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Trace elements and rare earth elements in wet deposition of Lijiang, Mt. Yulong region, southeastern edge of the Tibetan Plateau

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ABSTRACT

In order to investigate the compositions and wet deposition fluxes of trace elements and rare earth elements (REEs) in the precipitation of the southeastern edge of the Tibetan Plateau, 38 precipitation samples were collected from March to August in 2012 in an urban site of Lijiang city in the Mt. Yulong region. The concentrations of most trace elements and REEs were higher during the non-monsoon season than during the monsoon season, indicating that the lower concentrations of trace elements and REEs observed during monsoon had been influenced by the dilution effect of increased precipitation. The concentrations of trace elements in the precipitation of Lijiang city were slightly higher than those observed in remote sites of the Tibetan Plateau but much lower than those observed in the metropolises of China, indicating that the atmospheric environment of Lijiang city was less influenced by anthropogenic emissions, and, as a consequence, the air quality was still relatively good. However, the results of enrichment factor and principal component analysis revealed that some anthropogenic activities (*e.g.*, the increasing traffic emissions from the rapid development of tourism) were most likely important contributors to trace elements, while the regional/local crustal sources rather than anthropogenic activities were the predominant contributors to the REEs in the wet deposition of Lijiang city. Our study was relevant not only for assessing the current status of the atmospheric environment in the Mt. Yulong region, but also for specific management actions to be implemented for the control of atmospheric inputs and the health of the environment for the future.

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Introduction

Atmospheric concentrations of trace elements are affected by natural and anthropogenic processes (Pacyna, 1986). The trace elements emitted from anthropogenic sources, including fossil fuel combustion, metal smelting, industry, agriculture and large-scale land use, have increased since the late 19th century, leading to a substantial increase in trace elements in the atmosphere (Galloway et al., 1982). Wet deposition is known to be a crucial scavenging process by which trace elements return to terrestrial or aquatic surfaces (Bacardit and Camarero, 2010). Most importantly, many of the trace elements are potentially toxic to humans and other organisms, and thus, atmospheric wet deposition is of major significance in ecosystems. To date, numerous observations have been made targeting trace elements in precipitation to assess the current status of atmospheric contamination around the world (*e.g.*, Al-Momani, 2003; Kim et al., 2012; Zhou et al., 2012), indicating that the compositions and concentrations of trace elements vary greatly from region to region due to differences in sources, transport pathways, and residence time of trace elements in the atmosphere. Moreover, because of the systematic variation in their behavior due to the "lanthanide contraction," the rare earth elements (REEs) form a chemically coherent group of elements (Zhang and Liu, 2004), which have been regarded as potentially powerful tracers to investigate geochemical processes in the biogeochemical cycle of elements (Gabrielli et al., 2006). Therefore, the REEs have been widely used as potential tracers for environmental pollution studies (*e.g.*, Chiarenzelli et al., 2001; Olmez et al., 1991; Zhang and Liu, 2004). For example, previous studies have suggested that the compositions of particles released by coal-fired plants and refineries were strongly enriched in light REEs (LREEs) due to the use of zeolite cracking catalysts (Olmez and Gordon, 1985), and the REEs released from oil-fired power plants (*e.g.*, fly ash, bottom ash, and waste water) showed enrichment of the LREEs over heavy REEs (HREEs) (Watson, 1989).

The Tibetan Plateau (hereafter, TP), known as the "Roof of the World" and "the Third Pole", is a huge mountainous area of the Eurasian continent, with an average altitude of more than 4000 m a.s.l and an area of millions of square kilometers (Qiu, 2008). Over this vast area, the atmospheric environment may vary greatly in different parts of the TP (Huang et al., 2012, 2013a, 2015). As a result, a spatial array of chemical compositions of wet deposition from the TP is needed not only to effectively investigate spatial and temporal variations of the trace element loadings in the atmosphere, but also to provide insights for assessing the potential environmental risks accompanying increasing anthropogenic emissions in the context of rapid economic development. To date, a small number of datasets have been reported concerning trace elements in wet deposition over the TP (Cong et al., 2010, 2014; Liu et al., 2013; Huang et al., 2012, 2013a, 2013b, 2015). For example, previous studies on the wet deposition of trace elements in the TP have been conducted at Nam Co (Cong et al., 2010), Mt. Qomolangma (Cong et al., 2014) and Lulang station (Liu et al., 2013), respectively. However, those study sites were located remotely and considered background sites, and there are still great gaps in knowledge of this issue in the urban cities over the TP, which have been suffering from rapid economic development in recent decades. Studies on the trace elements in wet deposition of the urban cites in the TP have only been reported in Lhasa (Guo et al., 2015) and currently no measurements of REEs in wet deposition exist for the TP.

Lijiang, a famous tourist attraction and historic city, is located in the Mt. Yulong region on the southeastern edge of the TP, which has been suffering environmental problems with the rapid increase of anthropogenic activities in recent decades (Ning and He, 2007; Zhang et al., 2012b). Very few previous studies have been conducted on major ions in the precipitation of the Mt. Yulong region to differentiate the origins of chemical compositions, including crustal sources, local anthropogenic activities and sea salts from long-range atmospheric transport (Niu et al., 2013, 2014). Because of the large uncertainties in the measurements of major ions for the evaluation of environmental pollution related to anthropogenic contributions, these previous studies were insufficient to provide an accurate evaluation of the air quality in the Mt. Yulong region. Therefore, an investigation of the wet deposition of trace elements and REEs at Lijiang city from this study will not only expand the database for the evaluation of air quality in the TP but also will differentiate the relative contributions of different sources of atmospheric elements on the southeastern edge of the TP.

1. Methodology

1.1. Study area

Lijiang city (27°10′–27°40′N, 100°07′–100°10′E) is situated in the Mt. Yulong region on the southeastern edge of the TP (Fig. 1), which has become a popular city for tourism because the old town of Lijiang was listed as a World Heritage site in 1997. Since then, tourism has developed substantially and has become the mainstay of the economy of Lijiang city. The number of tourists visiting Lijiang city annually increased from 0.84 million in 1995 to almost 6 million in 2008 (Zhang et al., 2013). Meanwhile, the total number of traffic vehicles has increased from 9000 in 1995 to 87,000 in 2008 (Zhang et al., 2013).

The annual average temperature is 13.8°C, and the annual precipitation was 660 mm in 2012 according to the records from Lijiang Meteorological Observatory. During the monsoon period (from June to August), large amounts of moisture are transported northward and westward from the Indian Ocean and Pacific Ocean by the prevailing southwest and southeast monsoons (Pang et al., 2006). Therefore, more than 90% of the precipitation and the highest temperatures occur during the monsoon season. Conversely, Lijiang city receives very limited precipitation outside of the monsoon season due to the influence of the south limb of the westerlies.

