

# Phthalic acid esters (PAEs) in vegetable soil from the suburbs of Xianyang city, Northwest China

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**Abstract** This paper provided the first data on the concentration, distribution, congener profile, sources and potential risk of phthalic acid esters (PAEs) in soil of vegetable fields from the suburbs of Xianyang city, Northwest China. PAEs in all topsoil samples analyzed were detected, indicating that PAEs were ubiquitously environmental contaminants. The total concentration of six PAEs ( $\sum 6\text{PAEs}$ ) in soil ranged from 128.60 to 10,288.42  $\mu\text{g kg}^{-1}$ , with a mean of 638.30  $\mu\text{g kg}^{-1}$ . PAEs in soil belonging to the moderate level with comparison to the other researches were dominated by DnBP and DEHP which contributed to the application of agricultural plastic film and fertilizers. The concentrations of DMP and DnBP in 100 and 85 % topsoil samples exceeded the recommended soil allowable concentration used in New York, USA, which were 20 and 81  $\mu\text{g kg}^{-1}$ , and the concentrations of DnBP and DEHP in 5 and 3 % topsoil samples were above the environmental risk level (ERLs), which were 700 and 1,000  $\mu\text{g kg}^{-1}$ . The elevated level of PAEs in soil presented a potential risk to ecological environment and human health, especially for DMP, DnBP and DEHP.

**Keywords** Phthalic acid esters · Soil · Vegetable field · Xianyang city

## Introduction

Phthalic acid esters (PAEs) are a class/group of artificially synthesized organic compounds that are widely used as

additives or plasticizer in polyvinyl chloride, polyvinyl acetates, cellulose and polyurethanes to improve flexibility and resilience of plastic products; and also as non-plasticizers in consumer products such as cosmetics, personal care products, food packaging, medical products, floorings, wallpapers, paints, glues, electronic and automobile parts, and insect repellents (Staples et al. 1997; Abdel daiem et al. 2012; Fu et al. 2013). The global production of PAEs was approximately 6.0 million tons per year (Mackintosh et al. 2006), and the consumption of PAEs in China in 2011 was about 2.2 million tons (China Plastics Process Industry Union 2011). Nevertheless, PAEs are not covalently or chemically bound in the products and can release into the surrounding environment during manufacture, usage and disposal (Benson 2009). Due to the wide application of PAEs, PAEs have been detected frequently in environmental media such as water (Wang et al. 2008a, b; Zhang et al. 2012), air (Wang et al. 2008a, b; Pei et al. 2013), and sediment/soil (Liu et al. 2010; Vikelsøea et al. 2002; Peijnenburg and Struijs 2006; Ma et al. 2013; Li et al. 2006; Cai et al. 2005; Guan et al. 2007; Zeng et al. 2008; Kong et al. 2012; Yang et al. 2013). In addition, PAEs are characterized by the relatively low solubility in water and high *n*-octanol/water partition coefficient (*K*<sub>ow</sub>), they have stronger affinity to human and animals. At the same time, some PAEs can cause carcinogenicity, teratogenicity and teratogenicity to human and animals, and disrupt the normal endocrine activity of human and animals (Hu et al. 2003; Xu et al. 2008; Ma et al. 2013). Therefore, six PAEs, namely, dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), di-*n*-octyl phthalate (DnOP), di (2-ethylhexyl) phthalate (DEHP) and butylbenzyl phthalate (BBP), have been classified as priority pollutants by United States Environmental protection Agency (US EPA), and three of them (i.e. DMP, DnBP and

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DnOP) subsequently been listed as priority pollutants by China State Environmental Protection Agency.

The vegetable production bases which are usually seated at the connected part of urban and rural districts (Cai et al. 2005) provide all kinds of fresh vegetables to urban residents. Soil serves as the growth medium and nutrient provider for plant growth (Chen et al. 1997). Affected by anthropogenic activities such as industrial and agricultural production, traffic emission and waste disposal, soil has been heavily polluted by heavy metals (HMs), polycyclic aromatic hydrocarbons (PAHs) and PAEs, and become an important reservoir of these pollutants (Yang et al. 2013). These pollutants can enter into air through vapor volatilization, water and soil by leaching and human directly or indirectly via food chain, which pose a potential threat to ecological environment and human health.

Xianyang city is located at the middle part of Shaanxi Province, Northwest China. Promoted by China's Western Development Program and Integration of Xi'an and Xianyang, the speed of urbanization, industrialization and agricultural modernization of Xianyang city is very fast. The area of vegetable production of Xianyang accounts for 1/4 of the total area of vegetable production of Shaanxi Province. Some important vegetable production fields lie in the suburbs of Xianyang city, especially in south, southwest and southeast suburbs, which lies also in the urban connected part of Xianyang and Xi'an (capital of Shaanxi Province). The wide application of agricultural plastic film and fertilizer during agricultural production and the deposition of particulates containing PAEs may result in PAEs accumulation in soil. However, there was little information about PAEs contamination in vegetable soil in the suburbs of Xianyang city. Therefore, the objective of this paper is to investigate the concentration, distribution, congener feature, sources and potential risk of PAEs in vegetable soil from the suburbs of Xianyang city, NW China.

