Polycyclic aromatic hydrocarbons in soils along the coastal and estuarine areas of the northern Bohai and Yellow Seas, China

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Abstract Polycyclic aromatic hydrocarbons (PAHs) and their health risks in surface soils ($n=31$) collected from coastal and estuarine areas of the northern Bohai and Yellow Seas (CEANBYS), China, were investigated. Total concentrations of PAHs ranged from 6.6×10^1 to 9.2×10^2 ng g^{-1} dry weight, with an average of 3.1×10^2 ng g^{-1} dw. The locations where greater concentrations of PAHs were observed were all near factories emitting black smoke or on the edge of the urban areas. These observations are consistent with concentrations of PAHs in soils being influenced by human activities, especially industrialization and urbanization. Concentrations of PAHs were significantly correlated with concentrations of organic carbon in soils. The patterns of relative concentrations and types of PAHs observed as well as knowledge of the potential sources were consistent with the primary sources of PAHs in soils of the CEANBYS being derived from the pyrolytic processes such as combustion of fossil fuel. The incremental lifetime cancer risks of exposing to PAHs for child, youth, and adult were 1.6×10^{-6}, 1.2×10^{-6}, and 1.9×10^{-6}.

Keywords PAHs · Soil contamination · Risk assessment · Coastal areas

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Introduction

The Bohai Sea, together with nearby coastal and riverine areas, is a major commercial artery and has been a region of significant urbanization and industrialization. Rapid social and economic development has resulted in the area becoming contaminated with persistent organic pollutants (Liu et al. 2007; Wang et al. 2007; Zhang et al. 2009). The Yellow, Liaohe, Haihe, Luanhe, and Dalinghe rivers are the major fresh water sources, which discharge directly to the Bohai Sea. The drainage areas of these rivers are important agricultural and chemical production areas (China Statistical Yearbook 2007). The region has a cool continental monsoon climate, with an average annual temperature of 10.6 °C, and average annual precipitation of 580 mm. A northwest wind prevails in the coastal area.

Polycyclic aromatic hydrocarbons (PAHs) are of concern in both urban and rural areas in China (Mastral and Callen 2000; Zhang et al. 2009). Because of their

toxicity, mutagenicity, and carcinogenicity, PAHs have received considerable attention and is known about their toxic effects and even exposure of humans (Wilcke 2000; Peng et al. 2011). Emission of the 16 PAHs that are listed by the United Sates Environmental Protection Agency (USEPA) as priority pollutants have increased substantially in China from approximately 1.8×10^4 tons in 1980 to $>2.5 \times 10^4$ tons in 2003, with the greater emissions occurring in western and northern China (Xu et al. 2006). It has been reported that 1.6 % of the lung cancer observed in China is attributable to inhalation of PAHs in ambient air (Zhang et al. 2009). PAHs are released primarily from anthropogenic sources, such as vehicle exhaust, heat, and power generation from coal and other fossil fuels, petroleum refinery, straw and firewood burning, industrial processes, chemical manufacturing, oil spills, and as a constituent of coal tar (Mastral and Callen 2000; Yunker et al. 2002; Nam et al. 2003; Masih and Taneja 2006). Based on information for 2003, biomass burning, domestic coal combustion, coking industry, and petroleum combustion accounted for 60, 20, 16, and 3 % of PAHs emissions in China, respectively (Xu et al. 2006). The diversity of PAHs sources results in its ubiquity and complexity of origin in various environmental media. The spatial heterogeneity of concentrations of PAHs in soil is also affected by heterogeneity of soil property (Peng et al. 2011).

Once PAHs are released into the atmosphere, they attach to particles, and via dry and wet deposition, they tend to accumulate in soils. Because of their sparing solubility PAHs adsorb to soil particles, which limits their degradation (Sun et al. 2009). PAHs can be removed from soils through volatilization, leaching, fugitive dust, and absorption by plants (Zhang et al. 2011). Soils can play a role in the global fate and distribution of pollutants since they have been identified as a sink from which they can be rereleased into water or air (Tao et al. 2003; Demircioglu et al. 2011). The distributions of PAHs in regional soils provide information on sources of emission and for evaluating environmental and health risks associated with PAHs (Nam et al. 2003; Peng et al. 2011). Exposures to PAHs in the atmosphere not only result in occupational exposure such as those of traffic policemen (Hu et al. 2007), factory employees (Tsai et al. 2001), and Buddhist temple attendants (Liao and Chiang 2006), but also are potentially harmful to the general population (Zhang et al. 2009).

Several studies of PAHs in air, seawater, sediment, and biota have been conducted in the coastal areas of the Bohai Sea (Wu et al. 2005; Shi et al. 2005; Liu et al. 2007; Zhang et al. 2009), whereas few studies have systematically reported concentrations of PAHs and their health risk in soils of the coastal and estuarine areas of the northern Bohai and Yellow Seas (CEANBYS). The median concentration of $\sum 14$ PAHs was 1.1×10^4 ng g^{-1} dw (2.2×10^2–1.9×10^4 ng g^{-1} dw) in urban and rural soils in Dalian (Wang et al. 2007). The average concentration of $\sum 16$ PAHs was 2.3×10^3 ng g^{-1} dw (2.8×10^2–8.3×10^4 ng g^{-1} dw) in soils of the Liao River Basin (Song et al. 2008). Therefore, supplementary data on concentrations of PAHs in soils were needed to determine the risks posed by the PAHs to humans and to determine sources that can be controlled.

