



Preliminary assessment of size distribution of airborne metals and metalloids in the urban aerosols of Guiyang, southwest China

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ABSTRACT

Size-fractionated (7 fractions from <math><0.39\ \mu\text{m}</math> up to \text{PM}_{10.2}, and $\text{PM}_{2.1}$ concentrations in Guiyang were at relatively low levels (59.1–222, 48.6–192, and 33.2–131 $\mu\text{g}/\text{m}^3$). This is consistent with the small industrial scale of this city. In the winter, coal combustion was proven to be the dominant source of airborne PM, whereas in other seasons, road dust resuspension was considered the primary source. Al, Ti, Fe, Sr, and Ba were highly associated with soil particles in the road dust. Cu and Zn could be associated with vehicle emissions that accumulated in road dust, while As, Mo, Cd, Sb, and Pb (and another portion of Zn) could be associated with main local industrial emissions. Compared to the coarse PM, the fine PM typically exhibited lower concentrations of crustal elements but higher concentrations of anthropogenic elements. The anthropogenic elements exhibited higher water solubility than crustal elements. Almost all of the elements in the PM in the winter exhibited the highest water solubility because of the lowest pH of the PM in this season.

Keywords: Aerosols, metals, metalloids, size distribution



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Article History:

Received: 09 September 2014

Revised: 18 January 2015

Accepted: 19 January 2015

doi: 10.5094/APR.2015.072

1. Introduction

Atmospheric pollution is a significant environmental issue across the world, especially in cities. Aerosol particles are known to have negative health effects on humans (Anenberg et al., 2010; Cheng et al., 2013). Besides, the chemical composition and, especially, the toxic metal concentrations of aerosols are also crucial for the assessment of the risks to human health associated to aerosols (Voutsas and Samara, 2002; Heal et al., 2005; Schleicher et al., 2011). In the last three decades, economic development in China has been fast but has also increased the emission levels of metals and metalloids into the atmosphere, resulting in poor air quality and adverse effects on human health (Cheng et al., 2013). Many studies of airborne particulate matter (PM) have been conducted in China, mostly near northern cities, such as Beijing, Xi'an and Tianjin (Bi et al., 2007; Li et al., 2011; Schleicher et al., 2011), coastal cities or industrialized cities in Eastern and Southern China (Wang et al., 2003; Hu et al., 2014). Airborne PM in these areas is considered to be significantly affected by sand or dust storms (Zhang et al., 2010), intensively distributed industrial factories (Huang et al., 2013), and sea salt (Wang et al., 2006).

Guiyang City is located in inland (southwest) China. This city is not affected by sand or dust storms and has only a small amount of industrial activity (an iron and steel works, a coal-fired power plant, and an aluminum electrorefining plant) that can make significant contribution to air pollution. Guiyang is situated in a karst basin (elevation 1050 m) that is surrounded by hills and mountains, and the wind is weak throughout the year, which is unfavorable for the dispersion of atmospheric contaminants.

However, Guiyang is now undergoing rapid urbanization, and as a result, the quantity of residents, buildings and vehicles is growing fast. The traffic in Guiyang is very intense due to the rapid increase of vehicles and the limited urban area. In addition, coal combustion is still in domestic use, especially in the winter. The combination of these factors may uniquely influence the characteristics of the airborne contaminants. The aerosols of Guiyang were mainly addressed in terms of organic substances in TSP (Guoying et al., 1991; Hu et al., 2012), water-soluble ions in TSP (Xiao and Liu, 2004), mineral characteristics of PM_{10} (Xie et al., 2005), and metals in TSP (Wu et al., 2008). The study by Wu et al. (2008) reported the total concentrations and speciation of only five metals (Cd, Cr, Cu, Pb, and Zn) in TSP from Guiyang in 2006–2007. Our work aimed to elucidate the seasonal size distribution of PM-related metals and metalloids (Al, Ti, Mn, Fe, Cu, Zn, As, Sr, Mo, Cd, Sb, Ba, and Pb) in Guiyang, as well as the water solubility of these elements, to provide valuable information for risk-mitigation measures by the departments of public affairs.

2. Methodology

2.1. Area description

Guiyang City, the capital of Guizhou Province, is located in the southwest of China (26°34'N, 106°43'E). The area of the city is only 220 km², whereas the population is ca. 4 million, and the quantity of vehicles was 750 000 in 2011 and is increasing by ca. 150 vehicles per day. Therefore, this city has a high population density, and the traffic is very intense. Generally, the industry of Guiyang is undeveloped compared to other provincial capitals in China. An

iron and steel works and a coal-fired power plant are the two most important factories. There is also an aluminum electrorefining plant, but it is far away (ca. 25 km) from the urban area. Other main economic activities are correlated with tobacco, alcohol, tea, food, medicine, and construction. Guiyang has been undergoing rapid urbanization and economic development, and the air quality in this city is deteriorating. The prevailing winds are from the southeast in the spring and summer and from the north in the fall and winter. The climate is typically overcast, cloudy or rainy, and the wind speed is typically in the low range of <1.5 m/s.

2.2. Sample collection, pretreatment and analysis

Deionized water (18.2 MΩ cm) produced by a Milli-Q system (Millipore, Bedford, USA) was used throughout the experiment. Concentrated nitric acid (HNO₃, 69%), hydrochloric acid (HCl, 37%), and hydrofluoric acid (HF, 40%) were purified using a sub-boiling distillation system (SavilleX DST-1000, Minnetonka, USA) prior to use.