## Materials and methods

### Chemicals and materials

Six PAEs standard stock solution including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), di-*n*-octyl phthalate (DnOP), di (2-ethylhexyl) phthalate (DEHP) and butylbenzyl phthalate (BBP) were purchased from Supelco Company of US and their contents were all 2,000  $\mu\text{g mL}^{-1}$  in methanol medium. They were appropriately diluted with methanol during use. All organic reagents, namely, *n*-hexane, acetone, dichloromethane, methanol and acetonitrile, were HPLC Grade and purchased from J.T. Baker Company of US. Silica gel (80–100 Mesh), neutral alumina (100–200 Mesh) and

anhydrous sodium sulfate (Analytical Grade) were purchased from Qingdao Ocean Chemical Factory, Sinopharm Chemical Reagent Co., Ltd, and Tianjin Chemical Reagent Factory, respectively. They were first extracted for 48 h with dichloromethane in a Soxhlet apparatus, and then baked for 6 h at 180 °C, 12 h at 250 °C and 6 h at 150 °C before use, respectively. Filter papers were extracted for 48 h with dichloromethane before use.

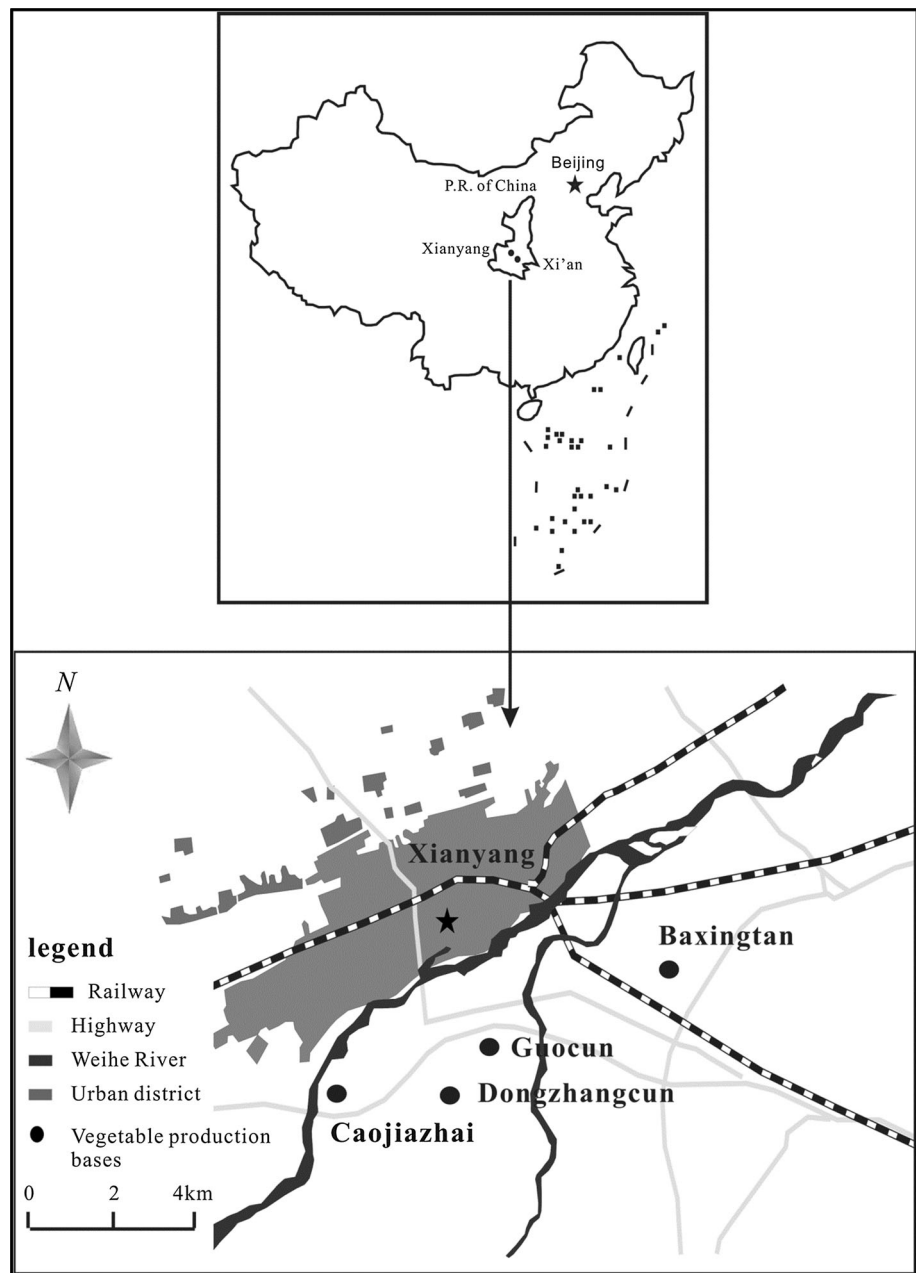
### Sample collection

According to the actual investigation, four typically vegetable production fields, namely, Dongzhangcun (relative near from urban district), Caojiazhai (common vegetable fields), Guocun (heavy traffic district and nearest from urban district) and Baxingtang (heavy traffic district), were selected in the suburbs of Xianyang city, NW China (Fig. 1). These vegetable fields have been applied agricultural plastic film and fertilizers during production. Based on the area of vegetable production fields, soil sampling sites were arranged in the four vegetable production fields of Dongzhangcun ( $n = 12$ ), Caojiazhai ( $n = 27$ ), Guocun ( $n = 4$ ) and Baxingtang ( $n = 16$ ). At each sampling site, 5 sub-topsoil samples (0–25 cm) were collected from the four corners and center of a 2 m  $\times$  2 m grid with a stainless steel shovel and mixed into a composite topsoil sample of  $\sim 1$  kg by a quartile method on the spot. A total of 59 topsoil samples were collected in September and October in 2013. The collected topsoil samples were stored in brown glass bottles, and then taken back to laboratory. All topsoil samples were air-dried in a cool, dark and ventilated place at room temperature. The air-dried topsoil samples were first crashed, then sieved through a 1 mm stainless steel sieve to remove small stones, plant debris and other refuse, and stored in brown glass bottles at  $-4$  °C before analysis.

