

Distribution, sources, and toxicity assessment of polycyclic aromatic hydrocarbons in surface soils of a heavy industrial city, Liuzhou, China

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Abstract As a heavy industrial city, Liuzhou has been facing a serious pollution problem. It is necessary to take steps to control and prevent environmental pollution wherever possible. Surface soil samples were collected from four communities in Liuzhou City, to determine the concentrations, distributions, sources, and toxicity potential of polycyclic aromatic hydrocarbons (PAHs) present. The mean concentrations of total PAHs in the surface soil are 756.43 ng/g for the heavy industrial area, 605.06 ng/g for the industrial area, 481.24 ng/g for the commercial–cum–residential area, and 49.93 ng/g for the rural area. Both the isomer ratio and principal component analyses for the PAHs prove that these pollutants originate mainly from coal, diesel, gasoline, and natural gas combustion. The pollution hierarchies and toxic equivalency factor of BaP prove that the city is subject to heavy pollution caused by industry, transportation, and daily human activities.

Keywords Polycyclic aromatic hydrocarbons · Heavy industrial city · Surface soil · Isomer ratio · Principal component analysis · Toxicity assessment

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are environmentally persistent, organic pollutants (POPs), which have carcinogenic, teratogenic, and mutagenic properties (Jiang et al. 2016; Ma et al. 2015). They are ubiquitous in environmental media, such as soil, water, sediment, and air (Yu et al. 2014a, b; Wang et al. 2011; Larsen and Baker 2003). Once they become part of the environment, PAHs can exist for a long time, and threaten the ecosystem and human health via the food chain. The United States Environmental Protection Agency (USEPA) has identified 16 kinds of PAHs as priority pollutants (Tan et al. 2007; Keth and Telliard 1979). Because of the high octanol-water partition coefficient ($\log K_{ow} = 3.37\text{--}6.75$), PAHs are easily adsorbed in the organic matter of soil, and persist there for a long time. Thus, soil is a major repository of PAHs in the environment (Wilcke 2000). It is well recognized that PAHs originate mainly from anthropogenic sources (Suman et al. 2016; Argiriadis et al. 2014; Luo et al. 2015), such as industrial activities, transport and daily human activities, and accidental fuel spills.

Many studies have been conducted on the concentrations and distributions of PAHs in soil (Yu et al. 2014a, b; Wilcke 2000; Wang et al. 2010; Essumang et al. 2011; Marusenko et al. 2011; Bortey-Sam et al. 2014).

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However, no comprehensive work has been done to address the accumulation and distribution of PAHs in surface soil in Liuzhou, Southwest China. Liuzhou is one of the most industrialized and economically proficient cities in Guangxi Province. It has a population of 1.6 million, and is home to more than 3400 companies, and 11 large state enterprises. Liuzhou has been subjected to the heavy anthropogenic influences resulting from rapid economic development and urbanization. The expansion in industries, increased population, growth in the highway, railway, aviation, and shipping networks, and increasing vehicular emissions are potential sources of PAH contamination. The objectives of this study are to determine the concentrations of select PAHs, identify the major sources of these pollutants, and evaluate the extent of pollution and their toxicity potential in the surface soil of Liuzhou.

Materials and methods

Introduction of four communities

Figure 1 shows the four communities. The heavy industrial area contains several companies that consume large

amounts of coal resources, such as the Liuzhou Iron & Steel Group Co., LTD., Liuzhou Chemical Co., LTD., and Guangxi Liudian Electric Co., LTD. The industrial area contains many machinery manufacturing companies such as Guangxi Liugong Machinery Co., LTD., SAIC-GM-Wuling Automobile Co., LTD., and Liuzhou Rolling Stock Plant. The commercial-cum-residential area comprises business establishments and residences. The rural area has the least industrial activities, and the main activities are agriculture and animal husbandry.

Sampling

Twenty-one soil samples were collected from four communities in Liuzhou in August 2015. The global positioning system (GPS) was used to locate the sampling positions. Soil samples (0–5 cm) were collected using a stainless steel scoop and stored in amber-colored wide-mouth packers. All soil samples obtained were stored at –4 °C before being transported to the laboratory (State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, China) for analysis. A map showing the sampling locations is presented in Fig. 1.

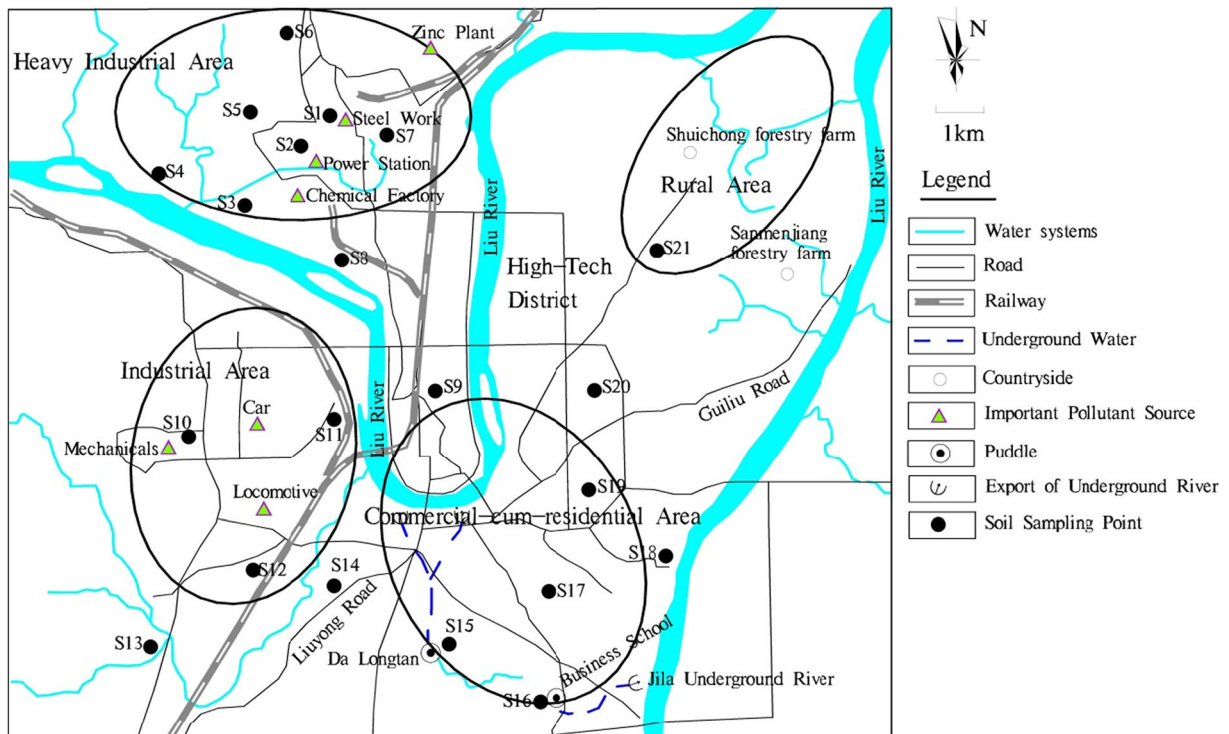


Fig. 1 Map showing the sampling locations

Sample extraction and cleanup

For the analysis of the PAHs, the soil samples were first dried naturally. Then, 10 g of each soil sample was evenly mixed with a certain amount of anhydrous sodium sulfate, activated copper sheets were added to remove elemental sulfur, the recovery indicators (naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12}) were added to indicate the recovery rates and Soxhlet extracted with 120 mL dichloromethane (DCM) for 24 h. N-hexane was used to replace the methylene chloride. Then, a 1:2 (v/v) alumina/silica gel column (DCM extract 48 h, silicon baked in oven at 180 °C and aluminum oxide at 240 °C for 12 h, after cooling both add 3% of its weight deionized water to activate) was used to separate and purify the samples with 40 mL 2:3 (v/v) dichloromethane/n-hexane to leach. Finally, the eluate was concentrated to 0.2 mL through a rotary evaporator and transferred to a 2 mL bottle. Simultaneously, hexamethyl benzene was added as an internal standard.

