



Evaluating the effectiveness of pollution control measures via the occurrence of DDTs and HCHs in wet deposition of an urban center, China[☆]



Ling-Chuan Guo^{a, e}, Lian-Jun Bao^{b, *}, Shao-Meng Li^c, Shu Tao^d, Eddy Y. Zeng^b

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, China

^c Air Quality Research Division, Environment Canada, 4905 Dufferin Street, Toronto, Ontario M3H 5T4, Canada

^d Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

^e University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 23 February 2016

Received in revised form

24 December 2016

Accepted 4 January 2017

Available online 30 January 2017

Keywords:

Wet deposition

Anthropogenic control

DDTs

HCHs

Urbanized districts

ABSTRACT

Wet deposition is not only a mechanism for removing atmospheric pollutants, but also a process which reflects loadings of atmospheric pollutants. Our previous study on wet deposition examined the effectiveness of short-term control measures on atmospheric particulate pollution, which were partly effective for organic pollutants of current input sources. In the present study, dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs), representative of legacy contaminants, were measured in the same samples collected throughout the entire year of 2010 in Guangzhou, a large urban center in South China. Concentrations of \sum DDT (sum of *o,p'* and *p,p'*-DDT, *o,p'* and *p,p'*-DDE, *o,p'* and *p,p'*-DDD, and *p,p'*-DDMU) and \sum HCH (sum of α -, β -, γ -, and δ -HCH) in wet deposition were in the ranges of nd–69 (average: 1.8 ng L⁻¹) and nd–150 ng L⁻¹ (average: 5.1 ng L⁻¹), respectively. In addition, the results of source diagnostics and backward air mass trajectories appeared to suggest the transport of antifouling paint derived DDTs from the coastal region off South China to Guangzhou. The combined wet and dry deposition flux of \sum HCH in the first quarter (January to March) was greater than that in the fourth quarter (October to December), while those of \sum DDT were comparable in the first and fourth quarters. Similar trends were also observed for the concentrations of \sum HCH and \sum DDT in aerosol samples. These results suggested the short-term pollution control measures implemented during the 16th Asian Games and 10th Asian Para Games (held in November and December 2010, respectively) did not work well for DDTs. The reduced input of HCHs during the fourth quarter was probably associated with the strict ban on lindane for food safety, which also exposed the weakness of control measures focusing mainly on the removal of atmospheric particulate matter.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Air pollution, closely associated with human health, has been a global concern (Ren et al., 2014; World Health Organization, 2011), and can be alleviated via natural processes and/or anthropogenic actions (Gong et al., 2010; Sheng et al., 2013; Wang et al., 2009). Wet deposition is a main mechanism for removal of pollutants from

the atmosphere, including particulate matter and organic pollutants (United Nations Environment Programme, 2002). On the other hand, examples of anthropogenic actions to improve air quality include the implementation of control measures during large events, e.g., administrative measures such as partial closure of selected heavy polluters, traffics restrictions, and dust control were implemented during the 2008 Beijing Olympic Games, 2010 Guangzhou Asian Games, and 2014 Asia-Pacific Economic Cooperation meeting in Beijing (Peoples Government of Beijing Municipality, 2008; 2014; Peoples Government of Guangzhou Municipality, 2010). A previous study confirmed the effectiveness of source control efforts before, during, and after the 2008 Olympic

[☆] This paper has been recommended for acceptance by Dr. Chen Da.

* Corresponding author.

E-mail address: baolianjun@jnu.edu.cn (L.-J. Bao).

Games, with lower concentrations of atmospheric particulate matter during the Olympic Games than during other time periods (Wang et al., 2009). While these control measures indeed substantially lessened air pollution by particulate matter (Zhou et al., 2010), their effectiveness in reducing the atmospheric levels of organic pollutants was variable (Cao et al., 2013).

Temporal trends of organic pollutants have been used to assess the effectiveness of long-term or short-term source control measures on reducing their concentrations in the atmosphere (Li et al., 2011; Liu et al., 2014). On the other hand, concentrations of organic pollutants in the atmosphere are also influenced by meteorological parameters, such as temperature, precipitation, and snow (Lohmann et al., 1999). Precipitation and snow can scavenge organic pollutants from the atmosphere (Poster and Baker, 1995; Wania et al., 1998, 1999). Hence use of the temporal trends of organic pollutants to evaluate the effectiveness of source control measures may incur large uncertainties if the number of air samples is insufficient to minimize the interferences of precipitation or snow. For instance, if most of air samples were collected after rainfall or snow, the derived decreasing trend of atmospheric organic pollutants would not be ascribed to the source control measures. In other words, meteorological parameters in study regions, especially tropical, subtropical and frigid zones, should be included in the assessment method. Therefore, atmospheric deposition fluxes of organic pollutants can be an alternative for assessing the effectiveness of source control measures on reducing the atmospheric loading of semi-volatile organic pollutants.

As a matter of fact, control measures were not always effective in removing organic aerosol components. Our previous study, targeting the consequences of source control measures for the 16th Asian Games and 10th Asian Para Games in November and December 2010 in Guangzhou, China, suggested that the measures worked well for removal of polycyclic aromatic hydrocarbons (PAHs), but not for polybrominated diphenyl ethers (PBDEs) by comparing their atmospheric deposition fluxes (including both wet and dry deposition) between the first and fourth quarters (Guo et al., 2014b). This was possibly because PAHs have overlapping emission sources with part of atmospheric particulate matter, i.e., incomplete combustion of fossil fuel and biomass. However, PBDEs embrace widely different emission sources (e.g., leaching of flame retardants from electronic/electric products and/or e-waste recycling activities) from atmospheric particulate matter (Guardia et al., 2006; Xu et al., 2006). As a consequence, the presence of overlapping emission sources allows portions of currently emitted pollutants to be removed along with atmospheric particulate matter. It has remained unclear whether the control measures were effective in lowering the levels of legacy contaminants with little discharge from current sources and the majority of residues in urban soil, as the effects of control measures may depend on both overlapping emission sources and atmospheric residues.

To address the above-mentioned issue, we analyzed the same samples for dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs), and combined with our previous efforts (Guo et al., 2014a, 2014b), further evaluated the effectiveness of the control measures. It has been demonstrated that DDTs and HCHs have the potential to cause endocrine damage in organisms (Tiedeken and Ramsdell, 2009; Willett et al., 1998) and increase the health hazards for humans as well as the ecosystem (Carreno et al., 2007; Daniel et al., 2001). Large amounts of DDT and HCH remnants have remained in the environment, particularly in South China (Guo et al., 2009; Wei et al., 2015), despite the phase-out of DDTs and HCHs in China in the 1980s and 1990s, respectively (Office of the National Coordination Group for Stockholm Convention Implementation, 2007). For instance, our previous study (Wei et al., 2015) showed that the soil inventory of DDT and its

metabolites including *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, and *p,p'*-DDMU in Guangzhou was estimated at 12.1 ± 17.7 tons, whereas that of HCHs (sum of α -HCH, γ -HCH, β -HCH, and δ -HCH) was estimated at 7.8 ± 10.2 tons. Expectedly, DDTs and HCHs in soil can transfer into the atmosphere through air-soil gaseous exchange and dust resuspension. In addition, small amounts of DDTs and HCHs were still used in China until recent years. For example, DDTs were utilized to fight against infectious diseases until 2001, and synthesized dicofol and anti-fouling paints containing residual DDTs were used for commercial purposes until 2014 (General Office of the State Council, 2007; Ministry of Environmental Protection of the People's Republic of China, 2014a, 2014c). Also, HCHs were used to control mites on crops until 2014 (Ministry of Environmental Protection of the People's Republic of China, 2014b). As a result, DDTs and HCHs may be appropriate candidates for assessing the effectiveness and limitation of pollution control measures on alleviation of air pollution by organic contaminants.

