

1 Phthalate esters and organochlorine pesticides in agricultural soils and vegetables from
2 fast-growing regions: a case study from eastern China

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19 **ABSTRACT**

20 The present study investigated phthalate esters (PAEs) and organochlorine pesticides (OCPs) in

21 agricultural soils and vegetables from eastern China. The concentrations of PAEs ranged from 109 to 5560
22 ng/g in soils and 60.1 to 2390 ng/g in cabbages, with average concentrations of 946 and 601 ng/g,
23 respectively. The concentrations of OCPs ranged from <0.1 to 662 ng/g in soils and <0.1 to 42.8 ng/g in
24 cabbages, with average concentrations of 134 and 11.6 ng/g, respectively. OCPs were mainly in the 0–30
25 cm surface soil layers, while PAEs could infiltrate in deep soil profiles to 70–80 cm layer. Potential source
26 analysis traced the occurrence of OCPs to both historical application and current usage, where- as building
27 materials and agricultural plastic film were possible input sources of PAEs in the ambient environment.
28 OCPs showed no apparent effect on soil microbial communities, whereas significant negative
29 relationship was observed be- tween PAEs and fungi in soils ($R = -0.54$, $p < 0.01$). Human health risk
30 assessment data revealed marginal noncarcinogenic risks and low carcinogenic risks in these soils. Notably,
31 PAEs posed a comparable or higher risk level compared with that of OCPs. This study suggests the need
32 for better regulation on pollution control and management of PAE-elevated sites to protect soil quality
33 and food safety.

34

35 INTRODUCTION

36 In recent years, soil pollution in China has become a significantly environmental issue due to the population
37 growth, eco- nomic development, and accelerated urbanization (Li et al. 2015; Teng et al. 2014). A large
38 number of fast-growing regions were potential pollution hotspots to the surrounding environment. The
39 intensified farming and industrial activities in these regions may lead to the elevated levels of various
40 contaminants in the environment (Cai et al. 2008; Zhong and Zhu 2013). Organic pollutants in agricultural
41 soils could influence microbial activities and enter the food chain through bioaccumulation, thus disturbing
42 the ecosystem and impairing human health (Fang et al. 2015).

43 Organochlorine pesticides (OCPs) such as dichlorodiphenyl-trichloroethanes (DDTs) and
44 hexachlorocyclohexanes (HCHs) were produced and extensively used in agriculture of China dur- ing the
45 1950s–1980s (Liu et al. 2015b). Although the production and agricultural use of DDTs and HCHs have been

46 phased out over the past three decades, the historical usage of these persistent OCPs has resulted in widespread
47 pollution of agricultural soils and vegetation in China (Tao et al. 2008; Wang et al. 2016).

48 Phthalate esters (PAEs) are widely used plasticizers and additives in a variety of products, including building
49 materials, home furnishings, food packaging, and polyvinylchloride (PVC) resins (Ma et al. 2015). Numerous
50 studies have demonstrated that some PAEs are endocrine disrupting compounds, with adverse effects on
51 metabolism and reproduction (Li and Ko 2012). As a result, some phthalates have been classified as priority
52 pollutants by the US Environmental Protection Agency (USEPA). In China, the production of plastic has reached
53 74 million tons by 2013, which accounts for approximately 24.8 % of the global production (PlasticsEurope
54 2015), and PAEs are gradually released into the environment from PAE-containing products during their
55 manufacture, use, and disposal (Wang et al. 2013). Yang et al. (2013a) observed the high concentrations of PAEs
56 in densely anthropo- genic activities areas (such as the urbanization and industrialization), and agriculture
57 influenced district.

58 The concentrations of PAEs have reached milligrams per kilogram in most agricultural soils across China
59 (Chen et al. 2012; Niu et al. 2014; Zeng et al. 2008). However, there is no available soil quality standard for
60 PAEs in China. More studies on the contamination of PAEs and associated environmental effects are required
61 to better understand the potential risk of these chemicals in soil environments.

62 Our recent study has revealed that the agricultural soils in the Yangtze River Delta (YRD) of China were
63 widely contaminated with various organic pollutants (Sun et al. 2016). The border of Jiangsu province and
64 Shanghai Municipality is such a pollution hotspot. A large number of industrial and commercial enterprises
65 does not only contribute to economic development but also possibly pose a serious threat to the
66 environmental quality. It is important to elucidate the soil- plant interactions with high-density sampling
67 to assess the pollution of OCPs and PAEs in agricultural fields and their associated impact on the
68 environmental quality and human health. This is crucial for managing environmental risks and developing
69 effective remediation and abatement strategies.

70 In the present study, DDTs, HCHs, and six priority control PAEs were determined in soils and vegetables

71 collected from the agricultural fields at the border of Jiangsu province and Shanghai Municipality in eastern
72 China. The objectives were to: (i) characterize the contamination status of OCPs and PAEs in agricultural
73 topsoils and soil profiles; (ii) analyze bioaccumulation of OCPs and PAEs by plants; (iii) identify the
74 correlations among soil microbiota, soil properties, and organic contaminants; and (iv) evaluate the
75 potential human health risks due to exposure to OCPs and PAEs in agricultural soils. The results can provide
76 important baseline information for soil quality assessments in fast-growing regions, especially in China.

77

78 **MATERIALS AND METHODS**

79 **Sample collection**

80 The studied region was located at the border of Shanghai Municipality and Jiangsu province, eastern
81 China. The 26 sampling sites were based in Jiading District of Shanghai, Kunshan, and Taicang cities
82 of Jiangsu. As shown in Fig. 1, there were nine sampling sites in area BA[^], which comprised an industrial
83 park and nearby villages. There were seven sampling sites in area BB[^], which comprised several villages
84 and vast areas of farmland. There were five sampling sites in area BC[^], where several residential areas were
85 under construction and many greenhouses were in use. A sampling site in each of the three areas (i.e., A, B,
86 and C) was included in our previous survey (Sun et al. 2016). These three areas have different industry and
87 agriculture types, and represent the different levels of rapid economic development. The other areas
88 including D, E, F, G, and H contained only one sampling site each. These five areas are evenly distributed
89 along the border of Jiangsu province and Shanghai Municipality. More detailed sampling locations are
90 presented in the Supporting information (SI).