Size-fractionated PM was collected from a lawn (25 m × 25 m) in the Institute of Geochemistry, Chinese Academy of Sciences. This institute is located in the urban area of Guiyang City, and the sampling site is more than 100 m away from the main traffic roads. A six-stage cascade impactor (Model 236; Staplex Inc., USA) was employed to collect the size-fractionated PM samples at a height of 1.2 m. Slotted cellulose filters (15×14.3 cm; Model TFAS810, USA) were soaked in ultra-pure HCl for three days to reduce the blank of metals and dried in advance. These filters were used to collect six size fractions of PM. A back-up filter (pore size: 1 μm) (17.7×22.7 cm) was used to collect the remaining (finest) particles. Samples were collected between May 14 and 18, 2011 (spring), between July 26 and 30, 2011 (summer), between October 30 and November 3, 2011 (fall), and between January 6 and 10, 2012 (winter). Each day during these periods, a set of size-fractionated PM samples were collected from around 8:00 a.m. at a flow rate of 565 L/min. Under the operational conditions, the collected particles were classified in the following seven size intervals: <0.39, 0.39–0.69, 0.69–1.3, 1.3–2.1, 2.1–4.2, 4.2–10.2, and ≥10.2 μm. Five set of samples were collected in each season, and a total of 20 set of samples (140 size-based subsamples) were obtained. After sample collection, the filters were preconditioned in a desiccator for at least 72 h to obtain a constant weight because the cellulose filter easily absorbs humidity in the air. The filters before and after sample collection were weighed by a micro balance (0.01 mg) to obtain the weight of the PM.

The sample digestion procedure was modified from Liang et al. (2000). Three of the ten strips of each slotted filter or a quarter of the back-up filter were placed into a Teflon crucible. One milliliter of HNO₃ and 0.2 mL of HF were added. The crucible was sealed within a stainless steel bomb and heated at 140 °C for 12 h. After cooling, the digestion bomb was opened and heated at 80–90 °C to dry the solution. Then, 0.5 mL of HNO₃ was added and evaporated until dry. The residue was re-dissolved in 0.5 mL of HNO₃ and diluted into 50 mL. A clean cellulose filter was also digested to prepare a digestion blank. To determine soluble metals and metalloids of PM, another three strips of each slotted filter or a quarter of a back-up filter were ultrasonically extracted with 15 mL of deionized water for 30 min and then filtered through a 0.45-μm cellulose filter (Millipore). The pH of the extract was determined by a Hanna pH meter.

After sample digestion and extraction, the metal and metalloid determination was conducted by a quadrupole ICP-MS (Platform ICP, Micromass Instrument Corporation, Manchester, UK). Multi-element standard solutions (Accu-Trace ICP-MS Calibration Standard, 10 μg/mL for each element) for ICP-MS analysis were purchased from AccuStandard Inc., New Haven, USA. These solutions were diluted in a matrix of 1% HNO₃ to different metal concentrations for the external calibration of analysis. Detection limits were calculated three times the standard deviation of determination blank – 1% HNO₃ (n=8). Metals and metalloids Al, Ti, Mn, Fe, Cu, Zn, As, Sr, Mo, Cd, Sb, Ba, and Pb were determined, and the corresponding detection limits for these elements were 0.2, 0.3, 0.3, 0.4, 0.2, 0.3, 0.3, 0.05, 0.05, 0.05, 0.05, 0.05, and 0.05 μg/L, respectively.

Method blanks, certified reference fly ash and soil (GBW08401 and GBW07404, China National Research Center of CRM's, Beijing, China), were included in the analysis. Method blank was conducted in the same procedure to samples. The blank of the cellulose filter and the recoveries for metals and metalloids in certified reference materials are presented in Table 1. The procedure blank caused by the cellulose filter was mostly <5% for the metal and metalloid concentrations of PM sample in most cases. Exception was for Fe whose blank values could be high as 10%. In these cases, the blank was subtracted for the analysis.

Statistical analysis of the dataset was conducted using SPSS software (V.18). Principal components analysis (PCA) was carried out by using a Varimax Rotation with Kaiser Normalization to identify the metals and metalloids in PM with similar sources or behaviors.

Table 1. Blank of cellulose filter (n=3) and recoveries for metals and metalloids in certified reference materials (n=4)

	Filter Blank (μg/g)	GBW07404 Soil		GBW08401 Fly Ash	
		Certified ^a	Recovery (%)	Certified ^a	Recovery (%)
Al	31±5			12.9±0.3	97±3
Ti	27±5	1.08±0.05	102±4	0.58±0.01	101±4
Mn	2.3±0.4	142±12	106±3	1.178±20	98±4
Fe	15±3	7.21±0.11	105±6	7.65±0.07	110±5
Cu	0.41±0.03	40±4	99±4	53±2	97±4
Zn	1.2±0.4	210±19	107±5	61±4	100±4
As	0.35±0.03	58±8	92±4	11.4±0.3	98±5
Sr	0.26±0.05	77±9	95±2		
Mo	0.15±0.04	2.6±0.4	95±3		
Cd	0.12±0.02	0.35±0.08	100±3	0.16±0.02	109±3
Sb	0.15±0.02	6.3±1.7	102±2		
Ba	0.42±0.04	213±31	90±2	1.450±59	98±2
Pb	0.40±0.02	58±7	105±3	33.8±2.2	95±3

^a The unit is % for Al, Ti, and Fe, and μg/g for other elements.

The meteorological parameters during the sampling periods were supplied by the Guizhou Bureau of Meteorology, the monitoring site of which is located 1.5 km from the sampling site.

3. Results and Discussion

The meteorological parameters during the sampling periods are listed in Table 2. In spring and fall, the weather was occasionally rainy (daily precipitation <1 mm in spring and <0.1 mm in fall), and in the summer, it was generally sunshiny. In the winter, it was either snowy or rainy (daily precipitation: 0.2–0.5 mm). The wind was characterized by a slow speed of <1.5 m/s.

