



# Significance of wet deposition to removal of atmospheric particulate matter and polycyclic aromatic hydrocarbons: A case study in Guangzhou, China



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## HIGHLIGHTS

- Increased use of cleaner energy lowers the PAH levels in rain from 2005 to 2010.
- Washout ratio of organic pollutants decreases with increasing rainfall intensity within 0–6 mm h<sup>-1</sup>.
- Wet deposition is significant for removing PM and PAHs, especially when rainfalls are scarce.

## GRAPHICAL ABSTRACT



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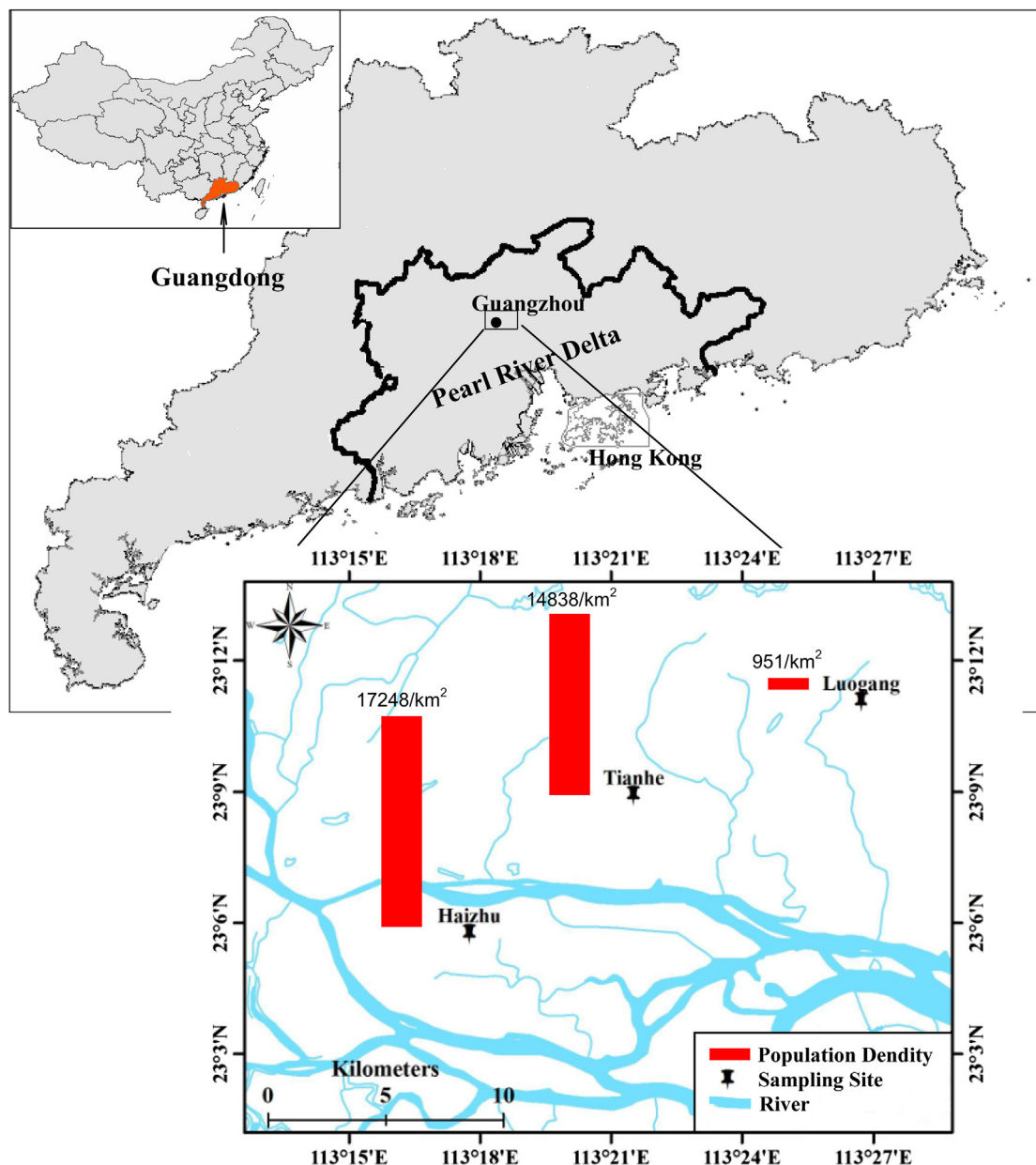
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## ABSTRACT

Rainwater samples were simultaneously collected from three locations in Guangzhou, a mega metropolitan center in South China, during the entire year of 2010, and analyzed for particulate matter (PM), total organic carbon and polycyclic aromatic hydrocarbons (PAHs), with the objectives of assessing the seasonality of washout effects and efficiency for removal of pollutants from the atmosphere by wet deposition. The contents of PM, particulate organic carbon, and dissolved organic carbon were in the ranges of 0.74–420 (average: 8.1 mg L<sup>-1</sup>), 0.16–40 (average: 1.3 mg L<sup>-1</sup>), and 0.34–6.9 mg L<sup>-1</sup> (average: 1.4 mg L<sup>-1</sup>), respectively. Concentrations of  $\Sigma_{15}\text{PAH}$  (sum of the 16 priority PAH compounds defined by the United States Environmental Protection Agency minus naphthalene) in wet deposition samples ranged from 39 to 1580 ng L<sup>-1</sup> with an average of 170 ng L<sup>-1</sup>. The PAH concentration levels were slightly abated compared to those acquired previously in Guangzhou during the year of 2005, probably indicating a favorable change of energy consumption patterns in the region. There were moderately significant negative correlations between washout ratios and rainfall intensities (0–4.3 mm h<sup>-1</sup>). The total annual fluxes of wet and dry depositions combined for PM and PAHs in the urban area of Guangzhou were 34 g m<sup>-2</sup> yr<sup>-1</sup> and 6.0 × 10<sup>2</sup> μg m<sup>-2</sup> yr<sup>-1</sup> with 50 and 57% being contributed from wet deposition, respectively. The monthly capacity for removal (CR) of PM and PAHs (calculated as the wet deposition flux dividing the total flux) varied widely with different months, and was lower during the dry weather season (January–March and October–December) than during the wet weather season (April–September). Finally, the air quality index related to PM<sub>10</sub> was negatively correlated to CR values of PM and PAHs, indicating the need to control the emissions of anthropogenically derived pollutants during the dry weather season.

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**Fig. 1.** Map showing the sampling sites (Tianhe, Haizhu and Luogang) in Guangzhou, China. The red bars indicate the population densities in these three sampling areas (Statistical Bureau of Guangzhou City, 2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 1. Introduction

Worsening air pollution in urban areas, a global environmental problem, is often associated with accelerated urbanization processes, and may adversely affect human health (WHO, 2011). To evaluate the magnitude of air pollution, indicative pollutants are often monitored and their trends are tracked. For example, among the six common air pollutants and 187 toxic air pollutants listed by the United States Environmental Protection Agency (USEPA), particulate matter (PM) and organic pollutants are the priority contaminants (USEPA, 2010). The USEPA in 1997 revised its air quality standards and proposed a standard for airborne PM less than 2.5  $\mu\text{m}$  diameter (PM<sub>2.5</sub>) to address potential health issues posed by these respirable particles, which are in a size range small enough to penetrate deeply into human lungs and therefore have direct and deleterious health effects (USEPA, 1997). Due

to the adoption and implementation of the air quality standards and regulations, levels of atmospheric PM and organic pollutants decreased, and at the same time air pollution was eased in the last 10 years (USEPA, 2010).

