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Particle deposition fluxes of BDE-209, PAHs, DDTs and chlordane in the Pearl River Delta, South China

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ABSTRACT

Year-round bulk air deposition samples were collected at 15 sites in the Pearl River Delta (PRD) on a bimonthly basis from Dec 2003 to Nov 2004, and the particle-phase deposition of BDE-209, PAHs, DDTs and chlordane was measured. The annual deposition fluxes of BDE-209, total PAHs (15 compounds), total DDT (sum of *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, and *o,p'*-DDT), and chlordane (sum of *trans*-chlordane and *cis*-chlordane) varied from 32.6 to 1970 $\mu\text{g m}^{-2}\text{yr}^{-1}$, 22 to 290 $\mu\text{g m}^{-2}\text{yr}^{-1}$, 0.8 to 11 $\mu\text{g m}^{-2}\text{yr}^{-1}$, and 0.25 to 1.9 $\mu\text{g m}^{-2}\text{yr}^{-1}$, respectively. Spatial variations were higher in the centre of the PRD and lower at the coastal sites for all compounds. The seasonal variations of deposition were found to be compound-dependent, influenced by a number of factors, such as the timing of source input, temperature, and precipitation etc. In particular, source input time affected the deposition fluxes of BDE-209 and high-weight PAHs, while temperature-dependent gas-particle partitioning was a key factor for DDT and light-weight PAH deposition. During the whole sampling period, the atmospheric deposition of BDE-209, ΣPAHs , ΣDDTs , and chlordane onto Hong Kong reached about 93, 86, 2.1 and 2.1 kg yr^{-1} , respectively, and onto the PRD reached about 13,400, 2950, 82, and 63 kg yr^{-1} . By comparing the calculated total air deposition with the burden in the soils, the half residual time of BDE-209 in soils was estimated to be 3 years.

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1. Introduction

Persistent organic pollutants (POPs) are chemical substances that persist in the environment, can be bioaccumulated through the food web, and may pose a risk of causing adverse effects to human health and ecosystems. Due to their semi-volatility and persistence, POPs are subjected to long-range transport through the atmosphere and ocean (Jones and de Voogt, 1999). Therefore, POPs released in the tropical and subtropical environments could be dispersed rapidly through air and water, and tend to be redistributed at a global scale (Tanabe, 1991; Wania and Mackay, 1996). The international community has now called for urgent global actions to reduce and eliminate releases of these chemicals.

The rapid socio-economic development during the past three decades in China produced a number of large scale industrial areas and mega-cities. Such areas can act as a source of POPs, such as polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs), and concern has been raised regarding their potential health effects. As one of the most prosperous economic regions in China, the Pearl River Delta (PRD) in south China has relatively high levels of

POPs pollution (Chan and Yao, 2008; Fu et al., 2003). In the last decade, the PRD has become an important region for POPs research in China. Previous studies illustrated the high PAH levels in the air and sediment originated from bio-fuel combustion and vehicle emission (Li et al., 2006a; Mai et al., 2003), the fresh input of DDT from dicofol and anti-fouling paint (Li et al., 2007, 2006b; Wang et al., 2007), and abnormally high levels of PBDEs in the atmosphere and sediments from widespread and large scale electronics, plastics and furniture manufacturers, and as well as from the processes of uncontrolled electronic-waste recycling (Chen et al., 2006; Li et al., 2009b; Mai et al., 2005; Wong et al., 2007). As a whole, BDE-209, DDT, chlordane, and PAHs were the most abundant POPs in the air, sediments, wild fishes and human breast milk of the PRD region (Bi et al., 2006; Chen et al., 2006; Fu et al., 2003; Mai et al., 2005). Atmospheric deposition plays an important role in the transport and fate of POPs on regional and global scales (Jones and de Voogt, 1999; Wania et al., 1998). Until now, there are relatively few studies to describe the deposition characteristics of OCPs, PAHs, and PCDD/F in this study area (Li et al., 2009a; Ren et al., 2007; Wong et al., 2004). In order to understand the regional transport and environmental fate of these pollutants, large scale investigation of POPs deposition date is needed (Lang et al., 2007).

In the present study, a year-round bulk (wet plus dry) deposition sampling campaign in urban, suburban, mountain and coastal sites was conducted in the PRD from Dec 2003 to Nov 2004. The spatial and temporal variations of particle deposition fluxes and the potential

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influences of the subtropical climate on the fate of POPs were investigated in the current study.

2. Materials and methods

2.1. Field site and sampling

Bulk deposition samples were collected at 15 locations across the PRD region (Fig. 1). Detailed site information is listed in Table 1. Deposition samples were collected from Dec 2003 to Nov 2004. The sampling program was conducted in six consecutive phases at every two calendar months. Bulk particle deposition (wet and dry) collection was achieved using a stainless steel funnel with a receiving area of 0.049 m², attached to a filter holder in a blinded screen house (for preventing sunlight, see Fig. 2). The bulk deposition samples were filtered *in situ* through pre-combusted (4 h at 450 °C) 90 mm diameter glass microfibre filters (GFF) (Whatman Type GF/F, nominal pore size 0.7 µm). Prior to the first sampling, the inner surface of the stainless steel funnel was washed with distilled water and wiped with pre-cleaned cotton wool. After sampling, the inner surfaces of the stainless steel funnels were wiped with pre-cleaned cotton. The soiled cotton and filter were combined together as particle deposition fluxes during the sampling period. A total of 90 samples were collected at the 15 monitoring stations across the PRD region.