PAH analysis

The concentrations of the PAHs were determined by a gas chromatograph and mass spectrometer (GC-MS, Agilent 6890 and 5975). The operational settings/conditions of the GC were as follows. The chromatographic column was equipped with a DB-5MS fused silica capillary column (30 m \times 0.25 mm \times 0.25 μ m). The chromatographic column was heated to 80 °C for 2 min. The temperature was then raised to 290 °C at the rate of 4 °C/min, and retained for 25 min. The GC used an auto-feeding device with no shunt. The temperature of the injection port was 280 °C. The carrier gas was high purity helium at a constant flow rate of 1.0 mL/min. The operational conditions of the MS were as follows. Electron impact ionization was used as the ion source and the scan parameters were set to full scan mode. The ion source temperature and connector temperature were 230 and 280 °C, respectively. The mass selective detector operated in the electron impact mode at 70 eV, its scanning range being 50–550 amu, at a scanning rate of once per second.

All the soil samples were analyzed for 16 PAHs listed by the USEPA as priority PAHs: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA),

chrysene (Chr), benzo(b)fluorantene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (InP), dibenzo(a,h)anthracene (DBA), and benzo(g,h,i)perylene (BgP).

Quality assurance and quality control (QA/QC)

Quality control (QC) makes data more reliable, controls errors so that they lie within a permissible range, and guarantees data accuracy, precision, and reliability. To ensure quality assurance (QA)/QC, the PAH analysis included parallel and blank sampling, as well as a check on appropriate recovery rates.

Each set of batch samples contained 10% parallel samples, and the error rate was set to $\leq 20\%$.

While pretreating the samples, adding a recovery indicator can control the loss of target material in the Soxhlet-extracted process. The quantitative data of all samples were calibrated through the recovery rate. The recovery rate was 72–96%.

Quantitation was performed using an internal standard calibration method (six-point calibration: 0.2, 0.5, 1, 2, 5, and 10 ppm), and all the correlation coefficients (r^2) for the calibration curves exceeded 0.99.

Source apportionment

The distribution and source of PAHs are very complex. During migration, isomers are equally diluted, and they have unique compositions and ratios in each state. Isomer ratio is a widely used concept to judge the sources of PAHs existing in different environmental media (Yunker et al. 2002; Bucheli et al. 2004; Bortey-Sam et al. 2014; Cachada et al. 2012; Škrbić et al. 2017).

Concentrations of individual PAHs change during the emission from the source, migration, and distribution because of the differences in the physical and chemical properties as well as modified external conditions. Factors that are prone to change, such as biodegradation rate, volatility, and atmospheric precipitation, affect calculations of the isomer ratio (Zheng et al. 2011). As a result, simply using ring number distribution and the isomer ratio method to determine sources of PAHs may not be enough. Thus, we applied SPSS 17.0 to conduct principal component analysis (PCA), which performed with a varimax rotation to identify the potential sources of the PAHs.

Table 1 Toxicity equivalency factor (TEF) and targets in the Dutch standard (Suman et al. 2016; Nisbet and Lagoy 1992)

| | Nap | Acy | Ace | Flu | Phe | Ant | Fla | Pyr | BaA | Chr | BbF | BkF | BaP | InP | DaA | BgP |
|--------|-------|-------|-------|-------|-------|------|-------|-------|-----|------|-----|-----|-----|-----|-----|------|
| TEF | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.01 | 0.001 | 0.001 | 0.1 | 0.01 | 0.1 | 0.1 | 1 | 0.1 | 1 | 0.01 |
| Target | 15 | | | | 50 | 50 | 15 | | 20 | 20 | | 25 | 25 | 25 | | 20 |

Soil toxicity assessment

Currently, China has no official quality standards pertaining to PAHs in soil, and there is no unified evaluation standard in the world (Yang et al. 2016). We use the pollution hierarchies and toxicity equivalency of BaP (TEQ_{BaP}) to quantitatively characterize its potential toxicity.

Based on the total PAH concentration in soil, Maliszewska-Kordybac (1996) classified pollution levels pertaining to PAHs into four categories: unpolluted (< 200 ng/g), weakly polluted (200–600 ng/g), polluted (600–1000 ng/g), and severely polluted (> 1000 ng/g).

BaP poses the highest risk of cancer (Liu et al. 2017), using BaP as a reference substance to evaluate the toxicity of the 16 PAHs. This study uses the toxicity equivalence of BaP ($TEQ_{BaP} = \sum c_i \cdot TEF_i$) (Wang et al. 2015; Tsai et al. 2004; Agarwal et al. 2009; Jiao et al. 2017) to quantitatively characterize potential toxicity. In the equation, c_i denotes the content of PAH (i), and TEF_i is toxicity equivalency factor of PAH (i) (Table 1).

Results and discussion

Concentrations of PAHs in four communities

Sixteen types of PAHs were detected in 21 soil samples. The statistical data for total PAHs in surface soil from sample positions in Liuzhou are summarized in Table 2.

The heavy industrial area contained eight sampling positions, including S1, a special sampling point located within the boundary of the Liuzhou Iron & Steel Group Co., LTD. The concentration of total PAHs at S1 is 38,865.97 ng/g. Except S1, this value ranged from 146.27 at S4 to 1250.92 ng/g at S7, the average being 756.43 ± 399.94 ng/g. Compounds containing 2–4 rings are the major components of the total PAH in this area, and comprise 74.84% of the total. The concentration of total PAHs decreased in the order $S7 > S6 > S8 > S5 > S2 > S3 > S4$, corresponding to the prevailing wind

direction in Liuzhou, which has a southeast prevailing wind in summer and northwest prevailing wind in winter. Thus, S6 and S8, located northwest and southeast of S1, respectively, recorded the third and fourth highest total PAH concentrations. S7 recorded the second highest total PAH concentration, which could be attributed to the high vehicle exhaust emissions in that area.