One of the main mechanisms for removal of PM and organic pollutants from the atmosphere is wet deposition. In addition, total organic carbon (TOC) in wet deposition, comprised of particulate organic carbon (POC) and dissolved organic carbon (DOC), can be used to evaluate the magnitude of organic pollution in precipitations. Similarly, levels of polycyclic aromatic hydrocarbons (PAHs) in rainwater may also be used to reflect air pollution by total hydrocarbons and investigate their removal patterns during wet deposition. Therefore, PM, TOC, and PAHs were selected as the target analytes in the present study to examine any possible link between the characteristics (e.g., amount and intensity) of wet deposition and its efficacy for removal of PM and organic pollutants from the atmosphere.

Guangzhou is located in the middle of the Pearl River Delta (PRD; Fig. 1), one of the economically fastest growing regions in China. With rapid urbanization and steadily increasing population, the city has gradually transformed itself into a mega urban center. Partly because of its geographic locality within the East Asian Monsoon boundary zone and at low altitudes, Guangzhou embraces heavy precipitations with clear seasonal pattern, i.e., the wet and dry weather seasons run from April to September and from October to March, respectively, with annualized precipitation rates of 1900 and 250 mm (Guangzhou Meteorological Bureau, 2010). As a result, Guangzhou was considered an appropriate site for investigating wet washout patterns and their role in mitigating air pollution under the premise of rapid urbanization and intensive anthropogenic activities.

To accomplish the above-stated objectives, rainfall samples collected in Guangzhou for the entire year of 2010 were analyzed for PM, TOC, and PAHs. In addition, dry deposition and aerosol samples were also collected and analyzed, from which the seasonal washout patterns and capability of wet deposition in removal of the target analytes from the atmosphere were examined. The results from the present study are expected to enhance the ongoing efforts in battling haze weathers in China, by better defining the role of wet deposition in removing PM and organic pollutants from the atmosphere, so that efficient control measures can be implemented in response to climatic conditions and pollutant input patterns.

## 2. Materials and methods

### 2.1. Sample collection and pretreatment

Three sites located at the districts of Haizhu, Tianhe, and Luogang, representative of heavy, moderate, and light urbanization in Guangzhou, were chosen for field sampling (Fig. 1). Individual samples at each sampling site were collected with six stainless steel platters of 76.5-cm diameter, operated manually, during each significant rainfall event (with precipitation higher than 1 mm within 48 h) over the entire year of 2010. The platters were exposed to the atmosphere during rainfalls only, but covered otherwise. If an individual rainfall within 48 h was less than 1 mm, samples collected from multiple precipitations at the same site were combined. A stainless steel brush was used to sweep particulates stuck to the platters into rainwater, which was collected into 10-L brown glass bottles (pre-cleaned with distilled water three times) and transported to the laboratory immediately. Overall, 157 rain samples were collected at three sampling sites, with 111 from April to September and 46 from October to March.

In addition, dry particle deposition and aerosol samples were also collected during the dry and wet weather periods, respectively, at Tianhe District. Dry deposition samples were taken monthly with a platter filled with distilled water; therefore, each sample was a cumulative collection of particles for the entire month during dry weather. Eleven aerosol samples (particle and gas separately) were collected from time to time (Table S1 of the Supplementary material; "S" indicates the tables and figures in the Supplementary material thereafter) using a high-volume air sampler containing a glass fiber filter (GF/F;  $20.3 \times 25.4 \text{ cm}^2$ ,  $0.6 \mu\text{m}$  nominal pore size; Whatman, Maidstone, England) for collecting particles and a polyurethane foam plug (PUF; 6.5 cm diameter and 8.0 cm thick with a density of  $0.03 \text{ g cm}^{-3}$ ) for collecting gases. Prior to sampling, GF/Fs were pre-baked at  $450^\circ\text{C}$  for 4 h, whereas PUF plugs were Soxhlet extracted for 48 h with methanol and for another 48 h with dichloromethane (DCM). Flow rates were carefully adjusted to prevent the breakthrough of PUF plugs.

Within 48 h upon collection, rainwater samples were filtered through 142-mm (diameter) pre-weighed GF/F glass fiber filters

( $0.7 \mu\text{m}$  pore size; Whatman, Maidstone, England), pre-baked at  $450^\circ\text{C}$  for 4 h. Loaded filters were wrapped with aluminum foil, whereas PUF plugs were stored in cleaned glass jars with aluminum foil-lined lids; they were all stored at  $-20^\circ\text{C}$  until analysis. Before extraction, each loaded filter was freeze-dried and re-weighed to obtain PM mass and divided into two parts and analyzed for POC and PAHs, respectively. Contents of PM and PAHs were determined in all particulate samples, but POC was determined in 163 samples only (including 157 wet deposition samples and six dry deposition samples) due to insufficient sample amounts for the remaining six dry deposition samples. In addition, only one third of wet deposition samples (54) were analyzed for DOC, because DOC measurements without acidification have to be done quickly (Wallace, 2011), which could not be easily achieved in the present study.

### 2.2. Sample extraction

Residual PAHs in filtered samples were retained in glass columns ( $400 \text{ mm} \times 25 \text{ mm}$  i.d.), packed with a mixture of XAD-2 and XAD-4 resins (1:1 in mass) ultrasonically cleaned with methanol prior to use. The columns were eluted three times each with 50 mL of methanol and three times each with 50 mL of a DCM:methanol mixture (1:1 in volume). The resins were extracted three times each with 50 mL of the DCM:methanol mixture in an ultrasonic bath. The extract and eluent were combined and spiked with known amounts of surrogate standards (naphthalene- $d_8$ , acenaphthene- $d_{10}$ , phenanthrene- $d_{10}$ , chrysene- $d_{12}$ , and perylene- $d_{12}$ ; AccuStandard, New Haven, CT, USA). The combined solution was further liquid–liquid extracted four times, each with a solution of 5 g of NaCl, 500 mL of distilled water, and 50 mL of DCM. Loaded GF/F filters were freeze-dried and weighed to obtain mass contents. Both the GF/F filters and PUF plugs were spiked with the surrogate standards and Soxhlet-extracted for 48 h with 220 mL of DCM:hexane:acetone (2:2:1 in volume).

All extracts were concentrated, solvent-exchanged to hexane, and further concentrated to 1 mL with a Zymark TurboVap 500 (Hopkinton, MA, USA). They were purified and fractionated with glass columns ( $400 \text{ mm} \times 10 \text{ mm}$  i.d.) packed with alumina: silica gel (1:2 in volume). The fraction containing PAHs was eluted with 85 mL hexane:DCM (7:3 in volume) mixture, concentrated to 1 mL and solvent-exchanged to hexane, and further concentrated to 0.5 mL under a gentle stream of  $\text{N}_2$ . Internal standards, i.e., 2-fluoro-1,1-biphenyl, *p*-terbenyl- $d_{14}$ , and dibenzo[*a,h*]anthracene- $d_{14}$  (AccuStandard) were added to each extract prior to instrument analysis.

