Distribution characteristics and health risk assessment of PAEs in urban soils of Changji City, Xinjiang, China

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Abstract

Recent studies have indicated that PAEs (phthalic acid esters) are significant environmental pollutants with carcinogenic, teratogenic, and mutagenic effects. Urban soils can act as both a source and sink for city contaminants. This paper takes Changji, Xinjiang in Northwest China as the study area and explores the pollution characteristics and health risks of PAEs in the urban soils of arid areas. The analysis results indicate average concentration occurrences of 13.77 mg/kg and ranges from 0.29 to 119.72 mg/kg in the study area. Dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) were the predominant PAEs in the urban soil of Changji. The highest average PAEs concentration appeared in winter, followed by autumn and spring and the lowest in summer; the seasonal variation was significant. The climate characteristics of arid regions and seasonal variations of source emissions were the primary influencing factors. The theoretical values of the non-carcinogenic and carcinogenic risk of PAEs were relatively small, all within the acceptable range. Values of non-carcinogenic risk and carcinogenic risk to children were much higher than the risks to adults. Children were the vulnerable groups most at risk for harmful pollutants, and the safety of their living environment should be the focus of more attention.

Keywords: urban soil; PAEs; pollution characteristics; health risk

Introduction

Phthalic acid esters (PAEs) are widely used in industrial production. PAEs are often used as plasticizers in the production of plastic to increase product plasticity and improve product strength. Additionally, PAEs compounds are used in the production of rubber, pesticide carriers, coatings, insect repellents, cosmetics, lubricants, defoamers, etc. PAEs and plastics bond via hydrogen bonding or van der Waals force, so the stability of the resulting product is relatively poor. In the production, use and final disposal of plastic products, PAEs can easily migrate from the plastic to the environment (Al-Natsheh et al. 2015, Kong et al. 2015). With the extensive application of plastic products, PAEs are a significant emission and widespread in the air, water, soil, sediment, biological and other environmental media (Kranich et al. 2013, Kong et al. 2015, Paluselli et al.,2018). The study also found that coal combustion can also release PAEs (Wang et al. 2015a). Recent studies have indicated that PAEs are significant environmental pollutants with carcinogenic, teratogenic, and mutagenic effects. PAEs are uniquely toxic to reproductive systems in humans and other animals. They are universally capable of interfering with normal endocrine activity, which leads to an abnormal reproductive system and behaviour. Six of the most widely used PAEs are classified as priority pollutants by the US Environmental Protection Agency (USEPA), and of these, three types have also been listed as environmental priority control pollutants in China (USEPA 2013, Yang 2013). The environmental behaviour of PAEs has become a hot topic in related fields.

PAEs are hydrophobic organic pollutants that are easily distributed to soil organic matter. PAEs continuously migrate in the environment through wet and dry deposition, sewage discharge, accumulation of waste plastic products, etc. and finally accumulate in the soil. It has been shown that PAEs are one of the most abundant in soil organic contaminants (Niu et al. 2014). Urban soils are a central part of the urban environment and can act as both a source and sink for urban environment pollutants. In the current accelerating process of urbanization, urban soil pollutants are not only a complex source of pollutants, but the pathways of human toxicity have become more complex. The primary routes for urban soil contaminants to enter the body include hand-mouth contact intake, respiratory inhalation and skin absorption (Li and Liu 2007). The potential ecological risks of PAEs pollution in urban soils should not be neglected, given their concealed and persistent risk in intensive urban human activities (Xia et al. 2011).

Human activities and natural conditions severely affect the fates of environmental pollutants. Arid regions in Xinjiang have a special natural environment, i.e., rare precipitation, significant evaporation, more wind and sand weather, large temperature differences between day and night. The urban soils in arid regions also have the characteristics of strong alkalinity and rich phosphorus content (Li and Liu 2007). Most studies on soil PAEs focus on cropland systems, and less on urban soils (Zeng et al. 2009, Niu et al. 2014, Li et al. 2015, Sun et al. 2016, Wang et al. 2015b). At present, the environmental behavior of urban soil PAEs and its influencing mechanism are still unclear, and relevant research on arid areas have not been reported. Therefore, the characteristics of PAEs pollution and its health risk assessment in urban soils in Xinjiang arid region have certain theoretical value and regional characteristics.

