Polycyclic aromatic hydrocarbons (PAHs) in surface soil from the Guan River Estuary in China: Contamination, source apportionment and health-risk assessment

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ABSTRACT: To analyse the distribution characteristics, potential sources and health risks of PAHs in the surface soil of the Guan River Estuary Industrial Area, 30 samples along the Guan River were collected. Sixteen types of PAHs were detected by gas chromatography-mass spectrometry (GC-MS). The results showed that the total content of the 16 PAHs (Σ16PAHs) ranged from 1212.8–12264.5 ng/g, and the arithmetic mean and median were 3504.8 ng/g and 2396.5 ng/g, respectively. The concentrations of 7 carcinogenic PAHs (Σ7carPAHs) ranged from 546.1–5742.3 ng/g, accounting for 34–54% of the Σ16PAHs. The pollution of the PAHs was intermediate compared with that of other industrial areas in China. Fluoranthene, pyrene and benzo[a] pyrene (BaP) are the main monomer PAHs. There was a weak positive correlation between the total organic carbon and the PAHs, and a negative correlation between the PAHs and the pH was found. The characteristic ratio and principal component analysis (PCA) show that the PAHs mainly come from combustion sources, especially the combustion process of coal and coke from industrial areas. The TEQBaP (toxic equivalency quantity relative to BaP) concentrations of 7 types of carcinogenic PAHs accounted for 99% of the Σ16TEQBaP. According to the Canadian soil environmental quality standard, 87% of the sampling site's PAH pollution values exceeded the safety value, suggesting that there is a potential ecological risk in the Guan River Estuary industrial area.

KEYWORDS: Guan River Estuary, polycyclic aromatic hydrocarbons (PAHs), pollution level, health-risk assessment

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a typical persistent organic pollutant. Persistent polycyclic aromatic hydrocarbons (PAHs) are widely distributed in different environmental media. Because of their carcinogenicity, PAHs increased concern for risk to the environment and human health and have become the target pollutants of environmental studies [1]. PAHs mainly come from the incomplete combustion process of fossil fuels, biomass and organic matter [2]. In 1976, the United States Environmental Protection Agency (US EPA) listed 16 types of PAHs as priority pollutants [3]. Studies have found that soil is the main sink of PAHs and that 90% of PAHs in the environment are stored in surface soil in the UK [4, 5]. PAHs generated by natural processes and human activities enter the environment and soil through a wet-dry deposition process. PAHs in soil pose a threat to human health through dusting, skin contact, and direct ingestion [6]. The pollution characteristics [7, 8], sources [9] and ecological risks [10, 11] of PAHs in surface soil have been extensively studied in China. However, there is no report on related research on PAHs in the Guan River Industrial Area. The Guan River is the main river in northern Jiangsu, China. In the most recent ten years, the Guan River Industrial Area has developed rapidly, especially with the establishment of steelmaking and thermal power and petrochemical industry bases. More and more news on pollution in the estuary area have been reported. Researchers have carried out related studies, but the existing research focuses on nutrients and heavy metal pollutants with few research results [12]. However, there are no reports about the PAHs in the soil. Therefore, this study analysed the PAHs in the surface soil of the Guan River Industrial Area. The purpose is to investigate the PAH pollution characteristics to discuss the factors affecting PAH enrichment, to analyse the pollutant sources and to conduct an ecological risk assessment, all with

a focus on providing basic data for managers to manage and control regional PAH pollution.

MATERIALS AND METHODS

Sample collection

In April 2017, surface soil samples were collected from an industrial area. The sampling points are shown in Fig. 1. The soil collection was based on a multi-point (5 points) mixed method. A stainless-steel shovel was used to collect 0–10 cm of the surface soil, and 30 soil samples were collected and returned to the laboratory for freeze-drying and impurity removal prior to analysis.

Extraction and purification

The soil samples (5 g), copper powder and anhydrous sodium sulfate were added to a filter tank along with the internal standard substances (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} (Dr. Ehrenstorfer Company, Germany)), 120 ml of acetone (HPLC grade, TEDIA Company, USA) and dichloromethane (HPLC grade, CNW, Germany) mixed solvents (volume ratio V:V = 1:1) in a Soxhlet extractor with a mean rate of 4 times/hour continuous reflux extraction for 20 h. The extract was concentrated by rotary evaporation to approximately 1 ml, brought back up to a volume of 25 ml with n-hexane, concentrated by rotary evaporation to approximately 1 ml again and transferred to a 2 ml brown vial. To reduce the influence of impurities on the PAH test, the concentrated liquid was transferred to a silica alumina column (volume fraction of silica and alumina was 2:1, wet filling) with hexane (15 ml) and a mixed solvent of dichloromethane and hexane (70 ml, volume fraction of V:V = 3:7) to elute the alkanes and aromatic hydrocarbons, respectively. The eluent containing the aromatic hydrocarbon component was concentrated to approximately 1 ml for analysis.

