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Chemical characterization of aerosol collected at Mt. Yulong in wintertime on the southeastern Tibetan Plateau

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ABSTRACT

In order to evaluate the chemical composition of aerosol on the southeastern Tibetan Plateau, aerosol samples were acquired at Mt. Yulong during January to February, 2010. Eighteen elements (Al, Si, P, S, Ca, Ti, K, Cr, Mn, Fe, Ni, Zn, As, Br, Ba, Pb, Sb and Cu) and major water-soluble ions (SO_4^{2-}, NO_3^-, Cl^-, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were detected. The results show that Ca, Fe, Al, Si, S, K and Ti are major elements which mainly originate from crustal material, while SO_4^{2-} and Ca^{2+} are the dominant anion and cation in the samples, respectively. Results of ion analysis indicate that our samples are alkaline and that the main compounds present are $CaCO_3$, $(NH_4)_2SO_{4,}$ and $CaSO_4$. The enrichment factors (EFs) determined for As, Br, Ca, Cu, S, Pb and Zn are greater than 10; in particular, EFs for As and Br are above 100. However, the high EF for As could be caused by crustal sources because the high level of As enrichment can be found commonly on the Tibetan Plateau. Analyses including Scanning Electron Microscope (SEM) observations, EF determinations, backward trajectories and correlation coefficients reveal that Al, Fe, Ca, Ti, Mn, Fe, K and Mg^{2+} mainly originate from crustal sources; Pb, Br, Cu, Ni, Zn and Sb come mainly from traffic-related emissions; and biomass burning influences Cl^-, Br, S and P.

1. Introduction

Aerosols have received increasing attention due to the roles they play in many climate and environmental processes (Andreae and Crutzen, 1997; Buseck et al., 2000; Bellouin et al., 2005). They can scatter or absorb both incoming solar radiation and thermal radiation emitted from Earth's surface, thereby directly altering the radiation balance. Aerosols can also act as condensation nuclei for cloud droplets, affecting cloud and precipitation formation and causing indirect radiative forcing (IPCC, 2007). Because aerosol may emit from different sources, they not only reflect and affect regional atmospheric environmental characteristics, but may also affect the global atmospheric environment due to long-distance transport. Understanding the chemical and physical properties of background aerosols is useful for determining source regions, elucidating the mechanism of long-range transport of anthropogenic pollutants, and validating both regional and global atmospheric models. In addition, data regarding the chemical composition of aerosols from remote areas can form a valuable reference for studying and evaluating the evolution of the atmosphere with respect to the rapid development of industry.

Investigation of aerosol chemistry in the Tibetan plateau to date has been limited on a spatial scale, mainly due to its remoteness and difficult topography. However, because the Tibetan plateau is far from any industrialized area and lightly populated, the plateau has been chosen as an ideal location from which to monitor the long-term changes in the global environment and to evaluate the various impacts of human activities. A limited number of studies have been conducted in the past, including short-term (Wake et al., 1994; Shrestha

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et al., 1997; Ming et al., 2007; Zhang et al., 2010) and long-term (Shrestha et al., 2000, 2002; Cao et al., 2009) aerosol chemistry investigations over the Tibetan plateau. However, in light of its vast area and very limited availability of data for the region, more investigation is needed to understand the chemical composition of aerosol over the Tibetan Plateau. On the southern slopes of Tibetan plateau, atmospheric circulation is controlled by monsoonal winds from the Indian Ocean during summertime and the westerlies during wintertime, which alternate every year, and the regional aerosol properties change accordingly (Shrestha et al., 2000).

Previous studies on Mt. Yulong included analyses of firn cores to reveal changes in isotopic and ionic composition in accumulated ice on a glacier (He et al., 2002; Pang et al., 2007). However, for aerosol, there has been only a short-term study of water-soluble ions present during the monsoon period at Mt. Yulong (Zhang et al., 2010) and a few reports at Lijiang city that is 25 km south away from Mt. Yulong (Zhang et al., 2007; Zhang et al., 2011). The purposes of this paper are to (1) investigate elemental and ionic composition of aerosol, and (2) identify their sources during wintertime.

2. Sampling site and methods

2.1. Site description

Mt. Yulong is located in the Hengduan Mountain range at the southeastern edge of the Tibetan plateau, 25 km north of

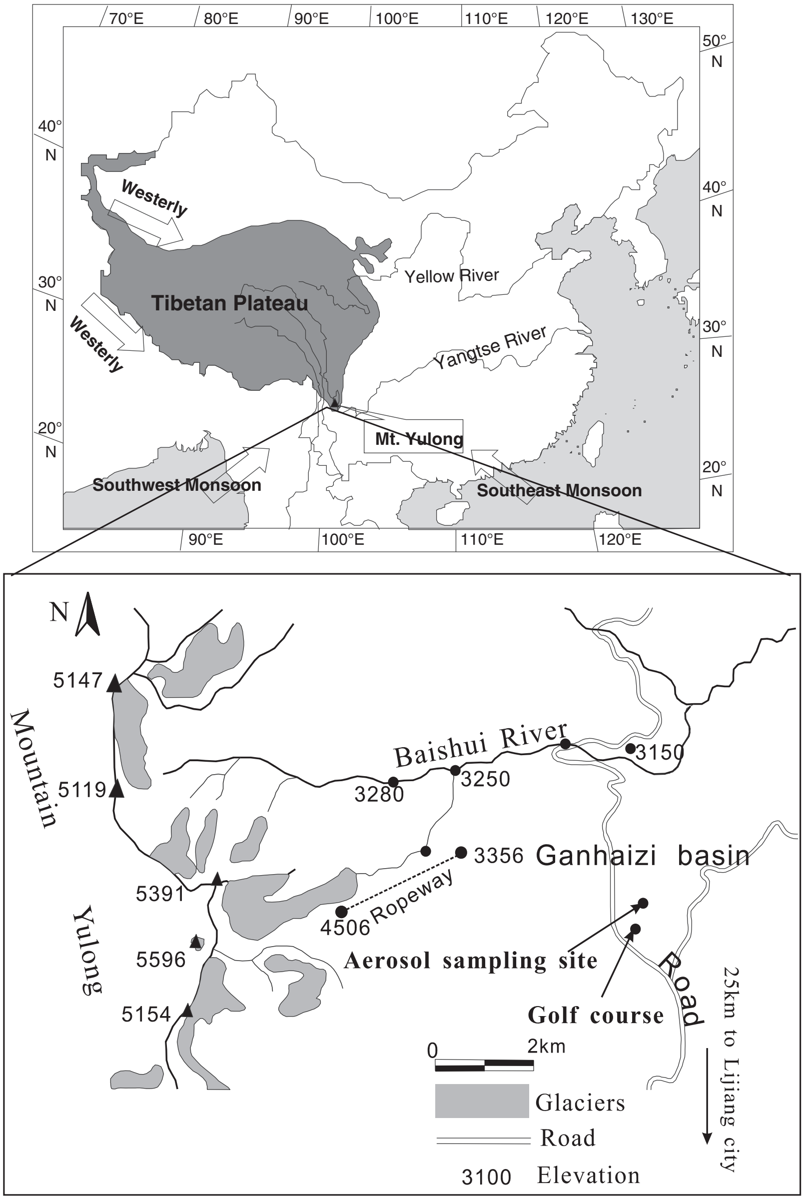


Fig. 1. Location of Mt. Yulong and the sampling site.