Materials and Methods

1.1 Overview of research area

Changji (86°24′–87°37.0′ E, 43°06′–45°20′ N) is in the northwestern part of China, in the centre of the Eurasian continent and is a relatively new city. As the satellite city of Urumqi (capital of Xin jiang, China), it has a typical continental arid climate. Recently, the Chinese government's western development policy has promoted the rapid urbanization. In this paper, Changji City was taken as the study area. Dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP) were selected as the target pollutants, which were listed as priority pollutants by the USEPA and have relatively high detectable contents in environmental medium. This study aimed to investigate the PAEs pollution characteristics and health risks in urban soils.

1.2 Sample Collection

Sampling was based on urban functional areas and the microenvironment in Changji City. According to land uses, the city was divided into heavy traffic, industrial and residential/educational areas. Five sampling points were selected and arranged in each of the above three functional areas, and a total of 15 sampling points were set. The 0 ~ 2 cm part of the surface layer of the soil was collected. Each point adopted the multi-point mixing method. The specific collection situation of the multi-point mixing method was as follows: Set a center point for each sampling point, and 6-7 point samples were collected around the center point, and then equal and uniformly mix to represent a sample. The soil samples were collected month by month and 15 samples per month were collected. There are 180 samples which were collected for this research. The sampling period was from March 2016 to February 2017. In the sampling process, sampling was conducted to avoid any plastic products and simultaneous recordied meteorological conditions, traffic, flow and other sampling micro-environment.

1.3 Sample analysis

1.3.1 Main Instruments and Reagents

The main instruments were as follows: a SHIMADZU GC-2010 gas chromatograph (GC), a RE-52AA rotary evaporator and HY-CXJ-type high-power ultrasonic cleaner. Four pure standard samples of DMP, DEP, DBP, DEHP and surrogate standards, consisting of 500 $g \cdot ml^{-1}$ each of DBP and DEHP

(Aldrich Chemicals, Gillingham, UK) were used. Benzyl benzoate, which was used as the internal standard, was acquired as a solid of 99% purity (Aldrich Chemicals, Gillingham, UK). Anhydrous sodium sulfate was baked at 420 °C for 12 h and stored in sealed glass jars. The filter paper was extracted with methanol and n-hexane with the Soxhlet extractor for 72 h before use. Water was filtered by Milli-Q and double distilled. All organic solvents used were of analytical grade and redistilled using a glass system. Laboratory glassware was soaked overnight in $K_2Cr_2O_7/H_2SO_4$ solution, washed with tap water and redistilled water, baked at 300 °C for 12 h, and then rinsed with acetone and n-hexane.

1.3.2. Experimental Methods

The samples were dried in a dry, ventilated place and passed through a 40-mesh screen to remove impurities and large particles and then passed through a 200-mesh sieve after drying to be extracted. Each soil sample was weighed to 2 g using an analytical balance. The samples were wrapped in qualitative filter paper and placed in a Soxhlet extractor. The samples were extracted with hexane and acetone (1: 1) for 8 h with the temperature controlled at 74.5 °C. The resulting solution was extracted with Floris cartridges to remove macromolecular organics and impurities. Moreover, the filtered solution was dried with nitrogen. Normal hexane was added to give a 1 mL test solution.

The PAEs were determined using Hydrogen Flame Gas Chromatography. The working conditions of the GC were as follows: the temperature of the vaporization chamber was 260 °C, the detector was a hydrogen flame ionization detector (FID) at a temperature of 260 °C. The nitrogen carrier gas, hydrogen gas, and air (all ≥99.999%) were kept at constant speeds of 30 mL/min, 40 mL/min, and 400 mL/min, respectively. The extracted samples were injected into the GC in split mode with a split ratio of 9:1. The injection volume was 1.0 μL, and the temperature was increased from 120 °C to 260 °C.

