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Wet and dry deposition fluxes of heavy metals in Pearl River Delta Region (China): Characteristics, ecological risk assessment, and source apportionment

Lyumeng Ye[1,**], *Minjuan Huang*[2,**], *Buqing Zhong*[3], *Xuemei Wang*[3,*], *Qiulan Tu*[1], *Haoran Sun*[1], *Chao Wang*[1], *Luolin Wu*[1], *Ming Chang*[3]

1. *School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, China*
2. *School of Atmospheric Sciences, Sun Yat-Sen University, Guangzhou 510275, China*
3. *Institute for Environmental and Climate Research Jinan University, Guangzhou 510632, China*

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ABSTRACT

The atmospheric deposition of heavy metals poses serious risks to the ecological system and human health. To advance our knowledge of atmospheric dry/wet heavy metal deposition in the PRD region, monthly fluxes were examined based on soluble/insoluble fractions of five heavy metal elements (Cu, Pb, Cd, Cr and Zn) in samples collected from January 2014 to December 2015 at Guangzhou (urban) and Dinghushan (suburban) sites. The ratios of wet/dry deposition fluxes indicated that heavy metal deposition was governed by wet deposition rather than dry deposition in the PRD region. Affected by the shifting of the Asian monsoon, wet deposition fluxes exhibited significant seasonal variation between summer monsoon seasons (April to September) and winter monsoon seasons (October to February) in this region. Cd was classified as an extremely strong potential ecological risk based on solubility and the Hakanson ecological risk index. Source contributions to wet deposition were calculated by PMF, suggesting that dust, biomass burning, industries, vehicles, long-range transport and marine aerosol sources in Guangzhou, and Zn fertilizers, marine aerosol sources, agriculture, incense burning, biomass burning, vehicles and the ceramics industry in Dinghushan, were the potential sources of heavy metals.

Introduction

With the rapid industrialization, agricultural modernization and urban expansion in China, the mining and smelting of metal minerals, thermal power, automobile exhaust and waste incineration emissions are the major sources of the atmospheric heavy metal pollutants. Recent research studies demonstrated that atmospheric heavy metal emissions have rapidly increased in a linear fashion during the past two decades (Tian et al., 2012a, 2012b). Heavy metals in the atmosphere eventually return to land and water surfaces by the processes of dry and wet deposition (in-cloud or below-cloud scavenging). The experimental results demonstrated that atmospheric deposition is the major source of heavy metals in soil (Gandois et al., 2010; Gray et al., 2003; Nicholson et al., 2003; Shen et al., 2016) and water environments (Sandroni and Migon, 2002;

* *Corresponding author. E-mail:* eeswxm@sysu.edu.cn (Xuemei Wang).
** Co-first authors.

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Wang et al., 2014), and causes persistent damage to these ecosystems. Public concern due to heavy metal transfer and accumulation in the food chain by atmospheric deposition into the ecosystem has increased rapidly with the substantial atmospheric emissions.

Since simultaneous measurements of atmospheric deposition to examine the relative importance of wet and dry deposition in removing airborne metals are lacking (Pan and Wang, 2015), monitoring observations have been performed, and wet deposition is considered to be the dominant removal mechanism for atmospheric pollutants, especially in monsoon areas with abundant rainfall (Sakata and Asakura, 2011). There are many studies focusing on the soluble fraction of the atmospheric heavy metal deposition (Avila and Rodrigo, 2004; Azimi et al., 2003; Hou et al., 2005; Moaref et al., 2014; Sakata et al., 2006), but recently researchers have paid more attention to the insoluble fraction (Baez et al., 2007; Fernandez-Olmo et al., 2014; Theodosi et al., 2010). Evaluation of the heavy metal soluble and particulate fractions is essential since the soluble and particulate forms have different fates in the environment, especially with respect to bioavailability (Theodosi et al., 2010).

The Pearl River Delta (PRD) region is located in the central Guangdong province in southern China, and has experienced remarkable economic development and urbanization during the past three decades (Lai et al., 2016). The PRD region is one of main industrial centers in China, and covers 4.17×10^4 km^2 land surface but hosts more than 5.8% of the Chinese population, and contributed more than 10.7% of the national Gross Domestic Product (GDP) in 2015 (Bereau of Statistics of Guangdong Province, 2016; National Bureau of statistics of China, 2016). With rapid development, the PRD region is becoming a major atmospheric emission region for heavy metals (Cu, Zn, Cd and Cr) in China (Duan and Tan, 2013). Although many measurements have been performed to analyze the characteristics of heavy metals in the airborne particles *i.e.*, TSP, PM_{10} and $PM_{2.5}$ (Lee et al., 2007; Tan et al., 2014, 2016; Zhu et al., 2015), atmospheric heavy metal deposition has yet to receive much attention. So far, there have been only a few research studies on atmospheric deposition in this region. Wong et al. (2003) and Huang et al. (2014) observed the bulk deposition of heavy metals. Huang et al. (2016) recorded the soluble mercury in atmospheric deposition from 2010 to 2012 in both Guangzhou and Dinghushan. To our knowledge, these published works have not examined the relative importance of the atmospheric input to the PRD region in either wet or dry deposition in soluble and particulate fractions. Moreover, source apportionment of atmospheric wet deposition of this region has not been well performed. The Pearl River Delta region is a typical region suffering from serious atmospheric pollution, and is located in the subtropical monsoon climate zone with abundant rainfall from April to September. Hence, we carried out this study: (1) to investigate the characteristics of atmospheric deposition for heavy metals (Cu, Pb, Cd, Cr and Zn) over two different underlying surfaces, *i.e.*, suburban and urban; (2) to determine the ecological risks of heavy metals induced by atmospheric deposition using the Hakanson potential ecological risk index; and (3) to identify the possible sources of typical heavy metals in wet deposition using positive matrix factorization (PMF).

1. Methodology

1.1. Site description

Two sites in the PRD region were selected for collecting atmospheric heavy metal deposition. The Guangzhou site is representative of urban areas, whereas the Dinghushan site, in the northwest of the PRD region, represents suburban areas. Both sites are shown in Fig. 1.

In Guangzhou (GZ), the south campus of Sun Yat-sen University (113°17′E, 23°06′N) was selected as the representative urban site. Guangzhou is in the center of the PRD region. The sampling site is located on the seventh floor (about 20 m above the ground) of the Geography and Environment Building in Sun Yat-sen University, and is surrounded by three main roads, which represents a typical urban surface.

The site in Dinghushan (DHS), on the third floor (about 10 m above the ground) of the Dinghushan Ecosystem Research Building (112°33′E, 23°10′N) at the foot of Dinghu Mountain, was also selected in this study, about 78 km away from Guangzhou. Dinghushan is 1132.2 ha in area, encompassing 132 ha of virgin forest landscape (approximately 12%). Dinghushan is located in the downwind area of Qingyuan City and Foshan City, which are in the heavy industrial area of Guangdong Province. The area around the Dinghushan site is an open terrain surrounding, and it is an excellent representative for a typical suburban surface.

1.2. Sampling and analytical method

An automated wet and dry sampler was used to collect the wet and dry deposition. The sampler consisted of two dishes (22 cm inner diameter with 11.5 cm height in DHS and 26 cm with 30 cm height in GZ, respectively), each equipped with a movable polyethylene cover which automatically covers the dry or wet sampler port depending on the rain. The dish collecting dry deposition is an aqueous surface with the water level kept at

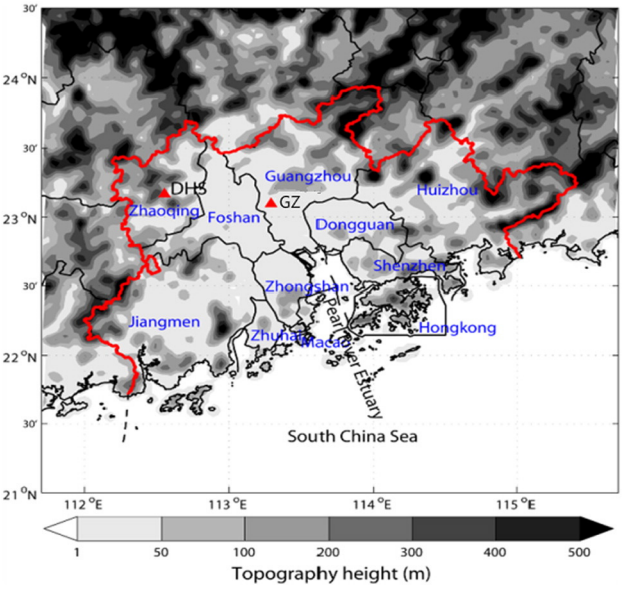

Fig. 1 – Locations of the sampling sites.

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about 2 cm. The same sampler was also applied by Wang et al. (2013).

Atmospheric wet and dry deposition samples were collected from January 2014 to December 2015 at both the GZ and DHS sites. Wet deposition samples were collected after the rain stopped and dry samples were collected biweekly. In total, 106 wet samples and 41 dry samples were collected at the GZ site, while 82 wet samples and 45 dry samples were collected at the DHS site during the study period.

The samples were filtered by a 0.45 μm mixed cellulose ester membrane (MCEM, ADVANTEC, Japan) with 47 mm diameter, and the filtrate was acidified to a pH of less than 2.0 by adding 1% HNO_3. The filter residue membrane was processed based on US Environmental Protection Agency (EPA) Method 3051 (US EPA, 2007) and the microwave-assisted method with nitric acid (HNO_3) was applied. A CEM Mars 6 microwave sample preparation system with temperature control was used to digest the filter residue membrane. Briefly, the filter was digested using 65% HNO_3 for the extraction of heavy metals. The preparation procedure for sample digestion is as follows: the temperature of each sample was increased from room temperature to 150°C in approximately 10 min and remained constant for 2 min, and then was raised to 190°C in approximately 5 min and remained constant for 30 min. After cooling, the sample digestion solutions were evaporated to near dryness, then diluted to 25 mL with 1% HNO_3 in a 50-mL polypropylene vial and immediately stored in a 4°C refrigerator before analysis.