2. Materials and methods

2.1. Sampling

Three field sampling sites are located at different urbanized districts of Haizhu, Tianhe, and Luogang, respectively (Fig. 1). Most precipitation samples were collected simultaneously at all sites, but a few samples were collected separately as some rainfalls occurred only at one or two sites. Overall, 157 precipitation samples were collected, with 111 collected during the wet weather season (April–September) and 46 during the dry weather season (January–March and October–December) in 2010. Additionally, 12 dry deposition samples, each integrated for one month during non-raining days, and 59 air samples from time to time were taken at the Tianhe District. Details about the sampling and preliminary treatment procedures were described previously (Guo et al., 2014a, 2014b), and a brief description is given herein. Precipitation samples were collected with stainless steel plates, and divided into filtrate and particulate samples via filtration in laboratory. Dry depositing particle samples were collected with a stainless plate filled with distilled water, and then all particles were retained on glass fiber filters (0.7 μm nominal pore size; Whatman, Maidstone, England) via filtration. In addition, particulate matter and gaseous samples were collected simultaneously with glass fiber filters and polyurethane foam (PUF) plugs, respectively, using a high-volume air sampler.

2.2. Sample analysis

Detailed procedures for sample extraction were described previously (Guo et al., 2014a; Yue et al., 2011). In brief, a known amount of the surrogate standards, i.e., PCB-67 and PCB-191, was spiked to each sample prior to extraction. Filtrate samples were processed with solid-phase extraction combining with liquid-liquid extraction, and filters loaded with particulates and PUF plugs were Soxhlet extracted for 48 h using a mixture of hexane, dichloromethane and acetone (2:2:1, v:v:v). All extracts were purified with glass columns consisting of neutral alumina and neutral silica gel, and finally stored in autosampler vials at -20 °C. Before instrumental analysis, a known amount of internal standard PCB-82 was added into each extract.

All samples were analyzed with a Shimadzu Model 2010 Plus GC-MS (Kyoto, Japan) in the electronic ionization mode equipped with a DB-5ms (60 m long \times 0.25 mm i.d. with 0.25 μm film thickness) capillary column (J&W Scientific, Folsom, CA, USA). The column temperature was initiated at 50 °C (held for 1 min),

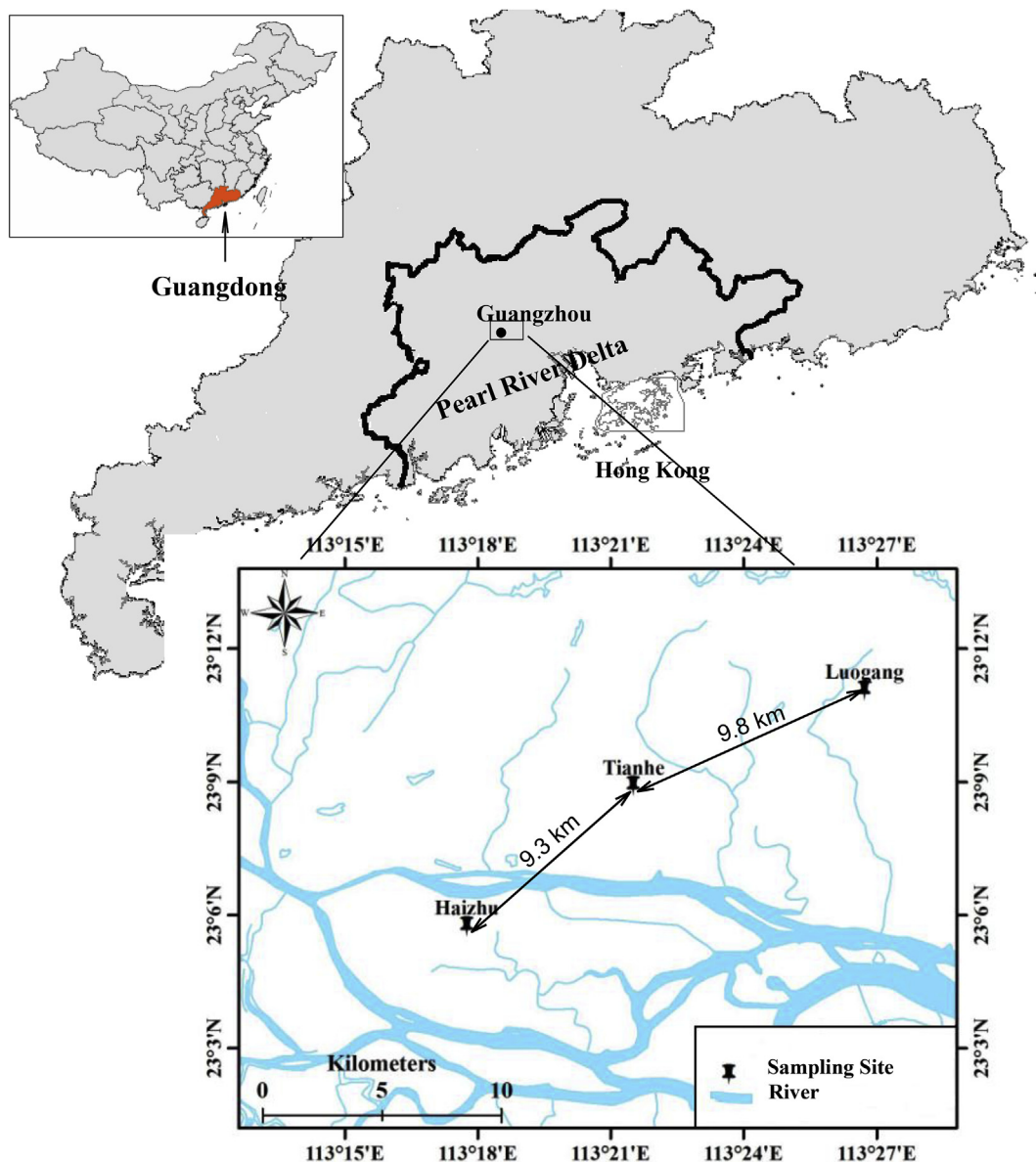


Fig. 1. Sampling sites of wet deposition (the black points) in Guangzhou, Pearl River Delta (the area surrounded by thick black line).

increased to 210 °C at 20 °C min⁻¹, 240 °C at 2 °C min⁻¹, 260 °C at 5 °C min⁻¹ and 280 °C at 20 °C min⁻¹ (held for 7 min), and finally ramped to 290 °C at 20 °C min⁻¹ (held for 11 min). The injection port temperature was initiated at 100 °C (held for 0.2 min), then increased to 280 °C at 400 °C min⁻¹ (held for 30 min). The transfer line and ion source temperatures were both maintained at 250 °C. The carrier gas was helium at a constant flow rate of 1.3 ml min⁻¹. DDTs and HCHs were quantified in the selective ion monitoring mode using characteristic ions (Table S1 of the Supplementary material; "S" indicates the tables and figures in the Supplementary material thereafter).

