Organochlorine pesticides in the atmosphere of Guangzhou and Hong Kong: Regional sources and long-range atmospheric transport

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Abstract

Organochlorine pesticides (OCPs) were measured in the atmosphere over the period of December 2003–December 2004 at four sampling sites in Guangzhou and Hong Kong. Gas phase and particle phase concentrations of 8 OCP species, including *trans*-chlordane (*t*-CHL), *cis*-chlordane (*c*-CHL), *p,p'*-DDT, *p,p'*-DDE, *o,p'*-DDT, α-endosulfan, α- and γ-hexachlorocyclohexane (HCH), were studied. OCPs were found predominantly in the gas phase in all seasons. *t*-CHL, *c*-CHL, *o,p'*-DDT, *p,p'*-DDT and α-endosulfan had significantly ($p < 0.001$) higher concentrations than other OCPs, with mean values (gas + particle) typically ranging from 103 to 1440 pg m^{-3}. In general, the concentrations of OCPs in summer were higher than that in winter, except for α-HCH which showed no clear seasonal pattern. Higher levels of γ-HCH and *o,p'*-DDT found in Guangzhou could be attributed to the present usage of lindane and dicofol in the Pearl River Delta (PRD) region. The very high concentrations of *p,p'*-DDT and α-endosulfan were observed at all sampling sites. The results of 7 days air back trajectory analysis indicated that the unusual high *p,p'*-DDT levels in summer in both cities could be related to the seasonal usage of DDT containing antifouling paints for fishing ships in the upwind seaports of the region. The high concentrations of α-endosulfan in winter in the study area suggested an atmospheric transport by the winter monsoon from the East China, where endosulfan is being used as insecticide in cotton fields. The consistency of the seasonal variation of concentrations and isomeric ratios of DDTs and α-endosulfan with the alternation of winter monsoon and summer monsoon suggested that the Asian monsoon plays an important role in the long-range atmospheric transport of OCPs.

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1. Introduction

Organochlorine pesticides (OCPs) are a group of persistent organic pollutants (POPs) which are to be eliminated or reduced on their release into the environment in many countries. Because of their

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persistence in the environment, and biological accumulation through the food web, OCPs can cause environmental damage, and affect human health (Colborn et al., 1996). Due to their volatility and persistence in the air, OCPs are subjected to long-range atmospheric transport (LRAT). Therefore, OCPs released in the tropical and subtropical environments could be dispersed rapidly through air and water, and tend to be redistributed on a global scale (Tanabe, 1991; Wania and Mackay, 1996). Many recent studies showed that the atmospheric transport from these regions across the Pacific Ocean was one of the major contributing sources for OCPs in the Canadian west coast and arctic regions (Bailey et al., 2000; Harner et al., 2005). The

Asian monsoon was supposed to have been playing an important role in the long-range atmospheric transport of POPs (Tanabe, 1991; Iwata et al., 1994).

The Pearl River Delta (PRD), including Hong Kong and Macao, located in the south coast of China, and covering an area of about 42,794 km^2, is one of the rapid developing regions in China over the last three decades (Fig. 1). The region is under strong influence of the Asian monsoon system. A few investigations on OCPs in various environmental media of the PRD have been conducted recently (Wong et al., 2002; Zhang et al., 2002; Monirith et al., 2003; Luo et al., 2004). These studies not only detected higher concentrations of
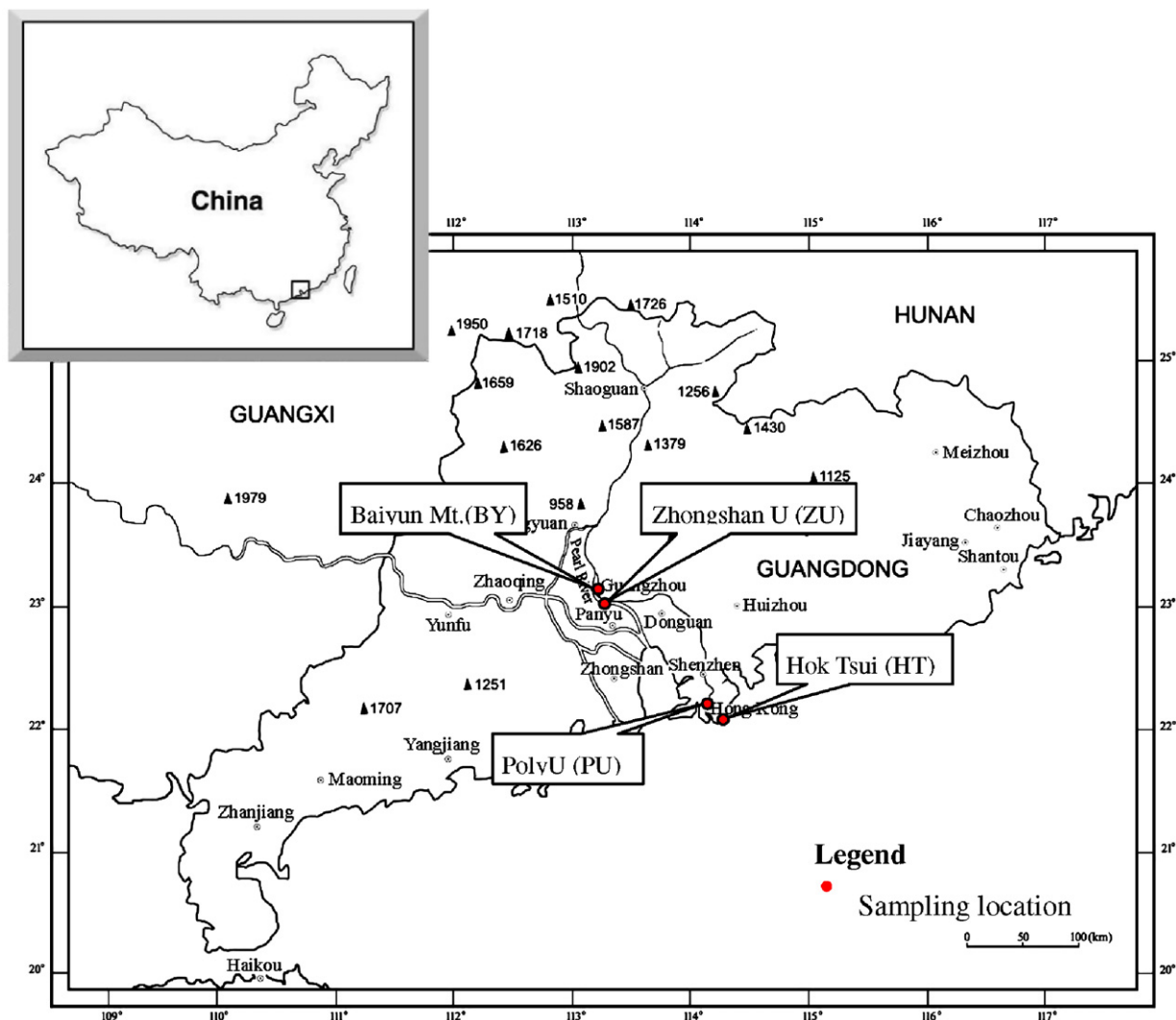

Fig. 1. Sampling locations.

