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# Characterizing the Gas-phase Organochlorine Pesticides in the Atmosphere over the Pearl River Delta Region

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## ABSTRACT

The organochlorine pesticides (OCPs) in the atmosphere were measured at four sampling sites located in Guangzhou (GZ), Zhaoqing (ZQ) and Hong Kong (HK) over the Pearl River Delta Region (PRDR) in one year duration from August 2006 to August 2007. Total 14 OCP species in the gas phase including 6 DDTs, 2 Chlordanes, 4 HCHs, HCB and heptachlor (HEP) were studied. It was found that Guangzhou had the highest concentration of DDTs and the mean concentrations of OCPs at these sampling sites were higher than those obtained in other rural/urban regions in the world. The concentrations of most OCPs in summer were higher than those in winter excluding TC, HCB and HCH. The ratios of $\alpha$- to $\gamma$-HCH and *o,p′*- to *p,p′*-DDT showed that HCHs in GZ and ZQ might come from the current usage of lindane and dicofol, but in HK might be from other sources. The results using 5 days backward air trajectory analysis indicated that the high concentrations of $\gamma$-HCH and HCB were mainly related to air mass through the potential source regions through long-range transport and local usage should not be overlooked.

***Keywords:*** Organochlorine pesticides; Gas phase; Pearl River Delta Region.

## INTRODUTION

Due to their semi-volatility, toxicity and persistence in the environment and biological accumulation via food chain, persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) and so on can cause environment pollution and influence human health. (Colborn *et al*., 1996; Chiu *et al*., 2010; Lin *et al*., 2010; Wang *et al*., 2010; Wu *et al*., 2010). According to Stockholm Convention on POPs, there are 12 POPs that must be eliminated or reduced. Most of them are polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs). Because of the long-range transport, POPs can be transported from their original places to remote areas of Earth with no historical usage and can be detected in the biosphere (Cheng *et al*., 2007; Wang *et al*., 2010). Some new sampling methods were used to characterize the OCPs including SPMD (Lohmann *et al*., 2001), PUF disk (Pozo *et al*., 2004), resin-based (Wania *et al*., 2003), Thin-Film (Harner *et al*., 2003) and Polymer-Coated Glass (Farrar *et al*., 2005) as the passive air samplers. These studies have shown that long-range transport has a significant impact on the dispersion of OCPs in the atmosphere.

The Pearl River Delta Region (PRDR), located on the south coast of China, has the subtropical monsoon climate with abundant sunshine and rainfall. The Asian monsoon system has a significant influence on this region. In summer, the monsoon is mostly from southwest while from northeast in winter. The PRDR is one of the highly populated, urbanized and industrialized regions in China. Several important cities, such as Guangzhou, Shenzhen, Dongguan, Foshan, Zhongshan, Zhuhai, Hong Kong and Macao are located there. The rapid urbanization and industrialization has resulted in a significant rise in pollutant emissions and therefore a severe degradation of air quality (Wang *et al*., 2005). A few investigations concerned OCPs pollution in this region have been concentrated in water (Luo *et al*., 2004), soil (Li *et al*., 2006), sediment (Zhang *et al*., 2003) and human breast milk (Wong *et al*., 2002). The related results showed that severe OCP pollutions in the PRDR are ubiquitous and harmful to human health. However, few researches on OCPs in atmosphere have been conducted (Li *et al*., 2007; Wang *et al*., 2007; Yang *et al*., 2008). Yang *et al*. (2008) conducted field measurement of OCPs weekly from April 2005 to March 2006 at two sampling sites to investigate the seasonal variation of OCPs in Guangzhou. Li *et al*. (2007) conducted sampling in Guangzhou and Hong Kong and

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found that the Asian monsoon plays an important role in the long-range atmospheric transport of OCPs. However, few studies in PRDR were focused on the central cities instead of some satellite cities around them. Liu *et al*. (2009) conducted field measurement from 37 Chinese cities and three background sites in 2005 in order to investigate the seasonal patterns of DDTs, chlordanes, hexachlorobenzenes and endosulfan in the atmosphere by using passive air samplers.

In order to characterize the levels, sources and transport of OCPs in atmosphere over the PRDR (two central cities and one satellite city), one year duration monitoring plan was performed simultaneously at four sampling sites from northern to southern of the PRDR using active polyurethane foam (PUF) air samplers and air mass back trajectory analysis.

## SAMPLING AND METHODOLOGY

### *Sampling Sites*

Total four atmospheric sampling stations including three urban sites, the Zhaoqing Institute (ZQ), Sun Yat-sen University campus in Guangzhou (GZ) and the Hong Kong Polytechnic University in Hong Kong (PU), and one rural site, Hok Tsui (HT) in Hong Kong which was located on the seaside, were established (Fig. 1).

Detailed description of sites of Hong Kong (PU) and Hok Tsui (HT) can be found at Ho *et al*. (2002). Briefly, the Hong Kong (PU) site, approximately 6 m above ground level and about 8 m away from the main traffic road, located in a mixed commercial and residential area with high traffic density. The Hok Tsui site, about 20 m above sea level is situated at the tip of Southern Hong Kong with least anthropogenic pollution. This site is considered as a rural sampling site.