Instrumental analysis

The concentration of the PAHs in the surface soil was tested by gas chromatography-mass spectrometry (GC-MS, Agilent, 7890A/5975C, USA). The gas chromatographic column was a DB-5 polysiloxane polymer column (30 m × 0.25 mm × 0.25 μm). The column warming procedure was as follows. The column was held at 55 °C for 2 min, heated to 280 °C at 20 °C/min and then heated to 310 °C at 10 °C/min for 5 min. The carrier gas was high-purity He, and the velocity was 1 ml/min. The scan mode was SIM

Table 1 Concentrations (ng/g) of the PAHs in the surface soil from the industrial area of the Guan River Estuary.

PAH	Min	Max	Mean	Median	SD
NaP	1.7	79.0	17.2	11.8	15.79
Acy	5.2	519.3	43.7	16.9	94.01
Ace	1.3	86.8	21.5	14.1	19.23
Fluo	6.9	129.9	36.8	23.7	35.44
Phe	56.2	915.6	295.7	217.7	235.52
An	13.1	250.1	68.8	47.4	68.60
Fl	176.7	2659.6	681.6	413.0	677.43
Pyr	189.2	2173.4	585.5	392.8	539.79
B[a]A	76.8	1457.6	290.4	204.9	279.19
Chry	102.0	1214.7	308.2	229.8	260.01
B[b+k]F	108.0	986.0	301.5	221.8	231.52
B[a]P	89.4	1737.6	336.6	234.8	326.03
InP	83.0	556.8	199.3	142.1	128.70
D[ah]A	21.9	287.4	74.4	50.7	66.66
B[ghi]P	93.2	770.2	243.6	170.3	174.46
Σ(2+3)	102.9	1359.8	483.8	343.6	363.72
Σ4	621.7	7237.2	1865.6	1225.9	1722.85
Σ(5+6)	447.5	3831.7	1155.4	830.7	860.82
Σ7carPAHs	546.1	5742.3	1510.4	1108.7	1207.19

mode. In this study, 16 United States Environmental Protection Agency (USEPA) priority controlled PAHs were detected and analysed: naphthalene (NaP), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phe), anthracene (An), fluoranthene (Fl), pyrene (Pyr), benzo[a] anthracene (BaA), chrysene (Chry), benzo[b] fluoranthene (B[b]F), benzo[k] fluoranthene (B[k]F), benzo[a] pyrene (BaP), indeno[1,2,3-cd] pyrene (InP), dibenz[a,h] anthracene (DahA) and benzo[ghi] perylene (BghiP).

Quality control and quality assurance (QC/QA)

A method blank, spiked blank and parallel experiment were used for quality assurance and quality control. The method blank experiment did not detect the target pollutants. The spike blank recovery range was between 74.7–106.3%. The relative standard deviation of each parallel sample was controlled within 3%. The detection limit was 0.07–0.12 ng/g.

