Source identification and eco-risk assessment of polycyclic aromatic hydrocarbons in the sediments of seawaters facing the former steel plant ILVA, Naples, Italy

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A B S T R A C T

The study was designed to complement the results of a previous investigation which revealed a worrying contamination scenario by polycyclic aromatic hydrocarbons, PAHs, in the Gulf of Pozzuoli, GoP, in the south of Italy. This former study also evidenced the pyrolytic source of PAHs from the dismissed metallurgical brownfield site of Bagnoli in the east side of GoP. The environmental toxicological risk assessment was also carried out. Sampling transects were drawn in the west edge of the gulf, T1 and T2, in the east side, T5, T6, in the proximity of the industrial plant and outside GoP, MdP, where pollution was expected to be low. ΣPAHs largely exceeded, from 36 up to >220 times, the regulatory standard in the east area. Lower exceeding values were determined in all the west side. FLT and PYR were the dominant hydrocarbons and PAHs distribution profiles were quite similar from west to east sides, meaning a common pollution source. Moreover, sediments appeared enriched by 4, 5 and 6 aromatic rings, 47.2%, 25.7%, and 14.0%. PAHs diagnostic ratios for source screening confirmed the pyrolytic origin of the PAH mixtures at all sites. ΣPAHcarc/ΣPAH showed that ∼50% of PAHs were of carcinogenic nature at all sites. The total benzo(a)pyrene, BaP, equivalent toxicity (TEQ) values highlighted a dramatic scenario especially in the east part of GoP, with values from twenty-four fold and six hundreds fold those reported by the literature for moderate and low ecological risk environment. The output of the risk assay assessment revealed a situation of high risk in the east side of GoP, whereas a moderate to high risk level was determined throughout all GoP.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the most widespread and dangerous pollutants for mankind and the environment. These compounds are formed by two or more condensed aromatic rings, with low affinity for water and low volatility, which further reduces as molecular weight increases. Many PAHs have toxic, mutagenic and/or carcinogenic properties. Three main sources of PAHs in the environment exist: petrogenic, pyrogenic and biological. The petrogenic source of crude oil shows a PAHs level from a few mg to ∼5 g per kg, with naphthalene as the main component, mean 60.5% and a maximum of ∼78% of total PAHs (Pampanin and Sydnes, 2013). Oil dispersions can be a consequence of human activities, i.e. pipeline spills, oil

tanker spills, offshore platforms and shipping accidents, intentional oil discharges as well as linked to natural petroleum seeps. The biological source of PAHs is mainly linked to the activity of plants, fungi, and bacteria, with generation of naphthalene, phenanthrene, and perylene (Krauss et al., 2005). The pyrogenic source includes electric power generation, refuse incineration, internal combustion engines, home heating, production of coke, carbon black, coal tar, and asphalt, and forest/grass fires. PAHs dispersed in the environment tend to be transported to the sea where, due to their poor solubility in water, aggregate with other suspended material and precipitate in sediments. Although PAHs are known as hydrophobic compounds, they have a certain water solubility which affects their marine dispersion (Guigue et al., 2017; Abdel-Shafy and Mansour, 2016). In the case of sediments present in relatively shallow waters, and within the *depth of closure*, PAHs can be moved by storm surges and return to suspension (Arienzo et al., 2019) and even reach the beaches.

Here, PAHs being semi-volatile substances, can constitute a not negligible human risk.

In previous works we examined the state of contamination of the coastal marine sediments of the GoP, embedded in the Gulf of Naples (GoN), Italy, by PAHs, metals and lanthanides (Arienzo et al., 2017; Trifuoggi et al., 2017, 2018). The impairment for the local fauna (Arienzo et al., 2019), and the drawing of a prototype system of sediment reclamation (Nastro et al., 2019) were also studied. The GoP is an area known for the beauty of its coasts, of volcanic nature with over fifty craters, both inland and offshore. However, the choice made at the beginning of the 20th century to implement in this site an industrial metallurgic plant and other dangerous productions, seriously compromised land, groundwater and coastal environments. GoP is a large bay, Fig. 1, placed on the Campanian Margin of the Tyrrhenian Sea and originated during a Pliocene extensional tectonic phase (Patacca et al., 1990; Sgrosso, 1998). GoP, mean depth ∼60 m, maximum depth 110 m, Somma et al. (2016), has a surface area of 33 km^2 and a volume of ∼2 km^3. Water exchange occurs between GoP and GoN through a Section 2 km wide and 100 m deep (De Maio et al., 1982). The purpose of this work was to complement the previous research with information on the toxicological risk of PAHs.

2. Material and methods

2.1. Sampling activities

Sediment sampling was carried out in June 2017 with a Van Veen grab on an equipped boat, the Antilia, of the Lega Navale of Pozzuoli. A total of 15 sampling points aligned along four transects located in the coast offshore direction were chosen. The transects T4 and T6 were offshore the ILVA plant, in the eastern part; T1 and T2-3, in the western area, and finally a fourth transect, Mdp, taken as external reference out of the GoP, in correspondence of Monte di Procida (MdP) (see Fig. 1 and Table 1). Sea depth, measured with an echo sounder, varied between 10 m up to ∼100 m while the geographical coordinates of the single points were measured by DGPS (Differential Global Positioning System).

2.2. Sample analysis

The sediments were collected in plastic bags, wrapped in aluminium foil and frozen at −20 °C . Sediment samples were analysed for granulometric parameters, TOC, and PAHs (Tables 1, 2). The granulometric analysis and TOC determination were carried out as in the previous work (Arienzo et al., 2017). Sixteen PAHs indicated from Environmental Protection Agency (EPA) as important toxicological contaminants were determined: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorine (FLR), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(ah)anthracene (DhA), indeno[1,2,3-cd] pyrene (IPY), benzo(ghi)perylene (BgP) (US EPA, 1977). Among them, benzo (a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(b) fluoranthene (BbF), benzo(k) fluoranthene (BkF), chrysene (Chry), dibenzo(a)anthracene (DBA), and indeno (1,2,3-c,d)pyrene (IP) were classified as possible or probable human carcinogens, and BaP is often chosen as a standard of the whole group of PAHs due to its high carcinogenic potency (IARC, 1987). For the analysis of PAHs the IRSA CNR 25 method was followed and modified as described in the previous work (Arienzo et al., 2017). Samples were analysed in triplicate, for all the investigated points. The percentage of recovery was estimated by analysing 10 replicates

of a fortified matrix, constituted by 13 PAHs at a known concentration. The range of the recovery percentage was 57%–130%, in accordance with current methods normed. The detection limit (LOD) and limit of quantification (LOQ) were calculated using the range method of prediction to 95% of linear regressions, for each investigated PHAs. The calculated average values of LOD and LOQ were 0.1 and 0.3 μg g^{-1}, respectively. The quality of the analytical results is assured by participation in ring tests for the determination of PAHs from sediments and similar matrices.

3. Results and discussion

3.1. Distribution and composition profiles of PAHs

Table 2 shows the concentrations, in μg g^{-1}, of PAHs in the different sampling points. The table also reports the environmental quality standards of sediments in marine-coastal and transitional water bodies provided by DM (0000).

