Environ Geochem Health (2020) 42:4313–4326
https://doi.org/10.1007/s10653-019-00502-4

ORIGINAL PAPER

Pollution characteristics of phthalate acid esters in agricultural soil of Yinchuan, northwest China, and health risk assessment

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Received: 26 June 2019 / Accepted: 18 December 2019 / Published online: 3 January 2020

Abstract Eighty-nine agricultural surface soil samples from different types of land of Yinchuan were collected and detected for sixteen phthalate acid ester (PAE) compounds; the pollution characteristics and pollution distribution were analyzed. In addition, the potential health risk exposures to local resident of six priority control phthalates by the US EPA were assessed. All soil samples were contaminated with PAEs, the total concentrations of Σ_{16}PAEs were between 0.391 and 11.924 mg kg^{-1}, and the mean concentrations were 4.427 mg kg^{-1} in soil. Among the sixteen PAE congeners, DMP was the most abundant component, which accounted for average 44.64% of the total PAEs, then DnBP and DEHP, which accounted for the average contribution rate, were 21.25% and 23.34%, respectively, and DpHP was not detected in all soil samples. Risk assessment indicated that the risk of non-carcinogenesis in this study was within the acceptable range; however, the carcinogenic risk of DEHP through intake dietary significantly exceeded the carcinogenic level recommended by the US EPA (1×10^{-6}) and therefore presented a potential carcinogenic risk. More considerable attention should be given to the PAEs contamination status in soils and potential effects on local resident health.

Keywords Phthalate acid esters · Pollution characteristic · Agricultural soil · Health risk assessment · Yinchuan

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Introduction

Due to the widespread application of phthalate acid esters (PAEs), this synthetic organic compound has been received more and more attention. They are mostly colorless transparent oily liquid, which is almost insoluble in water, but soluble in organic solvents, with high fat solubility and are difficult to volatilize. They have been used extensively in plastics, fertilizers, pesticides, toys, cosmetics, detergents, coatings and other industries. About 85% of them have been used in polyvinyl chloride as plasticizers to improve the ductility and softness (Yang et al. 2016). At present, the PAEs have been detected in soil (Sun et al. 2016; Zhou et al. 2012), air (Wang et al. 2012), water (Li et al. 2017; Shi et al. 2016), municipal sludge (Cai et al. 2003; Mo et al. 2001), municipal solid waste (Zheng 2007), fertilizer (Mo et al. 2005) and

sediments (Li et al. 2016a, b, c; Liu et al. 2010; Wang et al. 2014; Wang et al. 2016a, b; Zhang et al. 2016a, b).

PAEs are a kind of environmental hormones which are long-term residue in the environment, with bioaccumulation, semi-volatile and highly toxic. They are typical endocrine disruptors, and the toxicity to the human body is a chronic process. Through breathing, diet and skin contact, they directly enter to human and animal body, causing people to be widely, continuously exposed to PAEs. They also interfere with the normal levels of hormones in the human body, which leads to many adverse consequences, such as deformity of the human body, endocrine disorder, disease of reproductive system, decrease in sperm quantity and higher incidence of breast cancer (Wang et al. 2015). At present, US EPA has classified diethyl phthalate (DEP), dimethyl phthalate (DMP), di-*n*-butyl phthalate (DnBP), butylbenzyl phthalate (BBP), di-n-octyl phthalate (DnOP) and di (2-ethylhexyl) phthalate (DEHP) as the "priority-controlled toxic pollutants." In addition, the soil pollution control standards and governance standards have been also stipulated. In China, DEP, DnBP and DnOP have been listed in the priority control pollutants blacklist. Because of many applications of agricultural measures, such as the extensive use of plastic film, fertilizer, pesticide, sewage sludge and irrigation of wastewater, the PAEs pollution of soil in China was more and more prominent (Mo et al. 2008; Wang et al. 2015). As modified additives, PAEs are only physically combined with product molecules in the plastic products, not through chemical bonding to the high polymer carbon chain of the product. As a plasticizer in plastic products, the concentration of PAEs is from 10% to 60% (Wang et al. 2018); in the process of product use, PAEs are continuously released from plastics, through leaching, volatilization and sedimentation into the soil (He et al. 2015). Because of the increasing application of agricultural plastic films, the PAEs pollution of soil was particularly serious. Studies have shown that PAEs in facility agricultural soils were higher than the open field soil (Meng et al. 1996).

Yinchuan, the capital city of Ningxia Hui Autonomous Region, is the important city in northwest China. Although the ecological environment is relatively fragile, the soil types are diverse, which is very suitable for the development of agricultural production and various economic crops. In recent years, the use of plastic products has increased dramatically, the planting area of plastic film mulching is close to 1.85×10^4 hm^2 every year and the total amount of agricultural film use reached to 2322.4 t (Yang et al. 2013). With the aging, broken and low recovery rate of the plastic film, the residual PAEs in the soil become more and more serious; our research team have detected the soil of greenhouse vegetable fields in the eastern suburb of Yinchuan in 2018 and found that the soil was contaminated with a certain degree of PAEs, especially DMP, the exceeding rate even reached to 73.47% (Liang et al. 2018). But so far, there have been no relevant reports on the pollution characteristics of PAEs in other types of soil in Yinchuan. Therefore, in this study, sixteen kinds of PAE compounds were determined in the different types of agricultural soil in Yinchuan by gas chromatography–mass spectrometry; pollution levels and human health risk assessment were analyzed to provide basic data on PAEs pollution and agricultural product safety in this area.

