Environ Sci Pollut Res (2013) 20:5013–5027
DOI 10.1007/s11356-012-1379-x

RESEARCH ARTICLE

Wet precipitation chemistry at a high-altitude site (3,326 m a.s.l.) in the southeastern Tibetan Plateau

Bin Liu · Shichang Kang · Jimin Sun · Yulan Zhang · Ri Xu · Yongjie Wang · Yongwen Liu · Zhiyuan Cong

Received: 13 August 2012 / Accepted: 29 November 2012 / Published online: 20 January 2013

Abstract This paper presents the results of wet precipitation chemistry from September 2009 to August 2010 at a high-altitude forest site in the southeastern Tibetan Plateau (TP). The alkaline wet precipitation, with pH ranging from 6.25 to 9.27, was attributed to the neutralization of dust in the atmosphere. Wet deposition levels of major ions and trace elements were generally comparable with other alpine and remote sites around the world. However, the apparently greater contents/fluxes of trace elements (V, Co, Ni, Cu, Zn, and Cd), compared to those in central and southern TP and pristine sites of the world, reflected potential anthropogenic disturbances. The almost equal mole concentrations and perfect linear relationships of Na^+ and Cl^- suggested significant sea-salts sources, and was confirmed by calculating diverse sources. Crust mineral dust was responsible for a minor fraction of the chemical components (less than 15 %) except Al and Fe, while most species (without Na^+, Cl^-, Mg^{2+}, Al, and Fe) arose mainly from anthropogenic activities. High values of as-K^+ (anthropogenic sources potassium), as-SO_4^{2-}, and as-NO_3^- observed in winter and spring demonstrated the great effects of biomass burning and fossil fuel combustion in these seasons, which coincided with haze layer outburst in South Asia. Atmospheric circulation exerted significant influences on the chemical components in wet deposition. Marine air masses mainly originating from the Bay of Bengal provided a large number of sea salts to the chemical composition, while trace elements during summer monsoon seasons were greatly affected by industrial emissions from South Asia. The flux of wet deposition was 1.12 $kg N ha^{-1} year^{-1}$ for NH_4^+–N and 0.29 $kg N ha^{-1} year^{-1}$ for NO_3^-–N. The total atmospheric deposition of N was estimated to be 6.41 $kg N ha^{-1} year^{-1}$, implying potential impacts on the alpine ecosystem in this region.

Keywords Wet precipitation chemistry · Major ions · Trace elements · Atmospheric N deposition · Southeastern Tibetan Plateau

Responsible editor: Gerhard Lammel

B. Liu · J. Sun
Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, P.O. Box 9825, Beijing 100029, China

S. Kang · Y. Zhang · R. Xu · Y. Wang · Y. Liu · Z. Cong (✉)
Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, A4 Datun Road, Chaoyang District, Beijing 100101, China
e-mail: zhiyuancong@itpcas.ac.cn

S. Kang
State Key Laboratory of Cryospheric Sciences, Chinese Academy of Sciences, Lanzhou 730000, China

B. Liu · Y. Liu
Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

Introduction

Wet deposition in the atmosphere is a crucial removal process for airborne particulate matter (anthropogenic emissions, particle pollutants, and soil dusts) returning to earth's surface. Dissolved solutes in wet precipitation originate from diverse sources including natural sources (soil and mineral dusts, sea salts, volcanoes, and natural forest fires) and anthropogenic sources (fossil fuel burning, industrial activities, agricultural activities, and biomass burning). Moreover, the chemical composition of wet precipitation is influenced by the dynamics of the atmosphere, the atmospheric chemical reactions, and the removal processes in the atmosphere (Galy-Lacaux et al. 2009). Further, various components in wet deposition vary geographically. Wet precipitation chemistry can reveal the state of the atmospheric environment and the transport of chemical species emitted from various sources (Polkowska et al. 2011). Furthermore, acidic components (like nitrogen) from wet deposition exert complex impacts on natural ecosystems. For example, as a nutrient, nitrogen can enhance plant production in nitrogen-limited forests. However, excess nitrogen deposition can provoke a variety of negative impacts such as leaching of soil nutrients (Aber et al. 1998), eutrophication (Smith et al. 1999), and the reduction of biodiversity in forests (Bobbink et al. 2010). Therefore, wet depositions of the ionic components and trace elements have received a great deal of attention in the past decades.

Human activity has significantly affected the atmospheric environment in Asia. Asia has been estimated to have the largest amount of anthropogenic emissions of atmospheric trace metals (Pacyna and Pacyna 2001) and has suffered from atmospheric contamination of trace elements (Sakata and Asakura 2009; Zhou et al. 2012). Atmospheric brown cloud (ABC) principally consisting of emissions from fossil fuel combustion and biomass burning has been observed over entire South Asia, from the North Indian Ocean toward the southern slope of the Himalaya (Lelieveld et al. 2001). Pollutants from the biomass burning in Southeast Asia have impacted the chemical composition of the background atmosphere in the eastern Tibetan Plateau (TP) (Chan et al. 2006; Engling et al. 2011). The Asian monsoon and westerlies are responsible for dispersion and transport of the anthropogenic pollutants and airborne dusts from South Asia and inner Asia (Cong et al. 2007; Huang et al. 2007; Ming et al. 2008), resulting in potential threats to the ecosystems of continental Asia.

The TP, with extreme high altitude, is sensitive to atmospheric composition changes due to active atmosphere exchange created by monsoonal circulation and the westerlies. In recent years, exotic air pollutants were observed in measurement campaigns over the TP. For example, Cong et al. (2010) studied the trace elements in wet deposition on the central TP and noted that pollutants from South Asia might affect this region through long-range transport. Theoretically, the changed atmospheric chemistry will have considerable influence on the alpine ecosystem because of its vulnerable biotic communities. However, almost no work has been done to examine the probable effects of anthropogenic disturbances via wet deposition on the alpine ecosystem of the TP. Therefore, a comprehensive monitoring of wet deposition in the southeastern TP, where alpine forest is widely distributed, is essential to assess the changes of chemical composition in this specific region and its implications for the high-altitude environment of this biodiversity hotspot.

In this study, wet precipitation chemistry, including the pH, major ions, and elements, has been investigated throughout 1 year at a high-altitude forest site, the Southeastern Tibet Station for Observing Alpine Environment (SET Station). This work aims to (1) reveal the current wet deposition levels of major ions and elements in this region, (2) estimate the contributions of diverse sources to chemical species, (3) discern the influences of exotic and regional/local sources on the wet precipitation chemistry, and (4) assess the atmospheric nitrogen deposition and its possible effects on the high-altitude ecosystem.

Methodology

Monitoring site

The wet deposition samples were collected at the SET Station, the Chinese Academy of Sciences (94°44′E, 29°46′N, 3,326 ma.s.l.) (Fig. 1). The observation site of SET Station is flat grassland at the intersection of two rivers in the Lulang Valley, one of the main branches of Yarlung Tsangpo Grand Canyon. This canyon, formed by the Yarlung Tsangpo River (Brahmaputra), serves as a corridor for warm-humid air masses originating in the Indian Ocean to reach the inner part of the TP (Yang et al. 1989). High mountains, glaciers, alpine meadows, forest, and grassland are the main landscapes in this region, representing the mountain–valley geomorphologic features of the southeastern TP. The major human activities around the station are tourism and limited agricultural activities, thus the local emission of air pollution is small.

At SET Station, annual precipitation was 800–1,000 mm. Annual mean temperature was 5.6 °C, with dramatic seasonal differences, e.g., the lowest (−18.2 °C) in winter and the highest (25.2 °C) in summer (Wang et al. 2010). Monthly precipitation amounts at SET Station are presented in Fig. 2. Precipitation was lower in the dry season when the air masses were dominated by westerlies. In the wet season, precipitation was controlled by the South Asian monsoon, which brought abundant precipitation by the prevailing southwest wind from South Asia to the TP. Active interactions between unique geomorphological conditions and strong monsoons have bred diverse biomes and high-altitudinal distribution patterns of vegetation in this region, including the extreme northern limit of tropical rain forests (~29°N) and the highest alpine tree lines (4,400 m a.s.l.) in the world (Luo et al. 2002; Liang et al. 2011).