The results clearly show that, in all the three transects, the concentrations of all individual PAHs are significantly higher than the corresponding values of environmental quality standards and that there is a significant correlation ($p < 0.01$, $r = 0.71$) between ΣPAHs and TOC. In the case of T4, the levels of FLT, BbF, BkF, BaP exceed the environmental quality standard and up to >1000 times in T4-3. A similar trend was also observed by ΣPAHs. In the transect T4, ΣPAHs exceeds the value of the environmental quality standard from 36 up to >220 times in T4-3. In T6, ΣPAHs is from 23 to 156 times higher than the standard. In T1, located in the western part of the GoP, ΣPAHs also largely exceeds the reference by ∼15 times. In the case of MdP, data are only slightly higher than the reference values. However, it is interesting to note how ΣPAHs increases with a coast-offshore direction, with a value twice the standard in the MdP3, shifting to levels of bathymetrically higher deposition. This can be explained by the circulation models of the GoN elaborated by De Maio et al. (1985) and de Ruggiero et al. (2016) reporting two main flow patterns: (i) when the open sea currents flow towards southeast, the inner waters of bay are cut off in a slow cyclonic gyre, then the coastal waters slow motion could favour a high pollutant concentration; (ii) when the open sea currents flow towards northwest, some branches enter into the bay, then a fair renewal of sea waters occurs.

The results of the previous work (Arienzo et al., 2017) evidenced a strong PAH contamination of the sediments of the entire Gulf of Pozzuoli, with very high levels of individual PAHs in all GoP, with mean values higher than legal limits from one hundred twenty seven fold (NAP) to seven hundred twenty five fold (BaP). Transit axes of fine and very fine sands and diagnostic indexes revealed a common pyrolytic PAHs pollution spreading from the former Bagnoli plant to all the Gulf.

Fig. 2 shows the percentage compositions of the individual PAHs in all samples. Fig. 2a clearly reveals that FLT and PYR are the dominant hydrocarbons, as well as that the PAHs distribution profile is basically the same in GoP. The same distribution pattern was also observed in the case of MdP, Fig. 2b. This means a common origin of GoP contamination as highlighted by Arienzo et al. (2017), and that even the remote area of MdP is affected by the same pollution source. It is not a coincidence that the concentrations of PAHs increase from coast to offshore in MdP. In fact, it is possible that the diffusion of the contamination from the industrial site overcomes Capo Miseno (Fig. 1) by transport and subsequent deposition of suspended materials.

Fig. 3 shows the composition pattern of PAHs by ring size in GoP sediments (μg g^{-1}). PAHs with 4 aromatic rings (FLT, PYR, BaA, CHR) make up about half of the mixture, 47.2%, followed by those with 5 rings, (BbF, BkF, BaP, DhA), 25.7%, and 6 terms, (IPY and BgP), 14.0%. The 3 (IND, ACY, ACP, FLR, PHE, ANT) and 2-ring (NAP) components represent only 11.5 and 1.6%, respectively.
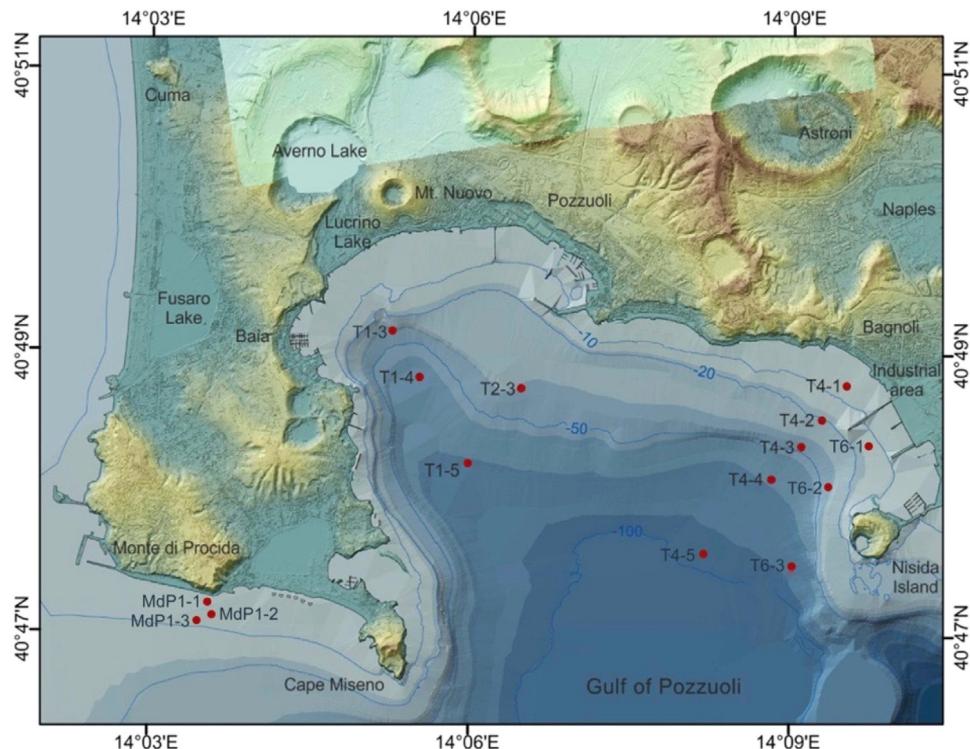
Fig. 1. Map of the sediment sampling in the Gulf of Pozzuoli. Depth is in metres bsl, coordinate system is WGS84 UTM Zone 33T (after Somma et al., 2016).
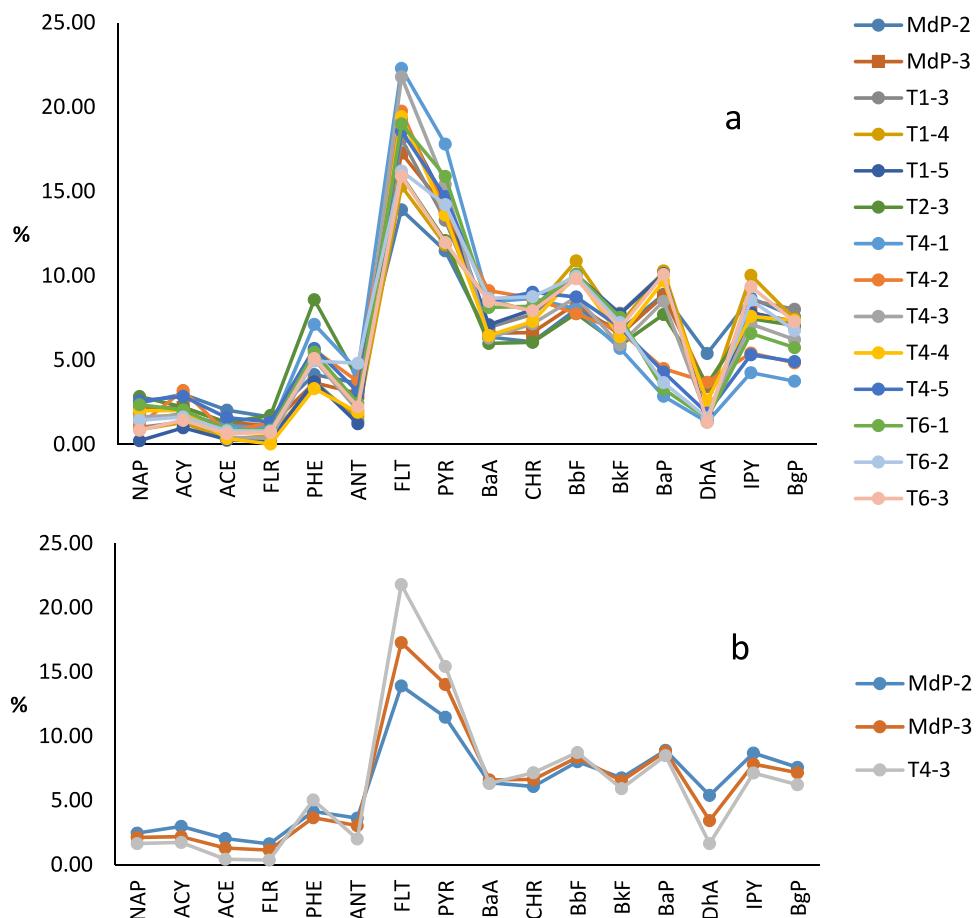

Fig. 2. Relative concentration in percentage of individual PAHs: (a) all sampling stations; (b) the MdP compared with T4-3.

