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Polycyclic aromatic hydrocarbons in marine sediments from the Rijeka Bay area, Northern Adriatic, Croatia, 1998–2006

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ABSTRACT

The first analyses of PAHs in marine sediments within Rijeka Bay started in 1998 at three sampling sites offshore from the petroleum refinery facilities and were extended in 1999 to three more sampling points in front of the repair shipyard within the same east industrial zone. The small Svezanj cove, lying between the shipyard and the petroleum refinery was chosen as the reference point. The concentrations of PAHs were considerably higher in the shipyard environment (average: 3009–6314 $\mu\text{g kg}^{-1}$ d.w.) in comparison to the petroleum refinery area (average: 279–919 $\mu\text{g kg}^{-1}$ d.w.), while the PAHs load at reference point was close to the latter level (average: 717 $\mu\text{g kg}^{-1}$ d.w.). The Phe/Anth and Flo/Py ratios indicate the dominant pyrogenic sources, except for the results from 1999 to 2000 with dominant petrogenic origin at some sites. A declining trend of total PAHs, and consequently toxicity indices was observed at all sites.

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Polycyclic aromatic hydrocarbons (PAHs) form a group of persistent organic pollutants. There are two major sources of PAHs in the environment: incomplete combustion of organic material (pyrogenic PAHs) and storm runoff, industrial discharges and petroleum spills (petrogenic PAHs), as they are constituents of crude oil. Therefore, petroleum refineries are important contamination sources to marine ecosystems with aliphatic and aromatic hydrocarbons including PAHs (Le Dreau *et al.*, 1997). Higher molecular weight PAHs are likely to bind to particulates, and to be deposited on surface waters, and subsequently to sediments. Petrogenic PAHs show the same tendency of binding to solid substrate and deposit into sediments. Due to the hydrophobic nature of PAHs, the elevated pressure and relatively low constant temperatures at the marine bottom favor the adsorption process in the sediment pores (Notar and Leskovšek, 2000). Besides these two anthropogenic sources, there is evidence of natural origin of some PAHs in lake and marine sediments, with perylene being a dominating compound. The main source is supposed to be PAH diagenesis from organic matter, having origin in the water column from in-lake/marine sources (Quiroz *et al.*, 2005; Nikolau *et al.*, 2009).

PAHs in marine sediments tend to accumulate to high concentrations. (Strictly, by definition: PAHs in sediments are given in weight fractions, but the term “concentration” is generally used to denote the sediments’ PAHs loading). These concentrations may fluctuate due to site specific biotic (microbial) degradation of PAHs, either aerobically (Cerniglia, 1992) or anaerobically within nitrate (Mac Rae and Hall, 1998) and/or sulfate-reducing

conditions (Coates *et al.*, 1997). Determination of PAHs in marine sediments is used to identify levels and sources of contamination by PAHs. Some PAHs are known to be toxic and increase toxic potency of sediments. However, there is inconsistency regarding relationships between PAHs concentrations and sediment toxicity. On the other hand, there is a positive correlation between PAH content and genotoxicity of sediments, attributed either to PAHs or their biotransformed metabolites. According to the literature, only sediments with high concentrations of PAHs ($>10 \text{ mg kg}^{-1}$ d.w.) have been found to be mutagenic, the majority of which effect is attributed to benzo(a)pyrene (Bihari *et al.*, 2006).

Marine organisms such as mussels are exposed to PAHs either by a direct route, i.e. uptake of the water soluble fraction of PAHs by gills, and/or by an indirect route through absorption of the smallest grain-size fraction of the sediment and the assimilation of PAHs through the digestive tract. As the bivalves like mussels filter the smallest size particles ($<60 \mu\text{m}$), the composition of the pollution bulk reservoir may differ from the composition of pollution mussels are exposed to (Baumard *et al.*, 1998). Therefore, as a part of biomonitoring, PAHs are often analyzed in mussels (Baumard *et al.*, 1998; Beliaeff *et al.*, 2002; Potrykus *et al.*, 2003) but also in other marine organisms used in the Mediterranean diet to estimate human exposure (Perugini *et al.*, 2007). In addition, although several laboratory studies have documented the importance of PAH phototoxicity (Swartz *et al.*, 1997), there is still a dilemma regarding environmental significance of this process (Mc Donald and Chapman, 2002).