### 2.3. Instrumental analysis

Contents of DOC in filtered samples were determined with a Shimadzu (Kyoto, Japan) TOC-VCPH analyzer. Oxygen was used as carrier gas at a flow rate of  $150 \text{ mL min}^{-1}$  and a pressure of 200 kPa. Each sample was repeatedly analyzed three times to acquire a mean value. For POC measurement, each loaded filter sample was divided equally into two subsamples, packed with tinfoil, and analyzed using an Elementar (Vario, EL III, Germany) elemental analyzer. Helium was used as carrier gas at a flow rate of  $230 \text{ mL min}^{-1}$  and a pressure of 120 kPa. The combustion tube temperature was maintained at  $950^\circ\text{C}$  before injection. After sample injection, oxygen was carried into the system at a rate of  $25 \text{ mL min}^{-1}$  and held for 80 s. The combustion tube temperature was raised to  $1800^\circ\text{C}$  and held for 5 s. To minimize any potential uncertainty, the measurements of POC and DOC in collected samples were performed within 48 and 24 h, respectively.

Concentrations of 16 priority PAH components (USEPA, 2008) were determined with a Shimadzu Model 2010 GC–MS equipped

with an AOC-20i auto injector (Kyoto, Japan). A TG-5ms (30 m × 0.25 mm i.d. with 0.25 μm film thickness) capillary column with helium as carrier gas at a flow rate of 1 mL min<sup>-1</sup> was used for chromatographic separation. The column temperature was programmed from 60 °C to 200 °C at a rate of 10 °C min<sup>-1</sup>, ramped to 250 °C at 5 °C min<sup>-1</sup>, and finally raised at 20 °C min<sup>-1</sup>–290 °C (held for 25 min). The injector temperature was set at 280 °C. Extract injection was conducted in the splitless mode, with a split time of 0.75 min after injection. Mass spectral data of PAHs were acquired in the selective ion monitoring mode.

#### 2.4. Quality assurance/quality control

Both POC and DOC were quantified by an external calibration method. The calibration for POC was done based on 15 mass levels with acetanilide (AccuStandard) as the standard, and the detection limit was defined as the lowest calibration mass (30 μg). Measurement precision was assessed by one triplicate analysis for every 10 samples (a total of 15 triplicate analyses), and the relative standard deviations were all smaller than 0.3%. In addition, DOC was quantified with five-point calibration with potassium hydrogen phthalate (AccuStandard) as the calibration standard, and the detection limit for DOC was 0.01 mg L<sup>-1</sup>. All DOC measurements were done three times and the relative standard deviations were all less than 10%; the average value of three measurements was reported. A laboratory blank was processed for each batch of 15 samples, and a procedural blank was processed for each batch of 30 samples. Analyte concentrations in all laboratory blanks were lower than the detection limit. The average POC and DOC contents in procedural blanks were 100 μg and 0.25 mg L<sup>-1</sup>, respectively, and were subtracted from all measured values in field samples.

A total of 19 field blanks, laboratory blanks and spiked blanks were analyzed with field samples for PAHs. If the field blank concentration of an analyte (Table S2) was higher than the lowest level on the calibration curve (0.02 μg mL<sup>-1</sup>), this lowest concentration level divided by sample volume (3–413 L) was defined as the reporting limit (0.037–3.3 ng L<sup>-1</sup>) for each target compound. In addition, the average concentrations of PAHs in the field blanks were subtracted from all measured concentrations to derive reporting concentrations. Due to high background levels in field blanks, naphthalene was excluded from data reporting. The recoveries of target compounds in spiked blanks were in the range of 40 ± 8% to 138 ± 6%. The recoveries of the surrogate standards were 45 ± 13% for naphthalene-*d*<sub>8</sub>, 62 ± 12% for acenaphthene-*d*<sub>10</sub>, 71 ± 13% for phenanthrene-*d*<sub>10</sub>, 78 ± 13% for chrysene-*d*<sub>12</sub> and 71 ± 14% for benzo[*g,h,i*]perylene-*d*<sub>12</sub> in filtrate samples, whereas they were 49 ± 12% for naphthalene-*d*<sub>8</sub>, 67 ± 14% for acenaphthene-*d*<sub>10</sub>, 73 ± 14% for phenanthrene-*d*<sub>10</sub>, 82 ± 15% for chrysene-*d*<sub>12</sub> and 76 ± 26% for benzo[*g,h,i*]perylene-*d*<sub>12</sub> in particulate samples. Measured concentrations were not corrected with the recoveries of the surrogate standards.

#### 2.5. Data analysis

All measured concentrations were normalized to water sample volume. The volume weighted mean (VWM) concentration of an analyte during a certain sampling period is defined as follows:

$$C_{VWM} = \frac{\sum(C_i \times V_i)}{\sum V_i} \quad (1)$$

where  $C_i$  is the concentration of an analyte in a wet deposition sample,  $V_i$  is the related sample volume, and the summation covers the number of rainfalls for the entire sampling period (often designated as a month or a year). Only  $C_{VWM}$  is discussed in the

remainder of this paper except where otherwise specified. The weighted standard deviation ( $SD_w$ ) for  $C_{VWM}$  is defined as follows:

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

where  $M$  is the number samples. The sum of 16 target PAHs minus naphthalene is labeled as  $\Sigma_{15}$ PAH. High molecular weight (HMW) PAHs include benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene; while low molecular weight (LMW) PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. In addition, PAH source diagnostic ratios used include benzo[*a*]anthracene/(benzo[*a*]anthracene + chrysene) and indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[*g,h,i*]perylene). The square of Spearman correlation coefficient ( $r^2$ ) was used to demonstrate the correlation between two variables, with  $p < 0.05$  as the criterion of significance. A one-way analysis of variance (ANOVA) with statistical significance defined at  $p < 0.05$  was used to evaluate the temporal trends of PM, POC, DOC, and PAH concentrations. A paired  $t$ -test was used to demonstrate the significant difference between two corresponding variables, with  $p < 0.05$  as the criterion of significance.

### 3. Results and discussion

#### 3.1. Occurrence and spatial distribution of particulate matter, total organic carbon and polycyclic aromatic hydrocarbons in wet deposition

Concentrations of PM, POC, and DOC in wet deposition samples (Table S3) were in the ranges of 0.74–420 (average: 8.1 ± 15 mg L<sup>-1</sup>), 0.16–40 (average: 1.3 ± 18 mg L<sup>-1</sup>), and 0.34–6.9 mg L<sup>-1</sup> (average: 1.4 ± 1.2 mg L<sup>-1</sup>), respectively. The annual  $C_{VWM}$  of POC (1.3 mg L<sup>-1</sup>) was higher than the levels obtained from forestry and semi-rural regions in the United States, i.e., 0.20 mg L<sup>-1</sup> in Hubbard Brook of New York (Likens et al., 1983) and 0.73 mg L<sup>-1</sup> in Wilmington of North Carolina (Kieber et al., 2006). Similarly, the annual  $C_{VWM}$  of DOC (1.4 mg L<sup>-1</sup>) in the present study was lower than other measurements conducted in urban and forest regions in North America and Asia, i.e., 1.9 mg L<sup>-1</sup> in Ithaca of New York (Likens et al., 1983), 3.0 mg L<sup>-1</sup> in North China (Pan et al., 2010), 3.6 mg L<sup>-1</sup> in Guangzhou (Xu et al., 2008), 6.7 mg L<sup>-1</sup> in Los Angeles (Kawamura et al., 2001), and 6.8 and 2.1 mg L<sup>-1</sup> (spring and summer) in Xi'an of China (Tian et al., 2011), but higher than those in coastal areas in north America (1.1 mg L<sup>-1</sup>) (Likens et al., 1983).

