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Spatial distribution characteristics, source analysis and risk assessment of polycyclic aromatic hydrocarbons in topsoil of a typical chemical industry park

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Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in soil and are difficult to degrade, posing a great threat to the ecological environment and human health. Therefore, research on the distribution characteristics and risks of PAHs is of great significance to protect human and ecosystem health. Taking a typical chemical industry park in Chongqing as an example, the spatial distribution characteristics of PAHs content in 54 topsoil samples in the typical area were analyzed, and the soil PAHs pollution was evaluated by incremental models such as single-factor index and Nemerow comprehensive index. A factor decomposition model Positive Definite Matrix Factorization (PMF) was used to analyze the sources of PAHs. The results showed that 16 kinds of optimally controlled PAHs were detected, and the content of ΣPAHs in the topsoil ranged from ND to 16.07 mg/kg, with an average value of 1.78 mg/kg; spatially, pollutant levels are higher in the south and southwest of the park as well as in the center; source analysis showed that Chongqing The PAHs pollution in this typical chemical industry park in the city is from coke combustion sources, traffic emission sources, biomass combustion sources, oil sources, coal combustion sources and oil leakage sources, and the contribution rates to PAHs are 10.7%, 35.2%, 20.7%, and 5.0%, 24.6%, and 3.7%; respectively. The health risk assessment of soil PAHs shows that there is no potential carcinogenic risk of PAHs in different age groups in this area, and the main exposure route of adults is dermal > ingestion > inhalation, and the main exposure route of children is ingestion > dermal > inhalation.

KEYWORDS

spatial distribution characteristics, polycyclic aromatic hydrocarbons (PAHs), source identification, risk assessment, chemical industry park

1 Introduction

The large amounts of polycyclic aromatic hydrocarbons (PAHs) and potential carcinogenicity have been creasing during the past few years, attracting the attention of researchers and scholars worldwide. PAHs are mainly by-products produced by incomplete combustion of fossil fuels (coal, petroleum, etc.) (Cui et al., 2022), and are a class of organic pollutants with neutral, non-polar molecules and semi-volatiles. More than 100 different

PAHs exist globally, including 16 PAHs of high concern (Zhang et al., 2023). PAHs adhere to organic matter in soil particles due to their lipophilicity and low solubility in water (Shukla et al., 2022). After these pollutants enter the soil, they are accumulated, stable, and not easy to flow. At the same time, due to the higher activity of pollutants in water, they are more likely to migrate or precipitate in surface and groundwater (Zhao et al., 2018). The uptake of carcinogenic PAHs by plants can lead to food chain contamination (Schwab and Dermody, 2021), and these pollutants can enter the food chain or seep into surface and groundwater, posing a great threat to human health and the environment (Zhang et al., 2018). Long-term contamination of soil by PAHs compounds can lead to significant deterioration of soil biological conditions (Devatha et al., 2019). For example, high concentrations of naphthalene, anthracene, pyrene, phenanthrene, and fluorene reduce phosphatase activity in soil (Mao et al., 2021). PAHs pollution not only adversely affects soil ecosystems, but also poses certain risks to human health in the long-term PAHs environment. Studies have shown that long-term human exposure to high doses of PAHs pollutants may lead to the occurrence of many diseases, including neurodegenerative diseases, cancer, respiratory diseases, etc. (Ambade et al., 2022a; Kurwadkar et al., 2022). Data from many occupational health studies suggest an association between lung cancer and exposure to PAH compounds, and evidence from García et al. (2023) suggested that short-term exposure to PAHs may lead to impaired lung function in asthmatics and may increase blood clots in patients with coronary artery disease risk that arises. Ambade et al. (2022b) studied the distribution of polycyclic aromatic hydrocarbons (PAHs) in the sediments of the Mahanadi estuary, determined their sources, and evaluated their ecological toxicity. They found that PAHs have potential risks and ecological risks to specific sources. Polycyclic aromatic hydrocarbons (PAHs) pollution is associated with various health problems (Li et al., 2023).

Ambade and Sethi Shrikanta (2021) proved the pollution of PAHs is caused by petroleum and combustion in the industrial production process. Kurwadkar et al. (2022) pointed out that large-scale emissions from vehicle traffic and industrial activities are the main reasons for the increase in PAH levels. Zhang et al. (2019) showed that the average concentration of PAHs in industrial areas was higher than that in parks and residential areas. Fundamentally, most of the pollutants come from human activities, especially industrial economic construction, because it requires a lot of underground raw materials (Cao et al., 2015). Johnsen and Karlson (2007) demonstrated that point sources such as industrial plants and direct discharge (oil spills) can significantly increase soil PAHs concentrations within a few meters to a few kilometers from the point source. Ambade and Sankar (2021) pointed out that PAHs can induce cancer through the inside of the bronchus. Kwon and Choi (2014) demonstrated that the PAH content of industrial sites is much higher than that of rural and urban sites.Ambade et al. (2020) reported by using principal component correlation (PCC) that the source of emissions may be industrial activity, automobiles, wood, coal, or dung cake burning. However, there has been no study on PAHs pollution of this typical chemical industry park selected in this article, a national industrial park approved by the Chongqing Municipal People's Government in December 2001. The planned area of the park is 31.3 square kilometers, which is divided into natural gas chemical area, petrochemical area, fine chemical area and chemical material area. It is an important platform for Chongqing's resource processing industry, and a comprehensive integration of natural gas chemical, petrochemical, biomass chemical, fine chemical and new material industries in Chongqing. After 5 years of development and construction, the park has basically formed the industrial base of petrochemical, natural gas, chlor-alkali, biomass, fine chemicals and new materials. Chongqing is located at the "Y"-shaped node where the "Silk Road Economic Belt and the 21st Century Maritime Silk Road" and the "Yangtze River Economic Belt" intersect. Regional PAHs pollution prevention and control measures are of great significance to promote ecological security and high-quality development in the Yangtze River Economic Belt, pollution prevention and protection and people's livelihood. The research in this article will help determine whether the PAHs produced by various factories or enterprises in the typical chemical park pose risks to the ecological environment and human health, so that timely measures can be taken to avoid the risks.

This paper takes the surface soil of a typical industrial park in Chongqing as the research object, and studies the monitoring results of 54 soil samples in the area, focusing on the following three issues: 1) The content of 16 optimally controlled PAHs in the soil of this typical chemical park; 2) Pollution degree and distribution of pollutants; 3) Evaluation of soil ecological risks of pollutants and health risks of people in the park.

2 Materials and methods

2.1 Overview of the study area

The research area is a typical chemical industry park in Chongqing. This area belongs to the ecological economic zone of the Three Gorges Reservoir area. It spans the north and south of the Yangtze River. The terrain is dominated by low mountains and hills. It is rainy in early summer, hot and often dry in midsummer, rainy in autumn, long frost-free period, large temperature difference, foggy and less sunshine. The annual average temperature of 10 years (2012–2021) is 18.7°C. The soil types are mainly paddy soil, alluvial soil, purple soil and yellow soil. With the development of the development strategy of the Yangtze River Economic Belt, the rapid industrial development and urbanization of Chongqing have made more and more pollutants enter the urban soil in various ways, thereby affecting the soil environmental quality and safety performance.