2.2. Extraction and analysis

Deuterated PAHs, 2,4,5,6-tetrachloro-*m*-xylene (TCmX), deca-chlorobiphenyl (PCB209), ¹³C₁₂-PCB138 and ¹³C₁₂-PCB180 were added to each of the samples prior to extraction. Activated copper granules were added to the collection flask to remove elemental sulfur. All deposition samples were Soxhlet-extracted with dichloromethane (DCM) for 40 h. The extract was concentrated and solvent exchanged to hexane. A portion (20%) of each sample was eluted on an 8 mm i.d. column with 1 g neutral alumina, 2 g of silica gel, and 1 g

Table 1
Sampling locations for atmospheric deposition in the Pearl River Delta (PRD).

Sample ID	Location	Elevation (m)	Longitude	Latitude
HH	Northeastern Hong Kong	40	114.19	22.54
TM	Tai Mo Shan, New Territories, Hong Kong	900	114.04	22.44
TO	Northwestern Hong Kong	120	113.84	22.24
HT	Cape D'Aguilar, Hong Kong	60	114.24	22.24
PU	Hong Kong Polytechnic University, Hong Kong	30	114.17	22.34
WT	Wu Tong Mountain	680	114.26	22.61
YM	Coast of DaYa Bay, Shenzhen	20	114.60	22.62
ZS	Southeastern Zhongshan	530	113.44	22.44
JM	Western margin of Pearl River Delta	280	112.91	22.69
QY	Northern suburban Qingyuan	609	113.12	23.79
SD	Countryside in Shunde City	10	113.08	22.84
NH	Countryside in Naihai City	10	112.96	23.00
GZ3	Northern urban Guangzhou	384	113.24	23.12
GZ2	Northeastern urban Guangzhou	110	113.35	23.15
GZ1	Zhongshan University, Centre urban Guangzhou	110	113.35	23.1

of sodium sulphate (all baked at 450 °C overnight). The solution was reduced to about 200 µL under a gentle stream of nitrogen. Internal standard hexamethylbenzene was added prior to the GC–MS analysis. The rest of each sample was eluted on an 8 mm i.d. column with 1 g neutral alumina, 2 g of silica gel, 4 g of 50% sulfuric acid silica gel, and 1 g of sodium sulphate. The solution was reduced and solvent exchanged to 25 µL of dodecane containing PCB-54 and BDE-77 as internal standard for OCPs and BDE-209, respectively.

The samples were analyzed by gas chromatography–mass spectrometry (GC–MS) with an EI⁺ source operating in selected ion mode (SIM) for PAHs and OCPs. PAHs were separated on a 30 m × 0.25 mm i.d. HP-5 capillary column (film thickness 0.25 µm). OCP analysis was carried out with a CP-Sil 8 CB capillary column (50 m length × 0.25 mm i.d., 0.17 µm film thickness). Split/splitless injection of a 1 µL sample was

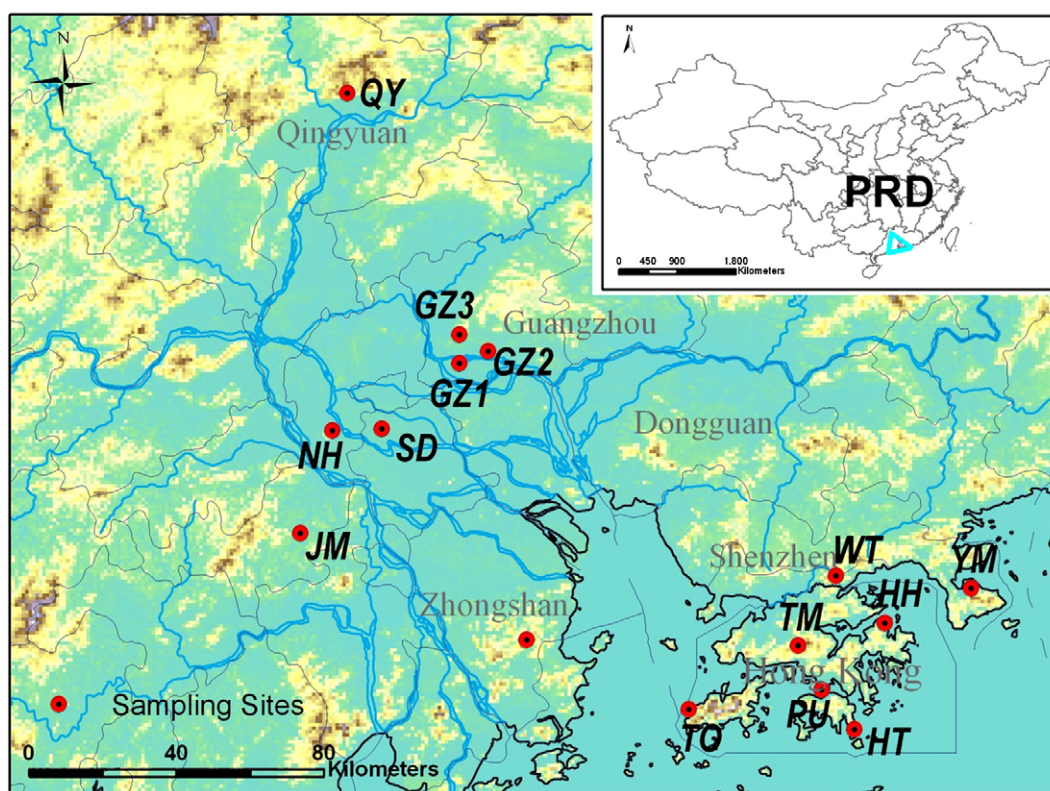


Fig. 1. Sampling locations for atmospheric deposition in the Pearl River Delta (PRD), south China.

