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Surface sediments collected from 10 stations of Taranto Gulf influenced by industrial waste waters were analysed for metals (Hg, Cd, Sn, As, Cu, Pb, Ni, V, Cr, Zn, Mn, Al and Fe), priority polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Data were compared with the published results from other coastal areas of the Mediterranean Sea and with Sediments Quality Guidelines (effect range low-effects range medium, threshold effects level-probable effects level indexes) for evaluation of probable toxic effects on marine organisms. Moreover, mean effects range medium (ERM) and mean probable effects level (PEL) quotients were used to evaluate the degree to which chemicals exceed guidelines. Results suggest an ecotoxicological risk for benthic organisms, mainly in sediments near ironed steel production plant of ILVA, where high concentrations of PAHs were found.

Keywords: PCBs; PAHs; metals; sediments; sediment quality indexes

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental organic contaminants, many of which are known to be carcinogenic and mutagenic [1]. PAHs are formed as a consequence of incomplete combustion or high-temperature pyrolytic process involving organic matter, and reach the marine environment via effluent discharges, urban run-off, atmospheric transport, accidental oil spill and leakages [2]. Polychlorinated biphenyls (PCBs) are a group of organic compounds consisting of 209 congeners that have been used extensively in electronic equipment, like transformers and capacitors, and as plasticisers in paints and rubbers sealants. They can be found in various areas of the environment all over the world and their properties suggest that they are a probable threat to human health [3]. Because of their high persistence, hydrophobic nature and low solubility in water, both PAHs and PCBs, are adsorbed on particulate matter and finally accumulate in marine sediments [4]. Metals in marine sediments have natural and anthropogenic origin: distribution and accumulation are influenced by sediment texture, mineralogical composition, reduction/oxidation state, adsorption and desorption processes and physical transport. Moreover, metals can be absorbed from the water column onto fine particles surfaces and accumulate in sediments; metals participate in various biogeochemical mechanisms, have significant mobility, can affect the ecosystems through bio-accumulation and bio-magnification processes

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and are potentially toxic for human health [5]. As a combined result of these factors, metal concentrations in the sediment change in space and time. In fact, during the last few decades, industrial and urban activities have contributed to the increase in metals contamination in the marine environment.

The coastal area of Taranto (Ionian Sea, southern Italy) is a marine ecosystem influenced by different anthropogenic pressure. Sediment contamination in this area is related to the discharges of two industrial plants: the 'ILVA' iron and steel factory, which is the most important steel production plant in Europe, and the 'ENI' petroleum refinery. The goal of this study was to determine the degree of contamination by metals, PAHs and PCBs of the surface sediments located near the industrial area and evaluate the potential toxic effects of contaminants on marine organisms using numerical Sediments Quality Guidelines (SQGs) [6–11]: effect range low-effects range medium (ERL-ERM), threshold effects level-probable effects level (TEL-PEL). Moreover, ERM and PEL quotients (m-ERM-Q and m-PEL-Q) [12,13] that consider the biological effects by a mixture of chemicals instead of the toxicity due to single pollutants were used to evaluate the degree to which levels of toxic contaminants exceed guidelines.

2. Materials and methods

Surface sediments (0–20 cm) were collected in June 2007 with a Van Veen grab sampler from four stations (1–4) located in the Mar Grande basin and six stations (5–10) of Taranto Gulf (Figure 1). Stations 1–4 were located in the harbour area where sediment contamination is influenced mainly by discharge activities of minerals and oil. Stations 5–10 were located in the area of Taranto Gulf influenced by industrial wastes ($\sim$150,000 $m^3 \cdot h^{-1}$ from ILVA coke plant and ENI refinery). For each station, three sampling were effected in order to obtain a representative sample.

Grain size distribution was effected through a series of sieves to establish the percentage of silt and clay (<0.063 mm), sand (2–0.063 mm) and coarser fraction (>2 mm) [14]. Before the grain size analyses, samples were treated with H_2O_2, washed with distilled water and then dried at 60 °C. Total organic carbon (TOC) was determined for each sample using the loss-on-ignition method [15], and the dry weight fraction was determined by weight loss at 105 °C.