91 In November 2014, a total of 26 pairs of topsoil (depth, 0–20 cm) and cabbage (*Brassica chinensis*) were
92 collected from the study region. Each composite sample consisted of five subsamples. In addition, three
93 vertical soil profiles were obtained. The soil profiles were excavated to a depth of 90 cm. Soil samples were
94 collected from the front of the soil trenches at 10-cm intervals. All the samples were packed in aluminum foil
95 and freeze-dried before being ground, homogenized, and stored at –20 °C until analysis.

97 **Sample preparation and analysis**

98 The target compounds in the analysis of the present study included α -HCH, β -HCH, γ -HCH, δ -HCH,
99 *p,p'*-DDT, *o,p'*- DDT, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDE, *o,p'*-DDE, dimethyl phthalate (DMP), diethyl
100 phthalate (DEP), dibutyl phthalate (DnBP), benzyl butyl phthalate (BBP), *bis*(2-ethylhexyl) phthalate
101 (DEHP), and di-*n*-octyl phthalate (DnOP).

102 The sample preparation and analysis procedures for OCPs and PAEs were adapted from the reported
103 methods (Wang et al. 2007, 2015). Briefly, 5 g of soil or 1 g of plant material was extracted with 30 mL of
104 a 1:1 (*v/v*) mixture of hexane and dichloromethane in an ultrasonic bath for 60 min twice. Surrogate
105 standards PCB-209 (20 ng) and deuterium-labeled DnBP (DnBP-D4) (20 ng) were added prior to extraction.
106 The two extracts were combined, concentrated to 1–2 mL and cleaned up by passing through a multilayer
107 column containing, from bottom to top, alumina oxide (6 g), neutral silica gel (12 g), and anhydrous sodium
108 sulfate (2 g). The column was eluted with 60 mL acetone/hexane (1:4, *v/v*). Then the eluent was reduced
109 to 0.5 mL with a gentle nitrogen flow.

110 PAEs were determined by an Agilent 7890B/5977A gas chromatography/mass spectrometry (GC/MS)
111 equipped with a DB-5 MS fused silica capillary column (30 m, 0.25 mm i.d.,
112 0.25 μ m film thickness) for chromatographic separation. The initial oven temperature was 90 °C, and then
113 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 and
114 kept for 3 min. The analysis of OCPs was carried out on an Agilent 6890N GC with a DB-5 column (30 m,
115 0.25 mm i.d., 0.25 μ m film thickness) and an electron capture detector (ECD). The oven temperature was
116 held at 80 °C for 2 min and programmed to increase at 10 °C/min to 140 °C, increase again at 4
117 °C/min to 280 °C, and held for 5 min

118

119 **Quality assurance and quality control**

120 A procedural blank, spiked blank, and sample duplicate were processed simultaneously with every batch of

121 ten samples. Trace DnBP and DEHP were detected in procedural blanks, though contact with plastics was
122 avoided throughout the experiment. The concentrations of PAEs were all blank corrected. The recovery
123 rates of PAEs and OCPs in the spiked samples ranged from 77.6 to 108.5 % and from 81.5 to 93.1 %,
124 respectively, where **relative standard deviation** (RSD) was <10 % ($n = 3$). The measured concentration
125 variations of pollutants in duplicates were <15 % ($n = 3$). The recovery rates of surrogate standards DnBP-D4
126 and PCB-209 were 84.5 ± 12.2 and 88.7 ± 14.6 %, respectively. Five-point standard calibration curves were used
127 for quantitative analysis. The limits of detection (LODs) were calculated as three times the signal-to- noise ratio
128 and fell in the range of 0.20–0.40 and 0.10–0.45 ng/g for PAEs and OCPs, respectively. Statistical analyses were
129 per- formed using SPSS 18.0, R, and Origin 8.0. Statistical significance was considered as $p < 0.05$.

130

131 **Soil microbiological and physicochemical analysis**

132 Extraction and analysis of microbial phospholipid fatty acids (PLFA) were performed by GC fitted with
133 MIDI Sherlock microbial identification system with reference to the reported method (He et al. 2013). The
134 biomasses of bacteria, fungi, actinomycetes, gram-positive bacteria, and gram-negative bacteria were
135 quantified, respectively. Soil pH was measured using a pH meter with a soil/water ratio of 1:2.5. The total
136 organic carbon (TOC), total nitrogen, and total phosphorus were analyzed by the reported methods (Liu
137 et al. 2015a).

138

139 **Health risk assessment**

140 The noncarcinogenic and carcinogenic risks of OCPs and PAEs to human were evaluated using the
141 methods recommended by the USEPA (1997), which have been widely adopted in the literature (Islam et
142 al. 2015; Niu et al. 2013; Wang et al. 2015). Among the studied pollutants, DEP, DnBP, BBP, DEHP, DnOP,
143 α -HCH, β -HCH, γ -HCH, and p,p' -DDT were regarded as noncarcinogenic compounds with respect to human
144 health, while BBP, DEHP, α -HCH, β -HCH, γ -HCH, p,p' -DDT, p,p' -DDD, and p,p' -DDE present
145 carcinogenic risk. Risks through nondietary (including soil ingestion, inhalation and dermal contact) and

146 dietary (i.e., intake of agricultural products harvested from the soils) pathways were all involved. The average
147 daily intake dose was estimated by the equations presented in SI. The noncarcinogenic risks of pollutants
148 were presented as hazard index (HI). The local residents are considered to be exposed to noncarcinogenic
149 risks if $HI > 1$. The carcinogenic risks are considered very low if the value of risk is less than 10^{-6} , low in
150 the range of 10^{-6} – 10^{-4} , moderate in the range of 10^{-4} – 10^{-3} , high in the range of 10^{-3} – 10^{-1} , and very high
151 if the value exceeds 10^{-1} .