HCHs and DDTs in water, sediment, fish, and human breast milk in Guangzhou, the center of the PRD, but also found a similar problem in Hong Kong where no HCHs and DDTs were presently in use. Studies on trace gases and ozone showed that the PRD was a receptor of many anthropogenic emissions from the Asian continent and Southeast Asia (Chan et al., 1998), but there were only a very limited number of reports about the behavior of atmospheric OCPs in south China (Cheng et al., 2000; Louie and Sin, 2003).

In an effort to better characterize OCPs in the air of the PRD, and to study the potential influence of the Asian monsoon on the transport of OCPs over this subtropical region, a year-round air sampling campaign was conducted in Guangzhou and Hong Kong, the two major cities in the PRD. The present work aims to study the seasonal patterns and the spatial distribution of OCPs in the air, particularly on the influences of Asian monsoon on the long-range transport of these contaminants in the low-latitude region.

2. Materials and methods

2.1. Sampling sites

The PRD has population of 38.7 millions and a land area of $42,794 \, \text{km}^2$ in 2000. Large cities, including Guangzhou, Hong Kong, Shenzhen, Fushan, Dongguang, Macao etc., form one of the most urbanized regions in South China. Public concerns arose when DDT concentrations in human breast milk in Guangzhou and Hong Kong were found to be the second highest in the world (Wong et al., 2002). To observe POPs in the region, four active atmospheric sampling stations were set up in 2003, including two urban sites, at the Hong Kong Polytechnic University, Hong Kong (PU) and Sun Yet-sen (Zhongshan) University, Guangzhou (ZU); and two suburban sites, at Hok Tsui (Cape D'Aguilar), Hong Kong (HT), and Baiyun Mountain, Guangzhou (BY).

2.2. Sampling method

Sampling was conducted concurrently at the four sampling sites for a consecutive 24 h period on a biweekly basis from December 2003 to December 2004. A total of 90 pairs of samples were collected from four sampling sites. Air volumes of $314-328 \, \text{m}^3$ were drawn through quartz microfibre filter (QFF) (Grade GF/A, $20.3 \times 25.4 \, \text{cm}$, Whatman, Maidstone, England), and subsequently through 6.5 cm in diameter $\times$ 7.5 cm in thickness (a density of $0.030 \, \text{g cm}^{-3}$) polyurethane foam (PUF) plugs using a high-volume sampler (of the Anderson type) at a flow rate of $0.217-0.228 \, \text{m}^3 \, \text{min}^{-1}$. Prior to sampling, QFFs were baked at 450 °C for 12 h to remove any organic contaminant, and PUF plugs were Soxhlet extracted for 48 h with methanol and then acetone for 24 h, followed by two overnight extractions using dichloromethane (DCM). PUF plugs were dried overnight in a vacuum desiccator and stored in solvent-rinsed glass jars with Teflon lined lids before use. During the sample collection, gloves were worn, and QFFs and PUFs were handled using acetone-rinsed stainless steel tongs. After sampling, loaded QFFs were wrapped with pre-baked aluminum foils and sealed with double layers of polyethylene bags, and PUFs were placed in solvent rinsed glass jars with Teflon lined lids, and then transported to the laboratory and stored at -20 °C until extraction. Meteorological data, such as temperature, relative humidity, wind speed/direction, and precipitation were recorded at each sampling station.

2.3. Extraction and analysis

QFFs and PUFs were spiked with 20 ng of 2,4,5,6-tetrachloro-*m*-xylene (TC*m*X) and deca-chlorobiphenyl (PCB209) as surrogates, and Soxhlet-extracted with dichloromethane (both DCM and hexane obtained from Merck & Co. Inc.) for 48 h. Activated copper granules were added to the collection flask to remove elemental sulfur. The extract was concentrated and solvent exchanged to *n*-hexane and purified on an 8 mm i.d. alumina/silica column packed, from the bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (10 cm, 3% deactivated), 50% (on a weight basis) sulfuric acid silica (10 cm), and anhydrous sodium sulfate (1 cm). Before use, neutral alumina, neutral silica gel, and anhydrous sodium sulfate were Soxhlet-extracted for 48 h with DCM, and then baked for 12 h in 250, 180, and 450 °C, respectively. The column was eluted with 50 ml of dichloromethane/hexane (1:1) to yield the OCPs fraction. The fraction was reduced to a final volume of 25 μL under a gentle stream of nitrogen and solvent exchanged to 25 μL of dodecane containing a known quantity of pentachloronitrobenzene (PCNB) as an internal standard.

GC–MS analysis was carried out on an Agilent-5975 GC-MSD system with a CP-Sil 8 CB capillary column (50 m length × 0.25 mm i.d., 0.25 µm film thickness), operating under selected ion monitoring (SIM) mode. The selected ion groups for most OCPs have been listed by Yeo et al. (2004). The oven temperature began at 60 °C for 1 min and increased to 290 °C (10 min hold time) at a rate of 4 °C min^{-1}. Split/splitless injection of a 1 µL sample was performed with a 12 min solvent delay time. Injector temperature was at 250 °C. The inlet degradation of DDT was checked daily and controlled within 15%.

2.4. QA/QC

All analytical procedures were monitored using strict quality assurance and control measures. Laboratory and field blanks consisted of PUF and QFFs were extracted and analyzed in the same way as samples. Four field blank samples (clean QFF and PUF) deployed at four sampling sites and six laboratory blanks were used. When the blank samples were analyzed, OCPs were not detected in the QFF and PUF blanks except CHLs in PUF field blank, which were detected at less than 2% of the mass in the samples, and they were appropriately subtracted from the sample concentrations.

Method detection limits (MDLs) of individual OCPs were as follows: 1.1 pg m^3 for α-HCH, 1.5 pg m^3 for γ-HCH, 1.4 pg m^{-3} for t-CHL and c-CHL, 1.8 pg m^{-3} for p,p′-DDE, 2.5 pg m^{-3} for o,p′-DDT, 3.6 pg m^{-3} for p,p′-DDT, and 3.9 pg m^{-3} for α-endosulfan. Concentrations lower than MDLs were considered non-detectable for quantified OCPs.

Before the extraction, each media was fortified with 20 ng of recovery standards TCmX and PCB209. Recoveries for TCmX and PCB209 were 75 ± 9% and 80 ± 13%, respectively. Data shown in this paper were corrected according to the recovery rates of the standards.