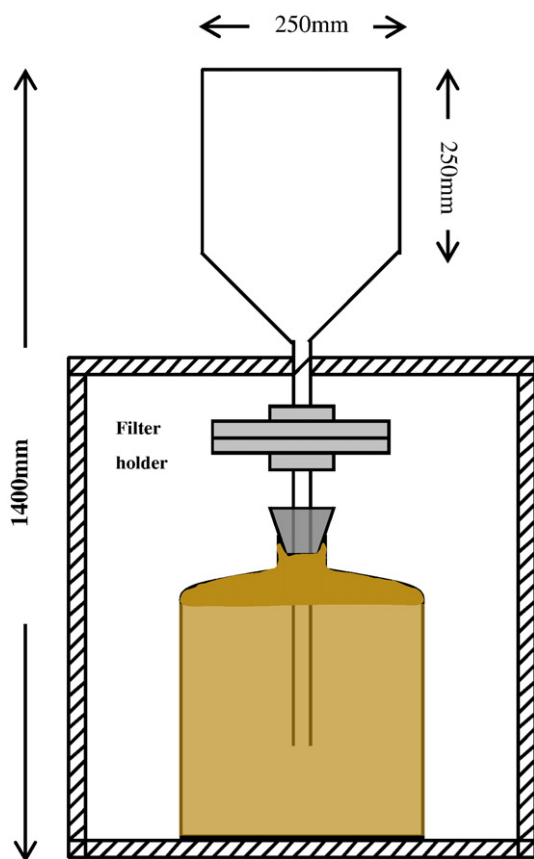


Fig. 2. Atmospheric deposition sampler used in this study.

performed with a 5 min solvent delay time. Injector temperature was at 250 °C. The inlet degradation of DDT was checked daily and controlled within 15%. Fifteen PAHs (acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (DbahA), and benzo[g,h,i]perylene (BghiP)) and six OCPs (*o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, *trans*-chlordane (TC) and *cis*-chlordane (CC)) were quantified in the deposition samples.

BDE-209 analysis was performed with a Shimadzu model 2010 gas chromatograph (GC) coupled with a model QP2010 mass spectrometer (MS) (Shimadzu, Japan) using negative chemical ionization (NCI) under SIM mode. A CP-Sil 13 CB (12.5 m × 0.25 mm i.d., 0.2 μm film thickness) capillary column was used. The oven temperature was programmed from 110 to 300 °C at a rate of 8 °C/min (held for 20 min) and the high-pressure splitless injection mode was used with a split time of 1 min. The limit of detection (LOD), defined as a signal of 3 times the noise level, for BDE-209 was 1.80 ng.

2.3. Quality control/quality assurance (QA/QC)

All chemical standards were purchased from Accustandard Co., U.S.A. All analytical procedures were monitored using strict quality assurance and control measures. Laboratory and field blanks (*i.e.*, filters and jars sent to/from field sites unopened) were extracted and analyzed in the same way as the samples. Analytical blanks consisted of at least six field and six laboratory blanks. There was no significant difference (*t* test significance <95%) between analyte concentrations in the laboratory and field blanks, indicating that contamination was negligible during the transport, storage, and analysis of the samples. Method detection limits (MDLs) were derived from the blanks, and quantified as three times the standard deviation of the mean blank

concentrations. In addition, peaks were only integrated when the signal-to-noise ratio was ≥ 3 ; otherwise, they were considered non-detectable (n.d.). The percentage of reference standard recoveries ranged from 55% to 107% for all samples. Reported values were corrected for the recovery rates and blanks.

3. Results and discussion

3.1. Introductory remarks on the data set

There might be some drawbacks using the stainless steel funnel as the sampling device for particle deposition. For example, the atmospheric deposition fluxes of vapor-phase POPs might be overestimated due to adsorption on the sampler's surface, whereas the particle-phase POPs might be underestimated during the dry seasons when particles stuck on the surface might be blown off by wind. Besides this, the 2-month sampling period of the particle deposition could be detrimental for some POPs as losses could occur due to volatilization, photodegradation or biological transformation. The loss might be reflected by the difference of BeP/BaP ratios between deposition and aerosol samples since BaP was easily decomposed by light and oxidants. The mean BeP/BaP value (1.87 ± 0.45) in deposition samples was higher than that in aerosol samples (1.02 ± 0.20) in a previous study (Li et al., 2006a). The observed values in the present study were presented without adjustments for the potential sampling bias.