Lijiang City in Yunnan Province, China (27°10'–27°40'N; 100°07'–100°10'E) (Fig. 1). Attractions ranging from modern temperate glaciers and beautiful scenery have resulted in the 400 km^2 area including Mt. Yulong becoming known as a world-known scenic tourism destination. Our sampling site is located at Ganhaizi Basin on the eastern side of Mt. Yulong (Fig. 1). Thousands of tourists travel to the Ganhaizi Basin (3100 m a.s.l.) in various types of vehicles every day. Some travel by buses to the ropeway at the glacier park at an elevation of 3350 m, and the rest travel to other sites in the Mt. Yulong scenic area by green buses. Overall, the Ganhaizi Basin serves as a transfer site for tourists. It is notice that a golf course is under constructed about 1 km southwest away our sampling site during the sampling period (Fig. 1).

2.2. Meteorology

The weather of the study region is controlled by Asian southwestern monsoonal circulation from May to October, and by the southern branch of the westerly circulation from November to April of the following year. During our sampling period, the major prevailing circulation is westerly. It is proved by the wind field at 500 hPa which is plotted by Grads software (Grads version 1.8) with the NCEP/NCAR Reanalysis data (http://www.esrl.noaa.Gov/psd/data/gridded/data.ncep.reanalysis.pressure.html). (Fig. 2). Meanwhile, an automatic weather station was set up about 300 m from the sampling site. We selected meteorological parameters such as air temperature, air pressure, relative humidity, and wind speed and direction, which were measured simultaneously during the sampling period. The prevailing winds measured at Ganhaizi are shown in Fig. 2. The circulation in the upper atmosphere is westerly, but the prevailing winds near the surface are mainly from the south caused by the local topography.

2.3. Sampling and analysis

Aerosol samples were collected about 7 m above the ground and 1.5 m above the roof of the Mt. Yulong Fire Brigade building at 3100 m a.s.l. (27°06.170′N, 100°11.545′ E) from 24 January to 27 February 2010. Teflon® Zefluor™ filters, 47 mm in diameter with 2 μm pore size (Pall Corporation, Port Washington, NY), were used for sampling. The sampler (Zambelli Easy Plus 1, Zambelli srl, Milan, Italy) was driven by 220 V alternating current. The volume of air sampled was measured by an in-line flow meter with a mean flow rate of 16.7 $L \cdot min^{-1}$. Corrections for ambient temperature and pressure allowed conversion of the measured volumes to standard (101325 Pa, 273 K) cubic meters. 17 samples were collected and only 14 samples whose sampling time is enough to 48 h (about 33 m^3) are selected to analysis. Both samples and 5 field bland filters were stored at 4 °C from field to laboratory before analyzing in the Institute of Earth Environment, Chinese Academy of Sciences (Xi'an).

Aerosol mass loadings were determined gravimetrically using a Sartorius MC5 electronic microbalance (Sartorius, Göttingen,Germany) with a sensitivity of 1 μg, and the detail processes were shown in Cao et al. (2007). In order to analyze the major ionic, elemental concentrations and individual particle, the samples and blank filters were cut into two pieces. Half of each filter sample was used to determine the aerosol ion mass concentrations. Three anions (SO_4^{2-}, NO_3^- and Cl^-) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were determined using aqueous extracts of the filters by ion chromatography (IC, Dionex 500, Dionex Corp, Sunnyvale, CA). To extract the water-soluble species from the filters, half of each filter was wetted with 50 μl ultra-pure ethanol, and the soluble components were then extracted with 10 ml Milli-Q water ($R \approx 18$ MΩ), and sonication in a water bath for 60 min. The samples were shaken twice on a mechanical shaker for 1 h each to completely extract the ionic compounds. The extracts were filtered with a 0.45 μm pore size microporous membrane, and the filtrates were stored at 4°C in a clean tube before analysis. Cation (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) concentrations were determined with a CS12A column (Dionex Corp.), using 20 mM methanesulfonate as an eluent. Anions (SO_4^{2-}, NO_3^- and Cl^-) were separated on an AS11-HC column (Dionex Corp.), using 20 mM KOH as the eluent. The

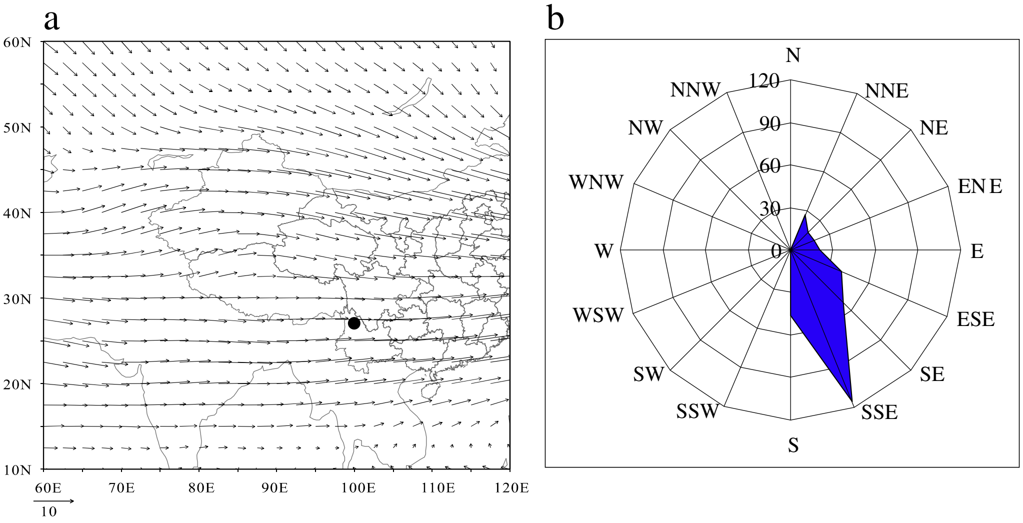


Fig. 2. Wind field at 500 hPa (a) and rose diagram of wind frequency at the surface (b) of the Ganhaizi Basin during the sampling period.

method detection limits (MDLs) were Na^+ (4.6 μg·L^{-1}), NH_4^+ (4.0 μg·L^{-1}), K^+ (10.0 μg·L^{-1}), Mg^{2+} (10.0 μg·L^{-1}), Ca^{2+} (10.0 μg·L^{-1}), SO_4^{2-} (20.0 μg·L^{-1}), NO_3^- (15.0 μg·L^{-1}) and Cl^- (0.5 μg·L^{-1}). Standard Reference Materials produced by the National Research Center for Certified Reference Materials, China, were analyzed for quality assurance purposes. The specific laboratory methods are the same as in Shen et al. (2009). Blank values were subtracted from sample concentrations.

