Atmospheric Environment 43 (2009) 4444–4452

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Concentrations, seasonal variations, and transport of carbonaceous aerosols at a remote Mountainous region in western China

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ARTICLE INFO

Article history:
Received 22 February 2009
Received in revised form
12 June 2009
Accepted 15 June 2009

Keywords:
Elemental carbon
Organic carbon
Carbonate carbon
Aerosol
Ice core
Remote atmosphere

ABSTRACT

Carbonaceous aerosol concentrations were determined for total suspended particle samples collected from Muztagh Ata Mountain in western China from December 2003 to February 2006. Elemental carbon (EC) varied from 0.004 to 0.174 μg m^{-3} (average = 0.055 μg m^{-3}) while organic carbon (OC) ranged from 0.12 to 2.17 μg m^{-3} and carbonate carbon (CC) from below detection to 3.57 μg m^{-3}. Overall, EC was the least abundant fraction of carbonaceous species, and the EC concentrations approached those in some remote polar areas, possibly representing a regional background. Low EC and OC concentrations occurred in winter and spring while high CC in spring and summer was presumably due to dust from the Taklimakan desert, China. OC/EC ratios averaged 10.0, and strong correlations between OC and EC in spring–winter suggest their cycles are coupled, but lower correlations in summer–autumn suggest influences from biogenic OC emissions and secondary OC formation. Trajectory analyses indicate that air transported from outside of China brings ~0.05 μg m^{-3} EC, ~0.42 μg m^{-3} OC, and ~0.10 μg m^{-3} CC to the site, with higher levels coming from inside China. The observed EC was within the range of loadings estimated from a glacial ice core, and implications of EC-induced warming for regional climate and glacial ice dynamics are discussed.

1. Introduction

Carbonaceous materials, comprising elemental carbon (EC, also referred to as black carbon and similar in chemical structure to graphite), organic carbon (OC, a large variety of organic compounds), and carbonate carbon (CC, an inorganic alkaline form, e.g., $CaCO_3$) (Mueller et al., 1971) are important components of the atmospheric aerosol, especially in the context of climate (Seinfeld and Pandis, 1998). While many aerosol particles (hereafter simply aerosols) cool the atmosphere by increasing the Earth's reflectivity, EC tends to warm it by absorbing both short-wave and long-wave solar radiation. As EC is essentially unreactive, it can be suspended in the atmosphere for a week or more and be transported over great distances.

The concentrations of EC in remote areas including polar regions and high-mountain areas have become of increasing interest owing to possible warming effects over snow- and ice-covered surfaces (Wolff and Cachier, 1998; Polissar et al., 1998; Lavanchy et al., 1999; Pereira et al., 2006). EC has thus been implicated as potentially playing a role in the melting of polar ice and snow (Clarke and Noone, 1985; Hansen and Nazarenko, 2004), which would be important in the context of changes in global ice volume, sea-level rise, etc. Measurements of carbonaceous aerosols in remote areas also can be used to trace the transport of pollution (Andreae, 2007).

Located in central Asia, the Tibetan Plateau is the world's highest and largest plateau, spanning an area of ~2.5 million km^2. The uplift of the Plateau caused changes in the monsoonal circulation in Asia (An et al., 2001), and several recent studies have investigated ways in which the western Tibet Plateau may affect large-scale climatic processes and the environment (Wu et al., 2006; Xu et al., 2006; Yu et al., 2006). Interest in the composition of air over the Tibetan Plateau also has increased recently, primarily in relation to studies of the South Asian Brown Cloud (Ramanathan et al., 2005; Bonasoni et al., 2008).

Most of the atmospheric chemistry studies conducted on the Tibetan Plateau have focused on its southern edge (Carrico et al., 2003; Sagar et al., 2004; Pant et al., 2006; Ming et al., 2008); in comparison, the data for other parts of the Plateau are far more

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doi:10.1016/j.atmosenv.2009.06.023

limited. Information on the atmospheric aerosol over the western part of the plateau is especially sparse, and in the case of carbonaceous aerosols, almost no data for the Plateau have been reported. The western edge of the Plateau is influenced by westerly winds, and therefore, the atmospheric circulation in that part of Plateau is distinctly different from that along its south edge (Fig. 1); so one would expect compositional differences in the air from the two parts of the Plateau.

Here we present the results of more than two years of ground-based observations of aerosol EC from Muztagh Ata (Fig. 1), a remote high-mountain site located on the western side of the Tibetan Plateau. The concentrations of the other carbonaceous species, OC and CC, also were determined. The primary objectives of this paper are (1) to characterize the seasonal variations of the carbonaceous aerosol, (2) to determine the relative contributions of EC, OC, and CC to total aerosol carbon (TC), and (3) to investigate the transport of these substances to Muztagh Ata. The integrated database from our study provides the first known information on carbonaceous aerosols from this remote area of western China.

2. Methodology

2.1. Research site

With a peak altitude of 7509 m, Muztagh Ata Mountain is located in the eastern part of the Pamir mountain range and on the western margin of the Tarim Basin. The mountain is topographically connected to the Kunlun Mountains and the Tibetan Plateau, which together compose one of the great high-altitude regions on the earth. The topography of the mountain is characterized by a gentle slope to the west and sharper gradients to the north and east. From the peak down to 5200 m, the mountain is covered by a perennial glacier. Snow and ice from the glacier sometimes extend to elevations below 4500 m. The area of snow coverage is on average about 275 km^2.