Materials and methods

Sampling

Representative plots were selected as sampling sites according to the agricultural production layout and planting type in the surrounding areas of Yinchuan. A sum of 89 agricultural soil samples (facility vegetable land 27, mulch farmland 8, farmland 26, woodland 11, orchard 12, grassland 5) were collected in Yinchuan from May to June 2018. The "W" five-point sampling method was adopted to collect the topsoil of 0–20 cm, and the location of the sampling point was recorded by GPS. Avoiding the edge of the greenhouse, the root of the crop and the place that just fertilized, particles of vegetation litter and roots and small stones were removed when sampling, five subsamples of soil were collected and mixed into a composite sample, and about 1 kg soil was left in a paper bag by the quartering method and then transported to the laboratory. The soils were stored in the brown jars and kept in − 4 °C refrigerator; then, the soil was being air-dried, ground and homogenized with 0.25-mm stainless-steel sieve in the shade and ventilated place at room temperature. Tomatoes, beans, celery, zucchini, eggplant and cucumber were

the main vegetables for long-term cultivation in the facility vegetable land, and the broccoli, rape and lettuce were the main short-term intercropping cultivation. The shortest time for facility vegetable greenhouses was 3 years, and the longest time was 16 years. Vegetables were mainly planted in mulched farmland, such as tomatoes, zucchini, eggplant and lettuce. Film was mulched in spring and autumn. There were mainly planted with wheat and corn in the farm land. The main trees in the woodland were pine, poplar, sand jujube, willow, young forest and nurseries. The soil of young forest and nurseries was covered with film. There were peach, apple, pear, plum and apricot trees in the orchard, and weeds grew in the waste grassland. The topographical map of Yinchuan and the sampling sites are shown in Fig. 1.

Chemicals and materials

Sixteen standard mixture of PAEs, including DEP, DMP, DnBP, BBP, DnOP, DEHP, bis (2-methoyethyl) phthalate (DMEP), diisobutyl phthalate (DIBP), DMP, dipentyl phthalate (DPP), di (2-ethoxyethyl) phthalate (DEEP), di-n-hexyl phthalate (DHXP), di-n-nonyl phthalate (DNP), di(2-*n*-butoxyethyl) phthalate (DBEP), bis (4-methyl-2-pentyl) phthalate(BMPP), dicyclohexyl phthalate (DCHP), dipentyl phthalate (DPHP) were obtained from O2SI, Inc. (Charleston, SC, USA), and their concentration was all 1000 μg mL^{-1}. The recovery indicator is benzyl benzoate (1000 μg mL^{-1}), which was of analytical grade and acquired from Dr. Ehrenstorfer (Augsburg, Germany); other chemicals and materials were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Diethyl ether, acetone and petroleum ether were of analytical grade, which were all distilled before use; methanol was of HPLC grade. Anhydrous sodium sulfate was baked at 400 ± 1 °C for 6 h; florisil, neutral silica gel and aluminum were activated prior to use in a muffle furnace.

Sample extraction

Soil sample was extracted following Rao's method (Liang et al. 2018; Rao et al. 2017). Five grams of soil was weighed into the 250-mL grinding mouth tapered bottle, mixed with 1 mL benzyl benzoate with concentration of 2 ug mL^{-1} and 90 mL acetone/petroleum ether (1:3 V/V) and then ultrasonicated for 30 min. The soil extracts were filtered into the round-bottom flask with a sand core funnel. The glass column (1.2 cm × 30 cm) was successively added with 4 g anhydrous sodium sulfate, 6 g florisil and 4 g anhydrous sodium sulfate and then prewashed the column with 10 mL petroleum ether/ethyl ether (10:0.4 V/V);

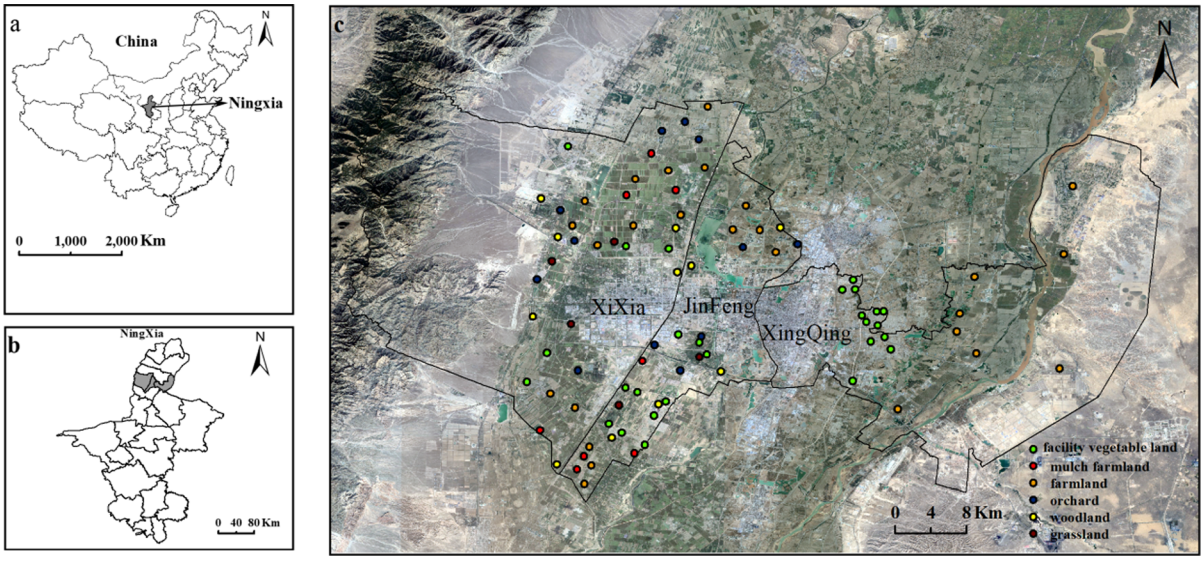

Fig. 1 The geographical locality of the Ningxia province in China (**a**); Yinchuan city in the Ningxia province (**b**); the sampling sites in Yinchuan (**c**)

then, the eluent was discarded. The extraction liquid in the round-bottom flask was concentrated and reduced to 3–5 mL with the rotary evaporator under low pressure at 35 °C; then, 90 mL of petroleum ether/ether (10:3 V/V) was used to eluted PAEs, all the eluent was collected to the heart-shaped bottle, condensed by rotary evaporation to exactly dryness, then was dissolved by the chromatographic-grade methanol and diluted to 2 mL. Finally, the known quantities of the internal standard were added to the sample, and then, they were through the 0.22-μm organic filter membrane before instrumental analysis.

Instrumental analysis

The extracted compounds were analyzed with the GC–MS 2010 Plus (Shimadzu, Japan), with the DB-5MS quartz capillary column (30 m × 0.25 mm × 0.25 μm) for the chromatographic separation. The GC column temperature was set at 60 °C for 1 min and programmed to increase to 220 °C at the rate of 20 °C min^{-1}, maintained for 1 min, then increased to 290 °C at the rate of 3 °C min^{-1} and maintained for 5 min. Then, 0.5 μL of the extract was injected onto the GC–MS in the splitless mode with the injection temperature of 260 °C. High-purity helium was used as the carrier gas, and the flow speed was kept at 1 mL min^{-1}. Mass spectrum conditions were as follows: the selective ion monitoring was SCAN mode, the temperature of ion source and transfer line was 230 °C and 280 °C and the post-run temperature was 280 °C for 5 min.