1.2. Sampling

From March to August 2012, a total of 38 wet deposition samples were collected from the Yulong Snow Mountain Glacial-Environmental Observation Station, Chinese Academy

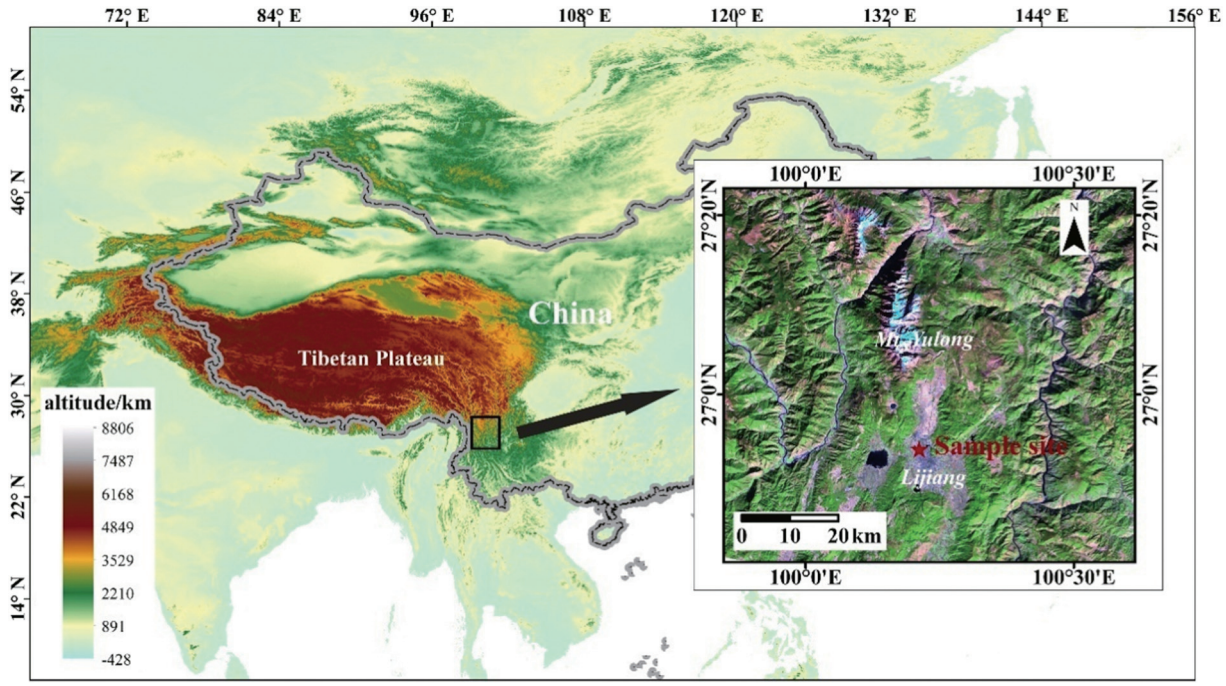

Fig. 1 – Map showing the Tibetan Plateau and the location of the sampling site.

of Sciences (CAS) in Lijiang city (26°54.07′N, 100°12.92′E). The samples were collected using inner removable high-density polyethylene (HDPE) plastic bags in a pre-cleaned HDPE bucket. To minimize the possible interference of dry deposition, the plastic bag was opened at the beginning of the precipitation event and was closed as quickly as possible at the end of precipitation process. The samples were transferred into new 50-mL polypropylene BD Falcon® centrifuge tubes and spiked with ultraclean grade HNO_3 (MOS Grade, Beihua Chemical, China) to achieve a concentration of 1% (*V*:*V*). Deionized water was flushed through the sampler and was then collected as a field blank solution weekly. All of the samples were stored in a refrigerator with temperature kept at 4°C until analysis, and extreme care was taken during the collection, handling, and storage of samples to minimize contamination. The details of the sample collection and sampling procedures are described elsewhere (Cong et al., 2010; Huang et al., 2012; Guo et al., 2015).

1.3. Analytical procedures and QA/QC

The concentrations of 40 elements were measured directly by inductively coupled plasma mass spectrometry (ICP-MS, X-7 Thermo Elemental) at the Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, CAS, in Beijing. The method detection limits (MDLs), defined as three times the standard deviation of the replicated blank measurements, are listed in Table 1. The certified trace elements in natural water (Standard Reference Material 1640a) from the National Institute of Standards & Technology (NIST), MD, USA, were measured repeatedly to evaluate their accuracy. The values for all of the measured elements agreed well with the certified values, with recoveries ranging from 96.1% for Mn to 109.3% for U. The corresponding relative standard deviation (RSD) values of all of the element concentrations measured in the reference material were defined as the analytical precision and were less than 5%. The concentrations of trace elements in the field blanks were generally less than the detection limits or <10% of those in the actual samples.

1.4. Enrichment factors and wet deposition calculation

Enrichment factors (EFs) relative to crustal material are often used to differentiate between elements originating from crustal material and those originating from anthropogenic activities (Kim et al., 2012) and are generally defined as:

$$EF_X = \frac{(C_X/C_R)_{precipitation}}{(C_X/C_R)_{crust}}$$

where X represents the element of interest, C_x is the concentration of *X*, and C_R is the concentration of a reference element. In this study, Al was used as an index for the reference material, and the average topsoil composition from the TP was used as the elemental reference (Li et al., 2009; Cong et al., 2014).

The annual wet deposition flux of trace elements at Lijiang city in 2012 was calculated as:

$$F_{iw} = C_i \sum_{j=1}^{j=n} P_j$$

where F_{iw} is the annual wet deposition flux for element *i*, C_i is the volume weighted mean (VWM) concentration (μg/L) of element *i* from April to August, and P_j (mm) is the precipitation amount in each wet deposition day.

Table 1 – Statistical data of the trace element and REEs concentrations in precipitation of Lijiang city.

Element	Unit	Detection limit	Average	SD	Max	Min	Elements	Unit	Detection limit	Average	SD	Max	Min
Li	μg/L	0.04	0.38	0.46	2.79	0.06	Cs	ng/L	1.54	17.83	22.87	127.90	<DL
B	μg/L	0.14	1.43	1.08	6.61	0.47	Ba	μg/L	0.009	3.44	10.12	56.92	0.15
Al	μg/L	0.08	113.82	325.69	1957.00	3.66	Pb	μg/L	0.004	1.93	2.37	11.88	0.19
Ti	μg/L	0.10	1.08	2.04	11.89	0.11	Bi	ng/L	0.65	33.85	26.82	162.60	14.13
V	μg/L	0.02	1.51	6.29	37.30	<DL	Th	ng/L	0.35	4.27	14.67	87.97	<DL
Cr	μg/L	0.03	0.31	0.43	2.35	0.06	U	ng/L	0.16	7.05	16.48	92.74	0.64
Mn	μg/L	0.01	3.41	4.24	23.49	0.41	La	ng/L	0.54	52.55	125.48	706.60	2.69
Fe	μg/L	1.24	31.39	52.32	247.00	3.09	Ce	ng/L	0.81	102.65	256.86	1459.00	4.42
Co	μg/L	0.00	0.03	0.04	0.21	0.01	Pr	ng/L	0.16	13.51	31.64	176.90	0.66
Ni	μg/L	0.06	0.24	0.40	2.33	<DL	Nd	ng/L	1.53	52.31	119.57	657.70	2.26
Cu	μg/L	0.09	0.59	0.89	5.24	<DL	Sm	ng/L	0.94	13.44	28.56	141.10	<DL
Zn	μg/L	0.06	7.62	9.58	55.25	1.10	Eu	ng/L	0.29	2.94	5.72	27.80	<DL
Ga	μg/L	0.00	0.02	0.04	0.26	0.00	Gd	ng/L	0.95	11.45	22.61	111.60	<DL
As	μg/L	0.16	0.42	0.42	1.78	<DL	Tb	ng/L	0.23	1.86	3.31	15.32	<DL
Rb	μg/L	0.01	0.18	0.21	0.97	0.02	Dy	ng/L	0.35	7.75	16.40	85.82	0.47
Sr	μg/L	0.00	1.55	1.86	7.54	0.16	Ho	ng/L	0.17	1.52	3.09	15.42	<DL
Y	ng/L	0.40	41.61	86.86	451.70	3.59	Er	ng/L	0.44	4.01	8.13	41.43	<DL
Mo	ng/L	3.69	46.68	88.52	423.90	5.17	Tm	ng/L	0.14	0.67	1.20	5.60	<DL
Cd	ng/L	2.80	83.25	123.69	645.40	6.00	Yb	ng/L	0.41	3.32	6.84	36.14	<DL
Sn	ng/L	8.05	69.91	32.40	189.80	43.18	Lu	ng/L	0.13	0.68	1.11	4.87	<DL

