

Original Research

Polycyclic Aromatic Hydrocarbons (PAHs) in Main urban area Soils of Changchun, Northeast China: Status, Sources, and Potential Toxic Risk Assessment

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Abstract

This study comprehensively investigated the occurrence, sources, and potential toxicity risks of 16 PAHs in main urban area surface soils of Changchun, northeast China. The 16 total PAHs (Σ_{16} PAHs) concentrations in surface soils decreased significantly along the commercial traffic district, industrial zone, residential zone, park zone, and outskirt farmland, ranging from 46.6 to 8870.8 ng/g, with a mean value of 1480.1ng/g and 4-ring PAHs were always the dominant constituents in all land used area soils. Based on ArcGIS mapping, higher concentrations of PAHs are mainly concentrated in the northeast region and the central historic district soils of Changchun city. Mixed pyrogenic sources and coal combustion were the dominant sources and contributed approximately 45% and 30% of the total soil PAHs, respectively. Toxicity risk assessment based on the toxic equivalent concentrations (BaP_{eq}) of soil PAHs indicated the potential toxicity risks detected in this study were relatively moderate compared with other global cities, while some special attention still should be paid to hotspots with high PAHs concentrations surrounding the commercial traffic area and industrial zone in the northeast pattern of Changchun city. This study could be potentially useful for local governments targeted to control toxicity exposure, promote actions to alleviate PAHs contamination.

Keywords: PAHs, urban soils, Changchun, principal component analysis, BaP_{eq}

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous persistent organic contaminants consisting of two or more fused aromatic rings [1]. They have attracted considerable research attention

due to their environmental persistence and significant health risk as carcinogens and mutagens [2-4]. Among hundreds of different PAHs, 16 PAH compounds have been listed as the priority pollutants by the United States Environment Protection Agency (US EPA) and seven of these priority pollutants have been classified as the probable human carcinogens by the International Agency for Research on Cancer (IARC) [5]. Based on their formation process, PAHs mainly originated

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from pyrogenic, petrogenic, and biogenic sources, and pyrogenic PAHs results from incomplete combustion of organic carbon such as vehicle emission have been reported as the most contributors [6].

In recent decades, the unprecedented rapid development of urbanization and industrialization in China has created giant economic growth, while simultaneously resulting in significant levels of urban environmental pollution, especially the continuous and increased emissions of potentially toxic PAHs [3]. It is reported that motor vehicles can contribute to approximately 36% of annual total PAH emissions [7]. Soil is the most important sink for PAHs in the terrestrial system and approximately 90% of the total PAHs retain in surface soil [8]. PAHs derived from anthropogenic activities can enter urban soils via dry or wet deposition after transporting in the atmosphere over long distances [9]. Further, urban soil PAHs can be also the source of atmospheric and water PAHs through volatilization and surface runoff, thereby increasing the urban ecological environment security and PAHs exposure to urban residents [10]. They can accumulate into human bodies through dermal contact and/or ingestion of contaminated food and pose a threat to inhabitants' health [11-12]. Therefore, understanding the occurrence, distribution and negative effects of PAHs in urban surface soil is a critical issue for ensuring urban public health.

Changchun, a major industrial center in northeastern China, is one of the most industrialized and economically significant cities in China and its environment has been subjected to heavy anthropogenic influences with rapid urbanization and industrialization. It has many industry segments such as the automotive industries, coal-fired power plants, metallurgy, iron and steel mills, construction material manufacturers, and chemical plants [13]. As a high population density city, the total population of Changchun had reached 9.06 million in 2020, including 5.81 million in the main municipal area, accounting for 64.08% of its total population [14]. The local energy structure is dominated by fossil fuels (coal, natural gas, and petroleum) and biomass combustion, which total consumed 17.5 million tons of standard coal energy (SCE) annually and resulted in large amounts of PAHs emitting into the environment [15]. Previous studies on PAHs in Changchun have mainly focused on atmospheric particulate matters [16-18]. Research showed that the total concentrations of 16 PAHs in the atmospheric particulate matter were 1.57 ng/m³ and 1.10 ng/m³ during the heating period and non-heating period [16]. However, limited studies have been investigated on PAHs pollution in different urban land used pattern soils of Changchun. Therefore, the objectives of this study are to (1) investigate the pollution levels and spatial distribution of PAHs in urban soils from different land used areas of Changchun; (2) identify possible sources of PAHs in urban soils from Changchun; and (3) assess toxic ecological risk of PAHs to residents.

Material and Methods

Study Area and Soil Sampling

Changchun (124°18'~127°02'E, 43°05'~45°15'N), with a total city area of 20593 km² and the district area of 543 km² [15], is the capital city of Jilin province, located in the hinterland of Songliao plain in northeast China. It has a north temperate zone continental climate, with an annual average temperature of 6.7°C, characterized by long and cold winters, while warm and short summers. The annual frost-free period lasts about 134-140 days and the heating period can last from October to the following March [19], which may further influence the levels of PAHs contamination in urban surface soil as the temperature is a very important factor in determining the degradation of soil PAHs [20]. The soil types are mainly dominated by black soil, dark brown soil, and meadow soil.

48 surface soil samples and 4 background samples were collected from the main urban district and suburban cultivated land of Changchun city in October 2019 (Fig. 1). The main urban district samples were divided into park zone (PZ) samples, industrial zone (IZ) samples, residential zone (RZ) samples, commercial traffic area (CT) samples, and outskirts farmland (OF) samples according to their different land used pattern locations. Each sampling site was set in a 10 m×10 m grid, and five surface subsamples (0-20cm) according to the diagonal rule were taken to mixed as one composite sample. All soil samples were freeze-dried at -50°C for 24 h and sieved to 80 mesh after removing stones, leaves and other impurities, then sealed in polyethylene bags and stored at -4°C until further analysis of total organic carbon (TOC) and PAHs.

Reagents and Materials

A composite standard solution of sixteen US EPA priority-listed PAHs was purchased from Tan-Mo Technology Co.; Ltd (Beijing, China), the names and abbreviations of PAHs are listed in Table 1. A deuterated PAHs mixture standard solution containing naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂ in dichloromethane solvent was used as the internal standard chemicals for quality monitoring during detection. 2-fluorophenyl and p-terphenyl-d₁₄ mixed in n-hexane and acetone (1:1) solvent were used as the surrogate standards for quality monitoring during the pretreatment process. Dichloromethane (DCM), n-hexane, acetone solvents at chromatographic grade, and anhydrous ethanol at analytical grade were purchased from Haodi Chemical reagent Co.; Ltd (Jilin, China). Granular diatomite (20-40 mesh) and quartz sand were purified at 400°C for 4 h, then kept in a desiccator using as desiccants and filters.

