Composition, Distribution and Sources of Polycyclic Aromatic Hydrocarbons in Sediments of the Gulf of Trieste, Northern Adriatic Sea

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The composition, distribution and the sources of polycyclic aromatic hydrocarbons (PAHs) in the surficial sediments of the Gulf of Trieste were investigated. To document the spatial PAH input, surficial sediment samples from 17 locations throughout the Gulf were analysed. The total PAH load determined in the surficial sediment samples are between 30 and 600 ng g^{-1}, and were the highest in the immediate vicinity of the Port of Trieste. The PAH contents decline rapidly with increasing distance from the shore. The ratios of methylphenanthrenes/phenanthrene and methylpyrene/pyrene are sensitive indicators of the origin of PAH pollution in the Gulf which is mostly pyrolitic. The phenanthrene/anthracene ratio was used to determine the approximate location and distance from the source of PAH pollution, while 1-methyl-7-isopropylphenanthrene (retene) was used as indicator for forest fires. A sediment depth profile indicates a major increase in the PAH concentrations after the First World War. © 2001 Elsevier Science Ltd. All rights reserved.

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Introduction

Polycyclic aromatic hydrocarbons (PAH) are widespread contaminants throughout the environment (Blumer, 1976; Suess, 1976; Harvey, 1996). PAH arise from the incomplete combustion of organic matter in flames, engines and industrial processes and from emissions of noncombustion-derived petrogenic (Hites *et al.*, 1977; Wakeham *et al.*, 1980). Natural sources of PAH include forest-fires, natural petroleum seeps and post-depositional transformation of biogenic precursors (Young and Cerniglia, 1995). The environmental concern about PAH is due to their potential to form highly carcinogenic and mutagenic derivatives such as diols and epoxides (Baird, 1995; Stegeman and Lech, 1991).

Once formed, PAH are known to enter the near-shore marine environment through the spillage of petroleum, industrial discharges, atmospheric fallout and urban run-off (Neff, 1979; Gevao *et al.*, 1998; Sharma *et al.*, 1997). Because of their low water solubility, (10^{-7}–10^{-10} mol m^{-3}), and their hydrophobicity, PAH in the aquatic environment rapidly become associated with inorganic and organic suspended particles (Gearing *et al.*, 1980; Chiou *et al.*, 1998) and subsequent deposition in sediments. The favourable partition coefficients and greater persistence of sedimentary PAH compared to PAHs in solution, means that, in general, sediments contain a PAH concentration which is a factor of 1000 or more higher than in the overlying water column. Therefore, sediments can be used to monitor PAH inputs to the aquatic environment. The importance of sediments as reservoirs for PAH is well documented (Nes and Oug, 1997; Prahl *et al.*, 1984; Maher and Aislabie, 1992).

The distribution of PAH in waters and sediments of the Mediterranean Sea has been the subject of several studies (Tolosa *et al.*, 1996; Lipiatou and Albaiges, 1994; Dachs *et al.*, 1997; Lipiatou *et al.*, 1997), but relatively few of these have focused on the PAH distribution in water and sediments of the Adriatic Sea (Marcomini *et al.*, 1986; Dujmov and Sucevic, 1989; Guzzella and de Paolis, 1994). The waters of the Gulf of Trieste in the northern Adriatic are extensively utilized for tourist and mariculture purposes as well as industrial, and agricultural activities in the hinterland. In consequence extensive areas of the marine environment of the Gulf are potentially affected by organic pollution. Also, freshwater inflow of the tributary rivers, like the Isonzo in the northern part of the Gulf, draining industrial and agricultural areas are a potential source of contamination. A detailed study was, therefore, conducted to investigate the composition, distribution, and the sources of PAH pollution in the Gulf of Trieste. From 17 sampling locations throughout the Gulf of Trieste, sediments were

taken and analysed for parent and alkylated PAH. In addition, the history of accumulation of PAH in recent Gulf sediments was determined by collecting a deeper core in the northern part of the Gulf of Trieste.

Materials and Methods

Sample collection and preparation

The sediment sampling sites are shown in Fig. 1, while their exact position was recorded using the global positioning system. The work described herein involves a sampling program undertaken in the winter of 1996. Surficial sediment samples (0–2 cm) were collected using a 40 mm diameter gravity core sampler (Meischner and Rumohr, 1974). In addition, one 3 m core was collected at station GT2.

Sediment samples were placed in glass pans (previously washed with methanol and heated at 400°C for 3 h), covered with aluminium foil and allowed to dry at room temperature for 5–6 days. The samples were then homogenized and sieved in a stainless steel sieve (particles 0.05–0.02 mm). After sieving, the samples were transferred into pre-cleaned glass bottles, wrapped with aluminium foil, and refrigerated (−25°C) prior to analysis.