1.3.3 Quality assurance and quality control

The results showed a good linear relationship, and the correlation coefficients of the four PAEs were all greater than 0.998. The detection limits of the DMP, DEP, DBP and DEHP standards were between 0.008 and 0.025 mg/L. To test the method precision, the determination of the 50 μg/mL mixed standard solution concentration was repeated five times. Among them, the relative deviations of DMP, DEP, DBP and DEHP were 2.0%, 1.6%, 2.2% and 4.2% respectively, both less than 5%. To ensure the reliability of the experimental data, the same sample was used for parallel determination, with a deviation threshold not to exceed 5%

Results and Discussion

2.1. Concentration of PAEs and Its Influencing Factors

When only these four PAEs were monitored, the average PAE concentration in the Changji City soil was 13.77 (0.29-119.72) mg/kg. Among them, average concentrations of DMP, DEP, DBP and DEHP in the soil were 0.87(ND -5.75) mg/kg, 1.53 (ND -11.18) mg/kg, 9.72 (0.15-102.36) mg/kg, 1.66 (ND-15.12) mg/kg. Respectively(Fig 1). DBP detected the highest proportion of four kinds of PAEs, followed by DEHP, and DMP content is relatively minimum. Relative to other PAEs, The total amount of DBP and DEHP are the most commonly used plasticizers, accounting for 50-60% of all plasticizers (Xia et al. 2011, Adeniyi et al. 2011). Thus, the emissions of these two PAEs in the urban environment are relatively large. Compared with other PAEs, DBP and DEHP belong to middle and high molecular weight PAEs with longer molecular chain, larger octanol-water partition coefficient and weaker activity. These PAEs are not easily degraded by microorganisms in the soil and do not migrate as quickly via runoff and leaching and hence rapidly accumulate in the soil. DMP, DEP molecular weight is relatively small, short alkyl chain, the migration speed is faster and more volatile (Zeng et al. 2009, Niu et al. 2014, Wang et al. 2015b, Langer et al. 2010). These factors might be the reason why DBP and DEHP were the primary PAE pollutants in the urban soil.

Presently, there is no control standard for PAE soil pollution in China. Therefore, this study was based on the control criteria for PAEs in the United States soils (USEPA 2013). In this study regions, DMP, DEP, DBP and DEHP in the urban soil samples exceeded this standard by varying degrees, DMP, DEP and DBP were exceeded the standard serious, particularly DBP which exceeded the standard by three orders of magnitude. Although the DMP, DEP and DEHP concentrations did not exceed the United States governance standards, DBP significantly exceeded the governance standards. PAEs pollution problems should arouse the concern of the relevant management (Tab 1).

The PAEs content found in Changji was much higher than that in other cities in China, e.g., Beijing, Tianjin and Anshan (Tab 1). The sampling time for Changji City was later than that in the other cities, so PAEs had accumulated in the soil for a longer time. Additionally, the Changji samples were collected during four seasons, so these PAE concentrations represent the annual average value. The samples from Beijing, Tianjin and Anshan were collected in summer, and these three cities are in temperate monsoon climate regions. In these regions, summer rainfall is plentiful and easily forms runoff. Runoff scouring exacerbates the migration of PAEs into the aquatic environment. Especially in summer, soil PAEs are more volatile, and these summer PAEs concentrations represented these cities' annual mean values, which might result in the artificially low PAE concentrations for these cities. The DEHP concentration in Guangzhou was about ten times that in Changji City. Guangzhou is an important industrial base in China and a comprehensive industrial manufacturing center in South China. Light industry is more developed, cosmetics, plastics and rubber production and other industries scale were larger, This might be the main reason that led to the large emissions of overall PAEs.

It is found that in addition to DMP, the Changji urban soil PAEs content was much higher than that of domestic agricultural soils. This result is consistent with other studies(Xia et al. 2011, Zeng et al. 2009). Urban soils are characterized by a high organic matter content (Li and Liu 2007). The soil organic matter content has a significant effect on the soil adsorption capacity of PAEs, which increases with the increase of organic matter content (Yang 2013). Additionally, the PAEs in agricultural soil are primarily from sewage and agricultural plastic film, while the PAEs in an urban environment are more complex and their emissions larger. Wang et al study also shows that the river bank deposits, PAEs content riverbank sediments in urban areas is much higher than suburban and rural(Sun et al. 2016, Wang et al. 2014). This discrepancy indicates that urbanization significantly increases PAE emissions in the local environments. This factor are also the primary reason that the PAE content in the urban soil was higher than that agricultural soil.