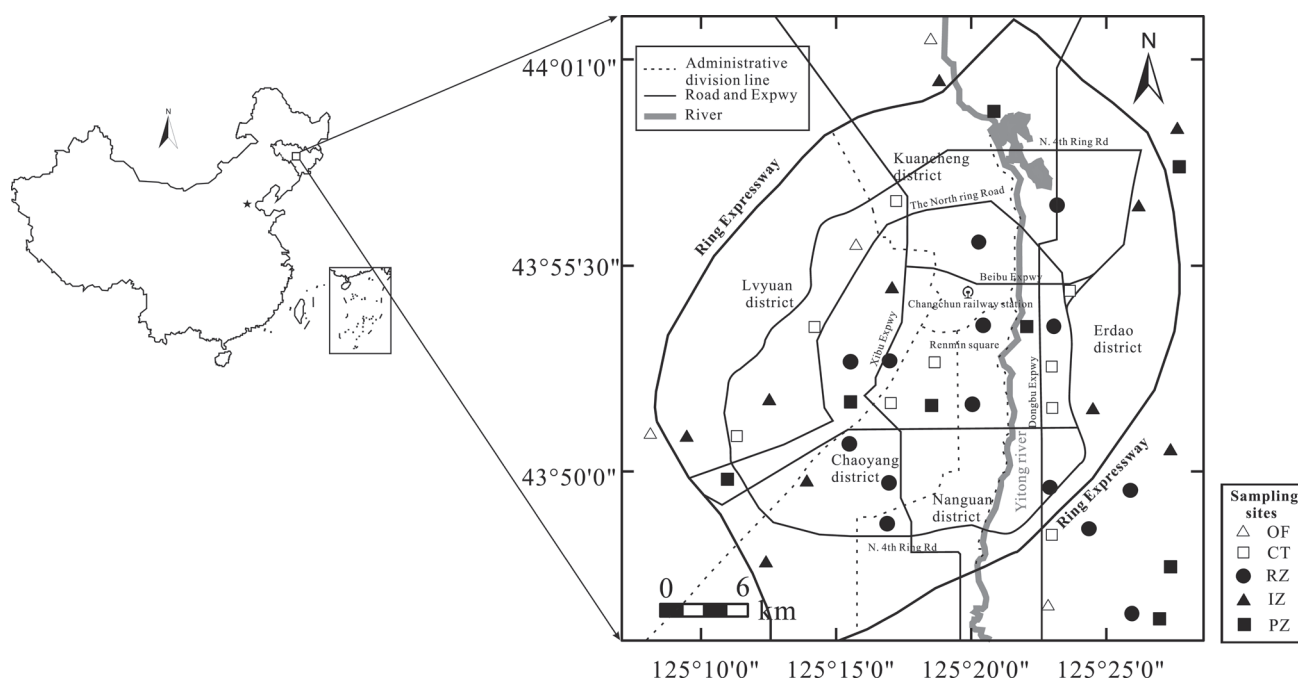


Fig. 1. Map of the soil sampling sites in the main urban district of Changchun, NE China (sampling sites including: park zone (PZ), industrial zone (IZ), residential zone (RZ), commercial traffic area (CT), and outskirts farmland (OF)).

Table 1. Retention time and precision for the determination of 16 PAHs by GC-MS.

PAH congeners	Abbreviations	Rings	RT ^a (min)	MDLs ^b (ng/g)	R ^c	DF ^d
Naphthalene	Nap	2	7.118	1.6	0.9964	90%
Acenaphthylene	Acy	2	9.972	0.8	0.9952	77%
Acenaphthene	Ace	2	10.430	0.5	0.9961	85%
Fluorene	Flu	2	12.111	0.8	0.9958	88%
Phenanthrene	Phe	3	15.626	2.1	0.9912	100%
Anthracene	Ant	3	15.780	1.8	0.9968	98%
Fluoranthene	Fla	3	19.680	3.6	0.9958	90%
Pyrene	Pyr	4	20.601	3.6	0.9963	96%
Benzo[a]anthracene	BaA	4	27.043	2.8	0.9960	100%
Chrysene	Chr	4	27.245	3.1	0.9957	100%
Benzo[b]fluoranthene	BbF	4	32.763	6.5	0.9956	88%
Benzo[k]fluoranthene	BkF	4	32.770	2.8	0.9963	98%
Benzo[a]pyrene	BaP	5	34.140	1.8	0.9966	100%
Indeno[1,2,3-cd] pyrene	IcdP	5	40.910	3.4	0.9966	81%
Dibenz[a,h]anthracene	DB(a,h)A	5	41.160	2.4	0.9964	58%
Benzo[ghi]perylene	BghiP	6	42.870	2.5	0.9976	88%

^a RT: Retention time; ^b MDLs: Method detection limits, they were experimentally calculated as 3.143σ , where σ is the standard deviation of the response of 7 parallel analyses for the blank sample (quartz sand) containing the standard solution of 20 ng/g;

^c R: Correlation coefficient of calibration curve; ^d DF: detection frequency

Extraction and Analysis of PAHs

Exactly 15.0g freeze-dried soil samples spiked with surrogate standard mixture were extracted with an accelerated solvent extractor (APLE-2000, Jitian Instrument Co., Ltd, Beijing, China) using a mixture of DCM-hexane (1:1, v/v). Soil samples were extracted 2 times under 100°C, 10MPa. The static time was 5 min, the flush volume was 60%, and the purge time was the 90s. The final extracts were concentrated to approximately 2ml with a vacuum rotary evaporator (Yarong Instrument Co., Ltd, Shanghai, China) with a 50°C water bath and 60RPM of spin rate, then cleaned up using a Florisil cartridges column (1000 mg, 6 ml) equipped on a solid phase setup. Before purification, 5 mL DCM and 10 mL n-hexane were added to activate the magnesium silicate column and the fraction was discarded. The extracts were then eluted with 10 mL DCM/n-hexane (2:8, v/v) through the column. All eluents were collected and concentrated to 1.0 mL, then transferred to a clean vial. Then internal standards were added to the bottle before instrumental analysis.

Sixteen US EPA priority-listed PAHs were detected on Clarus 580/680 gas chromatograph -SQ8 mass spectrometry (ClarusSQ8 GC-MS, PerkinElmer, USA), equipped with a DB-5 elastic quartz capillary column (30 m×0.25 mm×0.25 μm), using ultrapure helium (>99.999% pure) as the carrier gas. The sample extracts (each 1.0 μL) were injected in the splitless mode. The oven temperature program was set as follows: held at 80°C for 2 min, increased to 180°C at a heating rate of 20°C/min, holding for 5min, then raised to 240°C with 5°C/min, holding for 5min, finally from 240°C to 290°C at 10°C/min, and holding for 8min. The MS was operated in electron impact ionization mode with electron energy of 70eV. The inlet and transfer line temperature were both 280°C and the ion source temperature was 230°C. A composite standard of 16 PAHs solution was analyzed by GC-MS in MS scan mode to record the retention time of each target compound for the qualitative analysis (Table 1). Quantification of each PAH compound based on the selective ion monitoring (SIM) mode was carried out using internal standard calibrations with peak area.

Quality Assurance and Quality Control

Strict quality control procedures were applied to monitor the validity of data. The calculated calibration curves (gradient of 0,0.5,1,5,10 μg/mL concentration standard solutions containing individual PAHs) showed high-level linearity for all target analytes. The method detection limits (MDLs) for individual PAHs ranged from 0.5 to 6.5 ng/g, as described in detail in Table 1. One laboratory blank sample (equivalent quartz sand instead of soil sample) and one duplicate sample were run with every batch of 12 samples. The concentration of PAHs detected in the blank samples was negligible, and the relative standard deviation of PAH in random

duplicate was less than 15%. In addition, the surrogate standards and the deuterated PAHs mixture standard were added to all soil samples to monitor the procedural performance. Mean recovery of all samples for 2-fluorophenyl and p-terphenyl-d14 was 62% and 128%, respectively and the recoveries of five deuterated internal standards ranged from 89% to 109%.

Determination of Soil pH and TOC

Soil pH was determined with a pH meter (PB-21, Sartorius, Germany) in a 1:2.5 suspension H₂O. Soil total organic carbon (TOC) was determined through the potassium dichromate volumetric method, which is a standard method recommended by the Chinese Society of Soil Science [21]. Briefly, soil organic carbon was oxidized into carbon dioxide by quantitative potassium dichromate solution under the condition of oil bath heating, while potassium dichromate (K₂Cr₂O₇) is reduced to Cr³⁺. The remaining K₂Cr₂O₇ was titrated by FeSO₄ and the concentrations of soil TOC can be calculated quantitatively on basis of the change of potassium dichromate before and after oxidation of soil organic carbon.

Data Analyses Method

Both PAH diagnostic ratios and principal component analysis coupled with multivariate linear regression (PCA-MLR) were chosen in this study to identify the major sources of PAHs in the main urban area soils of Changchun. PCA-MLR is a commonly applied technique to quantitatively appoint the pollution sources of PAHs in the environment as it only needs to roughly understand the composition of pollutant emission sources without the accurate source component data. Principal component analysis (PCA) was used to reduce the dimensionality of receptor data, and extract valuable representative factors information from multivariate. Under utilizing the orthogonal transformation method, several principal components (PCs) can be extracted with different factor loadings which can indicate different pollution sources [22]. Multivariate linear regression (MLR) aims to appoint the relative contribution of each pollution source using ordinary least squares based on the identification of emission sources [23]. It is performed between the PCs and the sum of pollutants, and the standardized regression coefficients were used to calculate the relative contributions of various PAH sources. The model of MLR was as follows:

$$Z_{PAHs} = \sum_{i=1}^n m f_i + b$$

Where, Z_{PAHs} is the dependent variable represented by the standardized total 16 PAH concentration values; n is the number of extracted principal components

(PCs); m_i is the standardized regression coefficient; f_i is the standardized factor score of the PC_{*i*} and b is the regression constant. The contribution rate (W , %) of each pollution source was calculated as follows:

$$W = m_i / \sum m_i \times 100\%$$

Where i is the pollution source represented by each principal component; m_i is the regression coefficient corresponding to source i .

