



## Concentration and Influence Factors of Organochlorine Pesticides in Atmospheric Particles in a Coastal Island in Fujian, Southeast China

Liping Jiao<sup>1,2\*\*\*</sup>, Qibin Lao<sup>2,3,4+</sup>, Liqi Chen<sup>2\*</sup>, Fajin Chen<sup>4</sup>, Xia Sun<sup>2</sup>, Meixun Zhao<sup>1</sup>

<sup>1</sup> Key Laboratory of Marine Chemistry Theory and Technology (Ocean University of China), Ministry of Education; Laboratory for Marine Ecology and Environmental Science, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266071, China

<sup>2</sup> Key Laboratory of Global Change and Marine-Atmospheric Chemistry of State Oceanic Administration (SOA), Third Institute of Oceanography, SOA, Xiamen 361005, China

<sup>3</sup> Marine Environmental Monitoring Center of Beihai, SOA, Beihai 536000, China

<sup>4</sup> Guangdong Ocean University, Guangdong Province Key Laboratory for Coastal Ocean Variation and Disaster Prediction, Zhanjiang 524088, China

### 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 (not detected) to 27.25 pg m<sup>-3</sup> (an average of 4.30 ± 4.07 pg m<sup>-3</sup>) and ND to 13.16 pg m<sup>-3</sup> (an average of 3.11 ± 2.54 pg m<sup>-3</sup>) in 2006 and 2007 respectively, and the level are obviously lower than urban, industrial, suburban, and the similar research areas in the coastal areas of Europe. HCH (Hexachlorocyclohexane) and DDT (Dichlorodiphenyltrichloroethane) were the predominant contaminants, followed by Methoxychlor and Endrin, while the levels of Chlordane, Endosulfan, Aldrin and Dieldrin was relatively lower. 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 (total organic carbon) 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

Organochlorine pesticides (OCPs) are widely concerned as one class of important persistent organic pollutants

(POPs) due to their salient features of bioaccumulation, ubiquity and persistence. OCPs were extensively used around the world between the 1950s and the 1970s. As a consequence of their high toxicity to biota and humans, most OCPs were banned in most countries from the 1970s to the 1980s (Willett *et al.*, 1998; Wu *et al.*, 2011; Li *et al.*, 2014; Qu *et al.*, 2015). However, they could still be found in various environmental media on a global scale (Li *et al.*, 2009; Yu *et al.*, 2013; Gai *et al.*, 2014; Evenset *et al.*, 2016). Once these contaminants are released into the environment, some of the semi-volatile OCPs can undergo long-range atmospheric transport (LRAT) to remote pristine areas as gases or by adsorbing onto atmospheric aerosols (Wania and Mackay, 1993; Wu *et al.*, 2010; Lao *et al.*, 2017). Particulate matter (PM) in atmosphere is the main pollutant affecting

<sup>+</sup> These authors contributed equally to this paper.

\* Corresponding author.

Tel.: 86-592-2195351

E-mail address: chenliqi@tio.org.cn

\*\* Corresponding author.

Tel.: 86-592-2195660

E-mail address: jiaoliping@tio.org.cn

the regional air quality, and POPs in the gas phase are easily absorbed on PM and transported atmospherically (El-Mubarak *et al.*, 2015; Xing *et al.*, 2017). In fact, atmospheric particulates are considered to be the primary carrier for transferring organic contaminants in environments (Gai *et al.*, 2014; Ding *et al.*, 2015; Xing *et al.*, 2017; Lao *et al.*, 2018). Finally, PM coupled with POPs are either deposited in soils and water introducing the pollutants to the ground and aquatic environments, or are absorbed by organisms during transport (Zhu *et al.*, 2017). More importantly, OCPs associated with fine particles can enter biological respiratory systems, and might affect biota including human beings (Pagano *et al.*, 1996). Previous studies have shown that the concentration of PM was positively correlated with the morbidity and mortality of respiratory and cardiopulmonary diseases (Künzli *et al.*, 2000; Obot *et al.*, 2002; Baulig *et al.*, 2003). Information on the occurrence of OCPs in PM is available for urban settings (Wu *et al.*, 2005; Xu *et al.*, 2011; Ding *et al.*, 2015; El-Mubarak *et al.*, 2015), but background areas such as coastal islands are limited. Coastal areas are susceptible to the accumulation of semi-volatile organic compounds, such as OCPs, from atmospheric inputs (He and Balasubramanian, 2010a).

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

Pingtang Island (between 25°15'–25°45'N, 119°32'–120°10'E), located in southeastern China, is the fifth largest island in China and the largest island in Fujian Province. It is an area with a typical subtropical monsoon climate. Many studies have been conducted on the occurrence of OCPs in coastal areas of southeastern China (adjacent Pingtan areas), especially focusing on aquatic systems (i.e., sediment and water) and soils (Zhang *et al.*, 2003; Zhang *et al.*, 2011; Yang *et al.*, 2013; Qu *et al.*, 2015; Liu *et al.*, 2016). However, little information is available on the occurrence of OCPs in atmospheric particles in the coastal island.

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

and assessed the toxicological risk of OCPs.

## MATERIALS AND METHODS

### *Sampling Location and Sample Collection*

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

Air sampling was conducted continuously from January 2006 to November 2007, using a high-volume air sampler (EDPL5000, China), and the average gas flow rate of the sampler was 62.88 m<sup>3</sup> h<sup>-1</sup>. Each sample was collected continuously for three days during each sampling month, and a total of 10 samples were collected each month. A glass fiber filter (GFF: the diameter of 0.4 μm, 200 mm × 250 mm, American Whatman company) was used to collect the PM. The GFFs were annealed in an oven at 450°C for 4 h to remove organic residues before use. After sampling, the GFFs were removed from the sampler, wrapped with aluminum foil, placed in a darkened desiccator and transported to the laboratory as soon as possible. The collected PM mass (after freeze-dried) was calculated by subtracting the pre-weight from the post-weight of the GFF. After being weighed, the samples were stored in a freezer at -20°C until analysis.

### *Sample Pretreatment and Analysis*

Sample extraction and analysis method was accomplished by use of previously established and reported methods (Lam *et al.*, 2008; Lao *et al.*, 2018). Details about the sample extraction and analysis are presented in supplementary material (Text S1). Briefly, the samples were extracted using an accelerated solvent extraction instrument (ASE 200, Dionex, US), using 1:1 dichloromethane (HPLC grade, 99.9%, Product of Tedia, US)/hexane (HPLC grade, 99.9%, Product of Tedia, US) as the extracting solvent. The extract was concentrated and transferred into hexane using a rotary evaporation and then concentrated again to 1 mL under a gentle stream of nitrogen. Finally, the concentrated extract was further cleaned with a chromatography column. Then eluted with 100 mL of hexane/dichloromethane (v/v 1:1). The eluate was concentrated to 0.1 mL under a gentle stream of nitrogen and transferred into hexane for analysis. The determination of OCP (including α-HCH; β-HCH; γ-HCH; δ-HCH; Aldrin; Dieldrin; Endrin; Heptachlor; Heptachlor exoxide; α-chlordane; γ-chlordane; endosulfan I; endosulfan II; p,p'-DDT; p,p'-DDD; p,p'-DDE; Endrin aldehyde; Endosulfan sulfate; Endrin ketone; Methoxychlor) was performed on a gas chromatography/electron capture detector (GC/ECD) (Agilent 7890A with Ni<sup>63</sup> ECD) equipped with a DB-5 MS column (60 m × 0.25 mm × 0.25 μm film thickness). The temperature of the detector and injector was 300°C and 270°C, respectively. The oven temperature started at 80°C, increased to 210°C at 10°C min<sup>-1</sup>, then

increased to 250°C at a rate of 0.8°C min<sup>-1</sup>, and at last increased to 290°C at 10°C min<sup>-1</sup> before being held for 12 min. 1 µL of each sample was injected in splitless mode. Nitrogen was used as the carrier gas with a flow rate of 30 mL min<sup>-1</sup>.

