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# Seasonal Deposition Fluxes and Removal Efficiency of Atmospheric Polybrominated Diphenyl Ethers in a Large Urban Center: Importance of Natural and Anthropogenic Factors

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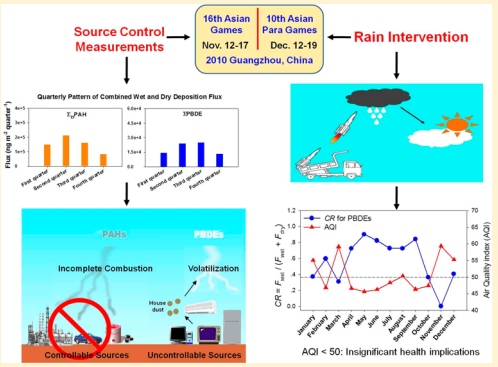
Supporting Information

**ABSTRACT:** Wet deposition is an effective and important mechanism for removal of atmospheric pollutants, particularly in urban regions. To examine the effectiveness of natural and anthropogenic factors in such removal mechanisms, we conducted a study in Guangzhou, a mega metropolitan center in South China. Rainwater and dry particle deposition samples were simultaneously collected from Guangzhou during the entire year of 2010, and analyzed for polybrominated diphenyl ethers (PBDEs), a group of pollutants mainly derived from industrial and household consumer products. Concentrations of ΣPBDE (sum of the 21 congeners of PBDEs) and BDE-209 in wet deposition samples ranged from 0.11 to 640 (average: 23 ± 36 ng $L^{-1}$) and 0.071 to 420 (average: 20 ± 31 ng $L^{-1}$), respectively. Assessed by conditional inference tree, particulate matter was recognized as the most important factor controlling concentration levels of PBDEs. The combined wet and dry deposition flux of ΣPBDE (1.4 (±1.2) × $10^4$ ng $m^{-2}$ $quarter^{-1}$) in the first quarter of 2010 was not significantly different from that (1.3 (±0.46) × $10^4$ ng $m^{-2}$ $quarter^{-1}$) in the fourth quarter, indicating that source control measures implemented by local governments for the 16th Asian Games and 10th Asian Para Games (held in November and December 2010, respectively) were ineffective in reducing the loadings of atmospheric PBDEs. In addition, the lower removal efficiency of ΣPBDE was found in the fourth quarter compared to other quarters. This result suggested that rain interventions conducted to maintain clear weather conditions for the Asian Games turned out to lower the efficacy for removal of PBDEs by wet deposition.




## INTRODUCTION

Air pollution is a global concern, and has been linked to a variety of human health issues.[1] In preparation for the Beijing Olympics Games held in 2008 (http://2008.olympic.cn/), the municipal government of Beijing implemented a series of control measures to ease air pollution (http://sports.cctv.com/20080414/109677.shtml). Some notable measures included partial closure of selected heavy polluters and traffic restrictions (i.e., alternate vehicle usage during weekdays based on the last digit (odd or even) of license plate numbers). Two years later, the government of Guangzhou in South China adopted similar strategies for reducing air pollution when hosting the 16th Asian Games on November 12−27, 2010 and 10th Asian Para Games on December 12−19 of the same year (http://huanbao.huizhou.gov.cn/hbzw/dqhj/xgzl/201010/P020101021625002284935.doc). Because Guangzhou is located in the East Asian Monsoon boundary zone, the local weather pattern is quite distinct, characterized by different wet weather (from April to September) and dry weather (from October to March) seasons with annualized precipitation rates of 1900 and 250 mm, respectively.[2] Therefore, not only were the 16th Asian Games and 10th Asian Para Games held during the dry weather season, but the local government also utilized artificial rain intervention to maintain clear sky.

To examine the effectiveness of the control measures, we analyzed precipitation samples collected during the entire 2010 for particulate matter (PM), total organic carbon, and polycyclic aromatic hydrocarbons (PAHs) and assessed the removal efficacy of these pollutants from the atmosphere through wet deposition.[3] We found that wet deposition was an

