

Concentration and influence factors of atmospheric organochlorine pesticides in a coastal island in Fujian, southeast China

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Abstract

Atmospheric particulate samples collected from Pingtan Island in Fujian province were analyzed for 20 organochlorine pesticides (OCPs) with the aims of elucidating the contamination levels and their influence factors, and providing more comprehensive and fundamental data for the risk assessment of OCPs in this coastal area. The concentration of total OCPs ranged from ND~27.25 pg m⁻³ (an average of 4.30 ± 4.07 pg m⁻³) and ND~13.16 pg m⁻³ (an average of 3.11 ± 2.54 pg m⁻³) in 2006 and 2007 respectively, and the level obviously lower than urban areas. HCH and DDT were the predominant contaminants, and those contaminants are mainly historical residues. Obvious seasonal variations in OCP levels correlate significantly with total particulate levels; higher concentrations of most OCP compounds appeared in winter, whereas lower concentrations appeared in summer. The distribution pattern of the level of most OCP compounds might be directly or indirectly influenced by meteorological conditions, and TOC is an important factor influencing the persistence of these OCPs in atmospheric particulates. The source of atmospheric particulates was traced by stable carbon isotopes, which indicate that the increased levels of OCPs in winter and spring influenced by the source of polluted air mass during the “heating season” of Northern China. The cancer risk probability was evaluated based on the residual levels of OCPs, and the results show that dermal contact was the primary pathway affecting human health, and the effect of OCP residuals in atmospheric particulates of the coastal area could not be neglected.

Keywords: Organochlorine pesticides; Fujian coastal area; Carbon stable isotope; Atmospheric particulates; Meteorological conditions

INTRODUCTION

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37 Organochlorine pesticides (OCPs) are widely concerned as one class of important
38 persistent organic pollutants (POPs) due to their salient features of bioaccumulation, ubiquity
39 and persistence. OCPs were extensively used around the world between the 1950s and the
40 1970s (Wu *et al.*, 2011). As a consequence of their high toxicity to biota and humans, most
41 OCPs were banned in most countries from the 1970s to the 1980s (Li *et al.*, 2014; Qu *et al.*,
42 2015; Willett *et al.*, 1998; Wu *et al.*, 2011). However, they could still be found in various
43 environmental media on a global scale (Evenset *et al.*, 2016; Gai *et al.*, 2014; Li *et al.*, 2009;
44 Yu *et al.*, 2013). Once these contaminants are released into the environment, some of the
45 semi-volatile OCPs can undergo long-range atmospheric transport (LRAT) to remote pristine
46 areas as gases or by adsorbing onto atmospheric aerosols (Lao *et al.*, 2017; Wania and
47 Mackay, 1993; Wu *et al.*, 2010). Particulate matter (PM) in atmosphere is the main pollutant
48 affecting the regional air quality, and POPs in the gas phase are easily absorbed on PM and
49 transported atmospherically (El-Mubarak *et al.*, 2015; Xing *et al.*, 2017). In fact, atmospheric
50 particulates are considered to be the primary carrier for transferring organic contaminants in
51 environments (Ding *et al.*, 2015; Gai *et al.*, 2014; Lao *et al.*, 2018; Xing *et al.*, 2017). Finally,
52 PM coupled with POPs are either deposited in soils and water introducing the pollutants to the
53 ground and aquatic environments, or are absorbed by organisms during transport (Zhu *et al.*,
54 2017). More importantly, OCPs associated with fine particles can enter biological respiratory
55 systems, and might affect biota including human beings (Pagano *et al.*, 1996). Previous
56 studies have shown that the concentration of PM was positively correlated with the morbidity
57 and mortality of respiratory and cardiopulmonary diseases (Baulig *et al.*, 2003; Künzli *et al.*,
58 2000; Obot *et al.*, 2002). Information on the occurrence of OCPs in PM is available for urban

59 settings (Ding *et al.*, 2015; El-Mubarak *et al.*, 2015; Wu *et al.*, 2005; Xu *et al.*, 2011), but
60 background areas such as coastal islands are limited. Coastal areas are susceptible to the
61 accumulation of semi-volatile organic compounds, such as OCPs, from atmospheric inputs
62 (He and Balasubramanian, 2010a).

63 China is a large agricultural and industrial country, and OCPs have been used in large
64 amounts, especially in the agricultural areas of southeast China (Qu *et al.*, 2015; Tieyu *et al.*,
65 2005). The total production of DDT and HCH was approximately 0.4 and 4.9 million tons,
66 prior to being phased out in 1983, which accounts for 20% and 33% of the global production,
67 respectively (Xu *et al.*, 2011). In China, chlordane was still used as a termiticide until 2008
68 (Wu *et al.*, 2011). Therefore, although most OCPs have been prohibited since approximately
69 three decades ago, the historical widespread usage of OCPs in China is responsible for high
70 residual levels in the environment. Generally, due to the differences in the usage of OCPs in
71 different regions, the occurrence at the regional scale displays a distribution pattern of south >
72 central > north (Hao *et al.*, 2008).

73 Pingtan Island (between 25°15'-25°45' N, 119°32'-120°10' E), located in southeastern
74 China, is the fifth largest island in China and the largest island in Fujian Province. It is an area
75 with a typical subtropical monsoon climate. Many studies have been conducted on the
76 occurrence of OCPs in coastal areas of southeastern China (adjacent Pingtan areas), especially
77 focusing on aquatic systems (i.e., sediment and water) and soils (Liu *et al.*, 2016; Qu *et al.*,
78 2015; Yang *et al.*, 2013; Zhang *et al.*, 2011; Zhang *et al.*, 2003). However, there is little
79 literature concerning the OCP distribution in atmospheric particulates of this region and
80 limited understanding of the contribution of OCPs in PM and of the effect of the LRAT of

81 contaminants from the source to coastal areas.

82 To obtain a more thorough understanding of OCPs in atmospheric particles in the coastal
83 island of southeastern China, two-year sampling of the total suspended PM of ambient air was
84 conducted in Pingtan. The aim of the study was to understand the contamination levels,
85 seasonal variations and potential sources of OCPs on Pingtan Island. Furthermore, we
86 analyzed the influencing factors (such as total organic carbon (TOC) and meteorological
87 conditions) and assessed the toxicological risk of OCPs.

88 **MATERIALS AND METHODS**

89 *Sampling Location and Sample Collection*

90 Pingtan is an island located in the southeast of China. It has a distinct monsoon climate,
91 with the prevailing wind in the southerly direction and frequent tropical storms in summer,
92 and prevailing wind in the northeasterly direction the rest of the year. The sampler was set up
93 on a coastal mountain with no direct pollution sources around the sampling site, located on
94 the southeast of Pingtan Island, about 15 meters above sea level.

95 Air sampling was conducted continuously from January 2006 to November 2007, using a
96 high-volume air sampler. A glass fiber filter (GFF: the diameter of 0.4 μm , 200 mm x 250 mm,
97 American Whatman company) was used to collect the PM. The GFFs were annealed in an
98 oven at 450°C for 4 h to remove organic residues before use. After sampling, the GFFs were
99 removed from the sampler, wrapped with aluminum foil, placed in a darkened desiccator and
100 transported to the laboratory as soon as possible. The collected PM mass (after freeze-dried)
101 was calculated by subtracting the pre-weight from the post-weight of the GFF. After being
102 weighed, the samples were stored in a freezer at -20°C until analysis.

103 ***Sample Pretreatment and Analysis***

104 Details about the sample extraction and analysis are presented in supplementary material
105 (Text S1). Briefly, the samples were extracted using an accelerated solvent extraction
106 instrument (ASE 200, Dionex, US), using 1:1 dichloromethane / hexane as the extracting
107 solvent. The extract was concentrated and transferred into hexane using a rotary evaporation
108 and then concentrated again to 1 mL under a gentle stream of nitrogen. Finally, the
109 concentrated extract was further cleaned with a chromatography column. Then eluted with
110 100 mL of hexane / dichloromethane (v/v 1:1). The eluate was concentrated to 0.1 mL under a
111 gentle stream of nitrogen and transferred into hexane for analysis. The determination of OCP
112 (including α -HCH; β -HCH; γ -HCH; δ -HCH; Aldrin; Dieldrin; Endrin; Heptachlor;
113 Heptachlor exoxide; α -chlordane; γ -chlordane; Endosulfan I ; Endosulfan II ; P, P'-DDT, P,
114 P'-DDD, P, P'-DDE, Endrin aldehyde, Endosulfan sulfate, Endrin ketone, Methoxychlor) was
115 performed on a gas chromatography/electron capture detector (GC/ECD) (Agilent 7890A with
116 Ni⁶³ ECD) equipped with a DB-5 MS column (60 m×0.25 mm×0.25 μ m film thickness). The
117 temperature of the detector and injector was 300°C and 270°C, respectively. The oven
118 temperature started at 80°C, increased to 210°C at 10°C min⁻¹, then increased to 250°C at a
119 rate of 0.8°C min⁻¹, and at last increased to 290°C at 10°C min⁻¹ before being held for 12 min.
120 1 μ L of each sample was injected in splitless mode. Nitrogen was used as the carrier gas with
121 a flow rate of 30 mL min⁻¹.

122 ***Quality Control and Quality Assurance (QA/QC)***

123 The identification of individual target OCPs was based on the retention time compared
124 with corresponding standards, and they were quantified using an internal standard. The GFFs,

125 which went through dichloromethane / hexane (v:v, 1:1) extraction for 24 h, and repeated 3
126 times before drying, are as the blank samples. The blank samples were added to unknown
127 samples to treat and measure together, and added a blank sample for every 20 unknown
128 samples, and no 20 OCPs target compounds were detected in all blank samples. Before
129 extraction, the blank samples and the samples were added 60 $\mu\text{g L}^{-1}$ internal standard
130 (2,4,6-trichlorobiphenyl) to monitor the recovery rate of extraction process, and the recovery
131 rate was in the range of 81.4%-115.3%, and all data were corrected for recovery.

132 ***Risk Assessment***

133 There are three pathways of human exposure to OCPs through ambient particles, dermal
134 contact, ingestion and inhalation. Cancer risks via those three pathways of ambient particles
135 were calculated from Eqs. (2), (3) and (4), which were derived from previous studies (Ding et
136 al., 2015; Ge et al., 2013), and each parameter is shown in Table S1.

$$137 \quad \text{ADD (ingest)} = \frac{C(\text{particle}) \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF}$$

138 (1)

$$139 \quad \text{ADD (dermal)} = \frac{C(\text{particle}) \times \text{SA} \times \text{AF}(\text{particle}) \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF}$$

140 (2)

$$141 \quad \text{ADD (inhale)} = \frac{C(\text{particle}) \times \text{IR}(\text{inhalation}) \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{AT}}$$

142 (3)

143 ***Meteorological Parameters***

144 The data of ambient temperature (T), wind direction (WD), wind speed (WS),
145 atmospheric pressure (AP), water vapor pressure (WVP), relative humidity (RH) and rainfall,
146 were from China Meteorological Data Sharing Service System (CMDSS), located in the site

147 of Pingtan meteorological observation station. The frequency of wind direction and the
148 temporal variations of wind speed and temperature from January 2006 to November 2007 are
149 plotted in Figure S1 and S2.