<DL means below detection limit.

1.5. *Principal component analysis*

Principal component analysis is a multivariate statistical method that is frequently used to simplify large and complex datasets to identify potential contamination sources. In this study, VARIMAX rotated principal component analysis was performed using SPSS 16.0 with the elemental data obtained by ICP-MS analysis.

2. Results and discussion

2.1. *Concentrations and wet deposition fluxes of trace elements and REEs*

The average, maximum and minimum concentrations for 40 elements in the wet deposition samples are shown in Table 1. The elements can be divided into three groups: Al and Fe, with an average concentration higher than 10 μg/L; B, Ti, V, Mn, Zn, Sr, Ba, and Pb, with concentrations between 1 and 10 μg/L; and other elements (Li, Cr, Co, Ni, Cu, Ga, As, Rb, Y, Mo, Cd, Sn, Cs, Bi, Th, U, and all REEs), with concentrations lower than 1 μg/L (Table 1). The concentrations differ by orders of magnitude from one element to another, with the highest concentrations at the 113.82 μg/L level for Al and the lowest concentrations at the 0.67 ng/L level for Tm. As shown in Fig. 2, most of the elements (except for Li, B, Pb and Bi) were statistically lower during the monsoon season than during the non-monsoon season (Mann–Whitney *U* test, $p < 0.05$). As a consequence of the strong seasonality of precipitation, with 90% of the precipitation occurring during the monsoon season at our study site (Pang et al., 2006), the lower concentrations of those elements observed during the monsoon season could be attributed to the dilution effect of increased precipitation (Cong et al., 2010). Due to limited precipitation and frequent dusty weather conditions, previous studies have suggested that suspended particulate matter could be easily accumulated in the air during the non-monsoon season (Zhang et al., 2012a). Consequently, the higher concentrations of trace elements and REEs in wet deposition during the non-monsoon season observed in this study were most likely attributable to the limited precipitation and higher dust loadings.

The concentrations of trace elements observed at different sites of the TP and other regions worldwide are listed in Table 2 for an overall comparison. As the Nam Co, Mt. Qomolangma and Lulang stations are regarded as remote and background sites in the TP (Cong et al., 2010, 2014; Liu et al., 2013), the concentrations of most trace elements in wet deposition at those sites were lower than those observed at Lijiang city from our present study. However, the concentrations of trace elements in wet deposition of Lijiang city were comparable to those determined in Lhasa, the biggest city of the TP (Guo et al., 2015). Although most of the urban sites in the TP are historic cities with very limited heavy industries compared to other polluted sites, as shown in Table 2, the rapid development of tourism in recent decades has inevitably led to an increase of local atmospheric contamination in those historic cities in the TP. For example, previous studies have suggested that the main energy sources (*e.g.*, gas and coal) of Lijiang city are largely consumed by hotels and motor vehicles (Zhang et al., 2013), reconfirming that local anthropogenic sources must be the most likely causes for the elevated levels of trace elements in the wet deposition of Lijiang city. Our findings are further supported by the previous findings that the concentrations of major ions from anthropogenic sources in wet deposition of Lijiang city were higher than those observed at a nearby rural site of Lijiang in the Mt. Yulong region (Niu et al., 2014).

Moreover, as shown in Table 2, the concentrations of trace elements in wet deposition of Lijiang city are higher than

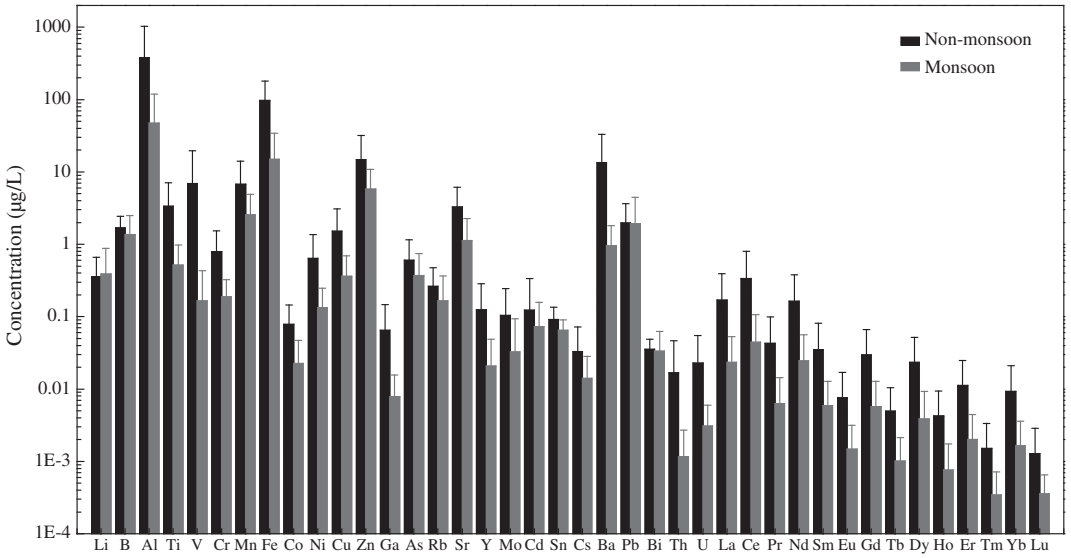

Fig. 2 – Comparison of concentrations of trace elements and REEs between monsoon and non-monsoon seasons. REEs: rare earth elements.

those determined at rural sites worldwide (*e.g.*, Chuncheon) and comparable to Kathmandu, but significantly lower than those observed at polluted urban/rural sites in middle/eastern China (Table 2). For example, most trace element concentrations at Lijiang city are around one order of magnitude lower than those observed at Tangshan (Table 2), which is considered a typical industrial city of eastern China, with high anthropogenic emissions from steel smelting, fugitive dusts and coal combustion (Li et al., 2012). Furthermore, the concentrations of trace elements in the wet deposition of Lijiang city are even found to be significantly lower than those determined at Mt. Heng (Table 2), a remote site in central China, which has been greatly influenced by regional anthropogenic emission sources (Zhou et al., 2012). As a result, these results have indicated that the atmospheric environment of Lijiang city can be considered relatively good as compared with the polluted urban/rural sites in middle/eastern China.

