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Atmospheric Deposition of Metals in TSP of Guiyang, PR China

Y. F. Wu · C. Q. Liu · C. L. Tu

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Abstract Total concentrations and speciation of metals had been studied in TSP of Guiyang from April 2006 and January 2007, PR China. The average concentration ranged from 14.48 ng m^{-3} for Cd to 1,161.45 ng m^{-3} for Zn. The concentrations of Cd, Cr, Pb and Zn were significantly higher during winter than those at other seasons. The environmentally mobile fractions of Cd and Zn were the highest in the three stages. The highest proportion of Pb was the fraction that bound to carbonate and oxide. Cr and Cu were clearly restricted to the fraction that bound to silicate and organic matter.

Keywords Atmospheric deposition · Metals · TSP · Guiyang

Rapid urbanization and industrial development in China during last decades has provoked some serious environmental concerns. Atmospheric deposition represents a major pathway of anthropogenic inputs of metals into the surface environment (Wong et al. 2003). Trace elements originate from both natural and anthropogenic sources. Natural sources include both geochemical and biochemical processes, while anthropogenic trace element sources are transportation, mining, energy production, smelting, refining, waste incineration, commercial applications and so on (Bem et al. 2003). Trace elements are of particular importance due to their potential toxicity for environment and human being. Metals are non-degradable, and can accumulate in the human body system, causing damage to a person's nervous system and internal organs (Lee et al. 2007). And from the view of environmental point, we need not only determine the total concentrations of metals in total suspended particles (TSP) but also ascertain how easily the metals that can be mobilized in the environment. Leaching is a procedure that has been applied to the extraction of metals from environmental analytical field. Hlavay et al. (1998) had used sequential leaching to assess the atmospheric particles at Tihany in Hungary, where the soluble fraction and environmentally mobile fraction of trace elements in air particulates were determined.

Guiyang is the capital of Guizhou Province (Fig. 1) and its altitude is 1,050 m. The total urban area of Guiyang is 8,084 km^2 and the population 1.56 million. It features an undulating topography, with high mountains and plateaus from north to south, hills and river valleys in the centre. It has a subtropical monsoon climate with annual average temperature of 15.6°C, relative humidity 77%, and an average annual rainfall of 1,177 mm. The prevailing wind direction is northeasterly in winter, and southerly in summer.

Materials and Methods

TSP samples were collected from 1 m above a building (5 m) roof's surface by Tissuquartz™ Filters (8 × 10 in., made by Pall Corporation, USA) using a special high-flow rate (1.06 m^3/min) sampler (KC-1000, made by Laoshan Institute for Electronic Equipment, China). The sampling site, located within the Institute of Geochemistry, CAS, belongs to a typical urban area and lies in the southeast of

Y. F. Wu (✉) · C. Q. Liu · C. L. Tu
State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 46 Guanshui Road, Guiyang, Guizhou Province 550002, People's Republic of China
e-mail: yongfengwu80@126.com

Y. F. Wu · C. L. Tu
Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

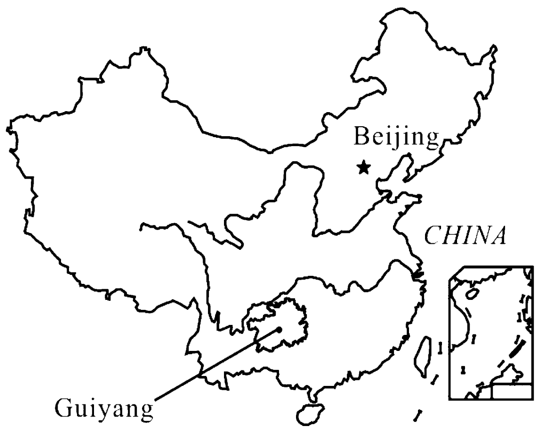

Fig. 1 The location of sampling site in Guiyang

the downtown of Guiyang. Prior to sampling, the filters were pre-baked at 500°C for 2 h in order to eliminate impurities. The sampling time was nominally 24 h with sampling starting at 6:00 pm We take four samples every month, from April 2006 and January 2007, so in total 40 samples were collected (1 day one sample).

One quarter of the filters was carefully cut using a pair of stainless steel scissors and transferred to PTFE beakers and 10 mL of concentrated HNO_3 was added to each sample. The beakers were placed on a hot spot at 95°C for 2 h, and 5 mL of HF and 1 mL $HClO_4$ were then added. The beakers were returned to the hot spot until the filters and particles had dissolved. Heating was continued for one hour to evaporate off the excess of HF, during which time 1 mL concentrated HNO_3 was added. Finally, the cooled solutions were transferred to 50 mL volumetric flasks and the solutions were diluted to volume with ultra-pure water.

A three-stage sequential leaching procedure was applied in our study. One quarter of the filters was carefully cut using a pair of stainless steel scissors and then transferred to a 50-mL centrifuge tube. The leaching experiments for the sampling filters were carried out mainly according to the procedure of Hlavay et al. (1998).

