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Contamination of phthalate esters, organochlorine pesticides and polybrominated diphenyl ethers in agricultural soils from the Yangtze River Delta of China

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ABSTRACT

To reveal the pollution status associated with rapid urbanization and economic growth, extensive areas of agricultural soils (approximately 45,800 km^2) in the Yangtze River Delta of China were investigated with respect to selected endocrine disruptor compounds (EDCs), including phthalate esters (PAEs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs). The residues of sum of 15 PAEs, sum of 15 OCPs and sum of 13 PBDEs were in the range of 167–9370 ng/g, 1.0–3520 ng/g, and b 1.0–382 ng/g, respectively. The OCPs residuals originated from both historical usage and recent input. Agricultural plastic film was considered to be an important source of PAEs. Discharge from furniture industry was potential major source of PBDEs in this region. The selected pollutants showed quite different spatial distributions within the studied region. It is worth noting that much higher concentrations of the EDCs were found on the borders between Shanghai and the two neighboring provinces, where agriculture and industry developed rapidly in recent years. Contaminants from both agricultural and industrial activities made this area a pollution hotspot, which should arouse more stringent regulation to safeguard the environment and food security.

INTRODUCTION

Soil is a major reservoir for a variety of pollutants (Zhang et al., 2011) and is a secondary emission source of contaminants to groundwater, surface water, and the air (Tao et al., 2008). In recent years, soils in China have been severely polluted by intensified farming activities, industrial operations and urban development (Cai et al., 2008). Multi- class environmental endocrine disruptor compounds (EDCs), such as phthalate esters (PAEs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs), may coexist in soils and accumulate in crops and human bodies through food chains, posing risks to ecosystem and human health (Hites, 2004; Lemaire et al., 2004; Net et al., 2015). Therefore, it is important to study the pollution of coexisting EDCs in soil.

PAEs have been prevalently used in the production of agricultural plastic film in China, which presents an important source of PAEs to farmland soils (Hu et al., 2003; Wang et al., 2013). Due to recent out- breaks of food safety issue in Taiwan and Mainland China, PAEs have aroused intensive public attention to their adverse effects on human health, especially reproductive physiology (Li and Ko, 2012). In addition, OCPs were produced and extensively used in agriculture in China during the 1950s–1980s (Li et al., 2001; Liu et al., 2015). Although the usage was terminated over thirty years ago, OCPs are still widely distributed in the environment and attract considerable scientific and regulatory interests due to their persistence, bioaccumulation and multiple endocrine disrupting risks to eco-systems and human health (Concha-Grana et al., 2006; Hu et al., 2010; Niu et al., 2013). In recent years, as emerging pollutants, PBDEs are of considerable concerns for their increasing detection rates and elevated levels in the environment (Wang et al., 2011; Luo et al., 2014) and human bodies (Hites, 2004; Chen et al., 2014). Their toxicity has also been widely studied in a variety of animal models (Messer, 2010), and significant

concerns of toxicity on human health such as hormonal deficits have been raised (Giordano et al., 2009).

The Yangtze River Delta (YRD), located in eastern China, is one of the most populated and economically prosperous regions in the world. The core part of the YRD consists of Shanghai, northern Zhejiang and south- ern Jiangsu, with a population more than 110 million. The YRD region accounts for more than 15% of China's GDP (Wuxi Municipal Bureau of Statistics, 2013). Intensive farming has also been conducted due to the demand for agricultural products from urban areas (Huang et al., 2011; Li et al., 2001). Numerous chemical manufactures are located on the provincial boards. Because of the high usage in industrial and agricultural productions, OCPs, PAEs, and PBDEs may coexist in farmlands of the YRD at elevated concentrations.

There have been several surveys on soil contamination in China (Hu et al., 2003; Niu et al., 2013; Tao et al., 2008; Zou et al., 2007). However, these studies generally focused on a single class of targeted contaminants in a limited number of samples and/or relatively small sampling area. Few studies have characterized the regional-scale spatial distribution of coexisting EDCs (i.e., PAEs, OCPs and PBDEs) in rapidly developing regions, such as the YRD. Thus, to reveal the pattern of the combined organic pollution in agricultural soils, we conducted an ex- tensive survey in the core YRD area. An evenly distributed sampling net- work composed of 241 sites was schemed to cover a terrestrial area of approximately 45,800 km2. We assessed the contamination status and spatial distributions of PAEs, OCPs and PBDEs in agricultural soils, as well as their potential sources in the YRD. This study is of considerable significance to risk management of PAEs, OCPs and PBDEs pollution using this fast developing region of China as a representative example.