Total metals (Hg, Cd, Sn, As, Cu, Pb, Ni, V, Cr, Zn, Mn, Al and Fe) were determined using the ICP-MS technique after acid digestion of sediments in a microwave oven. A microwave oven
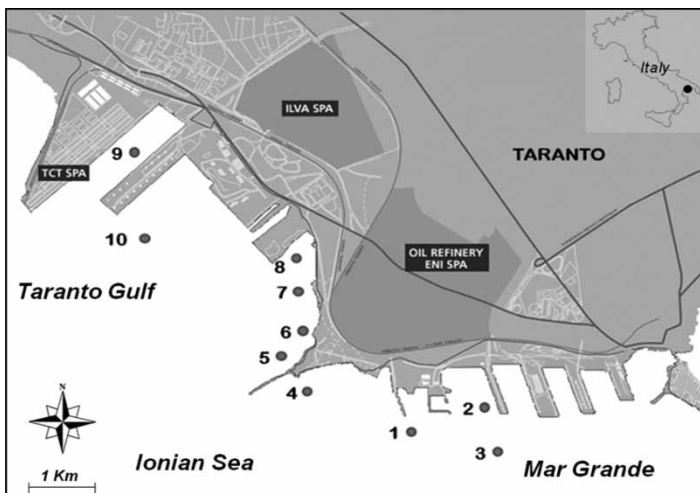

Figure 1. Sampling stations.

CEM model MARSX (CEM Corp., Matthews, NC) was used to accomplish sediment digestions [16]. For digestion, 0.2 g of dried sample was put into a PTFE vessel with 9 mL nitric acid, 2 mL hydrochloric acid and 3 mL hydrofluoric acid. For each digestion programme, a blank was prepared with the same amount of acid. After digestion, samples were diluted with 20 mL boric acid, to permit elimination of fluoride in excess by complexation. Each sample was filtered, diluted to 50 mL with ultra-pure water and analysed. All reagents were of analytical grade and must contain very low concentrations of trace metals. Nitric acid (70% w/w), hydrochloric acid (37% w/w) and hydrofluoric acid (48% w/w) were Instra-Analyzed (J.T. Baker, Phillipsburg, USA); boric acid was Ultrex Ultrapure Reagent (J.T. Baker, Phillipsburg, USA). Ultra-pure water, with conductivity $<0.1\,\mu S$, was obtained from a MILLI-QR system (Millipore, Bedford, MA, USA). For various metals, the relative standard deviation for triplicate analyses ranged from 5 to 13%. The accuracy and precision of the analytical procedures were checked by analysing a certified reference marine sediment IAEA356. Analytical results indicate good agreement between certified and determined values. Metals recovery was practically complete for most of them ($>95\%$): only in the case of Zn the recovery was equal to 88%.

For PAH and PCB analysis, samples were extracted and purified as described by Cardellicchio et al. [17]. Briefly, 15 g of wet samples were extracted with 90 mL acetone–hexane (1 : 1) using a automated Soxhlet system. In order to eliminate sulfur, 5 g of copper powder, activated with HCl (2 N), was added to solvent extraction directly in the Soxhlet apparatus. After extraction, total organic extract was purified by liquid chromatography on Florisil cartridge to remove polar compounds co-extracted. The purified extract was split in two fractions for PAH and PCB determination. For PAH analysis, a further clean-up on a silica gel column was effected, in order to separate the aliphatic hydrocarbons fraction (eluted with 30 mL *n*hexane) from the aromatic hydrocarbon fraction (eluted with 80 mL hexane–dichloromethane 3 : 2 mixture). This last fraction was concentrated and analysed by GC/MS, using selected ion monitoring (SIM). The mass spectrometer was used in electronic impact (EI) mode (70 eV electron energy) with ion source, quadrupole and transfer line temperatures of 200, 100 and 290 °C, respectively. The chromatographic column was a PTE-5 (Supelco Inc. Bellefonte), 30 m × 0.32 mm ID × 0.25 μm film thickness. Deuterated PAHs (naphthalene-d8, acenaphtene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12) were added to the sample, at the beginning of the extraction procedure, for recovery calculation. Anthracene-d10 was used as an internal standard: it was added to the sample prior to injection into the GC. The recovery of the different PAHs, determined with a standard reference materials NIST-SRM 1941b, ranged from 77 to 91%. The relative standard deviation for triplicate analyses ranged from 5 to 15%, while method detection limits for PAH compounds ranged from 0.7 to 10 μg·kg^{-1} d.w., for all examined compounds.