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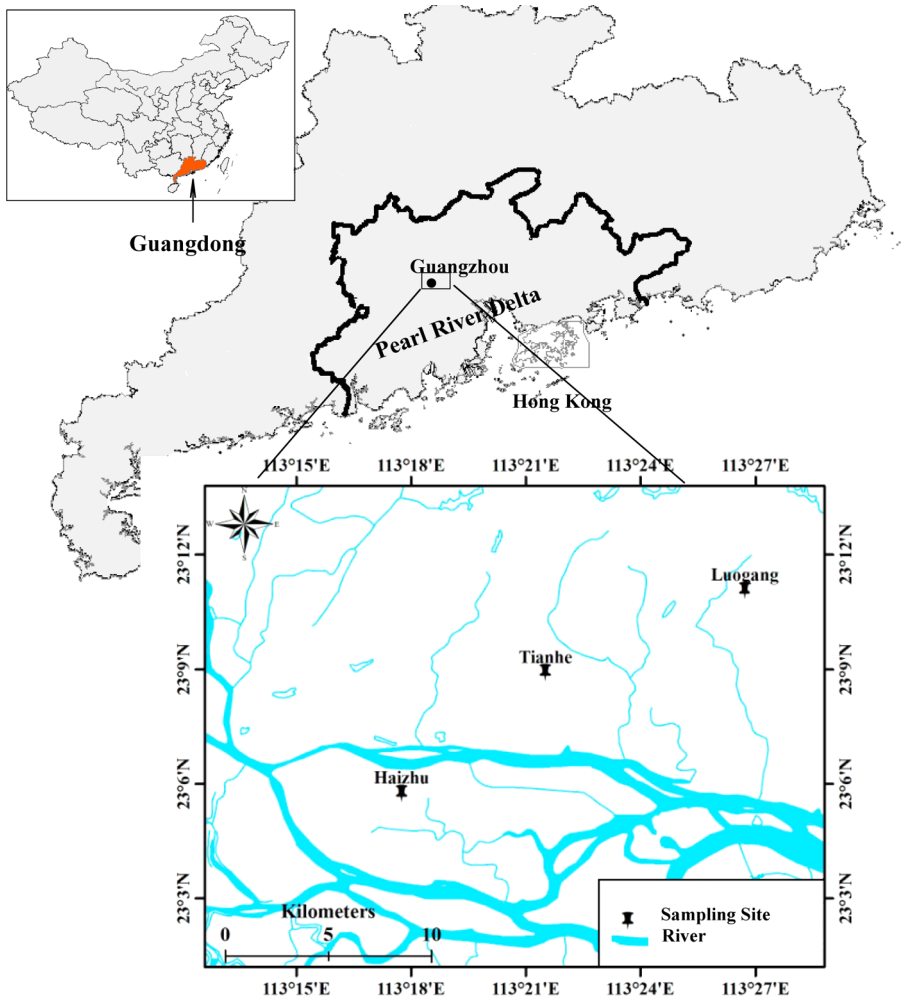


**Figure 1.** Sampling sites of wet deposition (the black points) in Guangzhou. The area surrounded by thick black line in Guangdong Province refers to the Pearl River Delta, China.

important mechanism to remove PAHs and PM from the atmosphere and the related removal rates in November 2010 would have been higher without artificial rain intervention. It is well-known that PAHs are mainly derived from incomplete combustion of fossil fuel and biomass, and automobile exhausts may be the major contributor of PAHs in urban areas in this context.[4,5] As a result, administrative policy limiting the usage of motored vehicles during a certain period of time may work well for PAHs, but not so for other pollutants of different sources. To test this hypothesis and provide further insights into the efficacy of the implemented pollution control measures, we analyzed the same samples for polybrominated diphenyl ethers (PBDEs) and calculated their deposition fluxes and removal efficiencies by wet deposition.

As the main constituents of brominated flame retardants, PBDEs have been widely used in an array of industrial and household products.[6] PBDEs can be leached into the environment during the processes of manufacture, consumer use, and primitive recycling of obsolete electronics devices.[7,8] Because of these attributes, emissions of PBDEs are difficult to control and not expected to show strong seasonal variability. Although previous studies have demonstrated that the source control measures implemented during the Beijing Olympic and Paralympic Games reduced the emission of hydrocarbons and polychlorinated dibenzo-*p*-dioxins and dibenzofurans,[9,10] the effectiveness of such source control measures for reduction of PBDEs in the atmosphere was not identified. Therefore, investigating into PBDEs in dry and wet deposition samples separately collected from Guangzhou would allow the examination of the efficacy for removal of organic pollutants by wet deposition, and therefore the effectiveness of pollution control measures from a different angle.

## MATERIALS AND METHODS

**Sample Collection and Pretreatment.** Three sites located in the districts of Haizhu, Tianhe, and Luogang of Guangzhou were chosen for field sampling (Figure 1). There were 40 and 19 rainfalls during the wet and dry weather seasons, respectively, in 2010. Samples were collected simultaneously for most of these rainfalls at three sites; a few rains occurred only at one or two sites and therefore were sampled separately. Overall, 157 wet deposition samples were collected with 111 during the wet weather season and 46 during the dry weather season. All rainfall samples were immediately transported to the laboratory where they were refrigerated at 4 °C. Within 48 h upon collection, the rainfall samples were filtrated through preweighed glass fiber filters (GF/F; 0.7 $\mu$m nominal pore size; Whatman, Maidstone, England), which were baked at 450 °C prior to use.


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In addition, 12 dry depositing particle samples, respectively integrating all nonraining days over every month of 2010, and 59 aerosol samples from February to November were also collected at the Tianhe district. Aerosol samples were taken via a high-volume air sampler. Approximately 480 $m^3$ of air was passed through a glass fiber filter (GF/F; 20.3 × 25.4 $cm^2$, 0.6 $\mu$m nominal pore size; Whatman, Maidstone, England) to trap airborne particles and subsequently a packed polyurethane foam (PUF) plug (6.5 cm diameter and 8.0 cm thick with a density of 0.03 g $cm^{-3}$) for collecting gaseous organics. All dry deposition particles and aerosol samples were transported to the laboratory and stored at −20 °C until further processing. Detailed sampling and preliminary treatment procedures were described in our previous study.[3]