The sampling site used for our study (38°17.30′N, 75°01.38′E) is located at the Fieldwork Observation Site of the Cold and Arid Regions Environmental and Engineering Institute, Chinese Academy of Sciences. It is situated close to the snow line on the western side of the Muztagh Ata Mountain, ~4500 m above sea level (asl) (Fig. 1). The annual temperature in this area varies greatly with altitude. At the mountain's peak, the average annual temperature is ~−20 °C, while at the observation site it is ~+4 °C, with absolute extremes ranging from −20.5 to 14.5 °C. The annual precipitation, which is mainly in the form of snow, averages less than 200 mm. This area is essentially free from local sources of residential pollution, but a few farmers do use the area for grazing during summer.

2.2. Aerosol sampling and analysis

Total suspended aerosol particle (TSP) samples were collected at the Muztagh Ata site from December 5, 2003 to February 17, 2006 with the use of custom-made samplers that operated at flow rates of 16 l min^{-1}. Aerosol samples were collected on 15 mm Whatman quartz microfibre filters (QM/A, Whatman LTD, Maidstone, UK), which were pre-combusted at 800 °C for 3 h prior to use. Power for the samplers was supplied by a solar energy panel and a storage battery. Under favorable conditions, each sample filter was collected over a one-week period, but during strongly overcast conditions, the energy provided by this system was insufficient to operate the pumps. When the sampling standard volume was larger than 30 m^3, the sample was regarded as valid and analyzed. During the study period, a total of 81 valid samples was obtained successfully under these challenging conditions. The sample numbers for spring, summer, autumn, and winter were 19, 21, 14, 27 and these are sufficiently similar that seasonal trends should not be seriously biased.

The TSP samples were analyzed for OC, EC, and CC using a Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). The total aerosol deposit on each filter covered an area of about 0.78 cm^2, and a 0.5 cm^2 punch from the filter was analyzed first for eight carbon fractions following the IMPROVE (Interagency Monitoring of PROtected Visual Environments) thermal optical reflectance (TOR) protocol (Cao et al., 2003; Chow et al., 2004). Approximately 1.6–68 μg of carbon deposited on each filter was used for the TOR analysis. This procedure produced four OC fractions (OC1, OC2, OC3, and OC4 at 120 °C, 250 °C, 450 °C, and 550 °C, respectively, in a He atmosphere); OP (a pyrolyzed carbon fraction determined when reflected or transmitted laser light attained its original intensity after O_2 was added to the analyzer's atmosphere); and three EC fractions [EC1, EC2, and EC3 at 550 °C, 700 °C, and 800 °C, respectively, in a O_2/He (2%/98%) atmosphere]. The detection limit for the carbon analyzer was 0.05 μg carbon cm^{-2} for a typical punch size of 0.5 cm^2.

A separate 0.08 cm^2 punch from each filter was analyzed for its CC content and for replicates of the eight carbon fractions. From experiments investigating possible interferences of CC for the OC and EC determinations, we found that CC has almost no effect on EC, but CC did interfere slightly with the determinations of the OC4

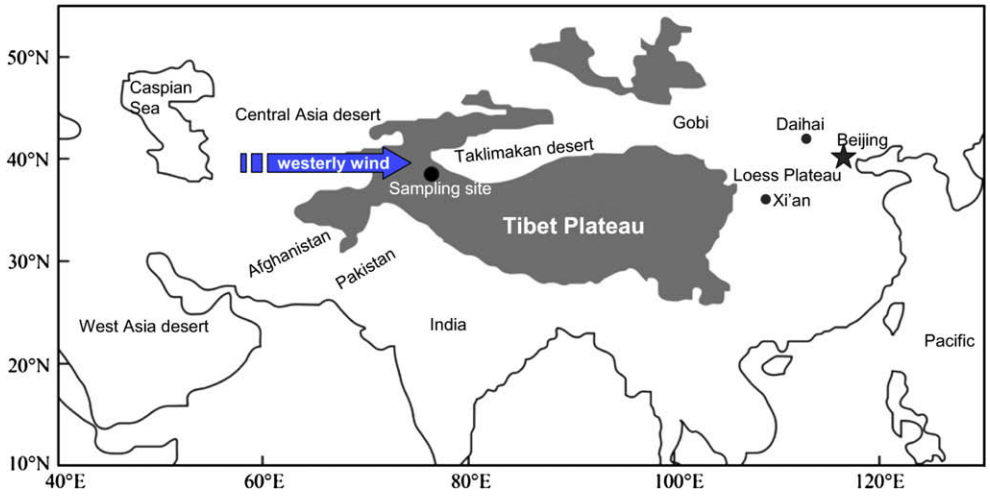

Fig. 1. Location of the Muztagh Ata Mountain sampling site in western Tibet Plateau.

fraction. To compensate for this, the OC concentrations were corrected for CC, but these corrections were small, of the order of 10%. Detailed discussion presents in Supplemented material. Quality Assurance/Quality Control (QA/QC) procedures for the EC, OC and CC analyses have been described in Cao et al. (2003, 2005).

2.3. Air-mass trajectory analysis

Aerosol concentration data typically show considerable variance, particularly in samples taken over 7 days or less. Numerous factors can influence the variability in EC, OC, and CC, but knowing the recent history of the air that was sampled can provide insights into the sources, physical processes, etc. that affected them. Temporal patterns in the concentrations of trace constituents in air are commonly evaluated with the use of back-trajectory analyses, and here we use the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT 4) model (www.arl.noaa.gov/ready/hysplit4.html) as a means of tracing the paths of the air parcels that were sampled.

Trajectories backwards-in-time were calculated up to 150 m agl (above ground level) for five days at 12:00 coordinated universal time (UTC) for each of the seven days the samples were collected. Although the effects of topographic features such as mountain-valley wind systems and the complex terrain of the Himalayas cannot be captured by the back-trajectories, they can provide insights into potential source regions, and they are useful for evaluating large-scale transport pathways. Meteorological factors, such as variations in the height of the planetary boundary layer, are not considered here, but they, too, may have contributed to the variance in the data.