BaP toxic equivalent concentration (BaP_{eq}) has been widely accepted and used to estimate the carcinogenic toxic risks of PAHs [24]. It was calculated and estimated based on the toxic equivalency factors (TEFs) that have been compiled by Tsai et al. (2004) [25]. The BaP_{eq} of each sample was calculated as follows:

$$BaP_{eq} = \sum_1^{16} TEQ_i = \sum_1^{16} C_i \times TEF_i$$

Where, BaP_{eq} is the toxic equivalent concentration of BaP in each sample (ng/g); TEQ_{*i*} is the equivalent concentration of the i -th individual PAH (ng/g); C_i is the concentration of the i -th individual PAH (ng/g), and TEF_{*i*} is the corresponding toxic equivalent factor of the i -th PAH relative to BaP (Table 4).

In addition, statistical analyses including correlation analysis, PCA-MRL, and descriptive statistics were implemented using IBM SPSS Statistics 21.0, and data graphical plots were conducted using Origin 8.0. The inverse distance weighted (IDW) map showing the spatial distribution of \sum_{16} PAHs was carried out with ArcGIS 10.4.

Results and Discussion

Concentrations and Pollution Levels of PAHs

Total concentrations of sixteen US EPA priority-listed PAHs (\sum_{16} PAHs) in main urban area soils of Changchun were in the range of 46.6-8870.8 ng/g, with a mean value of 1480.1 ng/g, which are nearly 10 times higher than those in the background area soils (Table 2). The mass concentration of \sum_{7car} PAH (Sum of 7 carcinogenic PAHs including BaA, Chr, BbF, BkF, BaP, IcdP, and DBahA) ranged from 21.6 to 6056.1 ng/g, with a mean value of 908.1 ng/g, accounting for 61.3% of \sum_{16} PAHs. According to the contamination classification system recommended by Maliszewska-Kordybach (1996) [26]: noncontaminated (\sum_{16} PAHs < 200 ng/g); weakly contaminated (200 ng/g < \sum_{16} PAHs < 600 ng/g); moderate contaminated (600 ng/g < \sum_{16} PAHs < 1000 ng/g)

Table 2. Concentrations (ng/g, dry weight) of individual PAHs in urban surface soil of Changchun city, NE China.

Compounds	Changchun city (52) ^k				Main urban area (48) ^k			Background area (4) ^k		
	Min	Max	Mean	SD ^b	Mean ₁	SD ₁ ^b	CV ₁ ^c	Mean ₂	SD ₂ ^b	CV ₂ ^c
Nap	n.d. ^a	44.9	7.7	7.8	7.6	8.2	108%	8.9	1.1	12%
Acy	n.d.	292.5	10.7	40.8	11.5	42.4	369%	0.9	0.4	39%
Ace	n.d.	83.2	7.6	14.4	8.1	14.9	184%	1.2	0.8	71%
Flu	0.4	194.3	12.4	28.1	13.2	29.1	221%	3.4	3.9	115%
Phe	n.d.	313.2	56.3	81.0	60.2	83.1	138%	8.7	4.9	56%
Ant	n.d.	312.6	55.7	77.1	59.6	79.1	133%	8.8	5.5	62%
Fla	n.d.	1024.4	147.2	239.6	158.1	246.3	156%	15.5	11.1	71%
Pyr	1.8	1046.1	157.4	247.7	169.2	254.4	150%	16.0	10.2	64%
BaA	3.0	874.9	111.4	176.6	119.7	181.4	152%	11.4	7.9	70%
Chr	n.d.	1556.1	143.3	251.1	153.5	258.8	169%	20.8	14.3	69%
BbF	n.d.	1479.1	200.6	330.4	215.9	339.6	157%	17.4	12.2	70%
BkF	n.d.	1394.4	209.0	334.6	225.1	343.5	153%	16.2	11.5	71%
BaP	1.9	542.8	94.6	141.7	101.8	145.2	143%	8.4	7.0	84%
IcdP	n.d.	478.8	73.4	108.2	79.0	110.9	140%	7.3	6.4	89%
DB(a,h)A	n.d.	74.4	12.5	18.2	13.2	18.8	142%	4.2	5.9	142%
BghiP	n.d.	489.9	78.7	115.5	84.5	118.4	140%	9.5	7.8	82%
2-ring PAHs ^d	1.9	606.9	38.3	85.7	40.3	89.0	221%	14.4	4.3	30%
3-ring PAHs ^e	8.9	1523.3	259.2	366.9	278.0	376.0	135%	33.0	21.2	64%
4-ring PAHs ^f	21.7	6188.7	821.7	1287.1	883.3	1321.	150%	81.7	55.5	68%
5-ring PAHs ^g	4.8	1094.6	180.5	264.7	193.9	271.3	140%	19.8	17.9	91%

Table 2. Continued.

6-ring PAHs ^h	n.d.	489.9	78.7	115.5	84.5	118.4	140%	9.5	7.8	82%
Σ_{16} PAHs ⁱ	46.6	8870.8	1378.4	2011.7	1480.1	2062	139%	158.3	98.0	62%
Σ_7 PAHs ^g	21.6	6056.1	844.8	1305.0	908.1	1339	148%	85.5	57.9	68%

^an.d.: not detected, lower than the limit of detection, calculated as half value of the method detection limit for mean;

^bSD: Standard Deviation; ^cCV: Coefficient of variation;

^dTwo rings: sum of Nap, Acy, Ace and Flu; ^eThree rings: sum of Phe, Ant and Fla; ^fFour rings: sum of Pyr, BaA, Chr, BbF, and BkF; ^g

Five rings: sum of BaP, IcdP, and DB(a,h)A; ^hSix rings: BghiP;

ⁱ Σ_{16} PAHs: sixteen US EPA priority-listed PAHs;

^g Σ_7 PAHs: sum of 7 carcinogenic PAHs including BaA, Chr, BbF, BkF, BaP, IcdP, and DBaA.

^k(): The digit in brackets is the number of samples.

and heavily contaminated (Σ_{16} PAHs > 1000 ng/g), 25% and 25% of Changchun main urban area sampling sites could be considered as noncontaminated and weakly contaminated, respectively. Whereas, 15% and 35% of the sampling sites would be considered as moderate contaminated and heavily contaminated and deserved further attention for their potential environmental and human health risks.

Levels of PAHs in urban surface soil from Changchun city were much higher than those in southern China and seaside cities, such as Hangzhou (611 ng/g), Shenzhen (360 ng/g), Nanjing (979.6 ng/g), Xian (1246 ng/g); Ulsan (960 ng/g) of Korea, Kumasi (442 ng/g) of Ghana; Viseu (169 ng/g) and Estarreja (98 ng/g) of Portugal (Table S1). As one of the inland

capital cities of the largest province of coal consumer in China, domestic heating in winter and coal combustion from coal-fired power plants as well as coke oven used in metallurgy, iron, and steel mills, machine manufacturing was assigned as a crucial source of soil PAHs in Changchun. Meanwhile, the lower annual average temperature in Changchun compared with the southern cities of China also contributed to a relatively high level of PAHs in the urban soil. Similar levels of PAHs were found in Dalian (1104 ng/g) and Zhengzhou (1567 ng/g) city of China as their similar development structure of transportation and industry with Changchun. On the other hand, the concentrations of Σ_{16} PAHs in Changchun urban soils were lower than those megacities, such as Beijing (1802.6 ng/g),

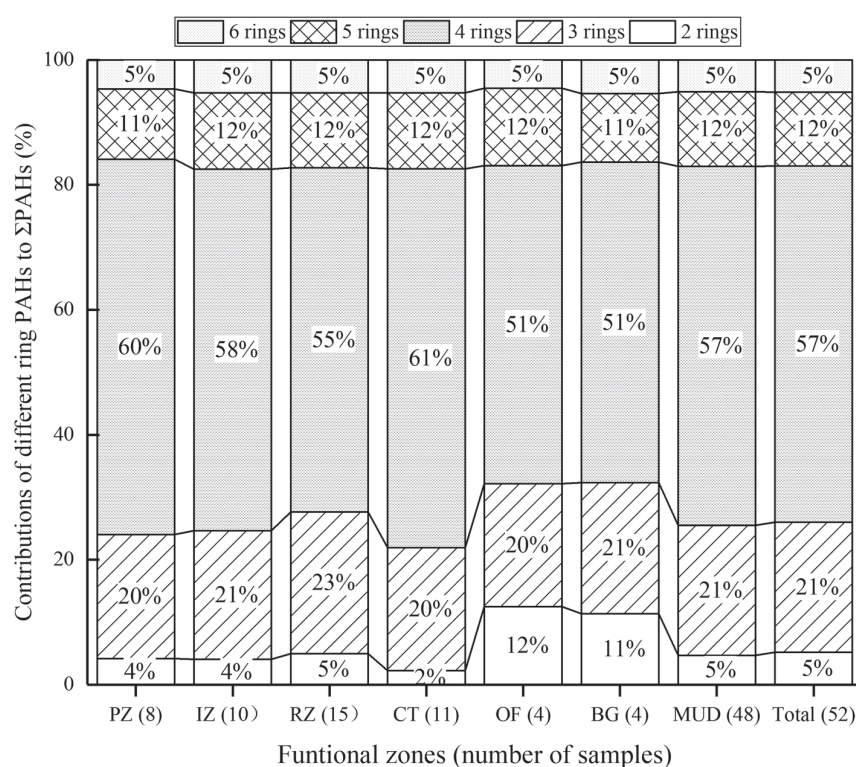


Fig. 2. Composition profiles plot of different ring PAHs in surface soils collected from the background (BG) area and different functional areas in main urban district (MUD), including park zone (PZ), industrial zone (IZ), residential zones (RZ), commercial traffic district (CT) and outskirts farmland (OF) of Changchun city, NE China.

