

Distribution of phthalate esters in topsoil: a case study in the Yellow River Delta, China

Yang Hongjun · Xie Wenjun · Liu Qing · Liu Jingtao · Yu Hongwen · Lu Zhaohua

Received: 21 August 2012 / Accepted: 4 April 2013 / Published online: 24 April 2013
© The Author(s) 2013. This article is published with open access at Springerlink.com

Abstract The Yellow River Delta (YRD) is a typical agricultural and petrochemical industrial area of China. To assess the current status of phthalate esters (PAEs) of soil residues, soil samples (0–20 cm) ($n=82$) were collected in Bincheng District, at the geographic center of the YRD. PAEs were detected in all topsoil samples analyzed, which indicated that PAEs are ubiquitous environmental contaminants. Concentrations of 11 PAEs are in the range of 0.794–19.504 $\mu\text{g g}^{-1}$, with an average value of 2.975 $\mu\text{g g}^{-1}$. It was presented that PAEs pollution in this area was weak and monotonously increasing along the rural–urban gradient. Higher concentrations were observed from roadsides (and/or gutters), densely

anthropogenic activities areas (such as the urbanization and industrialization), and agriculture influence district, which mainly originated from construction waste, municipal sewage, agricultural waste and pesticide, discarded plastic effusion and atmospheric depositions. Concentrations of PAEs were weakly positively correlated with soil organic carbon content and pH, which suggested both of them can affect the distribution of PAEs. The concentration of di (2-ethylhexyl) phthalate and di-*n*-butyl phthalate dominated in the 11 PAEs, with the average values of 0.735 and 1.915 $\mu\text{g g}^{-1}$, respectively, and accounted for 92.1 % of the whole PAEs' concentrations. No significant differences of PAE congener profiles were observed between our work and others previously reported, which is consistent with the use of similar commercial PAEs around the world.

Y. Hongjun (✉) · X. Wenjun · L. Qing · L. Jingtao · L. Zhaohua
Shandong Key Laboratory of Eco-Environmental Science for the Yellow River Delta, Shandong Provincial Engineering and Technology Research Center for Wild Plant Resources Development and Application of Yellow River Delta, Binzhou University,
391, 5th Yellow River Road,
Binzhou City 256603 Shandong Province, China
e-mail: sfyanghongjun@126.com

Y. Hongwen (✉)
Northeast Institute of Geography
and Agricultural Ecology, CAS,
Changchun, People's Republic of China
e-mail: yuhongwen@neigae.ac.cn

L. Zhaohua
Institute of Restoration Ecology,
China University of Mining and Technology,
Beijing, People's Republic of China

Keywords Phthalate esters · PTS · Rural–urban gradient · Yellow River Delta

Introduction

Soil is an important reservoir for many persistent toxic substances (PTS), including polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalate esters (PAEs), and so on. These PTS have been received worldwide attention due to their high resistance to degradation, high bioaccumulation, and having toxic properties (He et al. 2011).

PAEs have been widely used as plasticizers in polyvinyl chloride, polyvinyl acetates, polyurethanes, and cellulose. As non-plasticizers, they are an important

ingredient in flexible vinyl products, such as wiring and cabling, wall covering, and flooring. They could be used in vinyl blood bags and IV tubing used to help save lives as well (Staples et al. 1997). Up to now, the global production is estimated to be several million tons and will continue to increase. As a result, PAEs have become ubiquitous contaminants in various environmental compartment (Zeng et al. 2009; Cendrine et al. 2009; Liu et al. 2010; Yuan et al. 2010; Maraqa et al. 2011; Bradley and Smith 2011; Zhang et al. 2012). Elevated levels for PAEs are detected in different environmental matrices (Fromme et al. 2002; Teil et al. 2006; Zeng et al. 2008). Due to the teratogenicity, carcinogenicity, and mutagenicity (Xu et al. 2008; Liao et al. 2010), both the Environmental Protection Agency (EPA) of the USA and the China State Environmental Protection Administration have listed PAEs as environmental priority pollutants. Three phthalates (diethyl, di-*n*-butyl-, and di-*n*-octyl phthalate esters) are also listed in the black list of China's water priority pollutants by China National Environmental Monitoring Center.

The Yellow River Delta (between 117° 48' and 119° 45'E and 36° 52' and 38° 12'N), one of the largest deltas in China and characterized with a temperate, semi-humid continental monsoon climate, is located in the northeast of Shandong Province on the southern bank of the Bohai Sea (Qi and Luo 2007; Liu and Qi 2011). Recently, high-speed developing in economy promoted this area to an important agricultural and petrochemical area. Cotton, corn, wheat, and vegetables are major products for food source of the growing city population (Midmore and Jansen 2003). Nowadays, concerns have aroused on potential contamination of textiles and foodstuff with toxic contaminants (Midmore and Jansen 2003). Soil PAEs pollution in the region can be strongly influenced by agricultural operations, urbanization, and oil refinery production (Kaisarevic et al. 2007; Khai et al. 2007). It is therefore necessary to evaluate the current residues of PAEs in the region. However, little is known about soil PTS contamination in the YDR (Chen et al. 2012; Wang et al. 2011; Nie et al. 2010). The major purposes of this study were to investigate the concentrations, compositions, and distributions of 11 PAEs in the Bincheng District, an area representative of the YRD, and discuss their contamination profiles and possible sources of PAEs.

Materials and methods

Study area

Bincheng District (Fig. 1) is in Binzhou City, located at the center of the YRD, China, which covers about 740 km². The gross output values of agriculture and petrochemical industry accounted for roughly 10 and 30 % of the total output value, respectively. Soil in this area was derived from alluvial sediments of the Yellow River and is classified as Aquic Inceptisols (CST 2001).

Chemicals and materials

Eleven mono-PAE reference material, containing dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-propyl phthalate (DPRP), diisobutyl phthalate (DiBP), di-*n*-butyl phthalate (DnBP), di-*n*-pentyl phthalate (DnAP), di-*n*-hexyl phthalate (DnHP), benzyl butyl phthalate (BBP), di (2-ethylhexyl) phthalate (DEHP), di-*n*-nonyl phthalate (DnNP), and di-*n*-octyl phthalate (DnOP), were purchased from Dr. Ehrenstorfer (Augsburg, Germany) and were used to prepare a mixture solution of 1,000 µg mL⁻¹.

Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were cleaned with methanol (MeOH), dichloromethane (DCM), and *n*-hexane, respectively, using Soxhlet extractor for 72 h, activated at 180±1 and 250±1 °C for 12 h, and subsequently deactivated with 3 % (w/w) of deionized water (extracted with DCM/*n*-hexane), respectively. Anhydrous sodium sulfate was baked at 450 °C for 4 h and stored in sealed glass jars. Filter paper was extracted with methanol, DCM, and *n*-hexane with Soxhlet extractor for 72 h prior to use. To avoid contamination, no plastic equipment was used during sampling and processing. Water was filtered by Milli-Q and double distilled. All organic solvents used were of analytical grade and redistilled with glass system. All the laboratory glass apparatus were soaked in K₂Cr₂O₇ sulfuric acid solution for at least 12 h and rinsed with organic-free reagent water thoroughly and finally baked at 180 °C for 4 h.

Soil sampling and preparation

Topsoil samples (0~20 cm) (*n*=82) were collected from urban, suburban, and rural areas in September 2009, using a stainless steel shovel. Sample location coordinates were recorded with a handheld GPS receiver (Fig. 1). In the

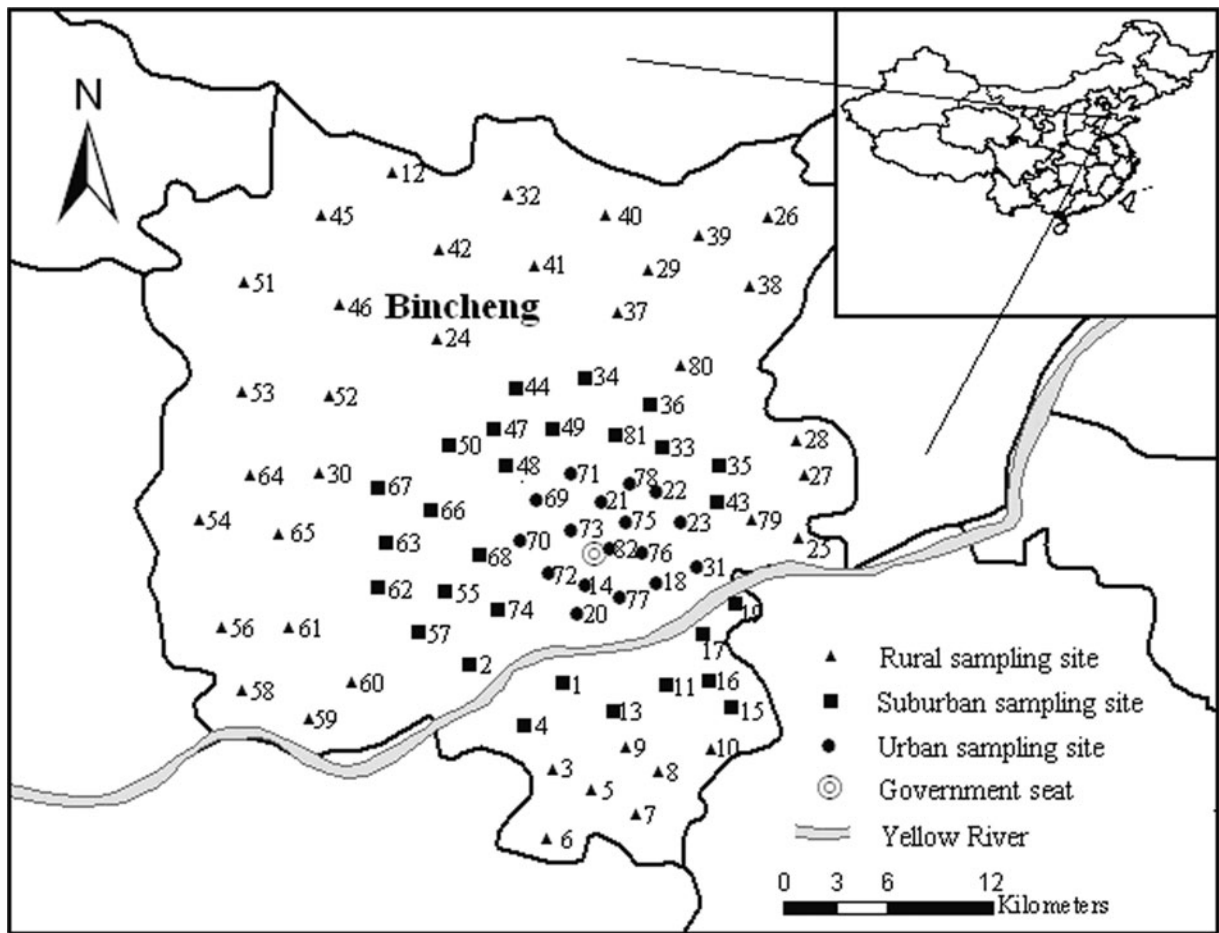


Fig. 1 Map of soil sampling sites for PAEs analysis in Bincheng District

rural and suburban areas, samples were mainly collected from farmland and woodland, and in the urban areas, samples were collected from residential, commercial, and industrial land. Samples were put into solvent-rinsed brown glass bottles with a Teflon cap and stored frozen ($-20\text{ }^{\circ}\text{C}$) until analysis. Before extraction, soil samples were freeze-dried and sieved to less than 2 mm.

Sample extraction and cleanup

Extraction of 11 PAEs congeners was conducted based on the method of Antoinette et al. (2009). Soil samples were extracted with dichloromethane/acetone (1:1 v/v) using a speed extractor (E-916, Büshi). A 5-g dry sample was mixed with 10 g of sand and placed in a 20-mL extraction cell with a temperature and pressure of $110\text{ }^{\circ}\text{C}$. The pressures employed were 1,500 psi for each protocol. The extraction stages were preheated 5 min, static solvent

extraction time 1 min, purge 2 min, and static cycle ($n=3$) 10 min. High-purity nitrogen was employed as the purge gas. The extracts were separated and concentrated to around 1 mL using rotary evaporation, and then concentrated extracts were cleaned and fractionated on a 10-mm i.d. 1:2 alumina/silica gel glass column packed, from the bottom to top, with neutral silica gel (12 cm), neutral alumina (6 cm), and anhydrous sodium sulfate (1 cm). The concentrated extracts were added into the column and washed with 40 mL of hexane. Then, PAEs were eluted with 40 mL mixed solvent of acetone/*n*-hexane (2:8, v/v). The extracts were concentrated using rotary evaporator and reduced to 1 mL under a stream of purified N_2 .