Materials and methods

Field samples were collected for each precipitation event at the SET Station. A total of 103 precipitation events were sampled from September 2009 to August 2010, using an inner removable high-density polyethylene (HDPE) plastic bag in a pre-cleaned HDPE bucket, which was placed 1.5 m above the ground. To minimize the possible interference of

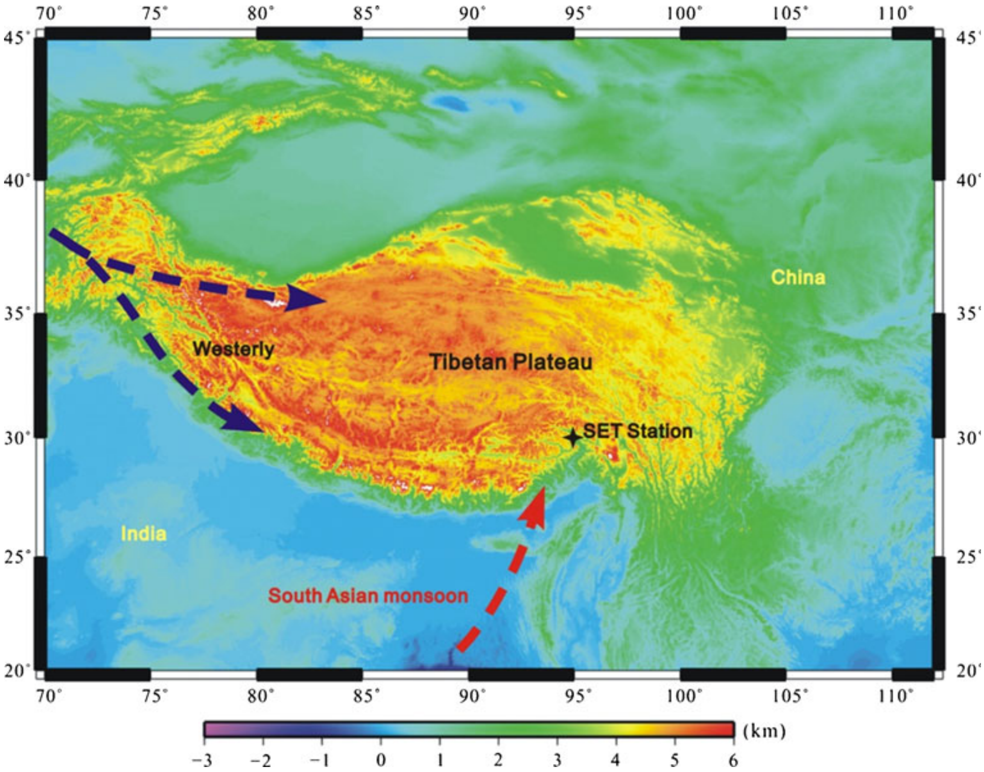


Fig. 1 Location of the SET Station and the dominant atmospheric circulation patterns in this region

dry deposition, the plastic bag was opened at the beginning of the precipitation event and was collected as quickly as possible at the end of precipitation process. Each sample was transferred into a pre-cleaned HDPE bottle and kept frozen until analysis in the laboratory. Field blanks (n=12) were also attained by 50 mL of ultrapure water used to wash the HDPE plastic bag and transferred into cleaned HDPE bottles. Air temperature, humidity, wind speed and direction, and precipitation amounts were also recorded by an automatic weather station (AWS). Total sampled precipitation amount was 728 mm, accounting for 81.2 % of the total precipitation (896.8 mm) in the investigation period. The pH of rainfall samples was determined by a pH meter (HI98128; Hanna Instruments).

At the Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Chinese Academy of Sciences, samples were filtered through 0.45-μm-pore-size PTFE filters (FHLC02500; Millipore). Major ions were analyzed using two ion chromatography systems (ICS-2500 and ICS-2000; Dionex, USA) equipped with an electrochemical detector. The detection limits of Ca^{2+} and SO_4^{2-} were 2 μg L^{-1}; other ions were 1 μgL^{-1}. After the major ions were

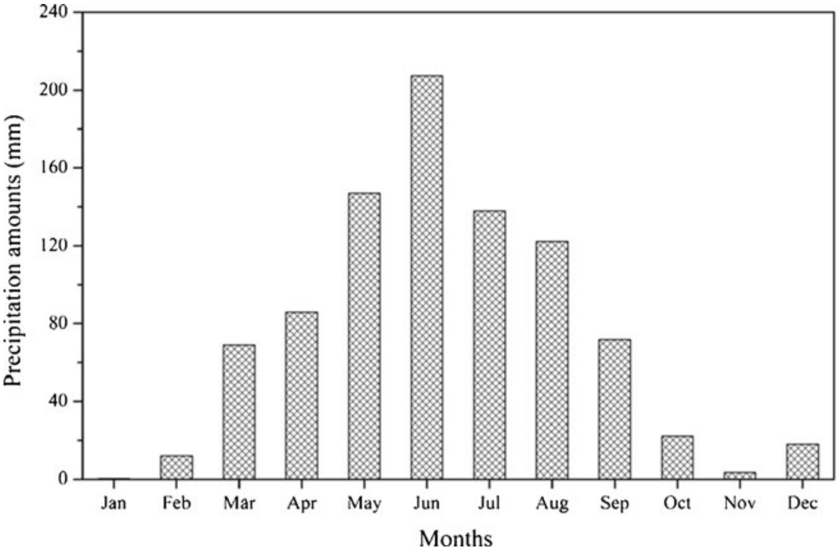


Fig. 2 Monthly precipitation amounts at the SET Station during the monitoring period

measured, samples were acidified to pH <2 with ultrapure HNO_3, then measured by inductively coupled plasma–mass spectrometry (ICP–MS; X-7 Thermo Scientific) for the concentrations of 15 elements (Al, Fe, Rb, Sr, Ba, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Cs, and Pb). The method detection limits (MDLs), defined as three times the standard deviation of replicate blank measurements, were Al, 0.043 μgL^{-1}; Fe, 0.351 μgL^{-1}; Rb, 0.005 μgL^{-1}; Sr, 0.003 μgL^{-1}; Ba, 0.008 μgL^{-1}; V, 0.015 μgL^{-1}; Cr, 0.033 μgL^{-1}; Mn, 0.008 μgL^{-1}; Co, 0.005 μgL^{-1}; Ni, 0.018 μgL^{-1}; Cu, 0.023 μgL^{-1}; Zn, 0.195 μgL^{-1}; Cd, 0.001 μgL^{-1}; Cs, 0.001 μgL^{-1}; and Pb, 0.003 μgL^{-1}. The accuracy and precision of trace elements was ascertained based on repeated measurement of the certified trace elements in natural water (Standard Reference Material 1640a) from the National Institute of Standards and Technology (NIST), Maryland, USA. Good agreements between measured and certified values were observed for all measured elements, with the recoveries ranging from 98 % for Co to 103 % for Sr.

Data quality

The ionic amounts measured in the field blanks were generally lower than 10 % those in the precipitation samples, while elemental field blanks were typically <15 % of the mean analyzed concentration. Field blank values were deducted from the measured values. For the purpose of quality assurance and quality control (QA/QC), 15 samples outside the range ($m-3\delta$, $m+3\delta$) were excluded with a statistical technique of data points in precipitation chemistry (Safai et al. 2004), where m=average value and δ=standard deviation. The ion balance between anions (Cl^-, SO_4^{2-}, and NO_3^-) and cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, and NH_4^+) was also evaluated by regression analysis. The result ($\Sigma_{\mathrm{anions}}=0.205\times\Sigma_{\mathrm{cations}}+0.214$, $R^2=0.557$) suggests an acceptable data quality. The value of the slope is 0.205 (indicating the ratio of total anions to total cations), which may reflect the absence of HCO_3^- in precipitation events (Li et al. 2007).

Backward air trajectory analysis

Based on the meteorological data of the National Centers for Environmental Prediction's (NCEP) Global Data Assimilation System (GDAS, global, 2006–present), trajectories were used to diagnose the air masses corresponding to the wet precipitation events at the SET Station; the samples were then categorized according to the dominant trajectory pathways. Five-day backward air trajectories were constructed using the HYSPLIT-4 online transport and dispersion model from the National Oceanic and Atmospheric Administration (NOAA) with 500 and 1,000 m (a.g.l.) ending levels (http://www.arl.noaa.gov/HYSPLIT_info.php).

Results and discussion

Ionic composition and pH value

The volume-weighted mean (VWM) concentrations and wet deposition fluxes (the VWM concentration multiplied by an annual precipitation amount, 896.8 mm, obtained by the AWS) of ions are shown in Table 1. The VWM concentrations of the cation Ca^{2+}, NH_4^+, Na^+, K^+, and Mg^{2+} were 34.0, 8.91, 6.73, 1.88, and 1.66 µEq/L, and 6.74, 2.62, and 2.33 µEq/L for anion Cl^-, SO_4^{2-}, and NO_3^-, respectively. They were lower than those reported in the northeastern TP (Tang et al. 2000) and the central TP (Li et al. 2007) (Table 1). Major ions, i.e., Ca^{2+}, Na^+, Cl^-, and NH_4^+, showed large variations with ranges of 0.11–151, 0.12–44.18, 0.23–43.98, and 0.37–41.81 µEq/L, respectively. Similar to the results observed by previous studies in the TP (Zhang et al. 2002, 2012a), Ca^{2+} was dominant in the chemical composition, with a relative contribution of 78 % in total concentrations of cations. The pH ranged from 6.25 to 9.27, with a mean value of 7.8, implying that the alkalinity of wet precipitation in the southeastern TP largely resulted from the neutralization of carbonate in the troposphere because the contribution of the low CO_2 partial pressure to the pH was negligible and the alkaline dust as a major cause to the high pH of precipitation was reported in the TP (Zhang et al. 2002).

As shown in Table 1, despite the fact that their fluxes were similar, the major ion concentrations of wet precipitation at the SET Station were apparently lower than those from other sites over the TP, probably caused by the diluting effects of monsoonal rainfall in the southeastern TP region. Compared to high-altitude precipitation monitored in East Asia (e.g., Mt. Lulin in Taiwan and Mt. Fuji in Japan) (Wai et al. 2008), the SET Station showed lower concentrations and fluxes in ionic constituents, especially for SO_4^{2-} and NH_4^+, reflecting the difference of chemical compositions in the Asian background atmosphere. It was interesting that in spite of lower values than those in Hawaii, the Na^+ and Cl^- at the SET Station showed apparently higher concentrations and/or fluxes compared to a high-altitude site in the Rocky Mountains, USA (http://nadp.sws.uiuc.edu/), and a remote site located in the central Amazonia rain forest (Pauliquevis et al. 2012). As shown below, this observation was a consequence of sea-salt contribution at the SET Station, though with a background atmosphere characteristic of the Asian continent.