The concentrations of Cd, Cr, Cu, Pb and Zn were measured by ICP-OES after calibration using Perkin Elmer high-purity standard in 5% high-purify HNO_3. The element concentrations of the procedural blanks were generally <5% of the mean analyte concentrations for all metals. Blanks (5% high-purify HNO_3) and quality control standards were measured at every 10 samples to detect contamination and drift. Three replicates of each of the solutions were measured and precision was generally lower than 2.0%.

Results and Discussion

The mean elemental concentrations of Cd, Cr, Cu, Pb and Zn in TSP collected at the site were summarized in Table 1. The mean concentrations for trace elements ranged from 14.48 ng m^{-3} for Cd to 1,161.45 ng m^{-3} for Zn.

The mean trace element concentrations in TSP of our study were compared with those in the urban areas of other major cities (see Table 1). In comparison with Beijing (Okuda et al. 2004), Guangzhou (Lee et al. 2007), Hong Kong (Lee et al. 2007) and Taichung (Fang et al. 2003), Guiyang had higher mean concentrations of Cd and Cr. And the mean concentration of Pb was higher in Beijing and Taichung. On the other hand, the mean concentrations of metals, including Cr, Cu, Pb and Zn, in Guiyang were higher than those in Ho Chi Minh (Hien et al. 2001) and Tokyo (Var et al. 2000). In the whole, we can see that the atmospheric trace metals pollution in Guiyang was significant compared with some cities in the world.

Guiyang had ample mineral and energy sources, and it was prestigious for its ferrous and non-ferrous metallurgy. These industries were all energy-material-waste intensive, generating relatively large amounts of ambient particles (Xie et al. 2005). The sampling site in Guiyang was close to many industrial installations and several of them were located to the south, so the meteorological conditions during the experiment favoured the transport of particulates from these sources.

Four campaigns represented different seasons in Guiyang as we can see from Fig. 2. April and May 2006 campaign represented the spring season, whereas June to August, September to November and December 2006 to January

Table 1 The mean trace elemental concentrations in TSP of Guiyang and other major cities in the world (ng m^{-3})

Location	Cd	Cr	Cu	Pb	Zn	References
China Beijing	6.80	19.00	110.00	430.00	770.00	Okuda et al. (2004)
China Guangzhou	7.85	20.90	82.30	269.00	1,190.00	Lee et al. (2007)
China Hong Kong	1.61	15.30	70.80	56.50	298.00	Lee et al. (2007)
Taiwan Taichung	8.50	9.30	198.60	573.60	395.30	Fang et al. (2003)
Vietnam Ho Chi Minh	–	8.63	1.28	146.00	203.00	Hien et al. (2001)
Japan Tokyo	–	6.09	30.32	124.70	298.70	Var et al. (2000)
China Guiyang	14.48	26.35	31.21	393.02	1,161.45	Present study

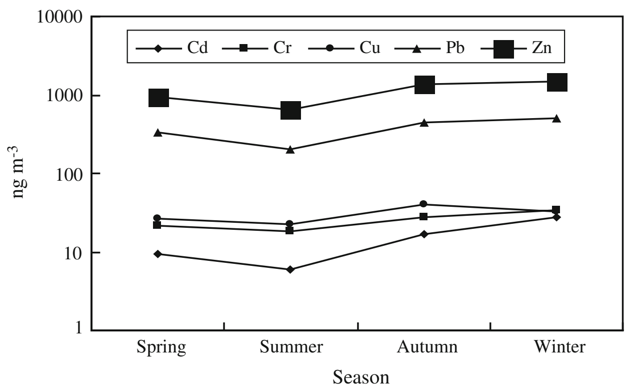

Fig. 2 The metal concentrations during four study periods

2007 campaigns represented summer, autumn and winter, respectively.

From Fig. 2, we can see the distinguished seasonal patterns in the metal concentrations in TSP of Guiyang. The concentrations of most elements (Cd, Cr, Pb and Zn) were significantly higher during winter than those at other seasons. The metal concentrations in TSP were relatively low during spring and summer seasons. This kind of seasonal pattern, with lower concentrations of metals in summer, was similar to those of other airborne primary pollutants in other studies (Wong et al. 2003).

In Guiyang, a subtropical region remote from sandstorm areas with humid climate and high vegetation coverage, the soil contribution to TSP was relatively lower compared with northern areas (Xie et al. 2005). Therefore, the major anthropogenic atmospheric metal sources in Guiyang were from coal-combustion. And coal was widely burnt for both industrial and domestic purposes. The main domestic coal consumption which comprised approximately 25% total coal consumption was diverted to house heating during cold seasons from late autumn through winter to early spring, which could explain partly the differences of metals among the seasons (Feng et al. 2003).