The concentrations of elements in aerosol samples with the remaining half of each filter were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry using the PANalytical Epsilon 5 XRF analyzer (PANalytical B.V., Almelo, The Netherlands). The Epsilon 5 XRF spectrometer uses three-dimensional polarizing geometry with 11 secondary targets (CeO_2, CsI, Ag, Mo, Zr, KBr, Ge, Zn, Fe, Ti, and Al) and one Barkla target (Al_2O_3) that supplies a good signal-to-background ratio, permitting such low detection limits. The X-ray source is a side window X-ray tube with a gadolinium (Gd) anode, which is operated at an accelerating voltage of 25–100 kV and a current of 0.5–24 mA (maximum power: 600 W). Characteristic X- radiationis detected by a germanium (Ge) detector (PAN 32). Each sample was irradiated for half an hour and a laboratory blank Teflon filter sample is also analyzed to evaluate analytical bias. The elements that were determined by the EDXRF method include Al, Si, P, S, Ca, K, Cr, Mn, Ti, Fe, Ni, Zn, As, Br, Ba, Pb, Sb and Cu with the detection limits (μg·cm^{-2}) of 0.115, 0.093, 0.014, 0.032, 0.007, 0.007, 0.003, 0.014, 0.005, 0.011, 0.003, 0.008, 0.000, 0.006, 0.052, 0.015, 0.033 and 0.010, respectively.

After elemental analysis, individual particles were observed by SEM using a computer-controlled JEOL JSM-6460 LV SEM (Japan Electron Optics Laboratory Co. Ltd., JP) under 20–25 kV accelerating voltage at work distance of 10 mm (Hu et al., 2009).

IC measures the soluble fraction of aerosol particles, and EDXRF has been proved as an effective tool to detect total elemental concentrations (Lindgren et al., 2006; Öztürk et al., 2011). In order to check data quality and study the ratio between soluble and insoluble components, the concentrations for S, Ca and K measured by IC and EDXRF are compared (Fig. 3). For sulfur, a comparison is made between the fraction of sulfur measured as SO_4^{2-} by IC and total elemental S measured by EDXRF (Fig. 3a). Fig. 3 shows the good correlation between the values of S, Ca and K detected by IC and EDXRF, which suggests that the quality of data obtained is accepted. The slopes of S, Ca and K are 1.12, 1.64 and 1.14, respectively. It is indicating that part of the sulfur, calcium and potassium due to the presence of insoluble mineral particle, in particular for calcium.

3. Results and discussion

3.1. Elemental composition

Average elemental and ionic compositions of total suspended particulate (TSP) collected at Mt. Yulong are summarized in Table 1. In a decreasing order, average concentrations were Ca, Fe, Al, Si, S and Ti, and the levels of remaining elements were lower than 100 ng·m^{-3}. Ca, Fe, Al and Si are the dominant elements, accounting for 81% (68%–94%) of all detected 18 elements, likely because the elements Ca, Fe, Al, and Si are commonly found in the Earth's crust, as for the report from data collected at Mt. Gongga (Yang et al., 2009), southeast of Tibetan Plateau in western Sichuan, China. The sum of elements detected accounted for about 12%–28% of the mass concentrations.

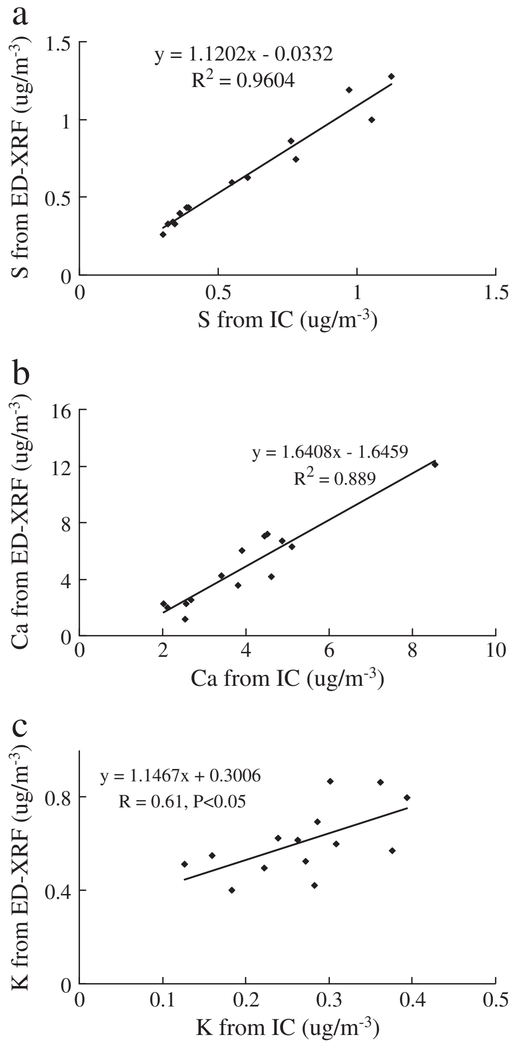


Fig. 3. Comparison of S, Ca and K concentrations measured by IC and EDXRF.

Elemental concentrations from earlier studies at different locations on the Tibetan Plateau are listed for comparison. Lijiang (Zhang et al., 2007) and Mt. Gongga are located relatively close to urban and suburban areas, while the Zhadang glacier (Li et al., 2007), Nam Co glacier (Cong et al., 2007), and Mt. Qomolangma (Mt. Everest) (Cong et al., 2010) are relative remote from industrialized areas and thus represent these sites with less pollution. First, concentrations of all elements in our samples are greater than those at Zhadang glacier, Nam Co, and Mt. Qomolangma, particularly crustal elements such as Ca, Al, and Fe, suggesting that the elemental composition of our samples maybe influenced by the golf course construction and human activity. Compared to the results of Lijiang (from 28 Dec 2003 to 6 Jan 2004) and Mt. Gongga (from January to December 2006), it is apparent

Table 1
Statistical summary of elemental and ionic concentration (ng/m^3) determined at Mt.Yulong and comparison with data over Tibetan Plateau.

Sample ID	Average	Min	Max	SD	Lijiang[a]	Mt.Gongga[b]	Zhadang glacier[c]	Nam Co[d]	Mt.Qomolangma[e]	Waliguan[f]
Al	1099.47	481.42	2233.96	460.27	223.9	688.4	57	131	55	2110–3410
Si	688.54	237.56	1306.32	319.89	619			550		
S	629.60	262.34	1276.70	336.06	71.7			101		
P	10.80	0.00	29.46	9.51						
Ca	4814.85	1181.94	12094.29	2942.48	580.1	848.6	51	251	451	2010–4280
Ti	149.94	59.35	352.83	76.07	18.1		4	10	5.1	106–220
V	1.76	0.00	4.91	1.33	2.8	1.4	0	0.06	1.4	3.02–5.88
Cr	3.16	0.91	5.04	1.12	3			1	3	
Mn	36.03	20.96	70.94	13.05	9.5		1	3.7	1.8	27.5–52.9
Fe	1258.31	550.16	2618.95	561.89	83.6	496.8	21	94	61	1720–3910
Ni	2.95	0.30	6.93	2.24	2.9	1.6		0.95	0.6	
Zn	71.75	29.61	192.83	48.22	13.2	247.6	2	1.8	1.4	9.5–26.3
As	3.61	1.58	6.74	1.29	6.2	6.1	0	0.04		0.70–3.37
Br	4.66	2.30	9.77	1.92	10.1					1.07–2.67
Sb	5.04	0.00	19.23	5.12						0.26–1.11
Ba	12.67	3.14	20.56	5.32		12	0			21.3–45.3
Pb	12.37	1.84	23.96	5.83	17.7	55.3	0		0.43	
Cu	4.95	2.73	8.96	1.87	5.1	3.6		0.56	0.31	
Na^+	122.57	85.78	328.16	61.72	72.02	100				
NH_4^+	372.18	112.68	842.45	277.96	794.53	1700				
K^+	269.44	126.56	393.39	79.17	335.07	310				
Mg^{2+}	86.82	48.95	157.98	26.88	353.99	80				
Ca^{2+}	3937.65	2021.72	8537.98	1690.90	3641.53	680				
Cl^-	263.12	134.97	461.68	83.10	569.00	260				
NO_3^-	577.08	295.65	970.23	190.46	902.17	880				
SO_4^{2-}	1775.16	900.05	3370.88	882.04	2336.93	4700				

[a] Elemental concentration of TSP collected at Lijiang, December 28, 2003~Janaury 6, 2004 (Zhang et al., 2007), ionic concentration of TSP collected at Lijiang, December 2008~Janaury 2009 (Zhang et al., 2011).