Table 1
Sampling locations associated to water depts, total organic carbon (TOC) and grain size of sediments from GoP.

Sampling station	Latitude (N)	Longitude (E)	Depth (m)	TOC (%)[a]	Class[b]
T1-3	40°49.114′N	14°5.251′E	45.1	1.8	Medium sand
T1-4	40°48.822′N	14°5.523′E	58.6	2.2	Coarse sand
T1-5	40°48.177′N	14°5.972′E	80.0	1.9	Very fine sand
T2-3	40°48.715′N	14°6.484′E	34.0	1.2	Fine sand
T4-1	40°48.774′N	14°9.515′E	7.7	4.2	Fine sand
T4-2	40°48.546′N	14°9.294′E	21.5	1.6	Fine sand
T4-3	40°48.347′N	14°9.091′E	47.8	6.4	Very fine sand
T4-4	40°48.115′N	14°8.819′E	71.5	3.2	Very fine sand
T4-5	40°47.554′N	14°8.198′E	98.0	1.8	Fine sand
T6-1	40°48.323′N	14°9.768′E	13.4	5.3	Fine sand
T6-2	40°48.038′N	14°9.352′E	37.1	3.2	Fine sand
T6-3	40°47.468′N	14°9.023′E	87.5	1.5	Fine sand
MdP-1	40°47.230′N	14°3.311′E	4.10		Medium sand
MdP-2	40°47.182′N	14°3.312′E	5.22		Medium sand
MdP-3	40°47.086′N	14°3.215′E	7.47		Medium sand

[a]TOC: total organic carbon.
[b]Classification of grain size sediment (Folk and Ward, 1957).

Table 2
Concentrations of individual PAHs in the sediments ($\mu g\ g^{-1}$).

PAH	NAP	ACY	ACE	FLR	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	DhA	IPY	BgP	Total PAH	Total PD[a] PAH
n° rings	2	3	3	3	3	3	4	4	4	4	5	5	5	5	6	6		
T1-3	0.345	0.455	0.082	0.087	1.29	0.499	6.24	4.58	2.39	2.66	3.43	2.68	3.50	0.511	2.94	2.76	34.4	13.2
T1-4	0.241	0.359	0.089	0.141	0.968	0.461	4.19	3.23	2.34	2.16	2.98	1.95	2.81	0.657	2.74	2.03	27.3	10.5
T1-5	0.069	0.305	0.089	0.079	1.15	0.379	6.00	4.47	2.20	2.48	3.12	2.39	3.14	0.449	2.42	2.26	31.0	11.4
T2-3	0.123	0.096	0.056	0.074	0.371	0.167	0.689	0.522	0.259	0.261	0.335	0.253	0.333	0.154	0.322	0.305	4.32	1.52
T4-1	6.74	8.56	5.19	4.67	33.4	20.5	104	83.4	39.6	40.6	37.7	26.7	13.4	6.24	19.9	17.6	469	123
T4-2	1.16	3.22	0.684	1.33	5.62	3.74	19.8	13.9	9.15	8.70	7.78	6.76	4.52	3.70	5.44	4.86	100	28.8
T4-3	8.83	9.31	2.32	1.94	27.1	10.8	117	82.9	33.9	38.4	46.9	31.8	45.6	8.83	38.4	33.4	538	177
T4-4	5.43	5.47	0.957	0.070	9.00	5.17	52.8	36.9	17.5	19.8	27.2	17.4	26.3	7.01	20.6	20.0	272	101
T4-5	3.31	3.64	2.02	1.71	7.27	3.98	23.7	18.8	10.8	11.53	11.2	8.89	5.49	2.37	6.79	6.28	128	39.1
T6-1	1.41	1.22	0.528	0.513	3.28	1.46	11.4	9.54	4.88	4.92	6.06	4.52	1.97	0.920	3.95	3.44	60.0	18.9
T6-2	5.24	5.91	2.93	2.86	17.9	17.5	58.8	51.6	31.4	31.8	36.1	26.2	13.3	5.71	31.0	24.5	363	123
T6-3	0.764	1.30	0.591	0.646	4.62	2.03	14.4	10.9	7.69	7.19	8.91	6.27	9.14	1.19	8.49	6.60	90.7	33.7
MdP-1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MdP-2	0.061	0.074	0.050	0.040	0.102	0.090	0.344	0.284	0.158	0.150	0.198	0.167	0.220	0.133	0.215	0.187	2.47	0.923
MdP-3	0.103	0.106	0.063	0.055	0.178	0.148	0.840	0.681	0.320	0.322	0.406	0.316	0.428	0.167	0.381	0.348	4.86	1.75
Legal limits[b]	0.035					0.045	0.110				0.040	0.020	0.030		0.070	0.055		0.800

[a]PD: priority dangerous: NAP, ANT, BbF, BkF, BaP, BgP according to the rules of the DLgs 10 December 2010, n. 219.
[b]DM (0000).

3.2. Diagnostic ratios for pyrogenic vs. petrogenic source determination

The distribution of hydrocarbons in a mixture provides valuable information on its origin. In fact, PAHs of petrogenic source (petroleum derived) are more shifted towards components with lower molecular weights, while pyrogenic mixtures (combustion derived) are dominated by 4-ring or higher molecular weight PAHs.

However, a clear pyrogenic origin to the mixture of PAHs found in the sediments was not observed. In fact, the long permanence of PAHs mixture, after its formation, first in the atmosphere, then in the marine waters and finally in the sediments, definitely alters its original composition as a consequence of physical, chemical and biological factors. Fig. 4 compares the mean individual PAHs composition of crude oil with that of GoP sediments. The PAHs pattern in sediments is markedly different respect with crude oil with a net dominance of higher molecular weight (HMW) compounds. In the atmosphere there is a first important separation between the low and high molecular weight, LMW and HMW. LMW are more volatile and tend to have a longer residence time in atmosphere than HMW, which are less polar and tend to aggregate with solid particles and precipitate

with dry or wet deposition. Once PAHs are adsorbed by sediments, they become less susceptible to degradation (Guzzella and Depaolis, 1994).

To distinguish the source of PAH mixtures, researchers have begun to make use of diagnostic indexes, which are generally ratios between two different PAHs isomers. The use of these ratios is based on the different thermodynamic stability of the isomers, which in turn is related to the greater or lesser presence of these components in the mixture (Yunker et al., 2002).

Table 3 shows a list of source indicators and their respective diagnostic ratios. These values were compared with those determined at each individual sampling station, Table 4. The set of results obtained confirms the pyrolytic origin of the PAH mixtures at all the examined sites. One of the most relevant and widely used diagnostic reports to distinguish an oil from a combustion source is ANT/(ANT+PHE), Yunker et al. (2002). This index is largely >0.1 in all GoP, meaning the predominance of the pyrogenic source.