RESULTS

Concentration characteristics

The concentration distribution and total contents of the 16 monomer PAHs (Σ16PAHs) in the surface soil of the Guan River Estuary Industrial Area are shown in Table 1. The concentrations of the Σ16 PAHs
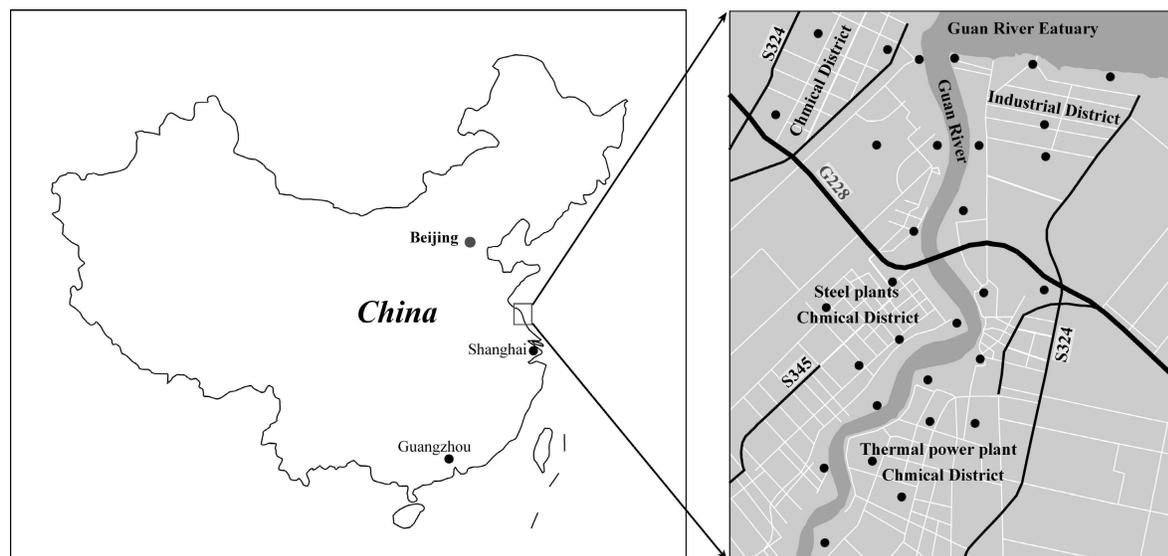
Fig. 1 Distribution map of the surface soil sampling points in the Guan River Estuary.

ranged from 1212.8–12264.5 ng/g with the arithmetic mean and median values of 3504.8 ng/g and 2396.5 ng/g, respectively. Among them, the mean concentration of the Σ4 ring PAHs was the highest (1865.6 ng/g), followed by the Σ(5+6) ring PAHs (1155.4 ng/g), and the lowest concentration was the Σ(2+3) ring PAHs (483.8 ng/g). The concentrations of the 7 carcinogenic PAHs (Σ7car PAHs) listed by the US EPA ranged from 546.1–5742.3 ng/g, had an arithmetic mean of 1510.4 ng/g and a median of 1108.7 ng/g and accounted for 34–54% of the Σ16PAHs. Maliszewska-Kordybach established the classification standard for PAH pollution in soil. Concentrations of Σ16PAHs < 200 ng/g represent uncontaminated soil, from 200–600 ng/g represent slightly polluted soil, 600–1000 ng/g represent polluted soil and > 1000 ng/g represent serious pollution [13]. According to this standard, all sampling points in the Guan River Estuary Industrial Area were seriously polluted, and the soil pollution problems in the study area should be further researched by the relevant departments.

Previous studies have shown that the median value of the PAHs in the surface soil in China is 730 ng/g [9], which is much lower than that determined in this study. The possible reason for this result is that this study mainly focuses on the pollution of PAHs in industrial area so that the sampling points are close to the pollution sources. Therefore, this study objectively reflects the actual situation. Compared with other industrial areas in China, the concentration of the Σ16PAHs was higher than those
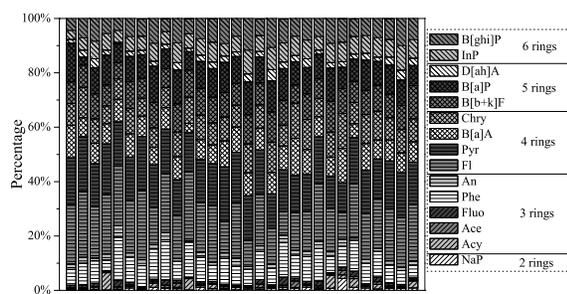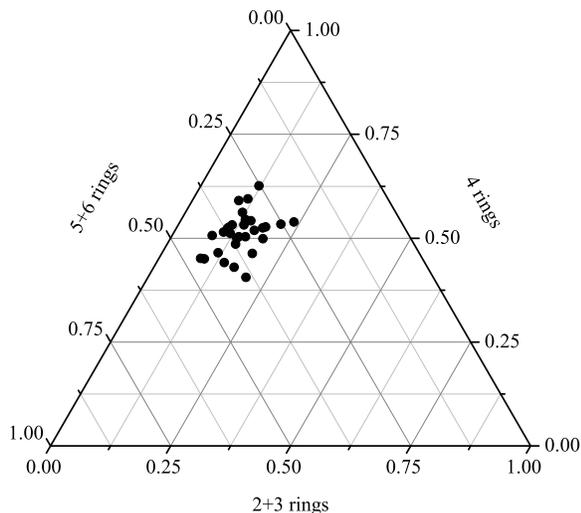

Fig. 2 PAH composition in surface soil from the Guan River Estuary.

determined for Nanjing (1060 ng/g) [14], Handan (398.9 ng/g) [15], Daqing (1839 ng/g) [16] and Shenyang (326.7 ng/g) [17], equivalent to that for Jinan (2700 ng/g) [18], and lower than that for Anshan (32100 ng/g) [19] and Dalian (6440 ng/g) [20]. Based on the PAH pollution in the surface soil in industrial areas, this study area has an intermediate pollution level.