Analysis

A combination of accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE) was used in order to quantitatively extract the PAH from the marine sediments (Notar and Leskovšek, 2000). Approximately 5 g of sample was mixed with 2 g of acti-vated copper powder necessary to decrease the amount of sulphur forming unsoluble copper sulphide and loaded into a 10 ml extraction cartridge. The residual volume was made using wetsupport (diatomaceous earth) addition (2 g). An internal standard mixture containing four deuterated PAH (acenaphthene-d10, chrysene-d12, phenanthrene-d10, perylene-d12) was added directly to the sample prior to the extraction (50 μl of mixture; concentration of each compound 200 μg ml^{-1}). Extraction of PAH was performed in two steps starting with ASE. The sealed extraction cartridge was then placed in a heated (120°C) extraction cell. Extraction started by filling and pressurizing (138 × 10^5 Pa, 2000 psi) the cell with methylene chloride. The extraction outlet valve was closed allowing 10 min static extraction. Following static extraction, the extraction outlet valve is then opened to perform a dynamic extraction with methylene chloride at a flow rate of 5–6 ml min^{-1}. The extract was then passed through the stainless steel outlet tube and trapped in the collection vial. The outlet tube was ice-cooled (0°C) to prevent the loss of highly volatile 2-3-ring PAH. When 60 ml of methylene chloride had passed through the extraction cartridge, the solvent supply pump valve was closed, and the carbon dioxide supply pump valve opened pressurizing the cell to 350 × 10^5 Pa (120°C), starting the dynamic step of supercritical fluid extraction. The consumption of supercritical carbon dioxide was 20 ml at a flow rate of 2–3 ml min^{-1}, and was trapped in the 60 ml of methylene chloride extract originating from the first (ASE) extraction step. The whole extraction time was 30 min. Cooling of the outlet tube during this step is not
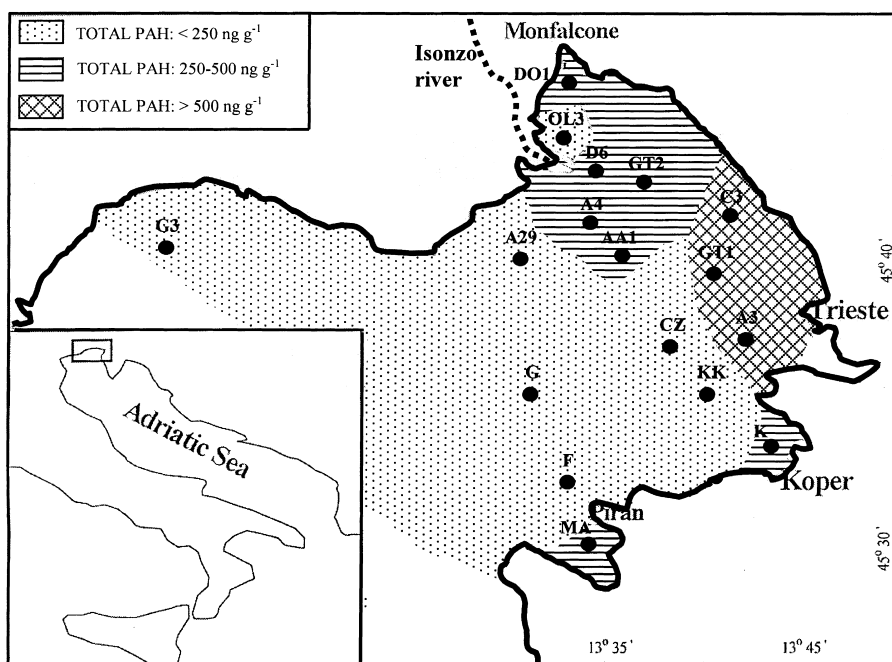

Fig. 1 Locations of 17 sampling stations in the Gulf of Trieste, northern Adriatic Sea, with clusters produced by cluster analysis of PAH concentrations.

necessary, because of the carbon dioxide expansion effect occurring along the outlet tube. All extracts were dried with anhydrous sodium sulphate and reduced in volume to 1 ml under a gentle stream of nitrogen at room temperature. Extracts were analysed without further purification of the sample.

Analysis of the marine sediment extracts was made using a Hewlett–Packard model 6890 GC/MSD with automatic liquid sampler gas chromatography with split/splitless injection and mass selective detection in the selected ion mode. The GC was equipped with a HP5-MS crosslinked 5% phenyl-methyl silicone capillary column (30 m × 0.25 mm id, 0.25 mm film thickness). A multiple selected ion monitoring (MS/SIM) method was capable of monitoring up to 12 ions (primary and confirming ions) in each of three retention time windows including selected ions of the internal standard. Response factors and retention times were determined in relation with four deuterated internal standards (acenaphtene-d10, chrysene-d12, phenanthrene-d10 and perylene-d12) and a standard PAH test mixture.

The average recoveries of PAHs, based on deuterated internal standards were 77% for 2-3-ring PAHs, 85% for 4-ring PAHs, 88% for 5-ring PAHs and 97% for 6-ring PAHs. Method detection limits (MDL) were statistically estimated. MDL values for PAHs compounds varied between 0.06 and 3.45 ng g^{-1}. The precision varied from 7% for fluoranthene to 19% for dibenzo(a,h)anthracene. The accuracy of the method was assessed by analysing a standard reference material (NIST, SRM 1941a). The method was accurate for all PAHs measured except for dibenzo(a,h)anthracene for which the measured concentration was too high and exceeded the accuracy interval.

Organic carbon and total nitrogen concentrations were determined using a CHNS Carlo Erba (mod. 1108) analyser after the acidification of the sediment samples to remove carbonates (Hedges and Stern, 1984). Analyses of ^{13}C isotopic composition of the CO_2 produced by ignition of organic matter in decarbonated samples in an oxygen atmosphere were performed with an Europa 20-20 mass spectrometer and the results expressed as deviations from the $^{13}C/^{12}C$ ratio of the Chicago PDB standard ($\delta^{13}C_{org}$ values). AMS $^{14}C_{org}$ dating in GT2 core samples were performed by Beta Analytic, Miami, FL, USA.

Results and Discussion

Composition

For a composition study, 22 PAH compounds were divided into four groups according to their number of aromatic rings. The PAH compounds representing 2-3-ring, 4-ring, 5-ring and 6-ring PAH are shown in Table 1. The sum concentration of the total number of PAH compounds in each sediment sample were characterized by calculating the total concentration of PAH for each group of PAH separately. This is in the present study called the PAH-group profile. The PAH-group profiles (Fig. 2) in all the surficial sediment samples are similar and show higher proportions of low molecular weight PAH (2-3-ring PAH, defined as $128 < m/z < 192$) with phenanthrene as dominant compound in most cases. The only exceptions are the samples A3, C3, AA1, GT1 and GT2, where the PAH-group profile is dominated by 4-ring PAH (defined as $202 < m/z < 234$) with fluoranthene and pyrene being the highest.