**Sample Extraction and Instrumental Analysis.** The procedures of extraction and purification were described in detail elsewhere[11] and only a brief description was given herein. Known amounts of the surrogate standards, i.e., $^{13}$C-PCB-141, PCB-204, PCB-209, and $^{13}$C-BDE-209 (AccuStandard, New Haven, CT), were added to each sample before extraction. The filtrated samples were processed by solid phase extraction combined with liquid−liquid extraction, whereas the GFF filters loaded with particulate samples (including wet deposition and aerosol) and PUF plug were processed with Soxhlet extraction. Half of each extract for measuring PBDEs was purified with a glass column packed with neutral alumina (6 cm), neutral silica gel (2 cm), sodium hydroxide silica (5 cm), neutral silica gel (2 cm), sulfuric acid silica gel (8 cm), and anhydrous sodium sulfate (2 cm) from bottom to top. The final extract was concentrated to 0.1 mL under a gentle nitrogen stream and stored in a 2.0 mL crimp-top vial at −20 °C. Known amounts of three internal standards, BDE-69, $^{13}$C-PCB-208, and $^{13}$C-BDE-139 (AccuStandard, New Haven, CT), were spiked to each extract before instrumental analysis.

Concentrations of PBDEs were determined with a Shimadzu Model 2010 gas chromatograph coupled with a QP 2010 plus mass spectrometer (Kyoto, Japan) in the negative chemical ionization mode. A DB-5ht (15 m × 0.25 mm i.d. with 0.10 $\mu$m film thickness) capillary column (J&W Scientific, Folsom, CA) was used for chromatographic separation. The column temperature was initiated at 110 °C (held for 5 min), increased to 200 °C at 40 °C $min^{-1}$ (held for 4 min) and 260 °C at 10 °C $min^{-1}$ (held for 1 min), and finally ramped to 320 °C at 15 °C $min^{-1}$ (held for 15 min). The injection port, transfer line, and ion source temperatures were 290, 300, and 250 °C, respectively. Helium was used as the carried gas at a constant flow of 1.5 mL $min^{-1}$, and methane was the reagent gas for the ionization source. Mass spectral data of PBDEs were acquired in the selective ion monitoring mode.

**Quality Assurance/Quality Control.** A total of 24 field blanks, laboratory blanks, and spiked blanks were analyzed with field samples. The recoveries of the target compounds in spiked blanks ranged from 67 ± 15% to 97 ± 42%. Recoveries of the surrogate standards, i.e. $^{13}$C-PCB-141, PCB-204, PCB-209, and $^{13}$C-BDE-209, were 66 ± 19%, 64 ± 17%, 70 ± 18%, and 69 ± 18% for filtrated samples, whereas they were 68 ± 20%, 69 ± 17%, 71 ± 15%, and 68 ± 17% for particulate samples. In addition, the surrogate standard recoveries were 65 ± 14%, 67 ± 16%, 71 ± 19%, and 68 ± 15% for gas aerosol samples and were 66 ± 12%, 70 ± 15%, 72 ± 16%, and 69 ± 18% for particulate aerosol samples. Data from 11 wet deposition samples were not reported due to operational errors during sample extraction; however, statistical analysis indicated no significant difference ($p > 0.05$) between all measurements with and without these data. Generally, the reporting limit of an analyte was defined as the lowest calibration concentration divided by the sample volume. If the concentration of an analyte in a field blank was higher than the lowest calibration concentration, then this concentration divided by the sample volume was defined as the reporting limit (Supporting Information (SI) Table S1). In addition, the average concentrations of PBDEs in the field blanks were subtracted from all measured concentrations to derive reporting concentrations.

**Data Analysis.** The volume weighted mean (VWM) concentration of an analyte during a certain sampling period is defined as follows:

$$C_{VWM} = \Sigma(C_i \times V_i)/\Sigma V_i \quad (1)$$

where $C_i$ is the concentration of an analyte in a wet deposition sample with a volume of $V_i$. The weighted standard deviation ($SD_W$) for $C_{VWM}$ was estimated by the following approach:[12]

$$SD_w = \sqrt{\frac{M \times \sum((C_i - C_{VWM})^2 \times V_i)}{(M-1) \times \sum V_i}} \quad (2)$$

Monthly wet deposition flux ($F_{wet}$) was estimated by $C_{VWM}$ of a target compound and monthly precipitation amount in 2010 ($Q$) (Table 1):

$$F_{wet} = C_{VWM} \times Q \times 10^{-3} \quad (3)$$

**Table 1. Monthly Volume Weighted Mean Concentrations (Weighted Standard Deviation) of ΣPBDE, BDE-209 (ng $L^{-1}$) and Particulate Matter (PM; mg $L^{-1}$) in Wet Deposition and Precipitation Amount ($Q$; mm) in Guangzhou, China in 2010**

| month | ΣPBDE[a] | BDE-209 | PM[b] | $Q$[c] |
|---|---|---|---|---|
| January | 22 (29) | 15 (24) | 8.5 (47) | 77 |
| February | 35 (85) | 26 (59) | 13 (43) | 73 |
| March | 35 (30) | 27 (23) | 18 (10) | 42 |
| April | 17 (16) | 11 (12) | 11 (10) | 210 |
| May | 17 (35) | 15 (37) | 4.0 (2.9) | 500 |
| June | 22 (21) | 18 (21) | 7.7 (7.9) | 360 |
| July | 32 (26) | 27 (25) | 12 (9.5) | 180 |
| August | 29 (28) | 26 (27) | 11 (9.1) | 150 |
| September | 19 (29) | 16 (26) | 5.8 (7.0) | 470 |
| October | 46 (16) | 41 (15) | 12 (7.6) | 31 |
| November | 460[d] | 420[d] | 30[d] | 0 |
| December | 88 (72) | 76 (63) | 28 (26) | 23 |