Instrumental analysis

The extracted compounds were determined with an Agilent 7890N gas chromatography coupled to an

Agilent 5975 mass spectrometer (GC-MS) (Agilent Technologies, Avondale, PA, USA), operating in electron impact and selective ion monitoring modes, and a HP-5MS capillary column (30 m×0.250 mm i.d., 0.25 µm film thickness; J&W Scientific). The transfer line and the ion source temperature were maintained at 280 and 230 °C, respectively. The column temperature program was initiated at 60 °C for 1.0 min, increased to 220 °C at a rate of 20 °C min⁻¹, held for 1.0 min, and finally ramped at 5 °C min⁻¹ to 250 °C and held for 9 min. The flow rate of the carrier gas helium was kept constant at 1.0 mL min⁻¹. The extracts (1.0 µL) were injected onto GC-MS in splitless mode with an inlet temperature of 250 °C.

Quantitative analysis was performed using the external calibration method based on five-point calibration curve for individual PAEs. Peak areas were calculated using Agilent ChemStation software. PAEs concentrations in this study are based on dry soil weights.

Quality control and quality assurance

Blanks covering the entire analytical procedure, from the extraction to GC analysis, were analyzed. Method blank was firstly run. The matrix blanks, the recoveries of PAEs, and the limits of detection were based on the measures of the deep layer soil samples from the rural area of Binzhou City, which was free of any interference for the target component. Only small concentrations of DnBP and DEHP were found in procedural blanks, and they were appropriately subtracted from those in the sample extracts. The instruments were calibrated daily with calibration standards. In addition, the average recovery experiments were done in triplicate by spiking the mixed standards with known amount of the PAEs in a matrix blank for each compound. Average recovery for PAEs varied from 85.0 to 110.0 %, and relative standard deviations for each compound were all below 15 %. Instrumental detection limits using the present methods were calculated by signal to noise ratio of 10 and ranged from 0.2 to 2.5 ng g⁻¹. The method detection limits (MDLs) were derived from the blanks and quantified as mean field blanks plus three times the standard deviation (3σ) of field blanks.

Soil TOC, TN, and pH analyses

Total organic carbon (TOC) and total nitrogen (TN) of the soil samples was measured with an Elementar

vario EL III elemental analyzer (Germany). Soil pH was measured by pH meter with a soil/water ratio of 1:2.5.

Statistical analysis

All statistical analysis was conducted using SPSS 11.0 for Windows. To detect significant differences for PAEs concentrations among areas and land uses, ANOVA and least significant difference were calculated. All significant differences reported are $p \leq 0.05$.

Results and discussion

Major characteristics of the soils

The properties of the collected soils, including pH, TOC, TN, and C/N ratio are presented in Table 1. The pH (H₂O) in the soils is all weakly basic, with a mean value of 7.88. The soil salinity owes much to the geographic position and pressures of human being activities, such as, annual rainfall is lower than evaporation, bricks and construction debris included in the soil all could increase the pH (Biasioli et al. 2006; Liu and Qi 2011). The content of total organic carbon and total nitrogen in the soil ranged from 0.72 to 2.05 % and 0.06 to 0.42 %, with higher mean values mostly resulted from the roadsides or gutters.

Concentrations of PAEs in the soils

The individual concentrations of 11 PAEs in the topsoil from Bincheng District of Yellow River Delta are shown in Table 2 and Fig. 2. PAEs were detected in all the topsoil samples analyzed, which indicated that PAEs were ubiquitous environmental contaminants. The total contents of the 11 PAEs varied considerably, ranging from 0.794 to 19.504 µg g⁻¹, with an average value of 2.975 µg g⁻¹. The contents of 11 PAEs in the soil samples of Bincheng District in Yellow River Delta are higher than that of Jiang Han Plain (Liu et al. 2010) (Σ16PAEs ranged from 252.6 to 2,515.7 ng g⁻¹) in China and are lower than that of urban (Zeng et al. 2009) (Σ16PAEs ranged from 1.67 to 322 µg g⁻¹) areas around Guangzhou, China, and are equivalent to peri-urban (Zeng et al. 2008) (Σ16PAEs ranged from 0.195 to 33.6 µg g⁻¹) around Guangzhou City. Σ6EPA-PAEs in the studied area accounted for 94.7 % of the total 11

Table 1 The main characteristics of Bincheng District soils in Yellow River Delta

Soil properties	Urban (n=17)			Suburb (n=28)			Rural (n=37)					
	Range	Mean±SD	Median	DF	Range	Mean±SD	Median	DF	Range	Mean±SD	Median	DF
pH (H ₂ O)	7.58–8.15	7.92±0.241	7.91	100	7.48–8.21	7.93±0.280	7.92	100	7.55–8.09	7.82±0.189	7.76	100
TOC (%)	0.78–2.04	1.21±0.349	1.13	100	0.72–2.05	0.99±0.225	0.95	100	0.74–1.94	0.95±0.212	0.91	100
Total nitrogen (%)	0.06–0.42	0.14±0.088	0.13	100	0.06–0.17	0.12±0.025	0.11	100	0.07–0.16	0.11±0.020	0.11	100
C/N ratio	4.07–16.48	10.14±3.256	9.73	100	5.72–13.78	8.75±1.826	8.35	100	6.31–11.83	8.67±1.487	8.45	100

Reported data were corrected by subtracting the mean blank values
 DF detectable frequency (percent)

PAEs. Significantly, the most high concentrations of Σ11PAEs in the study area were observed from roadsides (and/or gutters), which resulted from the accumulation of the contaminants washed off from roofs and/or grounds (Zeng et al. 2009). Another partial high concentrations of Σ11PAEs sites probably resulted from the densely anthropogenic activities or influence of industry and agriculture.

Among the 11 PAEs studied, DMP, DiBP, DnBP, DnHP, and DEHP were present in all samples with average contents of 0.030, 0.086, 0.735, 0.035, and 1.915 μg g⁻¹, respectively. DEP was with detectable frequencies (DF) of 51.2 %, and its average content was 0.138 μg g⁻¹. Other PAEs had low DF and contents. So, the dominant PAEs species in the topsoil samples from Bincheng District of Yellow River Delta are DEHP, DnBP, DiBP, DMP, and DEP. DEHP and DnBP in the studied area accounted for 92.1 % of the total 11 PAEs. The high fraction of DEHP and DnBP was similar to the composite characteristic of PAEs detected in various environmental matrix (Zhao et al. 1987; Ma et al. 2003a, b). There were no DnAP and BBP in all the soils. In JiangHan Plain, peri-urban and urban areas around Guangzhou, DnBP, DEHP, DiBP, DMP, and DEP were dominant PAEs congeners, whereas DMP, DiBP, DnBP, and DEHP were also present in all the soil samples (Zeng et al. 2008, 2009).