The cross plots of FLT/(FLT+PYR) vs. ANT/(ANT+PHE), FLT/(FLT+PYR) vs. BaA/(BaA+CHR), FLT/(FLT+PYR) vs. IPY/(IPY+BgP), IPY/(IPY+BgP) vs. BaA/(BaA+CHR) and their cut-off values are shown in Fig. 5. Once again all the specimens analysed resulted unequivocally of pyrolitic origin.
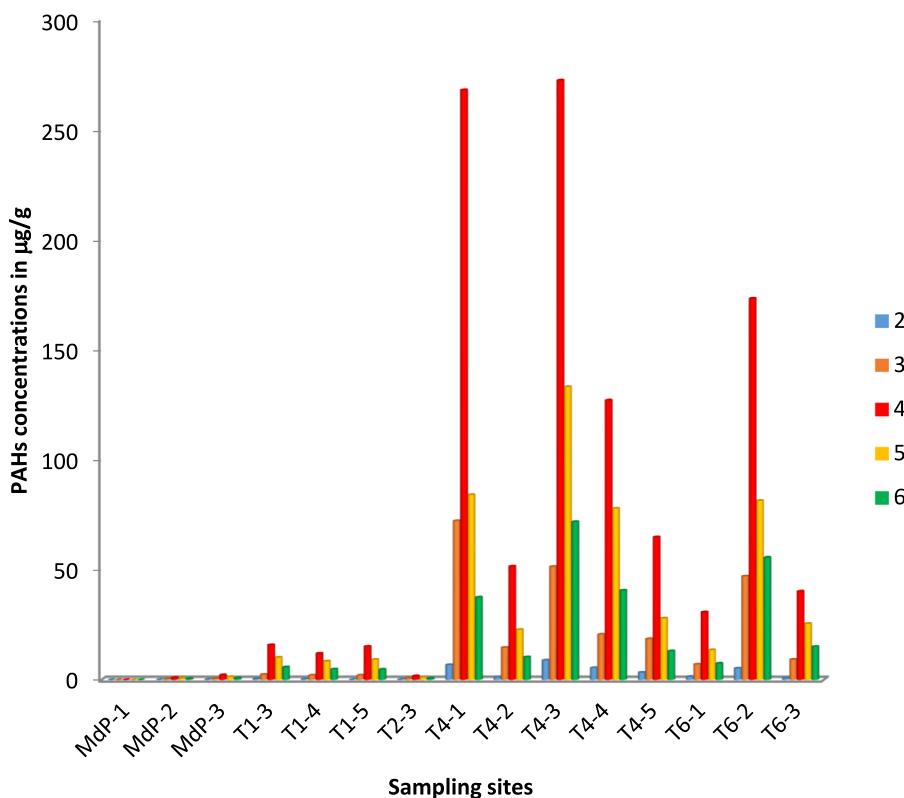
Fig. 3. PAHs distribution in samples of sediments in GoP reported as sum of 2, 3, 4, 5, and 6-ring PAHs (in $\mu g\ g^{-1}$).

Table 3
Source indicators and their respective diagnostic ratios.

Ratios	Petrogenic[c]	Petroleum burning /vehicular emission	Diesel	Coal combustion	Softwood combustion	Pyrogenic	Aluminium smelter emissions	References
PHE/ANT	>15					<10		Soclo (1986)
FLT/PYR	>1					≤1		Sicre et al. (1987)
CHR/BaA	>1					<1		Parlanti (1990)
LMW/HMW[a]	>1					<1		Soclo et al. (2000)
ΣCOMB/ΣPAHs	<1					~1		Ravindra et al. (2008a)
BbF/BkF							2,5–2,9	Hwang and Foster (2006)
BaP/BgP		>0.6						Tobiszewski and Namiesnik (2012)
IPY/(IPY+BgP)		0.18	0.37	0.56	0.62			Ravindra et al. (2008a)
ANT/(ANT+PHE)	<0.10	>0.10		>0.10	>0.10	>0.10		Pies et al. (2008)
FLR/(FLR+PYR)	<0.5						>0.5	Ravindra et al. (2008b)
FLT/(FLT+PYR)	<0.40	0.40–0.50		>0.50	>0.50	>0.40		De La Torre-Roche et al. (2009)
BaA/(BaA+CHR)	<0.20	>0.35		0.20–0.35	>0.35	>0.35		Akyüz and Çabuk (2010) and Yunker et al. (2002)
Ring456/TPAS[b]	<0.40	>0.50		>0.50	>0.50	>0.50		Arienzo et al. (2017).

[a]LMW: PHE, ANT, FLT, PYR. HMW: BaA, CHR, BbF, BkF, BaP, BgP, DhA.
[b]Ring456: Total 4–6 ring PAHs (mainly originated from combustion); ΣCOMB (FLT, PYR, BaA, CHR, BbF, BkF, BaP, BgP); ΣPAHs sum of total PAHs.
[c]Yan et al. (2004).

3.3. Toxicity assessment of PAHs

Several approaches are used to estimate the toxicity of polluting substances through Standard Quality Guidelines, SQGs. These include the determination of Effects Range-Low (ERL), Effects Range-Median (ERM), Threshold Effects Levels (TEL) and Probable Effects Levels (PEL) (Long and MacDonald, 1998). Toxicity was estimated based on BaP equivalents for the whole group of PAHs due to the classification of BaP as a group 1 carcinogen. Mumtaz and George (1995) and Obini et al. (2013) reported that BaP metabolites block DNA replication and is mutagenic. To assess the overall carcinogenic potency of a mixture of PAHs to mankind, the toxicity equivalence factors, (TEF), (Table 5) of the single PAHs were introduced relative to BaP, US EPA (1993) as adapted for PAH compounds by Nisbet and LaGoy (1992). The total BaP equivalent toxicity (TEQ) is consequently defined as the sum of the products of the concentrations of each carcinogenic with the relative toxicity equivalence factor as indicated below:

