E3S Web of Conferences **1**, 20008 (2013)
DOI: 10.1051/e3sconf/20130120008

Temporal determination of heavy metals in $PM_{2.5}$ from Guiyang, Guizhou province, southwestern China

G. Qiu[1], X. Feng[2], M. S. Landis[3] and N. Liu[4]

[1] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China, qiuguangle@vip.skleg.cn
[2] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China, fengxinbin@vip.skleg.cn
[3] US EPA, Office of Research and Development, Research Triangle Park, NC 27709, USA, landis.matthew@epamail.epa.gov
[4] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China, liunagy@163.com

Abstract. Twelve hours integrated $PM_{2.5}$ samples collected with a Weekly Air Particulate Sampler (URG Model 2000-01J) from September 2008 to November 2008 in Guiyang, China, were analyzed on the Kevex energy dispersive x-ray spectrometer (XRF) for elements. Monitoring results found elevated concentrations of heavy metals (Ti, Mn, Fe, Zn, and Pb) in $PM_{2.5}$ in Guiyang. The average concentrations were 30±22 ng m^{-3} for Ti, 250±400 ng m^{-3} for Mn, 340±280 ng m^{-3} for Fe, 290±330 ng m^{-3} for Zn, and 130±130 ng m^{-3} for Pb, respectively. Temporal variation patterns in the resulting data were also obtained. It is hypothesized that local anthropogenic sources and the seasonal variability result in the temporal variability.

Key words: Heavy metals, $PM_{2.5}$, Meteorological parameters, Anthropogenic sources

Introduction

The fine particles in ambient air have been reported to be associated with many health problems (Kim et al., 2004). The fractions smaller than 2.5 μm ($PM_{2.5}$) are getting more and more attention worldwide, which can result in the prolonged exposure, promoting or aggravating health problems (Figueroa et al., 2006). Because the $PM_{2.5}$ has a long residential time of several days to weeks in atmosphere, it can travel hundreds to thousands of kilometers. Previous studies indicated that smaller particles of $PM_{2.5}$ are water soluble and hygroscopic, and make them bio-available (Raes et al., 2000; Heal et al., 2005). On the other hand, the $PM_{2.5}$ has high concentrations of toxic trace metals, such as chromium (Cr), cadmium (Cd), titanium (Ti), manganese (Mn), nickel (Ni), lead (Pb), arsenic (As), zinc (Zn), etc. (Singh et al., 2002). Those toxic heavy metals incorporated with $PM_{2.5}$ may enter the body through inhalation and have been suggested as causative agents associated with adverse respiratory health effects.

Guiyang, the capital of Guizhou province, southwestern China, is classified as one of the most seriously air polluted cities in China. Its climate represents a typical subtropical humid monsoon with an average annual temperature of 15 ºC and 1100-1400 mm of precipitation. It has 3.7 million populations in 2008. Because of the abundant coal resources in Guiyang, the air pollution caused by coal combustion emission is considered as the most critical environmental issue.

Materials and Methods

The $PM_{2.5}$ measurements at the Monitoring Station Agency (MSA) in Guiyang (E: 106º43'03", N: 26º33'56") were conducted on the roof of an 8-story building using a Weekly Air Particulate Sampler (URG Model 2000-01J). The MSA site is located in residential area with a number of local industries, including a large coal-fired utility (1.5 km south), a cement plant (3.5 km south), and several non-ferrous metal smelters. The $PM_{2.5}$ samples were collected onto filters (Millipore, PGTRISLIDE^{TM}) at a flow rate of 10 L min^{-1}. During the sampling campaign, 12-hour integrated samples were collected each day from 8:00am/8:00pm (Daytime) to 8:00pm/8:00am (Nighttime). The sampled filters were stored individually

Table 1. The concentration range and average of the different components

Parameter	Range /ng m^{-3}	Average /ng m^{-3}
$PM_{2.5}$ /μg m^{-3}	3.7-190	53±27
Ti	0.39-160	30±22
Mn	0.017-3980	250±400
Fe	11-1870	340±280
Zn	6.7-2160	290±330
Pb	1.6-920	130±130

in petri dishes and were sealed in polyethylene bags with citric acid paper for preservation.

The sampled filters were analyzed for elements using the Kevex energy dispersive X-ray fluorescence spectrometer (XRF) at USEPA's National Exposure Research Laboratory. The certified reference standards of SRM1833-1111 and SRM1832-249 were analyzed to monitor the accuracy of the spectrometer. Laboratory blanks, field blanks, and duplicate samples were also determined for data quality control and assessment. The average concentrations for each element reported were higher than the limit of quantification (LOQ), which is defined as ten times the standard deviation of a set of blanks.

Results and Discussion

Concentrations of $PM_{2.5}$ and heavy metals measured in 12-hour integrated samples were presented in Table 1. The $PM_{2.5}$ showed elevated concentrations with a range of 3.7 to 190 μg m^{-3}. Heavy metals concentrations in $PM_{2.5}$, particularly Mn, Pb, and Zn, were highly elevated, ranging from 0.39 to 160 ng m^{-3} for Ti, 0.017 to 3980 ng m^{-3} for Mn, 11 to 1870 ng m^{-3} for Fe, 6.7 to 2160 ng m^{-3} for Zn, and 1.6 to 920 ng m^{-3} for Pb, respectively.

The distribution of the five heavy metals showed different temporal variation. High monthly average concentrations of Mn were record during September and October, while during September and November, the high levels of Ti, Fe, Zn, and Pb were presented. In the present study, notable diurnal variations characterized by reduced concentrations during daytime were observed among Mn, Fe, Zn, and Pb (Figure 1).

