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RESEARCH ARTICLE

# Occurrence and risk assessment of phthalate esters (PAEs) in agricultural soils of the Sanjiang Plain, northeast China

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**Abstract** This study looks at the pollution status of six priority control phthalate esters (PAEs) under different cultivation of agricultural soils in the Sanjiang Plain, northeast China. Results show the total concentration of PAEs ranged from 162.9 to 946.9 μg $kg^{-1}$ with an average value of 369.5 μg $kg^{-1}$. PAE concentrations in three types of cultivated soils exhibited decreasing order paddy field (532.1 ± 198.1 μg $kg^{-1}$) > vegetable field (308.2 ± 87.5 μg $kg^{-1}$) > bean field (268.2 ± 48.3 μg $kg^{-1}$). Di-(2-ethylhexyl) phthalate (DEHP) and di-*n*-butyl phthalate (DnBP) were the most abundant PAEs congeners. Compared with previous studies, agricultural soils in the Sanjiang Plain showed relatively low contamination levels. Anthropogenic activities such as cultivation practices and industrial emissions were associated with the distribution pattern of PAEs. Furthermore, human health risks of PAEs were estimated and the non-cancer risk shown negligible but carcinogenic risk of DEHP exceeded the threshold limits value. PAE contaminants originated from cultivation practices and intense anthropogenic activities result in placing the agricultural soils under a potential risk to human health and also to ecosystems in the Sanjiang Plain. Therefore, the contamination status of PAEs in agricultural soil and potential impacts on human health should attract considerable attention.

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**Keywords** Phthalate ester · Agricultural soils · Risk assessment · Sanjiang Plain · Northeast China

## Introduction

Phthalate esters (PAEs) are the predominant synthetic compounds of plasticizers that prevalently used to enhance durability, elasticity, and plasticity of polyvinyl chloride (PVC) products (Bergé et al. 2013; Bui et al. 2016). Approximately 8 million tons of PAEs were produced globally in 2011. Some PAEs such as DEHP have extensive application in the manufacture and processing of PVC products and other polymers, and accounts for 80% of the annual PAEs production in China (Gao and Wen 2016; Meng et al. 2014). Major studies have suggested that several PAEs may be suspect endocrine-disrupting chemicals (EDCs), and their environmental behavior and health risk have attracted considerable attention (Botton et al. 2016; Hotchkiss et al. 2008). Due to the potential adverse effects of PAEs, the United States Environmental Protection Agency (USEPA) has listed dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), butyl benzyl phthalate (BBP), DEHP, and di-*n*-octyl phthalate (DnOP) as priority environmental pollutants, which are also classified as priority water contaminant by the Chinese Environment Monitoring Center (Gao and Wen 2016). As there are no covalent bonds between PAEs and plastic substrates, PAEs can easily contaminate the environment and pose a health risk to humans from their manufacture, usage, and disposal (Fromme et al. 2007). Over time, PAE contamination has become a critical issue for agricultural soils, which act as natural reservoirs for pollutants (Kong et al. 2012). Several studies have reported soil PAE contamination in different regions of China (Niu et al. 2014), for example, the Yangtze River Delta (Sun et al. 2016), the

Shandong Peninsula (Chai et al. 2014), Beijing (Li et al. 2016), Guangzhou (Zeng et al. 2009), Nanjing (Wang et al. 2013a), Xianyang (Wang et al. 2015b), and Hebei Province (Zhang et al. 2015a).

The Sanjiang Plain is originally a floodplain in northeastern China that encompasses a large area of natural freshwater wetlands (Huang et al. 2013). Areas of the natural wetland in Sanjiang Plain have been altered to arable soils in past decades (Dong et al. 2015; Wang et al. 2016b). To date, the Sanjiang Plain is an important cereal production region with effective and intensive agricultural practices in China (Wang et al. 2015c). To maintain yields, continuous cropping and multiple agricultural activities are using agricultural plastic films, fertilizers, and pesticides which lead to more PAEs contaminate sources to the soil. However, there have been a few studies conducted on these agricultural soils in northeast China (Xu et al. 2008; Zhang et al. 2015b). Thus, to reveal the occurrence and distribution patterns of PAEs in agricultural soils of Sanjiang Plain, this study investigated the contamination status and health risk assessment of six priority control phthalates under different cultivation methods.

## Materials and methods

### Sampling

Thirty-six agricultural soil samples were gathered in May 2014, from three cultivated regions, including Qixinghe (46°39′–46°51′ N, 131°54′–132°28′ E), Naolihe (46°41′–46°55′ N, 132°31′–132°59′ E), and Honghe (47°37′– 47°53′ N, 133°23′–133°79′ E) in the Sanjiang Plain (Fig. 1). The sampling sites were chosen by cultivation types: paddy field, vegetable field, bean field. All sample sites had been originally reclaimed from natural wetlands. Surface soil (20 cm depth) samples were gathered by a pre-cleaned stainless steel tube soil sampler and transferred into solvent-rinsed aluminum containers. Any pieces of residual flora or roots were removed. For each samples location, a single 1.0 kg soil sample was a mixture of five sub-samples collected within a 5 m × 5 m area. All soil samples were cooled and stored in an ice box for transport from the field to the laboratory where samples were air-dried at ambient temperature, ground and sieved through a 2 mm stainless steel sieve, and stored at −20 °C until extraction.