The annual VWM concentrations of sodium (6.73 µEq/L) and chloride (6.74 µEq/L) were almost equivalent, constituting high fractions of the total ionic concentration. The linear relationship between Na^+ and Cl^- was perfect ($R^2=0.959$) (Fig. 3), and the VWM concentration ratio of Cl^-/Na^+ was 1, very close to the seawater ratio (1.16) observed

Table 1 The VWM (volume-weighted mean) concentrations (μEq/L) and fluxes ($kg ha^{-1} year^{-1}$) of major ions and pH values in wet precipitation at SET Station and other studied sites

Sites depiction pH	SET Station		Nam Co Station		Waliguan		Mt. Lulin		Mt. Fuji		Mt. Rocky		Cen. Amazonia		Hawaii	
	SE TP, 3,326 m		Cen. TP, 4,730 m		NE TP, 3,180 m		Taiwan, 2,860 m		Japan, 3,780 m		USA, 3,159 m		Tropic rain forest		Island in Pacific	
	7.8		6.59		6.38		5.12		4.66		5.33		4.9		4.61	
Varieties	VWM	Fluxes	Mean	Fluxes[a]	VWM	Fluxes[b]	VWM	Fluxes[c]	VWM	Fluxes[d]	VWM	Fluxes	VWM	Fluxes[e]	VWM	Fluxes
Cl^-	6.74	2.15	19.17	2.28	6.1	0.84	7.2	4.85	18.9	17.42	1.13	0.5	5.2	4.66[d]	19.46	19.19
NO_3^-	2.33	1.3	10.37	2.15	8.3	2	10.8	12.72	8.6	13.86	8.06	6.57	4.5	8.47	0.97	1.64
SO_4^{2-}	2.62	1.13	15.5	2.49	24	4.47	15.7	14.32	26.1	32.59	6.42	4.08	3.4	4.13	24.98	33.36
Na^+	6.73	1.39	15.44	1.19	8.7	0.78	2.9	1.27	18.5	11.06	1.26	0.38	3.8	2.21	15.27	9.74
NH_4^+	8.91	1.44	18.13	1.1	45.5	3.18	12.3	4.21	11.6	5.44	6.65	1.48	3.7	1.69	0.55	0.31
K^+	1.88	0.66	14.49	1.9	3.8	0.58	1.4	1.04	9.8	9.96	0.61	0.32	1.5	1.48	0.51	0.56
Mg^{2+}	1.66	0.18	7.43	0.3	12.1	0.57	1.7	0.39	1.5	0.47	2.23	0.38	1.93	0.59	3.13	1.05
Ca^{2+}	34.04	6.12	65.58	4.4	34	2.64	3.9	1.48	6.4	3.33	23.45	6.16	1.81	0.92	1.5	0.94

References for various sites are SET Station (present work); Nam Co Station (Li et al. 2007); Waliguan (Tang et al. 2000); Mt. Lulin and Mt. Fuji (Wai et al. 2008); Mt. Rocky and Hawaii (http://nadp.sws.uiuc.edu/); Cen. Amazonia (Pauliquevis et al. 2012)

[a] The annual precipitation amount was 335 mm investigated during 2005–2009 (Zhang et al. 2012a)

[b] The annual precipitation amount was 388 mm investigated in 1997 (Tang et al. 2000)

[c] The annual precipitation amount was 1,899.1 mm estimated by weekly samples in 2003–2005 (Wai et al. 2008)

[d] The annual precipitation amount was regarded as 2,600 mm according to observing precipitations above 1,500 m in Mt. Fuji (Ohsawa 1984)

[e] The annual precipitation amount was 2,538 mm reported in Pauliquevis et al. (2012)

in the central South Indian Ocean (Keene et al. 1986). These all supported the concept that the precipitation chemistry in the southeastern TP region was influenced by the air masses coming with sea-salt aerosols. In the southern slope of Mt. Everest, Nepal, high correlations of Cl^- and Na^+ as well as their similar ratios to sea salts were also measured in fresh snow due to the strong marine contribution (Valsecchi et al. 1999; Marinoni et al. 2001).

Wet deposition of elements

The VWM concentrations of the dissolved element Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Cd, Cs, Ba, and Pb were 0.46, 0.43, 0.06, 0.58, 1.78, 0.02, 0.14, 0.42, 10.24, 0.14, 1.17, 0.005, 0.011, 0.682, and 0.036 ng/g, respectively. The measured elements were compared with observing sites in the western, central, and southern areas of the TP (Table 2) (Kang et al. 2007; Aizen et al. 2009; Cong et al. 2010). As expected, the crust elements Al and Fe from the SET Station wet depositions were low because the land surface was usually well vegetated in this region. In contrast, a higher content of anthropogenic elements (V, Cr, Co, Ni, Cu, Zn, Cd, and Pb) compared to snow sampled in the southern TP in the central Himalayas (Kang et al. 2007) probably indicates the extra contribution of trace elements from exotic air masses coming with pollutants.

In order to assess the current wet deposition level of trace elements at the SET Station, data sets from other background or remote sites were also tabulated in Table 2. For V, Cr, Ni, Cu, Pb, Rb, Sr, and Ba, the amounts of wet deposition at the SET Station were comparable to those from other alpine sites (Pyrenees in Spain and Eastern Alps) (Bacardit and Camarero 2009; Gabrieli et al. 2011) and a background site (Florida, USA) (Landing et al. 2010), indicting a characteristic of background atmosphere. However, these species were considerably higher than those at pristine sites, such as rainfall in Paradise, New Zealand (Halstead et al. 2000) and snow in East Antarctica (Hur et al. 2007), which suggests that anthropogenic disturbances have influence on the chemical composition of wet deposition in this region.

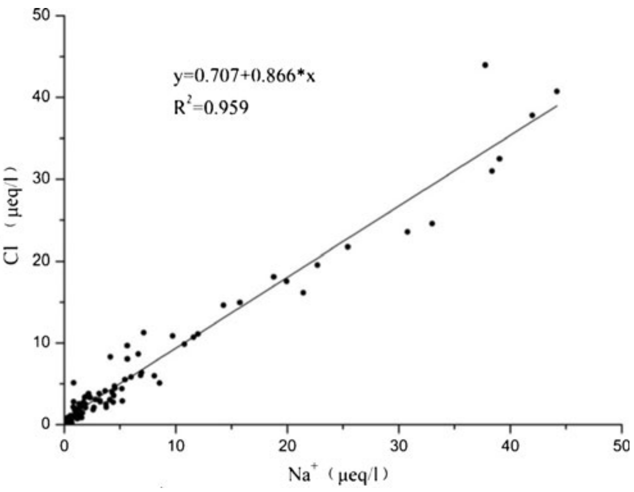


Fig. 3 The correlations of Na^+ and Cl^- (μEq/L) in wet precipitation events at the SET Station during the monitoring period

The wet deposition fluxes of Al and Fe >400 $\mu g m^{-2}\ a^{-1}$ (Table 2), despite representing the relative high elemental loading fluxes at the SET Station, were lower than those from other alpine sites (except Fe which was 1,596 $\mu g m^{-2}\ a^{-1}$ at the SET Station and 1,138 $\mu g m^{-2}\ a^{-1}$ in the Pyrenees), confirming the lower contribution of crust mineral dust in the southeastern TP. On the other hand, the fluxes of trace elements were generally similar to alpine/background sites in Europe and USA (Table 2), while higher than those (especially for V, Co, Ni, Cu, Zn, and Cd) reported in the central TP (Nam Co Station) and New Zealand (Paradise), revealing a possible trace element pollution in the atmosphere of the southeastern TP region.

Estimated contributions from diverse sources

Pearson correlation coefficients of major ions could give useful information for the contributions of ionic sources measured in wet precipitation (Table 3). The high correlation coefficients between Na^+, Cl^-, and K^+ may be caused mainly by the significant contributions of sea-salt aerosols to the wet precipitation, as indicated by a measurement from the southern slope of Mt. Everest (Valsecchi et al. 1999). HCO_3^-, Ca^{2+}, and Mg^{2+} showed positive correlations with each other, indicating the homologous alkaline species from soil dust. Clearly, the relationships among SO_4^{2-}, NO_3^-, and NH_4^+ largely resulted from the similarity of chemical behavior in wet precipitation and the co-emission of their precursors (i.e., SO_2 and NO_x) emitted from anthropogenic sources (Lu et al. 2011). Furthermore, Ca^{2+}, Mg^{2+}, $HCO_3^-SO_4^{2-}$, NO_3^-, and NH_4^+ exhibited notable relativities for each other, with the ranges of Pearson correlation coefficients from 0.42 to 0.97 in Table 3. K^+ was also positively correlated with Mg^{2+}, HCO_3^-, and NH_4^+ (with Pearson correlation coefficient 0.37, 0.43, and 0.55, respectively). These statistical correlations could be explained by the combining contributions of crust mineral dusts and soil dusts associated with the absorption of acid species in the troposphere (Calvo et al. 2010). These estimated sources are largely consistent with the results of wet precipitation chemistry reported in the Everest region (Valsecchi et al. 1999; Marinoni et al. 2001) and the central TP (Li et al. 2007).