In Bincheng District of Yellow River Delta, the contents of DEHP ranged from 0.431 to 6.320 μg g⁻¹, with an average value of 1.902 μg g⁻¹, which were higher than that in the soil samples from other areas of China (Zeng et al. 2008; Liu et al. 2010) and lower than partly areas of China (Ma et al. 2003a, b; Cai et al. 2005; Zeng et al. 2009). They were comparable to 23 arable soils throughout China (Hu et al. 2003; Li et al. 2006). DnBP contents in this study were from 0.136 to 2.058 μg g⁻¹, with an average of 0.735 μg g⁻¹, which are equivalent to the peri-urban areas around Guangzhou, China (Zeng et al. 2008), and higher than that in Jiang Han Plain (Liu et al. 2010), Netherlands (Peijnenburg and Struijs 2006), and Denmark (Vikelsøe et al. 2002) and lower than urban soils of Guangzhou City (Zeng et al. 2009) and Taizhou City of China (Liu et al. 2009). DiBP does not belong to priority pollutants, so there are limited reports about it in soils abroad even though it is ubiquitous in the environment (Zheng et al. 2007; Zeng et al. 2008, 2009; Liu et al. 2010). DiBP showed contents from 0.007 to 0.526 μg g⁻¹, with an average of

Table 2 Summary of the individual concentrations of PAEs (in microgram per gram dry weight) in Bincheng District soils of Yellow River Delta

PAEs	Urban (<i>n</i> =17)				Suburb (<i>n</i> =28)				Rural (<i>n</i> =37)			
	Range	Mean±SD	Median	DF	Range	Mean±SD	Median	DF	Range	Mean±SD	Median	DF
DMP	0.002–0.060	0.030±0.005	0.038	100	0.001–0.065	0.027±0.004	0.037	100	0.001–0.005	0.032±0.003	0.040	100
DEP	ND–0.004	0.001±0.001	0	47.1	0.001–11.239	0.353±0.351	0.002	100	ND–0.001	0	0	16.2
DPRP	ND–0.002	0	0	29.4	ND–1.709	0.053±0.051	0	39.3	ND	0	0	0
DiBP	0.015–0.123	0.049±0.008	0.040	100	0.007–0.526	0.104±0.021	0.069	100	0.040–0.514	0.089±0.015	0.075	100
DnBP	0.245–2.058	1.392±0.142	1.613	100	0.166–1.450	0.657±0.067	0.629	100	0.136–1.039	0.413±0.047	0.330	100
DnAP	ND	0	0	0	ND	0	0	0	ND	0	0	0
DnHP	0.016–0.019	0.018±0.001	0.018	100	0.016–1.227	0.061±0.378	0.016	100	0.016–0.100	0.019±0.001	0.016	100
BBP	ND	0	0	0	ND	0	0	0	ND	0	0	0
DEHP	1.465–6.320	3.399±0.323	3.200	100	0.710–4.473	2.701±0.172	1.442	100	0.431–2.449	1.224±0.105	1.128	100
DnNP	ND–0.001	0	0	17.6	ND–0.122	0.005±0.003	0	17.9	ND	0	0	0
DnOP	ND–0.044	0.011±0.003	0	41.2	ND–0.142	0.025±0.008	0	25.0	ND–0.068	0.005±0.001	0	16.2
ΣEPA-PAEs	1.987–8.454	4.832±0.966	4.722	100	1.007–16.007	2.765±0.105	2.179	100	0.716–3.251	1.674±0.325	1.472	100
Σ11PAEs	2.096–8.527	4.899±0.187	4.764	100	1.076–19.504	2.988±0.116	2.366	100	0.794–3.461	1.782±0.357	1.565	100

Reported concentrations were corrected by subtracting the mean blank values

DF detectable frequency (in percent), ND concentration was lower than the MDL

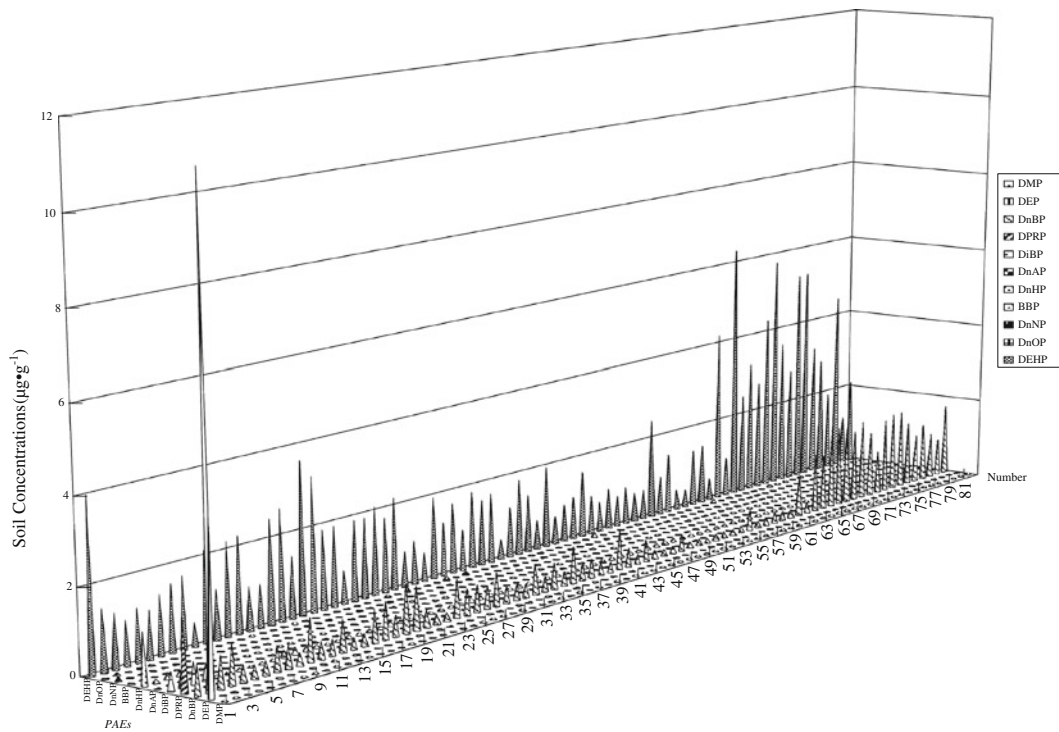


Fig. 2 Concentrations of 11 PAEs (in microgram per gram dry weight) congeners in Bincheng District soils of Yellow River Delta

0.086 $\mu\text{g g}^{-1}$, which is relatively higher than that of Panyu District, Tianhe District, Liwan District, and Baiyun District of Guangzhou City (Zeng et al. 2009) and Jiang Han Plain (Liu et al. 2010) and are lower than urban soil of Beijing (Li et al. 2006) and peri-urban soils of Guangzhou City (Zeng et al. 2008). This was in consistent with the fact that there are more abundant usages of DEHP, DnBP, and DiBP as plastic additives in China. Other PAEs have very low contents or below the MDL.