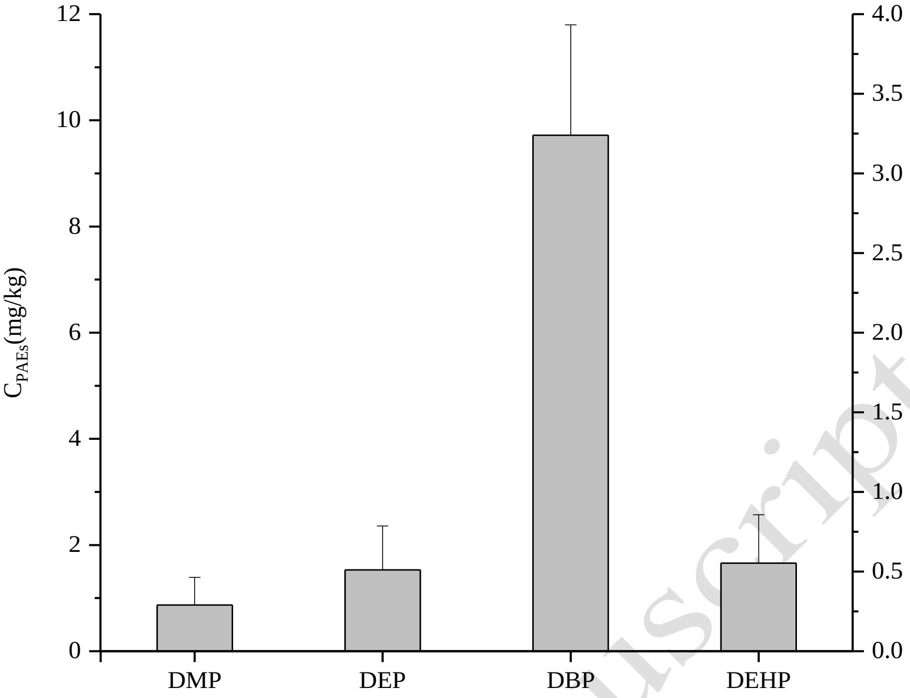

Figure 1. Concentration of PAEs

Table 1 Distribution of PAEs in Chinese soils (mg/kg)

	Sampling Location	DMP	DEP	DBP	DEHP	Sample Year	Data Sources
Control standards		0.02	7.10×10-2	8.10×10-2	4.35	Soil types	(USEPA 2013)
Governance Standards		2.0	7.1	8.1	50	-	(USEPA 2013)
Urban soil	Changji, Xinjiang	0.87	1.53	9.72	1.66	2015	This Research
	Tianjin	1.50×10-3	6.67×10-3	0.37	0.42	2008	(Zhu et al. 2012)
	Anshan, Liaoning	6.67×10-3	7.83×10-3	0.59	0.43	2008	(Zhu et al. 2012)
	Beijing	6.18×10-3	1.27×10-3	0.99	0.14	2008	(Xia et al. 2011)
	Guangzhou	-	-	1.80	14.8	2005	(Zeng et al. 2009)
Agricultural soils	China	1.48×10-2	2.79×10-3	6.58×10-2	8.21×10-1	2013	(Niu et al. 2014)

2.2. Seasonal Variation of PAEs and Its Influencing Factors

The concentrations of Σ_4PAEs in spring, summer, autumn and winter were 3.05 mg/kg, 2.19 mg/kg, 8.89 mg/kg and 46.76 mg/kg, respectively. The concentration of Σ_4PAEs was highest in winter, followed by autumn and spring, and minimum content in summer (Fig. 2). Four seasons change in Xinjiang are obvious, the winter was very cold, and there was a heating period during the autumn, winter and spring, starting from October of the year to the end of next year April, for up to six months or more. The primary heating method in Changji relies on coal combustion and the coal-burning process can release PAEs to the environment(Wang et al. 2015a). During the winter, the low temperatures were not conducive to PAEs volatilizing from the soil. Further, winter is the season with the least precipitation, and the precipitation was solid. Combined with the low temperatures, runoff erosion of soil PAEs and deep penetration to the soil does not easily occur during winter. These might be the reasons that the concentration of Σ_4PAEs was highest in winter.