The elements Pb, Cu, Zn, Cd and Cr were measured using an inductively coupled plasma optical emission spectrometer (Agilent| ICP-OES 700 Series) and graphite furnace-atomic absorption spectrophotometer (GF-AAS). Standard reference material (SRM) 2711a (MontanaIIsoil), matrix spike/matrix spike duplicates (MS/MSD), filter blanks and method blanks were processed and analyzed in parallel with the samples. The recoveries of target elements ranged from 88% to 120%.

1.3. Potential ecological risk

The Hakanson potential ecological risk index was originally used to determine the ecological risks of heavy metals in sediment (Li et al., 2013; Liu et al., 2009). Recently, more researchers have introduced it to Chinese atmospheric pollutant studies (Cui et al., 2011; Hu et al., 2011; Yao et al., 2013). The Hakanson potential ecological risk index was calculated using Eqs. (1)–(3):

$$C_f^i = \frac{c_i}{c_n^i} \tag{1}$$

$$E_r^i = T_r^i \times C_f^i \tag{2}$$

$$RI = \sum E_r^i \tag{3}$$

where, c_i (mg/kg) and c_n^i (mg/kg) are the total and background concentrations of heavy metals in soils, respectively. E_r^i is the ecological risk of each heavy metal and RI represents comprehensive potential ecological risk of multiple heavy metal elements. E_r^i is defined as the "toxic-response factor". c_s is the concentration of heavy metals in soils due to the wet and dry deposition (D_{tot}, mg/(m^2·year)) as well as the loss from soil through leaching or volatilization, and was calculated by Eqs. (4) and (5). The total heavy metal concentration (c_i) in soils was calculated by Eq. (6):

$$D_{tot} = D_{dry} + D_{wet} \tag{4}$$

$$c_s = \frac{D_{tot} \cdot [1 - \exp(-k_s \cdot t)]}{z \cdot k_s \cdot BD} \tag{5}$$

$$c_i = c_s + c_n^i \tag{6}$$

Parameters of the aforementioned equations are as following: c_n^i (Cd 0.034 mg/kg, Cr 43.25 mg/kg, Cu 14.38 mg/kg, Pb 34.38 mg/kg, Zn 48.75 mg/kg, Zhang et al., 2012b); T_r^i (Cd 30, Cr 2, Cu 5, Pb 5, Zn 1, Yao et al., 2013); Soil bulk density (BD, g/cm^3) 1.37 (http://www.soil.csdb.cn/); soil loss constant (k_s 0.06 year^{-1}, Lonati and Zanoni, 2012), lifetime (t, 30 years, Lonati and Zanoni, 2012), soil mixing depth (z 17.91 cm, http://www.soil.csdb.cn/).Taking local atmospheric deposition into consideration, the classifications of E_r^i and RI are delineated in Table 1 (Yao et al., 2013).

1.4. PMF analysis

The PMF model is a mathematical factor-based receptor model that interprets source types with a robust uncertainty estimate (Khan et al., 2016). PMF has been applied to determine the source apportionment of wet or dry deposition of ions, organic matter and heavy metals in many studies (Keeler et al., 2006; Wang et al., 2016). These successful applications demonstrate that PMF is a viable means to identify sources contributing to precipitation chemistry (Kitayama et al., 2010). In this study, 5 elements and 9 ions were included in the EPA PMF 5.0 model to investigate the sources of wet deposition. The input data included concentrations of chemical species and equation-based uncertainties. The equation-based uncertainty includes detection limits and error fractions (20%). If the concentration is less than or equal to the method detection limit (MDL) provided, the uncertainty (Unc) is calculated using a fixed fraction of the MDL (Eq. (7)).

$$Unc = \frac{5}{6} \times MDL \tag{7}$$

And if the concentration is greater than the MDL provided, the calculation (Eq. (8)) is

$$Unc = \sqrt{(\text{Error Fraction} \times \text{concentration})^2 + (0.5 \times MDL)^2} \tag{8}$$

Table 1 – E_r^i and RI classifications of Hakanson potential ecological risk.

E_r^i	RI	Grade	Ecological risk category
<40	<150	I	Low
40–80	150–300	II	Moderate
80–160	300–600	III	Considerable
160–320	600–12,000	IV	Strong
≥320	≥1200	V	Very strong

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2. Results and discussion

2.1. Dry deposition of heavy metals

2.1.1. Comparison of dry-deposited heavy metals between two sites

Table 2 shows the annual average dry deposition fluxes of Cu, Pb, Cd, Cr and Zn at the DHS and GZ sites from 2014 to 2015. As expected, the annual dry deposition fluxes of all investigated heavy metals at the GZ site in the present study were higher than the fluxes measured at the DHS site. The dry deposition fluxes of Cu and Zn at the urban site were more than two times higher than those at the suburban site. The significant variation between the two sites was related to local emissions, suggesting that human activities had a stronger impact at the urban site. Moreover, the forest canopy can serve as an interceptor of airborne particles to reduce the dry deposition velocity on forest land surfaces (Liu et al., 2012; Mao et al., 2013; Wang and Stuanes, 2003). Dry deposition fluxes of these metals in the PRD region were relatively lower than the monitoring results in the Jing-jin-ji area and central Taiwan with the exception of Zn, but relatively higher than those observed in Japan, USA and Greece, except for Cr (Table 2), which is linked to the moisture level of soil and intensive human activities in the PRD region.

2.1.2. Seasonal variations in dry deposition fluxes of heavy metals

Dry deposition is considered to be the predominant process to remove atmospheric pollutants from the atmosphere, especially during the dry season with lower precipitation. The climate in the PRD region is affected by the shifting of the Asian monsoon, and the strong temperature inversion and lower air pressure are favorable for accumulation of particulate matters in the winter monsoon season (dry season). The seasonal variations of dry deposition during the study period are shown in Figs. 2 and 3. As the deposition flux is non-normally distributed, a non-parametric test (Kruskal–Wallis test) is applied in this study. Median values (25th percentile–75th percentile) of dry deposition fluxes for heavy metals observed for different seasons are presented in Table 3. There is no significant difference in dry deposition fluxes for the investigated heavy metals between summer monsoon (April to September) and winter monsoon seasons (October to March) at both the GZ and DHS sites. According to Lee et al. (2007), long-range transport due to the Asian monsoon could have the most dominant effect on the seasonal variations in heavy metals in the PRD region, so we concluded that sources of dry deposition for heavy metals at both sites are similar throughout the year and are mainly from local and regional emission.

2.2. Wet deposition of heavy metals

2.2.1. Comparison of wet-deposited heavy metals between two sites

Annual average wet deposition fluxes of heavy metals at the DHS and GZ sites during the observation period are shown in Table 2. The wet deposition fluxes of Cd and Cr at the GZ site were relatively higher than those at the DHS site, whereas the Cu, Pb and Zn deposition fluxes of the GZ site are lower than those of the DHS site. The wet deposition fluxes of Cd and Cr at the GZ site are almost a factor of 2 and a factor of 1.5 higher than those at the DHS site, respectively, which is probably attributable to local emissions from human activities in the urban area (Hjortenkrans et al., 2007; Shao et al., 2013). Industrial uses, including electroplating, leather tanning, and textiles, are responsible for higher Cr deposition in the urban PRD, whereas coal and oil combustion could also release Cr (Hu and Cheng, 2013). Wet deposition of Cd was mainly derived from vehicular emissions and Cd used in local industries in the urban area. Surprisingly, unlike the spatial pattern of dry deposition, the

Table 2 – Annual monitoring of heavy metals deposition fluxes (mg/m^2/year) in the present study and comparisons with previous studies.

Study sites			Cu	Pb	Cd	Cr	Zn	References
Guangzhou, China	Wet deposition	Urban	13.17	10.4	0.83	6.04	105.64	This study
	Dry deposition		9.06	6.6	0.17	3.82	56.49	
	Total deposition		22.23	17	1	9.86	162.13	
Dinghushan, China	Wet deposition	Suburban	19.06	38.01	0.42	4.42	160.67	
	Dry deposition		4	4.83	0.15	1.54	25.11	
	Total deposition		23.06	42.84	0.57	5.96	185.78	
Matsuura, Japan (2004–2006)	Dry deposition	Suburban	3.01	1.55	0.058	4.28	–	Sakata and Asakura, 2011
	Wet deposition		1.2	6.14	0.23	0.34	–	(water surface)
Fort Crevecoeur State Park, Illinois, USA (2011.6–7)	Dry deposition	Urban	1.68	0.8	0.012	–	44.75	Lynam et al., 2015 (polypropylene surface)
Jing-jin-ji area (2007.12–2010.11)	Dry deposition	Urban	17.17	18.2	0.28	7.73	93.08	Pan and Wang, 2015
	wet deposition	Urban	2.46	7.19	0.23	0.38	73.02	(PU foam surface);
Finokalia, Greece (2005–2006)	Dry deposition	Suburban	2.28	0.72	0.048	2.28	9	Theodosi et al., 2010 (glass surface);
Taiwan, China (2009–2010)	Dry deposition	Urban	20.8	20.03	–	9.2	18.03	Zhang et al., 2012a (PU foam surface)
Mersin, Turkey (2003–2005)	Wet deposition	Urban	2.35	6.87	0.37	4.03	16.20	Ozsoy and Ornektekin, 2009
Kathmandu, Nepal (2011–2012)	Wet deposition	Urban	1.95	1.42	0.1	1.6	24.44	Tripathee et al., 2014

(–) not reported.

