Baseline

Origin, distribution and toxicological potential of polycyclic aromatic hydrocarbons in surface sediments from the Bushehr coast, The Persian Gulf

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ABSTRACT

To evaluate the hazards of polycyclic aromatic hydrocarbons (PAHs) in the Bushehr coastal zones, 12 surface sediments were analyzed. The $\sum_{14}$PAHs concentrations varied from 371 to 611 ng g^{-1} dw. The primary sources of the observed PAHs were pyrolytic processes, demonstrating the dominance of petroleum-related combustion inputs. The ERL/ERM and TEL/PEL values showed that there was a moderate level of toxicity risk for some PAHs. The toxicological significance of the pollutants was assessed using the toxic equivalency factor (TEF) to calculate both the toxic equivalent for dioxins (TEQ$_{TCDD}$) and the TEQ carcinogenic risks. Dibenz(a,h)anthracene exhibited the highest proportion in the TEQs, ranging from 49% to 56% (TEQ$_{carc}$) and from 29% to 39% (TEQ$_{TCDD}$) regarding the overall toxicity in the sampled sediments. This result suggests that the ambient dibenz(a,h)anthracene concentration represents the risk posed by PAHs in the sediments. Moreover, using a specific sediment criterion demonstrated the bioaccumulation potential of benzo(a)pyrene for humans in the sampled sediments.

Among the numerous marine environments, creeks are recognized as one of the richest marine habitats (Friday and Ingram, 1985). The high net productivity of organic matter, the dense presence of marine biota and extensive human activities transform creeks into hot spots of biodiversity (Abu-Hilal et al., 1994). Therefore, current accelerated pollutant discharges to these vulnerable environments and their subsequent toxic effects on the related biota and ultimately human beings may be a subject of interest for future risk estimates. Pollutants commonly called polycyclic aromatic hydrocarbons (PAHs) are of particular importance (Charles et al., 2012).

In this work, three important creeks (i.e., Soltani, Lashgari, and Podar) at Bushehr port, which is located on the northern end of the Persian Gulf, and an important fishery harbor for Bushehr (i.e., Rostami harbor) were investigated for PAH contamination. The distribution and origin of PAHs, ecological risk screening, potential human toxicity and a site-specific sediment criterion were also investigated.

The sediments were sampled from 3 creeks at the Bushehr port and a fishing port located along the southeastern Bushehr coast. Surficial sediment samples (0–5 cm) were collected from Podar (P; 28°58′12.80″N, 50°51′44.83″E), Soltani (S; 28°59′23.07″N, 50°50′28.50″E) and Lashgari (28°59′16.67″N, 50°52′44.92″E) creeks

and from the Rostami fishing port (R; 28°33′11.84″N, 51°3′7.70″E) using a stainless steel Van-Veen grab sampler on 21 and 22 February 2012. Three replicate samples were collected. The sediments were freeze-dried in the laboratory using an Operon Freeze-Dryer 5503 and stored at −20 °C before performing gas chromatography–mass spectroscopy (GC–MS) analysis.

The samples were extracted by applying the low-density homogeneous liquid–liquid extraction method with some modifications (Shamsipur and Hassan, 2010). Then, 1 g of freeze-dried and homogenized sediment (<63 μm) was extracted using 10 mL of methanol in an ultrasonic bath for 30 min. The extracted material was centrifuged for 3 min at 2500 rpm. Then, 6 mL of the organic layer (including the extracted compounds) was decanted in a separate container; the sediments were re-extracted and centrifuged two additional times. The supernatants of each sample were combined to form a unit sample. The methanolic phase was placed in a volumetric flask, and 1.0 mL of n-hexane was added to the flask. The flask was vigorously shaken for 3 min. By adding 8 mL of water into the solution, n-hexane was separated at the top of volumetric flask. After some time, a 500-μL aliquot of the upper phase was extracted. Activated copper powder was added to the extract for desulfurization. Finally, 1 μL of each sample was used for GC–MS analysis.

The loss on ignition (LOI) method was used to estimate the organic content in the sampled sediments. The total organic matter (TOM) was assayed by weighing approximately 1.5–2 g of the

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sediments (<63 µm) after placing the samples in a furnace (NABERTHERM, P330; Germany) at 450 °C for 8 h. The mass differences were related to the TOM percent using the appropriate formula. Half of the LOI amount (Gaspare et al., 2009) can be used to estimate the total organic carbon (TOC) content in a sample.