2.3. Quality assurance/quality control

A total of 24 procedural blanks, field blanks, and spiked matrix samples were processed with field samples. The recoveries of DDTs and HCHs in spiked matrix samples were in the range of 70± 12% to 105± 20%. The recoveries of surrogate standards were 92± 12% for PCB-67 and 83± 16% for PCB-191 in filtrate samples, whereas they

were 72± 18% for PCB-67 and 76± 15% for PCB-191 in particulate samples. In addition, the recoveries of surrogate standards were 109± 22% for PCB-67 and 94± 25% for PCB-191 in gas aerosol samples and were 83± 19% for PCB-67 and 83± 35% for PCB-191 in particulate aerosol samples. In general, the reporting limit of an analyte was calculated by the lowest calibration concentration multiplying the related final extract volume and divided by the sample volume. If the concentration of an analyte in a field blank was greater than the lowest calibration concentration, this concentration divided by the sample volume was defined as the reporting limit. As a result, the reporting limits of DDTs and HCHs in wet deposition and aerosol samples were 0.0024–0.33 ng L⁻¹ and 2.1 pg m⁻³ (Table S1).

2.4. Data analysis

The calculations of volume-weighted mean concentrations, wet and dry deposition fluxes of target compounds during a sampling period were described in details by our previous studies (Guo et al.,

2014a, 2014b), and are briefly presented in the Supporting material. The capacity for removal (CR), which describes the amounts of pollutants removed by rainfall washout from the atmosphere, is defined as

$$CR = F_{wet} / (F_{wet} + F_{dry}) \quad (1)$$

where F_{wet} and F_{dry} are wet and dry deposition fluxes of a target analyte during a sampling period. The sum of o,p' and p,p' -DDT, o,p' and p,p' -DDE, o,p' and p,p' -DDD, and p,p' -DDMU is labeled as $\sum DDT$, while the sum of α -, β -, γ -, and δ -HCH is designated as $\sum HCH$. The Spearman correlation between two variables was determined with the square of correlation coefficient (r^2). In all statistical analyses, the criterion of significance was defined as $p < 0.05$. All statistical analyses were performed with SPSS 13.0 (Chicago, IL, USA) and R software (R Development Core Team, Vienna, Austria).

2.5. Backward trajectory analysis

The 72 h backward trajectories were calculated for each month of 2010 in Guangzhou with Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (Version 4) (<http://ready.arl.noaa.gov/HYSPLIT.php>), which was designed by the National Oceanic and Atmospheric Administration's Air Resources Laboratory. Each day embraced two endpoints, i.e., 12 h for one endpoint. The altitude selected for computing the trajectories was 1000 m above the sea level, and meteorological data used for modeling were obtained from Global Data Assimilation System (<ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1>). A hierarchical clustering method was used to classify horizontal trajectories based on backward trajectory directions and group the data into clusters.

3. Results and discussion

3.1. Occurrence of DDTs and HCHs

Concentrations of $\sum DDT$ in precipitation samples were in the range of nd–69 (average: 1.8 ng L^{-1}), with p,p' -DDT (58%) and p,p' -DDMU (2.5%) as the most and least abundant components. Approximately 61% of DDTs in wet deposition was distributed in the particulate phase (Table S2). The annual volume-weighted mean concentration of $\sum DDT$ (1.8 ng L^{-1}) was lower than those in some large cities in temperate and tropical regions, e.g., 9.9 ng L^{-1} in Beijing (Yang et al., 2012) and 31 ng L^{-1} in Singapore (He and Balasubramanian, 2010), but greater than those in relatively small towns and rural regions, e.g., 0.094 ng L^{-1} in Senga Bay of Malawi (Karlsson et al., 2000), 0.23 ng L^{-1} in Point Petre of Canada (Melymuk et al., 2011), 0.53 ng L^{-1} in Lucknow of India (Malik et al., 2007), and 0.94 and 0.79 ng L^{-1} in Dongguan and Shunde of China (Yue et al., 2011). The annual volume-weighted mean concentration of $\sum DDT$ (1.8 ng L^{-1}) in the present study was also greater than that in large cities of cold regions such as 0.40 ng L^{-1} in Toronto (Melymuk et al., 2011) (Table 1).

Concentrations of $\sum HCH$ in precipitation samples were in the range of nd–150 ng L^{-1} (average: 5.1 ng L^{-1}), with γ -HCH (37%) and δ -HCH (13%) as the most and least abundant components, respectively. The annual volume-weighted mean concentration (4.0 ng L^{-1}) of $\sum HCH$ in the dissolved phase was higher than that (1.1 ng L^{-1}) in the particulate phase, suggesting that HCHs were predominant in the dissolved phase (Table S2). Similar to DDTs, the annual volume-weighted mean concentration of $\sum HCH$ (5.1 ng L^{-1}) in the present study was lower than those in large cities of Asia, e.g., 33 ng L^{-1} in Beijing (Yang et al., 2012) and 84 ng L^{-1} in

Singapore (He and Balasubramanian, 2010), and slightly greater than those in small towns and rural regions, e.g., 0.51 ng L^{-1} in Point Petre of Canada (Melymuk et al., 2011), 0.62 ng L^{-1} in Senga Bay of Malawi (Karlsson et al., 2000), and 0.68 ng L^{-1} in Toronto (Melymuk et al., 2011) (Table 1). The greater concentrations of $\sum DDT$ and $\sum HCH$ occurred in subtropical and tropical regions than in temperate and cold regions. These results may be ascribed to the higher demand for pesticides used to control diseases infection (malaria and typhoid fever) and the later phasing-out of pesticides in the subtropical and tropical regions than in the temperate and cold regions (Fang et al., 2012; He and Balasubramanian, 2010; Ministry of Environmental Protection of the People's Republic of China, 2014a; Park et al., 2001; United Nations Environment Programme, 2002; Yao et al., 2008).