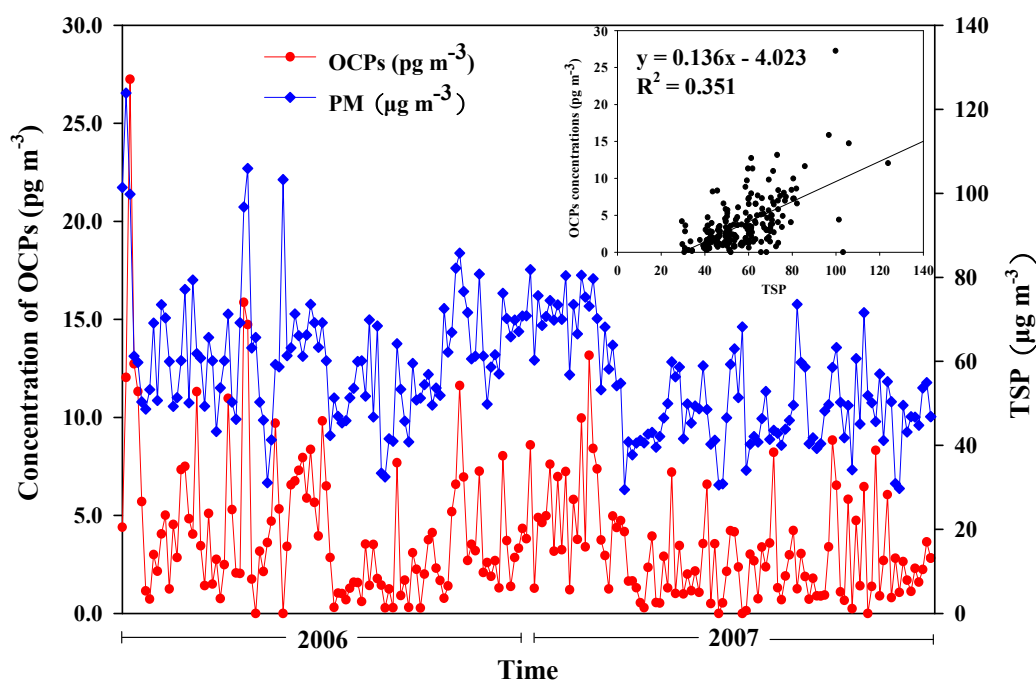
150 **RESULTS AND DISCUSSION**

151 *Atmospheric Concentrations and Seasonal Variations*

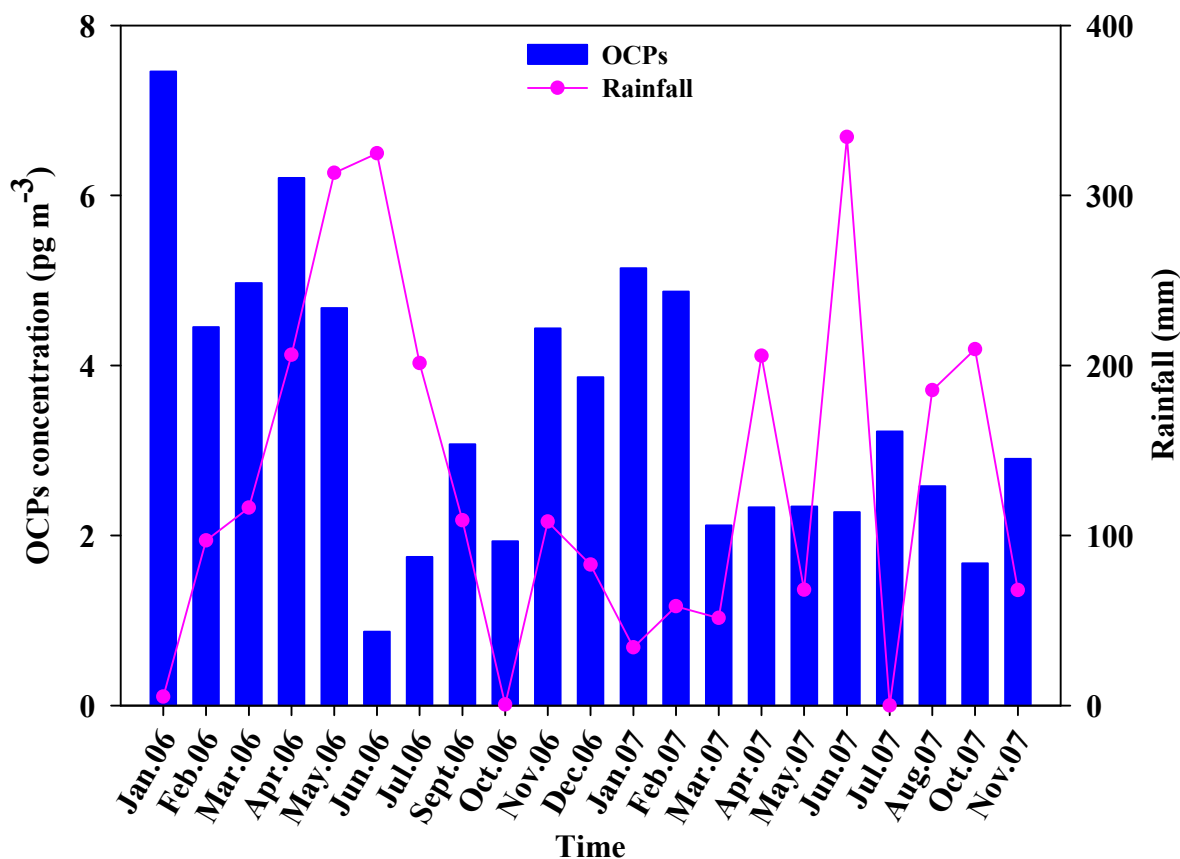
152 208 samples were collected from Pingtan Island from January 2006 to November 2007
153 (August 2006 and September 2007 were absent due to sampler maintenance). The results of
154 the OCP and PM levels are summarized in Figure 1, and the monthly average concentrations
155 of $\Sigma 20$ OCPs and rainfall over the two-year sampling period are plotted in Figure 2.

156 The total OCP concentration correlated well with TSP and exhibited a good correlation
157 coefficient (Figure 1), and ranged from ND~27.25 pg m^{-3} (an average of $4.58 \pm 5.00 \text{ pg m}^{-3}$)
158 and ND~13.16 pg m^{-3} (an average of $3.11 \pm 2.54 \text{ pg m}^{-3}$) in 2006 and 2007, respectively. For
159 individual compounds, DDT and HCH were the predominant contaminants in all samples,
160 followed by methoxychlor, while the remaining OCPs were found at relatively low levels.
161 Compared with other regions, much higher OCP concentrations in PM were found in the
162 major cities, such as Jinan (China, $\Sigma 18$ OCPs = $92 \pm 82 \text{ pg m}^{-3}$) (Xu *et al.*, 2011), Northern
163 China ($\Sigma 20$ OCPs = 0.14~34.72 pg m^{-3}) (Ding *et al.*, 2015), Konya (Turkey, $\Sigma 20$ OCPs = 186
164 $\pm 833 \text{ pg m}^{-3}$) (Ozcan and Aydin, 2009) and Riyadh (Saudi Arabia, $\Sigma 18$ OCPs = $183 \pm 235 \text{ pg}$
165 m^{-3}) (El-Mubarak *et al.*, 2015), indicating that the occurrence of OCPs in the coastal island
166 was relatively low. The highest OCP concentrations appeared in January 2006 and 2007, and
167 the seasonal distribution was in the following order: winter (5.96 pg m^{-3}) > spring (5.28 pg
168 m^{-3}) > fall (3.15 pg m^{-3}) > summer (1.31 pg m^{-3}) in 2006 and winter (4.63 pg m^{-3}) > summer

169 (2.69 pg m^{-3}) > fall (2.29 pg m^{-3}) > spring (2.26 pg m^{-3}) in 2007. The seasonality of rainfall
170 may partly be responsible for the monthly variations of OCPs level (Figure 2).The detailed
171 description of contamination characteristics of individual OCPs was shown in the following
172 sections.



173
174 Figure 1 Temporal variations of the total OCP concentrations and PM at Pingtan Island from
175 January 2006 to November 2007 (lack of the data of August 2006 and September 2007)



176

177 Figure 2 Seasonal variations of total OCP concentrations in PM of Pingtan Island from

178

January 2006 to November 2007

179 **HCH**

180 HCH was widely used in China as two formulations, one was technical HCH (60-70%
 181 α -HCH, 5-12% β -HCH, 10-12% γ -HCH, 6-10% δ -HCH), and the other was lindane
 182 (approximately 99% of γ -HCH).

183 In our study, HCH was one of the dominant OCPs in air at Pingtan Island and was
 184 detected in almost all samples. The concentration of Σ HCH isomers (α -, β -, γ -, δ -HCH) in the
 185 analyzed samples was ND~4.64 pg m⁻³ (an average of 1.10 ± 0.94 pg m⁻³) and ND~4.44 pg
 186 m⁻³ (an average 0.96 ± 0.75 pg m⁻³) in 2006 and 2007, respectively, which accounted for 25.5%
 187 and 30.9% of the total OCPs, respectively. The average annual concentrations of the HCH
 188 isomers were as follows: $\beta > \alpha > \gamma > \delta$ in both 2006 and 2007 (Figure 4). Seasonal variations

189 were observed at Pingtan for Σ HCH isomers (Figure 3). Higher Σ HCH concentrations were
190 observed in the cool season (from January to April 2006 and from October 2006 to February
191 2007), whereas lower concentrations were observed in the warm season. However, high HCH
192 concentrations could mainly be attributed to β -HCH, while an increasing proportion of
193 α -HCH appeared in the warm season (Figure 4).

194 Historically, HCH products were widely used in the southeastern region of China. High
195 HCH concentrations were detected in water, sediment and soil, and they could be
196 re-suspended or re-volatilized to the local atmosphere (Qu *et al.*, 2015; Zhang *et al.*, 2009;
197 Zhang *et al.*, 2003; Zheng *et al.*, 2010). Due to their high volatility, α - and γ -HCH tend to
198 evaporate into the gas phase (Wu *et al.*, 2010; Zheng *et al.*, 2010). However, β -HCH is the
199 most stable isomer and tends to accumulate in particles as a consequence of its far lower
200 Henry's law constant and its equatorially positioned chlorines (Zhang *et al.*, 2009). Thus, it
201 was concluded that a high concentration of β -HCH in atmospheric PM might be historical
202 residue from industrial and agricultural applications in southeastern China.