Shanghai (1970 ng/g), Lanzhou (2360 ng/g), Urumqi (5018 ng/g) of China; London (18000 ng/g) and Glasgow (11930 ng/g) of UK; Erbil (2296 ng/g) of Iraq and some other megacities with a comparatively larger population and heavier industries developed (Table S1). According to these comparison results, the PAHs pollution levels in Changchun urban soil are moderate and still should be paid enough attention.

Composition and Distribution of PAHs

The composition of different ring PAHs in different functional areas soils was exhibited in Fig 2. The 4-ring PAHs accounted for the majority (51.3%-60.6%, mean 57.0%) of the total PAHs in all land used pattern soils of Changchun city, followed by the 3-ring PAHs (19.7%-22.7%, mean 20.9%) and 5-ring PAHs (11.0%-12.2%, mean 11.8%), which indicated that pyrogenic source may be the dominant PAH source in surface soil of Changchun city [6]. High molecular weight PAHs (HMW-PAHs, 4-6 rings) accounted for the majority (67.6%-78.1%, mean 74.0%) of the total PAHs in main urban area soils from CT, IZ, PZ, and RZ, similar to the previous studies conducted in many cities [6, 12, 27]. These probably resulted from the higher persistence and the tendency to accumulate close to the emission sources of HMW-PAHs in soils [28]. It should be noted that a relatively high proportion of 2-ring PAHs was found in BG soil samples (11.4%) and OF soil samples (12.6%) compared with the soil samples from other functional areas, which can demonstrate that low molecular weight PAHs (LMW-PAHs, 2-3 rings) are more easily transported to remote areas via the atmosphere as their high volatility and low octanol-

water partition coefficient [29]. For the individual compounds, BkF accounted for the highest proportion (15.2%) of Σ_{16} PAHs, then followed by BbF (14.6%), Pyr (11.4%), Fla (10.7%), Chr (10.4%), BaA (8.1%) and BaP (6.9%).

The coefficient of variation (CV) can be used to exhibit spatial variation levels of PAHs in soil and strong anthropogenic activities usually correspond with a high level of CV [10]. PAHs contaminations in main urban area soils of Changchun city exhibited a strong spatial variability ($CV > 100\%$) (Table 2), while weak variation ($CV < 100\%$) for individual PAHs (except Flu and DB(a,h)A) was shown in background area soils, which indicated PAHs in urban surface soils of Changchun were strongly affected by anthropogenic activities. Concentrations of PAHs in urban surface soils varied greatly among different land used areas in Changchun city (Fig 3). The mean concentrations of Σ_{16} PAHs and Σ_7 PAHs all decreased in an order of $CT > IZ > RZ > PZ > OF > BG$. Similar research also exhibited that the concentrations of soil PAHs in the industrial areas, commercial districts, and heavy traffic areas were higher [30]. These are mainly due to the large motor vehicles with heavy vehicle exhaust, dense population, and public catering services in commercial traffic districts, leading to an increase in PAHs emissions [31]. Meanwhile, the "running, leaking, dripping and leaking" of raw materials, power fuel, and lubricating oil in the process of industrial production also results in the high PAHs concentration in the urban soil of industrial areas.

The spatially interpolated distribution of Σ_{16} PAHs contamination in the main urban area soil of Changchun city was exhibited using the IDW interpolation in Fig.4.

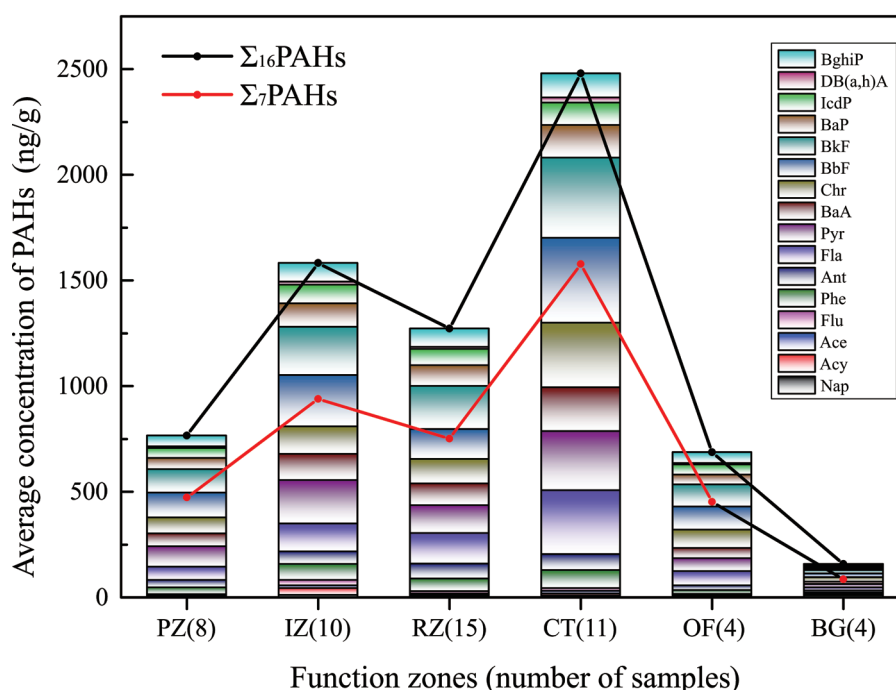


Fig. 3. Concentrations of PAHs in urban surface soils among different land used areas of Changchun city, NE China.

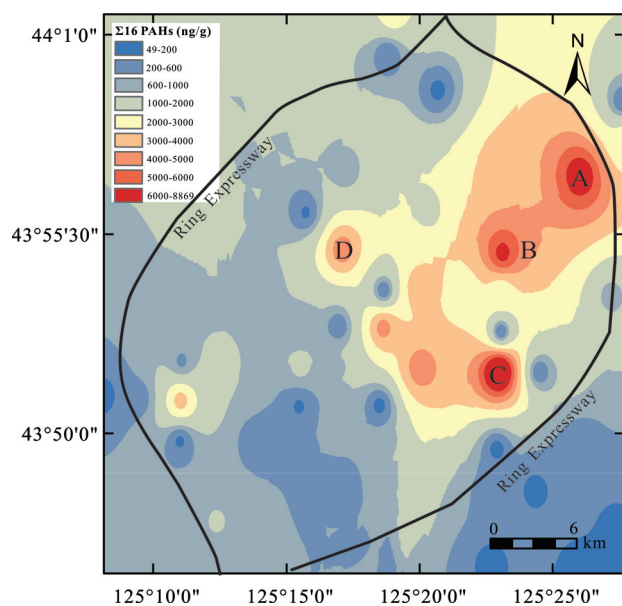


Fig. 4. Concentrations of PAHs in urban surface soils among different land used areas of Changchun city, NE China.