Concentrations of  $\Sigma_{15}$ PAH in wet deposition samples (Table 1) were in the range of 39–1580 ng L<sup>-1</sup> (average: 170 ± 130 ng L<sup>-1</sup>), with those in the particulate phase ranging from 22 to 980 ng L<sup>-1</sup> (average: 110 ± 93 ng L<sup>-1</sup>) and those in the dissolved phase varying between 17 and 780 ng L<sup>-1</sup> (average: 59 ± 52 ng L<sup>-1</sup>). The annual  $C_{VWM}$  of  $\Sigma_{15}$ PAH in Guangzhou (170 ng L<sup>-1</sup>) was lower than those obtained from industrial regions with high population densities in Europe and Asia, i.e., 210 ng L<sup>-1</sup> in Wielkopolski and 280 ng L<sup>-1</sup> in Pozan (Walna et al., 2001), 360 ng L<sup>-1</sup> in Paris (Ollivon et al., 2002), 430 ng L<sup>-1</sup> in Northern Greece (Manoli et al., 2000), 540 ng L<sup>-1</sup> in Hungary (Kiss et al., 1996), 580 ng L<sup>-1</sup> in Fortaleza of Brazil (Cavalcante et al., 2012), 1340 ng L<sup>-1</sup> in Ankara of Turkey (Gaga et al., 2009), and 1910 ng L<sup>-1</sup> in Guangzhou (Huang et al., 2009), but higher than those from small towns and rural areas in Europe, i.e., 72 ng L<sup>-1</sup> in west of Paris (Motelay-Massei et al., 2003), 93 ng L<sup>-1</sup> in Brno (Skrdliková et al., 2011), and 110 ng L<sup>-1</sup> in Northern Italy (Olivella, 2006).

Generally, concentrations of PM, POC, DOC and  $\Sigma_{15}$ PAH at all three sampling sites showed consistent seasonal patterns, with

**Table 1**  
Concentrations (volume weighted mean values  $\pm$  weighted standard deviation in parentheses;  $\text{ng L}^{-1}$ ) of PAHs (P for particulate phase and D for dissolved phase) in wet deposition of Guangzhou (2010) and other previous reports. The volume weighted means in the parentheses are annual average values.

Sampling time	Sites	PAH type	$\Sigma$ PAH	$\Sigma$ PAH (P)	$\Sigma$ PAH (D)	Reference
1994	Hungary	$\Sigma_{11}$ PAH <sup>a</sup>	(540)	(160)	(380)	Kiss et al. (1996)
1996–1997	Northern Greece	$\Sigma_{14}$ PAH <sup>b</sup>	(430)			Manoli et al. (2000)
1996–1999	Poznan, Poland	$\Sigma_{15}$ PAH <sup>c</sup>	(280)			Walna et al. (2001)
1996–1999	Wielkopolski Park	$\Sigma_{15}$ PAH <sup>c</sup>	(210)			Walna et al. (2001)
1999–2000	Paris, France	$\Sigma_{14}$ PAH <sup>d</sup>	49–990 (360)			Ollivon et al. (2002)
2000–2002	Ankara, Turkey	$\Sigma_{15}$ PAH <sup>c</sup>	(1340)	(710)	(630)	Gaga et al. (2009)
2001–2002	West of Paris, France	$\Sigma_{14}$ PAH <sup>d</sup>	1.1–220 (72)			Motelay-Massei et al. (2003)
2003–2004	Northern Italy	$\Sigma_{15}$ PAH <sup>e</sup>	(110)	26–30 (28)	67–84 (75)	Olivella (2006)
2005	Guangzhou, China	$\Sigma_{14}$ PAH <sup>f</sup>	(1910)	410–3100 (680)	620–3500 (1230)	Huang et al. (2009)
2005	Fortaleza, Brazil	$\Sigma_{10}$ PAH <sup>g</sup>	210–680 (580)			Cavalcante et al. (2012)
2006–2008	Brno, Czech	$\Sigma_{15}$ PAH <sup>e</sup>	2.8–570 (93)	140–510 (47)	0.74–330 (46)	Skrdlíková et al. (2011)
2010	Guangzhou, China	$\Sigma_{15}$ PAH <sup>e</sup>	39–1580 (170 $\pm$ 130)	22–980 (110 $\pm$ 93)	17–780 (59 $\pm$ 52)	Present study

<sup>a</sup> Sum of the 16 priority PAHs designated by the United States Environmental Protection Agency minus naphthalene, acenaphthylene, acenaphthene, indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene.

<sup>b</sup> Sum of 16 priority PAHs plus benzo[e]pyrene, but minus acenaphthylene, acenaphthene and fluorene.

<sup>c</sup> Sum of 16 priority PAHs minus acenaphthene.

<sup>d</sup> Sum of 16 priority PAHs minus naphthalene and acenaphthene.

<sup>e</sup> Sum of 16 priority PAHs minus naphthalene.

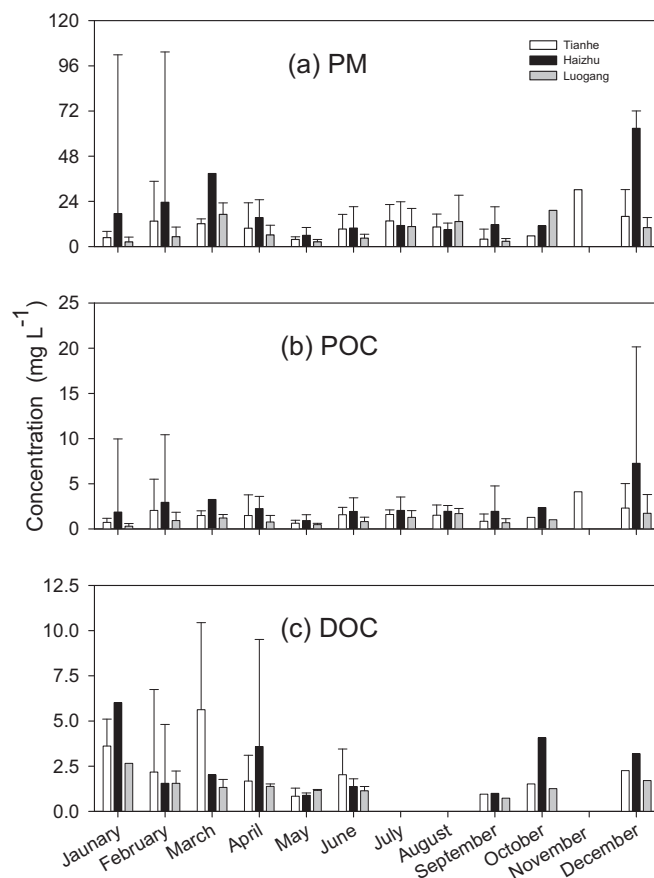
<sup>f</sup> Sum of 16 prior PAHs minus naphthalene and dibenzo[a,h]anthracene.

<sup>g</sup> Sum of 16 priority PAHs minus naphthalene, acenaphthylene, acenaphthene, anthracene, benzo[a]anthracene and dibenzo[a,h]anthracene.

