Atmospheric pollution for trace elements in the remote high-altitude atmosphere in central Asia as recorded in snow from Mt. Qomolangma (Everest) of the Himalayas

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ABSTRACT

A series of 42 snow samples covering over a one-year period from the fall of 2004 to the summer of 2005 were collected from a 2.1-m snow pit at a high-altitude site on the northeastern slope of Mt. Everest. These samples were analyzed for Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Sb, Pb, and Bi in order to characterize the relative contributions from anthropogenic and natural sources to the fallout of these elements in central Himalayas. Our data were also considered in the context of monsoon versus non-monsoon seasons. The mean concentrations of the majority of the elements were determined to be at the pg g^{-1} level with a strong variation in concentration with snow depth. While the mean concentrations of most of the elements were significantly higher during the non-monsoon season than during the monsoon season, considerable variability in the trace element inputs to the snow was observed during both periods. Cu, Zn, As, Cd, Sb, and Bi displayed high crustal enrichment factors (EF$_c$) in most samples, while Cr, Ni, Rb, and Pb show high EF$_c$ values in some of the samples. Our data indicate that anthropogenic inputs are potentially important for these elements in the remote high-altitude atmosphere in the central Himalayas. The relationship between the EF$_c$ of each element and the Al concentration indicates that a dominant input of anthropogenic trace elements occurs during both the monsoon and non-monsoon seasons, when crustal contribution is relatively minor. Finally, a comparison of the trace element fallout fluxes calculated in our samples with those recently obtained at Mont Blanc, Greenland, and Antarctica provides direct evidence for a geographical gradient of the atmospheric pollution with trace elements on a global scale.

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1.   Introduction

Greenland and Antarctic snow and ice records have provided historical indications of changes in the occurrence of toxic trace elements in the atmosphere in response to anthropogenic emissions of such elements. Among the most interesting results is the oldest hemispheric scale atmospheric pollution in the Northern Hemisphere for Pb and Cu during the Greco-Roman times, two millennia before the Industrial Revolution, especially due to ancient mining and smelting activities (Hong et al., 1994, 1996; Rosman et al., 1997). The atmospheric pollution from the mid-1700s to present times has also been documented for various heavy metals, including Pb, Cd, Cu, and Zn (Murozumi et al., 1969; Boutron et al., 1991; Candelone et al., 1995), Hg (Boutron et al., 1998), Pt, Pd and Rh (Barbante et al., 2001a). Reliable Antarctic snow and ice records have provided evidence that the natural cycles of trace elements such as Cr, Cu, Zn, Ag, Pb, Bi, and U have been greatly perturbed in the recent decades even in the remote Antarctic atmosphere. This is primarily due to the long-range transport of manmade pollutants from the surrounding source areas such as South America, South Africa, and Australia (Rosman et al., 1994; Wolff and Suttie, 1994; Wolff et al., 1999; Planchon et al., 2002, 2003; Vallelonga et al., 2002).

Although data obtained from Greenland and Antarctic snow and ice have shown that environmental pollution by trace elements has become global, the spatial data on the occurrence of trace elements in temperate to low-latitude snow and ice are required to better characterize the extent of human impact on natural geochemical cycles of these elements. Recently, several studies have reported changes in the occurrences of trace elements related to human activities in dated snow and ice from the Alps and high-altitude Bolivian ice cap (Van de Velde et al., 1999b, 2000a, b; Rosman et al., 2000; Barbante et al., 2001a,b, 2002; Schwikowski et al., 2004; Hong et al., 2004a).

Our understanding of the changing occurrence of trace elements in snow and ice from mid-latitude areas in Asia is of special interest, because the rapid economic growth and industrialization have occurred during the past decades, resulting in elevated levels of anthropogenic pollutants in the atmosphere (Lelieveld et al., 2001; Fang et al., 2005). Indeed, Asia is now the single largest source of anthropogenic trace element emissions to the atmosphere in the world (Pacyna and Pacyna, 2001). Very recently, the trace elements concentrations were measured in snow and firn core samples at high high-altitude sites in the eastern Tien Shan (Li et al., 2007) and on Mt. Muztagh Ata in the eastern Pamirs in northwest China (Li et al., 2006a,b), and on Mt. Everest in the Himalayas (Kang et al., 2007; Duan et al., 2007). Such data provided aspects of changing occurrence of various trace elements in snow and ice from one area to another. However, available data are not sufficient to understand the perturbation of atmospheric trace element cycles in Asia, because previous studies dealt with only few elements (Al, V, Cr, Mn, Co, Cu, Zn, Pb, and Bi).

Here, we present new data on 15 trace elements (Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Sb, Pb and Bi) in successive snow pit samples on the northeastern slope of Mt. Everest in the central Himalayas, spanning a one-year time period. Our data reveal changes in concentration, fallout fluxes and the relative importance of natural and anthropogenic contributions for such elements during monsoon versus non-monsoon periods. Our data are also compared with those obtained in recent Greenland, Antarctic and Mont Blanc snow.