The wet deposition fluxes of trace elements are important for evaluating atmospheric loadings and the inputs of trace elements, their geochemical cycling, and their impacts on the terrestrial/aquatic ecosystem (Cong et al., 2014). The relationships among daily wet deposition fluxes, precipitation amounts and concentrations of elements are shown in Table 3. The results suggest that the precipitation amount was the governing factor affecting the wet deposition fluxes for most elements. However, the wet deposition fluxes of elements such as Al, V and Ba were positively related to concentrations, indicating that the concentration rather than precipitation amount was the governing factor affecting the wet deposition fluxes for these elements. The wet deposition fluxes (μg/(m^2·year)) of trace elements at Lijiang city are shown in Table 2, along with comparisons to measurements from other regions worldwide. The wet deposition fluxes of most trace elements at Lijiang city were found to be one or two orders of magnitude higher than those observed at background sites in TP (*e.g.*, Nam Co and Mt. Qomolangma) (Cong et al., 2010, 2014). This is mainly due to the fact that both the trace element concentrations and precipitation amounts in Lijiang city were higher than those observed at the Nam Co and Mt. Qomolangma sites. Moreover, as shown in Table 2, the wet deposition fluxes of trace elements at Lijiang city were lower than those observed at Kathmandu, mainly due to the relatively low precipitation amount in Lijiang city. In addition, although the precipitation amount in Chuncheon was remarkably higher than that observed at Lijiang city, the wet deposition fluxes of trace elements in Chuncheon were comparable to Lijiang, which must be a result of the relatively low concentrations of trace elements in precipitation. Nevertheless, the wet deposition fluxes of trace elements in Lijiang city were found to be significantly lower than those determined in middle/eastern China (Table 2). Therefore, this study indicates that levels of wet deposition fluxes of trace elements from an urban site of the southeastern edge of the TP were moderate compared to other sites around the world shown in this study.

2.2. Potential sources of trace elements and REEs

The enrichment factors (EFs) of trace elements and REEs in the wet deposition of Lijiang city are shown in Fig. 3. EFs exhibited great variabilities among the different trace elements, with the highest for Cd (1273) and the lowest for Ti (0.46). The trace elements can be divided into three groups according to the EF results: non-enriched trace elements, such as Ti, V, Fe, Co, Ga, Rb, Y, Cs, Th, U, and all REEs, with EFs of <1 to 10; moderately enriched trace elements, such as Li, B, Cr, Mn, Ni, Cu, As, Sr, and Sn, with EFs ranging from 10 to 100; and highly enriched

Table 2 – Comparison of the trace element and REEs concentrations (μg/L) in precipitation and wet deposition fluxes (μg/(m^2·year)) in Lijiang city and other typical regions in the world.

	Lijiang city[a]		Lhasa[b]		Nam Co[c]		Lulang Sitation[d]	Mt. Qomolangma[e]		Mt. Heng[f]	Kathmandu[g]		Chuncheon[h]		Tangshan[i]	Northern China[j] (10 sites)
	Urban		Urban		Remote		Remote	Remote		Remote	Urban		Rural		Urban	Urban
	2012		2010–2012		2007–2008		2010	2009–2010		2009	2011–2013		2006–2009		2010	2007–2010
	Mean	Fluxes	VWM	Fluxes	VWM	Fluxes	VWM	Mean	VWM	VWM	VWM	Fluxes	VWM	Fluxes	VWM	Fluxes
Precipitation (mm)		660		400		490			286			1445.2		2196		
Li	0.38	283														
B	1.43	1007														
Al	113.82	27,110	130.5	43,662	12.6	5510	0.46	2.92	853	243.57	145.05	21,000	13.85	9690	247.7	45,000–120,000
Ti	1.08	395														
V	1.51	256	0.31	353	0.033	33	0.43	0.024	6.75	1.09			0.14	100	1.4	400–900
Cr	0.31	139	0.43	118	0.267	139	0.06	0.055	15.8	0.73	1.11	1600			1.0	300–700
Mn	3.41	1666	7.70	2423	0.565	297	0.58	0.59	168	12.68	5.76	8000	3.23	2260	28.1	8000–19,000
Fe	31.39	11,874	221.4	59,280	11.5	5020	1.78	4.55	1301	118.33	170.58	24,700			291.0	60,000–149,000
Co	0.03	15	1.56	462	0.051	7.1	0.02	0.031	8.75		0.69	1000			1.2	800–1200
Ni	0.24	91	0.58	171	0.221	97	0.14	0.146	41.8	1.09	0.49	710	0.52	370	1.4	500–2000
Cu	0.59	238	1.71	584	0.537	231	0.42	0.060	17.1	12.91	1.35	1950	1.73	121	5.4	1800–3800
Zn	7.62	3642	14.21	5211	6.09	266	10.24	0.47	134		16.91	24,440	9.90		88.7	22,000–90,000
Ga	0.02	5														
As	0.42	249	0.64	233				0.043		2.80			0.38	260	1.4	1000–2100
Rb	0.18	124														
Sr	1.55	783														
Y	0.042	13														
Mo	0.047	31						0.006								100–190
Cd	0.083	40	0.028	9.5	0.004	1.8	0.005	0.005	1.52	0.71	0.071	102	0.07	50	0.3	180–310
Sn	0.070	41	0.12	50				0.012								
Cs	0.018	9	0.32	82				0.044								
Ba	3.44	843					0.682						1.72	1200		
Pb	1.93	1117	1.59	516	0.141	60	0.036	0.036	10.4	8.48	0.98	1400	1.51	1060	18.3	5000–27,500
Bi	0.34	22	0.020	7				0.0004	0.16							
Th	0.043	1														
U	0.071	2	0.023	8.5				0.003	0.91							
La	0.053	14														
Ce	0.10	26														
Pr	0.014	4														
Nd	0.052	15														
Sm	0.013	3														
Eu	0.0029	0.71														
Gd	0.011	3														
Tb	0.0019	0.45														
Dy	0.0078	2														
Ho	0.0015	0.41														
Er	0.0040	1														
Tm	0.00067	0.14														
Yb	0.0033	0.93														
Lu	0.00068	0.10														

Table 3 – Correlation coefficients between fluxes and precipitation amounts, and between flux and concentration.