[b] elemental concentration of PM_{10} collected at Mt. Gongga, 2006 (Yang et al., 2009), ionic concentration of PM_{10} collected at Mt. Gongga, 2006 (Zhao et al., 2009).

[c] aerosol collected at Zhadang glacier, June 25 to October 15, 2006 (Li et al., 2007).

[d] aerosol collected at Nam Co, July–October, 2005(Cong et al., 2007).

[e] TSP collected at Mt.Qomolangma, May and June, 2005 (Cong et al., 2010).

[f] TSP collected at Waliguan, 1992–1995 (Wen et al., 2001).

that the concentrations of pollutant elements like Pb and As in our samples are lower than those at Lijiang and Mt. Gongga but crustal elements such as Al, Fe, and Ca exhibit higher concentrations. This indicated that the elements of our samples is mainly attributable to crustal sources because (1) the sampling site is located at a tourist transfer site, and the tourism activities are mainly during 7 a.m. to 6 p.m. at daytime, no human activity takes place there at night, and (2) during the sampling, a golf course was under construction near the sampling site, so the crustal dust is easily re-suspended by the local wind and likely had a significant influence on the elemental composition.

3.2. Water-soluble ionic composition

The sum concentrations of ions were accounted for about 11%–27% of mass concentration. The dominant anion and cation in the samples are SO_4^{2-} and Ca^{2+}, which account for 25% and 52% of the total ionic concentrations, respectively. However, previous studies have found that NH4+ is the dominant cation in aerosol collected at Tibetan Plateau (Wake et al., 1994; Shrestha et al., 1997, 2000). This difference may be attributed to the contributions from local dust/soil particles which are rich in calcium carbonate at Mt. Yulong. Because the lithology of Mt. Yulong consists primarily of limestone (Zhang et al., 2010), the concentration of Ca^{2+} is higher than the values at Lijiang City and Mt. Gongga. However, the concentrations of SO_4^{2-}, NO_3^- and $NH_4^+$are related to human activities and their concentration are lower than the corresponding values at those two sites. Therefore, the comparison indicates that crustal sources have a more significant influence than human activity at the sampling site in this study.

In order to evaluate the main detected ions and the acid–base balance of the aerosol particles, the ion balance is calculated as (Shen et al., 2009):

$$\begin{aligned}\text{CE (cation equivalent)} = {} & Na^+/23 + {NH_4}^+/18 + K^+/39 \\ & + Mg^{2+}/12 + Ca^{2+}/20\end{aligned}$$

$$\text{AE(anion equivalent)} = {SO_4}^{2-}/48 + {NO_3}^-/62 + Cl^-/35.5$$

The mean CE/AE ratio is 5.11 in our samples, indicating cations dominate the ionic composition during the sampling period and major anions are not detected. Previous studies have pointed out that anion deficiency is mainly attributable to failure to detect HCO_3^-/CO_3^{2-}, when the relationship between Ca^{2+} and $\triangle C$ (CE–AE) is significantly correlated (Wake et al., 1992; Sun et al., 1998). The correlation coefficient between Ca^{2+} and $\triangle C$ in this study is 0.9988 ($p<0.01$), suggesting that HCO_3^- /CO_3^{2-} should be the major undetected anion. So, the dominant inorganic compound in this sampling should be

$CaCO_3$, similar to the result found at Lijiang City (Zhang et al., 2011).

Because SO_4^{2-} and NH_4^+ are the important soluble inorganic components of tropospheric aerosols, more attention has been paid to those species and their ratio (Warneck, 1988; Gorzelska et al., 1994; Sun et al., 1998). Warneck (1988) suggests that ammonium and sulfate exist mainly as NH_4HSO_4 and $(NH_4)_2SO_4$, if the equivalence ratio of ammonium to non-sea-salt sulfate ranges from 0.5 to 1. When the equivalence ratio exceeds 1, the compounds exist mainly as $(NH_4)_2SO_4$ and NH_4NO_3. Shrestha et al. (1997) pointed out that the most prevalent compound of SO_4^{2-} and NH_4^+ is NH_4HSO_4, based on the fact that the mean equivalence ratio of NH_4^+ to SO_4^{2-} is 0.69 in aerosol collected in the Hidden Valley on the south slope of Himalayas. Because the mean equivalence ratio of NH_4^+ to SO_4^{2-} is 0.99 in the aerosol sampled at Lijiang City, Zhang et al. (2011) suggest that ammonium is mainly exists as $(NH_4)_2SO_4$. In this study, the mean equivalence ratio of NH_4^+ to SO_4^{2-} is 0.51, and the correlation coefficient between NH_4^+ and SO_4^{2-} is 0.94 ($P<0.01$), indicating that the main compound composed of NH_4^+ and SO_4^{2-} is NH_4HSO_4 in this study. However, our samples are cation excess which means the samples are alkaline (Shen et al., 2009), and the compound NH_4HSO_4 cannot exist in that situation. So, the chief compound of NH_4^+ and SO_4^{2-} is $(NH_4)_2SO_4$, and the excess SO_4^{2-} is likely being neutralized by $CaCO_3$, to form $CaSO_4$.

3.3. Elemental enrichment factors (EFs)

EFs are often used to differentiate between elements originating from crustal material and those originating from human activities (Al-Momani et al., 2005; Ragosta et al., 2008), and is generally defined as follows:

$$EF_X = (C_X/C_R)_{aerosol}/(C_X/C_R)_{crust},$$

where X represents the element of interest, C_X is the concentration of X, and C_R is the concentration of a reference element. The aerosol and crust subscripts refer to particles in the aerosol samples and crustal material, respectively. The reference element commonly used is Al, Si, Ti, and Fe, among others. In this study, Al was selected as the reference material, and Wedepohl's (1995) average upper continental crust composition was used as the elemental composition of the crust material.

The EFs of elements in our samples collected at Mt. Yulong are presented in Fig. 4. When the EF_X for a sample approaches unity, the dominant source for that element is crustal; if $EF_X > 10$, a significant fraction of the element is from anthropogenic sources. In our samples, elements such as Fe, Mn, K, Si, Ba and Ti have an EF value around 1, suggesting that they are mainly from soil dust. However, the EF values for As, Br, Ca, Cu, S, Pb and Zn are greater than 10, and values of As and Br are above 100 (127 and 205, respectively). These high EF values indicate that some portion of the concentration measurements for these elements is affected by anthropogenic sources, especially for As and Br. It is notice that Br, Pb, Cu and Zn appear to be simultaneously enriched in \our sample, because all of them can originate from fossil fuel combustion processes and traffic-related sources. Previous studies have proven the relationship between Pb and Br in exhaust emissions (Harrison and Srueges, 1983; Lee et al., 1994) and pointed out that the major sources of Cu in atmospheric particles are combustion of fossil fuels, industrial metallurgical processes, and waste incineration (Nriagu and Pacyna, 1988), which are also sources for Zn in the atmosphere (Rogge et al., 1993; Chueinta et al., 2000). This reveals that the air pollution in the region mainly came from traffic exhaust emissions due to the transfer of tourists on thousands of bus trips into and out of the Ganhaizi Basin.