For PCB analysis, the clean-up step was effected by concentrated sulfuric acid treatment for organic compounds removal. The purified extracts were concentrated and analysed by GC/ECD, using a Varian 3800 gas chromatograph. The column was a SPB-5 (Supelco), 60 m × 0.25 mm I.D. × 0.25 μm film thickness. PCBs were quantified only as Aroclor 1260. In this study, total PCBs were determined, because sediment quality guidelines were indicated only for total PCBs. Decachlorobiphenyl (IUPAC PCB congener 209) was used as a surrogate standard and added to the sample prior to extraction. The reproducibility and recovery of the analytical procedure were determined by measuring the PCB concentration in a certified marine sediment (IAEA-408). For triplicate analysis, the mean recovery percentage was $>75\%$, whereas reproducibility was good with mean standard deviation of 9%. The detection limit for total PCBs was 2.5 μg·kg^{-1} for dry sediments.

Multivariate analysis (principal component analysis; PCA) and correlation analysis (bivariate correlations) have been used to extract relationships among chemical data and environmental impacts on sediments [18–22]. The plot of scores and loadings allowed us to recognise groups of samples with similar behaviour and the correlations among the variables. The correlation analysis

was performed by Pearson correlation. All statistical analyses were performed with the software package STATISTICA® (StatSoft Inc, Tulsa, OK, USA).

3.   Results and discussion

3.1.   *Sediment characteristics*

Sediment grain size fractions were classified as fine (silt-clay; <0.063 mm), sand (0.063–2 mm) and gravel (>2 mm). In all samples, the percentage of sand ranged from 33 to 40.7%, except for stations GT5 (80.3%) and MG3 (49%); the percentage of silt-clay ranged from 36.5 to 61%, except for station GT5 (15.8%). Therefore, in general, most of the sediments in Taranto Gulf and Mar Grande basin can be considered fine sediments. Total organic carbon (TOC) ranged from 2.1 to 5.1%, with an average value of 3.9%. No statistically significant correlation among TOC and contaminant concentrations was found ($p < 0.05$), suggesting that the distribution and concentrations of contaminants in whole sediments are independent by organic carbon content.

3.2.   *Metals*

Metal concentrations in sediment samples are shown in Table 1. The highest concentrations of Hg, As, Pb, Zn, Mn, Fe, V, Cu and Cd were observed at station 9, influenced by discharge from the iron and steel factory (ILVA). The highest concentrations of Sn, Ni, Cr and Al were found at station 2, influenced by harbour activities. This results show that concentrations of Cd and Cu found in the sediments from Taranto Gulf and Mar Grande basin were higher than those reported for Ligurian Sea [23] and Venice Lagoon [24], whereas the levels of Pb, Ni and V were higher than those found for the northern [25] and southern Adriatic Sea [26]. Cr, Fe and Zn levels were higher than those reported for sediments from the Algerian Mediterranean coasts [27].

3.3.   *PAHs and PCBs*

Results for PAHs and PCBs are shown in Table 2. Total PCBs (quantified as Aroclor 1260) ranged from not detectable (stations 1 and 2) to 1780 µg·kg^{-1} d.w. (station 9). PCB levels in sediments from the Gulf of Taranto ranged from 85 to 1780 µg·kg^{-1} d.w.; they were higher than

Table 1.   Metal concentrations (mg·kg^{-1} d.w.) (mean of three determinations) in sampling stations.

Metals	Stations									
	1	2	3	4	5	6	7	8	9	10
Hg	0.2	0.2	0.3	0.2	0.6	0.6	0.5	0.3	0.9	0.6
Cd	2.7	3.9	1.5	1.6	1.7	2.9	2.7	1.8	3.9	2.8
Sn	8.9	21	9.8	11	4.5	7.7	6	4.5	13	5.9
As	12.6	17.1	12.6	16.4	19.4	27.4	24.5	19.2	32.8	30.1
Cu	13.9	27	47.5	16.3	9.4	24.3	13.1	2.7	51.6	20.6
Pb	37	28	22	20	55	86	86	72	133	74
Ni	84	107	37	30	27	54	46	32	50	62
V	109	151	58	49	67	99	95	68	143	122
Cr	127	165	70	61	53	88	79	65	113	106
Zn	75	98	78	88	190	366	316	224	629	268
Mn	595	616	438	411	687	995	1099	1195	3233	926
Al	56840	77626	30350	30190	26860	39520	36960	35600	54883	47500
Fe	27780	35254	30680	17890	30590	45460	51100	48360	130043	45480

Note: The relative standard deviation for metal analyses ranged from 5 to 13%.

Table 2. PAH and PCB concentrations ($\mu g \cdot kg^{-1}$ d.w.) (mean of three determinations) in sampling. stations.