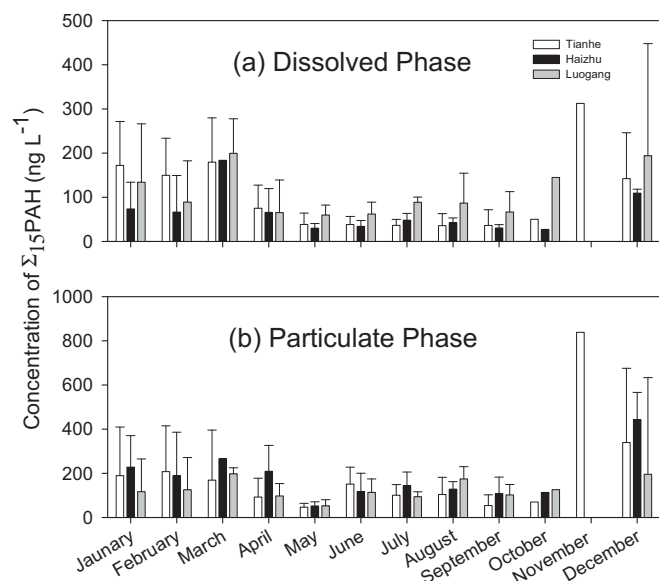
higher levels for the dry weather season (January–March and October–December) than the wet weather season (April–September) (Figs. 2 and 3; Table S4), i.e., air quality may have been better during the wet weather season than during the dry weather season in 2010. This conclusion has been widely supported by previous studies (Likens et al., 1983; Ollivon et al., 2002; Sun et al., 2006; Orlović-Leko et al., 2009). This seasonal variance appeared to associate with dilution effects (Pan et al., 2010), because precipitation amounts were negatively correlated with PM, TOC and  $\Sigma_{15}$ PAH concentrations in the present study. Besides, significant spatial variances were found for the concentrations of PM, POC, and DOC among three sampling sites ( $p < 0.05$  by ANOVA), with the highest and lowest levels occurring in Haizhu and Luogang (Fig. 2), respectively. However, no significant spatial variances were found for the concentrations of  $\Sigma_{15}$ PAH among the sampling sites ( $p > 0.05$  by ANOVA). This contrasting spatial distribution pattern remains difficult to comprehend. It has been determined that PAHs were mainly derived from domestic coal and straw burning and production residuals from petrochemical plants in suburban areas and automobile exhausts in urban districts of Guangzhou, which may have resulted in a relatively uniform distribution of PAHs throughout the entire city (Yang et al., 2010; Zhang et al., 2012). In contrast, the main sources of PM and TOC in urban districts were construction dusts and automobile exhausts, which explains the higher levels of PM and TOC in urban districts than in suburban areas (Zhou et al., 2009).

Significant correlation ( $r^2 = 0.53$ ,  $p < 0.05$ ) was observed between TOC and  $\Sigma_{15}$ PAH concentrations in the wet deposition samples, indicating that TOC and PAHs were simultaneously washed out by precipitations. Temporally, the concentration levels of TOC and PAHs in wet deposition from the present study were lower than those from previous studies also conducted in Guangzhou, i.e., the level of TOC in 2010 ( $2.5 \text{ mg L}^{-1}$ ) was lower than those in 2004 ( $7.1 \text{ mg L}^{-1}$ ) (Xu et al., 2008) and levels of PAHs in 2010 ( $170 \text{ ng L}^{-1}$ ) were lower than those in 2005 ( $1910 \text{ ng L}^{-1}$ ). On the other hand, the relative abundance of the low molecular weight (3 + 4-ring) PAHs, mainly derived from low-efficient combustion of domestic coal and biomass (Liu et al., 2012b), was reduced from 86% to 61% in 2010 (Huang et al., 2009). Furthermore, source diagnostic ratios of PAHs, including benzo[a]anthracene/(benzo[a]anthracene + chrysene) or indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[g,h,i]perylene),  $>0.35$

or  $> 0.5$  and in the range of 0.2–0.35 or 0.2–0.5 indicate coal or wood burning and petroleum combustion, respectively (Yunker et al., 1996, 2002). In the present study, the mean values of these two indices both decreased from 2005 (0.37 and 0.53) (Huang et al., 2009) to 2010 (0.29 and 0.46), uniformly suggesting similar



**Fig. 2.** Concentrations of particulate matter (PM), particulate organic carbon (POC) and dissolved organic carbon (DOC) in wet deposition samples collected from three districts (Tianhe, Haizhu and Luogang) of Guangzhou, China in 2010. The error bar is designated as weighted standard deviation.



**Fig. 3.** Concentrations of  $\Sigma_{15}\text{PAH}$  (sum of the 16 priority polycyclic aromatic hydrocarbons (PAHs) designated by the United States Environmental Protection Agency minus naphthalene) in the dissolved and particulate phases of wet deposition samples collected from three districts (Tianhe, Haizhu and Luogang) of Guangzhou, China in 2010. The error bar is designated as weighted standard deviation.

distribution patterns and lower proportion of coal combustion derived PAHs in 2010 than in 2005.

Existing data on the energy consumption patterns (Statistical Bureau of Guangzhou City, 2010) indicated that the consumed amounts of domestic coal and straw, two major sources of PAHs and suspended particles in China's atmosphere (Xu et al., 2006; Liu et al., 2012b), were much smaller in 2010 than in 2004 and 2005, i.e., the amounts of domestic coal consumed decreased approximately 74% (75%) from 2004 (2005) to 2012, and those of straw decreased 69% (68%). Our recent findings that the levels of sediment PAHs became steady or even lower in the PRD and adjacent coastal region may have been reflective of a shift in energy consumption patterns in South China, e.g., natural gas, liquefied petroleum gas and other environmentally friendly energy types have been increasingly used during the last few years (Zhang et al., 2011; Liu et al., 2012a).

### 3.2. Washout efficiency

Wet deposition is an important mechanism for mitigating air pollution by washing out PM and organics from the atmosphere to the ground. The washout ratio ( $W_T$ ), which describes how pollutants are removed by rainwater, is expressed as (He and Balasubramanian, 2009)

$$W_T = C_{\text{Rain}}/C_{\text{Air}} \quad (3)$$

where  $C_{\text{Rain}}$  and  $C_{\text{Air}}$  are the VWM concentrations of a target compound in paired rainwater and air samples, respectively. In the present study, the mean washout ratios of POC and PM were  $(3.5 \pm 3.0) \times 10^5$  and  $(3.1 \pm 1.6) \times 10^4$  (Table 2), respectively, and  $W_T$  of POC were within the range  $(1 \times 10^5 - 5 \times 10^5)$  obtained by Bidleman (1988). By definition,  $W_T, \text{POC} = 1000 \times C_{\text{PM}} \times f_{\text{OC}}/C_{\text{TSP}} \times f_{\text{OC}'}$ , where  $C_{\text{PM}}$  is the concentration of PM in wet deposition,  $C_{\text{TSP}}$  is the content of particles in aerosol, and  $f_{\text{OC}}$  and  $f_{\text{OC}'}$  are the fractions of organic carbon in wet deposition and aerosol, respectively. For PM,  $W_T, \text{PM} = 1000 \times C_{\text{PM}}/C_{\text{TSP}}$ . Thus,  $W_T, \text{POC} = W_T,$

$\text{PM} \times f_{\text{OC}}/f_{\text{OC}'}$ , and  $W_T, \text{POC}$  was higher than  $W_T, \text{PM}$  because  $f_{\text{OC}}/f_{\text{OC}'}$  was greater than 1 (Table S1).