3.2. General character of annual deposition fluxes

Annual particle deposition fluxes of the analytes were calculated, and the summary data are presented in Table 2 and Fig. 3. The results showed that the atmospheric deposition of BDE-209 was highest for all compounds analyzed in this study, ranging from $32.6 \mu\text{g m}^{-2}\text{yr}^{-1}$ at HT to $1970 \mu\text{g m}^{-2}\text{yr}^{-1}$ at SD with a geometric mean of $270 \mu\text{g m}^{-2}\text{yr}^{-1}$. The atmospheric bulk deposition fluxes of BDE-209 have been reported in some recent studies, from 3.0 to $550 \mu\text{g m}^{-2}\text{yr}^{-1}$ in Kyoto, Japan (Hayakawa et al., 2004), from 17 to $48 \mu\text{g m}^{-2}\text{yr}^{-1}$ in the coastal locations of Korea (Moon et al., 2007). The median deposition fluxes of BDE-209 in Sweden during 2001–2002 were $23.3 \mu\text{g m}^{-2}\text{yr}^{-1}$ near municipal solid waste incinerators, and were $5.4 \mu\text{g m}^{-2}\text{yr}^{-1}$ at an industrial and urban reference site (ter Schure et al., 2004). Average

Table 2

Summary of the annual atmospheric deposition ($\mu\text{g m}^{-2}\text{yr}^{-1}$) of selected POPs.

	Geometric mean	Average \pm std	Median	Range
BDE-209	270	610 ± 710	220	33–1970
Σ_{15} PAHs	100	140 ± 89	100	22–290
Acy	2.3	4.1 ± 6.0	2.2	0.22–2.5
Ace	0.70	0.82 ± 0.49	0.73	0.29–2.0
Flu	5.0	5.8 ± 3.0	5.9	1.7–12
Phe	36	82 ± 45	46	10–83
Ant	2.1	2.6 ± 1.5	2.0	0.56–5.2
Flua	14	20 ± 14	15	3.5–42
Pyr	7.0	11 ± 8.8	7.2	1.1–27
BaA	2.6	3.7 ± 2.7	2.6	0.59–7.7
Chr	6.4	10 ± 8.8	6.7	0.96–27
BbF	6.5	10 ± 8.9	7.6	1.1–30
BkF	2.9	4.1 ± 3.0	2.4	0.47–9.0
BaP	2.4	3.5 ± 2.8	2.7	0.37–9.3
Ind	4.7	6.8 ± 5.4	5.2	0.74–18
DbahA	1.1	1.6 ± 1.3	1.4	0.23–4.1
BghiP	4.5	6.5 ± 5.0	5.4	0.64–16
Σ DDTs	3.0	4.2 ± 3.8	3.0	0.80–11
<i>o,p'</i> -DDT	0.75	1.2 ± 1.2	0.69	0.23–3.6
<i>p,p'</i> -DDT	1.7	2.5 ± 2.2	1.6	0.38–6.2
<i>p,p'</i> -DDE	0.16	0.30 ± 0.24	0.26	<0.01–0.66
<i>p,p'</i> -DDD	0.28	0.43 ± 0.36	0.33	0.03–1.0
TC	0.96	1.1 ± 0.55	1.1	0.25–1.9
CC	0.96	1.1 ± 0.45	1.1	0.31–1.7

