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Elemental composition of aerosols collected in the glacier area on Nyainqêntanglha Range, Tibetan Plateau, during summer monsoon season

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In order to investigate the elemental composition in atmospheric aerosols and its sources in the glacier area over the Tibetan Plateau (TP), seven totally suspended particle samples were collected continuously at the col of the Zhadang glacier (30°28'N, 90°39'E, 5800 m a.s.l.), Nyainqêntanglha Range, southern TP, from June to October 2006. Twenty-seven elements (Li, Be, B, Na, Mg, Al, K, Ca, Sc, Ti, V, Fe, Mn, Zn, Ga, As, Rb, Sr, Y, Cd, Cs, Ba, TI, Pb, Bi, Th, U) were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The result indicates that the concentrations of most elements (especially crustal elements) are lower than values at the Nam Co Station during the same period of 2005, and also much lower than other sites in the TP such as Wudaoliang and Waliguan. This suggests that elemental compositions of aerosols in the Zhadang glacier area may represent the background levels of the middle/upper troposphere over the TP. Crustal enrichment factors (EFs) reveal that several elements (e.g. B, Zn, As, Cd, Pb and Bi) may have anthropogenic sources. The southern TP is mainly influenced by the summer Indian monsoon during the sampling period. Backward air mass trajectory analysis suggests that air masses in the region may originate from South Asia. Therefore, anthropogenic pollutants from South Asia may be transported by the summer Indian monsoon to the region which clearly affects the atmospheric environment in the southern TP during the summer monsoon season.

Nam Co, Tibetan Plateau, aerosol, elements, air pollutants

Aerosol is significant in the global climate change processes. It affects both atmospheric composition and radiative balance of the land surface, as well as the surface biological productivity of the ocean and the air-sea CO₂ exchange by means of depositing large amounts of mineral nutrients into the Ocean^[1,2]. The background value of aerosols from high elevations can also act as valuable data for validating global atmospheric models. In addition, anthropogenic pollutants absorbed on aerosols can be transported for a long distance^[3]. The status of global industrial pollution and evaluation of environmental quality can be revealed by heavy metal concentrations from remote and high elevation region^[4]. Anthropogenic heavy metal contaminations have been discovered from ice/snow and aerosols in both polar regions^[5–7]. Tibetan Plateau (TP), as the third polar region, has very sparse anthropogenic activities and thus is to be an ideal region to monitor global atmospheric environmental change, especially for low and mid latitudes. The pollutants from South Asia and Middle East have been detected in ice and snow over the TP^[4,8–10]. Chemical compositions in

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aerosols have been studied in the $TP^{[11-16]}$, among them pollutants from South Asia has been discovered in the Nam Co region during the summer monsoon season^[15].

Generally, there are two ways to investigate the background atmospheric pollutants in the TP, one is to recover atmospheric pollutants indirectly through ice and snow records, the other is to collect aerosols at relatively low place and measure the chemical composition directly. However, the latter is hard to exclude effects of very local human activities. Therefore the better way is to collect aerosol samples directly in the glacier area at high elevations, which has the advantage of reflecting large scale atmospheric condition and being far from local potential pollution sources due to high elevations^[17]. Here we present elemental compositions in aerosols collected in the Zhadang glacier on Nyaingêntanglha Range, southern TP, during summer monsoon season in 2006. The sampling site is 50 km away from the Nam Co station where a research ^[15] into aerosol composition was carried out.

1 Sampling methods and analysis

From June 25 to October 15, 2006, seven aerosol sam-

ples of total suspended particles were collected continuously on Teflon filters at the col of the Zhadang glacier (30°28'N, 90°39'E, 5800 m a.s.l.) on Nyaingêntanglha Range (Figure 1). The duration of each sample was set from one week to two weeks. The filter holder was protected with a rain cover and connected to a vacuum pump with average flow rate of 0.4 m^3/h . The pump was equipped with an automatic air mass flow meter (Taihe Automation Control and Instrument Corp.). The air volume was converted into standard condition according to the ambient conditions at the sampling site. The pump was powered by a combination of solar panel system and storage battery. Extreme cares were taken during all the operations for the purpose of avoiding any possible pollution. Blank samples also experienced the same operation as the samples. Totally 27 elements (Li, Be, B, Na, Mg, Al, K, Ca, Sc, Ti, V, Fe, Mn, Zn, Ga, As, Rb, Sr, Y, Cd, Cs, Ba, Tl, Pb, Bi, Th, U) were determined in aerosol samples by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (X-7; Thermo-elemental, USA) at the Institute of Tibetan Plateau Research, CAS. Values of all the measured elements were far higher than their relevant detection limit, which are three-fold of the



Figure 1 Location map of sampling site.