### Extraction and purification of PAEs

15 g topsoil sample and 5 g anhydrous sodium sulfate were weighed, mixed thoroughly, packed by filter paper, and placed into the extraction tube of Soxhlet apparatus. PAEs of topsoil sample were extracted for 24 h with 200 mL mixed solution of *n*-hexane and acetone ( $v:v = 1:1$ ). The extraction temperature was controlled at below 60 °C and the extraction rate was at 3–5 recycle per hour. The solution containing PAEs was reduced to approximately 1–2 mL by RE-52A model Rotary Evaporator (Shanghai Yarong Biochemical Instrument Factory), then added 20 mL *n*-hexane and continuously concentrated to about 1–2 mL to finish solvent exchange. The extracts were loaded on a glass purification column (30 cm L  $\times$  1 cm I.D.) of silica gel/neutral alumina (2:1), which was

**Fig. 1** Schematic map for geographic location of study area



6 cm neutral alumina, 12 cm silica gel and 1 cm anhydrous sodium sulfate from bottom to top, respectively. 20 mL *n*-hexane, 70 mL blended solution of dichloromethane and *n*-hexane (*v:v* = 3:7) and 40 mL mixed solution of acetone and *n*-hexane (*v:v* = 2:8) were used to elute fatty hydrocarbons, aromatic hydrocarbons and esters, respectively. The collected elution of esters was reduced to approximately 1–2 mL with the Rotary Evaporator, then evaporated to dryness in N<sub>2</sub> atmosphere by NAS-12 model Nitrogen Blowing Instrument (ABSON Scientific Instruments Group), at last dissolved with a little methanol and diluted to 1.5 mL.

**Instrument analysis**

The standard gradients and extracted solutions of PAEs were separated by a Hypersil ODS2 column (250 mm L × 46 mm I.D., 5 μm, Dalian Elite Analytical Instrument Co., Ltd) at Ultimate-3000 model high-performance liquid chromatography (HPLC) made by Dionex of US and equipped with a diode array detector (DAD). Acetonitrile (A) and water (B) were used as the mobile phases, the flow speed was 1 mL min<sup>-1</sup>, and the gradient conditions were: 0–4 min, A 60 %; 4–5 min, A 60–70 %; 5–11 min, A 70 %; 11–14 min, A 70–100 %; 14–22 min, A 100 %.

Other instrument conditions were injection volume 20  $\mu\text{L}$ , column temperature 30  $^{\circ}\text{C}$ , and detection wavelength 225 nm. PAEs were identified through the retention time and quantified through the external standard method.

#### Quality control and assurance

Plastic wares were prohibited in experiments. All glass wares used in experiments were first soaked in  $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$  solution, and then rinsed with tap water, distilled water and ultrapure water, respectively. They were dried for 2 h at 105  $^{\circ}\text{C}$ , then baked for 3 h at 350  $^{\circ}\text{C}$ , and pre-washed with corresponding organic reagents before use. A small volume of organic reagents was evaporated to dryness in an  $\text{N}_2$  condition and dissolved with 1.5 mL methanol, and PAEs were not detected. At the same time, the whole process blank experiment was conducted, only a few DMP ( $2 \mu\text{g L}^{-1}$ ) and DEP ( $3 \mu\text{g L}^{-1}$ ) were detected and lower than the limit of detection of instrument. Calculated as the three times ratio of signal to noise, the limit of detection of instrument for DMP, DEP, BBP, DnBP, DEHP and DnOP was 13, 28, 6, 71, 15 and  $11 \mu\text{g L}^{-1}$ , respectively. In addition, the results of recovery experiments by adding a certain volume of the standard stock solution of PAEs into some topsoil samples showed the recovery coefficient for PAEs ranged from 80 to 103 %, except for DEHP (73 %).

#### Statistics methods

The descriptive statistics, correlation analysis, principal component analysis and cluster analysis of PAEs data were conducted on SPSS 13.0.

## Results and discussions

### Concentration and distribution of PAEs in soil

The descriptive statistics of concentration for individual and total PAEs in topsoil from the whole and each vegetable production field in the suburbs of Xianyang city, NW China, are listed in Table 1. PAEs in the topsoil samples analyzed were detected frequently, which indicates PAEs were ubiquitously environmental contaminants. The concentration of individual PAEs in topsoil samples was in the range of low limit of detection (LLD) to  $6,313.35 \mu\text{g kg}^{-1}$ . The total concentration of six PAEs ( $\sum 6\text{PAEs}$ ) varied from 128.60 to  $10,288.42 \mu\text{g kg}^{-1}$ , with an average of  $638.30 \mu\text{g kg}^{-1}$ .