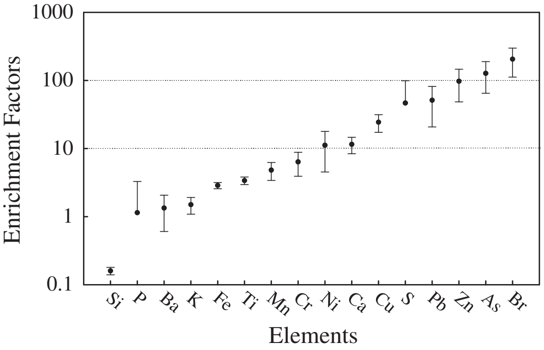


Fig. 4. Enrichment factors of elements in aerosol samples at Mt. Yulong.

Published EF values taken at different sites on the Tibetan Plateau were collected and listed in Table 2. It is found that As is enriched at most sites, including Nam Co and Zhadang glacier, far away any human activity, and it is also found at Lijiang and Mt. Gongga. Because arsenic is a metalloid that is distributed widely in the earth's crust, sources of it in the environment can be either natural or anthropogenic, or both (Roy and Saha, 2002). By collecting topsoil samples from the western Tibetan Plateau, Li et al. (2009) found that As was enriched in the topsoil and pointed out that the high EF value for As could not be solely assigned to anthropogenic sources. Moreover, research on the environmental background values of soils in Xizang indicated that the concentration of As in the soil there is higher than the average As level for the rest of China (Zhang, 1994). Hence, the high enrichment of As in our dataset may be influenced by crustal sources.

3.4. Possible elemental sources

In order to determine the possible sources of elements and ions in our samples, we used the SEM images firstly. Under SEM, it is easy to classify the mass into two groups: mineral particles from dust and soot from combustion processes (Fig. 5), and then backward trajectories and correlation coefficients were calculated. The hybrid single-particle Lagrangian integrated trajectory (HYSPLIT4) model (www.arl.noaa.gov/ready/hysplit4.html) for 6 days were calculated at the sampling site (27°06.170′N, 100°11.545′E; 100 m AGL (above ground level)) and with ending time corresponding to the end of each sample collection period (around 8 UTC). These calculated trajectories were plotted on Google Earth (Fig. 6a), showing that the air mass is mainly from northern Myanmar and the eastern edge of India where the forest is usually burning during our sampling period (Fig. 6b). Fig. 6b shows that the fire sites (http://firefly.geog.umd.edu/firemap/) distribute during our sampling period at South Asia and Southeast Asia. In that case, the material

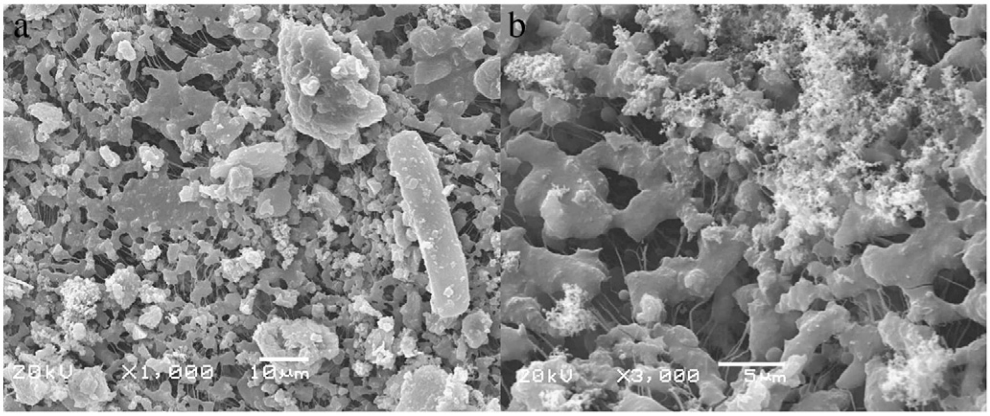
Table 2
Comparison of elemental EFs at different sites over the Tibetan Plateau.

Site	Location and altitude	Reference element	>100	10~100	1~10	<1	References
Lijiang	27°06.170′N, 100°11.545′E Southeastern Tibetan Plateau, 3100 m	Al	As, Br	Ni, Ca, Cu, S, Pb, Zn	P, Ba, Rb, K, V, Fe, Sr, Ti, Mn, Cr, Co	Si, Na, Mg,	This study
Lijiang	27°13′ N; 100°11′E, Southeastern Tibetan Plateau, 3100 m	Si	As, Se, Br, Pb	S, Ni, Zn	Mg, Ca, V, Cr, Mn, Cu	Al, K, Ti, Fe	Zhang et al., 2007
Mt. Gongga (PM_{10})	29°35′N, 101°59′E, Southeastern Tibetan Plateau, 1600 m	Al	As, Zn, Ag, Pb	Cu, Ti	Na, Mg, K, Ca, V, Fe, Ni, Ba		Yang et al., 2009
Waliguan	36°17′N, 100°54′E Northern Tibetan Plateau, 3814 m	Fe		As, Br, Cl, I, Sb, Se	Ba, Ca, K, Mg, Sc, Zn	Al, Mn, Na, Ti, V	Wen et al., 2001
Nam Co	30°46.44′N, 90°59.31′E, Central Tibetan Plateau, 4730 m.	Al		Cr, Ni, Cu, Zn, As	Mg, Si, K, Ti, V, Fe		Cong et al., 2007
Zhadang glacier	30°28′N, 90°39′E, Southern Tibetan Plateau, 5800 m	Al	As, Cd	B, Zn, Pb, Bi	Mg, Ca, Ga, Rb		Li et al., 2007
Mt. Qomolangma	27°59 N′, 86°55′E, central Himalayas, 6520 m,	Al	Cr	Ca, V, Ni, Cu, Zn, Pb	Na, Mg, K, Ti, Mn, Fe, Al		Cong et al., 2010

from biomass burning is being transported into the study region. In general, combining the correlation coefficients, elements and ions can be divided into the following three groups (Table 3):

(1) Crustal material
Because the lithology of Mt. Yulong is mainly carbonate, which is rich in calcium and magnesium, meanwhile, the correlation coefficient between Ca and Mg^{2+} is 0.84 ($p<0.01$), and that between Ca^{2+} and Mg^{2+} is 0.84 ($p<0.01$), suggesting that they are both from crustal sources. Moreover, all of the elements Al, Fe, Ti, Mn and K are significantly correlate with Ca and Mg^{2+} ($0.73<r<0.96$, $p<0.01$). Additionally, the EFs for these elements are lower than 10 except for that of Ca. These results indicate that Al, Fe, Ca, Ti, Mn, Fe and K are attributed to crustal sources.