Guangzhou (GZ): the station was located on a 15-high rooftop in the campus of Sun Yat-sen University. This site is about 100 m and 800 m away from the Pearl River Delta and the main traffic road -- Xingang Road, respectively. It represents an urban monitoring site which is also located in a mixed commercial and residential area.

Zhaoqing (ZQ): the site was located about 15 m above ground on the roof of a building in Zhaoqing University, which it is surrounded by farmlands, near the Xinghu Lake and Dinghu mountain landscape and famous scenery (about 10 km away). The site is about 200 m away from the main road of the Duanzhou District of Zhaoqing city.

### *Sample Collection*

The sampling duration was one year, starting from August 2006 to August 2007. Sampling was conducted simultaneously at the three sampling sites biweekly, while sampling was conducted at HT every three weeks due to the logistical problems. Totally, 78 samples were collected from four sampling sites. Meteorological conditions, such as temperature, relative humidity, wind speed and direction were recorded at each sampling site. Atmospheric samples were collected by a medium-volume sampler at a flow rate of 0.113–0.125 $m^3$/min for 24 hrs. The OCPs in the gas phase were trapped by polyurethane foam (PUF) cylinder (6.5 cm i.d. × 7.5 cm in height) after flowing through a quartz microfiber filter (QFF) (Grade GF/A, 20.3 × 25.4 cm, Whatman). Prior to sampling, the PUF cylinders were cleaned by Soxhlet extraction for 48 hrs by methanol, 24 hrs by acetone 48 hrs by dichloromethane (DCM), and then dried overnight in vacuum desiccator. All the PUFs were sealed with polyethylene bags and stored at 4°C before use. When the sampling ends, the PUFs were re-sealed using the original package materials, transported to the laboratory as soon as possible and stored at –18°C until extraction and analysis.

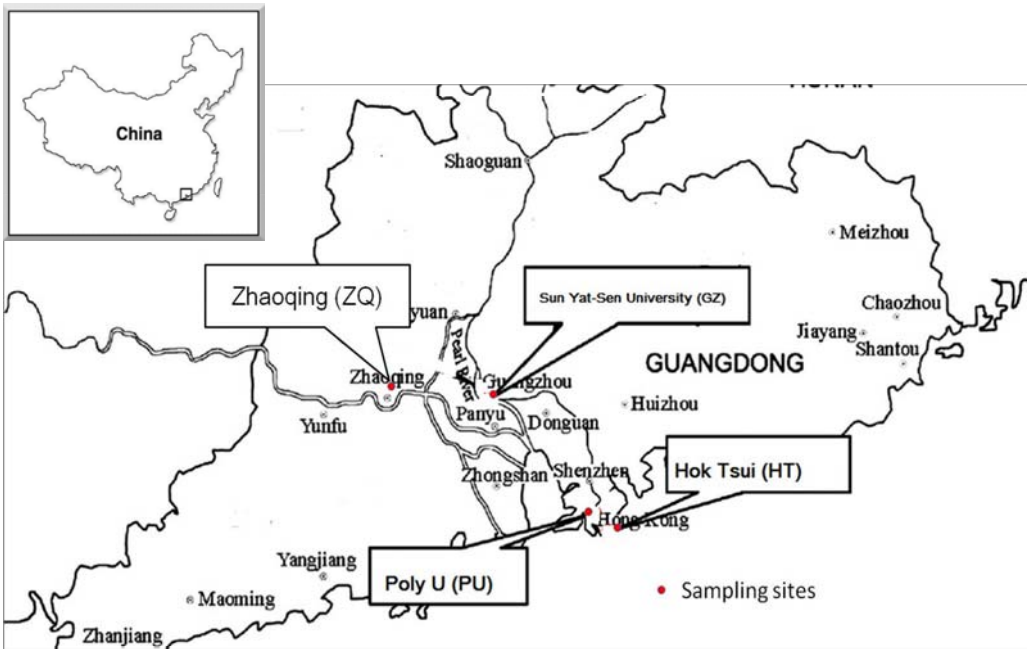


**Fig. 1.** Sampling locations over the Pearl Delta River region.

***Extraction and Analysis***

Add 2,4,5,6-tetracgkiri-m-xylene (TCmX) and decachlorobiphenyl in the sampled PUFs as recovery surrogates and activated copper granules in the collection flask to remove elemental sulfur. And then run Soxhlet extractor for 24 hrs using dichloromethane as reagent. The extract was concentrated by rotary evaporator and solvent exchanged to n-hexane and purified on an 8 mm i.d. aluminum/silica column packed, from the bottom to top, with neutral silica gel (3 g, 3% deactivated), neutral alumina (6 g, 3% deactivated), anhydrous sodium sulfate (1 g). The column was eluted with 10 mL of dichloromethane/ hexane (1/1, v/v) to yield the OCPs fraction. The fraction was purged to 200 μL under a gentle nitrogen stream. A known quantity of pentachloronitrobenzen (PCNB) was added as an internal standard prior to OCPs analysis. OCPs were analyzed using an Agilent 6890 GC equipped with a $^{63}$Ni electronic capture detector (ECD), a HP-5 column (30 m × 0.25 mm i.d × 0.25 μm film thickness) with a 2 m pre-column. The work conditions were as follows: Injector temperature, 80°C; oven temperature, the initial temperature, 100°C (hold for 1 min) and increased to 290°C (hold for 20 min) at a rate of 4 °C/min; the detector was operated at 315°C with helium as carrier gas at a rate of 1.0 mL/min; injection volume, 1 μL (splitless). Compounds were identified and quantified based on the retention time and peak area respectively.