Composition characteristics

The composition characteristics of the PAHs in the surface soil from the Guan River Industrial Area are shown in Fig. 2. The mean proportions of Fl, Pyr and BaP were the highest ($\geqslant$ 10%); Fl accounted for up to 18%, and Pyr and BaP accounted for 16% and 10%, respectively. These were followed by Phe (9%), Chry (9%), B[b+k]F (9%) and B[a]A (8%). Na, Acy, Ace and Fluo only represented 1%.

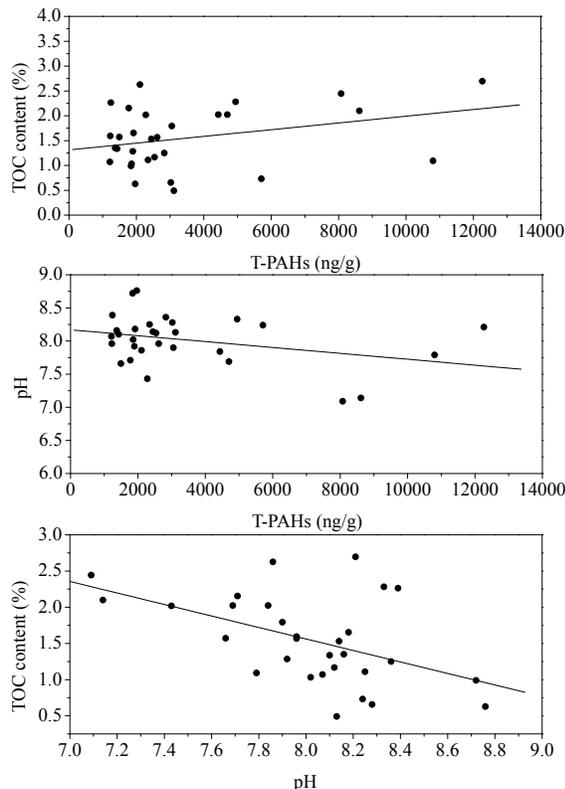Researchers have found that there is a high

Fig. 3 PAH composition in surface soil from the Guan River Estuary.

proportion of Phe, Fluo and Pyr in Chinese surface soil [14]. However, there are differences in various regions of China, mainly due to different pollutant emissions. The PAHs can be divided into 2-3 rings (low rings), 4 rings (middle rings) and 5-6 rings (high rings) according to the different ring numbers. In this study, the higher contribution of Fl, Pyr, B[a]A and Chry led to the highest proportion of 4-ring PAHs, accounting for 51%; this was followed by 5-ring and 6-ring PAHs, accounting for 21% and 13%, respectively (Fig. 3). The proportion of 3-ring and 2-ring PAHs is lower, only 12% and 3%, respectively [9]. This is similar to the studies in other parts of China. The low-ring PAHs in the atmosphere mainly exist in the gas phase and have a long-range migration ability. However, the high-ring PAHs mainly exist in the atmospheric particle phase and have a weak long-range migration ability [21, 22]. Therefore, point-source pollutant emission is the main source of high-ring PAHs in soil.

DISCUSSION

pH and TOC analyses

The total organic carbon (TOC) can affect physicochemical processes such as adsorption/analysis of soil materials and biodegradation and is considered a major factor affecting the accumulation of PAHs in soil. The TOC did not significantly change in this study (0.5–2.7%, mean 1.6%). A correlation analysis showed a weak positive correlation between the TOC and $\Sigma16$PAHs ($n = 30$, $r = 0.319$, $p < 0.01$) (Fig. 4). Previous researchers reported that there

Fig. 4 Effect of the pH and TOC on the T-PAH concentrations in the surface soil. T-PAH $= \Sigma16$PAHs.

