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The concentrations and sources of PAHs and PCBs in soil from an oil field and estuary in the Yellow River Delta, China

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The occurrence of organic pollutants [i.e. polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)] had been assessed in the soil samples collected from two sub-regions (an oil field and the Yellow River Estuary) in the Yellow River Delta (YRD), China. The concentrations of PAHs and PCBs in the soil were in the range of 157.8–481.7 $\mu\text{g kg}^{-1}$ (dry weight) and 5.6–56.6 $\mu\text{g kg}^{-1}$ (dry weight), respectively. The average concentration of PAHs in the soil samples from the oil field were 274.0 $\mu\text{g kg}^{-1}$, and that in the estuary soil samples were 244.4 $\mu\text{g kg}^{-1}$. The average concentration of PCBs in the soil samples from the oil field and the estuary were 24.2 $\mu\text{g kg}^{-1}$ and 10.8 $\mu\text{g kg}^{-1}$, respectively. The contribution of low molecular weight PAHs (two-ring and three-ring PAHs) was larger in the soil samples from the oil field than that in the estuary soil samples. Both PAHs and PCBs contaminations in the estuary area were lower than that in the oil field area. By using diagnostic ratios analysis, the main source of PAHs was attributed to petroleum input caused by the fuel oil or light refined petroleum products in the Gudong Oilfield. The amount of low-chlorine congeners (three to four chlorine atoms) PCBs in soil samples from the oil field were higher than that in the estuary soil samples. The congeners analysis of PCBs and the correlation analysis between the concentrations of PAHs and PCBs were employed. The results indicated that the emission of PCBs in YRD were influenced by both Gudong oilfield and other industrial sources.

KEYWORDS

polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), proportion, distribution, sources

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants, whose pollution are ubiquitous anthropogenic. Organic pollutants are typically persistent in the environment and are known to accumulate in soils, sediments, plants, animals and human beings (Harvey 1991; Kannan et al., 1995; Wilcke, 2000; Senthilkumar et al., 2001). PAHs are a large group of organic compounds with at least two condensed rings. Many PAHs are possessed of mutagenic, carcinogenic and teratogenic properties (Xue and Warshawsky, 2004). Because PAHs are ubiquitous

environmental contaminants, communities surrounding petroleum can be exposed at increased risk of cancer and other adverse health outcomes consequently (Kaldor et al., 1984; Pan et al., 1994; Lin et al., 2001). Being probably carcinogenic to humans, 16 PAHs has been identified as “priority pollutants” by the US Environmental Protection Agency (US EPA, 2002). Similar to PAHs, PCBs has been widely detected in various environmental media and biota in the Arctic (Muir and Norstrom, 2000; Ikonomou et al., 2002; Wit et al., 2006; Ross et al., 2008). A large number of persistent organic pollutants have been produced in China (Hua and Shang, 1996). It was reported that approximately 10,000 tons of PCBs were produced from 1965 to the early 1980s in China, accounting for about 1% of the global production (Zheng et al., 2012). Environmental pollution in soil by PAHs and PCBs is a matter of great concern because of their prolonged persistence, lipophilic nature and tendency to accumulate in animal and plant tissues. Concerns have focused on many coastal regions owing to high anthropogenic influence and various contamination sources (Liu et al., 2009a; Hu et al., 2009; Hui et al., 2009; Wang et al., 2011).

The Yellow River Delta (YRD) in China is a triangular-shaped region, which covers an area of 5450 km². The economy of the YRD region has developed rapidly. The Shengli Oil Field, the second largest oil field in China, is located in the YRD. Because of the ecological risk of YRD causing by oil production and refinement, a few studies on hydrocarbon pollutants and PAHs in YRD have been undertaken (Luo et al., 2005; Hui et al., 2009; Wang et al., 2011; Xie et al., 2011). Xie et al. (2011) had studied the distribution of PAHs in the topsoil of the YRD on a county-scale and Wang et al. (2011) tried to find out the source of PAHs in YRD. However, few people did such a contrastive research on the concentrations, distribution, and composition of PAHs and PCBs in the Oil soil and Estuary soil. The effect of the oil production and refinement in YRD to the adjacent soil environment in the regional-scale remains scarcely touched.

This paper represents the first contrastive study of the PAHs and PCBs in the soil samples from two different regions in the YRD, the Oil Filed soil *versus* the Estuary soil. The main objectives of the study were: 1) to assess the level of PAHs and PCBs contamination in the two different sub-regions in the YRD; and 2) to identify the sources of PAHs and PCBs in these areas using the analysis of PAHs isomer ratios and PCB congeners.

Materials and methods

Sampling

Thirty-seven soil samples were collected and analyzed for persistent organic pollutants in November 2018, among which twenty-five samples were taken from the Gudong Oilfield which is a part of Shengli Oilfield, and twelve samples were taken from

the estuary of the YRD. These samples were far away from industrial zones in order to avoid the influence of point pollution. Sampling locations are shown in Figure 1.

Soil samples (about 1 kg) were collected, and then put in cleaned polyethylene bags with zippers and transported on ice to the laboratory. These samples were dried using a freezing dryer and then grounded to pass through a 1 mm × 1 mm stainless steel sieve and fully homogenized. All the soil samples were kept at −20°C until chemical analysis.