As the aerosol samples were collected over a period of about one week, it is unlikely that a single back-trajectory calculation can adequately represent the movements of all the air that was sampled. Therefore, all back-trajectories associated with each sample were plotted on a single diagram, and the samples were then categorized according to the dominant trajectory pathways. To evaluate the effects of pollutant transport from outside of China, a simple classification scheme for the samples was developed. The trajectories were used to divide origins of the air sampled into two groups, that is, inside China (to the east) and outside China (to the west). The differences between the EC, OC, and CC concentrations in these two groups were then evaluated.

3. Results and discussion

3.1. Temporal variations of EC, OC, and CC

Temporal variations in the concentrations of EC tracked those of OC throughout the study period (Fig. 2), but the variations in concentrations differed in relative magnitude. That is, the EC concentrations varied by almost 50-fold, ranging from 0.004 μg m^{-3} on March 5, 2004 to 0.174 μg m^{-3} on June 23, 2004 while OC concentrations varied by only about 20-fold, ranging from 0.12 μg m^{-3} on the same day with EC lowest values to 2.17 μg m^{-3} on same day with EC highest values. The larger difference between the maximum-to-minimum ratios of EC compared with OC may be ascribed to the removal of EC during long-range transport and the formation of secondary OC plus the contribution of biogenic emissions to OC as discussed below.

A tendency for lower concentrations of EC and OC during the colder winter–spring seasons and higher levels for the warmer summer–autumn seasons can be seen in Fig. 2. Most of EC concentrations fluctuated around 0.05 μg m^{-3} while OC varied around 0.5 μg m^{-3}. The major peaks in EC always coincided with the high values of OC, and this implies that the same processes, including the effects of transport, caused the EC and OC concentrations to co-vary.

High concentrations of CC are most logically and simply explained by episodic dust events. A tendency for higher CC concentrations during spring and summer and lower levels in autumn and winter can be seen in Fig. 2, and this may be explained by the seasonal occurrence of dust storms. Note that elevated levels of water-soluble calcium, some if not most of which is likely in the form of CC, have been observed during dust events (Duvall et al., 2008). In the absence of such events, the CC concentrations tended to be low, often below detection. Carbonate was not detected in twenty-four of the filters, and the CC concentrations in thirty-four samples were less than 0.02 μg m^{-3}. The highest CC concentration (3.57 μg m^{-3}) occurred on June 23, 2004, and that peak in CC

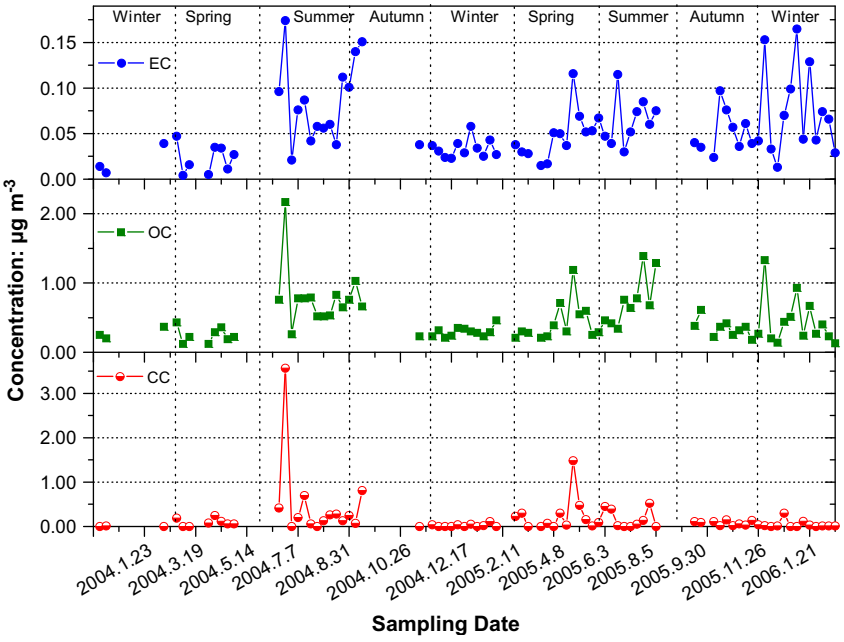

Fig. 2. Elemental carbon (EC), organic carbon (OC), and carbonate carbon (CC) concentrations at Muztagh Ata from December 5, 2003 to February 17, 2006.

coincided with the highest values of EC and OC. Other CC peaks (>0.5 μg m^{-3}) also were coincident with spikes in EC and OC concentrations; these occurred on July 13, September 14, 2004 and April 29 2005. Assuming the four CC peaks are indicative of desert dust, the simultaneous peaks in EC and OC suggest that pollutants were mixed with the dust on those occasions.

3.2. Seasonal variations of EC, OC, and CC

The highest seasonally-averaged EC concentration (0.071 μg m^{-3}) occurred during summer and the lowest during spring (0.038 μg m^{-3}) (Table 1). This was also true for OC whose seasonal average in summer was 0.77 μg m^{-3} and 0.36 μg m^{-3} in spring. Indeed, the seasonally-averaged EC and OC concentrations ranked in the same descending order of summer > autumn > winter > spring, and the high summertime averages of both species were around twice those of the lowest seasonal values. EC and OC concentrations tended to be high during the warmer months of June to November and low during the colder months of December to May (Fig. 2).

As there are minimal emissions of carbonaceous aerosol around the observation site (Bond et al., 2004), the variability in OC and EC is most easily explained by changes in the types of air masses sampled. Muztagh Ata can be influenced by free tropospheric air masses of different origins, but transport is predominantly from the west (Fig. 1). However, as synoptic scale air masses often changed during the sampling period of one filter, a meteorological analysis revealed no significant correlation of surface wind direction with either OC or EC. During convective events, which are most common in spring and summer, Muztagh Ata is influenced by air from the planetary boundary layer.