For PAHs,  $W_T$  can also be expressed as (Ligocki et al., 1985a, b; Bidleman, 1988)

$$W_T = C_{\text{Rain}}/C_{\text{Air}} = W_P \times \phi + W_G \times (1 - \phi) \quad (4)$$

where  $\phi$  is the particle-sorbed fraction in air,  $W_G$  is defined as  $1000 \times C_{\text{Rain, Dissolved}}/C_{\text{Air, Gas}}$  with  $C_{\text{Rain, Dissolved}}$  and  $C_{\text{Air, Gas}}$  being the dissolved and gaseous concentrations of PAHs in rain and air, respectively (Table S5). Similarly,  $W_P$  is defined as  $1000 \times C_{\text{Rain, Particle}}/C_{\text{Air, Particle}}$ , where  $C_{\text{Rain, Particle}}$  and  $C_{\text{Air, Particle}}$  are the particulate concentrations of PAHs in rain and air, respectively (Table S5). The washout ratios of the PAH target compounds in the present study were in the range of  $(2.9 \pm 0.42) \times 10^3$  (phenanthrene) to  $(6.2 \pm 1.0) \times 10^4$  (acenaphthylene) (Table 2), comparable to those in Singapore ( $8.9 \times 10^4$  to  $1.2 \times 10^6$ ) (He and Balasubramanian, 2009), Chesapeake Bay ( $10^4 - 10^6$ ) (Dickhut and Gustafson, 1995), and Lake Michigan ( $1.8 \times 10^2$  to  $8.2 \times 10^7$ ) (Offenberg and Baker, 2002).

Washout ratio is associated with rain events, i.e., precipitation amount and duration (Zhang et al., 2009). In fact,  $W_T$  can be strongly affected by rainfall intensity ( $I$ ;  $\text{mm h}^{-1}$ ), i.e., precipitation amount per unit time (Dickhut and Gustafson, 1995; He and Balasubramanian, 2009). In Guangzhou, 59% of the rainfall intensity values were in the range of 0–4.3  $\text{mm h}^{-1}$  (Guangzhou Meteorological Bureau, 2010), and was negatively correlated with  $W_T$  of PM, POC or PAHs ( $p < 0.05$ ). Previous studies in Singapore and Chesapeake Bay also mentioned that  $W_T$  decreased when  $I$  increased within 0–6  $\text{mm h}^{-1}$ . When  $I$  was greater than 6  $\text{mm h}^{-1}$ , however,  $W_T$  increased with increasing  $I$  (Dickhut and Gustafson, 1995; He and Balasubramanian, 2009). Semi-quantitatively, the correlative relationship between  $W_T$  and  $I$  can be used to predict concentrations of PM and PAHs in wet deposition through  $W_T$  with known  $I$  and aerosol concentrations. For PM, the correlative relationship was derived as:

$$\log W_T = -0.18I + 4.7 \quad (r^2 = 0.46) \quad (5)$$

For PAHs, both  $\log \phi$  and  $I$  were used as independent variables to obtain a better fit (Table 2). Moderate correlative relationships were found with  $r^2$  ranging from 0.63 to 0.87 (Table 2) for other 12 PAH compounds except for acenaphthene, fluorene and indeno[1,2,3-*cd*]pyrene; the insignificant regressions ( $p > 0.05$ ) for the three congeners were ascribed to two abnormal values (collected on September 4 and 12, respectively). An  $F$ -test indicated that  $W_T$  for PM and 11 PAHs (12 PAHs mentioned above except for dibenzo[*a,h*]anthracene) obtained by linear regression were within the 95% confidence interval of the measured values. Due to the low detection frequency (36%; 4/11) in the gas phase of aerosol (Table S5), the insignificant regression of dibenzo[*a,h*]anthracene by  $F$ -test ( $p > 0.05$ ) was probably resulted from the non-normal distribution. Therefore, the regression model was applicable for 11 PAHs. The fitted equations (Table 2), which are appropriate for regions with lower rainfall intensity (0–6  $\text{mm h}^{-1}$ ) including Guangzhou, can be employed to calculate  $W_T$  of 11 PAHs based on given rainfall intensities and particle-sorbed fractions of PAHs.

### 3.3. Wet deposition flux and removal capacity

Monthly wet deposition flux ( $F_{\text{wet}}$ ) can be estimated from  $C_{\text{VWM}}$  of a target analyte (Table S6) and monthly precipitation amount in 2010 ( $Q_{2010}$ ) (Table S7):

$$F_{\text{wet}} = C_i \times Q_i \times 10^{-3} \quad (6)$$

Monthly dry deposition flux ( $F_{\text{dry}}$ ) is estimated by the analyte mass ( $M$ ) in dry deposition particles sampled each month and

**Table 2**  
Washout ratio ( $W_T$ ) of particulate matter (PM), particulate organic carbon (POC) and PAH, and correlative relationships between  $\log W_T$  and two dependent variables (rainfall intensity ( $I$ ) within 0–4.3 mm h<sup>-1</sup> (Table S1) and particle fraction ( $\phi$ )) in Guangzhou.

Target analyte	$W_T$ (mean $\pm$ SD <sup>a</sup> )	Regression equation <sup>b</sup>	$r^2$
PM	$(3.1 \pm 1.6) \times 10^4$	$\log W_T = -0.18I + 4.7^c$	0.46
POC	$(3.5 \pm 3.0) \times 10^5$	$\log W_T = -0.13I + 5.6^c$	0.53
Acenaphthylene	$(6.2 \pm 1.0) \times 10^4$	$\log W_T = -0.48I + 1.1\log\phi + 6.1$	0.80
Acenaphthene	$(1.9 \pm 0.18) \times 10^4$	– <sup>d</sup>	
Fluorene	$(4.8 \pm 0.88) \times 10^3$	– <sup>d</sup>	
Phenanthrene	$(2.9 \pm 0.42) \times 10^3$	$\log W_T = -0.32I + 1.0\log\phi + 5.6$	0.63
Anthracene	$(6.0 \pm 0.29) \times 10^3$	$\log W_T = -0.44I + 1.0\log\phi + 5.9$	0.77
Fluoranthene	$(4.2 \pm 0.82) \times 10^3$	$\log W_T = -0.34I + 0.70\log\phi + 4.9$	0.80
Pyrene	$(4.8 \pm 0.70) \times 10^3$	$\log W_T = -0.37I - 0.097\log\phi + 3.8$	0.72
Benzo[a]anthracene	$(2.1 \pm 1.2) \times 10^4$	$\log W_T = -0.34I + 2.2\log\phi + 5.4$	0.80
Chrysene	$(2.9 \pm 0.49) \times 10^4$	$\log W_T = -0.21I + 2.6\log\phi + 5.4$	0.87
Benzo[b]fluoranthene	$(3.0 \pm 0.26) \times 10^4$	$\log W_T = -0.34I + 1.4\log\phi + 4.8$	0.68
Benzo[k]fluoranthene	$(3.2 \pm 1.7) \times 10^4$	$\log W_T = -0.35I + 6.8\log\phi + 5.1$	0.67
Benzo[a]pyrene	$(3.8 \pm 1.6) \times 10^4$	$\log W_T = -0.39I - 2.3\log\phi + 4.8$	0.70
Dibenzo[a,h]anthracene	$(6.3 \pm 0.93) \times 10^3$	– <sup>e</sup>	
Indeno[1,2,3-cd]pyrene	$(3.8 \pm 1.6) \times 10^4$	– <sup>d</sup>	
Benzo[g,h,i]perylene	$(4.5 \pm 1.8) \times 10^4$	$\log W_T = -0.43I - 0.78\log\phi + 4.9$	0.69

<sup>a</sup> Standard derivation of washout ratio was calculated based on the propagation of error in concentrations of wet deposition and aerosol samples.