### Chemicals

Six PAEs standard mixture solutions including DMP, DEP, DBP, BBP, DEHP, and DOP (1000 mg $L^{-1}$) and an isotope surrogate standard di-*n*-butyl phthalate-d4 (DnBP-D4, 100 mg $L^{-1}$) were acquired from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The six mixed phthalates ester standard stock solutions (1 mg $L^{-1}$) were prepared in *n*-hexane. High purity pesticide analytical grade acetone solvents were purchased from J.T. Baker (Philipsburg, USA) and residue grade *n*-hexane solvents were obtained from Tedia Company Inc. (Carson, CA, USA). Neutral aluminum ($Al_2O_3$) and anhydrous granular sodium sulfate ($Na_2SO_4$) were baked at 350 °C in an oven for 8 h. Neutral silica gel was sieved though 100-mesh and activated in advance to use.

### Sample extraction and analytical procedure

Five-gram samples were transferred to a cleaned and baked glass centrifuge tube containing 25 mL extraction solvent (acetone and hexane, 1:1 *v*/*v*) for 8 h, and ultrasonicated for 30 min. The liquids were spiked into the isotope surrogate standard filtered twice, and combined and concentrated to 1–2 mL on a rotary evaporator at 40 °C water bath at 80 rpm. Five milliliters of *n*-hexane was added for solvent-change and evaporated to 1 mL. The extract was purified by a column of neutral alumina-neutral silica gel-anhydrous sodium sulfate and made up to 1 mL. To minimize PAE contamination during field sampling and laboratory analysis, all glassware and containers were properly washed and rinsed with solvents and heated at 450 °C for 10 h prior to use; no plastic materials were involved during sampling and extraction procedures.

The extracted compounds were analyzed with an Agilent 6890 N gas chromatograph equipped with an Agilent 5973 N mass spectrometer (GC-MS) (Agilent Technologies, Avondale, PA, USA) operating in electron impact (EI) and selective ion monitoring (SIM) mode. A DB-5MS (Agilent; 30 m × 0.25 mm i.d.; 0.25 μm film thickness) fused-silica capillary column was used for chromatographic separation. The flow rate of the helium carrier gas was held at 1.0 mL $min^{-1}$. Oven temperature program was initiated at 60 °C for 1 min and increased to 220 °C at 20 °C $min^{-1}$, held for 1 min, then to 280 °C at 5 °C $min^{-1}$ and held for 4 min. Splitless mode was performed with a non-pulse injection volume of 1 μL. Each extract and the injector temperature was 250 °C. The GC-MS transfer line was set at 280 °C, and the post run temperature was 285 °C for 2 min.

### Quality analysis and quality control

Quality assurance was simultaneously carried out by analyzing a procedural and solvent blank, a spiked and sample duplicate blank every ten samples, and surrogate standards for each sample. The surrogate recoveries for DnBP-D4 were 86.3 ± 6.8%. The recovery rates of spiked samples of the six target PAEs ranged from 82.4 to 108.9%. The method detection limits of the six target PAEs were 3.75, 4.21, 2.76, 3.53, 6.84, and 4.11 μg $kg^{-1}$ for DMP, DEP, DnBP, BBP, DEHP, and DnOP, respectively. This indicates that the method is capable of determining PAEs at low levels in the agricultural