152

153 RESULTS AND DISCUSSION

154 OCPs residues in topsoils

155 A summary of the concentrations (ng/g dry weight) of OCPs in topsoil samples is presented in Table 1. The
156 concentrations of total HCHs in the agricultural soils ranged from <0.1 to 92.0 ng/ g, with a mean of 14.4 ng/g
157 and a detection rate of 84.6 % in all the soil samples. The HCH levels found in this study were higher than those
158 in agricultural soil collected across China (0.146–23.9 ng/g) (Niu et al. 2013), and those in soil collected in
159 the YRD region (0.376–30.3 ng/g) in our previous study (Sun et al. 2016). The total concentrations of DDTs and
160 their metabolites in the agricultural soils ranged from <0.1 to 659 ng/g, with a mean of 120 ng/g and a detection
161 rate of 88.5 %. The overall DDT concentrations in the present study were comparable with or higher than
162 those in agricultural soil from other regions of China (Tao et al. 2008; Zhang et al. 2012). The mean values
163 of total DDTs in the study area were higher than those in soil col- lected in the YRD region (mean of 56.2
164 ng/g) in our previous study (Sun et al. 2016). The agricultural soils in the study area may have been subjected
165 to relatively high levels of OCP pollu- tion. However, it has been reported that the OCP residues in the
166 environment were gradually decreasing after many years of for- bidden for application for agriculture in China
167 (Hu et al. 2010; Nakata et al. 2002).

168 Higher levels of OCPs were found in the sites located in area A, which probably reflected the presence of
169 point source pollution in this area. A large number of chemical factories within and surrounding the
170 villages may contribute to the OCPs pollution (Tang et al. 2016). In addition, local practices of pesticide

171 applications with respect to pest control needs may be another input source. Comparing with the industrial
172 area A, the natural and agricultural area B possessed much lower OCP residues. The concentrations of
173 DDTs in only one soil sample collected in site A1 exceeded less stringent grade II limits in Environmental
174 Quality Standard for Soil (GB-15618-1995) (China National Environmental Protection Agency 1995). The
175 concentrations of HCHs in all the samples complied with this environmental quality standard.

176 The ratios of selected compounds were useful for distinguishing whether the sources originated from the
177 historical usage or fresh application on agricultural soils in recent years. In China, technical HCH (α -HCH
178 60–70 %, β -HCH 5–12 %, γ -HCH 10–12 %, δ -HCH 6–10 %) was widely used for agriculture during the
179 1950s–1980s (Tao et al. 2008). Lindane (>99 % γ -HCH) was subsequently applied as a substitute (Li et al.
180 2001). The α -/ γ -HCH ratios in soil samples ranged from 0 to 0.60 in this study, which indicated fresh
181 application of lindane in recent years. The major source of DDT contamination in China was attributed to
182 the agricultural application of technical DDTs and dicofol (Yang et al. 2013b). In this study, the ratio of
183 (p,p' -DDE + p,p' -DDD)/ p,p' -DDT was greater than 1.0 in 73 % of the topsoils, suggesting DDT in soils
184 originated mainly from historical usage. Furthermore, a ratio of o,p' - DDT/ p,p' -DDT higher than 1.3 was
185 indicative of dicofol source while a range of 0.20–0.30 was indicative of technical DDT source (Qiu et al.
186 2005). The o,p' -DDT/ p,p' -DDT ratios ranged from 0 to 0.28, suggesting aged DDT as the prime source
187 of DDTs in the study area.

188

189 **PAEs residues in topsoils**

190 A summary of the concentrations (ng/g dry weight) of PAEs in topsoil samples is presented in Table 2. The
191 concentrations of six PAEs in the agricultural soils ranged from 109 to 5560 ng/g, with a mean of 946 ng/g.
192 The concentrations of PAEs in the study area were comparable with those in soils across China (75.0–6369
193 ng/g) (Hu et al. 2003; Niu et al. 2014). The mean values of total six PAEs in the study area were higher
194 than those in soil collected from vast area of the YRD region (mean of 670 ng/g) in our previous study (Sun
195 et al. 2016). It suggested that the agricultural soils have been widely contaminated with PAEs in this region.

196 According to the commonly used soil cleanup objectives from the USEPA (2015), DEHP in the soil sample
197 collected from site C1 exceeded the allowable concentration (3900 ng/g). DEHP exhibited the highest
198 concentration (mean, 796 ng/g) among the analyzed PAEs, followed by DnBP (mean, 91.8 ng/g). The
199 contribution of DEHP in total PAEs was in the range of 13.9 to 98.9 %. The average total contributions
200 of DMP, DEP, and BBP were 5.1 % to the total concentrations. The composition was similar to those
201 reported in other regions of China (Chai et al. 2014; Zhang et al. 2015b).

202 Higher levels of PAEs were found in the sites located in area C (mean of 2120 ng/g). Many new buildings
203 were under construction in this area. A wide range of new building materials could release PAEs to the
204 surrounding environment (Xia et al. 2011). The plastic used in greenhouses in this area may also be an
205 important source of PAEs pollution (Wang et al. 2015). The concentrations of PAEs found in Chinese farmland
206 soils were significantly higher than in other countries, such as the UK (Gibson et al. 2005) and Denmark
207 (Vikelsee et al. 2002). The PAEs pollution in China was likely to become more serious in the near future
208 because of the increasing use for PAE-containing building materials, home furnishings, and PVC in the
209 process of rapid urbanization. In addition, facility agriculture (i.e., controlled environment agriculture) is
210 an important developing direction in China. A large amount of agricultural plastic films input and
211 greenhouses construction could be possible emission sources of PAEs (Wang et al. 2015). This should draw
212 more attention for strategic planning and regulation on pollution management of PAEs in China.