Quality control and quality assurance

To avoid the influence of PAEs on the experiments in the environment, no plastic products were used in the experiment, and all glass products were first soaked in the solution of potassium dichromate and concentrated sulfuric acid for 24 h; then, they were rinsed clean with ultrapure water and organic solvents and were dried before being used. All the organic solvents were steamed twice through the whole glass system.

The recovery rate was used to test the reliability of the detection method, and the mixed standard solution of 16 kind of PAEs was added to all the samples at the concentrations of 1 mg kg^{-1}, 2 mg kg^{-1} and 3 mg kg^{-1}, respectively. The samples were pretreated according to the above steps, and the recovery rate of the samples was between 86.3% and 115.4%, in line with the requirements of trace analysis. In order to ensure the analysis reliability, the reagent blank test was carried out simultaneously in each ten samples during the sample determination. The surrogate benzyl benzoate recoveries ranged from 80 to 120%.

Sixteen kinds of PAEs with 0.01, 0.05, 0.1, 0.2, 0.5, 1, 1.5 and 2 μg mL^{-1} were used to draw the standard curve, and the correlation coefficient R^2 ranged from 0.995 to 0.999, satisfying the requirements.

Health risk assessment

Among the PAEs homologues, DEHP, BBP, DEP, DnBP, DMP and DnOP are the non-carcinogenic substances related to human health, and DEHP and BBP are carcinogenic substances. The main approaches that local residents take PAEs are dietary and non-dietary. Approaches of dietary are the food intake, which mainly refer to the intake of vegetables growing in plastic film greenhouse. Non-dietary approaches include inhalation, dermal contact and soil ingestion (Wang et al. 2015). The PAEs' non-carcinogenic risk and carcinogenic risk assessment models recommended by US EPA are as follows:

$$CR = \sum (ADD_i \times CFS) \quad (1)$$

CR (unitless) is the carcinogenic risk; ADD_i (mg $kg^{-1}days^{-1}$) is the average daily dosage, including dietary (food intake, ADD_{intake}) and non-dietary (soil ingestion, dermal contact and inhalation, ADD_{ingest}, ADD_{dermal}, ADD_{inhale}); CFS (mg kg^{-1}-$days^{-1}$) is the carcinogenic slope factor (DEHP is 0.014, BBP is 0.0019) (Zeng et al. 2016):

$$HQ = \sum \left(\frac{ADD_i}{RfD_i} \right) \quad (2)$$

HQ is the hazard quotient; RfDi (mg kg^{-1} $days^{-1}$) is the daily maximum permissible level of contaminants (DM is 10, DEP is 0.8, DBP is 0.1, BBP is 0.2, DEHP is 0.02, DNOP is 0.04).(Wang et al. 2018).

The calculation formula of PAEs intake by residents through food intake, inhalation, dermal contact and soil ingestion is as below:

$$ADD_{intake} = \frac{C_{soil} \times BAF \times IRF \times EF \times ED}{BW \times AT} \times CF \quad (3)$$

$$ADD_{ingest} = \frac{C_{soil} \times IRS \times EF \times ED}{BW \times AT} \times CF \quad (4)$$

$$ADD_{dermal} = \frac{C_{soil} \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (5)$$

$$ADD_{inhale} = \frac{C_{soil} \times EF \times ED \times Ij}{PET \times AT} \times 10^3 \quad (6)$$

The parameters for human risk assessment are listed in Table 1.

For non-carcinogens, if HQ > 1, there shows a non-carcinogenic risk. For carcinogens, if CR > 10^{-6}, there shows a carcinogenic risk.

Results and discussion

PAE concentrations and spatial distribution of agricultural soil in Yinchuan

The descriptive statistics of concentration for every PAEs' congener and total PAEs in agriculture soil in Yinchuan are presented in Table 2. Most of the PAEs congener was detected in all soil samples except DPhP; the total concentrations of Σ_{16}PAEs were between 0.391 and 11.924 mg kg^{-1}, with the mean and the median concentration of 4.277 and 4.427 mg kg^{-1}, respectively. In all the soil samples,

Table 1 Parameters of health risk assessment in this study

Parameter	Meaning	Unit	Numerical data	Source
C_{soil}	PAEs concentration of agricultural soil	mg kg^{-1}		This study
BAF	Bioaccumulation factor of PAEs from soil to crops;	–	DEP(0.108), DBP(0.108)	
DEHP(0.166), DNOP(0.166)	Wang et al. (2015)			
IRF	Daily intake of foods	mg day^{-1}	Adult 710000, children 236000	Wang et al. (2016a, b)
EF	Exposure frequency	days $year^{-1}$	350	Yang et al. (2017)
ED	Exposure duration	year	Adult 24, children 6	Niu et al. (2014)
BW	Body weight	kg	Adult 70, children 15	Yang et al. 2017
AT	Average lifetime exposure	days	Non-carcinogenic risk 365 × ED, carcinogenic 25550	Niu et al. (2014)
CF	Conversion factor	–	10^{-6}	Yang et al. 2017
IRS	Soil ingestion rate	mg day^{-1}	Adult 100, children 200	Wang et al. (2016a, b)
SA	Soil surface area	cm^2 day^{-1}	Adult 5700, children 2800	Wang et al. 2018
AF	Soil adherence factor	mg cm^{-2}	Adult 0.07, children 0.2	Wang et al. (2016a, b)
ABS	Fraction of pollutant absorbed dermal from the soil	–	0.1	Niu et al. (2014)
PEF	Particles emission factor	m^3 kg^{-1}	1.36×10^9	Wang et al. (2018)
Ij	Respiratory rate	m^3 day^{-1}	13.5	Wang et al. (2016a, b)

Table 2 Concentration (mg kg^{-1}) of PAEs and detection rate in soil of Yinchuan

