Aliphatic and polycyclic aromatic hydrocarbons in the Xihe River, an urban river in China's Shenyang City: Distribution and risk assessment

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ABSTRACT

The characteristics of petroleum hydrocarbons and the risks they pose to the ecosystem were studied in the Xihe River, which is an urban river located in Shenyang, China. High levels of aliphatic hydrocarbons (AHc) and polycyclic aromatic hydrocarbons (PAHs) were observed in the river due to the discharge of wastewater from industrial and municipal facilities for a long period of time. High-molecular-weight hydrocarbons, including unresolved complex mixtures (UCM) of n-alkanes between n-C16 and n-C32 and of PAHs with four to six rings, were the dominant hydrocarbons in the river, particularly in suspended particulate matter (SPM) and sediments. The AHc was mainly from petrogenic sources, whereas PAHs was from both pyrolytic and petrogenic source inputs. Our results suggest that there is a high risk of toxicity for the soils and groundwater of the study area. The overall toxicity in the sediments can be described using the toxic equivalent (*TEQ*) of dibenzo[*a,h*]anthracene (DBA) based on benzo(*a*)pyrene (*TEQ*$_{BaP}$) and dioxins (*TEQ*$_{TCDD}$) toxic equivalent concentrations. The TEQ values for benzo(*a*)pyrene (*TEQ*$_{BaP}$) and dioxins (*TEQ*$_{TCDD}$) presented a consistent assessment of sediment PAHs.

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1. Introduction

With increasing urbanization and industrialization, the environmental quality in cities has been deteriorating. A large quantity of untreated or partially treated wastewater is discharged into rivers and lakes near cities directly or via canals that generally contain persistent toxic organic compounds. These substances have severely damaged and jeopardized the ecosystems around cities [1–4]. Thus, the determination and monitoring of persistent toxic substances in urban water bodies is necessary and important for protecting urban ecological and human health. Among organic compounds, aliphatic hydrocarbons (AHc) and polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants [5]. Of these, PAHs represent a greater concern due to their documented carcinogenic, mutagenic, and toxic properties [6]. Though a considerable fraction of the hydrocarbons entering the water environment are removed by evaporation, most of them were distributed in the water, accumulated in the sediment and transferred to biota ultimately [7].

Shenyang is an important industrial city and an economic and cultural center of northeastern China. As a result of economic development and population growth during the past 40 years, the ecological environment and the health of residents have both been placed under significant stress [4,8]. In the past, most of Shenyang's industrial and urban wastewater was biologically treated and subsequently discharged into the Xihe River and used for agricultural irrigation due to local water shortages and the desire to recycle nutrients in the water to protect freshwater resources. Therefore, the Xihe River became the largest recipient of industrial effluents and domestic wastewater from Shenyang [9]. Although the U.S. Environmental Protection Agency has reported that the reuse of treated sewage water for irrigation is potentially safe for non-edible species [10], the wastewater nonetheless still contained some persistent organic pollutants capable of endangering food safety and human health [6]. A historical study of pollution of the Xihe River confirmed that the river has been subjected to severe inputs of inorganic and organic pollutants, such as heavy metals [11] and volatile hydroxybenzene compounds [12]. The purpose of the present study was to assess the characteristics of the organic contaminants in a typical urban river. Thus, the levels of AHc and PAHs were monitored in the water, suspended particulate matter (SPM) and surface sediments. In addition, a core sediment from a downstream section of the Xihe River was collected to determine trends in AHc and PAH pollution in this urban river during the past 40 years.

2. Materials and methods

2.1. Study area

Our research was carried out in western Shenyang (42°26′N, 122°38′E) in August 2005. The study area has a continental tem-

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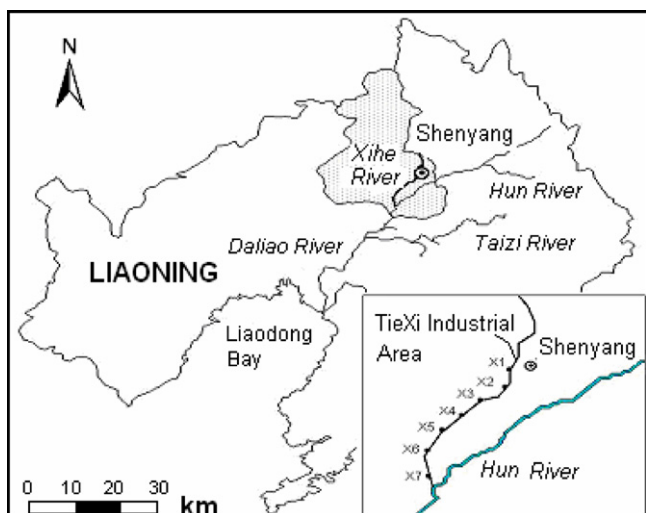(X. Quan).

Fig. 1. Location of the study area and sampling stations.

perate monsoon climate with a dry, cold winter and a warm, wet summer. The Xihe River is 78.2 km long, with a mean river width of 10.5 m and a mean water depth of 1.60 m in the low flow period, and it runs through the Tiexi industrial area of Shenyang, entering the Hun River in Chiyutuo village of Shenyang's Liaozhong town. Locations of the sampling stations are shown in Fig. 1.

2.2. Sampling and pretreatment

Water samples were collected from seven sites (X1–X7) at a depth of at 0.50 m using pre-cleaned dark glass bottles. All samples were stored in an icebox, immediately transported to the laboratory, and stored in a refrigerator at 4 °C before analysis. Water samples were filtered through partial four-fluorine ethylene filters (0.45 μm, d = 50 mm, Millipore, Billerica, MA, USA) to separate SPM from the water. The SPM samples were freeze-dried and wrapped in aluminum foil and then stored in a freezer at -20 °C until analysis.

Surface sediments (0–20 cm) were collected using a grab sampler (Van Veen bodemhappe, 2 L) from six sites (X1, X3–X7). A core sediment to a depth of 48 cm was also collected in the downstream reaches of the Xihe River near station X7 using a stainless-steel core sampler. The core was sectioned at 2 cm intervals for the top 10 cm and 3 cm intervals at greater depths. The surface and core sediments were kept in a freezer at -20 °C until they were analyzed. The frozen sediments were freeze-dried (FD-1A, China), ground with a mortar, and then stored in pre-cleaned dark glass bottles before extraction.