2.   Experimental

2.1.   Sampling site

On September 4, 2005, samples were collected at the East Rongbuk Glacier (28°01′08″N, 86°57′48″E, elevation 6576 m asl) on the northeastern slope of Mt. Everest in the central Himalayas (Fig. 1). A shallow snow pit was hand-dug by operators wearing full clean room garments and polyethylene gloves, using acid-cleaned plastic shovels. Approximately 10 cm of snow was then shaved away from the upwind wall using acid-cleaned ultra-clean low-density polyethylene (LDPE) scrapers. A continuous series of 42 snow samples were collected from the snow surface to a depth of 2.1 m at 5-cm intervals, by horizontally pushing an ultra-clean cylindrical Teflon container (5 cm in diameter, 35 cm in length) into the wall of the pit using an acid-cleaned LDPE hammer. The samples were then immediately transferred into ultra-clean 500 mL LDPE bottles. Extreme care was taken during collection, handling, and storage to minimize contamination. All equipment used for the sampling had been cleaned as described by Hong et al. (2000). All bottles were packed in double sealed acid-cleaned LDPE bags and were kept frozen until analysis.

2.2.   Analytical procedures

The samples were melted at room temperature inside class 10 clean benches in a class 1000 clean room at the Korea Polar Research Institute (KOPRI). Aliquots were then taken for various analyses with different analytical instruments installed in the class 100 clean chemistry laboratories available at KOPRI, and for oxygen isotopes at another institute.

Concentrations of V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Sb, Pb, and Bi were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Perkin Elmer Sciex, ELAN 6100) at KOPRI. All aliquots were acidified to 1% with Fisher "Optima" grade ultra-pure HNO_3. A quartz cyclonic spray chamber, a micro micro-flow nebulizer, a Pt sampler cone and a Pt skimmer cone were employed to enhance peak sensitivity. Tube and sample introduction system cleaning were carried out for at least 3 days using ultra-pure 5% and 1% HNO_3 solutions to reduce the blank level of each element. The instrument was optimized to obtain the maximum sensitivity and extended stability using a solution of 10 pg g^{-1} In; the maximum sensitivity varied between 10,000 and 20,000 counts s^{-1} (cps).

Detection limits, defined as three times the standard deviation on the five measurements of blank solution (1% (v/v) HNO_3 ultra-pure water solution), are reported in Table 1. A riverine water reference (SLRS-4, Riverine Reference Material for
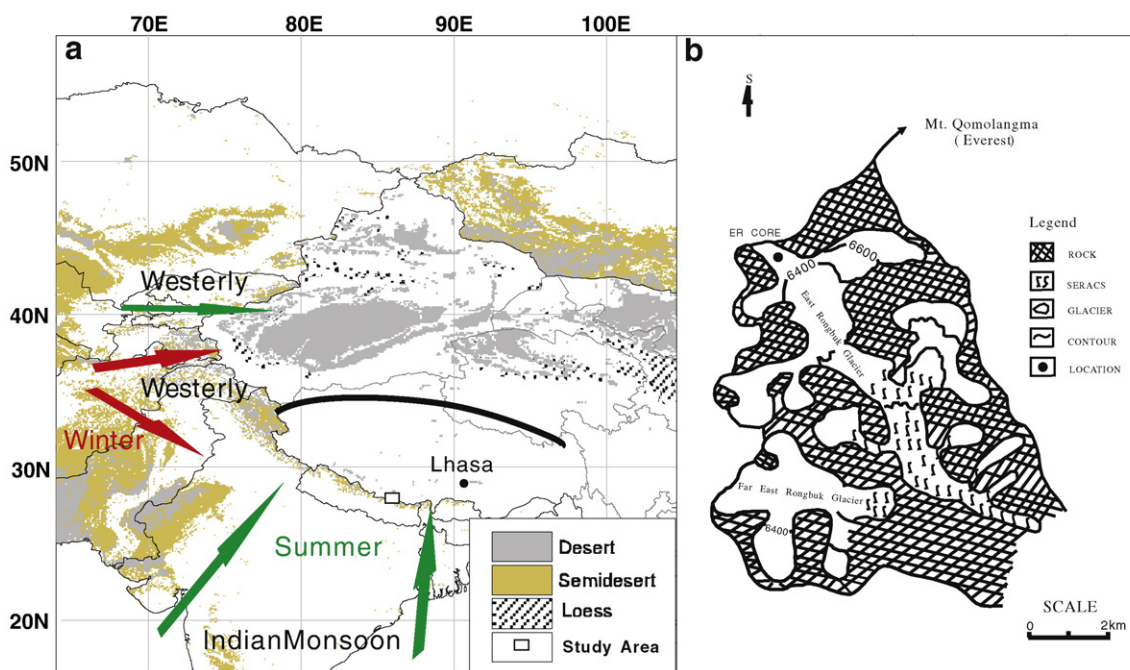
Fig. 1 – (a) Location map of the study area in the central Himalayas and distribution of dust sources and general patterns for winter and summer circulation systems. The thick line represents the northern border of the summer monsoon (34°–35°N in the middle of the plateau). (b) Map of the ER Glacier showing the snow pit site.

Trace Metals, National Research Council Canada, Ottawa, Canada) was used for quality control of the data, and good agreement between our data and the certified values was observed for most elements (Table 1).

Al contents were determined by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) using a Perkin Elmer 4110ZL instrument equipped with a Zeeman background corrector at KOPRI, and the precision was estimated to be better than ±5% at high concentration levels (Hong et al., 2000).

