

Atmospheric depositional fluxes and sources apportionment of organochlorine pesticides in the Pearl River Delta region, South China

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Abstract Organochlorine pesticides (OCPs) have variously been phased out in agricultural activities, but they are still widely detected in air, water, and soil systems due to their recalcitrant nature in the environment. The purposes of this study were to assess potential OCP pollution via dry and wet deposition over the fast developing Pearl River Delta area with 41,700 km², where the main effort has been focused on emerging pollutants such as petroleum hydrocarbons and PM_{2.5}. We quantified both the dry and wet deposition fluxes of 19 OCPs including dichlorodiphenyltrichloroethanes (DDTs), endosulfans (Endos), and hexachlorocyclohexanes (HCHs). The results showed that each year about 67.4, 42.0, 15.0, and 8.07 kg of total OCPs, DDTs, Endos, and HCHs were returned to the ground, among which 11.7, 10.4, 0.84, and 0.16 kg were in the dry deposition forms. The large spatial variations in OCP deposition fluxes indicated that OCP pollution in the air is mainly influenced on local scales because

evaporation from local soil is likely the major source of the phased out OCPs. Source analysis indicated that DDTs may be still in use as antifouling agent and/or dicofol, but Endos and HCHs were mainly derived from the residual of historical usage. The study suggests that the historical OCP pollutants are persistent at high levels in this area and should not be overlooked, while we tackle emerging pollutants.

Keywords Deposition flux · Pearl River Delta · DDT · Endosulfan · HCH

Introduction

Organochlorine pesticides (OCPs) had been widely used worldwide for enhancing agricultural production and for controlling vector-borne diseases before the 1980s (Shunthirasingham et al. 2010). Many OCPs including dichlorodiphenyltrichloroethanes (DDTs) have been gradually phased out due to their high bioaccumulation, toxicity, and persistence in the environment (Jones and de Voogt 1999; Nakata et al. 2002). However, these phased-out OCPs are still widely detected in air, water, and soil largely because OCPs associated with soils or dissolved in surface water are continuously evaporated to air and become highly dispersive on a large scale, resulting in secondary pollution long after they were banned for use.

Atmospheric deposition including both dry and wet deposition is responsible for returning pollutants such as OCPs from air to the ground surface, contaminating

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soil and water that may be far away from the source areas (Hippelein and McLachlan 2000). This process plays an important role in the transport and fate of pollutants on regional and global scales (Jones and de Voogt 1999). It is particularly important for the phased-out OCPs whose contamination may be overlooked, since their sources are believed to be terminated.

The purpose of this study was to quantify dry and wet deposition fluxes of OCPs for a fast developing area, where emerging pollutants such as petroleum hydrocarbons and PM_{2.5} are the major foci of environmental monitoring and research. The study area is the Pearl River Delta (PRD) located in the southern coast of China, which has undergone rapid urbanization and industrialization in the past three decades. It was estimated that the average annual application of OCPs from 1980 to 1995 reached 37.2 kg ha⁻¹, four times higher than the average annual application in China (Huang 2000). Although application of OCPs such as DDTs and hexachlorocyclohexanes (HCHs) in agriculture has presumably been banned in China since 1980s, fresh inputs of DDTs and HCHs have been identified due to continued but limited usage of lindane, dicofol, and DDT-containing antifouling paints (Qiu et al. 2005; Li et al. 2007). Heavy usage of OCPs in the PRD have resulted in the occurrence of OCPs at high levels in water (Luo et al. 2004), soil (Li et al. 2006), sediment (Zhang et al. 2003), and even human breast milk (Wong et al. 2002). Despite a long record of OCPs in different environmental compartments in this region, few data exist on atmospheric deposition, especially dry deposition fluxes of these contaminants. Previous studies concerned OCPs precipitation in two sites of Guangzhou (Huang et al. 2010), DDTs in air and precipitation of three urban sites in the PRD (Yue et al. 2011), and DDTs in particle deposition of the PRD (Li et al. 2010). Yue et al. also estimated indirectly dry depositional fluxes of DDTs in three urban sampling sites of the PRD (Yue et al. 2011). Compared to wet deposition, dry deposition is a slow pollution process and is seriously harmful to the plants.

This study focused on atmospheric bulk deposition and dry deposition of OCPs in the PRD. To better understand deposition processes that control the fate of OCPs in the PRD region, we set out a 16-month monitoring plan at ten sampling sites that belong to various environments. The passive deposition collectors were used to collect monthly bulk deposition (including wet and dry deposition) samples and dry deposition samples.