2.2 Sampling point layout and sample collection

Based on the grid point method required in "Technical Specifications for Soil Environmental Monitoring" (HJ/T 166-2004), combined with the actual sampling situation on site, a total of 54 points of surface soil were collected in a typical chemical park, and the sampling depth was 30 cm. The

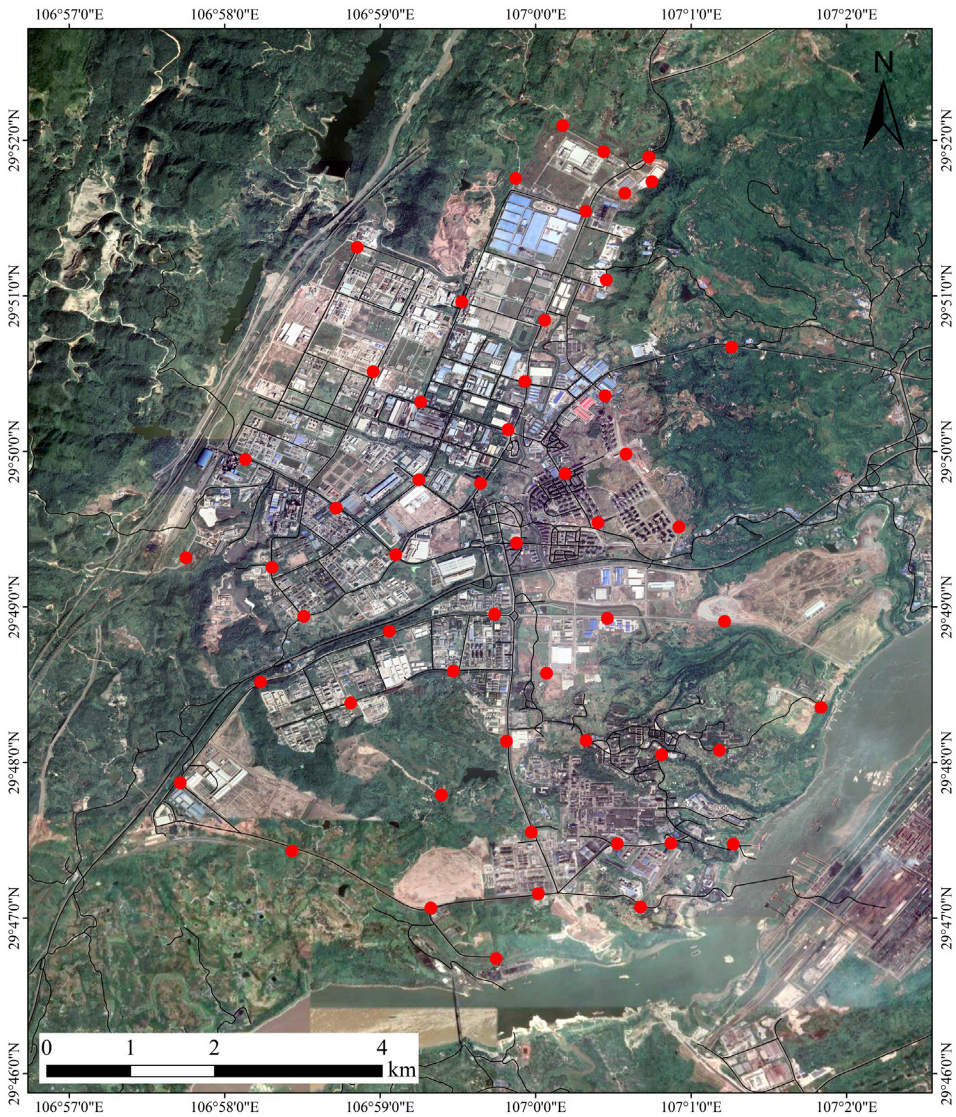

FIGURE 1
Schematic diagram of sampling point distribution.

distribution is shown in Figure 1. The specific method is based on the "five-point method" sampling, delineating a (5 m × 5 m) square plot at each sampling point, avoiding artificial fillings and removing sundries on the surface, and distributing stainless steel at the four corners and the center of the plot respectively. One soil sample was collected with a shovel, and the 5 soil samples were fully mixed in the field to obtain the soil sample (about 500 g) at this point. The collected samples were put into a brown ground glass bottle and stored in a low temperature seal and brought back to the experiment as soon as possible. The soil samples were placed in a cool indoor place to air dry naturally. After removing debris such as stones and animal and plant residues, they were ground and passed through a 2 mm sieve. The site number, sampling quantity, sampling site type, sampling depth, sample type, location and other information were marked, and some soil samples were freeze-dried and passed through a 60-mesh sieve to be tested for PAHs.

2.3 Sample processing and testing

2.3.1 Instrumental analysis

Vacuum freeze-drying was used for sample pretreatment, and gas chromatography-mass spectrometry (GC-MS) was used for sample determination.

2.3.2 Pressurized fluid extraction

Weigh 20 g of sample and about 10 g of diatomite and mix them evenly, then add a substitute (low concentration 2 μg, high concentration 5 μg) to assemble the extraction cell, pad an appropriate amount of quartz sand in the lower part, transfer all the samples to be extracted, and lay them on the upper part. A layer of quartz sand is covered with filter paper, transferred to the extraction apparatus, and the general conditions are set (preheating for 5 min, static extraction for 5 min, extraction pressure 103 bar, flushing volume 60%, solvent flushing for

1 min, gas flushing for 2 min), extraction solvent, The temperature and times are determined according to the optimization experiment, and the extract is collected (Ouyang et al., 2018).

2.3.3 Purification of extracts

Set the heating temperature conditions according to the instrument manual, and concentrate the extract to about 2 mL, to be purified.

2.3.4 Concentrate, add internal standard

Fix the magnesium silicate purification column on the solid phase extraction device, rinse the purification column with 4 mL of dichloromethane, add 5 mL of n-hexane, close the flow rate control valve after the column is full, and infiltrate for 5 min, slowly open the control valve, and continue to add 5 mL of n-hexane, before exposing the packing to air, close the control valve and discard the effluent. Transfer the concentrated extract to the small column, wash the concentrated vessel three times with 2 mL of n-hexane, and transfer all the washing liquid to the small column. Slowly open the control valve, close the control valve before the filler or copper powder is exposed to the air, add 5 mL of dichloromethane-n-hexane mixed solvent with a volume ratio of 1:9 for elution, slowly open the control valve and wait for the eluent to be saturated and purified After the column, close the control valve, soak for 2 min, slowly open the control valve, continue to add 5 mL of a mixed solvent with a volume ratio of dichloromethane-n-hexane of 1:9, and collect all the eluents for reconcentration.

2.3.5 Determination of samples

The purified test solution was concentrated by rotary evaporation, and an appropriate amount of the internal standard intermediate solution (the internal standard stock solution was diluted by a mixture of n-hexane and acetone with a volume ratio of 1:1) was added, and the volume was adjusted to 1.0 mL. 2 mL vial, to be tested.