	Range	Mean ± SD	Median	DF (%)
DMP	0.089–4.684	1.836 ± 0.878	1.818	100
DEP	0.004–6.017	0.25 ± 0.766	0.102	100
DIBP	0.009–0.984	0.252 ± 0.248	0.137	100
DnBP	0.018–2.652	0.919 ± 0.664	0.815	100
DEHP	0.069–2.693	0.96 ± 0.717	0.702	100
DMEP	0.012–0.467	0.246 ± 0.23	0.261	3.37
DHXP	0.005–0.006	0.006 ± 0.0003	0.006	6.74
DEEP	0.036–0.069	0.053 ± 0.023	0.053	2.25
DPP	0.004–0.008	0.005 ± 0.001	0.005	8.99
BMPP	0.005–0.007	0.006 ± 0.001	0.006	2.25
BBP	0.009–0.039	0.023 ± 0.013	0.02	6.74
DBEP	0.072–0.072	0.072±	0.072	1.12
DCHP	0.007–0.009	0.007 ± 0.001	0.008	3.37
DNP	0.005–0.005	0.005±	0.005	1.12
DnOP	0.033–1.354	0.685 ± 0.66	0.656	6.74
DPhP	ND			0
$\sum_{16}$PAEs	0.391–11.924	4.277 ± 1.847	4.427	
$\sum_{6}$PAEs	0.374–11.659	4.013 ± 1.736	4.063	

Note: ND presented not detected; $\sum_6$PAEs presented the total concentration of six priority control PAEs; $\sum_{16}$PAEs presented the total concentration of sixteen kinds of PAEs

46.07% of the soil samples were between 0.391 and 4.277 mg kg^{-1}, 51.69% of the soil samples were between 4.277 and 10 mg kg^{-1}, and 2.25% of the soil samples were greater than 10 mg kg^{-1}. The sum concentrations of the six priority control PAEs in soil ranged from 0.374 to 11.659 mg kg^{-1}, with the mean value of 4.013 mg kg^{-1}, and the median value was 4.063 mg kg^{-1}.

Due to the lack of data on the past levels in the study area, there is no conclusion about the temporal change of PAEs level in the different types of soil of Yinchuan.

Some studies on PAEs of soil in other regions or countries were conducted; the results showed that there were a certain variety of PAEs concentrations among those areas; and the PAE concentrations in our work were compared to those areas in Table 3. As it is shown in Table 3, the concentration of PAEs in different types of land from Yinchuan was lower than the soil in Shandong peninsula (range of Σ_{16}PAEs: 1.94–35.44 mg kg^{-1}; Chai et al. 2014). But the concentration of PAEs in this study was much higher than the soil in the greenhouse of Beijing (range of Σ_{15}PAEs: 0.14–2.13 mg kg^{-1}; Li et al. 2016a, b, c) and northeastern China (range of Σ_{15}PAEs: 1.37–2.83 mg kg^{-1}; Zhang et al. 2015). With the long history of greenhouse vegetable planting, Shandong Peninsula was the main agricultural planting area in China and the plastic film was used widely and frequently, which might lead to increase the PAEs contamination of soil in this area. In terms of other regions of different types of soil, the concentrations of Σ_6PAEs in this study (range of Σ_6PAEs: 0.374–11.659 mg kg^{-1}) were higher than those in the vegetable soil of Nanjing (range of Σ_6PAEs: 0.4–6.2 mg kg^{-1}) (Wang et al. 2015) and vegetable soil of Sanjiang Plain (range of Σ_6PAEs: 0.163–0.469 mg kg^{-1}) (Wang et al. 2017). However, the concentrations of Σ_6PAEs in the soil of Yinchuan were lower than the suburban soil of Yellow River Delta (range of Σ6 PAEs: 1.007–16.007 mg kg^{-1}) (Yang et al. 2013), the agricultural soils of Xianyang (range of Σ_6PAEs: 9.11–157.62 mg kg^{-1}) (Wu et al. 2015a, b) and the urban soils of Guangzhou (range of Σ_6PAEs: 1.123–298.539 mg kg^{-1}) (Zeng et al. 2009), which was one of the most industrialized regions in China and showed a rapid economic development. The extremely high concentration of Σ_6PAEs had reached to 1532.987 mg kg^{-1} in Xinjiang, because of the long history of cotton cultivation with plastic film (Guo and Ying 2011). Overall, the concentration of PAEs in agriculture soil of Yinchuan should be categorized as at the moderate level in China. Compared with the Netherlands, the UK and Denmark, the concentration

Table 3 Comparison of concentration of PAEs in soil of different regions (mg kg $^{-1}$)

Location	Soil types	DMP	DEP	DnBP	BBP	DEHP	DnOP	$\sum_6$PAEs	$\sum_{16}$PAEs	References
Beijing	Greenhouse soil	0.008	0.02	0.44	0.004	0.38	0.002	0.85	–	Li et al. (2016a, b, c)
Shandong Peninsula	Vegetable soil	0–1.179	0.01–1.90	0–9.855	0–4.786	0–2.943	0–5.873	0.01–26.536	1.37–18.81	Li et al. (2016a, b, c)
Shandong Peninsula	Greenhouse soil	ND–1.245	0.002–1.051	0.016–15.72	ND–5.691	0.073–5.327	ND–14.397	–	1.939–35.44	Chai et al. (2014)
Yellow River Delta	Suburb soil	0.001–0.065	0.001–11.239	0.166–1.450	ND	0.710–4.473	ND–0.142	1.007–16.007	–	
	Rural soil	0.001–0.005	ND–0.001	0.136–1.039	ND	0.431–2.449	ND–0.068	0.716–3.251	–	
Tianjin	Vegetable soil	0.002–0.101	0.002-0.114	0.013–0.285	0–0.358	0.028–4.17	0–9.78	0.05–10.4	–	Kong et al. (2012)
Xiangyang	Agriculture soil	0.15–8.04	0.13–14.09	0.69–18.24	ND–9.16	3.26–153.4	ND–2.31	9.11–157.62	–	Wu et al. (2015a,b)
Shantou	Vegetable soil	ND–0.087	ND–0.354	ND–7.652	ND–2.833	0.001–4.197	ND–0.323	0.018–9.303	–	Wu et al. (2015a,b)
Denmark	Agriculture soil	NA	NA	0.128	0.009	0.448	0.018	0.603	–	VikelsØe et al. (2002)
UK	Soil	0.0001	0.0009	0.0008	0.0008	0.076	0.014	0.0926	–	Gibson et al. (2005)
Netherland	Soil	NA	NA	0.006	0.0318	NA	NA	0.038	–	Peijnenburg and Struijs (2006)
Xianyang	Vegetable soil	0.0213–0.823	ND–0.067	0.037–6.313	ND–0.222	ND-3.871	ND–0.763	0.129–10.288	–	XU et al. (2014)
Nanjing	Vegetable soil	ND–0.04	ND–0.02	ND–2.08	ND–0.10	0.24–4.18	ND–2.64	0.40–6.20	–	Wang et al. 2015
Sanjiang plain	Vegetable soil	0.012–0.034	0.020–0.046	0.022–0.209	0–0.054	0.034–0.218	0–0.054	0.163–0.469	–	Wang et al. (2017)
	Paddy soil	0.013–0.049	0.033–0.097	0.015–0.354	0–0.072	0.077–0.583	0–0.163	0.268–0.947	–	Wang et al. (2017)
Xinjiang	Cotton soil	1.126	1.572	351.12	28.28	0.198	128.7	1532.987	–	Guo and Ying (2011)
Yinchuan	Agriculture soil	0.089–4.684	0.004–6.017	0.018–2.653	ND–0.039	0.069–2.693	ND–1.354	0.374–11.659	0.391–11.924	This study