Spatial distribution

The PAH concentrations (expressed in ng g^{-1} dry weight) in 17 surficial sediment samples are also presented in Table 1. The total PAH concentration in sediments varies from 34.67 to 682.29 ng g^{-1}. The analysis and comparison of the total PAH levels in this study is similar to international studies worldwide (Benlanchen et al., 1997; Johnson and Larsen, 1985) which reveal three classes of sediments with regard to the level of contamination. The majority of samples are classified as fairly contaminated (250 ng g^{-1} < total PAH < 500 ng g^{-1}), while the slightly contaminated (total PAH < 250 ng g^{-1}) and relatively highly contaminated samples (total PAH > 500 ng g^{-1}) consisted of some samples located in a restricted locations in the Gulf.

A hierarchical cluster analysis of the total PAH data separated sampling stations into two main groups with broadly similar molecular composition of parent PAH. The stations associated with the two main clusters form two zones: the zone in front of the city of Trieste and the rest of the Gulf. The latter zone can be subdivided into two subzones: stations affected by the river Isonzo outflow (OL3, D6, A4, GT2, AA1), and Bays of Panzano (D01), Koper (K) and Piran (MA), and those in the central part of the Gulf (G, F, CZ, KK, A29, G3). The station OL3 located in the vicinity of the river Isonzo outflow is similar to other stations located in the central part of the Gulf because it is less affected by the riverine input due to the major flow direction diverted southwest. The relatively highly contaminated sediments are mainly located in the area around Trieste (stations GT1, A3, C3), where the sum concentration of the total number of identified PAH is higher than 600 ng g^{-1}. This is due to contamination by port activities including oil transportation, and local industrial and sewage outfalls. Trieste is the largest human agglomeration and oil terminal in the Gulf. The less contaminated area is located in front of the principal riverine inflow of the Isonzo with a yearly average flow of about 160 m^3 s^{-1} (Širca et al., 1999). Higher PAH concentrations in the samples with a higher sand content collected in the vicinity of the river Isonzo outflow (D6 and A4) suggest that the larger riverine particles containing PAH are deposited at the Isonzo river mouth while finer particles are spread over a wider area. The fairly contaminated areas include also the Bays of Koper and Panzano with

TABLE 1

Total PAH concentrations (ng g^{-1} dry weight) and concentrations of 22 parent and alkylated PAHs for 17 sediment samples.

|	Analyte\sample	CZ	F	G	K	MA	KK	A29	A3	A4	C3	D01	D6	G3	OL3	AA1	GT1	GT2
												Sampling stations						
2-3-ring PAHs	Naphthalene	13.90	10.39	6.55	29.66	16.58	6.91	3.11	76.39	22.69	24.55	26.66	28.16	7.38	34.23	8.72	14.41	39.92
	2-Methylnaphthalene	18.34	11.96	8.60	18.58	27.65	21.23	1.22	14.45	7.73	11.50	18.78	14.22	3.15	12.85	5.30	8.09	12.76
	1-Methylnaphthalene	11.56	5.16	4.26	10.67	17.29	12.33	0.68	14.29	7.01	9.51	13.43	10.48	2.90	10.22	5.31	6.23	11.42
	Acenaphthylene	1.23	1.23	1.23	3.18	2.08	1.61	1.23	10.02	2.86	6.34	2.69	3.49	1.12	1.60	1.47	6.39	6.15
	Acenaphthene	1.04	1.49	0.97	2.85	1.80	1.00	2.05	4.64	2.27	2.99	2.49	4.51	1.57	2.09	0.76	1.53	1.91
	Fluorene	3.96	5.39	2.10	5.96	5.69	3.20	0.57	12.25	5.20	5.59	6.19	9.38	2.17	5.29	5.03	6.40	6.92
	Phenanthrene	17.63	15.15	9.69	27.36	23.08	10.51	3.15	50.31	25.31	49.19	37.75	32.19	6.43	30.76	12.55	44.90	42.03
	2-Methylphenanthrene	12.12	8.36	18.17	14.87	16.18	12.83	4.39	11.58	10.61	10.99	16.26	7.75	2.17	8.99	4.01	10.06	12.08
	1-Methylphenanthrene	7.45	7.45	5.64	11.17	14.06	9.88	1.59	7.22	8.51	6.77	11.18	6.87	1.90	6.31	3.82	5.34	6.72
	Retene	3.88	6.33	1.43	6.17	7.81	3.67	0.63	5.66	1.58	2.52	6.39	3.12	1.25	1.86	2.39	4.73	6.81
	Anthracene	2.20	1.51	1.92	4.92	4.34	1.80	0.83	11.35	2.65	12.64	3.65	2.18	0.83	1.21	2.10	16.59	7.11
	1-Methylanthracene	4.91	5.37	4.48	5.45	13.43	4.87	0.61	10.35	7.07	6.58	11.62	6.45	1.49	5.46	3.88	6.89	7.82
4-ring PAHs	Fluoranthene	17.48	9.77	10.39	42.94	33.08	9.43	1.64	69.53	27.85	80.40	30.47	32.55	6.93	10.49	25.65	63.14	54.36
	Pyrene	16.44	8.37	8.99	37.18	30.79	8.81	2.04	64.38	26.09	69.48	27.23	28.76	5.49	10.83	23.78	52.34	58.25
	1-Methylpyrene	5.07	4.04	3.63	11.02	14.84	6.89	0.63	13.95	4.90	8.04	7.00	4.95	1.33	3.28	2.13	3.32	3.60
	Benzo(a)anthracene	9.47	4.39	4.62	23.47	15.83	10.09	1.56	40.94	17.74	43.42	15.02	19.75	5.97	8.22	24.59	39.45	29.56
	Chrysene	9.49	6.09	6.09	21.62	16.26	8.71	1.69	51.48	23.92	54.63	23.15	22.31	5.94	9.52	21.97	43.30	34.06
5-ring PAHs	Benzo(b)fluoranthene	17.56	8.36	9.65	34.15	32.33	19.39	3.54	76.28	37.99	70.56	26.98	19.81	3.91	7.47	43.84	61.01	35.88
	Benzo(a)pyrene	8.40	4.27	4.73	23.52	16.22	13.00	0.83	44.52	19.77	53.31	16.11	20.11	3.00	4.07	26.72	42.39	24.22
	Dibenzo(a,h)anthracene	1.90	0.76	0.94	5.37	3.83	2.19	0.33	7.13	3.35	8.23	2.45	2.49	0.68	0.91	7.53	10.11	3.79
	Benzo(g,h,i)perylene	11.91	5.46	5.81	22.13	17.12	24.61	1.36	50.09	23.50	59.09	15.45	16.86	3.17	4.67	62.45	93.69	42.04
6-ring PAHs	Indeno(1,2,3-c,d)pyrene	10.68	5.39	5.50	24.97	17.65	15.32	1.00	35.49	18.87	42.21	14.92	14.39	2.48	5.74	34.78	58.49	31.29
Total PAH		206.61	136.65	125.39	387.20	347.95	208.27	34.67	682.29	307.44	638.54	335.85	310.74	71.28	186.08	328.79	598.80	478.70
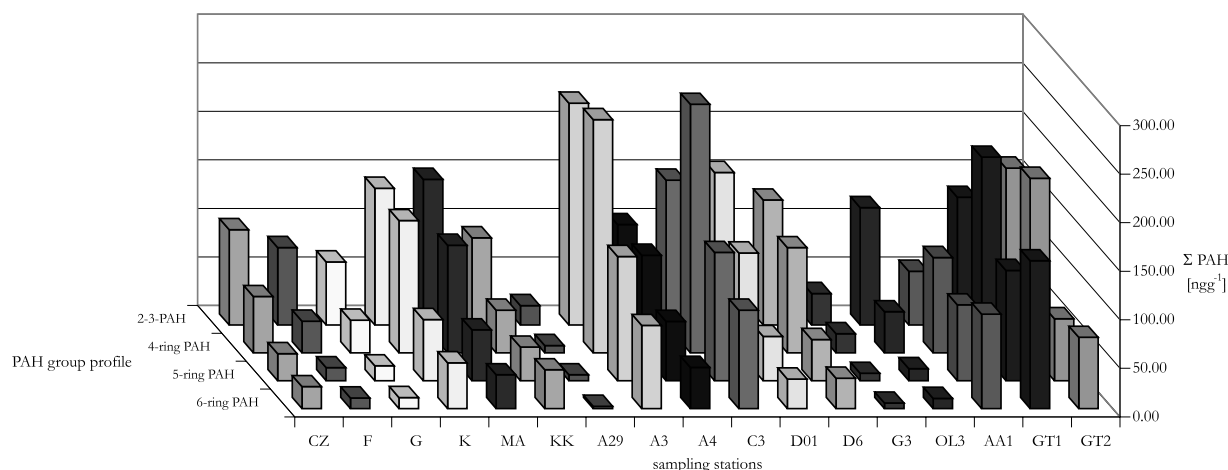
Fig. 2 Group profiles of sedimentary PAHs from the Gulf of Trieste.