***Quality Control***

The concentration OCPs were determined according to the retention times and peak areas of the calibration standards. All analytical procedures were monitored via strict quality control measures. Nine laboratory and three field blanks were subjected to the same experimental operations. No OCPs were detected in all the PUF blanks. Besides, recovery surrogates and internal standards were added into all samples and the mean recoveries for OCPs and surrogates in field samples were 72 and 110%, respectively. The final concentrations of OCPs were not corrected for recovery efficiency here.

***Backward Trajectories***

To investigate the transport of the OCPs, air backward trajectories were conducted using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSLPIT 4.9), developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (Draxler and Rolph, 2003). Due to the fact that the synoptic atmospheric conditions at two locations in the same city (i.e. the PU and HT sites in Hong Kong) were quite similar, we focused on the backtrajectories of three sampling sites (GZ, ZQ and PU) in the present study. Five days air back trajectories were calculated at 6 hours intervals (i.e. 0:00, 06:00, 12:00, 18:00 local time) for all the sampling days. Each trajectory was estimated for three starting altitudes (100 m, 500 m and 1000 m above ground level).

## RESULT AND DISCUSSION

***Concentrations of OCPs in Air***

Total of 78 PUF samples in the four sampling sites were collected. For these samples, 14 OCP species including *o,p′*-DDT, *p,p′*-DDT, *p,p′*-DDE, *o,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *tans*-Chlordane, *cris*-Chlordane, *α*-HCH, *β*-HCH, *γ*-HCH, *δ*-HCH, HCB and HEP were studied. The PRD region is a subtropical area with rain heat over the same period and its annual mean temperature ranging from 20 to 25°C. Therefore, in the present study, the samples were divided into two groups, winter and summer, according to its average temperature and the direction of monsoon. Winter season lasts from September through February, while summer season includes the six months from March through August.

The arithmetic mean concentrations with their standard deviations for the various analytes in the gas phase samples collected at four sampling sites in the two seasons has been shown in Tables 1 and 2.

**Table 1.** Mean concentration of OCPs (pg/m$^3$) in PRD in summer.

| OCPs | Concentration(pg/m$^3$) | | | |
|---|---|---|---|---|
| | GZ | ZQ | PU | HT |
| *o,p′*-DDT | 671 ± 535 | 198 ± 163 | 169 ± 165 | 137 ± 82 |
| *p,p′*-DDT | 177 ± 278 | 27 ± 17 | 32 ± 53 | 34 ± 22 |
| *p,p′*-DDE | 66 ± 115 | 30 ± 18 | 57 ± 68 | 98 ± 89 |
| *o,p′*-DDE | 951 ± 683 | 135 ± 111 | 159 ± 12 | 84 ± 76 |
| *o,p′*-DDD | 113 ± 48 | 132 ± 89 | 249 ± 268 | 88 ± 55 |
| *p,p′*-DDD | 142 ± 102 | 17 ± 19 | 15 ± 16 | 15 ± 8 |
| ΣDDTs | 2120 ± 925 | 539 ± 218 | 681 ± 326 | 456 ± 154 |
| TC | 114 ± 97 | 45 ± 27.27 | 238 ± 425 | 33 ± 44 |
| CC | 159 ± 154 | 54 ± 65.42 | 247 ± 436 | 79 ± 161 |
| *α*-HCH | 33 ± 21 | 119 ± 134.05 | 31 ± 15 | 34 ± 16 |
| *β*-HCH | 9 ± 5 | 10 ± 7.27 | N/A | N/A |
| *γ*-HCH | 378 ± 243 | 286 ± 338.37 | 233 ± 342 | 39 ± 27 |
| *δ*-HCH | 48 ± 2 | 31 ± 24 | N/A | N/A |
| HCB | 158 ± 101 | 135 ± 148 | 82 ± 71 | 114 ± 92 |
| HEP | 82 ± 106 | 26 ± 31 | 60 ± 51 | 30 ± 28 |

N/A -- data not available.