The industrial area included five sampling positions. Sampling point S11 was present in a vegetable field that uses sewage for irrigation and is located near a village road. This location recorded the highest concentration of 5273.19 ng/g, which was 4 to 24 times higher than the values at other locations. This result could be attributed to an as yet unknown pollution source. The concentration of total PAHs in other surface soil samples ranged from 225.07 at S10 to 1254.7 ng/g at S12, with an average of 605.06 ± 450.24 ng/g. The detected percentages of 2–3, 4, and 5–6 ring PAHs are 24.37, 50.42, and 25.2%, respectively. The order of concentrations of total PAHs is $S12 > S13 > S14 > S10$. As seen from Fig. 1, all the sampling sites are located near the trunk road, which means that the industrial area is also subjected to vehicular emissions.

The commercial–cum–residential area included seven sampling positions. The concentration of total PAHs in the surface soil samples ranged from 151.94 at S9 to 1106.02 ng/g at S17, with an average of 481.24 ± 355.22 ng/g. The percentages of 2–3, 4, and 5–6 ring PAHs are 25.12, 46.16, and 28.71%, respectively. These findings are very similar to the industrial area, and 4-ringed PAHs are the most abundant within the total PAHs. The total PAH concentrations decreased in the following order: $S17 > S15 > S16 > S19 > S18 > S20 > S9$. The commercial–cum–residential area is located southeast of the heavy industrial area, and is adjacent to the trunk road and the main residential area. Thus, the PAH concentrations here are strongly influenced by vehicular emissions, residential activities, and heavy industry.

The rural area included only one sampling position, and is located far away from the industry and commercial–cum–residential areas. The sample from this area

Table 2 Concentration of PAHs in surface soil from the sampling locations in Liuzhou City

| | Heavy industrial area | | | | | | | | | | | Industrial area | | | | | | | | | | |
|-------------------|-----------------------|--------|--------|--------|--------|---------|---------|--------|--------|---------|---------|-----------------|---------|---------|-----|-----|-----|--|--|--|--|--|
| | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S10 | S11 | S12 | S10 | S11 | S12 | S19 | S20 | S21 | | | | | |
| Nap | 2802.75 | 42.70 | 4.62 | 3.21 | 26.22 | 8.30 | 3.79 | 24.04 | 4.6 | 56.15 | 6.71 | 4.6 | 56.15 | 6.71 | | | | | | | | |
| Acy | 873.43 | 4.24 | 0.12 | 0.12 | 4.75 | 3.91 | 10.71 | 0.24 | 2.05 | 25.29 | 16.18 | 2.05 | 25.29 | 16.18 | | | | | | | | |
| Ace | 428.37 | 3.63 | 0.04 | 0.67 | 2.39 | 3.52 | 0.02 | 1.95 | 0.4 | 21.44 | 2.16 | 0.4 | 21.44 | 2.16 | | | | | | | | |
| Flu | 1000.88 | 11.38 | 5.01 | 2.22 | 7.63 | 14.57 | 2.34 | 10.05 | 2.57 | 31.16 | 7.69 | 2.57 | 31.16 | 7.69 | | | | | | | | |
| Phe | 7533.45 | 149.32 | 52.74 | 19.10 | 71.01 | 179.82 | 49.07 | 150.19 | 22.65 | 391.32 | 102.11 | 22.65 | 391.32 | 102.11 | | | | | | | | |
| Ant | 3432.82 | 20.26 | 7.34 | 3.28 | 22.71 | 53.79 | 19.05 | 21.38 | 4.29 | 162.49 | 26.43 | 4.29 | 162.49 | 26.43 | | | | | | | | |
| Fla | 256.84 | 72.62 | 28.85 | 10.19 | 49.20 | 86.46 | 88.53 | 73.21 | 18.53 | 397.73 | 107.16 | 18.53 | 397.73 | 107.16 | | | | | | | | |
| Pyr | 349.93 | 83.66 | 40.23 | 14.43 | 81.97 | 128.83 | 135.17 | 107.91 | 32.41 | 646.65 | 191.89 | 32.41 | 646.65 | 191.89 | | | | | | | | |
| BaA | 7473.60 | 42.01 | 25.80 | 9.21 | 50.30 | 94.25 | 122.03 | 60.03 | 17.77 | 480.90 | 91.74 | 17.77 | 480.90 | 91.74 | | | | | | | | |
| Chr | 5234.70 | 72.76 | 42.23 | 15.29 | 72.39 | 112.07 | 139.03 | 98.22 | 22.60 | 505.28 | 140.65 | 22.60 | 505.28 | 140.65 | | | | | | | | |
| BbF | 33.60 | 82.42 | 58.86 | 23.89 | 113.13 | 150.34 | 214.80 | 128.42 | 31.77 | 788.07 | 187.65 | 31.77 | 788.07 | 187.65 | | | | | | | | |
| BkF | 6568.61 | 21.42 | 15.52 | 6.05 | 29.23 | 43.87 | 64.21 | 32.38 | 9.01 | 242.47 | 51.80 | 9.01 | 242.47 | 51.80 | | | | | | | | |
| BaP | 1432.33 | 28.88 | 29.83 | 11.88 | 69.75 | 101.03 | 130.37 | 57.06 | 21.08 | 561.43 | 106.64 | 21.08 | 561.43 | 106.64 | | | | | | | | |
| InP | 487.98 | 30.34 | 30.54 | 12.94 | 83.98 | 95.78 | 147.87 | 61.57 | 19.75 | 489.16 | 108.94 | 19.75 | 489.16 | 108.94 | | | | | | | | |
| DaA | 715.05 | 6.38 | 5.12 | 2.11 | 11.11 | 18.13 | 23.55 | 10.50 | 1.39 | 85.75 | 16.88 | 1.39 | 85.75 | 16.88 | | | | | | | | |
| BgP | 241.62 | 25.96 | 25.71 | 11.66 | 70.40 | 80.2 | 100.37 | 49.05 | 14.13 | 387.88 | 90.08 | 14.13 | 387.88 | 90.08 | | | | | | | | |
| Σ_2-3 环 | 16,328.54 | 304.14 | 98.71 | 38.80 | 183.90 | 350.37 | 173.51 | 281.06 | 55.18 | 1085.58 | 268.43 | 55.18 | 1085.58 | 268.43 | | | | | | | | |
| Σ_4 | 19,660.44 | 302.27 | 182.64 | 68.87 | 347.02 | 529.36 | 675.24 | 426.95 | 113.55 | 2663.38 | 663.72 | 113.55 | 2663.38 | 663.72 | | | | | | | | |
| Σ_5-6 | 2876.99 | 91.56 | 91.20 | 38.60 | 235.23 | 295.21 | 402.17 | 178.18 | 56.35 | 1524.22 | 322.55 | 56.35 | 1524.22 | 322.55 | | | | | | | | |
| Σ PAHs Nap | 38,865.97 | 697.97 | 372.55 | 146.27 | 766.15 | 1174.95 | 1250.92 | 886.18 | 225.07 | 5273.19 | 1254.70 | 225.07 | 5273.19 | 1254.70 | | | | | | | | |