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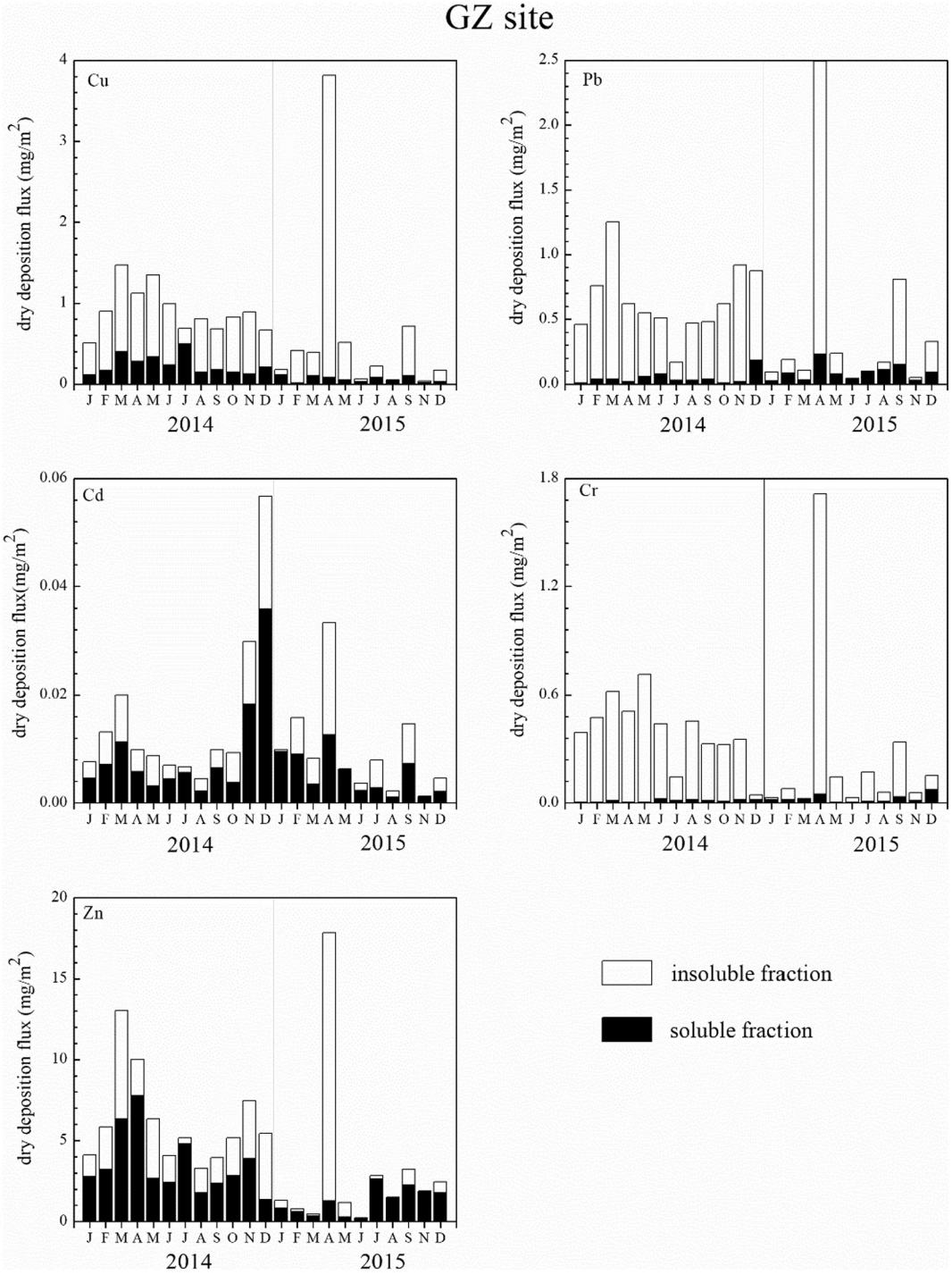

Fig. 2 – Monthly dry deposition fluxes at Guangzhou (GZ) site during 2014–2015.

wet deposition fluxes of Cu, Zn and Pb at the DHS site were approximately 1.5–4 times greater than those at the GZ site, respectively. The higher wet deposition fluxes of Cu and Zn might result from regional transport or local emission sources, depending on the particle size distribution of heavy metals in this region (Pan and Wang, 2015). Pb is the most widespread toxic metal on earth due to anthropogenic activities. The wet deposition of Pb at the DHS site was most likely contributed by long-range transport from South Asia and regional transport from the ceramic industry in the upwind direction of Dinghushan (Lee et al., 2007; Tan et al., 2016; Zhu et al., 2015). After the phase-out of leaded gasoline in China in the early 2000s, vehicle exhaust appears to no longer be an important local emission source of atmospheric Pb in urban areas (Duan and Tan, 2013). The long-range transport of air pollutants originating from south Asia has been demonstrated to have an impact on the wet deposition of trace elements in East Asia and even in the remote areas of western China (Lee et al., 2007; Tripathee et al., 2014). The wet deposition fluxes in the present study were relatively higher than the observed results in the

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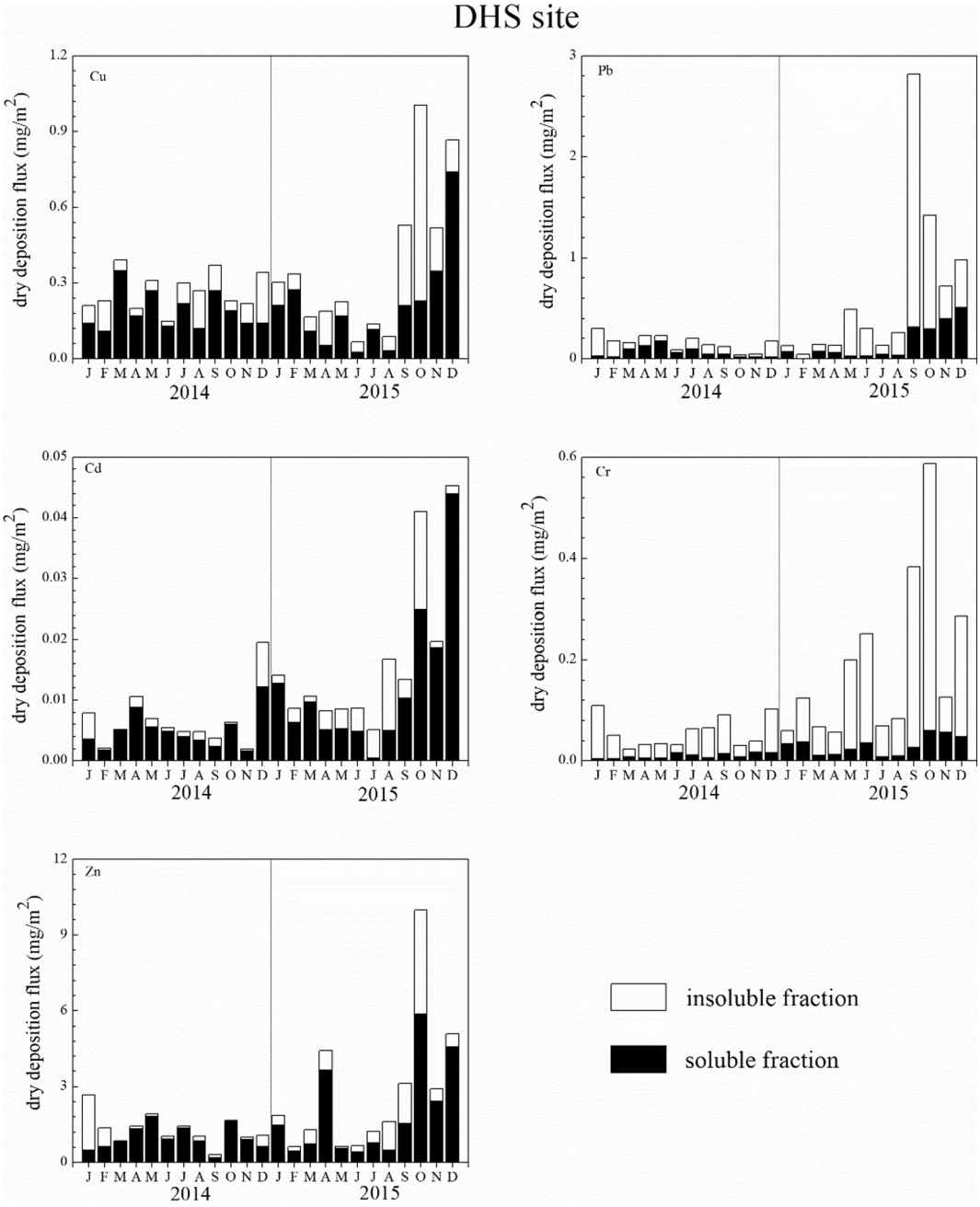

Fig. 3 – Monthly dry deposition fluxes at Dinghushan (DHS) site during 2014–2015.

Table 3 – Median values (25th percentile–75th percentile) for dry deposition fluxes observed for different seasons (unit: mg/m^2).

	GZ site			DHS site		
	Summer Monsoon season	Winter Monsoon season	*p*-Value [a]	Summer Monsoon season	Winter Monsoon season	*p*-Value [a]
Cu	0.700(0.442, 1.017)	0.509(0.282, 0.859)	0.3889	0.215(0.140, 0.305)	0.320(0.228, 0.423)	0.06438
Pb	0.474(0.168, 0.574)	0.467(0.148, 0.816)	0.7119	0.215(0.130, 0.270)	0.170(0.113, 0.405)	0.6856
Cd	0.007(0.006, 0.010)	0.010(0.008, 0.018)	0.1962	0.010(0.008, 0.010)	0.010(0.010, 0.020)	0.1944
Cr	0.047(0.025, 0.093)	0.228(0.028, 0.433)	0.1757	0.065(0.053, 0.118)	0.085(0.048, 0.123)	0.7497
Zn	3.620(2.500, 5.443)	4.104(1.594, 5.636)	1	1.325(0.945, 1.688)	1.510(1.043, 2.730)	0.4187

[a] From Kruskal–Wallis test.