#### Quality Control and Quality Assurance (QA/QC)

The sampling artifacts tended to occur when gas phase POPs adsorbed to particle and filter, resulting in an overestimation of POPs in atmospheric particles (Dachs and Eisenreich, 2000). Backup GFFs were used to monitor for gas phase adsorption of OCP compounds to a front filter. This method were reported by Mader and Pankow (2001), and the results showed that less than 5% of mass recovered from the primary GFF was absorbed into a secondary GFF.

The identification of individual target OCPs was based on the retention time compared with corresponding standards, and they were quantified using an internal standard. The GFFs, which went through dichloromethane/hexane (v:v, 1:1) extraction for 24 h, and repeated 3 times before drying, are as the blank samples. The blank samples were added to unknown samples to treat and measure together, and added a blank sample for every 20 unknown samples, and no 20 OCPs target compounds were detected in all blank samples. The method detected limits (MDLs) were defined as the average signal of the blanks plus three times the standard deviation of the blanks, and the MDLs of OCPs was 0.05–0.13 pg m<sup>-3</sup>. Concentrations lower than MDLs were considered non-detectable for quantified OCP compounds. Before extraction, the blank samples and the samples were added 60 µg L<sup>-1</sup> internal standard (2,4,6-trichlorobiphenyl, Accustandard, US) to monitor the recovery rate of extraction process, and the recovery rate was in the range of 81.4%–115.3%, and all data were corrected for recovery. The MDLs and recoveries of each OCP compound are presented in Table S1.

#### Risk Assessment

There are three pathways of human exposure to OCPs through ambient particles, dermal contact, ingestion and inhalation. Cancer risks via those three pathways of ambient particles were calculated from Eqs. (2), (3) and (4), which were derived from previous studies (Ge et al., 2013; Ding et al., 2015). The definition and value of each parameter are given in Table S2.

$$\text{ADD (ingest)} = \frac{C(\text{particle}) \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \quad (1)$$

$$\text{ADD (dermal)} = \frac{C(\text{particle}) \times \text{SA} \times \text{AF}(\text{particle}) \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \quad (2)$$

$$\text{ADD (inhale)} = \frac{C(\text{particle}) \times \text{IR}(\text{inhalation}) \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{AT}} \quad (3)$$

#### Meteorological Parameters

The data of ambient temperature (T), wind direction (WD), wind speed (WS), atmospheric pressure (AP), water vapor pressure (WVP), relative humidity (RH) and rainfall, were from China Meteorological Data Sharing Service System (CMDSS), located in the site of Pingtan meteorological observation station. The frequency of wind direction and the temporal variations of wind speed and temperature from January 2006 to November 2007 are plotted in Figs. S1 and S2.

## RESULTS AND DISCUSSION

#### Atmospheric Concentrations and Seasonal Variations

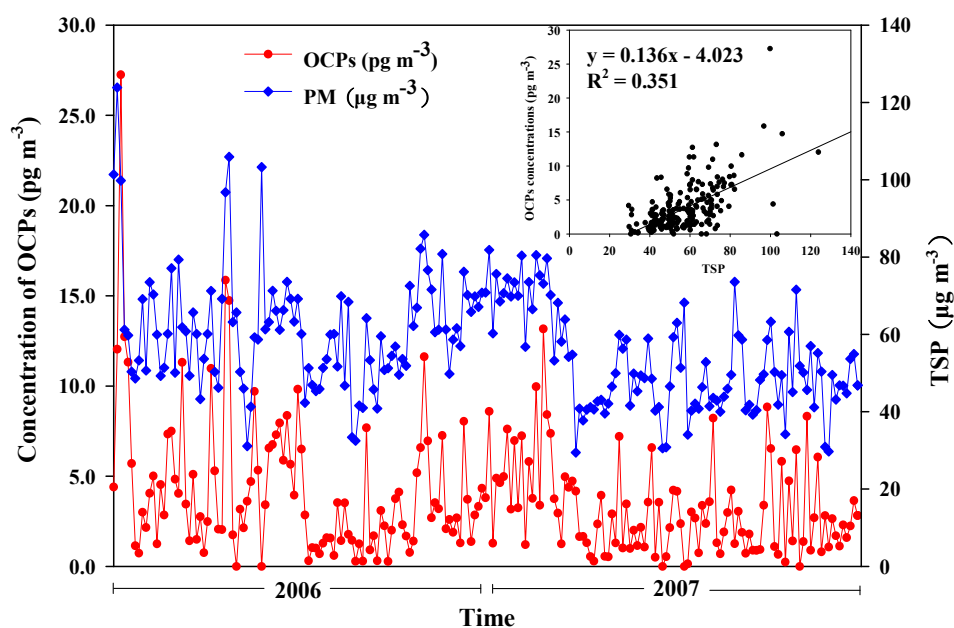
208 samples were collected from Pingtan Island from January 2006 to November 2007 (August 2006 and September 2007 were absent due to sampler maintenance). The results of the OCP and PM levels are summarized in Fig. 1, and the monthly average concentrations of  $\Sigma 20$  OCPs and rainfall over the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

The total OCP concentration correlated well with TSP and exhibited a good correlation coefficient (Fig. 1), and ranged from ND to 27.25 pg m<sup>-3</sup> (an average of 4.58 ± 5.00 pg m<sup>-3</sup>) and ND to 13.16 pg m<sup>-3</sup> (an average of 3.11 ± 2.54 pg m<sup>-3</sup>) in 2006 and 2007, respectively. The highest OCP concentrations were all observed in winter (December–February, 5.96 pg m<sup>-3</sup> and 4.63 pg m<sup>-3</sup> in 2006 and 2007, respectively), while relatively low concentrations in the other months except for a relatively high concentration in spring of 2006 (March–May, with an average of 5.28 pg m<sup>-3</sup>). The seasonality of rainfall may partly be responsible for the monthly variations of OCPs level, and rainfall was significantly low in winter (Fig. 2). For individual compounds, DDT and HCH were the predominant contaminants in all samples, followed by methoxychlor, while the remaining OCPs were found at relatively low levels. Compared with other regions, the levels of particle-bound OCPs and its compounds in Pingtan Island atmosphere were much lower than those in urban, industrial, suburban, and the similar research areas in the coastal areas of Europe (Table 1), indicating that the occurrence of OCPs in the coastal island was relatively low. The detailed description of contamination characteristics of individual OCPs was shown in the following sections.