Concentrations and fluxes of 19 typical OCPs were quantified for the sampled deposition. The spatial distribution, temporal variation, and sources of these pesticides in deposition were discussed. The results may be useful for us to understand the deposition flux of OCPs in the subtropical region.

Materials and methods

Materials and preparation

The 19 OCPs targeted in this study included α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor, aldrin, heptachlor epoxide A, heptachlor epoxide B, α -endosulfan (α -Endo), dieldrin, endrin, β -endosulfan (β -Endo), methoxychlor, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT. These chemicals were purchased from AccuStandard Inc. (New Haven, CT) and used as the external standards. 4,4'-dichlorobiphenyl (PCB15) was purchased from Ultra Scientific (North Kingston, RI) and used as the surrogate standard. 2,4,5,6-tetrachloro-*m*-xylene (TCMX) and decachlorobiphenyl (PCB209) at 99 % purity were purchased from Aldrich Chemical Company (St. Louis, MO) and used as the internal standards. Silica gel and aluminum oxide were purchased from Qingdao Chemical Company (Qingdao, China). They were extracted with dichloromethane (DCM), activated at 180 and 250 °C for 12 h, respectively, inactivated with 3 % deionized water, and stored in hexane.

Sampling

A total of 137 dry deposition samples and 149 bulk (dry + wet) deposition samples were collected simultaneously and monthly between Sept. 5, 2008 and Dec. 30, 2009 at ten well-selected locations in the PRD, South China (Fig. 1). As shown in the figure, Conghua is the background site located in a forest park in the north of the PRD; Huizhou is a suburban site in the eastern PRD, far from the center of the PRD; Nansha, Zhongshan, and Zhuhai are suburban sites located along the coastal line; the remaining five sites are urban sites among which Shenzhen is also a coastal site. At each site, a dry deposition collector and a bulk deposition collector were placed on the roof of well-selected building with a height of >10 m above the ground.



Fig. 1 Sampling locations

The dry deposition collector was designed and fabricated by South China Institute of Environmental Science, Chinese Ministry of Environmental Protection. It had a flat bottom Teflon bucket with an opening of 97 cm×56 cm and a depth of 60 cm. According to our observation, the bucket was deep enough to prevent the collected particles from being blown-away by gusty wind under field conditions. A precipitation sensor was installed to control the lid of the sampler according to real-time humidity. With the sensor, the lid was automatically closed during wet precipitation, and was set open for receiving dry deposition when rain had stopped for a minute. The Teflon buckets of the collector were cleaned with distilled water and dried prior to sampling. During sampling, leaves, insects and bird manure were removed from the bucket, and dry deposition was collected by gentle sweeping with a brush and stored in glass jars. The bucket was washed three times with distilled water and set up for the next collection. The dry deposition samples were brought back to the lab, freeze-dried, weighed, and stored at -18 °C before use.

The bulk deposition collector was a glass vessel (98 cm length×68 cm width×60 cm height) settled on a 50 cm high supporter. Distilled water was added into the vessel, and 1 g NaN₃ was added to reduce the effects of biodegradation before sampling. Leaves and insects were picked out using forceps before

sample preparation, and after the samples were brought back to the lab, they were immediately filtered through glass fiber filters (GF/F, 47 mm diameter, 0.7 μm pore size; Whatman International Ltd., Maidstone, England), which were pre-combusted at 450 °C for 5 h before use. The filtered matter and filtrate were defined as the particulate and the dissolved phase, respectively.

Sample extraction and clean up

Detailed laboratory procedures given elsewhere (Silgoner et al. 1998; Le Calvez 2002; Tor et al. 2006) were generally followed for sample extraction and clean up. In brief, the surrogate standards were added to all samples prior to extraction. For each bulk deposition sample, the filtered dissolved phase was extracted on an ENVI-Disk filtration system with C18 solid phase disks (47 mm diameter, 0.5 mm thickness; Supelco, Bellefonte, PA, USA), which was then combined with the glass fiber filters with the Soxhlet particulates extracted for 72 h with dichloromethane, and the solvent mixture was exchanged to hexane and further reduced to approximately 1 mL with a gentle N₂ flow.

Each dry deposition sample was weighed and placed in an ultrasonicated Teflon tube. The ultrasonic extraction was repeated six times for each sample, each time added 10 mL of acetone–hexane (v/v=1:1) mixture, ultrasonicated at 30 °C for 5 min, the Teflon tubes

were centrifuged, and the supernatant was transferred from each tube to a pre-combusted flask. The final extract for each sample was also concentrated to approximately 1 mL.