2.3.6 Pressurized fluid extraction

Take 1 mL of the extracted polycyclic aromatic hydrocarbon solution, dilute the solution to the desired concentration, and use GC-MS to quantify the concentration of each of the 16 polycyclic aromatic compounds.

2.3.7 Rotary evaporation concentration

According to the instructions of the instrument, the heating temperature conditions were set. If it was not necessary to purify, the extract was concentrated to about 2 mL, and the concentrated liquid was transferred to a calibrated concentration vessel with a disposable dropper. The bottom of the rotary evaporation bottle was washed twice with a small amount of acetone-n-hexane mixed solvent, and all the concentrated liquid was merged, and then concentrated to about 2 mL by nitrogen blowing.

2.3.8 Magnesium silicate purification column

The magnesium silicate purification column was fixed on the solid phase extraction device, and the purification column was rinsed with 4 mL dichloromethane. After the column was filled with 5 mL n-hexane, the flow rate control valve was closed for infiltration for 5 min. The control valve was slowly opened, and 5 mL n-hexane was added. Before the filler was exposed to the air, the control valve was closed and the effluent was discarded. The concentrated extract was transferred to a small column, and the concentrated vessel was washed three times with 2 mL n-hexane, and all the washing solution was transferred to the small column. Slowly open the control valve, close the control valve before the filler is exposed to air, add 5 mL dichloromethane-n-hexane mixed solvent for elution, slowly open the control valve to be eluted after the eluent is filled with the purification column, close the control valve, diffuse for 2 min, slowly open the control valve, continue to add 5 mL dichloromethane-n-hexane mixed solvent, and collect all the eluent, to be concentrated again.

2.3.9 Concentrate, add internal standard

After purification, the test solution was concentrated again according to the step of rotary evaporation concentration, and an appropriate amount of internal standard intermediate liquid was added to keep the internal standard concentration consistent with the internal standard concentration in the calibration curve, and the mixed solvent of acetone-n-hexane was used to constant the volume to 1.0 mL. After mixing, it was transferred to 2 mL sample bottle for testing.

2.3.10 Quality control

Quality control according to 10% parallel, 10% standard. The quality control of 16 polycyclic aromatic hydrocarbons in soil was also carried out.

2.4 Pollution assessment and health risk assessment

2.4.1 Pollution index method

The single factor index and the Nemerow comprehensive pollution index can comprehensively reflect the pollution status of soil samples. The calculation formula is:

$$P_i = C_i / S_i$$

$$P_{comprehensive} = \sqrt{\frac{(C_i/S_i)^2_{max} + (C_i/S_i)^2_{ave}}{2}}$$

In the formula, P_i is the pollution index of soil PAH monomer i; $P_{comprehensive}$ is the Nemerow comprehensive pollution index, reflecting the comprehensive pollution status of the soil sample; C_i is the measured content of PAHs in the sample (mg/g); S_i is the PAHs evaluation standard (mg/g) (Callén et al., 2014), using the second-level standard limit in the National Construction Land Soil Environmental Assessment Quality Reference Standard (GB 36600-2018). When P sum ≤ 0.7, no pollution, 0.7 < P sum ≤ 1, slight pollution, l < P sum ≤ 2, light pollution, 2 < P sum ≤ 3, moderate pollution, and P sum > 3, severe pollution.

2.4.2 Health risk assessment

The health risk assessment of PAHs in this paper adopts the carcinogenic health risk assessment model provided by the International Agency for Research on Cancer (IARC), as shown in the following formula:

10.3389/fenvs.2023.1209137

TABLE 1 PAHs in soil of an industrial park.

Name	Abbreviations	Number of rings	Toxicity equivalent factor (TEF)	Minimum mg/kg	Maximum mg/kg	Average mg/kg	Standard deviation mg/kg	Coefficient of variation %	Detection rate %
Naphthalene	Nap	2	0.001	ND	0.38	0.04	0.07	167.21	59.26
Acenaphthylene	Acy	3	0.001	ND	0.24	0.03	0.06	209.07	27.78
Acenaphthene	Ace	3	0.001	ND	0.11	0.01	0.02	207.52	16.67
Fluorene	Flu	3	0.001	ND	0.27	0.02	0.05	185.54	37.04
Phenanthrene	Phe	3	0.001	ND	1.67	0.17	0.31	178.36	94.44
Anthracene	Ant	3	0.01	ND	0.19	0.02	0.04	182.24	31.48
Fluoranthene	Fla	4	0.001	ND	1.78	0.20	0.37	184.18	83.33
Pyrene	Pyr	4	0.001	ND	2.18	0.24	0.47	192.58	81.48
Benzo(a)anthracene	BaA	4	0.1	ND	0.96	0.10	0.20	200.43	74.07
Chrysene	Chry	4	0.01	ND	1.37	0.15	0.29	186.49	83.33
Benzo(b) fluoranthene	BbF	5	0.1	ND	1.76	0.18	0.36	204.23	81.48
Benzo(k) fluoranthene	BkF	5	0.1	ND	1.02	0.09	0.17	199.40	75.93
Benzo(a)pyrene	BaP	5	1	ND	1.45	0.14	0.30	212.97	72.22
Dibenzo (a,h) anthracene	DahA	5	1	ND	0.30	0.03	0.05	209.12	35.19
Benzo (ghi)perylene	BghiP	5	0.01	ND	2.22	0.22	0.44	199.71	74.07
Indeno (1,2,3-cd) pyrene	InP	6	0.1	ND	1.48	0.14	0.27	198.39	74.07
∑PAHs		-	-	ND	16.07	1.78	3.28	184.52	62.62

$$ILCR_{ingestion} = \frac{CS \times \left(CSF_{ingestion} \times \sqrt[3]{BW/70}\right) \times IR_{ingestion} \times EF \times ED}{BW \times AT \times 10^6}$$

$$ILCR_{dermal} = \frac{CS \times (CSF_{dermal} \times \sqrt[3]{BW/70}) \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^6}$$

$$ILCR_{inhalation} = \frac{CS \times (CSF_{inhalation} \times \sqrt[3]{BW/70}) \times IR_{inhalation} \times EF \times ED}{BW \times AT \times 10^6}$$

where BW is body weight, $IR_{ingestion}$ and $IR_{inhalation}$ are the soil intake rate and the inhalation rate, EF is the exposure frequency, ED is the exposure duration, SA is the surface area of the skin, AF is the dermal adherence factor, ABS is the dermal adsorption factor, AT is the average life expectancy, and PEF is the particle emission factor. CS is the sum of converted concentrations of soil PAHs according to the toxic equivalents of BaP based on toxic equivalency factors (TEFs) given in Table 1 CSF, short for carcinogenic slope factor, is determined according to the cancer-causing ability, and $CSF_{ingestion}$, CSF_{dermal}, and $CSF_{inhalation}$ are 7.3, 25, and 3.85 (mg kg^{-1} d^{-1})$^{-1}$, respectively. Moreover, cancer risks were estimated for the residents with three groups according to age: child (0–10 years), and adult (19–70 years).