3.1. Concentrations of PM masses and metals and metalloids

The size-fractionated PM samples were analyzed for PM masses, total and water-soluble concentrations of metals and metalloids. In this preliminary study, the five set of PM samples from one location in May, July, October–November of 2011, and January of 2012 were representative of PM in spring, summer, fall,

and winter, respectively. More PM samples from different locations will be required to be collected and analyzed in further studies to make a more representative assessment.

For comparison with the standard parameters frequently used in air-quality evaluations, the concentrations of PM and the associated metals and metalloids were segregated into three size fractions, the total suspended particle (TSP), PM_{10.2}, and PM_{2.1} (Table 2). TSP represents the sum of seven size intervals, PM_{10.2} represents the sum of six size intervals (<0.39, 0.39–0.69, 0.69–1.3, 1.3–2.1, 2.1–4.2, and 4.2–10.2 μm), and PM_{2.1} the sum of four size intervals (<0.39, 0.39–0.69, 0.69–1.3, and 1.3–2.1 μm). During four seasons, the TSP concentrations were 59.1–222 μg/m³, the PM_{10.2} concentrations were 48.6–192 μg/m³, and the PM_{2.1} concentrations were 33.2–131 μg/m³. The highest TSP, PM_{10.2}, and PM_{2.1} concentrations occurred in the fall. This was possibly due to biomass burning, which was popular for the treatment of fallen tree leaves in the urban area (Wu et al., 2008), as well as that of crop straw in the suburb of Guiyang.

Table 2. Meteorological parameters during the sampling periods and concentrations of PM mass (μg/m³) and associated metals and metalloids (ng/m³) in the TSP, PM_{10.2} and PM_{2.1} fractions

		Spring			Summer			Fall			Winter		
T (°C)	Max	21±7			30.6±2.2			20.8±0.8			2±2		
	Min	15.4±3.3			23±0.7			12.4±1.9			−0.6±1.1		
RH (%)		53–92			61–73			81–92			92–98		
PM	Mean	TSP	PM _{10.2}	PM _{2.1}	TSP	PM _{10.2}	PM _{2.1}	TSP	PM _{10.2}	PM _{2.1}	TSP	PM _{10.2}	PM _{2.1}
	SD	88.6	76.1	51.1	59.1	48.6	33.2	222	192	131	94.6	81.5	59.6
Al	Mean	34.9	30.9	22.7	10.2	7.9	6.2	49	43	30	16.3	13.9	9.7
	SD	5 715	4 705	1 819	2 397	1 749	758	1 734	1 331	579	1 043	748	370
Ti	Mean	2 705	2 187	837	542	410	143	585	463	263	680	535	302
	SD	658	545	227	240	174	79.9	152	119	56.0	115	88.1	51.8
Mn	Mean	410	344	119	70	51	21.4	37	31	14.6	84	68.1	43.0
	SD	413	385	295	238	210	162	206	190	133	115	109	89.6
Fe	Mean	306	293	256	159	150	133	137	131	76	115	111	91.9
	SD	5 374	4 479	1 646	3 383	2 116	910	9 966	7 829	3 944	1 442	1 116	721
Cu	Mean	3 231	2 753	759	1 341	681	257	5 430	4 255	2 363	892	745	531
	SD	211	199	156	95.9	87.0	64.4	50.6	44.5	29.0	40.7	35.8	24.1
Zn	Mean	149	141	116	30.5	28.1	19.8	15.4	12.4	7.0	16.6	13.2	7.4
	SD	354	339	290	257	235	186	200	191	148	145	140	128
As	Mean	122	116	97	135	126	105	84	81	61	90	88	81
	SD	62.1	56.1	42.7	47.9	43.8	34.2	73.8	69.2	57.5	49.1	44.2	33.4
Sr	Mean	8.8	7.8	5.4	23.5	20.3	14.3	26.8	26.5	23.3	21.1	19.9	15.6
	SD	77.1	61.8	20.3	33.9	23.7	9.5	26.8	19.7	8.1	16.6	12.1	6.4
Mo	Mean	50.1	40.4	9.5	9.9	6.7	2.1	6.8	5.1	2.2	9.0	7.0	3.9
	SD	8.7	7.9	5.7	9.6	7.5	4.8	33.5	28.7	19.3	11.8	10.4	8.5
Cd	Mean	4.5	4.2	3.0	4.1	3.2	2.3	14.0	11.5	6.4	6.0	5.2	3.7
	SD	7.0	6.6	5.2	10.1	8.8	6.1	9.6	8.7	6.6	7.9	7.2	5.9
Sb	Mean	2.8	2.6	2.2	3.4	3.1	2.5	2.2	2.0	1.3	3.6	3.1	2.2
	SD	17.8	17.1	14.3	10.4	9.8	7.8	23.3	22.6	18.4	16.4	15.9	13.1
Ba	Mean	8.7	8.4	6.9	5.1	4.6	3.5	10.9	10.8	8.8	9.3	9.1	6.4
	SD	474	380	142	43.7	31.7	14.0	50.2	37.9	15.3	32.6	26.5	16.2
Pb	Mean	510	405	125	15.5	10.2	3.9	17.7	11.3	3.3	15.6	13.5	8.6
	SD	214	209	190	455	444	384	191	186	162	148	145	135
		57	56	47	326	323	267	80	78	67	57	56	51

RH: Relative humidity, SD: Standard deviation.

The concentrations of PM mass and associated metals and metalloids in the TSP, PM_{10.2}, and PM_{2.1} of each season are expressed as the mean value and standard deviation of samples (sample number: 5 for each season).