Chemicals

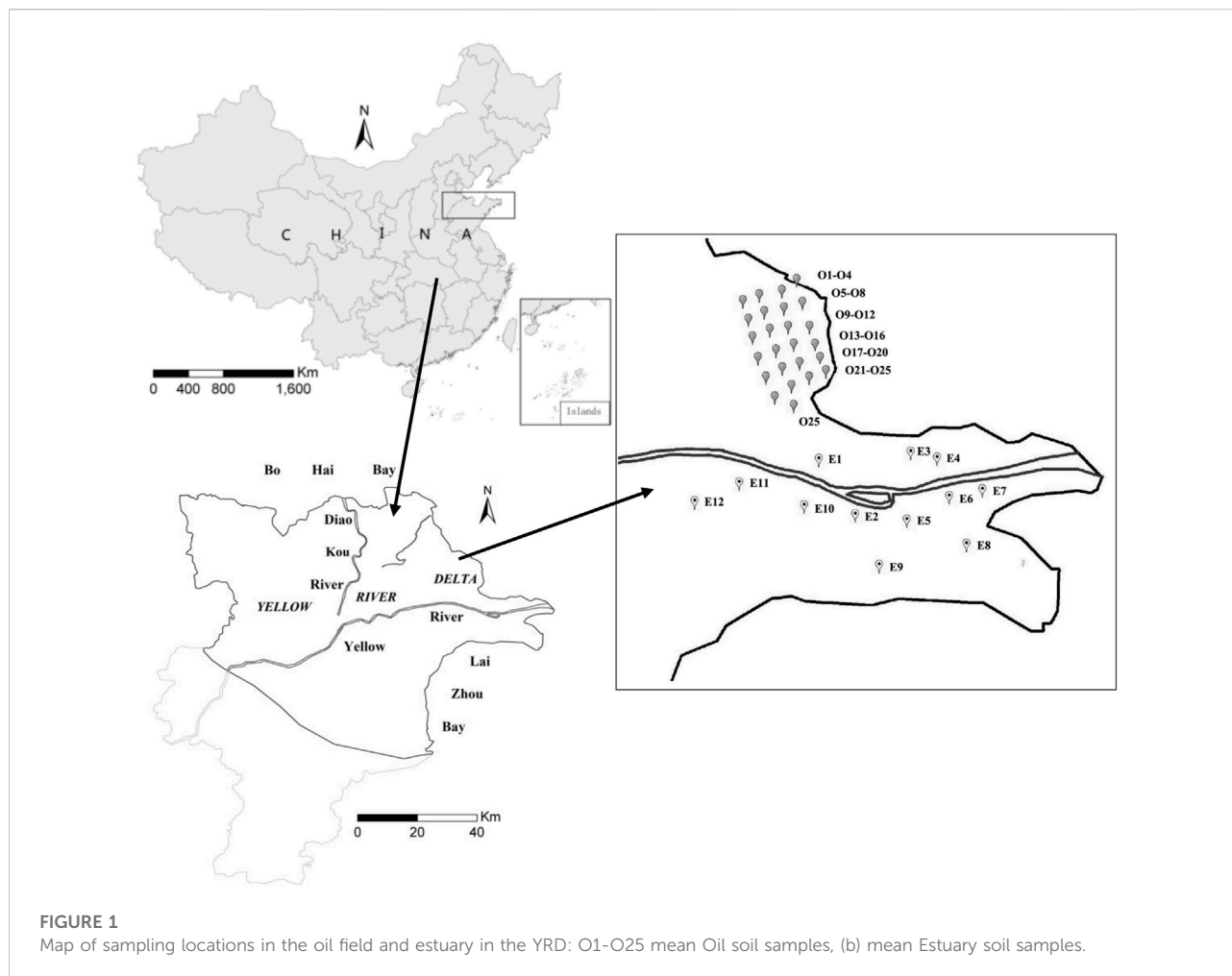
The EPA-610-16PAHs mixed standard solutions used in this study included acenaphthylene (Ace), acenaphthene (Acy), anthracene (Ant), benzo-a-anthracene (BaA), benzo-a-pyrene (BaP), benzo-b-pyrene (BbF), benzo-ghi-pyrene (Bgp), benzo-k-pyrene (BkF), chrysene (Chr), dibenz-ah-anthracene (DaA), fluorine (Fl), fluoranthene (Fla), indeno-123-cd-pyrene (Inp), naphthalene (Nap), phenanthrene (Phe) and pyrene (Pyr). Sixteen PAHs (16 compounds specified in EPA Method 610) in a mixture were purchased from Supelco company (United States). The PCBs mixed standard solutions including PCB28, PCB52, PCB101, PCB118, PCB153, PCB138 and PCB180 were purchased from o2si company (United States). Hexane and dichloromethane used for sample pretreatment were all pesticide analysis grades.

Sample extraction and clean-up

The mixture of soil sample (3 g) and quartz sand (10 g) was then Soxhlet-extracted with 20 ml of hexane and dichloromethane solvent mixture (1:1, v/v) for 48 h. The extract was concentrated to approximately 1 ml by a rotary evaporator (Buchi E-96, Switzerland).

For the determination of PCBs, the concentrated extract was treated with sulfuric acid (98%) before clean-up. A silica gel column chromatograph was used to clean up and fractionate the extract. The column was the glass column with an inner diameter of 25 cm × 1 cm and was filled with glass wool, 1 cm anhydrous Na₂SO₄, 1.5 cm silica gel, and 1 cm anhydrous Na₂SO₄ in turn. PCBs were eluted with 20 ml hexane. The hexane fraction was then evaporated to dryness and spiked with hexane retaining constant volume to 1 ml.

For the determination of PAHs, the extract was cleaned up with a silica gel column. The column was rinsed with 5 ml hexane and dichloromethane solvent mixture (9:1, v/v) before using. PAHs were eluted with 20 ml hexane and dichloromethane solvent mixture (1:1, v/v). The solvent mixture was evaporated to dryness and spiked with hexane retaining constant volume to 1.5 ml.



Instrument analysis

In the study, sixteen polycyclic aromatic hydrocarbons in soil had been analyzed using GC/MS (7890/5975). A capillary column HP-5 (30 m × 0.32 mm × 0.25 μm) was employed. The carrier gas was purified nitrogen at the flow rate of 1.0 ml min⁻¹. The temperature of the injector was maintained at 290 °C. For PAHs analysis, the splitless injection was employed. The column oven temperature program was as follows: The oven temperature was initially maintained at 80°C and held for 2 min, and then increased to 290°C at the rate of 6°C min⁻¹ and held for 5 min until the sample was completely out of the column. SIM mode was used for quantification of PAHs.