Determination of PAHs in marine sediments within Rijeka Bay began in 1998 at three locations facing the petroleum refinery facilities (Fig. 1; sites S02 and S03) including one next to the former

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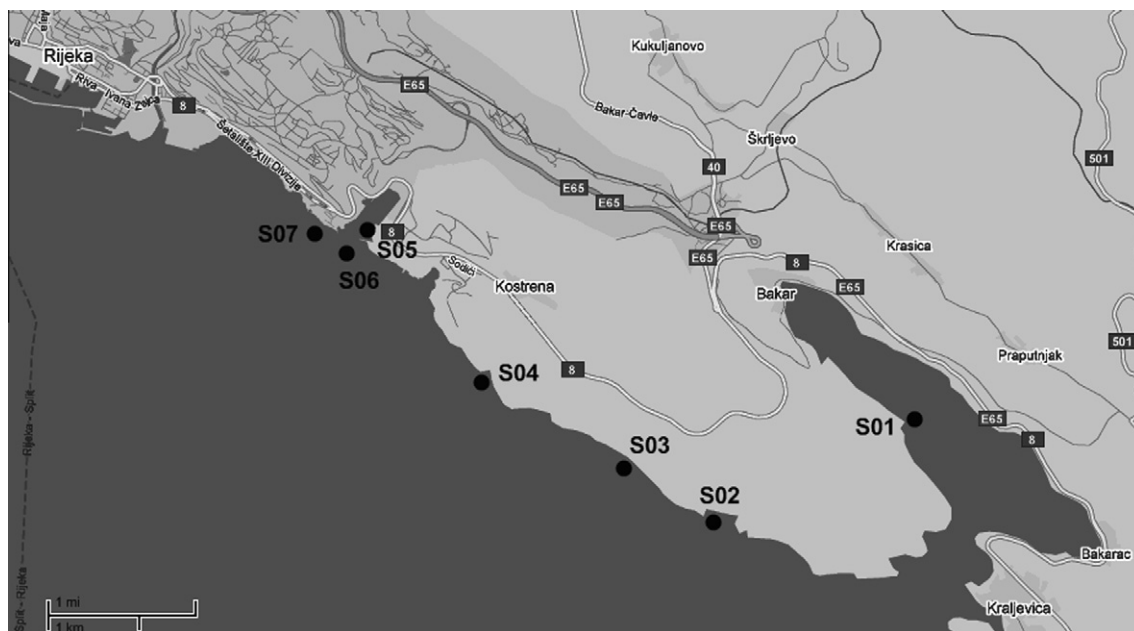


Fig. 1. Location of sampling sites in the east industrial zone of the city of Rijeka: S01, S02 and S03 in front of the petroleum refinery, S04 – reference recreational zone; S05, S06 and S07 in front of the repair shipyard.

coke plant area (site S01). In subsequent years, the monitoring has been extended to three locations in the vicinity of a repair shipyard (sites S05, S06 and S07). The Svežanj cove, located between these two industrial facilities, was chosen as a reference site (site S04). The first analyses of the obtained results as well as time trends of PAHs during the period 1998–2006 are presented in this work.

The samples of marine sediments were collected at three locations (Fig. 1) in front of the petroleum refinery:

S01: in front of the decantator, but also close to the former coke plant area that ceased its activity in 1994,

S02: in front of the petroleum harbor,

S03: beneath the waste water treatment facility,

The monitoring was extended to three more sites in the repair shipyard environment:

S05: the Martinšćica cove, the shipyard working area,

S06: cca 100 m from the entrance into Martinšćica cove, and

S07: west from the Martinšćica cove.

The Svežanj cove (site S04), situated between petroleum refinery and shipyard area, and well known as recreational zone was chosen initially as the reference point.

Samples of marine sediments were taken from the depth of 20–30 m that proved to be optimal for the vertical profile of PAHs.

Marine sediments were dried at 105 °C, and sieved through a 0.5 mm sieve. Samples of dry sediment (20 g) were extracted with cyclohexane (100 ml) in an ultrasonic bath (60 min). The cyclohexane extract was cleaned on a silica-gel column (10% moist) and HPLC with UV/fluorescence detector was used for quantitative determination of PAHs, according to our previously described method (Alebic-Juretic, 1994, 2005). The observed interference of sulfur was eliminated first by shaking the cleaned extract with elemental mercury, and since 2003 by adding elemental copper to the sediment samples prior to extraction in cyclohexane. As BaA and Chr were not always possible to separate by this method, they are given as the sum (BaA + Chr) in this work, similarly to BbF + BkF.

The samples of previously extracted and cleaned marine sediments (20 g) were spiked with a PAH mixture containing 4–10 µg of individual PAHs and analyzed according to the previously described procedure. The recovery of such a prepared samples

varied between 65.6% for indeno(1,2,3-c,d)pyrene (IP) and 104.7% for fluoranthene (Flo). The exception was anthracene (Anth) whose recovery was only 50%. Application of the method used to the sediment sample IAEA-159 during interlaboratory comparison gave satisfactory results as reported in Table 1 (IAEA, 2007).