In areas commonly affected by anthropogenic activities, both EC and OC typically are produced as primary particles, and combustion emissions are especially important sources for them (Chow et al., 1996; Cao et al., 2003). In our case, due to the remote location and high altitude of our observation site, there are no significant direct combustion sources nearby (Bond et al., 2004), and so the OC and EC were likely delivered by mid- and long-range transport (Liu et al., 2008). The wet removal of EC and OC probably has a weaker impact on the seasonality of these carbonaceous aerosols than transport because precipitation in the observation area is sparse and varies little from month-to-month. The annual mean precipitation at the Taxkorgen meteorological station (3100 m asl), about 60 km south-east of our station, has been only about 69 mm over the past 45 years.

Carbonate carbon is injected into the mid- to upper-troposphere during dust storms, and in the Asia/Pacific region, this form of carbon is mainly transported via the northwesterly winds of the winter monsoon (Cao et al., 2005; Li et al., 2008). At Muztagh Ata, CC exhibited seasonality that was different from EC and OC, i.e., the highest average CC (0.36 μg m^{-3}) was found during summer, which is the same as the other species, but the lowest CC concentrations occurred during winter (0.04 μg m^{-3}) instead of spring. More generally, the CC concentrations were highest during the warmest season, with the summertime concentrations two, three, and nine times those during spring, autumn and winter, respectively (Table 1). The seasonal standard deviations for CC were about twice the mean values; this was true in all four seasons and demonstrates relatively large variability in CC throughout the year.

Previous studies in China have shown that CC exhibits high concentrations in surface soils and dust particles from the Taklimakan desert, which is the world's second largest desert and located ~50 km to the east of our observation site (Wang et al., 2005). We examined possible reasons for the high CC contents observed during the week of 23 June 2004 as a case study. Observations at the Tazhong dust station (39°08′N, 83°8′E) demonstrated that a heavy dust storm occurred on the night of 25 June 2004 and the visibility was limited to 600 m (He Qing, Xinjiang Institute of Desert Research, personal communication). Forward air-mass trajectories for this site indicate that the dust plume was likely advected towards our Muztagh Ata station in the following days (Fig. S1).

In the Taklimakan region, dust loadings are high in spring and summer and low in autumn and winter; this is due at least in part to the fact that there are fewer dust storms when the desert soils are frozen. Temperature records from the sampling site showed that three coldest months of the year were December, January and February, with average monthly temperatures for 2004 and 2005 combined of −14.9, −13.3, −8.7, −5.2, −5.0, 3.5, 5.5, 5.3, 2.6, −4.2, −6.6, −11.6 °C, from January to December. Wu et al. (2006) concluded that dust records extracted from ice cores taken from Muztagh Ata Mountain reflected the contribution of dust storm from near Taklimakan desert, and these authors suggested that strong dust storms or local on flow could deliver dust particles to the region. Studies by Carrico et al. (2003) showed that long-range transport delivered desert dust to the Himalayas from arid regions in India and the Middle East and perhaps as far distant as the remote Sahara (>8000 km). Based on these results, we hypothesize that the high CC aerosol events at Muztagh Ata reflect the occurrence of dust storms, either from nearby deserts to the west (<100 km) or from upwind regions in central Asia (<500 km).

As most studies of carbonaceous aerosols at remote sites have measured only EC, we focus on those data for our evaluation of seasonal patterns. A first comparison shows that seasonal EC variations at Muztagh Ata Mountain are exactly opposite to those reported in urban and rural areas of China where the highest EC concentrations occur in winter and the lowest in summer (Cao et al., 2003, 2007; Han

Table 1
Statistical summary of carbonaceous aerosol particle concentrations for total suspended particle samples from Muztagh Ata Mountain (units for EC, OC and CC: μg m^{-3}).

	n[a]	Elemental carbon (EC)				Organic carbon (OC)				Carbonate carbon (CC)				OC/EC	
		Ave[b]	SD[c]	Max[d]	Min[e]	Ave	SD	Max	Min	Ave	SD	Max	Min	Ave	SD
Spring[f]	19	0.038	0.027	0.116	0.004	0.36	0.25	1.19	0.12	0.18	0.34	1.48	0.00	12.0	6.5
Summer[g]	21	0.071	0.035	0.174	0.021	0.77	0.42	2.17	0.26	0.36	0.76	3.57	0.00	11.9	5.4
Autumn[h]	14	0.062	0.040	0.151	0.024	0.40	0.23	1.03	0.18	0.12	0.20	0.81	0.00	7.1	3.5
Winter[i]	27	0.052	0.041	0.165	0.007	0.37	0.26	1.33	0.13	0.04	0.08	0.30	0.00	9.0	5.6
Annual	81	0.055				0.48				0.18				10.0	

[a] Number of samples.
[b] Ave: arithmetic mean value.
[c] SD: standard deviation.
[d] Max: maximum value.
[e] Min: minimum value.
[f] Spring includes March, April, and May in 2004, 2005.
[g] Summer includes June, July, and August in 2004, 2005.
[h] Autumn includes September, October, and November in 2004, 2005.
[i] Winter includes December 2003, December, January, and February of 2004 and 2005.