MATERIALS AND METHODS

Sampling

The study area covers 45,800 km2. A total of 241 topsoil samples (0– 15 cm depth) were collected from various farmlands in the YRD in June 2014, of which 30 sampling sites were located in Shanghai City, 90 were in Jiangsu Province, and 121 were in Zhejiang Province (Fig. 1). At each sampling site, soil from five cores were collected using a stainless steel and then composited into a single sample (approximately 1000 g). The distance between each core was 10–20 m and each sampling site covered an area of approximately 400 m2. The soil samples were packed in aluminum foil, sealed in kraft bags, transported to the laboratory within seven days and stored at −4 °C before analysis.

Chemicals and reagents

In the chemical analysis, 15 standards of PAEs were dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), dibutyl phthalate (DnBP), bis(2-methoxyethyl) phthalate (DMEP), bis(4-meth-yl-2-pentyl) phthalate (BMPP), bis(2-ethoxyethyl) phthalate (DEEP), dipentyl phthalate (DPP), dihexyl phthalate (DnHP), benzyl butyl phthalate (BBP), bis(2-n-

butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), bis(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP), and dinonyl phthalate (DNP). Also, 15 standards of OCPs were α -hexachlorocyclohexane (α -HCH), β -HCH, γ -HCH, δ -HCH, p,p ′ -dichlorodiphenyltrichloroethane (p,p′-DDT), o,p′-DDT, p,p′-DDD, o,p′-DDD, p,p′-DDE, o,p′-DDE, aldrin, endrin, heptachlor, heptachlor ep- oxide (HEPX), and hexachlorobenzene (HCB). In addition, 13 standards of PBDEs were BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, and 209. Deuterium-labeled DnBP (DnBP-D4), PCB-209 and BDE-75 were used as surrogate standards for PAEs, OCPs and PBDEs analysis, respectively. The stock standards were purchased from AccuStandard (New Haven, USA). All solvents were HPLC grade or pesticide grade. Florisil, silica gel and anhydrous sodium sulfate were activated in advance.

Sample preparation

The extraction and cleanup procedures for PAEs, OCPs and PBDEs were adapted from the reported methods (Wang et al., 2013; Wang et al., 2007). All samples were freeze-dried, ground and sieved through a stainless steel 75-mesh (0.5 mm) sieve. Soil pH was measured by a pH meter with a soil/water ratio of 1:2.5. Total organic carbon (TOC) was measured with an Elementar Vavio EL III elemental analyzer (Hanau, Germany). Duplicate samples were performed for all the soil samples. The relative standard deviation (RSD) for replicate analyses (n = 3) ranged from 2.5% to 9.2%. To avoid contamination, no plastic equipment was used during sampling and processing.

For PAEs analysis, an aliquot of 5 g sample was spiked with surrogate standard DnBP-D4 (20 ng) and extracted with 20 mL acetone/hexane (1:1; v/v) in an ultrasonic bath for 60 min. The extract was filtered into a flask and the procedure was repeated two more times. The extract was concentrated, solvent exchanged to hexane, and further reduced to approximately 1.0 mL using a rotary evaporator. Finally, the extract was transferred through a 0.22 μm membrane filter, and the volume was adjusted to 0.5 mL for sample injection before instrumental analysis.

For OCPs, the surrogate standard PCB-209 (20 ng) was added to a 5 g sample, followed by ultrasonically extraction using hexane/dichloro- methane (1:1; v/v) for 60 min. The extracts were concentrated and cleaned up by passing through a Florisil column (containing 6 g activated Florisil), and the column was eluted with 60 mL hexane/dichloro- methane (4:1; v/v). Then the elution was concentrated, the solvent was exchanged into hexane, and the volume was adjusted to 0.5 mL with a gentle nitrogen flow.

For PBDEs, a 10 g soil sample was spiked with surrogate standards BDE-75 (20 ng) and ultrasonically extracted in a mixture of hexane/di- chloromethane (1:1; v/v). The extract was concentrated and cleaned up by elution with 100 mL of hexane on a glass column packed with, from bottom to top, 1 g of activated silica gel, 4 g of basic silica gel (1.2% w/w), 1 g of activated silica gel, 8 g of acid silica gel (30%, w/w), 2 g of activated silica gel, and 4 g of anhydrous sodium sulfate. Elution with PBDEs was rotary-evaporated and concentrated to 0.5 mL, prior to instrumental analysis.

Instrumental analysis

The quantification of PAEs was carried out using an Agilent 7890B gas chromatograph (GC) coupled with a 5977A mass spectrometer (MS) detector using an electron impact (EI) ion source. Compounds separation was achieved using a DB-5 MS (J & W Scientific, Folsom, CA) fused silica capillary column (30 m, 0.25 mm i.d., 0.25 μm film thick- ness) with helium as the carrier gas at a constant flow of 1.0 mL/min. The initial oven temperature was 90 °C, and then increased at 15 °C/ min to 220 °C, and further to 260 °C at 1 °C/min. The post run was set at 300 °C, kept for 3 min. Selected ion monitoring (SIM) mode was used for quantitative determination (Table SI-1).