The final concentrated hexane solution was loaded to a chromatography column (30 cm, 10 mm i.d.) filled with cotton (0.5 cm), silica gel (12 cm), aluminum oxide (6 cm), and anhydrous sodium sulfate (1 cm). The column was sequentially eluted with 15 ml of hexane to remove aliphatic hydrocarbons and 70 mL of hexane–DCM (v/v=7:3) mixture to obtain the OCP fraction. The OCP fraction was exchanged to hexane, which was concentrated to 0.2 mL under a gentle stream of N₂. Each sample was spiked with 20 ng of TCmX and PCB209 as the internal standards before analysis on a gas chromatography-mass spectrometry (GC-MS).

Quantification

GC-MS analysis was carried out on an Agilent-5975c GC-MSD system with a CP-Sil 8CB-MS capillary column (50 m length, 0.25 mm i.d., and 0.12 μm film thicknesses) operated under single ion monitoring mode. Helium was used as the carrier gas under a constant flow rate (1.2 mL min⁻¹) mode. The oven temperature began at 60 °C for 1 min, increased to 180 °C at a rate of 20 °C min⁻¹, and held for 2 min; 2 °C min⁻¹ to 200 °C and held 2 min, 4 °C min⁻¹ to 260 °C, 15 °C min⁻¹ to 305 °C and held at 305 °C for 10 min. The ion source temperature and injector were set at 250 °C split/splitless injection of a 1-μL sample and performed with a 7-min solvent delay time. The inlet degradation of DDT was checked daily and controlled within 15 %.

Field blanks that underwent through the entire field sampling procedures were used to determine potential background contamination during sampling. Laboratory blanks were used to assess potential contamination during sample preparation procedures. The two types of blanks and all samples underwent identical extraction and purification procedures. GC-MS analysis showed that the 19 target OCPs in both the field blanks and the laboratory blanks were below their respective detection limits of the method. For all the blanks and samples, the mean recovery efficiencies of the surrogate standard were 97±8 %. The final results reported here for all samples were corrected with the recovery efficiencies.

Results and discussions

OCP concentrations and fluxes

A summary description of detection frequency, range, and mean concentrations of dry deposition for 19 individual OCPs is presented in Table 1. As shown in Table 1, for all the 137 dry deposition samples, the concentrations of total OCPs (ΣOCPs) ranged from 2.2 to 1247 ng g⁻¹ with an average concentration (C_{Ave}) of 95.5 ng g⁻¹. ΣDDTs (the sum of *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT) ranged from 1.1 to 1,237 ng g⁻¹, with C_{Ave} of 87.5 ng g⁻¹. ΣEndos (the sum of α-Endo and β-Endo) were the second important classes of OCPs, and their concentrations ranged from non-detected (nd) to 39.5 ng g⁻¹ with C_{Ave} of 5.4 ng g⁻¹. The level of α-Endo (ranged from nd to 6.4 ng g⁻¹, mean of 1.7 ng g⁻¹) is statistically significantly lower ($p<0.05$) than that of β-Endo (ranged from nd to 36.7 ng g⁻¹, mean of 3.7 ng g⁻¹). ΣHCHs (the sum of α-HCH, β-HCH, γ-HCH, and δ-HCH) ranged from nd to 15.0 ng g⁻¹, with C_{Ave} of 1.2 ng g⁻¹. The concentrations of heptachlor and aldrin ranged from nd to 13.9 ng g⁻¹ and nd to 3.4 ng g⁻¹, with C_{Ave} of 0.7 ng g⁻¹ and 0.7 ng g⁻¹, respectively. Heptachlor epoxide A and B, dieldrin, endrin, and methoxychlor were not detected in any of the samples.

The fluxes of dry deposition and bulk deposition were summarized in Table 2. The deposition fluxes of individual and ΣOCPs (in nanogram per square meter per month) were computed on a basis of 30 days per month from the measured OCP mass in each sample and the area of collector. As shown in Table 2, the dry deposition fluxes of ΣOCPs ranged from 0.02 to 521(mean 50.4)ng m⁻² month⁻¹. The fluxes of ΣDDTs accounted for about 80±17 % of ΣOCPs, ranged from 0.02 to 509(45.1)ng m⁻² month⁻¹. ΣEndos fluxes accounted for about 15±13 % of the total OCPs, ranged from nd to 40.6(3.71)ng m⁻² month⁻¹. The fluxes of ΣHCHs accounted for about 4±6 % of the total OCPs, ranged from nd to 8.12(0.66)ng m⁻² month⁻¹. Heptachlor and aldrin ranged from nd to 24.8 (0.47) and nd to 7.17(0.52)ng m⁻² month⁻¹, respectively.

