

Concentrations, Sources and Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Soils of Liaohe Estuarine Wetland

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Abstract Concentration, source, and risk of PAHs were investigated in 31 sites from surface soils of Liaohe estuarine wetland. Total PAHs concentrations ranged from 293.4 to 1735.9 ng/g with a mean of 675.4 ng/g. The 3- and 4-ring PAHs were the dominant species. The ratios of high-molecular weight PAHs to low-molecular weight PAHs and anthracene/(anthracene+phenanthrene) were calculated to apportion sources of PAHs. It was found that both pyrogenic and petrogenic PAHs sources were important. Effect range low and effect range median showed that the PAHs would occasionally cause adverse effects. The nemerow composite index revealed that about 41.9% soil sampling sites were safety; about 58.1% sites had different grades of PAHs pollution.

Keywords PAHs · Isomer ratio · Effect range low and effect range median · The nemerow composite index

PAHs are one of the most important classes of persistent organic contaminants that have been of scientific interest for several decades due to their widespread distribution in the environment and their impact on public health and the environment. These compounds exhibit mutagenic, carcinogenic and teratogenic effects and endocrine-disrupting activities (Zedeck 1980; Santodonato 1997). PAHs are

usually introduced into the environment as a result of anthropogenic activities, mainly including incomplete combustion of fossil fuel and burning of vegetation and organic matter. The estuaries are characterized by an immense biological diversity, a huge temporary variability in their environmental parameters as well as receiving large quantities of organic terrestrial matter and along with these, strange substances of a very diverse origin (Ruiz et al. 2011). Due to their ubiquity and persistence nature, soil ecosystem is an effective sink of PAHs. PAHs in soil may lead to direct or indirect exposure in humans. Therefore, studies on soil contamination by PAHs are crucial for protecting of human health and environment security. Information about PAHs contamination in soils of estuarine is essential in pollution control, management decisions and remediation. The objectives of the present work were to investigate the concentration levels and compositional characteristics of PAHs in soils of Liaohe estuarine wetland, to provide data for comparison with other soils, to identify the possible sources of PAHs by diagnostic ratios and to evaluate their risk.

Materials and Methods

Liaohe estuarine wetland surface soils were collected in 31 sites in August 2009 (in Fig. 1). Approximately the top 0–20 cm of soil was collected by a stainless steel grab sampler. All samples were frozen on dry ice immediately and transported to the laboratory with no exposure to light. In the laboratory samples were defrosted and ground to pass through a 100-mesh sieve and then stored in the pre-combusted amber glass jar in the dark at 4°C until analysis.

Standard mixture containing 16 PAHs (16 compounds specified in USEPA method 610) and deuterated PAHs

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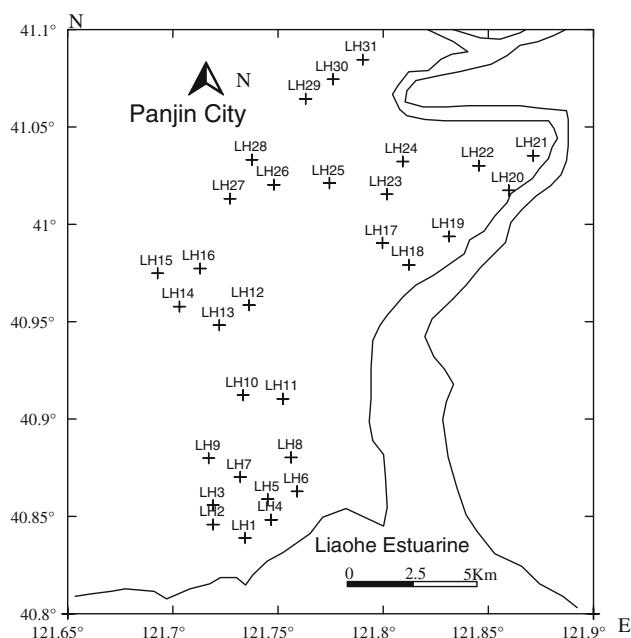


Fig. 1 Sampling sites of soils in Liaohe estuarine wetland

internal standard mixture (naphthalene-d₈; acenaphthene-d₁₀; phenanthrene-d₁₀ and chrysene-d₁₂) were procured from Supelco (Bellefonte, PA, USA). All solvents used for sample processing and analysis were of gas chromatograph grade.