The distribution of individual and total PAEs of soil from different vegetable production fields in the suburbs of Xianyang city, NW China, is also shown in Table 1. The maximum of individual and total PAEs in topsoil was found at Caojiazhai, except for DMP and DEP in Baxingtang. The order of mean concentration

**Table 1** Concentration of individual and total PAEs in soil ( $\mu\text{g kg}^{-1}$ )

Area	DMP	DEP	DnBP	DnOP	DEHP	BBP	$\sum 6\text{PAEs}$
Xianyang							
Min	21.26	LLD	36.63	LLD	LLD	LLD	128.60
Max	823.16	66.99	6,313.35	762.50	3,871.09	222.00	10,288.42
Mean	54.31	19.46	316.59	42.30	166.17	39.48	638.30
Dongzhangcun							
Min	21.26	LLD	52.61	LLD	39.20	LLD	217.88
Max	395.87	44.36	527.09	67.63	213.22	172.12	740.70
Mean	68.35	27.46	162.14	35.10	63.99	49.18	406.21
Caojiazhai							
Min	21.54	LLD	49.12	LLD	31.97	LLD	145.72
Max	62.51	51.44	6,313.35	762.50	3,871.09	222.00	10,288.42
Mean	28.35	12.61	504.51	48.28	292.52	35.06	921.34
Baxingtang							
Min	21.83	LLD	36.63	LLD	LLD	LLD	128.60
Max	823.16	66.99	459.41	103.67	161.17	93.47	1,171.53
Mean	76.75	24.80	159.71	33.43	58.61	33.16	386.46
Guocun							
Min	21.60	LLD	83.00	39.83	31.70	35.98	214.95
Max	320.13	41.76	230.90	73.84	98.59	135.65	802.25
Mean	97.61	20.25	139.06	58.93	50.12	65.47	431.43

LLD low limit of detection

for DMP was Guocun ( $97.61 \mu\text{g kg}^{-1}$ ) > Baxingtang ( $76.75 \mu\text{g kg}^{-1}$ ) > Dongzhangcun ( $68.35 \mu\text{g kg}^{-1}$ ) > Caojiashai ( $28.35 \mu\text{g kg}^{-1}$ ), DEP was Dongzhangcun ( $27.46 \mu\text{g kg}^{-1}$ ) > Baxingtang ( $24.80 \mu\text{g kg}^{-1}$ ) > Guocun ( $20.25 \mu\text{g kg}^{-1}$ ) > Caojiashai ( $12.61 \mu\text{g kg}^{-1}$ ), BBP and DnOP were Guocun ( $65.47$  and  $58.93 \mu\text{g kg}^{-1}$ ) > Dongzhangcun ( $49.18$  and  $35.10 \mu\text{g kg}^{-1}$ ), Caojiashai ( $35.06$  and  $48.28 \mu\text{g kg}^{-1}$ ) > Baxingtang ( $33.16$  and  $33.43 \mu\text{g kg}^{-1}$ ), and DnBP and DEHP were Caojiashai ( $504.51$  and  $292.52 \mu\text{g kg}^{-1}$ )  $\gg$  Dongzhangcun ( $162.14$  and  $63.19 \mu\text{g kg}^{-1}$ ) > Baxingtang ( $159.71$  and  $58.61 \mu\text{g kg}^{-1}$ ) > Guocun ( $139.06$  and  $50.12 \mu\text{g kg}^{-1}$ ). The total concentration of six PAEs of topsoil from different vegetable production field decreased in the order of Caojiashai ( $921.34 \mu\text{g kg}^{-1}$ )  $\gg$  Guocun ( $431.43 \mu\text{g kg}^{-1}$ ) > Dongzhangcun ( $406.21 \mu\text{g kg}^{-1}$ ) > Baxingtang ( $386.46 \mu\text{g kg}^{-1}$ ). The distribution patterns of PAEs in topsoil illustrated elevated levels of PAEs accumulated in vegetable soil of Caojiashai which lies in the southwestern suburb of Xianyang city.

#### Comparison of PAEs concentration in soil with other studies

Some studies on PAEs of urban or agricultural soils in other regions or countries were conducted in past decade (Li et al. 2006; Zeng et al. 2009; Cai et al. 2005; Guan et al. 2007; Yang et al. 2007; Xu et al. 2008; Zeng et al. 2008; Guo and Wu 2011; Tan et al. 2012; Kong et al. 2012; Vikelsøea et al. 2002; Peijnenburg and Struijs 2006), which were taken to compare to the present study in Table 2. As shown in Table 2, in general, the concentration of PAEs in urban soil was higher than that in agricultural soil, the concentration of PAEs of agricultural soil from the developed area was higher than that from the developing area, and DnBP and DEHP were higher than other individual PAEs compounds. In the present study, the concentration of DMP in soil was higher than that in most of other research results, except for urban soil of Guangzhou, vegetable soil of Lianxing and cotton soil of Xinjiang. DMP was higher than that in urban soil of Beijing and agricultural soil of Leizhou Peninsula, Guangdong province (Zhanjiang, Huizhou and Zhongshan), Guangzhou (Panyu, Tianhe and Baiyun) and Tianjin (orchard). DnBP and DEHP were lower than that in urban soil (Beijing and Guangzhou) and agricultural soil of Guangzhou and Shenzhen, Guangdong Province (paddy soil in Shantou and Dongguan), Handan, Harbin, Xinjiang and Denmark (high sludge application), while higher than that in agricultural soil of other regions (Leizhou Peninsula, Guangdong province and Tianjin). DnOP and BBP were higher than that in some of urban soil (Beijing and Guangzhou) and agricultural soil (Guangdong province, Leizhou Peninsula and