PAHs	Stations									
	1	2	3	4	5	6	7	8	9	10
Naph	n.d	n.d	15	10	n.d	n.d	199	283	372	164
Acy	n.d	n.d	17	10	68	506	336	826	1296	389
Ace	n.d	n.d	7	n.d.	n.d.	63	144	676	1340	83
Fl	n.d	n.d	16	4	5	267	270	846	1340	218
Phen	n.d	n.d	19	15	429	4655	1732	5041	9477	1893
Anthr	n.d	n.d	12	10	248	2252	889	3106	4799	1102
Fluo	n.d	n.d	194	189	3025	19039	8752	18111	35023	9890
Pyr	n.d	n.d	177	170	2524	15480	8478	16980	26969	9203
B[a]A	n.d	n.d	353	119	2556	11475	4874	10903	23527	6206
Chry	n.d	n.d	359	52	3477	15740	4164	1494	25325	6255
B[b]Fl	n.d	n.d	764	274	5900	24969	10650	17990	39714	10330
B[k]Fl	n.d	n.d	483	156	418	8635	4804	10727	19147	5254
B[a]P	n.d	n.d	454	166	4035	17729	7926	16533	33986	9951
IDP	n.d	n.d	481	138	3689	14401	5112	8033	23549	6419
DB[ah]A	n.d	n.d	164	78	870	3123	1463	2099	4816	1386
B[ghi]P	n.d	n.d	304	93	1674	9159	2719	5317	11766	681
Σ PAHs	0	0	3819	1484	28918	147493	62512	118965	262446	69424
PCBs	0	0	119	54	221	1436	85	723	1780	226

Notes: The relative standard deviation for PAHs analysed ranged from 5 to 15%, whereas for PCBs the reproducibility was good with a mean standard deviation of 9%. n.d., not detectable. Naph, naphthalene; Acy, acenaphthylene; Ace, acenaphthene; Fl, fluorene; Phen, phenanthrene; Anthr, anthracene; Fluo, fluoranthene; Pyr, pyrene; B[a]A, benz[a]anthracene; Chry, chrysene; B[b]Fl, benzo[b]fluoranthenes; B[k]Fl, benzo[k]fluoranthenes; B[a]P, benzo[a]pyrene; IDP, indeno[1,2,3-cd]pyrene; DB[ah]A, dibenz[a,h]anthracene; B[ghi]P, benzo[g,h,i]perylene.

levels determined for sediments of Mar Grande basin (n.d. to 119 $\mu g \cdot kg^{-1}$ d.w.). Moreover, PCB contamination in the Gulf of Taranto was comparable with contamination levels in the Venice Lagoon [28] and Alexander's harbour [29], but was higher (on average) than those reported for Naples harbour [30]. These results suggest that PCB contamination is strongly related to industrial sources and harbour activity.

As regard PAHs, the composition for analysed sediment was dominated by fluoranthene, benzo[b]fluoranthene and benzo[a]pyrene and more than four-ring PAHs. Levels of two- and three-ring PAHs were typically 10 times lower, except for phenanthrene which was the predominant PAH. While the relative PAH composition was similar between different stations, absolute concentrations varied by more fold for individual compounds and Σ PAHs. Highest PAH concentrations were found in sediment of the Gulf of Taranto influenced by 'ILVA' and 'ENI' waste waters (range 28,918–262,446 $\mu g \cdot kg^{-1}$ d.w.). The lowest levels were found in the Mar Grande with concentrations that ranged from not detectable to 3819 $\mu g \cdot kg^{-1}$ d.w. Compared with other marine coastal areas, sediments in the Gulf of Taranto, in particular those collected in stations 6, 8, 9, are the most polluted in Mediterranean Sea, whereas PAH contamination in stations of the Mar Grande, is generally comparable or lower [17,30–32].

In this study, in order to evaluate the origin and the sources of PAHs in marine sediments analysed, we used molecular indices based on ratios of selected PAH concentrations. The use of PAH ratios is not feasible, due to the variety of processes contributing to the distribution of PAHs in marine sediments. Despite this, information on major pollution sources for a particular area, can help to infer the primary factors that cause the appearance of these compounds in the environment.