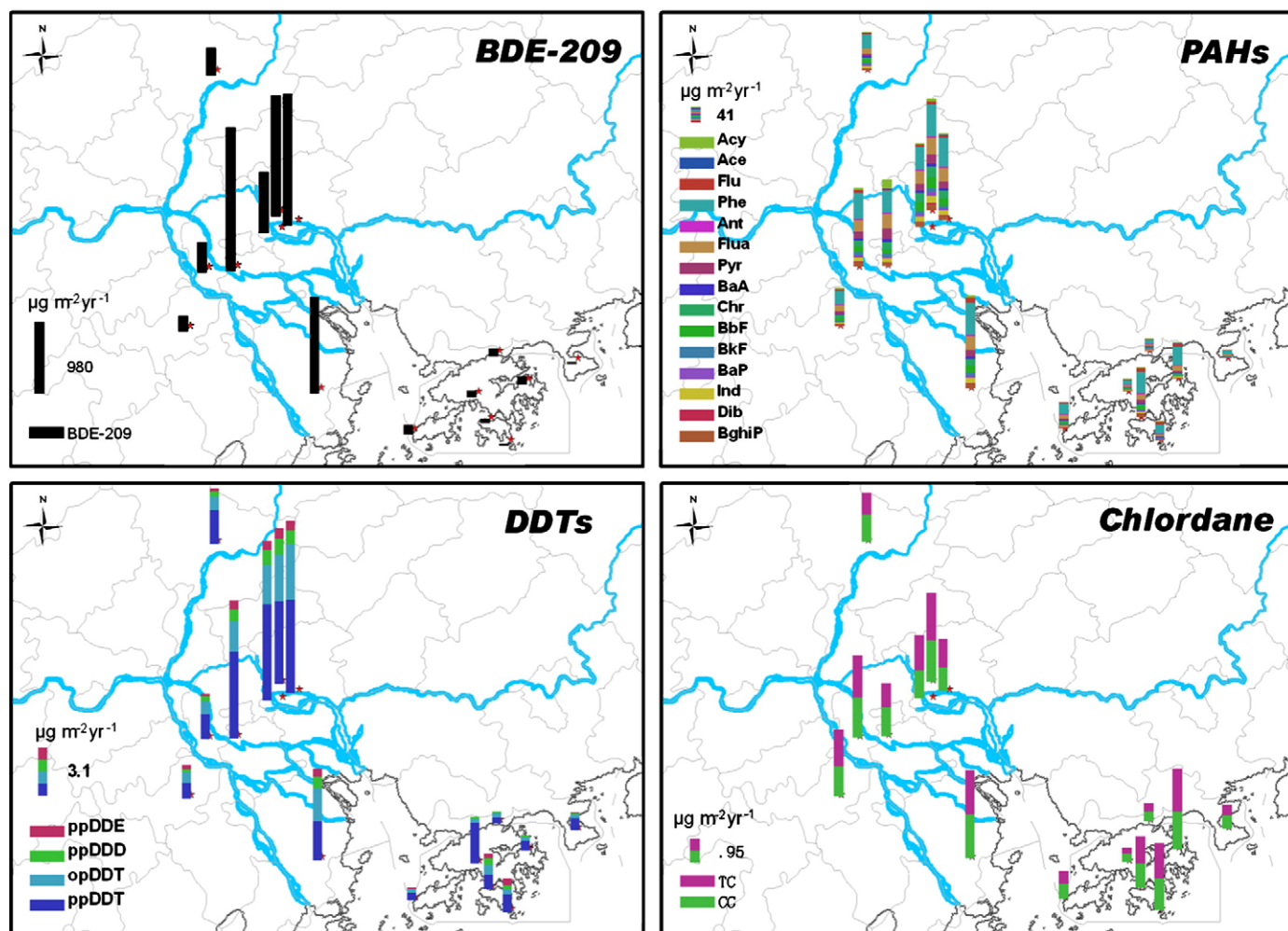


Fig. 3. Spatial trends of the annual deposition fluxes of BDE-209, PAHs, DDT, TC and CC in the Pearl River Delta (PRD).

particle-phase dry deposition fluxes of Σ_7 PBDEs (including BDE-209) for suburban and urban sites in Izmir, Turkey, were 24.7 and $47.0 \mu\text{g m}^{-2}\text{yr}^{-1}$, respectively (Cetin and Odabasi, 2007). Compared with these data, the centre of the PRD exhibited the highest deposition fluxes, while some coastal sites in the PRD were comparable to those reported values in the world.

Total PAH deposition fluxes ranged from $22 \mu\text{g m}^{-2}\text{yr}^{-1}$ at YM to $290 \mu\text{g m}^{-2}\text{yr}^{-1}$ at GZ3 with a geometric mean of $103 \mu\text{g m}^{-2}\text{yr}^{-1}$. Similar to the deposition profile reported by others (Halsall et al., 1997; Ollivon et al., 2002), the deposition profiles were dominated by Phe (35.9%), Flua (14.1%), Pyr (7.0%), BbF (6.7%), and Chr (6.6%) on an annual basis. These deposition fluxes in Guangzhou were slightly lower than the reported values at another site in Guangzhou during April 2001 to March 2002 (mean of $460 \mu\text{g m}^{-2}\text{yr}^{-1}$) (Li et al., 2009a). The deposition fluxes of BaP, which has the highest potential carcinogenicity and deposits mainly via wet and dry particles due to its particle-bound property, were chosen for comparison. In this study, the geometric mean of BaP were $2.4 \mu\text{g m}^{-2}\text{yr}^{-1}$, with a range of 0.37 to $9.3 \mu\text{g m}^{-2}\text{yr}^{-1}$. The results were similar to those reported in the Great Lakes region, from 2.6 to $9.4 \mu\text{g m}^{-2}\text{yr}^{-1}$ during 1988 to 1994 (Hoff et al., 1996), and were also comparable to that in the centre of Paris with a mean value $9.0 \mu\text{g m}^{-2}\text{yr}^{-1}$ (Ollivon et al., 2002). The current data in the PRD was significantly lower than that in Tianjin, China, which had a range of 1.46 to $400 \mu\text{g m}^{-2}\text{yr}^{-1}$ with the median value of $43 \mu\text{g m}^{-2}\text{yr}^{-1}$ (Wu et al., 2005).

The annual deposition fluxes of Σ DDT (sum of p,p' -DDD, p,p' -DDE, o,p' -DDT and p,p' -DDT) ranged from 0.80 to $11 \mu\text{g m}^{-2}\text{yr}^{-1}$ with a

geometric mean of $3.0 \mu\text{g m}^{-2}\text{yr}^{-1}$, and p,p' -DDT (56.8%) was the highest among all DDT compounds. Compared with the reference data, the values in the coastal region of the PRD (including the sampling sites in Hong Kong, see Fig. 3) were comparable to the Great Lakes (Hoff et al., 1996), Jersey City ($1.2 \mu\text{g m}^{-2}\text{yr}^{-1}$) and Corpus Christi Bay, Texas ($1.93 \mu\text{g m}^{-2}\text{yr}^{-1}$) of the U.S. (the data included dissolved phase) (Gioia et al., 2005; Park et al., 2002). However, in the centre of the PRD, the DDT deposition fluxes were much higher than those reported in the literatures (Gioia et al., 2005; Hoff et al., 1996; Park et al., 2001, 2002; Teil et al., 2004).

Bulk particle deposition fluxes of TC ranged from 0.25 to $1.9 \mu\text{g m}^{-2}\text{yr}^{-1}$ with a geometric mean of $0.96 \mu\text{g m}^{-2}\text{yr}^{-1}$, and CC ranged from 0.31 to $1.7 \mu\text{g m}^{-2}\text{yr}^{-1}$ with a geometric mean of $0.96 \mu\text{g m}^{-2}\text{yr}^{-1}$. The values in the PRD were comparable to those in the US Mid-Atlantic region (Gioia et al., 2005), and higher than in parts of the Great lakes region (Hoff et al., 1996).