213 **Vertical distributions of OCPs and PAEs in soil profiles**

214 The vertical concentrations and distributions of OCPs and PAEs at different depths in three collected
215 agricultural soil profiles are shown in Fig. 2. Higher OCPs concentrations were observed in the 0–30-
216 cm surface layers relative to the subsurface soils, because the upper 30 cm of the soil was a plow layer
217 formed through frequent cultivation and plowing activities. A rapid decline of OCPs concentrations to
218 marginal level was observed when the soil depth was >30 cm. This indicated that OCPs in agricultural
219 soils were less likely to contaminate the groundwater and subsurface environments. In contrast, the
220 vertical distributions of PAEs in soil profiles were not regular. The relatively higher PAEs concentrations

221 were observed in the 0–20 cm surface layers of site C, and the 0–10-cm surface layer of site A. However,
222 PAEs could be detected through each soil layer to a depth of 90 cm. In site B, the higher concentration
223 was even found in the 70–80-cm layer of the soil profile. There was no obvious variation tendency for the
224 vertical distribution of PAEs, in contrast to that of OCPs in soils. This suggested that PAEs may be easier
225 to infiltrate into the soil profile, imposing potential risks to the subsurface soil and groundwater
226 environments.

227 **OCPs and PAEs pollution in vegetables**

228 A summary of the concentrations (ng/g dry weight) of OCPs and PAEs in plant samples is presented in
229 Tables 1 and 2, respectively. Cabbage was selected as a bioindicator because it was commonly planted as
230 food items for local residents in East and South China. Residues of OCPs in cabbages ranged from <0.1 to
231 15.0 ng/g for total HCHs and from <0.1 to 39.3 ng/g for total DDT-related compounds. However, the
232 concentration of DDTs was comparable with that of HCHs in plants. It was probably because the higher
233 vapor pressures and lower octanol-water coefficient (K_{ow}) of HCHs make them easier to accumulate in
234 plants than DDTs (Walker et al. 1999). The concentrations of PAEs in cabbages ranged from 60.1 to 2390
235 ng/g, with a mean of 601 ng/g, of which DEHP was the predominant compound detected in most
236 vegetable samples.

237 The concentrations of OCPs and PAEs in the plants were significantly correlated with the concentrations
238 in soils ($R = 0.72–0.91$, $p < 0.01$), suggesting that OCPs and PAEs in cabbages originated mainly from
239 the soil. However, both translocation from roots to aerial tissues and evaporation from soil to ambient air
240 followed by foliar uptake were possible pathways of these pollutants entering the edible parts of cab-
241 bages. The bioconcentration factors (BCF) of compounds, i.e., the ratio of concentrations in the plant to
242 corresponding concentrations in soil, were in the range of 0–1.31 for total HCHs, 0–0.16 for total DDTs,
243 and 0.29–1.23 for total PAEs, respectively. The BCF values of cabbages in the present study were lower
244 than those of OCPs in tomatoes from the south-eastern region of Buenos Aires Province in Argentina
245 (Gonzalez et al. 2003). This difference in soil-plant transfer might be caused by the short life cycle of

246 cabbages in the current study. In addition, cultivation methods, soil properties, and climate might be other key
247 factors contributing to the BCF values (Zhang et al. 2015a).

248

249 **Correlations among soil properties, microbiota, and pollutants**

250 Soil pollution could affect microbial community activity and the soil ecosystems (Brantner and Senko
251 2014). Soil proper- ties are important factors affecting the fate of pollutants and microbial community
252 composition. A matrix of correlation coefficients between pollutant residues, microbial community
253 characteristics, and soil properties are shown in Table 3. Significant relationships were observed between
254 PAEs and soil pH ($R = 0.49$, $p < 0.05$, $n = 26$); however, other soil physicochemical properties showed no
255 apparent relationships with the pollution levels of OCPs and PAEs. Soil TOC and total nitrogen seemed to
256 impose greater effects than OCPs and PAEs on the soil microbial communities. Negative relation- ships
257 were observed between PAEs and fungi in soils ($R = -0.54$, $p < 0.01$, $n = 26$), which suggested that
258 fungi are sensitive to environmental stress due to PAEs, and PAEs pollution may reduce the abundance of
259 soil fungi. In contrast, there was no significant correlation between OCPs and soil microbiota, suggesting
260 that OCPs in the soils showed no significant effect on the composition of microbial communities.

261

262 **Human health risk assessments**

263 The noncarcinogenic and carcinogenic risks of OCPs and PAEs to local villagers living close to the farmlands
264 through multiple pathways were assessed (Fig. 3). The average noncarcinogenic risks of PAEs (HI = 0.150 for
265 children and 0.084 for adults) was higher than the average noncarcinogenic risks of OCPs (HI = 0.123 for
266 children and 0.068 for adults). Among the measured PAEs, the average HI in soils was highest for DEHP,
267 while the noncarcinogenic risks of OCPs were mainly derived from p,p' -DDT and γ -HCH. The estimated intake
268 doses of PAEs and OCPs in all the samples were within acceptable levels (HI < 1). The average carcinogenic
269 risk of OCPs (3.28×10^{-6} for children and 7.85×10^{-6} for adults) was slightly higher than those of PAEs (2.99
270 $\times 10^{-6}$ for children and 7.26×10^{-6} for adults). DEHP and γ -HCH were the dominant contributors to the

271 carcinogenic risks of PAEs and OCPs, respectively. The estimated carcinogenic risk levels of OCPs and PAEs
272 were all less than 10^{-4} , implying low or very low carcinogenic risks to both adults and children.

273 Intake of agricultural products is the primary exposure pathway and contributed to over 99 % of the total
274 risks. The risks derived from the tightly controlled DDTs were in the acceptable range now, nevertheless,
275 potential accumulation of PAEs in vegetables should receive more attention in future monitoring programs.
276 The health risks due to both PAEs and OCPs pollution in soil were generally low based on the assessment
277 in this study. However, the risks caused by PAEs reached a comparable level with those of OCPs. The
278 elevated concentration of PAEs in the environment in China should arouse more stringent regulation
279 (which is currently absent) to safeguard the soil environment and food quality.