2.3. Extraction and analyses of hydrocarbons

The extraction and analyses of hydrocarbons followed previously reported methods [13–16]. Filtered water samples (2 L) were extracted using a solid-phase extraction system from Supelco (USA). Fifteen grams of freeze-dried sediment were Soxhlet extracted using 250 mL of dichloromethane/hexane (1:1, v/v) for 24 h in a water bath maintained at 60 °C. SPM was subjected to the same extraction procedure as sediments. The extracts from the water, SPM, and sediment samples were passed through a 1:2 alumina:silica gel glass column containing 1 g of anhydrous sodium sulfate overlaying the silica gel for clean-up and fractionation. First, the aliphatic hydrocarbons were eluted with 15 mL of hexane. We then collected eluents containing PAHs by eluting the samples with 70 mL of hexane:dichloromethane (7:3, v:v) and concentrated the eluate to 0.50 mL under a gentle stream of purified N_2. Known quan-

tities of an internal standard were added to the fractions prior to analysis.

Samples were analyzed for AHc (from n-C8 to n-C38) including n-alkanes, unresolved complex mixtures (UCM) and isoprene (phytane and pristine) and for the following 16 non-alkylated polycyclic aromatic hydrocarbons (PAHs): naphthalene (Naph), acenaphthylene (Aceph), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenz[ah]anthracene (DBA), and benzo[ghi]perylene (BgP). AHc were analyzed using a Varian 3800 GC/FID with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 column (J& W Co., USA). The temperature was programmed from 50 °C (hold for 2 min) to 290 °C at 6 °C min^{-1} and was then maintained at 290 °C for 15 min. Hydrogen was used as the carrier gas at a flow of 1.20 mL/mim. PAHs were analyzed using a ThermoQuest GC/MS with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 MS column (ThermoQuest, San Jose, CA, USA) in selected ion mode. The temperature was programmed from 80 °C (hold for 2 min) to 120 °C increasing at 3 °C min^{-1}, then increasing at 5 °C min^{-1} to 200 °C, 200 °C to 290 °C at rate of 7 °C min^{-1} and hold for 15 min at 290 °C. Helium was used as the carrier gas at a flow of 1.00 mL/mim.

All data were subject to strict quality control procedures. The method detection limit (MDL) for n-alkanes and PAHs ranged from 1.30 to 3.10 ng L^{-1} and 18.6 to 79.6 ng L^{-1} for water samples and from 0.79 to 4.82 ng g^{-1} and 0.56 to 3.07 ng g^{-1} for sediment samples, respectively. The mean recovery of n-alkanes and PAHs were 79.1–111% and 60.8–120% for water samples and 69.4–114% and 63.8–97.7% for sediment samples, respectively. Each sample was analyzed in duplicate, and relative standard deviations were less than 15%. Additionally, the dissolved organic carbon (DOC) in water samples and the total organic carbon (TOC) for the sediments were determined using previously described methods [17].

3. Results and discussion

3.1. Aliphatic hydrocarbons in the water, SPM, and sediment

The values of AHc in the water and SPM samples are shown in Table 1. The total AHc concentrations from n-C8 to n-C38 ranged from 3.59 to 21.5 μg L^{-1} in water and from 20.02 to 688.8 μg L^{-1} in SPM. Unresolved complex mixtures (UCM) were not detected in water but made an important contribution to the total AHc (between 18.47 and 584.1 μg L^{-1}) in SPM. The AHc content was higher in the granular phase (SPM) than in the dissolved phase due to the hydrophobic characteristic of these organic compounds. We observed high levels of AHc in the upper and middle reaches of the river in the water and SPM (stations X1–X5) due to the discharge of municipal wastewater directly from Shenyang city, but observed lower levels of AHc in downstream reaches (stations X6 and X7) due to attenuation of the contaminants.

To describe the AHc composition in these samples, the ratio of low- to high-molecular-weight compounds was calculated (Table 1); the LMW/HMW ratios ranged from 0.04 to 0.93 in water and from 0.17 to 0.70 in SPM, and the values were higher in the upper and middle reaches of the river than they were farther downstream. The ratios were all lower than 1, indicating that there were petroleum and terrigenous inputs at these stations [18]. Aquatic organic matter (<n-C21) is preferentially remineralized during the sinking of particles and at the water-sediment interface [19]. Fig. 2a shows the composition and distribution patterns for the individual n-alkanes and PAHs in water and SPM. There was no discernible pattern of odd- to even-numbered carbon compounds. However,

Table 1
Concentrations of AHc and PAHs, and the calculated distribution indices in water and SPM of the Xihe River, Shenyang, China.

Station	AHc (μg L^{-1})		UCM (μg L^{-1})		LMW/HMW		DOC (mg L^{-1})	PAHs (ng L^{-1})		HPAH/TPAH	
	Water	SPM	Water	SPM	Water	SPM	Water	Water	SPM	Water	SPM
X1	10.6	88.02	nd	73.46	0.93	0.17	66.74	115.8	1382	1.00	0.98
X2	12.6	688.8	nd	584.1	0.40	0.66	66.92	92.33	164.4	0.66	1.00
X3	16.0	202.4	nd	173.9	0.51	0.70	43.22	91.63	192.4	1.00	1.00
X4	8.89	176.0	nd	144.1	0.30	0.63	69.28	111.4	93.30	1.00	1.00
X5	21.5	195.1	nd	156.8	0.27	0.51	65.58	39.23	149.3	0.47	0.87
X6	15.0	101.5	nd	83.43	0.06	0.33	52.52	249.6	218.3	1.00	0.85
X7	3.59	20.02	nd	18.47	0.04	0.23	43.22	55.82	366.6	0.63	0.95

UCM: unresolved complex mixtures; AHc: the total concentration of n-alkanes (n-C$_8$ to n-C$_{38}$) and UCM; LMW/HMW ratio: low molecular weight n-alkanes (<n-C21)/high molecular weight n-alkanes (>n-C20) [18]; HPAH/TPAH: ratio of the concentration of PAHs with four to six rings to the total concentration of PAHs; nd: not detected.

n-C20 and n-C21 were dominant in water, and there were two main peaks in SPM: a short chain from n-C16 to n-C18 and a long chain from n-C25 to n-C30. Petroleum usually shows a wide distribution of n-alkane sizes and no dominance in the ratio of even to odd numbers of carbon atoms [20].