The mass concentrations of TSP for each size fraction of airborne PM in Guiyang were compared with other cities in China. The annual average TSP concentration in 93 cities of China from 1981 to 2008 was 402 $\mu\text{g}/\text{m}^3$ (Zhang et al., 2010), and the median TSP mass concentration of Beijing from 2005 to 2008 was 373 $\mu\text{g}/\text{m}^3$ (Schleicher et al., 2011). The average PM_{10} concentrations of six cities in Northern China from 1999 to 2002 were 115–186 $\mu\text{g}/\text{m}^3$ (Bi et al., 2007). The PM_{10} and $\text{PM}_{2.5}$ concentrations in Nanjing in 2001 were 194–632 $\mu\text{g}/\text{m}^3$ and 149–423 $\mu\text{g}/\text{m}^3$ (Wang et al., 2003). The $\text{PM}_{2.5}$ concentrations in Beijing in 2000 and Tianjin in 2008 were 101 $\mu\text{g}/\text{m}^3$ (Zheng et al., 2005) and 144.6 $\mu\text{g}/\text{m}^3$ (Gu et al., 2011), respectively. The relatively low PM concentrations of Guiyang are consistent with the small industry scale of this city. In 2013, the gross domestic production (GDP) of Guiyang ranked only 29 among the 34 province–capital cities in China (NBSC, 2013).

Among the toxic metals and metalloids in TSP of four seasons, Pb and Zn were generally the most abundant, and Cd and Sb were the least abundant, whereas Cu and As were at a median concentration level. In contrast, a previous study on the TSP of Guiyang by Wu et al. (2008) reported a lower Cu concentration of 31.2 ng/m^3 , higher Cd and Zn concentrations of 14.5 ng/m^3 and 1161 ng/m^3 , respectively, and a similar Pb concentration of 393 ng/m^3 .

3.2. Extraction of water-soluble metals and metalloids in PM

Regarding the extraction of metals and metalloids in PM by water, the pH of the extracts is shown in Table 3. The pH of the extract of PM is generally in the range of neutral to slightly acidic (3.8–7.5). The extract of PM in the winter exhibited the lowest pH

compared to that of other seasons. This is consistent with the high usage of coal for heating in winter in Guiyang. The pH of the extract decreases as the particle size decreases. This trend has also been observed in the aerosols from Nanjing, China (Wang et al., 2003). This is because acidic substances released by coal or gasoline combustion were proven to be mainly enriched in fine PM (Andreae et al., 1987; Talbot et al., 1988), and basic substances from crustal materials were proven to be enriched mainly in coarse PM (Jacobson et al., 2000).

Table 3. Mean pH values of the water extracts of the size-fractionated PM

Size (μm)	Spring	Summer	Fall	Winter
≥ 10.2	7.3	7.1	7.4	6.7
4.2~10.2	7.2	7.5	7.3	6.2
2.1~4.2	7.1	7.3	7.0	5.5
1.3~2.1	6.7	7.0	6.6	4.4
0.69~1.3	5.7	6.8	5.9	3.9
0.39~0.69	5.5	5.6	5.2	3.9
<0.39	5.4	5.3	5.0	3.8

The water-solubility of metals and metalloids in PM is shown as a composite result in Table 4. The water-soluble proportion (WSP) of metals and metalloids in the fine PM is generally higher than that in the coarse PM. The PM of winter generally showed high WSP of metals and metalloids relative to those in the other seasons. For example, the WSPs of Al, Ti, Fe, Zn, Sr, Ba, and Pb in the TSP of winter were the highest among four seasons, and those of Mn, Cu, and Cd were the second highest.

Table 4. Water-soluble proportions (%) of metals and metalloids in the TSP, $\text{PM}_{10.2}$ and $\text{PM}_{2.1}$ fractions

		Spring			Summer			Fall			Winter		
		TSP	$\text{PM}_{10.2}$	$\text{PM}_{2.1}$	TSP	$\text{PM}_{10.2}$	$\text{PM}_{2.1}$	TSP	$\text{PM}_{10.2}$	$\text{PM}_{2.1}$	TSP	$\text{PM}_{10.2}$	$\text{PM}_{2.1}$
Al	Mean	1.3	1.4	3.0	2.0	2.3	3.6	3.2	3.8	7.3	10.7	14.4	26.3
	SD	0.7	0.7	1.3	0.6	0.6	1.1	1.0	1.1	1.9	6.1	8.2	15.0
Ti	Mean	8.3	8.8	15.5	13.3	15.9	25.3	25.5	29.7	49.5	32.1	38.2	52.3
	SD	2.9	3.1	5.7	1.1	1.4	2.4	5.8	6.9	12.0	10.0	11.9	16.2
Mn	Mean	36.0	36.7	40.1	54.0	59.9	70.9	68.2	72.6	85.0	57.9	58.7	60.8
	SD	25.7	25.7	26.6	47.3	53.4	66.9	63.7	68.6	74.7	51.5	52.3	55.7
Fe	Mean	0.5	0.6	1.4	1.1	1.6	3.2	0.4	0.5	0.8	4.7	6.0	8.6
	SD	0.3	0.3	0.7	0.4	0.7	1.3	0.1	0.1	0.2	2.3	2.9	3.9
Cu	Mean	14.3	13.7	13.8	33.0	34.1	38.4	26.2	27.8	33.7	28.3	29.9	31.3
	SD	8.3	7.6	7.5	16.0	16.3	18.6	6.2	6.8	8.8	7.0	7.5	6.3
Zn	Mean	38.4	39.0	43.5	47.3	50.2	58.0	62.1	64.7	77.7	71.9	73.7	74.8
	SD	27.4	27.4	30.0	33.3	35.8	42.7	24.2	25.2	29.9	36.5	37.5	38.4
As	Mean	23.2	24.2	27.6	45.1	47.6	54.7	52.5	55.0	62.0	28.9	30.2	33.5
	SD	7.2	7.9	9.8	13.0	14.1	16.0	24.9	26.5	30.5	8.5	8.7	9.0
Sr	Mean	44.7	44.7	62.4	42.0	46.8	63.7	60.6	67.1	97.9	68.5	75.7	90.4
	SD	23.4	22.9	29.5	4.9	5.6	6.0	8.9	9.9	15.1	28.4	30.4	34.2
Mo	Mean	76.2	75.4	81.1	47.6	54.0	64.2	12.3	12.9	14.9	30.8	30.4	27.4
	SD	31.0	32.3	41.1	3.7	4.4	6.2	3.3	3.7	4.8	4.6	4.6	5.2
Cd	Mean	74.9	73.0	72.3	36.9	37.3	40.3	54.8	56.0	62.5	66.7	66.9	66.6
	SD	13.5	13.1	13.0	3.6	4.0	5.3	10.8	11.2	13.1	12.8	13.7	14.8
Sb	Mean	26.8	26.4	27.4	39.1	39.5	43.6	38.0	38.3	42.5	28.2	28.0	29.5
	SD	11.5	11.8	13.3	6.6	6.9	8.0	17.6	18.0	20.6	11.8	11.9	13.2
Ba	Mean	4.3	4.7	7.4	26.3	30.5	43.6	30.5	35.4	60.2	48.4	54.5	67.2
	SD	2.7	2.8	3.8	4.6	5.3	8.0	6.9	8.2	12.8	10.7	12.1	13.9
Pb	Mean	5.8	5.9	6.3	6.6	6.7	7.5	9.9	10.1	11.4	37.4	38.1	40.6
	SD	4.8	4.9	5.4	4.8	4.7	5.2	5.4	5.5	6.3	15.2	15.5	16.2