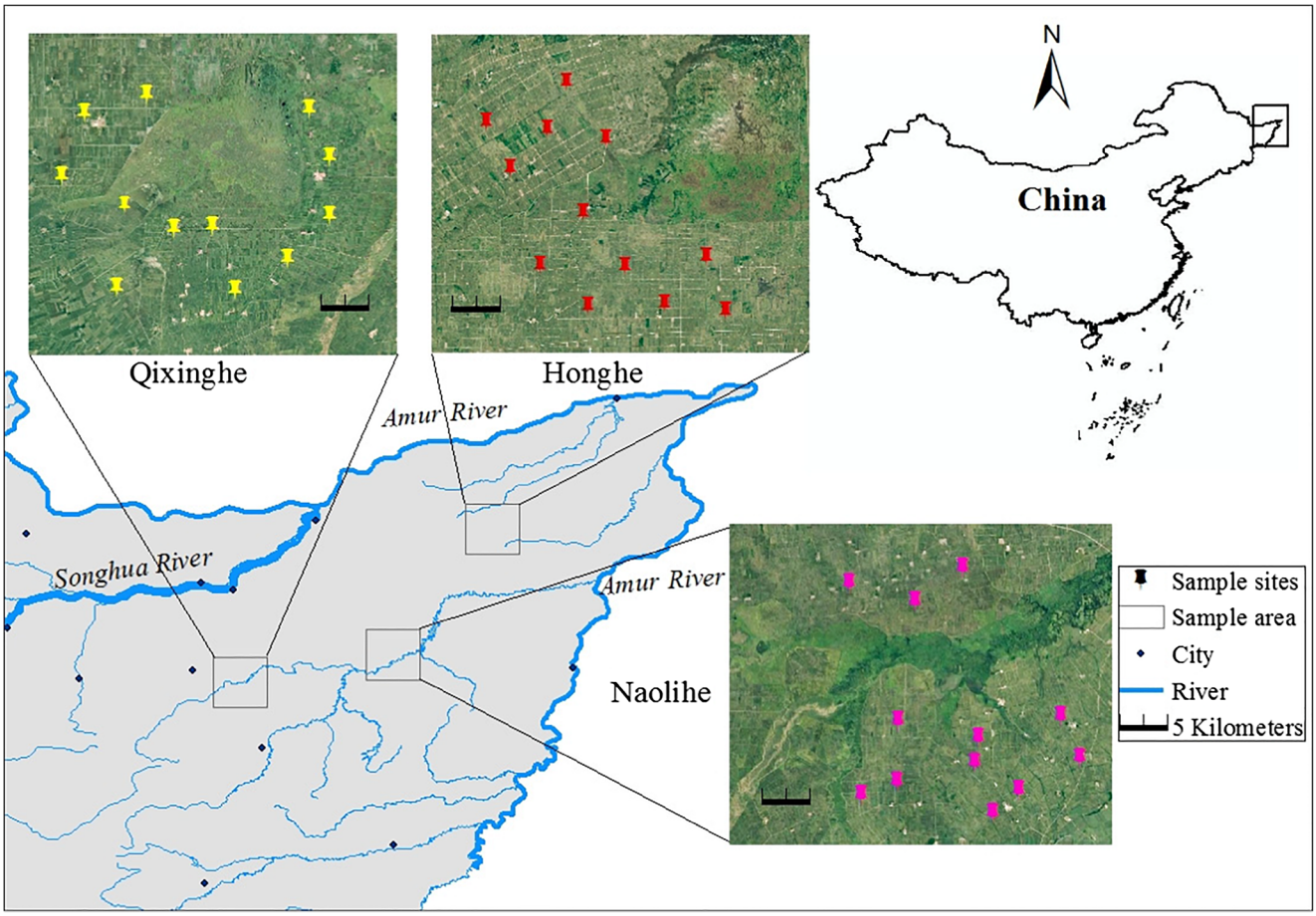


**Fig. 1** Sample sites of three agricultural areas in the Sanjiang Plain, northeast China

soils. Data analysis was conducted using SPSS 17.0 and Origin 8.0; data are presented as means ± standard deviation (SD). Excel 2016 established the Risk Assessment Model.

### Health risk assessment

To assess the potential health risk to inhabitants, non-cancer and carcinogenic risks of PAEs were evaluated based on risk assessment guidelines recommended by USEPA (2013), which have been widely applied in previous studies (Li et al. 2016; Wang et al. 2015a). PAEs can migrate to rice, cucumber, and cabbage, which are crops produced from the respective agricultural soils (Cai et al. 2015; Wang et al. 2016a; Zhao et al. 2015). The present study suggests that the local population eats the food harvested from the soils and is exposed to the soils via dermal and inhalation contact, which are the intake and exposure routines of PAEs to the body. Non-cancer risk assessment induced by PAEs was quantified by the hazard quotient (HQ) value determined by the average daily dosage (ADD, mg $kg^{-1}$ $day^{-1}$) and reference dosage (RfD) of these exposure pathways, including intake, ingestion, dermal absorption, and inhalation. To calculate the average daily dosage (ADD, mg $kg^{-1}$ $day^{-1}$) of these exposure pathways, the equations are listed in Table 1. The hazard quotient (HQ) stands for the health risks of the individual PAEs to human health through various exposure pathways; *j* represents the various exposure pathways. RfD is defined as the daily maximum allowable level of pollutant, including the reference dosage for ingestion and intake via contaminated food (RfDo, mg $kg^{-1}$ $day^{-1}$), the reference dosage for dermal contact ($RfD_{ABS} = RfD_o \times ABS_{GI}$, mg $kg^{-1}$ $day^{-1}$), and the reference dosage via inhalation ($RfC_i$, mg $m^{-3}$). RfCi was assumed equal to $RfD_o$; $ABS_{GI}$ is the portion of pollutant via the gastrointestinal tract absorption (unitless).

$$HQ_j = \frac{ADD_J}{RfD} \quad (1)$$

CR is the carcinogenic risk (unitless), CFS is the slope factor of the carcinogen ((mg $kg^{-1}$ $days^{-1}$)$^{-1}$) comprised of oral slope factors (SFO, (mg $kg^{-1}$ $day^{-1}$)$^{-1}$) for ingestion, dermal contact (SFO × $ABS_{GI}$ (mg $kg^{-1}$ $day^{-1}$)$^{-1}$), and inhalation unit risk (IUR, (mg $m^{-3}$)$^{-1}$).