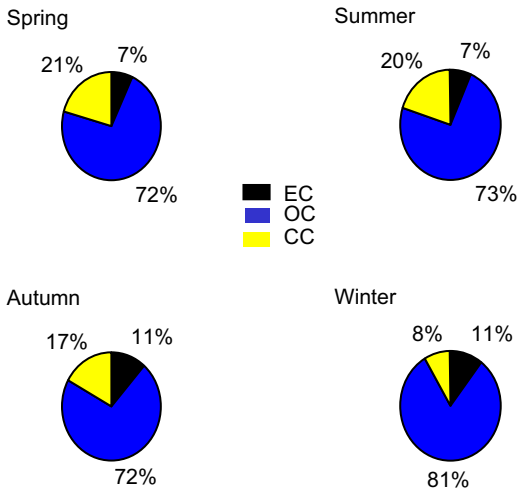

Fig. 3. Total carbon balance for four seasons (unit: percentage).

et al., 2008). Generally, the high wintertime EC concentrations in more populous areas have been linked to the burning of biofuels and fossil fuels for heating as wells as to particularly meteorological conditions, most notably increased stability of the lower troposphere.

On the other hand, the pattern of high summertime EC concentrations observed at our site, even under conditions favorable for atmospheric dispersion, is similar to what has been reported for the high-alpine Jungfraujoch station (Lavanchy et al., 1999) and various polar areas (Wolff and Cachier, 1998; Polissar et al., 1998; Pereira et al., 2006). In those areas, direct human influences are relatively weak, and EC and other pollutants are delivered by long-range transport. For example, Sagar et al. (2004) measured aerosol optical depths (AODs) at a high-altitude station in the central Himalayas, and they found extremely low AODs during winter and a remarkable increase in summer. Carrico et al. (2003) found that the lowest EC at Nepal (0.15 μg m^{-3}) occurred during the summer monsoon (June–September), increased in February–May (0.48 μg m^{-3}) and was highest during October–January (0.52 μg m^{-3}). The low summertime EC values in the latter study were ascribed to southerly airflow and the arrival of monsoonal rains.

3.3. Total carbon balance

The relative amounts of the three carbon fractions were calculated for each season, and the proportions of EC, OC, and CC relative to TC are illustrated in Fig. 3. The carbon balances are quite similar in spring and summer, i.e., EC, OC, and CC accounted for about 7%, 72%, and 21% of TC, respectively. In autumn, EC increased to 11% and CC decreased to 17% while in winter, CC decreased from 17% to 8% and OC increased from 72% to 81%. Thus, the contribution of CC to TC surpasses that of EC in all seasons except winter. Normally CC only accounts for less than 5% of TC in atmosphere (Japar et al., 1986), and the contribution of CC to TC was found to be less than that of EC even during a dust storm at Xi'an, China (Li et al., 2008). In winter, when dust storms are less frequent, we see the lowest percent contribution of CC for the year; thus, CC is a minor- but still important-component of the carbonaceous aerosol of the rural atmosphere over western China.

3.4. Relationship between EC and OC

As CC is a component of mineral dust, the processes responsible for its emission are different from those for EC or OC, and therefore the relationships between CC and the other two species are not discussed further here. Emitted from combustion sources, EC is often related to primary OC, and more generally, the relationships between the two species can provide insight into their origins (Chow et al., 1996). As shown in Fig. 4, strong OC and EC correlations (R^2: 0.75–0.77) in spring and winter suggest that the same emission and transport processes affect the two species, but the OC and EC correlations were lower in autumn (0.57) and summer (0.39), suggesting other influences.

Comparisons with other sites show that the OC and EC correlations at our site are higher than those at a rural area in Daihai where the $R^2 = 0.37–0.46$ (Han et al., 2008), but they are lower than in China's urban areas such as Beijing where the $R^2 = 0.54–0.99$ (Cao et al., 2007). Generally, in urban areas of northern China, OC and EC have two main sources, motor vehicle emissions and coal

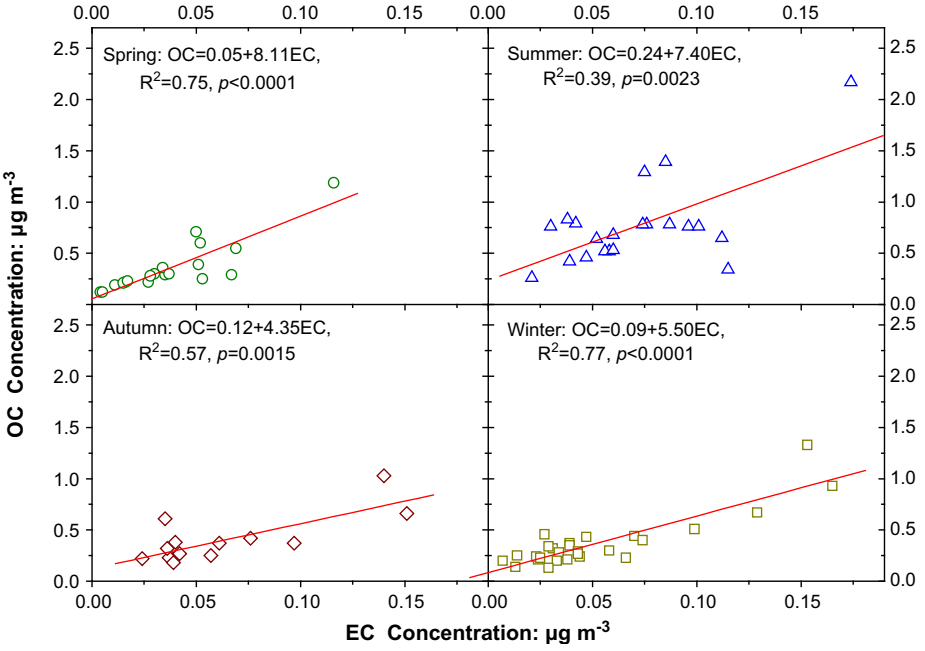

Fig. 4. Relationships between OC and EC for the four seasons.

combustion. In contrast, in rural and remote areas of China, additional sources and processes that occur during long-range transport can weaken the relationship between them (Han et al., 2008). This is the case because OC also can be produced by biogenic sources in addition to those just noted, and various chemical reactions can lead to the formation of secondary OC. The intercept of the seasonally calculated OC/EC regressions is highest in summer, perhaps due to a higher percentage of secondary OC present in the atmosphere at that time of year; this would be consistent with some findings of studies done in urban areas (Cao et al., 2007).