2.5. Back-trajectory calculation

To investigate the possible sources of OCPs, air mass backward trajectories were calculated using the HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, Version 4.7), a comprehensive modelling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (Draxler and Rolph, 2003). Because the synoptic atmospheric conditions at two locations in the same city (i.e. the PU and HT sites in Hong Kong, and the ZU and BY sites in Guangzhou) were quite similar, 7-day back trajectories ending at Hong Kong and Guangzhou at 0600 UTC, i.e. 14:00 local time for all sampling dates, were calculated. For the classification of air masses, these trajectories ended at the height of 500 m AGL (above ground level), a level of about half the height of the mean daytime planet boundary layer (PBL), to represent general transport conditions in the PBL.

3. Results and discussion

3.1. Concentrations of OCPs in air

The arithmetic mean concentrations with their standard errors, minimum and maximum values and median concentrations of the various analytes in both particle phase and gas phase in the air samples collected at four sampling sites are given in Tables 1–4, respectively. Due to the high atmospheric temperature in this subtropical area, the OCPs in this study were predominantly in gaseous phases. For α-HCH and γ-HCH, the particle-phase fraction was less than 1% in all seasons except some samples at the urban site in Guangzhou, where the fraction was less than 5% of the total. For t-CHL and c-CHL compounds, this fraction was less than 5% in the non-winter seasons and less than 15% during the winter months, except one sample attained to 32% at the urban site in Hong Kong. For α-endosulfan and the DDT compounds, the particle fraction was less than 20% in most samples; the fraction has occasionally reached as high as 75% in the winter season. Therefore, the sum of vapor phase and particulate phase was used in the data analysis, except only gas-phase in the Clausius–Clapeyron equation.

Among the analyzed compounds at the four sites, γ-HCH, t-CHL, c-CHL, o,p′-DDT, p,p′-DDT and α-endosulfan had high concentrations with the maximum values of 2640, 2030, 4190, 3380, 4530, and 2500 pg m^{-3}, respectively. α-HCH and p,p′-DDE showed similar ranges with the highest concentrations of 313 and 526 pg m^{-3}, respectively. The significantly high values of these compounds may imply the fresh inputs of those OCPs in this region. Chlordane was used as a termiticide of woods in many parts of the world, and was detected in high levels where the technical chlordane was

Table 1
Summary of air concentrations and Clausius–Clapeyron regression results of organochlorine pesticides in the urban site (PU) of Hong Kong during a 1-year period

(pg m^{-3})	Particle phase ($n = 24$)			Gas phase ($n = 24$)				
	Mean ± SD	Range	Median	Mean ± SD	Range	Median	ΔH (kJ mol^{-1})	r^2
α-HCH	nd	nd	nd	46 ± 28	5–109		ns	0.013
γ-HCH	nd	nd	nd	51 ± 64	5–261	24	ns	0.012
t-CHL	2 ± 2	nd–7	1	389 ± 381	6–1600	301	84 ± 35	0.203
c-CHL	2 ± 2	nd–7	1	380 ± 358	7–1500	316	ns	0.153
p,p′-DDE	1 ± 2	nd–8	1	54 ± 36	8–151	43	72 ± 24	0.304
p,p′-DDT	10 ± 9	nd–33	9	358 ± 719	6–2630	61	139 ± 36	0.406
o,p′-DDT	6 ± 7	nd–22	3	191 ± 188	7–673	126	88 ± 28	0.308
α-endosulfan	6 ± 7	nd–29	3	124 ± 212	nd–840	27	113 ± 51	0.207

nd, not detected; ns, not statistically significant.

Table 2
Summary of air concentrations and Clausius–Clapeyron regression results of organochlorine pesticides in the suburban site (HT) of Hong Kong during a 1-year period

(pg m^{-3})	Particle phase ($n = 24$)			Gas phase ($n = 24$)				
	Mean ± SD	Range	Median	Mean ± SD	Range	Median	ΔH (kJ mol^{-1})	r^2
α-HCH	nd	nd	nd	52 ± 26	19–112	46	ns	0.028
γ-HCH	nd	nd	nd	51 ± 116	4–579	20	ns	0.146
t-CHL	1 ± 1	nd–5	1	427 ± 563	15–2030	252	109 ± 35	0.306
c-CHL	2 ± 2	nd–8	1	406 ± 516	26–1940	225	100 ± 31	0.302
p,p′-DDE	2 ± 3	nd–12	2	195 ± 153	4–462	159	119 ± 25	0.513
p,p′-DDT	13 ± 14	nd–61	11	914 ± 1310	15–4530	387	202 ± 27	0.718
o,p′-DDT	5 ± 6	nd–23	3	229 ± 231	23–795	137	97 ± 22	0.308
α-endosulfan	3 ± 2	nd–10	2	101 ± 155	nd–528	46	ns	0.126

nd, not detected; ns, not statistically significant.

Table 3
Summary of air concentrations and Clausius–Clapeyron regression results of organochlorine pesticides in the urban site (ZU) of Guangzhou during a 1-year period

(pg m^{-3})	Particle phase ($n = 21$)			Gas phase ($n = 21$)				
	Mean ± SD	Range	Median	Mean ± SD	Range	Median	ΔH (kJ mol^{-1})	r^2
α-HCH	0 ± 1	nd–4	0	139 ± 71	41–313	126	ns	0.011
γ-HCH	4 ± 8	nd–24	0	523 ± 819	5–2640	79	149 ± 36	0.476
t-CHL	7 ± 7	nd–21	5	922 ± 424	192–1790	929	34 ± 13	0.251
c-CHL	12 ± 17	nd–75	9	1430 ± 979	191–4180	1360	ns	0.141
p,p′-DDE	11 ± 9	nd–30	7	222 ± 150	34–579	171	58 ± 16	0.442
p,p′-DDT	71 ± 84	nd–257	49	718 ± 781	22–2840	407	108 ± 21	0.578
o,p′-DDT	40 ± 48	7–172	15	912 ± 607	86–2010	881	62 ± 19	0.350
α-endosulfan	8 ± 6	nd–19	6	217 ± 302	nd–1080	64	ns	0.143

nd, not detected; ns, not statistically significant.

sprayed (Bidleman et al., 1998; Murayama et al., 2003). In China, technical chlordane is still being extensively used against termites in buildings, with an estimated amount of over 200 t year^{-1} in recent years (Xu et al., 2004). The PRD, located in the subtropics, always suffers from termites in rainy season, the high concentrations of t-CHL and c-CHL observed may be predominantly due to the

Table 4
Summary of air concentrations and Clausius–Clapeyron regression results of organochlorine pesticides in the suburban site (BY) of Guangzhou during a 1-year period