$$CR_j = ADD_J \times CFS \quad (2)$$

**Table 1** Equations of average daily dosage of pathways

| Human exposure pathways | Average daily dosage equations | Parameters, values, and units |
|---|---|---|
| Intake | $ADD_{intake} = (C_{soil} \times BAF \times IRF \times EF \times ED \times CF) / (BW \times AT)$ | $C_{soil}$, PAEs concentration agricultural soils (mg $kg^{-1}$); BAF, bioaccumulation factor of PAEs from soil to crops; IRF, daily intake of crops (2.0E+06 mg $day^{-1}$); EF, exposure frequency (350 days $year^{-1}$); ED, exposure duration (30 years); BW, body weight (65 kg); AT, lifetime (25,550 days); CF, conversion factor (1.0E−6 kg $mg^{-1}$) |
| Ingestion | $ADD_{ingest} = (C_{soil} \times IRS \times EF \times ED \times CF) / (BW \times AT)$ | IRS, soil ingestion rate (100 mg $day^{-1}$) |
| Dermal absorption | $ADD_{dermal} = (C_{soil} \times SA \times AF \times ABS \times EF \times ED \times CF) / (BW \times AT)$ | SA, soil surface area (5700 $cm^2$ $day^{-1}$); AF, soil adherence factor (0.07 mg $cm^{-2}$); ABS, fraction of contaminant absorbed dermally from the soil (0.1 unitless); |
| Inhalation | $ADD_{inhale} = (C_{soil} \times EF \times ED \times 10^3) / (PEF \times AT)$ | PEF, particles emission factor (1.36E+09 $m^3$ $kg^{-1}$) |

The local inhabitants take an appreciable non-cancer health risk if the HQ value is greater than 1 and very low carcinogenic risk if the CR value is less than $10^{-6}$. For the values of parameters for the risk assessment model, refer to Niu et al. (2014) and Wang et al. (2015a) listed in Table 2.

## Result and discussion

### Occurrence of PAEs in agricultural soils

The total concentrations of six priority control PAEs ($\sum_6$PAEs) in three types of agriculture soils in the Sanjiang Plain are presented in Table 3. The mean value of $\sum_6$PAEs exhibited decreasing order: paddy field (532.1 ± 198.1 μg $kg^{-1}$) > vegetable field (308.2 ± 87.5 μg $kg^{-1}$) > bean field (268.2 ± 48.3 μg $kg^{-1}$). Cultivation practices and management approaches in the agricultural production process may introduce and influence PAE contaminants in agricultural soils (Wang et al. 2013b; Xu et al. 2008). The total concentration of PAEs in paddy fields exhibited the highest levels, this might be explained by more intense anthropogenic disturbance such as the large input of organic fertilizers and more usage of farm machinery (Chen et al. 2013; Teng et al. 2015). Furthermore, a potential source might be derived from the rice seeding process uses of plastic film before being transported to the paddy fields. Across all the agricultural soils, $\sum_6$PAEs ranging from 162.85 to 946.92 μg $kg^{-1}$ with mean values of 369.49 ± 168.85 μg $kg^{-1}$ are below grade II limits of PAEs ($10^4$ μg $kg^{-1}$) for tillable soils as recommended by the Environmental Quality Standard for soil in China (China National Environmental Protection Agency 2008). The fact that PAEs were detected in all soils samples is not unexpected and suggests that they are omnipresent contaminants in the Sanjiang Plain agricultural soils.

**Table 2** Parameters for human risk assessment model

| PAEs | BAF | RfDo | SFO |
|---|---|---|---|
| DMP | 0.108 | 10 | – |
| DEP | 0.108 | 0.8 | – |
| DnBP | 0.108 | 0.1 | – |
| BBP | 0.166 | 0.2 | 1.90E−03 |
| DEHP | 0.166 | 0.02 | 1.40E−02 |
| DnOP | 0.166 | 0.04 | – |

$\sum_6$PAEs in the current study were compared to soils in other regions (Table 4), $\sum_6$PAEs were substantially similar to agricultural soils without film cover at Hebei and Tianjin, central China (Kong et al. 2012; Zhang et al. 2015a), but lower than the black soil collected from greenhouses in northeast China (Zhang et al. 2015b). $\sum_6$PAEs in greenhouse soils were found to be about 1940 to 354,400 μg $kg^{-1}$ in Shandong Province which has a high density urbanized population (Chai et al. 2014). Although none of the soil samples in our study was taken from beneath plastic films or from greenhouses, an abundance of PAEs may have been leached by agricultural mulching film and some frequently used fertilizers. Extensive usage and permanent emissions have yet resulted in their ubiquitous presence in soils (Net et al. 2015; Vikelsøe et al. 2002). PAE concentrations have reached milligram per kilogram in some agricultural regions of China (Li et al. 2016; Niu et al. 2014; Wang et al. 2013a; Zeng et al. 2008). Compared to reported studies in other countries, Chinese agricultural soils have considerably higher PAE concentrations than similar soils in Denmark or in the UK (Gibson et al. 2005; Vikelsøe et al. 2002). Furthermore, economic and urbanization levels might be important factors for PAE concentrations in agricultural soil; PAE levels observed in the Yangtze River Delta and in Guangzhou were considerably higher than in this study (Sun et al. 2016; Zeng et al. 2008). In China, rapidly increasing usage of chemical and developing industrial and agricultural activities might significantly elevate the accumulation of PAEs in soils (Cai et al. 2008; Niu et al. 2014; Zeng et al. 2009). It is worth noting that the prevalence and extensive usages of agricultural plastic