This study focused on the CEANBYS, China, including the following eight cities: Tangshan, Qinhuangdao, Huludao, Jinzhou, Panjin, Yinkou, Dalian, and Dandong (Fig. 1). The specific objectives of the present paper were to: (1) determine concentrations of PAHs in soils from the CEANBYS and investigate their regional differences, (2) identify possible sources and their relative contributions of PAHs in soils, and (3) evaluate incremental lifetime cancer risks to humans.

Materials and methods

Soil sampling and preparation

Thirty-one surface (0–20 cm) soil samples were collected along the CEANBYS, in May 2008 and numbered as: TS1-6 in Tangshan, QH1-3 in Qinhuangdao, HL1-4 in Huludao, JZ1-5 in Jinzhou, PJ1-2 in Panjin, and YK1-3 in Yingkou (Fig. 1). Soils collected from the northern shore of the Yellow Sea were numbered as: DL1-4 in Dalian and DD1-4 in Dandong.

Each sample was a composite of subsamples taken from the five locations within an area of about 100×100 m^2. Sample were dried at room temperature (Nadal et al. 2004), sieved through 100-mesh sieve, and stored at 4 °C in glass bottles prior to analysis. At the time of sampling, site description including land use pattern and major environmental features were recorded, and a global positioning system was used to locate the sampling sites. To eliminate the effects of
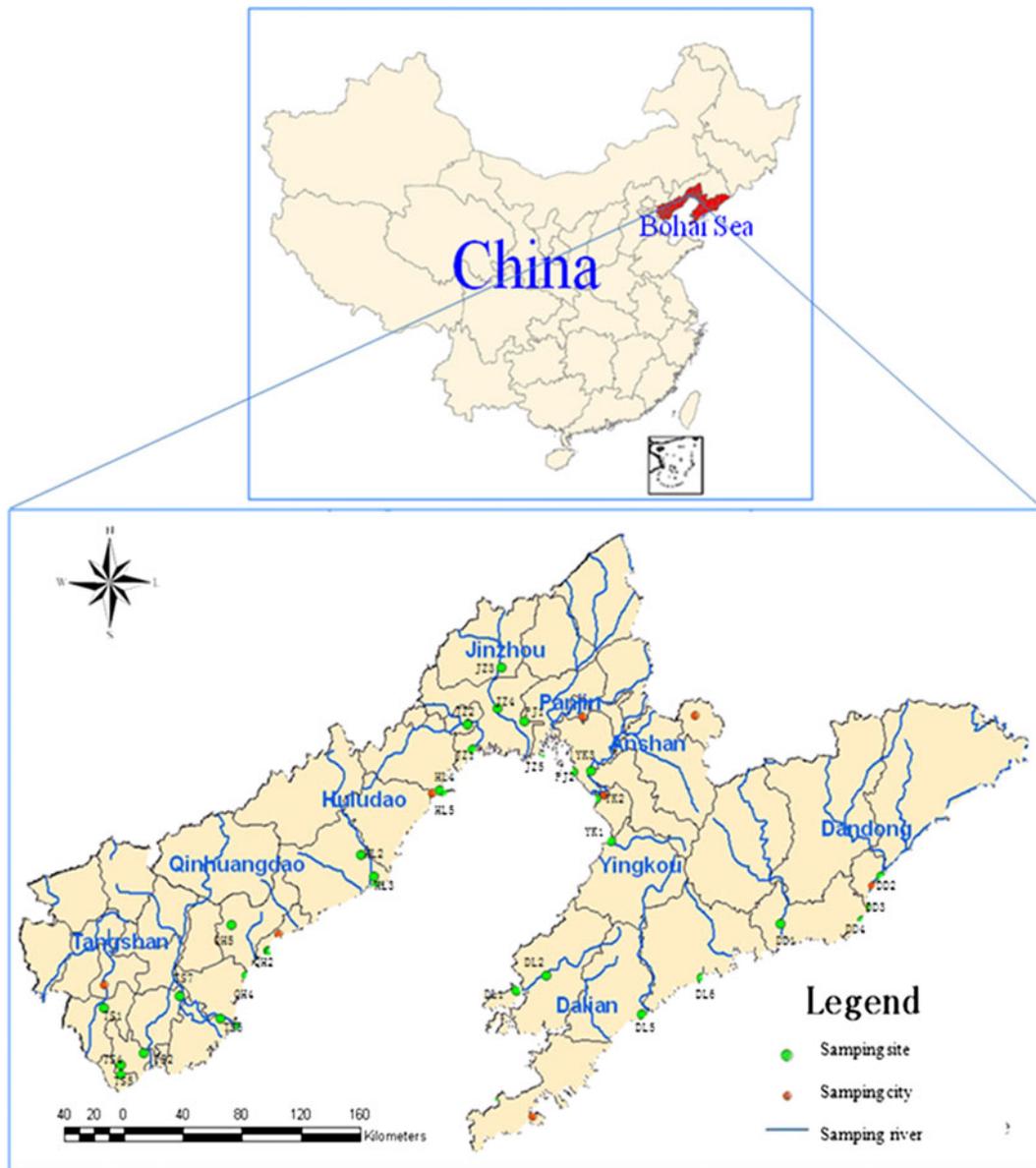
Fig. 1 Study area and sampling locations in the coastal and estuarine areas of the northern Bohai and Yellow Seas

vehicle exhaust emissions, each sample was collected at least 50 m from the nearby highway or road. Grass and other sundries were removed from the surface of each sample location before the sample was collected.