Compared to dry deposition, the bulk deposition fluxes of ΣOCPs were significantly higher than those in the dry deposition. As shown in Table 2, the bulk deposition ranged from 3.19 to 1,045(mean 180)ng m⁻² month⁻¹. The fluxes of ΣDDTs accounted for about 61±25 % of the total OCPs, ranged from 0.60 to 978(122)ng m⁻² month⁻¹,

Table 1 The concentrations (ng g⁻¹) of individual OCPs in dry deposition

Compounds	Range	Mean ± SD	Detection frequencies
<i>o,p'</i> -DDE	nd–6.8	0.3±0.6	64 %
<i>p,p'</i> -DDE	nd–90.1	4.5±10.4	95 %
<i>o,p'</i> -DDD	nd–11.1	0.9±1.3	87 %
<i>p,p'</i> -DDD	nd–45.8	3.3±5.1	96 %
<i>o,p'</i> -DDT	nd–129	10.5±17.6	99 %
<i>p,p'</i> -DDT	0.4–977	68.1±146.5	100 %
ΣDDTs	1.1–1237	87.5±176	
α-Endo	nd–6.4	1.7±1.5	81 %
β-Endo	nd–36.7	3.7±4.5	79 %
ΣEndos	nd–39.5	5.4±5.5	
α-HCH	nd–3.9	0.5±0.8	53 %
β-HCH	nd–6.5	0.2±0.6	36 %
γ-HCH	nd–4.6	0.3±0.5	67 %
δ-HCH	nd–13.4	0.3±1.2	27 %
ΣHCHs	nd–15	1.2±1.8	
Hept	nd–13.9	0.7±1.6	43 %
Aldrin	nd–3.4	0.7±0.6	93 %
ΣOCPs	2.2–1,247	95.5±177.2	

ND not detected, SD standard deviation

Table 2 The fluxes (ng m⁻² month⁻¹) of individual OCPs in dry deposition and bulk deposition

Compounds	Bulk deposition flux		Dry deposition flux		(%)
	Range	Mean ± SD	Range	Mean ± SD	
<i>o,p'</i> -DDE	nd–5.15	0.72±0.68	nd–1.58	0.16±0.28	22.8
<i>p,p'</i> -DDE	0.53–69.2	10.4±12.4	nd–23.9	2.28±4.29	21.9
<i>o,p'</i> -DDD	nd–31.76	2.56±3.39	nd–4.65	0.5±0.85	19.5
<i>p,p'</i> -DDD	nd–122	13.6±15.7	nd–18.3	1.83±2.95	13.4
<i>o,p'</i> -DDT	nd–155	19.4±22.3	nd–68.8	5.9±10.9	30.4
<i>p,p'</i> -DDT	nd–718	75±106	0.01–432	34.4±72.3	45.9
ΣDDTs	0.6–978	122±152	0.02–509	45.1±89.5	37.0
α-Endo	nd–93.4	15.3±17.1	nd–10.8	1.35±2.17	8.8
β-Endo	nd–319	18.9±31.3	nd–33.5	2.36±4.14	12.4
ΣEndos	nd–349	34.3±42.9	nd–40.6	3.71±5.94	10.8
α-HCH	nd–33	4.78±5.01	nd–6.61	0.36±0.87	7.5
β-HCH	nd–26.2	4.18±4.72	nd–0.79	0.08±0.14	1.8
γ-HCH	nd–30.7	5.99±6.03	nd–3.59	0.17±0.37	2.9
δ-HCH	nd–67.1	2.82±6.48	nd–1.76	0.06±0.18	2.1
ΣHCHs	0.33–96.3	17.8±16.8	nd–8.12	0.66±1.23	3.7
Hept	nd–24	2.74±4.53	nd–24.8	0.47±2.24	17.0
Aldrin	nd–13.1	3.22±2.35	nd–7.17	0.52±0.96	16.1
ΣOCPs	3.19–1,045	180±164	0.02–521	50.4±94.4	28.1

ND not detected, SD standard deviation

and it was above two times higher than in dry deposition. Σ Endos fluxes accounted for about $23 \pm 19\%$ of the total OCPs, ranged from nd to $349(34.3) \text{ ng m}^{-2} \text{ month}^{-1}$. The fluxes of Σ HCHs accounted for about $14 \pm 11\%$ of the total OCPs, ranged from 0.33 to $96.3(17.8) \text{ ng m}^{-2} \text{ month}^{-1}$. Heptachlor and aldrin ranged from nd to 24.0 (2.74) and nd to $13.1(3.22) \text{ ng m}^{-2} \text{ month}^{-1}$, respectively.