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Jing-jin-ji area, Matsuura, Japan, Mersin, Turkey, Kathmandu and Nepal (Table 2), probably due to the intensive manufacturing activities and high precipitation amounts in the PRD region.

2.2.2. Seasonal variations in wet deposition fluxes of heavy metals

Wet deposition may exhibit seasonal variations in regions controlled by emissions and meteorological conditions (*e.g.*, rainfall, wind speed, relative humidity and temperature). Airborne particulate matter and associated heavy metals were easily suspended in the air and returned to the land surface through the effect of rainfall scavenging. The PRD region is subject to the typical Asian monsoon climate, hot and humid with strong southeastern monsoon breezes from the South China Sea during the summer monsoon season (Yang et al., 2008). The Asian monsoon climate has been reported to result in seasonal variation of wet deposition, with contributions from different regional emission sources in the PRD region (Huang et al., 2010). The seasonal variations in wet deposition during the study period are shown in Figs. 4 and 5, and median values (25th percentile-75th percentile) for wet deposition fluxes observed for different seasons are presented in Table 4. The wet deposition fluxes of all investigated heavy metals in urban Guangzhou during the summer monsoon season are significantly higher than those measured during the winter monsoon season. As for the investigated heavy metals in the suburban area (Dinghushan site), there are also significant differences in wet deposition between summer monsoon and winter monsoon seasons, except for Zn. About 78% and 63% of precipitation occurred in the summer monsoon at the GZ site and DHS site, respectively, which indicates that higher wet deposition fluxes of heavy metals in the summer monsoon season corresponded to higher amounts of precipitation. Seasonal variations of wet deposition were also found in Chongqing, China (Peng et al., 2014) and Singapore (Hu and Balasubramanian, 2003). However, this is not the case for Zn at the DHS site, which exhibits no significant difference between the summer monsoon and winter monsoon seasons. This finding suggests that Zn in wet deposition in Dinghushan partly exists in coarse particulate form, and originates from local and regional emission sources.

2.2.3. Factors controlling wet deposition fluxes

To investigate the factors controlling the monthly wet deposition flux, the scavenging ratio (W) was introduced by Sakata et al. (2006) and Pan and Wang (2015). The scavenging ratio (W) is defined as:

$$W = \frac{C}{K}$$

C is the concentration of heavy metals in precipitation, and is related to the concentration of heavy metals in the air (*K*). When the precipitation amount is expressed as *P*, the wet deposition flux of heavy metals is related to *K*, *W* and *P* by

$$F = WKP$$

Here, the scavenging ratio (*W*) and atmospheric concentration (*K*) at all investigated sites were assumed to be constant, and the wet deposition flux would therefore increase proportionally with the amount of precipitation. What's more, when the atmospheric concentrations of heavy metal increase due to additional anthropogenic inputs (*e.g.*, long-range/regional transport), the wet deposition fluxes for the site would be larger than the expected amount based on the above equation and assumptions (*i.e.*, *W* and *K* are both constant). The relationship between wet deposition fluxes and precipitation amounts can be applied to evaluate the degree of impact from anthropogenic emissions at each site.

The results of the relationship between the monthly deposition fluxes and monthly precipitation amount for the GZ and DHS sites are shown in Figs. 6 and 7, respectively. The results show that the monthly wet deposition fluxes of heavy metals except for Cu have significant correlation with the monthly precipitation amount at the GZ site ($0.21 < r^2 < 0.75$, $p < 0.05$). In particular, 75% of the variance of wet deposition fluxes for Cr ($p < 0.001$) and 20%–47% of the variance for Cd ($p < 0.05$), Zn ($p < 0.05$) and Pb ($p < 0.001$) can be explained using the precipitation amount, suggesting that the wet deposition flux of these heavy metals increased in proportion to the precipitation amount and that the scavenging ratio and atmospheric concentration were constant (WK = constant). WK = constant may mean that there were no marked differences in the atmospheric concentrations of these four heavy metals in particulate form and in the scavenging ratio over the study period, which indicated that these heavy metals in atmospheric particles acted as condensation nuclei throughout the PRD region. However, the wet deposition flux of Cu had no significant correlation with the precipitation amount. For Cu, existing mostly in coarse particulate forms (particle diameter more than 4 μm), this indicated that the wet deposition of Cu in Guangzhou is strongly dependent on local and regional anthropogenic sources (Gong et al., 2006). Moreover, one or two large Pb, Cd and Zn monthly wet deposition fluxes were found to be higher than those expected based on the precipitation amount (in red circles) with the blue curves representing 95% prediction limits, which suggested the presence of a large contribution from long-range transport, probably from Northeastern China and South Asia, during the monsoon season, from anthropogenic sources (Lee et al., 2007).

The relationship between the monthly wet deposition flux and precipitation amount in Dinghushan is not significant for the five investigated heavy metals (Fig. 7), which is different from the GZ site. The results demonstrate that wet deposition fluxes for the investigated heavy metals at the DHS site are more likely to depend on the scavenging ratio and atmospheric concentration of heavy metals, probably due to local and regional anthropogenic sources. For heavy metals existing entirely in coarse particulate form, their wet deposition depends on the below-cloud scavenging of local emissions rather than regional emissions. However, for heavy metals existing in fine particulate form, which can act as condensation nuclei for the formation of precipitation, most of the wet deposition might arise from in-cloud scavenging, and regional emissions made more contribution to fine particles. Further investigation on the size distribution of trace metals in atmospheric aerosols will help distinguish the contributions of local and regional anthropogenic sources in the PRD region.

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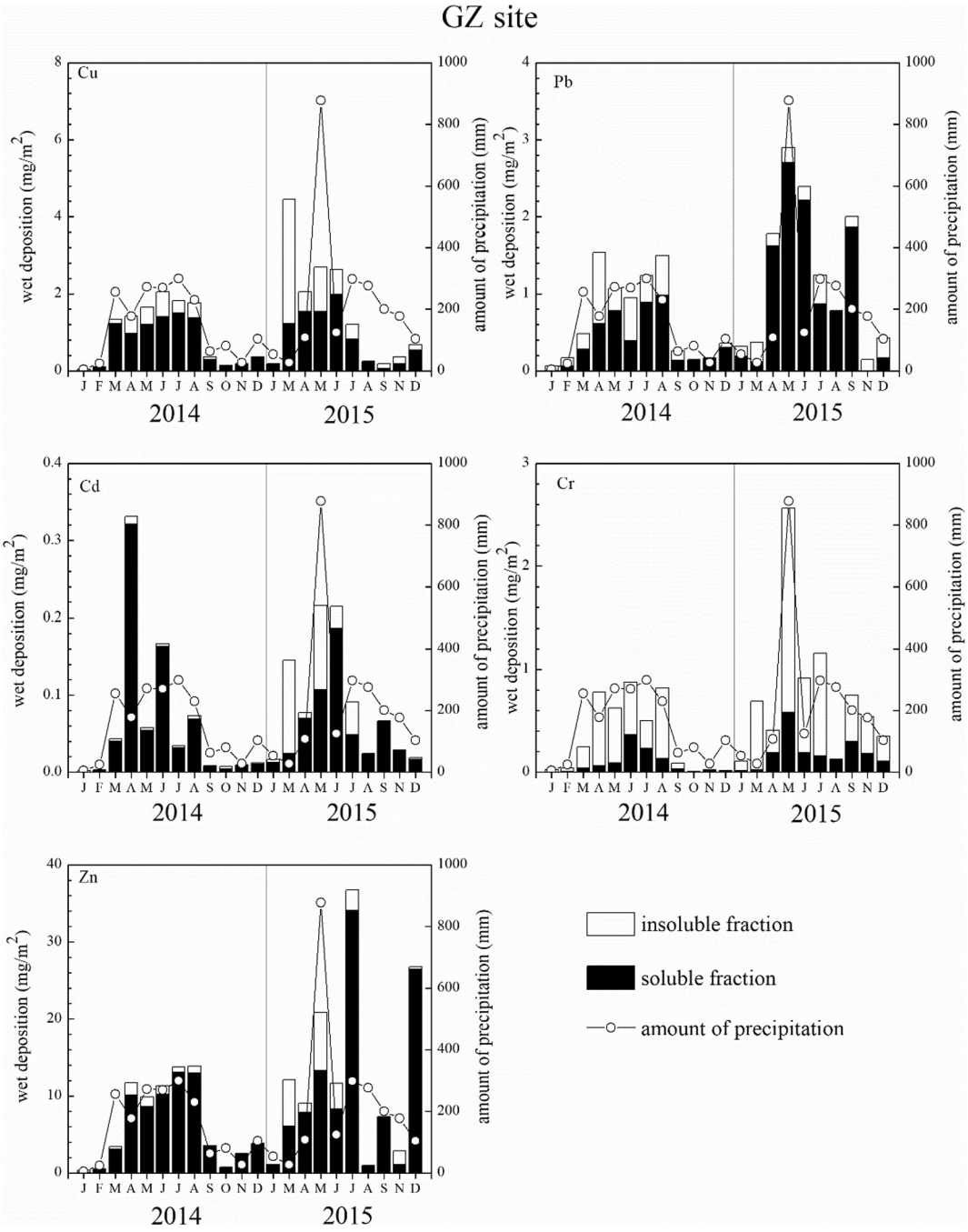

Fig. 4 – Monthly wet deposition fluxes and amount of precipitation at GZ site during 2014–2015.

2.3. Wet vs. dry deposition of heavy metals

A comparison of wet deposition flux and dry deposition flux at the two sites is provided in Fig. 8. The wet deposition fluxes of Cu, Pb, Cd, Cr and Zn exceeded their dry deposition fluxes at both sites. That is, the dry deposition of heavy metals shows a smaller contribution to atmospheric deposition, which indicates that their deposition is governed by wet deposition rather than dry deposition in the PRD region. Compared with dry deposition, the wet deposition of heavy metals is more likely to depend on the regional precipitation patterns and emissions, as mentioned by Pan and Wang (2015). This contrasts with the situation in semi-arid or arid regions, where dry deposition contributes primarily to the total annual deposition due to low precipitation. In addition, wet deposition is thought to be a cleansing mechanism for removing atmospheric pollutants with abundant precipitation. This mechanism is well-verified in the PRD region, where the climate is dominated by the subtropical monsoon.