(2) Traffic-related emissions
Emissions, including heavy metals, are one of the most significant environmental problems caused by existing transport systems (Weckwerth, 2001). Previous studies have proven that the main elements related to vehicle exhaust are Pb, Br, Zn, Ni and Cu. It is interesting to find a significant relationship between Pb and Br in this study, with a correlation coefficient of 0.64 ($p=0.01$) in our samples. Br in aerosols mainly comes from sources including marine aerosols, leaded gasoline combustion, biomass burning, and coal combustion (Gao et al., 2010), and is a good tracer element for motor vehicle exhaust together with Pb (Harrison and Srueges, 1983; Salma et al., 2000). The relationship between Br and Pb and the Br/Pb ratio has been used as an indicator of the influence of traffic emissions (Lee et al., 1994). Although direct emissions of Pb from vehicular exhaust were prohibited after 2003 in China, Pb is still persistent in road dust from earlier vehicular exhaust emissions because it can be resident for several decades to the soil (Miller and Friedland, 1994). Moreover, the average ratio of Br/Pb is 0.52 in our samples, which is greater than the Br/Pb ratio of 0.48 typical of ethyl (Liu et al.,



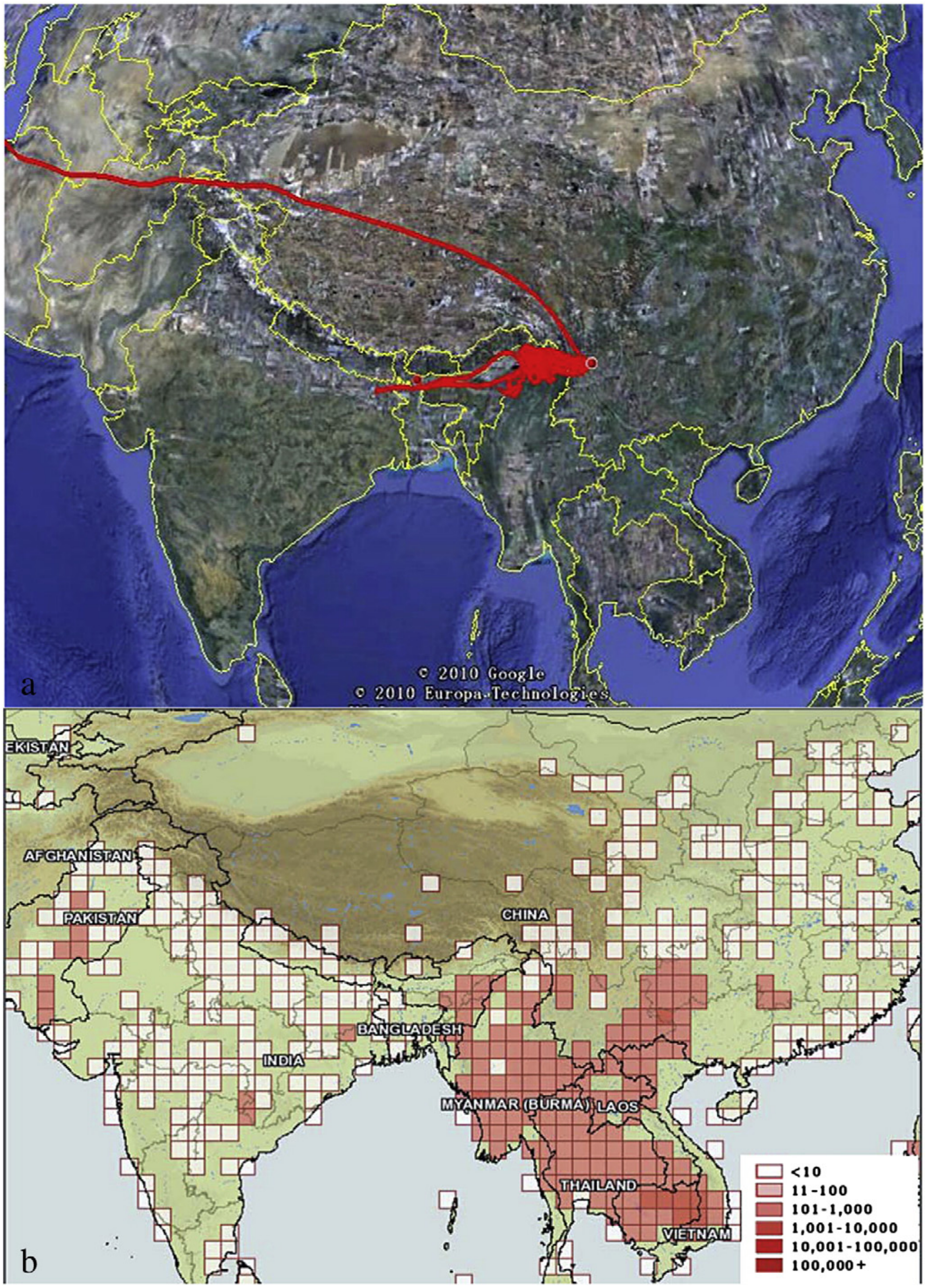


Fig. 6. Backward trajectories and distribution of fire sites during sampling period.

Table 3
Summary of species sources.

species	Sources
Al, Fe, Ca, Ti, Mn, Fe, K, Mg^{2+}	Crustal
Pb, Br, Cu, Ni, Zn, Br	Traffic
S, P, Cl^-, Br	Biomass burning

1995), and of 0.39 found in leaded gasoline, as reported by Lee et al. (1994). However, due to the volatility of Br during exhaust emission aging process, the Br/Pb ratio decrease (Salma et al., 2000; Voutsa et al., 2002). Because there is no heavy industry at Lijiang and no marine air mass arrived at Lijiang during sampling time (Fig. 6b), the higher ratio in our samples indicates there is excess

Br in our samples, which can be attributed to biomass burning. Good relationships are also found between Pb and Zn, Pb and Sb, Cu and Ni, Zn and Sb, with correlation coefficients of 0.62 ($p<0.02$), 0.57 ($p<0.05$), 0.88 ($p<0.01$), and 0.66 ($p<0.01$), respectively. Elemental Ni is regarded as an indicator of fuel burning and vehicular emissions (Pacyna, 1984; Cong et al., 2007), and Sb is related to shedding of brake-lining materials (Weckwerth, 2001). At the same time, the largest mass concentrations of Zn, Cu, and Ni appear in the same sample. Furthermore, EFs of Br, Pb, Zn, Cu and Ni are all greater than 10. Thus, Pb, Zn, Cu, Ni, Sb and a portion of Br are attributed to traffic-related emissions.

(3) Biomass burning

Biomass burning is a global phenomenon that is one of the major sources of airborne particulate matter and has an impact on the environment and climate (Houghton et al., 2001; Fiedler et al., 2010). Measurements of K have been widely used as a source tracer for biomass burning emissions and have been applied in source appointment studies (Khalil and Rasmussen, 2003; Hays et al., 2005). Because the air masses arrive at the sampling site through the forest fire regions (Fig. 6), the EF for K should be high. However, it is puzzling that EF value for K is close to 1, indicating that K is not enriched in our samples. Echalar et al. (1995) pointed out that potassium enrichment is lower from forest fires than from savanna fires, and that the EF for not only K but also for Cl and P is low from forest fires. On the other hand, K has a good relationship with crustal elements (the correlation coefficient between K and Al is 0.85 ($p<0.01$), and that between K and Mg is 0.88 ($p<0.01$)), even considering that crustal element concentration comprises 83% of the total elemental concentration. So, signal of K originating from forest fires may be obscured by the K originating from crustal sources.