	Flux *vs.* precipitation	Flux *vs.* concentration
Li	**0.45**	**0.93**
B	**0.57**	**0.82**
Al	0.22	**0.55**
Ti	**0.67**	0.10
V	–	**0.99**
Cr	**0.62**	0.17
Mn	**0.67**	0.19
Fe	**0.38**	0.32
Co	**0.61**	0.22
Ni	**0.55**	0.29
Cu	**0.59**	0.31
Zn	**0.67**	**0.44**
Ga	**0.52**	0.18
As	**0.57**	**0.50**
Rb	**0.52**	**0.72**
Sr	**0.52**	**0.44**
Y	**0.58**	0.22
Mo	**0.39**	**0.72**
Cd	**0.52**	0.30
Sn	**0.95**	–
Cs	**0.69**	0.23
Ba	0.28	**0.80**
Pb	**0.52**	**0.54**
Bi	**0.70**	**0.51**
Th	**0.56**	0.17
U	**0.73**	0.09
La	**0.59**	0.20
Ce	**0.54**	0.25
Pr	**0.62**	0.22
Nd	**0.62**	0.21
Sm	**0.58**	0.10
Eu	**0.58**	0.12
Gd	**0.47**	0.20
Tb	**0.56**	0.14
Dy	**0.57**	0.24
Ho	**0.58**	0.19
Er	**0.53**	0.19
Tm	**0.57**	0.11
Yb	**0.59**	0.17
Lu	**0.68**	–

Boldface means $p < 0.05$.

trace elements, such as Zn, Mo, Cd, Ba, Pb, and Bi, with EFs values more than 100. Generally, the trace elements with EFs >10 are considered to derive mainly from anthropogenic sources (*e.g.*, Cong et al., 2010; Tripathee et al., 2014; Guo et al., 2015). Therefore, Fig. 3 clearly indicates that some of the trace elements (Li, B, Cr, Mn, Ni, Cu, As, Sr and Sn) were moderately enriched and were derived from the influence of anthropogenic emissions. Furthermore, a few highly enriched elements (*e.g.*, Zn, Cd and Pb) were observed, which are mostly from the anthropologic sources in Lijiang city. Previous studies have suggested that Cd has been the most highly enriched trace element since the Industrial Revolution (Barbante et al., 2004). Similarly, Cong et al. (2014) has reported that the highest EF of Cd was found in the wet deposition of Mt. Qomolangma, on the southern edge of the TP. Therefore, the highest EF of Cd in our present study (Fig. 3) has reconfirmed that Cd is the trace element most sensitive to environmental pollution with the increasing atmospheric contamination over the TP.

Furthermore, the EFs of most trace elements and REEs (except for Fe, Ga and Th) were higher during the monsoon season than during the non-monsoon season (Fig. 3). These results have shown a significant seasonal variation and suggested that anthropogenic activities could result in distinct seasonality between the anthropogenic and crustal emissions of trace elements. Previous studies have suggested that increasing numbers of tourists and traffic (*e.g.* growing use of motor vehicles) in Lijiang city have caused an increase in anthropogenic emissions during the monsoon season (Cao et al., 2012), leading to the observation of high EFs of trace elements and REEs in the monsoon season (Fig. 3). In contrast, limited precipitation and dusty weather conditions occur frequently during the non-monsoon season (Niu et al., 2014), which could result in more loadings of crustal elements than in the monsoon season (Zhang et al., 2012a). Therefore, similar to what has been found in the wet deposition of Lhasa (Guo et al., 2015), the seasonal variations of EFs of trace elements in the precipitation of Lijiang city could be attributed to the fact that more anthropogenic emissions occurred in the monsoon season (*i.e.*, high EFs) and more loadings of crustal particles occurred during the non-monsoon season (*i.e.*, low EFs), respectively.

Principal component analysis (PCA) was performed for the entire dataset of 40 elements and is shown in Table 4. Three factors were identified, and 86% of the total variance in the dataset was explained. The first factor was associated with Al, Fe, Co, Ni, Cu, Zn, Ga, Sr, Y, Sn, Ba, Th, U, and all REEs, accounting for 55% of the total variation. This group contained most of the elements with EFs lower than 10 except for Ni, Cu, Zn, and Sn, indicating that the crustal sources contributed substantially to those elements grouped in the first factor. Previous studies have indicated that the compositions of REEs in anthropogenic and natural aerosols are significantly different, as presented earlier in Section 1 (Olmez and Gordon, 1985; Watson, 1989). The ratios of La to Ce, Nd, Sm, and Yb in the wet deposition of Lijiang were compared with those observed from the crustal, oil-fired plants and refineries, and are presented in Table 5. The REE ratios in the wet deposition of Lijiang city were found to be similar to the ratios from the

Notes to Table 2:
[a] This study, [b] Guo et al. (2015), [c] Cong et al. (2010), [d] Liu et al. (2013), [e] Cong et al. (2014), [f] Zhou et al. (2012), [g] Tripathee et al. (2014), [h] Kim et al. (2012), [i] Li et al. (2012), [j] Pan and Wang (2015).

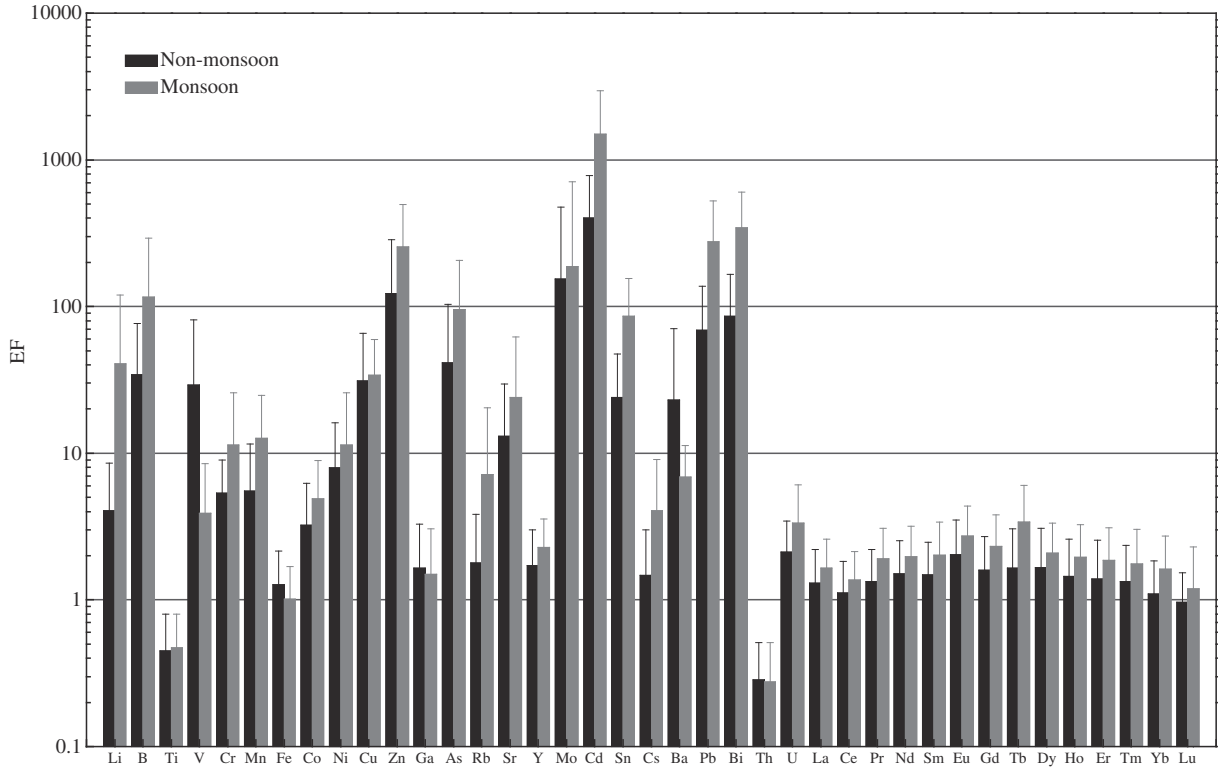

Fig. 3 – Mean enrichment factors for 40 elements (Al was a reference element and not shown) in precipitation of Lijiang city.