203 It has been suggested that the ratio of α - / γ -HCH in the environment was strongly
204 influenced by the usage of lindane (α - / γ -HCH < 0.1) and technical HCH (α - / γ -HCH at
205 3.6~15) (Zheng *et al.*, 2010). A α -/ γ -HCH ratio lower than 1 indicates that the amount of HCH
206 is primarily derived from local and recent lindane inputs, whereas a ratio higher than 7 is
207 attributed to LRAT or historical residue derived from technical HCH (Xu *et al.*, 2011). In our
208 study, the ratio ranged from 0.17 to 0.93 from January-March 2006, and a lower ratio
209 appeared in July 2007 (lower than 1), indicating higher local and recent inputs of lindane
210 during these periods. Whereas the ratios ranged from 1.09 ~ 6.00 in other months (except

211 March 2007), and these values indicated no preference between lindane and technical HCH.

212 Additionally, the α -/ γ -HCH ratio exhibited an increasing trend with time in 2006 and a

213 decreasing trend after March 2007 (Figure 3). However, an abrupt rise in the α -/ γ -HCH ratio

214 in March 2007 implied that there may be historical residue of technical HCH. α -HCH has a

215 longer atmospheric lifetime (120 d) than γ -HCH (96 d), and γ -HCH can be converted to α -

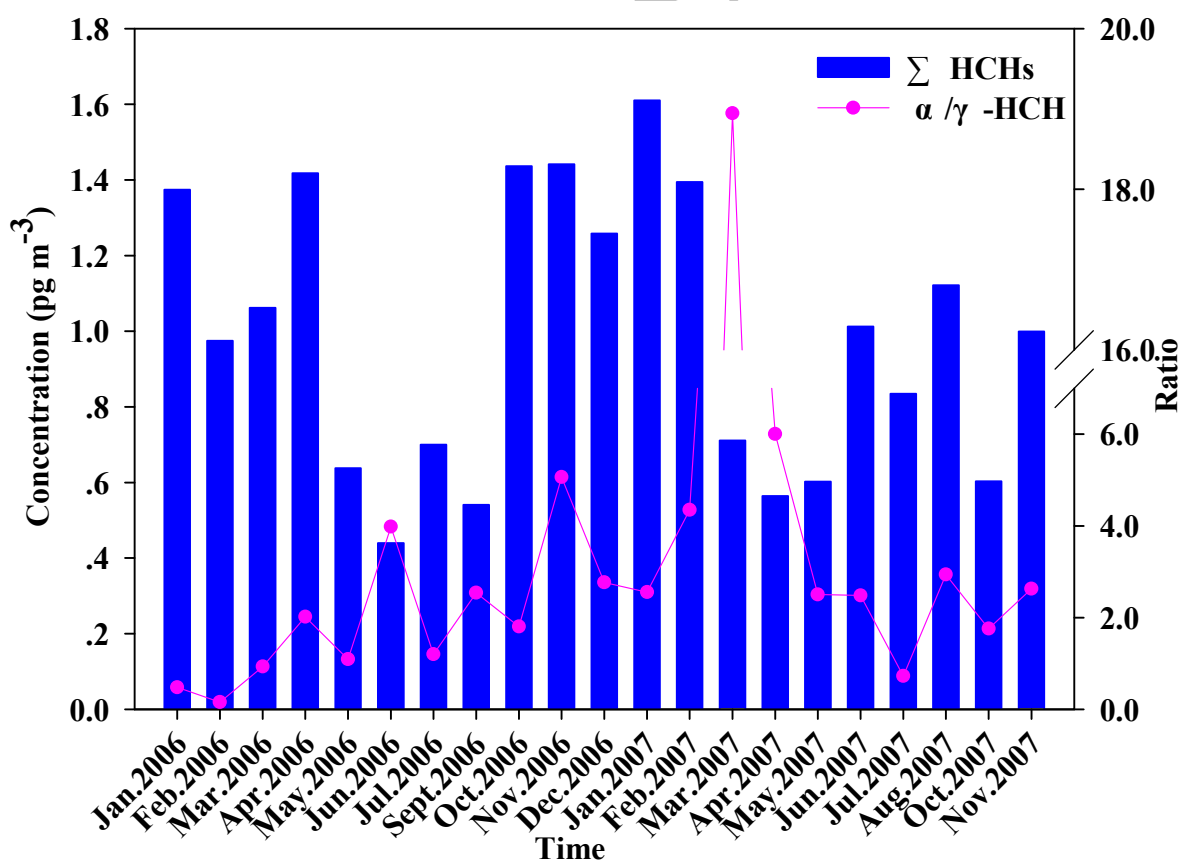
216 HCH by photoisomerization. Thus, all of these properties cause a lower residence time of

217 γ -HCH in atmospheric PM compared to that of α -HCH, leading to increase α -/ γ -HCH ratios

218 (Wu *et al.*, 2010). In addition, the extremely high value of α -/ γ -HCH in March 2007 may also

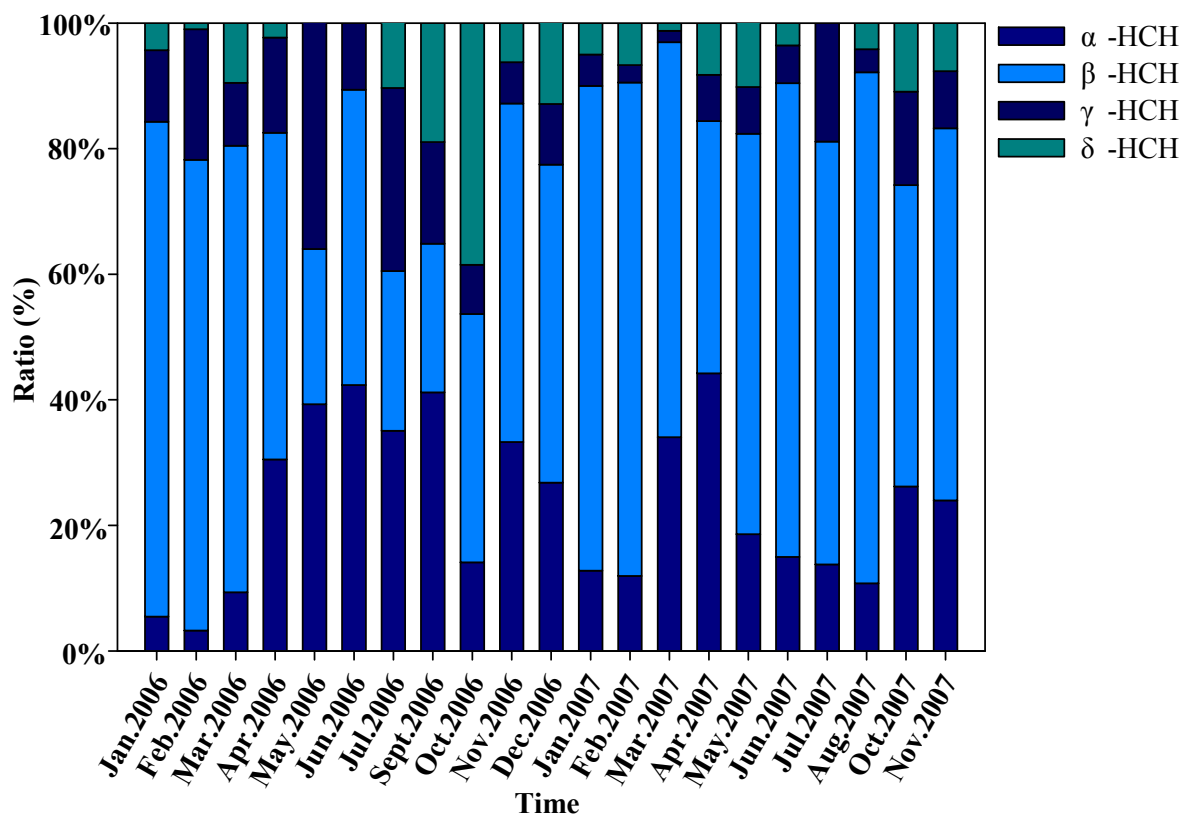
219 be explained by the re-volatilization of α -HCH from secondary sources, such as contaminated

220 sediments, soil and water surfaces (Bossi *et al.*, 2013).



221

222 Figure 3 Seasonal variations of Σ HCH concentrations and ratios of α - / γ -HCH in PM from



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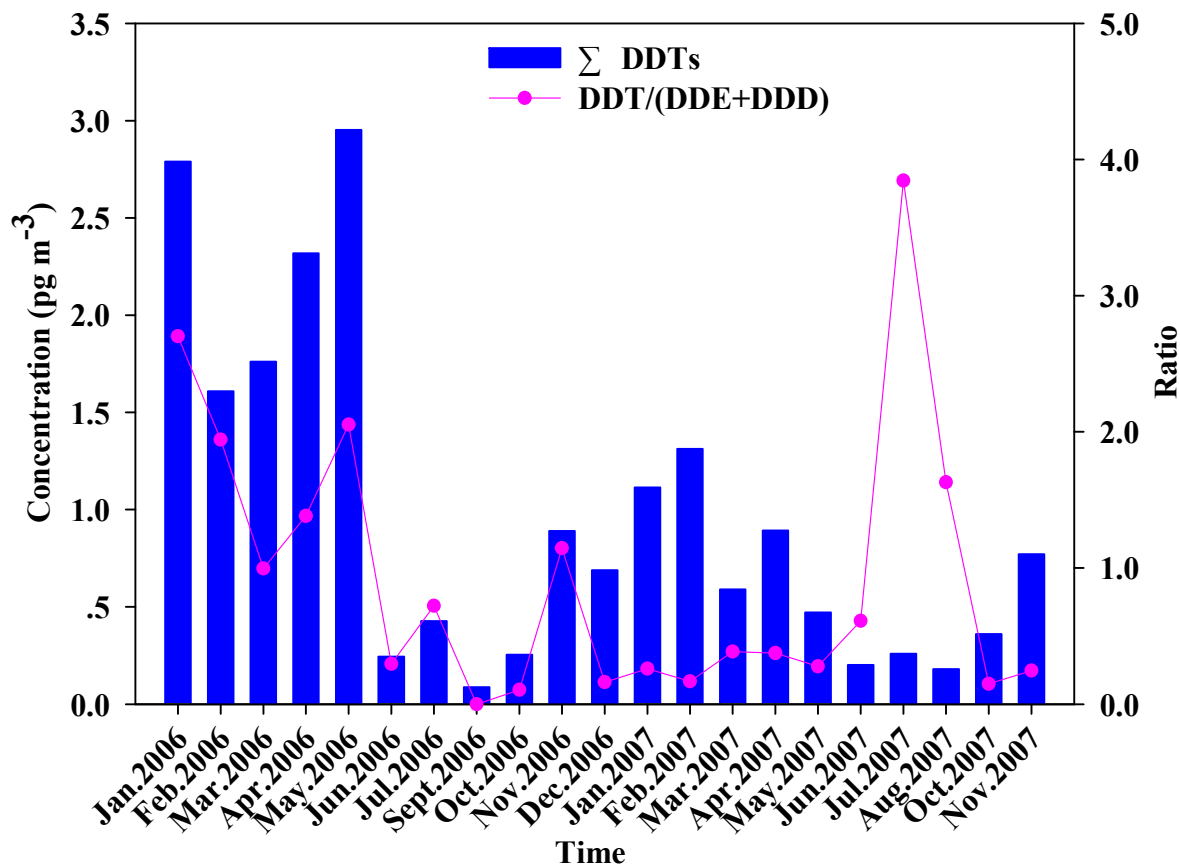
225 Figure 4 Distribution percent of the four HCH isomers in atmospheric PM from Pingtan
226 Island