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standard deviation (S. D.) of blank samples. The accuracy and precision of the analytical protocol were evaluated by Chinese Loess Reference Material (GBW07408). The recovery rate ranged from 81% (V) to 115% (Pb). For precision, the corresponding RSD values of element concentrations measured in the reference material should be less than 5% for most elements, except 13% for Cd.

An automatic weather station (Campbell Scientific, Inc.) was set up at the col of the Zhadang glacier, which measures wind speed and direction, air temperature, relative humidity and air pressure. The measurements were done every 60 seconds, averaged into 30 minutes by the datalogger, continuously, throughout the sampling period (Table 1). During the sampling period, the average air temperature was relatively low (-0.89° C) with a large range of 23.4°C, the relative humidity varied from 15.51% to 100% and the wind speed was relatively high. The prevailing winds were from south (Figure 2), reflecting the influence of the summer Indian monsoon.

 Table 1
 Meteorological parameters during sampling period

Parameters	Accuracy	Mean	S.D.	Range
Air pressure (hPa)	±0.25hPa	504.68	1.32	499.50-508.3
Air temperautre (°C)	±0.2°C	-0.89	2.31	-13.14 - 10.28
Relativity humidity (%)	±2-3%	79.74	15.25	15.51 - 100
Wind speed (m/s)	$\pm 0.3 \text{m/s}$	5.00	2.83	0-17.1

Mean value and S.D. computed from daily mean value, range derived from the minimum and maximum of relevant parameters during sampling period.



Figure 2 Frequencies of wind direction during sampling period.

2 Results and discussion

2.1 Elemental compositions in aerosols

Mean elemental compositions in aerosols collected in the Zhadang glacier are given in Table 2. By contrast,

the data from other sites in the TP, Antarctica and Beijing are also tabulated out. Na, Mg, Al, K, Ca and Fe are the major elements of the aerosols in the Zhadang glacier. The total concentration of these six elements accounts for about 95.2% of all the measured elements. Compared with data at Nam Co station during summer monsoon season, 2005, glacier site has clear low mass concentrations of crustal elements such as Al, K, Ca, Fe and Mn, among them concentrations of Ca and Mn are only one fifth of those at Nam Co station. Research has shown that the aerosol particles at low elevations in the TP derive mainly from local dust^[14], while the atmosphere over the glacier region at high elevations is much cleaner (lower dust aerosol) than at low elevations^[21]. Therefore the results of this study prove that aerosol particles of high elevations reflect the atmospheric background in a large scale region. The concentrations of As and Zn in the glacier region are similar to those of Nam Co station, which may indicate that these two elements have been long-range transported from South Asia by Indian summer monsoon^[15], and their concentrations are consistent in atmosphere at various elevations without the effect of local dust.

Mass concentrations of all the elements in the Zhadang glacier are much lower than those of Waliguan and Wudaoliang, which may be caused by higher dust loadings at two sites^[4]. Waliguan and Wudaoliang are closer to big deserts of the northwest China than our site. Similarly, most element concentrations in the glacial region are lower than those of the south slope of the Mt. Everest. Although the sampling site on Mt. Everest is located at the southern fringe of the TP, its relatively low elevation and sparse vegetation coverage and sampling period (pre-monsoon) will induce high aerosol concentrations^[18].

Hence the atmosphere over the Zhadang glacier is very clean, which could be considered as the representative of the middle/upper troposphere of the TP. However, the element concentrations in the glacier region are significantly higher than those in Antarctica. Because Antarctica is far from human inhabits and almost covered by ice and snow. Most element concentrations are lower than those of Beijing by several orders of magnitudes because of strong dust storm and serious pollution in Beijing^[20].