**Table 3** Detection rates and concentrations (μg $kg^{-1}$) of six priority control PAEs in three types agriculture soils

| PAEs | Paddy field | | | | Vegetable field | | | | Bean field | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Detection rate (%) | Mean ± S.D. | Range | Median | Detection rate (%) | Mean ± S.D. | Range | Median | Detection rate (%) | Mean ± S.D. | Range | Median |
| DMP | 100 | 27.8 ± 10.6 | 12.7–48.9 | 27.8 | 100 | 25.2 ± 6.4 | 11.6–34.3 | 26.9 | 100 | 21.2 ± 6.3 | 10.7–29.2 | 21.4 |
| DEP | 100 | 60.3 ± 20.6 | 32.6–97.0 | 61.1 | 100 | 36.4 ± 9.0 | 19.7–46.0 | 39.5 | 100 | 36.1 ± 9.0 | 24.7–58.6 | 35.5 |
| DnBP | 100 | 159.6 ± 91.7 | 15.4–354.2 | 179. 5 | 100 | 70.4 ± 63.1 | 22.1–208.5 | 41.9 | 100 | 29.9 ± 11.6 | 17.9–52.4 | 25.5 |
| BBP | 58.3 | 20.0 ± 22.3 | 0–72.1 | 19.2 | 50.0 | 12.4 ± 16.2 | 0–53.6 | 6.7 | 41.6 | 10.2 ± 12.8 | 0–29.3 | 0 |
| DEHP | 100.0 | 221.5 ± 127.2 | 77.2–583.4 | 202.6 | 100 | 136.5 ± 50.3 | 33.5–217.6 | 138.3 | 100 | 145.4 ± 29.5 | 86.9–187.6 | 154.9 |
| DnOP | 66.7 | 43.4 ± 50.8 | 0–162.5 | 32.4 | 75.0 | 27.4 ± 18.5 | 0–54.3 | 32.7 | 66.7 | 25.5 ± 25.7 | 0–85.4 | 26.825 |
| $\sum_6$PAEs | 100 | 532.1 ± 198.1 | 267.5–946.9 | 531.1 | 100 | 308.2 ± 87.5 | 162.9–468.9 | 299.4 | 100 | 268.2 ± 48.3 | 183.7–336.6 | 263.2 |

*ND* not detected

**Table 4** Contamination of the priority control PAEs in agricultural soils: comparison with other regions (μg $kg^{-1}$)

| Soil types and location | DMP | DEP | DnBP | BBP | DEHP | DnOP | $\sum_6$PAEs | Reference |
|---|---|---|---|---|---|---|---|---|
| Intensive agricultural soils, Sanjiang Plain, China | 10.7–48.9 | 19.7–97.0 | 15.7–354.2 | ND–72.1 | 33.5–583.4 | ND–162.7 | 161.0–946.9 | Present study |
| Greenhouse soils, Beijing, China | 2–23 | 1–360 | 6–1230 | 5–9 | 6–1220 | ND–25 | NG | Li et al. (2016) |
| Agricultural soils, Yangtze River Delta of China | 0.2–71 | 0.5–90.6 | ND–1500 | ND–12.2 | ND–9190 | ND–273 | NG | Sun et al. (2016) |
| Agricultural soils, Hebei, China | ND–34 | 23–34 | 35–54 | ND–116 | 66–263 | ND–69 | 191–457 | Zhang et al. (2015a) |
| Facility agricultural soils, northeast China | 71–453 | 63–851 | 51–950 | 17–139 | 517–2121 | 7.9–151 | NG | Zhang et al. (2015b) |
| Greenhouse soils, Shandong Peninsula, China | ND–1245 | 2–1051 | 16–15,722 | ND–5691 | 73–5323 | ND–14,397 | NG | Chai et al. (2014) |
| Intensive vegetable soils, Nanjing, China | ND-16 | ND–18 | ND–1410 | ND–41 | 34–9030 | ND–7040 | 150–9680 | Wang et al. (2013b) |
| Vegetable soils, Tianjin, China | 2–101 | 2–114 | 13–285 | 0.000–358 | 28–4170 | 0.000–9780 | 5–100,400 | Kong et al. (2012) |
| Agricultural soils, Guangzhou, China | 1–157 | 1–178 | 9–274 | ND–1580 | 107–2940 | ND–84 | 220–33,600 | Zeng et al. (2008) |
| Uncultured soils, Denmark | NA | NA | 21–450 | 0–32 | 12–1900 | 12–67 | NG | Vikelasoe et al. (2002) |
| Soil, UK | 0.1–26 | 0.2–18 | 7.9–8.0 | 0.2–0.8 | 22.2–75.8 | 11.5–13.7 | NG | Gibson et al. (2005) |

*NG* not given, *ND* not detected, *NA* not analyzed

films, fertilizers, and pesticides may possibly result in high contamination of PAEs in agricultural soils.