(pg m^{-3})	Particle phase ($n = 21$)			Gas phase ($n = 21$)				
	Mean ± SD	Range	Median	Mean ± SD	Range	Median	ΔH (kJ mol^{-1})	r^2
α-HCH	nd	nd	0	111 ± 69	28–272	87	ns	0.164
γ-HCH	nd	nd	0	285 ± 495	5–1630	49	83 ± 37	0.214
t-CHL	3 ± 8	nd–32	0	387 ± 279	56–1140	421	59 ± 21	0.301
c-CHL	4 ± 7	nd–28	1	674 ± 620	52–2490	504	ns	0.177
p,p′-DDE	5 ± 8	nd–30	2	145 ± 121	15–526	151	73 ± 19	0.442
p,p′-DDT	31 ± 45	nd–147	14	557 ± 900	4–2770	129	165 ± 30	0.617
o,p′-DDT	25 ± 42	nd–130	7	598 ± 748	14–3380	371	118 ± 21	0.623
α-endosulfan	11 ± 14	nd–51	6	348 ± 698	nd–2500	58	ns	0.175

nd, not detected; ns, not statistically significant.

current usage of technical chlordane as a termiticide in this area. In the past, large quantities of technical HCH and DDT had been used in China, and total of 4.9 million tons (HCH) and 0.4 million tons (DDT) were produced until the production was banned in 1983 (Hua and Shan, 1996). After that, as the substitutes, the purified γ-HCH isomer (lindane) and DDT-type pesticide (dicofol) has been produced in many factories (Qiu et al., 2004, 2005; Jaward et al., 2005). The extremely high values of γ-HCH and DDTs observed in this area were consistent with other research results, such as the high concentrations of HCHs and DDTs in water, sediment, fish, and human breast milk in the PRD (Wong et al., 2002; Zhang et al., 2002; Monirith et al., 2003; Luo et al., 2004). Endosulfan is another remaining OCPs registered in China for the control of cotton bollworm (Helicoverpa armigera) and native budworm (H. punctigera) in cotton crops, and regarded as a "soft" organochlorine because of its chemical properties, degradation rate, and metabolism in plants and animals (Gupta and Gupta, 1979). The annual production of endosulfan was about 2400 t in China. The eastern China plain is one of the major areas for cotton culture in the country, consisting of parts of the lower reaches of the Yellow River, Huaihe River, and the middle and lower reaches of the Yangtze River. No cotton is grown in the PRD. The high levels of α-endosulfan might be the outflow from the cotton production fields in eastern China.

HCHs, CHLs, o,p′-DDT, and α-endosulfan showed significant different concentrations between the two cities. The concentrations of these compounds were significantly ($p < 0.05$) higher in the air of Guangzhou than in Hong Kong. However, elevated concentrations of p,p′-DDE and p,p′-DDT at the HT site in Hong Kong were also observed. Besides this, the distribution of OCPs mean and median concentrations in Guangzhou and Hong Kong showed different patterns. For example, Guangzhou had higher t-CHL and o,p′-DDT than c-CHL and p,p′-DDT, and Hong Kong showed slightly higher c-CHL and p,p′-DDT than t-CHL and o,p′-DDT. While the concentration differences between the two cities may indicate that the agricultural areas (mostly around Guangzhou in the rural PRD) are a dominant source of most OCPs in the air of PRD, the different patterns of OCPs between the two cities may also suggest that there might be other types of emission sources coexistent in the region.

3.2. Comparison of OCPs with other countries

As shown in Table 5, atmospheric concentrations of OCPs in several places were compared with those in Guangzhou and Hong Kong. In India, which has been known as a large point source of HCHs and DDTs, the concentrations of α-HCH, γ-HCH, and p,p′-DDE were higher than that in the PRD. The comparable or higher concentrations of OCPs in the PRD than other places were observed in the current study. For example, α-HCH in the PRD showed similar levels to that in Korea and Japan. α-endosulfan in Guangzhou showed as high levels as in Seoul, where endosulfan is one of the remaining OCPs registered in Korea. The concentration of chlordane in Guangzhou and Hong Kong showed much higher value than other countries,

Table 5
Concentrations of OCPs (pg m^{-3}) in other cities

	α-HCH	γ-HCH	t-CHL	c-CHL	p,p'-DDE	p,p'-DDT	o,p'-DDT	α-Endosulfan
Taihu Lake, China[a]	74	46			212	124	767	307
July 23 to August 11, 2002 (Rural)	(21–164)	(18–96)			(55–502)	(34–394)	(80–2753)	(nd–888)
Parangipettai, India[b]	(530–27,400)	(380–8170)			(400–5790)	(60–1020)	(0–150)	
Seoul, Korea[c]	169±250	50.5±86.6	5.0±9.4	3.7±7.1	34.6±51.3	21.0±34.6		329±383
	(20.6–830)	(4.8–326)	(0.2–35.0)	(0.1–26.1)	(2.6–185)	(<1.0–121)		(89–1086)
Niigata, Japan[d]	103±67	40±22	70±89	61±76	5.3±4.2	6±7		
	(14–281)	(10–98)	(2–401)	(<1–329)	(<0.3–17.8)	(<2–25)		
Chicago, USA[e]	110±40	150±80	130±80	120±70		70±60		
Belize, Central America[f]		63±22	34±39	32±42	458±127	556±356	145±45	

[a]Qiu et al. (2004).
[b]Rajendran et al. (1999).
[c]Yeo et al. (2004).
[d]Murayama et al. (2003).
[e]Bidleman et al. (1998).
[f]Alegria et al. (2000).

although chlordane has been largely used to control termites around homes in Japan and the United States. o,p'-DDT had similar high levels to that in Taihu Lake region, China, where high concentration of o,p'-DDT was attributed to the dicofol usage (Qiu et al., 2004). Moreover, high concentrations of p,p'-DDT were detected in both Guangzhou and Hong Kong, which were higher than that in India and central America where technical DDT is still in use (Rajendran et al., 1999; Alegria et al., 2000). All of above results might indicate that there were fresh inputs of those OCPs in the PRD region.

3.3. Seasonal variation and sources

Generally, gas-phase concentrations of most OCPs in many cities of the world were higher in summer with higher ambient temperature than in winter with lower temperature (Murayama et al., 2003; Yeo et al., 2003, 2004; Gioia et al., 2005). This pattern is consistent with the theory of liquid-vapor equilibrium described by the Clausius–Clapeyron equation (Hoff et al., 1992, 1998; Bidleman et al., 1998; Cortes et al., 1998; Wania et al., 1998; Carlson and Hites, 2005):

$$\ln P = (-\Delta H/R)(1/T) + \text{constant} = m(1/T) + b, \tag{1}$$

where P is the SVOC partial pressure (Pa), ΔH is a characteristic environmental phase-transition energy of the compound (kJ mol^{-1}), R is the gas constant, and T is the average atmospheric tem-

perature (K) during the sampling period. It is suggested that a negative slope in the Clausius–Clapeyron plot indicates that gas-phase concentrations increase with increasing temperature. The slope of a line fitting to these data (m) multiplied by the negative universal gas constant ($-R$) gives a chemical's phase-transition energy (ΔH). In a dynamic environment, an increase in temperature can affect other processes that will lead to an increase or decrease in atmospheric gas-phase concentrations of pesticides, such as transfer across the air/water interface and partitioning from terrestrial surfaces. As a result, ΔH is useful to understand the environmental behavior of these compounds. The different ΔH values among the sites may reflect the different processes that control the concentrations of these compounds. While strong temperature dependence is indicative of partitioning between surfaces and the atmosphere, and can be indicative of seasonal pesticide use, a weaker dependence may be due to processes that have an opposite correlation with temperature, for example, long-range transport or the direction of local winds. This means the atmosphere transport also plays an important role in controlling the seasonal variations of OCPs in the air.