| | Commercial-cum-residential area | | | | | | | | | | | Rural area | | | | | | | | | | |
|-----|---------------------------------|-------|-------|--------|-------|--------|-------|-------|-------|-------|-------|------------|-------|--------|-------|--------|-------|-------|-------|-------|--|--|
| | S13 | S14 | S9 | S15 | S16 | S17 | S18 | S19 | S20 | S21 | S13 | S14 | S9 | S15 | S16 | S17 | S18 | S19 | S20 | S21 | | |
| Nap | 9.90 | 24.12 | 3.52 | 5.85 | 2.47 | 15.31 | 2.21 | 10.42 | 6.30 | 11.88 | 9.90 | 24.12 | 3.52 | 5.85 | 2.47 | 15.31 | 2.21 | 10.42 | 6.30 | 11.88 | | |
| Acy | 1.72 | 3.91 | 0.12 | 0.04 | 3.97 | 1.00 | 1.90 | 0.07 | 2.64 | 0.04 | 1.72 | 3.91 | 0.12 | 0.04 | 3.97 | 1.00 | 1.90 | 0.07 | 2.64 | 0.04 | | |
| Ace | 1.98 | 1.04 | 0.68 | 6.38 | 0.49 | 0.03 | 0.55 | 2.00 | 0.12 | 0.22 | 1.98 | 1.04 | 0.68 | 6.38 | 0.49 | 0.03 | 0.55 | 2.00 | 0.12 | 0.22 | | |
| Flu | 5.52 | 4.67 | 2.27 | 8.23 | 2.73 | 3.95 | 2.53 | 4.89 | 1.45 | 1.97 | 5.52 | 4.67 | 2.27 | 8.23 | 2.73 | 3.95 | 2.53 | 4.89 | 1.45 | 1.97 | | |
| Phe | 48.08 | 59.29 | 19.06 | 132.07 | 44.04 | 65.61 | 31.52 | 43.93 | 18.50 | 11.33 | 48.08 | 59.29 | 19.06 | 132.07 | 44.04 | 65.61 | 31.52 | 43.93 | 18.50 | 11.33 | | |
| Ant | 13.29 | 10.89 | 3.31 | 45.37 | 13.32 | 11.33 | 8.36 | 6.85 | 2.93 | 0.73 | 13.29 | 10.89 | 3.31 | 45.37 | 13.32 | 11.33 | 8.36 | 6.85 | 2.93 | 0.73 | | |
| Fla | 53.10 | 28.82 | 10.14 | 77.63 | 35.64 | 113.61 | 26.86 | 31.02 | 13.18 | 3.10 | 53.10 | 28.82 | 10.14 | 77.63 | 35.64 | 113.61 | 26.86 | 31.02 | 13.18 | 3.10 | | |
| Pyr | 73.65 | 41.64 | 14.46 | 112.00 | 53.29 | 133.18 | 40.11 | 41.83 | 20.00 | 3.23 | 73.65 | 41.64 | 14.46 | 112.00 | 53.29 | 133.18 | 40.11 | 41.83 | 20.00 | 3.23 | | |
| BaA | 45.74 | 23.73 | 9.67 | 70.34 | 42.81 | 113.11 | 26.18 | 25.26 | 10.71 | 1.72 | 45.74 | 23.73 | 9.67 | 70.34 | 42.81 | 113.11 | 26.18 | 25.26 | 10.71 | 1.72 | | |
| Chr | 52.71 | 40.18 | 15.41 | 67.48 | 53.12 | 62.59 | 25.83 | 38.12 | 16.93 | 2.82 | 52.71 | 40.18 | 15.41 | 67.48 | 53.12 | 62.59 | 25.83 | 38.12 | 16.93 | 2.82 | | |

Table 2 (continued)

| | Industrial area | | | | Commercial-cum-residential area | | | | | | Rural area | |
|--------------------|-----------------|--------|--------|--------|---------------------------------|---------|--------|--------|--------|-------|------------|--|
| | S13 | S14 | S9 | S15 | S16 | S17 | S18 | S19 | S20 | S21 | | |
| BbF | 72.48 | 56.20 | 25.24 | 87.84 | 80.19 | 115.47 | 39.80 | 46.67 | 24.98 | 5.10 | | |
| BkF | 22.50 | 14.23 | 6.10 | 27.86 | 23.87 | 51.12 | 11.58 | 14.72 | 7.20 | 1.04 | | |
| BaP | 44.46 | 29.13 | 12.76 | 64.60 | 48.11 | 232.05 | 27.81 | 25.45 | 14.08 | 1.72 | | |
| InP | 40.22 | 40.63 | 14.94 | 55.19 | 51.50 | 116.23 | 28.65 | 24.53 | 14.55 | 2.46 | | |
| DaA | 6.56 | 5.10 | 2.30 | 9.09 | 8.11 | 9.35 | 4.35 | 1.91 | 2.19 | 0.11 | | |
| BgP | 30.21 | 34.76 | 11.96 | 36.14 | 37.56 | 62.09 | 19.22 | 20.05 | 12.43 | 2.48 | | |
| Σ ²⁻³ 环 | 133.58 | 132.73 | 39.09 | 275.56 | 102.67 | 210.84 | 73.92 | 99.18 | 45.12 | 29.26 | | |
| Σ ⁴ | 267.08 | 175.99 | 70.89 | 365.51 | 253.28 | 475.46 | 143.50 | 166.60 | 79.82 | 13.91 | | |
| Σ ⁵⁻⁶ | 121.46 | 109.63 | 41.96 | 165.03 | 145.28 | 419.72 | 80.03 | 71.94 | 43.27 | 6.76 | | |
| ΣPAHs Nap | 522.12 | 418.35 | 151.94 | 806.11 | 501.23 | 1106.02 | 297.45 | 337.72 | 168.20 | 49.93 | | |

Unit: ng/g

was thus considered pristine and used for comparison. The total PAH concentration is 49.93 ng/g, three orders of magnitude lower than the highest value recorded at S1. The percentages of 2–3, 4, and 5–6 ring PAHs among the total PAHs are 58.6, 27.86, and 13.54%, respectively.

In conclusion, the heavy industrial area suffers from the most serious pollution followed by the industrial area, commercial-cum-residential area, and rural area. The findings prove that emissions from heavy industry, vehicular emissions, and human daily life are the main factors causing environmental pollution in Liuzhou.

PAH molecular composition analysis

According to the summary analyses of previous studies, an Ant/(Ant + Phe) ratio lower than 0.10 is usually taken as an indication of petroleum source while a ratio higher than 0.10 as dominance of combustion (Chen et al. 2005; Kuśmierz and Oleszczuk 2014). A BaP/BghiP ratio lower than 0.6 relates to non-traffic, and a ratio higher than 0.6 relates to the existence of traffic emissions (Bortey-Sam et al. 2014; Liu et al. 2016; Chen et al. 2016). A BaA/(BaA + Chr) ratio lower than 0.20 implies petroleum source, whereas a ratio from 0.20 to 0.35 is for either petroleum or combustion, and any ratio higher than 0.35 for combustion origin (Chen et al. 2005; Zheng et al. 2014; Yunker et al. 2002). An InP/(InP + BaP) ratio lower than 0.20 possibly indicates petroleum source, the ratios between 0.20 and 0.50 indicate liquid fossil fuel (vehicle and crude oil) combustion, and the ratios higher than 0.50 suggest grass, wood, and coal combustion (Chen et al. 2005; Zheng et al. 2014; Yunker et al. 2002).