Tables 2 and 3 show that the concentration of AHc ranged from 180.8 to 760.9 μg g^{-1} in surface sediments and from 320.9 to 1126 μg g^{-1} dry weight in core sediments, and UCM accounted for an important proportion of these compounds (154.6–642.5 μg g^{-1} in the surface sediments and 236.0–869.5 μg g^{-1} in the core sed-

Fig. 2. Distribution of individual n-alkanes and PAHs in water and SPM.

iments). UCM are often attributed to petroleum contamination, as they have a well-known relationship to degraded or weathered petroleum residues [21]. The relative degree of persistent and degraded compounds can be gauged using the UCM/R ratio [22]. The UCM/R value ranged from 4.19 to 7.91 in surface sediments (Table 2) and from 2.69 to 4.86 in core sediments (Table 3), which confirmed the widespread presence of important petroleum-related residues.

We found a different trend in the surface sediments compared to the distribution of AHc in the water and SPM. The highest level of AHc were observed in the middle reaches (X3) and downstream reaches (X7) of the river due to the deposition and transportation of contaminants. In the core sediments, the highest AHc level was found in the 10- to 13-cm layer and the 45- to 48-cm layer, and the same trend was found for UCM (Table 3). This may represent two periods of heavy pollution (in the 1990 s and the 1960 s) based on the relationship between layer thickness (48 cm) and the deposition time (>40 years).

For the AHc composition in the sediments, the LMW/HMW indices ranged from 0.20 to 0.47 in surface sediments (Table 2) and from 0.32 to 0.73 in the core sediments (Table 3). Low-molecular-weight hydrocarbons from petroleum contamination that enter the water environment are reduced by degradation and weathering, whereas high-molecular-weight hydrocarbons are reserved and mineralized in sediment. Pristane and phytane are the products of the geological alteration of phytol and are often used as indicators of petroleum contamination and of the depositional environment [23]. In our study, the ratio of pristine to phytane ranged from 0.69 to 1.17 in surface sediments (Table 2) and from 0.49 to 0.79 in the core sediments (Table 3), which reflects petroleum contamination and an anaerobic environment in the Xihe River. Fig. 3a presents the composition and distribution patterns of the individual AHc in sediments. There was no clear pattern of carbon compounds with odd to even numbers of carbon atoms, but long-chain AHc (from n-C21 to n-C28) were the dominant form in the sediments.

3.2. PAHs in the water, SPM, and sediments

Table 1 presents the concentrations of 16 PAHs in water and SPM. The total PAH concentration ranged from 39.23 to 249.6 ng L^{-1} in water and from 93.30 to 1382 ng L^{-1} in SPM. The PAH concentration was higher in the granular phase than in the dissolved phase due to the hydrophobic characteristics of these organic compounds. With respect to the PAH composition, PAHs with four to six rings were the dominant form based on the ratio of high-molecular-weight PAHs to total PAHs (HPAH/TPAH; Table 1), which indicated that pyrolytic processes might be an important contaminant input source [24]. Most PAHs investigated were not detected, and only dibenzo[a,h]anthracene was present at high levels in water and SPM (Fig. 2b). There is no commercial production or known use of dibenz[a,h]anthracene. It occurs as a component of coal tars, shale oils, and soots [25], and this might suggest that there is still simi-
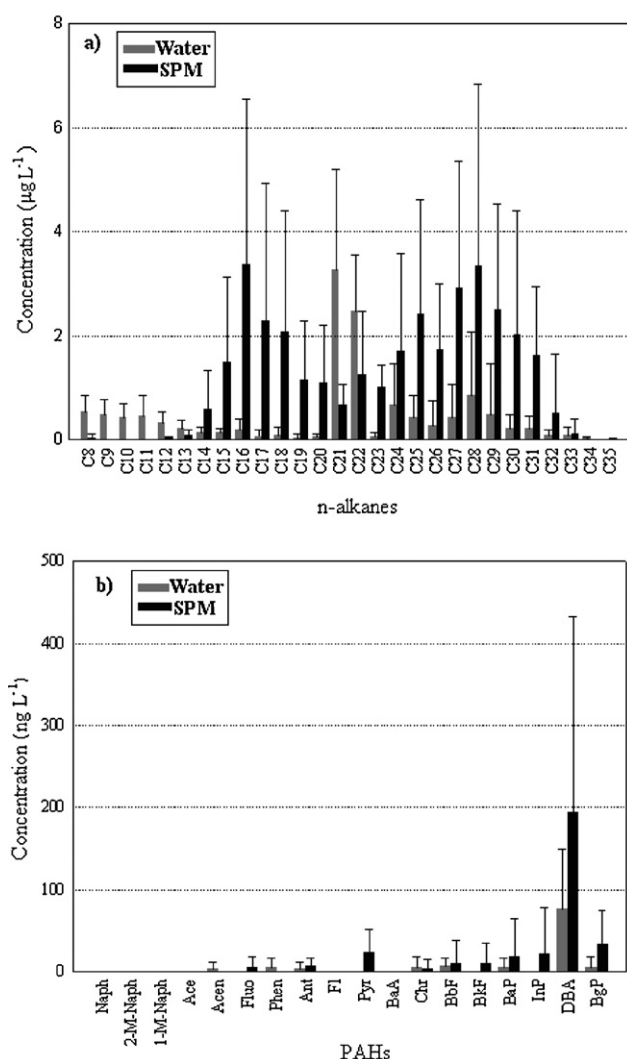
Table 2
Concentrations of AHc and PAHs, and calculated distribution indices in surface sediments collected at six stations along the Xihe River, Shenyang.