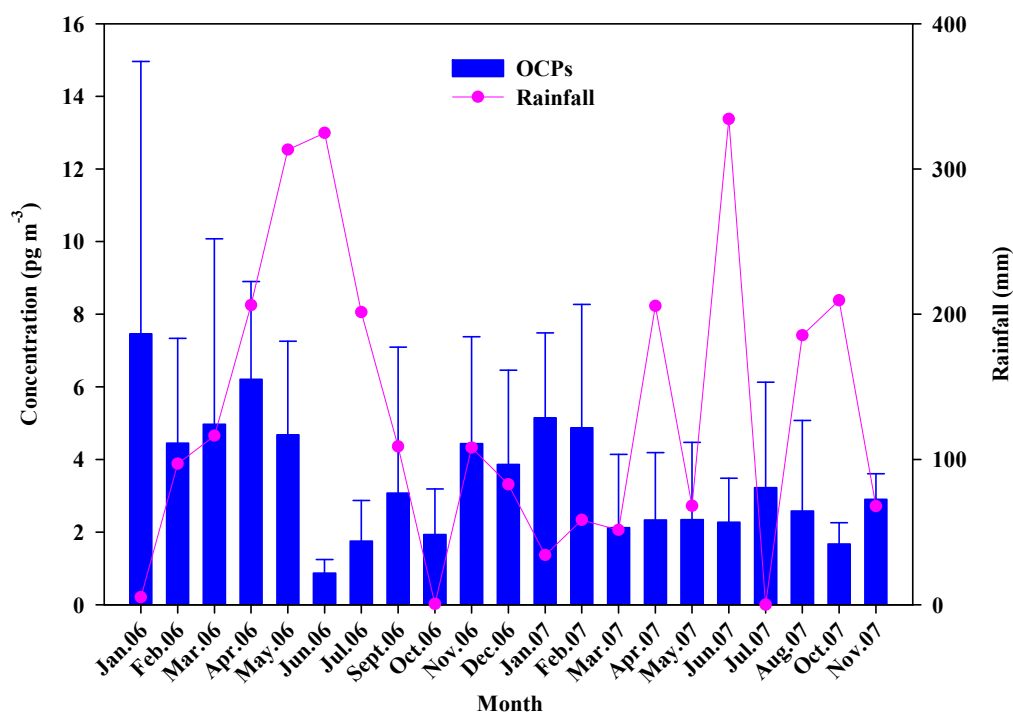
#### HCH

HCH was widely used in China as two formulations, one was technical HCH (60–70%  $\alpha$ -HCH, 5–12%  $\beta$ -HCH, 10–12%  $\gamma$ -HCH, 6–10%  $\delta$ -HCH), and the other was lindane (approximately 99% of  $\gamma$ -HCH).

In our study, HCH was one of the dominant OCPs in air at Pingtan Island and was detected in almost all samples. The concentration of  $\Sigma$ HCH isomers ( $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -HCH) in the analyzed samples was ND to 4.64 pg m<sup>-3</sup> (an average of 1.10 ± 0.94 pg m<sup>-3</sup>) and ND to 4.44 pg m<sup>-3</sup> (an average of 0.96 ± 0.75 pg m<sup>-3</sup>) in 2006 and 2007, respectively, which accounted for 25.5% and 30.9% of the total OCPs, respectively. The average annual concentrations of the HCH



**Fig. 1.** Temporal variations of the total OCP concentrations and PM at Pingtan Island from January 2006 to November 2007 (lack of the data of August 2006 and September 2007).



**Fig. 2.** Seasonal variations of total OCP concentrations in PM of Pingtan Island from January 2006 to November 2007.

isomers were as follows:  $\beta > \alpha > \gamma > \delta$  in both 2006 and 2007 (Fig. 4). Seasonal variations were observed at Pingtan for  $\Sigma\text{HCH}$  isomers (Fig. 3). Higher  $\Sigma\text{HCH}$  concentrations were observed in the cool season (from January to April 2006 and from October 2006 to February 2007, with an average of  $16.0^\circ\text{C}$ ), whereas lower concentrations were observed in the warm season ( $27.1^\circ\text{C}$ ). However, high HCH concentrations could mainly be attributed to  $\beta\text{-HCH}$ , while an increasing proportion of  $\alpha\text{-HCH}$  appeared in the

warm season (Fig. 4).

Historically, HCH products were widely used in the southeastern region of China. High HCH concentrations were detected in water, sediment and soil, and they could be re-suspended or re-volatilized to the local atmosphere (Zhang *et al.*, 2003; Zhang *et al.*, 2009; Zheng *et al.*, 2010; Qu *et al.*, 2015). Due to their high volatility,  $\alpha$ - and  $\gamma$ -HCH tend to evaporate into the gas phase (Wu *et al.*, 2010; Zheng *et al.*, 2010). However,  $\beta\text{-HCH}$  is the most stable

**Table 1.** Comparison of the concentrations of OCPs in atmospheric particles at different regions ( $\text{pg m}^{-3}$ ).

Site	region	Time	HCHs	DDTs	Chlordane	Endosulfan	Total OCPs	Reference
Beijing, China	Industrial/urban	2006	293	1019	731	241	2917	(Wang et al., 2008)
Konya, Turkey	urban	2006	17	83	3	72	186	(Ozcan et al., 2009)
Jinan, China	Urban	2009	26.1	10.1	4.8	13.2	92	(Xu et al., 2011)
Hong Kong	Urban	2003	ND	17	4	6	27	(Li et al., 2007)
Guangzhou, China	Urban	2003	4	122	19	8	153	(Li et al., 2007)
Hong Kong	Suburban	2003	ND	20	3	3	26	(Li et al., 2007)
Guangzhou, China	Suburban	2003	ND	71	7	11	89	(Li et al., 2007)
Korea	Land background	2008	71	3.5			76.71	(Jin et al., 2013)
Xining, China	Land background	2011	8.45	64.0	0.35			(Li et al., 2015)
Tianjun, China	Land background	2011	6.55	55.5	0.35			(Li et al., 2015)
Izmir, Turkey	Coastal	2005	4.4	2.0	1.6	7.1	29.4	(Odabasi et al., 2008)
Bight, Germany	Coastal	2009	9.2	1.2			12.4	(Mai et al., 2016)
Mudanya, Turkey	Coastal	2008	53.33	10.23	6.15	70.13	215.43	(Cindoruk, 2011)
Pingtian, China	Coastal	2006	1.16	1.35	0.05	0.13	4.58	This study
Pingtian, China	Coastal	2007	0.96	0.65	0.03	0.12	3.11	This study

isomer and tends to accumulate in particles as a consequence of its lower volatility and its equatorially positioned chlorines (Zhang et al., 2009).

It has been suggested that the ratio of  $\alpha$ -/ $\gamma$ -HCH in the environment was strongly influenced by the usage of lindane ( $\alpha$ -/ $\gamma$ -HCH < 0.1) and technical HCH ( $\alpha$ -/ $\gamma$ -HCH at 3.6–15) (Zheng et al., 2010). A  $\alpha$ -/ $\gamma$ -HCH ratio lower than 1 indicates that the amount of HCH is primarily derived from local and recent lindane inputs, whereas a ratio higher than 7 is attributed to LRAT or past usage of technical HCH derived from technical HCH (Xu et al., 2011). In our study, the ratio ranged from 0.17 to 0.93 from January–March 2006, and a lower ratio appeared in July 2007 (lower than 1), indicating higher local and recent inputs of lindane during these periods. Whereas the ratios ranged from 1.09–6.00 in other months (except March 2007), and these values indicated no preference between lindane and technical HCH. Additionally, the  $\alpha$ -/ $\gamma$ -HCH ratio exhibited an increasing trend with time in 2006 and a decreasing trend after March 2007 (Fig. 3). However, the  $\alpha$ -/ $\gamma$ -HCH ratio in March 2007 was much higher than 7, this might influence by the past usage of technical HCH, and transported through atmosphere to Pingtan Island.  $\alpha$ -HCH has a longer atmospheric lifetime (120 d) than  $\gamma$ -HCH (96 d), and  $\gamma$ -HCH can be converted to  $\alpha$ -HCH by photoisomerization (Brubaker and Hites, 1998). Thus, all of these properties cause a lower residence time of  $\gamma$ -HCH in atmospheric PM compared to that of  $\alpha$ -HCH, leading to increase  $\alpha$ -/ $\gamma$ -HCH ratios (Wu et al., 2010). In addition, the extremely high value of  $\alpha$ -/ $\gamma$ -HCH in March 2007 may also be explained by the re-volatilization of  $\alpha$ -HCH from secondary sources, such as contaminated sediments, soil and water surfaces (Bossi et al., 2013).