Aerosol Cl is mainly derived from marine sources and biomass burning (Khalil and Rasmussen, 2003; Na and Coker, 2009). The Cl^- to Na^+ ratio in seawater is 1.8, which is assumed to become 1.0 due to the loss of Cl^- during transport. The loss of Cl^- should be very important as our samples are collect during the non-monsoonal period. However, the average Cl^-/Na^+ ratio is 2.30 (~1.13–3.91) in our samples or in two-fold excess than 1, which suggests that additional Cl^- may come from biomass burning in our samples. Biomass burning also includes essential nutrients such as S, P, N, and K^+ (Kauffman et al., 1994; Yamasoe et al., 2000). A high EF for S (46.53) is found in our samples, and there is no large-scale industry emission in Lijiang-Mt. Yulong region. Thereby, it is suggesting that there is the contribution of S from biomass burning. At the same time, although the EF value of P is below than 10, the correlation coefficient between S and P is 0.88 ($P<0.01$) indicating both of them arise from the same source. So, it is concluded that part of S and P should be from biomass burning.

4. Conclusions

Elemental and ionic compositions of aerosol collected during wintertime at Mt. Yulong, on the southeastern edge of the Tibetan Plateau were analyzed for this study. The major elements found in aerosol included Ca, Fe, Al, Si, S, K, and Ti, and SO_4^{2-} and Ca^{2+} are the dominant anion and cation in the samples. Compared with other sites across the Tibetan Plateau, the atmosphere of Mt. Yulong is influenced by human activity, but the mass concentration is mainly related to crustal source components, resulting in samples that are alkaline, with the dominant compounds present including mainly $CaCO_3$, $(NH_4)_2SO_4$, and $CaSO_4$. Enrichment factors for As, Br, Ca, Cu, S, Pb, and Zn are greater than 10, and those for As and Br are over 100, indicating that their concentrations are influenced by anthropogenic sources. However, high enrichment of As in aerosol is found commonly over the Tibetan Plateau, indicating that high enrichment of As may be from natural sources. The detected elements may be divided into three groups according to sources. The first group (Al, Fe, Ca, K, Ti, Mn, Fe and Mg^{2+}) mainly originates from crustal sources. The second group (Pb, Br, Cu, Ni, Zn, and Sb) comes from traffic-related sources and the third group (S, P, Cl^- and Br) is related to long-distance transport of emissions from burning biomass.

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References

Al-Momani, I.F., Daradkeh, A.S., Haj-Hussein, A.T., Yousef, Y.A., Jaradat, Q.M., Momani, K.A., 2005. Trace elements in daily collected aerosols in Al-Hashimya, central Jordan. Atmos. Res. 73, 87–100.

Andreae, M.O., Crutzen, P.J., 1997. Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. Science 276 (5315), 1052–1058.

Bellouin, N., Boucher, O., Haywood, J., Reddy, M.S., 2005. Global estimate of aerosol direct radiative forcing from satellite measurements. Nature 438 (7071), 1138–1141.

Buseck, P.R., Jacob, D.J., Posfai, M., Li, J., Anderson, J.R., 2000. Minerals in the air: an environmental perspective. Int. Geol. Rev. 42 (7), 577–593.

Cao, J.J., Lee, S.C., Chow, J.C., Watson, J.G., Ho, K.F., Zhang, R.J., Jin, Z.D., Shen, Z.X., Chen, G.C., Kang, Y.M., Zou, S.C., Zhang, L.Z., Qi, S.H., Dai, M.H., Cheng, Y., Hu, K., 2007. Spatial and seasonal distributions of carbonaceous aerosols over China. J. Geophys. Res. 112, D22S11.

Cao, J.J., Xu, B.Q., He, J.Q., Lin, X.Q., Han, Y.M., Wang, G.H., Zhu, C.S., 2009. Concentrations, seasonal variations, and transport of carbonaceous aerosols at a remote Mountainous region in western China. Atmos. Environ. 43, 4444–4452.

Chueinta, W., Hopke, P.K., Paatero, P., 2000. Investigation of sources of atmospheric aerosol at urban and suburban residential areas in Thailand by positive matrix factorization. Atmos. Environ. 34 (20), 3319–3329.

Cong, Z.Y., Kang, S.C., Dong, S.C., 2010. Elemental and individual particle analysis of atmospheric aerosols from high Himalayas. Environ. Monit. Assess 160, 323–335.

Cong, Z.Y., Kang, S.C., Liu, X.D., Wang, G.F., 2007. Elemental composition of aerosol in the Nam Co region, Tibetan Plateau, during summer monsoon season. Atmos. Environ. 41, 1180–1187.

Echalar, F., Gaudichet, A., Cachier, H., Artaxo, P., 1995. Aerosol emissions by tropical forest and Savanna biomass burning: characteristic trace elements and fluxes. Geophys. Res. Lett. 22 (22), 3039–3042.

Fiedler, V., Arnold, F., Ludmann, S., Minikin, A., Pirjola, L., Dörnbrack, A., Schlager, H., 2010. African biomass burning plumes over the Atlantic: aircraft based measurements and implications for H_2SO_4 and HNO_3 mediated smoke particle activation. Atmos. Chem. Phys. Discuss. 10, 7699–7743.

Gao, Y.C., Sun, M.X., Wu, X.W., Liu, Y.D., Guo, Y.Q., Wu, J., 2010. Concentration characteristics of bromine and iodine in aerosols in Shanghai, China. Atmos. Environ. 44, 4298–4302.

Gorzelska, K., Talbot, R.W., Klemm, K., Lefer, B., Klemm, O., Gregory, G.L., Andonson, B., Barrie, A., 1994. Chemical composition of the atmospheric aerosol in the troposphere over the Hudson Bay lowlands and Quebec-Labrador regions of Canada. J. Gephys. Res. 99, 1763–1779.

Harrison, R.M., Srueges, W.T., 1983. The measurement and interpretation of Br/Pb ration in airborne particles. Atmos. Environ. 28, 311–328.

He, Y.Q., Yao, T.D., Theakstone, W.H., Cheng, G.D., Yang, M.X., Chen, T., 2002. Recent climatic significance of chemical signals in a shallow firn core from an alpine glacier in the South-Asia monsoon region. J. Asian Earth Sci. 20 (3), 289–296.

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. Atmos. Environ. 39, 6747–6764.

Houghton, J.T., Ding, Y., Griggs, D., 2001. Climate change: the Intergovernmental Panel on Climate Change Scientific Assessment. Cambridge University Press, IPCC, Cambridge, UK. 7701.

Hu, T.F., Lee, S.C., Cao, J.J., Chow, J.C., Watson, J.G., Ho, K.F., Ho, W.K., Rong, B., An, Z.S., 2009. Characterization of winter airborne particles at Emperor Qin's Terra-cott Museum, China. Sci. Total. Environ. 407, 5319–5327.

IPCC, 2007. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Kauffman, J.B., Cummings, D.L., Ward, D.E., 1994. Relationships of fire, biomass and nutrient dynamics along a vegetation gradient in the Brazilian cerrado. J. Ecol. 82, 519–531.

Khalil, M.A.K., Rasmussen, R.A., 2003. Tracers of wood smoke. Atmos. Environ. 37, 1211–1222.