In this study, the ratios of Ant/(Ant + Phe), BaP/BgP, IcdP/(IcdP + BaP), and BaA/(BaA + Chr) in soil are shown in the scatterplot (Figs. 2 and 3). As Fig. 2 shows, Ant/(Ant + Phe) ratios ranged from 0.12 to 0.31, except S21 has a ratio of 0.06. This indicates that the PAHs (except for S21) are derived from combustion, while the PAHs at S21 originated from petroleum. The BaP/BgP ratios ranged from 0.69 to 5.93, implying that vehicular emissions are the source of the PAHs at these locations. Notably, vehicular traffic has increased, as the road network has become more sophisticated; each village is easily accessible today via cement and asphalt roads, which extend in all directions. Figure 3 shows that the InP/(InP + BaP) ratios range from 0.25 to 0.59, indicating that these PAHs were derived from the combustion

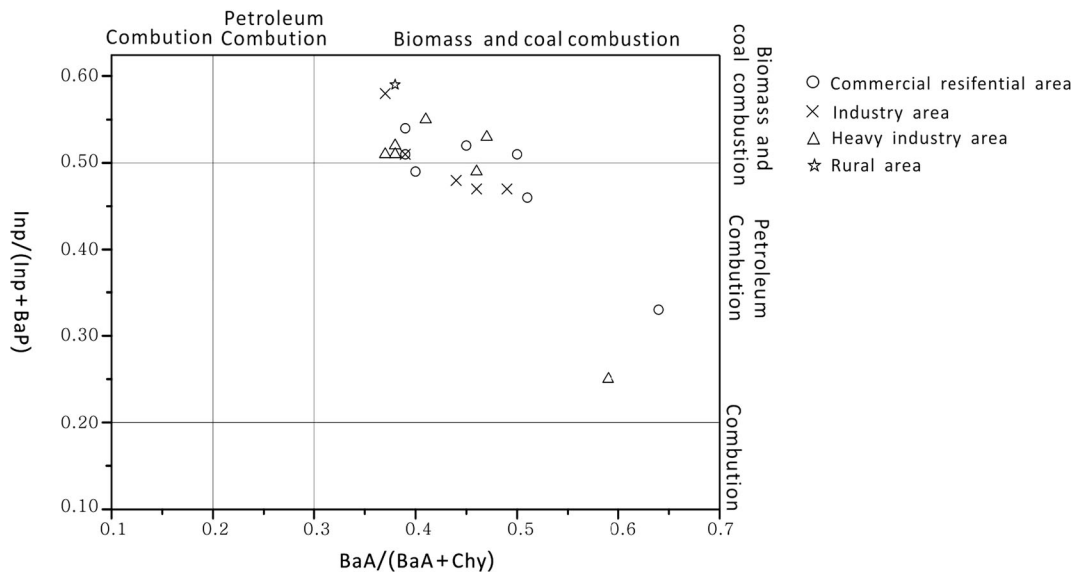


Fig. 2 Cross plot for the isomer ratios of BaA/(BaA + Chr) vs. InP/(InP + BaP) in the soil samples

of petroleum, biomass, and coal. Thus, pyrogenic sources are the main contributors of PAHs in the soil. However, the BaA/(BaA + Chr) ratios ranged from 0.37 to 0.64, and all values exceeding 0.3 imply that biomass and coal combustion are the sources of PAH concentrations.

The isomer ratios of the PAHs indicate that the PAHs in the sampled soil can be mainly attributed to mixed combustion sources. All the activities of the local population were undoubtedly the biggest contributor to

PAH pollution in the area. For instance, Liuzhou Iron & Steel Group Co., LTD (S1), Liuzhou Chemical Co., LTD (S8), and LiuGong Machinery Co., LTD (S10) consumed large amounts of hydrocarbon and coal resources and released considerable amounts of PAH pollutants. In addition, the Liujiang River has been called the “golden waterway,” as it bears the burden of water transportation. As remarked previously, the improved transportation (road) connectivity has added to the vehicular emissions. Thus, apportioning the extent of PAH

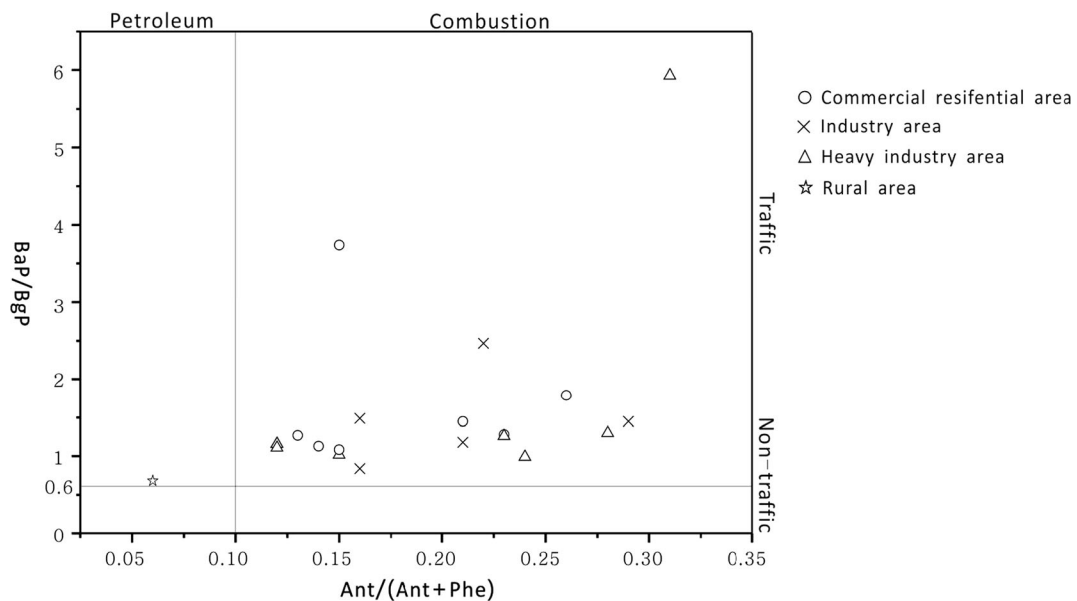
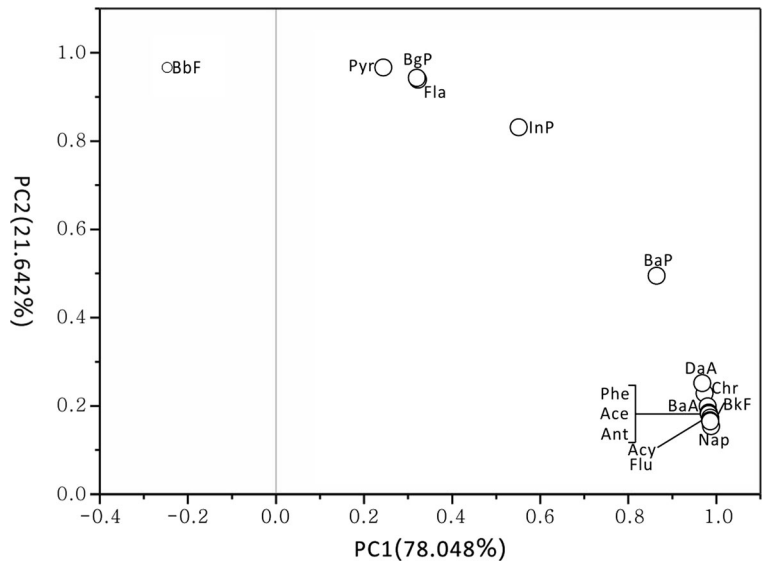


Fig. 3 Cross plot for the isomer ratios of Ant/(Ant + Phe) vs. BaP/BgP in the soil samples

Fig. 4 Principal components for the individual PAHs



pollution by source is evidently complicated; PAH concentrations are affected by many factors, including industry, transportation, daily human activities, and so on.