For OCPs, samples were quantified on an Agilent 6890N GC with a DB-5 column (30 m, 0.25 mm i.d., 0.25 μm film thickness) and an electron capture detector (ECD). Nitrogen was used for both carrier gas and makeup gas at flow rates of 1.0 mL/min and 50 mL/min, respectively. Oven temperature was initially set at 80 °C, held for 2 min, increased at 10 °C/min to 140 °C, increased again at 4 °C/min to 280 °C and held for 5 min. The injector temperature was 240 °C and the detector temperature was 300 °C.

The quantification of tri-through hepta-BDEs was performed on Agilent 6890N-5975C GC–MS using electron-capture negative ionization (ECNI) ion source. Extract was injected into a HP-5 (30 m,0.25 mm i.d., 0.1 μm film thickness) capillary column. The initial oven temperature was 90 °C, which was held for 2 min. It was increased to 210 °C at 25 °C/min, held for 1 min, then increased to 275 °C at 10 °C/min and held for 10 min and finally ramped to 310 °C at 25 °C/min and held for 10 min. Tri- to hepta-BDEs were quantified by monitoring m/z 79 ([79Br]−) and 81 ([81Br]−). Quantitative analysis of BDE-209 was performed on GC–MS with an EI ion source. The extract was injected into a DB-5MS (15 m, 0.25 mm i.d., 0.1 μm film thick- ness) capillary column. The initial oven temperature was 90 °C, which was held for 1 min. It was then increased to 320 °C at 20 °C/min and held for 2 min. BDE-209 was monitored at the molecular ion clusters $[M]^+$ and $[M + 2]^+$.

Quality assurance and quality control

Quality controls were implemented to ensure the correct identifica- tion and accurate quantification of the target analytes. A method-blank sample was included in every batch of 15 samples to control any sys- tematic contamination. Only small levels of DnBP, DiBP and DEHP were detected in procedural blank, ranging from 1.45 to 3.80 ng/g. The concentrations of PAEs in soils were all blank corrected. The recov- ery rates of 15 PAEs, 15 OCPs and 13 PBDEs in the spiked samples ranged from 72.2 to 106.1%, 76.5 to 95.9% and 71.5 to 93.2%, respectively, where RSD for replicate analyses of spiked samples was lower than 15% (n = 3). During routine sample analysis, a duplicate was included in every batch of 15 samples with RSD of detected concentration lower than 10% (n = 3). The recovery rates of surrogate standards DnBP-D4, PCB-209 and BDE-75 were 82.6 ± 14.8%, 91.2 ± 16.4%, and 85.0 ± 11.2%, respectively. Five-point standard calibration curves were employed every day for quantitative analysis. The limits of detection (LODs), calculated as signal-to-noise ratios of 3, were 0.05–0.28, 0.03–0.42 and 0.06–

1.0 ng/g dry weight for PAEs, OCPs and PBDEs, respectively.

Statistical analysis and spatial mapping

Statistical analyses including the Pearson's correlation analysis and the Ward hierarchical clustering analysis were performed using R (R Development Core Team, 2015). The concentrations of pollutants were log-transformed to approximate normal distributions prior to the statistical analyses, where 10−7 was assumed as the concentrations below LODs. Population density associated with each sampling site was extracted from a gridded population density dataset (Fig. SI-1), which was obtained from the Resource and the Environmental Science, Chinese Academy of Science (Fu et al., 2014). Statistical significance was considered as p b 0.05. Spatial distributions of the EDCs were simulated by using universal Kriging in ArcGIS 10.2 (ESRI, Redlands, CA, USA).

RESULTS AND DISCUSSION

Among the 241 soil samples analyzed in this study, PAEs and OCPs were detected in all samples, while PBDEs were detected in 92% of the samples. The high detection rates indicate the ubiquitous contamination by EDCs in the YRD farmland soils. The measured concentrations of PAEs, OCPs and PBDEs in soil are summarized in Table 1. The spatial distributions of PAEs, OCPs and PBDEs are presented in Fig. 1. All concentrations were reported on a dry weight (dw) basis.