Data analysis (e.g., mean, standard deviation, maximum, and minimum concentrations) was performed using appropriate statistical methods. The Kolmogorov–Smirnov test was used to test for normality in the data. Moreover, one-way ANOVA and Kruskal–Wallis tests were applied to determine significant differences ($p < 0.05$) between the TOC and PAH concentrations in the samples, respectively. Linear correlation using the Spearman technique was used to detect significant relationships among the studied variables (e.g., TOC, PAHs, and clay content). All statistical processes were performed using SPSS 17.5 and Excel 2007; the figures were created using the same software packages.

Table 1 lists the PAH concentrations for the sampled surface sediments. Fourteen of the 16 PAH compounds listed as priority pollutants according to the US EPA were analyzed, including naphthalene (Na), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Fl), phenanthrene (Ph), anthracene (An), fluoranthene (Flu), pyrene (Py), benz(a)anthracene [B(a)A], chrysene (Ch), benzo(b)fluoranthene [B(b)F], benzo(k)fluoranthene [B(k)F], benzo(a)pyrene [B(a)P], and dibenz(a,h)anthracene [D(a,h)A]. The sum of the individual PAH concentrations ($\sum_{14}$PAHs) varied from 371 ng g^{-1} dw at station R$_3$ to 611 ng g^{-1} dw at station S$_2$; the mean ranged from 388 to 600 ng g^{-1} dw, respectively. A CRM sample (IAEA-417) was tested in addition to the sampled sediments, demonstrating a recovery rate of 65–112% for the method applied in this study; the mean was 85%. Statistically, the studied areas were found to be more homogenously contaminated with PAH mixtures; no significant differences were observed in the PAH concentrations and clay contents among the individual sites points. Meanwhile, the TOC amounts exhibited significant differences among the sampling locations. A positive correlation between the PAH concentrations

and the TOC contents was observed, which supports the previously suggested relationship between sedimentary organic particles and lipophilic pollutants (Martínez-Lladó et al., 2007). Table 2 provides the PAH concentrations found in sediments from different locations around the world and those analyzed in this study. Several studies have divided PAH pollution into four categories, i.e., low (0–100 ng g^{-1}), moderate (100–1000 ng g^{-1}), high (1000–5000 ng g^{-1}) and very high (>5000 ng g^{-1}) on a per dry weight basis (Baumard et al., 1998; Chen and Chen, 2011). Based on these definitions, the surface sediments analyzed herein for the entire study area may be considered to be moderately polluted, particularly compared with other parts of the world (Table 2).

Fig. 1 depicts the distribution of PAHs according to the number of aromatic rings in the surface sediments collected from the studied areas. Based on these data, the 14 PAH compounds were divided into 2- or 3-ring, 4-ring, and 5- or 6-ring compounds. In this study, the 5-ring PAHs were dominant, ranging from 46% to 51%. The 2,3-ring compounds exhibited the least contribution (Fig. 1). Petroleum mixtures contain primarily 2- and 3-ring PAHs, while combustion products are dominated by 4- to 6-ring PAHs (Bouloubassi et al., 2012). In this study, the surplus of 5-ring PAHs suggests a common dominant pollution source, i.e., the combustion process. Therefore, the primary origin of the studied PAHs is likely the result of human activities. There are two primary processes that form these compounds: (1) fuel or organic matter combustion (pyrogenic) and (2) the discharge of crude oil (spill) and its derivatives in the global environment (petrogenic) (Guo et al., 2011). PAH diagnostic ratios have recently been used to identify the origin of pollutants in specific ecosystems. Because of the variability in the individual PAH responses to peripheral factors and different environmental fates, these ratios should be used with caution. Therefore, previous studies have advised using multiple diagnostic ratios. With regard to anthropogenic PAHs, the low-molecular weight parent (2- and 3-ring) PAHs have both petrogenic and combustion (low-temperature pyrolysis) sources, whereas

Table 1
Concentration (ng g^{-1} dry wet), calculated distribution indices and toxicity aspects of PAH compounds.