Seven PCBs in soil had been analyzed using Agilent 7890 GC-μECD. A capillary column HP-5 (30 m × 0.25 mm × 0.25 μm) was employed. Carrier gas was purified nitrogen at the flow rate of 2.0 ml min⁻¹. The temperature of injector and detector were maintained at 220 and 280°C. For PCBs analysis, Splitless injection was employed for PCBs analysis. The column oven temperature program was as follows: The oven temperature was initially maintained at 60°C and held for 1 min and then increased to

140°C at the rate of 20°C min⁻¹; subsequently, the oven temperature was increased to 260°C at the rate of 12°C min⁻¹ and held for 3 min until the sample was completely out of the column.

Quality assurance and quality control

The external standard method was used to determine the concentrations of target compounds. A procedural blank consisting of all chemicals and solvents was run to check for interferences and cross contamination. The recoveries ranged from 74.52 to 105.66% for sixteen PAHs and ranged from 73.2 to 96.3% for seven PCBs.

Results and discussion

Concentrations, proportions, and compositions of PAHs

The concentrations of PAHs in soil from the YRD were presented in Table 1. In the thirty-seven soil samples, most of the

TABLE 1 PAH concentrations ($\mu\text{g kg}^{-1}$), detect rates and proportions in different soil samples.

Compond	Total soil ($n = 37$)			Soil from the oil field ($n = 25$)					Soil from the estuary ($n = 12$)				
	Range	Mean	Detect rate	Range	Mean	Detect rate	SE	Proportion rate	Range	Mean	Detect rate	SE	Proportion rate
Nap	77.4–303.5	123.4	100	77.4–303.5	132.2	100	58.92	48.2	81.6–112.0	98.1	100	9.48	35.6
Acy	n.d.–37.9	5	97.3	n.d.–11.5	4.1	96	2.89	1.5	0.8–37.9	6.6	100	10.03	2.4
Ace	1.0–21.2	4	100	1.0–6.9	3.3	100	1.58	1.2	1.6–21.2	5.2	100	5.18	1.9
Fl	n.d.–102.7	21.1	97.3	n.d.–37.4	16.3	96	13.04	6	14.8–102.7	28.5	100	23.63	10.3
Phe	29.2–75.8	43.4	100	29.2–75.8	45	100	12.85	16.4	29.6–50.8	38.8	100	5.89	14
Ant	0.9–15.8	4	100	0.9–15.89	5.6	100	5.63	2	0.9–1.7	1.3	100	0.21	0.5
Fla	2.1–39.0	5.6	100	2.19–39.09	6.8	100	8	2.5	2.4–4.9	3.5	100	0.78	1.3
Pyr	0.7–32.5	18.6	100	0.7–32.5	17.5	100	10.39	6.4	4.6–30.1	19	100	7.06	6.9
BaA	0.7–23.9	3.9	100	0.8–19.2	4.3	100	4.53	1.6	0.9–23.9	3.6	100	6.53	1.3
Chr	n.d.–19.5	9	94.6	n.d.–15.2	7.1	92	4.36	2.6	1.2–19.5	12.4	100	5.99	4.5
BbF	n.d.–46.6	7.4	67.6	n.d.–15.62	5.8	56	5.72	2.1	n.d.–46.6	10.9	91.7	11.64	4
BkF	n.d.–2.4	0.6	59.5	n.d.–1.7	0.5	44	0.62	0.2	n.d.–2.4	0.8	75	0.67	0.3
BaP	n.d.–14.4	6.4	75.7	n.d.–14.0	5.7	68	4.84	2.1	n.d.–10.5	6.6	91.7	2.61	2.4
InP	n.d.–10.9	5	94.6	n.d.–8.5	3.9	92	2.43	1.4	0.7–10.9	6.9	100	3.33	2.5
DaA	0.3–7.8	1.3	100	0.3–6.3	1.4	100	1.48	0.5	0.3–7.8	1.2	100	2.13	0.4
BgP	n.d.–11.6	1.9	67.6	n.d.–11.6	2.5	48	3.49	0.9	n.d.–6.7	1	25	2.15	0.3
PAHs	157.7–481.7	269.4	100	157.7–481.7	274	100	91.21	100	222.2–408.3	244.4	100	48.06	100

nd.: not detected; SE: standard error of mean.

TABLE 2 Total PAH concentrations in soil samples reported in previous literature.

Sample	Number of PAHs	Total PAH concentration [$\mu\text{g kg}^{-1}$]	References
Agricultural soils from Shunde, Guangdong, China	16	33.7 to 350.0	Li et al. (2008)
Agricultural soil from Tianjin, China	16	1.1 to 6.3	Tao et al. (2004)
Soils in the Seine River basin, France	14	450.0 to 5650.0	Motelay-Massei et al. (2004)
Soils from Guiya, Guangdong, China	16	44.8 to 3206.0	Wong et al. (2007)
Surface sediments from the YRD, China	16	3.6 to 27.1	Wang et al. (2011)
Present study	16	157.8 to 481.7	Present study

TABLE 3 Classification of soil contamination by PAHs.

