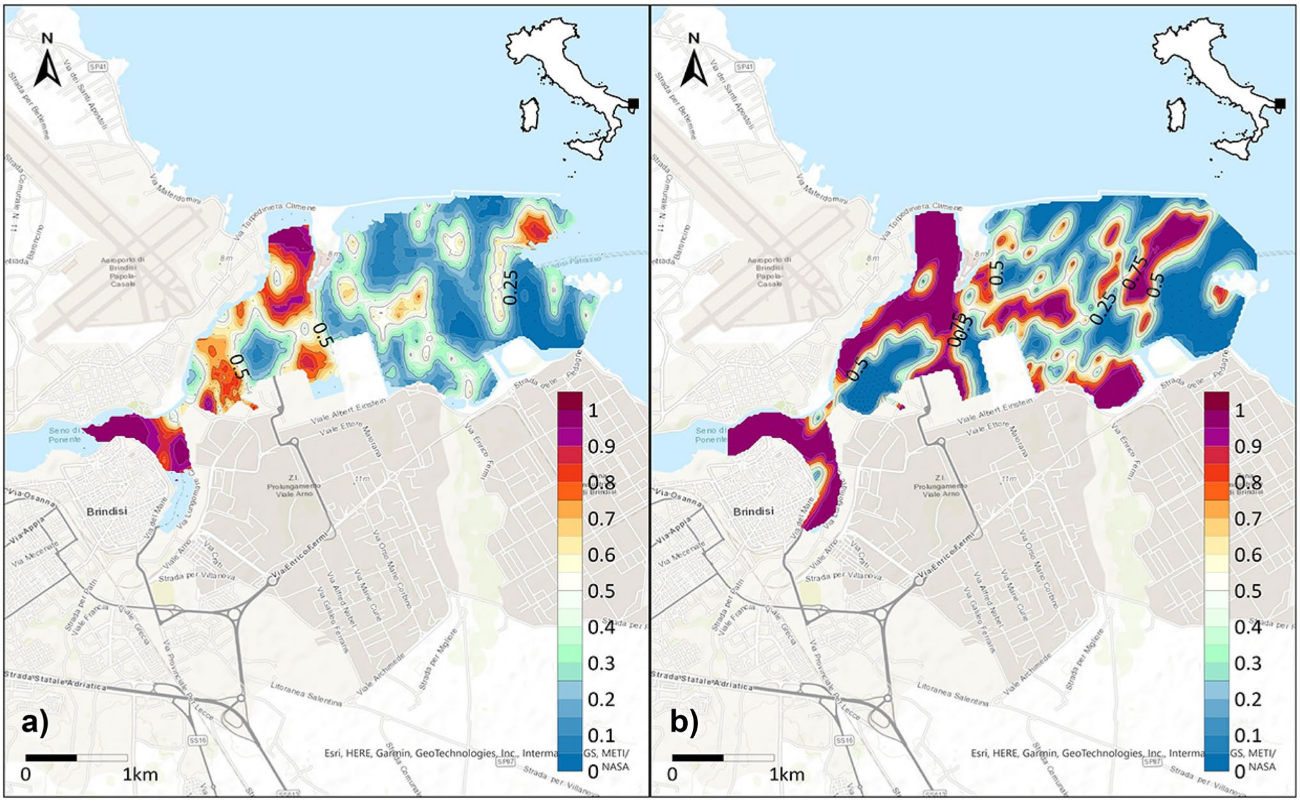


Fig. 6 Susceptibility map of the harbor of Brindisi: the probability of excess of the EQSs for at least one parameter: **a** MTEs; **b** OCs