Among the six PAEs congeners, four, DMP, DEP, DnBP, and DEHP, were detected in all soil samples, and the detection rates of BBP and DnOP were 47.9 and 68.7%, respectively. The average values of individual PAEs exhibited a declining order as DEHP, DnBP, DnOP, DEP, DMP, and BBP. Moreover, DEHP and DnBP were presented in considerably higher concentrations than the other PAEs congeners with concentrations ranging from 33.51 to 583.41 μg $kg^{-1}$ and 15.36 to 354.21 μg $kg^{-1}$, respectively. These distribution patterns were consistent with the widespread use of PAEs as plasticizers. For instance, 134,000 and 394,000 tons of DnBP and DEHP were produced globally (Xu et al. 2008). In addition, Wang et al. (2013a) reported that DnBP and DEHP account for more than 90% of $\sum_6$PAEs (2.95 mg $kg^{-1}$) in commercial organic fertilizers (Wang et al. 2013a). The mean concentrations of DnBP and DEHP in paddy fields were slightly higher than in vegetable and bean fields. This might be distinctly due to the constant cover of water on field surfaces during the growing season. In paddy fields, surface water prohibited air and light irradiation of the PAEs, thereby reducing their abiotic degradation through such processes as hydrolysis, photolysis, and photooxidation. Moreover, this present study showed manifestation that DEHP, DnBP, and DnOP accumulated relatively higher quantities than DMP, DEP, and BBP which are more degradable, but showed lower residual levels compared with other studies conducted with greenhouse or suburban agricultural soils (Chai et al. 2014; Cheng et al. 2015; Kong et al. 2012; Zeng et al. 2008). The lower molecular weights of PAEs such as DEP and DnBP are quite volatile with very low air-water partition coefficient values, so they will volatilize rapidly from bean and vegetable fields but very slowly from paddy fields which are aquatic environments. The biodegradation rate and volatility of DnBP was higher in bean and vegetable fields which were under aerobic conditions (Liu et al. 2010). Generally, soil oxidation-reduction conditions and aerobic microbial activities are also vastly reduced by surface water cover in paddy fields (Wang et al. 2013b). Meanwhile, aerobic biodegradation is the primary mineralization and process for the removal of PAEs in soils (Gao and Wen 2016). DEHP has the highest relative contribution rate to agricultural soils which may be attributed to its physicochemical properties including a relatively high molecular weight, low vapor pressure, low water solubility, and a greater octanol–water partition coefficient, which leads to increased binding with soil organic