<sup>b</sup> An *F*-test indicated that  $W_T$  for PM, POC and 11 PAHs obtained by linear regression were within the 95% confidence interval of the measured values, thus, these regression models were applicable for PM, POC and 11 PAHs.

<sup>c</sup>  $\phi$  was not used in the regression for PM and POC as no phase distribution was involved.

<sup>d</sup> The regressions were insignificant ( $p > 0.05$ ) for acenaphthene, fluorene and indeno[1,2,3-cd]pyrene due to two abnormal values (collected on September 4 and 12, respectively).

<sup>e</sup> The regression was insignificant by *F*-test ( $p > 0.05$ ) for dibenzo[a,h]anthracene, as a result of the abnormally distributed data based on the limited detection frequency (gaseous dibenzo[a,h]anthracene was detected in four of eleven aerosol samples only; Table S5).

sampling area, i.e., the area ( $A$ ) of the sampling platter used for rainfall collection:

$$F_{\text{dry}} = M_j/A \quad (7)$$

The mass of PM in each dry deposition sample is the mass of particles retained by GF/F filters, and the mass of POC or PAHs in each dry deposition sample is the product of OC or analyte mass-based concentration multiplied by PM content. Monthly fluxes of PM, POC and  $\Sigma_{15}$ PAH are listed in Table 3, and an annual flux is the sum of the monthly fluxes for 12 months (annual dry deposition flux of POC was not calculated because only the dry deposition fluxes in five months were obtained). The annual fluxes of PM, POC and  $\Sigma_{15}$ PAH in wet deposition were 17 g m<sup>-2</sup> yr<sup>-1</sup>, 2.7 g m<sup>-2</sup> yr<sup>-1</sup>

and  $3.4 \times 10^2 \mu\text{g m}^{-2} \text{yr}^{-1}$ , respectively, in the present study (Table 3). The total wet deposition amounts of PM, POC and  $\Sigma_{15}$ PAH in the entire Guangzhou area (calculated as the product of flux and total area ( $7.4 \times 10^9 \text{m}^2$ ) of Guangzhou) were  $1.2 \times 10^5$ ,  $2.0 \times 10^4$  and 2.5 tons yr<sup>-1</sup>, respectively. The dry deposition fluxes of PM and  $\Sigma_{15}$ PAH in the urban area of Guangzhou were 17 g m<sup>-2</sup> yr<sup>-1</sup> and  $2.6 \times 10^2 \mu\text{g m}^{-2} \text{yr}^{-1}$ , respectively, resulting in total dry deposition amounts of  $1.3 \times 10^5$  and 1.7 tons yr<sup>-1</sup> for PM and  $\Sigma_{15}$ PAH in the entire Guangzhou area. Clearly, the annual wet and dry deposition fluxes were within the same order of magnitude.

Wet deposition may be more easily boosted or reduced by human-related control measures as compared to dry deposition. In addition, good linear correlations were found between the wet deposition fluxes and precipitation amounts of both PM and PAHs

**Table 3**  
Monthly wet deposition flux ( $F_{\text{wet}}$ ), dry deposition flux ( $F_{\text{dry}}$ ) and the capacity for removal (CR;  $\text{CR} = F_{\text{wet}}/(F_{\text{wet}} + F_{\text{dry}})$ ) by wet deposition of particulate matter (PM), particulate organic carbon (POC) and  $\Sigma_{15}$ PAH in Guangzhou, China in 2010.

Month	$F_{\text{wet}}$			$F_{\text{dry}}$			CR		
	PM <sup>e</sup>	POC <sup>e</sup>	$\Sigma_{15}$ PAH <sup>a,f</sup>	PM <sup>e</sup>	POC <sup>e</sup>	$\Sigma_{15}$ PAH <sup>a,f</sup>	PM	POC	$\Sigma_{15}$ PAH <sup>a</sup>
January	0.66	0.076	23	1.5	– <sup>c</sup>	40	0.31	– <sup>c</sup>	0.37
February	0.94	0.14	19	1.6	– <sup>c</sup>	28	0.36	– <sup>c</sup>	0.41
March	0.77	0.069	11	0.94	– <sup>c</sup>	26	0.45	– <sup>c</sup>	0.30
April	2.2	0.32	43	1.5	– <sup>c</sup>	27	0.59	– <sup>c</sup>	0.61
May	2.0	0.33	48	0.74	– <sup>c</sup>	12	0.73	– <sup>c</sup>	0.79
June	2.8	0.51	60	2.2	– <sup>c</sup>	21	0.55	– <sup>c</sup>	0.74
July	2.1	0.30	31	2.7	0.10	17	0.43	0.74	0.64
August	1.6	0.26	29	1.6	0.077	15	0.51	0.77	0.65
September	2.7	0.52	60	0.70	0.029	7.7	0.80	0.95	0.88
October	0.36	0.042	5.6	1.3	0.099	23	0.22	0.30	0.20
November	– <sup>b</sup>	– <sup>b</sup>	– <sup>b</sup>	1.3	– <sup>c</sup>	25	– <sup>c</sup>	– <sup>c</sup>	– <sup>c</sup>
December	0.65	0.083	9.9	0.90	0.056	19	0.42	0.60	0.34
Entire year	17	2.7	340	17	– <sup>c</sup>	260	0.49	0.77 <sup>d</sup>	0.57

<sup>a</sup> Sum of the 16 priority PAHs designed by the United States Environmental Protection Agency minus naphthalene.

<sup>b</sup> Precipitation amount in November, 2010 was 0 from official report ([http://www.grmc.gov.cn/Article/2010/12/30/Article\\_5516.html](http://www.grmc.gov.cn/Article/2010/12/30/Article_5516.html)).

<sup>c</sup> Not calculated due to the lack of data.

<sup>d</sup> The ratio was calculated based on known data of five months.

<sup>e</sup> In g m<sup>-2</sup> mon<sup>-1</sup>.

<sup>f</sup> In  $\mu\text{g m}^{-2} \text{mon}^{-1}$ .