3.3. Geographical distribution of deposition fluxes

The geographical distribution of annual deposition fluxes is shown in Fig. 3. Generally, higher fluxes were observed in the centre area of the PRD (Guangzhou and surrounding sites), and lower fluxes were located in the coastal sites. Due to the different physicochemical properties and predominant source areas, varied spatial trends of individual compounds were observed. BDE-209 showed the strongest spatial variation from the centre to the coastal sites. The deposition fluxes at all sites could clearly be divided into three groups: the highest concentrations

occurred in the three sites in Guangzhou (GZ1, GZ2 and GZ3), and other two sites (SD and ZS) in Shunde and Zhongshan cities, with the concentrations ranging from 830 to 1970 $\mu\text{g m}^{-2}\text{yr}^{-1}$; the middle concentration group was composed of two margin sites (QY and JM) and one countryside site (NH) with the concentrations ranging from 220 to 390 $\mu\text{g m}^{-2}\text{yr}^{-1}$; the lowest concentration group consisted of seven coastal sites with the concentration ranging from 33 to 130 $\mu\text{g m}^{-2}\text{yr}^{-1}$. In the PRD, BDE-209 was the predominant congener of PBDEs, and was likely originated from uncontrolled e-waste recycling, and numerous textile, plastics, and electronics manufacturing operations (Mai et al., 2005). The spatial distributions of PBDEs in sediments and soils indicated that the centre of the PRD, including Guangzhou, Dongguan, and Shenzhen, was the predominant source area (Mai et al., 2005; Zou et al., 2007). In addition, ZS site is within the downwind area of the atmospheric outflow from Dongguan region during the winter monsoon season. Therefore, the high concentrations observed in the centre of the PRD were not unexpected. This spatial distribution pattern suggested that atmospheric deposition played an important role in transferring BDE-209 from air to soils and sediments.

Previous studies indicated that PAHs in the PRD region were predominantly originated from vehicle emission and coal combustion (Li et al., 2006a; Mai et al., 2003). The environmental levels of PAHs were usually linked to anthropogenic activities. The distribution pattern of particle deposition fluxes was similar to that obtained by SPMDs and pine needles (Liu et al., 2006). Levels were higher in the centre, and lower in the edge of the PRD, demonstrating the extent of human activities on these chemicals in this region. In addition, the downtown of Hong Kong (PU) was shown to be another source area for PAHs, probably due the heavy traffic near the sampling site.

Large quantities of technical DDT were used in agriculture in China, and a total of 0.4 million tons had been produced until the production ban in 1983 (Zhang et al., 2002). However, a number of recent studies found that high levels of DDT in the PRD environment could be attributed to the usage of dicofol, DDT containing anti-fouling paints for fishing ships, and even the illegal usage of technical DDT (Li et al., 2007, 2006b; Wang et al., 2007; Zhang et al., 2002). The spatial distribution of ΣDDT deposition fluxes was similar to that monitored by PUF passive samplers, in which the highest ΣDDT concentrations were found in the centre of the PRD, and lower levels were detected in Hong Kong (Wang et al., 2007). It is interesting to note that the higher ΣDDT concentrations in both deposition samples and PUF passive samples were observed at HT and TM (Wang et al., 2007). The spatial distribution inferred that both the industrial centre of the PRD and coastal harbours may be the two major source areas for DDTs in the region (Lin et al., 2009).

Technical chlordane was used mostly as an agricultural pesticide on corn and citrus, for home lawns and gardens, as well as a termiticide in house foundation. Previous studies revealed that chlordane was widespread in the PRD environment (Li et al., 2007, 2006b; Wang et al., 2007). In this study, similar deposition fluxes of chlordane were found in most parts of the PRD, and this spatial distribution was consistent with those of previous atmosphere and soil chlordane studies in this region (Li et al., 2007, 2006b; Wang et al., 2007).

3.4. Seasonal variation and controlling factors

In order to examine potential seasonal variations, the six sampling batches were regrouped according to the meteorological parameters. The weather of the PRD belongs to Group C of the Köppen climate classification scheme. The whole year can be divided into two distinct seasons, wet season and dry season, with the alternation of summer monsoon and winter monsoon. The wet season lasts from around April to September when the summer monsoon is prevailing. The weather is hot, humid and rainy, with about 90% of the rain falling between April and September during this sampling year. The dry season lasts from late

October to March when the Asian winter monsoon is dominant. The weather is cool and dry. The data obtained in the present study was divided into two groups, the dry season group, including three sampling phases from Dec 2003 to Jan 2004, from Feb to Mar 2004 and from Oct 2004 to Nov 2004 with an average rainfall of 0.8 $\text{mm m}^{-2}\text{day}^{-1}$ and the average temperature of 17.7 °C, and the wet season group, including another three sampling phases from Apr to May 2004, from Jun to Jul 2004, and from Aug to Sep 2004 with an average rainfall of 5.1 $\text{mm m}^{-2}\text{day}^{-1}$ and the average temperature of 27.5 °C.