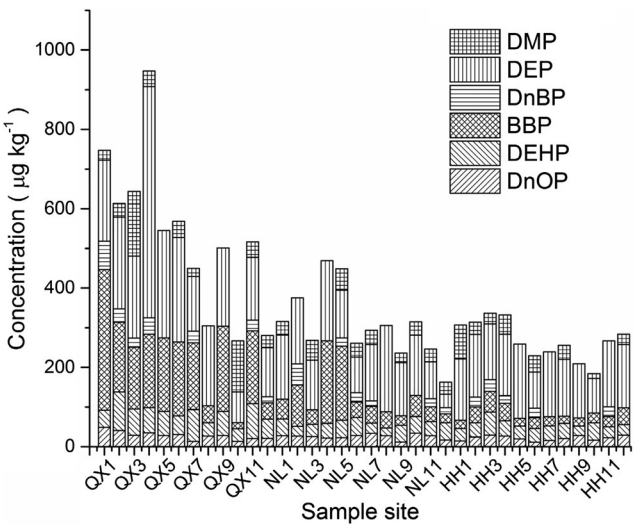


**Fig. 2** PAE concentrations in agricultural soils

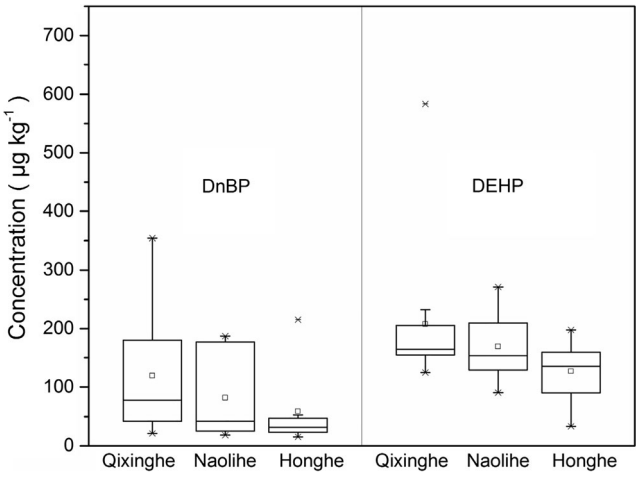


**Fig. 3** Distribution patterns of DnBP and DEHP in different agricultural areas in Sanjiang Plain

carbon (Zeng et al. 2008; Zhang et al. 2015b). DEHP and DnOP had the extremely high residual contaminations in soil from vegetable production systems using plastic films, with ranges of 34–9030 and up to 7040 μg $kg^{-1}$, respectively (Wang et al. 2013a). The distribution patterns of each PAE congeners were lower than in the studies with greenhouse or film-covered soil, but agree with soils under excessive fertilizer and without plastic film (Liu et al. 2010; Zhang et al. 2015a). The difference might be the absence of plastic film, as the PAEs content accounts for a high proportion of the weight in articles of plastic manufacture (Staples et al. 1997; Wang et al. 2013a), and thus the relatively lower concentrations of PAEs in the present study were not unexpected. Previous research has presented the contents of PAEs in a variety of commonly used fertilizers in China. With concentrations up to 2800 μg $kg^{-1}$, DEHP and DnBP accounted for higher proportions and concentrations in organic fertilizers containing organic matter, pesticide, and soil amendments (Mo et al. 2008). Therefore, different field management practices and degradation conditions might be attributed to the different levels of PAEs with cultivation types.

## Distribution of PAEs

Previous studies have reported that the level of residual PAEs in agricultural soils might be affected by the deposition atmospheric of pollutants, the use of agricultural mulching films, wastewater irrigation, the use of sewage sludge, fertilization, the use of poultry manure, and the use of pesticides (Wang et al. 2013a; Zeng et al. 2008, 2009). As Fig. 2 illustrates, $\sum_6$PAEs in soils from different agricultural areas of the Sanjiang Plain varied considerably. Sites QX1 (746.85 μg $kg^{-1}$), QX3 (643.46 μg $kg^{-1}$), and QX4 (946.92 μg $kg^{-1}$) exhibited relatively high levels of PAE contamination. These sites are adjacent to residential areas and compost fertilizers and poultry manure have been used for decades in the Qixinghe agricultural area, for the mean $\sum_6$PAEs 472.32 μg $kg^{-1}$. The mean $\sum_6$PAEs was 346.87 μg $kg^{-1}$ in the Naolihe agricultural areas which is downstream from Qixinghe and further away from residential areas. Meanwhile, samples sites in Qixinghe have been reclaimed for a long period, but samples sites in Naolihe have been reclaimed only in recent years. This distribution pattern was consistent with the cultivation history which could affect the accumulation and distribution processes of PAE residues in agricultural soils (Wang et al. 2013b).

To further understand possible sources of PAEs in the agricultural soils of the Sanjiang Plain, DnBP and DEHP, which are the most dominant PAEs, were compared between different agricultural areas (Fig. 3). They both exhibited similar distribution patterns in Qixinghe and Naolihe, but were lower in Honghe. Atmospheric deposition is known to be an unneglected contamination route; PAEs may be transported long distances via phase transfer into sediments and soils. This has been reported to be the key process for their occurrence in remote regions with less human activities, such as the Arctic Ocean and the Tibetan Plateau (Li et al. 2013; Xie et al. 2007). DnBP and DEHP were the predominant contaminants in atmospheric particulate matters attributed by industrial emissions and biomass burning (Kong et al. 2013; Tsai et al. 2015). There are no permanent residential areas within 10 km in the Honghe agricultural area, and the nearest industries are 60 km away from sample sites in Honghe agricultural areas which exhibited the lowest mean $\sum_6$PAEs value of 289.3 μg $kg^{-1}$. This is consistent with anthropogenic activities having strong associations with PAE residual levels in municipal sewage, domestic sludge, and landfill leachates (Gao et al. 2014; Marttinen et al. 2003; Meng et al. 2014). Significantly high contaminates of PAEs were found in the agricultural district of the Yellow River Delta, where PAEs originated

**Table 5** Hazard quotient to inhabitants from agricultural soils

| Congener | $HQ_{intake}$ | $HQ_{ingest}$ | $HQ_{dermal}$ | $HQ_{inhale}$ |
|---|---|---|---|---|
| DMP | $(6.48 \pm 2.13) \times 10^{-5}$ | $(1.95 \pm 0.64) \times 10^{-8}$ | $(7.79 \pm 2.56) \times 10^{-8}$ | $(9.34 \pm 3.06) \times 10^{-9}$ |
| DEP | $(1.16 \pm 0.46) \times 10^{-4}$ | $(3.50 \pm 1.39) \times 10^{-8}$ | $(1.40 \pm 0.55) \times 10^{-8}$ | $(1.67 \pm 0.66) \times 10^{-8}$ |
| DnBP | $(9.07 \pm 8.62) \times 10^{-4}$ | $(2.73 \pm 2.60) \times 10^{-7}$ | $(1.09 \pm 1.04) \times 10^{-7}$ | $(1.31 \pm 1.24) \times 10^{-7}$ |
| BBP | $(2.98 \pm 3.64) \times 10^{-4}$ | $(8.98 \pm 8.34) \times 10^{-8}$ | $(3.58 \pm 4.37) \times 10^{-8}$ | $(4.29 \pm 5.24) \times 10^{-8}$ |
| DEHP | $(1.76 \pm 0.91) \times 10^{-2}$ | $(5.30 \pm 2.73) \times 10^{-6}$ | $(2.12 \pm 1.09) \times 10^{-6}$ | $(2.54 \pm 1.30) \times 10^{-6}$ |
| DnOP | $(6.74 \pm 7.15) \times 10^{-5}$ | $(2.03 \pm 2.15) \times 10^{-8}$ | $(8.10 \pm 8.59) \times 10^{-9}$ | $(9.70 \pm 0.70) \times 10^{-8}$ |