industrial and port areas of Koper and Monfalcone (D01), with several coal, petroleum and other cargo-handling piers, and the Bay of Piran (MA) with its marinas. All these locations are also affected by smaller local freshwater inflows suggesting that fluvial and wastewater inflows dominate the PAH input (Prahl *et al.*, 1984). The total concentration of PAH determined in sediments declines quite rapidly with increasing distance from the shore. The slightly polluted sediment samples (A29, G and F) are located away from the major urban sites in the Gulf and contain the lowest percentage of clay and a lower (<1%) organic carbon content (Table 2).

The total concentration of parent PAHs in the surficial sediments show a significant correlation with the clay ($r = 0.76$) and organic carbon ($r = 0.65$) content. The latter indicates that PAH are associated with sedimentary organic matter and, thus, less available as a pollution source than those bound to soot particles (Pereira *et al.*, 1999). On the other hand, there is only a weak correlation ($r = 0.23$) between PAH levels and $\delta^{13}C_{org}$ values, indicating that sedimentary PAH do not reflect the sources, marine vs. terrigenous, of the bulk organic matter in the Gulf despite a significant correlation which was previously demonstrated between $\delta^{13}C_{org}$ values and clay contents (Faganeli *et al.*, 1998). The recent deposition of PAH at stations F, CZ and AA1 in the Gulf of Trieste, calculated using the ^{210}Pb sedimentation rates of 1.2–1.8 mm yr^{-1}, sediment density of 2.8–2.6 g cm^{-3} and porosity of 0.8 (Faganeli *et al.*, 1991; Covelli *et al.*, in press), is between the range 0.02–0.03 µg cm^{-2} yr^{-1} and, thus, lower than in some more polluted bays worldwide (Pereira *et al.*, 1999; Smith and Levy, 1990) but similar to those observed in the Mediterranean (Lipiatou *et al.*, 1997).

Among the individual PAH compounds identified, the dominant compounds in all samples are naphthalene, phenanthrene, fluoranthene and pyrene (Table 1). The

TABLE 2

Organic C and $\delta^{13}C_{org}$ values, and grain-size (%) analyses (Covelli and Fontolan, 1997; Ogorelec *et al.*, 1991) of surficial sediments in the Gulf of Trieste.

Sample station	Sediment fraction				
	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	Sand	Silt	Clay
CZ	1.32	−21.7	16.0	56.0	28.0
F	0.81	−23.2	66.0	22.0	12.0
G	0.52	−23.0	42.0	38.0	20.0
K	1.23	−21.6	2.4	62.6	35.0
MA	1.17	−21.0	8.0	64.0	28.0
KK	0.94	−21.6	22.0	50.0	28.0
A29	0.18	−23.7	10.4	71.7	17.9
A3	1.15	−30.2	10.5	44.7	44.8
A4	1.01	−22.1	23.3	48.5	28.3
C3	1.32	−22.3	1.4	43.2	59.4
D01	1.08	−26.4	78.7	15.6	4.7
D6	0.81	−25.5	30.5	56.4	13.1
G3	–	–	10	72	18
OL3	1.06	−25.8	29.8	58.0	7.2
AA1	1.20	−21.5	15.5	38.9	45.6
GT1	1.10	−22.3	2.5	43.5	54.0
GT2	1.20	−22.3	1.5	51.5	47.0

exception was observed in the relatively high polluted samples where the high molecular weight PAH (benzo[b]fluoranthene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene) were present in the same concentration range as the previously mentioned dominant PAH. These results agree with a similar study in the Adriatic Sea performed by Guzzella and de Paolis (1994). The only difference in our study is that photochemically labile anthracene is present in all sediments sampled.