$$TEQ = \sum_{i=1}^{n} C_i x TEF_i$$

where C_i represents the concentration of the ith PAH.
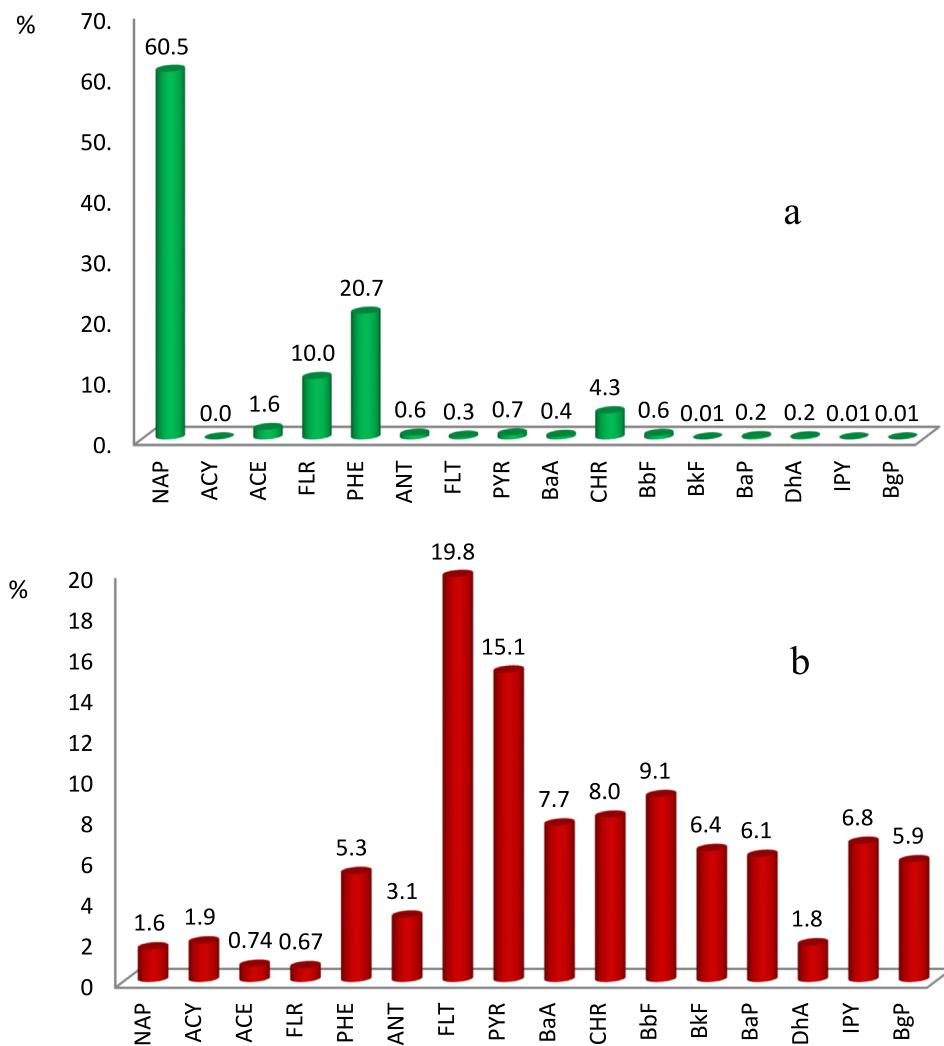
Fig. 4. Relative percentage distributions of individual PAHs in: (a) crude oil (mean of 48 different crude oils, Kerr et al. (1999) and (b) sediments of Gulf of Pozzuoli (mean of all the sampling sites).

Table 4
Diagnostic ratios determined at each individual sampling station.

Stations	PHE/ANT	FLT/PYR	CHR/BaA	LMW/HMW	ΣCOMB/ΣPAHs	BbF/BkF	BaP/BgP	IPY/(IPY+BgP)	ANT/(ANT+PHE)	FLR/(FLR+PYR)	FLT/(FLT+PYR)	BaA/(BaA+CHR)	Ring456/TPAS
T1-3	2.6	1.4	1.1	0.087	0.74	1.3	1.3	0.52	0.28	0.019	0.58	0.47	0.92
T1-4	2.1	1.3	0.92	0.090	0.72	1.5	1.4	0.57	0.32	0.042	0.56	0.52	0.92
T1-5	3.0	1.3	1.1	0.072	0.77	1.3	1.4	0.52	0.25	0.017	0.57	0.47	0.93
T2-3	2.2	1.3	1.0	0.26	0.61	1.3	1.1	0.51	0.31	0.12	0.57	0.50	0.79
T4-1	1.6	1.3	1.0	0.20	0.74	1.4	0.76	0.53	0.38	0.053	0.56	0.49	0.83
T4-2	1.5	1.4	1.0	0.19	0.70	1.2	0.93	0.53	0.40	0.087	0.59	0.51	0.84
T4-3	2.5	1.4	1.1	0.13	0.74	1.5	1.4	0.53	0.28	0.023	0.59	0.47	0.89
T4-4	1.7	1.4	1.1	0.11	0.73	1.6	1.3	0.51	0.36	0.0019	0.59	0.47	0.90
T4-5	1.8	1.3	1.1	0.21	0.71	1.3	0.87	0.52	0.35	0.084	0.56	0.48	0.83
T6-1	2.2	1.2	1.0	0.16	0.72	1.3	0.57	0.53	0.31	0.051	0.54	0.50	0.86
T6-2	1.0	1.1	1.0	0.17	0.69	1.4	0.54	0.56	0.49	0.052	0.53	0.50	0.86
T6-3	2.3	1.3	0.93	0.12	0.71	1.4	1.4	0.56	0.30	0.056	0.57	0.52	0.89
MdP-1	–	–	–	–	–	–	–	–	–	–	–	–	–
MdP-2	1.1	1.2	1.0	0.20	0.62	1.2	1.2	0.53	0.47	0.12	0.55	0.51	0.83
MdP-3	1.2	1.2	1.0	0.15	0.68	1.3	1.2	0.52	0.45	0.075	0.55	0.50	0.87

In a similar way, the mutagenic (MMC) and the carcinogenic (TCDD-TEF) equivalence factors (Table 5) relative to the mutagenicity of BaP (Durant et al., 1996) and to the carcinogenicity of 2, 3, 7, 8-tetrachlorodibenzodioxin (Willett et al., 1997), respectively, were defined. Table 6 shows the TEQ, the mutagenic
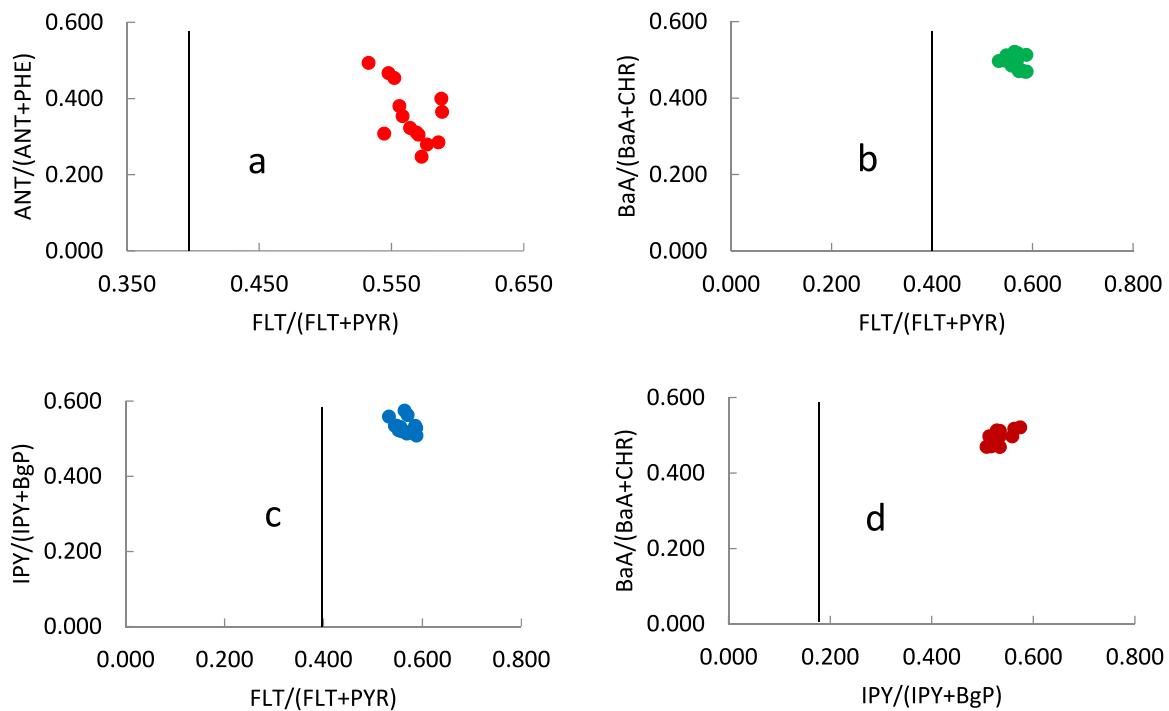
Fig. 5. Plots (a, b, c and d) of the diagnostic ratios calculated for the studied sediments.