### DDT

In our study, DDT compounds (including p,p'-DDT, p,p'-DDE and p,p'-DDD) were detected in most atmospheric PM samples, ranging from ND to  $17.36 \text{ pg m}^{-3}$  (an average of  $1.34 \pm 2.16 \text{ pg m}^{-3}$ ) and ND to  $5.22 \text{ pg m}^{-3}$  (an average of  $0.65 \pm 0.65 \text{ pg m}^{-3}$ ) in 2006 and 2007, respectively, accounting for approximately 31.1% and 21.0% of  $\sum$ OCPs. The annual mean DDT concentration in 2006 was more than 2-fold times higher than the average in 2007. Among the DDT isomers, p,p'-DDT was the most abundant compound, followed by p,p'-DDD and p,p'-DDE in 2006, while p,p'-DDD > p,p'-DDT > p,p'-DDE in 2007 (Fig. 6). A seasonal pattern of DDT compounds was similar to OCPs levels (Fig. 5). The DDTs level was relatively low compared with other urban regions, such as Jinan ( $1.4$ – $76 \text{ pg m}^{-3}$ ) (Xu et al., 2011), Tianjin ( $25$ – $2210 \text{ pg m}^{-3}$  in autumn and  $416$ – $3140 \text{ pg m}^{-3}$  in winter) (Wu et al., 2005) and northern China (Ding et al., 2015).

In the environment, p,p'-DDT can degrade to p,p'-DDE in aerobic environments and to p,p'-DDD in anaerobic environments (Yang et al., 2013). Hence, the ratio of p,p'-DDT over (p,p'-DDD + p,p'-DDE) can be used to trace the degree of degradation of the parent compounds and to distinguish recent inputs (the ratio > 1) from historical residues (the ratio < 1) (Li et al., 2007; Xu et al., 2011).

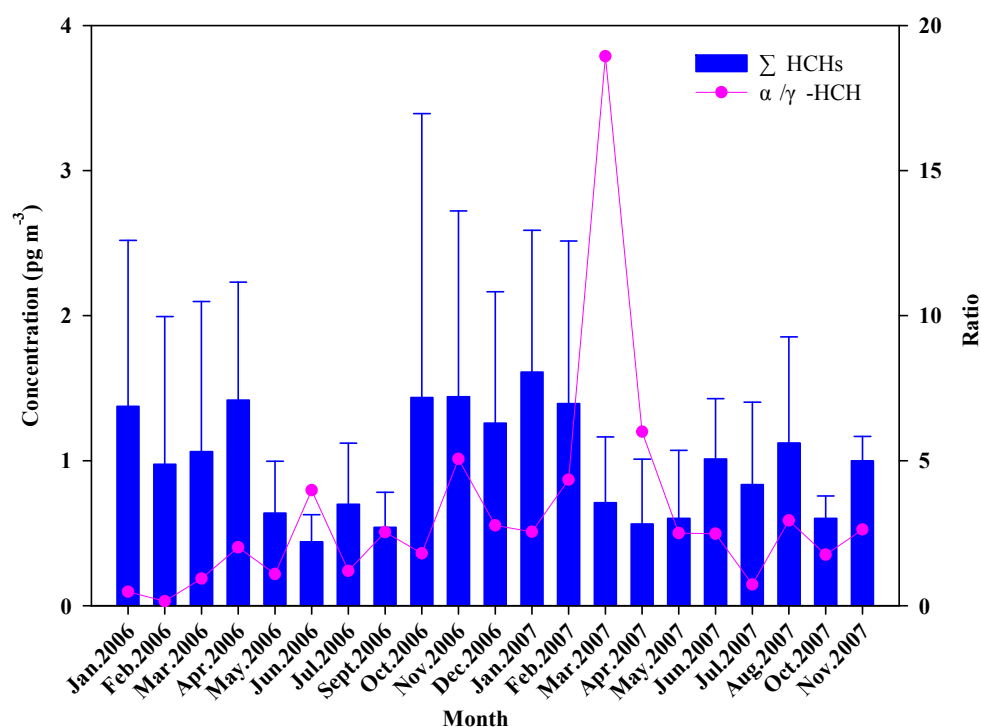


Fig. 3. Seasonal variations of  $\Sigma$ HCH concentrations and ratios of  $\alpha$ -/ $\gamma$ -HCH in PM from Pingtan Island from January 2006 to November 2007.

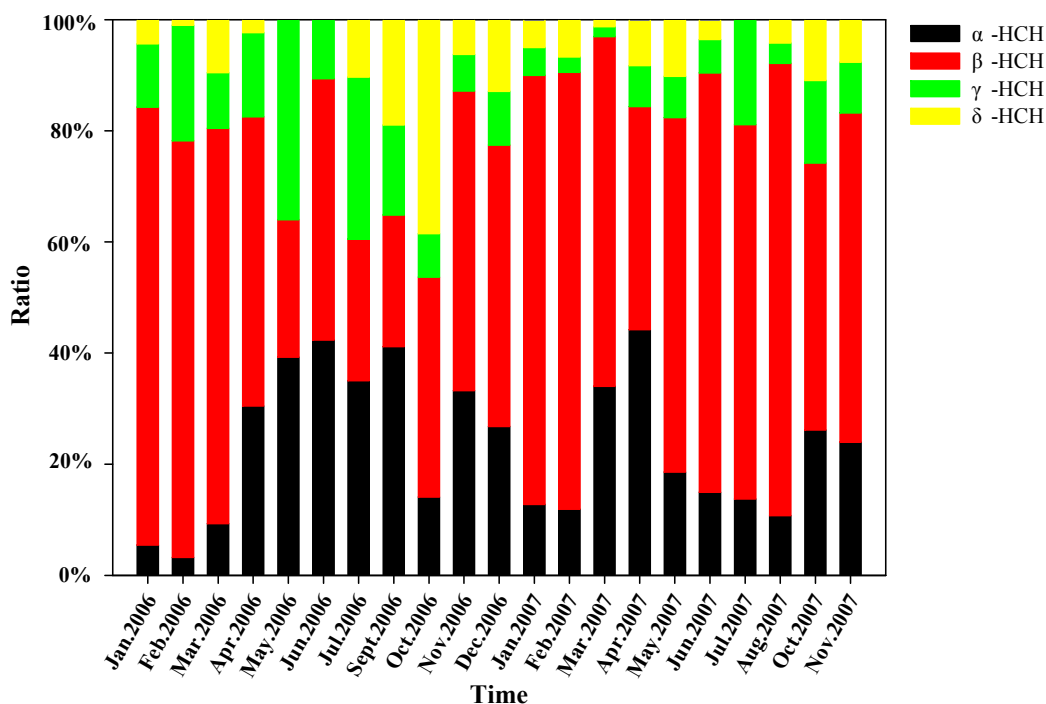
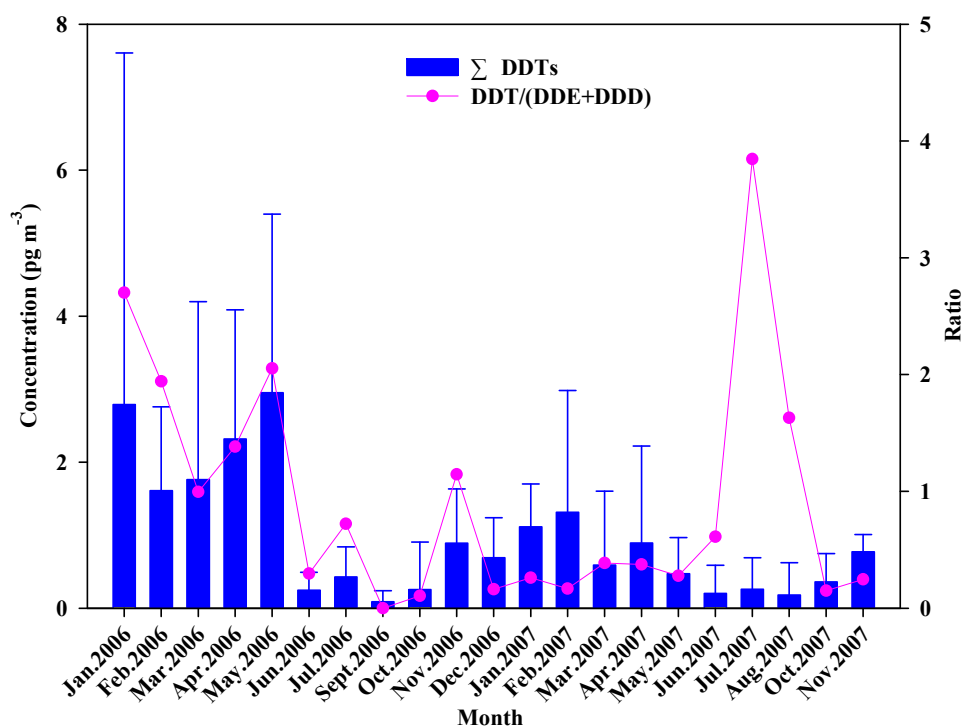