**Table 2.** Concentrations of OCPs (pg/m$^3$) in PRD in winter.

| OCPs | Concentration (pg/m$^3$) | | | |
|---|---|---|---|---|
| | GZ | ZQ | PU | HT |
| *o,p′*-DDT | 211 ± 190 | 272 ± 186 | 120 ± 66 | 66 ± 49 |
| *p,p′*-DDT | 55 ± 49 | 16 ± 15 | 17 ± 1 | 12 ± 13 |
| *p,p′*-DDE | 45 ± 40 | 28 ± 26 | 25 ± 15 | 33 ± 28 |
| *o,p′*-DDE | 608 ± 481 | 456 ± 483 | 145 ± 46 | 28 ± 17 |
| *o,p′*-DDD | 174 ± 128 | 107 ± 86 | 207 ± 140 | 64 ± 72 |
| *p,p′*-DDD | 72 ± 61 | 21 ± 28 | 17 ± 1 | 12 ± 11 |
| ΣDDTs | 1165 ± 539 | 900 ± 526 | 531 ± 162 | 215 ± 94 |
| TC | 116 ± 136 | 171 ± 233 | 282 ± 339 | 14 ± 17 |
| CC | 145 ± 163 | 121 ± 153 | 236 ± 334 | 12 ± 1 |
| *α*-HCH | 65 ± 64 | 112 ± 108 | 90 ± 34 | 46 ± 42 |
| *β*-HCH | 41 ± 39 | 28 ± 26 | N/A | N/A |
| *γ*-HCH | 410 ± 327 | 537 ± 447 | 261 ± 65 | 33 ± 23 |
| *δ*-HCH | 34 ± 25 | 88 ± 120 | N/A | N/A |
| HCB | 232 ± 140 | 394 ± 69 | 133 ± 109 | 102 ± 43 |
| HEP | 86 ± 119 | 220 ± 70 | 37 ± 18 | 9 ± 1 |

N/A -- data not available.

It was found that HCHs, chlordanes and *o,p′*-DDT had significant concentration differences among the three cities. The concentrations of these compounds in GZ, especially for the DDTs, were the highest. However, the elevated concentrations of *o,p′*-DDE and *o,p′*-DDD at ZQ and PU were also observed. Moreover, the distribution of OCPs concentrations in the three cities presented different patterns. GZ had the highest DDTs, while PU had higher chlordanes. These variations may be caused by different source emissions in this region.

Table 3 compared the concentrations of OCPs in the present study with those in other regions. In general, the levels of OCPs were much higher than those measured at other background/rural regions. For example, *α*-HCH in the PRD showed comparable levels to those in Japan. The concentrations of chlordane in PRD were much higher than those in other countries, especially in Japan and the United States where chlordane has been largely used to control termites around homes. The high levels of *o,p′*-DDT in GZ and ZQ were similar to those in Taihu Lake region, China, where the high concentration of *o,p′*-DDT was attributed to the use of dicofol (Qiu *et al*., 2005). However, it was also found that the concentrations of OCPs in this study (Table 3) were much higher than those collected in 2005–2006 (Yang *et al*., 2008), but they were comparable with those collected in 2003–2004 in Guangzhou (Li *et al*., 2007). It could be explained that there were 22 and 25 rainy days in May and June 2005, respectively. Moreover, there were total 11 rainy days during the whole sampling period in the present study. The lower concentrations in Guangzhou were related to the abundant rainfall in the year of 2005 (Yang *et al*., 2008).

**HCHs:** The seasonal variation of ∑HCHs was shown in Fig. 2. Tables 1 and 2 presented the mean concentrations of *α*-HCH and *γ*-HCH for summer and winter at the four sampling sites over the sampling period. With minor discrepancies, the concentrations of *α*-HCH and *γ*-HCH were higher in winter than those in summer. It suggested that the increasing usage of lindane on various purposes in winter. However, *γ*-HCH concentrations for these four sites (GZ, ZQ, PU, HT) were 394, 412, 247 and 36 pg/m$^3$, respectively, considerably higher among most reported data. It may indicate that there were fresh inputs of HCH in the PRD region. Among these four sampling sites, the concentration of HCHs of ZQ was the highest because of the developing agriculture usages there.

It has been widely recognized that HCH is available in two formulations: technical HCH and lindane. Typically, the percentages of HCH isomers over the technical HCH were 60–70%, 5–12%, 10–12%, 6–10% and 3–4% for α-, β-, γ-, δ- and ε-HCH, respectively (Cheng *et al*., 2007) and lindane account for 90% of *γ*-HCH. Usually, the isomer ratio of HCHs is used as an index to distinguish pollution sources. The *α*-HCH/*γ*-HCH ratio of technical HCH calibrated by relative vapor pressure at 25°C is > 1.9. High percentage of *γ*-HCH in lindane may reduce the ratio (Li *et al*., 1996). Generally, high *α*-HCH/*γ*-HCH ratio indicates the input of technical HCH and conversely from lindane (Iwata *et al*., 1993; Granier and Chevreuil *et al*., 1997; Haugen *et al*., 1998; Willet *et al*., 1998; Wu *et al*., 2005). The *α*-HCH/*γ*-HCH ratios in the atmosphere of GZ, ZQ were 0.12 ± 0.08 (0.02–0.35) and 0.48 ± 0.32 (0.06–1.5), respectively, lower than that of technical HCH. The low ratio of *α*-HCH/*γ*-HCH with high level of *γ*-HCH confirms the current usages of lindane in China. Previous studies showed that high levels of *γ*-HCH can be found in these areas where lindane was used (Granier and Chevreuil, 1997; Haugen *et al*., 1998; Li *et al*., 2007). Additionally, though the *α*-HCH/*γ*-HCH ratios in the atmosphere of PU and HT in Hong Kong were also low (0.76 ± 0.88 (0.2–3.8), 0.92 ± 1.01 (0.6–3.9), respectively), high *α*-HCH/*γ*-HCH ratios (> 3) were found at these two sites in July. Usually, the *α*-HCH/*γ*-HCH ratios were low in summer due to the usage of lindane as a seed dressing or as a general pesticide (Yang *et al*., 2008). The high levels of *α*-HCH/*γ*-HCH ratios in July at PU and HT indicated that there may be some other sources of HCHs in Hong Kong.