2.5 Positive definite matrix factorization (PMF)

Source apportionment of PAHs in topsoil using the PMF 5.0 model launched by the US Environmental Protection Agency (EPA) (Liu et al., 2019). The PMF model decomposes the sampling data into two matrices, namely, the contribution of the coefficients (C) and the number of factors (F), and uses the concentration and uncertainty data of the sample to weight each point to minimize the objective function Q:

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{n}\left[\left(x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}\right) \Big/ u_{ij}\right]$$

In the formula, Q is the cumulative residual error, i is the number of samples, j is the type of pollutants determined; p is the number of suitable factors found by the PMF model; f is the composition matrix of each source; g is the amount of each pollutant in the sample. Contribution matrix; u_{ij} is the uncertainty of the pollutant species in the sample, and the calculation method is as follows:

$$s_{ij} = \begin{cases} \frac{5}{6} \times L_{MDL}, & x_{ij} \le L_{MLD} \\ \sqrt{\left(RDS \times x_{ij}\right)^2 + \left(L_{MDL}\right)^2}, & x_{IJ} > L_{MLD} \end{cases}$$

Where RSD is the relative standard deviation of the compound concentration value, and L_{MDL} is the method detection limit.

3 Results and analysis

3.1 Content and composition of PAHs in soil

The contents of 16 PAHs in soil samples from 54 sampling points were studied, and the statistical results are shown in Table 1. The total content of 16 PAHs (ΣPAHs) was ND~16.07 mg/kg, with an average value of 1.78 mg/kg. The total content of low molecular weight PAHs with 2–3 benzene rings was ND~2.28 mg/kg, with an average value of 0.29 mg/kg, accounting for 16.29% of the content of ΣPAHs; The total content of molecular weight PAHs was ND~30.59 mg/kg, with an average value of 1.49 mg/kg, accounting for 83.24% of the content of ΣPAHs.

The coefficients of variation of the 16 PAH monomers in this typical chemical park were all greater than 100%, which belonged to strong variation, indicating that the soil pollution of the site showed strong heterogeneity. The coefficients of variation of Acy, Ace, BaA, BbF, BaP, and DahA were higher than 200%, indicating that LMWPAHs and HMWPAHs were greatly affected by external factors in the study area, resulting in strong variability.

The mass fractions of PAHs with different ring numbers were: four-ring (38.76%)> five-ring (37.08%)> three-ring (14.04%)> six-ring (7.87%)> two-ring (2.25%). Four-ring and five-ring PAHs accounted for 75.84% of the total PAHs. And studies have shown that oil spills usually produce 2 rings, low temperature or medium temperature combustion processes (such as coal combustion) usually produce 3 rings and 4 rings, and high temperature combustion processes (such as automobile exhaust) usually produce 5 rings (gasoline combustion) and 6 rings (diesel combustion) (Shi et al., 2021). Through preliminary analysis, coal combustion and transportation emissions are the main sources in the study area. The specific source analysis of PAHs in farmland soil is shown in Section 2.3.

3.2 Assessment of soil PAHs pollution

In 2018, the Ministry of Ecology and Environment issued the "Soil Environmental Quality Construction Land Polluted Soil Risk Control Standard (Trial)" (GB36600-2018), which stipulates risk screening and control values for 8 types of PAHs with high toxicity. The protection of construction land can be divided into the first type of land and the second type of land according to the exposure of the protection object. The second type of land includes industrial land, commercial facilities land, road traffic land, etc. Based on the risk screening value of the second type of land, single factor and Nemerow index method were used to judge the pollution level of soil PAHs in the study area. It can be seen from Table 2 that the single factor index values of all sampling points of the eight PAHs are less than 1, and they are all in a pollution-free state (Wei et al., 2020), indicating that the content of PAHs monomers in the surface soil of this typical chemical park is less than the corresponding risk screening value. The risk of pollutants to human health can be ignored. The pollution grading according to the Nemerow composite index showed that the pollution levels of these 8 PAHs were all pollution-free.

PMF5.0 was used to analyze the source of PAHs in soil (Ambade et al., 2023), 20 was selected as the initial starting point for iterative operation, and 2 to 8 factors were used for operation respectively. The comparison found that when the number of factors was 6, the simulation operation was the best in the 14th time, and Q_r is close to Q_t, and more than 95% of the samples have residuals between −3.0 and 3.0, and R^2 > 0.9.

The results of running the PMF model are shown in the Figure 2.

TABLE 2 Pollution indices of 8 PAHs.

PAH	One-factor index		Nemero composite index	Pollution level
	Maximum	Average		
Nap	0.0055	0.0007	0.0039	pollution-free
BaA	0.0640	0.0076	0.0456	pollution-free
Chry	0.0011	0.0001	0.0008	pollution-free
BbF	0.1173	0.0137	0.0835	pollution-free
BkF	0.0068	0.0007	0.0048	pollution-free
BaP	0.9665	0.1101	0.6878	pollution-free
InP	0.0985	0.0108	0.0700	pollution-free
DahA	0.1975	0.0206	0.1404	pollution-free

Source Analysis of Soil PAHs.