Briefly, freeze-dried and sieved soil subsamples (2.0 g) were mixed with anhydrous sodium sulfate and extracted twice with 20.0 mL n-hexane/dichloromethane (1:1 v/v). The extracts were concentrated to 1.0 mL by rotary vacuum evaporation and then purified and fractionated using the fully activated alumina/silica gel chromatographic column. The extracts were eluted with 30.0 mL dichloromethane/n-hexane (3:7 v/v). The PAHs fractions were concentrated to 1 mL under a gentle stream of nitrogen for instrumental analysis.

The analyses were performed using a Shimadzu 2010 series gas chromatograph equipped with a 30 m SPB-5 capillary column (0.32 mm i.d. and 0.25 µm film thickness). Samples containing PAHs were injected in the splitless mode of 1 µL using autosampler and subsequently analyzed by flame ionization detector. The gas chromatograph conditions for analysis were as follows: the injection port was set at 250°C. The column initial temperature was held at 80°C for 1 min, 15°C/min to 255°C with a holding time of 1 min, then at 1°C/min to 265°C, held for 1 min, and finally at 2.5°C/min to 295°C with a final holding time of 5 min. Helium/air was used as the carrier gas at a flow rate of 1.1 mL/min.

Recoveries ranged from 74.3% to 92.2% for all 16 target PAHs in soil samples. All samples were analyzed in quadruplicate, and the relative standard deviation varied from

1.5% to 18.1%. The limits of detection for the 16 PAHs were defined as three times signal-to-noise ratio and were between 0.1 and 0.5 ng/g. The method detection limit for the 16 PAHs were between 3.9 and 21.1 ng/g. All of the data were expressed on a dry weight basis.

Results and Discussion

The total concentrations of 16 PAHs in the present study varied greatly depending on the sampling location and ranged from 293.4 to 1735.9 ng/g with a mean value of 675.4 ng/g. The highest pollution levels were observed in site LH28, followed by sites LH27 and LH26 where oil wells located nearby them. The lowest concentrations of PAHs occurred in sites LH3, LH1 and LH2, probably due to the fact that these sites are far from extensive anthropogenic activities. Fluorene in all sites were 1,499.2 ng/g and the concentrations measured in sites LH26–LH28 were found to be 462.1 ng/g, contributing 30.8% of the total value. In comparison with other studies, observed concentrations were comparable to the corresponding concentration of 417.4 ng/g in Baiyangdian area (Zhao et al. 2009). The PAHs concentrations in this study were lower than those reported in vegetable soils of the Pearl River Delta (Cai et al. 2007) and urban soil of Beijing (Tang et al. 2005), in which the mean concentrations of PAHs were 1,503.0 and 3,917.0 ng/g, respectively. The levels of PAHs in the study area were significantly higher compared to the Yellow River Delta (Yuan et al. 2008) and soil of Yangtze Delta (Ping et al. 2007), where the average concentration of PAHs were 71.1 and 395.0 ng/g, respectively. As can be seen, the degree of soil contamination by PAHs in this study was moderate in comparison with some reported soils. To date, no guideline for assessing PAHs in soils has been developed specifically for China and only a few recommendations or guidelines exist worldwide. The concentration of about 100.0 ng/g is typical in the areas where no anthropogenic pollution sources occur (Trapido 1999). Also it has been suggested (Edwards 1983) that the typical endogenous PAHs in soil, resulting from plant synthesis and natural fires is in the range of 1.0–10.0 ng/g. Overall, soils from Liaohe estuarine wetland were contaminated above the natural level. The values in most stations were much higher than the guideline values in soils of Dutch (20.0–50.0 ng/g), mathematically indicating that majority of the sites contained relatively high PAHs concentrations. According to Polish standards, PAH levels can be characterized as pollution class I, II, III and IV when the sum of PAHs concentrations are 200.0–600.0, 600.0–1,000.0, 1,000.0–5,000.0 and 5,000.0–10,000.0 ng/g, respectively. On the basis of Polish standards, sites LH23, LH26–LH28 can be classified under pollution class III, i.e. polluted.