Sample	AHc (μg g^{-1})	UCM (μg g^{-1})	LMW/HMW	UCM/R	Pr/Ph	TOC (%)	PAHs (μg g^{-1})	L/H	Flu/Flu + Pyr	InP/InP + BgP
X1	218.3	193.8	0.47	7.91	0.71	8.54	11.1	0.48	0.56	0.29
X3	760.9	642.5	0.34	5.42	0.71	7.48	12.9	0.10	0.57	0.09
X4	180.8	154.6	0.22	5.90	1.17	3.87	0.34	0.06	0.54	0.38
X5	193.0	168.2	0.28	6.78	0.71	4.64	5.07	0.15	0.62	0.54
X6	233.8	196.9	0.39	5.33	0.96	5.98	1.52	0.29	0.40	0.38
X7	736.4	594.5	0.20	4.19	0.69	23.36	2.63	0.10	0.55	0.76

AHc: the total concentration of the n-alkanes (n-C$_8$ to n-C$_{38}$) and UCM; LMW/HMW ratio: low molecular weight n-alkanes (<n-C21)/high molecular weight n-alkanes (>n-C20) [18]; UCM/R: ratio of unresolved compounds to resolved compounds in gas chromatography; Pr: pristine; Ph: phytane; Flu: fluoranthene; Pyr: pyrene; InP: indeno[1,2,3-cd]pyrene; BgP: benzo[ghi]perylene; L/H ratio: ratio of the concentration of PAHs with two to three rings to the total concentration of PAHs with four to six rings.

lar pollution entering the Xihe River due to wastewater discharge and/or atmospheric fallout.

Tables 2 and 3 present total PAHs in the surface and core sediments from the Xihe River. The concentrations ranged from 0.34 to 12.9 μg g^{-1} dry weight in surface sediments and from 1.14 to 18.8 μg g^{-1} dry weight in the core sediments. Unlike AHc in sediments, high levels of PAHs were observed to have accumulated in surface sediments in the upper and middle reaches of the river (stations X1 and X3) due to direct wastewater discharge and the persistence of PAHs in the environment. In the core sediments, the distribution of PAHs concentration generally decreased with increasing depth (Table 3). Compared to the distribution of individual PAHs in water and SPM, many more individual PAHs were detected in sediments. PAHs with four to five rings were dominant in sediments (Fig. 3b). Similar PAH concentrations and compositions have been previously reported in soils of wastewater irrigation areas in Shenyang City [26], which may indicate similar input sources.

PAHs enter the river environment mainly via atmospheric fallout, urban runoff, municipal and industrial effluents, and oil leakage [27,28]. The source of PAHs is mainly anthropogenic [29], and these compounds are formed mainly via two mechanisms: fuel combustion (pyrolytic) and the discharge of crude oil byproducts (petrogenic). Their source can be identified by the ratios of individual PAH compounds, which differ among emission sources [17]. The ratio of low-molecular-weight PAHs to high-molecular-weight PAHs (L/H) ranged from 0.10 to 0.48 in surface sediments (Table 2) and from 0.09 to 3.14 in the core sediments (Table 3). This indicates that the PAHs had mixed sources, including both petro-genic and pyrolytic sources [24]. The ratios of Flu/(Flu + Pyr) and InP/(InP + BgP) confirmed the complexity of the PAH sources, with pyrolytic sources related to combustion of fossil fuels and crude oil [30].

3.3. The role of organic carbon in hydrocarbon concentrations

The dissolved organic carbon (DOC) in water ranged from 43.22 to 69.28 mg L^{-1} (Table 1), and the total organic carbon (TOC) in sediments ranged from 3.87 to 32.4% (Tables 2 and 3). These levels of organic carbon were high compared with the values in natural water columns [31,32], indicating that the study area was polluted. The organic matter in sediments generally plays an important role in controlling the distribution of many organic pollutants [32,33]. However, the only positive correlation observed was between TOC and PAHs ($r = 0.62$, $P = 0.001$, $n = 24$), which might be because the TOC and PAHs were mainly from the release of untreated wastewater, and PAHs have a highly hydrophobic nature and more easily tend to associate with the underlying sediments [34].

3.4. Assessment of contamination

Hydrocarbon pollutants endanger both ecosystems and human health. The concentrations of AHc detected in water, SPM, and sediments of the Xihe River were high enough to be close to the values characterizing areas with heavy petroleum pollution, such as the Black Sea (2–300 μg g^{-1} in sediments) [23], the coastal area near the Shuaiba industrial area (6.70–2067 μg g^{-1} in sediments) [29], Bassein-Mumbai (2.90–39.2 μg L^{-1} in water; 0.90–108 μg g^{-1} in

Table 3
Concentrations of AHc and PAHs, and the calculated distribution indices, in the core sediments of the Xihe River, Shenyang.

Sample	AHc (μg g^{-1})	UCM (μg g^{-1})	LMW/HMW	UCM/R	Pr/Ph	TOC (%)	PAHs (μg g^{-1})	LMW/HMW	Flu/Flu + Pyr	InP/InP + BgP
0–2 cm	446.3	361.8	0.32	4.29	0.61	26.9	14.7	0.82	0.65	0.73
2–4 cm	482.5	387.7	0.40	4.09	0.54	26.7	10.8	3.14	0.65	0.44
4–6 cm	480.8	397.5	0.41	4.77	0.59	24.7	5.15	1.35	0.89	0.37
6–8 cm	512.9	410.7	0.42	4.02	0.55	24.8	13.9	1.81	0.56	0.30
8–10 cm	514.5	422.2	0.49	4.57	0.49	29.9	18.4	0.99	0.54	0.44
10–13 cm	936.9	751.0	0.34	4.04	0.63	30.0	11.6	0.20	0.75	0.22
13–16 cm	507.0	420.5	0.53	4.86	0.60	29.0	11.2	0.65	0.52	0.67
16–19 cm	489.5	399.5	0.60	4.43	0.63	30.1	18.8	1.30	0.47	0.13
19–21 cm	559.5	454.5	0.54	4.33	0.60	26.5	9.27	1.21	0.45	0.48
21–24 cm	428.9	338.8	0.48	3.76	0.53	24.5	15.3	2.21	0.52	0.47
24–27 cm	489.3	386.1	0.49	3.74	0.54	26.6	7.58	1.98	0.51	0.41
27–30 cm	390.8	295.6	0.52	3.11	0.68	22.4	6.78	1.18	0.53	0.54
30–33 cm	632.8	487.3	0.63	3.35	0.61	32.4	9.94	1.78	0.52	0.89
33–36 cm	638.5	505.8	0.46	3.81	0.63	19.7	2.46	0.34	0.68	0.61
36–39 cm	320.9	236.0	0.51	2.78	0.59	19.2	2.63	0.37	0.62	0.87
39–42 cm	482.1	351.4	0.40	2.69	0.52	8.50	3.91	0.09	0.62	0.09
42–45 cm	463.6	362.5	0.40	3.59	0.50	7.47	1.91	0.25	0.97	0.87
45–48 cm	1126	869.5	0.73	3.39	0.79	4.17	1.14	0.12	0.03	0.69