PAEs

The detection rates of DMP, DEP, and DiBP were all 100%, while the de- tection rates of DnBP, DMEP, BMPP, DEEP, DPP, DnHP, BBP, DBEP, DCHP, DEHP, DnOP and DNP were 99, 98, 76, 92, 63, 34, 93, 43, 7, 99, 99 and 94%, respectively. The total concentrations of 15 PAEs ranged from 167 to 9370 ng/g (mean: 782 ng/g). Among the analyzed PAEs, DEHP exhibit- ed the highest concentration (mean: 546 ng/g), followed by DnBP (mean: 94.9 ng/g) and DiBP (mean: 86.0 ng/g). The composition was similar to those reported in other regions (Zhang et al., 2015; Chai et al., 2014) where DEHP was also the dominated compound. The total concentrations of the six PAEs (DMP, DEP, DnBP, DnOP, DEHP and BBP) ranged from 68 to 9330 ng/g, which were below the less stringent grade II limits for PAEs (10 mg/kg) in arable soils published by the

220 Environmental Quality Standard for Soil in China (GB-15618-2008) (China National
221 Environmental Protection Agency, 2008). Nonetheless, according to the commonly used soil
222 cleanup objectives (US EPA, 2015), DEHP in three soil samples exceeded allowable
223 concentration (3900 ng/g). The levels of PAEs in this study were comparable to those in field
224 soils across China (75.0– 6369 ng/g) (Hu et al., 2003; Niu et al., 2014; Zhang et al., 2015). Our
225 results were lower than those in soils from vegetable greenhouses in Shan-dong Province, China,
226 in which the concentration of ΣPAEs reached up to 35,400 ng/g due to the usage of plastic film
227 (Chai et al., 2014).

228 Many studies have suggested that the increased PAEs in agricultural soils might be caused by the
229 application of plastic films, fertilizers and atmospheric deposition (Zeng et al., 2008). PAEs are
230 mostly used as plasticizers in the polymer industry. The phthalate content in a plastic product
231 could be 10–60%. It has been reported that the agricultural consumption of plastic films in China
232 in 2011 was approximately 2.29 million tons, and the mulching area reached 19.8 million ha
233 (Department of Rural Survey National Bureau of Statistics of China, 2012). The production and
234 utilization of agricultural plastic films have increased in recent years, which is often recognized
235 as a major source of PAEs in farmland soils (Hu et al., 2003). Among plasticizers of PAEs, DEHP,
236 DiBP and DnBP are widely used. It is found that DEHP and DnBP are two dominant PAE
237 components in white and black mulch film used in agricultural production (Wang et al., 2013).
238 As shown in Fig. 1, higher contents of total PAEs in soils were observed in Zhejiang, while the
239 total PAE levelswere relatively lowin Shanghai andmost of the surveyed region of Jiangsu. The
240 studied area in Zhejiang is located in the Hangjiahu Plain,where a huge amount of plastic
241 filmswere used for agricultural production.

242

OCPs

The total concentrations of 15 OCPs ranged from 1.0 ng/g to 3520 ng/ g, with a mean of 59.3 ng/g. DDTs were predominant OCPs in most samples, and the concentrations of DDTs ranged from 0.13 to 3515 ng/g (mean: 56.2 ng/g). HCHs also extensively existed in the farmland soils, with HCHs ranging from 0.37 to 30.3 ng/g (mean: 2.46 ng/g). In addition to DDTs and HCHs, other important OCPs including HCB, he contamination status in the YRD soils. The detection rates of α-HCH, β- HCH, γ-HCH, δ-HCH, HCB, heptachlor, aldrin, endrin, HEPX, o,p´-DDE, p,p´-DDE, o,p´-DDD, p,p´-DDD, o,p´-DDT and p,p´-DDT were 91, 67, 99, 74, 59, 7, 54, 6, 28, 44, 99, 23, 71, 38 and 79%, respectively, suggesting the wide occurrence of OCPs in the YRD soil.

According to the Environmental Quality Standard for Soil (GB-15618- 2008) (China National Environmental Protection Agency, 2008), the less stringent grade II limits for HCHs and DDTs in agricultural soils are 50 and 100 ng/g, respectively. The results of this study showed that the concentrations of HCHs in agricultural soils in the YRD were all below 50 ng/g. Nevertheless, the concentrations of DDTs in 16 soil samples exceeded this safety standard, accounting for 6.6% of the total samples. The residue levels of DDTs and HCHs in this study were comparable to the studies in Haihe Plain of China (DDTs: mean 64.0 ng/g; HCHs: mean 3.90 ng/g), which accommodates similar industrial and agricultural activities (Tao et al., 2008). Concentrations of OCPs in soils of this study were much higher than the levels of OCPs in soils of Three Gorges Dam region, China (DDTs: mean, 1.80 ng/g; HCHs: mean, 1.27 ng/g; OCPs: mean, 6.49 ng/g) (Liu et al., 2015). Overall, the total levels of OCPs were higher in agricultural soils in Shanghai than Jiangsu and Zhejiang (Fig. 1). It is worthy to note that a relatively high level of OCPs (total 3250 ng/g) was detected in Taicang, Jiangsu, where many pesticide factories and chemical plants

were located in the vicinity (within 500–1000 m) of the sampling sites in farmlands, which might be a major pollution source of OCPs. We are conducting further study on soil–plant interactions with high-density sampling to explore possible reasons and environmental impacts of high OCPs pollution in this area.