Table 5

Values of toxicity (TEF), mutagenic (MMC), and carcinogenic (TCDD-TEF) equivalence factors for PAH and the carcinogenic (+).

PAHs	TEF	MMC	TCDD-TEF	Carc
ACE	0.001			
ACY	0.001	0.00056		
ANT	0.01			
BaA	0.1	0.082	0.000025	+
BbF	0.1	0.25	0.00253	+
BkF	0.1	0.11	0.00487	+
BgP	0.01	0.19		
BaP	1	1	0.000354	+
CHR	0.01	0.017	0.00020	+
DhA	5	0.29	0.00203	+
FLT	0.001			
FLR	0.001			
IPY	0.1	0.31	0.00110	+
NAP	0.001			
PHE	0.001			
PYR	0.001			

Table 6

Values of TEQ, MEQ, (μg g^{-1}), CEQ (ng g^{-1}) and share of carcinogenic PAH in ΣPAH for sediments of GoP.

Stations	TEQ μg g^{-1}	MEQ μg g^{-1}	CEQ ng g^{-1}	ΣPAHcarc/ΣPAH
T1-3	5.20	6.48	27.8	0.53
T1-4	4.51	5.43	22.8	0.57
T1-5	4.64	5.72	24.8	0.52
T2-3	0.61	0.673	2.9	0.44
T4-1	32.7	41.0	274	0.39
T4-2	11.3	11.8	69.7	0.46
T4-3	70.3	85.1	358	0.45
T4-4	42.0	49.0	204	0.50
T4-5	11.8	14.3	88.3	0.45
T6-1	4.91	6.61	45.4	0.45
T6-2	32.1	44.3	277	0.48
T6-3	18.4	17.0	69.7	0.54
Mean	19.9	24.0	122	0.48
SD	20.8	25.6	122	0.05
Min	0.61	0.67	2.9	0.39
Max	70.3	85.1	358	0.57
MdP2	0.43	0.44	1.9	0.50
MdP3	0.74	0.83	3.5	0.48

equivalent (MEQ), and the carcinogenic equivalent (CEQ) computed as linear combinations of the PAH concentrations and respective equivalence factors. Additionally, the ratios of the sum of the carcinogenic PAH (ΣPAHcarc) (US EPA, 2008) concentrations to the sum of the concentrations of the 16 determined PAH (ΣPAH) were computed.

The results are quite alarming since at all sites $\sim$50% of PAHs are of carcinogenic nature. The mean of TEQ and MEQ were 20 and 24 μg g^{-1}, respectively. Peaks of 70.3 and 85.1 μg g^{-1} were revealed at T4-3 which is the most polluted station. These values were higher, from $\sim$ six hundreds and seven hundreds fold relative to a low ecological risk environment (Li et al., 2014), to $\sim$ twenty-four and thirty-four fold relative to moderate polluted sites (Adeniji et al., 2019a,b). Table 6 also reports high values of CEQ, 127 ng g^{-1}, with a maximum of 358 ng g^{-1} at T4-3. MdP data appeared markedly lower, even if values were still of concern.

3.4. Risk assessment of PAHs

The presence of PAHs in the aquatic environments constitutes a very high risk for ecosystems. Consequently, the use of an ecosystem risk assessment was introduced to quantify the risk generated by the presence of a mixture of PAHs on the biosphere (Wu et al., 2011). Cao et al. (2010) advanced the method by employing the toxic equivalency factors for the USEPA-listed 16 PAHs. Normally a risk quotient, RQ, represents the ratio between the concentration of a contaminant present in the environment, in our case a PAH, and the expected optimal value, C_{QV}, for the same contaminant.

$$RQ = C_{PAHs}/C_{QV}$$

Based on scientifically derived risk limits, maximum permissible concentrations (MPCs) and the negligible concentrations

Table 7

Recommended RQ (NCs) and RQ (MPCs) values of PAHs(ng/g) in sediment (Cao et al., 2010).

PAHs	Recommended NCs	Recommended MPCs
ACE	1.2	120
ACY	1.2	120
ANT	1.2	120
BaA	3.6	360
BbF	3.6	3600
BkF	24	2400
BgP	75	7500
BaP	27	2700
CHR	107	107 00
DhA	27	2700
FLT	26	2600
FLR	1.2	120
IPY	59	5900
NAP	1.4	140
PHE	5.1	510
PYR	1.2	120

(NCs) were defined for the different PAHs. MPCs are concentrations above which the risk of adverse effects is considered unacceptable; NC is defined as MPC/100 which accounts for synergistic effects from the presence of other substances (Cao et al., 2010). The values used in this work are those suggested by Cao et al. (2010) (Table 7).

Consequently, the RQNCs and RQMPCs were defined as follows:

$$RQ_{NCs} = C_{PAHs}/C_{QV(NCs)}$$

$$RQ_{MPCs} = C_{PAHs}/C_{QV(MPCs)}$$

where $C_{QV(NCs)}$ and $C_{QV(MPCs)}$ indicate the quality values of the NCs and MPCs of PAHs in the medium respectively. The $RQ_{\Sigma PAHs}$, $RQ_{\Sigma PAHs(NCs)}$, and $RQ_{\Sigma PAHs(MPCs)}$ are defined as follows:

$$RQ_{\Sigma PAHs} = \Sigma RQ_i(RQ_i \geq 1)$$

$$RQ_{\Sigma PAHs(NCs)} = \Sigma RQ_{i(NCs)}(RQ_{i(NCs)} \geq 1)$$

$$RQ_{\Sigma PAHs(MPCs)} = \Sigma RQ_{i(MPCs)}(RQ_{i(MPCs)} \geq 1)$$

Naturally, only values of RQ(NCs) and RQ(MPCs) of individual PAHs ≥1 were considered when calculating RQPAHs(NCs) and RQ PAHs(MPCs) of PAHs.

Tables 8 and 9 report the values of different RQ while Table 10 reports the risk classifications of individual PAHs and ∑PAHs elaborated by Cao et al. (2010).

Based on the comparison of data from Tables 8 and 9 with the risk threshold expressed in Table 10, we can state a moderate risk for all sites except for MdP1, that is risk free, and a high risk situation for T4-1, T4-3 and T6-2. However, the individual RQ_{CNs} and RQ_{MPCs} values indicate in addition to the three already cited hotspots, T1-3, T1-4, T1-5, T4-2, T4-4, T4-5, T6-1 and T6-3 express high risk in ≥9 of 16 analysed PAHs.

4. Conclusions

PAH contamination extends over the west edge of GoP, suggesting that a similar scenario could be found beyond the east side of GoP, due to sediment transport. The source screening of indexes confirm the combustion origin of PAHs in GoP as well MdP sediments. Risk assessment analysis indicates most of the GoP sediments are considered a high toxicity risk.

CRediT authorship contribution statement

Luciano Ferrara: Supervision, Writing - original draft and editing. **Marco Trifuoggi:** Data curation, Visualization, Investigation. **Maria Toscanesi:** Data curation, Visualization, Investigation.

Table 8

Values of risk quotient, RQ, with respect to negligible concentrations, NCs, in different sampling sites with respect to individual PAHs and to ∑PAHs.