The low molecular weight/high molecular weight (LMW/HMW) ratio was the first index calculated [33,34]. The LMW PAHs have 2–3 rings (i.e. Naph + Acy + Ace + Fl + Phen + Anthr) and are acutely toxic to many aquatic organisms, while HMW PAHs have 4–6 rings (i.e. Flu + Pyr + B[a]A + Chry + B[b]Fl + B[k]Fl + B[a]P + IDP + DB[ah] + B[ghi]P) and are strongly carcinogenic, especially B[a]Pyr [35]. The theory of this origin index was based on the fact that PAHs from

pyrogenic sources (incomplete combustion of fossil fuels or wood) are depleted in low-molecular PAHs and enriched in high molecular mass compounds leading to LMW/HMW ratios <1. Petrogenic sources of PAHs (fuel oil or light refined petroleum products) are dominated by LMW PAHs and have LMW/HMW ratios >1. In this study, values of the LMW/HMW ratio were relatively low (range 0.02–0.10), indicating a pyrolytic origin of PAHs for all stations. Another method to estimate the origin of the PAHs in sediments uses the ratios Phen/Anthr and Fluo/Pyr. Phenanthrene and anthracene are two structural isomers. Because of their different physico-chemical properties, they could behave differently in the environment and could lead to different values for their Phen/Anthr ratio [36]. Pyrolysis of organic matter at very high temperature generates PAHs, characterised by a low Phen/Anthr ratio (<10), whereas the slow maturation of petroleum at lower temperatures leads to much larger values of the Phen/Anthr ratio (>25) [37,38]. In conclusion, phenanthrene is thermodynamically more stable than anthracene, so a Phen/Anthr ratio <10 is characteristic of pyrolytic pollution. In the same way, the Fluo/Py ratio is also discriminating. Fluoranthene is less thermodynamically stable than pyrene and a predominance of fluoranthene over pyrene is characteristic of pyrolytic products, whereas in petroleum-derived PAHs, pyrene is more abundant than fluoranthene. During the combustion process, pyrolytic products are usually characterised by a fluoranthene/pyrene ratios >1 [31,39,40]. In Figure 2, Phen/Anth was plotted against Fluo/Pyr for all stations: the resulting plot showed that all sediments were grouped and were characterised by Phen/Anth < 10 and Fluo/Pyr > 1, which are typical of pyroltic input.

In order to evaluate the results obtained, PCA was applied on a dataset of 10 sampling stations, 13 metals (Hg, Cd, Sn, As, Cu, Pb, Ni, V, Cr, Zn, Mn, Al and Fe), $\sum$PAHs, $\sum$PCBs and TOC (untransformed data). Five principal components were extracted. They covered 89.8% of the variance and the scatter plot of scores on the first two principal components PC1 and PC2 shows a separation among the stations (Figure 3). In fact, station 9 has the most negative score, compared with all other stations on PC1, whereas station 2 has the most positive score, compared with all other stations on PC2. Loading of variables on the first two principal components shows that Fe, Mn, As, Pb, Hg, Zn, Cd, V, $\sum$PAHs and $\sum$PCBs are the dominant variables on PC1, whereas Al, Cr, Sn and Ni are dominant on PC2 (Figure 4). Results obtained by PCA, showed that sediments from stations 9 and 2 differ from the remainder, in fact station 9 has the highest concentrations of Fe, Mn As, Pb, Hg, Zn, ΣPAHs and ΣPCBs, whereas station 2 has the highest concentrations of Al, Cr, Sn and Ni. These results confirm that highest contaminant levels were found in sediment influenced directly by 'ILVA' iron and steel factory and 'ENI' petroleum refinery.

3.4. *Risk assessment*

The effects of metals, PCBs and PAHs in sediments were evaluated by use of SQGs which provide a scientifically defensible basis for evaluating probable toxic effects of sediment on marine
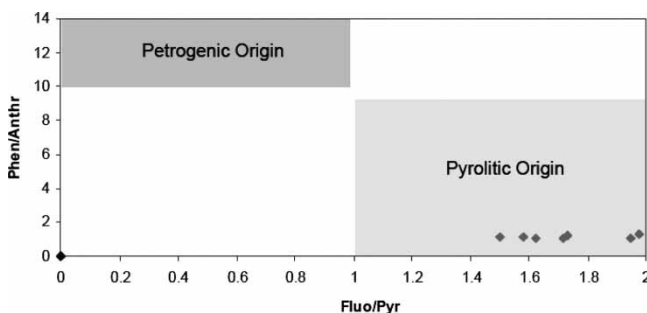