The ratios between a parent compound and its metabolites can pro- vide useful information on the pollution source. A ratio of (p,p ´ - DDD + o,p ´ -DDD + p,p ´ -DDE + o,p ´ -DDE)/(p,p ´ -DDT + o,p ´ -DDT) great- er than 1.0 indicates aged DDT while a ratio much less than 1.0 indicates new input (Harner et al., 1999). In this study, the ratios were lower than 1.0 in 87% of the samples, indicating a new input of DDT in the soils. This new input of DDT is most likely to be the pesticide dicofol which con- tains DDT, as reported in other surveys (Qiu et al., 2005). However, there might also be other unidentified source of DDTs such as anti- fouling paints, which requires further investigation. Comparing the dis- tributions of total DDT concentrations and (p,p ´ -DDD + o,p ´ -DDD + p,p ´ -DDE + o,p ´ -DDE)/(p,p ´ -DDT + o,p ´ -DDT) ratios (Fig. SI-2), it suggested that DDT in soils from border of Zhejiang Province and Shanghai City mainly originated from historical usage, whereas DDT in soils from border of Jiangsu Province and Shanghai City mainly originated from new input.

Technical HCHs contains 60–70% α-HCH, 5–12% β-HCH, 10–12% γ- HCH, and 6–10% δ-HCH (Li et al., 2006; Tao et al., 2008). In China, tech- nical HCH has been forbidden, but lindane (N 99% γ-HCH) is still being used. The ratios of α-/γ-HCH in soil samples ranged from 0 to 14.8 in this study. The higher ratios of α-/γ-HCH (N 3.0) were only found in 1% of the samples collected, suggesting that the HCHs in the soil samples might originate from historical usage of technical HCH but recent input of lindane most likely contributed to the occurrence of low concentra- tions of HCHs in YRD agricultural soils (Fig. SI-3). Except for DDT and HCH, the

289 other OCPs (e.g., HCB, heptachlor, aldrin, endrin and HEPX) were found to be minor pesticides
290 with lower detection rates.

291

292 **PBDEs**

293 PBDEs were detected in 92% of the soil samples. The total concentr tion of 13 PBDEs in all soil
294 samples ranged from b 1.0 to 382 ng/g with a mean of 12.4 ng/g, while the concentrations of
295 BDE-209 were from b 1.0 to 109 ng/g with an average of 6.67 ng/g. BDE-209 was the dominant
296 congener of the total PBDEs in the soils, followed by BDE-47, 99 and 154. The results indicate
297 that the commercial deca-BDE and penta-BDE were the major contaminants as reported (Leung
298 et al., 2007). This finding was consistent with the fact that commercial "deca-" product (BDE-
299 209 as its main component) is one of the most commonly used flame retardants across the world,
300 followed by "penta-BDE" commercial mixture.

301 The levels of low-brominated PBDE congeners (i.e., tri- to hepta-BDEs) in the present study
302 were lower than those in surface soils from e-waste recycling site in Guiyu (0.441–2768 ng/g)
303 (Leung et al., 2007; Wang et al., 2005) and Taizhou (824.4–948.6 ng/g) (Cai and Jiang, 2006).
304 As for BDE-209, the concentration was also lower than those in soils from e-waste recycling site
305 (Leung et al., 2007). In addition, our results were similar to or slightly higher than those in surface
306 soils from nonpoint contaminated sites. Zou et al. (2007) reported the concentrations of low-
307 brominated congeners (0.13–3.81 ng/g) and BDE-209 (2.38–102 ng/g) in the surface soils
308 sampled from the Pearl River Delta.

309 The PBDE concentrations in soils were higher for the sampling sites in Zhejiang Province than
310 those in Jiangsu Province and Shanghai City (Fig. 1). PBDEs are a class of flame retardants used

311 in furniture, textiles and electronic products. Furniture industry developed rapidly in Zhejiang
312 Province. In the first two seasons of year 2015, furniture enterprises in Zhejiang produced
313 approximately 35% of the total furniture production in China. The amounts of furniture made in
314 Zhejiang Province were nearly ten times as those in both Jiangsu Province and Shanghai City
315 (Zhiyan Consulting Group, 2015). PBDEs might be released to surrounding soils during the
316 process of production/disposal of furniture and its wastewater (Watkins et al., 2013). In addition,
317 there were numerous electronic-waste-polluted areas in the south to the sampling sites in
318 Zhejiang Province, which could be another potential source of PBDEs via long-range
319 atmospheric transport and deposition (Cai and Jiang, 2006). Further integration of sample
320 analysis, model simulation, and land use information should be conducted in future studies.