The atmospheric deposition ($\text{ng m}^{-2}\text{day}^{-1}$) of individual compounds in the dry and wet seasons was calculated on a daily basis. As shown in Fig. 4, various seasonal trends of different compounds at the different sampling sites were found. Atmospheric deposition of PAHs exhibited statistically significant seasonal differences, where deposition fluxes tended to be higher in the dry seasons than in the wet seasons. For DDTs, the deposition fluxes at the most sampling sites were also higher in the dry season than in the wet seasons, whereas for BDE-209 and chlordane, the deposition fluxes at the most sampling sites were higher in the wet seasons than in the dry seasons. In general, several factors could be responsible for the seasonal variations of atmospheric POPs deposition fluxes, such as the seasonality of contaminant sources, temperature, precipitation and photolysis. The seasonality of contaminant sources was found to be the most important factor in controlling the deposition fluxes (Wania et al., 1998). The aerosols with higher PAH concentrations in the dry season were found in Guangzhou in a previous study, which seasonal trends were consistent with this study (Li et al., 2006a). Besides the POP concentrations in aerosols, which directly affect the variation of particulate deposition fluxes, temperature is generally thought to be a crucial factor in controlling behaviours of POPs, such as the partition between gas/particles (Bidleman, 1988; Yamasaki et al., 1982). Impact of the ambient temperature on the deposition fluxes was shown by the significant correlations between the deposition fluxes and temperature for PAHs and DDT, with higher concentrations in winter and lower values in summer. In addition, there was significant increase in the contribution of the lighter PAHs to total PAHs in the dry season (Fig. 4). The same seasonal trends of DDT and PAH deposition fluxes were observed in previous studies, which was also attributed to the vapor–particle partitioning for semi-volatile organic compounds (SOCs) driven by temperature (Teil et al., 2004). The negative correlation between gas–particle partition coefficients of atmospheric *p,p'*-DDT, collected at the two sites by active air samplers in Hong Kong and Guangzhou, and ambient temperature ($r^2 > 0.70$, $p < 0.005$) was evidence of this (Li et al., 2007). Besides, the increase of atmospheric particle loading during this season might be another important factor. It is known that the PRD has been suffering worse environmental pollution in winter due to low temperature, low wind speed, less precipitation and the formation of atmospheric inversions. From January to March, Asia Brown Cloud (ABC), also called Asian haze, a cocktail of aerosol, ash, soot and other particles, hovered over most of the tropical Indian Ocean, South, Southeast and East Asia (Taylor, 2003). According to the data from the Guangdong Provincial Bureau of Meteorology, the frequency of haze appeared in Guangzhou in February and March 2004 was 14 and 19 days per month. The seasonal trends of atmospheric particle concentrations at the four sites collected by active air samplers in Hong Kong and Guangzhou also showed that the highest value was in February and March (Li et al., 2007).

The intensity and rate of precipitation could affect the atmospheric washout ratio of pollutants, which can influence the deposition fluxes of POPs (Dickhut and Gustafson, 1995). In the present study, the total amount of precipitation in summer (from April to September) varied from 652 to 1280 mm among the different sampling sites, with a mean value of 956 mm. During the six months of the dry season, the precipitation only amounted in the aggregate to a range of 88 to 174 mm (mean value of 138 mm). The frequent rainfalls in summer facilitate the transport of contaminants from air to ground and aquatic

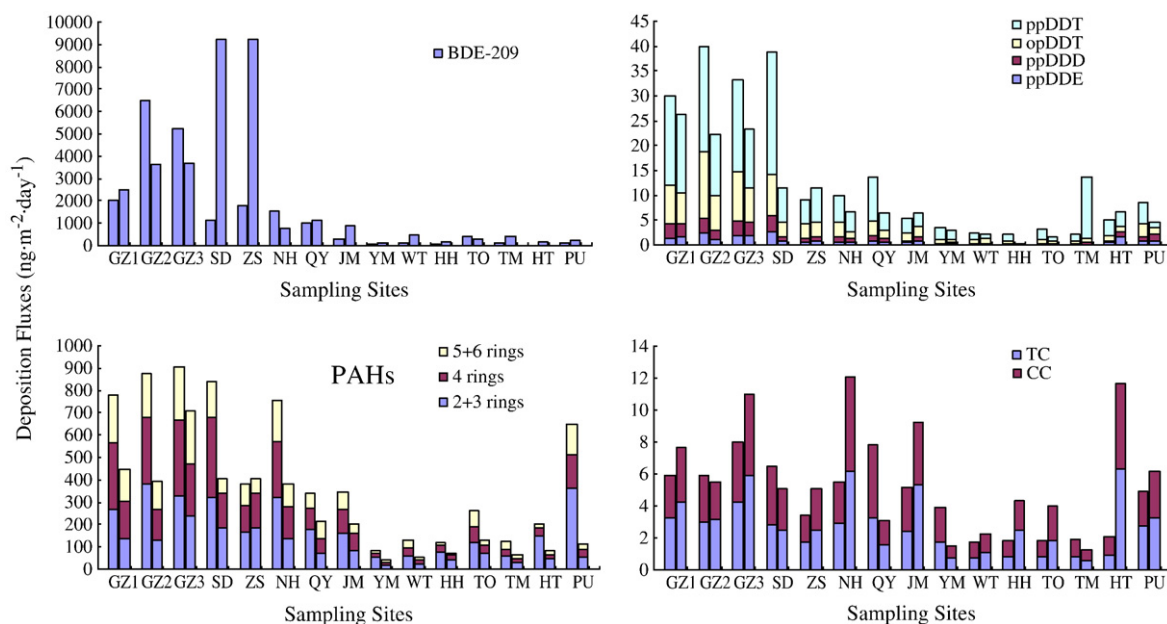


Fig. 4. Comparison of deposition fluxes in the dry season (left) and the wet season (right) at the all sampling sites in the PRD. For PAHs, 2 + 3 rings including Acy, Ace, Flu, Phe, and Ant; 4 rings including Flua, Pyr, BaA, and Chr; 5 + 6 rings including BbF, BkF, BaP, Ind, Dib, and BghiP.

environments. However, only chlordane deposition fluxes at some sites increased with increasing precipitation, and no significant correlations between the rainfall and other targeted compounds were found in the present study.