Because of no data were available on past levels of PAEs in this area, no conclusion can be made about temporal changes in PAEs levels in the soils of Bincheng District in Yellow River Delta.

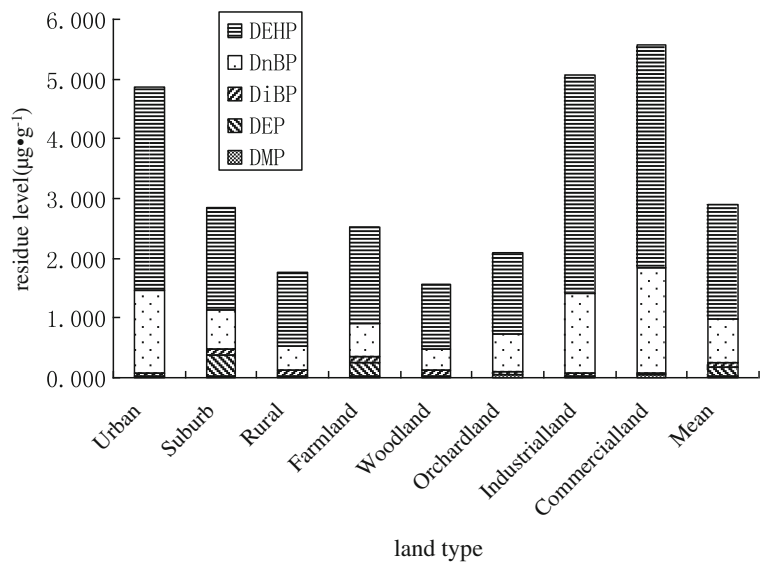
PAEs congener profiles and distribution in the soils

Dominant PAEs concentrations and distribution in top-soil from different areas and land use in Bincheng District of Yellow River Delta are shown in Table 2 and Fig. 3. Figure 3 presented the geographical distribution of the total 11 PAEs concentrations in the soils from the Bincheng District of Yellow River Delta, showing that a decreasing trend exists following the

distance away from the urban center of Binzhou City. Along the rural–urban gradient, PAEs concentrations increased significantly (Fig. 3). In the urban, suburban, and rural samples, the five dominant PAEs showed average contents of 4.899, 2.988, and 1.782 $\mu\text{g g}^{-1}$, respectively. PAEs concentrations in urban soil were about three times higher than those in rural soil and were twice higher than in suburban soil. The increased trend was obvious for DEHP and DnBP. The result above indicated that PAEs probably have caused serious contamination to urban soil in Binzhou City. It was worth nothing that DnBP, DEHP, $\Sigma 6\text{EPA-PAEs}$, and $\Sigma 11\text{PAEs}$ in urban soil were much higher than those in rural soil, probably reflecting the significant effect of anthropogenic activities, such as the urbanization and industrialization. The similar results were reported at soil (Li et al. 2006) and atmosphere (Zhao et al. 1987) of Beijing, where the level of PAEs in urban area was much higher than that in the rural area.

From the Fig. 3, it could be concluded that the difference of dominant PAEs concentrations between different kinds of land types existed. The result showed that the average total contents of the five dominant PAEs for commercial land, industrial land, farm land, orchard

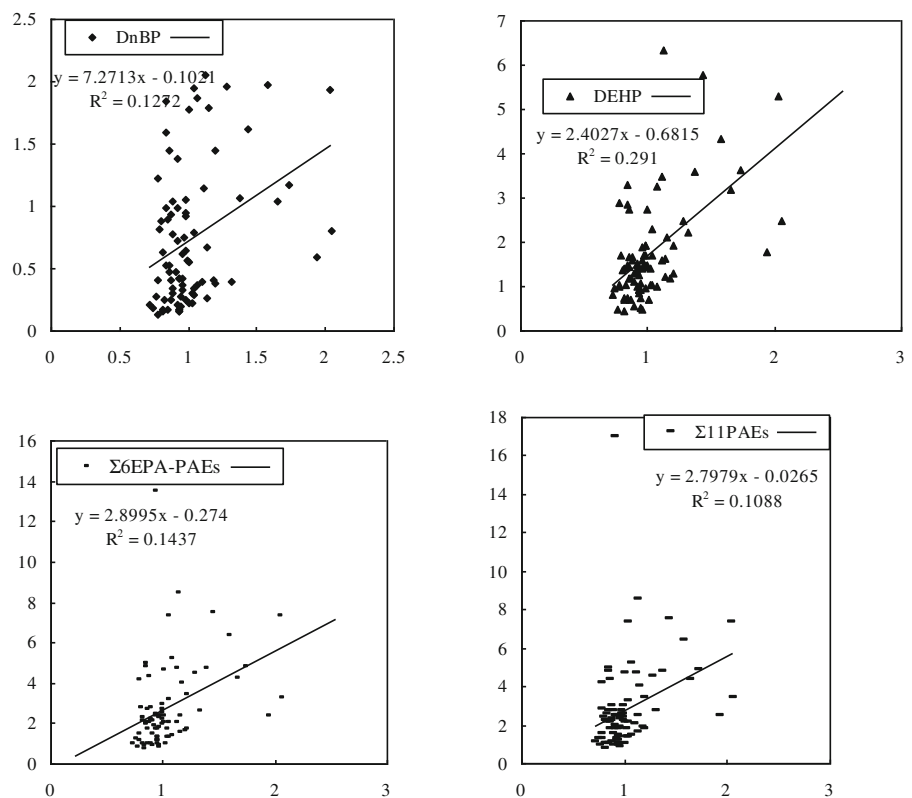
Fig. 3 Dominant PAEs concentrations and distribution in topsoil from different areas and land use in Bincheng District



land, and wood land are 5.566, 5.055, 2.521, 2.092, and 1.555 $\mu\text{g g}^{-1}$. Obviously, the higher PAEs concentrations were found in commercial and industrial areas, which was now the architectural area, where a significant amount of the used plastic materials (including floor lacquers, wrapping materials, wall papers, tiles,

and synthetic leathers) were discarded, and a large industrial complex comprising chemical manufacturing factories located in the field, and a lot of cosmetics and plastic living supplies were used in this area. Next was farmland and orchard land, and there was no obvious difference between them. Residual levels of PAEs are

Fig. 4 Correlations of PAEs (DnBP, DEHP, $\Sigma 6\text{EPA-PAEs}$, $\Sigma 11\text{PAEs}$) concentrations with the proportion of total organic carbon (TOC) in Bincheng District soils of Yellow River Delta