Generally, the monthly $\sum DDT$ and $\sum HCH$ concentrations (Table S3) were greater during the dry weather season than during the wet weather season (Fig. 2), probably resulted from dilution effects as verified by the negative correlations between the precipitation amounts and concentrations of $\sum DDT$ ($r^2 = 0.65$, $p < 0.05$) and $\sum HCH$ ($r^2 = 0.56$, $p < 0.05$). Spatially, no significant variance ($p > 0.05$, paired t -test) was observed for $\sum DDT$ and $\sum HCH$ concentrations among three sampling sites. Similar spatial distributions were also found for PAHs and PBDEs (Guo et al., 2014a, 2014b). As described before, the similar spatial distribution patterns for these semi-volatile organic contaminants probably indicated strong atmospheric convective mixing over the city, although these contaminants were derived from different sources.

3.2. Source diagnostics

Multiple studies showed that two primary metabolites of DDT, i.e., DDD and DDE, were more stable than their parent compounds in the environment (Aislabie et al., 1997; Mackay et al., 2006). As a result, the ratio of DDT/(DDD + DDE) has been used to diagnose the source of the prevailing DDT (Qiu et al., 2004). The ratio greater than 0.5 indicates fresh inputs of DDTs. In the present study, the median value of DDT/(DDD + DDE) was 1.6 in precipitation and 2.3 in aerosol samples, indicating moderate levels of newly emitted DDTs in the study region. Furthermore, the median value of o,p' -DDT/ p,p' -DDT was 0.27, which was similar to the ratios in anti-fouling paints that ranged from 0.2 to 0.33 (Yu et al., 2011). Apparently, DDTs have remained ubiquitous in the region, with anti-fouling paint as a viable new source of DDTs.

In addition, the DDT/(DDD + DDE) value was slightly higher for the wet weather season (median value: 1.7) than for the dry weather season (median value: 1.4) ($p < 0.05$, t -test), indicating that higher new emissions occurred in the wet weather season than in the dry weather season. Such seasonality was examined through backward trajectory of air mass (Fig. 3 and Fig. S1). During the wet weather season, the summer monsoon dominates air masses in southern China so that most air masses in Guangzhou originate from the South China Sea. On the contrary, air masses in Guangzhou during the dry weather season mostly originate from northern China. Because the coastal regions off southern China are known to be sites of DDT contamination (Zhang et al., 2010), summer monsoon can carry DDTs to the atmosphere of Guangzhou. Moreover, more anti-fouling paints are used during the wet weather season, as fishing boat maintenance mainly occurs during the fish moratorium period (May 16 to August 1 in 2010) (Agriculture-Fisheries and Conservation Department of Hong Kong, 2000).

Two major sources of HCHs are technical HCH (with α -HCH/ γ -HCH between 3 and 7) and lindane (with α -HCH/ γ -HCH far below 1) (Iwata et al., 1993; Qiu et al., 2004). The median value of α -HCH/ γ -HCH in the present study was 0.81, suggesting lindane as the major source of HCHs. Although use of technical HCH in China was

Table 1
Concentrations (volume weighted mean values in parentheses \pm weighted standard deviation, ng L^{-1}) of ΣDDT and ΣHCH (P for particulate phase and D for dissolved phase) in the present study and other previous reports.

ΣDDT						
Year	Site	Type	ΣDDT	$\Sigma\text{DDT (P)}$	$\Sigma\text{DDT (D)}$	Reference
1997–1998	Senga Bay, Malawi	Rural	(0.094) ^a			Karlsson et al. (2000)
2005	Lucknow, India	Urban	nd–6.2 (0.53 \pm 1.4) ^b			Malik et al. (2007)
2005	Guangzhou, China	Urban	(0.99 \pm 0.31) ^c			Huang et al. (2010)
2006–2007	Guangzhou, China		(1.5 \pm 0.64) ^d			Yue et al. (2011)
	Shunde, China		(0.79 \pm 0.14) ^d			Yue et al. (2011)
	Dongguan, China		(0.94 \pm 0.18) ^d			Yue et al. (2011)
2007–2008	Singapore	Urban	(31) ^e	(17) ^e	(14) ^e	He and Balasubramanian (2010)
2007–2009	Burlington, Canada	Peri-urban	(0.49) ^b			Melymuk et al. (2011)
2007–2009	Toronto, Canada	Urban	(0.40) ^b			Melymuk et al. (2011)
2007–2009	Point Petre, Canada	Rural	(0.23) ^b			Melymuk et al. (2011)
2009–2011	Beijing, China	Urban	(9.9) ^b	(4.9) ^b	(4.9) ^b	Yang et al. (2012)
2010	Guangzhou, China	Urban	nd–69 (1.8 \pm 4.8) ^f	nd–66 (1.1 \pm 4.3) ^f	nd–20 (0.69 \pm 1.6) ^f	the present study
ΣHCH						
Year	Site	Type	ΣHCH	$\Sigma\text{HCH (P)}$	$\Sigma\text{HCH (D)}$	Reference
1997–1998	Senga Bay, Malawi	Rural	(0.62) ^g			Karlsson et al. (2000)
2005	Lucknow, India	Urban	nd–330 (23 \pm 49) ^g			Malik et al. (2007)
2005	Guangzhou, China	Urban	(2.4)	(0.23 \pm 0.10) ^h	(2.2 \pm 0.77) ^g	Huang et al. (2010)
2007–2008	Singapore	Urban	(84) ^g	(5.7) ^g	(78) ^g	He and Balasubramanian (2010)
2007–2009	Burlington, Canada	Peri-Urban	(0.53) ^h			Melymuk et al. (2011)
2007–2009	Toronto, Canada	Urban	(0.68) ^h			Melymuk et al. (2011)
2007–2009	Point Petre, Canada	Rural	(0.51) ^h			Melymuk et al. (2011)
2009–2011	Beijing, China	Urban	(33) ^g	(9.3) ^g	(24) ^g	Yang et al. (2012)
2010	Guangzhou, China	Urban	nd–150 (5.1 \pm 12) ^g	nd–51 (1.1 \pm 3.1) ^g	nd–130 (4.0 \pm 10) ^g	the present study

^a Sum of *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDE.

^b Sum of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD.

^c Sum of *p,p'*-DDT and *o,p'*-DDT.

^d Sum of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, and *o,p'*-DDD.

^e Sum of *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD.

^f Sum of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDE, *o,p'*-DDE, and *p,p'*-DDMU.

^g Sum of α -HCH, β -HCH, γ -HCH, and δ -HCH.

^h Sum of α -HCH and γ -HCH.