Sources

The mixture of PAH present in a particular sample in many cases mirrors the sources that produce the PAH. Source temperature is a significant parameter and has a significant role on PAH formation. Alkyl substituted PAH are formed at low temperatures (400–800°C) while only a small amount of alkylated PAH are formed at higher temperatures (2000°C) (Blumer, 1976). Several methods can be used to determine the probable sources of PAH. The common method is the calculation of the specific alkylated PAH/parent PAH or parent PAH/parent PAH ratios (Blumer and Youngblood, 1975; Sporstol et al., 1983).

In the present study, the ratios of methylpyrene/pyrene (MPy/Py), methyphenanthrene/phenanthrene (MPhe/Phe), phenanthrene/anthracene (Phe/Anth) and fluoranthene/pyrene (Fluo/Py) were examined. The MPy/Py ratio is reported to be <1 for PAH derived from combustion sources, while MPy/Py ratio >2 suggests a petroleum source (Maher and Aislabie, 1992). MPy/Py ratios calculated for all sediments in our study is <1. The highest value of this ratio (0.78) was observed in sediment G. Considering this criteria the PAH in the sediments investigated in our study originate from combustion sources. The MPhe/Phe ratio is between 0.5 and 1 for phenanthrenes originating from combustion processes and 2–6 for sediments dominated by fossil-fuel phenanthrenes (Prahl and Carpenter, 1983). Surprisingly, the MPhe/Phe ratio >2, which indicates fossil-fuel sources, was noticed at sediment G located at the entrance of the Gulf of Trieste and at the sediment KK located at the entrance of the Bay of Koper. The Phe/Anth and Fluo/Py ratios enable us to determine the combustion source of pollution under the following conditions: in the particular sediment the Phe/Anth ratio should be <10 and Flu/Py ratio be >1. However, the results of all ratios examined (Table 3) are ambiguous. In general no more than two criteria are used to determine possible sources (Pereira et al., 1999; Benlanchen et al., 1997) because using more criteria can lead to different and ambiguous interpretation of the results. Therefore, the reliability of the results using these ratios should be checked by amounts of particular PAH compounds. For example, pyrolitic PAH include all parent compounds except phenanthrene and anthracene, because their unspecific origin (pyrolitic or fossil fuel) depends on the temperature of formation. On the

TABLE 3

PAH ratios in the sediment samples from the Gulf of Trieste.

Sample station\ ratio	MPy/Py	MPhe/Phe	Phe/Anth	Fluo/Py
CZ	0.31	1.11	8.02	1.06
F	0.48	1.04	10.05	1.17
G	0.40	2.46	5.06	1.16
K	0.30	0.95	5.56	1.15
MA	0.48	1.31	5.31	1.07
KK	0.78	2.16	5.83	1.07
A29	0.31	1.89	3.80	0.80
A3	0.22	0.37	4.43	1.08
A4	0.19	0.76	9.55	1.07
C3	0.12	0.36	3.89	1.16
D01	0.26	0.73	10.34	1.12
D6	0.17	0.45	14.78	1.13
G3	0.24	0.63	7.75	1.26
OL3	0.30	0.50	25.40	0.97
AA1	0.09	0.62	5.97	1.08
GT1	0.06	0.34	2.71	1.21
GT2	0.06	0.45	5.91	0.93

other hand, the predomination of alkylated and 2-3 ring PAH indicate a petrogenic source of pollution. Considering all the studied source definition criteria and the meteo-marine situation of the Gulf of Trieste, the weathered petroleum and pure combustion sources are the principal sources of contamination, except samples G and KK, which most likely originate from oil pollution. This assumption is supported by the phenanthrene/anthracene ratio, which is higher in remote areas compared to the urban sites, presumably because of selective photooxidation of anthracene during long-term transport (Irwan et al., 1998).

Retene (1-methyl-7-isopropylphenanthrene) is considered to be a characteristic PAH compound formed during the burning of coniferous timber. Generally, it is also thought to be a biomarker for diagenesis of coniferous material (Laflamme and Hites, 1978). Retene was determined in all sediments investigated indicating the influence of the terrigenous input. The highest amounts were noticed in samples MA in the Bay of Piran and F at the Bay entrance, K in the Bay of Koper and D1 in Panzano Bay.

Sedimentary record of PAH pollution

A 320 cm long core (GT2) was used for a historical reconstruction of PAH contamination in the Gulf of Trieste. The vertical profile of C_{org} shows a decrease in the upper 14.5 cm until reaching a nearly constant value of about 0.6–0.8% in the whole of the marine sequence-characterized by $\delta^{13}C_{org}$ values of between −22.8‰ and −23.2‰, and lower C/N (4–8, atomic) ratios. The sequence below 160 cm has between −25.2‰ and 26.9‰ $\delta^{13}C_{org}$, and higher C/N ratios (11–16, atomic) of prevalently terrigenous origin with C_{org} contents up to 1.6%, typical for peat presence. The $^{14}C_{org}$ dating shows the presence of rather old sedimentary organic matter throughout the core, and the terrigenous sequence is according to $^{14}C_{org}$ dating approximately 9000 years old

TABLE 4
PAH concentrations in the gravity core GT2 (ng g^{-1} dry weight).