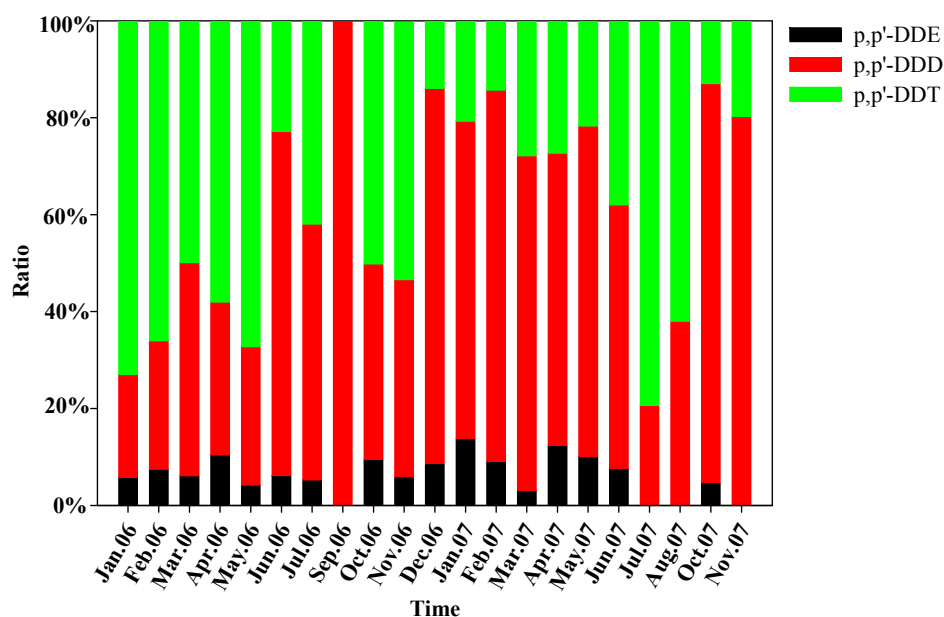
Fig. 4. Distribution percent of the four HCH isomers in atmospheric PM from Pingtan Island.

The results in our study showed that the ratio was 1.38 in 2006 and 0.35 in 2007 (Fig. 5), indicating that recent usage of DDT might have the greatest influence on the 2006 results, while historical residual dominated the 2007 results. Remarkably, though the DDTs concentration was relatively low in summer, the highest ratio appeared in July 2007,

which might have been influenced by DDT-containing antifouling paints commonly used on fishing boats in the coastal regions. To prevent the adhesion of marine organisms such as mollusks and barnacles, DDT-containing antifouling paints are often used on fishing boats by the fishermen (Li *et al.*, 2007; Zheng *et al.*, 2010). Furthermore, during periods



**Fig. 5.** Temporal variations of  $\Sigma$ DDT concentrations and ratios of p,p'-DDT / (p,p'-DDE + p,p'-DDD) in atmospheric PM of Pingtan Island from January 2006 to November 2007.



**Fig. 6.** Distribution percentage of three DDT isomers in atmospheric PM from Pingtan Island.

when fishing was prohibited and the boats were not working, a large amount of the antifouling paints were used, resulting in newly generated DDT occurring at Pingtan Island with summer monsoons.

#### Chlordane

Technical chlordane is a mixture of over 140 different components, with the major constituents being trans-chlordane (TC), cis-chlordane (CC) and heptachlor (HEPT)

(Bidleman *et al.*, 2002; Wu *et al.*, 2011). In the environment, HEPT will be metabolized to heptachlor epoxide (HEPX), which is more stable in the air and carcinogenic (Bidleman *et al.*, 1998a). The concentrations of  $\Sigma$ chlordanes (sum of TC, CC, HEPT, HEPX) ranged from ND to  $2.37 \text{ pg m}^{-3}$  (average of  $0.39 \pm 0.55 \text{ pg m}^{-3}$ ) and ND to  $2.81 \text{ pg m}^{-3}$  ( $0.32 \pm 0.54 \text{ pg m}^{-3}$ ) in 2006 and 2007, respectively. The three main components of technical chlordane (TC, CC and HEPT) were only sporadically detected in all samples

from Pingtan Island. However, HEPX was the most abundant compound, accounting for approximately 71.4% and 78.7% of  $\Sigma$ chlordane. The seasonal cycle of  $\Sigma$ chlordane concentration was also similar to total OCPs level (Fig. 7).

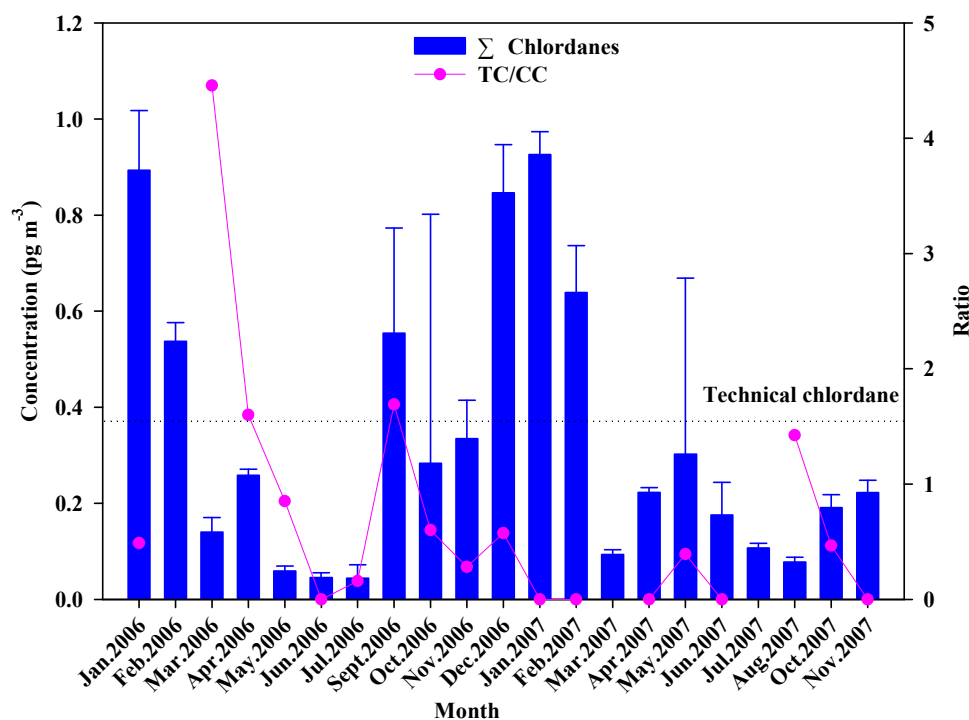
Chlordane was generally used as a termiticide, insecticide and herbicide in China during the past decades, with a usage rate of 200 tons per year (Zhang *et al.*, 2009; Wu *et al.*, 2011). However, no serious pollution by TC and CC was observed in our study. Once released into the terrestrial ecosystem, chlordane tended to bind with soil particles. Thus, it was not easily transported to Pingtan Island, which is isolated and far away from the source of the pollution. Concentrations of HEPT are mostly below the detection limit in the Pingtan atmospheric PM because HEPT is rapidly transformed to HEPX in the environment (Bossi *et al.*, 2013), this may be responsible for the higher HEPX level whereas lower HEPT in our study. However, relatively high chlordane concentrations appeared in spring and fall, which might be attributed to the application of pesticides in spring and the tilling of soil in fall.