was a significant correlation between the TOC and the $\Sigma16$PAHs when the $\Sigma16$PAH concentration was above 2000 ng/g [23]. In this study, the mean concentration was 3504.8 ng/g, which is much larger than 2000 ng/g. However, the TOC and PAHs did not show a significant correlation. Studies have found that soil microorganisms play a role in the metabolism of organic matter. This reduces the impact of the TOC on the enrichment of the PAHs. This may be the main reason for the weak correlation between the TOC and PAHs. Changes in the soil pH change the TOC, affecting the PAH content changes [24]. We found a weak negative correlation between the pH and $\Sigma16$PAHs ($n = 30$, $r = -0.338$, $p < 0.01$), and a moderate negative correlation between the TOC and pH ($n = 30$, $r = -0.493$, $p < 0.01$). The TOC content in more acidic soil is less because as the free organic matter in acidic soil decreases, the TOC solubility increases, making it easier for the TOC to drain. However, the organic-mineral complexes in soil are decomposed and destroyed under the action of the acid, becoming less complex particles, which are easily

Table 2 Rotated component matrix.

PAH	Component		
	1	2	3
NaP	−0.032	−0.039	0.973
Acy	0.157	0.903	−0.053
Ace	0.718	−0.271	0.293
Fluo	0.902	−0.248	−0.031
Phe	0.907	−0.181	0.024
An	0.871	0.062	−0.059
Fl	0.943	0.218	−0.123
Pyr	0.949	0.243	−0.095
B[a]A	0.916	0.132	0.023
Chry	0.953	0.127	−0.017
B[b+k]F	0.949	0.251	0.016
B[a]P	0.773	0.293	0.073
InP	0.889	0.347	0.049
D[ah]A	0.856	0.209	−0.034
B[ghi]P	0.907	0.205	0.043
% Variance	68.771	9.896	7.179
% Commutative	68.771	78.667	85.846

Table 3 TEQ calculated as the TEF of the individual PAH relative to BaP (ng/g).

TEQ	TEF	Min	Max	Mean	SD
NaP	0.001	ND	0.08	0.02	0.016
Acy	0.001	ND	0.52	0.04	0.092
Ace	0.001	ND	0.09	0.02	0.019
Fluo	0.001	0.01	0.13	0.04	0.035
Phe	0.001	0.06	0.92	0.30	0.232
An	0.01	0.15	2.50	0.69	0.675
Fl	0.001	0.17	2.66	0.68	0.666
Pyr	0.001	0.19	2.17	0.59	0.531
B[a]A	0.1	7.68	145.76	29.04	27.450
Chry	0.01	1.02	12.15	3.08	2.556
B[b+k]F	0.1	10.80	98.60	30.15	22.763
B[a]P	1.0	89.41	1737.58	336.55	320.549
InP	0.1	8.30	55.68	19.93	12.654
D[ah]A	1.0	21.86	287.38	74.42	65.486
B[ghi]P	0.01	0.93	7.70	2.44	1.715
TEQ of 7 PAHs		139.07	2337.15	493.17	
TEQ of 16 PAHs		140.58	2353.92	497.99	

TEQ = toxic equivalency quantity; TEF = toxic equivalency factor; ND = not detected.

lost, resulting in the decrease in the organic matter content. The PAHs may be released simultaneously with the organic matter.

Source apportionment

The relative abundances of different molecular weight PAHs can be used to identify the source of the contaminants. Researchers have found that low molecular weight (LMW, 2+3 rings) PAHs originate mainly from oil spills, while high molecular weight (HMW, > 4 rings) PAHs are derived from fossil fuel combustion [24]. The LMW/HMW ratios were less than 1 (Fig. 5), and the highest ratio was only 0.313, which suggested that the PAHs in the soil mainly come from the incomplete combustion of fossil fuels such as coal. Each PAH pollution source has its own unique composition and ratio. Therefore, some specific PAH isomers, such as An/(An+Phe), Fl/(Fl+Pyr), BaA/(BaA+Chry) and InP/(InP+BghiP), are often used to distinguish the source of PAHs in different environmental media [25]. As shown in Fig. 5, the An/(An+Phe) scatter points are mainly distributed in the region for the incomplete combustion emissions from wood, coke and coal and partly in the area of oil leakage and combustion. The Fl/(Fl+Pyr) scatter points are mainly distributed in the areas of incomplete combustion emissions from gasoline, wood, coke and coal and partly in the region of diesel combustion and leakage. The scatter points for BaA/(BaA+Chry) and InP/(InP+BghiP) are mainly

found in the coke, coal and diesel combustion regions. Overall, the PAHs mainly come from fossil fuel and petroleum combustion and partly from oil spills.