A relatively high concentration of Σ_{16} PAHs in soil was recorded in the northeast region and the central historic district of Changchun city, similar to the results from the previous study on the distribution of PAHs in vegetable soils in Changchun suburb [32]. The northern and eastern portions of the city have been mainly dominated by the coal-fired power plants, metallurgy plants, iron, and steel mills and large numbers of cement plants [13] and the central historic district of the city have experienced substantial development with the higher residential and commercial activities and traffic levels over the past decades. Liu et al. (2010) found that PAHs concentrations in the soils from old urban areas were high due to the process of long-term artificial accumulation [33]. Four sections with hotspots showed the highest concentrations of PAHs in Changchun urban soils which approach the major emission sources of PAHs geographically. Section A and D are located in the IZ surrounding the machinery plants, biopharmaceutical factories, and the coal-fired power plants; Sections B and C are located in the CT which is around complex vehicle traffic and commercial activities, such as lots of building material markets and catering services. It should be noted that the prevalence of southwest wind in Changchun throughout the year may also result in the migration of atmosphere PAHs with the wind force action and deposited into the soils in the northeast region.

Correlation Analysis between PAHs and Soil Basic Properties

PAHs residues in soil often bind with soil organic matter as their hydrophobicity and lipophilicity. Once deposited into the soil, most PAHs will be absorbed by soil organic matter and the strong sorption will

inhibit their degradation and leaching [21]. Therefore, the soil organic matter, especially the soil total organic carbon (TOC) is considered to be a very important factor related to soil PAHs pollution. Previous research had shown a high positive correlation between soil TOC and PAHs residues [34]. To further identify the impacts of TOC on soil PAHs pollution in this study, Pearson's correlation analysis was applied to evaluate the relationship among the individual PAHs and soil TOC (Table S2, Supplementary material). Soil TOC varied from 0.56% to 4.79%, with a mean of 1.63%. Pearson's correlation coefficients between soil properties (pH and TOC) and PAHs showed that there was a significantly positive correlation between soil TOC and Σ_{16} PAHs ($r = 0.408$, $p < 0.01$), Σ_7 PAHs ($r = 0.427$, $p < 0.01$), Σ_{LMW} PAHs ($r = 0.301$, $p < 0.05$) and Σ_{HMW} PAHs ($r = 0.423$, $p < 0.01$), but poorly related with soil pH in urban soil from Changchun. Individual PAHs (except Acy, Ace, Flu, Ant, and Chr) were also positively correlated with TOC ($0.275 \leq r \leq 0.539$, $p < 0.05$). The results of the above correlation analysis further certificate that TOC is a key factor affecting the fate of PAHs in soil, especially for high molecular weight PAHs in soil.

Source Identifications and Contributions

Identifying the potential sources of soil PAHs is essential for assessing the environmental risk and controlling the environmental pollution of PAHs [21]. PAHs emitted from different sources would exhibit different molecular compositions [35]. Generally, LMW-PAHs (2-3 rings) mainly result from petroleum pollution, and HMW-PAHs (4-6 rings) are always related to the incomplete combustion of coal, wood, and petroleum products as well as vehicle emissions [36]. Therefore, the ratio of LMW-PAHs to HMW-PAHs can be used to identify pyrogenic (< 1) and petrogenic (> 1) sources of PAHs in soils [37]. In this study, the ratio of LMW-PAHs to HMW-PAHs was far below 1, which can preliminarily conjecture that pyrogenic source related to combustion was the dominant source for PAHs in the urban surface soils of Changchun.

PAHs molecular diagnostic ratios can effectively provide specific source identification information as the pairs of PAHs with the same molar mass and similar physicochemical properties are often emitted as a group under different combustion conditions [38-39]. According to the previous reports, a ratio of $\text{Ant}/(\text{Ant}+\text{Phe}) < 0.1$ indicates the petrogenic sources (crude oil or raw coal) and that > 0.1 indicates the pyrogenic sources [40]. Meanwhile, $\text{BaA}/(\text{BaA}+\text{Chr}) < 0.2$ demonstrates petrogenic source; 0.2-0.35 indicates mixed pyrogenic sourcing including incomplete combustion of coal and biomass (such as wood or grass) and > 0.35 suggests petroleum combustion [36]. In addition, both ratios of $\text{IcdP}/(\text{IcdP}+\text{BghiP}) < 0.20$ and $\text{Fla}/(\text{Fla}+\text{Pyr}) < 0.4$ likely imply the petrogenic sources, whereas 0.2-0.5 and 0.4-0.5 of these two ratios indicate

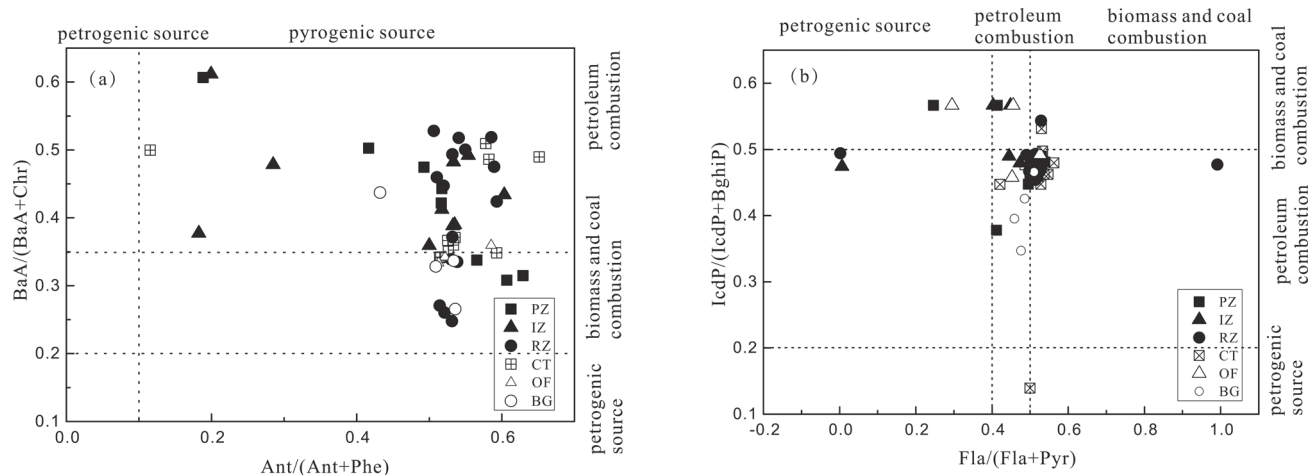


Fig. 5. Diagnostic ratios for source analysis of PAHs in the surface soil of Changchun city, NE China

petroleum combustion sources, respectively, and >0.5 of these two ratios both suggest the incomplete combustion of coal and biomass. In this study, the above four PAHs molecular diagnostic ratios of all 52 sampling sites from Changchun city were calculated and plotted in Fig 5. The ratios of $\text{Ant}/(\text{Ant}+\text{Phe})$ and $\text{BaA}/(\text{BaA}+\text{Chr})$ were ranged from 0.10 to 0.65 and from 0.25 to 0.61 respectively, indicating that pyrogenic sources were dominant for PAHs in surface soils. 65% of sampling sites including nearly all industrial zone and commercial traffic area and some residential and park zone samples exhibited the petroleum combustion sources, the remaining 35% sampling sites contained background samples, some park, and residential samples showed the signature of biomass and coal combustion sources. On the other hand, the ratios of $\text{Fla}/(\text{Fla}+\text{Pyr})$ and $\text{IcdP}/(\text{IcdP}+\text{BghiP})$ ranged from 0 to 0.48 and 0.14 to 0.57, respectively, suggesting that PAHs in urban soil from Changchun were primarily derived from petroleum combustion sources, biomass and coal combustion sources and the mixed sources of petroleum, biomass and coal combustion. Significantly, the petrogenic source may be also a contributor to the soil PAHs pollution in the main urban area of Changchun city.