Class of soil contamination	$\sum 16\text{PAH}$ ($\mu\text{g kg}^{-1}\text{d.w.}$)
Not contaminated	<200
Weakly contaminated	200-600
Contaminated	600-1000
Heavily contaminated	>1000

sixteen PAH compounds were observed with high detect rates. Twelve of them were detected in over 90% of the soil samples. The detect rates of BbF (67.6%), BkF (59.5%), BaP (75.7%) and BgP (67.6%) were relatively low. The concentrations of PAH compounds in the YRD were compared with those reported from elsewhere as listed in Table 2. Total PAHs had been detected in all the soil samples, which ranged from 157.8 to 481.7 $\mu\text{g kg}^{-1}$ (dry weight, DW). The concentrations observed in this study were higher than those in agricultural soils reported in Shunde (ranged from 33.7 to 350 $\mu\text{g kg}^{-1}$) (Li et al., 2008) and Tianjin (ranged from 1.08 to 6.25 $\mu\text{g kg}^{-1}$) (Tao et al., 2004), as well as the concentrations in sediments at the YRD (3.6–27.1 $\mu\text{g kg}^{-1}$) (Wang et al., 2011). However, the concentrations detected in this study were significantly lower than those reported in Seine River basin (ranged from 450 to 5650 $\mu\text{g kg}^{-1}$) (Motelay-Massei et al., 2004) and Guiya (ranged from 44.8 to 3206 $\mu\text{g kg}^{-1}$) (Wong et al., 2007). A slight difference was found between the samples from the oil field (274.0 $\mu\text{g kg}^{-1}$) and the estuary (244.4 $\mu\text{g kg}^{-1}$). Maliszewska-Kordybach (1996) established the classification of soil contamination by PAHs, which was summarized in Table 3. According to the classification, both the Oil soil and Estuary soil samples can be considered as weakly contaminated.

The proportions of individual compounds in PAHs in samples from the oil field and the estuary were depicted in Table 1. On the whole, the proportion of Nap in all the samples was the highest among the sixteen individual compounds, which accounted for 48.2% in the soil samples from the oil field and 35.6% in the estuarine samples. But the standard error of mean of Nap in the oil soil samples was 59.0%, which showed great different with the

other twenty-four soil samples collected from the oil field. The standard error of mean of Nap in the estuarine samples was only 9.48%. Following Nap, the proportion of Phe was higher than the other 14 compounds. The main compounds of PAHs in the samples from the oil field and the estuary were the same. The contributions of Nap and Phe to total PAHs in the samples from the oil field and the estuary were 64.7 and 56.0%, respectively. The proportions of Nap and Phe in the samples from the oil field were significantly higher than those in the soil samples from the estuary. Conversely, the Fl, Chr, BbF, and Inp in the oil field samples were obviously lower than those in the estuarine samples.

Furthermore, the compositions of different benzenes had been analyzed in order to obtain accurate information about the characteristics of PAHs. The compositions of different benzenes in total PAH in the samples from the oil field and the estuary were shown in Figure 2. As seen in Figure 2, the proportions of low-molecular-weight (LMW) PAHs (2- and 3-ring) in all samples are higher than 70%. Samples from the oil field contain a proportionally higher amount of low-ring PAHs. In all samples, there's high amount of LMW PAHs, which was the same as the profiles reported in Bincheng (Xie et al., 2011). However, the result was different from those reported in Beijing and Tianjin, China, which were characterized by high molecular-weight (HMW) PAHs (Wang et al., 2010). Compared with the estuary sites, the proportions of LMW PAHs in the oil field samples were close to 80%. It was reported that the high amount of LMW PAHs observed in soil samples from Tianjin industrial near shore area could be due to the input of the oil exploitation and biological processes (Jiao et al., 2009). The high content of phenanthrene in the sediments could be related to the petroleum input from local derived products (Yunker et al., 1996; Shi et al., 2005), while low-temperature combustion inputs could be also responsible for naphthalene and phenanthrene and their alkylated homologs (Mai et al., 2001). Soil petroleum contamination was characterized by high concentrations of LWM PAHs, particularly Nap and Phe (Aislabie et al., 1999; Nadal et al., 2007). In the present study, the abundance of LMW PAHs in soil samples from the oil field was higher than that from the estuary. The composition of different benzenes probably indicated the impact of petroleum in the study area, especially for the oil Filed region.

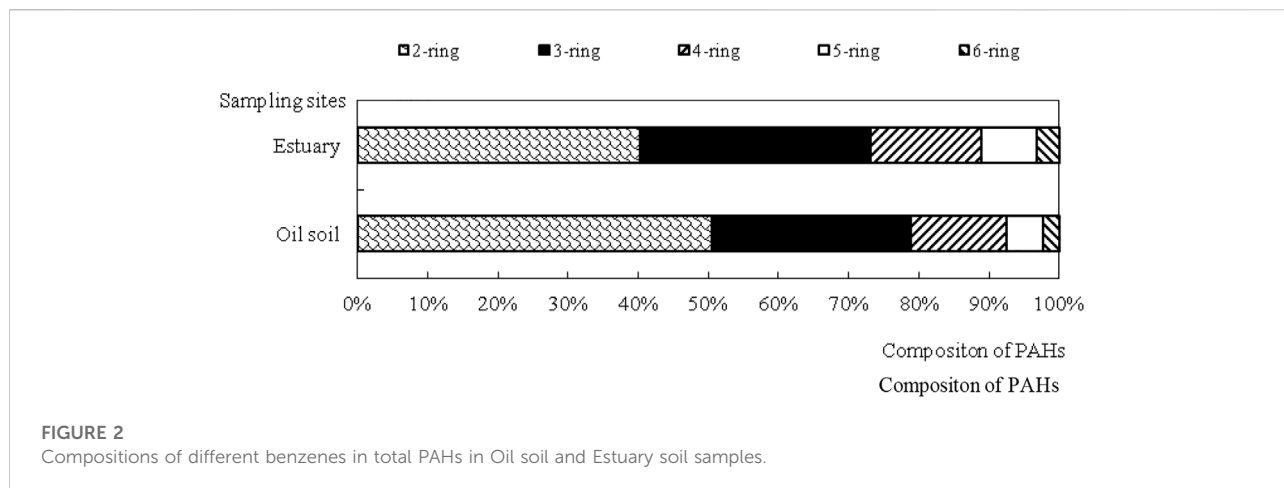


FIGURE 2 Compositions of different benzenes in total PAHs in Oil soil and Estuary soil samples.