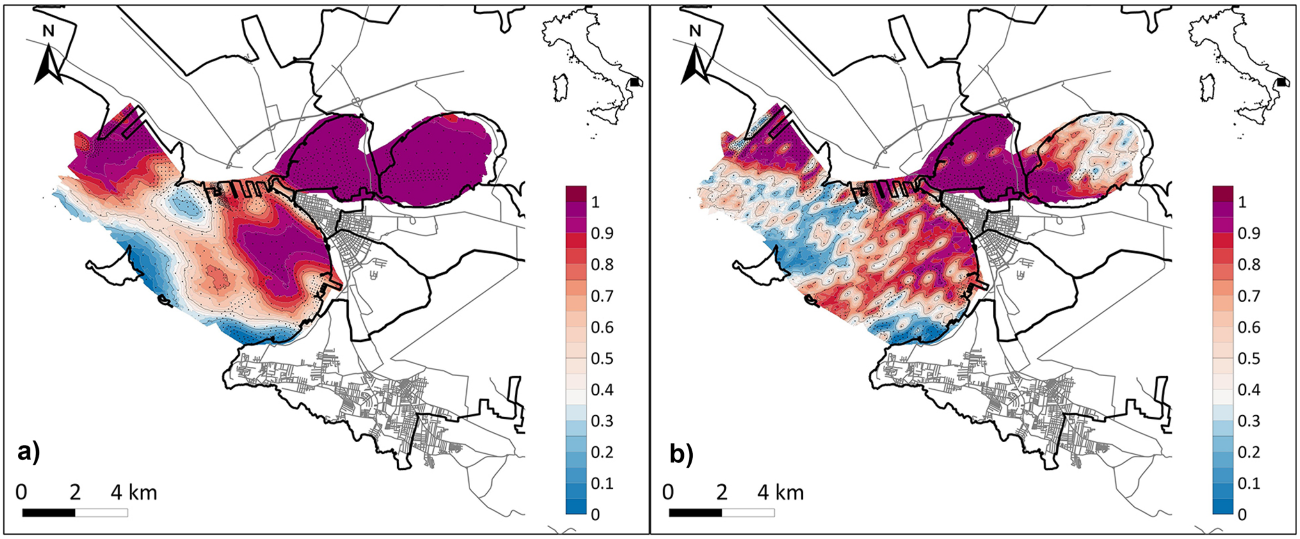


Fig. 7 Susceptibility map of the harbor area of Taranto: the probability of excess of the EQSs for at least one parameter; **a** MTEs; **b** OCs

sector (Mar Piccolo) and in large part of the western one (Mar Grande) where, however, all the probability classes were represented (Fig. 7a). As regards the OCs, a large area at the highest probability of excess of the EQSs was present in the western Mar Piccolo and unevenly in the Mar Grande (Fig. 7b). The prevalence of high probability classes in this area is, at least partially, due to the fine texture of sediment, mainly silty, recognized by HCA and CA, that facilitates the accumulation of contaminants. The CA associated this harbor with Hg and PCBs; both were among the parameters with the highest significance in the logistic model (Tables 5 and 6).

4 Conclusion

Currently, the national legislation does not consider the EQSs suitable tools for defining the chemical status in highly critical environmental areas such as harbors, considered, on the contrary, pressure sources. Applying a statistical approach, this study tried to compare the distribution of concentration data with the EQSs of sediments based on a specific dataset containing a wide number of records from many Italian harbors. Their different characteristics as regards size, sediment textures, and type and degree of contamination ensured to consider the highest variability of data for testing the applicability of the EQSs.

The placement of the EQSs of MTEs very close to the overall medians of all parameters in Johnson's charts demonstrated that they are suitable reference values; their application allowed the discrimination of a considerable number of observations exceeding them, pointing to the widespread metal contamination of the Italian harbors. This distribution is evident in the maps obtained through the logistic model, where wide areas with a homogeneous probability of excess EQSs were highlighted. Moreover, it was recognized that, overall, Cd, Hg, and Pb were the MTEs mostly contributing to the contamination of the Italian harbors due to their high variability. It was also observed that the EQSs of some MTEs were frequently exceeded in harbors affected by a natural enrichment due to a geochemical anomaly. In these cases, the Italian law allows changing the EQSs to assess chemical status with local background values in coastal areas where the geochemical anomaly is scientifically demonstrated (Romano et al. 2022).

The EQSs of all OCs resulted higher than the overall medians; however, due to their wide range of concentrations, most parameters exceeded by many orders of magnitude such values. These characteristics correspond to a patchy distribution of areas with very high concentrations confirmed by the susceptibility maps, where spots with the highest probability of excess of the EQSs were evident, demonstrating their capacity to define areas with different degrees of contamination.

The logistic model applied in this study, based on the excess of the EQSs for at least one parameter, represented a robust tool to define areas at high susceptibility in the harbors and confirmed their adaptability also in these highly impacted areas.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11368-023-03549-0.

Data availability The datasets used and/or analyzed during the current study will be available from the corresponding author upon reasonable request.

Declarations

Competing interest The authors declare no competing interests.

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