227 **DDT**

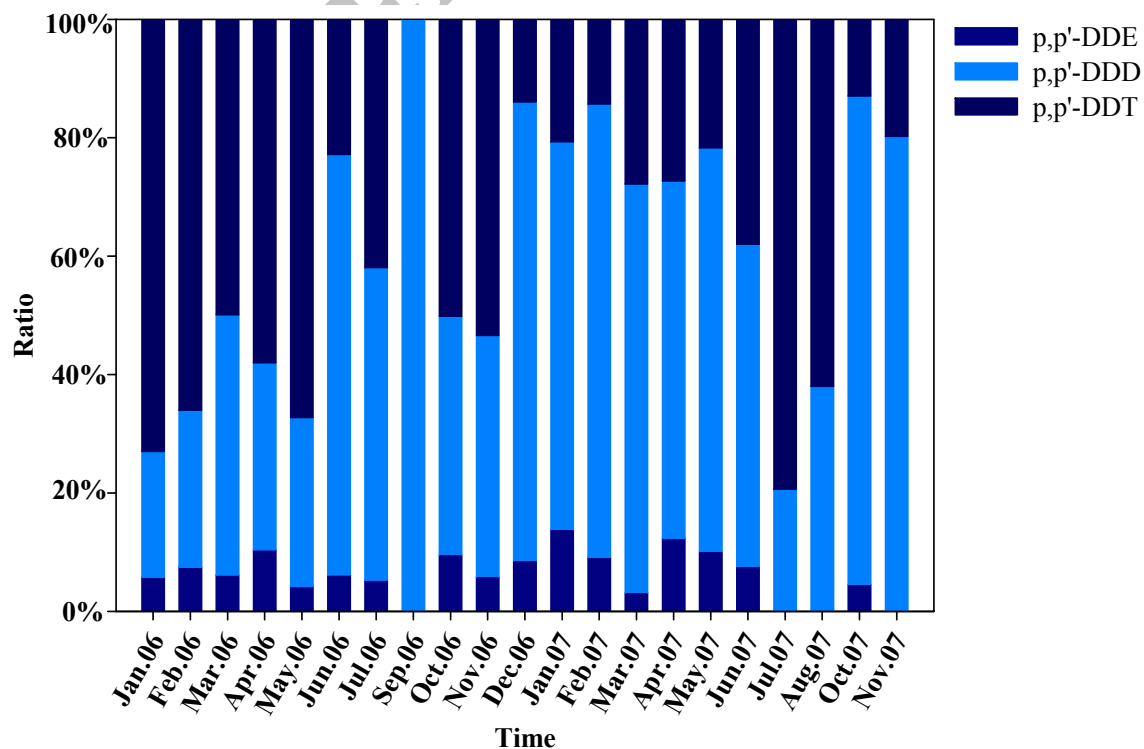
228 In our study, DDT compounds (including p,p'-DDT, p,p'-DDE and p,p'-DDD) were
229 detected in most atmospheric PM samples, ranging from ND ~ 17.36 pg m^{-3} (an average of
230 $1.34 \pm 2.16 \text{ pg m}^{-3}$) and ND ~ 5.22 pg m^{-3} (an average of $0.65 \pm 0.65 \text{ pg m}^{-3}$) in 2006 and
231 2007, respectively, accounting for approximately 31.1% and 21.0% of ΣOCPs . The annual
232 mean DDT concentration in 2006 was more than 2-fold times higher than the average in 2007.
233 Among the DDT isomers, p,p'-DDT was the most abundant compound, followed by
234 p,p'-DDD and p,p'-DDE in 2006, while p,p'-DDD > p,p'-DDT > p,p'-DDE in 2007 (Fig. 6). A
235 seasonal pattern of DDT compounds was similar to OCPs levels (Figure 5). The DDTs level

236 was relatively low compared with other urban regions, such as Jinan (1.4~76 pg m⁻³) (Xu *et*
237 *al.*, 2011), Tianjin (25~2210 pg m⁻³ in autumn and 416 ~3140 pg m⁻³ in winter) (Wu *et al.*,
238 2005) and northern China (Ding *et al.*, 2015).

239 In the environment, p,p'-DDT can degrade to p,p'-DDE in aerobic environments and to
240 p,p'-DDD in anaerobic environments (Yang *et al.*, 2013). Hence, the ratio of p,p'-DDT over
241 (p,p'-DDD + p,p'-DDE) can be used to trace the degree of degradation of the parent
242 compounds and to distinguish recent inputs (the ratio > 1) from historical residues (the ratio <
243 1) (Li *et al.*, 2007; Xu *et al.*, 2011). The results in our study showed that the ratio was 1.38 in
244 2006 and 0.35 in 2007 (Figure 5), indicating that recent usage of DDT might have the greatest
245 influence on the 2006 results, while historical residual dominated the 2007 results.
246 Remarkably, though the DDTs concentration was relatively low in summer, the highest ratio
247 appeared in July 2007, which might have been influenced by DDT-containing antifouling
248 paints commonly used on fishing boats in the coastal regions. To prevent the adhesion of
249 marine organisms such as mollusks and barnacles, DDT-containing antifouling paints are
250 often used on fishing boats by the fishermen (Li *et al.*, 2007; Zheng *et al.*, 2010). Furthermore,
251 during periods when fishing was prohibited and the boats were not working, a large amount of
252 the antifouling paints were used, resulting in newly generated DDT occurring at Pingtan
253 Island with summer monsoons.



254
 255 Figure 5 Temporal variations of Σ DDT concentrations and ratios of p,p'-DDT / (p,p'-DDE +
 256 p,p'-DDD) in atmospheric PM of Pingtan Island from January 2006 to November 2007



257
 14

258 Figure 6 Distribution percentage of three DDT isomers in atmospheric PM from Pingtan
259 Island

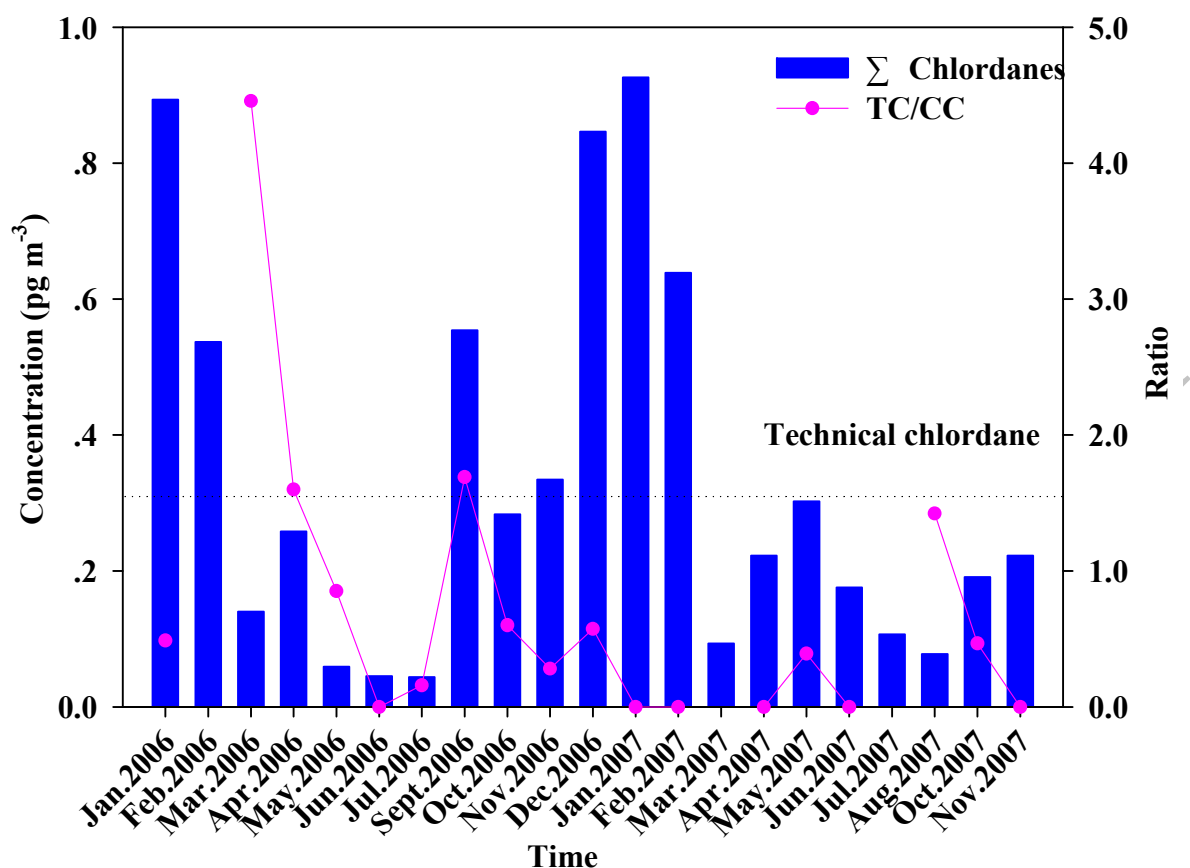
260 **Chlordane**

261 Technical chlordane is a mixture of over 140 different components, with the major
262 constituents being trans-chlordane (TC), cis-chlordane (CC) and heptachlor (HEPT)
263 (Bidleman *et al.*, 2002; Wu *et al.*, 2011). In the environment, HEPT will be metabolized to
264 heptachlor epoxide (HEPX), which is more stable in the air and carcinogenic (Bidleman *et al.*,
265 1998a). The concentrations of Σ chlordanes (sum of TC, CC, HEPT, HEPX) ranged from
266 ND~2.37 pg m^{-3} (average of $0.39 \pm 0.55 \text{ pg m}^{-3}$) and ND~2.81 pg m^{-3} ($0.32 \pm 0.54 \text{ pg m}^{-3}$) in
267 2006 and 2007, respectively. The three main components of technical chlordane (TC, CC and
268 HEPT) were only sporadically detected in all samples from Pingtan Island. However, HEPX
269 was the most abundant compound, accounting for approximately 71.4% and 78.7% of
270 Σ chlordane. The seasonal cycle of Σ chlordane concentration was also similar to total OCPs
271 level (Figure 7).