SD: Standard deviation, Sample number: 5 for each season.

3.3. The size distribution of metals and metalloids in airborne PM

C_f/C_c is the ratio of the concentration of an element in the fine PM (<2.1 μm) divided by its concentration in the coarse PM (2.1–10.2 μm). This ratio is used here because it can be used to judge the presence of an element between the fine and coarse PM (Karanasiou et al., 2007), and the knowledge about the presence of toxic elements between the fine and coarse PM can help better understand the risks to human health. $C_f/C_c > 1$ means the element is more distributed in the fine PM than in the coarse PM, whereas $C_f/C_c < 1$ means the opposite trend. The C_f/C_c ratios based on the mean concentrations of elements in PM are listed in Table 5. Al, Ti, Fe, Sr and Ba exhibited C_f/C_c ratios in the range of 0.79–1.0 (mean values), indicating that lower or equivalent proportions of these elements were present in the fine PM in comparison with the coarse PM. Mn, Cu, Zn, As, Mo, Cd, Sb and Pb exhibited C_f/C_c ratios in the range of 2.6–9.2 (mean values), indicating the major presence of these elements in the fine PM. The major presence of toxic elements (Cu, Zn, As, Cd, Sb, and Pb) in the fine PM of Guiyang may result in high health risks of residents because fine PM can deposit in the lungs and reach the alveoli (Hu et al., 2014). The major presence of Mn, Zn, Cd, and Pb in the fine PM is in agreement with the results of previous studies on aerosols in a roadside environment in Northern Greece (Samara and Voutsas, 2005), an urban road tunnel in Portugal (Pio et al., 2013), the urban environments in Athens (Karanasiou et al., 2007) and Hongkong (Jiang et al., 2014).

Table 5. Concentration ratios (C_f/C_c) of the elements in the fine (<2.1 μm) and coarse (2.1–10.2 μm) PM fractions

	C_f/C_c				
	Spring	Summer	Fall	Winter	Mean
Al	0.63	0.76	0.77	1.0	0.79
Ti	0.71	0.85	0.90	1.4	1.0
Mn	3.3	3.4	2.3	4.7	3.4
Fe	0.58	0.76	1.0	1.8	1.0
Cu	3.7	2.9	1.9	2.1	2.6
Zn	5.9	3.8	3.4	10.6	5.9
As	3.2	3.6	4.9	3.1	3.7
Sr	0.49	0.67	0.70	1.1	0.74
Mo	2.6	1.8	2.1	4.4	2.7
Cd	3.9	2.2	3.1	4.4	3.4
Sb	5.1	4.1	4.3	4.8	4.6
Ba	0.60	0.80	0.68	1.6	0.91
Pb	10	6.5	6.9	13	9.2

Based on their size distributions, the metals and metalloids on PM can be generally classified into two groups. Al, Ti, Fe, Sr, and Ba were more significantly associated with the coarse PM, whereas Mn, Cu, Zn, As, Mo, Cd, Sb, and Pb were more significantly associated with the fine PM. The distribution of the elements in PM can be governed by the sources and behaviors of both PM and the elements (Allen et al., 2001; Samara and Voutsas, 2005), which is discussed below.

3.4. Sources of metals and metalloids in airborne PM

Enrichment factors. Enrichment factors (EFs) of elements in PM relative to the earth's upper crust can help distinguish between elements originating from anthropogenic sources and those from natural sources. EFs have been used in numerous studies for the source apportionment of airborne contaminants (Schleicher et al., 2011). In this work, EFs were calculated as:

$$EF = (C_{\text{element}}/C_{\text{reference}})_{\text{PM}} / (C_{\text{element}}/C_{\text{reference}})_{\text{crust}} \quad (1)$$

where C_{element} and $C_{\text{reference}}$ are the concentrations of the target element and the reference element, respectively. Here, Al was taken as the reference element. The average EFs of metals and metalloids in TSP, $\text{PM}_{10.2}$, and $\text{PM}_{2.1}$ are presented in Table 6.