For a better insight on the controlling factors of the OCPs temporal trends, the plots of the 7-day back trajectories ending at Hong Kong and Guangzhou during the measurement period (December 2003–December 2004) are presented in Figs. 6a–b. In general, three categories of air masses can be identified during the annual cycle, (1) CI—air masses

coming from the north or northeast that originated from the continental inland areas of northern China, Mongolia, Central Asia and Siberia and reaching the South China region through the inland areas of China; (2) CT—air masses from the north or northeast that originated from continental inland areas of the northern China, reaching the South China region through the Southeast China coast; (3) SS—air masses coming from the south, southwest, or east that originated mostly from the sea, including the South China Sea, the Indian Ocean and the Pacific Ocean (Lee et al., 2007). The characteristics of the long-range transport pattern of the air masses arriving at the South China region exhibited a clear seasonal pattern throughout the annual cycle. From December 2003 to March 2004, the whole South China region was generally dominated by the air masses CI and CT, due to the Asian winter monsoon. Since early April 2004, the region had begun to be influenced by the marine air masses SS, although sometimes the continental air masses occasionally affected the study sites. At the end of the annual cycle, from mid August 2004 to December 2004, the air masses CI and CT were again dominant.

The Clausius–Clapeyron equation was applied for each gas-phase pesticide group at each sampling site in this study, and the ΔH values and the linear regression coefficient values (r^2) are given in Tables 1–4.

3.3.1. α-HCH and γ-HCH

For α-HCH, the ΔH values and the linear regression coefficient values (r^2) shown in Tables 1–4 indicates that there is no significant correlation between α-HCH concentrations and temperature. Unlike α-HCH, γ-HCH displayed significantly stronger temperature dependence ($p < 0.05$) at two sites in Guangzhou than those at two sampling sites in Hong Kong. Many studies have shown that a steep slope indicates that air concentrations are controlled by re-volatilization from surfaces, while a flatter slope indicates that advection of air is governing atmospheric concentration levels (Cortes et al., 1998; Yeo et al., 2003). The differences of slopes in this study suggested that α-HCH levels both in Hong Kong and Guangzhou and γ-HCH at Hong Kong sites may be governed primarily by transport, whereas the γ-HCH levels in Guangzhou were driven by temperature changes via evaporation from nearby terrestrial surfaces.

The similar levels of α-HCH as reported in other adjacent countries (Table 5) and no obvious peak appeared in the whole year data at the four sampling sites may imply no current usage of technical HCHs in the PRD region, and the major sources of α-HCH could be the residue of previously used technical HCHs or might be due to possible phototransformation of γ-HCH to α-HCH (Pacyna and Oehme, 1988; Barrie et al., 1992). Previous studies showed that in the areas where lindane was used or in the nearby areas, high concentrations of γ-HCH, ranging from several hundred to several thousand $pg\,m^{-3}$ can be detected (Granier and Chevreuil, 1997; Haugen et al., 1998). High concentrations of γ-HCH in the center of the PRD indicated that lindane was still used in this region. The average of the α/γ ratio observed in the air during the sampling period was 2.8 for Guangzhou and 1.6 for Hong Kong, also suggesting a current input of lindane in the study area (Fig. 2).

3.3.2. Chlordane

Gas-phase t-CHL were significantly correlated with $1/T$ ($p < 0.05$) among all sampling sites in the PRD, with relatively lower r^2 values ranging from 0.203 to 0.306, whereas gas-phase c-CHL had no correlation with $1/T$ for all sampling sites except at the suburban site in Hong Kong with also lower r^2 values of 0.302. This result indicated that the concentrations of those compounds were not strongly correlated with ambient temperature. Fig. 3 shows the seasonal variations of chlordane and the ratios of t-CHL/c-CHL. In Hong Kong, clearly seasonal patterns were observed, and the high concentration and relative uniform t-CHL/c-CHL ratios of about 1 were recorded in summer and autumn, and the opposite results were noted in winter and spring. Whereas, in Guangzhou, there was no clear seasonal variation, and the ratios of t-CHL/c-CHL varied from 0.27 to 1.44 throughout the whole year.