The occurrence of some extremely high OC/EC ratios (>20) in our samples can best be explained by the dilution of EC in the atmosphere coupled with the formation of secondary OC during the transport; however, the ratios are affected more by changes in the OC fraction than EC. Although OC/EC ratios can vary substantially among different source emissions (Mazzera et al., 2001; Chen et al., 2007), high ratios have been linked to OC from biomass burning (Han et al., 2008). To the best of our knowledge there are few, if any, other sources creating OC/EC ratios higher than 20, and therefore the occurrences of extremely high OC/EC ratios are best explained by impacts from biomass burning and possibly other sources besides motor vehicles and coal combustion.

Overall, the OC/EC ratios in our study varied from 2.9 to 32.1 with an annual average of 10.0 (Table 1). Seasonally-averaged OC/EC ratios were higher in spring (12.0) and summer (11.9) and somewhat lower in winter (9.0) and autumn (7.1). These seasonally averaged OC/EC ratios all were far higher than the average ratio of 4.0 reported for fourteen Chinese cities (Cao et al., 2007). We note that the loadings of carbonaceous aerosols at Muztagh Ata have important implications for climate. In particular, if the high OC particle concentrations observed at this high-altitude site are typical of the mid-troposphere over a large area of western China, then their scattering of solar radiation could lead to cooling, and this would tend to counteract any warming influences.

3.5. Long-range transport of carbonaceous aerosols

The prevailing winds in the study area are westerly, and back-trajectories for autumn and winter show a relatively simple pattern: they arrived at Muztagh Ata mainly from regions to the west of China. Those air parcels typically passed over Afghanistan, Pakistan, India and central Asia; and the important implication of this is that much of the aerosol load brought to the site under those conditions probably originated outside of China (Fig. 5). In contrast, the winds occasionally come from the east for part of the spring and throughout summer, and the trajectories for those two seasons are considerably more complicated and variable than in the colder parts of the year.

Indeed, the EC, OC, and CC concentrations for samples stratified by trajectory show that the air masses that originated inside China had higher concentrations of all carbonaceous species than those that started outside of China (Table 2). No comparisons were possible for autumn and winter because none of the dominant trajectory pathways for those seasons began outside of China. Overall, the average concentrations for the "inside China" trajectories were about 1.4, 1.6, and 5.0 times those in the "outside China" group, and some implications of this are discussed below.

The relationships between carbonaceous aerosol species and trajectories were complex, however, and this simple trajectory-based comparison is arguably an oversimplification to some extent. Nonetheless, the trajectory-stratified data do suggest that there are large-scale differences in the relative proportions of the carbonaceous species emitted by sources to the east versus west of the sampling site. That is, CC apparently accounts for a higher proportion of the carbonaceous aerosol in the air transported from the east

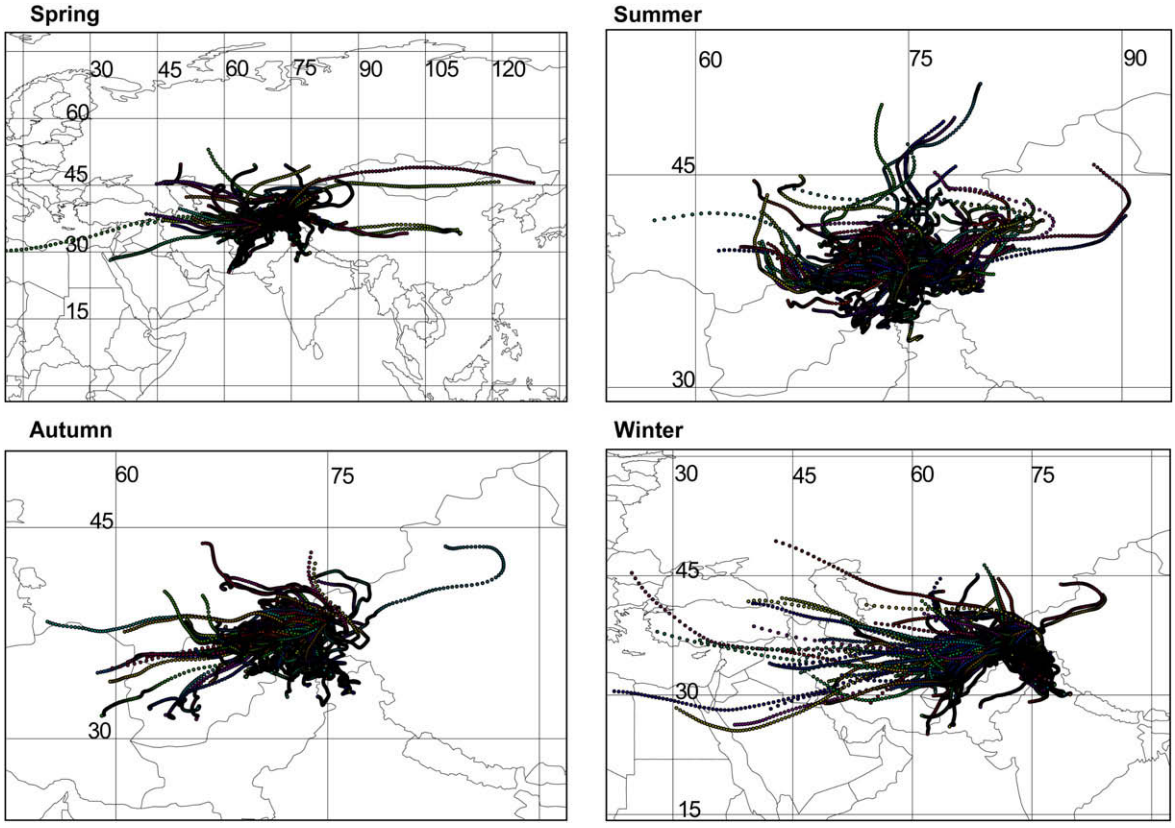

Fig. 5. Five-day backward-in-time trajectories for Muztagh Ata separated by season.