Note: ND presented not detected, "–"presented the study not involved. NA presented not available

of PAEs in China's soil was significantly higher than those countries. Firstly, the consumption of plastic film in China was much higher than that of other countries. Studies had shown that the annual production of PAEs in the world reached 600×10^4 t. China's annual consumption of PAEs was up to 87×10^4 t (Li et al. 2016a, b, c); secondly, the film thickness in China was generally 0.006 – 0.008 mm, while it was generally 0.02 – 0.05 mm in other countries; the film thickness in China was much lower than the foreign film thickness of 0.02 mm. Although it reduced the production cost, it also reduced the flexible strength of the film, making the recovery and utilization more difficult (Yan and Cheng 2011). In addition, different kinds of fertilizers, pesticides and other chemicals could cause significant increase in PAEs concentration in soil (He et al. 2015).

In order to see the concentration distribution more intuitively, the space distribution of the concentration of Σ_{16}PAEs is shown in Fig. 2, and the sampling points of 84, 83 and 73 were all the facility vegetable lands, in which the concentration of PAEs was the highest (Σ_{16}PAEs: 11.924, 10.668 and 7.781 mg kg^{-1}).

Pollution characteristics of different types of land of soil in Yinchuan

The PAEs concentration in soil of different types of land was different (Table 4). The average concentration of $\sum_{16}$PAEs in facility vegetable land was the highest (4.913 ± 2.473 mg kg^{-1}), followed by the mulched farmland, woodland, orchard and grassland. In general, the difference between the PAEs concentration of different types of land was not significant, the distribution of concentration was relatively homogeneous, there was no serious local deviation, the reasons may be as follows: (1) Investigation and statistics data show that there were fewer factories involved in the production and use of phthalate esters in this region, so the difference of PAEs concentration was not obvious. Furthermore, the volatilization of building materials and the air deposition were the important reasons to increase the pollutant concentration in the study area. (2) The extensive use of agricultural film was an important reason for the higher PAEs concentration in soil of facility vegetable land and mulched farmland than in other types of land. According to the preliminary investigation, there was a long history of filming in agriculture soil of Yinchuan; the shed age of the greenhouse in some

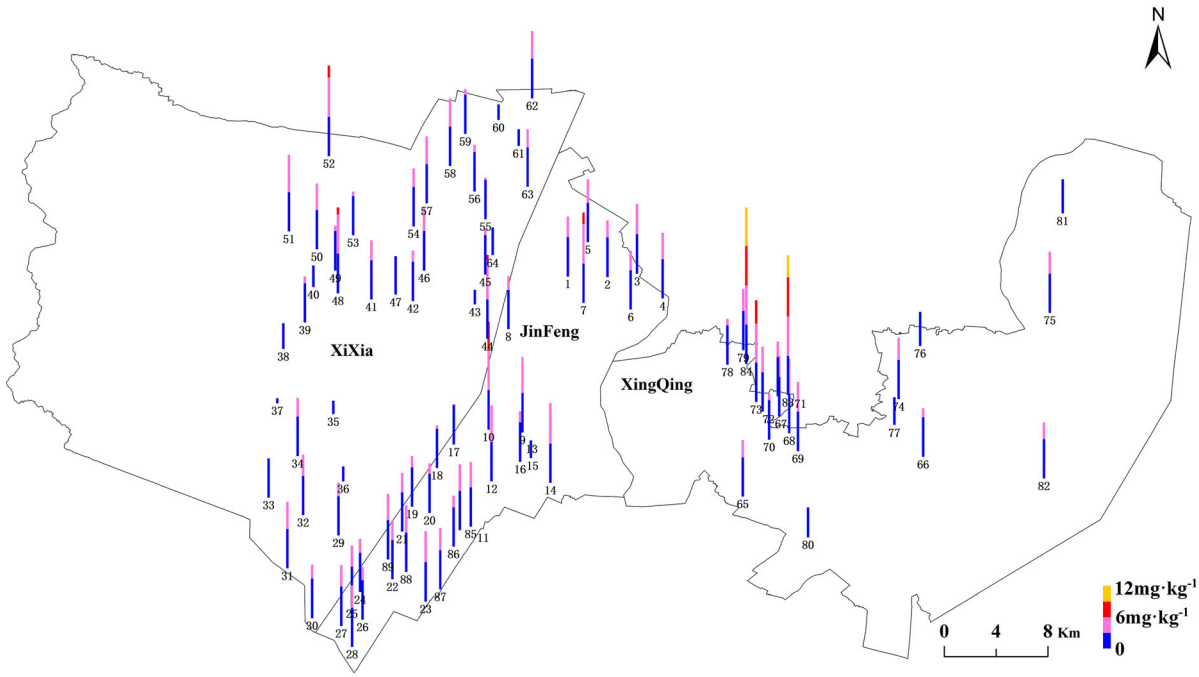

Fig. 2 Concentration and geographical distribution of PAEs in agriculture soil of Yinchuan

Table 4 The PAEs concentration in soil of different types of land in Yinchuan (mg kg $^{-1}$)