Photodegradation is another factor in determining the seasonal variation of the atmospheric deposition fluxes of POPs (Kajiwara et al., 2008; Söderström et al., 2004). The BeP/BaP ratios in different seasons might be an indicator to illustrate the impact of photodegradation. The similar BeP/BaP ratios in summer (1.84 ± 0.16) and in winter (1.85 ± 0.32) were obtained in this study, which suggested that the frequently washing air particles down to the sheltered filters during the summer seasons might reduce the extent of potential photodegradation process.

3.5. Annual deposition in Hong Kong and the PRD

Based on the atmospheric deposition values in typical areas, i.e. urban and rural, it is possible to assess the annual POPs atmospheric particulate deposition over a wider region. In this study, we estimated the atmospheric deposition of POPs in Hong Kong and the PRD region, respectively.

Hong Kong (1107 km²) is relatively “green” as the urban area (262 km²) makes up less than 25% of land area. Taking the values at the PU station as the urban deposition fluxes, and the mean values at other four sites in Hong Kong representing the remaining landscape, the particle deposition fluxes of BDE-209, Σ_{15} PAHs, BaP, Σ DDTs, and chlordane (TC + CC) in Hong Kong were estimated at 93, 86, 1.7, 2.1 and 2.1 kg yr⁻¹, respectively.

The PRD (41,700 km²) is composed of nine cities. Urban and rural residential areas accounted for about 11% of land surface, agriculture lands, such as paddy and crop fields, garden plots, grasslands, reservoirs, and ponds, etc, accounted for 52%, and forest accounted for 37%. In this study, the mean value of the deposition fluxes in the centre of the PRD, including GZ1, GZ2, GZ3, ZS, NH, SD sampling sites, was considered as the average urban and residential areas deposition fluxes, and the mean value of JM and QY, and the mean value of YM and WT were considered as the agriculture lands and forest deposition fluxes, respectively. In this way, the atmospheric particle deposition of BDE-209, Σ_{15} PAHs, BaP, Σ DDTs, and chlordane (TC + CC) in the PRD region was estimated at 13,400, 2950, 70, 82, and 63 kg yr⁻¹, respectively.

The atmospheric deposition of particle-phase BDE-209 is known to be one of the major sources of BDE-209 in soil. The inventory of BDE-209 in the PRD soils was estimated at 44.4 t in 2002 (Zou et al., 2007). In addition, a recent study analyzing 30 year depositional sediment cores found that BDE-209 increased exponentially after 1990, and higher concentrations appeared in 1995 in the PRD (Chen et al., 2007). Therefore, we assumed the BDE-209 in soils accumulated from 1995 with the average deposition fluxes of 13.4 t yr⁻¹. By comparing the estimated total deposition between 1990 and 2002 (107 t) with the estimated burden in soil (44.4 t) in 2002, the half residual time of BDE-209 in soils of the PRD was roughly estimated at about 3 years. There was uncertainty in calculating the half time of BDE-209, but the longer time in natural soils compared to other experiments (Kajiwara et al., 2008; Söderström et al., 2004) suggested that soil plays an important role determining the fate of BDE-209 in the environment.

4. Conclusion

The annual deposition fluxes of BDE-209, Σ_{15} PAHs, Σ DDTs, and chlordane (TC + CC) varied from 32.6 to 1970 $\mu\text{g m}^{-2}\text{yr}^{-1}$, from 22 to 290 $\mu\text{g m}^{-2}\text{yr}^{-1}$, from 0.8 to 11 $\mu\text{g m}^{-2}\text{yr}^{-1}$, and from 0.25 to 1.9 $\mu\text{g m}^{-2}\text{yr}^{-1}$, respectively. The deposition fluxes were higher in the centre of the PRD and lower at the coastal sites for all compounds. The seasonal variations of deposition fluxes were different for individual compounds. PAHs and DDTs showed higher fluxes in the dry season (winter), and lower ones in the wet season (summer), whereas BDE-209 and chlordane showed no significant difference between the dry season and the wet season. Source seasonality might affect the deposition fluxes of BDE-209 and high-weight PAHs, while temperature-dependent gas-particle partition may be a key factor affecting DDT and light-weight PAH deposition. The annual atmospheric depositions of BDE-209, Σ_{15} PAHs, Σ DDTs, and chlordane (TC + CC) were estimated about 93, 86, 2.1 and 2.1 kg yr⁻¹, respectively in Hong Kong, and about 13,400, 2950, 82, and 63 kg yr⁻¹ in the PRD region. The half residual time of BDE-209 in soils was estimated to be about 3 years.

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