Denmark), while lower than other urban and agricultural soils. The total concentration of six PAEs of soil was higher than that in agricultural soil of Leizhou Peninsula, Guangdong Province (vegetable soil, sugarcane soil and orchard; Zhanjiang, Huizhou, Zhongshan, Zhuhai and Shunde) and Tianjin (farmland and orchard), while lower than that in urban soil (Beijing and Guangzhou), vegetable soil (Guangzhou, Shenzhen and Tianjin) and agricultural soil of Guangdong province (paddy soil and banana soil; Shantou, Dongguan and Guangzhou). For the present study, in the whole, the concentration of individual and total PAEs of soil belonged to the moderate level.

Occurrence of elevated levels of PAEs in soil from the vegetable production fields in the suburbs of Xianyang city, NW China, may be related to local anthropogenic activities such as application of agricultural plastic film, fertilizers, sewage sludge and sewage irrigation in agricultural production, emission of cosmetics and personal care products of local residents, discard of waste plastics, volatilization of building materials and home furnishes materials (e.g. wall paper, paints and floorings) of surrounding buildings, atmospheric deposition of particulate matters containing PAEs.

#### PAEs congener profile in soil

Understanding of the difference in PAEs congener profile may reflect the environmental sources of PAEs (Zeng et al. 2008; Kong et al. 2012). PAEs composition patterns were analyzed in topsoil of the whole and each vegetable production field in the suburbs of Xianyang city, NW China (Fig. 2). Of the six individual PAEs studied, DMP, DnBP and DEHP were detected in all topsoil samples analyzed, except for DEHP which was not detected only in one topsoil sample. BBP, DnOP and DEP were detected in 80, 64 and 53 % topsoil samples, respectively. The concentration of DMP, DEP, BBP, DnBP, DEHP and DnOP of topsoil ranged from 21.26 to 823.16, LLD to 66.99, LLD to 222.00, 36.63 to 6,313.35, LLD to 3,871.09 and LLD to 762.50  $\mu\text{g kg}^{-1}$ , respectively; and the mean concentration decreased in the order of DnBP ( $316.59 \mu\text{g kg}^{-1}$ ) > DEHP ( $166.17 \mu\text{g kg}^{-1}$ )  $\gg$  DMP ( $54.31 \mu\text{g kg}^{-1}$ ) > DnOP ( $42.30 \mu\text{g kg}^{-1}$ ) > BBP ( $39.48 \mu\text{g kg}^{-1}$ ) > DEP ( $19.46 \mu\text{g kg}^{-1}$ ). In the whole vegetable production fields in the suburbs of Xianyang city, NW China, the most abundant PAE in soil was DnBP (45.86 %) and the second was DEHP (18.81 %), followed by DMP (11.91 %) and BBP (10.34 %); DnOP (7.67 %) and DEP (5.40 %) were relatively low. In different vegetable production fields of Xianyang suburbs, the most abundant PAE in soil was still DnBP which varied from 34.44 to 53.77 %, followed by DMP (16.38 %) and DEHP (16.36 %) in Dongzhangcun, DEHP (22.36 %) in Caojiashai, DEHP (16.38 %) and