[a]Sum of 21 BDE congeners including BDE-15, −17, −28, −47, −66, −77, −99, −126, −138, −153, −154, −181, −183, −190, −196, −203, −204, −206, −207, −208, and −209. [b]Obtained by Guo et al.[3] [c]Obtained from http://www.grmc.gov.cn/Article/2010/12/30/Article_5516.html. [d]A wet deposition sample (4 L) was collected at Tianhe District on November 5, though the precipitation amount was 0 mm during November based on official report.[2]

Dry deposition flux was estimated by two methods. The first method obtained $F_{dry}$ as follows:

$$F_{dry} = M/A \quad (4)$$

where $M$ is the product of mass-based analyte concentration multiplied by the mass of PM, and $A$ is the area of the dry deposition particle collector. The second method calculated the

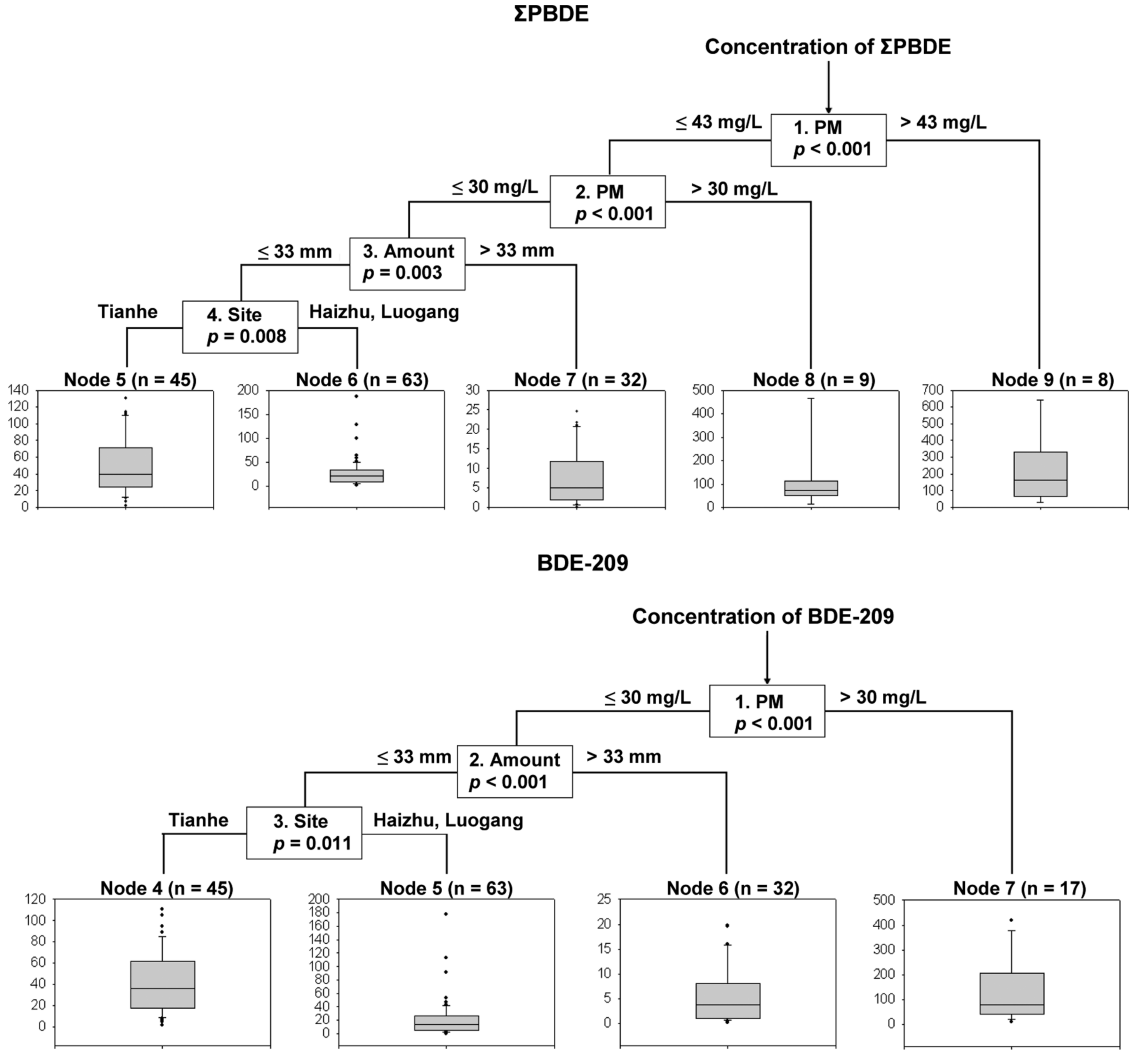


**Figure 2.** Conditional inference trees of ΣPBDE and BDE-209. The variables include sampling site (abbreviated as Site), average temperature between two adjacent rainfalls (Temperature), concentration of PM in each rainfall (PM), and precipitation amount of each rainfall (Amount). The concentrations of ΣPBDE and BDE-209 are expressed in ng $L^{-1}$, and $n$ is the number of samples.