272 Chlordane was generally used as a termiticide, insecticide and herbicide in China during
273 the past decades, and it could still be found as termiticide as late as 2008 with a usage rate of
274 200 tons per year (Wu *et al.*, 2011; Zhang *et al.*, 2009). However, no serious pollution by TC
275 and CC was observed in our study. Once released into the terrestrial ecosystem, chlordane
276 tended to bind with soil particles. Thus, it was not easily transported to Pingtan Island, which
277 is isolated and far away from the source of the pollution. Concentrations of HEPT are mostly
278 below the detection limit in the Pingtan atmospheric PM because HEPT is rapidly
279 transformed to HEPX in the environment (Bossi *et al.*, 2013), this may responsible for the

280 higher HEPX level whereas lower HEPT in our study. However, relatively high chlordane
281 concentrations appeared in spring and fall, which might be attributed to the application of
282 pesticides in spring and the tilling of soil in fall.

283 The TC/CC ratio has previously been used to understand the emission history and
284 degradability of chlordane (Shen *et al.*, 2005; Wu *et al.*, 2011). The ratio in technical
285 chlordane is 1.56, and the value decreases for weathered chlordane. Relatively uniform
286 TC/CC ratios of below 1.56 were recorded during the sampling period (Figure 7), reflecting
287 the main influence by weathered chlordane. A higher ratio in March 2006, indicating newly
288 generated chlordane during this period. Although the partitioning properties and atmospheric
289 deposition rates of TC are similar to CC, TC is generally more volatile and precipitated from
290 the atmosphere faster than CC (Bidleman *et al.*, 2002; Wu *et al.*, 2011). Thus a decrease in the
291 TC/CC ratio with LRAT from far sources is expected (Wu *et al.*, 2011). Therefore, the
292 relatively low concentrations of TC and CC in Pingtan Island exhibit a low TC/CC ratio
293 (Figure 7), and likely occur from aged sources.



294

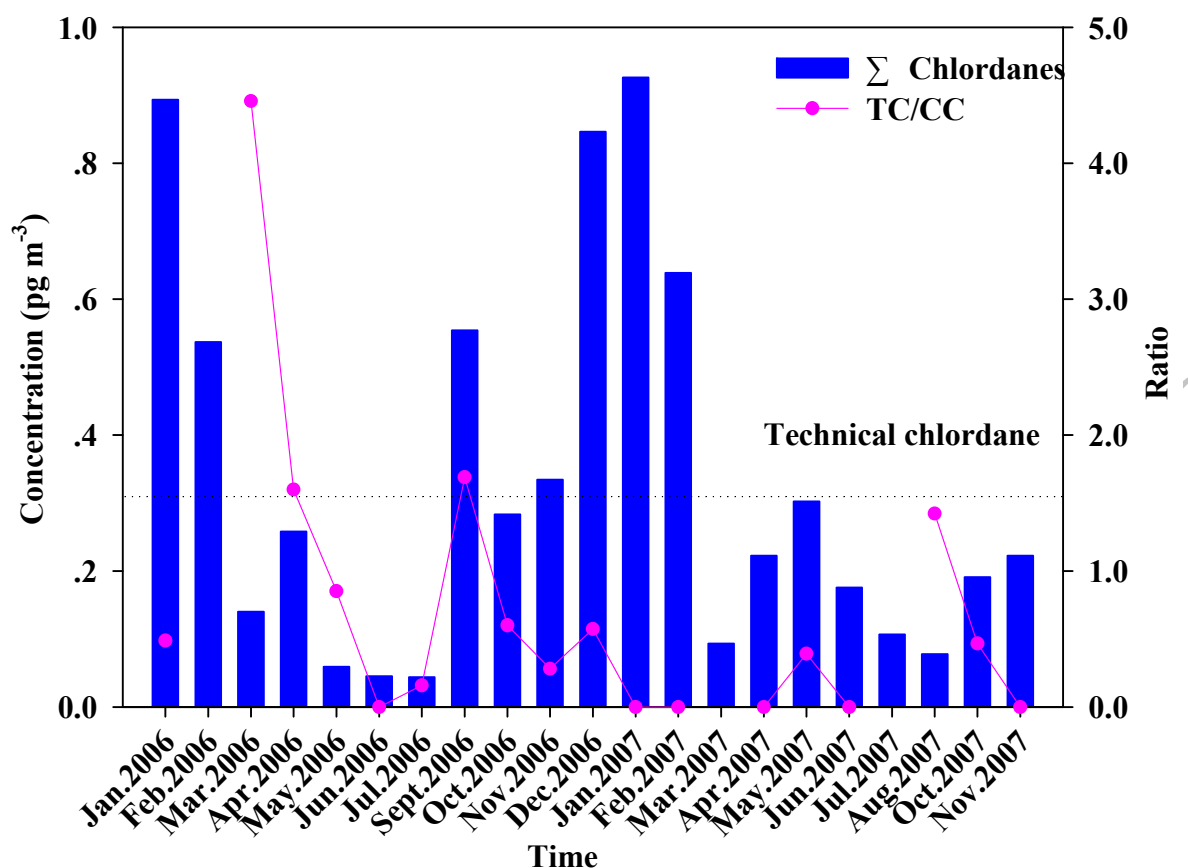
295 Figure 7 Seasonal variations of the Σ chlordane concentration and ratio of TC/CC in
 296 atmospheric PM from Pingtan Island during the sampling period

297 **Endosulfan**

298 Endosulfan was once widely used in agriculture as a pesticide for cotton, teas, tobacco
 299 and fruit plantations, and for the control of disease vectors. China is one of the largest
 300 consumers of endosulfan, and the manufacture and usage of endosulfan occurs mostly in the
 301 eastern cities (Gai *et al.*, 2014; Qu *et al.*, 2015). Technical endosulfan is a mixture of two
 302 isomers, endosulfan I (70%) and endosulfan II (30%), and they are broken down to
 303 endosulfan sulfate (EndoSO₄) in the environment (Pozo *et al.*, 2011). In this study, endosulfan
 304 I, II and EndoSO₄ exhibited low abundances in all samples, and the concentration of
 305 Σ endosulfan compounds (sum of I, II, EndoSO₄) in 2006 and 2007 ranged from ND~0.97 pg

306 m^{-3} and $\text{ND}\sim 3.88 \text{ pg m}^{-3}$, respectively. Those values are far lower than the other urban regions,
307 such as Jinan (China) (Xu *et al.*, 2011), northern China (Ding *et al.*, 2015), and Guangzhou
308 and Hong Kong (Li *et al.*, 2007), reflecting that Pingtan Island was less affected by
309 endosulfan pollution. Unlike the other OCP compounds, the highest endosulfan
310 concentrations observed in September 2006 and May 2007, whereas it appeared in relatively
311 low levels during the rest of the year (Figure 8). The elevated concentrations of endosulfan in
312 those two months may be associated with its use to control pests in tea planting, since Fujian
313 province is a large tea producing area with a long history.

314 The endosulfan I / II ratio is approximately 2.3 in the technical mixture, and a ratio less
315 than 2.3 indicates aged endosulfan, whereas ratios greater than 2.3 indicate newly generated
316 inputs (Qu *et al.*, 2015). As shown in Fig. 8, most values were less than 2.3 except for
317 September 2006 and May 2007, indicating the presence of aged endosulfan. The lower ratio
318 seen for most samples primarily results from the higher vapor pressure and Henry's law
319 constant for endosulfan I than II, suggesting that endosulfan I tends to evaporate from surface
320 environments to the gas phase (Jia *et al.*, 2010). Moreover, studies on the degradation of
321 endosulfan I and II to EndoSO_4 have shown that endosulfan I degrades more readily to
322 EndoSO_4 than II does (Jia *et al.*, 2010; Leonard *et al.*, 2001). Therefore, the significantly
323 higher concentrations of endosulfan in September 2006 and May 2007 and the higher
324 endosulfan I / II ratio suggest that endosulfan was derived from newly generated applications
325 during this period.



326

327 Figure 8 Seasonal variations in the Σ endosulfan concentration and endosulfan I / II in
 328 atmospheric PM from Pingtan Island during the sampling period

329 **Other OCP Compounds**

330 Aldrin, dieldrin, endrin and methoxychlor were also detected in our study. Aldrin was one
 331 of the most widely used OCPs in the world until it was banned in the 1970s due to its high
 332 toxicity and harm to ecological systems. After being released into the environment, aldrin was
 333 rapidly metabolized to dieldrin (Gioia *et al.*, 2005). In industrial production, dieldrin was
 334 mainly produced by the epoxidation of aldrin and was widely used in the control of soil pests.
 335 Endrin is a stereoisomerism of dieldrin and was used extensively for insect control on cotton,
 336 citrus fruit. Technical endrin is a mixture of endrin and its metabolites, endrin aldehyde and
 337 endrin ketone. Although those contaminants were never used in large amounts in China

338 (Wang *et al.*, 2008), they can be detected in our study.

339 The concentration of aldrin were ND~0.88 pg m⁻³ and ND~0.40 pg m⁻³ in 2006 and 2007,
340 respectively, The dieldrin concentrations were NA~1.42 pg m⁻³ and NA~0.93 pg m⁻³ in 2006
341 and 2007, respectively. Σ Endrin (sum of endrin, endrin aldehyde and endrin ketone) was
342 ND~2.91 pg m⁻³ and ND~2.28 pg m⁻³ in 2006 and 2007, respectively. Compared with other
343 regions, the residual levels of aldrin, dieldrin and endrin were far lower than those reported
344 for different sampling sites, such as New Jersey (Gioia *et al.*, 2005) and Beijing(Wang *et al.*,
345 2008) but were similar to the remote area in Station Nord (North-East Greenland) (Bossi *et al.*,
346 2013). However, the results showed a much higher concentration of aldrin than dieldrin,
347 which was similar to the research of Wang (Wang *et al.*, 2008) in Beijing, indicating the
348 newly generated input of aldrin in Pingtan Island. They may transport to the island by
349 atmosphere from the countries that those contaminants frequently used (Wang *et al.*, 2008).

350 Methoxychlor is an environmental estrogen that is gradually becoming a substitute for
351 DDT because of its lower toxicity and bioaccumulation in organisms, and it can be widely
352 used in pest control for vegetables and fruits. However, due to its longer half-life and its
353 potential to cause damage to the reproductive development of organisms, more attention has
354 been focused on the effects of methoxychlor. The concentration of methoxychlor varied
355 between ND~11.95 pg m⁻³ and ND~5.53 pg m⁻³ in 2006 and 2007, respectively. The level of
356 methoxychlor was much higher than Chlordane and endosulfan which had been widely used
357 in China in history, became one of the dominant components of OCPs during the sampling
358 period. Compared to other regions, the levels in our study were similar to the methoxychlor
359 found in PM_{2.5}, PM₅ and PM₁₀ (0.97 pg m⁻³, 0.94 pg m⁻³ and 1.0 pg m⁻³, respectively) in

360 Jinan, but slightly lower than that in TSP (2.2 pg m^{-3}) in Jinan (Xu *et al.*, 2011). Meanwhile, it
361 was far lower than those recorded for the Western Black Sea Region (Turkey, 91.9
362 pg/m^3)(Yenisoykarakaş *et al.*, 2012). The results indicate that the unrestricted use of
363 methoxychlor has greater uncertainty and potential risks in the environment.