Lee, D.S., Garland, J.A., Fox, A.A., 1994. Atmospheric concentrations of trace elements in urban areas of the United Kingdom. Atmos. Environ. 28 (16), 2691–2713.

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, C.L., Kang, S.C., Cong, Z.Y., 2007. Elemental composition of aerosols collected in the glacier area on Nyainqêntanglha Range, Tibetan Plateau, during summer monsoon season. Chin. Sci. Bull. 52 (24), 3436–3442.

Lindgren, E.S., Henriksson, D., Lundin, M., Therning, P., Laursen, J., Pind, N., 2006. Possible indicators for biomass burning in a small Swedish city as studied by energy dispersive x-ray fluorescence (EDXRF) spectrometry. X-Ray Spectrom. 35, 19–26.

Liu, X.D., Hopke, P.K., Cohen, D., Bailey, G., 1995. Sources of fine particle lead, bromine, and elemental carbon in southeastern Australia. Sci. Total. Environ. 175, 65–79.

Miller, E.K., Friedland, A.J., 1994. Lead migration in forest soils: response to changing atmospheric inputs. Environ. Sci. Technol. 28, 662–669.

Ming, J., Zhang, D.Q., Kang, S.C., Tian, W.S., 2007. Aerosol and fresh snow chemistry in the East Rongbuk Glacier on the northern slope of Mt. Qomolangma (Everest). J. Geophys. Res. 112, D15307.

Na, K., Coker, D.R., 2009. Characterization and source identification of trace elements in $PM_{2.5}$ from Mira Loma, Southern California. Atmos. Res. 93, 793–800.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 320, 735–738.

Öztürk, F., Zararsiz, A., Klrmaz, R., Tuncel, G., 2011. An approach to measure trace elements in particles collected on fiber filters using EDXRF. Talanta 83 (3), 823–831.

Pacyna, J.M., 1984. Estimation of atmospheric emissions of trace elements from anthropogenic sources in Europe. Atmos. Environ. 18, 41–50.

Pang, H.X., He, Y.Q., Theakstone, W.H., Zhang, D.D., 2007. Soluble ionic and oxygen isotopic compositions of a shallow firn profile, Baishui glacier No.1, southeastern Tibetan Plateau. Ann. Glaciol. 46, 325–330.

Ragosta, M., Caggiano, R., Macchiato, M., Sabia, S., Trippetta, S., 2008. Trace elements in daily collected aerosol: level characterization and source identification in a four-year study. Atmos. Res. 89, 206–217.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 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 (9), 1892–1904.

Roy, P., Saha, A., 2002. Metabolism and toxicity of arsenic: a human carcinogen. Curr. Sci. 82 (1), 38–45.

Salma, I., Maenhaut, W., Dubtsov, S., Zemplen-Papp, E., Zaray, G., 2000. Impact of phase out of leaded gasoline on the air quality in Budapest. Microchem. J. 67, 127–133.

Shen, Z.X., Cao, J.J., Arimoto, R., Han, Z.W., Zhang, R.J., Han, Y.M., Liu, S.X., Okuda, T., Nakao, S., Tanaka, S., 2009. Ionic composition of TSP and $PM_{2.5}$ during dust storms and air pollution episodes at Xi'an, China. Atmos. Environ. 43, 2911–2918.

Shrestha, A.B., Wake, C.P., Dibb, J.E., 1997. Chemical composition of aerosol and snow in the high Himalaya during the summer monsoon season. Atmos. Environ. 31, 2815–2826.

Shrestha, A.B., Wake, C.P., Dibb, J.E., Mayewski, P.A., Whitlow, S.I., Carmichael, G.R., Ferm, M., 2000. Seasonal variations in aerosol concentrations and compositions in the Nepal Himalaya. Atmos. Environ. 34, 3349–3363.

Shrestha, A.B., Wake, C.P., Dibb, J.E., Whitlow, S.I., 2002. Aerosol and Precipitation Chemistry at a Remote Himalayan Site in Nepal. Aerosol Sci. Technol. 36, 441–456.

Sun, J.Y., Qin, D.H., Mayewski, P.A., Dibb, J.E., Whitlow, S., Li, Z.Q., Yang, Q.Z., 1998. Soluble species in aerosol and snow and their relationship at Glacier 1, Tien Shan, China. J. Geophys. Res. 103 (D21), 28021–28028.

Voutsa, D., Samara, C., Kouimtzis, T., OchsenkÜhn, K., 2002. Elemental composition of airborne particulate matter in the multi-impacted urban area of Thessaloniki, Greece. Atmos. Environ. 36, 4453–4462.

Wake, P.C., Mayewski, P.A., Wang, P., Yang, J., Xie, Z.C., 1992. Anthropogenic sulfate and Asian dust signals in snow from Tien Shan, northwest China. Ann. Glaciol. 16, 45–52.

Wake, P.C., Dibb, E.J., Mayewski, P.A., Li, Z.Q., Xie, Z.C., 1994. The chemical composition of aerosols over the Eastern Himalayas and Tibetan Plateau during low dust periods. Atmos. Environ. 28 (4), 301–306.

Wen, Y.P., Xu, X.B., Tang, J., Zhang, X.C., Zhao, Y.C., 2001. Enrichment characteristics and origin of atmospheric aerosol elemental at Mt. Waliguan. Q. J. Appl. Meteorol. 12 (4), 400–408.

Warneck, P., 1988. Chemistry of the natural atmosphere. Int. Geophys. Ser. 41, 334–337.

Weckwerth, G., 2001. Verification of traffic emitted aerosol components in the ambient air of Cologne (Germany). Atmos. Environ. 35, 5525–5536.

Wedepohl, H.K., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta 59, 1217–1232.

Yamasoe, M.A., Artaxo, P., Miguel, A.H., Allen, A.G., 2000. Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements. Atmos. Environ. 34, 1641–1653.

Yang, Y.J., Wang, Y.S., Wen, T.X., Li, W., Zhao, Y.N., Li, L., 2009. Elemental composition of $PM_{2.5}$ and PM_{10} at Mount Gongga in China during 2006. Atmos. Res. 93, 801–810.

Zhang, N.N., He, Y.Q., Theakstone, W.H., Pang, H.X., 2010. Chemical Composition of Aerosol and Fresh Snow and Tourism Influences at Baishui Glacier No. 1 from Mt. Yulong, Southeastern Tibetan Plateau. J. Earth Sci. 21 (2), 199–209.

Zhang, N.N., He, Y.Q., Wang, C.F., He, X.Z., Xin, H.J., 2011. The chemical characteristic of soluble ions in total suspended particles (TSP) at Lijiang winter time. Environ. Sci. 32 (2), 26–33.

Zhang, P., 1994. Research of the environmental background values of soil in Xizang. Sci. Geograph. Sin. 14 (1), 49–55.

Zhang, R.J., Zou, H., Shen, Z.X., Wang, W., 2007. Size distribution of Chemical characteristics of aerosol at Lijiang of Yunnan province. Plat. Meteorol. 26 (6), 1319–1323.

Zhao, Y.N., Wang, Y.S., Wen, T.X., Yang, Y.J., Li, W., 2009. Observation and analysis on water-soluble inorganic chemical composition of atmospheric aerosol in Gongga Mountain. Environ. Sci. 30 (1), 9–13.