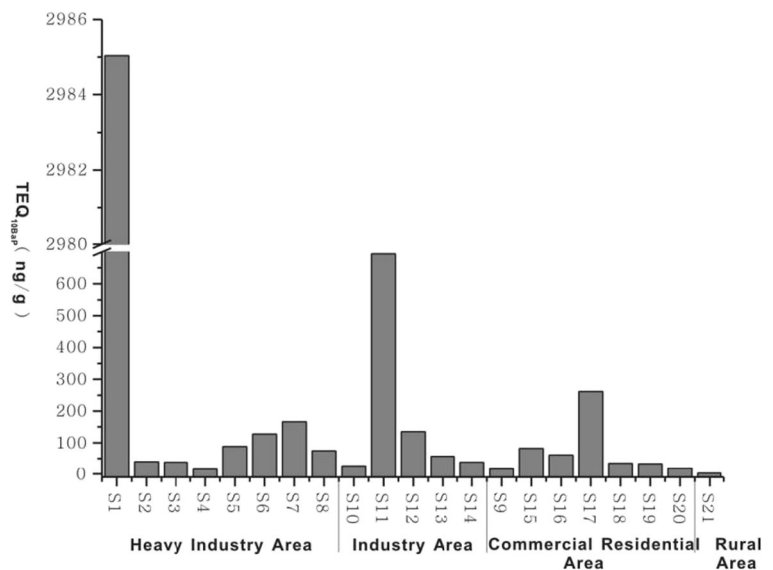
Source identification by PCA

To further identify the possible sources of PAHs in this study area, PCA is used to conduct quantitative assessments. Figure 4 shows the principal components for the individual PAHs.

As shown in Fig. 4, there were two principal components. The accumulated variance contribution rate was

99.69%, and PC1 explained 78.05% of the total variance, while Nap, Acy, Ace, Flu, Phe, Ant, BaA, Chr, BkF, BaP, and DaA were characterized by strong loadings. Nap is associated with unburned fossil derived fuel or alkyl substituted PAHs indicating petrogenic source (Deka et al. 2016; Dobbins et al. 2006; Yunker et al. 1996), whereas Acy, Ace, Flu, Phe, Ant, BaA, and Chr are typical markers for coal combustion (Duval and Friedlander 2004; Larsen and Baker 2003; Simcik et al. 1999; Ge et al. 2017; Wang et al. 2016). BkF, BaP, and DaA are markers for petroleum combustion, especially diesel and gasoline combustion related to

Fig. 5 Concentration of TEQ_{10BaP} in the sampled soil



vehicular emissions (Sofowote et al. 2008; Larsen and Baker 2003). Therefore, PC1 represents mixed combustion sources. PC2 explained 21.64% of the total variance, and Fla., Pyr, BbF, InP, and BgP were characterized by strong loadings. Fla. and Pyr are often derived from coal combustion (Khairy and Lohmann 2013), while BbF, InP, and BgP are connected with petroleum combustion (Khairy and Lohmann 2013; Netto et al. 2006). Therefore, PC2 obviously represents combustion sources.

In conclusion, the PAHs in the surface soil in Liuzhou can be mainly attributed to coal combustion and vehicular emissions (diesel and gasoline combustion). The former source is likely to be attributed to the large number of heavy industry enterprises, and the latter, to vehicles.

Soil toxicity assessment

By Maliszewska-Kordybac's (1996) classification, soil samples from S4, S14, S20, and S21 are considered unpolluted; S3, S10, S13, S14, S16, S18, and S19 are weakly polluted; S2, S5, S8, and S15 are polluted; and S1, S6, S7, S11, S12, and S17 are severely polluted. According to Fig. 1, the severely polluted and polluted soil samples are mainly located in the heavy industrial area. While all the weakly polluted and unpolluted soil samples are located relatively far away from the pollution sources in each community.

Figure 5 shows the TEQ_{BaP} level for ten PAHs using the Dutch standard. TEQ_{10BaP} ranges from 2.33 to 2985.04 ng/g, with an average of 237.67 ng/g. When TEQ_{10BaP} < 33 ng/g, there is no risk, but when TEQ_{10BaP} ≥ 33 ng/g, a risk exists. The concentration at S1 is 90 times higher, indicating that Liuzhou Iron & Steel Group Co., LTD is the largest source of PAH pollution. Only six soil samples show PAH concentrations under 33 ng/g, while 13 soil samples are under 8 times of 33 ng/g. In conclusion, the surface soil of Liuzhou City is widely polluted with PAHs, which pose a potential ecological risk to the ecosystem and human health.

Conclusions

1. The concentrations of total PAHs in the surface soil from 21 sites in Liuzhou City ranged from 49.93 ng/g at S21 to 38,865.97 ng/g at S1, the average being

2991.1 ng/g. The results indicate that PAH pollution in the city is serious, especially at locations near the industries, the trunk road, and the main residential area. The prevailing wind direction adds to the problem.

2. The results of the isomer ratio analysis and PCA indicate that the analyzed PAHs in the soil are mainly attributed to mixed combustion sources, such as coal combustion by the industry, diesel and gasoline combustion attributable to vehicular emissions, and natural gas combustion by residents.
3. The soil toxicity assessment indicates that the city is suffering from serious PAH pollution, underscoring the need for urgent government action.

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References

- Agarwal, T., Khillare, P. S., Shridhar, V., & Ray, S. (2009). Pattern, sources and toxic potential of PAHs in the agricultural soils of Delhi, India. *Journal of Hazardous Materials*, 163, 1033–1039. <https://doi.org/10.1016/j.jhazmat.2008.07.058>.
- Argiriadis, E., Rada, E. C., Vecchiato, M., Zambon, S., Ionescu, G., Schiavon, M., Ragazzi, M., & Gambaro, A. (2014). Assessing the influence of local sources on POPs in atmospheric depositions and sediments near Trento (Italy). *Atmospheric Environment*, 98, 32–40. <https://doi.org/10.1016/j.atmosenv.2014.08.035>.
- Bucheli, T. D., Blum, F., Desaulles, A., & Gustafsson, Ö. (2004). Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere*, 56, 1061–1076. <https://doi.org/10.1016/j.chemosphere.2004.06.002>.
- Bortey-Sam, N., Ikenaka, Y., Nakayama, S. M. M., Akoto, O., Yohannes, Y. B., Baidoo, E., Mizukawa, H., & Ishizuka, M. (2014). Occurrence, distribution, sources and toxic potential of polycyclic aromatic hydrocarbons (PAHs) in surface soils from the Kumasi Metropolis, Ghana. *Science of the Total Environment*, 496, 471–478. <https://doi.org/10.1016/j.scitotenv.2014.07.071>.