OCP deposition fluxes obtained in this study were comparably lower than those reported previously in the literatures (Wang et al. 2007; Huang et al. 2010; Li et al. 2010; Li et al. 2011; Yue et al. 2011). The bulk deposition fluxes of OCPs of our study were lower than Huang's report of wet deposition fluxes of 756, 842, and $298 \text{ ng m}^{-2} \text{ month}^{-1}$ for Σ HCHs, Σ Endos ($\alpha + \beta$) and Σ DDTs (p,p' -DDD+ p,p' -DDT) during the rainy season of 2005 in Guangzhou (Huang et al. 2010). The bulk deposition fluxes of DDTs of our study were also lower than those (67 to $917 \text{ ng m}^{-2} \text{ month}^{-1}$, with mean value of $350 \text{ ng m}^{-2} \text{ month}^{-1}$) reported for the particle deposition in 15 sites of the PRD in 2004 (Li et al. 2010). The dry deposition fluxes and total deposition fluxes of Σ DDTs obtained in this study were also comparably lower than those estimated by Yue et al. for the PRD region from October 2006 to September 2007 (Yue et al. 2011). The lowered deposition fluxes found in our study might be due to the reduction of DDT levels in the atmosphere resulting from its natural dissipation and sequestration in environmental compartments including soil.

The annual deposition of each OCP in both dry and bulk forms can be estimated for the entire study area ($41,700 \text{ km}^2$) using a patchwise approach and averaged flux values for urban (11 %), agricultural (52 %), and forest (37 %) patches (Li et al. 2010). The estimated total dry deposition of DDTs, Endos, and HCHs in the PRD region were about 10.4, 0.84, and 0.16 kg year, respectively, and the bulk (wet + dry) deposition of DDTs, Endos, and HCHs in the PRD region were about 42.0, 15.0, and 8.07 kg year, respectively. Note that our estimated annual bulk deposition of DDTs was about half of the previous study (82 kg year) conducted in 2004 (Li et al. 2010), 4 years before our study. It is apparent that such a difference between the two studies cannot be explained solely via natural reduction of DDT contamination levels. Methods of sample collection and chemical analysis and locations of sampling sites may be among the major factors causing variations in estimated pollutant deposition rates.

Geographical distribution

A striking feature of the results is that the concentrations and fluxes of the OCPs demonstrated large spatial variations. Figures 2 and 3 show the geographical distribution of deposition concentrations and fluxes of OCPs in the PRD. In general, higher concentrations and fluxes were observed in the central area of the PRD (i.e., Nansha, Shunde, and Guangzhou), and the lower ones were found in both the coastal sites (i.e., Shenzhen and Zhuhai) and remote sites (i.e., Conghua and Huizhou) of the PRD.

For the dry deposition samples (Fig. 2), the higher concentrations of Σ DDTs were found in Nansha, Shunde, and Guangzhou, with C_{Ave} of 297, 234, and 162 ng g^{-1} ; the median level concentrations of Σ DDTs were found in four sites (Zhuhai, Zhongshan, Dongguan, and Sanshui) with C_{Ave} of 58.3, 55.6, 34.0, and 22.1 ng g^{-1} , and the lower concentrations of Σ DDTs were found in the three sites located either in well-preserved area (Conghua, with C_{Ave} of 13.6 ng g^{-1}) or far from the center of the PRD (Huizhou, with C_{Ave} of 5.1 ng g^{-1}) and well-buffered coastal lines (Shenzhen, with C_{Ave} of 12.9 ng g^{-1}). Σ Endos were found with the highest concentrations of 11.5 ng g^{-1} from Guangzhou; the lower concentrations of Σ Endos were found in