Land types	$\sum_{16}$PAEs			$\sum_{6}$PAEs		
	Range	Mean ± SD	Median	Range	Mean ± SD	Median
Total(n = 89)	0.391–11.924	4.277 ± 1.847	4.427	0.374–11.659	4.013 ± 1.736	4.063
Facility vegetable land(n = 27)	1.121–11.924	4.913 ± 2.473	4.635	1.075–11.659	4.748 ± 2.363	4.388
Mulched farmland (n = 8)	3.171–5.355	4.461 ± 0.834	4.624	3.106–4.939	4.084 ± 0.683	4.158
Farmland (n = 26)	2.106–5.124	3.949 ± 0.927	4.277	1.997–4.987	3.704 ± 0.863	3.826
Woodland (n = 11)	0.391–6.396	4.254 ± 1.856	4.497	0.374–6.347	3.879 ± 1.700	4.158
Orchard (n = 12)	1.139–6.877	3.920 ± 2.168	4.204	1.082–6.244	3.517 ± 1.841	3.853
Grassland (n = 5)	1.038–4.490	3.164 ± 1.316	3.532	1.004–4.406	3.020 ± 1.303	3.494

sampling sites was even up to 16 years. (3) The reason for the higher average of PAEs concentration in woodlands in this area may be the deposition of phthalate esters in the air. The dominant wind direction in this region was southeast wind in spring and northwest wind in winter. The woodland and orchard were mainly distributed in the northwest with a certain altitude, which has a certain resistance effect on the air flow, so that the deposition of PAEs in the air relatively was easier in here than in other places. In addition, some of the woodlands were found to be nurseries and the soil was covered with plastic film. (4) The heavy use of agricultural materials such as pesticides and fertilizers, and agricultural nonpoint source pollution were the important reasons of PAEs pollution in soil of woodland, farmland and orchard, while the concentration of PAEs in the soil of grassland was low due to less human influence.

PAE congener profiles of agricultural soil in Yinchuan

In the present study, DEP, DMP, DnBP, DIBP and DEHP were detected at the frequency of 100%; there were no DpHP in all soil samples; among the rest of PAE congeners, DPP was detected in eight samples, and the detectable frequency was the highest (8.99%); then, BBP, DnOP and DHXP (6.74%) were detected in six samples, respectively; DMEP and DCHP were detected only in three samples, respectively, and the detectable frequency was 3.37%; DEEP and BMPP were detected only in two samples, respectively, and the detectable frequency was 2.25%; the detectable frequency of DNP and DBEP was the lowest (1.12%), which was only detected in one sample. The relative contributions of each PAEs' monomer in the soil are shown in Fig. 3. Among all the soil samples, it was obvious that DMP exhibited the highest concentration in the study areas, with the contribution rate ranging from 2.67 to 83.20%, the average contribution rate was 44.64%, followed by DEHP and DnBP, with the contribution rate ranging from 3.02 to 55.88%, and from 1.57 to 75.92%, the average contribution rate was 23.34% and 21.25%, respectively. DMP, DEHP and DnBP accounted for 89.23% of the Σ_{16}PAEs concentrations, indicating that they were the dominant pollutants of PAEs in the agriculture soil of Yinchuan. The sequence of average concentration of the six priority control compounds in the soil was DMP > DEHP > DnBP > DnOP > DEP > BBP.

The percentage composition of each PAEs' monomer in the soil of different types of land is shown in Fig. 4. In the soil of different types of land, DMP, DEHP and DnOP were still the main monomer pollutants of PAEs. The average percentage of DMP in the concentration of $\sum_{16}$PAEs from high to low was facility vegetable land (51.39%), grassland (50.72%), woodland (42.09%), farmland (41.32%), orchard (39.83%) and mulched farmland (39.57%); the average percentage of DEHP in the concentration of $\sum_{16}$PAEs from high to low was orchard (33.13%), woodland (30.73%), grassland (27.24.20%), mulched farmland (21.63%), farmland (21.63%) and facility vegetable land (16.65%); the average percentage of DnBP in the concentration of $\sum_{16}$PAEs from high to low was farmland (26.50%), mulched farmland (26.39%), facility vegetable land (21.03%), grassland (15.23%) and orchard (14.62%).