**Table 2** Comparison of PAEs concentration between this study and other studies ( $\mu\text{g kg}^{-1}$ )

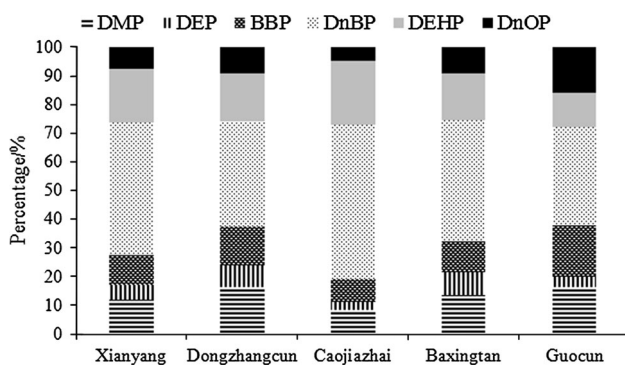
Regions	Soil description		DMP	DEP	DnBP	DnOP	DEHP	BBP	$\Sigma$ 6PAEs	References
Xianyang	Vegetable soil	Dongzhangcun, Guocun, Caojiazhai and Baxingtang	54.31	19.46	316.59	42.30	166.17	39.48	638.30	In this study
Beijing	Urban soil		10	16	790	31	1,875	29	2,751	Li et al. (2006)
Guangzhou	Urban soil	Roadsides	152	92	8,130	561	63,200	402	72,537	Zeng et al. (2009)
		Residents areas	74	34	2,060	17	16,100	32	18,317	Zeng et al. (2009)
		Parks	67	36	2,010	4	29,400	47	31,564	Zeng et al. (2009)
Guangzhou and Shenzhen	Vegetable soil	Guangqing	60	60	3,750	0	6,200	240	10,310	Cai et al. (2005)
		Yuewang	0	630	5,480	330	15,240	490	22,170	Cai et al. (2005)
		Shanmei	20	500	9,160	30	10,960	220	20,840	Cai et al. (2005)
		Tangjia	0	1,110	10,760	30	14,760	410	27,060	Cai et al. (2005)
		Loucun	0	60	4,340	30	9,250	0	13,680	Cai et al. (2005)
		Jiazitang	0	560	7,480	130	9,290	210	17,670	Cai et al. (2005)
		Beixing	0	350	14,060	0	8,250	230	22,888	Cai et al. (2005)
		Faji	0	50	9,740	0	8,840	390	19,030	Cai et al. (2005)
Lianxing			230	500	18,450	0	16,190	250	35,620	Cai et al. (2005)
Leizhou Peninsula	Agricultural soil	Sugarcane soil, paddy field, pot garden and fruit garden	18.06	4.61	282.3	7.09	140.7	5.08	76.31	Guan et al. (2007)
Guangdong Province	Agricultural soil	Vegetable soil	20	90	230	30	150	50	560	Yang et al. (2007)
		Paddy soil	20	50	490	60	170	130	920	Yang et al. (2007)
		Banana soil	30	190	410	20	120	20	810	Yang et al. (2007)
		Sugarcane soil	30	60	300	20	70	10	490	Yang et al. (2007)
		Orchard	20	60	200	30	110	10	430	Yang et al. (2007)
		Shantou	30	50	570	40	170	190	1,050	Yang et al. (2007)
		Zhanjiang	20	5	280	10	140	10	460	Yang et al. (2007)
		Dongguan	10	280	340	80	290	80	1,080	Yang et al. (2007)
		Huizhou	4	10	150	10	90	2	260	Yang et al. (2007)
		Zhongshan	10	2	240	20	140	10	420	Yang et al. (2007)
		Zhuhai	40	110	120	60	60	20	400	Yang et al. (2007)
Shunde	30	370	110	10	0	10	520	Yang et al. (2007)		
Handan	Agricultural soil	Non-cultivated, crop, greenhouse and vegetable fields	n.a	n.a	10,460	n.a	4,860	n.a	n.a	Xu et al. (2008)
Harbin	Agricultural soil	Non-cultivated, crop, greenhouse and vegetable fields	n.a	n.a	7,600	n.a	2,350	n.a	n.a	Xu et al. (2008)
Guangzhou	Agricultural soil	Panyu	5	8	95	ND	729	ND	837	Zeng et al. (2008)
		Haizhou	26	52	1,080	ND	2,750	454	4,362	Zeng et al. (2008)
		Tianhe	6	6	121	7	597	4	741	Zeng et al. (2008)
		Liwan	25	39	323	9	4,090	35	4,521	Zeng et al. (2008)
		Baiyun	9	12	89	ND	610	25	745	Zeng et al. (2008)
Xinjiang	Agricultural soil	Cotton fields	1,126	1,572	28,280	n.a	128,700	n.a	n.a	Guo and Wu (2011)
Huizhou	Agricultural soil	Pot garden, paddy field and fruit garden	3.61	9.23	150.6	9.95	88.28	2.14	310.5	Tan et al. (2012)
Tianjin	Agricultural soil	Farmland	18	25	73	69	264	73	521	Kong et al. (2012)
		Vegetable	24	24	68	790	618	54	1,580	Kong et al. (2012)
		Orchard	9	11	66	80	152	16	333	Kong et al. (2012)



**Table 2** continued

Regions	Soil description		DMP	DEP	DnBP	DnOP	DEHP	BBP	Σ6PAEs	References
Denmark	Agricultural soil	Uncultured	n.a	n.a	2.1	1.2	16	0.09	n.a	Vikelsøea et al. (2002)
		Manured 40 years	n.a	n.a	1.6	4.3	25	0.12	n.a	Vikelsøea et al. (2002)
		Manured 5 years	n.a	n.a	0.5	1.2	12	0.38	n.a	Vikelsøea et al. (2002)
		Artificially fertilized	n.a	n.a	1.1	1.5	40	0.06	n.a	Vikelsøea et al. (2002)
		Low sludge	n.a	n.a	1.3	1.3	13	0.06	n.a	Vikelsøea et al. (2002)
		Normal sludge	n.a	n.a	1.7	0.61	38	0.01	n.a	Vikelsøea et al. (2002)
		High sludge	n.a	n.a	439	52	1,110	29	n.a	Vikelsøea et al. (2002)
	Do 2 years later	n.a	n.a	453	251	1,900	32	n.a	Vikelsøea et al. (2002)	
Netherlands	Soil		n.a	n.a	6	31.8	n.a	n.a	n.a	Peijnenburg and Struijs (2006)

ND not detectable, n.a not available data



**Fig. 2** Composition of PAEs in vegetable soil from the suburbs of Xianyang City

DMP (13.50 %) in Baxingtang, BBP (17.85 %), DMP (16.28 %), DnOP (15.85 %) and DEHP (11.96 %) in Guocun. In the whole, the PAEs of soil from the vegetable production fields of Xianyang suburbs were dominated by DnBP and DEHP, which were corresponded with other studies of soil (Hu et al. 2003; Cai et al. 2005; Guan et al. 2007; Liu et al. 2009; Zeng et al. 2008, 2009; Tan et al. 2012; Wang et al. 2013; Yang et al. 2013).