In the international market, technical chlordane is a mixture of over 140 different components, the most abundant of components are trans-chlordane (t-CHL, 13%), cis-chlordane (c-CHL, 11%), heptachlor (5%) and trans-nonachlor (5%), and the ratios of t-CHL/c-CHL in technical chlordane are 1.2:1.0 (Bidleman et al., 2002). In this study, the t-CHL/c-CHL ratios were 0.78 ± 0.33 and 0.95 ± 0.18 in Guangzhou and Hong Kong, respectively. These values were significantly ($p < 0.001$) different with that of technical chlordane. The lower
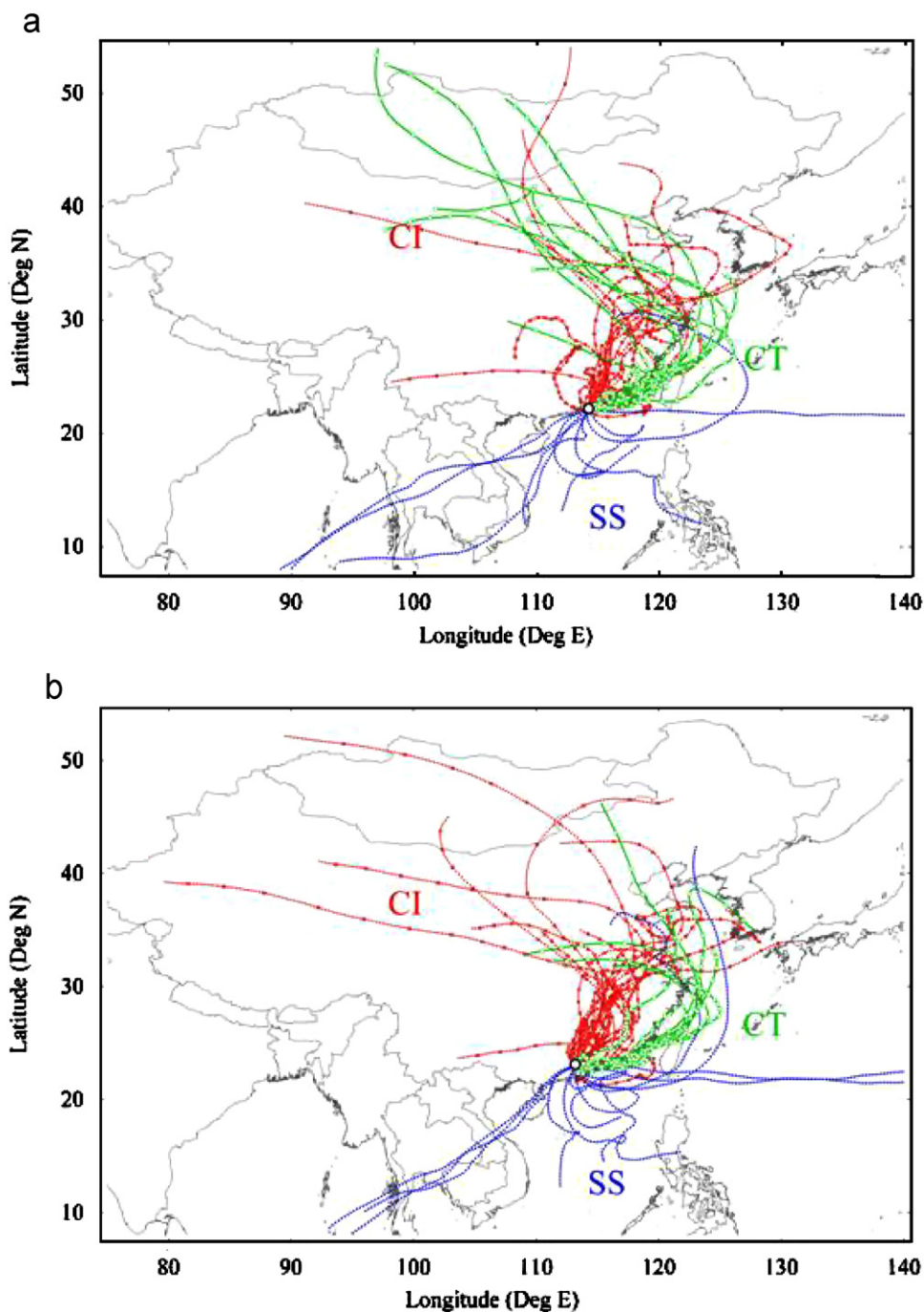
Fig. 2. The back trajectories of air masses in (a) Hong Kong and (b) Guangzhou. Air mass categories: CI—continental inland areas; CT—coastal areas; SS—marine sources.

t-CHL/c-CHL ratios in Guangzhou were similar to those in the pine needles in Beijing (Xu et al., 2004), and were likely attributed to the different values of half-life of t-CHL and c-CHL or the different compositions of t-CHL and c-CHL in the mixture of technical chlordane used in China. Fig. 4 displays the t-CHL/c-CHL ratios with the logarithm of the sum of the concentrations of t-CHL and c-CHL in
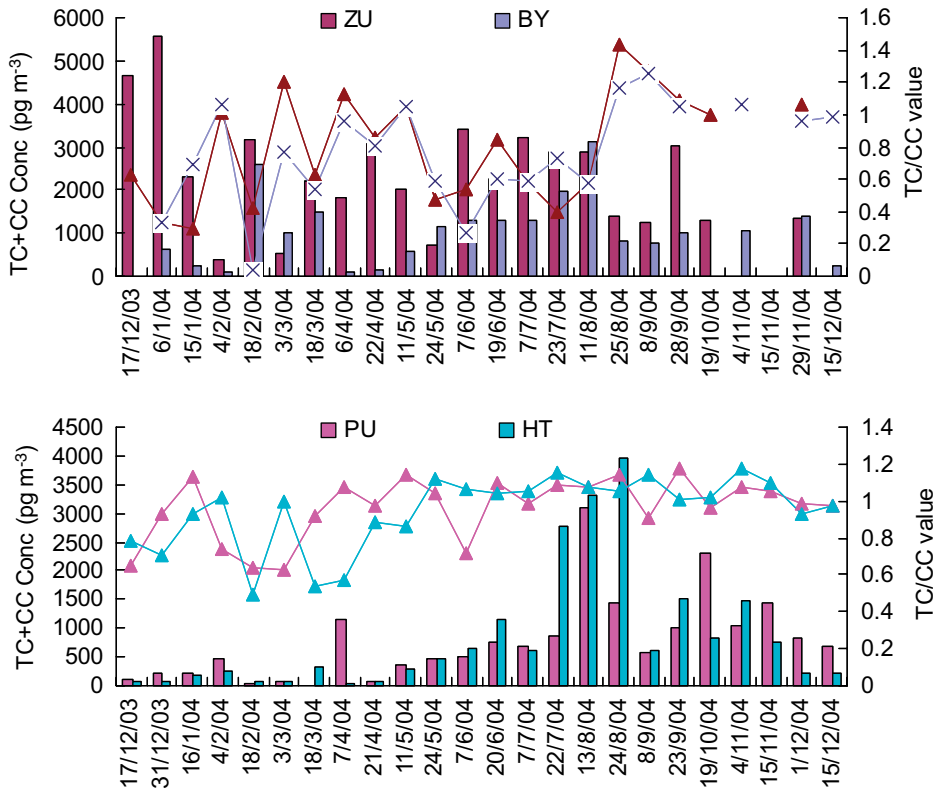
Fig. 3. Seasonal variations of chlordane concentration and ratio of *T*-CHL/CC in urban and suburban areas of Hong Kong and Guangzhou, South China.
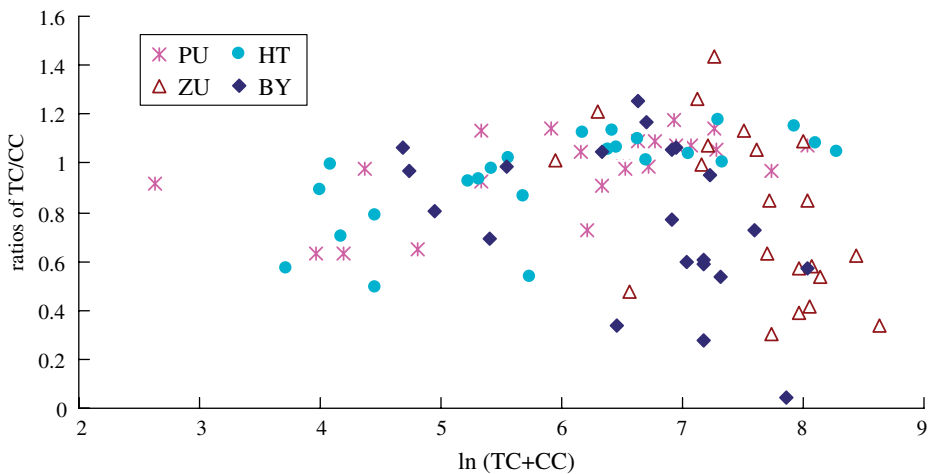