AHc: the total concentration of the n-alkanes (n-C$_8$ to n-C$_{38}$) and UCM; LMW/HMW ratio: low molecular weight n-alkanes (<n-C21)/high molecular weight n-alkanes (>n-C20) [18]; UCM/R: ratio of unresolved compounds to resolved compounds in gas chromatography; Pr: pristine; Ph: phytane; Flu: fluoranthene; Pyr: pyrene; InP: indeno[1,2,3-cd]pyrene; BgP: benzo[ghi]perylene; L/H ratio: ratio of the concentration of PAHs with two to three rings to the total concentration of PAHs with four to six rings.
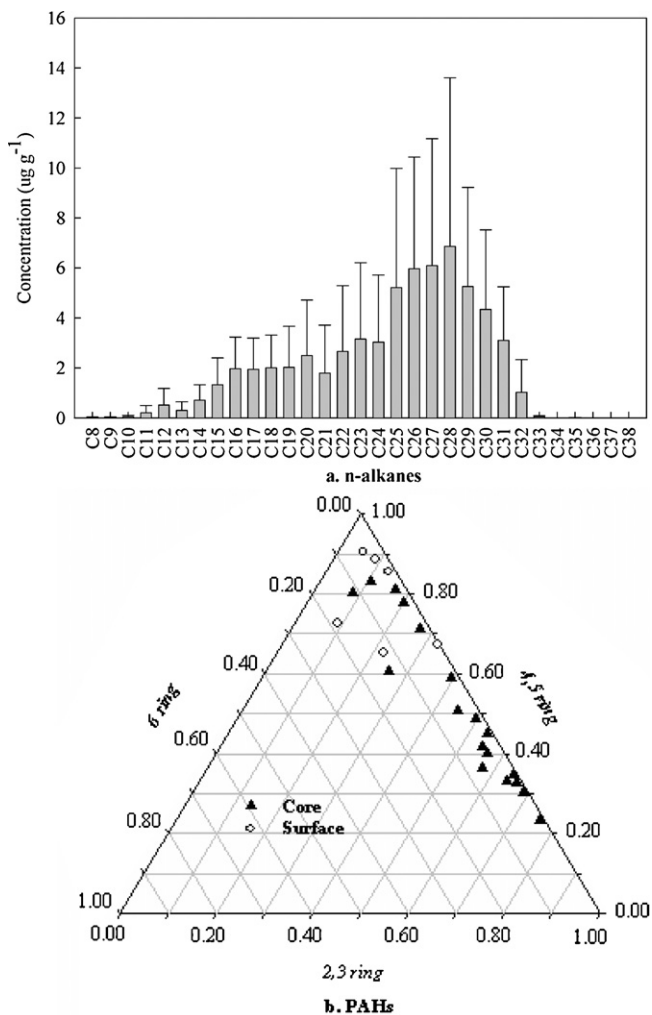
Fig. 3. Distribution of individual (a) n-alkanes and (b) PAHs with different numbers of rings in surface and core sediments from the Xihe River.

sediments) [7], and the Arabian Gulf (779 μg g^{-1} in sediments) [34]. UNEP [35] defines hydrocarbon concentrations in heavily polluted sediments as levels greater than 10 μg g^{-1} dry weight. Large quantities of AHc are gradually deposited and transported downstream by water currents in these areas, spreading the pollution beyond its source region.

The PAH concentrations in water and SPM were low compared to those in Taiwan's heavily polluted Gao-Ping River (10–9400 ng L^{-1} in water) [36], the river in Tianjing (45.81–1272 ng L^{-1} in water and 938–64,200 ng g^{-1} in SPM) [32], and the Seine River and estuary (4–36 ng L^{-1} in water and 1000–14,000 ng g^{-1} in SPM) [37]. Compared to PAH concentrations reported in the literature for domestic wastewater, the total concentrations measured in the Xihe River water column, including both the water and SPM, reached levels as high as those reported by Gasperi et al. [38] (from 0.24 to 3.1 μg L^{-1}). However, total PAHs concentration was high in sediments, with levels close to those in the most contaminated estuaries, bays, and rivers of economically developed areas around the world, such as China's Jiulong River Estuary (59–1177 ng g^{-1}) [39], Spain's Santander Bay (20–344,600 ng g^{-1}) [40], Narragansett Bay (569–216,000 ng g^{-1}) [41], and Tianjing in China (787–1,943,000 ng g^{-1}) [17].

We observed that sediments accumulated more AHc and PAH compounds than the water, especially in the core sediments, indicating long-term inputs of AHc and PAHs from wastewater discharge during the past 40 years. Pollution of the river by petroleum

hydrocarbons occurs mainly through human activities: approximately 65.3% of these substances is discharged through municipal and industrial wastes, urban and river runoff, oceanic dumping, and atmospheric fallout; 26.2% is derived from discharges during transportation, dry docking, tanker accidents, and de-blasting, etc.; and the remaining 8.50% comes from fixed installations such as coastal refineries, offshore production facilities, and marine terminals [42]. Under high loads of organic matter from through sewage and other anthropogenic sources, river sediments are expected to be anoxic [9], and as a result, petroleum residues deposited in the sediments are expected to be preserved due to very low rates of microbial degradation [43]. A number of new sewage treatment plants have been established in the upper reaches of the Xihe River, and improved monitoring of the Xihe River's environment will allow managers to regulate the discharge of wastewater and wastes from Shenyang, reducing future concentrations of AHc and PAHs in the water.