earth's crust (Table 5), but significantly lower than those of anthropogenic emissions emitted from oil-fired power plants and refineries (Olmez et al., 1991). Therefore, the results from this study suggest that the earth's crust should be the major sources of REEs in the wet deposition of Lijiang city rather than anthropogenic sources. Moreover, note that the trace elements grouped in this factor also contained Ni, Cu, Zn, and Sn with high loading values and high EFs as indicated in Fig. 3. Previous studies have suggested that exhaust emissions from vehicles could emit various amounts of Ni, Cu and Zn (Pakkanen et al., 2003). Furthermore, in general Ni has been regarded as an indicator of fuel burning and vehicular emissions (Pacyna and Pacyna, 2001), Zinc (Zn) was mainly derived from various industrial sources and the abrasion of rubber tires on roads (Rogge et al., 1993) and Cu in urban aerosols mainly originated from brake wear of vehicles (Weckwerth, 2001). Therefore, the anthropogenic emissions from the increasing numbers of tourists and traffic vehicles were also expected to be important sources of the trace elements grouped in the first factor.

The second factor accounted for 28% of the total variance included high loading values for Ti, Cr, Mn, Fe, Co, As, Cd, Cs, Pb and Bi (Table 4), which could be attributed to anthropogenic sources such as solid waste incineration (Pacyna and Pacyna, 2001). For example, Cr and Cd are generally considered to be important contaminants from solid waste treatment (Kulshrestha et al., 2009). Although leaded gasoline has been phased out gradually since the 1980s, relatively high levels of Pb may still exist in the environment (McConnell and Edwards, 2008; Özsoy and Örnektekin, 2009), and solid waste incineration could account for the major portion of the Pb in the urban atmosphere (Sakata et al., 2000). Furthermore, refuse burning was reported to be one of the important anthropogenic sources for Bi (Ferrari et al., 2000). Similarly, with the presence of hundreds of thousands of tourists in Lijiang city, the increased incineration of solid wastes most likely contributed a large amount of trace elements, as grouped in the second factor, to the wet deposition in our study area. Finally, the third factor accounted for 14% of the total variance, with high loadings of Li, B and Mo (Table 4). Previous studies have suggested that recent consumption of Li has increased greatly due to use in rechargeable cells (Shimamura et al., 2007). Therefore, it is reasonable to deduce that these elements grouped in the third factor might possibly be attributed to the emissions from electronic waste burning.

2.3. Patterns of REEs

EFs and PCA analysis, as discussed earlier, indicated that the REEs in the wet deposition of Lijiang city were significantly contributed by crustal sources rather than anthropogenic sources. In order to further investigate the potential source regions of REEs in Lijiang city, REE patterns normalized using the upper crustal concentration (UCC) were used to enable comparison with those observed from other potential sources, and are presented in Fig. 4. From Fig. 4, REE patterns in wet

Table 4 – Factor loading normalized with VARIMAX rotation.

	F1	F2	F3
Li	0.115	0.100	**0.879**
B	0.029	0.202	**0.954**
Al	**0.982**	0.008	0.098
Ti	0.489	**0.788**	−0.059
V	0.259	−0.061	0.073
Cr	**0.515**	**0.657**	0.037
Mn	0.422	**0.889**	0.055
Fe	**0.685**	**0.650**	0.002
Co	**0.606**	**0.759**	0.083
Ni	**0.953**	0.175	0.131
Cu	**0.916**	0.209	0.210
Zn	**0.833**	0.134	0.317
Ga	**0.962**	0.169	0.153
As	0.084	**0.799**	0.071
Rb	0.203	0.618	**0.690**
Sr	**0.589**	**0.587**	**0.501**
Y	**0.900**	0.424	0.044
Mo	0.202	0.018	**0.849**
Cd	0.076	**0.955**	0.019
Sn	**0.528**	−0.104	0.164
Cs	0.198	**0.951**	0.119
Ba	**0.891**	−0.047	0.270
Pb	0.089	**0.729**	0.115
Bi	−0.020	**0.533**	0.238
Th	**0.978**	0.042	0.120
U	**0.944**	0.298	0.094
La	**0.953**	0.284	0.072
Ce	**0.960**	0.256	0.073
Pr	**0.947**	0.301	0.072
Nd	**0.937**	0.332	0.069
Sm	**0.940**	0.285	0.008
Eu	**0.901**	0.395	0.030
Gd	**0.921**	0.344	0.000
Tb	**0.871**	0.452	0.013
Dy	**0.905**	0.413	0.048
Ho	**0.899**	0.417	0.031
Er	**0.910**	0.392	0.018
Tm	**0.902**	0.344	0.073
Yb	**0.933**	0.332	0.045
Lu	**0.915**	0.279	−0.035

deposition of Lijiang city were flat and the middle REEs were slightly enriched, which showed similar patterns to those in the topsoil of TP (Li et al., 2009). However, the results were significantly different from the patterns showing enriched LREEs in the topsoil sampled in other parts of Yunnan province (Lijiang is one of prefectures in Yunnan Province). This phenomenon could be mainly explained by the fact that the samples of topsoil in other parts of Yunnan province were mainly collected from traditional industrial regions, and the REE patterns showing enrichment in light REEs had been greatly influenced by anthropogenic activities (Fu et al., 2000). Furthermore, the REE patterns in the wet deposition of Lijiang city were also remarkably different from Taklimakan sand and Delhi sediments (Chang et al., 2000; Jayant and Rajamani, 1999), which showed flat patterns of REEs with a negative Eu anomaly (Fig. 4). Considering that our study site is a tourism city with negligible industrial sources, our study has further suggested that regional/local crustal sources should be the dominant sources of REEs in the wet deposition of Lijiang city.

3. Conclusions

The concentrations and wet fluxes of 40 elements were measured in the precipitation of Lijiang city from March to August in 2012. The concentrations of trace elements were significantly higher than those measured at remote and background sites over the TP, but much lower than those observed in polluted industrial sites and even remote sites in eastern China, indicating that the atmospheric environment in Lijiang city was relatively good. The EF and PCA analysis showed that most of the trace elements in the precipitation of Lijiang city were mainly derived from anthropogenic sources, such as the increasing traffic emissions, while the REEs in the precipitation of Lijiang city were most likely attributable to regional/local crustal sources. With the ongoing rapid development of the economy and increase of anthropogenic emissions in the foreseeable future, our study supports the implementation of specific management actions for the control of atmospheric inputs and the health of the environment at Lijiang city.