- Cachada, A., Pato, P., Rocha-Santos, T., da Silva, E. F., & Duarte, A. C. (2012). Levels, sources and potential human health risks of organic pollutants in urban soils. *Science of the Total Environment*, *430*, 184–192. <https://doi.org/10.1016/j.scitotenv.2012.04.075>.
- Chen, L. G., Ran, Y., Xing, B. S., Mai, B. X., He, J. H., Wei, X. G., Fu, J. M., & Sheng, G. Y. (2005). Contents and sources of polycyclic aromatic hydrocarbons and organochlorine pesticides in vegetable soils of Guangzhou, China. *Chemosphere*, *60*, 879–890. <https://doi.org/10.1016/j.chemosphere.2005.01.011>.
- Chen, Y. C., Chiang, H. C., Hsu, C. Y., Yang, T. T., Lin, T. Y., Chen, M. J., Chen, N. T., & Wu, Y. S. (2016). Ambient PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) in Changhua County, central Taiwan: seasonal variation, source apportionment and cancer risk assessment. *Environmental Pollution*, *218*, 372–382. <https://doi.org/10.1016/j.envpol.2016.07.016>.
- Deka, J., Sarma, K. P., & Hoque, R. R. (2016). Source contributions of Polycyclic Aromatic Hydrocarbons in soils around oilfield in the Brahmaputra Valley. *Ecotoxicology and Environmental Safety*, *133*, 281–289. <https://doi.org/10.1016/j.ecoenv.2016.07.031>.
- Dobbins, R. A., Fletcher, R. A., Jr, B. A. B., & Hoefft, S. (2006). Polycyclic aromatic hydrocarbons in flames, in diesel fuels, and in diesel emissions. *Combustion and Flame*, *144*, 773–781. <https://doi.org/10.1016/j.combustflame.2005.09.008>.
- Duval MM, Friedlander SK (2004) Source resolution of polycyclic aromatic hydrocarbons in Los Angeles atmosphere: application of a CMB with first order decay. USEPA Report EPA-600/2-81-161, Washington, DC. <https://www.researchgate.net/publication/236505332>
- Essumang, D. K., Kowalski, K., & Sogaard, E. G. (2011). Levels, distribution and source characterization of polycyclic aromatic hydrocarbons (PAHs) in topsoils and roadside soils in Esbjerg, Denmark. *Bulletin of Environmental Contamination and Toxicology*, *86*, 438–443. <https://doi.org/10.1007/s00128-011-0232-0>.
- Ge, W., Cheng, Q. Q., Chai, C., Zeng, L. S., Wu, J., Chen, Q. H., Zhu, X. W., & Ma, D. (2017). Pollution characteristics and source analysis of polycyclic aromatic hydrocarbons in agricultural soils from Shandong. *Environmental Sciences*, *38*, 1587–1596(in chinese). <https://doi.org/10.13227/j.hjxk.201608199>.
- Jiang, Y. F., Yves, U. J., Sun, H., Hu, X. F., Zhan, H. Y., & Wu, Y. Q. (2016). Distribution, compositional pattern and sources of polycyclic aromatic hydrocarbons in urban soils of an industrial city, Lanzhou, China. *Ecotoxicology and Environmental Safety*, *126*, 154–162. <https://doi.org/10.1016/j.ecoenv.2015.12.037>.
- Jiao, H. H., Bian, G., Chen, X., Wang, S. L., Zhuang, X. L., & Bai, Z. H. (2017). Distribution, sources, and potential risk of polycyclic aromatic hydrocarbons in soils from an industrial district in Shanxi, China. *Environmental Science and Pollution*, *24*, 12243–12260. <https://doi.org/10.1007/s11356-017-8553-0>.
- Keth, L. H., & Telliard, W. A. (1979). Priority pollutants: I. A perspective view. *Environmental Science & Technology*, *13*, 416–423. <https://doi.org/10.1021/es60152a601>.
- Khairy, M. A., & Lohmann, R. (2013). Source apportionment and risk assessment of polycyclic aromatic hydrocarbons in the atmospheric environment of Alexandria, Egypt. *Chemosphere*, *91*, 895–903. <https://doi.org/10.1016/j.chemosphere.2013.02.018>.
- Kuśmierz, M., & Oleszczuk, P. (2014). Biochar production increases the polycyclic aromatic hydrocarbon content in surrounding soils and potential cancer risk. *Environmental Science and Pollution Research*, *21*, 3646–3652. <https://doi.org/10.1007/s11356-013-2334-1>.
- Larsen, R. K., & Baker, J. E. (2003). Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environmental Science & Technology*, *37*, 1873–1881. <https://doi.org/10.1021/es0206184>.
- Liu, B., Xue, Z. Q., Zhu, X. L., & Jia, C. R. (2016). Long-term trends (1990–2014), health risks, and sources of atmospheric polycyclic aromatic hydrocarbons (PAHs) in the U.S. *Environmental Pollution*, *220*, 1171–1179. <https://doi.org/10.1016/j.envpol.2016.11.018>.
- Liu, W., Ma, L., Abuduwaili, J., & Li, Y. M. (2017). Distribution, source analysis, and ecological risk assessment of polycyclic aromatic hydrocarbons in the typical topsoil of the Issyk-Kul Lake Basin. *Environment Monitoring and Assessment*, *189*, 398. <https://doi.org/10.1007/s10661-017-6113-1>.
- Luo, X., Zheng, Y., Lin, Z., Wu, B., Han, F., Tian, Y., Zhang, W., & Wang, X. (2015). Evaluating potential non-point source loading of PAHs from contaminated soils: a fugacity-based modeling approach. *Environmental Pollution*, *196*, 1–11. <https://doi.org/10.1016/j.envpol.2014.09.011>.
- Ma, W. L., Liu, L. Y., Tian, C. G., Qi, H., Jia, H. L., Song, W. W., & Li, Y. F. (2015). Polycyclic aromatic hydrocarbons in Chinese surface soil: occurrence and distribution. *Environmental Science and Pollution Research*, *22*, 4190–4200. <https://doi.org/10.1007/s13566-014-3648-3>.
- Maliszewska-Kordybach, B. (1996). Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. *Applied Geochemistry*, *11*, 121–127. [https://doi.org/10.1016/0883-2927\(95\)00076-3](https://doi.org/10.1016/0883-2927(95)00076-3).
- Marusenko, Y., Herckes, P., & Hall, S. J. (2011). Distribution of polycyclic aromatic hydrocarbons in soils of an arid urban ecosystem. *Water, Air, & Soil Pollution*, *219*, 473–487. <https://doi.org/10.1007/s11270-010-0721-5>.
- Netto, A. D. P., Krauss, T. M., Cunha, I. F., & Rego, E. C. P. (2006). PAHs in SD: polycyclic aromatic hydrocarbons levels in street dust in the central area of Niterói City, RJ, Brazil. *Water, Air, & Soil Pollution*, *176*, 57–67. <https://doi.org/10.1007/s11270-006-9145-7>.
- Nisbet, I. C. T., & Lagoy, P. K. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology*, *16*, 290–300. [https://doi.org/10.1016/0273-2300\(92\)90009-X](https://doi.org/10.1016/0273-2300(92)90009-X).
- Simcik, M. F., Eisenreich, S. J., & Lioy, P. J. (1999). Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmospheric Environment*, *33*, 5071–5079. [https://doi.org/10.1016/S1352-2310\(99\)00233-2](https://doi.org/10.1016/S1352-2310(99)00233-2).
- Škrbić, S. D., Đurišić-Mladenović, N., Tadić, D. J., & Cvejanov, J. D. (2017). Polycyclic aromatic hydrocarbons in urban soil of Novi Sad, Serbia: occurrence and cancer risk assessment. *Environ Sci Pollut*, *24*, 16148–16159. <https://doi.org/10.1007/s11356-017-9194-z>.