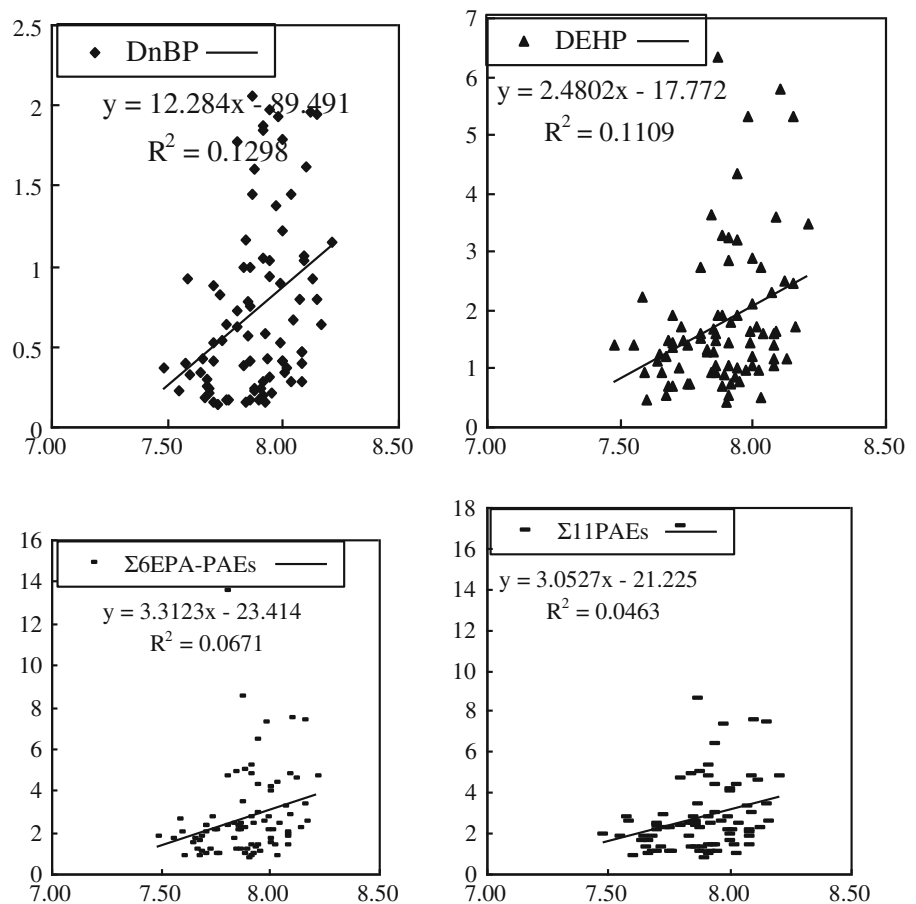
affected by application history and agricultural practices (Boul et al. 1994). Hence, this difference reflected intensive agricultural activities and more PAEs input in this area as compared to the woodland region. Dominant PAEs concentrations in farmland and orchard land soil was visibly higher than in woodland soil, which suggested that PAEs mainly originated from agricultural production in the farmland and orchard land area, such as plastic mulching for cotton, greenhouse for vegetables, apple bagging, and applications of pesticide.

The concentration and distribution features of PAEs in the study soils were subject to the urbanization process, agricultural plastic films, petroleum and chemical pollution and sewage sludge in the study area, human activities, agricultural practices, soil communities as well as meteorological factors such as rainfall and temperature, etc. PAEs in the soil may transfer to lower horizons or stay in the surface soil, and both can cause long-term harm to human health and ecosystem.

Correlation: PAE vs. TOC and PH

Various factors determine the distribution, air-to-soil transport, and fate of organic pollutants in soils. Soil organic matter has been shown to be important in mobility of hydrophobic organic contaminants (HOCs) in soil (Cousins et al. 1999; Wang et al. 2006). PAEs are hydrophobic and more likely to be adsorbed by soil organic matter. As a result, the content of TOC could affect the PAEs concentrations in soils. As shown in Fig. 4, correlation coefficient (R^2) ranged from 0.11 for $\Sigma 11$ PAEs to 0.29 for DEHP ($n=82$), which indicated a weakly positive correlation between PAEs and TOC in the investigated soils. However, another individual PAE species correlated with TOC at the insignificant levels. This proved that TOC can affect the distribution of PAEs in this area. Similar results were also reported by Zeng et al. (2008) and Agarwal and Bucheli (2011). A key character for soil–air partitioning of PAEs is their vapor pressure (Lu 2009). This parameter determines a

Fig. 5 Correlations of PAEs (DnBP, DEHP, $\Sigma 6$ EPA-PAEs, $\Sigma 11$ PAEs) concentrations with the pH in Bincheng District soils of Yellow River Delta



compound's vapor particle partitioning and thus the fraction that is available for long-range atmospheric transport and phase transfer into soil organic matters. As shown in the text, PAE profile in this study was characterized by the dominance of DnBP and DEHP, which accordingly resulted in the weakly correlation between TOC and Σ PAEs.

The pH of soils in the study area ranged from 7.48 to 8.21, with an average of 7.88. A weak positive correlation of the DnBP, DEHP, Σ 6EPA-PAEs, and Σ 11PAEs concentrations and pH was observed in the investigated soils (Fig. 5). The correlation coefficient (R^2) ranged from 0.05 for Σ 11PAEs to 0.13 for DnBP ($n=82$). Similar positive relationships between pH and HOCs were also observed in the forest soils in Germany (Wenzel et al. 2002), urban soil in Hong Kong (Zhang et al. 2006) and Guangzhou peri-urban soils of China (Zeng et al. 2008). pH can affect the HOCs in soils through the influence of the structure of humus (Wenzel et al. 2002).

Potential risk assessment of the soil

The concentrations of PAEs detected in the present study were used to assess the potential risk from the topsoils from Bincheng District of Yellow River Delta by comparing with the soil cleanup guidelines used in New York, USA (Department of Environmental Conservation 1994), due to the shortage of local standard for identifying soil pollution.