To evaluate the various contributions of wet precipitation chemistry at the SET Station, we classified the estimated sources into three types (crust mineral dusts, sea salts, and anthropogenic sources) according to the aforementioned speculation. The fractions of these sources were further

Table 2 The VWM (volume-weighted mean) concentrations (ng/g) and fluxes (μgm^{-2} a^{-1}) of trace elements measured in wet precipitation at SET Station and comparisons with other sites

Sites	SET Station, SE TP		Nam Co Station, Central TP		Himalayas, South TP	Pamirs, West TP	Eastern Alps		Pyrenees, Spain		Florida, USA		Paradise, New Zealand		East Antarctica
Depiction	3,326 m		4,730 m		6,513 m	5,365 m	3,532 m		2,000 m		Background		Island		Polar site
Varieties	VWM	Fluxes	VWM	Fluxes	Mean	Mean	Mean	Fluxes	VWM	Fluxes[a]	VWM	Fluxes[b]	VWM	Fluxes	Mean
Al	0.46	413	12.6	5,510	4.5	46	3.44	2,715	11	12,518	53.4	93,450	–	–	0.165
V	0.43	385	0.033	33	0.139	0.137	0.14	111	–	–	0.274	480	–	–	0.00056
Cr	0.06	53.8	0.267	139	0.034	0.146	0.045	36	–	–	0.099	173	–	–	–
Mn	0.58	520	0.565	297	2	4.199	0.825	650	2.9	3,300	1.13	1,978	0.073	130	0.0037
Fe	1.78	1,596	11.5	5,020	11.5	48	5.34	4,220	1	1,138	26	45,500	2.1	3700	0.045
Co	0.02	17.9	0.051	7.1	<D.L.	0.06	0.013	10	–	–	0.0298	52	–	–	–
Ni	0.14	126	0.221	97	0.061	–	0.19	151	0.22	250	0.374	655	–	–	–
Cu	0.42	377	0.537	231	0.343	–	0.155	122	0.44	501	0.313	548	0.013	23	0.0053
Zn	10.24	9183	6.09	266	2.032	–	0.955	755	7.11	8091	2.19	3833	0.038	69	–
Cd	0.005	4.48	0.004	1.8	<D.L.	0.012	0.007	5.2	–	–	0.007	12	0.00036	0.65	0.00021
Pb	0.036	32.3	0.141	60	0.005	0.461	0.108	85	0.34	387	0.306	536	0.02	37	0.004
Cs	0.011	9.86	–	–	0.046	0.012	–	–	–	–	0.004	7	–	–	–
Rb	0.14	126	–	–	–	–	0.044	–	–	–	–	–	–	–	–
Sr	1.17	1049	–	–	–	0.951	0.68	–	–	–	0.86	1,505	–	–	–
Ba	0.682	612	–	–	–	0.817	0.38	300	–	–	1	1,750	–	–	0.004

References for various sites are SET Station (present work); Nam Co Station (Cong et al. 2010); Himalayas (Kang et al. 2007); Eastern Alps (Gabrieli et al. 2011); Pyrenees (Bacardit and Camarero 2009); Florida (Landing et al. 2010); Paradise (Halstead et al. 2000); East Antarctica (Hur et al. 2007). <*D.L.* indicates the concentration was below the detection limit

[a] The annual precipitation amount (June 2005–May 2006) was 1,138 mm from Bacardit and Camarero (2009)

[b] The annual precipitation amount was 1,750 mm from Florida Water Resources Manual (http://sofia.usgs.gov)

Table 3 Pearson correlations matrix of the ionic VWM (volume-weighted mean) concentrations in wet precipitation of SET Station

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}
Na^+	1								
NH_4^+	0.48	1							
K^+	0.93	0.55	1						
Mg^{2+}	0.31	0.67	0.37	1					
Ca^{2+}	0.22	0.24	0.24	0.60	1				
HCO_3^-	0.41	0.42	0.43	0.69	0.97	1			
Cl^-	0.98	0.50	0.92	0.31	0.20	0.39	1		
NO_3^-	0.21	0.69	0.28	0.66	0.53	0.56	0.19	1	
SO_4^{2-}	0.18	0.71	0.28	0.76	0.47	0.51	0.17	0.86	1

The concentration of HCO_3^- was estimated by the formula $\Sigma_{cations}-\Sigma_{anions}$ (Li et al. 2007)

calculated by the following methods. Non-sea salt was calculated, using Na as a tracer, with the following equation:

$$[X]_{ss} = [Na^+]_{rain} * [X/Na^+]_{sea} \quad (1)$$

where $[X]_{ss}$ is the concentration of chemical species originating from sea salts for the desired ion/element in precipitation ($[X]_{rain}$), $[X/Na^+]_{sea}$ were from Keene et al. (1986) and KK Turekian (Oceans 1964, http://www.seafriends.org.nz/oceano/seawater.htm) for seawater ionic and elemental composition, respectively. It should be noted that the uncertainty caused by a possible Na^+ enrichment from other sources (such as minerals) during atmospheric transport was estimated to be slight according to the correlations of Cl^- and Na^+ (Fig. 3). Crust fractions were assessed with tracers of crust-originated elements (Al, Fe, Si, Rb, and Ca) in a variety of studies for atmospheric deposition (e.g., Lammel et al. 2003; Lu et al. 2011). In this work, we used the formula

$$[X]_{cm} = [Fe]_{rain} * [X/Fe]_{crust} \quad (2)$$

to assess the contributions of crust mineral dust in precipitation. $[X]_{cm}$ is the crust-originated concentration of the desired ion/element in a wet precipitation event. $[X/Fe]_{crust}$ is from the <2 μm of surface soils on the western TP (Li et al. 2009) [the fractions of S and N from crust mineral dust were calculated, according to their relative abundances in the upper crust (Rudnick and Gao 2003)]. Anthropogenic sources ($[X]_{as}$) in wet precipitation events were evaluated by subtracting the contributions of crust mineral dusts and sea salts (e.g., Lu et al. 2011), which is Formula 3.

$$[X]_{as} = [X]_{rain} - [X]_{ss} - [X]_{cm} \quad (3)$$

The fractions of sea salts presented large ranges in wet precipitation events (29.7–100 % for Cl^-, 3.3–100 % for Mg^{2+}, 1.9–71.1 % for K^+, 0.1–100 % for NO_3^-, and 0.1–100 % for SO_4^{2-}). With mean values of 85.6 %, 47.1 %, 24.5 %, and 8.8 %, respectively, Cl^-, Mg^{2+}, SO_4^{2-}, and K^+ confirmed the significant contributions of sea-salt aerosols (Fig. 4), largely resulting from rainfalls associated with the strong South Asian monsoon in summer (Fig. 2). Moreover, the "moisture passage" effect for humid air masses (Yang et al. 1989) and "leaking wall" effect for aerosols (Cao et al. 2011) from the Bay of Bengal and northeastern India can enhance the contribution of sea salts to the chemical composition in wet deposition. For trace elements, sea salt contributed a small fraction to the wet precipitation, with median values of 0.05 % for Rb, 0.54 % for Sr, 0.006 % for Ni, and others <0.005 %. Mineral dusts generally appeared in the coarse mode, thereby they are significantly removed by atmospheric dry deposition, which is an important reason for the low fraction of dissolved crust mineral dusts, with mean values of <5 % for all ions and <15 % for trace elements (without Al and Fe) in Fig. 4. Excluding Na^+, Cl^-, and Mg^{2+}, anthropogenic activities contributed the largest proportion to the content of major ions. For NO_3^- and SO_4^{2-}, the greatly anthropogenic fractions (>70 %) were largely caused by the precursor gases SO_2 and NOx from industrial activities coming with exotic air masses. The mean values of 49.1 % and 97.3 % for anthropogenic fractions of Mg^{2+} and Ca^{2+}, respectively, may partly result from agricultural soil caused by breeding livestock and cultivating land. Furthermore, anthropogenic K^+ (86.5 %) was ascribed to biomass burning, which was observed at Tengchong in the eastern edge of the southeastern TP (Chan et al. 2006; Engling et al. 2011). Thus, the quantitative contributions from various sources demonstrates the combined impacts of anthropogenic sources, sea salts, and crust mineral dusts on the wet precipitation chemistry in the southeastern TP.

Temporal variations of chemical species

During the study periods, the contents of the chemical species (except Ca^{2+}, V, Cr, Zn, and Ba) in wet deposition displayed significant fluctuations, with lower values of month/year-concentration (VWM month-concentration/year-concentration) in the wet season because of the dilute effect caused by monsoonal rainfall for most species in wet

