Atmospheric Research 153 (2014) 87–97

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Seasonal variations of trace elements in precipitation at the largest city in Tibet, Lhasa

Junming Guo [a,c,d], Shichang Kang [a,b,*], Jie Huang [a,c], Qianggong Zhang [a], Lekhendra Tripathee [a,c,d], Mika Sillanpää [c]

[a] Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences (CAS), Beijing 100101, PR China
[b] State Key Laboratory of Cryospheric Sciences, Cold and Arid Regions Environmental and Engineering Research Institute, CAS, Lanzhou 730000, PR China
[c] Laboratory of Green Chemistry, Lappeenranta University of Technology, Mikkeli 50130, Finland
[d] University of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:
Received 18 April 2014
Received in revised form 27 July 2014
Accepted 30 July 2014
Available online 9 August 2014

Keywords:
Trace elements
Wet deposition
Seasonal variations
Lhasa
Tibet

ABSTRACT

Precipitation samples were collected from March 2010 to August 2012 at an urban site in Lhasa, the capital and largest city of Tibet. The volume weighted mean (VWM) concentrations of 17 trace elements in precipitation were higher during the non-monsoon season than in the monsoon season, but inverse seasonal variations occurred for wet deposition fluxes of most of the trace elements. Concentrations for most of trace elements were negatively correlated with precipitation amount, indicating that below-cloud scavenging of trace elements was an important mechanism contributing to wet deposition of these elements. The elements Al, Sc, V, Cr, Mn, Fe, Mn, Ni, and U displayed low crustal enrichment factors (EFs), whereas Co, Cu, Zn, As, Cd Sn, Pb, and Bi showed high EF values in precipitation, suggesting that anthropogenic activities might be important contributors of these elements at Lhasa. However, this present work indicates a much lower anthropogenic emission at Lhasa than in seriously polluted regions. Our study will not only provide insights for assessing the current status of the atmospheric environment in Lhasa but also enhance our understanding for updating the baseline for environmental protection over the Tibetan Plateau.

1. Introduction

Since the Industrial Revolution, human activities have been the most important influence on the atmospheric environment on a global scale (Galloway et al., 1982; Nriagu, 1996). With the increased anthropogenic activities in the past hundred years and associated urban development, the environment is deteriorating in terms of increases of different types of atmospheric pollutants, such as trace elements, which poses a great threat to human and ecosystem health and, thus, highlights the importance of pathways for scavenging of atmospheric pollutants through atmospheric deposition such as precipitation (Galloway et al., 1982). Precipitation processes play an important role in the chemical transformation and removal of components that are important in determining air quality, in chemical reactions involving other components, and in the radiative balance in Earth's atmosphere (Andreae and Rosenfeld, 2008). Knowledge of these processes enhances understanding of the seasonal patterns and the contributions from different sources of atmospheric pollutants (Al-Momani et al., 1998). Atmospheric deposition is generally known as the most important pathway of trace element input into ecosystems, and, thus, represents a critical environmental and scientific issue. As a result, much attention has been paid to the study of the composition of trace elements in precipitation to understand the current status of the

* Corresponding author at: Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences (CAS), Building 3, Courtyard 16, Lincui Road, Chaoyang District, Beijing, China 100101. Tel./fax: +86 10 84097092.
E-mail address: shichang.kang@itpcas.ac.cn (S. Kang).

http://dx.doi.org/10.1016/j.atmosres.2014.07.030
0169-8095/

atmospheric environment worldwide (Cong et al., 2010; Kim et al., 2012; Liu et al., 2013; Roy and Négrel, 2001). In recent decades, intensified anthropogenic activities (e.g., industrial processes, fuel combustion, and waste incineration) have led to an increased emission of trace elements, which are the most important precursors of air pollution, into the atmosphere (Vuai and Tokuyama, 2011). Numerous observations of precipitation chemistry have been conducted in urban areas globally (e.g., North America, central Europe, and southern China), and composition of trace elements in precipitation has been investigated systematically (Conko et al., 2004; Koulousaris et al., 2009; Kyllönen et al., 2009; Roy and Négrel, 2001; Zhou et al., 2012).