Table 2
Concentrations (units: μg m^{-3}) of elemental carbon (EC), organic carbon (OC) and carbonate carbon (CC) for two air-mass trajectory groups.

Season	Trajectories from outside China				Trajectories from inside China			
	EC	OC	CC	Number	EC	OC	CC	Number
Spring	0.032	0.29	0.06	10	0.045	0.44	0.32	9
Summer	0.054	0.64	0.16	12	0.094	0.93	0.63	9
Autumn	0.062	0.40	0.12	14	ND[a]	ND	ND	0
Winter	0.052	0.37	0.04	27	ND	ND	ND	0
Average	0.050	0.42	0.10		0.069	0.69	0.48	

[a] ND stands for no data – no trajectories from inside China occurred in these seasons.

because the east/west difference in CC is greater than that for either EC or OC. This is consistent with the argument presented above that dust storms in and around the Taklimakan inject CC-containing dust into the atmosphere and that this material can be brought to Muztagh Ata by easterly winds (Fig. 5).

Our observation site is along the pathway of the planetary westerly winds (Fig. 1), and these winds can bring with them material from two high BC emission centers in the Northern Hemisphere, i.e., Western Europe and South Asia (India) (Fig. 2 in Bond et al., 2004). The influence of these winds is year-round, and therefore the carbonaceous aerosol can be used to evaluate the influence of transport from central Asia and possibly even western Europe. If one assumes that the influences of anthropogenic emissions from nearby sources were negligible under westerly flow, then those samples can be regarded as representing a background of non-Chinese emissions. On this basis, the transport of materials from outside China would appear to result in annually-averaged backgrounds of roughly 0.05 μg m^{-3} EC, 0.42 μg m^{-3} OC, and 0.10 μg m^{-3} CC (Table 2).

3.6. Comparison EC with other rural, alpine, and remote area measurements

Average EC and OC concentrations in Muztagh Ata are summarized in Table 3, and data for selected rural, high alpine, background, and polar areas are included for comparison. The average EC and OC concentrations in Muztagh Ata are 0.055 and 0.48 μg m^{-3}, respectively; these can be seen to be about two orders-of-magnitude lower than what has been reported for metropolitan areas or other mountain rural areas (Cao et al., 2007; Han et al., 2008), and more than ten-fold lower than in rural areas in China (Qu et al., 2006). EC concentrations appear to be far lower than those in rural background areas around the world, differences among methods notwithstanding (Table 3) (Hatakeyama, 1993, 1995; Chow et al., 1994; Malm et al., 1994; Kim et al., 2000; Salma et al., 2004; Tanner et al., 2005). EC at Muztagh Ata also is about one-tenth of that reported for high-alpine sites in the central Himalayas (Carrico et al., 2003; Pant et al., 2006), presumably due to stronger anthropogenic influences there. That is, the sites in Nepal (Manora Peak and Langtang) were closer to sources of anthropogenic emissions and possibly influenced by the Asian Brown Cloud (Carrico et al., 2003; Pant et al., 2006).

In general, EC concentrations in the interiors of the continents are far higher than those in oceanic and polar areas simply because EC is mainly anthropogenic in origin. Further comparisons of the data show that the concentrations of EC at Muztagh Ata are lower than those in polar areas affected by local human activities (Polissar et al., 1998), of the same order or slightly higher than those in areas with no clear local emissions from combustion activities (Mazzera et al., 2001), and about ten-fold higher than those in pristine polar areas (Wolff and Cachier, 1998; Pereira et al., 2006). As Muztagh Ata has EC concentrations comparable to some polar areas, they may be seen as defining or approaching a background level for inland Asia.

3.7. Comparison between atmospheric EC values and EC measurements in ice cores

Liu et al. (2008) recently determined the EC concentrations in an ice core taken from a glacier close to our observation station. Their results show annual average EC contents varied between 6.5 and 124.6 ng g^{-1} from 1955 to 2000. Two high EC-concentration periods were found, the first in 1955–1965 and the second in 1974–1989; and two low-value periods were found in 1966–1973

Table 3
Elemental carbon (EC) and organic carbon (OC) concentrations at Muztagh Ata and selected rural, high-alpine, and remote areas.