( $r^2 = 0.71$  and  $p < 0.05$  for PM;  $r^2 = 0.92$  and  $p < 0.05$  for PAHs) (Fig. S1). Thus, similar to  $W_T$ , the capacity for removal (CR) of pollutants scavenged by wet deposition from the atmosphere is defined as:

$$CR = F_{\text{wet}} / (F_{\text{wet}} + F_{\text{dry}}) \quad (8)$$

where  $F_{\text{wet}}$  and  $F_{\text{dry}}$  are wet and dry deposition fluxes of a target analyte during a sampling period (Table 3). Comparison of Eqs. (3) and (8) implicates that CR reflects the efficiency for removal of pollutants through wet deposition during a given period, whereas  $W_T$  represents the instantaneous effectiveness for scavenging of pollutants by rain events. In addition, the range of CR from 0 to 1 is more robust than that of  $W_T$  varying between 0 and  $\infty$ . In the present study, the CR values were 0.31–0.80 for PM and 0.20–0.88 for PAHs (Table 3). Generally, the CR values of PM and PAHs in the wet weather season were greater than those in the dry weather season. Likewise, there were significant linear correlations between the monthly precipitation amounts and CR values for both PM ( $r^2 = 0.71$ ) and PAHs ( $r^2 = 0.79$ ) (Fig. S2). These results suggested that CR can be used as another parameter for describing the effectiveness of wet deposition in moving particulate and pollutants from the atmosphere.

Air quality index (AQI) has been used to report daily air pollution levels and associated public health risk to human in China (Ministry of Environmental Protection of the People's Republic of China, 2012). In the present study, only the AQI related to  $PM_{10}$  was used. The correlative relationships between AQI and monthly CR values for PM ( $CR_{\text{PM}}$ ) and PAHs ( $CR_{\text{PAHs}}$ ) in 2010 were established as

$$AQI_m = -15CR_{\text{PM}} + 57 \quad (r^2 = 0.37, p < 0.05) \quad (9)$$

$$AQI_m = -14CR_{\text{PAHs}} + 57 \quad (r^2 = 0.52, p < 0.05) \quad (10)$$

where  $AQI_m$  was calculated as the monthly average value from daily monitoring data (Table S7), which was published by the Environmental Protection Bureau of Guangzhou (2010). By definition, the AQI equal or lower than 50 indicates good air quality with insignificant health risk (Ministry of Environmental Protection of the People's Republic of China, 2012). Substituting the AQI values (equal or lower than 50) to Eqs. (9) and (10) resulted in  $CR_{\text{PM}}$  and  $CR_{\text{PAHs}}$  values equal or higher than 0.47 and 0.50, respectively, suggesting that air pollution would be greatly alleviated when certain amounts of PM and PAHs were removed by wet deposition at these CR values.

To quantify the wet deposition removal effects on reduction of air pollution, the expected wet deposition fluxes ( $F_{\text{wet}}^{\text{exp}}$ ) of PM and PAHs in 2010 were estimated by Eq. (11):

$$F_{\text{wet}}^{\text{exp}} = CR_{50} \times F_{\text{dry}} / (1 - CR_{50}) \quad (11)$$

where  $F_{\text{dry}}$  is monthly dry deposition flux,  $CR_{50}$  (0.47 for PM and 0.50 for PAHs) represents the removal capacity for the expected amounts of PM and PAHs by wet deposition with AQI being equal to 50. Generally, the actual wet deposition fluxes of PM and PAHs were higher than the expected fluxes for the wet weather season, but lower than those for the dry weather season (Table S8). In particular, the differences ( $F_{\text{wet}}^{\text{exp}} - F_{\text{wet}}$ ) for PM and PAHs ( $1.2 \text{ g m}^{-2} \text{ mon}^{-1}$  and  $25 \text{ } \mu\text{g m}^{-2} \text{ mon}^{-1}$ , respectively) were the greatest in November. Coincidentally, the 16th Asian Games (<http://en.olympic.cn/games/asian/2011-02-11/2125066.html>) was held on November 12–27, 2010 in Guangzhou. The local government implemented a series of control measures for reduction of traffic and industrial emissions

and precipitations (<http://huanbao.huizhou.gov.cn/hbzw/dqjh/xgzl/201010/P020101021625002284935.doc>). However, the AQI value (59) in November was still higher than those in other months (46–55) except for March (59) (Table S7). This was probably due to no precipitation in November (Table S7) because of effective rain control. If the precipitation amount in November 2010 was assumed to be 78 mm, an average amount of November in both 2009 and 2011 (Statistical Bureau of Guangzhou City, 2010, 2012), the wet deposition fluxes of PM and PAHs in November 2010 would be  $0.84 \text{ g m}^{-2} \text{ mon}^{-1}$  and  $15 \text{ } \mu\text{g m}^{-2} \text{ mon}^{-1}$  calculated from the correlations between  $F_{\text{wet}}$  and  $Q$  ( $F_{\text{wet, PM}} = 0.004Q_{2010} + 0.71$ ,  $F_{\text{wet, PAHs}} = 0.10Q_{2010} + 11$ ; Fig. S1). Based on Eqs. (9) and (10), AQI value would decrease to 51 and 52 from 59, as the CR values for PM and PAHs would increase to 0.39 and 0.38, respectively. These results indicate that air pollution would have been better eased without artificial rain intervention for the 16th Asian Games.

### 3.4. Implications for regional variability of pollutant removal capacity

Calculated  $CR_{\text{PAHs}}$  values were quite different based on previously reported data from different regions (Table S9) (Golomb et al., 2001; Bodnár and Hlavay, 2005; Gigliotti et al., 2005). Two factors possibly contributed to these differences. The first factor is the disparity in the annual precipitation amounts, and consequently wet deposition fluxes, e.g., 2100 mm in Guangzhou and 1180 mm in Jersey City (Table S10). Thus  $CR_{\text{PAHs}}$  of Guangzhou (0.57) and Jersey City (0.27) differed substantially although both regions had similar annual combined wet and dry deposition fluxes, i.e., 600 and  $590 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$  for Guangzhou and Jersey City (Gigliotti et al., 2005), respectively. The second factor in the likelihood that variable dry deposition fluxes in different regions may also have influences on CR values, even if the regions share similar precipitation amounts and wet deposition fluxes. For example, due to different dry deposition fluxes ( $430$ ,  $220$ , and  $38 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$  for Jersey City, New Brunswick, and Tuckerton, respectively), higher  $CR_{\text{PAHs}}$  value occurred in Tuckerton (0.69), but lower values appeared in Jersey City (0.27) and New Brunswick (0.26), although these three areas had similar wet deposition fluxes ( $76$ ,  $160$  and  $84 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$ ) for Jersey City, New Brunswick and Tuckerton (Gigliotti et al., 2005). Golomb et al. (2001) showed that different dry deposition fluxes of PAHs among different regions were mainly associated with different types of source inputs and emission amounts, e.g., the much higher  $F_{\text{dry}}$  value in Nahant than that in Wolfs Neck (Table S9) was likely due to higher emissions of PAHs from civil aircraft and automobile exhausts (Golomb et al., 2001). Therefore, the CR value of PAHs in a region could be improved through increasing the precipitation amounts and decreasing emissions. For this reason, the conclusions derived in Guangzhou can be applied to other regions, e.g., the difference between  $F_{\text{wet}}^{\text{exp}}$  and  $F_{\text{wet}}$  for PM can also be used to evaluate the removal effect of wet deposition on reduction of air pollution in other regions.

## 4. Conclusions

The results from the present study suggested that wet deposition can play a major role in reducing air pollution by removing PM and other pollutants from the atmosphere under favorable climatic conditions, i.e., a combination of coordinating precipitation amount and intensity. Equally important is implementation of well-planned control measures, cohesive with the seasonality of meteorological patterns, to curb anthropogenically derived pollution inputs. Although the present study was conducted in a subtropical and heavy Monsoon-affected region, its findings should be applicable for other environments, perhaps with proper calibration.



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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2013.11.012>.

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