flux ($F_{dry}'$) by the concentration ($C_p$) of a target analyte in a particulate-phase aerosol sample and deposition velocity ($v_d$):

$$F_{dry}' = C_p \times v_d \quad (5)$$

The capacity for removal ($CR$) of pollutants scavenged by wet deposition from the atmosphere is defined as follows:

$$CR = F_{wet}/(F_{wet} + F_{dry}) \quad (6)$$

where $F_{wet}$ and $F_{dry}$ are wet and dry deposition fluxes of a target analyte during a sampling period. The sum of 21 PBDE congeners including BDE-15, -17, -28, -47, -66, -77, -99, -126, -138, -153, -154, -181, -183, -190, -196, -203, -204, -206, -207, -208, and -209 is labeled as ΣPBDE. The square of Spearman correlation coefficient ($r^2$) was used to demonstrate the correlation between two variables. A Welch's $t$-test was used to determine the significant difference between two samples with unequal variances. In all statistical analyses, the criterion of significance was defined as $p < 0.05$.

A stochastic model, i.e., conditional inference tree (CIT), used to identify the key factors responsible for the distribution of PBDEs in wet deposition, is constructed based recursive binary partitioning algorithm using a function:

$$D(Y|X) = D(Y|X_1, X_2..., X_m) = D(Y|f(X_1, X_2..., X_m)) \quad (7)$$

where $Y$ is a response variable, $X = (X_1, X_2..., X_m)$ is an $m$-dimensional covariate vector and $f(X_1, X_2, ..., X_m)$ is a function of the covariate.[13,14] The recursive binary partitioning algorithm for a given population $\Phi_n$ with $n$ samples ($\Phi_n = \{(X_i, X_{1i}, ..., X_{mi}); i = 1, 2, ..., n\}$) is constructed using the corresponding case weight vector ($W = (w1, w2, ..., w_n)$). Each node of the tree is represented by $W$, which is processed by significance test to ensure the quality of splits and remove the missing values. The details of the algorithm were described by Hu and Cheng.[14] Concentrations of ΣPBDE and 21 BDE congeners are selected as $Y$. The variable $X$ includes four factors governing the concentrations of PBDEs in wet deposition, i.e., sampling site (abbreviated as Site), average temperature between two adjacent rainfalls (Temperature), concentration of PM in each rainfall (PM), and precipitation amount of each rainfall (Amount). The Site is a categorical attribute including three sampling sites, i.e., Haizhu, Tianhe, and Luogang. The choices of variables and general partitioning procedures are summarized in the SI. The R software (R Development Core Team, Vienna, Austria) was used for the construction of CIT.

Table 2. Daily Wet Deposition Fluxes ($F_{wet}$; ng m$^{-2}$ d$^{-1}$) and Dry Deposition Fluxes ($F_{dry}$; ng m$^{-2}$ d$^{-1}$) of ΣPBDE and BDE-209 Around the World[a]

| | | | ΣPBDE | | | BDE-209 | | | |
|---|---|---|---|---|---|---|---|---|---|
| sites | sampling period | type | $F_{wet}$ + $F_{dry}$ | $F_{wet}$ | $F_{dry}$ | $F_{wet}$ + $F_{dry}$ | $F_{wet}$ | $F_{dry}$ | reference |
| China | | | | | | | | | |
| Guangzhou | biweekly (2003−2004) | urban | 2300[b] | | | 2200 (270−6000) | | | 17 |
| | monthly (2007−2008) | urban | 220 (69−530)[c] | | | 200 (62−510) | | | 18 |
| | four periods (2006−2007) | urban | | 250[d] | | | 230 | | 11 |
| | August and December 2010 | urban | | | | | | 89, 82[e] | 36 |
| | | | | | | | | 119, 122[f] | 36 |
| | 2010 | urban | 210 (130−360)[g] | 130[g] | 75[g] | 170 (110−300) | 110 | 59 | present study |
| Hong Kong | biweekly (2003−2004) | urban | 260[b] | | | 260 (29−1100) | | | 17 |
| Dongguan | four periods (2006−2007) | semirural | | 44[d] | | | 39 | 70, 41 | 11 |
| Shunde | four periods (2006−2007) | semirural | | 58[d] | | | 48 | 300, 180 | 11 |
| Qingyuan | monthly (2007−2008) | rural | 25 (4.7−65)[c] | | | 12 (1.8−41) | | | 18 |
| Longtang | monthly (2007−2008) | E-waste | 400 (73−980)[c] | | | 360 (64−860) | | | 18 |
| World | | | | | | | | | |
| Lund, Sweden | two perids (2001−2002) | urban | 58[h,i] | 40[h,i] | 18[h,i] | 44[i] | 33[i] | 11[i] | 29 |
| Malmo, Sweden | two periods (2001−2002) | industry | 180[h,i] | 82[h,i] | 99[h,i] | 140[i] | 64[i] | 77[i] | 29 |
| Daeyeon, Korea | monthly (2004) | urban | 140 (73−240)[j] | | | 130 (69−240) | | | 30 |
| Gijang, Korea | monthly (2004) | suburban | 61 (41−130)[j] | | | 55 (39−90) | | | 30 |
| Wolpo, Korea | monthly (2004) | urban | 96 (63−140)[j] | | | 90 (61−110) | | | 30 |
| Haengam, Korea | monthly (2004) | rural | 48 (28−65)[j] | | | 46 (25−61) | | | 30 |
| Lake Maggiore, Italy | March 2005 | industry | 17[l] | | | | | | 19 |