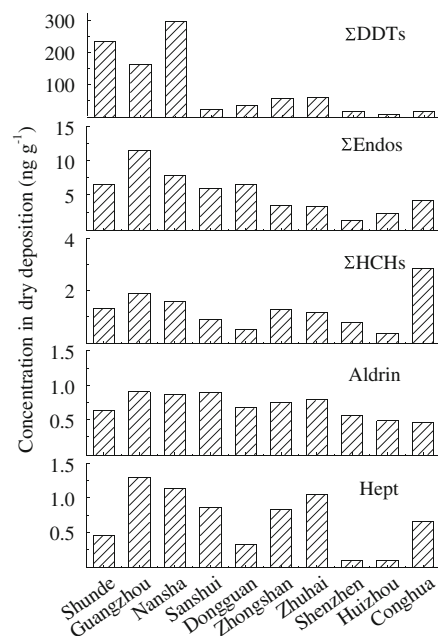


Fig. 2 Spatial variation of average concentration in dry deposition

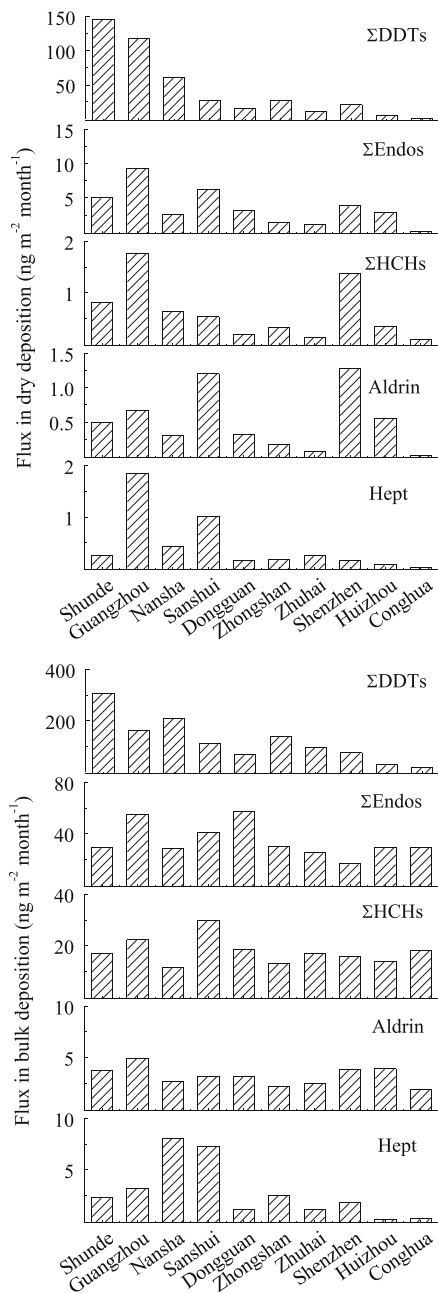


Fig. 3 Spatial variation of average flux in dry deposition and bulk deposition

Huizhou and Shenzhen with C_{Ave} of 2.2 and 1.3 $ng\ g^{-1}$, and the medium concentration group ranged from 3.3 to 7.8 $ng\ g^{-1}$ from the rest sites. The highest C_{Ave} of Σ DDTs was over 50 times greater than the lowest, and the highest C_{Ave} of Σ Endos was 9 times greater than the lowest. The concentrations of Σ HCHs, aldrin, and heptachlor were

too low to compute spatial variance in dry deposition samples.

The dry deposition fluxes of individual classes of OCP were shown in Fig. 3, where the highest fluxes of Σ DDTs were found in Shunde and Guangzhou at 146 and 118 $ng\ m^{-2}\ month^{-1}$. At all other sites, Σ DDT fluxes were under 65 $ng\ m^{-2}\ month^{-1}$, with the lowest flux in Conghua at 0.55 $ng\ m^{-2}\ month^{-1}$. The highest flux of Σ Endos was found in Guangzhou at 9.35 $ng\ m^{-2}\ month^{-1}$, followed by Shunde and Sanshui sites at 4.98 and 6.27 $ng\ m^{-2}\ month^{-1}$, respectively, and the lowest in Zhongshan, Zhuhai, and Conghua at 1.35, 1.04, and 0.14 $ng\ m^{-2}\ month^{-1}$, respectively. The highest flux of Σ DDTs was over 250 times greater than the lowest one, and the highest flux of Σ Endos was 66 times greater than the lowest one. This spatial distribution of OCP fluxes is consistent with that of the OCP concentrations in dry deposition as described above.

The bulk deposition fluxes of individual classes of OCP were shown in Fig. 3, where the highest fluxes of Σ DDTs found in Shunde, Nansha, Guangzhou, Zhongshan, and Sanshui at 307, 210, 163, 141, and 110 $ng\ m^{-2}\ month^{-1}$. At all other sites, Σ DDT fluxes were under 100 $ng\ m^{-2}\ month^{-1}$, with the lowest flux in Conghua and Huizhou at 17.3 and 27.2 $ng\ m^{-2}\ month^{-1}$. The highest flux of Σ Endos was found in Dongguan, Guangzhou, and Sanshui at 57.7, 55.4, and 40.9 $ng\ m^{-2}\ month^{-1}$. At all other sites, Σ Endos fluxes were under 30 $ng\ m^{-2}\ month^{-1}$, with the lowest flux in Shenzhen at 16.4 $ng\ m^{-2}\ month^{-1}$. The average fluxes of Σ HCHs ranged from 11.3 to 29.9 $ng\ m^{-2}\ month^{-1}$, with the highest flux in Sanshui and the lowest in Nansha. The highest flux of Σ DDTs was 18 times greater than the lowest one, and the highest flux of Σ Endos was 3.5 times greater than the lowest one.