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Table 5 – Ratios of REEs in precipitation of Lijiang city.

	Monsoon		Non-monsoon		Earth crust[a]	Oil-fired power plant[a]	Refinery[a]
	Mean	Range	Mean	Range			
La/Ce	0.58	0.54–0.63	0.55	0.48–0.68	0.5	1.8	1.25
La/Nd	1.04	0.69–1.26	1.03	0.84–1.17	0.84	2.4	1.83
La/Sm	7.97	3.74–14.74	5.38	3.51–8.85	4.9	28	20
La/Yb	18.34	10.56–25.74	16.82	13.14–19.55	12	135	950

[a] Olmez and Gordon (1985).

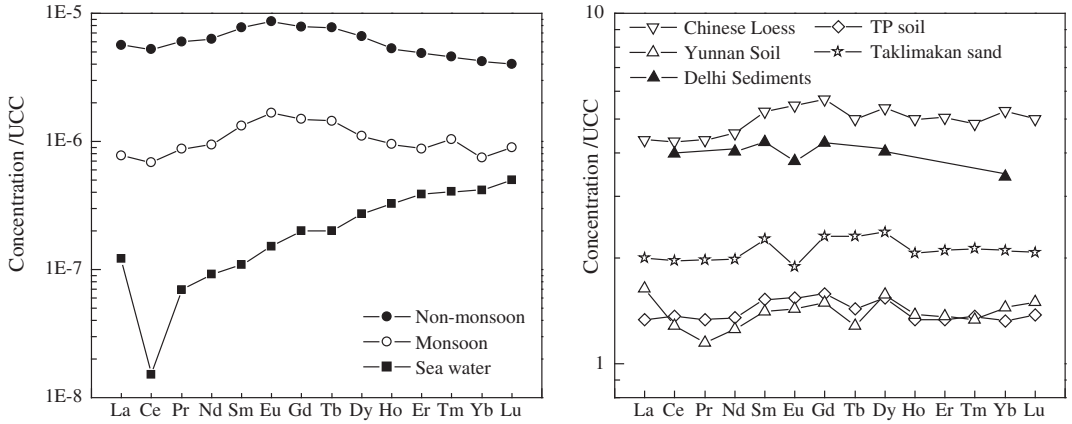

Fig. 4 – UCC-normalized REE patterns in precipitation of Lijiang during monsoon and non-monsoon seasons (average value) compared with TP soil (Li et al. 2009), Yunnan soil (Fu et al., 2000), Pacific seawater (Alibo and Nozaki, 1999), China loess (Ding et al., 2001), Delhi sediments in Thar Desert (Tripathi and Rajamani, 1999) and Taklimakan sand (Chang et al., 2000). Data for China loess, Delhi sediments and Taklimakan sands were multiplied 4, 3, and 2 times for comparison. REE: rare earth elements;

REFERENCES

Alibo, D.S., Nozaki, Y., 1999. Rare earth elements in seawater: Particle association, shale-normalization, and Ce oxidation. Geochim. Cosmochim. Acta 63, 363–372.

Al-Momani, I., 2003. Trace elements in atmospheric precipitation at Northern Jordan measured by ICP-MS: Acidity and possible sources. Atmos. Environ. 37, 4507–4515.

Bacardit, M., Camarero, L., 2010. Atmospherically deposited major and trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: The seasonal record of long-range fluxes over SW Europe. Atmos. Environ. 44, 582–595.

Barbante, C., Schwikowski, M., Döring, T., Gäggeler, H.W., Schotterer, U., Tobler, L., et al., 2004. Historical record of European emissions of heavy metals to the atmosphere since the 1650s from Alpine snow/ice cores drilled near Monte Rosa. Environ. Sci. Technol. 38, 4085–4090.

Cao, W., He, Y., Li, Z., Wang, S., Wang, C., Chang, L., 2012. A correlation analysis between climate comfort degree and monthly variation of tourists in Lijiang. Sci. Geol. Sin. 32, 1459–1464 (in Chinese with English abstract).

Chang, Q., Mishima, T., Yabuki, S., Takahashi, Y., Shimizu, H., 2000. Sr and Nd isotope ratios and REE abundances of moraines in the mountain areas surrounding the Taklimakan Desert, NW China. Geochem. J. 34, 407–427.

Chiarenzelli, J., Aspler, L., Dunn, C., Cousens, B., Ozarko, D., Powis, K., 2001. Multi-element and rare earth element composition of lichens, mosses, and vascular plants from the central Barrenlands, Nunavut, Canada. Appl. Geochem. 16, 245–270.

Cong, Z., Kang, S., Zhang, Y., Li, X., 2010. Atmospheric wet deposition of trace elements to central Tibetan Plateau. Appl. Geochem. 25, 1415–1421.

Cong, Z., Kang, S., Zhang, Y., Gao, S., Wang, Z., Liu, B., et al., 2014. New insights into trace element wet deposition in the Himalayas: Amounts, seasonal patterns, and implications. Environ. Sci. Pollut. Res. 1-10.

Ding, Z.L., Sun, J.M., Yang, S.L., Liu, T.S., 2001. Geochemistry of the Pliocene red clay formation in the Chinese Loess Plateau and implications for its origin, source provenance and paleoclimate change. Geochim. Cosmochim. Acta 65, 901–913.

Ferrari, C., Hong, S., Van de Velde, K., Boutron, C., Rudniev, S., Bolshov, M., et al., 2000. Natural and anthropogenic bismuth in Central Greenland. Atmos. Environ. 34, 941–948.

Fu, S., Yan, C., Wu, S., Yang, X., 2000. Content and distribution characteristics of rare earth elements in typical soil of Guizhou Province. Acta Pedol. Sin. 37, 109–115 (in Chinese with English abstract).

Gabrielli, P., Barbante, C., Turetta, C., Marteel, A., Boutron, C., Cozzi, G., et al., 2006. Direct determination of rare earth elements at the subpicogram per gram level in antarctic ice by ICP-SFMS using a desolvation system. Anal. Chem. 78, 1883–1889.

Galloway, J.N., Thornton, J.D., Norton, S.A., Volchok, H.L., McLean, R.A.N., 1982. Trace metals in atmospheric deposition: A review and assessment. Atmos. Environ. 16, 1677–1700.

Guo, J., Kang, S., Huang, J., Zhang, Q., Tripathee, L., Sillanpää, M., 2015. Seasonal variations of trace elements in precipitation at the largest city in Tibet, Lhasa. Atmos. Res. 153, 87–97.

Huang, J., Kang, S., Zhang, Q., Yan, H., Guo, J., Jenkins, M., et al., 2012. Wet deposition of mercury at a remote site in the Tibetan Plateau: Concentrations, speciation, and fluxes. Atmos. Environ. 62, 540–550.