While the analyses of PAHs in marine sediments were performed regularly twice a year in the petroleum refinery maritime area, the samples were collected and analyzed only six times within the repair shipyard area during the period studied (roughly once a year and omitted in 2003 and 2005). In spite of that, the number (N) and sampling period (yrs) of collected samples were enough for establishing a time trend in concentrations. Average concentrations of total PAHs are provided in Table 2.

Though it was anticipated that the most polluted area would be in front of the petroleum refinery, due to possible discharges and oil spillage, the results were contrary to expectations. The refinery area, with its limited access to maritime traffic (sites S02 and S03) was in fact less polluted with PAHs comparative to the shipyard area, in spite of an accidental oil spill in 2000 that resulted in multiple increases in PAH concentrations at site S03. The marine sediments from S01, also belonging to the petroleum refinery area, are still heavily polluted with PAHs, due to the fact that a coke plant was active in this vicinity until 1994. The shipyard area showed the worst pollution with PAHs, especially the entrance into

Table 1

The results of interlaboratory comparison tests for the determination of PAHs in marine sediments.

PAH	C (ng/g)	z-score
Anth	2.7	–1.57
Chr	59.2	0.04
Flo	117	0.20
Py	73.3	–0.67
BbF	19.3	–1.84
BaA	28.1	–1.23
BaP	22.1	–1.33

$z \leq 2$ = acceptable;
C = concentration.

Table 2
Total PAHs in marine sediments of the Rijeka Bay area ($\mu\text{g kg}^{-1}$ d.w.).

Site	N	C	Range	Sampling time span
S01	16	919	256–2295	1998–2006
S02	16	269	57–892	1998–2006
S03	16	616	53–6655	1998–2006
S04	17	717	103–2075	1998–2006
S05	6	5148	2653–9957	1999–2002, 2004, 2006
S06	6	6314	1026–12,532	1999–2002, 2004, 2006
S07	6	3009	960–6943	1999–2002, 2004, 2006

N – number of samples analyzed;
C – concentration.

the Martinšćica cove (S06). The sediment loadings were several times higher than in front of the petroleum refinery area.

Located in the recreational area between the shipyard and the refinery, Svezanj cove (site S04) was initially chosen as a reference site, but the PAHs loadings there were found to be unexpectedly high. Contributing factors include a relatively heavy traffic of private boats, whose high numbers with (small) fuel consumption contribute to PAH deposition into sediments.

Concentrations of PAHs in marine sediments from Rijeka Bay area are consistent with the results of similar studies in the Adriatic sea area (Table 3), particularly those from the neighboring Rovinj and Venice lagoon (Bihari et al., 2006; Frignani et al., 2003), while the Trieste area was surprisingly less polluted with PAHs (Guzzella and De Paolis, 1994; Notar et al., 2001). The highest loadings of PAHs in marine sediments from the Mediterranean area were found in the densely populated urban zones (Baumard et al., 1998; Cardellicchio et al., 2007), industrial sites (Frignani et al., 2003) and harbors (Bihari et al., 2006; Baumard et al., 1998; El Nemr et al., 2007). Thus, the maximal loadings were found in the beginning of nineties at the harbor of Venice (Fattore et al., 1997). The same hot-spots can be identified in the Black sea area (Readman et al., 2002), Siberian coastline (Dahle et al., 2003), Northern China (Wang et al., 2007) and Singapore coast (Basheer et al., 2003), though the loadings levels are lower (Table 3). On the other hand, up to 100 times higher loadings of PAHs in marine

sediments can be observed during the nineties in urban areas of Canada (Simpson et al., 1998) and industrial zones in the USA (Miles and Delfino, 1999).

Due to the presence of a petroleum refinery and boat traffic in the shipyard, it was expected petrogenic PAHs would dominate in marine sediments. Surprisingly, the Phe/Anth and Flo/Py ratios indicated pyrolytic PAHs to be dominant (Fig. 2). Petrogenic PAHs were found in five cases at sites 1, 2, 4 (two times) and 5, all of them at the end of 1999 and the beginning of 2000 which coincides with the major oil spill in the area.

Prevailing pyrolytic PAHs in the shipyard area can be explained by the use of heavy diesel fuel in boats, as well as their higher consumption during maintenance in the shipyard. The dominance of pyrolytic PAHs in marine sediments has been found in most Mediterranean countries with high maritime traffic, including harbors and urban areas (Bihari et al., 2006; Cardellicchio et al., 2007; Notar et al., 2001; Baumard et al., 1998; Frignani et al., 2003; El Nemr et al., 2007). Petrogenic PAH predominance has been found in some Siberian locations, though in that case pyrolytic sources were also identified (Dahle et al., 2003).