The composition pattern of PAHs by ring size in the soil was shown in Fig. 2. The 3- and 4-ring PAHs, accounting for 36.6% and 22.8% of the total PAHs concentrations respectively, were the most abundant in the samples. Concentrations of 6-ring PAHs were very low, only contributed 0.6%–26.4% to the total PAHs. Overall, except for sites LH11–13, LH18, LH20–LH22, samples were primarily enriched in low-molecular weight PAH (2–3 rings PAH = 54.1%–69.4%) and depleted in high-molecular weight PAH (4–6 rings = 30.6%–45.9%). In contrast, sites LH11–LH13, LH18, LH20–LH22 had different proportion of each PAH composition, in which 2–3 rings PAHs and 4–6 rings PAHs accounted for 41.1%–49.0% and 51.0%–58.9%, respectively. Naphthalene, as the sole 2-ring PAH in this study, occupied a relatively high percentage and accounted for 20.4% of the total PAHs concentrations. The 3-ring

PAHs of acenaphthene, phenanthrene, fluorene and the 4-ring PAHs of pyrene dominated in this area, each accounting for 11.0%, 10.2%, 7.2%, and 7.9% of the total concentrations, respectively. At all the sites, dibenzo(a,h)anthracene was not detected, probably due to a series losses caused in pretreatment and measurement process.

Based on characteristics in PAHs composition and distribution pattern, the sources of anthropogenic PAHs can be distinguished by several isomer ratios. In general, pyrogenic sources are enriched in high-molecular weight 4–6 rings PAHs and depleted in low-molecular weight 2–3 rings PAHs. In contrast, petrogenic sources are dominated by low-molecular weight PAHs. Therefore, pyrogenic sources lead to ratios of high-molecular weight PAHs/low-molecular weight PAHs >1.0, while petrogenic sources had high-molecular weight PAHs/low-molecular weight PAHs

Fig. 2 Contribution of different ring numbers of PAHs to the total burden of PAHs in 31 soil samples

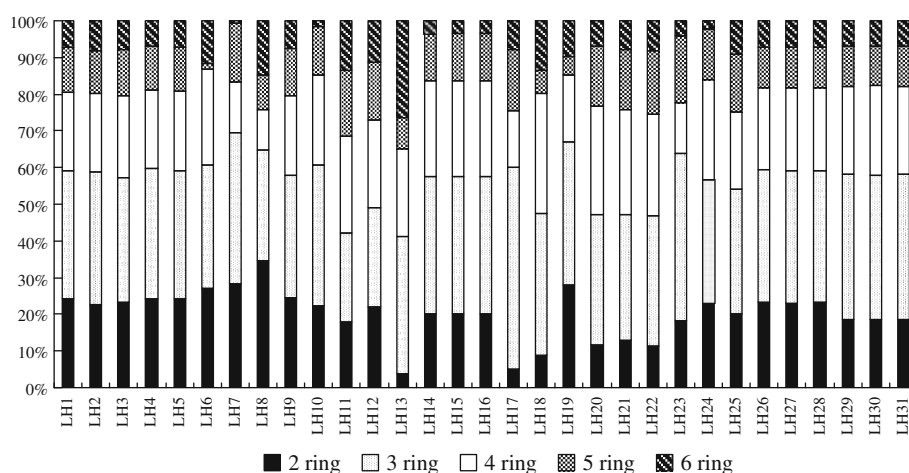


Table 1 Ratios of Ant/Ant+Phe and HMW/LMW in soil samples

Sites	LH1	LH2	LH3	LH4	LH5	LH6	LH7	LH8
HMW/LMW	0.69	0.70	0.75	0.68	0.69	0.65	0.44	0.55
Ant/Ant+Phe	0.17	0.13	0.13	0.17	0.17	0.15	0.37	0.21
Sites	LH9	LH10	LH11	LH12	LH13	LH14	LH15	LH16
HMW/LMW	0.73	0.65	1.37	1.04	1.43	0.73	0.73	0.73
Ant/Ant+Phe	0.15	0.16	0.53	0.51	0.42	0.17	0.17	0.17
Sites	LH17	LH18	LH19	LH20	LH21	LH22	LH23	LH24
HMW/LMW	0.66	1.10	0.49	1.12	1.11	1.14	0.57	0.77
Ant/Ant + Phe	0.16	0.18	0.10	0.20	0.25	0.27	0.12	0.06
Sites	LH25	LH26	LH27	LH28	LH29	LH30	LH31	
HMW/LMW	0.85	0.69	0.69	0.69	0.72	0.72	0.72	
Ant/Ant+Phe	0.22	0.19	0.19	0.18	0.18	0.17	0.18	

HMW/LMW high-molecular weight PAHs/low-molecular weight PAHs

Ant/Ant+Phe anthracene/(anthracene+phenanthrene)