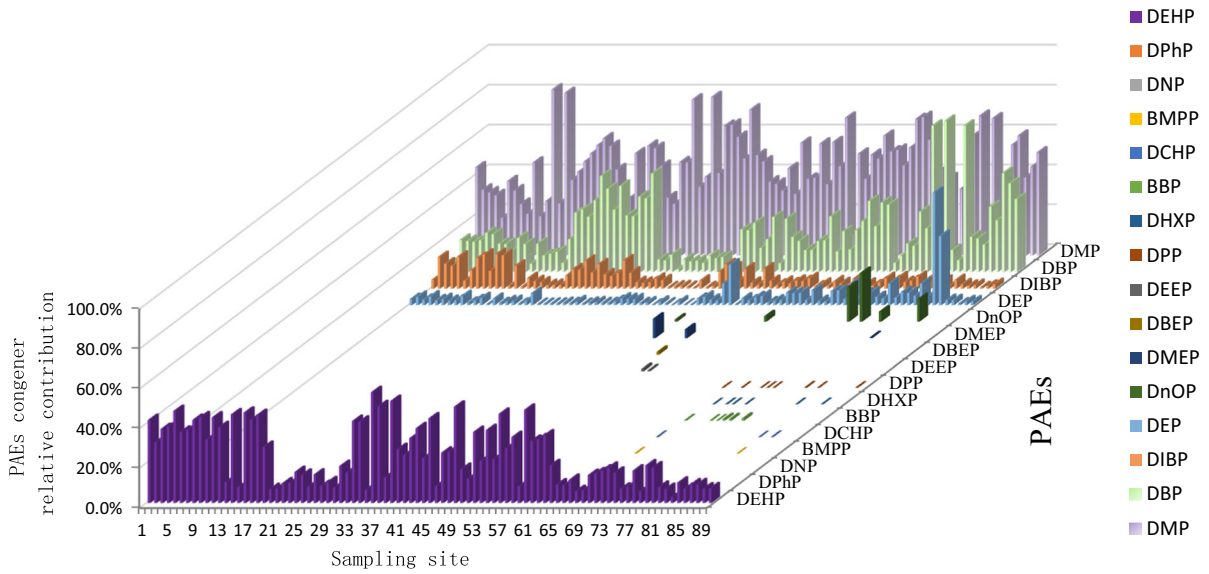

Fig. 3 Relative contributions of 16 PAE congeners in the soil of Yinchuan

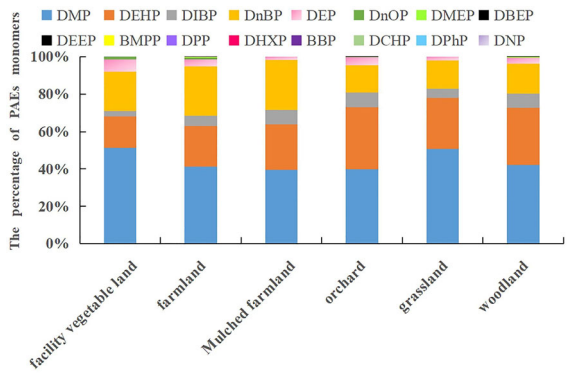

Fig. 4 Profiles of PAEs in different types of soil of Yinchuan

Previous studies had shown that DnBP, DMP, DEP and DEHP were the main monomer pollutants of PAEs in the soil in most regions of China. DMP, DnBP and DEHP had high concentrations in the soil of facility vegetable land in some regions, and some special regions with high concentrations of DEHP and DIBP. For example, DnBP and DEHP were the main monomer pollutants of PAEs in the soil of Changping, Shunyi and Yanqing facility vegetable base of Beijing (Li et al. 2016a, b, c), in the soil of Chaoyang and Chaonan districts in Shantou (Wu et al. 2015a,b), in the agricultural soil of Zhongshan (Li et al. 2015), while DMP, DnBP and DEHP were the main monomer pollutants of PAEs in vegetable soil of Xianyang suburbs (Xu et al. 2014). The main monomer pollutants of PAEs in the soil of different functional areas in Chongqing were DEHP, DBP and DIBP (Yang et al. 2018). The concentrations of DEHP, DIBP and DnBP in the soil of waste plastics disposal sites in Hebei Province (Wang et al. 2016a, b) were significantly higher than other monomers.

Compared to the reported studies in other areas, the concentration range of DMP in this study was 0.089–4.684 mg kg^{-1}, the average concentration was 1.836 ± 0.878 mg kg^{-1} and the concentration was higher than the Shandong vegetable soil (Chai et al. 2014) (ND–1.245 mg kg^{-1}), Tianjin vegetable soil (Kong et al. 2012) (0.002–0.101 mg kg^{-1}), Chongqing urban park soil (Yang et al. 2018) (0.0025–0.01 mg kg^{-1}), Huizhou agricultural soil (Tan et al. 2012) (ND–0.029 mg kg^{-1}) and Nanjing vegetable soil (Wang et al. 2015) (0–0.040 mg kg^{-1}). DMP belonged to short-chain PAE compounds with high water solubility and was easy to be biodegraded (Chen et al. 2016), but DMP was observed as the most abundant PAE compound in this study area, and the average concentration was considerably higher than the concentration of the other research areas, which indicated that the pollution frequency of DMP in Yinchuan was very high, and the rate of soil contamination was much higher than the rate of microbial degradation. DMP was commonly used in personal care products, cosmetics, coatings, special adhesives, anti-mosquito oil (crude oil), spray insecticides,

rodenticides and plasticizers, epoxy resin and other industrial products (Zhang et al. 2016a, b). With the rapid development of urbanization and economy in Yinchuan, the density of mobile population in the suburbs has increased, the waste of life garbage and construction waste has been greatly increased and discarded carelessly, such as personal care products, cosmetics, and some paint and interior decoration materials, which released these short-chain PAE compounds from the material to the soil environment, which may be one of the main reasons for the higher concentration of DMP in the soil of Yinchuan. The sampling time in this study was from May to June, that is exactly the time crops blossomed and bore fruits. Pesticides and fertilizers were applied more frequently, and DMP was often used as the solvent of chemical fertilizers, pesticides and insecticides. Moreover, most of the facility vegetable land and some farmland were covered with film again in spring. In addition, in recent years, the acreage of mulched soil has been expanding, agricultural chemical waste and plastic waste have been increasing and discarded at random, which makes PAEs in these chemicals to be absorbed by plants and enriched and transferred in the soil through atmospheric volatilization and deposition. The decomposition of macromolecular esters by microbial and leaching resulted in the residue of short-chain PAEs in the soil environment, which might be another reason for the high concentration of DMP in agricultural soil of Yinchuan.

DnBP and DEHP were the main plasticizing substances in plastic products in our country, although there was no significant correlation between the greenhouse age and the PAEs concentration, but the consumption of plastic films would lead to the continuous input of the PAEs into the soil, which lead to increase the amount of DnBP and DEHP in the soil. Because of larger molecular weight and relatively low solubility in water, DnBP and DEHP were easy to be adsorbed and enriched in soil, but not easily degraded by biodegradation or other degradation pathways. In Yinchuan, DnBP and DEHP were the main PAE compounds in the soil; this result was consistent with the previous reports in other regions, such as Zhongshan city (Li et al. 2015), Tianjin city (Zhao et al. 2018), Shandong province (Cui et al. 2013), Xian city (Wang et al. 2018) and Yellow River Delta (Yang et al. 2013).

Since the lack of relevant standards for PAEs pollution in soil in China, this study analyzed the PAEs pollution status in agricultural soil in Yinchuan by referring to the control and treatment standards of PAEs compounds in the soil of the USA. Compared with the control standard, the standard exceeding ratios of DMP, DEP, DnBP, DnOP and DEHP were 100%, 98.87%, 95.51%, 33.33% and 1.123%, respectively, and the highest over-standard multiples were 234, 38, 32, 138 and 112 times of the control standard, respectively. None of the BBP exceeded the control standard. Compared with the treatment standard, the standard exceeding ratios of DMP were 42.7%, and the remaining monomers did not exceed the treatment standard. In general, the agricultural soil of Yinchuan suffered varying degrees of contamination of PAEs, among which short-chain PAEs were most serious.