Sample extraction and fractionation

PAHs were extracted, isolated, and analyzed according to previously published procedures of Jiao et al.

(2009). The limit of quantification (LOQ) ranged from 1.7 to 4.9 $ng\,g^{-1}$ dry weight with those of the individual PAHs (Table 1). All the results are expressed on a dry weight basis.

Soil pH was measured by use of pH meter placed in a suspension of 10 g of air-dried soil in 25 ml deionized water. Total organic carbon (TOC) was quantified by using Universal CHNOS Elemental Analyzer (Elementar Vario EL III, Hanau, Germany).

Table 1 Parameters used in the incremental lifetime cancer risk assessment

Exposure variables	Unit	Child		Youth		Adult	
		Male	Female	Male	Female	Male	Female
Body weight (BW)	kg	17.2	16.5	47.1	44.8	60.2	53.1
Exposure frequency (EF)	day year^{-1}	350	350	350	350	350	350
Exposure duration (ED)	Year	6	6	14	14	30	30
Inhalation rate (IR_{air})	m^3 day^{-1}	10.9	10.9	17.7	17.7	17.5	17.5
Intake rate (IR_{soil})	mg day^{-1}	200	200	100	100	100	100
Dermal surface exposure (SA)	cm^2 day^{-1}	1,800	1,800	5,000	5,000	5,000	5,000
Dermal adherence factor (AF)	mg cm^{-2}	0.2	0.2	0.2	0.2	0.07	0.07
Dermal adsorption fraction(ABS)	Dimensionless	0.1	0.1	0.1	0.1	0.1	0.1
Dermal exposure ratio to soil(FE)	Dimensionless	0.61	0.61	0.61	0.61	0.61	0.61
Average life span (AT)	day	25,550	25,550	25,550	25,550	25,550	25,550
Soil dust produce factor(PEF)	m^3 mg^{-1}	6.2×10^9	6.2×10^9	6.2×10^9	6.2×10^9	6.2×10^9	6.2×10^9

Quality assurance and quality control

Laboratory quality control procedures included analyses of method blanks (solvent), spiked blanks (standards spiked into solvent), and matrix spikes. The analysis of matrix spikes and samples was performed in duplicate. Instrument stability and response were checked by injecting NIST standard solutions (DFTPP) periodically. The instrument was calibrated daily, and the relative percentage of differences between the five-point calibration and the daily calibrations were <20 % for all of the target analyses. The recoveries of surrogate standards were within the range, of 58.7±7.4 % (Nap) to 99.3±5.8 % (Flu).

Health risk assessment

Incremental lifetime cancer risks (ILCRs) of PAHs in soils along CEANBYS was evaluated following USEPA standard models. In order to reduce computation, it was assumed that exposure in different areas was via the same routes, including direct ingestion, dermal contact, and inhalation exposure as followed (Eqs. 1, 2, and 3).

$$\text{ILCRs}_{\text{ingestion}} = \frac{\text{CS} \times \left(\text{CSFingestion} \times \sqrt[3]{(\text{BW}/70)} \right) \times \text{IRsoil} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \tag{1}$$

$$\text{ILCRs}_{\text{dermal}} = \frac{\text{CS} \times \left(\text{CSFdermal} \times \sqrt[3]{(\text{BW}/70)} \right) \times \text{SA} \times \text{FE} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \tag{2}$$

$$\text{ILCRs}_{\text{inhalation}} = \frac{\text{CS} \times \left(\text{CSFinhalation} \times \sqrt[3]{(\text{BW}/70)} \right) \times \text{IRair} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times \text{PEF}} \tag{3}$$

Where: CS is the PAHs concentration of soils (ng g^{-1}), CSF is the carcinogenic slope factor (mg kg^{-1} day^{-1})$^{-1}$, BW is the body weight (kg), AT is the average life span (day), EF is the exposure frequency (day year^{-1}), ED is the exposure duration (year), IR$_{air}$ is the inhalation rate (m^3 day^{-1}), IR$_{soil}$ is the rate of

intake of soil (mgday^{-1}), SA is the dermal surface exposure (cm^{2}day^{-1}), FE is the dermal exposure ratio to soil, AF is the dermal adherence factor (mgcm^{-2}), ABS is the dermal adsorption fraction, and PEF is the soil dust produce factor (m^{3}kg^{-1}).