<1.0 (Soclo et al. 2000). Another ratio used extensively to delineate sources of PAHs contamination is anthracene/(anthracene+phenanthrene). Budzinski et al. (1997), Yunker et al. (2002) reported an anthracene/(anthracene+phenanthrene) ratio lower than 0.1 is usually taken as an indication of petroleum unburned, while a ratio higher than 0.1 indicates a dominance of combustion effect. In this study, the high-molecular weight PAHs/low-molecular weight PAHs ratios in most sites were much lower than 1 (Table 1), indicating that petrogenic sources were the primary sources of PAHs in Liaohe estuarine wetland. It was noted that high-molecular weight PAHs/low-molecular weight PAHs ratios ranging from 0.8 to 1.2 were observed at several sites (LH12, LH18, LH20, LH21, and LH25), which were located in reed field area. This result suggested that petrogenic and pyrogenic sources were significant and comparable in these sites. The ratio of anthracene/(anthracene+phenanthrene) was employed to distinguish between PAHs from combustion or petroleum in the study. These ratios were also included in Table 1. Anthracene/(anthracene+phenanthrene) ratios were higher than 0.1, except for site LH19 and LH24, indicating pyrogenic was the main PAH source. However, anthracene/(anthracene+phenanthrene) ratio in site LH19 site was near the boundary of mixed sources and pyrogenic sources, suggesting that the contributions from both sources are significant.

To assess potential environmental impacts of PAHs in soils, PAH levels in soils of Liaohe estuarine wetland were compared with threshold effect concentrations, i.e., effect range low and effect range median (Long et al. 1995). Effect range low (40,22 ng/g) and effect range median (44,792 ng/g) delineate three concentrations ranges for PAHs. PAHs concentrations less than effect range low suggest that the probability of a negative toxic effective is lower than 10%. However, concentrations higher than effect range median indicate that the probability exceeds 50%. Concentrations of total PAHs in soils from Liaohe estuarine wetland ranged from 293.4 to 1,735.9 ng/g in August 2009 and were far less than effect range low. Thus, the probability of adverse effects caused by PAHs alone would be low. The concentrations of all individual PAHs detected were lower than effect range low values except for

Table 3 Classification criteria for polluted index of soil environmental quality

Grade	Composite index	Appraisal result
1	$p \leq 0.7$	Safety domain
2	$0.7 < p \leq 1.0$	Precaution domain
3	$1.0 < p \leq 2.0$	Slightly polluted domain
4	$2.0 < p \leq 3.0$	Moderately polluted domain
5	$p > 3.0$	Seriously polluted domain

p The nemerow composite index

Table 2 Standard pollution criteria of PAH components for soil (ng/g)

Compound	ERL	ERM	This study		Number of sites		
			Average	Max	<ERL	ERL -ERM	>ERM
Naphthalene	160	2,100	137.9	403.4	22	9	0
Acenaphthylene	44	640	74.5	193.5	6	25	0
Acenaphthene	16	500	39.0	101	0	31	0
Fluorene	19	540	48.4	154.5	11	20	0
Phenanthrene	240	1,500	69.1	144.1	31	0	0
Anthracene	853	1,100	16.0	34.1	31	0	0
Fluoranthene	600	5,100	34.0	75.3	31	0	0
Pyrene	665	2,600	53.4	154.3	31	0	0
Benzo(a)anthracene	261	1,600	37.4	81.9	31	0	0
Chrysene	384	2,800	29.5	99.5	31	0	0
Benzo(b)fluoranthene	320	1,880	36.6	97.5	31	0	0
Benzo(k)fluoranthene	280	1,620	32.7	158.4	31	0	0
Benzo(a)pyrene	430	1,600	14.5	77.2	31	0	0
Indeno(1,2,3,cd)pyrene	—	—	20.8	54.3	—	—	—
Dibenzo(a,h)anthracene	63.4	260	0.0	0	31	0	0
Benzo(g,h,i)perylene	430	1,600	31.9	88.2	31	0	0
Total	4022	4,4792	675.4	1,735.9	31	0	0

ERL effect range low, ERM effect range median, Max maximum

Table 4 The nemerow composite indexes in soils of Liaohe estuarine wetland

Sites	LH1	LH2	LH3	LH4	LH5	LH6	LH7	LH8
p	0.52	0.49	0.51	0.54	0.53	1.29	1.28	1.12
Sites	LH9	LH10	LH11	LH12	LH13	LH14	LH15	LH16
p_n	0.55	0.72	0.75	1.48	0.57	0.77	0.78	0.78
Sites	LH17	LH18	LH19	LH20	LH21	LH22	LH23	LH24
p_n	0.56	0.42	1.23	0.61	0.60	0.55	1.48	0.99
Sites	LH25	LH26	LH27	LH28	LH29	LH30	LH31	
p_n	1.49	2.96	2.92	2.95	1.13	1.13	1.13	

p The nemerow composite index

naphthalene, acenaphthylene, acenaphthene and fluorene (Table 2). The latter showed values above effect range low but below effect range median, indicating occasional adverse effects may occur in the area.