In summary, the trend of geographical distribution of OCP fluxes in bulk deposition was similar to that found for the dry deposition, but the variations in bulk deposition were much smaller than in the dry deposition. This is likely because OCPs in both dry and bulk deposition were primarily emitted from soil and other surficial materials via evaporation. While larger spatial variation of OCP fluxes in the dry deposition may be due to the great heterogeneity of the particulate matter, the spatial variation in the bulk deposition may reflect uneven distribution of OCPs in surface soils. In fact, the spatial distribution described above is consistent with previous reports of OCP concentrations in atmosphere (Li et al. 2007; Wang et al. 2007; Yang et al.

2008; Li et al. 2011) or other environmental compartments (Chen et al. 2005; Li et al. 2006; Ma et al. 2008). The coincidence of spatial variations of OCPs in both bulk deposition and topsoil suggested that atmospheric OCPs are highly affected by local sources within this study area.

Nansha is the home of fishing boats in the Pearl River Estuary. Maintenance of fishing boats includes painting of the boats with DDT-containing antifouling paints. Inappropriate disposal of DDT containing water or materials could result in contamination in local aquatic and even atmospheric environment. The total urban area of Guangzhou of today is probably over four times greater than 30 years ago. Many of these newly developed areas were historically suburban of the old town of Guangzhou, such as the area of Guangzhou sampling site in this study. Compared to remote areas such as Conghua and Huizhou, these suburban areas were economically more advanced even 30 years ago. Farmers in the suburban could afford to use DDT for agricultural activities, whereas those in remote areas could not. Accumulatively, DDT contamination in the suburban areas is likely more severe in Guangzhou.

Sources

From the above analysis, DDTs, Endos, and HCHs are the three classes of OCPs having high depositional fluxes and possessing high risk to environmental receptors especially human beings in the PRD. Their possible sources and deposition processes are discussed below.

The ratio of DDT/ (DDD + DDE) was widely used in the literature for tracing the degree of DDT transformation and for identifying recent inputs of fresh Σ DDT (Lee et al. 2001) because DDT can be slowly biodegraded to more stable but equally toxic metabolites (DDE and DDD) (Hitch and Day 1992). If no fresh DDT was introduced, the relative percentage of DDT in Σ DDTs should gradually decrease, whereas the fraction of DDT metabolites should increase proportionally (Pereira et al. 1996; Lee et al. 2001). As a result, the DDT/ (DDD + DDE) ratio decreases as a function of time. In this study, our data showed that the ratios of DDT/ (DDD + DDE) in dry deposition and bulk deposition samples ranged from 1.9 to 31.4 and 1.0 to 8.3, with average ratios of 7.5 and 3.1, respectively, consistent with the previous studies in the PRD region (Yang et al. 2008; Huang et al. 2010). These results also implied that there were fresh inputs of DDT in the

PRD. The ratios of o,p' -DDT/ (o,p' -DDD+ o,p' -DDE) and p,p' -DDT/ (p,p' -DDD+ p,p' -DDE) were also >1, with average ratios of 3.5 and 8.4 for dry deposition and 6.5 and 2.7 for bulk deposition, respectively.

Moreover, the ratio of o,p' -/ p,p' -DDT is used widely in the literature for distinguishing whether the DDTs found in the samples were derived from technical DDT or DDT-based dicofol. Regardless of aging in the environment, a ratio of 0.2 to 0.3 indicates technical DDT, and a ratio of 7.0 ± 2.2 (mean \pm standard deviation) is related to DDT-based dicofol (Qiu et al. 2005). In our study, the average ratios of o,p' -/ p,p' -DDT in all ten sites ranged from 0.01 to 1.50 in dry deposition samples, and ranged from 0.16 to 1.10 in bulk deposition samples, with average value of 0.30 ± 0.24 and 0.36 ± 0.17 . This suggested that DDTs in deposition samples were mainly derived from the technical DDT. Since the usage of technical DDT for cropping in the PRD was banned officially in 1983 (Wong et al. 2002), the potential other usages may include DDT-based dicofol and technical DDT-containing antifouling paints used on fishing boats. The ratios of o,p' -/ p,p' -DDT in certain samples, such as those collected in Nov. and/or Dec. from Guangzhou (0.96), Sanshui (1.04), Conghua (0.95), Huizhou (0.84), and Shenzhen (1.37) and in April to Aug 2009 from Conghua, Sanshui, Shenzhen, and Huizhou were significantly higher than 0.2–0.3, suggesting that DDT-based dicofol was used in the PRD. The ratios being much smaller than 7 also indicated that the amount of DDT-based dicofol used may be proportionally smaller compared to the technical DDT.