Regarding TSP, EFs are low in the cases of Ti and Sr. The EF of Fe is low for the spring, summer, and winter, but moderately high for the fall. The EF of Ba is low for the summer, fall and winter, but moderately high for the spring. The EF of Mn is moderately high. The EFs are high for Cu, Zn, Mo, and Pb, and extremely high for As, Cd, and Sb. The EFs of these elements of $\text{PM}_{10.2}$ and $\text{PM}_{2.1}$ are generally similar to those of TSP. In previous studies, low EF values for Al, Ti, Fe, Sr, and Ba and high EF values for Cu, Zn, As, Cd, Sb, and Pb have been observed in the PM from Beijing (Schleicher et al., 2012; Schleicher et al., 2013; Chen et al., 2014). In addition, high EF values for Cu, Zn, Cd, and Pb have been observed in the PM from Shanghai (Hu et al., 2014), Hongkong (Jiang et al., 2014), Thessaloniki, Greece (Samara and Voutsas, 2005), Kanazawa, Japan (Wang et al., 2005), and Delhi, India (Srivastava et al., 2009). It is presumed that when the EF of a specific element is >5, then a significant fraction of the element was contributed from non-crystal sources (Voutsas and Samara, 2002; Samara and Voutsas, 2005). Therefore, Ti, Fe, Sr, and Ba are considered to be mostly contributed from crustal sources, except that Ba in the spring and Fe in the fall were also affected by anthropogenic sources. Mn, Cu, Zn, As, Mo, Cd, Sb, and Pb are mostly from anthropogenic sources.

Table 6. EFs for elements in the TSP, coarse and fine PM relative to the earth crustal values (reference element: Al)

	Spring			Summer			Fall			Winter			Crust ^a ($\mu\text{g/g}$)
	TSP	Coarse PM	Fine PM	TSP	Coarse PM	Fine PM	TSP	Coarse PM	Fine PM	TSP	Coarse PM	Fine PM	
Ti	3.1	3.0	3.3	2.7	2.5	2.8	2.4	2.2	2.6	2.9	2.6	1.0	3 000
Mn	9.7	4.2	22	13.3	6.4	29	16	10	31	15	6.8	8.8	600
Fe	2.2	2.3	2.1	3.2	2.8	2.8	13	12	16	3.2	2.4	1.2	35 000
Cu	119	47	276	129	73	273	94	67	161	125	99	57	25
Zn	70	19	180	121	56	278	131	65	289	157	36	106	71
As	583	249	1 259	1 071	518	2 421	2 280	832	5 325	2 524	1 532	1 307	1.5
Sr	3.1	3.3	2.6	3.2	3.3	2.9	3.5	3.5	3.2	3.7	3.5	1.1	350
Mo	81	41	169	214	146	340	1 035	670	1 784	605	271	331	1.5
Cd	1 011	378	2 361	3 444	2 272	6 582	4 553	2 327	9 374	6 233	2 890	3 542	0.098
Sb	1 254	392	3 167	1 736	780	4 156	5 391	2 269	12 747	6 327	2 915	3 847	0.2
Ba	12	12	11	2.7	2.6	2.7	4.2	4.4	3.9	4.6	4.0	1.7	550
Pb	151	26	420	762	242	2,038	442	126	1 128	569	109	395	20

Coarse PM (2.1–10.2 μm); Fine PM (<2.1 μm).

^a Data from Taylor and McLennan (1995).

The EFs of the crustal elements Ti, Fe, Sr, and Ba in the fine PM are generally similar to those in the coarse PM. However, a typically significant increase of the EF value with the decrease of particle size was observed for the anthropogenic elements Mn, Cu, Zn, As, Mo, Cd, Sb, and Pb (Table 6), indicating a high anthropogenic contribution of these elements to the fine PM. This is consistent with the decreasing pH trend with the decrease in particle size (Table 3). The decrease in the pH means a higher anthropogenic contribution because the anthropogenic processes such as fossil fuel combustions are usually accompanied by the generation of acidic gases (Hu et al., 2000). A similar trend for Cu, Zn, Cd, and Pb has also been observed in previous studies (Samara and Voutsas, 2005; Srivastava et al., 2009).

Correlations between elemental concentrations and PM masses.

The correlations between the elemental concentrations in TSP and the PM masses of four seasons (Table 7) are used to help identify the sources of PM. Interestingly in winter, the typical anthropogenic elements (Zn, As, Cd, and Pb) and PM are significantly positively correlated, whereas the crustal elements (Al, Ti, Fe, Sr, and Ba) and the PM are negatively correlated. This indicates that the PM from the winter was mostly contributed by anthropogenic sources and least contributed by crustal sources. This is consistent with the rainy or snowy weather during the sampling period in the winter that lessened the influence of crustal sources. The PM in winter can be most significantly generated by coal combustion. In winter, the weather in Guiyang is cold and humid and there is no central heating system for the entire city, coal is used for heating in many households. The importance of coal combustion for PM in winter is also supported by the lowest pH of the water extract of the PM from the winter (Table 3) because coal combustion emits a large amount of acidic substances, such as SO₂ and NO_x (Hu et al., 2000).

Table 7. Correlation coefficients between the metal and metalloid concentrations in TSP and the PM masses of four seasons

	Spring (n=5)	Summer (n=5)	Fall (n=5)	Winter (n=5)
Al	-0.02	0.22	-0.21	-0.46
Ti	-0.03	0.28	-0.23	-0.50
Mn	0.32	0.18	0.44	0.34
Fe	0.21	0.41	-0.23	-0.43
Cu	0.30	0.18	0.40	0.40
Zn	0.44	0.39	0.63	0.81^b
As	0.51	0.43	0.53	0.87^b
Sr	0.09	0.27	-0.20	-0.52
Mo	0.66	0.81^b	0.84^b	0.90^a
Cd	0.46	0.45	0.72	0.80^b
Sb	0.40	0.33	0.55	0.73
Ba	0.19	0.28	-0.16	-0.56
Pb	0.48	0.28	0.63	0.85^b

^a $P < 0.01$, ^b $P < 0.05$.