The wet/dry ratios of heavy metals and their order varied between the two sites. The wet/dry ratios for heavy metals at the GZ site are relatively lower than those at the DHS site, indicating

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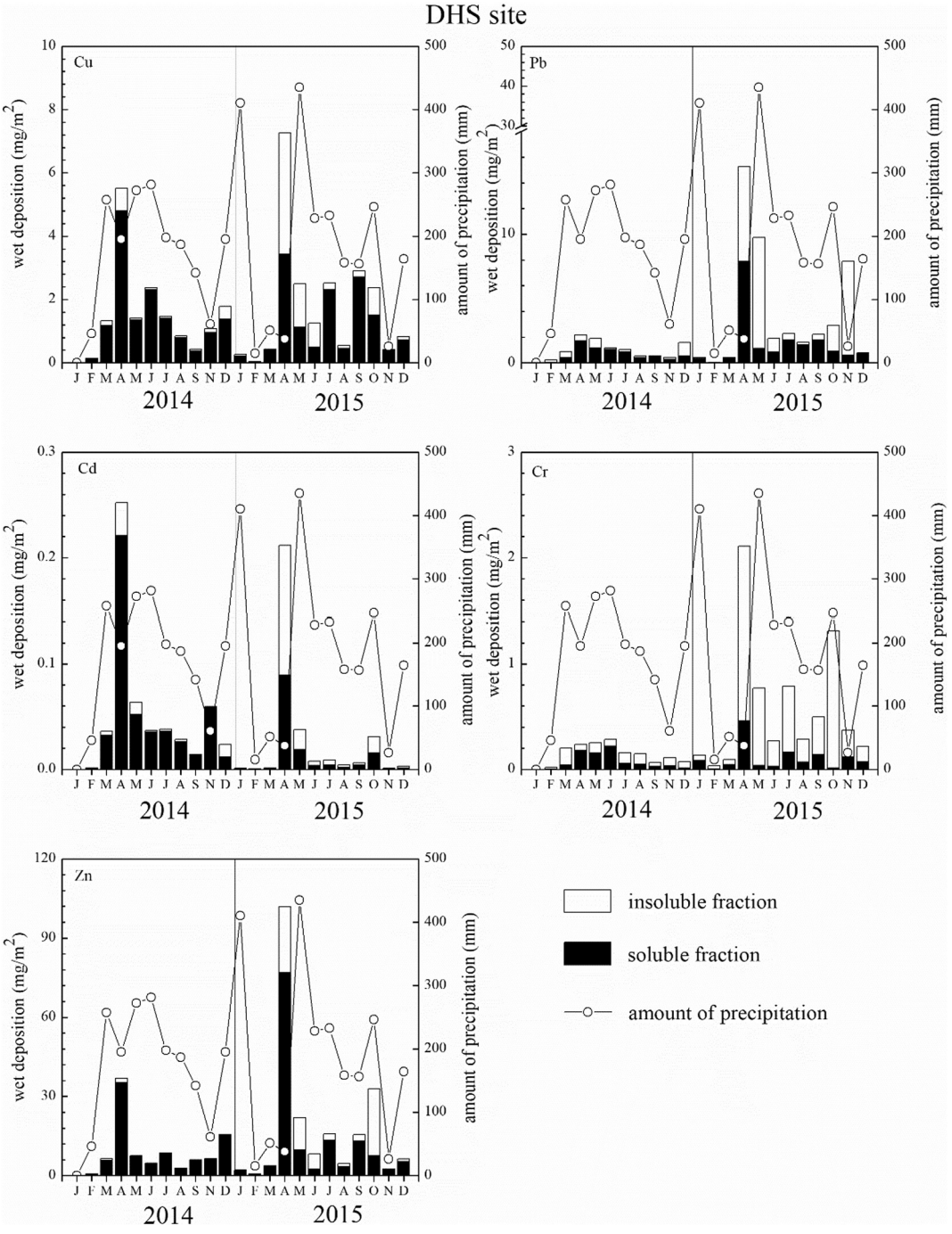

Fig. 5 – Monthly wet deposition fluxes and amount of precipitation at DHS site during 2014–2015.

that the cleansing mechanism of wet deposition at the DHS site is more important than at the GZ site. The average ratios of annual wet/dry deposition fluxes for heavy metals decreased in the order of Cd > Zn > Pb > Cr > Cu at the GZ site and Pb > Zn > Cu > Cr > Cd at the DHS site. Beyond the differences in emission sources, different land uses and size distributions of heavy metals in atmospheric aerosols are considered to influence the heavy metal wet/dry ratios of the two sites.

Higher settling velocity of particulate matter has been found for urban surfaces (Roupsard et al., 2013; Wang and Stuanes, 2003), whereas the forest canopy in natural land surfaces has a favorable absorption effect on particulate matter. Former studies have identified the effect of plant growth on PM-retention, which significantly influences the dry deposition in the forest canopy (Liu et al., 2012; Mao et al., 2013; Wu and Wu, 2015). The land use difference led to more heavy metal dry deposition flux at the GZ site than at the DHS site.

The size distribution of heavy metals in atmospheric aerosols is another factor influencing the differences between wet and dry deposition flux. In the study of Goossens (2008), dry deposition associated with coarse particles was predominantly determined by gravity while fine particles were

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Table 4 – Median values (25th percentile-75th percentile) for wet deposition fluxes observed for different seasons (unit: mg/m^2).

	GZ site			DHS site		
	Summer Monsoon season	Winter Monsoon season	*p*-Value [a]	Summer Monsoon season	Winter Monsoon season	*p*-Value [a]
Cu	1.706(0.997, 2.045)	0.275(0.150, 0.601)	0.02	1.925(1.150, 2.614)	0.635(0.299, 1.267)	0.01
Pb	1.368(1.040, 1.835)	0.244(0.152, 0.3676)	0.00	1.898(1.116, 2.227)	0.602(0.422, 1.395)	0.03
Cd	0.075(0.052, 0.179)	0.014(0.008, 0.026)	0.00	0.032(0.009, 0.045)	0.002(0.001, 0.029)	0.02
Cr	0.478(0.765, 0.886)	0.073(0.026, 0.321)	0.00	0.277(0.216, 0.565)	0.123(0.077, 0.212)	0.04
Zn	11.476(8.618, 13.794)	2.707(0.855, 3.721)	0.02	8.409(5.673, 17.317)	5.006(2.171, 6.453)	0.06

[a] From Kruskal–Wallis test.

affected by turbulence, and the intensity of the turbulence could increase the dry deposition velocity (Roupsard et al., 2013). Nowadays, deposition fluxes of heavy metals have been found to be size-dependent in research studies (Lyu et al., 2017; Pan and Wang, 2015). Sakata and Asakura (2011) indicated that heavy metals associated with coarse particles (>2.5 μm in diameter) have shorter atmospheric lifetimes caused by gravitational settling and inertial deposition, which easily govern the dry deposition. The particle size distribution is dependent on the intrinsic properties of particulate matter (Jiang et al., 2016; Liu et al., 2011) and heavy metal properties (Duan et al., 2014; Duan and Tan, 2013; Wang et al., 2015). Particles will experience hygroscopic growth at relatively higher humidity conditions. In addition, different heavy metals are prone to exist in different modes, such as coarse, accumulation and Aitken modes. Airborne Cd and Pb in Japan were found to mainly exist in the coarse particles (5–15 μm) and also in fine particles (<2.5 μm) (Sakata et al., 2006). Similarly, airborne Cr in North China displayed a bimodal distribution at 0.43–0.65 μm and 4.7–5.8 μm, while Cu and Pb existed entirely as fine particles in similar size ranges (Pan and Wang, 2015). In Beijing, however, Cu showed peaks at around 4.7–5.8 μm in addition to that at 0.43–0.65 μm and Pb showed only one peak at 0.43–0.65 μm. These results indicate that the size distributions of heavy metals in the atmospheric aerosols vary by region. Since there is no data on the particle size distributions of heavy metals in the air in the study region, further research on atmospheric PM concentrations and measurement of the particle size distribution at the two sites is necessary to better understand the factors controlling the deposition of heavy metals in the PRD region.

2.4. Potential ecological risk

Atmospheric deposition is considered to make an important contribution to the amount of heavy metals in the ecosystem (Huang et al., 2016). Table 5 lists the results of Hakanson potential ecological risk for the 5 studied heavy metals induced by atmospheric deposition in Guangzhou and Dinghushan. The potential ecological risk of the deposited heavy metals follows the order of Cd > Cu > Zn > Pb > Cr in Guangzhou and Cd > Cu > Pb > Zn > Cr in Dinghushan. The potential ecological risk indexes of Pb, Cr and Zn in Guangzhou as well as Cr and Zn in Dinghushan are lower than 40 (Yao et al., 2013), indicating that these metals are basically ecological-risk-free. However, Cd is classified as an extremely high potential ecological risk both in Guangzhou (2032.72) and Dinghushan (2881.55). Cadmium is particularly ecologically hazardous because of its easy uptake by plants, its tendency to accumulate in crops, and its persistent nature once it is in the environment.

2.5. Solubility of heavy metals in atmospheric deposition

Solubility is essential as it is related to the availability to humans and the ecosystem (Shao et al., 2017; Wang et al., 2015). In dry deposition, the contribution of the soluble fraction to total dry deposition is usually less than that of the insoluble fraction for all metals (Figs. 2 and 3). In particular, Cr and Pb show the greatest insolubility; respectively 86.13% and 74.59% at the GZ site, and 76.16% and 61.06% at the DHS site average insoluble contribution to the total dry deposition.