**Table 3.** Comparison of OCP concentrations (pg $m^{-3}$) at PRD with other sites.

| Sampling sites | Types | Time | α-HCH | γ-HCH | *o,p´*-DDT | *p,p´*-DDT | *p,p´*-DDE | TC | CC |
|---|---|---|---|---|---|---|---|---|---|
| GZ | Urban | 06–07 | 49 | 394 | 441 | 116 | 56 | 115 | 152 |
| ZQ | Suburban | 06–07 | 116 | 412 | 235 | 22 | 29 | 108 | 88 |
| PU | Urban | 06–07 | 61 | 247 | 145 | 25 | 41 | 260 | 242 |
| HT | Coastal | 06–07 | 40 | 36 | 102 | 23 | 66 | 24 | 46 |
| GZ [a] | Urban | 05–06 | 46 | 35 | 155 | 79 | 51 | 130 | 79 |
| Taihu Lake, China [b] | Urban | 2002 | 74 | 46 | 767 | 124 | 212 | -- | -- |
| Sigapore [c] | Coastal | | 30–259 | 24–208 | – | 1.6--10.8 | 0.4–0.9 | -- | -- |
| Seoul, Korea [d] | Rural | 99–00 | 34–1977 | 5–332 | 1--308 | -- | 1.6--30 | -- | -- |
| Niigata, Japan [e] | Coastal | 99–01 | 92 | 32 | -- | 6 | 5 | -- | -- |
| European [f] | Urban | 2002 | 14--100 | 9--390 | -- | 0.6--190 | 0.4--25 | -- | -- |
| Alabama, USA [g] | Farm | 96–97 | 92 | 50 | -- | -- | 10 | 47 | 25 |
| Signy Island, Antarctica [h] | Background | 94–95 | 2.7 | 22 | 0.2 | 0.28 | 0.4 | 0.9 | 0.21 |

[a] Yang *et al*., 2008; [b] Qiu *et al*., 2004; [c] Jaward *et al*., 2005; [d]Yeo *et al*., 2003; [e] Murayama *et al*., 2003; [f] Jaward *et al*., 2004; [g] Jantunen *et al*., 2000; [h] Motelay-Massei *et al*., 2005.