Multivariate linear regression (MLR) analysis in combination with PCA allows quantitatively apportioning the relative contributions of various identified sources to the total sum of pollutants. In this study, PCA subjected to the normal-varimax rotation of Kaiser standardization was performed on 16 PAHs of 52 samples. Before the interpretation of results, Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity tests were performed to examine the validity of PCA. KMO and Bartlett's test results were 0.76 and 2257.96, respectively ($df = 120$, $p < 0.01$), indicating that PCA may be a valuable tool in the discrimination of distinct PAHs sources [24]. Four principal components of PC1, PC2, PC3, and PC4 with the rotated eigenvalue >1 were extracted, which have cumulatively explained 95.68%

of the total variance. For each factor, the PAHs with relatively high loadings are marked in bold in Table 3. PC1 accounts for 47.12% of the total variance and is highly loaded by BghiP, IcdP, BaP, Ant, BkF, BaA, Chr, Pyr, BbF, DBahA, Phe. Among these PAHs, BghiP, BaP, IcdP, Chr, and DBahA have been identified as typical tracers of vehicular PAHs [41]. BaA, BaP, and BghiP are typical markers of petroleum combustion [42]. BkF is usually derived from diesel-powered vehicles and BghiP is predominated from the gasoline engine emission [34]. Whereas, Phe, Ant, Pyr, BaA, BbF, and BkF are markers for fuel and coal combustion [43-44]. Changchun has one of the largest transportation hubs and is an industrial manufacturing center dominated by automobiles industries, electricity-thermal production, and coal is one of the most important industrial energy. In addition, Changchun is the cradle of the automobile industry and rail transit manufacturing industry and the car parc of Changchun has reached 2.10 million in 2019 [15]. Thus, PC1 was identified as a mixed source contribution from fossil fuel combustion emission and the traffic emission. PC2 explained 20.76% of the total variance and was highly loaded by Acy, Ace, and Flu, which can be interpreted as the coking and biomass burning source. This is because Acy and Ace are the dominant PAH compounds released during wood and biomass burning, and Flu is a typical marker for coke oven source [45]. In 2019, the consumption amount of coke and other coke products for industrial production in Changchun has reached 9100 tons. Biomass waste as fuel is mainly used for thermal power and heating and the consumption amount achieved 132722 tons of SCE in 2019 [15]. PC3 explained 18.89% of the total variance with a heavier loading of Fla and the relatively high loadings of BbF and Pyr. Pyr and Fla are typical representative markers for coal combustion [46], therefore, PC3 was deduced to represent the coal combustion source. PC4 with the highest loading of Nap contributed 8.91% of the total variance. Nap is a kind of volatile PAH associated with the evaporation of

Table 3. Varimax normalized matrix of 16 PAHs in the surface soils from Changchun city.

PAH compounds	Principal components			
	PC 1	PC 2	PC 3	PC 4
Nap	0.176	0.473	0.147	0.834
Acy	0.071	0.974	0.014	0.133
Ace	0.315	0.737	0.456	0.322
Flu	0.223	0.938	0.213	0.137
Phe	0.697	0.495	0.393	0.267
Ant	0.872	0.141	0.323	-0.158
Fla	0.381	0.384	0.782	0.07
Pyr	0.689	0.269	0.557	0.252
BaA	0.812	0.158	0.515	0.158
Chr	0.727	0.029	0.600	0.002
BbF	0.660	0.152	0.646	0.31
BkF	0.856	0.168	0.383	0.225
BaP	0.885	0.24	0.275	0.261
IcdP	0.948	0.218	0.146	0.161
DBahA	0.716	0.172	0.514	0.39
BghiP	0.969	0.17	0.125	0.091
Eigenvalue	7.539	3.321	3.023	1.426
% of Variance	47.12%	20.76%	18.89%	8.91%
Cumulative %	47.12%	67.88%	86.77%	95.68%

Note: The bold data (>0.500) represents a higher weightage of PAH.

petroleum products during fuel handing and refueling operations.

In order to further analyze the relative contributions of various sources quantitatively, the standardized PCA factor scores and the standardized Σ_{16} PAHs concentrations were used as the independent and dependent variables, respectively, for the multivariate linear regression. The regression was run using a forward stepwise method under the significance level of 0.05 using IBM SPSS Statistics 21.0. The obtained regression equation was expressed as follows:

$$Z_{PAHs} = 0.787f_1 + 0.255f_2 + 0.526f_3 + 0.192f_4$$

$$(R^2 = 0.998, p < 0.001)$$

Where, Z_{PAHs} were the standardized concentration of Σ_{16} PAHs; f_{1-4} were the standardized factor scores of PC_{1-4} ; R^2 was the obtained decision coefficients; p was the conditional probability of model significance test.

The obtained decision coefficient of the regression model was 0.998, which indicated a good fit goodness of the regression equation. Source contributions from the four PCs to the total PAH burden in Changchun urban surface soil could be calculated from the standardized factor regression coefficients according to the calculation method described in Data analyses method, and the results are presented in Table 4. PC 1 (mixed sources of fossil fuel combustion emission and vehicular emission), PC 2 (coking and biomass burning), and PC 3 (coal combustion) contributed over 44.72%, 14.19% and 29.89% of the total PAH source to the city surface soil, respectively. The remaining 10.91% source of PC 4 may come from evaporative and leakage of petroleum products.

For further verifying the reliability of the PCA-MLR source apportionment method and exploring the spatial distribution of PAHs pollution sources in the main urban area of Changchun city, the spatially interpolated distribution for the four principal components factor scores was conducted using the IDW interpolation in Fig. 6. As the first major source of soil PAHs contamination, the mixed sources (PC1) containing fossil fuel combustion emission and vehicular emission exhibited the most similar distribution characteristics with the PAHs contaminations in the central historic district and northeast portions of Changchun city, and the mixed sources (PC1) corresponding to the PAHs contamination hotspot of section A in Fig. 5. Similarly, the coal combustion source (PC3) is the second-largest soil PAHs contamination source mainly corresponding to the hotspot of section C surrounding the thermal power plants in the southeast region. Coking and biomass burning sources (PC2) and petroleum sources (PC4) can be considered as the main sources of the hotspots of section D and section B, respectively. The spatial distribution of the principal components factor scores can well correspond to the area with high PAHs contaminations, which also indicated the effectiveness of PCA-MLR for source apportionment in urban soil PAHs pollution.

Table 4. Multiple regression statistics using standardized factor scores of four principal components for PAHs.

PCs	Representative source	Standardized regression coefficients	Source contribution	Decision coefficients
PC1	Mixed sources of fossil fuel combustion emission and vehicular emission	0.787	44.72%	0.998
PC2	Coking and biomass burning source	0.255	14.19%	
PC3	Coal combustion source	0.526	29.89%	
PC4	Petroleum source	0.192	10.91%	

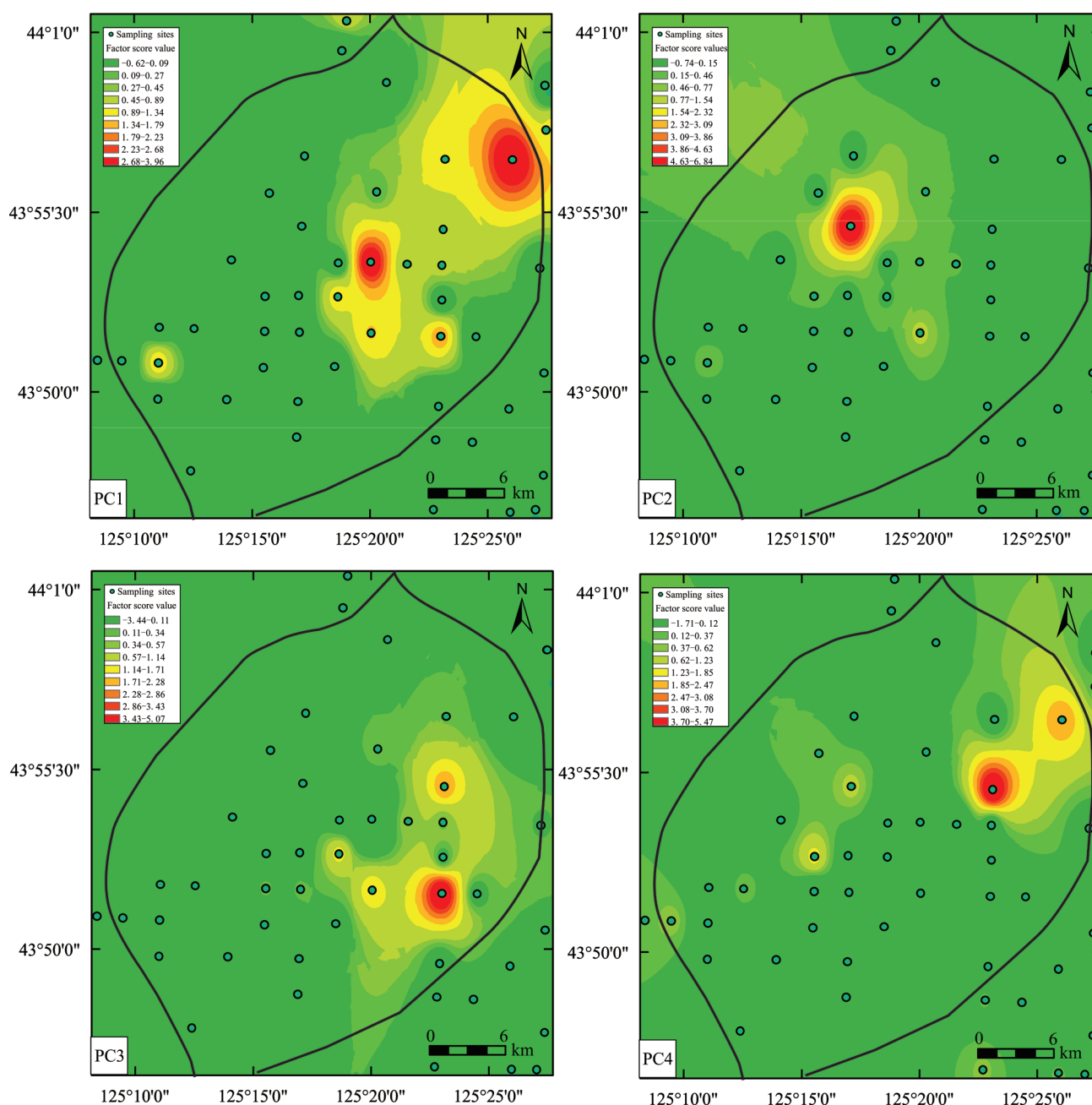


Fig. 6. Spatial distribution of the four principal components factor scores in main urban district soils of Changchun city, NE China.