The percentage solubility of heavy metals in precipitation was found to decrease in the order Zn, 86.82% > Cd, 84.00% > Cu, 76.14% > Pb, 63.69% > Cr, 34.63% at the GZ site; and Cd, 89.28% > Zn, 83.48% > Cu, 83.32% > Pb, 61.96% > Cr, 36.49% at the DHS site. Cr existed mainly in the insoluble fraction at the DHS and GZ sites, respectively, with levels lower than those observed in Mexico City but higher than in Edinburgh (Baez et al., 2007; Mukhtar and Limbeck, 2013). More than 80% Cd solubility was found in Guangzhou and Dinghushan, which is worth noting due to its ecological and health hazards as mentioned in Section 2.4. Cadmium acetate, cadmium sulfate and halogenated cadmium are the common soluble species in the atmosphere emitted from vehicles, MSW incineration and metal smelters, *etc.* (Cheng et al., 2014, 2015; Wang et al., 2017). Therefore, relevant action should be taken to control cadmium pollution in the atmosphere and to diminish its potential ecological and health risk.

2.6. Source apportionment by PMF

Heavy metal elements (Cu, Pb, Cd, Cr and Zn) and ions (F^-, Cl^-, NO_3^-, SO_4^{2-}, K^+, Mg^{2+}, Na^+, Ca^{2+}) were added to improve the model calculation in the EPA PMF analysis. Initially, PMF factors were resolved using the numbers from 50 runs. The number of factors was changed to optimize the goodness-of-fit parameter Q over the theoretical Q (Khan et al., 2016).

2.6.1. Source apportionment for wet deposition in Guangzhou

Based on the PMF model, 7 factors were finally determined for Guangzhou and identified as the following possible sources,

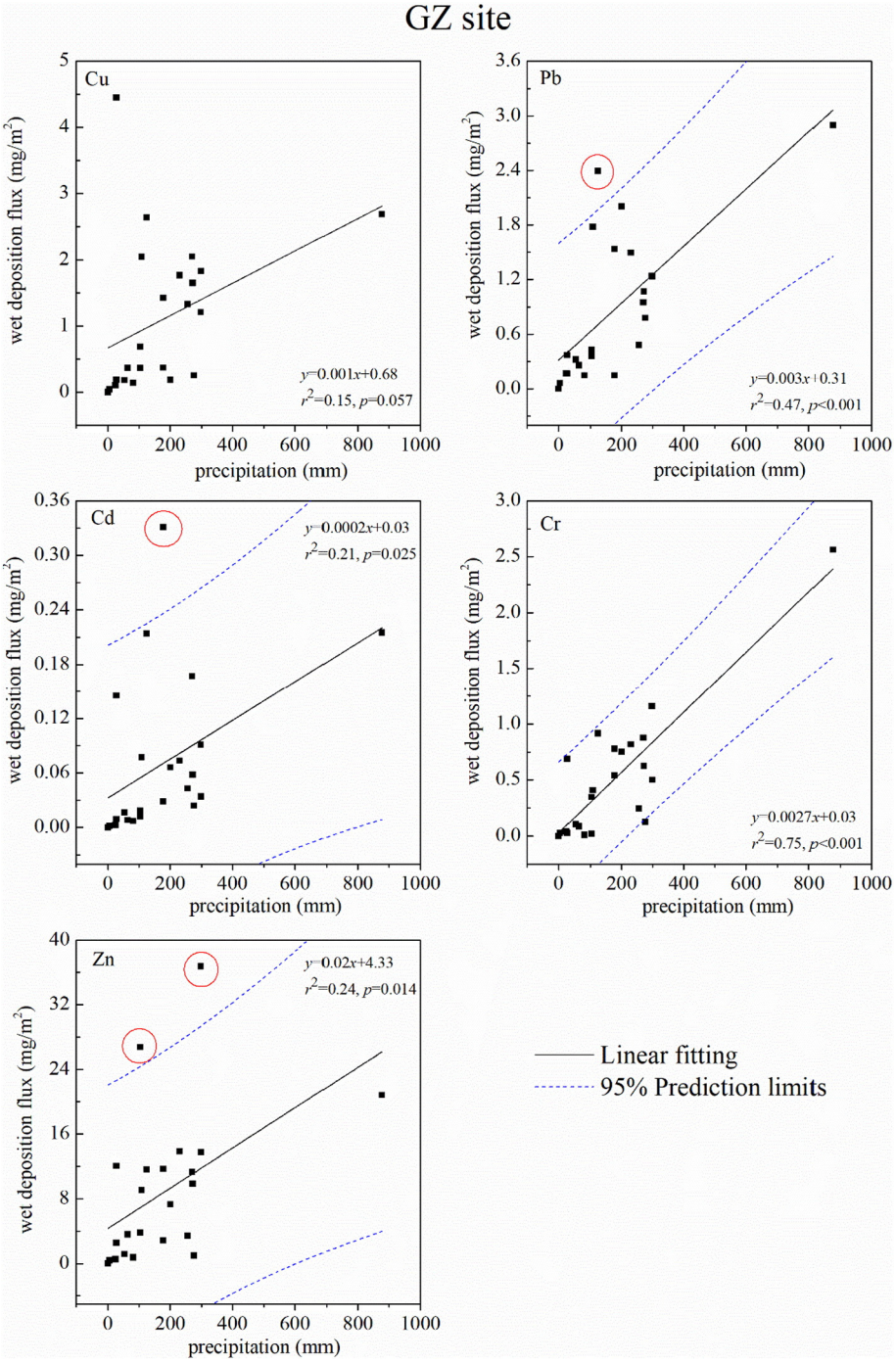

Fig. 6 – Monthly deposition flux of heavy metals vs. precipitation at GZ site during 2014–2015.

for which the factor profiles (% of species and contributions) are illustrated in Fig. 9.

Factor 1 is mainly dominated by Ca^{2+} (73.1%), K^+ (43.6%) and Mg^{2+} (42.3%) ions, suggesting that this source is related to the dust or crustal source (Xu et al., 2008). Researchers cited these ions as markers for the mineral dust source from rapid development activities such as construction, renovation of road surfaces, *etc.* (Khan et al., 2016).

Factor 2 has high contribution by Cr (53.3%) and K^+ (27.1%). Coal combustion is one of the important sources of atmospheric Cr, while K^+ is a good marker of biomass burning. Biomass burning has been reported as an important contributor to atmospheric pollutants in the PRD region (Dai et al., 2013; Zhang et al., 2015b), and burning of coal combined with biomass is relatively prevalent in China. Therefore, these results suggest that factor 2 is strongly related to coal and biomass burning.

Factor 3 has predominant contributions from Pb (79.7%), Cu (76.2%), Zn (46.8%), Cr (46.6%) and Cd (36.1%) and much less from other species (<5%), which are good indicators of industry emissions (Duan and Tan, 2013).

Factor 4 contains substantial Cd (42.1%), F^- (36.6%), SO_4^{2-} (29.6%) and NO_3^- (26.7%). The F^- in the precipitation mainly

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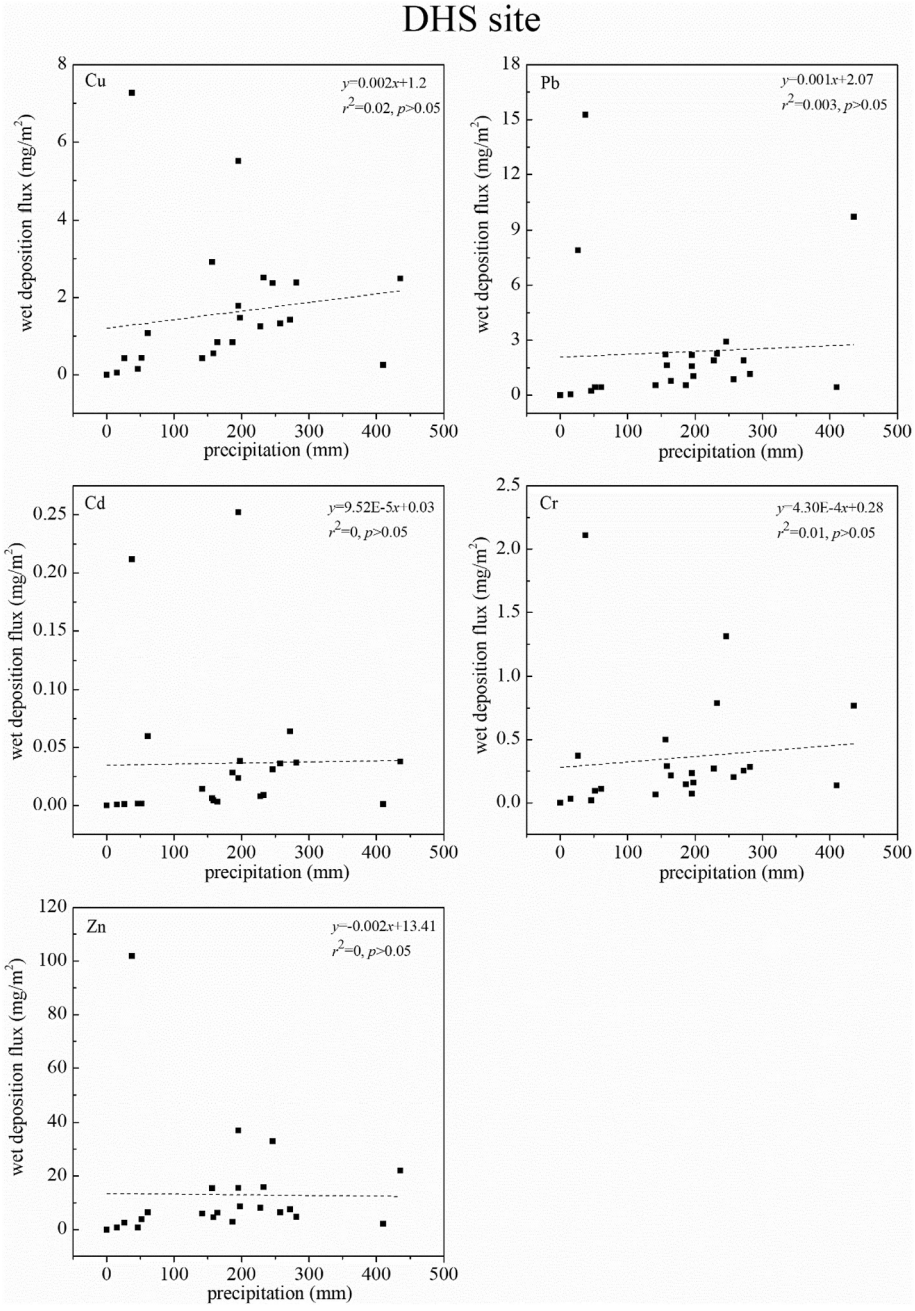