Note that, compared to the previous studies on the PRD, our o,p' -/ p,p' -DDT ratios were far lower than those reported for precipitation (1.10–6.84) in 2005 (Huang et al. 2010). Our ratios were also lower than those (0.2–6.8) measured for the particle and gas phases in the winter, spring, and fall seasons of 2004, but were close to those of the summer season (<1) (Li et al. 2007). It is apparent that, after 3 to 4 years, the ratio of o,p' -/ p,p' -DDT observed in the atmospheric samples collected from this region has significantly decreased, suggesting that the usage of DDT-based dicofol was proportionally decreased compared to technical DDT. It is possible that DDT-based dicofol has been replaced gradually with alternative pesticides, whereas technical DDT-based antifouling paints may be used continuously.

The ratio of α -/ β -endosulfan can be used to assess the relative age of their residues in the environment. In

general, α - and β -endosulfan in technical endosulfan accounts for 70 and 30 %, respectively, and the ratio of α -/ β -Endo in technical product is about 2.33 (Rice et al. 1997). This ratio decreases since α -Endo decomposes faster (five to eight times) than β -Endo in the environment (Awasthi et al. 1997; Siddique et al. 2003; Gioia et al. 2005). In this study, the average ratio of α -/ β -endosulfan was 0.62 and 1.14 from dry deposition and bulk deposition samples, which was much lower than about 2.33, suggesting that endosulfan was aged and that there was little or no considerable fresh input of technical endosulfan in the PRD. The ratio of 0.62 was consistent with the ratios (about 0.4) reported for particulate phase of precipitation in Guangzhou (Huang et al. 2010). Previous studies proposed that the residues of endosulfan in the atmosphere of the PRD region may be mainly transported by the Asian winter monsoon from the cotton fields of Eastern China (Li et al. 2007; Huang et al. 2010). According to our data, endosulfan had large spatial variation in the PRD, and its concentrations were higher in the center of the PRD than in the surrounding areas, especially in Guangzhou (11.5 ng g⁻¹) where endosulfan concentration was eight times higher than in Shenzhen (1.3 ng g⁻¹). This uneven spatial distribution strongly indicated that local sources of endosulfan in these areas were more important than the input from large transport scale.

The ratio of α -/ γ -HCH is used for identifying the sources of HCH. In general, γ -HCH is much less stable in both aquatic and atmospheric systems due to its much faster hydrolytical and photolytical reaction rates (Liu et al. 2003). The technical HCH banned in 1983 has a α -/ γ -HCH ratio of 5.8, while lindane has γ -HCH >99 % of HCH isomers and is currently used for pest control. Therefore, a ratio of α -/ γ -HCH >5.8 indicates historical usage of technical HCH, and a lower ratio or near zero suggests recent input of lindane or from the residues of lindane and technical HCH. In this study, the average ratios of α -/ γ -HCH for the dry deposition and the bulk deposition samples were 2.81 and 0.93, respectively, indicating that the sources of HCHs could be the residual of previously used technical HCH and lindane.

Conclusions

This study reported concentrations and fluxes of 19 OCPs associated with dry deposition and bulk deposition samples collected passively from ten sites settled

in the PRD region. The results indicated that, even though the production of DDT and HCH has been banned in China since 1980s, residues of these highly resistant OCPs were still present in atmospheric deposition at relatively high concentrations. The absence of large spatial variation of atmospheric deposition OCP levels suggests that atmospheric deposition of OCPs were mainly affected by volatilized gas phase OCP concentrations in air from the local soil residuals. The annual bulk depositions of Σ DDTs, Σ Endos, and Σ HCHs in the PRD region were estimated about 42.0, 15.0, and 8.07 kg year, and they are significantly higher than those dry deposition about 10.4, 0.84, and 0.16 kg year. Source analysis indicated that DDTs may have fresh inputs due to continued uses of technical DDT-based antifouling paints. Endos and HCHs appeared to be attributed to historical usage. This study provides baseline data that are key to atmospheric pollution control, exposure assessment, and policies for safe use of OCPs in this highly populated and rapidly developing region.

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