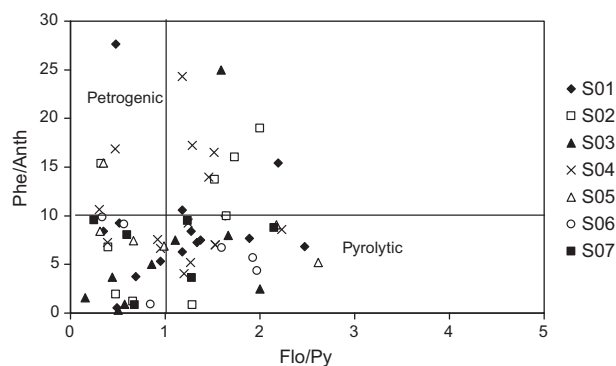


Fig. 2. Pyrolytic vs petrogenic PAHs in the marine sediments from the Rijeka Bay area.

Table 3
Comparison of PAHs concentrations in sediments from different marine coastal areas.

Country	Sites	Year of survey	Concentr. range ($\mu\text{g kg}^{-1}$ d.w.)	Reference
Italy	Coastline Bari-Trieste	1990	31–527	Guzzella and De Paolis, 1994
	Mar Piccolo, Taranto	2001	380–12750	Cardellicchio et al., 2007
	Venice lagoon	1998	315–16474	Frignani et al., 2003
	Venice lagoon	1992	184–201678	Fattore et al., 1997
	Gulf of Trieste	1996–97	600–800	Heath et al., 2006
It/Slovenia	Gulf of Trieste	1996	30–600	Notar et al., 2001
Croatia	Rovinj area	NA	32–13681	Bihari et al., 2006
	Rijeka Bay area	1998–06	53–12532	This work
Greece	Crete	1994	15–159	Gogou et al., 2000
France	Coastline- Toulouse	1995	45–13000	Baumard et al., 1998
	Corsica	1995	1–20500	ibid
	Aquitaine*	NA	4–853	Soclo et al., 2000
Egypt	Coastline	1999	88–6338	El Nemr et al., 2007
Marocco	Coastline	1999	27–254	Er-Raioui et al., 2009
Turkey	Bosphorus, Black sea	1995	14–531	Readman et al., 2002
Ukraine	Coastline- Odessa	1995	7–635	ibid
Russia	Sochi, Black sea	1995	61–368	ibid
(Siberia)	SE Kara Sea, Shelf	1993–94	36 ± 16	Dahle et al., 2003
	SW Kara Sea	1993–94	215	ibid
	Baydaratskaya Bay	1993–94	18 ± 8	ibid
	Gulf of Ob	1993–94	42 ± 24	ibid
	Yenitsei Bay	1993–94	105 ± 23	ibid
China	Laizhou Bay, Bohai Sea	2004	3–297	Wang et al., 2007
Singapore	SW-NE coast	2001	15–94	Basheer et al., 2003
USA	Florida#	NA	50–1086000	Miles and Delfino, 1999
Canada	Kitimat, BC	NA	1169–3576574	Simpson et al., 1998

* Atlantic ocean coast; #- $\mu\text{g/kg}$; NA-not available

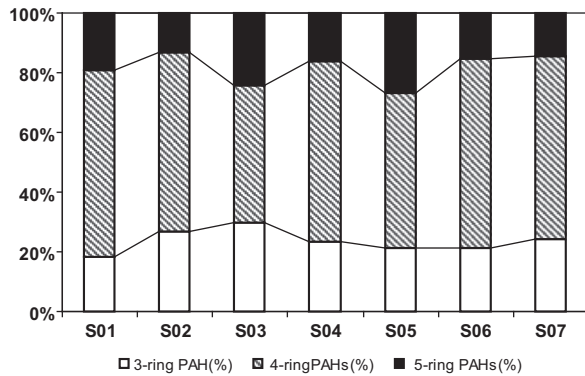


Fig. 3. Distribution patterns (%) of 3–5 ring PAHs in marine sediments.

The ratio of 3-, 4- and 5- ring PAHs at selected sites can be used to indicate their origin (Fig. 3). Thus, the highest percentage of 3- ring PAHs, characteristic for petrogenic source, was found at sites S02 and S03, in front of the petroleum refinery. However, the highest percentage of 5-ring PAHs was found at sites S01 (close to the former coke plant area) and S06 (within the shipyard area), indicating fuel combustion as major sources.