Fig. 7 – Monthly deposition flux of heavy metals vs. precipitation at DHS site during 2014–2015.

originates from anthropogenic emissions (Ge et al., 2016). Aucelio et al. (2007) and Hjortenkrans et al. (2007) reported that lubricating oil and some tire wear from vehicles release Cd into the atmosphere. SO_4^{2-} shows a significant relationship with NO_3^- ($p < 0.001$), which may be attributable to their similar chemical behaviors in precipitation and the co-emission of their precursors SO_2 and NOx from vehicle exhaust.

Factor 5 has the predominant ions of NH_4^+(77.1%), NO_3^-(29.2%) and SO_4^{2-}(15.5%), and has less than 20% contribution from heavy metals, indicating that it is a mixture of aged pollutants associated with long range transport. NH_4^+, NO_3^- and SO_4^{2-} are indicators of secondary aerosol and long-range transport (Tan et al., 2014).

Factor 6 is mainly dominated by Na^+ (57.7%), Mg^{2+} (33.8%) and F^- (23.6%) ions, suggesting that this source is related to marine aerosol sources. This factor may represent effective marine cloud condensation nuclei from the South China Sea near the PRD region.

Factor 7 features Cl^- (80%) and SO_4^{2-} (37.6%), with relatively lower Na^+ (10.7%). Although there is a correlation between Na^+ and Cl^- in the precipitation ($p < 0.05$), the Cl^-/Na^+ molar ratio in precipitation, with an average value of 11.72 (ranging from 0.30 to 60.00) is much higher than that of seawater along the South China Sea (Cl^-/Na^+ = 3.82, (Zhang et al., 2015a)). This indicates that Cl^- may not all come from sea salt, but may be due to the release of HCl during reactions between nitric and sulfuric acid

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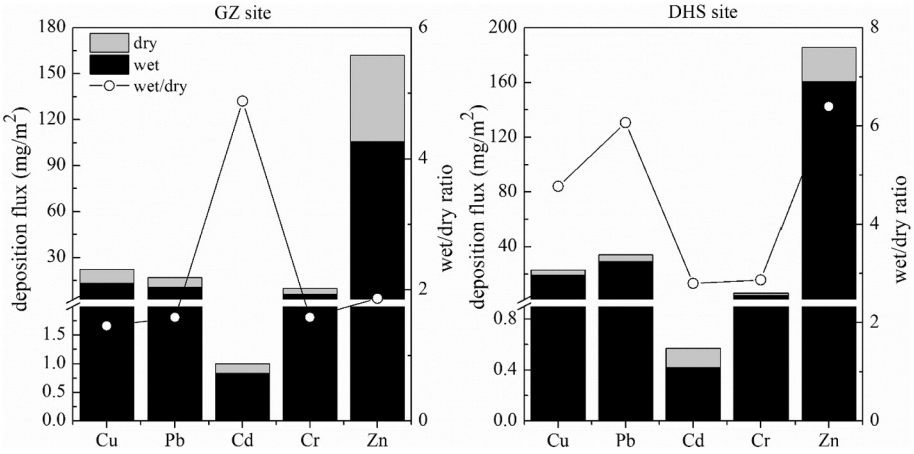

Fig. 8 – Composition of heavy metals in dry and wet deposition and ratios of wet to dry deposition flux.

(Wang et al., 2008). Moreover, the use of gasoline with lead chorobromide as an additive often produces gasified HCl (Li et al., 2010).

Source contributions of Cu, Pb, Cd, Cr and Zn in precipitation in Guangzhou calculated by the EPA PMF 5.0 model are shown in Fig. 11. Dust, biomass burning, industries, vehicles, long-range transport, sea salt and others are the sources contributing to the wet deposition of heavy metals in Guangzhou. Industries contribute about 76.2%, 79.7%, 36.1%, 53.3% and 46.8% of Cu, Pb, Cd, Cr and Zn, respectively; at the same time, vehicles contribute about 8.5%, 6.7%, 42.1% and 25.0% of Cu, Pb, Cd and Zn, respectively. These results suggest that industrial and vehicle emissions are the dominant sources.

2.6.2. Source apportionment for wet deposition in Dinghushan

In the same way, 7 factors were finally determined for Dinghushan and identified as arising from the following possible sources, with factor profiles (% of species and contributions) illustrated in Fig. 10.

Factor 1 is mainly dominated by SO_4^{2-} (56.1%), Zn (42.3%), Cl^- (32.1%) and NO_3^- (27.8%). As the DHS site is located at the foot of Dinghu Mountain and surrounded by farmland, zinc salts such as $ZnSO_4$ in fertilizer applied to the vegetable and tree fields and ZnO aqueous solutions sprayed on leaves are commonly used, suggesting that this source is related to Zn fertilizers (Ozsoy and Ornektekin, 2009). Factor 2 contributes high percentages of Na^+ (75.3%), Mg^{2+} (65.2%) and Ca^{2+} (38.8%) ions, showing that this source is related to the marine aerosol sources. Factor 3 contains substantial NH_4^+(87.7%) and Cu (25.1%), indicating an agricultural source (Huang et al., 2015; Wang et al., 2013; Zheng et al., 2012).

Factor 4 features Cd (75.5%), Ca^{2+} (33.9%), Pb (22.3%) and Zn (21%), suggesting that this source is related to incense burning. Qing Yun temple is one of typical famous Buddhist–Taoist combined temples in the PRD region, with an endless stream of pilgrims, located at the top of Dinghu Mountain. Lau and Luk (2001) once reported that both joss paper and stick ashes containing higher amounts of heavy metals were found in the air around the temple, and researchers further determined that Cd, Pb and Zn were the dominant components (Fang et al., 2003; See and Balasubramanian, 2011).

Factor 5 had a high percentage of K^+ (58.2%), which indicates that biomass burning contributes to this factor. In the suburban area, the burning of paddy straw, rape straw and other biomass fuel for activities such as cooking or heating can emit K, which is evident in the suburban areas of Shenzhen and Beijing, China. Additionally, post-harvest field burning is another typical source of biomass burning in the suburban regions (Khan et al., 2016).

Factor 6 has predominant traces of Cr (81.7%), Cu (30.3%) and Pb (25.0%). Diesel exhaust from vehicles and lubricant oil combustion are the major sources of atmospheric Cr, Cu and Pb (Adamiec et al., 2016; Pulles et al., 2012).

Factor 7 contains substantial F^- (52.2%), Pb (51.2%) and NO_3^- (37.2%). Atmospheric fluoride is recognized as a tracer of the ceramics industry (Tan et al., 2014). Peng et al. (2007) reported that Pb is one of the dominant heavy metals in the flue gas of the ceramics industry. Since industrial relocation took place in Guangdong Province, more ceramics industries were moved from Foshan to Zhaoqing (where Dinghushan is located).

The source contributions of Cu, Pb, Cd, Cr and Zn in precipitation in Dinghushan calculated from the EPA PMF 5.0 model are shown in Fig. 11. Zn fertilizers, marine aerosol sources, agriculture, incense burning, biomass burning, vehicles and the ceramics industry are the sources contributing to the wet deposition of heavy metals in Dinghushan. Local and regional emissions are the dominant sources for Dinghushan, with the ceramics industry, incense burning and vehicles contributing more than 50% of Pb, Cd and Cr.

Table 5 – Hakanson potential ecological risk of 5 heavy metals from atmospheric deposition at DHS and GZ sites.

Site	E_r^i					RI
	Cu	Pb	Cd	Cr	Zn	
GZ	48.82	19.02	5032.72	4.59	19.86	5125.00
DHS	50.46	40.32	2881.55	3.56	22.61	2998.50

GZ: Guangzhou; DHS: Dinghushan.