3.5. Toxicity assessment for PAHs in sediments

PAHs always occur in sediments as a complex mixture of compounds, leading to cumulative effects on the ecological environment [44]. The mean concentration of PAHs (8292 ng g^{-1}) in the sediments of the Xihe River was higher than the low effects range (ER-L = 4022 ng g^{-1}), but less than the median effects range (ER-M = 44,792 ng g^{-1}) [45], indicating that there are negative biological effects of PAHs in the Xihe River's sedimentary environment.

The equivalent concentrations of PAHs such as benzo[a]pyrene and 2378-TCDD (a dioxin) based on the values of the toxic equivalency factor (TEF) and the calculated toxic equivalent (TEQ) for BaP (TEQ$_{BaP}$) and dioxins (TEQ$_{TCDD}$) values were determined to assess the toxicity and carcinogenic potential of the PAHs [46,47]. The total toxic equivalent for all PAHs was calculated using the following equation:

$$TEQ_{BaP} = \sum C_i \times TEF_i$$

where C_i is the concentration of PAHs, and i is the number of PAHs. Given the agreement of the selected parameters between the TEQ$_{BaP}$ and TEQ$_{TCDD}$, the high molecular weight PAHs, including BaA, Chr, BbF, BkF, BaP and InP, were used to calculate the toxic potency. Table 4 summarizes the toxic equivalency factors and concentrations of these PAHs. The average TEQ$_{BaP}$ in the Xihe River sediments was 601 in the core sediments and 808 in surface sediments. Dibenzo[a,h]anthracene (68%) and benzo(a)pyrene (25%) were the individual PAHs that contributed most to the total TEQ$_{BaP}$. The average TEQ$_{TCDD}$ was 2.27 in surface sediments and 1.96 in the core sediments. Dibenzo[a,h]anthracene (45%) and benzo[k]fluoranthene (36%) were the individual PAHs that contributed most to the total TEQ$_{BaP}$. The high proportion of dibenzo[a,h]anthracene in the TEQ value may indicate that the risk posed by PAHs in sediments in the study area can be represented by the concentration of this compound. This differs from the results of other studies in which the toxicity of PAHs was based on benzo(a)pyrene [47]. This difference may result from different pollution sources and different sediment properties. In our study, dibenzo[a,h]anthracene is the major component of the PAHs in the water, which confirms that it may serve as a good indicator of PAH levels. We found a strong and significant linear correlation between TEQ$_{BaP}$ and TEQ$_{TCDD}$ (r = 0.85, P < 0.0001, n = 24) (Fig. 4), which suggests that TEQ$_{BaP}$ and TEQ$_{TCDD}$ present a consistent assessment of the PAH levels in sediments. The potential toxicity of PAHs is higher in surface sediments than that in deep sediments, which may indicate that recent contamination levels are higher than they were in the past. The TEQ value, including both TEQ$_{BaP}$ and TEQ$_{TCDD}$, was higher in the sediments of the Xihe River than was found in pre-

Table 4
Average concentrations of PAHs in sediments, and the toxic equivalent (TEQ) and toxic equivalency factor (TEF) values.

PAHs	TEF_{BaP}[a]	TEF_{TCDD}[b]	Mean PAH concentration in sediment (ng g^{-1})	
			Surface	Core
Benzo(a)pyrene	0.10	0.000025	210	86.4
Chrysene	0.01	0.00020	790	495
Benzo[b]fluoranthene	0.10	0.0025	18.8	61.9
Benzo[k]fluoranthene	0.10	0.0048	180	143
Benzo[a]pyrene	1.00	0.00035	247	114
Dibenzo[a,h]anthracene	1.00	0.0020	503	446
Indeno[1,2,3-cd]pyrene	0.10	0.0011	85.3	69.9
ΣPAHs	–	–	2034	1415
TEQ_{BaP}	–	–	808	601
TEQ_{TCDD}	–	–	2.27	1.96

[a] Toxic equivalency factors based on benzo(a)pyrene (BaP) [47].
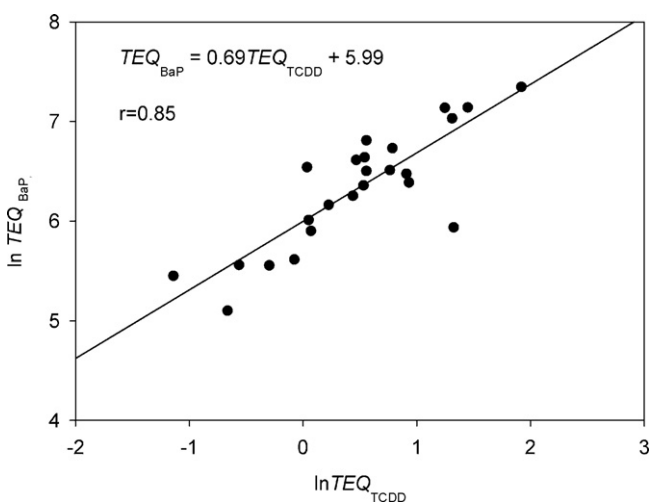[b] Toxic equivalency factors based on 2378-TCDD (dioxin) [49].

Fig. 4. The correlation between TEQ_{TCDD} and TEQ_{BaP} for sediments in the Xihe River.

vious research [48,49]. This indicates that a serious ecological risk exists in the Xihe River.

4. Conclusions

In this study, we investigated contamination by petroleum hydrocarbons, including aliphatic hydrocarbons (AHc) and polycyclic aromatic hydrocarbons (PAHs), in the water and sediments of the Xihe River, an urban river in Shenyang, China. We found long-term contamination caused by the discharge of wastewater from Shenyang, leading to high levels of AHc and PAHs in the Xihe River water and sediments. The high organic carbon levels that we detected indicated that the study area was severely polluted, and the high levels of AHc and PAHs in the sediments might be strongly affected by this pollution. The concentrations of the organic pollutants that we measured were highest in the sediments, followed by the levels in SPM and water. Substances with high molecular weight were more abundant than those with low molecular weight in the AHc and PAH fractions. The distribution and composition of both AHc and PAHs varied greatly between the water, SPM, and sediments, possibly as a result of temporal variation in the historical inputs from various contamination sources. The AHc were mainly derived from petroleum contamination and wastewater discharge, whereas PAHs came from both pyrolytic (combustion of fossil fuels) and petrogenic sources (from wastewater discharge and atmospheric fallout). The discharge of wastewater from industrial and municipal sources in Shenyang is the main source of the AHc and PAHs. Based on our results, the sediments in this river present a danger of high potential toxicity for soils and shallow groundwater near the river. Although the concentrations of individual hydrocarbons varied, dibenzo[a,h]anthracene (DBA) accounted for the majority of the toxic equivalent values and can potentially be used as an overall indicator of PAH toxicity in the sediments of the Xihe River.