TABLE 4 The concentrations of PCB congeners ($\mu\text{g kg}^{-1}$) in different soil samples.

Compound	Total soil (<i>n</i> = 37)			Oil soil (<i>n</i> = 25)			Estuary (<i>n</i> = 12)		
	Range	Mean	Detect rate	Range	Mean	Detect rate	Range	Mean	Detect rate
PCB28	n.d.–8.8	5.0	94.6	n.d.–8.8	6.5	92.0	0.8–4.5	1.8	100.0
PCB52	1.5–23.5	4.3	100.0	1.7–23.5	5.3	100.0	1.5–3.4	2.1	100.0
PCB101	n.d.–6.6	0.7	59.5	n.d.–2.8	0.8	44.0	n.d.–0.9	0.5	91.7
PCB118	n.d.–7.2	1.1	56.8	n.d.–5.1	1.4	48.0	n.d.–1.5	0.6	75.0
PCB153	n.d.–12.2	2.9	86.5	n.d.–12.2	3.3	80.0	0.4–3.8	2.0	100.0
PCB138	n.d.–10.2	2.1	89.2	n.d.–8.9	2.7	84.0	0.2–2.4	0.8	100.0
PCB180	n.d.–13.7	3.8	97.3	2.8–13.7	4.1	96.0	1.5–6.9	3.1	100.0
Total PCBs	5.6–56.6	38.9	100.0	11.5–56.6	24.2	100.0	5.6–19.0	10.8	100.0

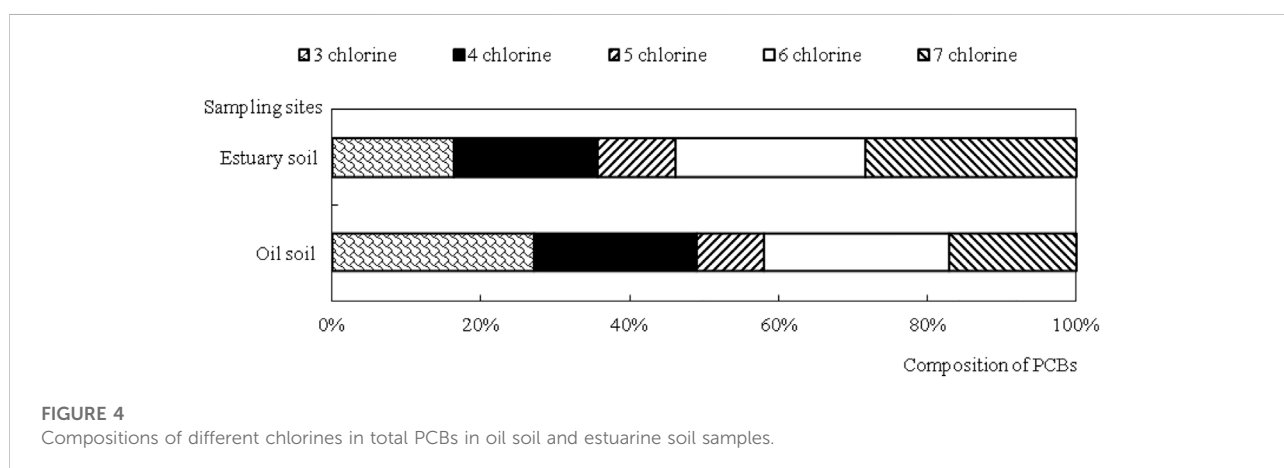
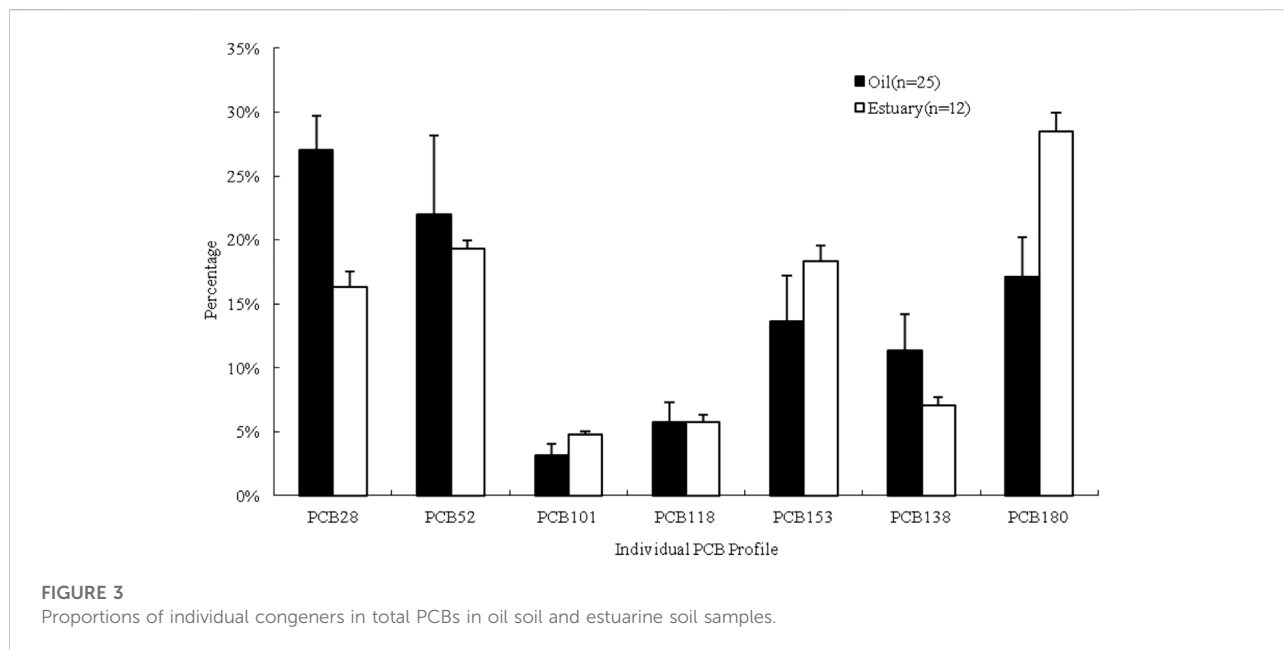
TABLE 5 Total PCB concentrations in soil samples reported from literature [$\mu\text{g kg}^{-1}$].