PAEs include a large number of compounds, which vary in alkyl chain length and branching, which exhibit a difference of water solubility, *n*-octanol/water partition coefficient (*K<sub>ow</sub>*) and vapor pressure. The longer the alkyl chain, the lower is the solubility and the higher is the *n*-octanol/water partition coefficient (Staples et al. 1997), which are frequently rate limiting for biodegradation, volatilization and subsurface transport.

Source identification of PAEs in soil

Diagnosis of environmental sources of pollutants is important to risk management and environmental remediation.

Multivariate statistical analysis (e.g. correlation analysis, principal component analysis and cluster analysis) can be used to check relationship between contaminants and simplify large datasets (Zeng et al. 2009; Kong et al. 2012). In this study, they were applied to identify the environmental sources of PAEs.

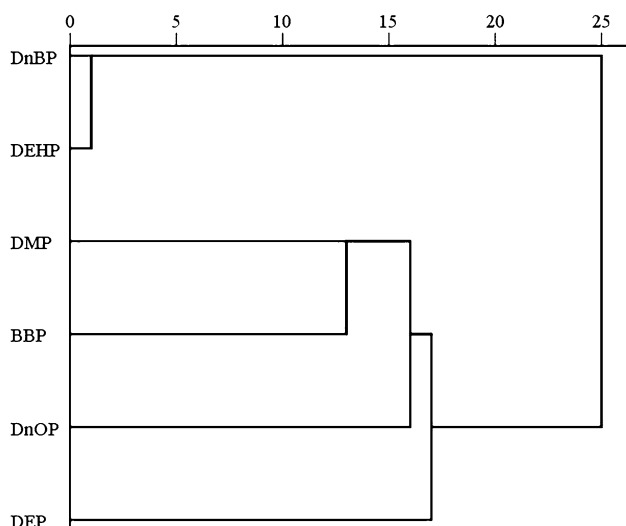
Pearson correlation analysis showed that a significantly positive correlation only existed between DnBP and DEHP ( $R = 0.979$ , at the 0.01 level), indicating that DnBP and DEHP have a similar source or environmental behaviors. Principal component analysis (Table 3) with the correlation coefficient matrix and the variance rotation with Kaiser Normalization extracted four principal components, DnBP and DEHP, DMP and BBP, DEP, and DnOP, with eigenvalues >1 explaining 33.190, 18.642, 18.379 and 16.735 % of the total variation, respectively. Cluster analysis (Fig. 3) separated the studied six individual PAEs into four clusters, DnBP and DEHP, DMP and BBP, DnOP, and DEP, which are consistent with the results of principal component analysis. At the same time, the later three clusters formed a new cluster in a higher level, demonstrating they have another common source.

PAEs have a wide variety of uses and are an important part of our lives. PAEs with lower molecular weight, such as DMP, DEP and DnBP are typically used in cosmetics and personal care products. DnBP is also used in epoxy resins, cellulose esters and special adhesive formulations (IARC 2000; Abdel daiem et al. 2012). Longer/branching alkyl chain PAEs, such as BBP, DnOP and DEHP have been widely used as plasticizers in the polymer industry to improve flexibility, workability and general handling properties and about 80 % of all PAEs are used for this purpose (IARC 2000; Hens and Caballos 2003; Abdel daiem et al. 2012). The content of PAEs in a finished plastic product ranges from 10 to 60 % by weight (IARC 2000; Abdel daiem et al. 2012).

**Table 3** Result of principal component analysis for PAEs

PAEs compounds	Component				Communities
	1	2	3	4	
DMP	-0.098	<b>0.581</b>	-0.570	-0.084	0.679
DEP	-0.106	0.144	<b>0.866</b>	-0.062	0.787
BBP	0.051	<b>0.871</b>	0.151	0.071	0.789
DnBP	<b>0.990</b>	0.018	-0.039	0.066	0.987
DEHP	<b>0.988</b>	-0.008	-0.042	0.092	0.986
DnOP	0.110	0.038	-0.031	<b>0.988</b>	0.990
Initial eigenvalues	1.991	1.119	1.103	1.004	
Variance/%	33.190	18.642	18.379	16.735	
Cumulative variance/%	33.190	51.832	70.211	86.946	

Factor loading values of >0.5 are shown in bold

**Fig. 3** Result of cluster analysis for PAEs

In this study, the PAEs of soil were controlled by DnBP and DEHP, which was consistent with the fact that DnBP and DEHP were mainly used as plasticizers in China. The world production of DnBP and DEHP reached 134 and 394 thousand tons, respectively (Xu et al. 2008). Of the commercial PAEs, the share of DEHP is about 50–60 %. Studies showed that the level of soil PAEs pollution was related to the usage amount and residual rates of agricultural plastic film (Chen et al. 2013) and phthalic acid esters (e.g. DnBP, DEHP and DMP) were one of the most abundant organic compound of fertilizers (Mo et al. 2008). Therefore, DnBP and DEHP of soil came mainly from the application of agricultural plastic film and fertilizers in local agricultural production (Hu et al. 2003; Mo et al. 2008; Kong et al. 2012; Wang et al. 2013). In recent years, the speed of urbanization of Xianyang city is very fast, especially in Guocun, in which, the mobile population was large and building construction was developed. In this study, the concentration of DMP, BBP and DnOP in

vegetable soil from Guocun was highest. Therefore, other PAEs compounds, DMP, BBP, DEP and DnOP, had composited sources: emission of cosmetics and personal care products for DMP and DEP; volatilization of building and decoration materials for BBP and DnOP; atmospheric deposition of particulate matters containing PAEs for DMP, DEP, BBP and DnOP (Zeng et al. 2009; Kong et al. 2012; Yang et al. 2013).