Huang, J., Kang, S., Wang, S., Wang, L., Zhang, Q., Guo, J., et al., 2013a. Wet deposition of mercury at Lhasa, the capital city of Tibet. Sci. Total Environ. 447, 123–132.

Huang, J., Kang, S., Zhang, Q., Guo, J., Chen, P., Zhang, G., et al., 2013b. Atmospheric deposition of trace elements recorded in snow from the Mt. Nyainqêntanglha region, southern Tibetan Plateau. Chemosphere 92, 871–881.

Huang, J., Kang, S., Zhang, Q., Guo, J., Sillanpää, M., Wang, Y., et al., 2015. Characterizations of wet mercury deposition on a remote high-elevation site in the southeastern Tibetan Plateau. Environ. Pollut. 206, 518–526.

Jayant, K.T., Rajamani, V., 1999. Geochemistry of the loessic sediments on Delhi ridge, eastern Thar desert, Rajasthan: implications for exogenic processes. Chem. Geol. 155, 265–278.

Kim, J.E., Han, Y.J., Kim, P.R., Holsen, T.M., 2012. Factors influencing atmospheric wet deposition of trace elements in rural Korea. Atmos. Res. 116, 185–194.

Kulshrestha, A., Satsangi, P.G., Masih, J., Taneja, A., 2009. Metal concentration of PM 2.5 and PM 10 particles and seasonal variations in urban and rural environment of Agra, India. Sci. Total Environ. 407, 6196–6204.

Li, C.L., Kang, S.C., Zhang, Q.G., 2009. Elemental composition of Tibetan Plateau top soils and its effect on evaluating atmospheric pollution transport. Environ. Pollut. 157, 2261–2265.
Li, Y., Pan, Y., Yuesi, W., Yingfeng, W., Li, X., 2012. Chemical characteristics and sources of trace metals in precipitation collected from a typical industrial city in Northern China. Environ. Sci. 33, 3712–3717 (in Chinese with English abstract).
Liu, B., Kang, S., Sun, J., Zhang, Y., Xu, R., Wang, Y., et al., 2013. Wet precipitation chemistry at a high-altitude site (3,326 m asl) in the southeastern Tibetan Plateau. Environ. Sci. Pollut. Res. 20, 5013–5027.
McConnell, J.R., Edwards, R., 2008. Coal burning leaves toxic heavy metal legacy in the Arctic. Proc. Natl. Acad. Sci. U. S. A. 105, 12140–12144.
Ning, B., He, Y., 2007. Tourism development and water pollution: Case study in Lijiang Ancient Town, China Population. Resour. Environ. 17, 123–127 (in Chinese with English abstract).
Niu, H., He, Y., Zhu, G., Xin, H., Du, J., Pu, T., et al., 2013. Environmental implications of the snow chemistry from Mt. Yulong, southeastern Tibetan Plateau. Quat. Int. 313, 168–178.
Niu, H., He, Y., Lu, X.X., Shen, J., Du, J., Zhang, T., et al., 2014. Chemical composition of rainwater in the Yulong Snow Mountain region, Southwestern China. Atmos. Res. 144, 195–206.
Olmez, I., Gordon, G.E., 1985. Rare-earths: Atmospheric signatures for oil-fired power-plants and refineries. Science 229, 966–968.
Olmez, I., Sholkovitz, E.R., Hermann, D., Eganhouse, R.P., 1991. Rare-earth elements in sediments off southern California: A new anthropogenic indicator. Environ. Sci. Technol. 25, 310–316.
Özsoy, T., Örnektekin, S., 2009. Trace elements in urban and suburban rainfall, Mersin, Northeastern Mediterranean. Atmos. Res. 94, 203–219.
Pacyna, J.M., 1986. Atmospheric trace elements from natural and anthropogenic sources, toxic metals in the atmosphere. Wiley, New York.
Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ. Rev. 9, 269–298.
Pakkanen, T.A., Kerminen, V.M., Loukkola, K., Hillamo, R.E., Aarnio, P., Koskentalo, T., et al., 2003. Size distributions of mass and chemical components in street-level and rooftop PM 1 particles in Helsinki. Atmos. Environ. 37, 1673–1690.
Pan, Y.P., Wang, Y.S., 2015. Atmospheric wet and dry deposition of trace elements at 10 sites in Northern China. Atmos. Chem. Phys. 15 (2), 951–972.
Pang, H., He, Y., Lu, A., Zhao, J., Ning, B., Yuan, L., et al., 2006. Synoptic-scale variation of δ 18O in summer monsoon rainfall at Lijiang, China. Chin. Sci. Bull. 51, 2897–2904.
Qiu, J., 2008. China: The third pole. Nature News 454, 393–396.
Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R., 1993. Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: Roads as sources and sinks. Environ. Sci. Technol. 27, 1892–1904.
Sakata, M., Kurata, M., Tanaka, N., 2000. Estimating contribution from municipal solid waste incineration to trace metal concentrations in Japanese urban atmosphere using lead as a marker element. Geochem. J. 34, 23–32.
Shimamura, T., Iwashita, M., Iijima, S., Shintani, M., Takaku, Y., 2007. Major to ultra trace elements in rainfall collected in suburban Tokyo. Atmos. Environ. 41, 6999–7010.
Tripathee, L., Kang, S., Huang, J., Sharma, C.M., Sillanpää, M., Guo, J., et al., 2014. Concentrations of trace elements in wet deposition over the Central Himalayas, Nepal. Atmos. Environ. 95, 231–238.
Tripathi, J.K., Rajamani, V., 1999. Geochemistry of the loessic sediments on Delhi ridge, eastern Thar desert, Rajasthan: Implications for exogenic processes. Chem. Geol. 155 (3), 265–278.
Watson, J.G., 1989. Receptor models in air resources management. Air & waste management assoc, Pittsburgh, PA.
Weckwerth, G., 2001. Verification of traffic emitted aerosol components in the ambient air of Cologne (Germany). Atmos. Environ. 35, 5525–5536.
Zhang, J., Liu, C.Q., 2004. Major and rare earth elements in rainwaters from Japan and East China Sea: Natural and anthropogenic sources. Chem. Geol. 209, 315–326.
Zhang, N., Cao, J., Ho, K., He, Y., 2012a. Chemical characterization of aerosol collected at Mt. Yulong in wintertime on the southeastern Tibetan Plateau. Atmos. Res. 107, 76–85.
Zhang, N., He, Y., Cao, J., Ho, K., Shen, Z., 2012b. Long-term trends in chemical composition of precipitation at Lijiang, southeast Tibetan Plateau, southwestern China. Atmos. Res. 106, 50–60.
Zhang, N., Cao, J., Xu, H., Zhu, C., 2013. Elemental compositions of PM2.5 and TSP in Lijiang, southeastern edge of Tibetan Plateau during pre-monsoon period. Particuology 11, 63–69.
Zhou, J., Wang, Y., Yue, T., Li, Y., Wai, K.-M., Wang, W., 2012. Origin and distribution of trace elements in high-elevation precipitation in Southern China. Environ. Sci. Pollut. Res. 19, 3389–3399.