[a]The Ranges, if Available, are Listed in the Parentheses. [b]Sum of 10 BDE congeners including BDE-28, -47, -66, -99, -100, -138, -153, -154, -183, and -209. [c]Sum of 17 BDE congeners including BDE-15, -17, -28, -47, -66, -99, -138, -153, -154, -183, -190, -196, -203, -206, -207, -208, and -209. [d]Sum of 15 BDE congeners including BDE-17, -28, -47, -49, -66, -99, -100, -153, -154, -183, -196, -206, -207, -208, and -209. [e]Sampled at a high of 100 and 150 m in August 2010, respectively. [f]Sampled at a high of 100 and 150 m in December 2010, respectively. [g]Sum of 21 BDE congeners including BDE-15, -17, -28, -47, -66, -77, -99, -126, -138, -153, -154, -181, -183, -190, -196, -203, -204, -206, -207, -208, and -209. [h]Sum of 9 BDE congeners including BDE-28, -47, -66, -99, -100, -153, -154, -183, and -209. [i]Median level. [j]Sum of 20 BDE congeners including BDE-3, -7, -15, -17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -183, and -209. [k]Sum of 7 BDE congeners including BDE-28, -47, -99, -100, -153, -154, and -209. [l]Sum of 8 BDE congeners including BDE-28, -47, -99, -100, -153, -154, -183, and -209.

## RESULTS AND DISCUSSION

**Occurrence of PBDEs in Wet Deposition.** Concentrations of ΣPBDE in wet deposition were in the range of 0.11−640 ng L$^{-1}$, with an average of 23 ± 36 ng L$^{-1}$ and a median of 22.6 ng L$^{-1}$ (SI Table S2). BDE-209 was the main component of ΣPBDE, contributing an average of 83% to the total concentration, followed by BDE-47 (5.6%) and BDE-99 (1.6%) (SI Figure S1). This compositional profile was consistent with previous results from analyses of aerosol and particle samples collected across China,[15,16] suggesting that PBDEs were mainly derived from technical Deca-BDE.[11,17,18] In addition, the annual $C_{VWM}$ of ΣPBDE was much greater in the particulate phase (22 ± 35 ng L$^{-1}$) than in the dissolved phase (3.0 ± 4.9 ng L$^{-1}$) (SI Table S2), obviously due to the predominance of BDE-209 in the particulate phase (19 ± 31 and 1.6 ± 4.4 ng L$^{-1}$ in the particulate and dissolved phases, respectively). Overall, the annual $C_{VWM}$ of ΣPBDE in wet deposition of the present study areas was much greater than those in rural or semirural regions in Europe, Asia and North America ($p < 0.05$), i.e., 1.3 ng L$^{-1}$ in Lake Maggiore of Italy,[19] 9.1 and 12 ng L$^{-1}$ in Dongguan and Shunde of China,[11] 0.65, 0.73, and 1.0 ng L$^{-1}$ in Sturgeon Point, Sleeping Bear Dunes, and Eagle Harbor around the Great Lakes,[20] but was comparable to or slightly lower than those obtained in urban regions of Europe, Asia, and North America ($p < 0.05$), i.e., 38 ng L$^{-1}$ in Paris,[21] 51 ng L$^{-1}$ in Guangzhou[11] and 94 ng L$^{-1}$ in Chicago[20] (SI Table S2). Therefore, the concentrations of PBDEs in wet deposition from Guangzhou were in the middle of the global range, and abundant PBDEs occurred in wet deposition collected in urban regions across the globe.

Higher monthly ΣPBDE concentrations (Table 1) generally occurred during the dry weather season compared to the wet weather season, which was attributed to dilution effects as corroborated by a negative correlation between the precipitation amounts and ΣPBDE concentrations ($r^2 = 0.81$, $p < 0.05$).[3,22] Spatially, no significant variance of ΣPBDE concentrations ($p > 0.05$; paired $t$-test) was found among the sampling sites with different urbanization levels.[23] Similar seasonal and spatial patterns were also observed for PAHs.[3] This similarity between PBDEs and PAHs probably suggested strong atmospheric convective mixing in Guangzhou,[24] as these two groups of contaminants are mainly derived from completely different sources, i.e., volatilization from electronic products for PBDEs and incomplete combustion of fossil fuel and biomass for PAHs.[4,8]

**Key Factors Controlling the Occurrence of PBDEs in Wet Deposition.** Detailed CIT results for ΣPBDE and BDE-209 are shown in Figure 2, whereas those for individual BDE congeners are displayed in SI Figure S2. Generally, the CITs of ΣPBDE and individual BDE congeners shared some common features. First, the most important splitting factor of the root nodes for ΣPBDE and 20 BDE congeners except for BDE-183 was PM content, indicating a strong contribution from PM. In addition, PM content was also the first splitting factor for the

left branches in CITs of ΣPBDE and 12 BDE congeners (Figure 2 and SI Figure S2). Thus, the distribution of PBDEs in wet deposition was dictated by PM, which was also demonstrated by the significant positive correlation between monthly ΣPBDE concentrations and PM ($r^2$ = 0.81, $p$ < 0.05). However, the PM contents were high for low molecule weight (LMW) PBDEs (defined as di-BDEs to hepta-BDEs) and low for high molecule weight (HMW) PBDEs (defined as octa-BDE, nona-BDE, and deca-BDE), e.g., the PM node for CIT of BDE-209 was characterized by lower PM content (30 mg $L^{-1}$) than those of BDE-47 (43 mg $L^{-1}$) and BDE-17 (60 mg $L^{-1}$). This may be resulted from different octanol−water partition coefficients for these target compounds (SI Table S3),[25,26] i.e., HMW PBDEs are tend more likely to affiliate with particulate matter compared to LMW PBDEs.