Although the PM of winter is considered to originate mostly from coal combustion that is a significant source for many metals and metalloids (Reddy et al., 2005), the highest concentrations of metals and metalloids in PM did not occur in the winter (Table 2), implying that the metals and metalloids in PM of the spring, summer and fall originated primarily from other significant sources than coal combustion. In Guiyang, the wind is usually weak, resulting in poor ventilation of the urban basin as well as the poor exchange of PM with other regions. This indicates the significance of local sources rather than long-range transport for the PM.

Principal component analysis. The result of PCA was given in Table 8. Three factors were separated for elements in TSP with eigenvalues >1, explaining a sum of 77% of the overall variance in the data set. Factor 1 was strongly correlated with Al, Ti, Mn, Cu, Zn, Sr, and Ba. Loadings on Al, Ti, and Mn were attributed to the matrix components of soil particles in the road dust (Steinnes, 1995; Gerdol et al., 2002). Their correlation with other elements indicates the co-existence of traffic-related sources such as tire wear, brake wear, and road wear. Tire wear and brake wear were the main sources for Zn and Cu (Weckwerth, 2001; Sternbeck et al., 2002; Hjortenkrans et al., 2007). Sr and Ba are thought to originate from soil dust because of their main existence in coarse particles (Table 5) and the high correlations of Sr and Ba with crustal elements (Wang et al., 2005; Pio et al., 2013). Therefore, Factor 1 can be interpreted as representing the road dust that includes soil particles as well as previously deposited particles from traffic-related sources, such as tire-wear, brake-wear and road-wear debris (Karanasiou et al., 2007; Hussein et al., 2008), etc. Factor 2 was primarily associated with Fe, As, Mo, and Sb. The coal in Guizhou province was reported to exhibit high concentrations of As, Mo, and Sb (Zhang et al., 2002) and these elements were highly volatile in the combustion (Wei et al., 2012). Therefore, Factor 2 can be assigned to coal combustion in the coal-fired power plant. However, Fe was identified in Factor 2 instead of Factor 1 although it was identified by EFs to be associated with crustal sources. This is possibly because of the disturbance of high Fe contribution from unidentified sources in the fall. Factor 3 is associated with Mn, Zn, Cd, and Pb. High loadings of Mn and Zn in this factor in addition to their appearance in Factor 1 indicates other sources for these two elements. As reported in previous studies (Nriagu and Pacyna, 1988; Chan et al., 1997; Heal et al., 2005; von Schneidmesser et al., 2010), Mn and Zn, along with Cd and Pb, are highly associated with emissions from industrial metallurgical processes, so Factor 3 can be attributed to the metallurgical processes in the iron and steel works that is 2 km away.

Table 8. Principal components analysis for metal and metalloids in TSP

	F1	F2	F3
Al	0.98	0.02	0.07
Ti	0.97	-0.02	-0.01
Mn	0.61	0.07	0.51
Fe	0.24	0.84	0.03
Cu	0.55	-0.10	-0.09
Zn	0.77	0.10	0.51
As	0.20	0.80	0.17
Sr	0.96	0.06	0.01
Mo	-0.28	0.87	-0.01
Cd	-0.40	0.35	0.60
Sb	-0.09	0.83	-0.03
Ba	0.91	0.07	-0.15
Pb	0.02	-0.07	0.91
% Variance	40.5	22.8	13.7
Eigenvalue	5.27	2.96	1.78
% of Cumulative	40.5	63.3	77.0

3.5. Bio-accessibility of airborne metals and metalloids

For risk assessment of a metal, it is important to know its bio-accessible fraction instead of the total metal content. The bio-accessibility of a metal means the availability of metal for absorption when dissolved in body fluid. For the assessment of bio-accessible metal fractions within PM, metal leaching by

various agents such as ultrapure water, weak acids, physiological sodium chloride solution and single chelating agents, buffer solutions and synthetic bodily fluids have been used (Mukhtar and Limbeck, 2013). Because typical lung fluid has a near-neutral pH and difficulties and high expenses are associated with the use of real serum (Voutsas and Samara, 2002), water extraction was used for the assessment of bio-accessibility of metals in some previous studies (Mukhtar and Limbeck, 2013, and references therein) as well as the present study.

Table 4 shows the average WSP of the elements in three size ranges (TSP, PM_{10.2}, and PM_{2.1}). The average WSP of metals and metalloids in TSP for the four seasons is >50% for Mn, Zn, Sr, and Cd, 20–50% for Cu, As, Mo, Sb, and Ba, 10–20% for Ti and Pb, and <5% for Al and Fe. This result is compared with that of previous studies. In the study on PM₁₀ and PM_{2.5} in Lahore, Pakistan, the WSP of elements was reported at a similar level for Zn, Sr, and Cd (>50%), As, Mo, Sb (25–40%), Pb (6.4–23%), Al, Fe (<2%), and at a lower level for Mn (25–40%), Ba (11–30%), Cu (13%), Ti (<0.3%) (von Schneidmesser et al., 2010). In the study on PM in Pune, southwest India, the WSP of elements in PM₁₀ was reported at a similar level for Zn, Sr, Cd (≥50%), Cu, Ba (25–45%), at a higher level for Pb (25–45%), Al, Fe (≤20%), and at a lower level for Mn (25–45%) (Yadav and Satsangi, 2013). In the study on PM₁₀ and PM_{2.5} in Edinburgh, UK, the WSP of elements was reported at a similar level for Zn, Cd (>50%), Cu (35–45%), at a higher level for As (50%), Pb (35–45%), Fe (<10%), and at a lower level for Mn (35–45%), Ti (<10%) (Heal et al., 2005). In the study on PM from Beijing, the WSP of elements in TSP was reported at a similar level for As, Cu (20–40%), Al and Fe (<5%), at a lower level for Zn, Sr, Cd (approximately 40%), Mn (20–40%), Pb (<10%) (Schleicher et al., 2011). In the sequential extraction of fine particles (<0.61 μm) in Seville, Spain, the WSP of elements was reported at a similar level for Cu (26.5%) and Fe (3.7%), and at a lower level for Mn (32.5%), Cd (24.9%), Ti (7.7%), and Pb (3.8%) (Espinosa et al., 2002). Costa and Dreher (1997) reported a similar level of WSP for Zn (57–91%) and Cu (18–33%) in PM from four cities in USA, Germany and Canada. In the study on PM from Hong Kong by Jiang et al. (2014), the authors used the ratio of the concentrations of water-extracted metals and those of acid digestion to represent the water-solubility of metals. They reported similar level of WSP for Zn, Cd (>60%), Mo (20–60%), higher level of WSP for Fe, Pb (20–60%), Al (<20%), lower level of WSP for Mn (20–60%).