In spite of occasional peaks, all sites show a declining trend in PAHs during the period studied (Fig. 4). This is likely due to improved environmental protection, including the use of fuel with lower sulfur content. The highest decline rate was observed at the highly contaminated S01 (a former coke-plant area). It is reasonable to believe that this trend will continue. In spite of two peaks in 2002 and 2004, the declining trend was visible at the recreational site S04. The highest variation was found in the shipyard environment, partly because of the smaller number of analyses (due to difficulties in management at the beginning of 2000 that resulted in a reduction of repair activities). In spite of that, there was a weak declining trend in this area, as well.

On the contrary, no clear trend was observed in PAH content in sediments from the Gulf of Trieste data during 1990 (Guzzella and De Paolis, 1994), 1996 (Notar et al., 2001) and 1997 (Heath et al., 2006). One of the possible reasons for this is the fact that samples were taken at different sampling points. A common feature was found in analyses of sediment cores collected in the neighboring Gulf of Trieste (Heath et al., 2006) and Venice lagoon (Frignani et al., 2003), revealing a similar history of pollution by PAHs. Starting at the beginning of the 20th century, and the post World War I period (Notar et al., 2001), PAH loadings reached a maximum in the post World War II period, coinciding with increased industrialization and urbanization of the region, and followed by a slow decline afterward. Although petrogenic sources may have influenced some samples, the main sources of sediment PAHs were high temperature combustion processes. Similar studies in the Barents Sea also did not show a significant decline in concentrations of PAHs in sediments from 2001 to 2005 relative to the results of 1992–1998, though PAH profiles were altered due to pyrogenic dominance (Dahle et al., 2009).

Analyses of sediment pollution have been the basis for the development of different approaches to ecotoxicological risk evaluation. As a result, Sediment Quality Guidelines (SQG) have been developed taking into account “biological effects database for sediments” (BEDS) which contains information on the effects of sediment-associated contaminants, including spiked-sediment toxicity test data, matching sediment chemistry and biological effects data from field studies. Numerical SQG were derived using the information in both the “effects data set” and the “no effect data set”. Statistical evaluation led to two sediment quality assessment values for each pollutant. If concentrations with no biological effects were

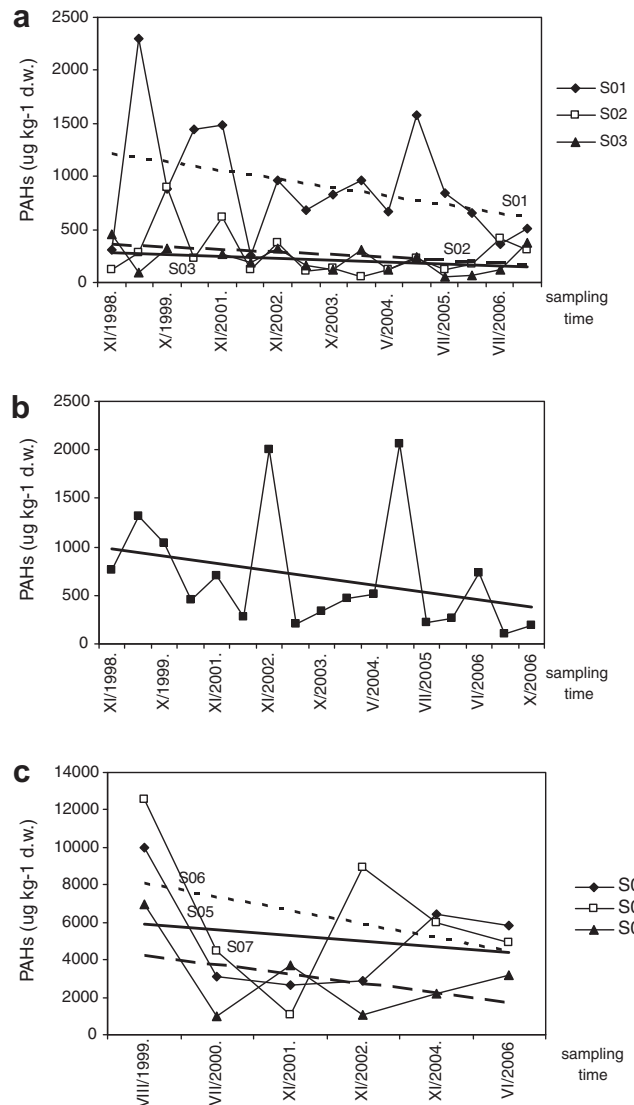


Fig. 4. Time trend in PAHs in marine sediments (a) in the refinery area (accidental loading at site S03 omitted); (b) at the reference site S04; and (c) from the shipyard environment.

excluded, the “effects range low” (ERL) and the “effects range medium” (ERM) values were defined (Long and Morgan, 1990). The ERL was calculated as the “lower” 10th percentile and the ERM as the 50th percentile of the “effects” concentration.