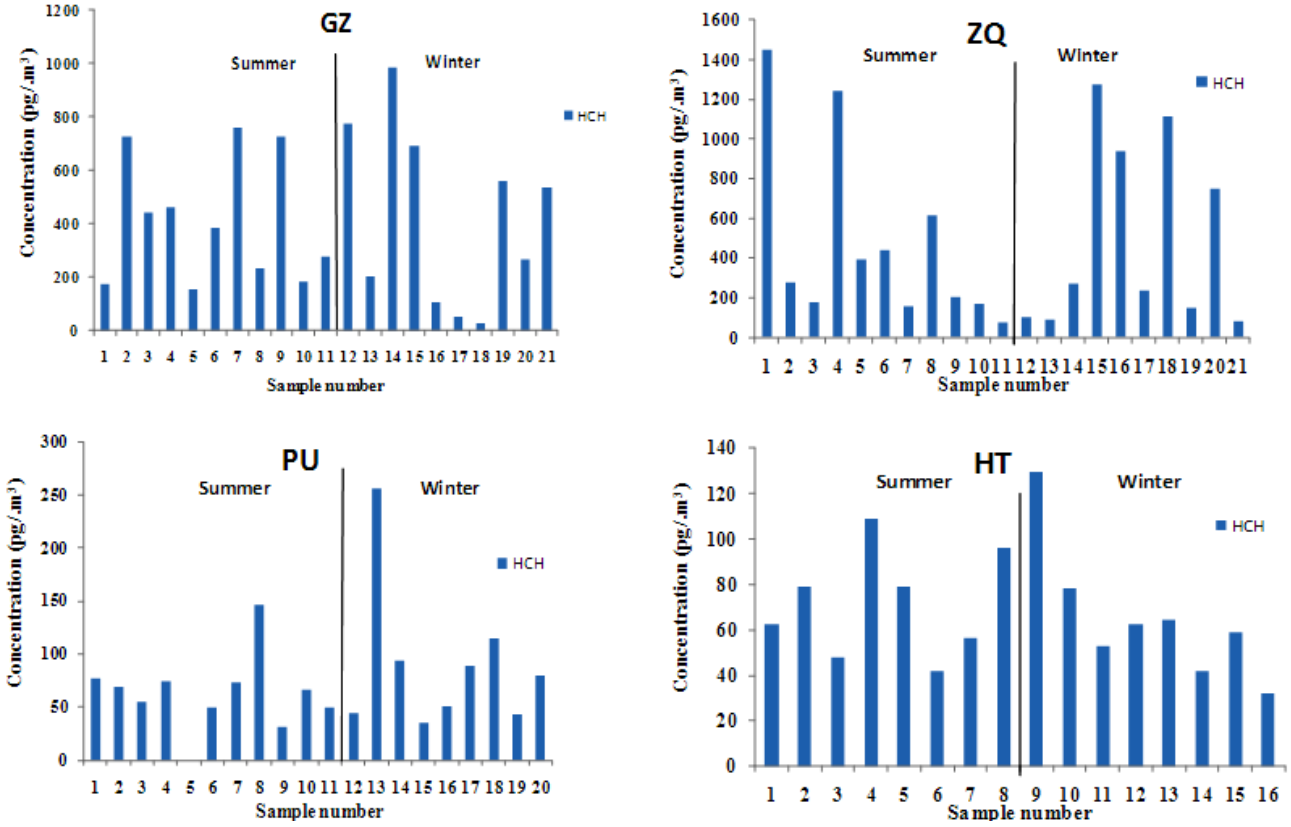


**Fig. 2.** Seasonal variations of total HCH concentrations at four sampling sites*.

**Chlordane:** Technical chlordane including *trans*- and *cis*-chlordanes (TC and CC) was widely used as agricultural pesticides on farm, public lawn and as a termiticide in house foundation.

The correlation values ($R^2$, $p < 0.05$) between the chlordane concentrations with temperature ranged from 0.008 to 0.055 for TC and 0.002 to 0.109 for CC, among all the sampling sites. The low $R^2$ values indicated that the concentrations of those compounds were less related to the ambient temperature. In this work, the mean concentrations of individual compounds in GZ, ZQ, PU and HT sites were 115, 108, 260 and 24 pg/$m^3$ for TC, and 152, 88, 242 and 46 pg/$m^3$ for CC, respectively. The concentrations were higher than those measured in other remote regions. Table 1 and 2 presented the mean concentrations of Chlordanes in different seasons. It was found that there were great seasonal variations at ZQ and HT, but minor variations at GZ and PU. This was agreeable to the results reported by Qiu *et al*. (2004).

Generally, the most abundant of components of technical

chlordane are *trans*-chlordane (TC, 13%), *cis*-chlordane (CC, 11%), heptachlor (5%) and *trans*-nonachlor (5%), respectively. The ratio of TC/CC in technical chlordane is 1.2 (Li *et al*., 1998). The changes of TC/CC ratio can be used to identify the "age" of the pollutions due to the photo degradation and a ratio of TC/CC < 1 is generally taken to be indicative of aged chlordane (Halsall *et al*., 1998; Bailey *et al*., 2000; Jantunen *et al*., 2000; Bidleman *et al*., 2002; Hung *et al*., 2005; Cheng *et al*., 2007). The relative liquid phase vapor pressure of TC/CC at 25°C is 1.00:0.72 (Hinckley *et al*., 1990; Yang *et al*., 2008). The TC/CC ratio (> 1.2) could be an indicator of fresh input of technical chlordane. In this work, the TC/CC ratio at GZ was relatively low (1.03 ± 0.26). This result is agreeable to some of the previous studies (Xu *et al*., 2004; Li *et al*., 2007). However, the TC/CC ratios at ZQ, PU and HT were 1.20 ± 0.27, 1.35 ± 0.29 and 1.44 ± 0.39, respectively. It indicated that there were some fresh inputs of technical Chlordanes in Zhaoqing and Hong Kong.

**DDTs:** DDT isomers have been widely used to control insects and pests in the farm, gardens and anti-fouling paint for ships as an additive (Ho *et al*., 2002). Technical DDT was produced since 1950s in China and was banned in 1983. In present study, GZ had the highest ∑DDTs concentration followed by ZQ. The concentration of ∑DDTs was comparable with other study in this area (Li *et al*., 2007) and higher than those of other areas (Table 3). Furthermore, some previous studies also shown that there was no apparent decline in DDT concentrations in PRD (Wang *et al*., 2007; Yang *et al*., 2008). The high levels of DDT indicated that there may be some other sources in this region, such as the usage of kelthane (Yang *et al*., 2008), anti-fouling paints containing DDT and so on (Li *et al*., 2007; Wang *et al*., 2007).

For the four sampling sites, there were clear seasonal variations for DDTs during the entire sampling sites. In general, the concentrations of DDTs were higher in summer than those in winter (Li *et al*., 2007; Yang *et al*., 2008) due to their volatility (Rajendran *et al*., 2005). On the other hand, technical DDT was applied in south and southeast China (Li and Macdonald, 2005), thus, the higher levels and seasonal variation of DDTs in PRD may be influenced by long range transport and the usage of anti-fouling paints (Wang *et al*., 2007).