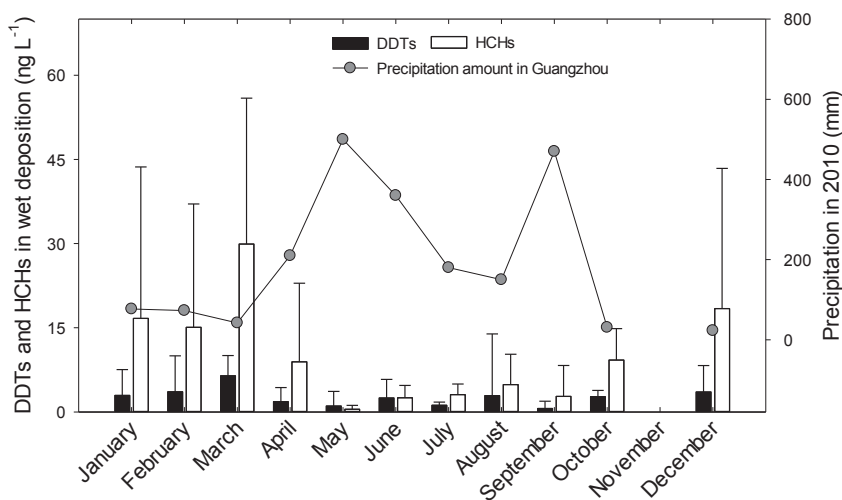


Fig. 2. Concentrations of DDTs and HCHs in wet deposition and monthly precipitation amount in Guangzhou in 2010.

banned in the 1980s, lindane in small amounts had still been produced and used in agriculture to control locust until 2014, when the Stockholm Convention was strictly complied (Ministry of Environmental Protection of the People's Republic of China, 2014b).

3.3. Deposition flux

The annual wet deposition fluxes of ΣDDT and ΣHCH were $(3.7 \pm 10) \times 10^3$ and $(1.0 \pm 2.6) \times 10^4$ $\text{ng m}^{-2} \text{yr}^{-1}$, whereas those

annual dry deposition fluxes were $(2.3 \pm 0.45) \times 10^3$ and $(5.6 \pm 1.1) \times 10^3$ $\text{ng m}^{-2} \text{yr}^{-1}$ (Table S4). The total annual atmospheric (combined wet and dry) deposition flux of ΣDDT was $(6.0 \pm 8.2) \times 10^3$ $\text{ng m}^{-2} \text{yr}^{-1}$, which was comparable to those of various previous studies around the world (Table S5), e.g., Rio de Janeiro City in Brazil (2.2×10^3 $\text{ng m}^{-2} \text{yr}^{-1}$) (Meire et al., 2013), Shunde (3.3×10^3 $\text{ng m}^{-2} \text{yr}^{-1}$), Dongguan (3.4×10^3 $\text{ng m}^{-2} \text{yr}^{-1}$), and Guangzhou of China (6.7×10^3 $\text{ng m}^{-2} \text{yr}^{-1}$) (Yao et al., 2008), and several rural regions in Canada (1.1×10^3 to 8.2×10^3 ng m^{-2}

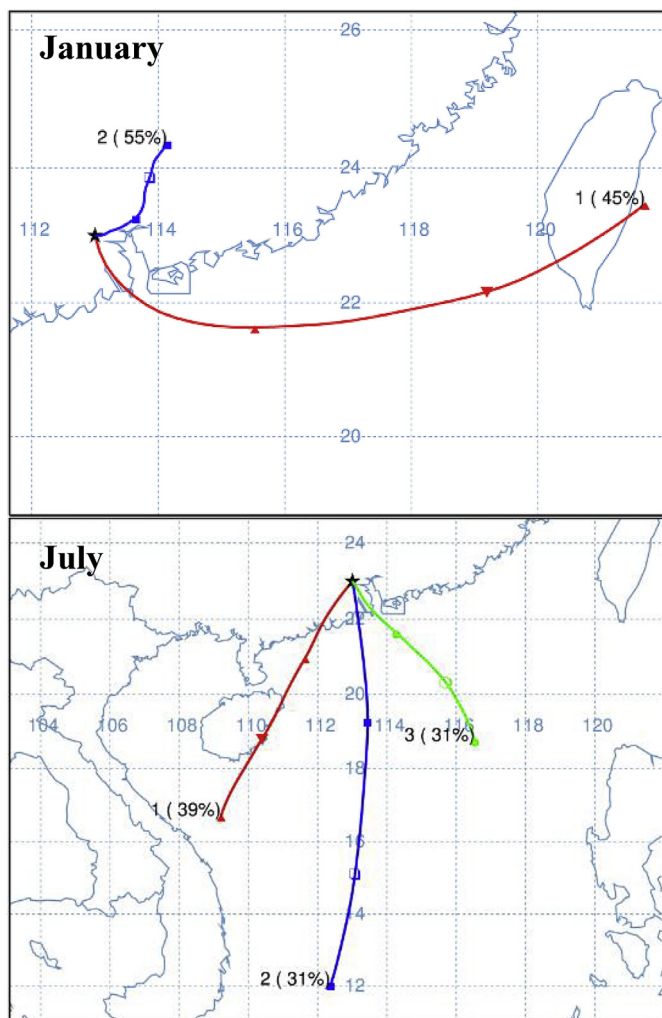


Fig. 3. The hierarchical clustering results of 72 h backward trajectories of Guangzhou in January and July 2010, representing dry weather season and wet weather season, respectively. The trajectories of different colors represent air masses derived from different directions. The percentage in parenthesis represents the proportion of air mass from each direction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

yr^{-1}) (Yue et al., 2011), and much smaller than that obtained in Galveston Bay of Texas, USA ($1.9 \times 10^6 \text{ ng m}^{-2} \text{ yr}^{-1}$) (Park et al., 2001). The total annual atmospheric deposition flux of ΣHCH was $(1.6 \pm 2.3) \times 10^4 \text{ ng m}^{-2} \text{ yr}^{-1}$, greater than those in several regions in Brazil (0.37×10^2 to $0.95 \times 10^2 \text{ ng m}^{-2} \text{ yr}^{-1}$) (Meire et al., 2013), Kensington in Canada ($9.8 \times 10^2 \text{ ng m}^{-2} \text{ yr}^{-1}$) (Yao et al., 2008), Tenerife in Spain ($1.2 \times 10^3 \text{ ng m}^{-2} \text{ yr}^{-1}$) (van Drooge et al., 2001), and several rural regions in Canada (2.8×10^3 to $4.7 \times 10^3 \text{ ng m}^{-2} \text{ yr}^{-1}$) (Yao et al., 2008), and smaller than that obtained in Galveston Bay of Texas, USA ($1.7 \times 10^6 \text{ ng m}^{-2} \text{ yr}^{-1}$) (Park et al., 2001).

On the other hand, the atmospheric deposition flux (combined wet and dry deposition fluxes) of ΣDDT ($(1.2 \pm 1.5) \times 10^3 \text{ ng m}^{-2} \text{ quarter}^{-1}$) in the first quarter (January–March) was not significantly different from that ($(0.87 \pm 0.43) \times 10^3 \text{ ng m}^{-2} \text{ quarter}^{-1}$) in the fourth quarter (October–December) ($p > 0.05$, t -test; Fig. 4), which was similar to the previously reported pattern of ΣPBDE (sum of 21 BDE congeners) from the same samples (Guo et al., 2014b). Similar flux levels between the two quarters were not dependent on precipitation amount, as the two quarters embraced