Na^+, Ca^{2+}, and SO_4^{2-} were analyzed with a Dionex 320 ion chromatograph, using a CS 12 column for cations and an AS 11 column for anion at KOPRI. Analytical precision ranged between 5% and 10%.

Oxygen isotope ratios were measured by Stable Isotope Ratio Mass Spectrometer (GV Instruments, Optima) at the Korea Basic Science Institute.

2.3. Assignment of seasonality to snow deposits

Our snow samples were dated by combining the depth profiles of oxygen isotopes ($\delta^{18}O$), major ions (Ca^{2+} and SO_4^{2-}) and Al content (as a reference element of the mineral dust) showing a very strong difference in concentrations between monsoon and non-monsoon seasons.

In the southern Tibetan Plateau, the seasonal distribution of $\delta^{18}O$ present in precipitation is characterized by more depleted $\delta^{18}O$ levels during the summer monsoon season, and enriched $\delta^{18}O$ levels during the non-monsoon period (Kang et al., 2000, 2002a; Tian et al., 2003). Such a seasonality of $\delta^{18}O$ in the precipitation is strongly related to varying moisture contributions from southerly air masses during the summer monsoon season and westerly air masses during the non-monsoon seasons (fall, winter and spring).

Glaciochemical studies of snow and ice in the central Himalayas have also revealed seasonal differences in major ions (e.g. Ca^{2+} and SO_4^{2-}) related to the influx of mineral dust between monsoon and non-monsoon seasons (Shrestha et al., 2000; Kang et al., 2004). Concentrations of major inorganic ions are enhanced during the non-monsoon period due to the strong influence of dust from central Asia, while they are low

Element	Mass no.	Detection limit	This study	Certified
V	51	1.6	0.37±0.01	0.32±0.03
Cr	53	5.9	0.37±0.01	0.33±0.02
Mn	55	2.8	3.48±0.12	3.37±0.18
Co	59	0.5	0.046±0.001	0.033±0.006
Ni	60	1.5	0.96±0.02	0.67±0.08
Cu	63	0.9	1.81±0.05	1.81±0.08
Zn	66	16.9	1.30±0.08	0.93±0.10
As	75	1.3	0.78±0.03	0.68±0.06
Rb	85	0.4	1.60±0.05	–
Sr	88	0.4	29.6±1.1	26.3±3.2
Cd	114	0.5	0.014±0.001	0.012±0.002
Sb	121	0.5	0.251±0.010	0.23±0.04
Pb	208	0.3	0.078±0.002	0.086±0.009
Bi	209	0.1	0.0028±0.0002	–

Table 1 – Detection limits (pg g^{-1}) calculated from 3σ of 5 replicates of blank solution and analytical results (ng g^{-1}) of certified reference material SLRS-4

during the monsoon season in response to the moisture originating from the Indian Ocean and increased regional precipitation, both of which can dilute the concentration levels of such ions.

In our snow samples, very characteristic patterns for $\delta^{18}O$, Ca^{2+}, SO_4^{2-}, and Al were well defined, as indicated in Fig. 2. The highest $\delta^{18}O$ values were found at the 0–5 cm and 185–190 cm depth intervals. When considering that the snow samples were collected on September 4, 2005, the second $\delta^{18}O$ maximum value at 185–190 cm was assigned to the winter layer in 2004/2005. The snow layers with more depleted $\delta^{18}O$ values, occurring below 200 cm, likely represent the fall of 2004. The concentration profiles of Ca^{2+}, SO_4^{2-}, and Al show relatively low values from the top to a depth of 115 cm, which is related to monsoon snow deposition following the striking peaks of Ca^{2+} and Al at the depth intervals at 115–125 and 190–200 cm, which represents non-monsoon snow layers. Much higher SO_4^{2-} concentrations are observed at the depth intervals below 160 cm.

Combining well-defined $\delta^{18}O$, Ca^{2+}, SO_4^{2-}, and Al concentration profiles, we can divide our snow pit layers into a non-monsoon period and a summer monsoon period as marked by a dashed line in Fig. 2, which covers approximately one full year of snow accumulation, from the fall of 2004 to the summer of 2005. Our dating is in general agreement with the mean snow accumulation rate of 50 cm water equivalent per year (cm w.e.a^{-1}), which is estimated from an ice core at the same site, and an annual precipitation of 65 cm w.e.a^{-1} reported by the closest meteorological station at Nyalam (Tian et al., 2003; Xu et al., 2007).

3.   Results and discussion

3.1.   Characteristics of the data

The concentrations of 14 trace elements determined in the 42 depth intervals are shown in Fig. 3, which indicate the depth profiles of the observed variations in concentrations of the measured elements. To the best of our knowledge, some of these elements have never been determined in successive snow pit samples collected at a high-altitude location in the Himalayas.

The concentration ranges and the ratios between maximum and minimum concentrations for each element are summarized in Table 2. The concentration levels differ by orders of magnitude from one element to another, with the highest concentrations at the ng g^{-1} level for Al, Mn, Zn, and Rb, and the lowest concentrations at the sub-pg g^{-1} level for Sb and Bi. The ratios between maximum and minimum concentrations range from 5 for Cd to 341 for Bi, indicating a stark variation in concentration with depth (Table 2).