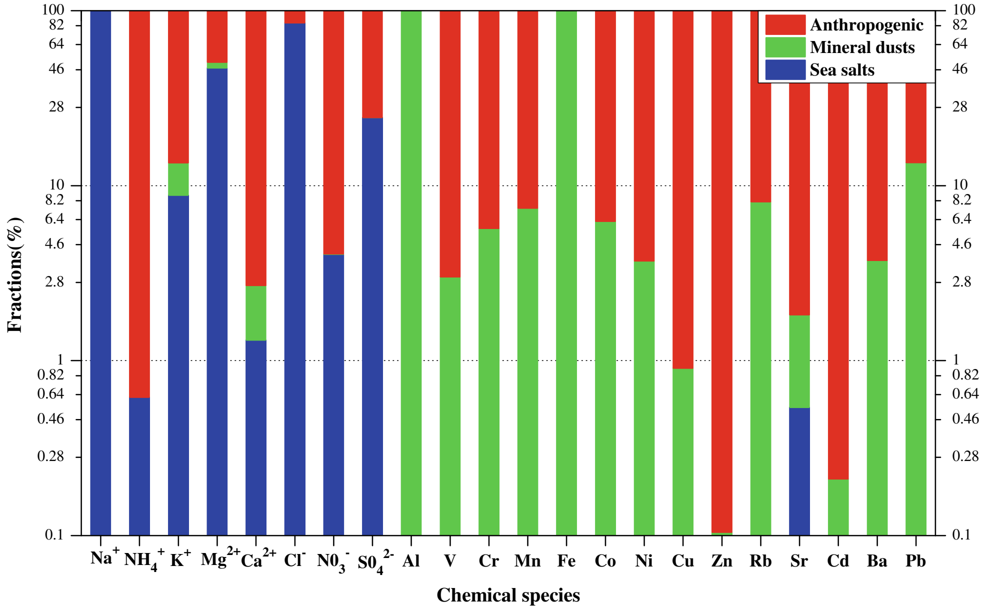


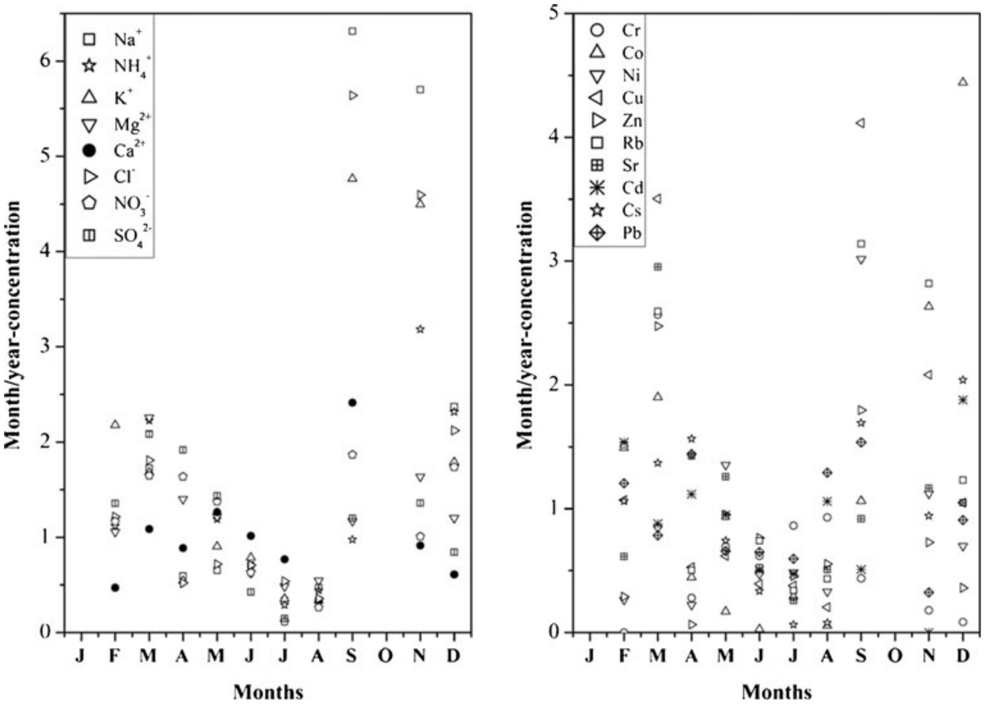
Fig. 4 The mean fractions of sea salts, mineral dust, and anthropogenic sources in wet precipitation at the SET Station

deposition (Fig. 5). Moreover, the monthly variations of ionic fluxes generally showed positive correlation with monthly precipitation amount, though the degrees varied in different months for various ions (Fig. 6), suggesting the effective scavenging of the soluble chemical species from the atmosphere in the wet deposition process. Obviously, the low wet precipitation fluxes for ions in the dry season (October, November, December, January, and February) were caused by sparse precipitation events when atmosphere circulation was dominated by continental masses. The highest amounts of monthly precipitations were in the monsoon season (May, June, July, and August) in the southeastern TP region, but the peak fluxes of the anthropogenic sources (SO_4^{2-}, NO_3^-, NH_4^+, and Mg^{2+}) were during the pre-monsoon season and the earlier period of the monsoon season (March, April, May, and June), reflecting the possible accumulating effect of atmospheric pollutants in the mountain–valley geomorphologic region along the southern slope of the high plateau. The monthly flux of Ca^{2+} was higher in the wet season (differing from the seasonal variations of dust constituents carried by Asian dust storms in rainwater) and was relatively constant in month/year-concentration (indicating a slight influence from the altered atmospheric circulation), which probably was caused by the diverse sources of airborne dust in the atmosphere.

Burning of biofuels (wood, dung, and agricultural waste) is a major source of energy in India (Lelieveld et al. 2001), and the large-scale practice of open biomass burning occurs during the periods of pre-monsoon in northern India and Nepal (Ram and Sarin 2010). Eliminating the contributions of sea salts and crust mineral dusts, anthropogenic source potassium (as-K^+) at the SET Station is an excellent tracer for biomass burning smoke. The apparently high values and peaks of as-K^+ in the dry season (Fig. 7) may result from the impacts of biomass burning in South Asia because such changes coincide with the South Asian haze outburst (Ramanathan et al. 2001). Moreover, monitoring results from the National Aeronautics and Space Administration (NASA), USA (http://firms.modaps.eosdis.nasa.gov/firemap/), indicating many dense fire points in the Indian subcontinent during those seasons, were additional evidence for this inference. The above results indicate that biomass burning emissions from South Asia influenced the chemical compositions of wet precipitation in the southeastern TP and was in accordance with the results of observed black carbon in this region (Cao et al. 2011).

In previous studies, fossil fuel combustion was identified to be a main source of carbonaceous aerosols in the South Asian haze layer (Novakov et al. 2000). Owing to excluding the effects of sea salts and dusts in the atmosphere, the anthropogenic sources sulfate (as-SO_4^{2-}) and nitrate (as-NO_3^-) are credible tracers of fossil fuel emissions. The large variability of as-SO_4^{2-} and as-NO_3^- (Fig. 7), with higher values in winter and spring, demonstrates the significant contributions of fossil fuel combustion to the haze cloud in South Asia. The co-source of as-SO_4^{2-} and as-NO_3^- emitted from fossil fuel combustion was further suggested by a significant correlation ($R^2=0.67$, $p=0.01$) and the same large peaks in Fig. 7. The long-range transport of South Asian pollutants was also observed in previous measurement campaigns over the TP (Cong et al. 2007, 2010; Ming et al. 2010), while the as-K^+, as-SO_4^{2-}, and as-NO_3^- of the SET Station wet precipitation was a clear signature, owing to its unique geomorphological condition and geographical location (Yang et al. 1989; Cao et al. 2011).

Fig. 5 The monthly variations of month/year-concentration ratios for chemical species of SET Station wet precipitation, from January (*J*) to December (*D*)



The features of various air masses

The trajectories achieved by HYSPLIT reveal three types of air masses arriving at the SET Station, including air masses coming from West Asia and the northwestern Indian subcontinent driven by the westerlies from November to February (corresponding to 11 % of the total samples, Fig. 8a), the summer monsoon from the Bay of Bengal across the northeastern part of the Indian subcontinent in wet season (May–August) (62 %, Fig. 8b), and regional air masses from the southern slope of the Eastern Himalayas in the transferring episodes of atmospheric circulation (including September, October, March, and April) (27 %, Fig. 8c).

The significant characteristics of diverse air masses were revealed by the relative contributions of various sources. As displayed in Fig. 9, the fractions of sea salts in Mg^{2+}, NO_3^-, and NH_4^+ were relatively high in samples dominated by the summer monsoon, indicating the effects of sea-salt aerosols from the Bay of Bengal. Furthermore, a southerly maritime signal during the summer monsoon was also identified in sampled precipitation and aerosols in the Nepal Himalayas (Shrestha et al. 2002). The lowest contribution of sea salt aerosols in samples controlled by regional air masses was reasonable, reflecting the continental characteristic of relatively stagnant air masses. That the anthropogenic fractions, both for NH_4^+ and K^+, were higher in regional masses and westerlies than in the summer monsoon may partly result from active agricultural activities and biomass burning in those periods. The relative high anthropogenic fractions for NO_3^-, Mg^{2+}, Cl^-, and Ca^{2+} in summer monsoon samples likely result from the influences of polluted air masses from Bangladesh and northeastern India.

High fractions of crust mineral dust (such as Ca^{2+}, V, Cr, Cd, Co, and Rb) were often monitored in samples

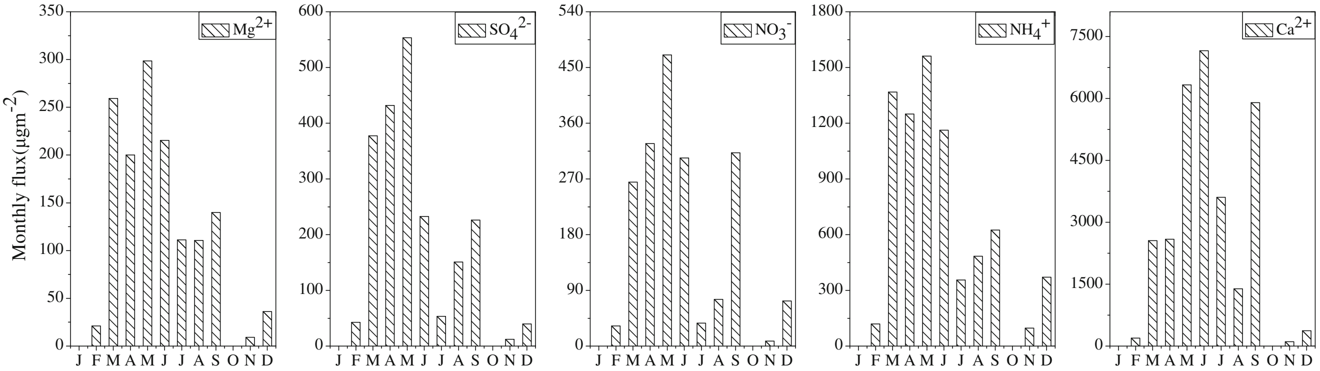


Fig. 6 The variations of monthly flux (μg m^{-2}) for selected ions of wet precipitation at the SET Station, from January (*J*) to December (*D*)