Although the partitioning properties and atmospheric deposition rates of TC are similar to CC, TC is generally more volatile and precipitated from the atmosphere faster than CC (Bidleman *et al.*, 2002; Wu *et al.*, 2011). Thus a decrease in the TC/CC ratio with LRAT from far sources is expected (Wu *et al.*, 2011). The TC/CC ratio has previously been used to understand the emission history and degradability of chlordane (Shen *et al.*, 2005; Wu *et al.*, 2011). The ratio in technical chlordane is 1.56, and the value decreases for weathered chlordane, which is the degradation products from the past usage of chlordane. Relatively uniform TC/CC

ratios of below 1.56 were recorded during the sampling period (Fig. 7), reflecting the main influence by the past usage of chlordane. Therefore, the relatively low concentrations of TC and CC in Pingtan Island exhibit a low TC/CC ratio in most month during the sampling period (Fig. 7), and likely occur from aged sources. However, the concentrations of CC in February 2006, March and August 2007 were all below than MDLs (Fig. 7, the broken line), and a higher ratio in March 2006, indicating newly generated chlordane during this period. Indeed, chlordane can still be found as termiticide until 2008 (Wu *et al.*, 2011), the high TC/CC ratio may influence by the usage of chlordane to control the breeding of termites during the period.

### Endosulfan

Endosulfan was once widely used in agriculture as a pesticide for cotton, teas, tobacco and fruit plantations, and for the control of disease vectors. China is one of the largest consumers of endosulfan, and the manufacture and usage of endosulfan occurs mostly in the eastern cities (Gai *et al.*, 2014; Qu *et al.*, 2015). Technical endosulfan is a mixture of two isomers, endosulfan I (70%) and endosulfan II (30%), and they are broken down to endosulfan sulfate (EndoSO<sub>4</sub>) in the environment (Pozo *et al.*, 2011). In this study, endosulfan I, II and EndoSO<sub>4</sub> exhibited low abundances in all samples, and the concentration of  $\Sigma$ endosulfan compounds (sum of I, II, EndoSO<sub>4</sub>) in 2006 and 2007 ranged from ND TO 0.97  $\mu\text{g m}^{-3}$  and ND to 3.88  $\mu\text{g m}^{-3}$ , respectively. Those values are far lower than the other urban regions, such as Jinan (China) (Xu *et al.*, 2011), northern China (Ding *et al.*, 2015), and Guangzhou and Hong Kong (Li *et al.*, 2007),



**Fig. 7.** Seasonal variations of the  $\Sigma$ chlordane concentration and ratio of TC/CC in atmospheric PM from Pingtan Island during the sampling period. The concentrations of CC in February 2006, March and August 2007 were all below than MDLs.



reflecting that Pingtan Island was less affected by endosulfan pollution. Unlike the other OCP compounds, the highest endosulfan concentrations observed in September 2006 and May 2007, whereas it appeared in relatively low levels during the rest of the year (Fig. 8). The elevated concentrations of endosulfan in those two months may be associated with its use to control pests in tea planting, since Fujian province is a large tea producing area with a long history.

The endosulfan I/II ratio is approximately 2.3 in the technical mixture, and a ratio less than 2.3 indicates aged endosulfan, whereas ratios greater than 2.3 indicate newly generated inputs (Qu *et al.*, 2015). As shown in Fig. 8, most values were less than 2.3 except for September 2006 and May 2007, indicating the presence of aged endosulfan. The lower ratio seen for most samples primarily results from the higher vapor pressure and Henry's law constant for endosulfan I than II, suggesting that endosulfan I tends to evaporate from surface environments to the gas phase (Jia *et al.*, 2010). Moreover, studies on the degradation of endosulfan I and II to EndoSO<sub>4</sub> have shown that endosulfan I degrades more readily to EndoSO<sub>4</sub> than II does (Leonard *et al.*, 2001; Jia *et al.*, 2010). Therefore, the significantly higher concentrations of endosulfan in September 2006 and May 2007 and the higher endosulfan I/II ratio suggest that endosulfan was derived from newly generated applications during this period.

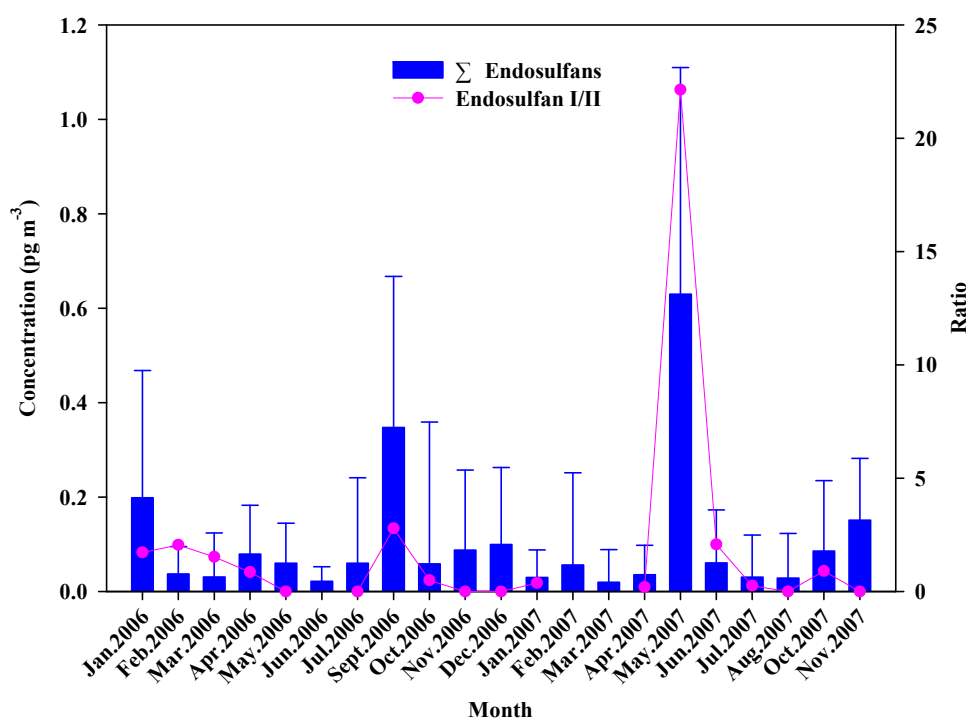
#### Other OCP Compounds

Aldrin, dieldrin, endrin and methoxychlor were also detected in our study. Aldrin was one of the most widely used OCPs in the world until it was banned in the 1970s due

to its high toxicity and harm to ecological systems. After being released into the environment, aldrin was rapidly metabolized to dieldrin (Gioia *et al.*, 2005). In industrial production, dieldrin was mainly produced by the epoxidation of aldrin and was widely used in the control of soil pests. Endrin is a stereoisomerism of dieldrin and was used extensively for insect control on cotton, citrus fruit. Technical endrin is a mixture of endrin and its metabolites, endrin aldehyde and endrin ketone. Although those contaminants were never used in large amounts in China (Wang *et al.*, 2008), they can be detected in our study.