Figure 2. Plot of the Phen/Anthr values against the Fluo/Pyr values for the analysed sediments.
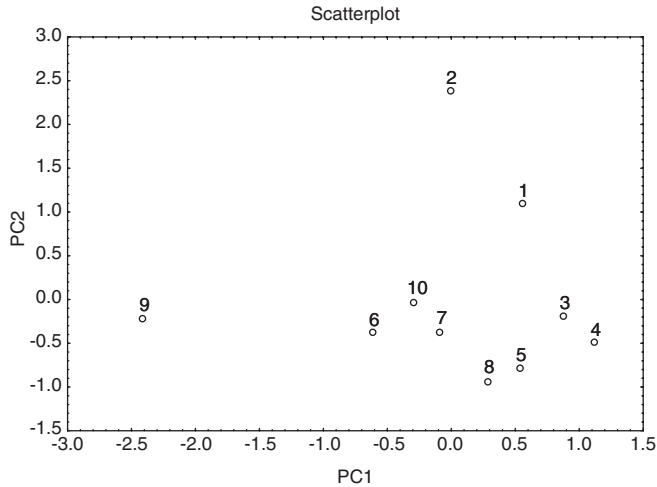
Figure 3. Principal component analysis (PCA) of loadings for PCBs, PAHs and metals.
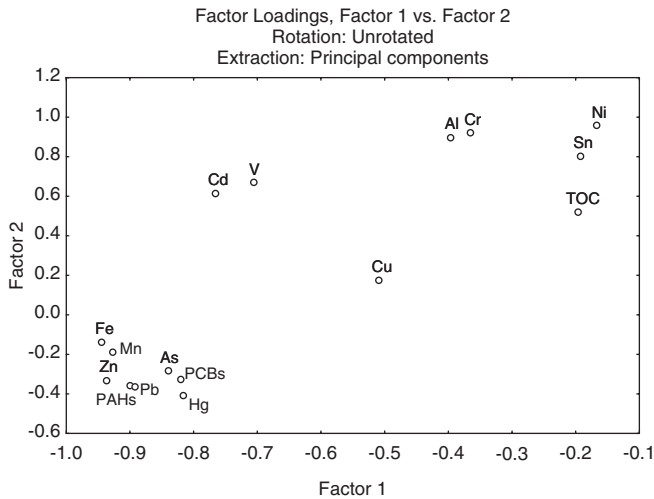

Figure 4. Scatter plot of the scores for the first two principal components obtained using PCBs, PAHs and analysed metals.

organisms. The two different approaches chosen were ERL/ERM and TEL/PEL. The ERL/ERM values (effects range low and effects range medium) were determined assembling a large dataset: for each chemical, data were arranged in order of increasing concentration. Concentrations not associated with an effect ('no-effect' data) were excluded; the ERL was calculated as the lower 10th percentile of 'effects' concentrations and the ERM as the 50th percentile of 'effects' concentrations. The method for TEL/PEL values (threshold effects level and probable effects level) [8] was similar to the method for deriving ERL/ERM values, but both 'effect' and 'no effect' data were used in calculating TEL and PEL values. Essentially, the TEL corresponds to the ERL and the PEL to the ERM. The TEL was calculated as the geometric mean of the 15th percentile concentration of the effects set and the 50th percentile concentration of the no-effects dataset. Similarly, the PEL was the geometric mean of the 50th percentile of the effects data and the 85th percentile of the no-effects data. The TEL (or ERL) and PEL (or ERM) values define three concentration ranges for a chemical, including those that were rarely (below the TEL or ERL),

Table 3. SQGs values for metals (mg/Kg d.w.) and relative percentage of stations including in the range of Sediment Quality Guidelines.

Metals	SQG ERL–ERM	% of stations			SQG TEL–PEL	% of stations		
		<ERL	ERL-ERM	>ERM		<TEL	TEL-PEL	>PEL
As	8.2–70	0	100	0	7.24–41.6	0	100	0
Cd	1.2–9.6	0	100	0	0.68–4.21	0	100	0
Cr	81–370	40	60	0	52.3–160	0	90	10
Cu	34–270	80	20	0	18.7–108	50	50	0
Pb	46.7–218	40	60	0	30.2–112	30	90	10
Hg	0.15–0.71	0	90	10	0.13–0.7	0	90	10
Ni	20.9–51.6	0	60	40	15.9–42.8	0	40	60
Zn	150–410	40	50	10	124–271	40	30	30

Table 4. SQGs values for PCBs and PAHs (μg/Kg d.w.) and relative percentage of stations including in the range of Sediment Quality Guidelines.