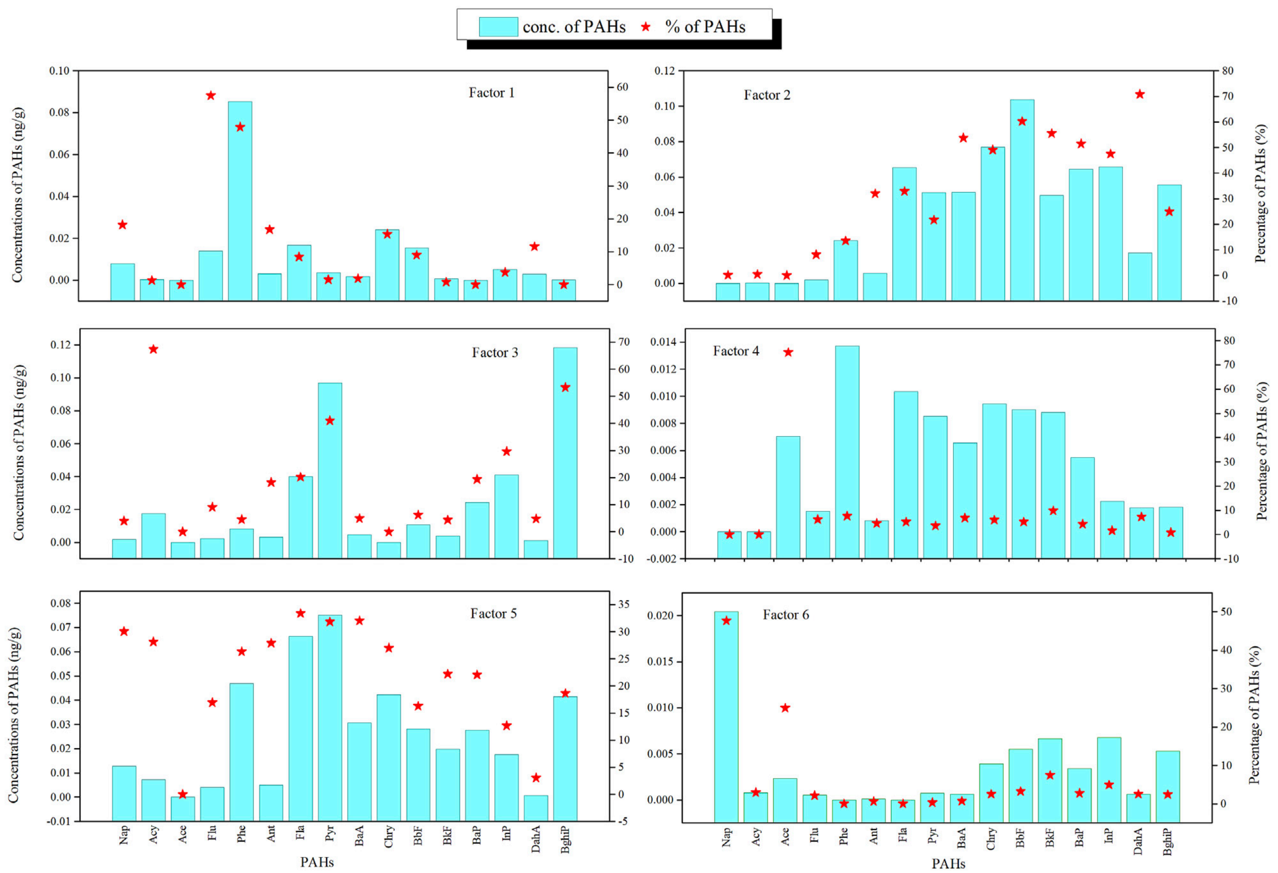

FIGURE 2
Source apportionment of soil PAHs based on PMF model.

Factor 1 accounts for 10.7% of the total source, and the loadings of Flu and Phe are relatively high. Flu is mainly the product of coke combustion (Simoneit, 2002), and Phe is mainly related to coke oven combustion (Zhang et al., 2021). From this, it is inferred that factor 1 is the source of coke combustion; factor 2 accounts for 35.2% of the total sources, and the loadings of DahA, BbF, BkF, and BaA are relatively high. Among them, DahA and BbF are considered to be important compounds in gasoline combustion (Yao et al., 2013), and

TABLE 3 Carcinogenic risk of different pathways in adults and children.

Crowd	Statistics	$ILCRs_{ingestion}$	$ILCRs_{dermal}$	$ILCRs_{inhalation}$	CR
Aldult	maximum	5.626×10^{-6}	1.175×10^{-5}	6.939×10^{-11}	1.738×10^{-5}
	minimum	1.164×10^{-12}	2.432×10^{-12}	1.436×10^{-17}	3.596×10^{-12}
	average	5.382×10^{-8}	1.124×10^{-7}	6.639×10^{-13}	1.663×10^{-7}
Child	maximum	5.887×10^{-6}	2.214×10^{-6}	1.878×10^{-11}	8.101×10^{-6}
	minimum	1.218×10^{-12}	4.581×10^{-13}	3.886×10^{-18}	1.676×10^{-12}
	average	5.632×10^{-8}	2.118×10^{-8}	1.797×10^{-13}	7.750×10^{-8}

Spatial distribution of soil PAHs.

are typical indicators of traffic emission sources. BkF and BaA are in diesel combustion exhaust gas (Yc et al., 2020). In summary, the analysis shows that the main factor 2 represents the transportation emission source; the factor 3 accounts for 20.7% of the total source, and the loads of Acy, BghiP, and Pyr are higher, and Acy is considered to be the product of biomass combustion (Yang et al., 2020). BghiP is an indicator of gasoline combustion products (Zheng et al., 2016), and Pyr is mainly an indicator of straw combustion (Liu et al., 2018). In summary, factor 3 represents a mixed source of biomass combustion and transportation emissions; factor 4 accounts for 5.0% of the total source, and Ace load Studies have shown that Ace is a representative indicator of petroleum sources (Han et al., 2022), so factor 4 is petroleum sources; factor 5 accounts for 24.6% of the total sources, the loadings of Fla, BaA, and Pyr are higher, and the main sources of Fla, BaA, and Pyr are It is coal combustion (Tian et al., 2009). Some enterprises in the chemical park use coal as energy, which makes coal an important source of soil PAHs pollution in the area; factor 6 accounts for 3.7% of the total source, and Nap and Ace loads are high. The sources of Nap mainly include Oil spill and oil volatilization (Abdel-Shafy and Mansour, 2016), Ace is a representative indicator of oil source (Wei et al., 2022), and comprehensive analysis factor 6 represents oil spill source. To sum up, the main sources of PAHs in the topsoil of the chemical park are coke combustion sources, traffic emission sources, biomass combustion sources, oil sources, coal combustion sources and oil leakage sources.

3.3 Health risk assessment of soil PAHs

The lifetime cancer risk increment model was used to calculate the carcinogenic risks (ILCRs) and total risks (CR) of soil PAHs to children and adults under the three exposure routes of ingestion, inhalation, and dermal. The results are shown in Table 3. In general, except for the pathway of accidental ingestion, the mean values of ILCRs and CR in adults were higher than those in children, indicating that the carcinogenic risk of PAHs in soil was higher than that in children.

This risk can be ignored when the ILCRs is 10^{-6} or less (Hoseini et al., 2016), and there is a potential risk when the ILCRs are between 10^{-6} and 10^{-4}. The carcinogenic risks in this study were all less than 10^{-6}, indicating a low carcinogenic risk.

ArcGIS was used to draw the spatial distribution map of surface soil PAHs (Figure 3), and the overall distribution was more concentrated in the south and less distributed in the north. The spatial distribution characteristics of Nap, Acy, Flu, and Lnp are roughly similar, with the majority in the south, and there is also a region with higher content in the south to the middle; Phe, Ace, Ant, Pla, Pyr, and Bghip are all higher in the southwest direction; BaA, The content of Chry, BbF, BkF, Bap, and DahA is higher in the central and southern parts, and there is a high value area in the west of the central part.

4 Discussion

The content of PAHs in the surface soil of this typical chemical industry park was determined to be ND~16.07 mg/kg, with an average value of 1.78 mg/kg. Its content is much lower than that of the soil of a large chemical site in northeast China (the average content of PAHs is 67 mg/kg) (Qu et al., 2021) and the soil of a chemical park in Shandong Province (the average content of PAHs is 3.0898 mg/kg) (Wang et al., 2015), and higher than that of an electronic waste dismantling area in southeast China (average PAHs content of 1.035 mg/kg) (Jin et al., 2020).