- Sofowote, U. M., Mccarry, B. E., & Marvin, C. H. (2008). Source apportionment of PAH in Hamilton Harbour suspended sediments: comparison of two factor analysis methods. *Environmental Science & Technology*, *42*, 6007–6014. <https://doi.org/10.1021/es800219z>.
- Suman, S., Sinha, A., & Tarafdar, A. (2016). Polycyclic aromatic hydrocarbons (PAHs) concentration levels, pattern, source identification and soil toxicity assessment in urban traffic soil of Dhanbad, India. *Science of the Total Environment*, *545–546*, 353–360. <https://doi.org/10.1016/j.scitotenv.2015.12.061>.
- Tan, W. J., Li, Z. L., Ding, A. Z., & Wang, J. S. (2007). Biodegradation of polycyclic aromatic hydrocarbons (PAHs) in soil and groundwater: a review. *Ecology and Environment*, *16*, 1310–1317(in chinese). <https://doi.org/10.16258/j.cnki.1674-5906.2007.04.035>.
- Tsai, P. J., Shih, T. S., Chen, H. L., Lee, W. J., Lai, C. H., & Liou, S. H. (2004). Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station workers. *Atmospheric Environment*, *38*, 333–343. <https://doi.org/10.1016/j.atmosenv.2003.08.038>.
- Wang, C. L., Zou, X. Q., Zhao, Y. F., & Li, B. J. (2016). Source apportionment and ecological risk assessment of polycyclic aromatic hydrocarbons in surface water from Yangtze River, China: based on PMF model. *Environmental Sciences*, *37*, 3789–3797(in chinese). <https://doi.org/10.13227/j.hjxx.2016.10.016>.
- Wang, C. H., Wu, S. H., Zhou, S. L., Wang, H., Li, B. J., Chen, H., Yu, Y. N., & Shi, Y. X. (2015). Polycyclic aromatic hydrocarbons in soil from urban to rural areas in Nanjing: concentration, source, spatial distribution and potential human health risk. *Science Total Environment*, *527–528*, 375–383. <https://doi.org/10.1016/j.scitotenv.2015.05.025>.
- Wang, W., Huang, M. J., Kang, Y., Wang, H. S., Leung, A. O. W., Cheung, K. C., & Wong, M. H. (2011). Polycyclic aromatic hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: status, sources and human health risk assessment. *Science Total Environment*, *409*, 4519–4527. <https://doi.org/10.1016/j.scitotenv.2011.07.030>.
- Wang, W. T., Simonich, S. L. M., Xue, M., Zhao, J. Y., Zhang, N., Wang, R., Cao, J., & Tao, S. (2010). Concentrations, sources and spatial distribution of polycyclic aromatic hydrocarbons in soils from Beijing, Tianjin and surrounding areas, North China. *Environmental Pollution*, *158*, 1245–1251. <https://doi.org/10.1016/j.envpol.2010.01.021>.
- Wilcke, W. (2000). Polycyclic aromatic hydrocarbons (PAHs) in soil—a review. *Journal of Plant Nutrition and Soil Science*, *163*, 229–248. [https://doi.org/10.1002/1522-2624\(200006\)163:3%3C229::AID-JPLN229%3E3.0.CO;2-6](https://doi.org/10.1002/1522-2624(200006)163:3%3C229::AID-JPLN229%3E3.0.CO;2-6).
- Yang, K., Jiang, J. J., Liu, F., Bai, Z. K., Peng, M., Zhao, C. D., Li, K., Liu, Y. H., Bo, W., Li, X. H., & Cheng, H. X. (2016). Polycyclic aromatic hydrocarbons (PAHs) in the topsoils of typical reclaimed area in Pingshuo opencast coal mine: status, source and risk. *Earth Science Frontiers*, *23*, 281–290(in chinese). <https://doi.org/10.13745/j.esf.2016.05.027>.
- Yu, B. B., Xie, X. J., Ma, L. Q., Kan, H. D., & Zhou, Q. X. (2014a). Source, distribution, and health risk assessment of polycyclic aromatic hydrocarbons in urban street dust from Tianjin, China. *Environmental Science and Pollution Research*, *21*, 2817–2825. <https://doi.org/10.1007/s11356-013-2190-z>.
- Yu, G. G., Zhang, Z. H., Yang, G. L., Zheng, W. R., Xu, L. H., & Cai, Z. (2014b). Polycyclic aromatic hydrocarbons in urban soil of Hangzhou: status, distribution, sources, and potential risk. *Environment Monitoring Assessment*, *186*, 2775–2784. <https://doi.org/10.1007/s10661-013-3578-4>.
- Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., & Sylvestre, S. (2002). PAH in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, *33*, 489–515. [https://doi.org/10.1016/S0146-6380\(02\)00002-5](https://doi.org/10.1016/S0146-6380(02)00002-5).
- Yunker, M. B., Snowdon, L. R., Macdonald, R. W., Smith, J. N., Fowler, M. G., Skibo, D. N., McLaughlin, F. A., Danyushevskaya, A. I., Petrova, V. I., & Ivanov, G. I. (1996). Polycyclic aromatic hydrocarbons composition and potential sources for sediment samples from the Beaufort and Barents Sea. *Environmental Science & Technology*, *30*, 1310–1320. <https://doi.org/10.1021/es950523k>.
- Zheng, T. H., Ran, Y., & Chen, L. G. (2014). Polycyclic aromatic hydrocarbons (PAHs) in rural soils of Dongjiang River Basin: occurrence, source apportionment, and potential human health risk. *Journal of Soils and Sediments*, *14*, 110–120. <https://doi.org/10.1007/s11368-013-0753-8>.
- Zheng, W. D., Lichwa, J., & Yan, T. (2011). Impact of different land use on polycyclic aromatic hydrocarbons contamination in coastal stream sediments. *Chemosphere*, *84*, 376–382. <https://doi.org/10.1016/j.chemosphere.2011.03.067>.