different precipitation amounts (192 mm for the first quarter and 54 mm for the fourth quarter). Furthermore, the concentrations of ΣDDT in air (gaseous + particle) samples collected in the fourth quarter ($0.52 \pm 0.30 \text{ ng m}^{-3}$) were not significantly different from those in other quarters (0.36 ± 0.34 , 0.90 ± 0.44 , and $0.69 \pm 0.28 \text{ ng m}^{-3}$ in the first, second, and third quarters, respectively) ($p > 0.05$). The volume-weighted mean concentrations of ΣDDT in wet deposition in the first and fourth quarter were 4.0 and 3.0 ng L^{-1} , respectively. Apparently, the short-term pollution control measures implemented in the fourth quarter for the 16th Asian Games and 10th Asian Para Games were not effective in removing DDTs from the atmosphere, similar to the situation for PBDEs (Guo et al., 2014b). On the other hand, the deposition fluxes of particulate matter were greater in the first quarter ($6.4 \text{ g m}^{-2} \text{ quarter}^{-1}$) than in the fourth quarter ($4.5 \text{ g m}^{-2} \text{ quarter}^{-1}$) in our previous study ($p < 0.05$) (Guo et al., 2014a), indicating that these control measures were effective in reducing atmospheric particles. The correlation between monthly particulate matter levels and DDTs concentrations ($r^2 = 0.24$, $p > 0.05$) was weak. As a consequence, sources of particulate matter were neither overlapped with the sources of currently emitted DDTs, nor overlapped with the release of residual DDTs.

The atmospheric deposition flux of ΣHCH in the fourth quarter ($(2.7 \pm 1.3) \times 10^3 \text{ ng m}^{-2} \text{ quarter}^{-1}$) was much smaller than those in other three quarters ($(5.4 \pm 4.7) \times 10^3$, $(3.9 \pm 8.7) \times 10^3$, and $(3.6 \pm 3.6) \times 10^3 \text{ ng m}^{-2} \text{ quarter}^{-1}$ for the first, second, and third quarters, respectively) ($p < 0.05$, t -test; Fig. 4). The lower flux level in the fourth quarter can not be ascribed to different precipitation amounts, as the monthly deposition flux of ΣHCH was not correlated with precipitation amount ($p > 0.05$). Also, the ΣHCH concentration in air (gaseous + particle) samples collected in the

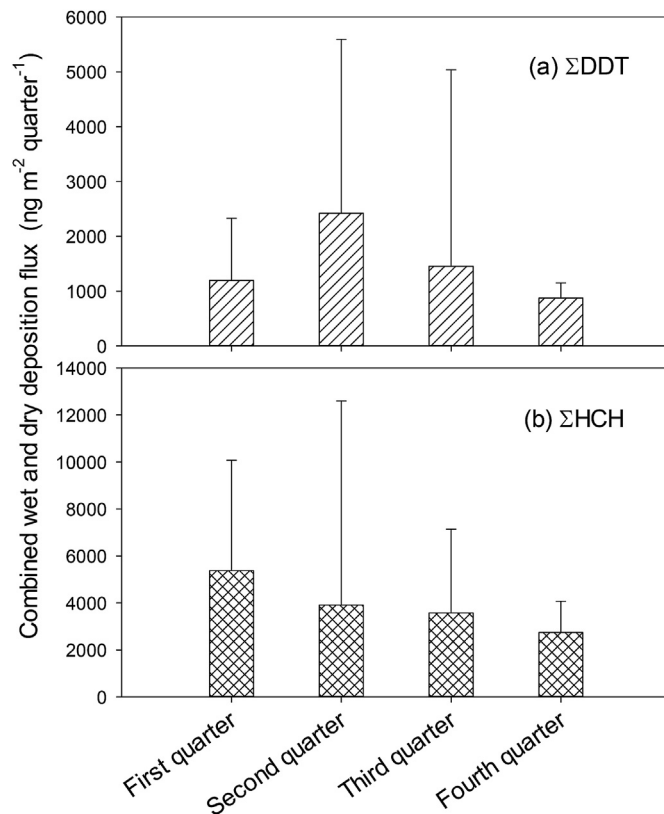


Fig. 4. Combined wet and dry deposition fluxes of ΣDDT and ΣHCH in individual quarters of 2010 in Guangzhou, China.

fourth quarter ($0.74 \pm 0.36 \text{ ng m}^{-3}$) was lower than those in other quarters (1.9 ± 2.0 , 4.0 ± 5.5 , and $1.6 \pm 1.2 \text{ ng m}^{-3}$) ($p > 0.05$). The volume-weighted mean concentration of $\sum\text{HCH}$ in wet deposition in the fourth quarter (13 ng L^{-1}) was slightly lower than that in the first quarter (19 ng L^{-1}). Similar seasonal trends were also found with PAHs (Guo et al., 2014b). These findings indicated an apparent decrease of atmospheric HCH levels in the fourth quarter, probably in response to the short-term control measures enforced by the local governments. However, the implemented control measures were designed mainly to remove atmospheric particulate matter, whereas HCHs were largely affiliated with the gaseous phase (more than 95%) (Table S2). Hence, reduced emissions of HCHs were most likely to result from the strict ban on the use of several pesticides including lindane due to the concern about food safety. Obviously, control measures effective for removal of atmospheric particulate matter were not effective for some legacy organic contaminants.

3.4. Removal capacity by wet deposition and effects of meteorological parameters

Wet deposition can scavenge organic compounds from the atmosphere. The capacity for removal (CR) by wet deposition was 0.64, 0.79, 0.70, and 0.29 for $\sum\text{DDT}$ and 0.68, 0.77, 0.73, and 0.26 for $\sum\text{HCH}$ in the four quarters, respectively. The apparently lower removal capacities in the fourth quarter were mainly attributed to smaller amount of precipitations during the fourth quarter (Table S2), i.e., CR was positively correlated with monthly precipitation amount ($r^2 = 0.46$ and $p < 0.05$ for $\sum\text{DDT}$, $r^2 = 0.71$ and $p < 0.05$ for $\sum\text{HCH}$). In fact, the artificial rain interventions taken in the upwind regions of Guangzhou in November and early December 2010 were implemented by the local governments to keep clear sky during the 16th Asian Games and 10th Asian Para Games (Peoples Government of Guangzhou Municipality, 2010). This intervention led to no rain in November in Guangzhou and thereby reduced the removal efficiency of pollutants from the atmosphere by wet deposition.

On the other hand, the similar variations were also observed for the monthly CRs of $\sum\text{DDT}$ and $\sum\text{HCH}$ and air temperature (Fig. S2). Except for greater precipitation amount at higher temperature in Guangzhou, this observation was in agreement with the finding that the highest deposition fluxes of PCBs occurred in June–September with the highest temperature in the vicinity of a steel manufacturing plant (Xu et al., 2011), indicating the effects of temperature on the re-emission of pollutants from their residues in water, soil, or plants into the atmosphere (He and Balasubramanian, 2010). In addition, the relative humidity (59–82%) was uniform throughout the year of 2010 in Guangzhou, implying that the relative humidity is not a concern when the scavenging effects of pollutants from wet deposition are evaluated.