280

281 **CONCLUSION**

282 The agricultural soils and vegetable in the fast-growing areas in China have been subjected to relatively high
283 levels of OCPs and PAEs pollution. DEHP and *p,p'*-DDT contributed to most of the detected PAEs and OCPs,
284 respectively. Historical usage was regarded as the primary source of DDTs, whereas HCHs may originate
285 from fresh application of lindane in recent years. A large number of new building materials and plastic
286 used in greenhouses could release PAEs to the ambient environment. The OCPs residues were accumulated
287 in the surface plow layer, while PAEs were easier to infiltrate in soil, resulting in potential risks to the deep
288 soil layers and ground- water. The soil ecosystem function was not significantly influenced by PAE and
289 OCP pollution. The human health risks due to both PAEs and OCPs pollution in soil were generally low
290 based on the assessment in this study. However, given the increasing usage of PAEs in various products,
291 continual monitoring, and environmental health risk assessments are needed in some pollution hotspot
292 regions.

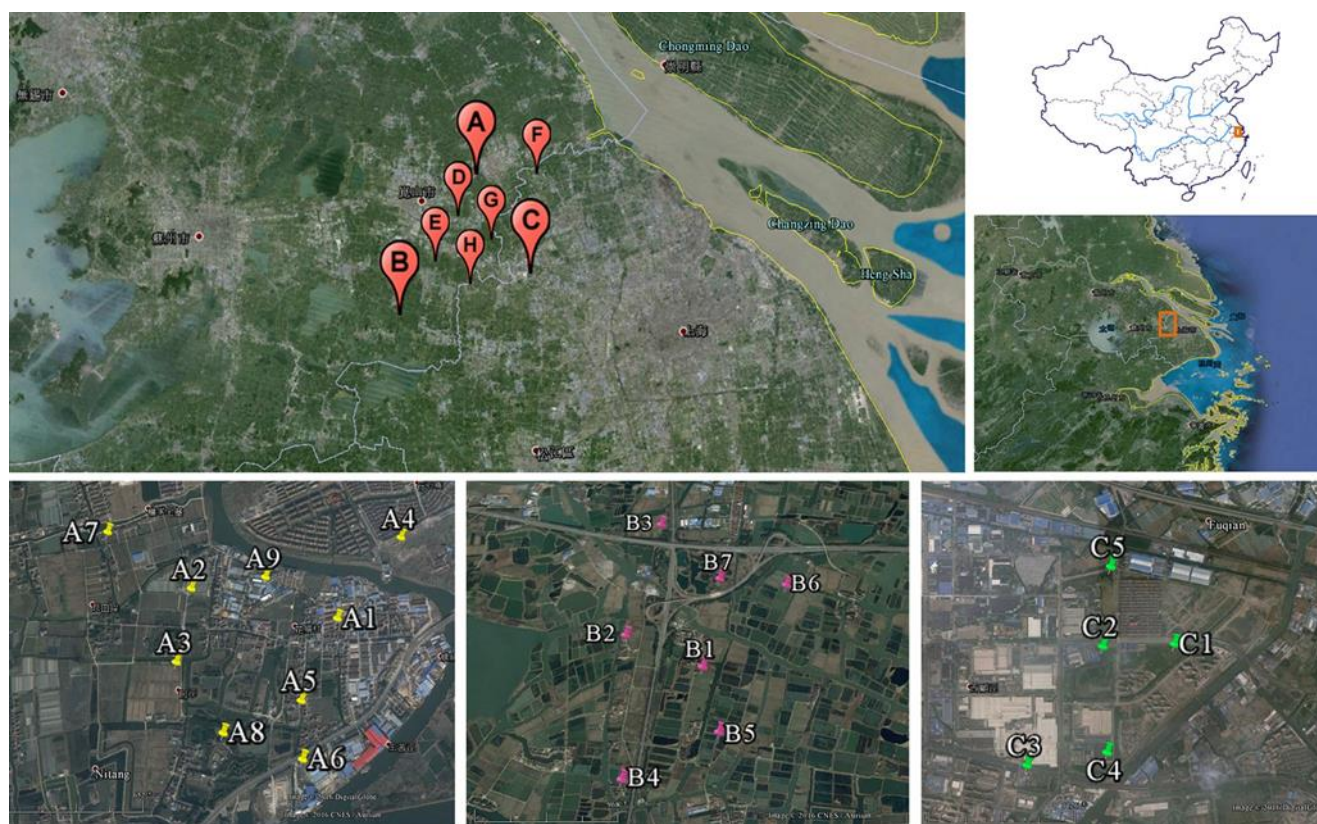
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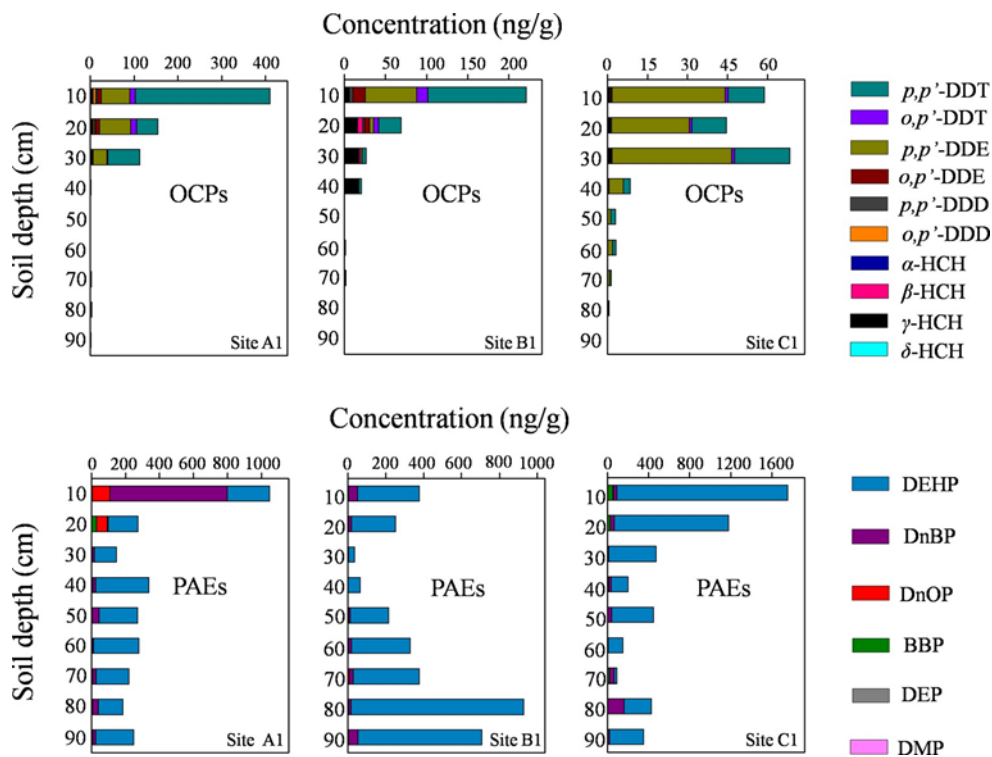
299 **LIST OF TABLES AND FIGURES**