A principal component analysis (PCA) was used to further judge the sources of the PAHs. Three main factors were extracted by the SPSS software (Table 2). The 4-ring PAHs (Pyr, BaA, Chry and B[b+k]F) in factor 1 have a higher loading and represent the significant source of coal combustion as some findings were obtained in the literature [15, 26]. The high loading of Acy in factor 2 suggests an oil spill source [27]. Acy is considered a product of a petroleum source, including the leakage and spillage of petroleum during production and transport. The high loading of a 2-ring (NaP) PAH in factor 3 also represents an oil source [28].

Risk assessment

The mean TEQBaP concentration of the 16 types of PAHs (Σ16TEQBaP) in the soil was 498 ng/g (Table 3). The highest concentration was 2218.4 ng/g, and the lowest was 156.9 ng/g. The 7 types of carcinogenic PAHs (Σ7cTEQBaP) had concentrations that ranged from 156.1–2210.1 ng/g with a mean value of 495.6 ng/g, which accounted for the 99% of Σ16TEQBaP. The results showed that the risk of toxicity was mainly from the 7 types of carcinogenic PAHs, especially
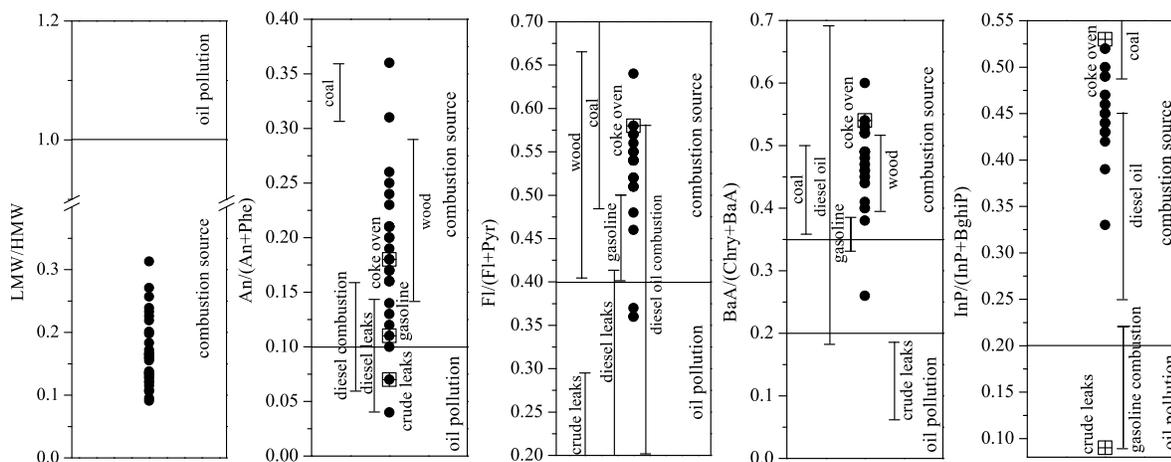
Fig. 5 Source apportionment of the characteristic ratios of the PAHs.

BaP (336.6 ng/g) and D[ah]A (74.4 ng/g). The Canadian soil environmental quality standard stipulates a safety value for Σ16TEQBaP in soil of 600 ng/g. The concentration of Σ16TEQBaP in soil around a coking plant was evaluated by multiplying the concentration by a coefficient of 3 [29]. In this study, the calculated Σ16TEQBaP concentration ranged from 470.6–6655.1 ng/g, and 87% of the sampling points exceeded the safety value, which indicated that there is a potential risk in the industrial area of the Guan River Estuary. Due to limited data, it is impossible to conduct a more comprehensive statistical analysis, and a risk assessment of the PAHs needs to be further studied.

CONCLUSION

The concentration range of the Σ16PAHs was from 1212.8–12264.5 ng/g. The PAHs were mainly 4-ring PAHs, followed by 5- and 6-ring PAHs, while 2-3 ring PAHs represent the lowest content. Fl, Pyr, BaP are the main monomer PAHs; the Fl ratio was as high as 18%, and the ratios of Pyr and BaP were 16% and 10%, respectively. There is a weak positive correlation between the TOC and PAHs, and the biological community may reduce the effect of the TOC on the PAH enrichment. However, there was a moderate negative correlation between the pH and TOC. The results of the principal component analysis showed that the PAHs were mainly derived from coal combustion and partly from oil leakage. The concentration of the Σ7cTEQBaP accounts for 99% of the Σ16TEQBaP. BaP and D[ah]A are the highest carcinogenic risk monomer PAHs.

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