321

322 **Characteristics of coexisting pollutants**

323 Cluster analysis was performed to identify homogeneous groups and combined characteristics of
324 these selected EDCs in the YRD agricultural soils. The 43 pollutants were classified into three
325 major groups (Fig. 2). Basically, PBDEs, PAEs and OCPs were spontaneously separated into dif-
326 ferent groups. The first major group contained most PBDEs (BDE-17, 28, 66, 71, 85, 100, 138,
327 153, and 183), heptachlor and endrin. All the PAEs were included in the second major group.
328 This group also contained BDE-99, BDE-154, BDE-209, HCB, HEPX, δ-HCH and γ-HCH. The
329 third major group mainly consisted of OCPs such as o,p´-DDD, p,p´-DDD, o,p´-DDE, p,p´
330 -DDE, o,p´-DDT, p,p´-DDT, α-HCH, β-HCH and aldrin, while BDE-47 was also assigned
331 to this group. Generally, in the same group, there is a close correlation of concentrations of two
332 compounds under the same branch. For example, DiBP and DnBP were very close to each other

in cluster, suggesting their positive correlation in soils as expected. Based on the cluster analysis, some contaminant characteristics of coexisting compounds may be speculated: firstly, the compounds are of the same kind of pollutant or share common sources; secondly, these compounds have transformation relationship (e.g., o,p ´ -DDD, p,p ´ -DDD, o,p ´ -DDE, p,p ´ -DDE, o,p ´ -DDT and p,p ´ -DDT in the third group); thirdly, several compounds have similar sorption affinity or transport behavior after long-term contamination although they belong to different class of contaminants. On the other hand, the result of cluster analysis provided useful information when the same class of pollutant was not classified to the same group. α-HCH and β-HCH were in the third group, but γ-HCH was assigned to the second group, implying the new input of lindane in the YRD region. The cluster analysis in this study could serve to provide a useful reference for predicting the spatial distribution of coexisting organic contaminants in a large and rapidly developing region such as YRD.

Soil properties such as TOC and pH are important factors affecting the occurrence and behaviors of EDCs. In this study, the contents of soil TOC ranged from 0.15% to 3.98%, with a mean value of 1.48%. For pH, the mean value was 6.14 and measurements ranged from 4.24 to 8.48. Positive but weak relationships were observed between the pairs of PAEs and TOC ($R = 0.390$, p b 0.001, $n = 241$; R: correlation coefficient, p: significance level, n: sample size), PBDEs and TOC ($R = 0.392$, p b 0.001, $n = 241$), as well as OCPs and TOC ($R = 0.307$, p b 0.001, $n = 241$). No outlier or extreme values were removed. It suggests that the studied lipophilic EDCs might be adsorbed to soil organic matter to varying extent depending on their characteristics and interactions. However, the correlation coefficients (R) were not strong, and other fac- tors such as sources and land management practices had higher effects on the spatial distributions of the three kinds of

EDCs than the soil organic matter content did. No clear correlation was found between pH and the concentrations of any target EDCs.

The spatial distributions and relationships between population density of sampling sites and the concentrations of pollutants were also analyzed (Fig. SI-1). Positive correlation was observed between PAEs and population density ($R = 0.261$, $p < 0.001$, $n = 241$), and between PBDEs and population density ($R = 0.223$, $p < 0.001$, $n = 241$). OCPs showed marginal correlation with population density ($R = 0.115$, $p = 0.074$, $n = 241$), which might be due to their long-term historical usage in agricultural production.

The overall level of the three classes of EDCs was relatively low in Jiangsu. It is interesting that much higher concentrations of PAEs, OCPs and PBDEs were found on the borders between Shanghai and Jiangsu, and the borders between Shanghai and Zhejiang. On one hand, many chemical factories were built near the borders to save cost and reduce pollution in downtown, which might be major emission sources of pollutants in the YRD. On the other hand, there were many vegetable production bases along these borders, which played an important role in food provision to Shanghai. In recent years, agriculture and industry have developed rapidly in the same terrestrial areas along the borders due to economic advantages and political concerns of these special geological locations. These severely polluted areas should arouse more stringent regulation to safeguard the environment and food security.