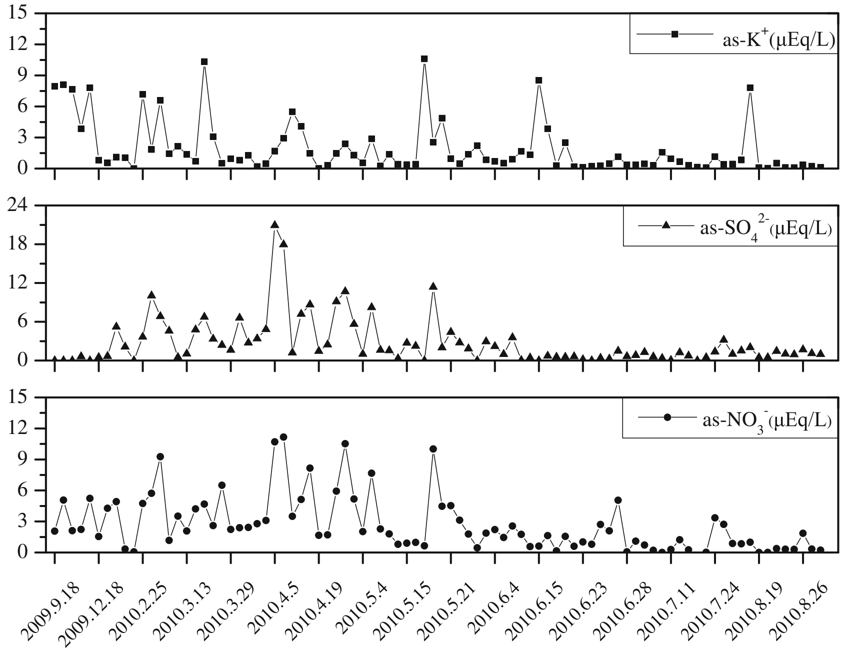


Fig. 7 The temporal variations of as (anthropogenic source)-K^+, as-SO_4^{2-}, and as-NO_3^- in wet precipitation at the SET Station

dominated by the regional and/or westerly air masses, being concordant with more dust aerosols from the arid region in dry seasons. However, for most of the trace elements, the highest anthropogenic fractions were observed in monsoonal rainfall, a result of the huge industrial emissions in South Asia (Pacyna and Pacyna 2001). From the point of view of discerning the diffusion of regional emissions, anthropogenic fractions observed in monsoonal rainfall at the SET Station were significant because these processes were associated with atmospheric dynamics. Therefore, they provide strong evidence of the transport of anthropogenic trace elements from South Asia.

Atmospheric nitrogen deposition

Nitrogen is crucial for the alpine ecosystem. High flux of atmospheric nitrogen deposition was modeled near the biodiversity hotspots of high-altitude Asia (Phoenix et al. 2006), which need verification from field monitoring. The wet deposition of NH_4^+–N, NO_3^-–N, and total inorganic nitrogen (TIN) at the SET Station was calculated based on their VWM concentration multiplied by annual precipitation amounts (Table 4). With a flux of 1.12 kgNha^{-1}year^{-1}, ammonia accounted for 79.27 % of TIN wet deposition. The nitrogen originating from nitrate accounted for the remaining 20.73 %, with a flux of 0.29 kgNha^{-1}year^{-1}.

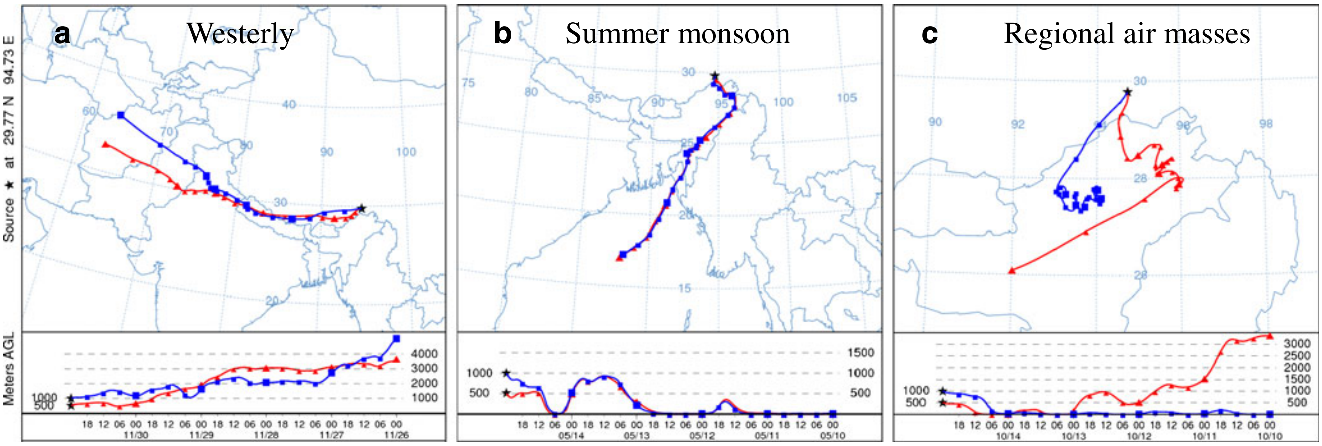


Fig. 8 Five-day back trajectories for the typical westerly (corresponding to 11 % of the total samples), summer monsoon (62 %), and regional air masses (27 %) reaching the SET Station

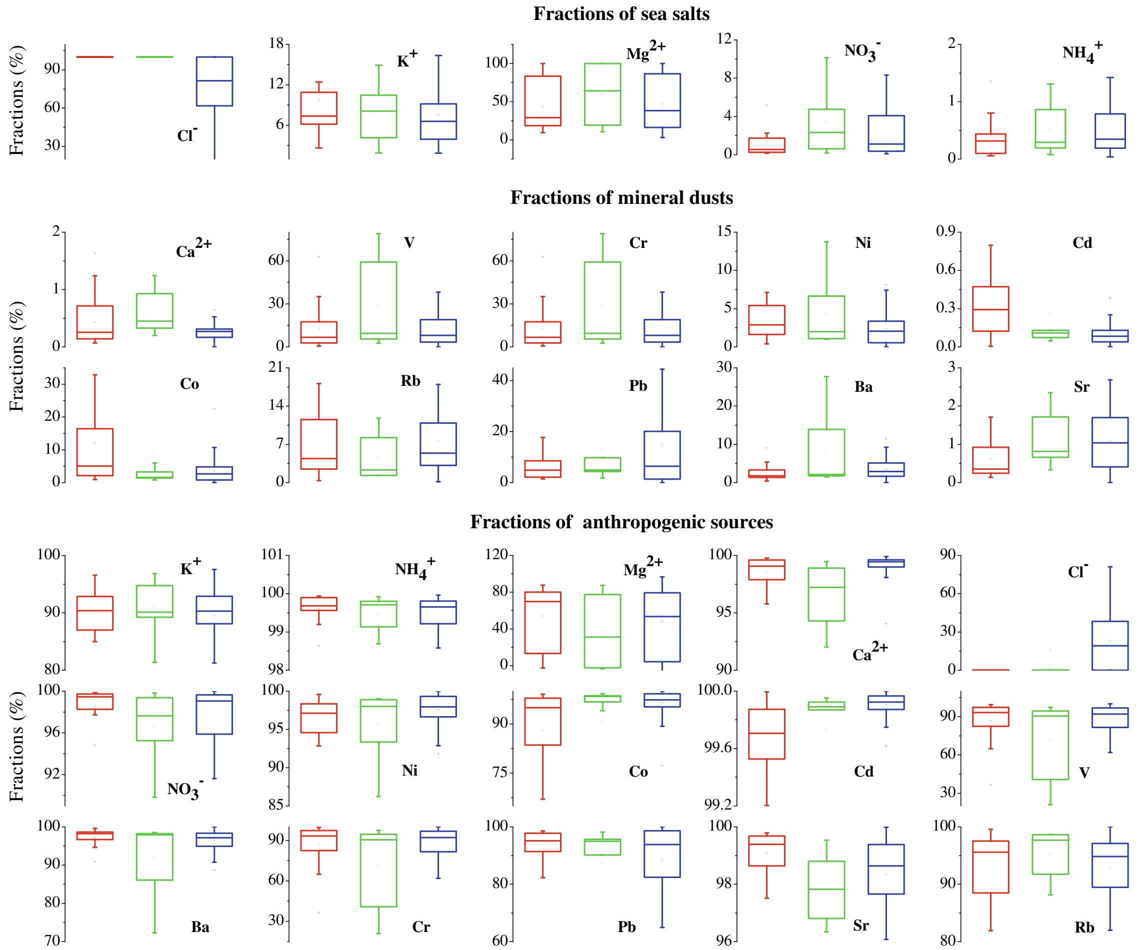


Fig. 9 The variations of fractions (medians, *line* within the *boxes*; percentiles 10–25–75–90, *boxes* and *whiskers*) in different air masses (*red*—regional air masses, *green*—westerly, *blue*—summer monsoon) in wet precipitation at the SET Station

As displayed in Table 4, the current wet deposition levels of IN in remote or background regions within various ecosystems around the world varied over a large range. The annual flux of TIN at the SET Station ranged from an alpine meadow at Nam Co Station in the central TP (Zhang et al. 2012a) to a montane forest at Mt. Ailao in southwestern China (Liu et al. 2003) (Table 4). This reflects the different influences of anthropogenic activities on the different alpine ecosystems in western China. When compared with wet depositions of Mt. Fuji in Japan (Wai et al. 2008), Rocky Mountains in the USA (http://nadp.sws.uiuc.edu), the dry savanna in Africa (Galy-Lacaux et al. 2009), and the tropical rain forest in the Amazon Basin (Pauliquevis et al. 2012), the wet deposition flux of TIN at the SET Station was lower.