300

301 Fig. 1 Map showing the sampling sites in the border of Jiangsu province and Shanghai Municipality,
302 eastern China. There were nine, seven, and five sites in A, B, and C, respectively. The three sampling
303 sites with soil profiles are A1, B1, and C1

304

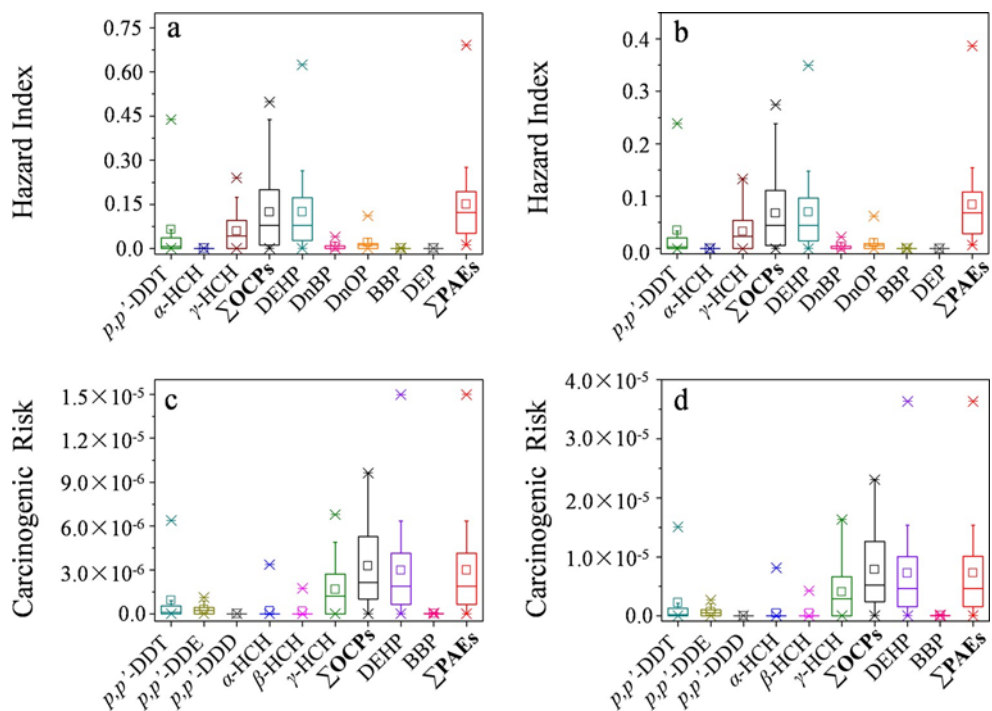


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306

307 Fig. 2 Vertical distributions of the concentrations and compositions of organic contaminants in
 308 agricultural soils of the study area

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310

311 Fig. 3 Noncarcinogenic risks to a children and b adults and carcinogenic risks to c children and d adults
 312 through dietary and nondietary exposure pathways to different organic contaminants

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Table 1 Concentrations (ng/g, dry weight) of OCPs in agricultural soil and vegetable samples

Compound	Soil					Vegetable				
	Min.	Max.	Mean	SD	Detectable rate (%)	Min.	Max.	Mean	SD	Detectable rate (%)
α -HCH	ND	4.67	0.47	0.96	38.5	ND	1.12	0.06	0.24	7.7
β -HCH	ND	3.70	0.58	0.95	38.5	ND	2.05	0.20	0.59	11.5
γ -HCH	ND	84.2	12.8	21.8	76.9	ND	12.9	3.19	3.52	61.5
δ -HCH	ND	7.45	0.57	1.72	19.2	ND	2.14	0.26	0.60	19.2
<i>o,p'</i> -DDE	ND	18.7	1.73	3.96	30.8	ND	1.34	0.10	0.35	7.7
<i>p,p'</i> -DDE	ND	79.8	29.0	20.6	88.5	ND	6.85	1.86	1.89	69.2
<i>o,p'</i> -DDD	ND	7.33	0.78	2.05	15.4	ND	2.05	0.13	0.46	7.7
<i>p,p'</i> -DDD	ND	4.77	1.18	1.26	69.2	ND	ND	ND	ND	0.0
<i>o,p'</i> -DDT	ND	15.3	1.77	3.30	46.2	ND	1.52	0.15	0.43	11.5
<i>p,p'</i> -DDT	ND	613	85.7	156	88.5	ND	38.3	5.61	10.7	53.8
Total OCPs	ND	662	134	163	88.5	ND	42.8	11.6	11.8	88.5

317 *SD* standard deviation, *ND* non-detectable

318

319 Table 2 Concentrations (ng/g, dry weight) of PAEs in agricultural soil and vegetable samples

Compound	Soil					Vegetable				
	Min.	Max.	Mean	SD	Detectable rate (%)	Min.	Max.	Mean	SD	Detectable rate (%)
DMP	ND	28.4	10.6	8.99	76.9	ND	31.6	3.36	8.42	15.4
DEP	ND	19.6	3.40	4.57	61.5	ND	20.1	1.88	5.39	11.5
DnBP	ND	659	91.8	163	57.7	ND	720	99.6	178	42.3
BBP	ND	78.3	11.6	20.6	61.5	ND	81.4	10.4	18.1	46.2
DEHP	28.9	5520	796	1120	100	ND	2250	450	523	84.6
DnOP	3.26	167	32.6	42.2	100	ND	200	36.3	53.6	69.2
Total PAEs	109	5560	946	1130	100	60.1	2390	601	538	100