Determination of the carcinogenic slope factor, based on the cancer-causing ability of BaP that CSF$_{ingestion}$, CSF$_{dermal}$, and CSF$_{inhalation}$ of BaP were 7.3, 25, and 3.85/(μgg^{-1}day^{-1}), respectively (USEPA 1994; Knafla et al. 2006; Peng et al. 2011). The cancer potency of the PAHs was calculated as the sum of the concentrations of individual PAH multiplied by their BaP relative potency factors to report equivalents of BaP (Table 2) (Nisbet and LaGoy 1992; Liao and Chiang 2006). Parameters necessary for the calculations were based on China's Health Statistical Yearbook (2007) and Risk Assessment Guidance of Beijing Municipal Environmental Protection Bureau (2007) (Table 1). The risks of cancer for children, youths, and adults were calculated separately. Total risks were the sum of risks associated with each exposure route.

Data analysis

SPSS 12.0 and Sigma Plot® 11.0 (Karnataka, India) for windows were employed for statistical analysis. For calculation of means, concentrations that were less than the LOQ were assigned a value of zero. Relationships between concentrations of individual PAHs and soil properties were investigated using Spearman correlation analysis for the non-normal

Table 2 Characteristics and concentrations of measured PAHs in soils (ngg^{-1}dw)

PAHs	Rings	DL[e]	TEF	Range	Aver	Med	DR[f] (%)
Nap	2	1.8	0.001	0.0–47	12±10	10.1	94
Acy	3	2.2	0.001	0.2–19	3.7±4.4	1.7	100
Ace	3	1.8	0.001	0.0–15	3.5±3.7	2.8	94
Fl	3	1.7	0.001	2.2–73	10±12	7.6	100
Phe	3	2.2	0.001	4.1–98	42±28	37.9	100
An	3	2.9	0.01	0.6–23	4.9±4.5	3.4	100
Flu	4	3.7	0.001	3.7–93	30±24	24.0	100
Pyr	4	3.1	0.001	3.7–97	31±24	22.3	100
BaA	4	3.6	0.1	4.2–90	24±22	16.6	100
Chr	4	3.4	0.01	1.2–82	21±20	12.3	100
BbF	5	2.6	0.1	6.2–2.1×10^2	51±51	29.3	100
BkF	5	4.9	0.1	0.2–27	6.4±6.8	3.4	100
BaP	5	3.9	1	4.6–58	19±16	11.4	100
Inp	6	4.7	0.1	8.9–100	29±25	15.1	100
DBA	5	3.5	1	0.8–5.6	1.5±1.0	1.2	100
BgP	6	2.7	0.01	5.6–61	21±14	16.5	100
∑16PAHs[a]				66–9.2×10^2	(3.1±2.3)×10^2	2.2×10^2	
∑2–3 r PAHs[b]				23–1.7×10^2	76±42	76	
∑4–6 r PAHs[c]				42–7.9×10^2	(2.3±2.0)×10^2	1.4×10^2	
∑7PAHcars[d]				29–5.5×10^2	(1.5±1.4)×10^2	81	

[a] Sum concentration of 16 PAHs compounds

[b] Sum concentration of six lesser molecular PAHs compounds (weight Nap, Ace, Acy, Fl, Phe, and An)

[c] Sum concentration of nine lesser molecular weight PAHs compounds (Pyr, BaA, Chr, BbF, BkF, BaP, Inp, DBA, and BgP)

[d] Sum concentration of seven carcinogenic PAHs compounds (Flu, BaA, BbF, BkF, BaP, Inp, and DBA)

[e] Detection limits for each of the 16 individual PAHs

[f] Detectable ratio (detectable ratio=the number above the LOQ for each PAH×100 %/31)

distribution data. The detectable ratio (DR) equal to the number above LOQ of each PAH individuals× 100 %/35.

Results and discussion

PAHs concentrations

Total concentrations of PAHs (sum of 16 priority PAHs, $\sum$16PAHs) and concentrations of individual PAHs in 31 soils collected along the CEANBYS are presented in the Table 2. Except for Nap and Ace, the detectable ratio, which is calculated as the ratio samples with concentrations greater than the LOQ for each PAH, were 100 %. The relatively larger DR of PAHs in the soil of the CEANBYS is consistent with the ubiquity of PAHs.

Concentrations of $\sum$16PAHs varied among soils from 66 to 9.2×10^2 ng g^{-1} dw, with an average of 3.1×10^2 ng g^{-1} dw. Concentrations of $\sum$16PAHs varied among soils from 29 to 5.5×10^2 ng g^{-1} dw, with an average of 1.5×10^2 ng g^{-1} dw. Total concentrations of PAHs were not normally distributed, with a median of 2.2×10^2 ng g^{-1} dw while the mean concentration was 3.1×10^2 ng g^{-1} dw. Even individual PAHs congeners exhibited similar distribution patterns. The skewed concentration distribution after log transformation reflected that in the CEANBYS, the $\sum$16PAHs contents of soils were rather small. The location with the greatest concentration of $\sum$16PAHs in top soils was in the vicinity of Dalian (DL6). The next greatest concentrations were 8.2×10^2 and 8.0×10^2 ng g^{-1} dw, which were observed in soils from Dandong city (DD3) and Huludao city (HL5), respectively. The locations with greater concentrations of $\sum$16PAHs were near factories that were emitting black smoke or on the edges of the urban areas, which indicated PAHs accumulations in soil were influenced by human activities, especially industrialization and urbanization (Nadal et al. 2004; Wang et al. 2007).