2.2 Possible sources

(i) Enrichment factors. Enrichment factors (EFs) were

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Elements	Zhadang glacier				Other sites of Tibetan Plateau				Antarctic ^{e)}	Beijing ^{f)}
	Min	Max	Mean	S.D.	Nam Co ^{a)}	Waliguan ^{b)}	Everest c)	Wudaoliang ^{d)}	-	
Li	0.007	0.191	0.053	0.061						
Be	0	0.009	0.002	0.003						
В	0	2.138	0.541	0.814						
Na	0.135	43.697	12.023	13.972		541-1150		11713.72		1600
Mg	2.049	64.257	17.793	20.956	12	1430-3230	490	4118.56		2040
Al	4.91	188.125	57.071	60.308	131	2110-3410		21390.48	1.875	5330
К	2.479	96.212	26.997	30.69	82	1190-2200	392			
Ca	3.978	144.963	51.139	59.83	251	2010-4280	483			9050
Sc	0	0.035	0.01	0.011		0.52-1.4	0.16	3.83		
Ti	0.12	12.44	3.675	4.059	10	106-220	73	716.13		330
V	0	0.661	0.281	0.212	0.06	3.02-5.88	1.3		0.036	
Fe	0	69.971	21.167	23.243	94	1720-3910	500	10453.67		3730
Mn	0	2.5	0.839	0.74	3.7	27.5-52.9	11.4	192.5		110
Zn	0.096	8.566	2.446	2.702	1.8	9.5-26.3	11.2		0.13	330
Ga	0	0.06	0.016	0.02				6.55	0.0005	
As	0	0.37	0.135	0.13	0.04	0.70-3.37	0.14			20
Rb	0.019	0.466	0.141	0.147		6.2-14.9	1.9	40.96	0.0062	
Sr	0.022	1.279	0.317	0.42				94.36	0.684	20
Y	0.002	0.058	0.018	0.019				4.33		
Cd	0	0.043	0.009	0.014			0.04		0.0013	2.43
Cs	0.004	0.064	0.021	0.02			0.22		0.0002	
Ba	0	1.39	0.466	0.549					0.0103	
Tl	0.001	0.009	0.003	0.003					0.0002	
Pb	0.081	0.762	0.294	0.217			4.4		0.041	110
Bi	0	0.02	0.006	0.006					0.0003	
Th	0.002	0.039	0.012	0.012			0.21	2.72		
U	0.001	0.016	0.004	0.005			0.026		0.0003	

 Table 2
 Elemental concentrations (ng/m³) in aerosols collected in the Zhadang glacier and compared with data from other sites

Tibetan Plateau

a) Aerosols collected at Nam Co station, July—October, 2005, 4718 m a.s.l.^[15]; b) aerosols collected at Waliguan, northeastern TP, 1992–1995, 3814 m a.s.l.^[11]; c) aerosols collected in the south slope of the Mt. Everest, March—May, 2002, 5100 m a.s.l.^[18]; d) aerosols collected at Wudaoliang, July—August, 1994, 4612 m a.s.l.^[16]; e) aerosols collected at Antarctic Peninsula, January, 2000—December, 2001^[19]; f) PM10 aerosols collected at Beijing Normal University, summer of 2002^[20].

originally used to investigate the element origins in Antarctic atmosphere dust^[22], which has been widely utilized in the evaluation of heavy metals in environmental geochemistry. Generally, Al was selected as the reference material for EF calculation. Taylor and McLennan's^[23] average upper continental crust composition was used as the elemental composition of the crust material. EFs are defined as follows:

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

where *X* represents the element of interest; EF_X the *EF* of *X*; C_X the concentration of *X*, and C_R the concentration of a reference element. In this study Al was selected as the reference material, and elements with an *EF*

higher than 10 are considered to be of anthropogenic origin^[15].

Figure 3 shows the EFs of elements in aerosol samples collected in the Zhadang glacier. Crustal elements such as Mg, Ca, Ga and Rb have EF values around one, indicating they are attributable predominantly to natural dust. Values of elements such as B, Zn, As, Cd, Pb, and Bi are greater than 10, with values of As and Cd being even higher than 100, suggesting these elements are affected by anthropogenic pollutants, especially for As and Cd. These enriched elements originate from a wide variety of anthropogenic sources except small quantities of natural sources. Pb emitted from battery production, trash burning, smelting industry as well as the petrol



Figure 3 Enrichment factors of elements in aerosols in the Zhadang glacier area.

burning^[24]. Zn may be derived from combustion of fossil fuels, industrial metallurgical process and waste incineration^[25,26]. Cd is widely utilized in alloying, electroplating and dyeing Industries^[27]. There are still sparse industry activities on the TP while the heavy metal contamination is widely exists in big cities in South Asian. For example, concentration of anthropogenic elements in fine fraction is higher than that in the course fraction, and the fine fraction is increasing with time in Visakhapatnam of India^[28]. Meanwhile, heavy metal concentrations of aerosol in summer monsoon season in Delhi are higher than in other seasons^[28]. In addition, EF values of Cd and Pb in aerosols in Delhi are above $50000^{[24]}$, and EF values of As, Zn and Pb in Dhaka are around 1000^[29]. Therefore we suggest that the pollution elements in the glacier are mainly from these big cities. The natural dust in the TP may also have some contribution to the high As EF value because of the relatively high As concentration in the Tibetan soil^[30].