Generally, contents of *o,p′*-DDT and *p,p′*-DDT in technical DDT ranged from 15 to 21% and from 65 to 85%, respectively. However, the average ratios of *o,p′*-DDT/*p,p′*-DDT in this work were 5.3 ± 2.1 (GZ), 5.4 ± 1.9 (ZQ), 4.1 ± 2.2 (PU) and 4.4 ± 1.5 (HT), respectively. The results were different from the percentages of *o,p′*-DDT and *p,p′*-DDT in the technical DDT. That might indicate that there were new emissions due to the application of dicofol, an acaricide form of technical DDT and used mainly on some crops in China (Qiu *et al*, 2004; Yang *et al*., 2008). Additionally, Wang *et al* (2007) reported that the anti-fouling paint within DDT additive used for fishing boats was also an important source for the DDT pollution in the PRD region.

**HCB:** HCB has several uses in industry and agriculture (Barber *et al*., 2005; Cheng *et al*., 2007; US Fish & Wildlife service). In China, it was also the intermediate product in the process of OCPs production. Particularly, HCB is currently used as a precursor in the manufacture of sodium pentachlorophenol for schistosome control in central and eastern China. Recent annual HCB production in China has been ca. 2000 t by a current manufacturer located in Tianjing, China (Wang *et al*., 2007). Though the production of HCB has been ceased in many countries, HCB occurs widely in the environment due to some incomplete combustion and its long half-life. The summer average concentrations of HCB were 158 ± 101 (GZ), 135 ± 148 (ZQ), 82 ± 71 pg/m$^3$ (PU) and 114 ± 92 (HT), and the winter average were 232 ± 140, 394 ± 69, 133 ± 109 and 102 ± 43 pg/m$^3$ (HT), respectively. It could be found that the concentration of HCB was close or higher in winter at the four sites. HCB concentrations in the European atmosphere were estimated to be quite uniform with the $c_{max}/c_{min}$ ratio (the ratio of the maximum concentration versus the minimum concentration of HCB) of 6 (Jaward *et al*., 2004). Some passive air sampling studies (Jaward *et al*., 2004, 2005) had shown that the $c_{max}/c_{min}$ ratio of HCB across China was 45, while the ratios in Korea, Janpan and Europe were in the range of 4 to 6. In this study, the ratios of $c_{max}/c_{min}$ were in range of 4.2 to 5.7 for the four sites, which was consistent with other study in PRD (Wang *et al*., 2007). Thus, the less fluctuation of HCB concentration in the PRD against the nationwide distribution may indicate that there was long-range transport of HCB from inland and North China to PRD. This can be confirmed by the seasonal variations of HCB and following backward trajectories analysis (Tables 1 and 2, Figs. 3 and 4).

### *Atmospheric Transport (LRAT) Trajectories*

As discussed above, LRAT could be the major factor that influenced the concentrations of OCPs in PRD region. In order to investigate the influence of the distant sources, backward air trajectory analysis was used to distinguish the long-range transport of air mass from potential source regions. In the present study, due to the fact that the PU site is very close to HT site in Hong Kong, the latitude and longitude for the two sites were almost the same. This feature can cause some deviation in the back trajectories simulations and result in inaccuracy. Thus, in this study, the backward trajectories analysis of GZ, ZQ and PU were conducted.

As shown in Fig. 3, the corresponding trajectories could be divided into two major types (N- and SW-type) according to their directions. N-type trajectory: air mass originated from Russia and pass through the northern part of China and the coast of South China Sea, traveled across Inner Mongolia, Liaoning province, Hebei province, Shandong province, Zhejiang province and ended at PRD region. SW-type trajectory: air mass originated from the coast of southeastern China and the South China Sea, mostly traveled across the South China Sea and the southern part of Vietnam. The rest of the trajectories were not regular at three heights, thus these trajectories were not