Known as the "roof of the world", the Tibetan Plateau is one of the most imposing topographic features on the Earth's surface and is sparsely populated, with an average population density of 2.5 people per km^2 (Qiu, 2008). However, with the implementation of "the Western Regions Development Strategy" by the Chinese government at the end of the past century, the Tibet Autonomous Region (hereafter, Tibet) has become one of the fastest growing economic areas in China (TARS and TGTINBS, 2012). As a result, cities in Tibet have experienced dramatic urbanization and industrialization, which has caused increased energy requirement and industrial production. Moreover, religious activities of local residents in urban areas contribute a certain fraction of atmospheric pollution (Gong et al., 2011). Therefore, the unique location, the structure of energy consumption, and the religious activities make urban areas in Tibet special atmospheric environments that are much different from other regions of the world, and are becoming a subject of scientific interest and public concern (Cong et al., 2011; Gong et al., 2011; Huang et al., 2010, 2013). However, there is limited data available on wet deposition of elements, in terms of concentrations and deposition fluxes at urban areas in Tibet (Huang et al., 2013). Huang et al. (2013) reported the seasonal variations of Hg concentrations and wet deposition fluxes in Lhasa; however, no information on other trace elements has been presented. Therefore, this work aims to investigate seasonal variations of trace element concentrations and wet deposition fluxes, to assess trace elements levels compared with those from other regions worldwide. This work is very important for understanding the potential impacts of trace elements on ecosystems and their environmental risks, and for providing baseline information from which the effective reductions of anthropogenic trace element emission over the Tibetan Plateau may be considered.

2. Methodology

2.1. Study area and sampling site

Lhasa is located in a narrow west-east valley in the southern part of the Tibetan Plateau (Fig. 1). Climatologically, Lhasa is characterized by a wet monsoon season and a dry non-monsoon season. The annual mean precipitation amount is approximately 400 mm, which occurs mainly in the monsoon season (Tian et al., 2007). During the monsoon season (July through September), low pressure over the Tibetan Plateau brings warm air masses from the Indian Ocean to the plateau. The large-scale atmospheric circulation patterns over the Tibetan Plateau are mainly dominated by westerlies during other seasons (Bryson, 1986; Yanai and Wu, 2006), resulting in limited precipitation.

The sampling site was located at the Lhasa branch of the Institute of Tibetan Plateau Research (29°38′N, 91°38′E, 3640 m a.s.l.; Fig. 1B) in the western part of Lhasa. The site is regarded as an urban site, where air quality is mainly influenced by emissions from industrial sources, including power plants, cement production facilities, vehicular traffic, and religious activities of local residents (Cong et al., 2010; Gong et al., 2011; Huang et al., 2013).

2.2. Precipitation sampling

A total of 157 precipitation samples were collected from March 2010 to August 2012. Precipitation samples were obtained by an automated precipitation sampler (SYC-2, Laoshan Electronic Instrument Complex Co., Ltd.). Briefly, the sampler consists of a rain sensor, rain container and a dust preventing cover. When there was rain, the rainfall sensor would activate the cover to open automatically, thereby exposing the container to wet precipitation. The container was closed when the sensor became dry after the rain. The details of the precipitation collection procedures are described elsewhere (Cong et al., 2010; Huang et al., 2013; Li et al., 2007). After collection, precipitation was transferred into new 50 mL polypropylene BD Falcon® centrifuge tubes for trace element analyses, and all samples were spiked with ultraclean grade HNO_3 (BV-III Grade, Beihua Chemical, China) to achieve a concentration of 1% (*v:v*) (Kaspari et al., 2009; Shimamura et al., 2006; Zhang et al., 2008). The field blanks were also evaluated monthly. During the field blank sampling procedure, deionized water was flushed through the sampler and was then collected as a field blank solution. All samples were stored in a room with temperature kept at 4 °C until analysis, and extreme care was taken during the collecting, handling, and storage of samples to minimize contamination.

The total precipitation amount for each precipitation day from 2010 to 2012 was recorded by an automatic rain gage located in the western part of Lhasa (Fig. 1B). The amount of precipitation sampled during our study period bracketed most of the large precipitation events, accounting for 93.4% and 93.2% of total precipitation in 2010 and 2011, respectively.

2.3. Analytical procedures and QA/QC

Concentrations of 17 elements (Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sn, Cs, Pb, Bi, and U) were analyzed directly by inductively coupled plasma mass spectrometry (ICP-MS, X-7 Thermo Elemental) at the Institute of Tibetan Plateau Research, Chinese Academy of Sciences, in Beijing. Elemental concentrations were quantified by use of external calibration standards. An analytical standard was analyzed after the initial calibration, and once every five samples. The method detection limits (MDLs), defined as three times the standard deviation of replicated blank measurements, is listed in Table 1. The accuracy of the analytical protocol was ascertained based on repeated measurements of an externally certified reference solution (AccuTrace™ Reference Standard). The recoveries ranged from 90% for Cr to 105% for Ni. Regarding the analytical precision, the corresponding RSD values of all element concentrations measured in the reference material were less than 5%. Most of trace