PAH	NAP	ACY	ACE	FLR	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	DhA	IPY	BgP	RQ$_{\Sigma PAHs(NCs)}$
T1-3	247	379	69	72	253	416	240	3813	664	25	952	112	130	19	50	37	7476
T1-4	172	299	74	118	190	384	161	2695	651	20	827	81	104	24	46	27	5874
T1-5	50	254	74	66	226	316	231	3726	611	23	867	100	116	17	41	30	6748
T2-3	88	80	47	62	73	139	26	435	72	2.4	93	11	12	5.7	5.5	4.1	1155
T4-1	4815	7137	4324	3892	6543	17 062	4018	69 516	11 004	379	10 470	1113	496	231	337	234	141 571
T4-2	828	2680	570	1110	1102	3116	763	11 591	2543	81	2161	282	167	137	92	65	27 288
T4-3	6309	7758	1932	1620	5309	8980	4506	69 096	9430	359	13 029	1325	1689	327	650	446	132 765
T4-4	3879	4555	798	58	1765	4308	2030	30 766	4869	185	7552	724	974	260	350	266	63 338
T4-5	2361	3032	1684	1428	1426	3316	913	15 644	3010	108	3103	370	203	88	115	84	36 885
T6-1	1010	1017	440	427	644	1216	439	7946	1354	46	1682	188	73	34	67	46	16 629
T6-2	3740	4926	2444	2380	3514	14 548	2262	42 979	8718	297	10 041	1092	493	212	526	327	98 498
T6-3	546	1081	492	538	906	1689	555	9053	2137	67	2475	261	338	44	144	88	20 415
MdP-2	43	61	42	33	20	75	13	237	44	1.4	55	7.0	8.1	4.9	3.6	2.5	651
MdP-3	74	88	52	46	35	123	32	568	89	3.0	113	13	16	6.2	6.4	4.6	1269

Table 9

Values of risk quotient, RQ, with respect to maximum permissible concentrations, MPCs, in different sampling sites with respect to single PAHs and to their mix. Only values ≥ 1 were reported.

PAH	NAP	ACY	ACE	FLR	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	DhA	IPY	BgP	RQ$_{\Sigma PAHs(MPCs)}$
T1-3	2.5	3.8			2.5	4.2	2.4	38	6.6		9.5	1.1	1.3				72
T1-4	1.7	3.0		1.2	1.9	3.8	1.6	27	6.5		8.3		1.0				56
T1-5		2.5			2.3	3.2	2.3	37	6.1		8.7	1.0	1.2				64
T2-3						1.4		4.3									5.7
T4-1	48	71	43	39	65	171	40	695	110	3.8	104.7	11.1	5.0	2.3	3.4	2.3	1416
T4-2	8	27	5.7	11	11	31	7.6	116	25		21.6	2.8	1.7	1.4			270
T4-3	63	78	19	16	53	90	45	691	94	3.6	130.3	13.2	16.9	3.3	6.5	4.5	1328
T4-4	39	46	8.0		18	43	20	308	49	1.9	75.5	7.2	9.7	2.6	3.5	2.7	633
T4-5	24	30	17	14	14	33	9.1	156	30	1.1	31.0	3.7	2.0		1.2		367
T6-1	10	10	4.4	4.3	6.4	12	4.4	79	14		16.8	1.9					164
T6-2	37	49	24	24	35	145	23	430	87	3.0	100.4	10.9	4.9	2.1	5.3	3.3	985
T6-3	5.5	11	4.9	5.4	9.1	17	5.6	91	21		24.7	2.6	3.4		1.4		202
MdP-2								2.4									2.4
MdP-3						1.23		5.7									6.9

Table 10

Risk classifications of individual PAHs and $\sum$PAHs (Cao et al., 2010).

Individual PAHs	RQ_{CNs}	RQ_{MPCs}	ΣPAHs	$RQ_{\Sigma PAHs(NCs)}$	$RQ_{\Sigma PAHs(MPCs)}$
Risk-free	0		Risk-free	$= 0$	
			Low risk	$\geq 1; <800$	$= 0$
Moderate risk	≥ 1	<1	Moderate risk$_1$	≥ 800	$= 0$
			Moderate risk$_2$	<800	≥ 1
High risk		≥ 1	High risk	≥ 800	≥ 800

Carlo Donadio: Visualization, Investigation. **Diana Barra:** Visualization, Investigation. **Giuseppe Aiello:** Visualization, Investigation. Michele Arienzo: Supervision, Writing - original draft and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abdel-Shafy, H.I., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. Egypt. J. Pet. 25, 107–123.

Adeniji, A.O., Okoh, O.O., Okoh, A.I., 2019a. Distribution pattern and health risk assessment of polycyclic aromatic hydrocarbons in the water and sediment of Algoa Bay, South Africa. Environ. Geochem. Health 41, 1303–1320.

Adeniji, A.O., Okoh, O.O., Okoh, A.I., 2019b. Levels of polycyclic aromatic hydrocarbons in the water and sediment of Buffalo River estuary, South Africa and their health risk assessment. Mar. Pollut. Bull. 84, 418–423.

Akyüz, M., Çabuk, H., 2010. Gaseparticle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. Sci. Total Environ. 408, 5550–5558.

Arienzo, M., Donadio, C., Mangoni, O., Bolinesi, F., Stanislao, C., Trifuoggi, M., Toscanesi, M., Di Natale, G., Ferrara, L., 2017. Characterization and source apportionment of polycyclic aromatic hydrocarbons (pahs) in the sediments of gulf of Pozzuoli (Campania, Italy). Mar. Pollut. Bull. 124, 480–487. http://dx.doi.org/10.1016/j.marpolbul.2017.07.006.

Arienzo, M., Toscanesi, M., Trifuoggi, M., Ferrara, L., Stanislao, C., Donadio, C., Villari, G., De Vico, G., Carella, F., 2019. Contaminants bioaccumulation and pathological assessment in *Mytilus galloprovincialis* in coastal waters facing the brownfield site of Bagnoli, Italy. Mar. Pollut. Bull. 140, 341–352.

Cao, Z., Liu, J., Li, Y.L.Y., Ma, M., Xu, J., Han, S., 2010. Distribution and ecosystem risk assessment of polycyclic aromatic hydrocarbons in the Luan river. China Ecotoxicol. 19, 827–837.

De La Torre-Roche, R.J., Lee, W.Y., Campos-Díaz, S.I., 2009. Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: analysis of a potential problem in the United States/Mexico border region. J. Hazards Mater. 163, 946–958.

De Maio, A., Moretti, M., Sansone, E., Spezie, G., Vultaggio, M., 1982. Circolazione costiera. Analisi dinamica e idrologica di una situazione osservata nel Golfo di Napoli. In: Convegno Risorse Biologiche e Inquinamento Marino del P.F. Oceanografia e Fondi Marini. pp. 609–624.

De Maio, A., Moretti, M., Sansone, E., Spezie, G., Vultaggio, M., 1985. Outline of marine currents in the Bay of Naples and some considerations on pollutant transport. Il Nuovo Cimento 8C (6), 955–969.

de Ruggiero, P., Napolitano, E., Iacono, R., Pierini, S., 2016. A high-resolution modelling study of the circulation along the Campania coastal system, with a special focus on the Gulf of Naples and adjacent areas. Cont. Shelf Res. 122, 85–101.

DM, 14 April 2009, nr 56. Gazzetta Ufficiale, Serie Generale n. 124, 30–05-2009. Suppl. Ordinario n. 83.

Durant, J.L., Busby, Jr., W.F., Lafleur, A.L., Penman, B.W., Crespi, C.L., 1996. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. Mutat. Res. Genet. Toxicol. 371, 123–157.

Folk, R.L., Ward, W.C., 1957. Brazos river bar: a study in the significance of grain size parameters. J. Sediment. Petrol. 27, 3–26.