During the spring and autumn, heating was just beginning or nearing completion, so less coal was burned, and PAE emissions were reduced. In addition, compared with winter, temperatures are relatively high in spring and autumn, and so did the volatilization of soil PAEs to the atmosphere. Compared with winter, there was an inevitable increase in precipitation in spring and autumn. Thus, the possibility of runoff formation also increases and causes runoff scouring and rainwater infiltration of PAEs into the soil. These factors raised the possibility of soil PAEs migrating to the water environment.

In summer, PAE emissions from coal-fired heating were missing. Concurrently, the highest temperatures occurred in Xinjiang, so the chance of PAEs volatilizing from the soil into the atmosphere are maximized. The precipitation also reached a maximum for the year, increasing runoff scouring and rainwater infiltration, which might be the reason for the occurrence of the lowest soil PAE concentrations in summer. The seasonal variation of DBP and DEHP was consistent with Σ_4PAEs, but the seasonal variation of DMP and DEP was not. This discrepancy may be related to the characteristics and seasonal variations in relevant sources of DMP and DEP (Langer et al. 2010, Li et al. 2016). Hu et al. found that soil PAEs with lower and higher molecular weights occur in different states, with significant differences in migration, transformation and bioavailability (Hu et al. 2007).

Studies show that there are distinct seasonal variations of ΣPAEs in farmland (agricultural soil), but that concentrations are highest in summer, contrary to the seasonal variation of urban soil (Wang 2015). There were a large number of plastic film left in the facility farmland. During summer, the temperature reaches the highest of the year, and the temperature of the plastic film in the soil. This factor leads to a substantial reduction of the bond strength between the plastic molecules and PAEs. The accelerated release of PAEs in the mulch film plays a major role in PAEs enrichment in the soil. The PAEs from differences sources was the reason why the variation of PAEs concentration seasonal variation in urban soil and farmland soil are primarily.