References

[1] G. Magazzù, G. Romeo, F. Azzaro, F. Decembrini, F. Oliva, A. Piperno, Chemical pollution from urban and industrial sewages in Augusta Bay (Sicily), Water Sci. Technol. 32 (1995) 221–229.
[2] P. Thanh-Thao, P. Suzie, B. Charles, M. Serge, Composition of PCBs and PAHs in the Montreal urban community wastewater and in the surface water of the St. Lawrence River (Canada), Water Air Soil Pollut. 111 (1998) 251–270.
[3] Q. Shen, K.Y. Wang, W. Zhang, S.C. Zhang, X.J. Wang, Characterization and sources of PAHs in an urban river system in Beijing, China, Environ. Geochem. Health 31 (2009) 453–462.
[4] Y.F. Song, B.M. Wilke, X.Y. Song, P. Gong, Q.X. Zhou, G.F. Yang, Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals (HMs) as well as their genotoxicity in soil after long-term wastewater irrigation, Chemosphere 65 (2006) 1859–1868.
[5] R.E. Countway, R.M. Dickhut, E.A. Canuel, Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary, Org. Geochem. 34 (2003) 209–224.
[6] S.A. Stout, A.D. Uhler, S.D. Emsbo-Mattingly, Comparative evaluation of background anthropogenic hydrocarbons in surficial sediments from nine urban waterways, Environ. Sci. Technol. 38 (2004) 2987–2994.
[7] M.K. Chouksey, A.N. Kadam, M.D. Zingde, Petroleum hydrocarbon residues in the marine environment of Bassein-Mumbai, Mar. Pollut. Bull. 49 (2004) 637–647.
[8] H.M. Ren, J.D. Wang, X.L. Zhang, Assessment of soil lead exposure in children in Shenyang, China, Environ. Pollut. 144 (2006) 327–335.
[9] P.D. Tai, P.J. Li, T.H. Sun, Y.F. Song, M. Mizuochi, Y. Inamori, CH4 emission from Xihe canal for drainage of municipal sewage in Shenyang City, Acta. Sci. Circumst. 23 (2003) 138–141 (in Chinese).
[10] D. Saucedo, T.W. Sammis, G.A. Picchioni, J.G. Mexal, Wastewater application and water use of Larrea tridentate, Agric. Water Manage. 82 (2006) 343–353.
[11] S.J. Pang, A.L. Jing, C. Liu, Characteristics analysis for contaminative sediment of Xihe, Environ. Prot. Sci. 29 (2003) 30–31 (in Chinese).
[12] X.Y. Song, L.N. Sun, X. Wang, X.X. Li, T.H. Sun, Organic contamination status of Xihe River surface water and its riverbank underground water, Chin. J. Ecol. 26 (2007) 2057–2061 (in Chinese).
[13] B.X. Mai, J.M. Fu, G. Zhang, Z. Lin, Y. Min, G. Sheng, X. Wang, Polycyclic aromatic hydrocarbons in sediments from the Pearl river and estuary, China: spatial and temporal distribution and sources, Appl. Geochem. 16 (2001) 1429–1445.
[14] I. Tolosa, S.D. Mora, M.R. Sheikholeslami, J.P. Villeneuve, J. Bartocci, C. Cattini, Aliphatic and aromatic hydrocarbons in coastal Caspian sea sediments, Mar. Pollut. Bull. 48 (2004) 44–60.
[15] W. Guo, M.C. He, Z.F. Yang, C.Y. Lin, X.C. Quan, H.Z. Wang, Distribution of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River watershed, China, Chemosphere 68 (2007) 93–104.

[16] W. Guo, M.C. He, Z.F. Yang, C.Y. Lin, X.C. Quan, H.Z. Wang, Occurrence of aliphatic hydrocarbons in water, suspended particulate matter and sediments of Daliao River system, China, Bull. Environ. Contam. Toxicol. 84 (2010) 519–523.

[17] Z. Shi, S. Tao, B. Pan, W. Fan, X.C. He, Q. Zuo, S.P. Wu, B.G. Li, J. Cao, W.X. Liu, F.L. Xu, X.J. Wang, W.R. Shen, P.K. Wong, Contamination of rivers in Tianjin, China by polycyclic aromatic hydrocarbons, Environ. Pollut. 134 (2005) 97–111.

[18] M.P. Zakaria, S. Tsutsumi, K. Ohno, J. Yamada, E. Kouno, H. Kumata, Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs, Environ. Sci. Technol. 36 (2002) 1907–1918.

[19] F.G. Prahl, L.A. Muehlhausen, Lipid biomarkers as geochemical tools for paleooceanographic study, in: W.H. Berger, V.S. Smetacek, G. Wefer (Eds.), Productivity of the Ocean: Present and Past, Wiley, Chichester, 1989, pp. 271–289.

[20] M.G. Commendatore, J.L. Esteves, Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina), Mar. Pollut. Bull. 48 (2004) 910–918.

[21] J.M. Readman, R.F.C. Mantoura, M.M. Rhead, A record of polycyclic aromatic hydrocarbons (PAH) pollution obtained from accreting sediments of the Tamar estuary, UK: Evidence for non equilibrium behaviour of PAH, Sci. Total Environ. 66 (1987) 73–94.

[22] B.R.T. Simoneit, Some applications of computerized GC-MS to the determination of biogenic and anthropogenic organic matter in environment, Int. J. Environ. Anal. Chem. 12 (1982) 177–193.

[23] J.W. Readman, G. Fillmann, I. Tolosa, J. Bartocci, J.P. Villeneuve, C. Catini, L.D. Mee, Petroleum and PAH contamination of the Black Sea, Mar. Pollut. Bull. 44 (2002) 48–62.