Concentrations of $\sum$16PAHs from the CEANBYS were comparable to results of two surveys from rural and suburban. Total concentrations of $\sum$16PAHs in soils varied from 28 to 8.4×10^4 ng g^{-1} with arithmetic means of 5.5×10^2 ng g^{-1} (Zuo et al. 2007) in the western watershed of the Bohai Sea, and from 63 to 4.1×10^4 ng g^{-1} with arithmetic means of 3.9×10^2 ng g^{-1} near Beijing Guanting Reservoir (Jiao et al. 2009),

and $4.1 \times 10^2 \pm 78$ ng g^{-1} and $2.2 \times 10^2 \pm 6$ ng g^{-1} from suburban area and rural area of Dalian (Wang et al. 2007).

Compared with the soils of urban areas of the CEANBYS, average concentrations of $\sum$16PAHs in soils of urban or industrial CEANBYS, such as urban area of Dalian ($6.5 \times 10^4 \pm 5.7 \times 10^4$ ng g^{-1}) (Wang et al. 2007) and the Liao River Basin (2.3×10^4 ng g^{-1}) (Song et al. 2008), were 7- to 20-fold greater than the concentrations observed in this study. Average regional concentrations of $\sum$16PAHs were distributed as follows: urban > suburban > rural gradient (Wang et al. 2007). Concentrations of PAHs reported here were not representative of the urban areas with the most industry and greater populations, such as the concentration of ($6.5 \times 10^4 \pm 5.7 \times 10^4$ ng g^{-1}) of Dalian sites near traffic (Wang et al. 2007). The variability observed in the soils of the CEANBYS reflected the difficulty of accurately characterizing PAHs distributions in regional soils due to limitations of field sampling. Sampling locations need to be selected according to scope of the investigation (Peng et al. 2011). Besides, soil-borne PAHs are susceptible to losses due to their volatility and degradability that are more effective in the summer months (Masih and Taneja 2006).

There were statistically significant ($\alpha = 0.05$) Spearman correlations among individual PAHs, except DBA (Table 2), which is consistent with 15 PAHs originating from similar sources. The sources were located in close proximity to sampling locations (Chung et al. 2007). BaP can be used as a marker for some combustion-derived PAHs (Magi et al. 2002). A significant correlation between concentrations of BaP and $\sum$16PAHs ($r^2 = 0.65$, $\alpha < 0.01$) was consistent with combustion being the primary sources of soil PAHs in this area.

Organic matter content is known to be one factor that relates to accumulation of PAHs in soils (Wilcke 2000; Wang et al. 2007) by influencing sorption/desorption and/or biodegradation. Some studies have found a positive relationship (Jiao et al. 2009), and some have shown little or no relationship between total concentration of $\sum$16PAHs and TOC content (Zhang et al. 2006). Concentrations of $\sum$16PAHs and concentrations of individual PAHs were investigated relative to total organic content (TOC). TOC measured in the coastal soil samples varied considerably from 0.20 to 3.1 % and were significantly

Table 3 Correlation matrix of PAHs concentrations and TOC content in soils

	TOC	Nap	Acy	Ace	Fl	Phe	An	Flu	Pyr	BaA	Chr	BbF	BkF	BaP	Inp	DBA	BgP	∑PAHs
TOC	1	0.48	0.43	0.35	0.43	0.42	0.48	0.75	0.59	0.78	0.74	0.75	0.59	0.68	0.77	0.26	0.57	0.73
Nap	++	1	0.24	0.43	0.36	0.34	0.39	0.66	0.53	0.65	0.73	0.60	0.67	0.64	0.62	−0.01	0.42	0.64
Acy	+	−	1.00	0.38	0.41	0.42	0.59	0.56	0.60	0.65	0.39	0.49	0.47	0.44	0.50	0.30	0.41	0.61
Ace	−	+	+	1.00	0.70	0.53	0.54	0.49	0.47	0.42	0.44	0.45	0.52	0.42	0.37	0.08	0.36	0.58
Fl	+	+	+	++	1.00	0.58	0.77	0.56	0.46	0.41	0.45	0.36	0.43	0.25	0.38	0.02	0.44	0.64
Phe	+	−	+	++	++	1.00	0.68	0.69	0.83	0.51	0.50	0.60	0.45	0.56	0.41	0.22	0.51	0.75
An	++	+	++	++	++	++	1	0.78	0.67	0.67	0.62	0.57	0.65	0.53	0.59	0.26	0.55	0.82
Flu	++	++	++	++	++	++	++	1.00	0.91	0.93	0.92	0.88	0.80	0.82	0.86	0.33	0.71	0.98
Pyr	++	++	++	++	++	++	++	++	1.00	0.82	0.79	0.86	0.68	0.80	0.72	0.35	0.69	0.92
BaA	++	++	++	+	+	++	++	++	++	1.00	0.89	0.85	0.80	0.85	0.90	0.36	0.60	0.90
Chr	++	++	+	+	+	++	++	++	++	++	1.00	0.89	0.76	0.81	0.89	0.29	0.75	0.90
BbF	++	++	++	+	+	++	++	++	++	++	++	1.00	0.81	0.85	0.88	0.32	0.80	0.88
BkF	++	++	++	++	+	+	++	++	++	++	++	++	1.00	0.78	0.77	0.39	0.63	0.81
BaP	++	++	+	+	−	++	++	++	++	++	++	++	++	1.00	0.81	0.39	0.57	0.81
Inp	++	++	++	+	+	+	++	++	++	++	++	++	++	++	1.00	0.24	0.68	0.82
DBA	−	−	−	−	−	−	−	−	−	+	−	++	+	+	−	1.00	0.12	0.35
BgP	++	+	+	+	+	++	++	++	++	++	++	++	++	++	++	−	1.00	0.75
∑PAHs	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	−	−	1