**Table 6.** Carcinogenic risk to inhabitants from agricultural soils

| | $CR_{intake}$ | $CR_{ingest}$ | $CR_{dermal}$ | $CR_{inhale}$ |
|---|---|---|---|---|
| BBP | $(5.66 \pm 6.91) \times 10^{-8}$ | $(1.71 \pm 2.08) \times 10^{-11}$ | $(6.81 \pm 8.31) \times 10^{-11}$ | $(8.15 \pm 9.95) \times 10^{-12}$ |
| DEHP | $(4.93 \pm 2.53) \times 10^{-6}$ | $(1.49 \pm 0.76) \times 10^{-10}$ | $(5.93 \pm 3.04) \times 10^{-10}$ | $(1.01 \pm 0.52) \times 10^{-13}$ |

from sewage sludge and agricultural wastes (Yang et al. 2013). Furthermore, PAEs ranging from 9.8 to 18.0 mg $kg^{-1}$ were reported in sewage sludge compost of rice straw and 2.24–6.84 mg $kg^{-1}$ in poultry manure (Cai et al. 2007; Wang et al. 2013a). Cultivation practices in the Sanjiang Plain are intensive, with more anthropogenic contamination sources supplying excessive amounts of pesticides and herbicides by aerial spraying (Sun et al. 2012).

### Risk assessment of PAEs

In this study, the non-cancer and carcinogenic risks of PAEs to local inhabitants through dietary and non-dietary routes were evaluated. Table 5 indicates that the non-cancer risks of PAEs via multiple pathways are all within acceptable criteria (HQ <1). Among the different exposure pathways, the intake dietary route was distinctly higher than the non-dietary route, including ingestion, dermal contact, and inhalation pathways. With the individual PAE non-cancer risks, despite the HQ value of DEHP by food, $1.76 \pm 0.91 \times 10^{-2}$ produced from agriculture was close to the threshold. Among the six PAEs congeners, BBP and DEHP exhibited potential carcinogenic risks (Ji et al. 2014). BBP had very low risk by non-dietary routes, and for the intake route the CR value was $5.66 \pm 6.91 \times 10^{-8}$ which is much lower than $1 \times 10^{-6}$. Meanwhile, carcinogenic risk exposure of DEHP via intake route was $4.93 \pm 2.53 \times 10^{-6}$, higher than $1 \times 10^{-6}$, but through non-dietary routes was far less than $1 \times 10^{-6}$ (Table 6). Therefore, DEHP and BBP exhibit potential non-cancer and carcinogenic risks to humans who intake the crops from those agricultural soils.

The results indicate that PAEs in agricultural soils of the Sanjiang Plain have an insignificant non-cancer risk to human health. This is consistent with former reports for other regions (Chen et al. 2012; Niu et al. 2014). The CR value of DEHP via the dietary route ranged from $2.26 \times 10^{-6}$ to $1.71 \times 10^{-5}$ within the low risk criteria which indicated an acceptable exposure scenario. It is in conformity with the risk assessment results of PAEs in greenhouse vegetable soils in Nanjing, and municipal soils in Beijing, where the CR values of DEHP were also below $10^{-4}$ (Li et al. 2016; Wang et al. 2015a). It is worth noting that DEHP, present in all of the agricultural soil samples, showed potential adverse health effects to the local population via the dietary route, which coincides with the report by Niu et al. (2014). Previous research showed that the human food chain could be contaminated via the bioaccumulation process of PAEs in vegetables, rice, and wheat (Fu and Du 2011; Tan et al. 2016; Zhao et al. 2015). Dietary intake is the crucial route of PAEs for humans, particularly for DEHP. Overall, although the human risk assessment of PAEs in agricultural soils was low in the Sanjiang Plain, efforts must be taken to evaluate and minimize the risks to human.

## Conclusion

The PAEs were omnipresent in agricultural soils of the Sanjiang Plain. The results show that DEHP and DnBP are predominant PAEs contaminations. PAE residues exhibited in decreasing order as paddy fields > vegetable fields > bean fields. A comparison with other regions showed that the agricultural soils in the Sanjiang Plain were polluted with PAEs, but their status is relatively low. The distribution of PAEs varied in different agricultural areas, indicating anthropogenic activities such as cultivation practices and industrial emissions may affect the accumulation of PAEs. Furthermore, risk assessment results indicate that the inhabitants of the local agricultural region are primarily at risk from agricultural crop intake by the dietary route. The non-cancer risks were negligible to human health, but carcinogenic risks of DEHP exceeded the threshold limits. Therefore, PAEs pollution in agricultural soils should be paid more attention and should be continually monitored.

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