Fig. 4. The logarithm of the sum of *T*-CHL and CC concentrations correlated with the *T*-CHL/CC ratios.

the two studied cities. In Hong Kong, high values of *t*-CHL/*c*-CHL, similar to technical chlordane, accompanied with high *t*-CHL + *c*-CHL concentra-

tions were observed. In Guangzhou, the opposite was held with lower *t*-CHL/*c*-CHL ratios at higher *t*-CHL + *c*-CHL concentrations. We analyzed the

commercially available technical chlordane in Guangzhou market, and found a t-CHL/c-CHL ratio of 0.76. Compared with this ratio, there was no significant ($p = 0.383$) difference from that observed in Guangzhou (0.78 ± 0.33). However, this values was significantly ($p < 0.001$) lower than that (0.95 ± 0.18) in Hong Kong. Therefore, the different patterns of t-CHL and c-CHL at two cities might be attributed to potentially different sources of commercially available technical chlordane in Guangzhou and Hong Kong.

3.3.3. DDT isomers

Correlations between $\ln p$ vs. $1/T$ the DDTs were statistically significant at the four sampling sites ($p < 0.01$). ΔH estimated for o,p'-DDT at Guangzhou and Hong Kong were similar. Hok Tsui site (suburban of Hong Kong) had the highest value of p,p'-DDT and p,p'-DDE. Values found for ΔH of p,p'-DDT were significantly higher than those for other DDT isomers, and the linear regression coefficient values (r^2) for p,p'-DDT was also higher than other compounds. The strong relationship between temperature and gas-phase concentration and higher ΔH values in the PRD suggest significant partitioning of DDTs between air and the surface. Considering the generally higher DDTs concentrations in this region, the PRD are close to the atmospheric sources of DDT.

The ratios of DDT isomers have been used to identify the possible DDT sources. A small value of DDT/(DDE + DDD) ratio is indicative of aged (microbially degraded) DDT, and a value much greater than 1 indicates fresh application. More o,p'-DDT than p,p'-DDT in the environment can demonstrate the dicofol-type DDT usage (Qiu et al., 2004). The DDT isomer concentrations and ratios of o,p'-DDT/p,p'-DDT and p,p'-DDE/p,p'-DDT at the four monitoring sites (PU, HT, ZU and BY) over the 1-year period are plotted as a time series in Figs. 5a–d. Distinguished seasonal patterns were found in the DDT isomer concentrations at the four sampling sites. The consistence of the seasonal variation of concentrations and isomeric ratios of DDTs with the alteration of winter monsoon and summer monsoon was also observed. During the Asian winter monsoon season (from December 2003 to March 2004), relatively lower concentrations of total DDTs with more o,p'-DDT than p,p'-DDT in Guangzhou and Hong Kong were recorded. This is in consistency with the compositional characteristics of DDTs in the Taihu Lake region, as well as East

China Sea (Iwata et al., 1993; Qiu et al., 2004), suggesting the usage of dicofol in the PRD. Whereas during the summer monsoon season (from early April 2004 to mid-August 2004), especially from mid-June 2004 to mid-August 2004, the unusually high levels of p,p'-DDT were observed at all sampling sites (Fig. 2). The compositions of DDTs changed to more p,p'-DDT than o,p'-DDT, similar to that of technical DDT. This change might be due to the usage of technical DDT or/and inputs from DDT-containing products. The production and usage of technical DDT in the PRD and in Hong Kong was banned in 1983 and 1988, respectively (Wong et al., 2002). The potential sources of DDT during this season might come from DDT containing anti-fouling paints used on fishing boats in the PRD region, and DDTs transported by the Asian monsoon from other areas. Anti-fouling paints are mainly used to prevent the adhesion of sea organisms like barnacles. According to the recent investigation, the average annual production of DDT was 4519 t during 2000–2003 in China, and there was no DDT import from other countries. About 4% of total DDT production was used as the additive for the production of anti-fouling paint for fishing ships. The coastal area of Guangdong province has ca. 60,000 fishing ships, which is above 1/5 of the total number in China. It can be estimated that about 30–60 t of DDT may be introduced to the coastal environment of Guangdong, including the PRD.

In 1995, fisheries administrations suspended fishing activities during the summer months on the East China, Yellow, and Bohai Seas in order to protect marine resources. In 1999, the protected area was expanded to include the South China Sea (from 1 June 1 to 1 August). During the suspension season, many boats were in the maintenance (i.e. painting), and large quantities of DDT accompanied with anti-fouling paints usage were introduced into the environment. Moreover, with the prevailing southeasterly or southwesterly wind (Fig. 2), the PRD was suffering from those high concentrations of DDT from the upwind South China Sea where many fishing boats anchored for maintenance in seaports during this period. Several types of antifouling paints in PRD market was analyzed (unpublished data by the research group), the most remarkable one had p,p'-DDT, o,p'-DDT, and p,p'-DDE concentrations of 368, 151, and 6 μg g^{-1}, respectively. The compositions of more p,p'-DDT than o,p'-DDT in anti-fouling paint was consistent