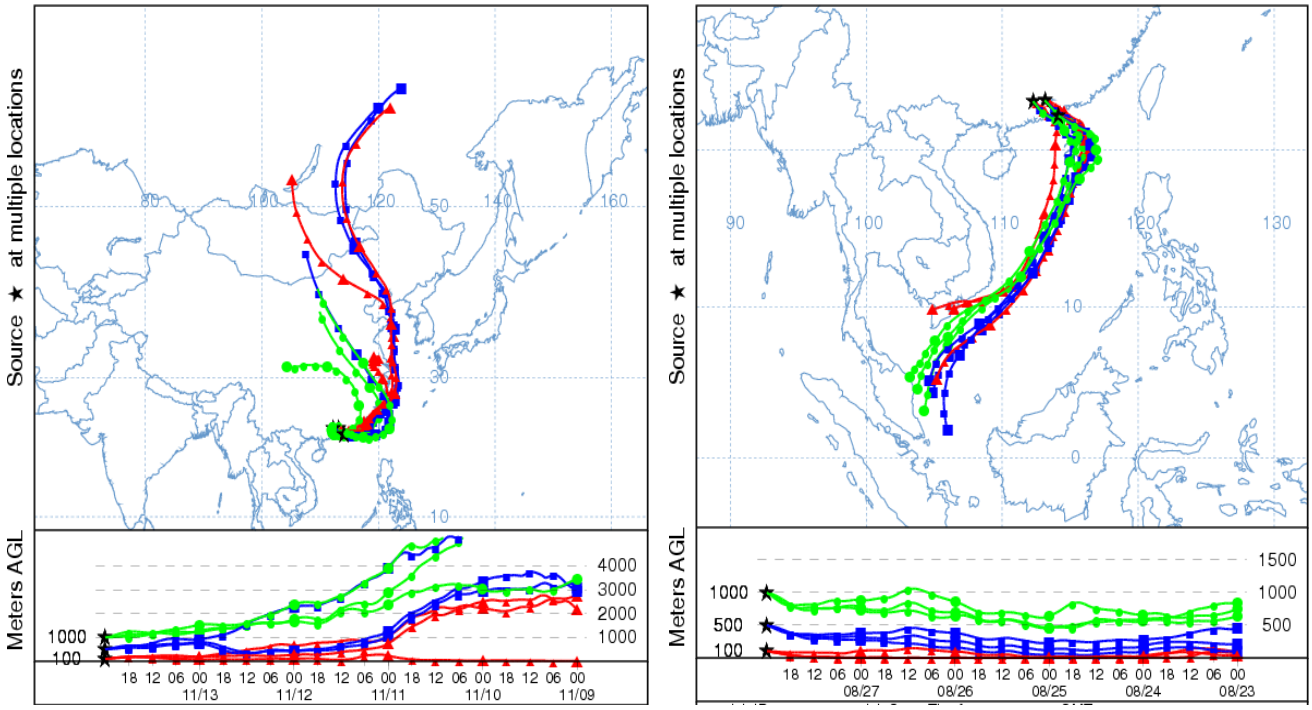


**Fig. 3.** Two major types of backward trajectories in the PRD region.

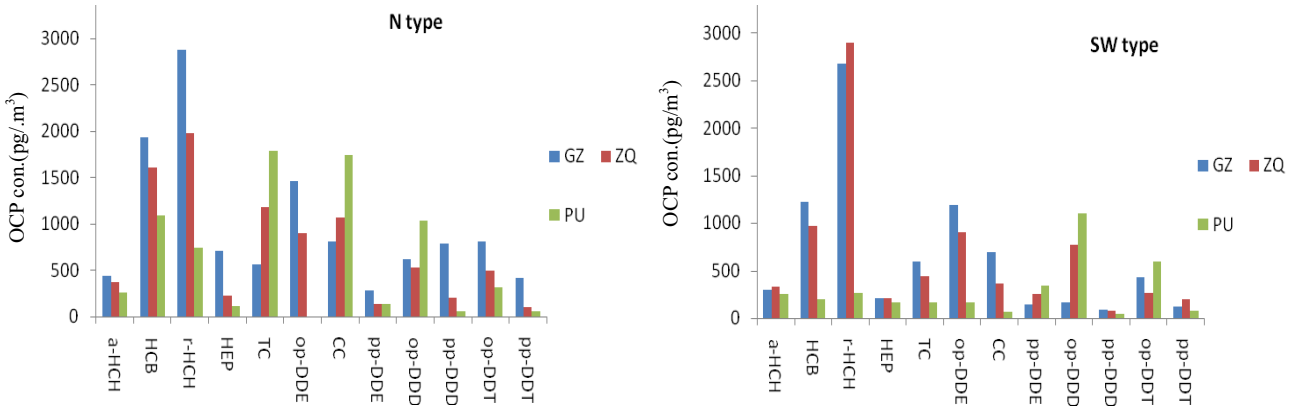


**Fig. 4.** Total concentrations of OCPs of the SW and N-type at three sites.

grouped to a special cluster. Fig. 4 showed the total concentrations of different OCPs with the same type of cluster. For N-type trajectory, γ-HCH, CHLs (Chlordanes) and HCB had higher concentrations compared with DDTs. It may indicate that significant amounts of HCH and HCB, especially HCB, may come from the northern part of China, particularly in Tianjin, where most of HCB producers were concentrated. Zheng *et al.* (2010) found that there were high levels of HCB in Tianjin. Furthermore, the slightly fluctuation of HCB indicated that long-range transport was a major source of HCB. The monsoon occurs mostly in winter and brings HCB from the northern China to the PRD region. It is consistent with the seasonal variations of HCB and ∑HCH, which had the higher concentration in winter. While the air mass was from the South China Sea (the SW type), the concentrations of OCPs were lower than that of N-type trajectories due to dilution effects by the clean monsoon from the sea.

## CONCLUSIONS

The concentrations of OCPs in the atmosphere at the PRD region were higher than those at other rural/urban regions in the world. The distribution of OCP concentrations in these three cities showed different patterns and had similar seasonal variations. The high levels of OCPs may be attributed to the seasonal usage of pesticides and/or long-range transport. Two types of air mass clusters were identified according to their directions and potential source regions. The lack of temperature dependence of OCPs especially CHLs and HCB suggested that the concentration variation may be attributed to the long-range transport of these pollutants. The low value of coefficient of correlation showed that the correlation of

OCPs and OC was low while the concentration fluctuation of OCPs was similar.

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