PAHs	SQG ERL–ERM	% of stations			SQG TEL–PEL	% of stations		
		<ERL	ERL-ERM	>ERM		<TEL	TEL-PEL	>PEL
Naph	160–2100	60	40	–	35–391	60	40	–
Acy	44–640	40	40	20	6–128	30	20	50
Ace	16–500	50	30	20	7–89	40	30	30
Fl	19–540	50	30	20	21–144	50	–	50
Phen	240–1500	40	10	50	87–544	40	10	50
Anthr	85–1100	40	30	30	47–245	40	–	60
Fluo	600–5100	40	10	50	113–1494	40	–	60
Pyr	665–2600	40	10	50	153–1398	20	20	60
B[a]A	261–1600	40	–	60	75–693	20	20	60
Chry	384–2800	30	20	50	108846	30	10	60
B[a]P	430–1600	30	10	60	89–763	20	20	60
DB[ah]A	63–260	20	20	60	6–135	20	10	70
Total PAHs	4022–44792	40	20	40	1684–16770	30	10	60
Total PCBs	23–180	20	30	50	22–189	20	30	50

Notes: Naphthalene, Naph; Acenaphthylene, Acy; Acenaphthene, Ace; Fluorene, Fl; Phenanthrene, Phen; Anthracene, Anthr; Fluoranthene, Fluo; Pyrene, Pyr; Benz[a]anthracene, B[a]A; Chrysene, Chry; Benzo[b]fluoranthenes, B[b]Fl; Benzo[k]fluoranthenes, B[k]Fl; Benzo[a]pyrene, B[a]P; Indeno[1,2,3-cd]pyrene, IDP; Dibenz[a,h]anthracene, DB[ah]A; Benzo[g,h,i]; B[ghi]P.

occasionally (above the TEL or ERL, but below a PEL or ERM) and frequently (above the PEL or ERM) associated with adverse effects. When contaminant concentrations exceed PEL or ERM, sediment samples were predicted to be toxic. In this study, comparison of chemical concentrations of metals, PCBs and PAHs with SQGs is summarised in Tables 3 and 4.

In 40% of the stations (1, 2, 6, 10), the Ni level exceeded the ERM value, whereas only in station 9, were the Hg and Zn levels higher than ERM level. TEL/PEL analysis showed that Cr, Pb and Hg concentrations were higher than PEL values only in station 9, whereas Zn levels were higher than PEL value in stations 6, 7, 9. Finally for Ni, the PEL level is exceeded in 60% of the stations.

As regard PCBs, concentrations were higher than ERM and PEL values in 50% of stations. For PAHs we considered only the compounds analysed in this study which have an assigned SQG value. Contamination level of PAHs were above ERM in 40% of the stations, whereas PEL is exceeded in 60%. In particular, PAHs concentration, in station 9, was ∼10 times greater than the PEL value.

Finally, to assess the potential effects of all contaminants in sediments, mean ERM quotients (m-ERMq) and mean PEL quotients (m-PELq) were used [13]. Briefly, the concentrations of metals, PCBs and 12 PAHs were divided by their respective ERM and PEL values. The mean of the quotients for all chemicals ($n = 21$) was then calculated. The resulting index provides a
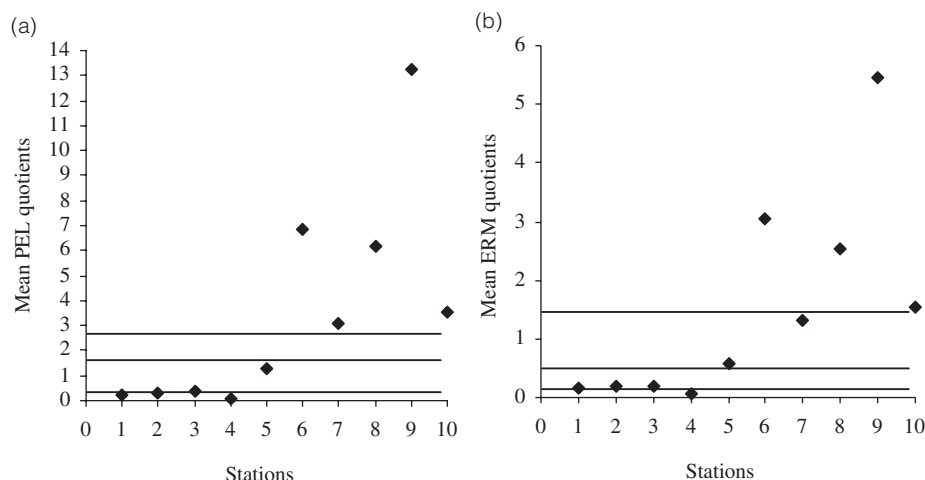
Figure 5.   Distribution of mPELq (a) and (b) mERMq in priority levels for sediments. The three lines represent boundaries between the four priority levels: highest, medium-high, medium-low and lowest.

method for the evaluation of synergic effects of contaminants in sediments and defines four relative priority levels for contaminated sites: highest (mERMq > 1.5 and mPELq > 2.3), medium–high (mERMq ranged from 0.51 to 1.5; mPELq ranged from 1.51 to 2.3), medium–low (mERMq ranged from 0.11 to 0.5; mPELq ranged from 0.11 to 1.59 and lowest (mERMq < 0.1 and mPELq < 0.1).