The results of soil PAHs contamination evaluation showed that the overall pollution status of the typical industrial park was relatively optimistic, and all sample sites were free of PAHs pollution. Compared with other areas in China, the pollution level is comparable to that of the three chemical industry areas in Tianjin Binhai New Area (Cai et al., 2008), and is significantly lower than that of the core area of Ningdong Energy and Chemical Industry Base (Wei et al., 2020). Compared with foreign countries, it is comparable to the soil in the chemical industry area of Tarragona Province, Spain (Nadal et al., 2004), and is significantly lower than the industrial soil in the Seine River Basin in France (Motelay-Massei et al., 2004) and the urban soil in New Jersey, United States (Mielke et al., 2004). The reason for the absence of PAHs in the soil of this typical industrial park in Chongqing is that the city has a subtropical monsoon humid climate, with warm winters and early springs, hot summers and cool autumns, abundant rainfall, with climatic characteristics such as high temperature and strong evaporation, which is conducive to the volatilization and photolysis of PAHs in the soil. On the other hand, as the country and Chongqing Municipality have been actively recommending the construction of ecological civilization and the implementation of the strategic goal of protecting the Yangtze River ecological environment in recent years. The industrial park has

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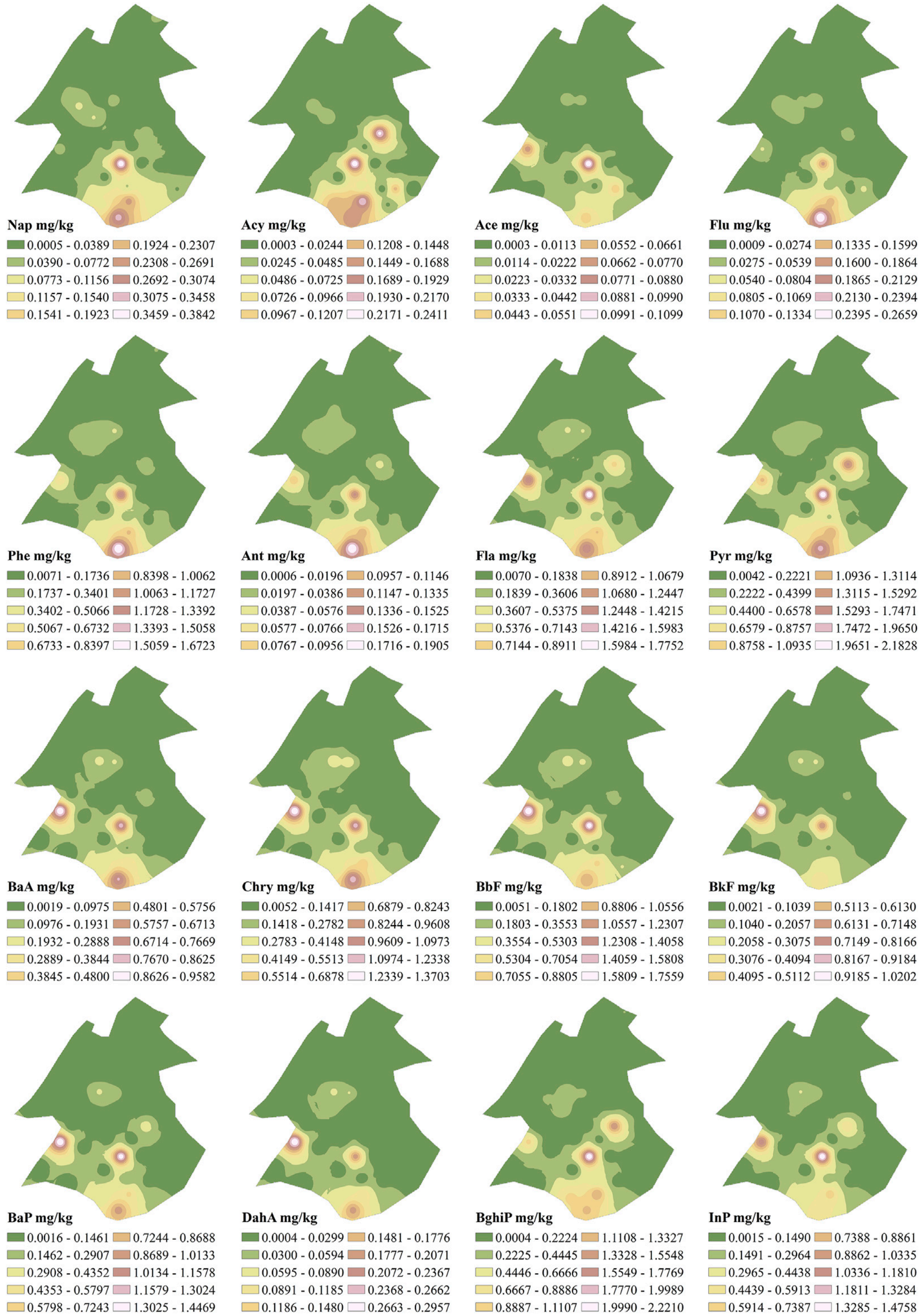

FIGURE 3
Spatial distribution of soil PAHs in a typical chemical industry park.

carried out comprehensive improvement of the environment and taken active pollution prevention and control measures, using new technologies with low energy consumption and environmental protection instead of traditional energy-consuming and high-polluting technologies and processes, which has played a positive role in environmental improvement and reduced the accumulation of soil PAHs to a certain extent.

The PMF method was used to analyze the sources of PAHs in the soil of the park. The six factors were: Coke combustion source (10.7%), traffic emission source (35.2%), biomass combustion/

traffic emission mixed source (20.7%), and petroleum source (5.0%), coal combustion sources (24.6%), and oil spill sources (3.7%). The factories in the chemical park in this study include petrochemical, natural gas, chlor-alkali, biomass, fine chemical and new material industries. Therefore, the source composition spectrum obtained by source analysis is consistent with the actual situation, and the results are relatively reasonable. The highest contribution rate is the factor 2 traffic emission source, which is also consistent with the results that the content of PAHs in this study is basically low and the pollution level is low.

It can be seen from the spatial interpolation map that the contents of 16 PAH monomers are distributed differently in the chemical industry park, with a patchy distribution, and the content in the southern part of the park is obviously higher than that in the northern part. There are 4 high-value distribution areas of PAHs in the park, which are the southernmost part of the park, the center of the park to the south, the center of the park to the west, and the center of the park to the east. The PAHs content gradually decreases from the polluted area to the surrounding areas, and the content in the entire northern part is lower. The frequent industrial production and heavy traffic in the southern part of the park may cause the higher content of polycyclic aromatic hydrocarbons in the southern part.

5 Conclusion

(1) The total content of 16PAHs in this typical chemical industry park in Chongqing is below 16.07 mg/kg. The degree of PAHs pollution is light, and the coefficient of variation of PAHs is relatively high, indicating that the soil pollution of the site presents strong heterogeneity.
(2) The health risk evaluation of soil PAHs shows that there is no potential carcinogenic risk of PAHs in this area to people of different ages. And the main exposure routes for adults were dermal contact > accidental ingestion > respiratory inhalation, and for children were accidental ingestion > dermal contact > respiratory inhalation.
(3) The contribution rates of coke combustion sources, traffic emission sources, biomass combustion sources, oil sources, coal combustion sources and oil leakage sources of soil PAHs in the park were 10.7%, 35.2%, 20.7%, 5.0%, 24.6%, and 3.7%, respectively. From the spatial distribution map of PAHs content, it can be seen that the content of PAHs is higher in the south of the park, and the high-value areas are mainly distributed in the central and southern regions.

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

Conceptualization, YZ and GS; methodology, JN; software, ZW; validation, XZ, LW, and XL; formal analysis, SM and ZW; investigation, YZ and GS; writing—original draft preparation, YZ, JN, and ZW; writing—review and editing, YZ and GS; supervision, YZ and GS. All authors contributed to the article and approved the submitted version.