364 ***Influence Factor***

365 ***Meteorological Parameters***

366 Theoretically, meteorological conditions and the proximity to sources are two dominant
367 factors that affect POPs levels in the atmospheric environment (Lao *et al.*, 2018; Lee and
368 Jones, 1999; Wang *et al.*, 2015). Therefore, to investigate the influence of related
369 meteorological factors on atmospheric OCP concentrations in Pingtan Island, a correlation
370 analysis between OCP concentrations and meteorological parameters was carried out in this
371 study. The results of correlation analysis are presented in Table S2.

372 Negative correlations were observed between most of the OCP concentrations and T,
373 suggesting that higher temperatures might contribute to the transfer of those OCP compounds
374 from the particulate phase into the gaseous phase, whereas lower temperatures promote the
375 absorption on those particles. As semi volatile contaminants, OCPs reach an equilibrium
376 between the particulate phase and gaseous phase mainly controlled by temperature (He and
377 Balasubramanian, 2010b). Among the meteorological parameters, OCP concentrations were
378 positively correlated to atmospheric pressure and negatively correlated to water vapor
379 pressure. However, relative humidity showed negative correlations with chlordane levels in
380 the air but were positively associated with endosulfan. In Pingtan Island, the relative humidity
381 and water vapor pressure are high and uniform throughout the year (especially in summer,

382 figure 2) due to frequent rainfall and marine exposure, and scavenging effects of contaminants
383 can be caused by precipitation and wet deposition (He and Balasubramanian, 2010b). For
384 wind speed, previous studies suggested that winds could play an important role in reducing
385 contaminants level in local sources by increasing the atmospheric dispersion and dilution
386 (Castro-Jiménez *et al.*, 2011; He and Balasubramanian, 2010b; Miguel. *et al.*, 2004). However,
387 wind speed was positively correlated with chlordane levels in the air, but no significant
388 correlation was found with other OCP compounds. This observation suggested that wind
389 could play an important role in the concentration of chlordane, which could assist in the
390 re-suspension of particulate matters from soil particles under strong wind events (Bidleman *et*
391 *al.*, 1998b).

392 ***Total Organic Carbon (TOC)***

393 OCPs tend to absorb in to particulate organic matter because of their high lipophilicity.
394 Thus, the TOC content in particulates is an important factor influencing POPs in soil or
395 particle-air exchange and transportation (Bajwa *et al.*, 2016; Devi *et al.*, 2013; Gai *et al.*, 2014;
396 Qu *et al.*, 2015). To investigate the influence of TOC on the OCP levels, a correlation analysis
397 between contaminant concentrations and TOC was carried out, and the results are presented in
398 Table S3.

399 The concentrations of α -HCH, p,p'-DDD and total OCPs in atmospheric PM at Pingtan
400 Island exhibited a significant positive correlation with the TOC content. This result suggests
401 that the PM organic matter could promote the adsorption of these compounds, and play an
402 important role in controlling the distribution of these contaminants in atmospheric PM.
403 However, the rest of the OCP compounds showed no significant correlation with TOC,

404 suggesting that the distribution pattern of those compounds at Pingtan Island does not reach
405 the absorption equilibrium status with organic matter. Previous studies demonstrated that
406 certain artificial conditions may strike this equilibrium status (Gao *et al.*, 2013), such as waste
407 incineration and frequent plowing with the robust agricultural activities may affect the fate of
408 OCPs and TOC in atmospheric PM.

409 ***Effect of TSP and Source Analysis***

410 As shown in Figure 1, the concentration of total OCPs in Pingtan Island exhibited a
411 significant positive correlation with the TSP content, most likely because of their presence in
412 TSP via the gas-particle partitioning process (Xing *et al.*, 2017). In addition, a significant
413 correlation was observed between TOC and TSP content ($R^2=0.548$, $p<0.01$) and among OCP
414 compounds (Table S2), suggesting that they may be derived from similar sources. To further
415 investigate the influence factor of OCPs concentrations distribution pattern in atmospheric
416 particulates in Pingtan Island, the stable ^{13}C isotope of TOC in PM was measured to trace
417 possible sources of the atmospheric PM.

418 The stable ^{13}C isotope as a tool for distinguishing from various sources. For example, the
419 $\delta^{13}\text{C}$ values of C_4 terrestrial vegetation range from ~ -14 to -12% , and the $\delta^{13}\text{C}$ values of
420 marine organic carbon sources (-22 to -18%) differ from those of fossil fuel organic carbon
421 (-30 to -23%) (Boutton, 1991; Fry and Sherr, 1989; Wozniak *et al.*, 2012) and C_3 terrestrial
422 vegetation (-32 to -29%) (Cao *et al.*, 2011; Moura *et al.*, 2008). Specifically, the $\delta^{13}\text{C}$ values
423 for motor vehicle exhaust (-28 to -26%) (Widory, 2006) are lower than those for coal
424 combustion (-24.9 to -21%) (Cao *et al.*, 2011; Widory, 2006). In our study, TOC $\delta^{13}\text{C}$ values
425 ranged from -27.8% to 24.6% during the sampling period, with an average value of $-26.5 \pm$

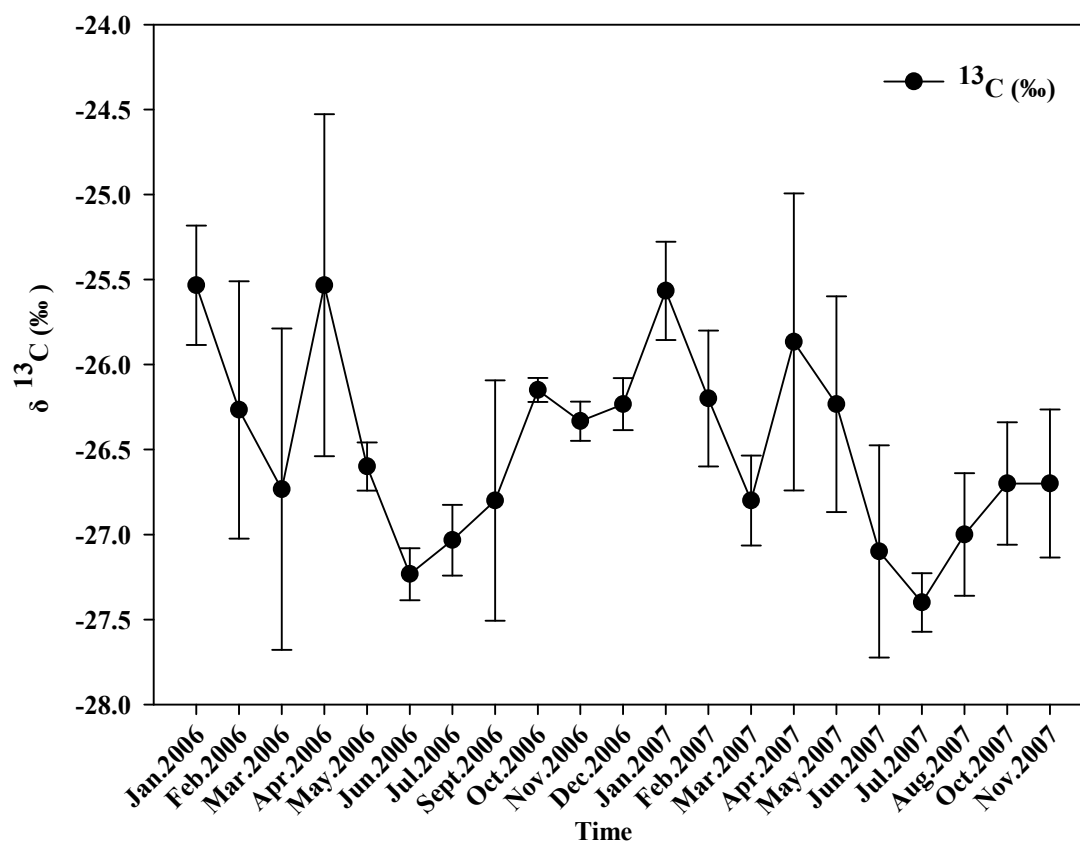
426 0.7‰. The values are more close to the values from coal combustion and motor vehicle than
427 other sources, indicating that the atmospheric particulates in Pingtan Island mainly from these
428 two sources. In addition, a clear seasonal variation of $\delta^{13}\text{C}$ values was found, the higher
429 values observed for $\delta^{13}\text{C}$ were found in winter and spring whereas the lower values were
430 observed in summer (Figure 9), which is consistent with the seasonal distributions of the OCP
431 concentrations. The higher $\delta^{13}\text{C}$ values in the cool season seem also to be influenced by
432 marine organic carbon sources, while the lower values in the summertime seem to be
433 influenced by C_3 terrestrial vegetation. However, air mass trajectory analyses (Figure S3)
434 showed that the air mass was mainly originate from the northern mainland China during the
435 sampling periods, whereas the air mass sources in summer mainly derived from the ocean.
436 Consequently, marine organic carbon sources and C_3 terrestrial vegetation is unlikely to be
437 responsible for the higher $\delta^{13}\text{C}$ values in the cool season and lower in summer. Therefore, the
438 sources of atmospheric PM in the Island are mainly influenced by coal combustion (in cold
439 season) and vehicle exhaust. In addition, a lower atmospheric load of OCPs can be expected
440 when air masses from the ocean (low pollutant loads), this therefore may be responsible for
441 the lower OCPs level in summer. On the contrary, when air masses are coming from northern
442 mainland China (high pollutant loads), high atmospheric OCPs in atmospheric particles would
443 be transported to the island therefore increasing OCPs inputs to Pingtan during the winter and
444 spring.

445 As mention above, particulates in Pingtan Island mainly from coal combustion and
446 vehicle exhaust. To further distinguish the influence of these two sources on air quality in
447 Pingtan Island, we calculate the contribution rate of the two sources by following,

448
$$C = AX + B(1 - X) \quad (4)$$

449 where A represents the $\delta^{13}\text{C}$ values for motor vehicle exhaust, B represents the $\delta^{13}\text{C}$ values for
450 coal combustion, C represents the mixed value (experimental data), and X represents the
451 contribution rate of motor vehicle exhaust. The values for motor vehicle exhaust and coal
452 combustion were selected from Widory (Widory, 2006) reported in the references, with
453 average values of -23.6‰ and -27.9‰, respectively. The contribution rate of the organic
454 contaminant source of atmospheric PM had an average of 67% from motor vehicle exhaust
455 emissions and 33% from coal combustion, showing that automobile exhaust had the largest
456 influence during the sampling period (Table 1). Previous studies suggested that the emissions
457 of POPs from diesel engines was also an important source (Cheruiyot *et al.*, 2017). Recently,
458 the selective catalytic reduction have been added into the heavy-duty diesel engine to reduce
459 emissions of nitrogen oxide, but it also could be the source of POP emissions due to
460 accumulation of organic particulates, and this provide the carbon matrix or necessary
461 precursors for their formation (Chen *et al.*, 2017; Cheruiyot *et al.*, 2017). However, it is noted
462 that the contribution rate of coal combustion increased obviously from summer (18% and
463 17%) to winter (47% and 44%) and spring (38% and 37%). Thus, the higher OCP
464 concentrations of atmospheric PM that appeared in winter and spring may be influenced by
465 coal combustion during the heating season in Northern China. By combining the air mass
466 sources mainly from the northern mainland China during the cool season, suggesting that
467 higher OCPs and PM levels appearing during the season may be strongly influenced by coal
468 burning in northern China during the heating season. In addition, previous studies also
469 demonstrate that extremely high OCPs level in atmospheric particles during the season (Ding

470 *et al.*, 2015), and this may be transported to the island with the air mass.