4. Conclusions

Results from the present study suggested that wet deposition in Guangzhou contained moderate concentration levels of DDTs and HCHs compared to other regions worldwide. Lower DDTs and HCHs concentrations in wet deposition were found in the wet weather season than in the dry weather season. The seasonality for the source diagnostic index, $\text{DDT}/(\text{DDD} + \text{DDE})$, and air mass indicated that DDTs derived from anti-fouling paint may have been transported from the coastal region off South China to Guangzhou. In addition, the effects of pollution control measures adopted by local governments in preparation for the 16th Asian Games and 10th Asian Para Games seemed limited, i.e., these measures did not work for DDTs and HCHs.

Acknowledgements

The present study was financially supported by the National Natural Science Foundation of China (Nos. 41390240 and 41329002). We thank Xian-Lin Luo and Bao-Zhong Zhang for assistance in sample collection and Wei-Hao Feng for laboratory support. This is contribution No. IS-2333 from GIGCAS.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2017.01.004>.

References

- Agriculture-Fisheries and Conservation Department of Hong Kong, 2000. Information Note on Fishing Moratorium in the South China Sea. <http://legco.gov.hk/yr99-00/english/panels/hs/papers/1555e01.pdf> (accessed on December 11, 2016).
- Aislabie, J.M., Richards, N.K., Boul, H.L., 1997. Microbial degradation of DDT and its residues—a review. *N. Z. J. Agric. Res.* 40, 269–282.
- Cao, H., Hidemichi, F., Shunsuke, M., 2013. Environmental impact of the 2008 Beijing Olympic Games. *Economics* 30, 1–17.
- Carreno, J., Rivas, A., Granada, A., Lopez-Espinosa, M.J., Mariscal, M., Olea, N., Olea-Serrano, F., 2007. Exposure of young men to organochlorine pesticides in Southern Spain. *Environ. Res.* 103, 55–61.
- Daniel, V., Huber, W., Bauer, K., Suesal, C., Conrath, C., Opelz, G., 2001. Associations of blood levels of PCB, HCHs, and HCB with numbers of lymphocyte subpopulations, in vitro lymphocyte response, plasma cytokine levels, and immunoglobulin autoantibodies. *Environ. Heal. Perspect.* 109, 173–178.
- Fang, M., Choi, S.-D., Baek, S.-Y., Jin, G., Chang, Y.-S., 2012. Deposition of polychlorinated biphenyls and polybrominated diphenyl ethers in the vicinity of a steel manufacturing plant. *Atmos. Environ.* 49, 206–211.
- General Office of the State Council, 2007. State Plan on Performance of Stockholm Convention in China. <http://www.china-pops.org/guide/popskt/200807/P020121210421015511833.pdf> (accessed on May 2, 2015).
- Gong, P., Wang, X., Sheng, J., Yao, T., 2010. Variations of organochlorine pesticides and polychlorinated biphenyls in atmosphere of the Tibetan Plateau: role of the monsoon system. *Atmos. Environ.* 44, 2518–2523.
- Guardia, M.J.L., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* 40, 6247–6254.
- Guo, L.-C., Bao, L.-J., She, J.-W., Zeng, E.Y., 2014a. Significance of wet deposition to removal of atmospheric particulate matter and polycyclic aromatic hydrocarbons: a case study in Guangzhou, China. *Atmos. Environ.* 83, 136–144.
- Guo, L.-C., Bao, L.-J., Wu, F.-C., Yue, Q., Zeng, E.Y., 2014b. Seasonal deposition fluxes and washout of atmospheric polybrominated diphenyl ethers in a large urban center: importance of natural and anthropogenic factors. *Environ. Sci. Technol.* 48, 11196–11203.
- Guo, Y., Yu, H.-Y., Zeng, E.Y., 2009. Occurrence, source diagnosis, and biological effect assessment of DDT and its metabolites in various environmental compartments of the Pearl River Delta, South China: a review. *Environ. Pollut.* 157, 1753–1763.
- He, J., Balasubramanian, R., 2010. Semi-volatile organic compounds (SVOCs) in ambient air and rainwater in a tropical environment: concentrations and temporal and seasonal trends. *Chemosphere* 78, 742–751.
- Huang, D.Y., Peng, P.A., Xu, Y.G., Sun, C.X., Deng, H.M., Deng, Y.Y., 2010. Distribution, regional sources and deposition fluxes of organochlorine pesticides in precipitation in Guangzhou, South China. *Atmos. Res.* 97, 115–123.
- Iwata, H., Tanabe, S., Sakai, N., Tatsukawa, R., 1993. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environ. Sci. Technol.* 27, 1080–1098.
- Karlsson, H., Muir, D.C.G., Teixeira, C.F., Burniston, D.A., Strachan, W.M.J., Hecky, R.E., Mwitwa, J., Bootsma, H.A., Grift, N.P., Kidd, K.A., Rosenberg, B., 2000. Persistent chlorinated pesticides in air, water, and precipitation from the Lake Malawi area, Southern Africa. *Environ. Sci. Technol.* 34, 4490–4495.
- Li, Y., Wang, T., Wang, P., Ding, L., Li, X., Wang, Y., Zhang, Q., Li, A., Jiang, G., 2011. Reduction of atmospheric polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) during the 2008 Beijing Olympic Games. *Environ. Sci. Technol.* 45, 3304–3309.
- Liu, L.-Y., Salamova, A., Hites, R.A., 2014. Interstudy and intrastudy temporal trends of polychlorinated biphenyl, pesticide, and polycyclic aromatic hydrocarbon concentrations in air and precipitation at a rural site in Ontario. *Environ. Sci. Technol. Lett.* 1, 226–230.
- Lohmann, R., Green, N.J.L., Jones, K.C., 1999. Detailed studies of the factors controlling atmospheric PCDD/F concentrations. *Environ. Sci. Technol.* 33, 4440–4447.
- Mackay, D., Shiu, W.Y., Ma, K.-C., Lee, S.C., 2006. In: CRC Press (Ed.), *Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals*, second ed. Taylor & Francis Group, Boca Raton, FL.
- Malik, A., Singh, V.K., Singh, K.P., 2007. Occurrence and distribution of persistent