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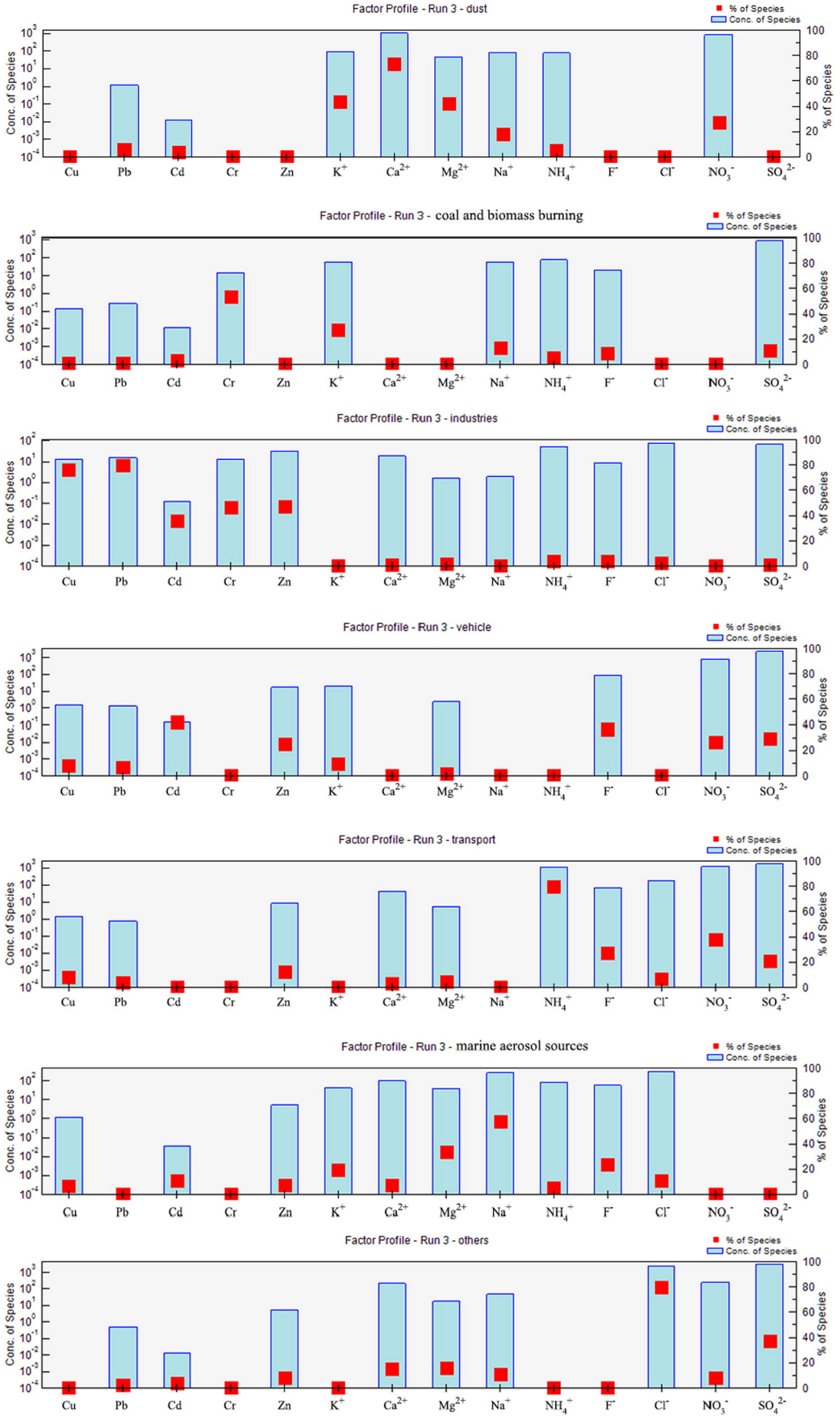

Fig. 9 – Factor profiles (% of species and contributions) obtained from US Environmental Protection Agency (EPA) positive matrix factorization (PMF) model in Guangzhou.

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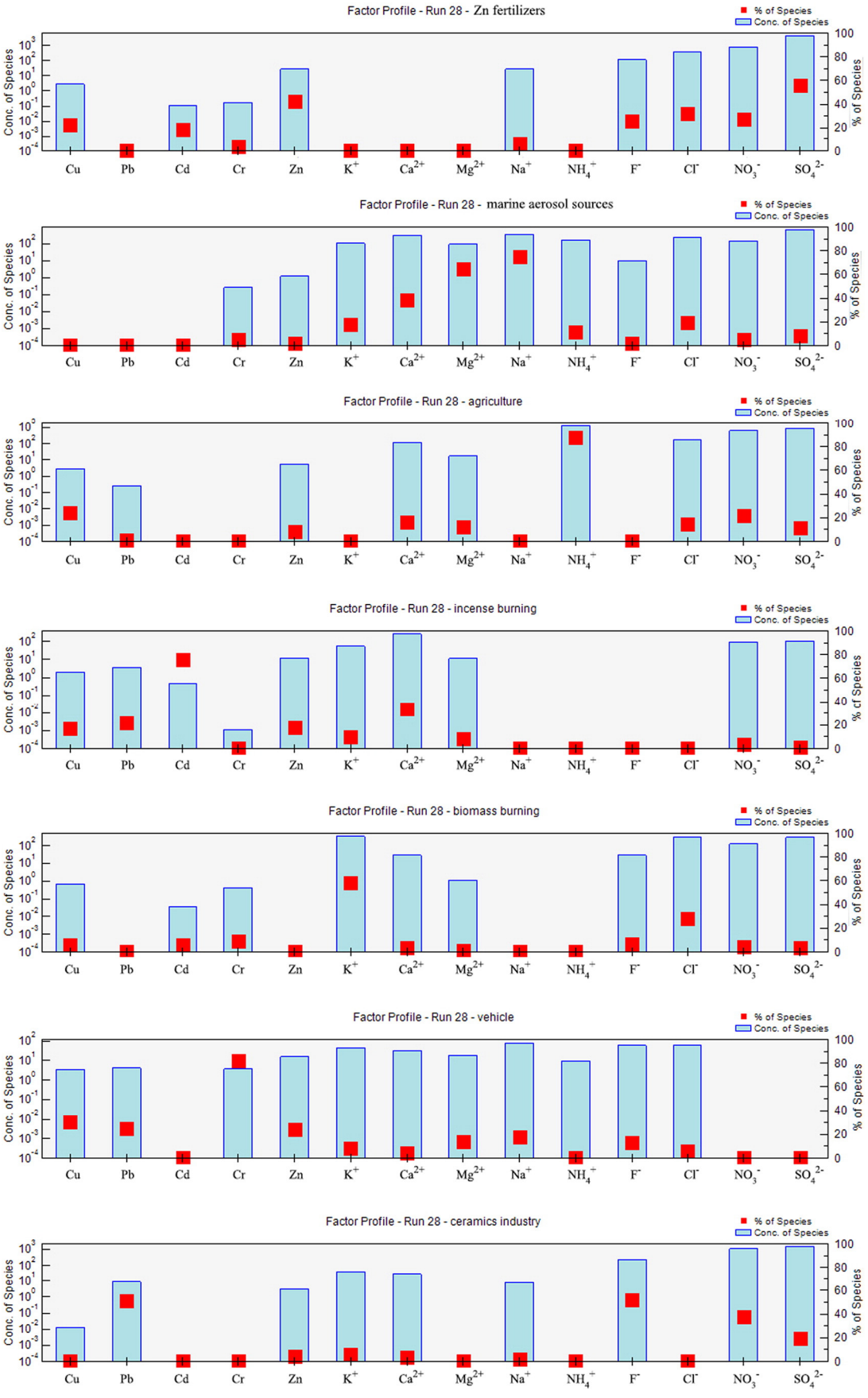

Fig. 10 – Factor profiles (% of species and contributions) obtained from US Environmental Protection Agency (EPA) PMF model in Dinghushan.

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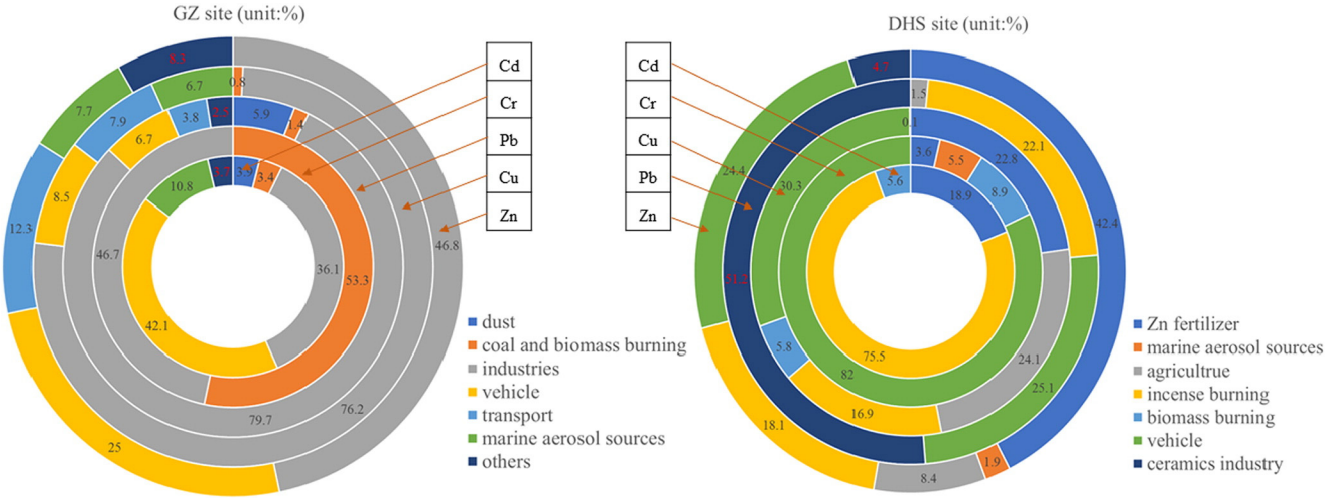

Fig. 11 – Source contributions calculated from US Environmental Protection Agency (EPA) PMF model.

3. Conclusions

The present study investigated the characteristics and ecological risk of atmospheric heavy metal wet and dry deposition in the PRD region and their potential sources. Affected by the regional pattern of precipitation, heavy metal wet deposition presented significant seasonal variation, and deposition was governed by wet deposition rather than dry deposition in the PRD region. Compared with other measurements around the world, the deposition flux in the PRD region was relatively higher, probably due to intensive manufacturing activities, suggesting that heavy metal control is still greatly needed. Cd was classified as an extremely strong potential ecological risk based on its solubility and the Hakanson ecological risk index. A PMF method was applied for source analysis of wet deposition of heavy metals, suggesting that substantial contributions were from local and regional sources. Meanwhile, distant sources also likely contributed to the wet deposition. Since size distribution is essential in source analysis and determination of the deposition mechanism, more information on the size distribution of atmospheric heavy metals in the PRD region is called for in future study.

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