Analyte	Core depth												
	1.25 cm	6.5 cm	10.25 cm	14.5 cm	18.5 cm	54.5 cm	79.5 cm	115 cm	195 cm	235 cm	275 cm	295 cm	315 cm
Naphthalene	39.92	15.99	25.87	16.36	13.37	14.45	17.88	16.97	22.18	10.46	15.89	11.37	13.25
2-Methylnaphthalene	12.76	8.58	12.46	10.21	8.68	8.50	7.41	3.85	8.29	5.72	4.89	4.87	2.17
1-Methylnaphthalene	11.42	6.87	11.91	9.57	7.07	6.38	6.76	3.82	7.99	4.85	4.66	3.96	2.05
Acenaphthylene	6.15	7.41	6.01	5.14	3.56	1.62	1.63	1.24	1.41	1.23	1.23	1.23	1.23
Acenaphthene	1.91	1.53	2.88	1.83	1.34	0.99	0.99	0.73	0.98	0.64	1.04	0.98	0.48
Fluorene	6.92	7.10	8.68	8.30	5.70	4.16	3.37	2.43	6.33	5.11	5.96	5.22	1.59
Phenanthrene	42.03	36.85	50.50	37.29	31.27	26.92	16.15	9.96	19.42	17.38	16.14	18.18	3.49
2-Methylphenanthrene	12.08	16.22	12.57	11.55	10.31	8.28	7.38	5.45	9.02	9.02	4.86	7.82	2.60
1-Methylphenanthrene	6.72	14.38	10.87	10.17	9.59	8.03	6.31	3.14	6.51	7.16	4.00	4.67	0.38
Retene	3.60	4.88	3.15	4.88	4.17	1.61	0.89	0.89	1.37	1.67	0.85	1.10	0.98
Anthracene	7.11	6.20	9.60	6.31	4.72	1.36	0.60	0.63	1.01	1.05	1.36	1.45	0.20
1-Methylanthracene	6.81	10.53	7.11	7.21	6.96	5.93	3.78	1.90	4.39	5.33	2.67	4.26	1.17
Fluoranthene	54.36	57.14	71.30	47.85	34.81	5.47	3.74	2.72	4.47	5.15	7.45	6.18	0.83
Pyrene	58.25	167.39	74.74	156.22	90.22	28.01	13.49	3.99	7.48	7.17	9.49	8.45	3.86
1-Methylpyrene	7.82	45.04	10.61	46.65	26.89	10.52	5.26	1.91	3.48	5.19	3.44	4.27	1.54
Benzo(a)anthracene	29.56	37.07	39.45	33.87	23.55	5.80	5.82	5.30	5.52	7.64	6.96	7.00	3.55
Chrysene	34.06	43.52	43.01	31.15	21.64	11.16	6.74	2.63	6.09	5.92	4.94	4.14	1.07
Benzo(k)fluoranthene	35.88	65.46	51.43	51.64	22.68	8.13	5.50	3.54	5.20	4.14	4.44	4.08	3.54
Benzo(a)pyrene	24.22	45.32	45.79	33.88	21.76	4.07	2.28	2.28	2.63	2.61	2.28	2.59	2.28
Benzo(g,h,i)perylene	42.04	75.22	73.78	54.27	39.00	5.32	4.83	3.59	5.81	5.91	4.18	4.55	1.09
Dibenzo(a,h)anthracene	3.79	8.39	8.14	5.33	3.91	1.26	0.73	0.33	0.33	0.98	0.43	0.40	0.00
Indeno(1,2,3-c,d)pyrene	31.29	47.69	43.25	33.11	25.87	5.11	3.78	2.69	5.72	6.66	4.59	4.91	1.35
Total PAH	478.70	728.81	623.13	622.79	417.07	173.08	125.33	79.99	135.65	120.98	111.74	111.68	48.69
Phe/Anth	5.91	5.94	5.26	5.91	6.63	19.75	26.85	15.93	19.14	16.58	11.90	12.55	17.61
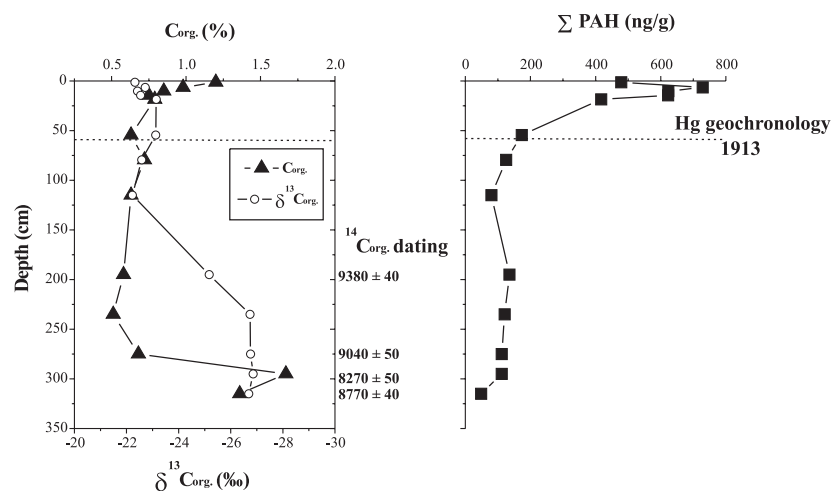
Fig. 3 Sediment core GT2. Distributions of organic C, $\delta^{13}C_{org}$ values, $^{14}C_{org}$ datation, Hg geochronology (Fontolan et al., 1999) and total PAH concentrations.

originating from the period of the last transgression in the Gulf of Trieste and northern Adriatic (Ogorelec et al., 1988). The mean accumulation rate from the upper 72.5 cm deep marine part of the core is, about 0.2 mm yr^{-1} which is about 30-fold lower than that calculated from the Hg contents (Fontolan et al., 1999). This was previously correlated with ^{210}Pb and can be used as a geochronological tracer in recent sediments of the Gulf of Trieste (Covelli et al., in press) giving a recent sedimentation rate of about 6 mm yr^{-1}. The difference is likely the result of increased sedimentation. Concentra-

tions of PAH (Table 4) decrease from the surface to deeper layers. Lower surficial than subsurficial PAH contents are probably a result of a shift from coal to oil and gas energy sources. Using Hg as a recent geochronological tracer (Krom et al., 1994; Covelli et al., in press) it emerges that the sediment layers located at the depth of 55 cm dated to 1913, during the maximal production of Hg in Idrija and the pollution of the Gulf of Triste (Covelli et al., in press). Below are only low levels of PAH. Hg geochronology suggests that the present-day PAH accumulation flux amounts to 0.14 µg

cm^{-2} yr^{-1} while in sediments deposited before the First World War it averages < 0.05 µg cm^{-2} yr^1. The PAH pollution in the Gulf increased after the First and especially the Second World War. The PAH contents in the terrigenous peat layer [14]C_{org} dated to about 9000 years BP (before present), with the exception at the depth of 315 cm, are in the same range as pre-industrial marine sediments (Fig. 3).