Table 4 Comparisons of wet deposition levels (kg N ha^{-1} year^{-1}) of inorganic nitrogen in remote or background regions within various ecosystems around the world

Sites	Ecosystems	Periods	NO_3^-–N	NH_4^-–N	TIN	References
SET Station, SE TP	Alpine forest (3,326 m)	2009–2010	0.29	1.12	1.41	Present study
Nam Co Station, Cen. TP	Alpine meadow (4,730 m)	2005–2009	0.27	0.43	0.70	Zhang et al. 2012a
Mt. Ailao, SW China	Montane forest (2,450 m)	1998–1999	0.90	2.70	3.60	Liu et al. 2003
Mt. Fuji, Cen. Japan	Alpine forest (3,780 m)	2001–2004	3.13	4.22	7.35	Wai et al. 2008
Mt. Rocky, Western USA	Alpine forest (3,159 m)	2010	1.48	1.15	2.63	http://nadp.sws.uiuc.edu
Balbina, Cen. Amazonia	Tropical rain forest	1998–2001	1.91	1.31	3.22	Pauliquevis et al. 2012
Niger, Northern Africa	Dry Savanna	1994–2005	0.80	1.26	2.06	Galy-Lacaux et al. 2009
Hawaii Island	Northern Pacific	2005	0.37	0.24	0.61	http://nadp.sws.uiuc.edu

However, the input of inorganic nitrogen through wet deposition was noticeable in this background atmosphere, compared with measurements from Hawaii, owing to the effects of the terrestrial sources and the long-range transport of exotic air masses.

The wet deposition of dissolved organic nitrogen is significant in remote forest ecosystems, which was estimated according to the ratio of dissolved organic nitrogen to total dissolved nitrogen (67 %) in the southeastern TP region (Zhang et al. 2012b), with the flux of 2.86 $\mathrm{kgNha^{-1}year^{-1}}$. Therefore, the total N import from wet precipitation was 4.27 $\mathrm{kgNha^{-1}year^{-1}}$ at the SET Station. In addition, dry deposition another main way of atmospheric nitrogen input. However, measuring dry deposition is difficult, particularly for dry deposition in the alpine ecosystem. In the Rocky Mountain region of Colorado, a similar altitude and environment, dry deposition generally constitutes 25 % to 47 % of total atmospheric N deposition (wet deposition plus dry deposition) (Burns 2003, and references therein). Thus, dry deposition flux of N in the southeastern TP was estimated to be 2.14 $\mathrm{kgNha^{-1}year^{-1}}$, assuming its amount to be half that of measured wet deposition in other high-altitude regions (Baron and Campbell 1997). It was worthy to stress that the above evaluations omitted the significant fog and cloud depositions in the atmosphere of alpine forest ecosystems; thus, the total atmospheric deposition of N should be higher than 6.41 kgN $\mathrm{ha^{-1}year^{-1}}$ in this region, which is about two times the global terrestrial with an average value of 3.5 $\mathrm{kgNha^{-1}year^{-1}}$ (Phoenix et al. 2006).

Lichens and bryophytes are important species in the alpine forest of the southeastern TP, and are sensitive to increased N inputs (Bobbink et al. 2010). Meanwhile, the assessed amount of atmospheric N deposition (6.41 kgN $\mathrm{ha^{-1}year^{-1}}$) reached an estimated effect threshold (5–15 kg $\mathrm{Nha^{-1}year^{-1}}$) for nitrogen deposition impacts in alpine ecosystems (Bobbink et al. 2010). This implies that the long-range transport of air masses containing nitrogen may impact the alpine ecosystem in this region.

Summary and conclusions

Wet precipitation chemistry at a remote forest site in the southeastern Tibetan Plateau had been examined. Although wet deposition levels at the SET Station were generally comparable to those in other alpine and background sites reported in the world, the potential anthropogenic disturbances of atmospheric trace elements in the southeastern TP was verified by calculating diverse sources. Sea salts were significant sources for ions in wet precipitation. Crust mineral dust was mainly responsible for the crust elements Al and Fe.

With an apparently diluting effect and effective scavenging by monsoonal rainfall, the seasonal variabilities of chemical species were striking and important. As-K^+, a perfect tracer of biomass burning with high concentrations during the non-monsoon season, revealed the influence of biomass burning on the wet precipitation chemistry. High values of as-SO_4^{2-} and as-NO_3^- in winter and spring demonstrated the large contribution of fossil fuel combustion during those seasons. These clear signatures of the long-range transport of South Asian pollutants monitored at the SET Station were credited to its unique geomorphological condition and geographical location.

Atmospheric circulation exerted significant effects on the variations of chemical components in wet deposition, which were revealed by combining backward air trajectories analysis. Marine air masses from the Bay of Bengal provided a large number of sea salts to the chemical composition of wet precipitation. Relatively high fractions of crust mineral dusts were often observed in the regional and westerly air masses, while striking anthropogenic fractions of trace elements in the summer monsoon season were greatly induced by industrial emissions from South Asia.

It is important to monitor wet precipitation at the SET Station to understand anthropogenic disturbances to alpine ecosystems on the southeastern TP. Affected by the exotic air masses, the flux of wet deposition was 1.12 $\mathrm{kgNha^{-1}year^{-1}}$ for NH_4^+–N and 0.29 $\mathrm{kgNha^{-1}year^{-1}}$ for NO_3^-–N. The conservative atmospheric import of N was 6.41 kgN $\mathrm{ha^{-1}year^{-1}}$ and reached the effect threshold of nitrogen deposition, implying potential impacts on the alpine ecosystem of the southeastern TP as emissions increase in South Asia.

Acknowledgments This research was supported by the National Natural Science Foundation of China (41075089, 40830743, 41271073). The authors appreciate the support of the K.C. Wang Education Foundation, Hong Kong, and the Youth Innovation Promotion Association, CAS. We thank the staff at the SET Station for collecting the samples, and Shi Yanyun and Gao Shaopeng, who performed the chemical analysis. Special thanks to Betsy Armstrong for the English editing. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the HYSPLIT transport and dispersion model in this publication.

References

Aber J, McDowell W, Nadelhoffer K, Magill A, Berntson G, Kamakea M, McNulty S, Currie W, Rustad L, Fernandez I (1998) Nitrogen saturation in temperate forest ecosystems. BioScience 48:921–934

Aizen VB, Mayewski PA, Aizen EM, Joswiak DR, Surazakov AB, Kaspari S, Grigholm B, Krachler M, Handley M, Finaev A (2009) Stable-isotope and trace element time series from Fedchenko glacier (Pamirs) snow/firn cores. J Glaciol 55:1–18

Bacardit, M., Camarero, L. (2009) Fluxes of Al, Fe, Ti, Mn, Pb, Cd, Zn, Ni, Cu, and As in monthly bulk deposition over the Pyrenees (SW Europe): the influence of meteorology on the atmospheric component of trace element cycles and its implications for high mountain lakes. J Geophys Res 114:G00D02. doi:10.1029/2008JG000732

Baron JS, Campbell DH (1997) Nitrogen fluxes in a high elevation Colorado Rocky Mountain basin. Hydrol Process 11:783–799

Burns DA (2003) Atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming—a review and new analysis of past study results. Atmos Environ 37:921–932

Bobbink R, Hicks K, Galloway J, Spranger T, Alkemade R, Ashmore M, Bustamante M, Cinderby S, Davidson E, Dentener F (2010) Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. Ecol Appl 20:30–59

Calvo AI, Olmo FJ, Lyamani H, Alados-Arboledas L, Castro A, Fernandez-Raga M, Fraile R (2010) Chemical composition of wet precipitation at the background EMEP station in Viznar (Granada, Spain) (2002–2006). Atmos Res 96:408–420

Cao J, Tie X, Xu B, Zhao Z, Zhu C, Li G, Liu S (2011) Measuring and modeling black carbon (BC) contamination in the SE Tibetan Plateau. J Atmos Chem 67:45–60

Chan CY, Wong KH, Li YS, Chan LY, Zheng XD (2006) The effects of Southeast Asia fire activities on tropospheric ozone, trace gases and aerosols at a remote site over the Tibetan Plateau of Southwest China. Tellus B 58:310–318

Cong ZY, Kang SC, Liu XD, Wang GF (2007) Elemental composition of aerosol in the Nam Co region, Tibetan Plateau, during summer monsoon season. Atmos Environ 41:1180–1187

Cong ZY, Kang SC, Zhang YL, Li XD (2010) Atmospheric wet deposition of trace elements to central Tibetan Plateau. Appl Geochem 25:1415–1421

Engling G, Zhang YN, Chan CY, Sang XF, Lin M, Ho KF, Li YS, Lin CY, Lee JJ (2011) Characterization and sources of aerosol particles over the southeastern Tibetan Plateau during the Southeast Asia biomass-burning season. Tellus B 63:117–128