When both “effects” and “no effects” data were used in calculations, the “threshold effects level” (TEL) and “probable effects level” (PEL) values were determined (FDEP, 1994). The TEL values were calculated as the geometric mean of the 15th percentile of the “effects” data and 50th percentile of the “no-effect” dataset, while the PEL values were determined as the geometric mean of the 50th percentile of the “effects” and 85th percentile of the “no effects” data. Basically, the ERL corresponds to TEL, and ERM to the PEL value. Both sets of values, PEL/TEL and ERL/ERM, define three concentration ranges for a chemical, including those that can be found rarely (below ERM or TEL), occasionally (above ERL or TEL but below ERM or PEL), and frequently (above ERM or PEL) associated with adverse effects on marine organisms. Exceedances of ERM or PEL values classify the sediment as potentially toxic. ERL/ERM and TEL/PEL values are not available for BbF + BkF, IP, BeP and BghiP (Cardellicchio et al., 2007).

Table 4
Sediment Quality Guideline (SQG) values ($\mu\text{g kg}^{-1}$ d.w.) for PAHs and percentages of samples within the SQG ranges for particular sites.

PAHs	SQG range ERL–ERM	% of samples	S01	S02	S03	S04	S05	S06	S07
Ace	16–500	<ERL	25.0	68.8	68.8	41.2	16.7	0	0
		ERL–ERM	75.0	31.2	25.0	52.9	83.3	66.7	66.7
		>ERM	0	0	6.2	5.9	0	33.3	33.3
Phe	240–1500	<ERL	100.0	100.0	93.7	100.0	16.7	16.7	83.3
		ERL–ERM	0	0	6.3	0	83.8	83.3	16.7
		>ERM	0	0	0	0	0	0	0
Anth	85–1100	<ERL	93.7	100.0	93.7	100.0	66.7	50.0	83.3
		ERL–ERM	6.3	0	6.3	0	3.3	50.0	16.7
		>ERM	0	0	0	0	0	0	0
Flo	600–5100	<ERL	100.0	100.0	100.0	100.0	33.3	33.3	83.3
		ERL–ERM	0	0	0	0	66.7	66.7	16.7
		>ERM	0	0	0	0	0	0	0
Py	665–2600	<ERL	100.0	93.7	93.7	100.0	66.7	16.7	66.7
		ERL–ERM	0	6.3	6.3	0	33.3	83.3	33.3
		>ERM	0	0	0	0	0	0	0
BaA + Chr	614–4400	<ERL	93.7	100.0	93.7	100.0	16.7	16.7	66.7
		ERL–ERM	6.3	0	6.3	0	83.3	83.3	33.3
		>ERM	0	0	0	0	0	0	0
BbF + BkF	–								
BaP	430–1600	<ERL	100.0	93.7	75.0	100.0	50.0	33.3	83.3
		ERL–ERM	0	6.3	25.0	0	50.0	66.7	16.7
		>ERM	0	0	0	0	0	0	0
IP	–								
Σ PAH	4022–44,792	<ERL	100.0	100.0	93.7	100.0	50.0	16.7	83.3
		ERL–ERM	0	0	6.7	0	50.0	83.3	16.7
		>ERM	0	0	0	0	0	0	0

ERL – effects range low;
ERM – effects range medium.

Table 5
Sediment Quality Guideline (SQG) values ($\mu\text{g kg}^{-1}$ d.w.) for PAHs and percentages of samples within the SQG ranges for particular sites.