Analytes	P$_1$	P$_2$	P$_3$	L$_1$	L$_2$	L$_3$	S$_1$	S$_2$	S$_3$	R$_1$	R$_2$	R$_3$	Rec. (%)	ER-L	ER-M	TEL	PEL	TEF^{TCDD}	TEF^{CARC}
Na	18.4	16	14	16.2	15.2	17.2	15.3	17.5	16	25.9	22.8	18.8	65	160	2100	34.6	391		
Ac	19.7	20	19.5	19.7	18.7	20.7	20.5	20.9	20.7	19.8	19.8	19.5	–	44	640	5.9	128		
Ace	21.5	22.7	20.6	19.7	18.6	20.6	23.4	21.9	20	20.1	19.7	20	66	16	500	7	89		
Fl	23.1	28.1	20.6	22.4	21.4	23.4	26.2	24.1	22.6	23.5	25.4	20.8	90	19	540	21.2	144		
Ph	27.9	34.5	23.4	20.6	19.6	21.6	19.7	23.9	20.4	21.9	24	19.8	88	240	1500	86.7	544		
An	16.2	21.2	12.3	10.5	9.5	11.5	12.4	17.8	11.6	10.4	20.6	10.3	84	85.3	1100	46.9	245		
Flu	21.2	22.1	21.9	16.5	15.5	17.5	17	23.9	16.9	17	17	16.4	87	600	5100	113	1494		
Py	24.3	27.8	24.3	17.2	16.2	18.2	18.8	30.9	17	18.2	21.7	16.4	88	665	2600	153	1398		
BaA	44.3	48.6	47.5	32.9	31.9	33.9	31.9	69.3	30.5	30.5	34.9	30.4	86	261	1600	74.8	693	25×10^{-6}	0.1
Ch	29.5	26.8	41.2	17.3	16.3	18.3	16.1	54	16.3	16.5	17.7	15.3	80	384	2800	108	846	2×10^{-4}	0.001
BbF	49	58.3	49	38.7	37.7	39.7	37.8	74.5	36.8	57.7	43.6	37.1	87	NA	NA	NA	NA	25×10^{-4}	0.1
BkF	34.5	37.3	39.6	22.9	21.9	23.9	21.3	53	21	21.3	20.9	20.8	112	NA	NA	NA	NA	48×10^{-4}	0.01
BaP	68	70.6	68	61	60	62	59.1	82.2	59.3	58	59	58.5	85	430	1600	88.8	783	35×10^{-5}	1
Da,hA	98.9	100.1	86.6	72.4	71.4	73.4	68.1	97.4	66.6	66.7	67.1	66.8	83	63.4	260	6.2	135	2×10^{-3}	1
$\sum$PAHs	496	534	488	388	373	401	387	611	376	407	414	371		4000	45,000				
LMW/HMW	0.34	0.36	0.29	0.39	0.38	0.40	0.44	0.26	0.42	0.43	0.47	0.42							
An/(An + Ph)	0.37	0.38	0.34	0.34	0.33	0.35	0.39	0.43	0.36	0.32	0.46	0.34							
B(a)A/(B(a)A + Ch)	0.60	0.64	0.54	0.66	0.66	0.65	0.66	0.56	0.65	0.65	0.66	0.67							
Flu/(Flu + Py)	0.47	0.44	0.47	0.49	0.49	0.49	0.47	0.44	0.50	0.48	0.44	0.50							
$\sum$CPAHs/$\sum$ PAHs	0.65	0.64	0.68	0.63	0.64	0.63	0.60	0.70	0.61	0.61	0.58	0.61							
TEQ$_{TCDD}$	0.51	0.55	0.52	0.37	0.36	0.39	0.35	0.67	0.35	0.4	0.37	0.35							
TEQ$_{CARC}$	177	182	165	141	138	143	134	194	133	134	134	132							
TOC%	3.67	4.79	4.24	1.7	1.8	1.69	3.73	4.26	4.11	2.33	2.35	2.37							
SC$_{oc}$ (ng g^{-1})	25	33	29	11	12	11	26	29	28	16	16	16							

Rec; Recovery.
LMW/HMW; Sum of lower-molecular weight parent (2, 3-ring) PAHs/Sum of higher-molecular weight parent (4, 5-ring) PAHs.
$\sum$CPAHs/$\sum$PAHs; Sum of potentially carcinogenic PAHs (i.e., B(a)A, Ch, B(b)F, B(k)F, B(a)P, and D(a,h)A)/Sum of parent PAHs.
TEFs^{TCDD} is based on Qiao et al. (2006).
TEFs^{CARC} is based on USEPA (1993).