471

472 Figure 9 Seasonal variations of $\delta^{13}\text{C}$ values during the sampling period in Pingtan Island

473

Table 1 Estimated values of the organic contaminant sources of air particulates

Season	$\delta^{13}\text{C}$ (‰)	Motor vehicle exhaust (%)	Coal combustion (%)
winter-06	25.9 ± 0.7	53	47
spring-06	26.3 ± 1.0	62	38
summer-06	27.1 ± 0.2	82	18
fall-06	26.4 ± 0.4	65	35
winter-07	26.0 ± 0.4	56	44
spring-07	26.3 ± 0.7	63	37
summer-07	27.2 ± 0.4	83	17

fall-07	26.7 ± 0.4	72	28
average	26.5 ± 0.6	67	33

474 **Risk Assessment**

475 The toxicity assessment of OCPs was calculated by the equations described in Section 1.4.
476 According to the literature, an average daily dose (ADD) between 10^{-6} and 10^{-4} denotes a
477 potential risk, whereas lower values ($< 10^{-6}$) indicate a very low risk and the higher values ($>$
478 10^{-4}) indicate a high potential health risk (Ding *et al.*, 2015; Ge *et al.*, 2013; Qu *et al.*, 2015).
479 As shown in Table S4, the estimated cancer risks for chlordane, endosulfan, aldrin, dieldrin,
480 endrin and methoxychlor are all well below 10^{-6} , suggesting the potential effect of those
481 compounds could be negligible. However, the estimated risks for DDT, HCH and the total
482 accumulation of OCPs are slightly above the threshold value (10^{-6}) indicated potential risk,
483 most notably, the higher levels of OCPs in the cold season. Therefore, the effect of those OCP
484 compound residuals in the atmospheric PM of Pingtan Island cannot be neglected. For
485 different exposure pathways, the increasing trend in cancer risk for all OCP compounds is
486 calculated as follows: dermal contact $>$ inhalation $>$ ingestion. The carcinogenic risk through
487 ingestion and inhalation of OCP compounds containing atmospheric PM is $10^{-2}\sim 10^{-3}$ times
488 less than that through dermal contact with OCP compound-containing particulates, and the
489 ADD values of all OCP compounds through ingestion and inhalation are below 10^{-6} , and thus,
490 of these three exposure pathways, dermal contact of OCP particulates is the primary pathway
491 contributing to human health risks.

492 **CONCLUSIONS**

493 The present study provided a 2-year dataset of the level of OCP contamination in

494 atmospheric PM at Pingtan Island, China. The level of OCPs in particulate samples obviously
495 lower than urban areas in China. DDT and HCH being the most dominant OCPs, and those
496 contaminants are mainly historical residues. Distinct seasonal variations in the OCP
497 concentrations correlated significantly with total particulate levels, and higher concentrations
498 of most of the OCP compounds appeared in winter (except for endosulfan), whereas the lower
499 concentrations appeared in summer. Correlation analysis results showed that the
500 concentrations of most OCP compounds in the coastal area were mainly influenced by
501 meteorological conditions. The close relationship between TOC and percentages of the OCP
502 compounds suggests that the former is an important factor affecting the persistence of these
503 OCPs in atmospheric PM. The isotopic signatures indicate that motor vehicle exhaust and
504 coal combustion were two major sources for the atmospheric particulates, and the higher
505 levels of OCPs in winter and spring might be influenced by coal combustion during the
506 heating season in Northern China. Compared to other regions, contamination from residual
507 OCPs in Pingtan Island may be considered minimal, but it still poses a potential carcinogenic
508 risk for exposed populations. Therefore, the effect of OCP residuals in atmospheric PM on
509 Pingtan Island cannot be neglected.

510

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519 REFERENCES

520 Bajwa, A., Ali, U., Mahmood, A., Chaudhry, M. J., Syed, J. H., Li, J., Zhang, G., Jones, K. C.,
521 Malik, R. N. (2016). Organochlorine pesticides (OCPs) in the Indus River catchment
522 area, Pakistan: Status, soil-air exchange and black carbon mediated distribution.
523 *Chemosphere* 152:292-300.

524 Baulig, A., Sourdeval, M., Meyer, M., Marano, F., Baeza-Squiban, A. (2003). Biological
525 effects of atmospheric particles on human bronchial epithelial cells. Comparison with
526 diesel exhaust particles. *Toxicol In Vitro* 17:567-573.

527 Bidleman, T. F., Jantunen, L. M. M., Wiberg, K., Harner, T., Brice, K. A., Su, K., Falconer, R.
528 L., Leone, A. D., Aigner, E. J., Parkhurst, W. J. (1998a). Soil as a Source of Atmospheric
529 Heptachlor Epoxide. *Environ.sci.technol* 32:1546-1548.

530 Bidleman, T. F., Jantunen, L. M. M., Wiberg, K., Harner, T., Brice, K. A., Su, K., Falconer, R.
531 L., Leone, A. D., Aigner, E. J., Parkhurst, W. J. (1998b). Soil as a Source of Atmospheric
532 Heptachlor Epoxide. *Environ. Sci. technol* 32:1546-1548.

533 Bidleman, T. F., Jantunen, L. M., Helm, P. A., Brorström-Lundén, E., Juntto, S. (2002).
534 Chlordane enantiomers and temporal trends of chlordane isomers in arctic air. *Environ.*
535 *Sci. Technol.* 36:539-544.

536 Bossi, R., Skjøth, C. A., Skov, H. (2013). Three years (2008-2010) of measurements of
537 atmospheric concentrations of organochlorine pesticides (OCPs) at Station Nord,

538 North-East Greenland. *Environ. Sci. Proc. Impacts* 15:2213-2219.

539 Boutton, T W. (1991). Stable Carbon Isotope Ratios of Natural Materials: II. Atmospheric,
540 Terrestrial, Marine, and Freshwater Environments.

541 Cao, J. J., Chow, J. C., Tao, J., Lee, S. C., Watson, J. G., Ho, K. F., Wang, G. H., Zhu, C. S.,
542 Han, Y. M. (2011). Stable carbon isotopes in aerosols from Chinese cities: Influence of
543 fossil fuels. *Atmos. Environ.* 45:1359-1363.

544 Castro-Jiménez, J., Mariani, G., Vives, I., Skejo, H., Umlauf, G., Zaldívar, J. M., Dueri, S.,
545 Messiaen, G., Laugier, T. (2011). Atmospheric concentrations, occurrence and deposition
546 of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau,
547 France). *Environ. Pollut.* 159:1948-1956.

548 Chen, C. Y., Lee, W. J., Wang, L. C., Chang, Y. C., Yang, H. H., Young, L. H., Lu, J. H., Tsai,
549 Y. I., Cheng, M. T. and Mwangi, J. K. (2017). Impact of high soot-loaded and
550 regenerated diesel particulate filters on the emissions of persistent organic pollutants
551 from a diesel engine fueled with waste cooking oil-based biodiesel. *Appl. Energy*
552 191:35-43.

553 Cheruiyot, N. K., Wang, L. C., Lin, S. L., Yang, H. H., and Chen, Y. T. (2017). Effects of
554 selective catalytic reduction on the emissions of persistent organic pollutants from a
555 heavy-duty diesel engine. *Aerosol Air Qual. Res.* 17:1558-1565.

556 Devi, N. L., Chakraborty, P., Shihua, Q., Zhang, G. (2013). Selected organochlorine pesticides
557 (OCPs) in surface soils from three major states from the northeastern part of India.
558 *Environ. Monit. Assess.* 185:6667-6676.

559 Ding, S., Dong, F., Wang, B. (2015). Polychlorinated biphenyls and organochlorine pesticides

560 in atmospheric particulate matter of Northern China: distribution, sources, and risk
561 assessment. *Environ. Sci. Pollut. R.* 22:1-11.

562 El-Mubarak, A. H., Rushdi, A. I., Al-Mutlaq, K. F., Bazeyad, A. Y., Simonich, S. L. M.,
563 Simoneit, B. R. T., 2015. Occurrence of High Levels of Persistent Organic Pollutants
564 (POPs) in Particulate Matter of the Ambient Air of Riyadh, Saudi Arabia. *Arab. J. Sci.*
565 *Eng.* 40:81-92.

566 Evenset, A., Hallanger, I. G., Tessmann, M., Warner, N., Ruus, A., Borgå, K., Gabrielsen, G.
567 W., Christensen, G., Renaud, P. E. (2016). Seasonal variation in accumulation of
568 persistent organic pollutants in an Arctic marine benthic food web. *Sci. Total Environ.*
569 542:108-120.

570 Fry, B., Sherr, E. B. (1989). $\delta^{13}\text{C}$ Measurements as Indicators of Carbon Flow in Marine and
571 Freshwater Ecosystems. *Contrib. Mar. Sci.* 27:13-47.

572 Gai, N., Pan, J., Tang, H., Chen, S., Chen, D., Zhu, X., Lu, G., Yang, Y. (2014).
573 Organochlorine pesticides and polychlorinated biphenyls in surface soils from Ruorgai
574 high altitude prairie, east edge of Qinghai-Tibet Plateau. *Sci. Total Environ.* 478:90-97.

575 Gao, J., Zhou, H., Pan, G., Wang, J., Chen, B. (2013). Factors influencing the persistence of
576 organochlorine pesticides in surface soil from the region around the Hongze Lake, China.
577 *Sci. Total Environ.* 443:7-13.

578 Ge, J., Woodward, L. A., Li, Q. X., Wang, J. (2013). Composition, distribution and risk
579 assessment of organochlorine pesticides in soils from the Midway Atoll, North Pacific
580 Ocean. *Sci. Total Environ.* 452-453:421-426.

581 Gioia, R., Offenberg, J. C., Totten, L., Du, S., Eisenreich, S. (2005). Atmospheric

582 concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic
583 region. *Atmos. Environ.* 39:2309-2322.

584 Hao, H., Bo, S., Zhao, Z. (2008). Effect of land use change from paddy to vegetable field on
585 the residues of organochlorine pesticides in soils. *Environ. Pollut.* 156:1046-1052.

586 He, J., Balasubramanian, R. (2010a). The exchange of SVOCs across the air-sea interface in
587 Singapore's coastal environment. *Atmos. Chem. Phys.* 10:1837-1852.

588 He, J., Balasubramanian, R. (2010b). Semi-volatile organic compounds (SVOCs) in ambient
589 air and rainwater in a tropical environment: concentrations and temporal and seasonal
590 trends. *Chemosphere* 78:742.