Spearman correlation coefficient were shown

− No significant correlations were found, + correlation is significant at the 0.05 level (two-tailed), ++ correlation is significant at the 0.01 level (two-tailed)

positively correlated ($r^2=0.54$, $\alpha<0.01$) with concentrations of ∑16PAHs (Table 3). This positive correlation also existed between TOC and concentrations of individual PAHs, except for Ace and DBA. These results are with the PAHs being associated with organic carbon in soil along the CEANBYS. Soil pH was measured between 5.03 and 8.29, and was not correlated with concentrations of ∑16PAHs.

Regional differences in ecological exposure of PAHs

Concentrations of ∑16PAHs in soils along the CEANBYS were related to discharges as well as other human activities. The mean concentration of ∑16PAHs in soils from Liaoning province ($3.5×10^2$ ng g^{-1} dw) was greater than that in soil from Hebei province ($2.1×10^2±5.7×10^4$ ng g^{-1} dw; Fig. 2). Since China's traditional industrial base is in the Liaoning area, industrial and economic activities in that region were greater than those in Hebei. Also more fossil fuels, such as coal and petroleum, were consumed in Liaoning.

Concentrations of ∑16PAHs in soils of urban areas were the greatest at Huludao ($4.9×10^2$ ng g^{-1} dw),

followed by Dandong ($4.2×10^2$ ng g^{-1} dw), and the least concentration was in Tangshan ($1.6×10^2$ ng g^{-1} dw; Fig. 2). Mining and refineries and smelting of non-ferrous metals in the Huludao were some of the primary sources of PAHs. Even in a tourist city, such as Qinhuangdao, which has little industry,
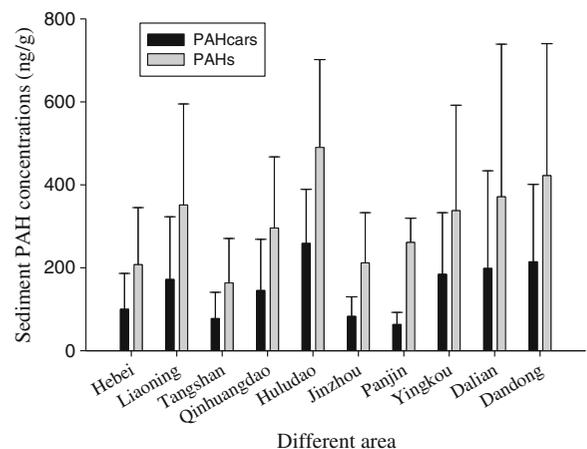

Fig. 2 Regional difference among concentrations of PAHs in soils

concentrations of $\sum$16PAHs in soil were as great as $2.9 \times 10^2\,\mathrm{ng\,g^{-1}}$ dw.

Relative proportions of PAHs components and possible sources

The relative proportions of individual PAH contributing to $\sum$16PAHs in soils along the CEANBYS were used to determine possible sources (Fig. 3). Higher molecular weight PAHs, such as BbF, Inp, Flu, and Pyr, were the dominant components in soils. It was different from the pattern in the western watershed of Bohai Sea(Phe>Nap≈FLu≈BkF>Chr≈BbF> Pyr)(Zuo et al. 2007), which suggested a different source pattern. The proportions of PAHs with different numbers of rings varied among soils along the CEANBYS. Four-ring PAHs homologues (39 %) were the main contributors to $\sum$16PAHs (Fig. 3) and there was a four-ring>five-ring>three-ring>six-ring>two-ring gradient. This result was consistent with the typical pattern of relative concentrations of PAHs observed in soils from other polluted areas (Wilcke 2000), and was similar to the pattern of the concentrations of individual PAHs in soils of Liao River Basin (Song et al. 2008). The four- to six-ring PAHs, which were considered to originate from combustion (Metre et al. 2000), represented approximately 76 % of the $\sum$16PAHs found in soils along the CEANBYS, which is consistent with combustion being the primary origin for PAHs along the CEANBYS.