323 *SD* standard deviation, *ND* non-detectable

324

325 Table 3 Correlation coefficients (*R*, *n* = 26) between pollutant residues, microbial community characteristics, and soil properties

	OCPs	PAEs	Bacteria	Fungi	Actinomycete	F/B	GN/GP	TOC	pH	TP	TN
OCPs	1										
PAEs	0.17	1									
Bacteria	0.28	-0.35	1								
Fungi	0.06	-0.54**	0.74**	1							
Actinomycete	0.23	-0.34	0.90**	0.72**	1						
F/B	-0.14	-0.13	-0.47*	0.14	-0.40*	1					
GN/GP	0.22	-0.30	0.35	0.50**	0.37	0.30	1				
TOC	0.30	0.03	0.49*	0.09	0.56**	-0.56**	-0.03	1			
pH	0.26	0.49*	-0.22	-0.23	-0.23	0.12	0.21	-0.18	1		
TP	0.10	0.04	0.12	0.16	0.17	0.05	-0.14	0.22	-0.01	1	
TN	0.23	-0.10	0.52**	0.25	0.59**	-0.49*	0.16	0.54**	-0.26	0.15	1

327 *F/B* PLFAs ratio of fungi to bacteria, *GN/GP* PLFAs ratio of gram-negative bacteria to gram-positive bacteria, *TP* total phosphorus, *TN* total nitrogen

328 *Correlation is significant at the 0.05 level; **correlation is significant at the 0.01 level

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331 **REFERENCES**

332

333 Brantner JS, Senko JM (2014) Response of soil-associated microbial communities to intrusion of coal
334 mine-derived acid mine drainage. *Environ Sci Technol* 48:8556–8563

335 Cai QY, Mo CH, QT W, Katsoyiannis A, Zeng QY (2008) The status of soil contamination by semivolatile
336 organic chemicals (SVOCs) in China: a review. *Sci Total Environ* 389:209–224

337 Chai C, Cheng HZ, Ge W, Ma D, Shi YX (2014) Phthalic acid esters in soils from vegetable greenhouses
338 in Shandong Peninsula, East China. *PLoS One* 9:e95701

339 Chen L, Zhao Y, Li LX, Chen BH, Zhang YH (2012) Exposure assess- ment of phthalates in non-
340 occupational populations in China. *Sci Total Environ* 427:60–69

341 China National Environmental Protection Agency (1995) Environmental quality standard for soils. GB-
342 15618-1995

343 Fang YY, Nie ZQ, Yang YM, Die QQ, Liu F, He J, Huang QF (2015) Human health risk assessment of
344 pesticide residues in market-sold vegetables and fish in a northern metropolis of China. *Environ Sci*
345 *Pollut Res* 22:6135–6143

346 Gibson R, Wang MJ, Padgett E, Beck AJ (2005) Analysis of 4- nonylphenols, phthalates, and
347 polychlorinated biphenyls in soils and biosolids. *Chemosphere* 61:1336–1344

348 Gonzalez M, Miglioranza KSB, de Moreno JEA, Moreno VJ (2003) Occurrence and distribution of
349 organochlorine pesticides (OCPs) in tomato (*Lycopersicon esculentum*) crops from organic produc-
350 tion. *J Agr Food Chem* 51:1353–1359

351 He Y, Ding N, Shi JC, Wu M, Liao H, JM X (2013) Profiling of microbial PLFAs: implications for
352 interspecific interactions due to intercropping which increase phosphorus uptake in phosphorus lim-
353 ited acidic soils. *Soil Biol Biochem* 57:625–634

354 Hu XY, Wen B, Shan XQ (2003) Survey of phthalate pollution in arable soils in China. *J Environ Monit*
355 5:649–653

356 Hu WY et al (2010) Spatial variability and temporal trends of HCH and DDT in soils around Beijing
357 Guanting reservoir, China. *Environ Geochem Hlth* 32:441–449

358 Islam S, Ahmed K, Al-Mamun H (2015) Distribution of trace elements in different soils and risk assessment:
359 a case study for the urbanized area in Bangladesh. *J Geochem Explor* 158:212–222

360 Li JH, Ko YC (2012) Plasticizer incident and its health effects in Taiwan.

361 *Kaohsiung J Med Sci* 28:S17–S21

362 Li YF, Cai DJ, Shan ZJ, Zhu ZL (2001) Gridded usage inventories of technical hexachlorocyclohexane
363 and lindane for China with 1/6 degrees latitude by 1/4 degrees longitude resolution. *Arch Environ Con*
364 *Tox* 41:261–266

365 Li XN, Jiao WT, Xiao RB, Chen WP, Chang AC (2015) Soil pollution and site remediation policies in
366 China. *Environ Rev* 23:263–274