Mean measured concentrations in all samples varied between 1.2 pg g^{-1} for Sb and 121 ng g^{-1} for Al (Table 2). When compared with previous reliable data, which were obtained from the firn core (28°03′N, 86°96′E, 6518 m asl) from the col of the East Rongbuk Glacier on the northern slope of Mt. Everest, our mean concentration values tend to be at a similar level, despite difference in time periods investigated (Table 3).

To compare the relative concentrations between monsoon and non-monsoon seasons, the mean concentrations of monsoon and non-monsoon snow, as determined in Fig. 2, were calculated, and are provided in Table 2. They indicate the seasonal differences in the concentrations for the measured elements. The non-monsoon concentration levels of most of the measured elements (except for Cr and Cd) are more than two-fold higher compared to monsoon values. This agrees well with documented values for major inorganic ions, for which the concentrations are higher in non-monsoon snow due to the strong influence of crustal dust from central Asia (Thompson et al., 2000; Kang et al., 2004; Xu et al., 2007).

3.2.   Depth profiles of changes in heavy metal concentrations

In our snow pit profiles, a striking feature is that the enhanced concentration levels of trace elements appear to be linked to the pronounced Al peaks (Fig. 2), originating from the mineral dust in both non-monsoon and monsoon snow layers. As depicted in Fig. 3, distinct concentration peaks at the 115–125 cm depth
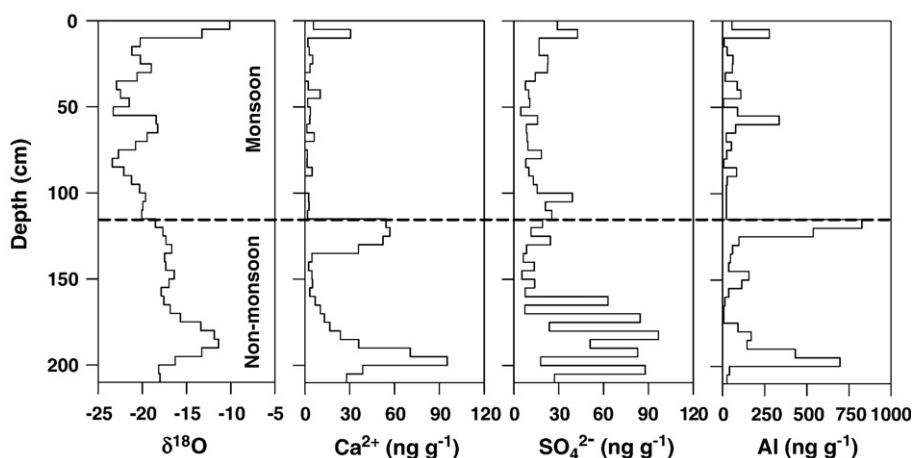

Fig. 2 – Depth profiles of $\delta^{18}O$, Ca^{2+}, SO_4^{2-}, and Al concentrations in the snow samples from a 2.1-m snow pit on the northern slope of Mt. Everest. Dotted line represents the seasonal boundary between monsoon and non-monsoon seasons.
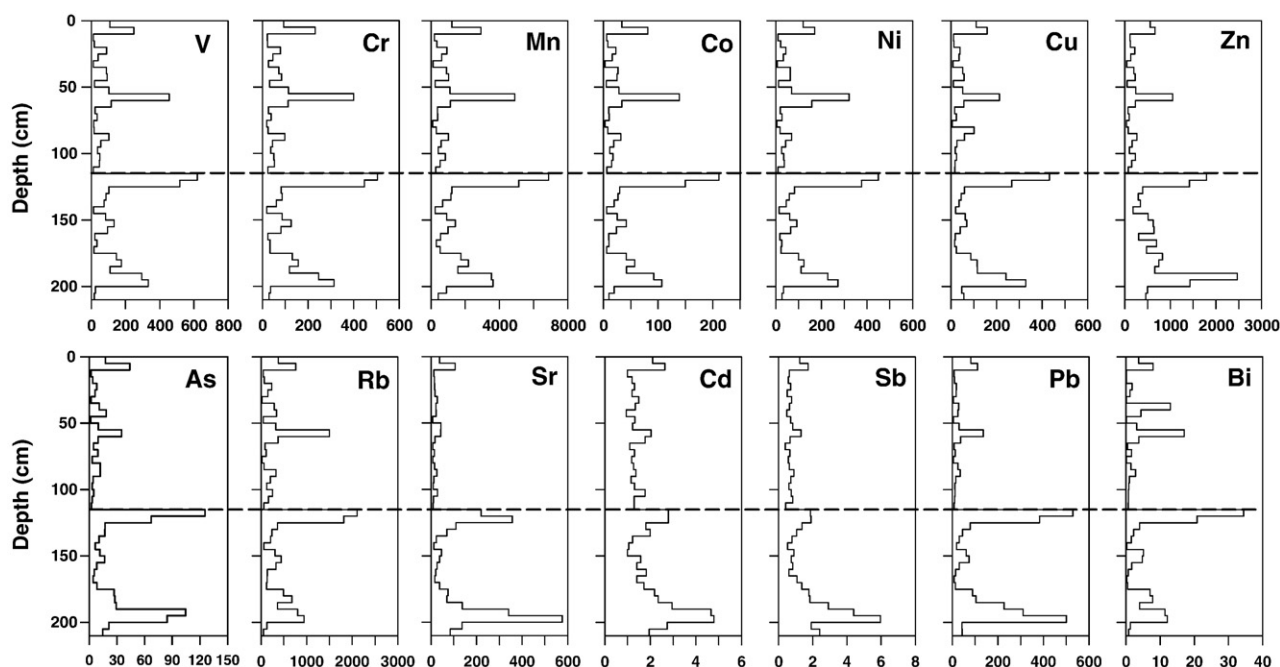
Fig. 3 – Depth profiles of V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Sb, Pb, and Bi concentrations (pg g^{-1}) measured in our snow pit samples from Mt. Everest in the central Himalayas. Dotted line represents the seasonal boundary between monsoon and non-monsoon seasons as indicated in Fig. 2.