Influence of anthropogenic emissions has been detected in ice/snow and aerosols on the TP. By studies on chemical components in snow pits at different sites in the TP, Xiao et al.^[4,21] reported that spatial distribution of dust aerosol shows low loading in the south while high in the north, however, heavy metal concentrations have a reverse pattern, suggesting the heavy metals over the TP come primarily from anthropogenic sources emitting in South Asia. The former aerosol studies over the TP also support the result^[9,11,15]. The long-range transport contaminants from South Asia couldn't be discovered at Waliguan^[9] and Wudaoliang^[11], since the north extent of the summer Indian monsoon only reaches to the Tanggula Mountains in the central TP^[31]. Although heavy mental pollutants were detected at the Nam Co station during summer monsoon season^[15], the glacier site in our study seems to be more sensitive to reflecting pollutants from South Asia than Nam Co station, which is supported by higher EF values of Zn and As at the glacier site.

(ii) Transport pathways. In order to further investigate air masses transport pathways during the summer, 7-day backward trajectories (100 500, 1000 m above ground level, AGL) were computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT-4) model developed by State Oceanic Adminstration and China Meteorological Administration (http://www.arl.noaa.gov/ready/hysplit4.html). Up to 20% errors of the traveled distance are typical of those trajectories computed from analyzed wind field^[32]. Thus, calculated air mass pathways indicate the general airflow rather than the exact pathway of an air mass. Generally, most air masses come from the Bay of Bengal and Indian subcontinent during the summer monsoon season. Figure 4 is a typical backward trajectory during the sampling period, showing air masses from the Bay of Bengal passing through India and Bangladesh, and crossing the Himalaya then reaching to sampling site.

During the last two decades, South Asia has been undergoing rapid industrial and economic development, which induces fast increasing of aerosols and gaseous pollutants emissions. The air pollution in both India and Bangladesh is becoming serious^[24,33,34]. The brown cloud made of atmospheric contaminants observed in Indian subcontinent in 2002 has aroused considerable attention to air pollution in this region^[35]. It will produce multifarious impacts on agriculture and climate on local and regional scales. Recent studies have suggested that deep convection associated with the Indian summer monsoon can lift boundary layer pollution from India into the upper troposphere, and then the strong Tibetan anticyclone formed during this period will 'trap' anthropogenic emissions lifted from the northeast India into the TP directly^[36]. Besides, the contaminants in the southern slope of Mt. Everest can also be transported into the TP by means of valley wind^[37]. Moreover, studies on the precipitation stable isotope ratio in the TP revealed that the Indian summer monsoon may reach the Tanggula Mountains^[31]. These evidences indicate that pollutants derived from South Asia can be transported to the Nyaingêntanglha Range region during the Indian sum- mer monsoon season.



Figure 4 A typical HYSPLIT backward trajectory during the sampling period.

3 Conclusions

Concentrations of 27 elements of aerosols collected in the Zhadang glacier, southern TP, during the summer monsoon season were measured. Analysis results suggest concentrations of most elements, especially crustal elements, are lower than those at lower elevations of the same region during the same period and other sites in the TP. Thus the atmosphere of the glacier region is very clean during the summer, which may represent the background levels of the middle/upper troposphere.

For the first time atmospheric pollutants from South Asia are revealed by aerosol samples collected in the glacier region. These results support heavy metal pollutants in the atmosphere over the southern TP which were also detected in ice/snow in the TP. According to EF calculations, elements of B, Zn, As, Cd, Pb and Bi have high enrichment, and the EF values are higher than those at low elevations in the same region. This indicates that the glacier region reflects the pollution from South Asia more sensitively. Both relatively serious pollution status in the big cities in India and Bangladesh and air masses in the region coming predominantly from South Asia during the summer support that the atmospheric environment of the Nyainqêntanglha Range has been affected by pollutants from South Asia.

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