Risk assessment of PAEs in Yinchuan

DEP, DMP, DnBP, BBP, DEHP and DnOP may represent non-carcinogenic risk; DEHP and BBP exhibit potential carcinogenic risk. In this study, the human health risk exposure to PAEs through dietary and non-dietary approaches was evaluated. The risk assessment results are shown in Fig. 4a and b. For all the samples, the non-cancer risk through dietary and non-dietary approaches was far less than the recommended allowable level (HQ < 1) and did not represent a threat to the exposed population. For the adults and children, the mean non-carcinogenic risk exposed to dietary route from high to low in turn was DEHP (7.75×10^{-2} and 1.21×10^{-1}), DnOP (2.76×10^{-2} and 4.30×10^{-2}), DnBP (9.65×10^{-3} and 1.50×10^{-2}) and DEP (3.29×10^{-4} and 5.11×10^{-4}); the mean non-carcinogenic risk exposed to non-dietary route from high to low in turn was DEHP (7.85×10^{-4} and 2.79×10^{-3}), DnOP (2.8×10^{-4} and 9.94×10^{-4}), DnBP (1.50×10^{-4} and 5.34×10^{-4}), DEP (5.12×10^{-6} and 1.82×10^{-5}), DMP (3.00×10^{-6} and 1.07×10^{-5}), BBP (1.84×10^{-6} and 6.55×10^{-6}). In general, the value of non-carcinogenic risk of various intake approaches was as follows: food intake > dermal contact > inhalation > soil ingestion. The carcinogenic exposure risk of BBP and DEHP through non-dietary approach was very low (4.53×10^{-10} and 1.42×10^{-7}), which was within the recommended allowable level (CR $< 10^{-6}$).

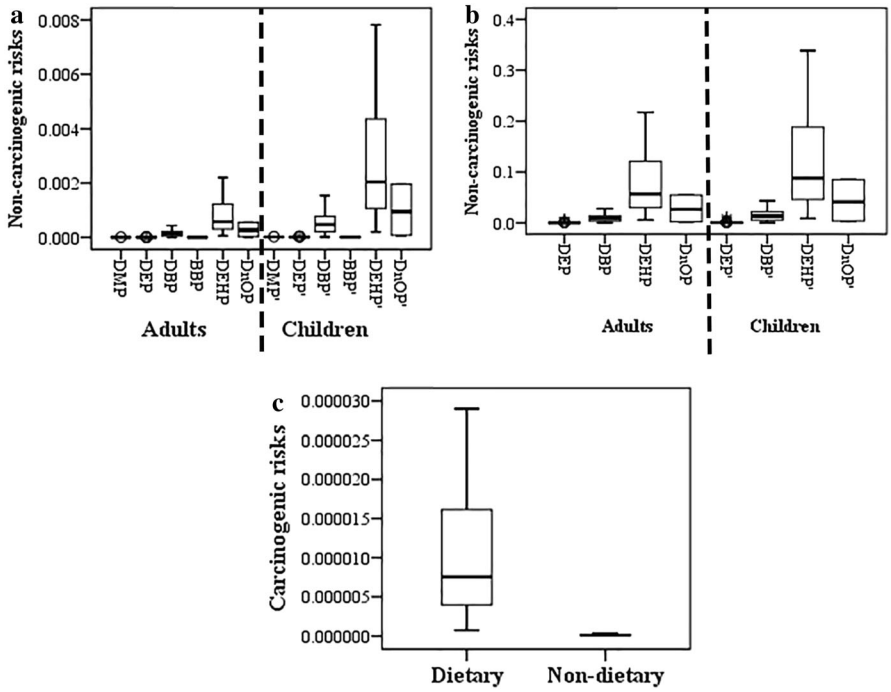

Fig. 5 Non-carcinogenic risk of PAEs through non-dietary route (**a**); non-carcinogenic risk of PAEs through dietary route (**b**); carcinogenic risk of DEHP (**c**)

However, carcinogenic risk of DEHP exposure through dietary approach was higher than 1×10^{-6} ($1.03 \times 10^{-5} \pm 7.65 \times 10^{-6}$), which exceeded the carcinogenic level recommended by the EPA and therefore presented a potential carcinogenic risk (Fig. 4c), and 40% of the samples represented potential carcinogenic risk through the dietary approach to the exposed residents.

It was similar to the agriculture soil in Sanjiang Plain and the mainland in China (Niu et al. 2014); DEHP may accumulate in vegetables, plants and so on and cause harm to human health through the food chain. Based on these calculations, as far as the non-carcinogenic risks of PAEs were concerned, there were few health threats to local inhabitants. But DEHP exhibited potential carcinogenic risk to the human health, the dietary was the main route to threaten the health of residents for carcinogenic risks, and further research was required to control the migration of PAEs from soil to plants.

The PAEs might be cumulative through bioaccumulation process and threaten the human health through the food chain (Fu and Du 2011; Tan et al. 2016; Zhao et al. 2015). Although the results showed low health risk of PAEs in Yinchuan at present, the long-term exposure should be paid attention, and the potential harm to human health of PAE contamination should receive constant attention (Fig. 5).

Conclusion

The present study has provided the contamination level of PAEs in the agricultural soil of Yinchuan, China. The total concentration of Σ_{16}PAEs ranged from 0.391 to 11.924 mg kg^{-1}; the mean and the median concentrations were 4.277 and 4.427 mg kg^{-1}, respectively. Among the sixteen PAEs monomers, DEP, DMP, DnBP, DIBP and DEHP were detected in the frequency of 100%, with DpHP being completely undetected. The total contribution of DMP, DBP and DEHP accounted for 89.23% of the Σ_{16}PAEs concentrations, indicating that they were the main pollutants in the agricultural soil of Yinchuan. The risk assessment results revealed that the risk of non-carcinogenic in this study was within the acceptable range, but the carcinogenic risk of DEHP through dietary routes exceeded the threshold level by the US EPA. DEHP may accumulate in vegetables and plants and do harm to human health by the dietary route. So, effective measures should be taken to control the

migration of PAEs from soil to plants. Meanwhile, the pollution of PAEs in soil and human health threats should receive more attention.

Acknowledgements This study was supported by the Key research and development project "Study on key techniques of PAEs pollution control and soil remediation" (No. 2016KJHM29) and "Study and demonstration on the key technology of antibiotic pollution control and soil remediation of organic fertilizer source" (No.2018BEG03005) from Ningxia science and technology department.

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