interval, corresponding to the non-monsoon period, are observed for all measured elements, except for Cd and Sb. The profiles of elements such as Zn, As, Sr, Cd, Sb, and Pb show noticeable concentration peaks in the snow layer at 190–200 cm depth interval, which is also associated with non-monsoon period (Fig. 2). Higher concentrations of V, Cr, Mn, Co, Ni, and Cu are also observed at this depth interval.

For the snow layers deposited during the monsoon period, clear enhancements in the concentrations are observed at 55–60 cm for V, Cr, Mn, Co, Ni, Cu, Zn, Rb, and Bi. For As and Pb, these peaks are relatively less pronounced. Bi also displays an elevated concentration level at the 35–40 cm depth interval, and the remaining measured elements show slightly enhanced concentrations at 5–10 cm.

From our depth profiles of trace element concentrations, it appears that although the mean non-monsoon concentrations of the majority of the measured trace elements are significantly higher than the mean monsoon concentration, variability in the trace element input occurs in both the non-monsoon and the monsoon seasons in the remote high-altitude atmosphere on Mt. Everest. This is likely associated with local parameters controlling transport and input of such elements, as discussed in Section 3.4.

3.3. Estimates of natural versus anthropogenic contributions

Trace elements in the atmosphere originate from natural sources such as rock and soil dust, sea-salt spray, volcanoes, wild forest fires and continental and marine biogenic sources (Nriagu, 1989). On a global scale, however, the emissions of trace elements into the atmosphere from various manmade sources are known to exceed those from natural sources (Nriagu and Pacyna, 1988; Nriagu, 1989). The degree to which elements are introduced from rock and soil dust can be assessed by calculating a crustal enrichment factors (EF$_c$). EF$_c$ is defined as the concentration ratio of a given element to that of Al (which is a good approximation of rock and soil dust), normalized to the

Table 2 – A statistical summary of heavy metal concentrations determined in 42 snow samples from a 2.1-m snow pit on Mt. Everest

Metal	Concentration (pg g^{-1})					
	Min	Max	Max/ Min	Mean value		
				All samples	Monsoon	Non-monsoon
Al[a]	6	827	150	121	66	187
V	11	620	55	111	78	153
Cr	19	505	26	104	76	138
Mn	102	6884	68	1302	895	1794
Co	3	211	83	36	24	49
Ni	4	450	113	85	60	116
Cu	6	432	78	76	49	109
Zn	39	2469	64	475	225	778
As	2	125	83	20	10	32
Rb	20	2106	104	372	258	510
Sr	8	576	75	70	23	126
Cd	1	5	5	2	1	2
Sb	0.4	6	15	1	1	2
Pb	5	530	118	77	28	137
Bi	0.1	34	341	5	3	6

[a] Concentrations in ng g^{-1}.

Table 3 – Comparison of our mean concentration values with previous reliable data obtained at the same location																
	Year	Altitude (m)	Mean concentration (pg g^{-1})													
			Al[a]	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Cd	Sb	Pb	Bi
This study (28°01′N, 86°57′E)	2004–2005	6576	121	111	104	1302	36	85	76	475	20	372	70	2	1	77	5
Everest firn core[b] (28°03′N, 86°96′E)	1999–2002	6518	38	75	101	2043	37	–	–	–	32	–	–	–	–	–	4

[a] Concentrations in ng g^{-1}.
[b] From Kang et al. (2007).

same concentration ratio characteristic of the upper continental crust. For example, the EF_c for V is thus:

$$EF_c = \frac{(V/Al)_{snow}}{(V/Al)_{crust}}.$$

Here, we have used the data for the upper continental crust given by Wedepohl (1995). The primary uncertainty in these calculations is attributed to the differences between chemical composition of local soil and reference crustal composition. EF_c values should therefore be qualitatively used in evaluating the relative contribution from rock and soil dust. If the calculated values of EF_c are near unity, rock and soil dust is a dominant source for the element. Conversely, if EF_c values are larger than unity, important contribution from other natural or anthropogenic sources is indicated.