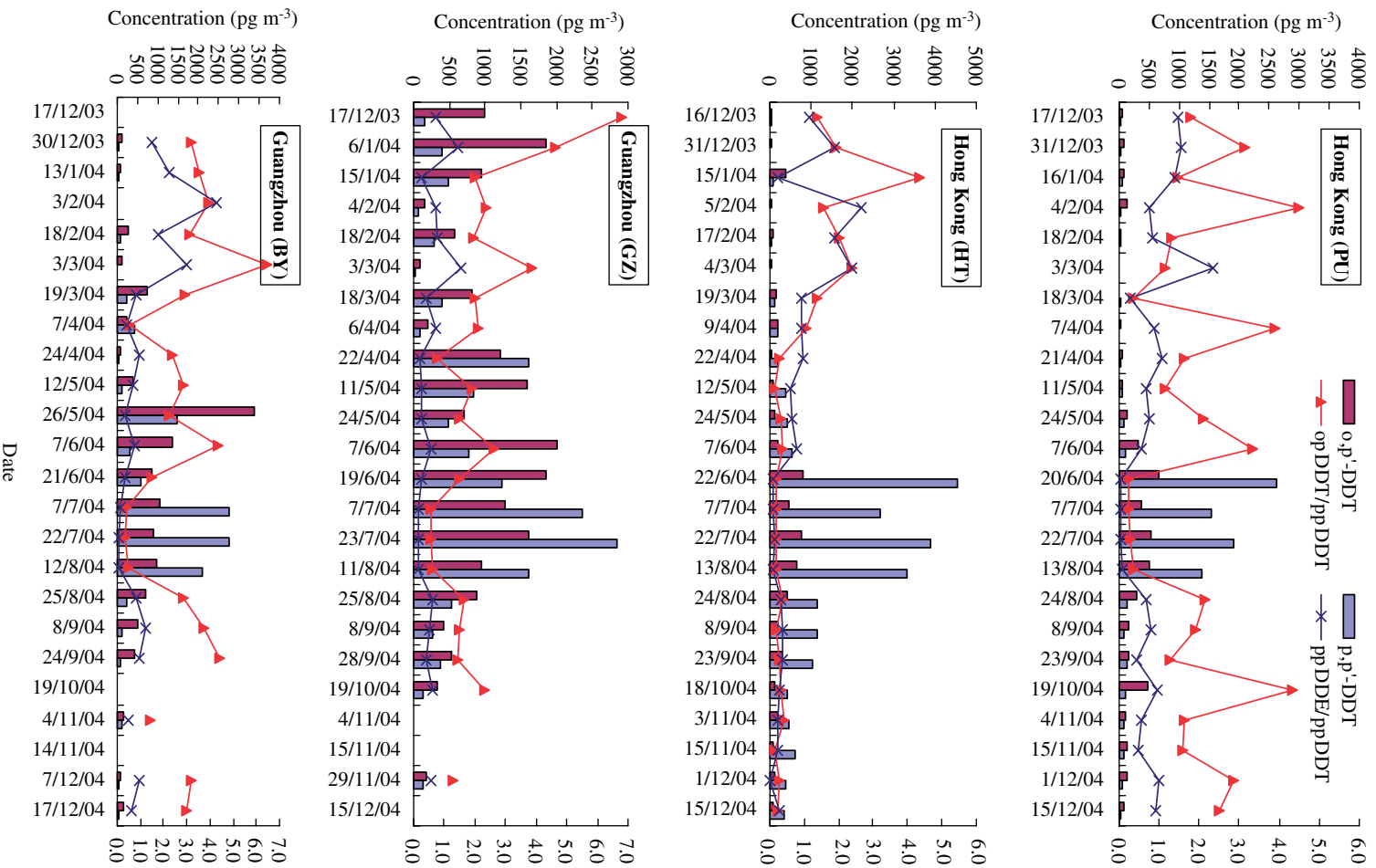Fig. 5. The DDT isomer concentrations and ratios of o,p'-DDT/p,p'-DDT and p,p'-DDE/p,p'-DDT in urban and suburban areas of Hong Kong and Guangzhou, South China.

with the fact observed in the PRD atmosphere during the summer monsoon season. From mid August 2004 to December 2004, the Asian winter monsoon were again dominant, the concentration of p,p'-DDT significantly decreased, and the compositions of DDT changed to more o,p'-DDT than p,p'-DDT characteristic among all sampling sites except at Hok Tsui (suburban of Hong Kong) site. Hok Tsui (Cape D'Aguilar) is located in the southeastern tip of Hong Kong Island (22°13′N, 114°15′E, with an elevation of 60 m above sea level). The site is in a relatively clean area of Hong Kong, situated on a cliff with 240° of ocean view stretching from northeast to southwest. The air masses passed through the east part of the South China coast before arriving at the Hok Tsui under the east-northeast (E–NE) flow in the winter monsoon season. The high concentrations of p,p'-DDT at this station might be due to the air/water exchange or pollutant flow-in from upwind position, such as Xiamen, where highest p,p'-DDT was observed by passive air sampling from September 2004 to November 2004 (Jaward et al., 2005). Further investigation is needed to verify the potential long range transport of OCPs at the sampling site.

3.3.4. α-Endosulfan

α-Endosulfan showed no significant ($p > 0.05$) or weak ($r^2 = 0.207$, $p = 0.032$) correlation with temperature at all sampling sites. The seasonal variation of α-endosulfan was different from the variation of temperature (Fig. 6), whereas, the maximum values were obtained in late August and September 2004. In general, high concentrations of α-endosulfan were observed was in the Asian winter monsoon season with predominantly northeast wind direction. The results of back-trajectory analysis showed the continental air masses passed through the cotton culture region in eastern China where endosulfan was widely used for the control of caterpillar. The coincidence of high levels in both cities might be attributed to alien source carried by the Asian winter monsoon.

4. Conclusions

Elevated concentrations of OCPs (especially γ-HCH, t-CHL, c-CHL o,p'-DDT, and p,p'-DDT) were found in the center of the PRD (Guangzhou) of the low-latitude subtropical region, showing significant local pollution. The potential sources of those pollutants might be the local usage of lindane, chlordane, dicofol and DDT containing anti-fouling paints. Distinct seasonal trends were found in OCPs concentrations in both Hong Kong and Guangzhou, with high concentrations of DDTs during the summer period, and low concentrations during the winter time, while opposite seasonal variability was observed with α-endosulfan concentrations in the PRD. The high levels of those OCPs could be attributed to the seasonal usage of pesticides and the long range atmospheric transport driven by the Asian monsoon. The very high p,p'-DDT levels in summer at both cities were probably related to the seasonal usage of DDT containing antifouling paints for fishing boats. The high concentrations of α-endosulfan in winter in the study area suggested an atmospheric transport by the winter monsoon from the East China, where endosulfan is being used as insecticide in cotton fields.
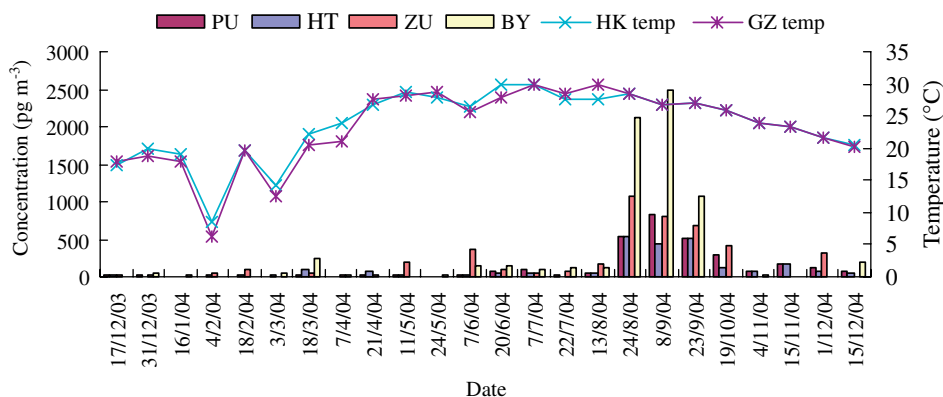

Fig. 6. α-Endosulfan concentrations and the ambient temperature in urban and suburban areas of Hong Kong and Guangzhou, South China.

Acknowledgments

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