Guigue, C., Tedetti, M., HuyDang, D., Mullot, J., Garnier, C., et al., 2017. Remobilization of polycyclic aromatic hydrocarbons and organic matter in seawater during sediment resuspension experiments from a polluted coastal environment: Insights from Toulon Bay (France). In: Environmental Pollution, Vol. 229. Elsevier, pp. 627–638. http://dx.doi.org/10.1016/j.envpol.2017.06.090.hal-01635969.

Guzzella, L., Depaolis, A., 1994. Polycyclic aromatic hydrocarbons in sediments of the Adriatic sea. Mar. Pollut. Bull. 28, 159–165.

Hwang, H.M., Foster, G.D., 2006. Characterization of polycyclic aromatic hydrocarbons in urban stormwater runoff flowing into the tidal Anacostia river, Washington, DC, USA. Environ. Pollut. 140, 416–426.

IARC, 1987. Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42. In: IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, vol. Supplement 7, International Agency for Research on Cancer, Lyon.

Kerr, J.M., Melton, H.R., McMillen, S.J., Magaw, R.I., Naughton, G., Little, G.N., 1999. Polyaromatic hydrocarbon content in crude oils around the world. In: Conference paper from the 1999 SPE/EPA Exploration and Production Environmental Conference Held in Austin, Texas, USA, 28 February–3 March.

Krauss, M., Wilcke, W., Martius, C., Bandeira, A.G., Garcia, M.V.B., Amelung, W., 2005. Atmospheric versus biological sources of polycyclic aromatic hydrocarbons (PAHs) in a tropical rain forest environment. Environ. Pollut. 135, 143–154.

Li, G.L., Lang, Y.H., Gao, M.S., Yang, W., Peng, P., Wang, X.M., 2014. Carcinogenic and mutagenic potencies for different PAHs sources in coastal sediments of Shandong Peninsula. Mar. Pollut. Bull. 84, 418–423.

Long, E.R., MacDonald, D.D., 1998. Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. Hum. Ecol. Risk Assess 4, 1019–1039.

Mumtaz, M., George, J., 1995. Toxicological Profile for Polycyclic Aromatic Hydrocarbons. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, Ga, USA.

Nastro, R.A., Gambino, E., Toscanesi, M., Arienzo, M., Ferrara, L., Trifuoggi, M., 2019. Microbial fuel cells (MFCs) remediation activity of marine sediments sampled at a dismissed industrial site: What opportunities? J. Clean. Prod. 235, 1559–1566.

Nisbet, I.C.T., LaGoy, P.K.I., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300.

Obini, U., Okafor, C.O., Afuikwu, J.N., 2013. Determination of level of polycyclic aromatic hydrocarbon in soil contaminated with spent motor engine oil in abakaliki auto mechanic village. J. Appl. Sci. Environ. Manag. 17, 169–175.

Pampanin, D.M., Sydnes, M.O., 2013. Polycyclic aromatic hydrocarbons a constituent of petroleum: presence and influence in the aquatic environment. Hydrocarbon, Vladimir Kutcherov and Anton Kolesnikov. IntechOpen, http://dx.doi.org/10.5772/48176.

Parlanti, E., 1990. Utilisation des hydrocarbures comme traceurs d'origine de la matière organique sédimentaire en milieu marin. In: Etude du Golfe du Lyon et du Golfe de Gascogne (Programme Ecomarge). University Bordeaux I, Bordeaux, France, p. 289, PhD thèses Nr 495.

Patacca, E., Sartori, R., Scandone, P., 1990. Tyrrhenian basin and apenninic arcs: kinematic relations since late tortonian times. Mem. Soc. Geol. Ital. 45, 425–451.

Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T., 2008. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. Chemosphere 72, 1594–1601.

Ravindra, K., Bencs, L., Wauters, E., de Hoog, J., Deutsch, F., Roekens, E., Bleux, N., Bergmans, P., Van Grieken, R., 2008a. Seasonal and site specific variation in vapor and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. Atmos. Environ. 40, 771–785.

Ravindra, K., Wauters, E., Taygi, S.K., Mor, S., Van Grieken, R., 2008b. Assessment of air quality after the implementation of CNG as fuel in public transport in Delhi, India. Environ. Monit. Assess. 115, 405–417.

Sgrosso, I., 1998. Possibile evoluzione cinematica miocenica nell'orogene centro-sudappenninico. Boll. Soc. Geol. Ital. 117, 679–724.

Sicre, M.A., Marty, J.C., Saliot, A., 1987. Aliphatic and aromatic hydrocarbons in different sized aerosols over the mediterranean sea: occurrence and origin. Atmos. Environ. 21, 2247–2259.

Soclo, H., 1986. Etude de la Distribution des Hydrocarbures Aromatiques Polycycliques dans les Sédiments Marins Récents, Identification des Sources (Ph.D. Thesis). University Bordeaux I, Bordeaux, France, p. 158.

Soclo, H.H., Garrigues, P., Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar. Pollut. Bull. 40, 387–396.

Somma, R., Iuliano, S., Matano, F., Molisso, F., Passaro, S., Sacchi, M., Troise, C., De Natale, G., 2016. High-resolution morpho-bathymetry of Pozzuoli bay, southern Italy. J. Maps 12, 222–230.

Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119.

Trifuoggi, M., Donadio, C., Ferrara, L., Stanislao, C., Toscanesi, M., Arienzo, M., 2018. Levels of pollution of rare earth elements in the surface sediments from the Gulf of Pozzuoli (Campania, Italy). Mar. Pollut. Bull. 136, 374–384. http://dx.doi.org/10.1016/j.marpolbul.2018.09.034.

Trifuoggi, M., Donadio, C., Mangoni, O., Ferrara, L., Bolinesi, F., Nastro, R.A., Stanislao, C., Toscanesi, M., Di Natale, G., Arienzo, M., 2017. Distribution and enrichment of trace metals in surface marine sediments in the gulf of Pozzuoli and off the coast of the brownfield metallurgical site of Ilva of Bagnoli (Campania, Italy). Mar. Pollut. Bull. 124, 502–511. http://dx.doi.org/10.1016/j.marpolbul.2017.07.033.

US EPA, 1977. Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants. U.S. Environmental Protection Agency, Environment Monitoring and Support Laboratory, Cincinnati.

U.S. EPA, 1993. Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons, Environmental Criteria and Assessment Office. Office of Health and Environmental Assessment, CincinnatiU.S.

US EPA, 2008. Polycyclic Aromatic Hydrocarbons (PAHs) - EPA Fact Sheet. National Center for Environmental Assessment, Office of Research and Development, Washington, DC, USA.

Willett, K.L., Gardinali, P.R., Sericano, J.L., Wade, T.L., Safe, S.H., 1997. Characterization of the H4IIE rat hepatoma cell bioassay for evaluation of environmental samples containing polynuclear aromatic hydrocarbons (PAHs). Arch. Environ. Contam. Toxicol. 32, 442–448.

Wu, B., Zhang, R., Cheng, S.P., Ford, T., Li, A.M., Zhang, X.X., 2011. Risk assessment of polycyclic aromatic hydrocarbons in aquatic ecosystems. Ecotoxicology 20, 1124–1130. http://dx.doi.org/10.1007/s10646-011-0653-x.

Yan, B., Benedict, L., Chaky, D.A., Bopp, R.F., Abrajano, T.A., 2004. Levels and patterns of PAH distribution in sediments from New York/New Jersey harbor complex. Northeast. Geol. Environ. Sci. 26, 113–122.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser river basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33, 489–515.