Fig. 4 shows the mean values and the ranges of crustal enrichment factors for the measured trace elements. The average EF_c values are observed to be highly variable between elements, with the lowest value determined for Sr (0.2) and the highest determined for Cd (38). The mean values of EF_c are relatively lower for V, Cr, Mn, Co, Ni, Rb, Sr, and Pb, (all less than 5), indicating that for these metals, the contribution from rock and soil dust is likely important. For Cu, Zn, As, Cd, Sb, and Bi, the mean EF_c values range from 6 to 38, and such elements are considered moderately to highly enriched, representing an important contribution from other natural sources or anthropogenic sources (Barbante et al., 2003; Hong et al., 2004a). The wide range of EF_c values for each element is an indicator of the differences in crustal contributions from one sample to another.
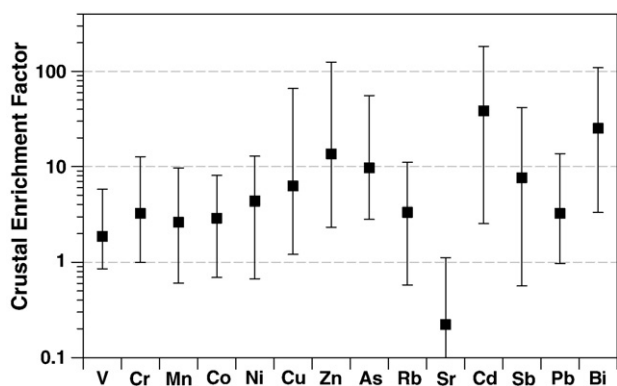

Fig. 4 – Mean crustal enrichment factors for 14 metals in our snow pit samples from Mt. Everest in the central Himalayas. The bars show the ranges in EF_c values on a logarithmic y-scale.

Volcanoes are significant sources of trace elements in the atmosphere. The contribution from volcanic emissions has been tentatively estimated from the concentration of non-sea-salt sulphate (nss-SO_4^{2-}), assuming that approximately 10–15% of nss-SO_4^{2-} originated from volcanoes (Boutron and Patterson, 1986). However, this approach for estimating volcanic input is not appropriate for our samples, as nss-SO_4^{2-} at higher altitudes of the central Himalayas is primarily of crustal origin (Wake et al., 1993; Marinoni et al., 2001). Although our data do not allow us to make quantitative estimates of the volcanic contribution, recent studies have demonstrated that volcanic emissions could be a significant natural source of As, Cd, and Bi during the late Quaternary period (Hong et al., 2004b, 2005; Gabrielli et al., 2005). Since the lowest EF_c values are above 2 for these metals in our samples, it is likely that volcanic contributions for these elements were significant.

The contribution from sea-salt spray can be evaluated from Na concentrations measured in each sample (after correction for Na contributed from rock and soil dust) and the element to Na ratios in surface ocean waters. We observed that all Na in our snow samples was crustal in origin, and thus, the sea-salt spray contributions are negligible.

Other possible sources for introduction of trace elements include wild forest fires and continental and marine biogenic sources (Nriagu, 1989). The contributions from these sources cannot be estimated from our data. However, based on the inventory of atmospheric emissions of trace elements from natural sources (Nriagu, 1989), it is likely that such contributions cannot explain the significantly high EF_c values observed for elements in our samples.

Overall, a large fraction of elements such as Cu, Zn, As, Cd, Sb, and Bi excess above rock and soil dust contribution in our samples is likely of anthropogenic origin. For Cr, Ni, Rb and Pb, for which high EF_c values are shown in some of the samples, anthropogenic inputs appear partly important (Fig. 4). Thus, our observations suggest that the atmospheric cycles of these elements are influenced by human activities, even in the high-altitude atmosphere in the central Himalayas.

Recently, Pacyna and Pacyna (2001) assessed the global and regional emissions of anthropogenic trace elements to the atmosphere from specific source categories. In Asia, fossil fuel combustion is a major source of Cr, Ni, and Sb, while non-ferrous metal production is the largest source of atmospheric Cu, Zn, As, and Cd. Combustion of leaded, low-leaded, and unleaded gasoline is the dominant contributor to the emission of Pb. Furthermore, Rb and Bi, two metals that have not been studied by Pacyna and Pacyna (2001), are likely input by biomass burning and fossil fuel combustion, respectively (Plessow et al., 2001; Morawska and Zhang, 2002).

3.4. Changes in anthropogenic contributions between monsoon and non-monsoon

Previous studies have documented that the temporal changes in snow chemistry at high altitudes are strongly related to monsoon and non-monsoon seasons (Marinoni et al., 2001; Balerna et al., 2003; Kang et al., 2004, 2007). To identify the seasonality of anthropogenic contributions to Cr, Ni, Cu, Zn, As, Rb, Cd, Sb, Pb, and Bi in our samples, the EF_c values of a specific element in each sample were plotted against the concentration of Al (Fig. 5). As discussed, Al concentration is a reliable measure of crustal dust, which exhibits low concentrations in the Himalayan atmosphere during summer monsoon season and high concentrations during the winter to spring non-monsoon seasons (Thompson et al., 2000; Kang et al., 2004, 2007; Xu et al., 2007).

As evident from Fig. 5, most of the elements show high EF_c values at low Al concentrations and low EF_c values at high Al concentrations in both monsoon and non-monsoon seasons, when Al concentrations are below 200 ng g^{-1}. However, Pb and Bi exhibit a less obvious relationship. Such patterns indicate that the anthropogenic contributions to the inputs of these elements become significant during both monsoon and non-monsoon seasons, when the levels of atmospheric loading of crustal dusts are low.