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

Methoxychlor is an environmental estrogen that is gradually becoming a substitute for DDT because of its lower toxicity and bioaccumulation in organisms, and it



**Fig. 8.** Seasonal variations in the  $\Sigma$ endosulfan concentration and endosulfan I/II in atmospheric PM from Pingtan Island during the sampling period.

can be widely used in pest control for vegetables and fruits. However, due to its longer half-life and its potential to cause damage to the reproductive development of organisms, more attention has been focused on the effects of methoxychlor. The concentration of methoxychlor varied between ND to 11.95  $\text{pg m}^{-3}$  and ND to 5.53  $\text{pg m}^{-3}$  in 2006 and 2007, respectively. The level of methoxychlor was much higher than Chlordane and endosulfan which had been widely used in China in history, became one of the dominant components of OCPs during the sampling period. Compared to other regions, the levels in our study were similar to the methoxychlor found in  $\text{PM}_{2.5}$ ,  $\text{PM}_5$  and  $\text{PM}_{10}$  (0.97  $\text{pg m}^{-3}$ , 0.94  $\text{pg m}^{-3}$  and 1.0  $\text{pg m}^{-3}$ , respectively) in Jinan, but slightly lower than that in TSP (2.2  $\text{pg m}^{-3}$ ) in Jinan (Xu *et al.*, 2011). Meanwhile, it was far lower than those recorded for the Western Black Sea Region (Turkey, 91.9  $\text{pg m}^{-3}$ ) (Yenisoykarakas *et al.*, 2012). The results indicate that the unrestricted use of methoxychlor has greater uncertainty and potential risks in the environment.

### **Influence Factor**

#### *Meteorological Parameters*

Theoretically, meteorological conditions and the proximity to sources are two dominant factors that affect POPs levels in the atmospheric environment (Lee and Jones, 1999; Wang *et al.*, 2015; Lao *et al.*, 2018). Therefore, to investigate the influence of related meteorological factors on atmospheric OCP concentrations in Pingtan Island, a correlation analysis between OCP concentrations and meteorological parameters was carried out in this study. The results of correlation analysis are presented in Table S3.

Negative correlations were observed between most of the OCP concentrations and T, suggesting that higher temperatures might contribute to the transfer of those OCP compounds from the particulate phase into the gaseous phase, whereas lower temperatures promote the absorption on those particles. As semi volatile contaminants, OCPs reach an equilibrium between the particulate phase and gaseous phase mainly controlled by temperature (He and Balasubramanian, 2010b). Among the meteorological parameters, OCP concentrations were positively correlated to atmospheric pressure and negatively correlated to water vapor pressure. However, relative humidity showed negative correlations with chlordane levels in the air but were positively associated with endosulfan. In Pingtan Island, the relative humidity and water vapor pressure are high and uniform throughout the year (especially in summer, Fig. 2) due to frequent rainfall and marine exposure, and scavenging effects of contaminants can be caused by precipitation and wet deposition (He and Balasubramanian, 2010b). For wind speed, previous studies suggested that winds could play an important role in reducing contaminants level in local sources by increasing the atmospheric dispersion and dilution (Miguel *et al.*, 2004; He and Balasubramanian, 2010b; Castro-Jiménez *et al.*, 2011). However, wind speed was positively correlated with chlordane levels in the air, but no significant correlation was found with other OCP compounds. This observation suggested that wind could play an important role in the concentration of chlordane,

which could assist in the re-suspension of particulate matters from soil particles under strong wind events (Bidleman *et al.*, 1998b).

#### *Total Organic Carbon (TOC)*

OCPs tend to absorb in to particulate organic matter because of their high lipophilicity. Thus, the TOC content in particulates is an important factor influencing POPs in soil or particle-air exchange and transportation (Devi *et al.*, 2013; Gai *et al.*, 2014; Qu *et al.*, 2015; Bajwa *et al.*, 2016). To investigate the influence of TOC on the OCP levels, a correlation analysis between contaminant concentrations and TOC was carried out, and the results are presented in Table S4.

The concentrations of  $\alpha$ -HCH, p,p'-DDD and total OCPs in atmospheric PM at Pingtan Island exhibited a significant positive correlation with the TOC content. This result suggests that the PM organic matter could promote the adsorption of these compounds, and play an important role in controlling the distribution of these contaminants in atmospheric PM. However, the rest of the OCP compounds showed no significant correlation with TOC, suggesting that the distribution pattern of those compounds at Pingtan Island does not reach the absorption equilibrium status with organic matter. Previous studies demonstrated that certain artificial conditions may strike this equilibrium status (Gao *et al.*, 2013), such as waste incineration and frequent plowing with the robust agricultural activities may affect the relationship between OCPs and TOC in atmospheric PM.

#### *Effect of TSP and Source Analysis*

As shown in Fig. 1, the concentration of total OCPs in Pingtan Island exhibited a significant positive correlation with the TSP content, most likely because of their presence in TSP via the gas-particle partitioning process (Xing *et al.*, 2017). In addition, a significant correlation was observed between TOC and TSP content ( $R^2 = 0.548$ ,  $p < 0.01$ ) and among OCP compounds (Table S3), suggesting that they may be derived from similar sources. To further investigate the influence factor of OCPs concentrations distribution pattern in atmospheric particulates in Pingtan Island, the stable  $^{13}\text{C}$  isotope of TOC in PM was measured to trace possible sources of the atmospheric PM.

The stable  $^{13}\text{C}$  isotope as a tool for distinguishing from various sources. For example, the  $\delta^{13}\text{C}$  values of  $\text{C}_4$  terrestrial vegetation range from approximately  $-14$  to  $-12\text{‰}$ , and the  $\delta^{13}\text{C}$  values of marine organic carbon sources ( $-22$  to  $-18\text{‰}$ ) differ from those of fossil fuel organic carbon ( $-30$  to  $-23\text{‰}$ ) (Fry and Sherr, 1989; Boutton, 1991; Wozniak *et al.*, 2012) and  $\text{C}_3$  terrestrial vegetation ( $-32$  to  $-29\text{‰}$ ) (Moura *et al.*, 2008; Cao *et al.*, 2011). Specifically, the  $\delta^{13}\text{C}$  values for motor vehicle exhaust ( $-28$  to  $-26\text{‰}$ ) (Widory, 2006) are lower than those for coal combustion ( $-24.9$  to  $-21\text{‰}$ ) (Widory, 2006; Cao *et al.*, 2011). In our study, TOC  $\delta^{13}\text{C}$  values ranged from  $-27.8\text{‰}$  to  $24.6\text{‰}$  during the sampling period, with an average value of  $-26.5 \pm 0.7\text{‰}$ . In addition, a clear seasonal variation of  $\delta^{13}\text{C}$  values was found, the higher values observed for  $\delta^{13}\text{C}$  were found in winter and