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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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References

Abdel-Shafy, H. I., and Mansour, M. S. M. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Petroleum* 25 (1), 107–123. doi:10.1016/j.ejpe.2015.03.011

Ambade, B., Sankar Tapan, K., Kumar, A., and Sethi Shrikanta, S. (2020). Characterization of PAHs and n-alkanes in atmospheric aerosol of Jamshedpur city, India. *J. Hazard. Toxic, Radioact. Waste* 24 (2), 04020003. doi:10.1061/(ASCE)HZ.2153-5515.0000490

Ambade, B., and Sankar, T. K. (2021). Source apportionment and health risks assessment of black carbon Aerosols in an urban atmosphere in East India. *J. Atmos. Chem.* 78 (3), 177–191. doi:10.1007/s10874-021-09418-9

Ambade, B., and Sethi Shrikanta, S. (2021). Health risk assessment and characterization of polycyclic aromatic hydrocarbon from the hydrosphere. *J. Hazard. Toxic, Radioact. Waste* 25 (2), 05020008. doi:10.1061/(ASCE)HZ.2153-5515.0000586

Ambade, B., Sethi, S. S., and Chintalacheruvu, M. R. (2023). Distribution, risk assessment, and source apportionment of polycyclic aromatic hydrocarbons (PAHs) using positive matrix factorization (PMF) in urban soils of East India. *Environ. Geochem. Health* 45 (2), 491–505. doi:10.1007/s10653-022-01223-x

Ambade, B., Sethi, S. S., Giri, B., Biswas, J. K., and Bauddh, K. (2022a). Characterization, behavior, and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the estuary sediments. *Bull. Environ. Contam. Toxicol.* 108 (2), 243–252. doi:10.1007/s00128-021-03393-3

Ambade, B., Sethi, S. S., Kurwadkar, S., Mishra, P., and Tripathee, L. (2022b). Accumulation of polycyclic aromatic hydrocarbons (PAHs) in surface sediment residues of Mahanadi River Estuary: Abundance, source, and risk assessment. *Mar. Pollut. Bull.* 183, 114073. doi:10.1016/j.marpolbul.2022.114073

Cai, Q. Y., Mo, C. H., Wu, Q. T., Katsoyiannis, A., and Zeng, Q. Y. (2008). The status of soil contamination by semivolatile organic chemicals (SVOCs) in China: A review. *Sci. Total Environ.* 389 (2-3), 209–224. doi:10.1016/j.scitotenv.2007.08.026

Callén, M., Iturmendi, A., López, J., and Mastral, A. M. (2014). Source apportionment of the carcinogenic potential of polycyclic aromatic hydrocarbons (PAH) associated to airborne PM10 by a PMF model. *Environ. Sci. Pollut. Res.* 21, 2064–2076. doi:10.1007/s11356-013-2116-9

Cao, S., Duan, X., Zhao, X., Wang, B., Ma, J., Fan, D., et al. (2015). Health risk assessment of various metal(loid)s via multiple exposure pathways on children living near a typical lead-acid battery plant, China. *Environ. Pollut.* 200, 16–23. doi:10.1016/j.envpol.2015.02.010

Cui, Z., Wang, Y., Du, L., and Yu, Y. (2022). Contamination level, sources, and health risk of polycyclic aromatic hydrocarbons in suburban vegetable field soils of Changchun, Northeast China. *Sci. Rep.* 12 (1), 11301. doi:10.1038/s41598-022-15285-5

Devatha, C. P., Vishnu Vishal, A., and Purna Chandra Rao, J. (2019). Investigation of physical and chemical characteristics on soil due to crude oil contamination and its remediation. *Appl. Water Sci.* 9 (4), 89. doi:10.1007/s13201-019-0970-4

García, T. C., Ruano-Ravina, A., Candal-Pedreira, C., López-López, R., Torres-Durán, M., Enjo-Barreiro, J. R., et al. (2023). Occupation as a risk factor of small cell lung cancer. *Sci. Rep.* 13 (1), 4727. doi:10.1038/s41598-023-31991-0

Han, B., Gao, W., Li, Q., Liu, A., Gong, J., Zheng, Y., et al. (2022). Residues of persistent toxic substances in surface soils of Ny-Ålesund in the arctic: Occurrence, source, and ecological risk assessment. *Chemosphere* 303, 135092. doi:10.1016/j.chemosphere.2022.135092

Hoseini, M., Yunesian, M., Nabizadeh, R., Yaghmaeian, K., Ahmadkhaniha, R., Rastkari, N., et al. (2016). Characterization and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in urban atmospheric Particulate of Tehran, Iran. *Environ. Sci. Pollut. Res.* 23 (2), 1820–1832. doi:10.1007/s11356-015-5355-0

Jin, R., Zheng, M., Lammel, G., Bandowe, B. A. M., and Liu, G. (2020). Chlorinated and brominated polycyclic aromatic hydrocarbons: Sources, formation mechanisms, and occurrence in the environment. *Prog. Energy Combust. Sci.* 76, 100803. doi:10.1016/j.pecs.2019.100803

Johnsen, A. R., and Karlson, U. (2007). Diffuse PAH contamination of surface soils: Environmental occurrence, bioavailability, and microbial degradation. *Appl. Microbiol. Biotechnol.* 76 (3), 533–543. doi:10.1007/s00253-007-1045-2

Kurwadkar, S., Sethi, S. S., Mishra, P., and Ambade, B. (2022). Unregulated discharge of wastewater in the Mahanadi River Basin: Risk evaluation due to occurrence of polycyclic aromatic hydrocarbon in surface water and sediments. *Mar. Pollut. Bull.* 179, 113686. doi:10.1016/j.marpolbul.2022.113686

Kwon, H.-O., and Choi, S.-D. (2014). Polycyclic aromatic hydrocarbons (PAHs) in soils from a multi-industrial city, South Korea. *Sci. Total Environ.* 470-471, 1494–1501. doi:10.1016/j.scitotenv.2013.08.031

Li, C., Li, Z., and Wang, H. (2023). Characterization and risk assessment of polycyclic aromatic hydrocarbons (PAHs) pollution in particulate matter in rural residential environments in China-A review. *Sustain. Cities Soc.* 96, 104690. doi:10.1016/j.scs.2023.104690

Liu, H., Yu, X., Liu, Z., and Sun, Y. (2018). Occurrence, characteristics and sources of polycyclic aromatic hydrocarbons in arable soils of Beijing, China. *Ecotoxicol. Environ. Saf.* 159, 120–126. doi:10.1016/j.ecoenv.2018.04.069

Liu, J., Liu, Y. J., Liu, Z., Zhang, A., and Liu, Y. (2019). Source apportionment of soil PAHs and human health exposure risks quantification from sources: The yulin national energy and chemical industry base, China as case study. *Environ. Geochem Health* 41 (2), 617–632. doi:10.1007/s10653-018-0155-3

Mao, Y., Zhang, L., Wang, Y., Yang, L., Yin, Y., Su, X., et al. (2021). Effects of polycyclic aromatic hydrocarbons (PAHs) from different sources on soil enzymes and microorganisms of Malus prunifolia var. Ringo. *Archives Agron. Soil Sci.* 67 (14), 2048–2062. doi:10.1080/03650340.2020.1820488