CONCLUSION

The intensified agricultural activities and rapid urban development has led to ubiquitous existence of many EDCs in the environments. This work revealed the current status of EDCs in agricultural

soils across the core YRD area, which is one of the most populated and economically prosperous regions in China. The residuals of selected pollutants illustrated quite different spatial distributions. The concentrations of PAEs and PBDEs were higher in Zhejiang. Agricultural plastic film was considered major source of PAEs. Discharge from furniture industry as well as atmospheric transport and deposition from electronic waste sites were potential sources of PBDEs. Shanghai showed a higher loading of OCPs, which might originate from both historical usage and recent input. It is noted that much higher concentrations of contaminants were found along the borders between Shanghai and the two neighboring provinces. Contaminants from both agricultural and industrial activities made this area a pollution hotspot, which should arouse more public attention. Ubiquitous presence of coexisting EDCs and their potential risks to residents via multiple pathways should draw more attention and regulatory control.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.12.012.

LIST OF FIGURES AND TABLES

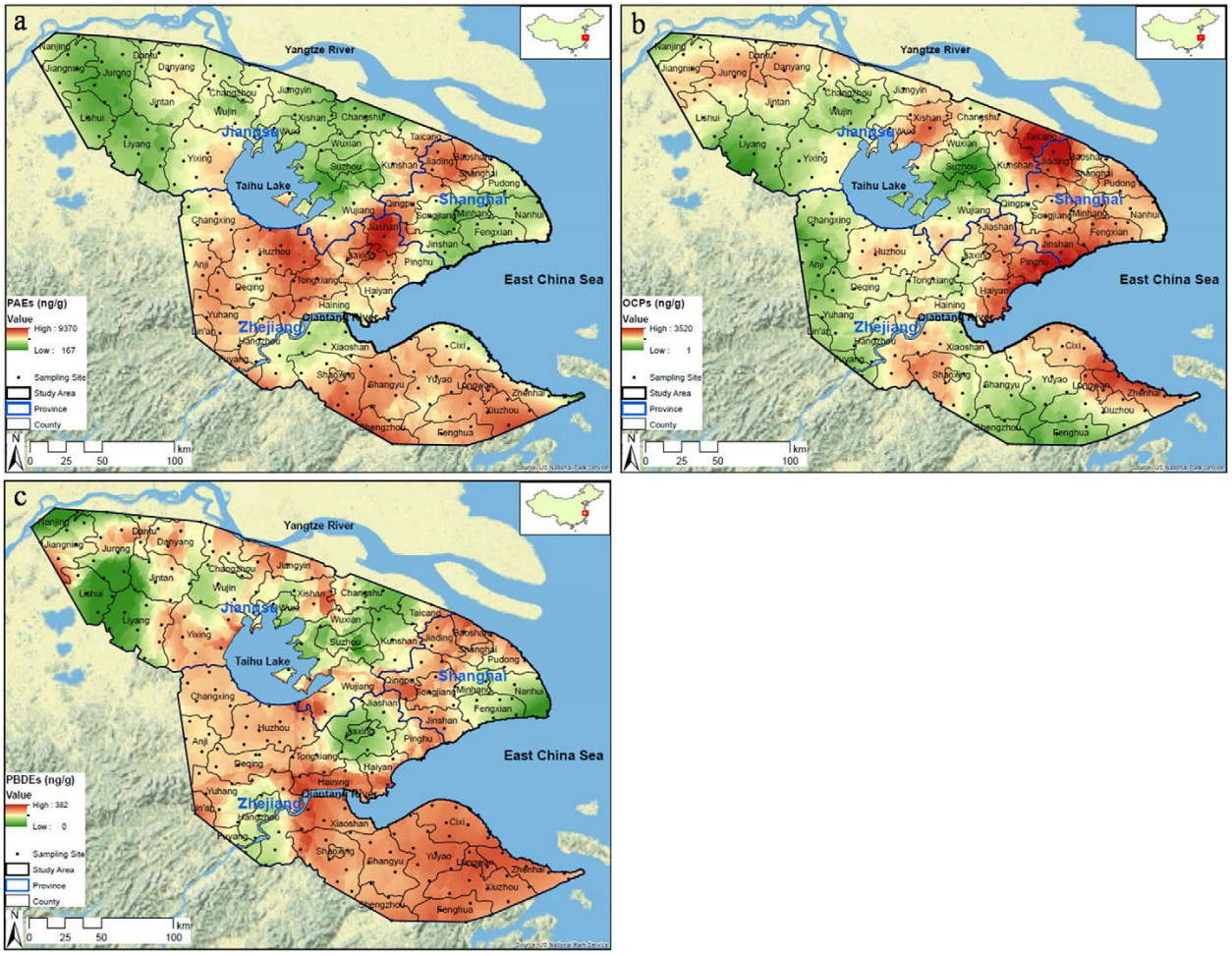

Fig. 1. Spatial distributions of (a) PAEs, (b) OCPs and (c) PBDEs in agricultural soils of YRD region.