Second, precipitation amount, the splitting factor in CITs of ΣPBDE and 19 PBDE congeners, was lower for greater PBDE concentrations, confirming the importance of dilution effects. The median concentration of ΣPBDE (38 mg $L^{-1}$) in wet deposition samples with precipitation amounts less than 33 mm was five times higher than that (7.7 mg $L^{-1}$) in samples with precipitation amounts greater than 33 mm. In contrast, other factors were not as decisive as PM content and precipitation amount. For example, spatial variance was the splitting factor in CITs of ΣPBDE and five BDE congeners (BDE-15, -47, -153, -208, and -209) only; thereby it was not a controlling factor in the occurrence of PBDEs in wet deposition. Furthermore, none of the nodes in CIT was spitted with temperature, although temperature was regarded as a primary factor governing the emission of PBDEs into air.[15,18] It appears that PM and precipitation amount were more important than spatial variance and temperature in controlling the occurrence of PBDEs in wet deposition, probably because they are directly related to phase partitioning and washout processes, respectively.[27,28]

**Deposition Flux.** The annual deposition flux of an analyte is defined as the sum of 12 monthly deposition fluxes (SI Table S4). In the present study, the annual $F_{wet}$ of ΣPBDE and BDE-209 were 4.8 (±6.2) × $10^4$ and 4.0 (±5.0) × $10^4$ ng $m^{-2}$ $yr^{-1}$, respectively (SI Table S5). Similarly, the annual $F_{dry}$ of ΣPBDE and BDE-209 were 2.7 (±0.55) × $10^4$ and 2.2 (±0.43) × $10^4$ ng $m^{-2}$ $yr^{-1}$, respectively (SI Table S5). In addition, the annual $F_{dry}'$ of ΣPBDE and BDE-209 were 3.4 (±0.68) × $10^4$ and 2.5 (±0.51) × $10^4$ ng $m^{-2}$ $yr^{-1}$, respectively (SI Table S5). As expected, there was no significant difference ($p$ > 0.05; $t$-test) between the annual $F_{dry}$ and $F_{dry}'$ of individual BDE congeners. This finding indicated that PBDEs in dry particles did not degrade substantially during long-term sampling (e.g., one month); subsequently, the approaches based on eqs 4 and 5 were equivalent in measuring dry deposition fluxes of PBDEs. As a result, the dry deposition fluxes of PBDEs obtained from both two methods were deemed comparable.

The combined daily wet and dry deposition fluxes of ΣPBDE (210 ng $m^{-2}$ $d^{-1}$) and BDE-209 (170 ng $m^{-2}$ $d^{-1}$) in the present study were greater than those obtained in other urban regions ($p$ < 0.05), e.g., Lund of Sweden (58 ng $m^{-2}$ $d^{-1}$ for ΣPBDE)[29] and Daeyeon of South Korea (140 and 130 ng $m^{-2}$ $d^{-1}$ for ΣPBDE and BDE-209, respectively),[30] and comparable to those (220 and 200 ng $m^{-2}$ $d^{-1}$ for ΣPBDE and BDE-209, respectively) also obtained in Guangzhou ($p$ < 0.05),[18] but lower than those (400 and 360 ng $m^{-2}$ $d^{-1}$ for ΣPBDE and BDE-209, respectively) in Longtang of South China ($p$ < 0.05), one of China's largest regions for e-waste recycling (Table 2).[18] Undoubtedly, e-waste recycling could be an important source contributing to wet and dry depositions of PBDEs in the study region.[31] It is also interesting to note that a strong correlation was observed between population densities and combined daily wet and dry deposition fluxes of ΣPBDE ($r^2$ = 0.81, $p$ < 0.05) for five urban regions in the world (SI Figure S3). A plausible explanation for this good correlation is that PBDEs in urban regions were predominantly derived from volatilization of household electronic products.

On a quarterly basis, the combined wet and dry deposition flux of ΣPBDE (1.4 (±1.2) × $10^4$ ng $m^{-2}$ $quarter^{-1}$) in the first quarter (January to March) was not significantly different from that (1.3 (±0.46) × $10^4$ ng $m^{-2}$ $quarter^{-1}$) in the fourth quarter (October to December) (Figure 3). However, the same