In all the soil samples from Bincheng District of Yellow River Delta, DnBP concentrations greatly exceeded the recommended allowable soil concentration for DnBP used in New York, USA ($0.081 \mu\text{g g}^{-1}$). The concentrations of DEHP in the study area, which was very close to the urban soil of Beijing, such as sampling sites 67, 72, 75, 76, and 80 (Fig. 1), where are nearby a construction site and refuse processing plant, were exceeding the recommended allowable soil concentrations ($4.35 \mu\text{g g}^{-1}$). Data showed that 69.5 % of the samples for DMP exceeded the recommended allowable soil concentrations ($0.02 \mu\text{g g}^{-1}$). DEP and DnOP concentrations in all the soil samples were far below the recommended allowable soil concentrations, 0.071 and $1.20 \mu\text{g g}^{-1}$, respectively, except site 1, which was nearby the Yellow River. The maximum values of DMP, DEP, DnBP, and DEHP occurred in the study area soils were over 1.5–158 times higher than above the recommended allowable soil concentrations used in New York, USA. However, compared with PAEs cleanup standard set for USA soils,

which is $2.0 \mu\text{g g}^{-1}$ for DMP, $7.1 \mu\text{g g}^{-1}$ for DEP, $8.1 \mu\text{g g}^{-1}$ for DnBP, and $50.0 \mu\text{g g}^{-1}$ for DEHP. In whole, all of these concentrations for individual PAE congeners in this study were far below the recommended soil cleanup levels used in New York, USA. It implied that no remediation measures were taken with respect to PAEs in the topsoils from Bincheng District of Yellow River Delta. However, the ecological and health effects of these PTS through food chain at the relatively lower concentrations still need further attention according to their possible biological magnifications.

Conclusion

This study has provided the firsthand data on the levels of the 11 PAEs in the topsoil from Bincheng District of Yellow River Delta. The total contents of the 11 PAEs varied considerably, ranging from 0.794 to $19.504 \mu\text{g g}^{-1}$, with an average value of $2.975 \mu\text{g g}^{-1}$, which were classified as weak pollution on the whole, with several sites in the urban area reaching the moderate and severe levels. Along the rural–urban gradient, PAEs concentrations increased significantly. The extent of PAEs pollution in the agricultural soils was far below the recommended values in soil cleanup guidelines used in New York, USA. The high concentrations were observed from roadsides (and/or gutters), densely anthropogenic activities areas (such as the urbanization and industrialization), and agriculture influence district, which mainly originates from construction waste, municipal sewage, agricultural waste and pesticide, discarded plastic effusion, and atmospheric depositions. Both the soil organic carbon content and pH can affect the distribution of PAEs. DEHP, DnBP, DiBP, DMP, and DEP are the most abundant PAEs. DEHP and DnBP, as the dominant PAEs in the studied area, accounted for 92.1 %. No significant differences of PAE congeneric profiles were observed between our work and others previously reported, which is consistent with the use of similar commercial PAEs around the world. Moreover, data on PAEs in the Yellow River Delta are processed for more accurate evaluation.

Acknowledgments This work was financially supported by The National Key Technology R&D Program of China (grant no. 2011BAC02B01-05), the Scientific Award Fund for the Excellent Middle-Aged and Young Scientists of Shandong Province (2008BS09024), Binzhou University research project (BZXYFB20110501), and Shandong Province “Yellow and Blue” construction special funds project (no. 2011-huang-19).

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

Agarwal, T., & Bucheli, T. D. (2011). Is black carbon a better predictor of polycyclic aromatic hydrocarbon distribution in soils than total organic carbon? *Environmental Pollution*, *159*, 64–70.

Antoinette, M. R., Brougham, C. A., Fogarty, A. M., & Roche, J. J. (2009). Accelerated solvent-based extraction and enrichment of selected plasticizers and 4-nonylphenol, and extraction of tin from organotin sources in sediments, sludges and leachate soils. *Analytica Chimica Acta*, *634*, 197–204.

Biasioli, M., Barberis, R., & Ajmone-Marsan, F. (2006). The influence of a large city on some soil properties and metals content. *Science of the Total Environment*, *356*, 154–164.

Boul, H. L., Garnham, M. L., Hucker, D., Baird, D., & Aislabie, J. (1994). Influence of agricultural practices on the levels of DDT and its residues in soil. *Environmental Science and Technology*, *28*, 1397–1402.

Bradley, O. C., & Smith, S. R. (2011). Review of ‘emerging’ organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. *Environment International*, *37*, 226–247.

Cai, Q. Y., Mo, C. H., Li, Y. H., Zeng, Q. Y., Wang, B. G., Xiao, K. E., Li, H. Q., & Xu, G. S. (2005). Preliminary study of PAEs in soils from typical vegetable fields in areas of Guangzhou and Shenzhen, South China. *Acta Ecol Sin*, *25*, 283–288 (in Chinese).

Cendrine, D., Teil, M. J., Chevreuil, M., & Blanchard, M. (2009). Phthalate removal throughout wastewater treatment plant: case study of Marne Aval station (France). *Science of the Total Environment*, *407*, 1235–1244.

Chen, C., Zhao, H., Chen, J., Qiao, X., Xie, Q., & Zhang, Y. (2012). Polybrominated diphenyl ethers in soils of the modern Yellow River Delta, China: occurrence, distribution and inventory. *Chemosphere*, *88*(7), 791–797.

Chinese Soil Taxonomy Research Group (CST), Li, F. (ed) (2001) Chinese Soil Taxonomy. Beijing: Science.

Cousins, I. T., Gevaio, B., & Jones, K. C. (1999). Measuring and modelling the vertical distribution of semivolatile organic compounds in soils. I: PCB and PAH soil core data. *Chemosphere*, *39*, 2507–2518.

Department of Environmental Conservation (1994) New York, USA, determination of soil cleanup objectives and cleanup levels (TAGM 4046). <http://www.dec.ny.gov/regulations/2612.html>.

Fromme, H., Kqchler, T., Otto, T., Pilz, K., Mqller, J., & Wenzel, A. (2002). Occurrence of phthalates and bisphenol A and F in the environment. *Water Research*, *36*, 1429–1438.

He, H., Hu, G. J., Sun, C., Chen, S. L., Yang, M. N., Li, J., Zhao, Y., & Wang, H. (2011). Trace analysis of persistent toxic substances in the main stream of Jianguo section of

the Yangtze River, China. *Environmental Science and Pollution Research*, *18*, 638–648.

Hu, X. Y., Wen, B., & Shan, X. Q. (2003). Survey of phthalate pollution in arable soils in China. *Journal of Environmental Monitoring*, *5*, 649–653.

Kaisarevic, S., Andric, N., Bobic, S., Trickovic, J., Teodorovic, L., Vojinovic-, M. M., & Kovacevic, R. Z. (2007). Detection of dioxin-like contaminants in soil from the area of oil refineries in Vojvodina region of Serbia. *Bull. Environ. Contam. Toxicol*, *79*, 422–426.