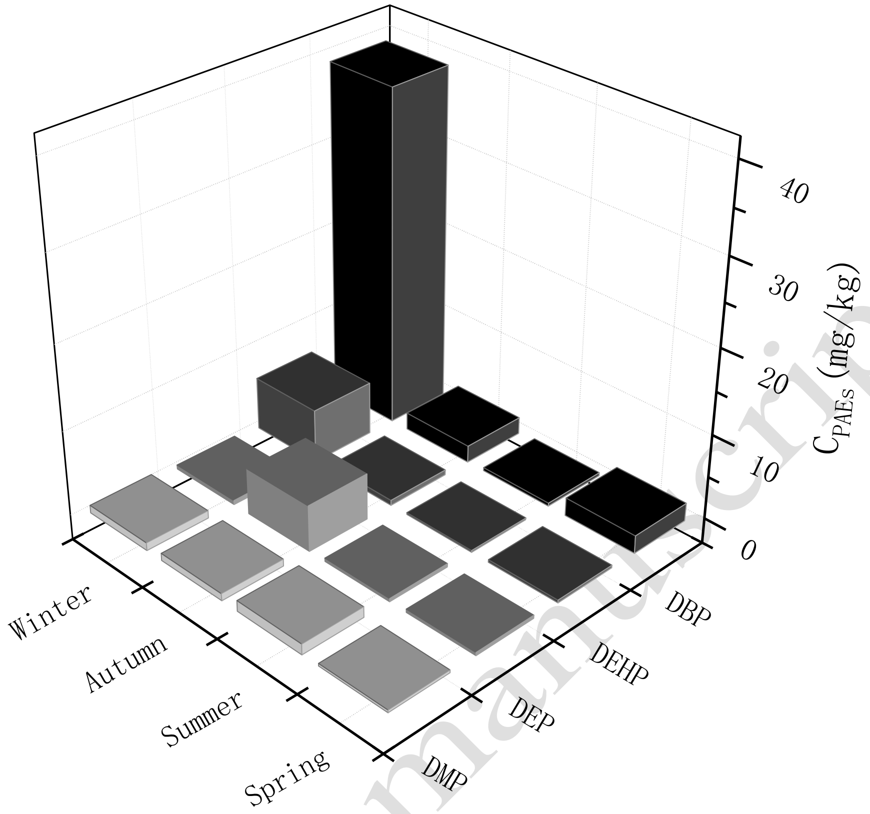

Figure 2 Seasonal Variation of PAEs

2.3. Health Risk Assessment

To evaluate the toxicity of PAEs, scholars had evaluated the exposure and health risks of PAEs in the atmosphere, water and other environmental media (Niu et al. 2014, Wang et al. 2015b, Li et al. 2016, Bui et al. 2016). Among these evaluations, the risk assessment of soil is primarily for that in agricultural soil (Niu et al. 2014, Duan et al. 2010). There are few reports evaluating urban soils. Given the concealment and persistence of urban soil pollutants and the large urban population, it is urgent and necessary to conduct health risk assessments of PAEs in urban soils.

According to the migration cycles of urban soil surface pollutants in the environment, three exposure routes of urban soil PAEs to the human body were determined: hand-mouth contact intake, respiration inhalation, and direct skin absorption (Li and Liu 2007). The health risk assessment of urban soil in the study area was conducted using the US EPA human exposure risk assessment model (USEPA 2004). Health risks include carcinogenic and non-carcinogenic risks. DEHP is one of the more toxic PAEs. The *global harmonized system of classification and labelling of chemicals* (GHS) defines two types of carcinogens: one class of substances includes *known carcinogens*, and the other class includes substances that are *suspected carcinogens.* DEHP has been classified in the Category *known to be a carcinogenic* substance (Chang 2011). DEHP has been banned from use in child care supplies, toys, cosmetics and medical devices (Bui et al. 2016, Buzek and Ask 2009). The high toxicity and low degradability of DEHP mean more focus should be on its health risk (Bui et al. 2016, Sampson and De Korte 2011) The PAEs were divided into non-carcinogenic (DEP, DBP and DEHP) and carcinogenic (DEHP) categories; DEHP was classified as both a non-carcinogen and a carcinogen to evaluation it. There were no sound DMP evaluation parameters. Therefore, the evaluation in this study was only for DEP, DBP, and DEHP.

2.3.1 Calculation of Exposure Dose

The exposure dose was calculated according to the soil concentration and exposure route of PAEs as follows:

Hand-mouth contact intake:

$$D_{ing} = C_{(\mathrm{PAEs})} \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \qquad (1)$$

Respiration inhalation:

$$D_{inh} = C_{(\mathrm{PAEs})} \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \qquad (2)$$

Direct skin absorption:

$$D_{der} = C_{(\mathrm{PAEs})} \times \frac{SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \qquad (3)$$

where D is the exposure dose of each PAE and the other physiological parameters values are shown in Tab 2.

2.3.2 Non-carcinogenic Risk Assessment

To obtain the noncarcinogenic contaminants Hazard Index, the non-carcinogenic contaminant exposure dose is divided by the reference dose:

$$HI = \sum \left(\frac{D}{\mathrm{R}_{fD}} \right)$$

where R_{fD} is the reference dose (Tab 2) and HI is the total non-carcinogenic hazard index, it meaning the integrated non-carcinogenic risks of the pollutants multiple exposure pathways.When the calculation result is less than 1, the risk is considered low or negligible. If the result is greater than 1, it believes there is a non-carcinogenic risk (USEPA 2004).

Table 2 Health risk assessment parameters of PAEs

Parameters	Physiological parameters	Unit	Value	Data Sources
C	Concentration of Soil PAEs	mg/kg	Average value	This research
IngR	Percentage of pathways through ingestion	mg/d	200 (child) 100 (adult)	(USEPA 2011)
InhR	Inhalation frequency	m^3/d	7.63 (child) 20 (adult)	
EF	Exposure frequency	d/a	180	
ED	Exposure time	a	6 (child) 24 (adult)	
SA	Exposure to skin surface area	cm^2	2800 (child) 5700 (adult)	
SL	Skin adhesion	mg/cm^2	0.2 (child) 0.07 (adult)	
ABS	Skin absorption factor	1/d	0.1	
BW	Mean body weight	kg	15 (child) 70 (adult)	
AT	Mean exposure time	d	ED × 365 (non-carcinogenic), 70 × 365 (Carcinogenic)	
PEF	Surface dust content factor	m^3/kg	1.3610^9	(Maxwell et al. 1978)
R_{fd}	Reference dose	mg/kg·d	8.00E-1 (DEP), 1.0E-1 (DBP), 2.00E-2 (DEHP)	(USEPA 1996, 2002)
SF	Carcinogenic slope	$(mg/kg\cdot d)^{-1}$	1.40E-2 (DEHP)	