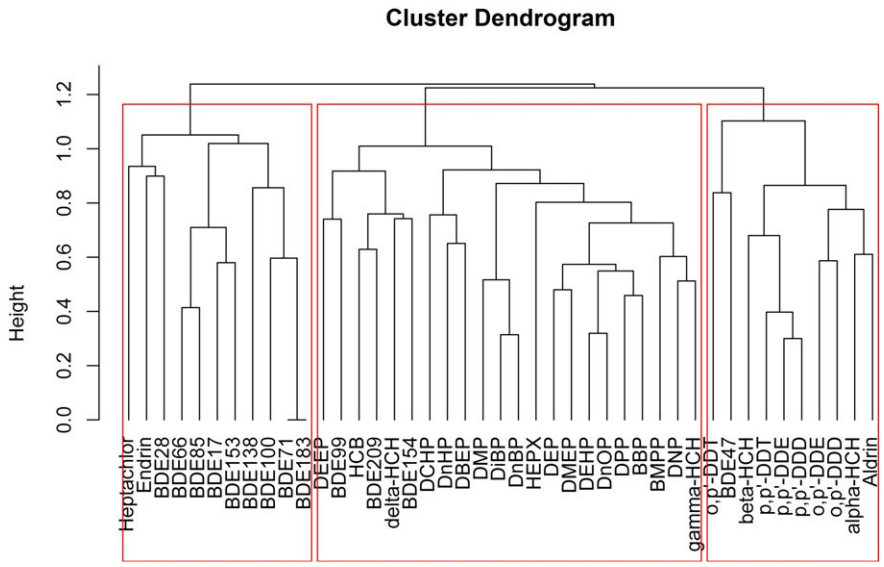

Fig. 2. Dendrogram for 241 soil samples from YRD region through cluster analysis.

Table 1
Concentrations (ng/g, dry weight) of PAEs, OCPs, and PBDEs in agricultural soil samples in YRD.

Compound	Detection rate (%)	Mean (ng/g)	Median (ng/g)	Min. (ng/g)	Max. (ng/g)
DMP	100	23.0	20.4	0.2	71.0
DEP	100	3.8	2.2	0.5	90.6
DiBP	100	86.0	71.0	0.4	474
DnBP	99	94.9	73.9	ND[a]	1500
DMEP	98	2.0	1.2	ND	40.1
BMPP	76	1.4	0.8	ND	9.90
DEEP	92	3.3	0.8	ND	151
DPP	63	2.2	0.2	ND	151
DnHP	34	0.5	0.1	ND	7.40
BBP	93	1.0	0.6	ND	12.2
DBEP	43	18.3	0.5	ND	680
DCHP	7	35.3	1.4	ND	265
DEHP	99	546	349	ND	9190
DnOP	99	6.9	2.0	ND	273
DNP	94	8.3	3.9	ND	434
∑PAEs	100	782	559	167	9370
α-HCH	91	0.6	0.4	ND	9.00
β-HCH	67	0.9	0.4	ND	29.4
γ-HCH	99	0.9	0.8	ND	6.60
δ-HCH	74	0.4	0.3	ND	1.50
HCB	59	0.9	0.4	ND	21.5
Heptachlor	7	0.7	0.6	ND	2.20
Aldrin	54	0.7	0.2	ND	8.70
Endrin	6	0.6	0.3	ND	5.70
HEPX	28	0.4	0.3	ND	3.30
o,p′-DDE	44	2.5	0.5	ND	31.2
p,p′-DDE	99	6.2	1.6	ND	167
o,p′-DDD	23	0.9	0.4	ND	5.80
p,p′-DDD	71	1.3	0.5	ND	29.4
o,p′-DDT	38	7.0	2.1	ND	226
p,p′-DDT	79	56.1	9.0	ND	3240
∑OCPs	100	59.3	13.2	1.0	3520
BDE-17	3	1.01	0.26	ND	6.19
BDE-28	5	40.1	1.39	ND	344
BDE-47	17	8.76	0.21	ND	212
BDE-66	4	0.26	0.14	ND	0.97
BDE-71	1	3.28	3.28	ND	4.16
BDE-85	3	3.31	1.73	ND	10.3
BDE-99	43	2.08	0.17	ND	114
BDE-100	1	1.48	0.33	ND	4.07
BDE-138	8	2.93	2.70	ND	7.78
BDE-153	3	2.01	0.58	ND	5.45
BDE-154	64	0.75	0.49	ND	12.1
BDE-183	1	15.6	15.6	ND	30.9
BDE-209	92	6.67	3.01	ND	109
∑PBDEs	92	12.4	4.02	ND	382

[a] ND, none-detectable.

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