PAHs from different sources have different molecular compositions. Molecular indices based on ratios
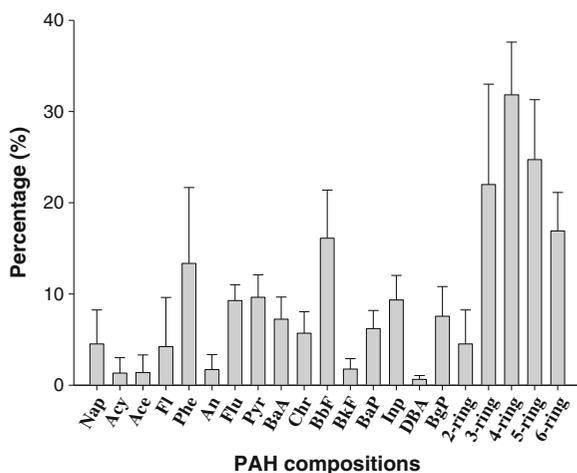
of concentrations of individual PAHs in soils can be used to distinguish PAHs originating from pyrogenic processes, such as fossil fuel combustion and vegetation fires, from those released in petroleum from oil spills. Two specific ratios of concentrations of PAHs ratios were calculated as follows: BaA/(BaA+Chr) and Flu/(Flu+Pyr), which have been frequently employed in published studies (Budzinski et al. 1997; Khim et al. 1999; Yunker et al. 2002).

Values of BaA/(BaA+Chr) ratios were greater than 0.35, which confirmed that combustion was the primary source of PAHs in soil from this area (Fig. 4). Furthermore, values of the Flu/(Flu+Pyr) ratios can be used to distinguish different combustion origins, such as burning of liquid fossil fuel or coal, wood, and grass. The Flu/(Flu+Pyr) ratio at Panjin, Petro China Liaohe Oilfield Company, which is the third oilfield of China located in this area. It is consistent with this industry being the primary source of PAHs in Panjin. The values of the Flu/(Flu+Pyr) ratios in the other 30 sites were greater than 0.4, which confirmed that general combustion origins the primary source of PAHs along north coastal area of the Bohai Sea. The values of the Flu/(Flu+Pyr) ratios were greater than 0.5 in almost 50 % of the sampling sites, which indicates grass, wood, or coal combustion were the main PAHs sources in this area. The values of the Flu/(Flu+Pyr) ratios were between 0.4 and 0.5 in approximately 50 % of the sampling sites, which indicates combustion of liquid fossil fuel was also the main PAHs source in this area. In this area, there are more than 8,000 industrial enterprises, and its gross industrial output value reached 2.9×10^7 million US dollar,

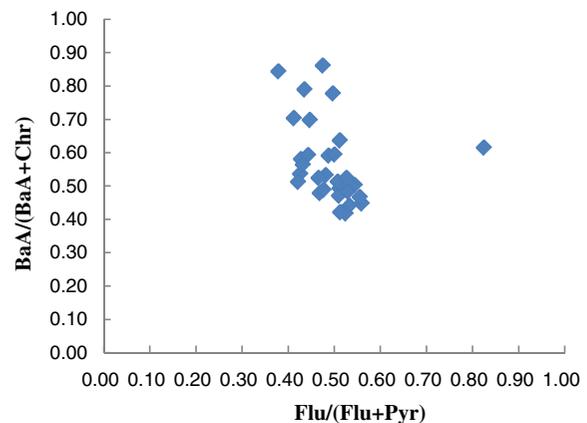**Fig. 3** Histogram of concentrations of PAHs in soils

Fig. 4 Plots of PAHs index pair ratios for source identification in soils

Table 4 ILCRs of three contact routes for three age groups (lg transformation)

	Child		Youth		Adult	
	Male	Female	Male	Female	Male	Female
Average	6.1×10^{-7}	6.3×10^{-7}	4.6×10^{-7}	4.8×10^{-7}	7.0×10^{-7}	7.6×10^{-7}
Min	1.5×10^{-7}	1.5×10^{-7}	1.1×10^{-7}	1.1×10^{-7}	1.7×10^{-7}	1.8×10^{-7}
Max	2.0×10^{-6}	2.0×10^{-6}	1.5×10^{-6}	1.5×10^{-6}	2.2×10^{-6}	2.4×10^{-6}
Median	3.7×10^{-7}	3.8×10^{-7}	2.9×10^{-7}	2.9×10^{-7}	4.2×10^{-7}	4.6×10^{-7}
90 percentile	1.6×10^{-6}	1.7×10^{-6}	1.2×10^{-6}	1.3×10^{-6}	1.9×10^{-6}	2.0×10^{-6}

representing 6.1 % of China (China City Statistical Yearbook 2007), and the factories rely on coal for energy. In addition, millions of tons of fuel oil are used for transportation and other purposes in this area annually. Automobiles may have been the sources of PAHs originating from liquid fossil fuel combustion.