- trace organics in rainwater in an urban region (India). *Bull. Environ. Contam. Toxicol.* 79, 639–645.
- Meire, R.O., Targino, A.C., Torres, J.P.M., 2013. Bulk atmospheric deposition of persistent toxic substances (PTS) along environmental gradients in Brazil. *Environ. Sci. Pollut. Res.* 20, 2046–2053.
- Melymuk, L., Robson, M., Diamond, M.L., Bradley, L.E., Backus, S., 2011. Wet deposition loadings of organic contaminants to Lake Ontario: assessing the influence of precipitation from urban and rural sites. *Atmos. Environ.* 45, 5042–5049.
- Ministry of Environmental Protection of the People's Republic of China, 2014a. The Anti-fouling Paints Containing DDTs Has Been Stopped. <http://finance.chinanews.com/life/2014/10-25/6716272.shtml> (accessed on May 2, 2015).
- Ministry of Environmental Protection of the People's Republic of China, 2014b. Notice on Amendments to Annexes a, B and C to the Stockholm Convention Has Come into Force. http://www.mep.gov.cn/gkml/hbb/bgg/201404/t20140401_270007.htm (accessed on May 2, 2015).
- Ministry of Environmental Protection of the People's Republic of China, 2014c. The Synthesize of Dicofof Has Been Stopped. http://news.xinhuanet.com/politics/2014-05/20/c_1110779851.htm (accessed on May 2, 2015).
- Office of the National Coordination Group for Stockholm Convention Implementation, 2007. National Implementation Plan on Stockholm Convention on POPs. <http://www.china-pops.org/guide/popskt/200807/P020121210421015511833.pdf> (accessed on July 3, 2016).
- Park, J.S., Wade, T.L., Sweet, S., 2001. Atmospheric deposition of organochlorine contaminants to Galveston Bay. *Tex. Atmos. Environ.* 35, 3315–3324.
- Peoples Government of Beijing Municipality, 2008. Notice on Air Quality Control Measures during Olympic Games and Paralympic Games. http://www.gov.cn/zwgk/2008-04/14/content_944313.htm (accessed on May 2, 2015).
- Peoples Government of Beijing Municipality, 2014. Notice on Air Quality Control Measures during Asia-Pacific Economic Cooperation (APEC) Meetings. <http://zhengwu.beijing.gov.cn/zfjd/hj/t1371578.htm> (accessed on May 2, 2015).
- Peoples Government of Guangzhou Municipality, 2010. Air Quality Control Measures during Asian Games and Asian Para Games. http://www.mep.gov.cn/zhxx/hjyw/201412/t20141218_293140.htm (accessed on May 2, 2015).
- Poster, D.L., Baker, J.E., 1995. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 2. scavenging of polycyclic aromatic hydrocarbons by rain. *Environ. Sci. Technol.* 30, 349–354.
- Qiu, X., Zhu, T., Li, J., Pan, H., Li, Q., Miao, G., Gong, J., 2004. Organochlorine pesticides in the air around the Taihu Lake, China. *Environ. Sci. Technol.* 38, 1368–1374.
- Ren, J., Wang, X., Xue, Y., Gong, P., Joswiak, D.R., Xu, B., Yao, T., 2014. Persistent organic pollutants in mountain air of the southeastern Tibetan Plateau: seasonal variations and implications for regional cycling. *Environ. Pollut.* 194, 210–216.
- Sheng, J., Wang, X., Gong, P., Joswiak, D.R., Tian, L., Yao, T., Jones, K.C., 2013. Monsoon-driven transport of organochlorine pesticides and polychlorinated biphenyls to the Tibetan Plateau: three year atmospheric monitoring study. *Environ. Sci. Technol.* 47, 3199–3208.
- Tiedeken, J.A., Ramsdell, J.S., 2009. DDT exposure of zebrafish embryos enhances seizure susceptibility: relationship to fetal *p,p'*-DDE burden and domoic acid exposure of California sea lions. *Environ. Heal. Perspect.* 117, 68–73.
- United Nations Environment Programme, 2002. Regionally Based Assessment of Persistent Toxic Substances: South East Asia and South Pacific. <http://www.unep.org/dgef/Portals/43/publications/seaandsp.pdf> (accessed on January 27, 2016).
- van Drooge, B.L., Grimalt, J.O., Torres-García, C.J., Cuevas, E., 2001. Deposition of semi-volatile organochlorine compounds in the free troposphere of the eastern north Atlantic Ocean. *Mar. Pollut. Bull.* 42, 628–634.
- Wang, W., Primbs, T., Tao, S., Simonich, S.L.M., 2009. Atmospheric particulate matter pollution during the 2008 Beijing Olympics. *Environ. Sci. Technol.* 43, 5314–5320.
- Wania, F., Hoff, J.T., Jia, C.Q., Mackay, D., 1998. The effects of snow and ice on the environmental behaviour of hydrophobic organic chemicals. *Environ. Pollut.* 102, 25–41.
- Wania, F., Mackay, D., Hoff, J.T., 1999. The importance of snow scavenging of polychlorinated biphenyl and polycyclic aromatic hydrocarbon vapors. *Environ. Sci. Technol.* 33, 195–197.
- Wei, Y.-L., Bao, L.-J., Wu, C.-C., He, Z.-C., Zeng, E.Y., 2015. Assessing the effects of urbanization on the environment with soil legacy and current-use insecticides: a case study in the Pearl River Delta, China. *Sci. Total Environ.* 514, 409–417.
- Willett, K.L., Ulrich, E.M., Hites, R.A., 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. *Environ. Sci. Technol.* 32, 2197–2207.
- World Health Organization, 2011. Tackling the Global Clean Air Challenge. http://www.who.int/mediacentre/news/releases/2011/air_pollution_20110926/en/index.html (accessed on May 12, 2015).
- Xu, S.-S., Liu, W.-X., Tao, S., 2006. Emission of polycyclic aromatic hydrocarbons in China. *Environ. Sci. Technol.* 40, 702–708.
- Xu, Y., Zhang, G., Li, J., Liu, X., Li, X., 2011. Atmospheric polybrominated diphenyl ethers (PBDEs) and Pb isotopes at a remote site in Southwestern China: implications for monsoon-associated transport. *Sci. Total Environ.* 409, 4564–4571.
- Yang, G.S., Ma, L.L., Xu, D.D., Liu, L.Y., Jia, H.L., Chen, Y., Zhang, Y.B., Chai, Z.F., 2012. Temporal variations of organochlorine pesticides in precipitation in Beijing, China. *Atmos. Environ.* 61, 614–619.
- Yao, Y., Harner, T., Blanchard, P., Tuduri, L., Waite, D., Poissant, L., Murphy, C., Belzer, W., Aulagnier, F., Sverko, E., 2008. Pesticides in the atmosphere across Canadian agricultural regions. *Environ. Sci. Technol.* 42, 5931–5937.
- Yu, H.Y., Shen, R.L., Liang, Y., Cheng, H., Zeng, E.Y., 2011. Inputs of antifouling paint-derived dichlorodiphenyltrichloroethanes (DDTs) to a typical mariculture zone (South China): potential impact on aquafarming environment. *Environ. Pollut.* 159, 3700–3705.
- Yue, Q., Zhang, K., Zhang, B.Z., Li, S.M., Zeng, E.Y., 2011. Occurrence, phase distribution and depositional intensity of dichlorodiphenyltrichloroethane (DDT) and its metabolites in air and precipitation of the Pearl River Delta, China. *Chemosphere* 84, 446–451.
- Zhang, W., Ye, Y., Hu, D., Ou, L., Wang, X., 2010. Characteristics and transport of organochlorine pesticides in urban environment: air, dust, rain, canopy throughfall, and runoff. *J. Environ. Monit.* 12, 2153–2160.
- Zhou, Y., Wu, Y., Yang, L., Fu, L., He, K., Wang, S., Hao, J., Chen, J., Li, C., 2010. The impact of transportation control measures on emission reductions during the 2008 Olympic Games in Beijing, China. *Atmos. Environ.* 44, 285–293.