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

[25] IARC (International Agency for Research on Cancer), IARC monographs on the evaluation of the carcinogenic risk of chemicals to, humans. Polynuclear aromatic compounds, Part 4, bitumens, coal-tars and derived products, shale-oils and soots, in: IARC Monographs on the Evaluation of Carcinogenic Risk of the Chemical to Man, vol. 35, World Health Organization, Lyon, France, 1985, pp. 88, 91, 164, 225.

[26] X.J. Li, P.J. Li, X. Lin, Z.Q. Gong, S.X. Fan, Z. Le, E.A. Verkhozina, Spatial distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in soils from typical oil-sewage irrigation area, Northeast China, Environ. Monit. Assess. 143 (2008) 257–265.

[27] J. Tolosa, J.M. Bayona, J. Albaiges, Aliphatic and polycyclic aromatic hydrocarbons and sulfur/oxygen derivatives in northwestern Mediterranean sediments: spatial and temporal variability, fluxes, and budgets, Environ. Sci. Technol. 30 (1996) 2495–2503.

[28] D.L. Wetzel, E.S. Van Vleet, Accumulation and distribution of petroleum hydrocarbons found in mussels (*Mytilus galloprovincialis*) in the canals of Venice, Italy, Mar. Pollut. Bull. 48 (2004) 927–936.

[29] M.U. Beg, T. Saeed, S. Al-Muzaini, K.R. Beg, M. Al-Bahloul, Distribution of petroleum hydrocarbon in sediment from coastal area receiving industrial effluents in Kuwait, Ecotoxicol. Environ. Safe. 54 (2003) 47–55.

[30] X.J. Luo, S.J. Chen, B.X. Mai, Y.P. Zeng, G.Y. Sheng, J.M. Fu, Distribution and sources of polycyclic aromatic hydrocarbons in sediments from rivers of Pearl River delta and its nearby South China Sea, Environ. Sci. 25 (2005) 129–134 (in Chinese).

[31] K.H. Johannesson, J.W. Tang, J.M. Daniels, W.J. Bounds, D.J. Burdige, Rare earth element concentrations and speciation in organic rich blackwater of the Great Dismal Swamp, Virginia, USA, Chem. Geol. 209 (2004) 271–294.

[32] Z. Shi, S. Tao, B. Pan, W.X. Liu, W.R. Shen, Partitioning and source diagnostics of polycyclic aromatic hydrocarbons in rivers in Tianjin, China, Environ. Pollut. 146 (2007) 492–500.

[33] S.E. McGroddy, J.W. Farrington, Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts, Environ. Sci. Technol. 29 (1995) 1542–1550.

[34] I. Tolosa, S.J. de Mora, S.W. Fowler, J.P. Villeneuve, J. Bartocci, C. Cattini, Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf and the Gulf of Oman, Mar. Pollut. Bull. 50 (2005) 1619–1633.

[35] UNEP, Determination of Petroleum Hydrocarbons in Sediments, Reference Methods For Marine Pollution Studies, United Nations Environment Programme, 1992, No. 20.

[36] R. Doong, Y.T. Lin, Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan, Water Res. 38 (2004) 1733–1744.

[37] M.B. Fernandes, M.A. Sicre, A. Boireau, J. Tronczynski, Polyaromatic hydrocarbon (PAH) distribution in the Seine River and its estuary, Mar. Pollut. Bull. 34 (1997) 857–867.

[38] J. Gasperi, V. Rocher, S. Azimi, S. Garnaud, G. Varrault, R. Moilleron, Contribution of domestic effluents to hydrocarbon levels of dry weather flow in combined sewers, Urban Water. J. 3 (2006) 225–233.

[39] K. Maskaoui, J.L. Zhou, H.S. Hong, Z.L. Zhang, Contamination by polycyclic aromatic hydrocarbons in the Jiulong River estuary and western Xiamen Sea, China, Environ. Pollut. 118 (2002) 109–122.

[40] J. Viguri, J. Verde, A. Irabien, Environmental assessment of polycyclic aromatic hydrocarbon (PAHs) in surface sediments of the Santander Bay, Northern Spain, Chemosphere 48 (2002) 157–165.

[41] P.C. Hartmann, J.G. Quinn, R.W. Cairns, J.W. King, The distribution and sources of polycyclic aromatic hydrocarbons in Narragansett Bay surface sediments, Mar. Pollut. Bull. 48 (2004) 359–370.

[42] GESAMP, Impact of Oil and Related Chemicals and Wastes on the Marine Environment Reports and Studies, vol. 50, IMO/FAO/UNESCO/WHO, Joint Group of Experts on the Scientific Aspect of Marine Pollution (GESAMP), IMO, London, 1993, p. 180.

[43] IOC-UNESCO, The Determination of Petroleum Hydrocarbons in Sediments, Manuals and Guides No. 11, 1982, p. 38.

[44] R.A. Hites, R.E. Laflamme, J.G. Windsor Jr., Polycyclic aromatic hydrocarbons in marine/aquatic sediments: their ubiquity, Adv. Chem. Ser. 185 (1980) 289–311.

[45] E.R. Long, D.D. MacDonald, S.L. Smith, F.D. Calder, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, Environ. Manage. 19 (1995) 81–97.

[46] P. Norramit, V. Cheevaporn, N. Itoh, K. Tanaka, Characterization and carcinogenic risk assessment of polycyclic aromatic hydrocarbons in the respirable fraction of airborne particles in the Bangkok metropolitan area, J. Health. Sci. 51 (2005) 437–446.

[47] Z. Wang, J.W. Chen, P. Yang, X.L. Qiao, F.L. Tian, Polycyclic aromatic hydrocarbons in Dalian soils: distribution and toxicity assessment, J. Environ. Monitor. 9 (2007) 199–204.

[48] V.M. Savinov, T.N. Savinova, G.G. Matishov, S. Dahle, K. Naes, Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) in bottom sediments of the Guba Pechenga, Barents Sea, Russia, Sci. Total. Environ. 306 (2003) 39–56.

[49] M. Qiao, C.X. Wang, S.B. Huang, D.H. Wang, Z.J. Wang, Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China, Environ. Int. 32 (2006) 28–33.