#### Potential risk analysis of PAEs in soil

Due to shortage of local standard for evaluating pollution level of soil PAEs (Cai et al. 2005; Yang et al. 2007; Zeng et al. 2008, 2009; Kong et al. 2012), in the present study, the concentration of PAEs recorded was used to assess the potential risk of soil from the vegetable production fields in the suburbs of Xianyang city, NW China, by comparing to the soil cleanup guidance used in New York, USA (Department of Environmental Conservation, New York, USA 1994). The concentration of DMP in all topsoil samples analyzed exceeded the recommended soil allowable concentration for DMP used in New York, USA ( $20 \mu\text{g kg}^{-1}$ ) and the highest of DMP in topsoil reached to over 40 times the recommended soil allowable value. The concentration of DnBP in 85 % topsoil samples studied was higher than the recommended soil allowable concentration for DnBP used in New York, USA ( $81 \mu\text{g kg}^{-1}$ ) and the maximum of DnBP in topsoil accounted for 79 times the recommended soil allowable value. The concentrations of other individual PAEs were below the soil recommended allowable concentration used in New York, USA, which were 71, 1,215, 4,350 and  $1,200 \mu\text{g kg}^{-1}$  for DEP, BBP, DEHP and DnOP, respectively. Luckily, the concentrations of all individual PAEs in all topsoil sample detected didn't exceed the recommended soil cleanup level value used in New York, USA, which were 2,000, 7,100, 8,100, 50,000, 50,000, and  $50,000 \mu\text{g kg}^{-1}$  for DMP, DEP, DnBP, BBP, DEHP and DnOP, respectively. These implied



that no remediation measures were required for PAEs in soils from the vegetable production fields in the suburbs of Xianyang city. Similar conclusion has been drawn in Guangzhou (Zeng et al. 2008) and Tianjin (Kong et al. 2012). However, Zeng et al. (2008) suggested that further attention should be paid to the ecological and healthy effects of PAEs through food chain at the relatively lower concentrations for their possible biological magnifications in higher trophic organisms including human beings.

In addition, based on the ecotoxicology and environmental chemistry of DnBP and DEHP, the environmental risk levels (ERLs) for DnBP and DEHP in soil or sediment were considered as 700 and 1,000  $\mu\text{g kg}^{-1}$  (Van Wezsel et al. 2000). The concentrations of DnBP and DEHP in 5 and 3 % topsoil samples of Xianyang suburbs were above this standard.

## Conclusions

Phthalic acid esters (PAEs) were ubiquitously environmental contaminants. This study provides the first data on the concentration, distribution, congener profile, source and potential risk of PAEs in soil from the vegetable production fields in the suburbs of Xianyang city, Northwest China. PAEs were detected in all topsoil samples analyzed. The individual PAEs varied from low limit of detection (LLD) to 6,313.35  $\mu\text{g kg}^{-1}$ ; the total concentration of six PAEs ( $\sum 6\text{PAHs}$ ) ranged from 128.60 to 10,288.42  $\mu\text{g kg}^{-1}$ , with a mean of 638.30  $\mu\text{g kg}^{-1}$ . The PAEs of soil belonging to the moderate level compared to the other researches were dominated by DnBP and DEHP, and accumulated in Caojiashai in the southwestern suburbs of Xianyang city. DnBP and DEHP of soil contributed to the application of agricultural plastic film and fertilizers during agricultural production; DMP, DEP, BBP and DnOP had the composited sources: emission of cosmetics and personal care products, volatilization of building and decoration materials, and atmospheric deposition of particulate matters containing PAEs. The concentrations of DMP and DnBP in 100 and 85 % topsoil samples exceeded the recommended soil allowable concentration used in New York, USA, which were 20 and 81  $\mu\text{g kg}^{-1}$ . The concentrations of DnBP and DEHP in 5 and 3 % topsoil samples were above the environmental risk level (ERLs), which were 700 and 1,000  $\mu\text{g kg}^{-1}$ . The elevated level of PAEs in soil presented a potential risk to ecological environment and human health, especially for DMP, DnBP and DEHP.

In present study, the potential risk of PAEs in soil was just analyzed on the basis of current guide values and limits of soil from other countries. Although no remediation measures are required in studied soil, the further attention should be paid to the ecological and healthy risk of PAEs at

relatively low concentration. Actually, predicted no-effect concentration (PNEC) is often used in ecological risk assessment to determine low-risk concentration for chemicals. Therefore, the calculation of PNEC of PAEs in soil environment may be more evaluable to understand their ecological risk. However, to obtain PNEC of PAEs of native species in soil environment, we should first collect and study the ecotoxicity data of PAEs of soil environmental or calculate PNEC of PAEs of native species in aquatic environment according to the aquatic ecotoxicity data of PAEs, then calculate PNEC of PAEs in soil environment using assessment factor method or equilibrium method. This needs to conduct a systematic research. Therefore, the future research will focus on PNEC of PAEs in environmental compartments to reveal the ecological risk of PAEs.

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