The Nemerow composite index (p value) for all the soil sampling sites was utilized for the degree of soil environmental pollution and integrative assessment of soil environmental quality. The values of 9 PAHs collected for this study were compared to the target values specified for soils in the environmental standards of the Canada. The risk assessment indexes used were naphthalene, phenanthrene, anthracene, pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3,cd)pyrene and dibenzo(a,h)anthracene (Aannokkee 1990). Its equation is as follows:

$$P = \sqrt{\frac{(\bar{P}_i)^2 + (P_{i\max})^2}{2}}$$

where, $P_i = C_i/S_i$, P_i is the pollution index, C_i is the measured concentration of PAHs, S_i is the required standard, \bar{P}_i is the average value of the individual pollutants indexes and $P_{i\max}$ is the maximum value of the individual pollutants indexes (Ge et al. 2005). Based on State Environmental Protection Administration of China (SEPA) 2004, environmental quality is divided into five environmental pollution grades (Table 3).

The nemerow composite indexes of the PAHs ranged from 0.42 to 2.96 (Table 4), 41.9% of these sites had a value of safety. 32.3% of these sites had a value of slightly polluted. The p values in site LH26–LH28 which were from reed field oil well area were relatively higher than other sampling sites and had a value of moderately polluted. Sites LH10, LH11 and 3 sites from reed degraded area (sites LH14–LH16) should be paid attention where the soil samplings were precaution. In a word, about 58.1% of all soil sampling sites were got different grades pollution and about 41.9% were safety.

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References

- Aannokkee GJ (1990) MT-TNO research into the biodegradation of soils and sediments contaminated with oils and PAHs. In: Wolf K et al (eds) Contaminated soil. Kluwer Academic Publisher, New York
- Budzinski H, Jones I, Bellocq J, Pierard C, Garrigues P (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Mar Chem 58:85–97
- Cai QY, Mo CH, Li YH, Zeng QY, Katsoyiannis A, Wu QT, Férard JF (2007) Occurrence and assessment of polycyclic aromatic hydrocarbons in soils from vegetable fields of the Pearl River Delta, South China. Chemosphere 68:159–168
- Edwards NT (1983) Polycyclic aromatic hydrocarbons(PAH's) in the terrestrial environment. J Environ Qual 12:427–441
- Ge CJ, An Q, Dong YH (2005) Residue and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soils around a steel mill. Rual Eco Environ 21: 66–69, 73
- Long ER, MacDonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuary sediments. Environ Manag 19:81–97
- Ping LF, Luo YM, Zhang HB, Li QB, Wu LH (2007) Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, east China. Environ Pollut 147:358–365
- Ruiz Y, Suarez P, Alonso A, Longo E, Villaverde A, San JF (2011) Environmental quality of mussel farms in the Vigo estuary: Pollution by PAHs, origin and effects on reproduction. Environ Pollut 159:250–265
- Santodonato J (1997) Review of the estrogenic and anti-estrogenic activity of polycyclic aromatic hydrocarbons: relationship to carcinogenicity. Chemosphere 34:835–848
- Soclo HH, Garrigues P, Ewald M (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar Pollut Bull 40:387–396
- Tang L, Tang XY, Zhu YG, Zheng MH, Miao QL (2005) Contamination of polycyclic aromatic hydrocarbons (PAHs) in urban soils in Beijing, China. Environ Int 31:822–828
- Trapido M (1999) PAHs in estonian soil: contamination and profiles. Environ Pollut 105:67–74

- Yuan HM, Zhao GM, Pang SJ, Gao JY, Ye SY (2008) Polycyclic Aromatic Hydrocarbons(PAHS) exposure and their source analysis in the northern Wetland of the yellow river delta. *Mar Geol Quat Geol* 28:57–62
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33:489–515
- Zedeck MS (1980) Polycyclic aromatic hydrocarbons: review. *J Environ Pathol Toxicol* 3:537–567
- Zhao J, Zhou HD, Lu J et al (2009) Distribution and source of polycyclic aromatic hydrocarbons (PAHs) in soils of Baiyangdian area. *Chin J Ecol* 28:901–906