Sediments from Gulf of Taranto exhibited the highest potential toxicity because mPELq were included in highest range for stations 6, 7, 8, 9, 10 and in the medium–low range for station 5 (Figure 5a). As regards mERMq, stations 6, 8, 9 and 10 were also in the highest range (Figure 5b), whereas stations 7 and 5 were located in the medium–high range. Stations 1, 2, 3 localised in Mar Grande basin, were in medium–low range, whereas station 4 was in lowest level for mPELq and mERMq quotients. Moreover, in stations 1 and 2, the m-PELq and mERMq values were influenced only by metal levels, whereas in stations 3 and 4, metals and organic compounds accounted for ∼50% of m-PELq and mERMq values. In the other stations, indeed, PAH contamination influenced the quotient values with percentage that ranged from 89% (stations 10) to 93% (station 9).

Results showed that the high PAH concentrations, mostly in the stations of the Gulf of Taranto, influenced significantly mPELq and mERMq compared with the other contaminants; in these stations it is possible to predict a possible environmental risk for benthic organisms.

3.5. *Total concentrations of carcinogenic PAHs*

Several PAHs and especially their metabolites, are known to be carcinogenic, but ecoxicological data are sufficient for derivation of a carcinogenic potency factor only for benzo[a]pyrene [41]. The toxicity equivalency factor (TEF) was used to quantify the carcinogenicity of other PAHs relative to benzo[a]pyrene and to estimate benzo[a]pyrene equivalent doses. In this study, we converted seven potentially carcinogenic PAHs to B[a]A, B[b]Fl, B[k]Fl, B[a]P, IDP, DB[ah] and Chry, with one toxic concentration for each sediment using the corresponding TEF proposed by US EPA [42]. The total toxic benzo[a]pyrene equivalent TEQ (TEQ = Σ Ci × TEFi), calculated for stations 3–10, varied from 299 (station 4) to 47,672 ngTEQ·g^{-1} (station 9). The spatial distribution of TEQ was site specific, showing higher values in samples collected near industrial areas influenced directly by the 'ILVA' iron and steel factory. Therefore, the proximity to industrial wastewater and the emission of atmospheric particles from steel factories were the most important determining factor for the distribution of PAHs in this study.

Among different carcinogenic PAHs, contribution to the total TEQ (average values) decreased in the order: B[a]P (65%), DB[ah]A (13%), B[b]Fl (10%), IDP (4.8%), B[a]A (4.1%), B[k]Fl (0.46%), Cry (0.03%). In comparison with other studies, TEQ values were higher than those found in the literature for the Mediterranean Sea, such as the sediment from Naples harbour or those from Catalonia [30,43], confirming that sediments in the Gulf of Taranto, were especially toxic and potentially carcinogenic.

4.   Conclusions

The results obtained in this study showed that concentrations of total and individual PAHs, PCBs and metals in surface sediments varied significantly among sampling stations. The highest levels of PAHs, PCBs, Fe, Mn As, Pb, Hg, Zn, were found in stations which were closer to the ILVA iron and steel factory, whereas Al, Cr, Sn and Ni were higher in the Mar Grande stations, influenced mainly by harbour discharge activities. Using fingerprint analysis, PAHs in the sediments showed a pyrolytic origin for all samples. Moreover, total TEQ, calculated for carcinogenic PAHs, suggests a relatively high level of toxicity, with values higher than literature-reported results for the area. To evaluate sediment contamination and potential ecotoxicological effects associated with the observed concentrations, different SQGs have been used in this study. The comparison with SQGs suggested a possible environmental risk for benthic marine organisms in Taranto Gulf, where overall PAH concentrations were higher than the sediment guidelines values. Although some SQGs have been found to be relatively good predictors of significant site contamination, they also have several limitations. False-positive and false-negative predictions are frequently in the 20–30% range for many chemicals and higher for others. Therefore, SQGs can be used in a 'screening' manner or in a 'weight-of-evidence' approach for a preliminary assessment of correlations between chemical concentrations and possible toxic effects on marine organisms. An efficient control of the input are necessary, nevertheless, for promoting a recovery of the quality in the marine environment.

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