591 Jia, H., Liu, .L, Sun, Y., Sun, B., Wang, D., Su, Y., Kannan, K., Li, Y. F. (2010). Monitoring
592 and Modeling Endosulfan in Chinese Surface Soil. *Environ. Sci. Technol.* 44:9279-9284.

593 Künzli, N., Kaiser, R., Medina, S., Studnicka, M., Chanel, O., Filliger, P., Herry, M., Horak, F.,
594 Puybonnieuxtexier, V., Quénel, P. (2000). Public-health impact of outdoor and
595 traffic-related air pollution: a European assessment. *Lancet* 356:795-801.

596 Lao, Q., Jiao, L., Chen, F., Chen, L., Sun, X. (2018). Influential Factors and Dry Deposition
597 of Polychlorinated Biphenyls (PCBs) in Atmospheric Particles at an Isolated Island
598 (Pingtan Island) in Fujian Province, China. *Atmos.* 9:59-76.

599 Lao, Q., Jiao, L., Chen, F., Chen, L. (2017). Review on Researches of Legacy POPs and
600 Emerging POPs in the Arctic Regions. *Adv. Earth Sci.* 32:128~138.

601 Lee, R. G. M., Jones, K. C. (1999). The Influence of Meteorology and Air Masses on Daily
602 Atmospheric PCB and PAH Concentrations at a UK Location. *Environ. Sci. Technol.*
603 33:705-712.

604 Leonard, A. W., Hyne, R. V., Lim, R. P., Leigh, K. A., Le, J., Beckett, R. (2001). Fate and
605 toxicity of endosulfan in Namoi River water and bottom sediment. *J. Environ. Qual.*
606 30:750-759.

607 Li, J., Gan, Z., Guo, L., Xu, W., Li, X., Lee, C. S. L., Ding, A., Tao, W. (2007).
608 Organochlorine pesticides in the atmosphere of Guangzhou and Hong Kong: Regional
609 sources and long-range atmospheric transport. *Atmos. Environ.* 41:3889-3903.

610 Li, Y., Niu, J., Shen, Z., Zhang, C., Wang, Z., He, T. (2014). Spatial and seasonal distribution
611 of organochlorine pesticides in the sediments of the Yangtze Estuary. *Chemosphere*
612 114:233-240.

613 Li, Y., Zhang, Q., Ji, D., Wang, T., Wang, Y., Wang, P., Ding, L., Jiang, G. (2009). Levels and
614 Vertical Distributions of PCBs, PBDEs, and OCPs in the Atmospheric Boundary Layer:
615 Observation from the Beijing 325-m Meteorological Tower. *Environ. Sci. Technol.*
616 43:1030-1035.

617 Liu, J., Qi, S., Yao, J., Yang, D., Xing, X., Liu, H., Qu, C. (2016). Contamination
618 characteristics of organochlorine pesticides in multimatrix sampling of the Hanjiang
619 River Basin, southeast China. *Chemosphere* 163:35-43.

620 Miguel, A. H., Eiguren-Fernandez, A., Jaques, P. A., Froines, J. R., Grant, B. L., Mayo, P. R.,
621 Sioutas, C. (2004). Seasonal variation of the particle size distribution of polycyclic
622 aromatic hydrocarbons and of major aerosol species in Claremont, California. *Atmos.*
623 *Environ.* 38:3241-3251.

624 Moura, J. M. S., Martens, C. S., Moreira, M. Z., Lima, R. L., Sampaio, I. C. G., Mendlovitz,
625 H. P., Menton, M. C. (2008). Spatial and seasonal variations in the stable carbon isotopic

626 composition of methane in stream sediments of eastern Amazonia. *Tellus B. Phys.*
627 *Meteorol.* 60:21–31.

628 Obot, C. J., Morandi, M. T., Beebe, T. P., Hamilton, R. F., Holian, A. (2002). Surface
629 components of airborne particulate matter induce macrophage apoptosis through
630 scavenger receptors. *Toxicol. Appl. Pharm.* 184:98-106.

631 Ozcan, S., Aydin, M. E. (2009). Organochlorine Pesticides in Urban Air: Concentrations,
632 Sources, Seasonal Trends and Correlation with Meteorological Parameters. *Clean– Soil,*
633 *Air, Water* 37:343-348.

634 Pagano, P., Zaiacomo, T. D., Scarcella, E., Stefania Bruni, A., Calamosca, M. (1996).
635 Mutagenic Activity of Total and Particle-Sized Fractions of Urban Particulate Matter.
636 *Environ. Sci. Technol.* 30:3512-3516.

637 Pozo, K., Harner, T., Lee, S. C., Sinha, R. K., Sengupta, B., Loewen, M., Geethalakshmi, V.,
638 Kannan, K., Volpi, V. (2011). Assessing seasonal and spatial trends of persistent organic
639 pollutants (POPs) in Indian agricultural regions using PUF disk passive air samplers.
640 *Environ. Pollut.* 159:646-653.

641 Qu, C., Yang, D., Zhang, J., Chen, W., Sandy, E. H., Xing, X., Qi, S., Huang, H., Yohannes, H.
642 K., Yang, J. (2015). Risk assessment and influence factors of organochlorine pesticides
643 (OCPs) in agricultural soils of the hill region: A case study from Ningde, southeast China.
644 *J. Geochem. Explor.* 149:43-51.

645 Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C., Bidleman, T. F. (2005). Atmospheric
646 distribution and long-range transport behavior of organochlorine pesticides in North
647 America. *Environ. Sci. Technol.* 39:409-420.

648 Tieyu, W., Yonglong, L., Hong, Z., Yajuan, S. (2005). Contamination of persistent organic
649 pollutants (POPs) and relevant management in China. *Environ. Int.* 31:813-821.

650 Wang, X., Li, X., Cheng, H., Xu, X., Zhuang, G., Zhao, C. (2008). Organochlorine pesticides
651 in particulate matter of Beijing, China. *J. Hazard. Mater.* 155:350-357.

652 Wang, Y., Li, Q., Wang, S., Wang, Y., Luo, C., Li, J., Zhang, G. (2015). Seasonal and diurnal
653 variations of atmospheric PAHs and OCPs in a suburban paddy field, South China:
654 Impacts of meteorological parameters and sources. *Atmos. Environ.* 112:208-215.

655 Wania, F., Mackay, D. (1993). Global fractionation and cold condensation of low volatility
656 organochlorine compounds in polar regions. *Ambio* 22:10-18.

657 Widory, D. (2006). Combustibles, fuels and their combustion products: A view through
658 carbon isotopes. *Combust. Theor. Model.* 10:831-841.

659 Willett, K. L., Ulrich, E. M., Hites, R. A. (1998). Differential Toxicity and Environmental
660 Fates of Hexachlorocyclohexane Isomers. *Environ. Sci. Technol.* 32:2197-2207.

661 Wozniak, A. S., Bauer, J. E., Dickhut, R. M., Xu, L., Mcnichol, A. P. (2012). Isotopic
662 characterization of aerosol organic carbon components over the eastern United States. *J.*
663 *Geophys. Res.* 117:13303.

664 Wu, S. P., Tao, S., Zhang, Z. H., Lan, T., Zuo, Q. (2005). Distribution of particle-phase
665 hydrocarbons, PAHs and OCPs in Tianjin, China. *Atmos. Environ.* 39:7420-7432.

666 Wu, X., Lam, J. C., Xia, C., Kang, H., Sun, L., Xie, Z., Lam, P. K. (2010). Atmospheric HCH
667 concentrations over the Marine Boundary Layer from Shanghai, China to the Arctic
668 Ocean: role of human activity and climate change. *Environ. Sci. Technol.* 44:8422-8428.

669 Wu, X., Lam, J. C., Xia, C., Kang, H., Xie, Z., Lam, P. K. (2011). Atmospheric concentrations

670 of DDTs and chlordanes measured from Shanghai, China to the Arctic Ocean during the
671 Third China Arctic Research Expedition in 2008. *Atmos. Environ.* 45:3750-3757.

672 Xing, J., Cui, K., Tang, H., Lee, W. J., Wang, L. C., Zhu, J., Lee, W., Mwangi, J. and Lee, Y.
673 (2017). Part II: PM_{2.5} and Polychlorinated Dibenzo-p-dioxins and Dibenzofurans
674 (PCDD/Fs) in the Ambient Air of Northern China. *Aerosol Air Qual. Res.* 17: 1550-1569.

675 Xu, H., Du, S., Cui, Z., Zhang, H., Fan, G., Yin, Y. (2011). Size distribution and seasonal
676 variations of particle-associated organochlorine pesticides in Jinan, China. *J. Environ.*
677 *Monitor.* 13:2605-2611.

678 Yang, D., Qi, S., Zhang, J., Wu, C., Xing, X. (2013). Organochlorine pesticides in soil, water
679 and sediment along the Jinjiang River mainstream to Quanzhou Bay, southeast China.
680 *Ecotox. Environ. Safe.* 89:59-65.

681 Yenisoykarakas, S., M., Ö., Gaga, E. O. (2012). Seasonal variation, sources, and gas/particle
682 concentrations of PCBs and OCPs at high altitude suburban site in Western Black Sea
683 Region of Turkey. *J. Environ. Monitor.* 14:1365-1374.

684 Yu, H. Y., Li, F. B., Yu, W. M., Li, Y. T., Yang, G. Y., Zhou, S. G., Zhang, T. B., Gao, Y. X.,
685 Wan, H. F. (2013). Assessment of organochlorine pesticide contamination in relation to
686 soil properties in the Pearl River Delta, China. *Sci. Total Environ.* 447:160-168.

687 Zhang, J., Qi, S., Xing, X., Tan, L., Gong, X., Zhang, Y., Zhang, J. (2011). Organochlorine
688 pesticides (OCPs) in soils and sediments, southeast China: A case study in Xinghua Bay.
689 *Mar. Pollut. Bull.* 62:1270-1275.

690 Zhang, L. F., Liang, D., Shi, S. X., Li, Z., Zhang, T., Huang, Y. (2009). Organochlorine
691 pesticides contamination in surface soils from two pesticide factories in Southeast China.

692 *Chemosphere* 77:628-633.

693 Zhang, Z. L., Hong, H. S., Zhou, J. L., Huang, J., Yu, G. (2003). Fate and assessment of
694 persistent organic pollutants in water and sediment from Minjiang River Estuary,
695 Southeast China. *Chemosphere* 52:1423-1430.

696 Zheng, X. Y., Chen, D. Z., Liu, X. D., Zhou, Q. F., Yue, L., Wen, Y., Jiang, G. B. (2010).
697 Spatial and seasonal variations of organochlorine compounds in air on an urban-rural
698 transect across Tianjin, China. *Chemosphere* 78:92-98.

699 Zhu, J., Tang, H., Xing, J., Lee, W. J., Yan, P. and Cui, K. (2017). Atmospheric Deposition of
700 Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Two Cities of Southern China.
701 *Aerosol Air Qual. Res.* 17: 1439-1449.

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