The Phe/Anth ratio calculated for GT2 sediment core is presenred in Table 4 also. As core depth increases, the Phe/Anth value tends to increase. A significant increase of Phe/Anth ratio was observed at about 50 cm, indicating a shift of a major PAH source. The low Phe/Anth values of the upper core sections indicate that PAH received by the sediment during 1913 to approximately 1997 probably came from a nearby source.

Conclusions

This study documents the first comprehensive analysis of PAH in surficial marine sediments in the Gulf of Trieste. Relative to other urbanized coastal areas worldwide, the measured PAH content of the Gulf of Trieste sediments can be considered low to moderately contaminated. The PAH group profile shows the predominance of 2-3-ring PAH in all samples with some exceptions, where the 4-ring PAH were present as the dominating group. Two main sources of PAH in the studied area have been found: pyrolitic and petrogenic. The dominant sources of PAH appear, however, to be the combustion processes through run-off, industrial and sewage discharges, and atmospheric input rather than the oil spills. However, it is important to emphasize that the ratio of pyrolitic to petrogenic input of PAH can be continuously changed, because of the intense tanker traffic in the Gulf. The area of the Port of Trieste was found to be the most contaminated area in the Gulf of Trieste followed by the area affected by the Isonzo river outflow, Bays of Koper and Panzano with port activities and smaller freshwater inflows, and the Bay of Piran with a marina and some freshwater inflows. This observation suggests fluvial and outfall sources of PAH, and localized deposition in coastal sediments. Sediment chronology of PAH suggests that the Gulf of Trieste has been significantly modified by urbanization and industrialization after the First World War. Information from this study should be useful in designing future strategies for environmental protection and management of the Gulf of Trieste.

Baird, C. (1995) Environmental Chemistry, pp. 276–278. W.H. Freeman and Company, New York.

Benlanchen, K. T., Chaoui, A., Budzinski, H., Bellocq, J. and Garrigues, Ph. (1997) Distribution and sources of polycyclic aromatic hydrocarbons in some mediterranean coastal sediments. Marine Pollution Bulletin 34, 298–305.

Blumer, M. (1976) Polycyclic aromatic compounds in nature. Scientific American 234, 34–35.

Blumer, M. and Youngblood, W. W. (1975) Polycyclic aromatic hydrocarbons in soils and recent sediments. Science 188, 53–55.

Chiou, C. T., McGroddy, S. E. and Kile, D. E. (1998) Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. Environmental Science and Technology 32, 264–269.

Covelli, S. and Fontolan, G. (1997) Application of a normalization procedure in determining regional geochemical baselines. Environmental Geology 30, 34–45.

Covelli, S., Faganeli, J., Horvat, M. and Brambati, A. Mercury contamination of coastal sediments as the result of a long-term cinnabar minig activity (Gulf of Trieste, northern Adriatic Sea). Applied Geochemistry (in press).

Dachs, J., Bayona, J. M., Raoux, C. and Albaiges, J. (1997) Spatial, vertical distribution and budget of polycyclic aromatic hydrocarbons in the western Mediterranean seawater. Environmental Science and Technology 31, 682–688.

Dujmov, J. and Sucevic, P. (1989) Contents of polycyclic aromatic hydrocarbons in the Adriatic Sea determined by UV-fluorescence spectroscopy. Marine Pollution Bulletin 20, 405–409.

Faganeli, J., Planinc, R., Pezdič, J., Smodiš, B., Stegnar, P. and Ogorelec B. (1991) Marine geology of the Gulf of Trieste (northern Adriatic): Geochemical aspects. Marine Geology 99, 93–103.

Faganeli, J., Pezdič, J., Ogrinc, N., Čermelj, B. and Kovač N. (1998) $\delta^{13}C$ as a tracer of the origin and fluxes of organic matter in the Adriatic. RMZ – Materials and Geoenvironment 45, 26–35.

Fontolan, G., Faganeli, J. and Covelli, S. (1999) Geochemical background levels of contaminants in sediments of the Gulf of Trieste (northern Adriatic). I-SLO Scientific Cooperation Project, Final report.

Gearing, P. J., Gearing, J. N., Pruell, R. J., Wade, T. L. and Quinn, J. G. (1980) Partitioning of No. 2 fuel oil in controlled estuarine ecosystem, sediments and suspened particulate matter. Environmental Science and Technology 14, 1129–1135.

Gevao, B., Jones, K. C. and Hamilton-Taylor, J. (1998) Polycyclic aromatic hydrocarbons (PAH) deposition to and processing in a small rural lake, Cumbria UK. Science of the Total Environment 215, 231–242.

Guzzella, L. and de Paolis, A. (1994) Polycyclic aromatic hydrocarbons in sediments of the Adriatic Sea. Marine Pollution Bulletin 28, 159–165.

Harvey, R. G. (1996) Polycyclic Aromatic Hydrocarbons. Wiley, New York, pp. 8–11.

Hedges, J. I. and Stern, J. H. (1984) Carbon and nitrogen determination of carbonate-containing solids. Limnology and Oceanography 29, 657–663.

Hites, R. A., Laflame, R. E. and Farrington, J. W. (1977) Sedimentary polycyclic aromatic hydrocarbons-the historical record. Science 198, 829–831.