The seasonal patterns of the air mass trajectories that dominate in the central Himalayas are well characterized with respect to both monsoon and non-monsoon seasons (Fig. 1). During the summer monsoon season, air masses move from the south, which brings moisture from the Indian Ocean. During the winter, the westerly winds feed the moisture, which originates in the northern Atlantic Ocean and is augmented by evaporation from the Mediterranean Sea (Thompson et al., 2000). The loading of crustal species in the atmosphere of the Himalayas in spring is generally highest in response to the strong influence of Asian dust (Wake et al., 1994). Such mechanisms controlling atmospheric circulation in the central Himalayas are well

illustrated by snow and ice records retrieved from that region. The highest concentrations of crustal components have been measured during the non-monsoon season, while the lowest have been measured during the summer monsoon season (Thompson et al., 2000; Kang et al., 2002b, 2007; Xu et al., 2007).

Based on a seasonal difference in air mass trajectories that are dominant during monsoon and non-monsoon seasons in the central Himalayas, the inputs of anthropogenic trace elements to snow during the summer are related to local and regional transport from South Asia, including India, Bangladesh and Nepal. In contrast, during the non-monsoon season, both local and long-range transports of anthropogenic pollutants from distant western areas (likely inclusive of the Mediterranean region) are likely to influence the atmospheric chemistry in the central Himalayas.

3.5. Comparison of trace element concentrations and fallout fluxes with other data

To understand the current situation of the input of trace elements to the snow at high altitude in the central Himalayas, we compared our concentration levels with those observed in recent Greenland and Antarctic snow (as representative areas remote from the anthropogenic pollutant sources) and in recent Mont Blanc snow in the central Europe (as a representative area close to the pollutant sources). Since the concentrations of elements in the snow could be dependent upon snow accumulation rates, the trace element fallout fluxes were also calculated by combining the annual mean concentration of each element with an annual mean snow accumulation rate (expressed in g H$_2$O cm^{-2} yr^{-1}) at each site. The annual mean concentrations and fallout fluxes of heavy metals in recent snow samples, reported by others, are listed in Table 4. Rb and Sr are not listed in Table 4, since no data were available at the other sites.

As indicated, mean concentration levels of crustal elements (Al, V, Mn and Co) at Mt. Everest are comparable to
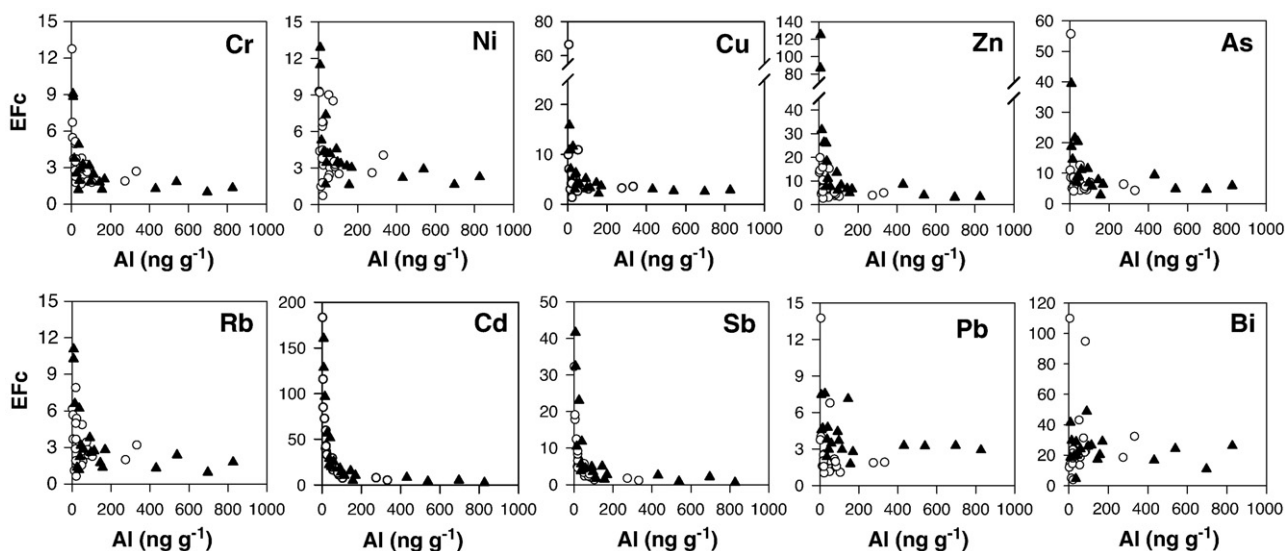

Fig. 5 – Crustal enrichment factor (EF$_c$) versus Al concentration plot for each metal with moderate to high EF$_c$ values in our snow pit samples. Open circles represent the data corresponding to summer monsoon season and full triangles to non-monsoon season as indicated in Fig. 2.