Toxicity Risk Assessment of PAHs

The potential toxicity of PAHs depends on the natural toxicity of PAHs and their concentration [22], the total BaP_{eq} of 16 PAHs in soil samples ranged from 2.42 to 980.25 ng/g, and the mean concentration in main urban area soils and background soils was 181.79 and 17.18 ng/g, respectively. The total BaP_{eq} of 7 carcinogenic PAHs was approximately that of 16 PAHs, and accounted for 98.97% contributions of the total BaP_{eq} of 16 PAHs (Table 5), suggesting that the 7 carcinogenic PAHs were the primary contributors to the total carcinogenic potency of the PAHs in the soil samples, and among which BaP was the largest contributor with an average contribution rate of 55.94%,

followed by BkF (12.36%), BbF (11.84%), DB(a,h)A (7.08%) and BaA (6.59%). A strong correlation between BaP_{eq} values and the concentrations of $\Sigma_{16}PAHs$ in Changchun city soils ($r^2 > 0.96$) was found (Fig. 7). The comparison of the toxic equivalent concentrations of PAHs in different land used areas (Fig. 8) exhibited that the concentrations of BaP_{eq} in commercial traffic district soils were highest, followed by industrial zone soils and those in background soils were lowest, which is corresponded to the comparison result of the PAHs concentrations in different land used areas.

The total BaP_{eq} concentration of 16 PAHs in Changchun urban soil was lower than that in urban soil of Shanghai, China (236 ng/g) [27], Lisbon, Portugal (229 ng/g) [12], Sydney, Australia (440 ng/g) [22]

Table 5. Total toxic equivalent concentrations of PAHs (ng/g) in surface soil of Changchun city, NE China.

Compounds	TEF ^a	Carcinogenic group ^b	BaP _{eq} (ng/g)			Toxicity contribution rate
			Concentration range	Mean ₁ ^c	Mean ₂ ^d	
Nap	0.001	2B	0-0.05	0.01	0.01	0.00%
Acy	0.001	3	0-0.29	0.01	0.00	0.01%
Ace	0.001	3	0-0.08	0.01	0.00	0.00%
Flu	0.001	3	0-0.19	0.01	0.00	0.01%
Phe	0.001	3	0.003-0.31	0.06	0.01	0.03%
Ant	0.01	3	0-3.13	0.60	0.09	0.33%
Fla	0.001	3	0-1.02	0.16	0.02	0.09%
Pyr	0.001	3	0-1.05	0.17	0.02	0.09%
BaA	0.01	2B	0.30-87.49	11.97	1.14	6.59%
Chr	0.1	2B	0.05-15.56	1.53	0.21	0.85%
BbF	0.1	2B	0-147.91	21.54	1.74	11.84%
BkF	0.1	2B	0-139.44	22.51	1.62	12.36%
BaP	1	1	1.90-542.80	101.79	8.35	55.94%
IcdP	0.1	2B	0-47.88	7.87	0.64	4.32%
DBahA	1	2A	0-74.4	12.71	3.25	7.08%
BghiP	0.01	3	0-4.90	0.84	0.09	0.46%
$\Sigma_{16}\text{Bap}_{\text{eq}}$ ^e	-	-	2.42-980.25	181.79	17.18	100.00%
$\Sigma_{7\text{car}}\text{Bap}_{\text{eq}}$ ^f	-	-	2.29-971.05	179.92	16.95	98.97%

^a TEF: Toxic equivalency factor;

^b 1: intensely carcinogenic to humans; 2A: probably carcinogenic to humans; 2B: possibly carcinogenic to humans; 3: not classifiable as to its carcinogenicity to humans; D: inadequate information to assess carcinogenic potential

^c mean₁: Average concentration in build-up area soils; ^d mean₂: Average concentration in background soils;

^e $\Sigma_{16}\text{Bap}_{\text{eq}}$: Sum of the 16 US EPA identified PAHs as priority-listed controlled environmental pollutants;

^f $\Sigma_{7\text{car}}\text{Bap}_{\text{eq}}$: Sum of 7 carcinogenic PAHs including BaA, Chr, BbF, BkF, BaP, IcdP, and DBahA.

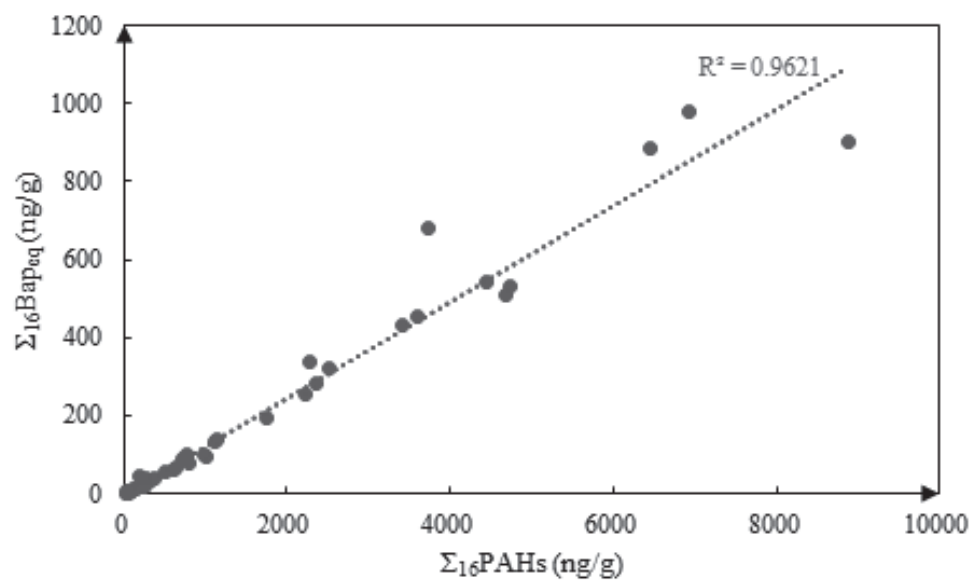


Fig. 7. Correlation between toxic equivalent concentration (Bap_{eq}) and total of 16 PAHs in surface soils of Changchun city, NE China (n = 52).