Health risk assessment

To place the current concentrations of PAHs into risk perspective, concentrations of $\sum16$PAHs in soils were compared with threshold concentrations for effects. Because environmental standards for PAHs in soils have not been established in China and the sampling sites were mainly distributed away from urban areas and industrial areas, standards from several more developed countries were reviewed and a standard derived based on criteria used to evaluate concentrations of PAHs on ecological endpoints in European agricultural soils, as well as from an estimation of risks of human exposure (Paterson and McKay 1989; Maliszewska-kordybach 1996). The threshold values

of this classification were: unpolluted ($<2 \times 10^2 \, \mathrm{ng\,g}^{-1}$ dw), weakly polluted (2×10^2–$6 \times 10^2 \, \mathrm{ng\,g}^{-1}$ dw), moderately polluted ($6 \times 10^{2-3} \, \mathrm{ng\,g}^{-1}$ dw), and severely polluted ($>10^3 \, \mathrm{ng\,g}^{-1}$ dw). According to this classification, 65 % of the soils would be considered to be contaminated with PAHs that were sufficient to potentially affect soil organisms.

Incremental life cancer risks were employed to explore the potential risks to humans. The ILCR accounts for integrated lifetime risks of being exposed to soil-borne PAHs through direct ingesting, dermal contacts, and inhalation collectively. The 90 % cumulative probability ILCRs for adults exposed to the average PAHs concentration of soils in CEANBY were 1.9×10^{-6} for male and 2.0×10^{-6} for female, respectively (Table 4), which were the greatest risk among three age groups. The risks for youths were less than for children and adults. Cancer risks of women exposed to PAHs was slightly greater than that for men, however, the difference was not significant. This was mainly due to the differences of body weight between men and women. In regulatory terms, an ILCR of 10^{-6} or
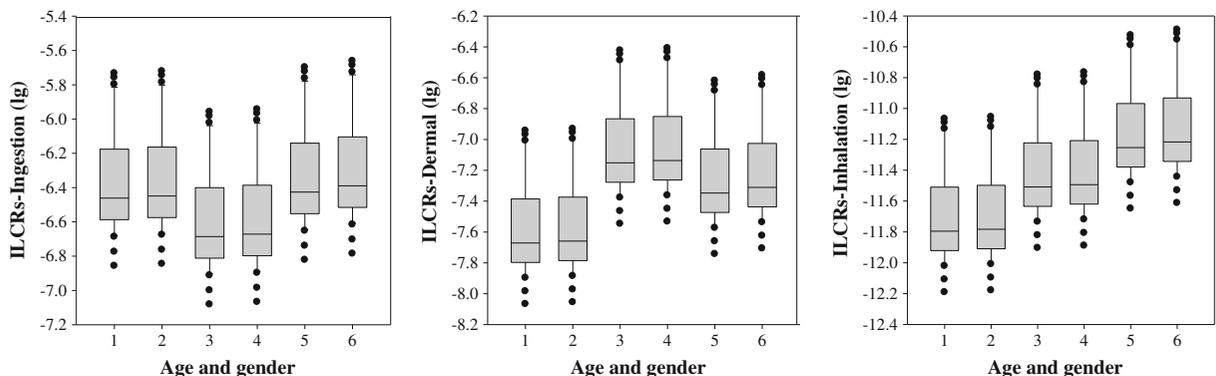

Fig. 5 ILCRs in different exposure approaches and different types of people. 1 represent male child; 2 represent female child; 3 represent male youth; 4 represent female youth; 5 represent male adult; 6 represent female adult

less denotes virtual safety and an ILCR of greater than 10^{-4} denotes potentially great risk (Liao and Chiang 2006). The average estimated ILCRs for children, youths, and adults are all less than 10^{-6}. The 90th percentile of estimated ILCRs for children, youths, and adults all exceeded 10^{-6}. While PAHs were pervasive in soils of the CEANBY, the cancer risk due to exposures to PAHs was deemed to be extraordinary (Peng et al. 2011).

The probability of ILCR through soil ingestion by children (3.3×10^{-7}) and adults (3.4×10^{-7}) were similar and were greater than those to youths (2.0×10^{-7}; Fig. 5). Children are naturally active, and the soil ingestion can be significantly greater than that by youths and adults, which leads to greater cancer risk caused by soil ingestion. As for adults, although the IR_{soil} was relatively small, longer exposure time and combined effects can result in cancer risk in adults that is similar to the risk caused by soil ingestion in children. Due to a lesser rate of ingestion of soil and shorter exposure time, the value of ILCRs for youths was smaller.

The magnitudes of ILCRs among the three age groups did not exceed 10^{-6} based on exposure through skin contact. Among them, the ILCRs value for youths was the greatest, followed by that for adults, and the ILCRs for children were the least. This was due to the lesser skin surface areas in children, which led to smaller ILCRs caused by skin contacts. Alternatively, although youths have smaller skin surface areas compared to adults, their dermal adherence factor is larger (0.2 for youth, and only 0.07 for adults), and the impacts of these factors resulted in the ILCR of youths to become the greatest, and the smallest for children.

The ILCRs caused by inhalation of soil particles were small among the three age groups, which were approximately 10^{-11}, less than 10^{-6}. This indicated that the cancer risk caused by the inhalation of soil particles was negligible. Because of the longer exposure time and the greater air intake amount, the ILCRs for adults were the greatest and the ILCRs for children were the smallest.

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