Non-carcinogenic risk assessment results are shown in Tab 3. For adults, the non-carcinogenic risk of PAEs in urban soils was DBP> DEHP> DEP, and children’s risk was characterized as DEHP> DBP> DEP. Although the average non-carcinogenic risk values of the three PAEs were all less than 1, total non-carcinogenic hazard index of DEHP and DBP were relatively higher. However, the non-cancer risk from PAEs to children was greater than to adults by approximately an order of magnitude. The primary reasons for this difference are that children's physical characteristics and living habits make them more likely to be exposed to pollutants and they are more sensitive to pollutants. Although the theoretical non-carcinogenic risk values of PAEs are within acceptable range, they may still be harmful to the health of susceptible people, Especially the maximum risk of DBP and DEHP has exceeded 1 × 10^{-3} for children. Children are even more Sensitive risk receptors, The safety of children's living environment should be the focus of attention.

2.3.3 Carcinogenic Risk Assessment

For carcinogenic substances, the exposure dose multiplied by the corresponding cancer slope factor (*SF*) results in the carcinogenic risk

$$(\mathrm{Risk})_T = \sum (D \times SF)$$

where *SF* is the carcinogenic slope (Tab 2) and $(\mathrm{Risk})_\mathrm{T}$ is the total carcinogenic risk. This expression shows the variety of exposure pathways for pollutants in a comprehensive carcinogenic risk assessment and the probability of cancer in a population. $(\mathrm{Risk})_\mathrm{T}$ is not more than 10^{-6} for the upper limit of acceptable cancer risk

(USEPA 2004).

In the carcinogenic risk assessment shown in Tab 3, the average carcinogenic risk for DEHP in adults and children was below 10^{-6}, within the acceptable safety range. Meanwhile, the average carcinogenic risk for DEHP in children was much higher than that for adults. Specifically, the greatest cancer risk value was more than 10^{-7}. Therefore, the DEHP may be a health hazard to children and other susceptible populations so the potential cancer risk should not be ignored.

Table 3 Health risk assessment of PAEs in urban soils

Child		DEP	DBP	DEHP
Non-carcinogenic risk	Ave	1.61E-5	8.71E-4	5.45E-4
	Max	8.8E-4	1.88E-3	1.39E-3
Carcinogenic risk	Ave			1.69E-8
	Max			1.55E-7
Adult		DEP	DBP	DEHP
Non-carcinogenic risk	Ave	1.90E-6	7.85E-5	8.15E-5
	Max	1.78E-5	1.01E-4	7.5E-4
Carcinogenic risk	Ave			7.84E-9
	Max			7.00E-8

Conclusions

(1) ∑PAEs content reached 13.77 (0.29-119.72) mg/kg, DBP and DEHP were the primary PAE pollutants in the Changji urban soil. Generally, PAE concentrations were higher in urban soils than in agricultural soils. As PAEs in an urban environment are more complex and are emitted in greater volumes and and higher organic matter concentration, these primary might be the reason that the higher soil PAE content in urban soils.

(2) PAEs had obvious seasonal variations with the highest concentrations occurring in winter, followed by autumn and spring, while the lowest concentrations occurred in summer. The climatic characteristics of arid regions and the seasonal variation of emission sources were the primary influencing factors. Additionally, seasonal variations in PAEs in urban soils were not consistent with those in agricultural soils, which were primarily due to the different soil PAEs sources.

(3) The average non-carcinogenic risk values of the three PAEs were all less than one. However, the risk value of DEHP and DBP were relatively higher. The non-cancer risk of PAEs to children was higher than the risk to adults by approximately an order of magnitude. DEHP average carcinogenic risk values were lower than 10^{-6}, but the average carcinogenic risk of DEHP to children was much higher than the risk to adults. All the theoretical values of the non-carcinogenic and carcinogenic risk of PAEs were within the acceptable safety range. Nevertheless, PAEs may still be harmful to the health of children and other susceptible populations.

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