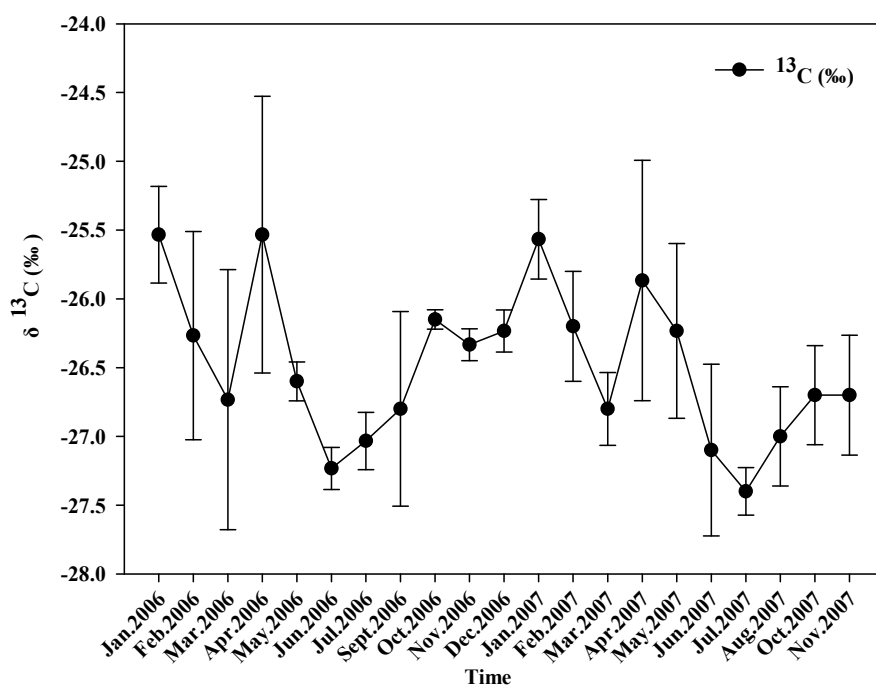
spring whereas the lower values were observed in summer (Fig. 9), which is consistent with the seasonal distributions of the OCP concentrations. The higher  $\delta^{13}\text{C}$  values in the cool season seem also to be influenced by marine organic carbon sources and coal combustion, while the lower values in the summertime seem to be influenced by  $\text{C}_3$  terrestrial vegetation and motor vehicle. However, air mass trajectory analyses (Fig. S3) showed that the air mass in the cool season was mainly originate from the northern mainland China during the sampling periods, whereas the air mass sources in summer mainly derived from the ocean. Consequently, marine organic carbon sources and  $\text{C}_3$  terrestrial vegetation is unlikely to be responsible for the higher  $\delta^{13}\text{C}$  values in the cool season and lower in summer. Therefore, the sources of atmospheric PM in the Island are mainly influenced by coal combustion and vehicle exhaust. In addition, a lower atmospheric load of OCPs can be expected when air masses from the ocean (low pollutant loads), this therefore may be responsible for the lower OCPs level in summer. On the contrary, when air masses are coming from northern mainland China (high pollutant loads), high atmospheric OCPs in atmospheric particles would be transported to the island therefore increasing OCPs inputs to Pingtan during the winter and spring.

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

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

where A represents the  $\delta^{13}\text{C}$  values for motor vehicle

exhaust, B represents the  $\delta^{13}\text{C}$  values for coal combustion, C represents the mixed value (experimental data), and X represents the contribution rate of motor vehicle exhaust. The values for motor vehicle exhaust and coal combustion were selected from Widory (Widory, 2006) reported in the references, with average values of  $-27.9\text{‰}$  and  $-23.6\text{‰}$ , respectively. By using the values of motor vehicle exhaust ( $-27.9\text{‰}$ ), coal combustion ( $-23.6\text{‰}$ ), the contribution rate of those two sources in atmospheric PM of Pingtan was calculated according to their  $\delta^{13}\text{C}$  measured values. The calculated results for the contribution rate of those two sources are presented in Table 2, and atmospheric PM had an average of 67% from motor vehicle exhaust emissions and 33% from coal combustion, showing that automobile exhaust had the largest influence during the sampling period. Previous studies suggested that the emissions of POPs from diesel engines was also an important source (Cheruiyot *et al.*, 2017). Recently, the selective catalytic reduction have been added into the heavy-duty diesel engine to reduce emissions of nitrogen oxide, but it also could be the source of POP emissions due to accumulation of organic particulates, and this provide the carbon matrix or necessary precursors for their formation (Chen *et al.*, 2017; Cheruiyot *et al.*, 2017). But it is noted that the contribution rate of coal combustion increased obviously from summer (18% and 17%) to winter (47% and 44%) and spring (38% and 37%). By combining the air mass sources mainly from the northern mainland China during the cool season (Fig. S3), suggesting that higher OCPs and PM levels appearing during the season may be strongly influenced by coal burning in northern China during the heating season. In addition, previous studies also demonstrate that extremely high OCPs level in atmospheric particles during the season



**Fig. 9.** Seasonal variations of  $\delta^{13}\text{C}$  values during the sampling period in Pingtan Island; the error bars are the standard deviation of monthly  $\delta^{13}\text{C}$  values.

**Table 2.** 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

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

### Risk Assessment

The toxicity assessment of OCPs was calculated by the equations described in Section 1.4. According to the literature, an average daily dose (ADD) between  $10^{-6}$  and  $10^{-4}$  denotes a potential risk, whereas lower values ( $< 10^{-6}$ ) indicate a very low risk and the higher values ( $> 10^{-4}$ ) indicate a high potential health risk (Ge *et al.*, 2013; Ding *et al.*, 2015; Qu *et al.*, 2015). As shown in Table S5, the estimated cancer risks for chlordane, endosulfan, aldrin, dieldrin, endrin and methoxychlor are all well below  $10^{-6}$ , suggesting the potential effect of those compounds could be negligible. However, the estimated risks for DDT, HCH and the total accumulation of OCPs are slightly above the threshold value ( $10^{-6}$ ) indicated potential risk, most notably, the higher levels of OCPs in the cold season. But considering that our study mainly focus on OCP in atmospheric particles, some relatively high volatility OCP compounds (e.g.,  $\alpha$ -HCH,  $\gamma$ -HCH, TC and CC) may reside in the gas phase. Therefore, the OCP compounds in the gas phase would likely gradually absorbed into atmospheric particles when the temperature drop during winter, and the effect of those OCP compound residuals in the atmospheric PM of Pingtan Island cannot be neglected. For different exposure pathways, the increasing trend in cancer risk for all OCP compounds in atmospheric particles is calculated as follows: dermal contact  $>$  inhalation  $>$  ingestion. The carcinogenic risk through ingestion and inhalation of OCP compounds containing atmospheric PM is  $10^{-2}$ – $10^{-3}$  times less than that through dermal contact with OCP compound-containing particulates, and the ADD values of all OCP compounds through ingestion and inhalation are below  $10^{-6}$ , and thus, of these three exposure pathways, dermal contact of OCP particulates is the primary pathway contributing to human health risks.

### CONCLUSIONS

The present study provided a 2-year dataset of the level of OCP contamination in atmospheric PM at Pingtan Island, China. The level of OCPs in particulate samples obviously lower than urban, industrial, suburban, and the similar research areas in the coastal areas of Europe. DDT and HCH being the most dominant OCPs, and those contaminants are mainly historical residues. Distinct seasonal

variations in the OCP concentrations correlated significantly with total particulate levels, and higher concentrations of most of the OCP compounds appeared in winter (except for endosulfan), whereas the lower concentrations appeared in summer. Correlation analysis results showed that the concentrations of most OCP compounds in the coastal area were mainly influenced by meteorological conditions. The close relationship between TOC and percentages of the OCP compounds suggests that the former is an important factor affecting the persistence of these OCPs in atmospheric PM. The isotopic signatures indicate that motor vehicle exhaust and coal combustion were two major sources for the atmospheric particulates, and the higher levels of OCPs in winter and spring might be influenced by coal combustion during the heating season in Northern China. Compared to other regions, contamination from residual OCPs in Pingtan Island may be considered minimal, but it still poses a potential carcinogenic risk for exposed populations. Therefore, the effect of OCP residuals in atmospheric PM on Pingtan Island cannot be neglected.

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### SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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