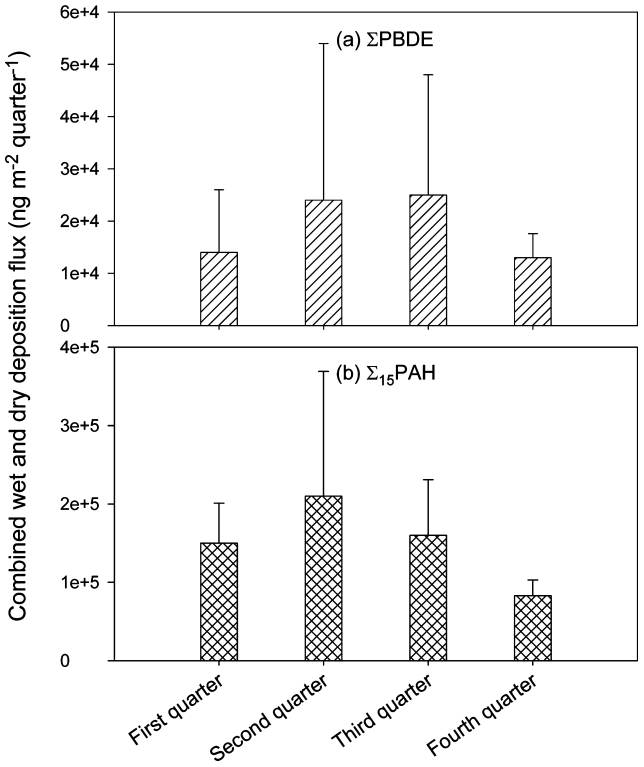


**Figure 3.** Combined wet and dry deposition fluxes of ΣPBDE and $\Sigma_{15}$PAH in four quarters of 2010 in Guangzhou, China. Data for $\Sigma_{15}$PAH (sum of the 16 priority PAHs designated by the United States Environmental Protection Agency minus naphthalene) were acquired from our previous study.[3]

samples had the greater ($p$ < 0.05) combined deposition flux of $\Sigma_{15}$PAH (sum of the 16 priority PAHs designated by the United States Environmental Protection Agency minus naphthalene) in the first quarter (15 (±5.1) × $10^4$ ng $m^{-2}$ $quarter^{-1}$) than in the fourth quarter (8.3 (±2.0) × $10^4$ ng $m^{-2}$ $quarter^{-1}$) (Figure 3). Moreover, the concentrations of ΣPBDE in aerosol samples of the fourth quarter (0.67 ± 0.52 ng $m^{-3}$) were comparable with those in three other quarters (0.48 ± 0.60, 0.77 ± 0.44, and 0.80 ± 0.54 ng $m^{-3}$ for the first, second and third quarters, respectively) ($p$ > 0.05; independent $t$-test). By comparison, the concentrations of $\Sigma_{15}$PAH in aerosol samples of the fourth quarter (58 ± 31 ng $m^{-3}$) were lower than those in the second quarter (106 ± 48 ng $m^{-3}$) ($p$ < 0.05; independent $t$-test). These quarterly patterns of ΣPBDE and $\Sigma_{15}$PAH concentrations suggested that contaminant source control measures implemented by the local governments in preparation for the 16th Asian Games and 10th Asian Para

Games were only partially efficient. Apparently, these measures, including removing half of the registered motored vehicles off the roads under an even−odd license plate system from 8:00 to 20:00, partial closure of heavy pollution emitting outlets (e.g., power plants and industrial boilers) and no use of high-emission fuels (e.g., coal and heavy oil) in restaurants,[32] indeed resulted in reduced emissions of PAHs, but did not yield similar results for PBDEs. Apparently, any policy and/or regulation intended for reducing emissions of organic pollutants need to take into account the differences in emission sources of contaminants, such as PBDEs and PAHs.

**Removal Efficiency by Wet Deposition.** Wet deposition is an important mechanism for removing contaminants from the atmosphere. The annual *CR* value of ΣPBDE, a parameter describing the effectiveness of wet deposition in removing pollutants from air, was 0.64 in 2010 in Guangzhou, indicating that wet deposition appeared to play a dominant role in scavenging organic pollutants from the atmosphere in a subtropical region with high humidity. On a quarterly basis, the *CR* values of ΣPBDE were 0.42, 0.83, 0.78, and 0.26 in the first, second, third, and fourth quarters, respectively. This pattern was also similar to that of $\Sigma_{15}$PAH.[3] The lower removal efficiency of ΣPBDE in the fourth quarter was mainly ascribed to lower amounts of precipitation and subsequent lower wet deposition flux in November. As mentioned above, the local governments conducted artificial rain interventions in November in an attempt to maintain clear sky during the 16th Asian Games and 10th Asian Para Games.[33] The rain interventions, i.e., cloud seedings were taken in Qiaoqing, Yunfu, and Qingyuan, which lie in the upwind regions of Guangzhou in November and December 2010.[33] Spraying with dry ice or silver iodide by rockets allowed high concentrations of artificial ice nuclei to accumulate into cold clouds, which drastically reduced the concentrations of supercooled droplets and thereby inhibited the growth of ice particles through riming and deposition, subsequently dissipated the clouds and suppressed the growth of precipitable particles (maths.ucd.ie/met/msc/fezzik/Synop-Met/Ch06-6-8-Slides.pdf). In addition, the average value of air quality index, an index for daily air pollution levels and associated public health risk to humans in China,[34] was 59 in November 2010 in Guangzhou,[35] indicating that hypersensitive individuals should reduce outdoor exercise. Therefore, these results further demonstrated that artificial rain intervention would lower the removal efficiency of pollutants by wet deposition, which would subject local residents to higher health risk through respiratory exposure.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Additional tables and figures containing reporting limits, wet and dry deposition fluxes, and results for CITs for all BDE congeners. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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