Sample	Number of PCBs	Total PCB concentration	References
Soils along the altitudinal gradients of Balang Mountain, the east edge of the Tibetan Plateau	25	0.06 to 0.29	Zheng et al. (2012)
Soils from Ny-Ålesund and London Island, Svalbard, the Arctic	25	0.56 to 0.98	Zhu et al. (2015)
Soils in the Seine River basin, France	7	0.09 to 150.00	A; Motelay-Massei et al., 2004
Soils from a coastal city—Tianjin, China	7	0.03 to 4.36	Li et al. (2011b)
Soils from Guiya, Guangdong Province, China	36	3.34 to 458.00	Wong et al. (2007)
Present study	7	5.60 to 56.60	Present study

Concentrations, proportions, and compositions of PCBs

The concentrations of individual congeners of PCB and the total concentration on the basis of dry weight are presented in

Table 4. The concentrations of total PCB in the thirty-seven soil samples ranged from 5.6 to 56.6 $\mu\text{g kg}^{-1}$, with a mean value of 38.9 $\mu\text{g kg}^{-1}$. Five of seven PCB congeners were observed over 80%. As listed in **Table 5**, the total concentration of PCBs in the soil from the Yellow River Delta was higher than that from



Balang Mountain, Ny-Ålesund and London Island, and Tianjin, but it is lower than that in the soil from Guiya, India. Concentrations of PCBs reported in the present study were lower comparing with the Australian and New Zealand ecological investigation level ($1000 \mu\text{g kg}^{-1}$) and the Canadian guidelines for soil ($1300 \mu\text{g kg}^{-1}$) (ANZECC and NHMRC, 1992; CCME, 2003). The detection frequencies of PCB congeners in the samples from the oil field samples were lower than the estuarine ones. However, the mean concentrations of PCB congeners in the samples from the oil field were higher than the ones from the estuary, which were 24.2 and $10.8 \mu\text{g kg}^{-1}$, respectively.

From Figure 3, we can see that the proportions of individual congeners in total PCBs in soil samples from the oil field and the estuary. The proportions of the former samples differed from that of the latter ones. Among all congeners in the samples from

the oil field, PCB-28 (27%) exhibited higher concentration, followed by PCB-52 (22%), PCB-180 (17.1%), PCB-153 (13.6%), PCB-138 (11.3%), PCB-118 (5.8%), and PCB-101 (3.2%). In the soil samples collected from the estuary, the concentrations of PCBs congeners were in the following order: PCB-180 (28.5%) > PCB-52 (19.4%) > PCB-153 (18.4%) > PCB-28 (16.3%) > PCB-138 (7%) > PCB-118 (5.7%) > PCB-101 (4.7%). Compositions of different chlorines in total PCBs in soil samples from the oil field and the estuary were shown in Figure 4. As illustrated in Figure 4, difference of the composition of PCBs was observed in the samples collected from the two different sites. The proportions of high-chlorine congeners (PCB101, PCB118, PCB153, PCB138 and PCB180) were 49.0%, and those of (PCB28 and PCB52) were 51.0% in Oil soil sites. The proportions are approximately similar between

high-chlorine congeners and low-chlorine congeners in Oil soil sites. The proportions of various PCBs congeners in the samples from the oil field and the estuary showed significant difference. In the samples from the estuary, the total percentage of the congeners that contain five to seven chlorine atoms (PCB101, PCB118, PCB153, PCB138, and PCB180) were higher than that with three to four chlorine atoms (PCB28 and PCB52). Unlike the estuarine samples, percentage of the high-chlorine congeners are approximately similar to that of the low-chlorine congeners in the oil field samples.

PAHs source identification

Low-molecular-weight/high-molecular-weight hydrocarbon ratio (LMW/HMW) have been frequently used to identify the sources of PAHs (A. Melnyk et al., 2015). Pyrogenic sources, such as the combustion derived PAHs, were depleted in LMW 2-ring PAHs and enriched in HMW four to six ring PAHs, leading to the LMW/HMW ratios were less than 1 (Soclo et al., 2000 and Rocher et al., 2004). In contrast, petrogenic sources, such as fuel oil or light refined petroleum products, are dominated by LMW PAHs and have LMW/HMW ratios larger than 1. Therefore, LMW/HMW ratios have been used to determine the source of PAHs, where the LMW acronym defines the total concentration of six PAHs (Nap + Acy + Ace + Flu + Phe + Ant), and the HMW acronym defines the total concentration of 10 PAHs (Fla + Pyr + BaA + Chy + BbF + BkF + BaP + InP + DaA + BgP). In this study, the LMW/HMW ratios of PAHs in all the oil field samples were larger than 1 with a mean ratio of 4.06; the LMW/HMW ratios of PAHs in all the estuarine soil samples were larger than 1 with a mean ratio of 2.81. These results confirmed that the sources of PAHs in all the soil samples in the study area were petrogenic. Although the LMW/HMW ratios in the samples from the two sites are significantly different from each other, both of them identified the petrogenic PAHs sources. Gudong Oilfield is part of Shengli Oilfield and might play an important role in the distribution of PAHs due to the operation of oil exploration and refineries.