Strong anti-correlations was detected between $PM_{2.5}$ and wind speed ($r=-0.31$, $p<0.01$) as well as $PM_{2.5}$ and relative humidity ($r=-0.46$, $p<0.01$) (Table 2). The results confirm the fact that strong winds prevent the accumulation of air pollutants and that the rainfall constituted a mechanism of purification of the atmosphere. Table 2 presents also the correlations coefficient between $PM_{2.5}$ and Ti, Mn, Fe, Zn, Pb as well as between the five metal concentrations. All of the heavy metals were positive correlated with $PM_{2.5}$ and were positive correlated with each other, indicating that those heavy metals are readily bond to fine particles and seem to be associated with local sources.

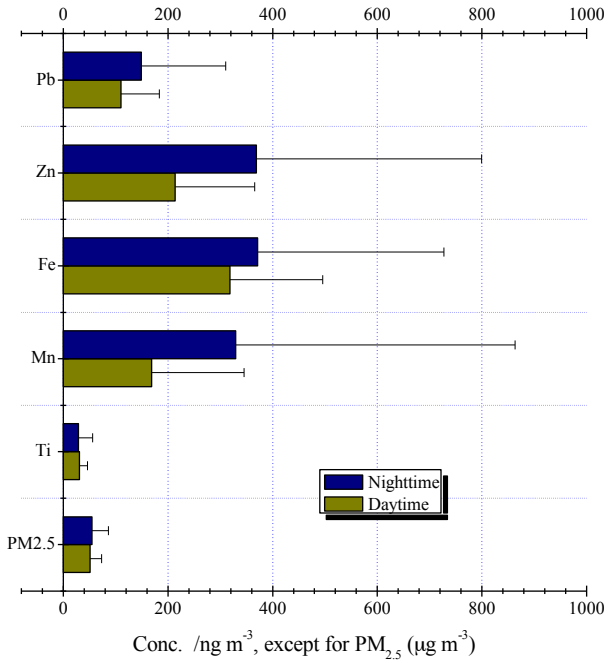

Fig. 1 The average concentrations of $PM_{2.5}$ and heavy metals during daytime and nighttime in Guiyang

High concentrations of $PM_{2.5}$ and heavy metals observed in Guiyang might suggest high emissions of fine atmospheric aerosol. The widely ranges of the heavy metals in $PM_{2.5}$ reflected the direct emissions of local sources. Because of Guiyang as an important coal produced and non-ferrous yielded city, the coal-fired power plants, residential coal-burning, and Pb-Zn producing might play an important role for measured high values of those heavy metals.

Conclusions

This study presents ambient $PM_{2.5}$ as well as its heavy metals concentrations in Guiyang city, Guizhou province. The temporal variation patterns in the resulting data suggest local anthropogenic activities impacted the sites. Concentrations of heavy metals, particularly Mn, Pb, and Zn, were significantly elevated in $PM_{2.5}$. Identification

Table 2. Correlations among $PM_{2.5}$, heavy metals and meteorology parameters (WS-Wind Speed, RH-Relative Humidity, T-Temperature)

	$PM_{2.5}$	Ti	Mn	Fe	Zn	Pb	WS	RH	T
$PM_{2.5}$	1								
Ti	.75**	1							
Mn	.37**	.21*	1						
Fe	.76**	.82**	.25*	1					
Zn	.68**	.64**	.43**	.74**	1				
Pb	.62**	.53**	.66**	.54**	.66**	1			
WS	-.31**	-.23*	-.25*	-.22*	-.25*	-.34**	1		
RH	-.46**	-.40**	-.16	-.38**	-.31**	-.43**	-.033	1	
T	.042	.047	.26*	-.029	.14	.26*	.090	-.28**	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

and quantification of the major atmospheric $PM_{2.5}$ sources in and around Guiyang and development of a detailed emission inventory in Guiyang is needed to further elucidate $PM_{2.5}$ as well as trace elements distribution characteristics.

Acknowledgements

This research was performed while the authors held a U.S. National Research Council Associateship Award at U.S. EPA's National Exposure Research Laboratory (NERL). It has been reviewed by the Agency and approved for publication. It also was financially supported by the Natural Science Foundation of China (No. 40773067). We also acknowledge Mr. Kangdi Han for the field sampling assistance.

References

Figueroa DA, Rodríguez-Sierra CJ, Jiménez-Velez BD. Concentrations of Ni and V, other heavy metals, arsenic, elemental and organic carbon in atmospheric fine particles ($PM_{2.5}$) from Puerto Rico. Toxicology and Industrial Health 2006; 22:87-99.

Heal MR, Hibbs LR, Agius RM, Beverland IJ. Total and water-soluble trace metal content of urban background PM_{10}, $PM_{2.5}$, and black smoke in Edinburgh, UK. Atmospheric Environment 2005; 39:1417-1430.

Kim JJ, Smorodinsky S, Lipsett M, Singer BC, Hodgson AT, Ostro B. Traffic-related air pollution near busy roads – the East Bay children's respiratory health study. American Journal of Respiratory and Critical Care Medicine 2004; 170:520-526.

Raes F, Dingenen RV, Vignati E, Wilson J, Putaud JP, Seinfeld JH, Adams P. Formation and cycling of aerosols in the global troposphere. Atmospheric Environment 2000; 34:4215-4240.

Singh M, Jaques PA, Sioutas, C. Size distribution and diurnal characteristics of particle-bound metals in source and receptor sites of the Los Angeles Basin. Atmospheric Environment 2002; 36:1675-1689.