In spring, it was evident that metal concentrations were generally elevated comparing to summer campaign. The reason may be because there was less rain in spring, therefore metals that deposited in the surface in winter time could enter into TSP. Apart from the fact as mentioned above, there were still some domestic coal burning activities occurred during this season, which could also be responsible for the high metals in TSP.

In summer, the major atmospheric metals sources were from industries because there was no domestic coal-consumption burning during this period of time. Wind direction may carry significantly higher concentrations of metals, because southern wind was dominant in summer of Guiyang. Dense industrial point sources were located to the south of the sampling site within 20 km and some small coal-fired boilers were situated near the research site. It was evident that the industrial point sources and some small coal-fired boilers were atmospheric metal sources.

In autumn, combustion of leaves was one of the main ways to deal with the falling leaves in Guiyang, which was an important atmospheric metal source. At the same time, some families began to heat their houses by burning coals during this period. All these sources could obviously contribute to the high average metal concentrations observed in the sampling period.

In winter, metal concentrations in TSP were enhanced due to intensive domestic coal use for house heating and the impacts from the industry area. Hence emissions from domestic coal burning were the primary atmospheric metals in winter.

Sequential leaching with various extractant solutions was performed to determine the chemical forms of the studied elements in an attempt to identify how easily the metals can be mobilized in the environment.

As shown in Table 2, the fraction of Cd resulted in association with the environmentally mobile fraction (stage I) (61.4%), and smaller amounts of Cd compounds were found in the fraction bond to carbonate and oxide (stage II) (25.7%) and bound to organic matter and silicate (stage III) (12.9%). Lum et al. (1982) reported that Cd in urban aerosol was almost completely in exchangeable form. Cadmium, liberated during combustion processes, had been shown to occur in elemental and oxide forms whereas emissions from incineration were predominantly as $CdCl_2$ (Hlavay et al. 1998).

Cr was mostly emitted to the atmosphere from coal-combustion, the metal industry and waste incineration (Hlavay et al. 1998). In our research, we thought that coal-combustion was the major reason for Cr in TSP of Guiyang. The principal world-wide anthropogenic sources of Cu were metal extraction and industrial uses. So the industry of Guiyang City may contribute to the Cu concentration in TSP. According to the results presented in Table 2, Cr and Cu were clearly restricted to the environmentally immobile fraction (stage III), and thus they did not have any direct impact on the respiratory systems of human being. Thus our results were in agreement with those obtained for the fraction of Cr in urban particles at Tihany in Hungary by Hlavay et al. (1998).

Table 2 Distribution of the metals in stages I–III from TSP in Guiyang (n = 40) (ng m^{-3})

Element	Stage I	Stage II	Stage III
Cd	8.61 ± 4.07	3.58 ± 1.68	1.83 ± 0.75
Cr	1.18 ± 0.30	2.86 ± 0.72	21.24 ± 5.10
Cu	6.93 ± 1.56	5.85 ± 1.24	17.60 ± 3.83
Pb	146.24 ± 68.32	174.01 ± 61.64	56.93 ± 30.75
Zn	505.70 ± 261.53	318.14 ± 149.05	302.79 ± 146.31

Pb in urban and industrial areas was emitted by different sources and each of these industries emitted lead with different form. The obtained results showed that atmospheric lead in Guiyang was mainly in stages I and II (Table 2), that was to say that lead in TSP was more mobile in Guiyang City. Emissions from vehicle exhausts had dominated the contribution of lead to the atmosphere, although smelting operations also contributed to the atmospheric lead load, emitting both PbO and Pb^0 (Hlavay et al. 1998). The relative significance of lead sources in the atmosphere was currently changing world-wide as a result of the decline in the use of leaded vehicle fuels.

Zn compounds were usually used for wheel manufacturing, metal alloys, pesticides, ceramic and plastic molding. And Guiyang was an important industrial base in China. Therefore, it was expected to observe high concentration of Zn in TSP of the surrounding environment. In addition, an increase in zinc concentration in TSP was also expected if soil re-suspension processes occurred. Speciation of zinc in the different solutions was presented in Table 2. We found that Zn was mainly in the form of environmentally mobile fraction, therefore it had important influence to the respiratory systems of human being.

In conclusion, the present study showed that Cd had the minimum total concentration 14.48 ng m^{-3}, while Zn had the maximum 1,161.45 ng m^{-3} of the five metals that we studied. The metals in TSP of Guiyang had something to do with coal-burning. There was clear pattern for the five metals during the period of sampling. The concentrations of the metals except Cu were significantly higher during winter season than those at other seasons. The metal concentrations in TSP were relatively low during spring and summer seasons. Cd and Zn had the highest proportion of environmentally mobile fraction in the three stages. The fraction bound to carbonate and oxide of Pb was the highest. Cr and Cu were restricted to the fraction that bound to silicate and organic matter and they had little impact on the respiratory systems of human being.

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