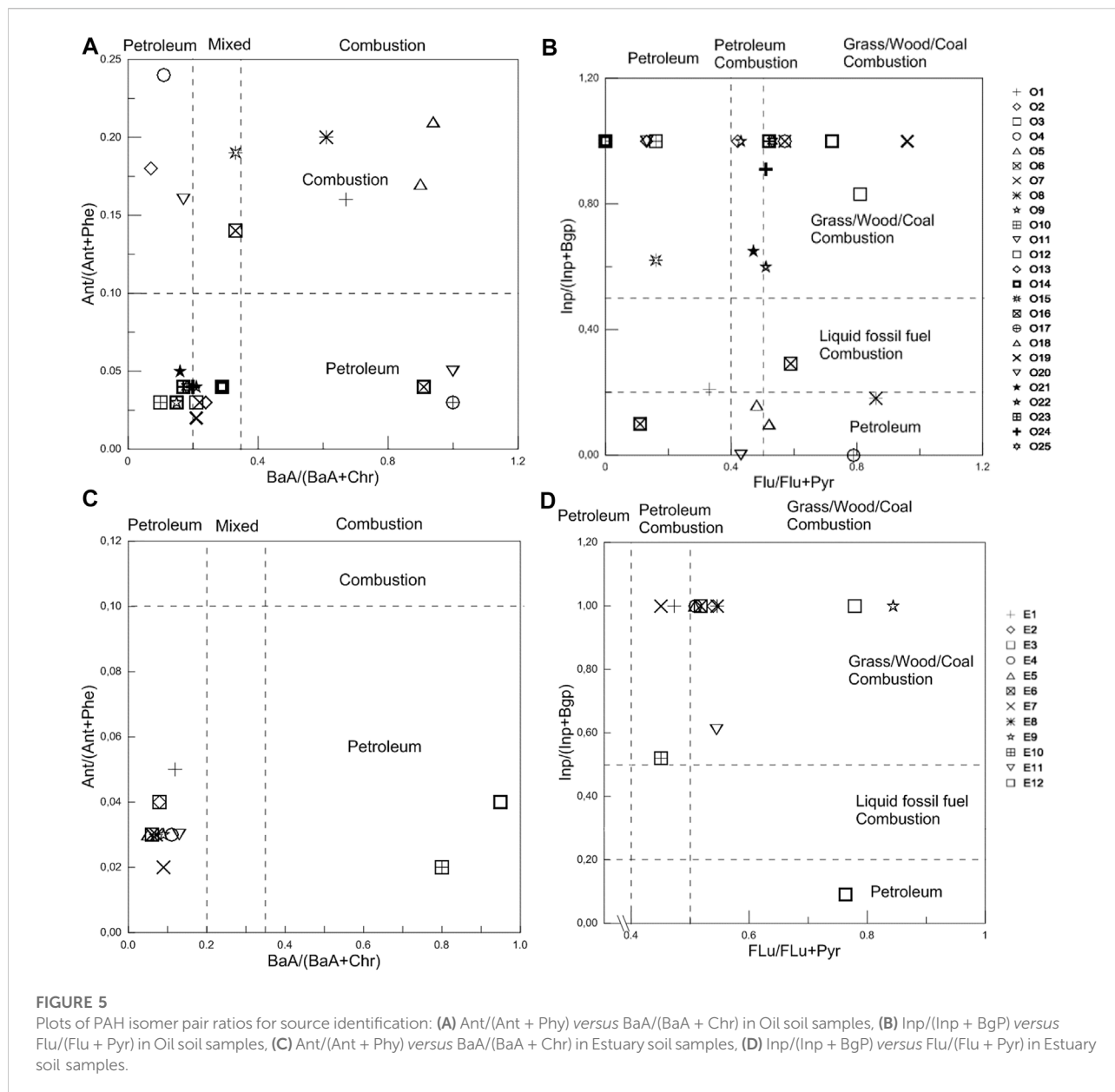
PAH isomer ratios such as Ant/(Phe + Ant), BaA/(BaA + Chr), Flu/(Flu + Pyr) and Inp/(Inp + BgP) were also extensively used to identify the PAHs sources (Yunker et al., 2002; Yang et al., 2009). Ant/(Phe + Ant) ratio < 0.10 is indicated as petroleum input or diagenetic source, whereas values > 0.10 is characteristic of combustion process. Flu/(Flu + Pyr) ratio less than 0.4 indicates petroleum input, between 0.4 and 0.5 indicates liquid fossil fuel combustion, and larger than 0.5 indicates grass, wood or coal combustion. BaA/(BaA + Chr) ratio less than 0.20 implies petroleum input, between 0.20 and 0.35 indicates petroleum or combustion, and larger than 0.35 implies combustion of vegetation and fossil fuel. Inp/(Inp + BgP) ratio below 0.20 shows petroleum, from 0.20 to 0.50 to liquid fossil fuel combustion, while a ratio over 0.50 has been attributed

to grass, wood and coal combustion (Yunker et al., 2002). In this study, the Flu/(Flu + Pyr) ratios of oil field samples and estuarine samples are 0.31 and 0.18, relatively. These indicated that petroleum input is an important source of PAHs in soil at the Yellow River Delta. Meanwhile, BaA/(BaA + Chr) ratios ranged from 0.10 to 0.90 in the oil field samples, and 0.07 to 0.95 in the estuarine samples. These ranges suggested that the PAHs sources in this study area were complicated. Moreover, most of the Inp/(Inp + BgP) ratios were over 0.50, which indicated the major sources were combustion of grass, wood and coal. For each soil sample, the PAH isomer ratios were paired and plotted in Figure 5 [Ant/(Phe + Ant) against BaA/(BaA + Chr) and Inp/(Inp + BgP) against Flu/(Flu + Pyr)]. It is clearly demonstrated that eight samples from the oil field (O9, O10, O12, O19, O21, O23, O24, O25) and ten samples from the estuary region (E1, E2, E4, E5, E6, E7, E8, E9, E11, E12) exhibited evidence of petroleum derived pollution, while other samples may be derived primarily from biomass and coal combustion. Moreover, the plots of Inp/(Inp + BgP) against Flu/(Flu + Pyr) shows that the PAHs in most samples mainly originated from combustion. Nevertheless, petroleum-derived pollution cannot be ignored in this case. Consequently, the isomer ratios noted above could not yet verify the sources of PAHs clearly in this study. The use of petroleum biomarkers has been proved to be more realistic for investigating petroleum contribution (Silva and Bicego, 2010; Tobiszewski and Namieśnik, 2012) and could be applied in the future study.