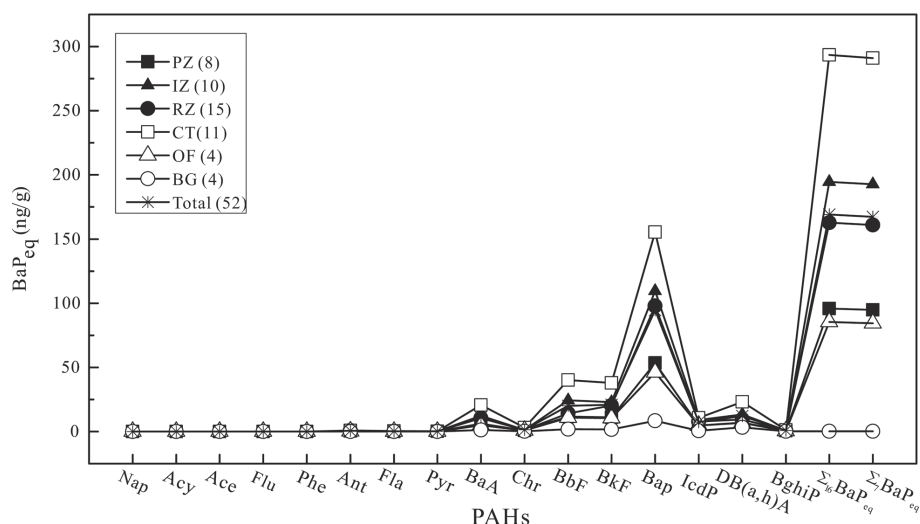


Fig. 8. Comparison of BaP_{eq} for 16 PAHs in urban surface soils among different land used areas of Changchun city, NE China (The digit in brackets represents the number of sampling sites).

and that found in Orlando and Tampa city, Florida, USA (4-3742 (452) ng/g and n.d.-9706(802) ng/g) [6]; while similar to the level found in Beijing, China (180.7 ng/g) [33], Nanjing, China (193.9 ng/g) [47], but higher than that in Lanzhou, China (5.93-205(136) ng/g) [34], Erbil, Iraq (3.26-362.84 (174.32) ng/g) [48], Kumasi, Ghana (1.24-188.2 ng/g) [11]. Compared with the average BaP_{eq} concentrations of the Σ_{16} PAHs in urban soils in China (191.55 ng/g) [49], 30% of the soil samples in Changchun city had BaP_{eq} concentrations that exceeded the average value of urban soils in China. Canadian Soil Quality Guidelines provide a BaP_{eq} reference guideline of 600 ng/g based on the PAHs' carcinogenic effects for the protection of the environment and human health [50]. Among 48 urban soil samples, 4 samples including 1 RZ sample in the central historic district, 2 CT samples, and 1 IZ sample nearby building materials markets in the east of the city had concentrations exceeding the safety value. The above results suggest that the potential toxic risk for exposure to soil PAHs in Changchun city was moderate, while the carcinogenic potency of PAHs still poses serious potential health risks in some sampling sites.

Conclusions

Significant differences (at least one order of magnitude) were observed in Σ_{16} PAH concentrations between main urban area soils and background area soils of Changchun city, which indicated the intensive anthropogenic activities were a key factor resulting in the continuous and increased emissions of potentially toxic PAHs in the urban soil environment. 4 ring PAHs accounted for the majority (51.3%-60.6%) of the total PAHs in urban soils. For the individual PAHs, BkF, BbF, Pyr, Fla, Chr, BaA, and BaP were the dominant

constituents. The PAHs in the main urban area soils of Changchun city primarily derived from pyrogenic sources, especially coal, fossil fuel combustion, and vehicle emissions. Soil TOC was an important factor affecting the accumulation of PAHs according to the correlation analysis. Distribution maps demonstrated that higher concentrations of PAHs mainly concentrated in the northeast region with business districts and heavy traffic loads and the central historic district soils of Changchun city. The total BaP_{eq} of 16 PAHs ranged from 2.42 to 980.25 ng/g, with a mean value of 181.79 ng/g. PAHs contaminations and their toxicity levels detected in main urban area soils of Changchun city are relatively moderate compared with other global cities, while 35% of the sampling sites would be considered contaminated with heavily PAHs (>1000 ng/g) based on the Maliszewska-Kordybach classification. Overall, this information demonstrates that some forms of considerable attention and remediation programs may be required for these heavily contaminated sampling sites to reduce their potential adverse health effect for residents exposed to harmful PAH contaminants.

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Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Material

Table S1. Comparison of PAHs concentration with related studies in domestic and foreign cities around the world (ng/g).

Country	City	No. of PAHs	PAHs (ng/g)		Reference
			Range	Mean	
UK	London	16	4000-66000	18000	[1]
	Glasgow	15	1487-51882	11930	[2]
Iraq	Erbil	16	24.3-6129.1	2296	[3]
India	Dhanbad	13	1019-10856	3488	[4]
Indonesia	Kalimantan	16	4690-22670	11720	[5]
Russia	Moscow	17	4288-8655	5385	[6]
Portugal	Viseu	16	6.0-790	169	[7]
	Estarreja	16	27-2016	98	[7]
Korea	Ulsan	16	65-12000	960	[8]
Ghana	Kumasi	22	14.8-2084	442	[9]
China	Hangzhou	16	181-1980	611	[10]
	Shenzhen	16	2-6745	360	[11]
	Nanjing	16	41.2-7016.7	980	[12]
	Xian	16	149.9-5770	1246	[13]
	Dalian	14	219-18727	1104	[14]
	Zhengzhou	16	49.9-11565	1567	[15]
	Urumqi	16	331-15799	5018	[16]
	Lanzhou	16	82.2-10900	2360	[17]
	Shanghai	16	83-7220	1970	[18]
	Beijing	16	8.5-13126.6	1803	[19]
	Changchun	16	46.6-8870.8	1480	In this study

Table S2. Pearson correlation coefficient matrix for individual PAHs and soil properties in surface soil samples of Changchun city (n = 52, p<0.05).

	Nap	Acy	Acc	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	IcdP	DB(a,h) A	BghiP	Σ_{16} PAHs	Σ_7 PAHs	Σ_{LMW} PAHs	Σ_{HIMW} PAHs	TOC	pH
Nap	1																					
Acy	0.574**	1																				
Acc	0.725**	0.780**	1																			
Flu	0.630**	0.951**	0.899**	1																		
Phe	0.644**	0.547**	0.850**	0.736**	1																	
Ant	0.162	0.147	0.475**	0.377**	0.786**	1																
Fluo	0.446**	0.405**	0.744**	0.614**	0.805**	0.640**	1															
Pyr	0.522**	0.553*	0.753**	0.559**	0.895**	0.812**	0.790**	1														
BaA	0.426**	0.249	0.666**	0.465**	0.880**	0.846**	0.764**	0.906**	1													
Chr	0.236	0.120	0.535**	0.323*	0.725**	0.771**	0.714**	0.793**	0.947**	1												
BbF	0.524**	0.259	0.721**	0.471**	0.854**	0.752**	0.806**	0.965**	0.939**	0.869**	1											
BkF	0.475**	0.268	0.641**	0.461**	0.891**	0.814**	0.712**	0.859**	0.979**	0.899**	0.893**	1										
BaP	0.526**	0.332*	0.657**	0.512**	0.925**	0.839**	0.690**	0.876**	0.938**	0.806**	0.866**	0.975**	1									
IcdP	0.421**	0.306*	0.574**	0.466**	0.864**	0.874**	0.580**	0.839**	0.898**	0.773**	0.806**	0.936**	0.975**	1								
DB(a,h)A	0.588**	0.286*	0.713**	0.486**	0.878**	0.758**	0.756**	0.952**	0.919**	0.814**	0.970**	0.902**	0.911**	0.860**	1							
BghiP	0.344*	0.255	0.511**	0.413**	0.822**	0.884**	0.549**	0.801**	0.891**	0.789**	0.774**	0.927**	0.958**	0.994**	0.828**	1						
Σ_{16} PAHs	0.496**	0.342*	0.735**	0.552**	0.929**	0.852**	0.822**	0.948**	0.985**	0.904**	0.958**	0.967**	0.953**	0.910**	0.950**	0.891**	1					
Σ_7 PAHs	0.458**	0.256	0.669**	0.463**	0.888**	0.836**	0.761**	0.917**	0.995**	0.934**	0.951**	0.984**	0.953**	0.915**	0.942**	0.904**	0.990**	1				
Σ_{LMW} PAHs	0.546**	0.558**	0.854**	0.759**	0.934**	0.755**	0.952**	0.874**	0.842**	0.740**	0.848**	0.820**	0.742**	0.742**	0.831**	0.706**	0.904**	0.841**	1			
Σ_{HIMW} PAHs	0.467**	0.275*	0.682**	0.482**	0.900**	0.850**	0.763**	0.938**	0.992**	0.919**	0.957**	0.978**	0.958**	0.925**	0.952**	0.911**	0.994**	0.998**	0.851**	1		
TOC	0.539**	0.075	0.255	0.127	0.422**	0.162	0.275*	0.377**	0.383**	0.249	0.439**	0.470**	0.494**	0.417**	0.486**	0.381**	0.408**	0.427**	0.301*	0.423**	1	
pH	0.145	0.142	0.203	0.18	0.129	0.06	0.238	0.119	0.062	0.078	0.125	0.029	0.016	-0.03	0.073	-0.033	0.097	0.063	0.206	0.066	-0.015	1

Σ_{LMW} PAHs: low molecular weight PAHs (2–3-ring PAHs); Σ_{HIMW} PAHs: high molecular weight PAHs (4–6-ring PAHs); TOC: total organic carbon
 **Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed)

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