Gabrieli J, Carturan L, Gabrielli P, Kehrwald N, Turetta C, Cozzi G, Spolaor A, Dinale R, Staffler H, Seppi R, dalla Fontana G, Thompson L, Barbante C (2011) Impact of Po Valley emissions on the highest glacier of the Eastern European Alps. Atmos Chem Phys 11:8087–8102

Galy-Lacaux C, Laouali D, Descroix L, Gobron N, Liousse C (2009) Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger). Atmos Chem Phys 9:1579–1595

Halstead MJR, Cunninghame RG, Hunter KA (2000) Wet deposition of trace metals to a remote site in Fiordland, New Zealand. Atmos Environ 34:665–676

Huang J, Minnis P, Yi Y, Tang Q, Wang X, Hu Y, Liu Z, Ayers K, Trepte C, Winker D (2007) Summer dust aerosols detected from CALIPSO over the Tibetan Plateau. Geophys Res Lett 34: L18805. doi:10.1029/2007GL029938

Hur SD, Cunde X, Hong S, Barbante C, Gabrielli P, Lee K, Boutron CF, Ming Y (2007) Seasonal patterns of heavy metal deposition to the snow on Lambert Glacier basin, East Antarctica. Atmos Environ 41:8567–8578

Kang SC, Zhang QG, Kaspari S, Qin DH, Cong ZY, Ren JW, Mayewski PA (2007) Spatial and seasonal variations of elemental composition in Mt. Everest (Qomolangma) snow/firn. Atmos Environ 41:7208–7218

Keene WC, Pszenny AAP, Galloway JN, Hawley ME (1986) Sea-salt corrections and interpretation of constituent ratios in marine precipitation. J Geophys Res 91:6647–6658

Lammel G, Brüggemann E, Gnauk T, Müller K, Neusüss C, Röhrl A (2003) A new method to study aerosol source contributions along the tracks of air parcels and its application to the near-ground level aerosol chemical composition in central Europe. J Aerosol Sci 34:1–25

Landing WM, Caffrey JM, Nolek SD, Gosnell KJ, Parker WC (2010) Atmospheric wet deposition of mercury and other trace elements in Pensacola, Florida. Atmos Chem Phys 10:4867–4877

Lelieveld J, Crutzen PJ, Ramanathan V, Andreae MO, Brenninkmeijer CAM, Campos T, Cass GR, Dickerson RR, Fischer H, de Gouw JA, Hansel A, Jefferson A, Kley D, de Laat ATJ, Lal S, Lawrence MG, Lobert JM, Mayol-Bracero OL, Mitra AP, Novakov T, Oltmans SJ, Prather KA, Reiner T, Rodhe H, Scheeren HA, Sikka D, Williams J (2001) The Indian Ocean Experiment: widespread air pollution from South and Southeast Asia. Science 291:1031–1036

Li CL, Kang SC, Zhang QG (2009) Elemental composition of Tibetan Plateau top soils and its effect on evaluating atmospheric pollution transport. Environ Pollut 157:2261–2265

Li CL, Kang SC, Zhang QG, Kaspari S (2007) Major ionic composition of precipitation in the Nam Co region, Central Tibetan Plateau. Atmos Res 85:351–360

Liang E, Wang Y, Eckstein D, Luo T (2011) Little change in the fir tree-line position on the southeastern Tibetan Plateau after 200 years of warming. New Phytol 190:760–769

Liu W, Fox JED, Xu Z (2003) Nutrient budget of a montane evergreen broad-leaved forest at Ailao Mountain National Nature Reserve, Yunnan, southwest China. Hydrol Process 17:1119–1134

Lu X, Li LY, Li N, Yang G, Luo D, Chen J (2011) Chemical characteristics of spring rainwater of Xi'an city, NW China. Atmos Environ 45:5058–5063

Luo T, Li W, Zhu H (2002) Estimated biomass and productivity of natural vegetation on the Tibetan Plateau. Ecol Appl 12:980–997

Marinoni A, Polesello S, Smiraglia C, Valsecchi S (2001) Chemical composition of fresh snow samples from the southern slope of Mt. Everest region (Khumbu–Himal region, Nepal). Atmos Environ 35:3183–3190

Ming J, Cachier H, Xiao C, Qin D, Kang S, Hou S, Xu J (2008) Black carbon record based on a shallow Himalayan ice core and its climatic implications. Atmos Chem Phys 8:1343–1352

Ming J, Xiao CD, Sun JY, Kang SC, Bonasoni P (2010) Carbonaceous particles in the atmosphere and precipitation of the Nam Co region, central Tibet. J Environ Sci China 22:1748–1756

Novakov T, Andreae MO, Gabriel R, Kirchstetter TW, Mayol-Bracero OL, Ramanathan V (2000) Origin of carbonaceous aerosols over the tropical Indian Ocean: biomass burning or fossil fuels? Geophys Res Lett 27(24):4061–4064

Ohsawa M (1984) Differentiation of vegetation zones and species strategies in the subalpine region of Mt. Fuji. Plant Ecol 57:15–52

Pacyna JM, Pacyna EG (2001) An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ Rev 9:269–298

Pauliquevis T, Lara LL, Antunes ML, Artaxo P (2012) Aerosol and precipitation chemistry measurements in a remote site in Central Amazonia: the role of biogenic contribution. Atmos Chem Phys 12:4987–5015

Phoenix GK, Hicks WK, Cinderby S, Kuylenstierna JCI, Stock WD, Dentener FJ, Giller KE, Austin AT, Lefroy RDB, Gimeno BS, Ashmore MR, Ineson P (2006) Atmospheric nitrogen deposition in world biodiversity hotspots: the need for a greater global perspective in assessing N deposition impacts. Glob Chang Biol 12:470–476

Polkowska Ż, Górecki T, Namieśnik J (2011) Determination of atmospheric pollutants in wet deposition. Environ Rev 19:185–213

Ram K, Sarin MM (2010) Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over Northern India. J Aerosol Sci 41:88–98

Ramanathan V, Crutzen PJ, Lelieveld J, Mitra AP, Althausen D, Anderson J, Andreae MO, Cantrell W, Cass GR, Chung CE, Clarke AD, Coakley JA, Collins WD, Conant WC, Dulac F, Heintzenberg J, Heymsfield AJ, Holben B, Howell S, Hudson J, Jayaraman A, Kiehl JT, Krishnamurti TN, Lubin D, McFarquhar G, Novakov T, Ogren JA, Podgorny IA, Prather K, Priestley K, Prospero JM, Quinn PK, Rajeev K, Rasch P, Rupert S, Sadourny R, Satheesh SK, Shaw GE, Sheridan P, Valero FPJ (2001) Indian

Ocean Experiment: an integrated analysis of the climate forcing and effects of the great Indo-Asian haze. J Geophys Res 106:28371–28398. doi:10.1029/2001JD900133

Rudnick R, Gao S (2003) Composition of the continental crust. Treatise Geochem 3:1–64

Safai PD, Rao PSP, Mornin GA, All K, Chate DM, Praveen PS (2004) Chemical composition of precipitation during 1984–2002 at Pune, India. Atmos Environ 38:1705–1714

Sakata M, Asakura K (2009) Factors contributing to seasonal variations in wet deposition fluxes of trace elements at sites along Japan Sea coast. Atmos Environ 43:3867–3875

Shrestha AB, Wake CP, Dibb JE, Whitlow SI (2002) Aerosol and precipitation chemistry at a remote Himalayan site in Nepal. Aerosol Sci Tech 36:441–456

Smith VH, Tilman GD, Nekola JC (1999) Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environ Pollut 100:179–196

Tang J, Xue H, Yu X, Cheng H, Xu X (2000) The preliminary study on chemical characteristics of precipitation at Mt. Waliguan. Acta Sci Circumst 04:420–425 (in Chinese with English abstract)

Valsecchi S, Smiraglia C, Tartari G, Polesello S (1999) Chemical composition of Monsoon deposition in the Everest region. Sci Total Environ 226:187–199

Wai KM, Lin NH, Wang SH, Dokiya Y (2008) Rainwater chemistry at a high-altitude station, Mt. Lulin, Taiwan: comparison with a background station, Mt. Fuji. J Geophys Res 113:D06305. doi:10.1029/2006JD008248

Wang Y, Ma Y, Zhu Z, Li M (2010) Variation characteristics of meteorological elements in near surface layer over the Lulang valley of southeastern Tibetan Plateau. Plateau Meteorol 01:63–69 (in Chinese with English abstract)

Yang Y, Gao D, Li B (1989) Study on the moisture passage on the lower reaches of the Yarlung Zangbo River. Sci China Ser B 05:580–593

Zhang DD, Peart MR, Jim CY, La J (2002) Alkaline rains on the Tibetan Plateau and their implication for the original pH of natural rainfall. J Geophys Res 107:4198. doi:10.1029/2001jd001332

Zhang Y, Kang S, Li C, Cong Z, Zhang Q (2012a) Wet deposition of precipitation chemistry during 2005–2009 at a remote site (Nam Co Station) in central Tibetan Plateau. J Atmos Chem. doi:10.1007/s10874-012-9236-3

Zhang Y, Song L, Liu XJ, Li WQ, Lü SH, Zheng LX, Bai ZC, Cai GY, Zhang FS (2012b) Atmospheric organic nitrogen deposition in China. Atmos Environ 46:195–204

Zhou J, Wang Y, Yue T, Li Y, Wai KM, Wang W (2012) Origin and distribution of trace elements in high-elevation precipitation in southern China. Environ Sci Pollut R 19:3389–3399