PAHs	SQG range TEL–PEL	% of samples	S01	S02	S03	S04	S05	S06	S07
Ace	7–89	<TEL	25.0	50.0	56.3	29.5	0	0	0
		TEL–PEL	50.0	37.5	25.0	52.9	0	16.7	0
		>PEL	25.0	12.5	18.7	17.6	100.0	83.3	100.0
Phe	87–544	<TEL	62.5	93.7	87.5	82.4	0	16.7	0
		TEL–PEL	37.5	6.7	12.5	17.6	50.0	33.3	83.3
		>PEL	0	0	0	0	50.0	50.0	16.7
Anth	47–245	<TEL	93.7	100.0	93.7	94.1	50.0	16.7	83.3
		TEL–PEL	6.3	0	6.3	5.9	50.0	83.3	0
		>PEL	0	0	0	0	0	0	16.7
Flo	113–1494	<TEL	67.5	87.5	87.5	70.6	0	16.7	16.7
		TEL–PEL	32.5	12.5	12.5	29.4	83.3	50.0	83.3
		>PEL	0	0	0	0	16.7	33.3	0
Py	153–1398	<TEL	68.8	93.7	93.7	82.4	0	16.7	16.7
		TEL–PEL	31.2	6.3	6.3	17.6	83.3	66.6	83.3
		>PEL	0	0	0	0	16.7	16.7	0
BaA + Chr	183–1539	<TEL	50.0	100.0	87.5	70.6	0	0	0
		TEL–PEL	50.0	0	12.5	29.4	83.3	83.3	100.0
		>PEL	0	0	0	0	16.7	16.7	0
BbF + BkF	–								
BaP	89–763	<TEL	68.8	87.2	75.0	70.6	0	16.7	33.3
		TEL–PEL	31.2	12.5	18.7	29.4	83.3	66.6	66.7
		>PEL	0	0	6.3	0	16.7	16.7	0
IP	–								
Σ PAH	655–6676	<TEL	31.2	93.7	93.7	58.8	0	0	0
		TEL–PEL	68.8	6.3	6.3	41.2	83.3	66.7	83.3
		>PEL	0	0	0	0	16.7	33.3	16.7

TEL – threshold effects level;
PEL – probable effects level.

Classification of sediment samples according to ERL/ERM values for particulate sites are given in Table 4, while Table 5 contains the same classification according to TEL/PEL values. Since Chr and BaA were not always separated by the HPLC method used, they are reported as the sum, and so were the respective values for ERL/ERM and TEL/PEL values.

Considering ERL/ERM classification (Table 4), most PAHs concentrations of the sediment samples are below ERL at sites S01, S02, S03 and S04, while ERM values are exceeded for Ace at sites

S05, S06 and S07 (33%). Similar results are obtained regarding TEL/PEL values. Results of individual and sum of PAHs are mostly below TEL values for sites S01, S02, S03 and S04 (Table 5). The PEL values are exceeded for Ace (83–100%), Phe (17–50%), Flo (16–33%), Py and BaA + Chr and total PAHs (17%) at sites S05, S06 and S07.

In order to assess the synergetic effects of all contaminants, mean of ERM quotients (mERMq) and PEL quotients (mPELq) were calculated for each determined PAH (Long and Mac Donald, 1997).

The ERM/PEL quotients are obtained dividing the concentration of particular PAH with its ERM/PEL value, while the mean value of thus obtained quotients for all PAHs determined the mERMq/mPELq indices. This approach defines four relative priority levels for contaminated sites: highest: (mERMq > 1.5 and mPELq > 2,3), medium-high (nERMq = 0.51–1.5; mPELq = 1.51–2.3), medium-low (nERMq = 0.11–0.5; mPELq = 0.11–1.5) and lowest (mERMq < 0,11 and mPELq < 0,11) (Cardallicchio et al., 2007).

Classification of marine sediments according to the mERMq indices are given in Fig. 5. Most of the sediment samples from sites S01, S02, S03 and S04 are in the low range regarding ecotoxicological risk. The exceptions are samples from sites S04 and S01 that are in the medium low and a single sample from S03 being positioned in the medium high range. Most of the sediment samples from sites S05, S06 and S07 are in the medium low range, with some samples from the turn of the millennium in medium high range.

Classification of sediment samples according to mPELq are given at Fig. 6. Most of the sediment samples from sites S01, S02, S03 and S04 are classified in medium low range, with a single sample at site S03 from 2000 classified in high range. Most of the sediment samples from sites S05, S06 and S07 are classified in the medium low range, four samples from sites S05 and S06 at medium high, while three samples at sites S05, S06 and S07 from 1999 were classified at high range.

In conclusion, the Phe/Anth and Flo/Py ratios indicated that most PAHs were of pyrolytic origins, except for a few occurrences of oil spillage when petrogenic PAHs dominated. Average loadings of total PAHs in marine sediments from sites S02 and S03 (located at petroleum refinery area) were similar to levels found in the petroleum refinery environment in Venice lagoon during the mid-nineties (Fattore et al., 1997). Higher loadings determined in 2000 at site S03 (waste treatment plant facilities) were due to an accidental crude oil spill. Elevated loadings of total PAHs at site