Irwan, A. L., Razak, A. A., Ni, F., Gin, M. F. and Christensen, E. R. (1998) Polycyclic aromatic hydrocarbons in the sediment of the Milwaukee harbour estuary, Wisconsin, USA. Water, Air, and Soil Pollution 101, 417–434.

Johnson, A. C. and Larsen, P. F. (1985). The Distribution of Polycyclic Aromatic Hydrocarbons in the Surficial Sediments of Penobscot Bay (Maine, USA) in Relation to Possible Sources and to Other Sites Worldwide. Marine Environmental Research 15, 1–16.

Krom, M. D., Kaufman, A. and Hornung, H. (1994) Industrial mercury in combination with natural Pb210 as time-dependent tracers of sedimentation and mercury removal from Haifa Bay, Israel. Estuarine, Coastal and Shelf Science 38, 625–642.

Laflamme, R. E. and Hites, R. A. (1978) The global distribution of PAH in recent sediments. Geochimica et Cosmochimica Acta 42, 289–303.

Lipiatou, E. and Albaiges, J. (1994) Atmospheric deposition of hydrophobic organic chemicals in the northwestern Mediterranean Sea: Comparison with the Rhone River input. Marine Chemistry 46, 153–164.

Lipiatou, E., Tolosa, I., Simo, R., Bouloubassi, I., Dachs, J., Marti, S., Sicre, M. A., Bayona, J. M., Grimalt, J. O., Saliot, A. and Albaiges, J. (1997) Mass budget and dynamics of polycyclic aromatic hydrocarbons in the Mediterranean Sea. Deep-Sea Research II 44, 881–905.

Maher, W. A. and Aislabie, J. (1992) Polycyclic aromatic hydrocarbons in nearshore marine sediments of Australia. *Science of the Total Environment* **112**, 143–164.

Marcomini, A., Pavoni, B., Donazzolo, R. and Orio, A. A. (1986) Combined preparative and analytical use of normal-phase and reversed-phase high-performance liquid chromatography for the determination of aliphatic and polycyclic aromatic hydroacrbons in sediments of the Adriatic Sea. *Marine Chemistry* **18**, 71–84.

Meischner, D. and Rumohr, J. (1974) A light-weight high-momentum gravity corer for subaqueous sediments. *Senckenbergiana Maritima* **6**, 105–117.

Neff, J. M. (1979) *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment-Sources, Fates and Biological Effects*, pp. 7–33. Applied Science, London.

Nes, K. and Oug, E. (1997) Multivariate approach to distribution patterns and fate of polycyclic aromatic hydrocarbons in sediments from smelter-affected Norwegian fjords and coastal waters. *Environmental Science and Technology* **31**, 1253–1258.

Notar, M. and Leskovšek, H. (2000) Determination of polycyclic aromatic hydrocarbons in marine sediments using a new ASE-SFE extraction technique. *Fresenius Journal of Analytical Chemistry* **366**, 846–850.

Ogorelec, B., Mišič, M. and Faganeli, J. (1991) Marine geology of the Gulf of Trieste (northern Adriatic): sedimentological aspects. *Marine Geology* **99**, 79–92.

Pereira, W. E., Hostettler, F. D., Luoma, S. N., van Geen, A., Fuller, C. C. and Anima, R. J. (1999) Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, CA. *Marine Chemistry* **64**, 99–113.

Prahl, F. G. and Carpenter, R. (1983) Polycyclic aromatic hydrocarbons (PAH)-Phase association in Washington coastal sedimentary particulates from Dadob Bay, Washington DC. *Geochimica et Cosmochimica Acta* **47**, 1013–1023.

Prahl, F. G., Crecellus, E. and Carpenter, R. (1984) Polycyclic aromatic hydrocarbons in Washington coastal sediments: An evaluation of atmospheric and riverine routes of introduction. *Environmental Science and Technology* **18**, 687–693.

Sharma, M., McBean, E. A. and Marsalek, J. (1997) Source characterization of polycyclic aromatic hydrocarbons in street and creek sediments. *Water Quality Research Journal of Canada* **32**, 23–35.

Smith, J. N. and Levy, E. M. (1990) Geochronology for polycyclic aromatic hydrocarbon contamination in sediments of the Sagvenay Fjord. *Environmental Science and Technology* **24**, 874–879.

Sporstol, S., Gjos, N., Lichtenthalter, R. G., Gustavsen, K. O., Urdal, K., Oreld, F. and Skei, J. (1983) Source identification of aromatic hydrocarbons in sediments using GC/MS. *Environmental Science and Technology* **17**, 282–286.

Stegeman, J. J. and Lech, J. J. (1991) Cytochrome P-450 monooxygenase system in aquatic species: Carcinogen metabolism and biomarkers for carcinogen and pollutant exposure. *Environmental Health Perspectives* **90**, 101–109.

Suess, M. J. (1976) The environmental load and cycle of polycyclic aromatic hydrocarbons. *Science of the Total Environment* **6**, 239–250.

Širca, A., Horvat, M., Rajar, R., Covelli, S., Žagar, D. and Faganeli, J. (1999) Estimation of mercury mass balance in the Gulf of Trieste. *Acta Adriatica* **40**, 75–85.

Tolosa, I., Bayona, J. M. and Albaiges, J. (1996) Aliphatic and polycyclic aromatic hydrocarbons and sulfur/oxygen derivatives in northwestern Mediterranean sediments: Spatial and temporal variability, fluxes, and budgets. *Environmental Science and Technology* **30**, 2495–2503.

Wakeham, S. G., Schaffner, C. and Giger, W. (1980) Polycyclic aromatic hydrocarbons in recent lake sediments: I. Compounds having anthropogenic origins. *Geochimica et Cosmochimica Acta* **44**, 403–413.

Young, L. Y. and Cerniglia, C. E. (1995) *Microbial Transformation and Degradation of Toxic Organic Chemicals*. Wiley, New York.