PCBs source identification

The distributions of PCBs could be influenced by the soil characteristics, the stability of different PCB congeners, and the function of emission sources. It is difficult to establish the correlation between the PCB congener profiles and the sources, especially in the condition of multi-sources.

Variety of methods have been tested to identify the sources of PCBs. The dominant component of PCBs could be used to identify the source of PCBs (Yu et al., 2014). Principal component analysis (PCA) has also been used to track the PCBs sources (Li et al., 2011a). The proportions of the individual PCB congeners from four categories of sampling sites, including industrial, urban, suburban, and remote sites, were normalized to congener 153 and used to find the spatial trend and to identify the source of PCBs (A. Motelay-Massei et al., 2004). According to Motelay-Massei's study, homogeneous proportions (the amount of light compounds equals to that of the heavy ones) indicated that the PCB signature is preserved over a short transport distance. The predominant PCBs are the high-molecular-weight PCBs at the urban sites. The lightest molecular weight PCBs contributes to the remote sites. The mode of PCB deposition on the soil is uncovered by those results. Different from the less chlorinated congeners, which



are easier to be transported over longer distances, the most chlorinated congeners tend to be adsorbed on particles and to settle near sources by dry or wet deposition.

The concentrations of PCB congeners in the samples from the oil field and the estuary were normalized to congener 153 and shown in Table 6.

As listed in Table 6, the samples from the two kinds of sites were both characterized by a signature with high proportions of the congeners with lightest and the heaviest molecular weight, and low proportions of compounds with intermediate molecular weight. This suggested the existence of two potential sources, local and remote. The concentrations of PCBs in the oil field samples were found higher than those in the estuarine samples.

This was probably because the sampling sites were located in the Gudong oil field. According to the congener index listed in Table 6, the proportion of the heaviest congener, PCB180, was higher than other congeners. According to Motelay-Massei's study, the remote sites are characterized by a greater contribution of the lightest molecular weight PCBs. There're some other sources away from the estuarine sites.

Because PCBs were chemically synthesized, it was hard to determine their points of origin according to molecular ratios (Wolska et al., 2012). But, after owning data on the origins of PAHs, the probable emission sources of PCBs could be attempted to pinpoint by comparing and seeking mutual correlations (Lidia et al., 2014). In this study, two different

TABLE 6 Concentrations proportions of the seven congeners normalized to congener 153.

PCB	Oil sites		Estuary sites	
	Range	Mean	Range	Mean
28	0–0.66	1.65	0.24–7.53	1.61
52	0.31–4.10	1.79	0.57–3.72	1.60
101	0–2.55	0.45	0–1.56	0.50
118	0–2.96	0.56	0–2.10	0.55
153	1	1	1	1
138	0–3.98	1.01	0.09–1.87	0.56
180	0–6.68	1.59	0.65–5.41	2.16

sources were identified by comparing the congeners normalized to congener 153. In order to obtain more accurate identification of the sources of PCBs, the relationships between PAHs and PCBs in different sites were discussed. The maximum correlation index in the oil field is 0.359, and the maximum correlation index in the estuarine sites is -0.323 . Correlation was not significant ($r^2 = 0.396$ and 0.576) as indicated by the Spearman correlation test ($\alpha = 0.05$). This would appear to indicate that, besides the petrogenic sources, other industrial sources also influenced the emission of PCBs.

Conclusion

Both PAHs and PCBs were detected with high frequency at YRD, and the average concentrations of PAHs in the samples from the oil field and the estuary were $274.0 \mu\text{g kg}^{-1}$ and $244.4 \mu\text{g kg}^{-1}$, relatively, which can be considered as weakly contaminated. The average concentrations of PCBs in the oil field samples and the estuarine samples were $24.2 \mu\text{g kg}^{-1}$ and $10.8 \mu\text{g kg}^{-1}$, respectively. Overall, the contamination in the estuarine area is weaker than that in the oil field area. In all samples, the proportions of low-molecular-weight (LMW) PAHs (2- and 3-ring) were higher than 50%. The contributions of Nap and Phe to total PAHs in oil field samples and estuarine samples were high, which were 64.7 and 56.0%, respectively. In the present study, the abundance of LMW PAHs in the oil field area was higher than that in the estuary area. According to the source identification, oil exploration and refineries in Gudong Oilfield could contribute to the PAHs contamination observed in the samples collected from the oil field. The analysis of diagnostic ratios and LMW/HMW ratios indicated that petrogenic PAHs were more significant in the samples from the oil field due to the production activities. The PCB28 and PCB52 congeners had the highest proportions in the majority of soil samples, especially in

the oil field samples. And the highest contents of PCBs in soil samples of estuaries (PCB180 and PCB52) were different from those in the oil field samples. The low-chlorine congeners (three to four chlorine atoms) PCBs in the oil field samples were more abundant than that in the estuarine samples. The analysis of congeners of PCBs and the correlation index between PCBs and PAHs showed that the emission of PCBs in the oil field area were influenced by the petrogenic sources from Gudong Oilfield and other industrial sources. The soil environmental management of the YRD could reference from the study.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

CJ was responsible for the experimental design and writing; LY was responsible for supporting CJ's experiments; YS was responsible for the correction of the paper.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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