Table 4 – Comparison with the data of annual mean concentrations (in pg g⁻¹) and fallout fluxes (pg g⁻¹ cm⁻² yr⁻¹) in recent snow at various sites

Location	Time period investigated	Altitude (m)	Accumulation rate (g H_2O cm⁻² yr⁻¹)		Al[a]	V	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb	Bi
This study	2004–2005	6576	84[b]	Mean concentration	121	111	104	1302	36	85	76	475	20	2	1	77	5
				Fallout flux	10,164	9324	8736	109,368	3024	7140	6384	39,900	1680	151	101	6468	378
Mont Blanc, France[c,d,e,f,g]	1990–1991	4304	350	Mean concentration	72	203	160	1451	207	130	79	626		5	14	572	2
				Fallout flux	25,200	71,050	56,000	507,850	72,450	45,500	27,650	219,100		1750	4900	200,200	700
Greenland[h]	1991–1995	3270	23	Mean concentration	7				6		5	51		1	1	17	3
				Fallout flux	168				133		108	1173		28	18	391	58
Antarctica[i]	1998–2002	1850	29	Mean concentration	0.2	0.5	2[j]	4	7		5	4[j]	10	0.2		4	0.03
	1983–1986[j]	1500[j]	5.6[j]	Fallout flux	5	13	9[j]	108	197		155	21[j]	289	6		117	0.81

[a] Mean concentrations in ng g⁻¹ and fallout fluxes in ng g⁻¹ cm⁻² yr⁻¹.
[b] Mean snow accumulation rate estimated by an assumption of mean snow density of 0.4 g cm⁻³.
[c] Van de Velde et al. (1999b).
[d] Van de Velde et al. (2000b).
[e] Rosman et al. (2000).
[f] Barbante et al. (2002).
[g] Van de Velde (1999a).
[h] Barbante et al. (2003).
[i] Hur et al. (2007).
[j] Planchon et al. (2002).

those at Mont Blanc, but fallout fluxes are significantly lower at Mt. Everest, indicating larger dust contributions at Mont Blanc. On the other hand, the concentrations and fallout fluxes of these elements in our samples are three and four orders of magnitude higher than those determined in Greenland and Antarctica, respectively. This situation is due to the relative proximity of Mt. Everest to dust sources, compared to Greenland and Antarctica.

The situation is very different for elements for which anthropogenic contributions are important, including Cr, Ni, Cu, Zn, As, Cd, Sb, Pb, and Bi, all of which display moderate to high enrichment (Table 4). Concentration levels of Cr, Ni, Cu, and Zn in our samples show comparable values to those observed in Mont Blanc snow, but fallout fluxes are one order of magnitude lower than those at Mont Blanc. When compared with the data from Greenland and Antarctica, however, our samples show values that are one or two orders of magnitude higher for concentrations, and up to three orders of magnitude higher for fallout fluxes. Our Pb concentration value is one order of magnitude smaller than that reported for Mont Blanc snow, and greater than in Antarctica, while they are comparable with those measured in Greenland. The situation is similar for Sb, for which our mean concentration level is lower than that at Mont Blanc, but comparable to that in Greenland. Fallout fluxes of Sb and Pb are the highest at Mont Blanc, which is expected due to higher snow accumulation rates and proximity to possible anthropogenic sources. The concentration levels of Cd and Bi at Mt. Everest are similar to those at Mont Blanc and Greenland. However, fallout fluxes are lower relative to Mont Blanc, and greater relative to Greenland and Antarctica, likely due to the differences in snow accumulation rates. Finally, as shown in Table 4, the mean concentration of As reported for recent Antarctic snow is similar to our samples, while the As fallout flux is approximately six-fold higher at Mt. Everest than in Antarctica.

Overall, fallout fluxes of anthropogenically-derived trace elements at Mt. Everest are higher than those observed in recent Greenland and Antarctic snow, while they are lower than those at Mont Blanc. Together with the high EF_c values observed for such elements in our snow samples, our comparison of fallout fluxes clearly suggests that the high-altitude atmosphere in the central Himalayas has been polluted.

Our observations are in disagreement with recent suggestion by Kang et al. (2007) that anthropogenic contributions to the high-altitude Mt. Everest atmospheric environment were negligible. Their conclusion was mainly based on the fact that the concentration levels of trace elements at Mt. Everest were comparable with those observed in recent Arctic and Antarctic snow samples, without considering the large differences in snow accumulation rates at each site. Further, they compared their concentration levels to those observed in surface snow samples collected during a traverse along a 2200 km route in East Queen Maud Land, Antarctica (Ikegawa et al., 1999). Similarly, we suspect that the data reported by Ikegawa et al. (1999), may have suffered from severe contaminations during field sampling, laboratory analysis, or both, due to incomplete use of ultra-clean procedures such as those previously described (Patterson and Settle, 1976; Boutron, 1990; Hong

et al., 2000). In fact, portions of their data are unexpectedly high, with Pb values up to 1000 pg g^{-1} and Zn values up to 500 pg g^{-1}; most concentration values recorded for Pb and Zn in recent Antarctic snow are below 10 pg g^{-1} (Boutron et al., 1990; Suttie and Wolff, 1992; Wolff et al., 1999; Planchon et al., 2002; Hur et al., 2007).

Further studies of the changes in the trace element concentrations in snow and ice at different sites on the Tibetan Plateau will be necessary to characterize their seasonal occurrences, and to better assess the degrees of contribution of anthropogenic pollution for trace elements in central Asia. Determination of Pb isotopic compositions in snow and ice archives would also be valuable as tracers to confidently identify the differing natural and anthropogenic contributions to the fallout of Pb in this region.

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