- 367 Liu J, He XX, Lin XR, Chen WC, Zhou QX, Shu WS, Huang LN (2015a) Ecological effects of combined
368 pollution associated with E-waste recycling on the composition and diversity of soil microbial com-
369 munities. *Environ Sci Technol* 49:6438–6447
- 370 Liu MX, Yang YY, Yun XY, Zhang MM, Wang J (2015b) Occurrence and assessment of organochlorine
371 pesticides in the agricultural topsoil of Three Gorges Dam region, China. *Environ Earth Sci* 74:5001–5008
- 372 Ma TT, Wu LH, Chen L, Zhang HB, Teng Y, Luo YM (2015) Phthalate esters contamination in soils and
373 vegetables of plastic film green- houses of suburb Nanjing, China and the potential human health risk.
374 *Environ Sci Pollut Res* 22:12018–12028
- 375 Nakata H et al (2002) Organochlorine pesticides and polychlorinated biphenyl residues in foodstuffs and
376 human tissues from China: status of contamination, historical trend, and human dietary exposure. *Arch*
377 *Environ Con Tox* 43:473–480
- 378 Niu LL, Xu C, Yao YJ, Liu K, Yang FX, Tang ML, Liu WP (2013) Status, influences and risk assessment of
379 hexachlorocyclohexanes in agri- cultural soils across China. *Environ Sci Technol* 47:12140–12147
- 380 Niu LL, Xu Y, Xu C, Yun LX, Liu WP (2014) Status of phthalate esters contamination in agricultural soils
381 across China and associated health risks. *Environ Pollut* 195:16–23
- 382 PlasticsEurope (2015) Plastics—the Facts 2014/2015. [http://www. plasticseurope.org/](http://www.plasticseurope.org/)
- 383 Qiu XH, Zhu T, Yao B, Hu JX, Hu SW (2005) Contribution of dicofol to the current DDT pollution in China.
384 *Environ Sci Technol* 39:4385–4390
- 385 Sun JT et al (2016) Contamination of phthalate esters, organochlorine pesti- cides and polybrominated diphenyl
386 ethers in agricultural soils from the Yangtze River Delta of China. *Sci Total Environ* 544:670–676
- 387 Tang ZW, Huang QF, Nie ZQ, Yang YF, Yang J, Qu D, Cheng JL (2016) Levels and distribution of
388 organochlorine pesticides and hexachlorobutadiene in soils and terrestrial organisms from a former
389 pesticide-producing area in Southwest China. *Stoch Env Res Risk A* 30:1249–1262
- 390 Tao S, Liu WX, Li Y, Yang Y, Zuo Q, Li BG, Cao J (2008) Organochlorine pesticides contaminated surface soil
391 as reemission source in the Haihe plain, China. *Environ Sci Technol* 42:8395–8400
- 392 Teng YG, Wu J, Lu SJ, Wang YY, Jiao XD, Song LT (2014) Soil and soil environmental quality monitoring
393 in China: a review. *Environ Int* 69:177–199
- 394 USEPA (1997) Exposure factors handbook. US Environmental Protection Agency, Office of Research
395 and Development, Washington, DC EPA/600/P-95/002F
- 396 USEPA (2015) Region 9, Regional Screening Levels [http://www.epa. gov/region9/superfund/prg/](http://www.epa.gov/region9/superfund/prg/)
- 397 Vikelsoe J, Thomsen M, Carlsen L (2002) Phthalates and nonylphenols in profiles of differently dressed soils.
398 *Sci Total Environ* 296:105–116 Walker K, Vallero DA, Lewis RG (1999) Factors influencing the distri-
399 bution of lindane and other hexachlorocyclohexanes in the environment. *Environ Sci Technol* 33:4373–
400 4378
- 401 Wang YW, Zhang QH, Lv JX, Li A, Liu HX, Li GG, Jiang GB (2007) Polybrominated diphenyl ethers
402 and organochlorine pesticides in sewage sludge of wastewater treatment plants in China. *Chemosphere*
403 68:1683–1691
- 404 Wang J, Luo YM, Teng Y, Ma WT, Christie P, Li ZG (2013) Soil con- tamination by phthalate esters in
405 Chinese intensive vegetable pro- duction systems with different modes of use of plastic film. *Environ*
406 *Pollut* 180:265–273

- 407 Wang J, Chen GC, Christie P, Zhang MY, Luo YM, Teng Y (2015) Occurrence and risk assessment of
408 phthalate esters (PAEs) in vegetables and soils of suburban plastic film greenhouses. *Sci Total Environ*
409 523:129–137
- 410 Wang BB, Wu CF, Liu WX, Teng Y, Luo YM, Christie P, Guo D (2016) Levels and patterns of
411 organochlorine pesticides in agricultural soils in an area of extensive historical cotton cultivation in
412 Henan province, China. *Environ Sci Pollut Res* 23:6680–6689
- 413 Xia XH, Yang LY, Bu QW, Liu RM (2011) Levels, distribution, and health risk of phthalate esters in
414 urban soils of Beijing, China. *J Environ Qual* 40:1643–1651
- 415 Yang HJ, Xie WJ, Liu Q, Liu JT, Yu HW, Lu ZH (2013a) Distribution of phthalate esters in topsoil: a case
416 study in the Yellow River Delta, China. *Environ Monit Assess* 185:8489–8500
- 417 Yang D, Qi SH, Zhang JQ, Wu CX, Xing XL (2013b) Organochlorine pesticides in soil, water and sediment
418 along the Jinjiang River main-stream to Quanzhou Bay, Southeast China. *Ecotox Environ Safe* 89: 59–65
- 419 Zeng F et al (2008) Phthalate esters (PAEs): emerging organic contaminants in agricultural soils in peri-
420 urban areas around Guangzhou, China. *Environ Pollut* 156:425–434
- 421 Zhang AP, Chen ZY, Ahrens L, Liu WP, Li YF (2012) Concentrations of DDTs and enantiomeric fractions
422 of chiral DDTs in agricultural soils from Zhejiang Province, China, and correlations with total organic
423 carbon and pH. *J Agr Food Chem* 60:8294–8301
- 424 Zhang AP, Luo WX, Sun JQ, Xiao H, Liu WP (2015a) Distribution and uptake pathways of
425 organochlorine pesticides in greenhouse and conventional vegetables. *Sci Total Environ* 505:1142–
426 1147
- 427 Zhang Y, Wang PJ, Wang L, Sun GQ, Zhao JY, Zhang H, Du N (2015b) The influence of facility agriculture
428 production on phthalate esters distribution in black soils of Northeast China. *Sci Total Environ* 506: 118–
429 125
- 430 Zhong YC, Zhu LZ (2013) Distribution, input pathway and soil-air exchange of polycyclic aromatic
431 hydrocarbons in Banshan Industry Park, China. *Sci Total Environ* 444:177–18