Essentially, the present study showed a much higher water solubility of Ti (19.8–35.7% for TSP, PM_{10.2}, and PM_{2.1}) than did previous studies. This can be explained by the huge construction projects in Guiyang. The decoration of new buildings can result in a high proportion of labile Ti in the dust because Ti is used in paints as a whitener (Neal et al., 2011). Compared to the other elements, Al and Fe exhibited the lowest solubility because they are primarily associated with silicates and oxides in PM and are not readily dissolved at a pH of approximately 7 (Tessier et al., 1979), and Fe in a water–solid system is readily sorbed (Tang et al., 2002). The anthropogenic elements (Cd, Zn, Mn, Mo, As, and Sb) were considered to be mostly bound on the surface of PM and thus showed high water solubility (Heal et al., 2005). The high solubility of Sr and the relatively high solubility of As and Sb is consistent with their high presence in a soluble form in the water–solid interactions (Zhang et al., 2009).

The water-solubility of metals and metalloids in PM differs as the size decreased. Compared to that in TSP, almost all metals and metalloids in PM_{2.1} exhibited higher water solubility (Table 4). This has also been observed in previous studies (Heal et al., 2005; von Schneidmesser et al., 2010). This trend can be caused by the increase of the particle surface area (Heal et al., 2005) that makes the PM be more intimately in contact with water and the different chemical states of an element in various size fractions due to different source emissions or atmospheric processes (von Schneidmesser et al., 2010; Jiang et al., 2014). Soluble metals may

play a more significant role in chronic and acute adverse health effects than the total metals (Jiang et al., 2014). Therefore, the highest water-solubility combined with the highest total concentrations of metals and metalloids in the fine PM fraction will highly increase the negative health effects of fine PM.

The water solubility of metals and metalloids in PM also differs between the seasons. The water solubility of Al, Ti, Fe, Zn, Sr, Ba, and Pb in the TSP of winter was the highest, and the water solubility of Mn and Cd in the TSP of winter was the second highest among the results for the four seasons (Table 4). This is consistent with the fact that the PM from the winter exhibited the lowest pH, which favors the dissolution or desorption of many elements. The water solubilities of As and Sb in the PM of winter were lower because these two elements exist as negatively charged oxy-anions (Ferguson and Gavis, 1972; Vink, 1996) in water and usually show a lower solubility with decreasing pH (Bowell and Bruce, 1995).

Due to the dissimilar water solubilities, the water-soluble concentrations of elements may differ from the sequence of their concentrations in PM. The average water-soluble concentrations of toxic elements in TSP are in the order of Zn (122 ng/m³)>Pb (29 ng/m³)>As (22.2 ng/m³)>Cu (21.6 ng/m³)>Sb (5.6 ng/m³)>Cd (4.9 ng/m³), which differs from the order of average total concentration of Pb>Zn>Cu>As>Sb>Cd (Table 2). Therefore, among the toxic elements, Zn, Pb, and As posed the highest risk to enter the human bodily fluids.

4. Conclusions

The airborne PM in Guiyang was considered primarily to originate from local sources. In the winter, coal combustion was proved to be the dominant source, whereas in the other seasons, the traffic-related emissions were considered the primary sources. The metals and metalloids in PM can be generally classified as crustal elements (Al, Ti, Fe, Sr, and Ba) and anthropogenic elements (Mn, Cu, Zn, As, Mo, Cd, Sb, and Pb). In particular, Al, Ti, Fe, Sr, and Ba were considered highly associated with soil particles in the road dust. Cu and a portion of Zn were associated with vehicle emissions that accumulated in road dust. As, Mo, Cd, Sb and Pb as well as another portion of Zn were associated with local industrial emissions, while As, Mo and Sb could be attributed to coal combustion and Mn, Zn, Cd and Pb could be attributed to metallurgical processes.

The crustal elements showed enrichment in the coarse PM, whereas the anthropogenic elements showed enrichment in the fine PM. As the PM size decreased, the metals and metalloids exhibited higher water solubility. The water solubility of the metals and metalloids in PM differs among the seasons, and almost all of the elements in the PM from the winter exhibited the highest water solubility. Among the toxic elements in PM, Zn, Pb, and As pose the highest risk to enter human bodily fluids because they exhibited the highest water-soluble concentrations in TSP among the investigated ones. For the urban planning and air pollution control in Guiyang, mitigation measures should be focused with priority on the Zn, Pb, and As – related sources, which includes vehicle emissions, metallurgical industry, and coal combustion.

Acknowledgment

This work was supported by the Chinese National Natural Science Foundation (Grant No. 41273150 and 41003053).

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