Khai, N. M., Ha, P. Q., & Öborn, I. (2007). Nutrient flows in small-scale peri-urban vegetable farming systems in Southeast Asia—a case study in Hanoi. *Agriculture, Ecosystems & Environment*, *122*, 192–202.

Li, H. X., Ma, L. L., Liu, X. F., Fu, S., Cheng, H. X., & Xu, X. B. (2006). Phthalate ester pollution in urban soil of Beijing, People’s Republic of China. *Bulletin of Environmental Contamination and Toxicology*, *77*, 252–259.

Liao, T. T., Shi, Y. L., Jia, J. W., & Wang, L. (2010). Sensitivity of different cytotoxic responses of vero cells exposed to organic chemical pollutants and their reliability in the bio-toxicity test of trace chemical pollutants. *Biomedical and Environmental Sciences*, *23*(3), 219–229.

Liu, X., & Qi, S. (2011). Wetlands environmental degradation in the Yellow River Delta, Shandong Province of China. *Procedia Environmental Sciences*, *11*, 701–705.

Liu, W. L., Shen, C. F., Zhang, Z., & Zhang, C. B. (2009). Distribution of phthalate esters in soil of e-waste recycling sites from Taizhou City. *China*, *82*, 665–667.

Liu, H., Liang, H., Liang, Y., Zhang, D., Wang, C., Cai, H., & Shvartsev, S. L. (2010). Distribution of phthalate esters in alluvial sediment: a case study at JiangHan Plain, Central China. *Chemosphere*, *78*, 382–388.

Lu, C. (2009). Prediction of environmental properties in water–soil–air systems for phthalates. *Bulletin of Environmental Contamination and Toxicology*, *83*, 168–173.

Ma, L. L., Chu, S. G., & Xu, X. B. (2003a). Phthalate residues in greenhouse soil from Beijing suburbs, People’s Republic of China. *Bulletin of Environmental Contamination and Toxicology*, *71*, 394–399.

Ma, L. L., Chu, S. G., & Xu, X. B. (2003b). Organic contamination in the greenhouse soils from Beijing suburbs. *China J Environ. Monit*, *5*, 786–790.

Maraqa, M. A., Zhao, X., Lee, J., Allan, F., & Voice, T. C. (2011). Comparison of nonideal sorption formulations in modeling the transport of phthalate esters through packed soil columns. *Journal of Contaminant Hydrology*, *125*, 57–69.

Midmore, M. J., & Jansen, H. G. P. (2003). Supplying vegetables to Asian cities, is there a case for peri-urban production? *Food Policy*, *28*, 13–27.

Nie, M., Xian, N., Fu, X., Chen, X., & Bo, L. (2010). The interactive effects of petroleum-hydrocarbon spillage and plant rhizosphere on concentrations and distribution of heavy metals in sediments in the Yellow River Delta, China. *Journal of Hazardous Materials*, *174*(1–3), 156–161.

Peijnenburg, W. J. G. M., & Struijs, J. (2006). Occurrence of phthalate esters in the environment of the Netherlands. *Ecotoxicology and Environmental Safety*, *63*, 204–215.

Qi, S., & Luo, F. (2007). Environmental degradation in the Yellow River Delta. *Shandong Province, China, Ambio*, *36*(7), 610–611.

- Staples, C. A., Peterson, D. R., Parkerton, T. F., & Adams, W. J. (1997). The environmental fate of phthalate esters, a literature review. *Chemosphere*, *4*, 667–749.
- Teil, M. J., Blanchard, M., & Chevreuil, M. (2006). Atmospheric fate of phthalate esters in an urban area (Paris-France). *Science of the Total Environment*, *354*, 212–223.
- Vikelsøe, J., Thomsen, M., & Carlsen, L. (2002). Phthalate and nonylphenols in profiles of differently dressed soils. *Science of the Total Environment*, *296*, 105–116.
- Wang, X. J., Piao, X. Y., Chen, J., Hu, J. D., Xu, F. L., & Tao, S. (2006). Organochlorine pesticides in soil profiles from Tianjin, China. *Chemosphere*, *64*, 1514–1520.
- Wang, C., Wang, W., He, S., Du, J., & Sun, Z. (2011). Sources and distribution of aliphatic and polycyclic aromatic hydrocarbons in Yellow River Delta Nature Reserve, China. *Applied Geochemistry*, *26*(8), 1330–1336.
- Wenzel, K. D., Manz, M., Hubert, A., & Schüürmann, G. (2002). Fate of POPs (DDX, HCHs, PCBs) in upper soil layers of pine forests. *Science of the Total Environment*, *286*, 143–154.
- Xu, G., Li, F. S., & Wang, Q. H. (2008). Occurrence and degradation characteristics of dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) in typical agricultural soils of China. *Science of the Total Environment*, *393*, 333–340.
- Yuan, S. Y., Huang, I. C., & Chang, B. V. (2010). Biodegradation of dibutyl phthalate and di-(2-ethylhexyl) phthalate and microbial community changes in mangrove sediment. *Journal of Hazardous Materials*, *184*, 826–831.
- Zeng, F., Cui, K. Y., Xie, Z. Y., Wu, L. N., Liu, M., Sun, G. Q., Lin, Y. J., Luo, D. L., & Zeng, Z. X. (2008). Phthalate esters (PAEs): emerging organic contaminants in agricultural soils in peri-urban areas around Guangzhou, China. *Environmental Pollution*, *156*, 425–434.
- Zeng, F., Cui, K. Y., Xie, Z. Y., Wu, L. N., Luo, D. L., Chen, L. X., Lin, Y. J., Liu, M., & Sun, G. X. (2009). Distribution of phthalate esters in urban soils of subtropical city, Guangzhou, China. *Journal of Hazardous Materials*, *164*, 1171–1178.
- Zhang, H. B., Luo, Y. M., Zhao, Q. G., Wong, M. H., & Zhang, G. L. (2006). Residues of organochlorine pesticides in Hong Kong soils. *Chemosphere*, *63*, 633–641.
- Zhang, L., Dong, L., Ren, L., Shi, S., Zhou, L., Zhang, T., & Yeru, H. (2012). Concentration and source identification of polycyclic aromatic hydrocarbons and phthalic acid esters in the surface water of the Yangtze River Delta, China. *Journal of Environmental Sciences*, *24*, 335–342.
- Zhao, Z., Quan, W. Y., & Tian, D. H. (1987). Phthalate esters in the atmosphere particulates of Beijing urban area. *Environmental Sciences*, *6*, 29–34. in Chinese.
- Zheng, Z., He, P. J., Shao, L. M., & Lee, D. J. (2007). Phthalic acid esters in dissolved fractions of landfill leachates. *Water Research*, *41*, 4696–4702.