Mielke, H. W., Wang, G., Gonzales, C. R., Powell, E. T., Le, B., and Quach, V. N. (2004). PAHs and metals in the soils of inner-city and suburban New Orleans, Louisiana, USA. *Environ. Toxicol. Pharmacol.* 18 (3), 243–247. doi:10.1016/j.etap.2003.11.011

Motelay-Massei, A., Ollivon, D., Garban, B., Teil, M. J., Blanchard, M., and Chevreuil, M. (2004). Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere* 55 (4), 555–565. doi:10.1016/j.chemosphere.2003.11.054

Nadal, M., Schuhmacher, M, and Domingo, J., L. (2004). Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environ. Pollut. -London Then Barking-* 132 (1), 1–11. doi:10.1016/j.envpol.2004.04.003

Ouyang, Z., Gao, L., and Yang, C. (2018). Distribution, sources and influence factors of polycyclic aromatic hydrocarbon at different depths of the soil and sediments of two typical coal mining subsidence areas in Huainan, China. *Ecotoxicol. Environ. Saf.* 163, 255–265. doi:10.1016/j.ecoenv.2018.07.024

Qu, M., Guang, X., Zhao, Y., and Huang, B. (2021). Spatially apportioning the source-oriented ecological risks of soil heavy metals using robust spatial receptor model with land-use data and robust residual kriging. *Environ. Pollut. (Barking, Essex 1987)* 285, 117261. doi:10.1016/j.envpol.2021.117261

Schwab, A. P., and Dermody, C. L. (2021). "Chapter Two - pathways of polycyclic aromatic hydrocarbons assimilation by plants growing in contaminated soils," in *Advances in agronomy*. Editor D. L. Sparks (Cambridge, Massachusetts, United States: Academic Press), 193–250.

Shi, R., Li, X., Yang, Y., Fan, Y., and Zhao, Z. (2021). Contamination and human health risks of polycyclic aromatic hydrocarbons in surface soils from Tianjin coastal new region, China. *Environ. Pollut.* 268, 115938. doi:10.1016/j.envpol.2020.115938

Shukla, S., Khan, R., Bhattacharya, P., Devanesan, S., and AlSalhi, M. S. (2022). Concentration, source apportionment and potential carcinogenic risks of polycyclic aromatic hydrocarbons (PAHs) in roadside soils. *Chemosphere* 292, 133413. doi:10.1016/j.chemosphere.2021.133413

Simoneit, B. R. T. (2002). Biomass burning — A review of organic tracers for smoke from incomplete combustion. *Appl. Geochem.* 17 (3), 129–162. doi:10.1016/s0883-2927(01)00061-0

Tian, F., Chen, J., Qiao, X., Wang, Z., Ping, Y., Wang, D., et al. (2009). Sources and seasonal variation of atmospheric polycyclic aromatic hydrocarbons in Dalian, China: Factor analysis with non-negative constraints combined with local source fingerprints. *Atmos. Environ.* 43 (17), 2747–2753. doi:10.1016/j.atmosenv.2009.02.037

Wang, C., Wu, S., Zhou, S., Wang, H., Li, B., Chen, H., et al. (2015). Polycyclic aromatic hydrocarbons in soils from urban to rural areas in Nanjing: Concentration, source, spatial distribution, and potential human health risk. *Sci. Total Environ.* 527-528C, 375–383. doi:10.1016/j.scitotenv.2015.05.025

Wei, C., Sg, A., Jing, Z. A., Yw, A., Yg, A., Yi, Z. A., et al. (2020). Post relocation of industrial sites for decades: Ascertain sources and human risk assessment of soil polycyclic aromatic hydrocarbons. *Ecotoxicol. Environ. Saf.* 198, 110646. doi:10.1016/j.ecoenv.2020.110646

Wei, P., Li, Y., Ren, X., and Duan, K. (2022). Crude oil price uncertainty and corporate carbon emissions. *Environ. Sci. Pollut. Res.* 29 (2), 2385–2400. doi:10.1007/s11356-021-15837-8

Yang, J., Sun, P., Zhang, X., Wei, X. Y., Huang, Y., Du, W. N., et al. (2020). Source apportionment of PAHs in roadside agricultural soils of a megacity using positive matrix factorization receptor model and compound-specific carbon isotope analysis. *J. Hazard. Mater.* 403, 123592. doi:10.1016/j.jhazmat.2020.123592

Yao, H., Zhang, S., Xue, X., Yang, J., Hu, K., and Yu, X. (2013). Influence of the sewage irrigation on the agricultural soil properties in Tongliao City, China. *Front. Environ. Sci. Eng.* 7 (2), 273–280. doi:10.1007/s11783-013-0497-0

Yc, A., Ming, X. B., Bw, B., Cl, A., Xl, A., Mh, A., et al. (2020). Spatiotemporal distribution, source, and ecological risk of polycyclic aromatic hydrocarbons (PAHs) in the urbanized semi-enclosed Jiaozhou Bay, China. *Sci. Total Environ.* 717, 137224. doi:10.1016/j.scitotenv.2020.137224

Zhang, C., Shan, B., Zhao, Y., Song, Z., and Tang, W. (2018). Spatial distribution, fractionation, toxicity and risk assessment of surface sediments from the Baiyangdian Lake in northern China. *Ecol. Indic.* 90, 633–642. doi:10.1016/j.ecolind.2018.03.078

Zhang, Q., Meng, J., Su, G., Liu, Z., Shi, B., and Wang, T. (2021). Source apportionment and risk assessment for polycyclic aromatic hydrocarbons in soils at a typical coking plant. *Ecotoxicol. Environ. Saf.* 222, 112509. doi:10.1016/j.ecoenv.2021.112509

Zhang, Y., Guo, Z., Peng, C., and He, Y. (2023). Introducing a land use-based weight factor in regional health risk assessment of PAHs in soils of an urban agglomeration. *Sci. Total Environ.* 887, 163833. doi:10.1016/j.scitotenv.2023.163833

Zhang, Y., Peng, C., Guo, Z., Xiao, X., and Xiao, R. (2019). Polycyclic aromatic hydrocarbons in urban soils of China: Distribution, influencing factors, health risk and regression prediction. *Environ. Pollut.* 254, 112930. doi:10.1016/j.envpol.2019.07.098

Zhao, D., Zhang, P., Ge, L., Zheng, G. J., Wang, X., Liu, W., et al. (2018). The legacy of organochlorinated pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in Chinese coastal seawater monitored by semi-permeable membrane devices (SPMDs). *Mar. Pollut. Bull.* 137, 222–230. doi:10.1016/j.marpolbul.2018.10.004

Zheng, X., Yang, Y., Liu, M., Yu, Y., Zhou, J. L., and Li, D. (2016). PAH determination based on a rapid and novel gas purge-microsyringe extraction (GP-MSE) technique in road dust of Shanghai, China: Characterization, source apportionment, and health risk assessment. *Sci. Total Environ.* 557-558, 688–696. doi:10.1016/j.scitotenv.2016.03.124