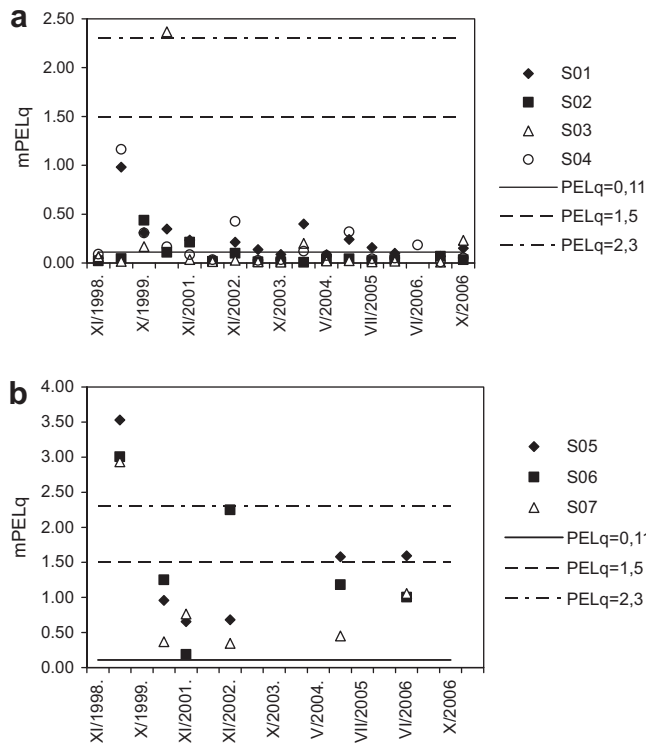


Fig. 6. Distribution of mPELq in priority levels (highest, medium high, medium low and lowest) for Rijeka Bay stations as follows: (a) petroleum refinery (S01, S02 and S03) and remote stations (S04); and (b) shipyard stations (S05, S06 and S07).

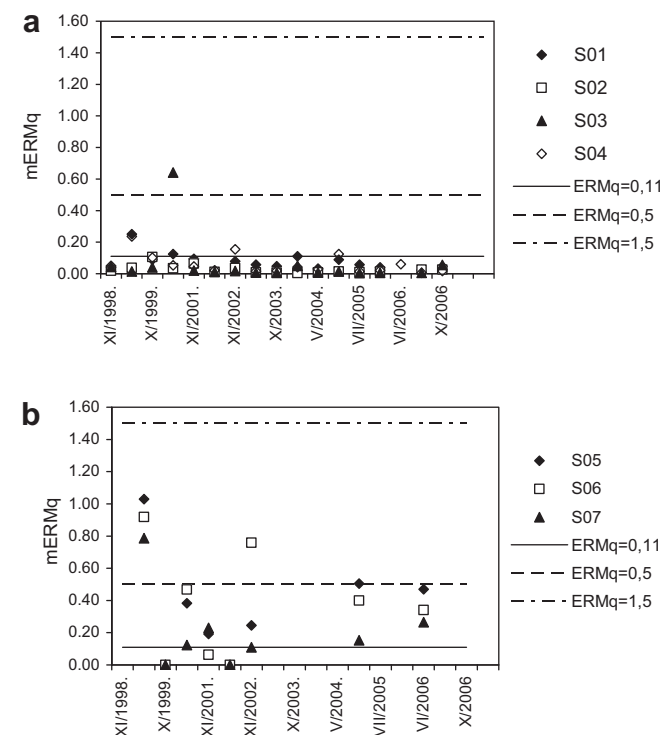


Fig. 5. Distribution of mERMq in priority levels (highest, medium high, medium low and lowest) for Rijeka Bay stations as follows: (a) petroleum refinery (S01, S02 and S03) and remote stations (S04); and (b) shipyard stations (S05, S06 and S07).

S01 were likely to be the result of contamination by a coke plant that operated in this area in the period 1979–1994.

The total PAH loadings in the repair shipyard environment (sites S05–S07) were several times higher relative to the petroleum refinery in the vicinity. That leads to the conclusion that high sulfur content fuel used during ship maintenance at the harbor/shipyard is responsible for such a high loadings of total PAHs in marine sediments. In addition, an unexpectedly high loading of total PAHs was observed at the remote site S04 located in the recreational area. High traffic of small boats, but also high traffic of road vehicles used to reach the recreational beach and boardwalk area might be responsible for these results. Therefore, this site could be considered as the reference only for the shipyard area. Long-term monitoring of total PAHs in marine sediments at all sites indicated a declining trend, due to environmental protection actions and/or diminishing sulfur content in the fuel used by ships and boats.

An estimation of ecotoxicity according to ERL/ERM and TEL/PEL values indicated samples from sites S05, S06 and S07 from the turn of the millennium may provide potential ecotoxicological risks to marine organisms. A similar result is provided by mERMq and mPELq indices.

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