Location	Size fraction[a]	Type of location	Period	Mean EC (μg m^{-3})	Mean OC (μg m^{-3})	Carbon analysis method[b]	References
Muztagh Ata	TSP	Remote mountain (4500 m asl)	Dec.2003–Feb.2005	0.055	0.48	TOR	This study
Daihai	TSP	Mountain rural	2005–2007	3.10	19.9	TOR	Han et al., 2008
Zhuzhan	PM_{10}	Rural background	Aug. 2004–Feb. 2005	0.34	3.13	TOR	Qu et al., 2006
Nagano		Rural	Oct. 1991	1.02	1.07		Hatakeyama (1993)
Nagano		Rural	Nov. 1992	1.58	1.38		Hatakeyama (1995)
Okinawa		Rural	Oct. 1991	2.06	2.67		Hatakeyama (1993)
San Nicolas Is.	$PM_{2.5}$	Rural	1987	0.1	0.81	TOR	Chow et al., 1994
Marblemount	$PM_{2.5}$	Rural	1990	0.44	3.06		Malm et al., 1994
Kosan	$PM_{2.5}$	Island background	1994–1999	0.26	3.24	TMO	Kim et al., 2000
Kangwha	$PM_{2.5}$	Island background	1996–1999	0.88	6.34	TMO	Kim et al., 2000
Tennessee Valley	$PM_{2.5}$	Mountain background	Jul.–Aug., 2001	0.55	3.3		Tanner et al., 2005
Budapest	$PM_{2.0}$	Near city background	23 Apr. - 5 May 2002	0.19–0.64	2.9–5.5	TOT	Salma et al., 2004
Halley Station, Antarctic	TSP	Polar pristine	1992–1995	0.0003–0.002	–	Aethalometer	Wolff and Cachier, 1998
Ferraz, Antarctic	TSP	Polar pristine	1993, 1997, and 1998	0.0083	–	Aethalometer	Pereira et al., 2006
Langtang, Nepal	$PM_{2.5}$	High-alpine (3920 m asl)	Dec. 1998–Oct. 2000	0.38	2.0	TOT	Carrico et al., 2003
Manora Peak, Central Himalayas	TSP	High-alpine (1950m asl)	Dec. 2004	1.36	–	Aethalometer	Pant et al., 2006
National Park Service locations in Alaska	TSP	Near Polar	1986–1995	0.1–5	–	Aethalometer	Polissar et al., 1998
Radar Sat Dome, McMurdo, Antarctica	PM_{10}	Polar remote	Austral summers of 1995–1997	0.042	0.101	TOR	Mazzera et al., 2001
Hut Point, McMurdo, Antarctica	PM_{10}	Polar remote	Austral summers of 1995–1998	0.129	0.149	TOR	Mazzera et al., 2001

[a] Size fractions: TSP = total suspended particles; PM_{10} and $PM_{2.5}$ – particles less than or equal to 10 and 2.5 μm, respectively.
[b] Carbon analysis methods: TOR – thermal optical reflectance, TOT – thermal optical transmittance, TMO – thermal manganese dioxide oxidation.

and 1990–1995. Here we used a method based on the work of Davidson et al. (1993) to estimate BC concentrations in the atmosphere

$$C_a = \rho_a \times C_s/\omega$$

where C_a is the concentration of the substance of interest in the atmosphere (ng m^{-3}), ρ_a is the air density (g m^{-3}) corrected to standard temperature and pressure, C_s is the species concentration (ng g^{-1}) in snow, and ω is the scavenging ratio (dimensionless) for the specific species by snow fall. A value for ω of 125 was adopted and used for our estimation (Ming et al., 2008) as no measurements of ω are unavailable at our site.

The estimated annual EC concentrations calculated from the ice core were 31–600 ng m^{-3}, and our annual EC average of 56 ng m^{-3} falls into the lower end of this range. Therefore, it appears that the 2003–2004 EC values may reflect relatively clean conditions at Muztagh Ata. As noted above, interest in EC in polar regions stems from the fact that it absorbs solar radiation and so it can both warm the atmosphere and darken snow/ice surfaces after deposition thus accelerating melting (Hansen and Nazarenko, 2004). The estimated average atmospheric BC concentration over the East Rongbuk Glacier on Mt. Everest was nearly 80 ng m^{-3} (Ming et al., 2008), similar to our annual EC average of 56 ng m^{-3}, and it was estimated that BC loadings of this order could induce radiative forcing of ~1–4.5 W m^{-2}. Along the same lines, Flanner et al. (2007) estimated that the instantaneous BC-induced radiative forcing over the Tibet Plateau averaged 1.5 W m^{-2}, but exceeded 20 W m^{-2} at sometimes during spring. The significance of this is that BC suspended in the atmosphere or deposited onto snow and ice surfaces can affect the regional radiative balance and this in turn could influence glacial mass-balance dynamics, that is, the accretion and melting of glacial ice.

4. Conclusions

More than two years of observations of EC and related species OC and CC were made at the Muztagh Ata Mountain, a high Himalayan site, in western China. The carbonaceous aerosols were characterized by low EC concentrations, high OC/EC ratios, and relatively high CC loadings compared with other remote parts of the earth. Indeed, the Muztagh Ata EC concentrations were of the same order as those in some remote polar areas, suggesting that the EC concentrations can at times approach a background for inland Asia. The EC and OC concentrations were strongly correlated and followed same descending order of summer > autumn > winter > spring. The CC concentrations were elevated during the warmer months, especially the summer when transport from the east was most common, and that most likely due to the influence of dust from the Taklimakan.

The observed temporal variations are best explained by differences in the composition of the air brought to the site under different flow regimes. Relatively low concentrations of carbonaceous materials are transported to the site from regions to the west and outside of China. When flow to the site was from the east, however, as indicated by trajectory analysis, emissions from nearby Taklimakan desert contributed CC and anthropogenic sources in the interior of China increased the concentrations of EC and OC. Differences in the relative abundances of the species as a function of transport showed the greatest effect for CC, which again can be explained by the influences of dust sources to the east.

In areas to the west of China and upwind of Muztagh Ata, emissions from human activities involving transportation, farming, etc. will likely strengthen in the future, and therefore one would expect the emissions of carbonaceous aerosol to increase commensurately. This is important in the context of glacial ice dynamics because higher concentrations of EC particles would tend to warm the regional climate and possibly lead to melting of the Himalayan glaciers, whereas high concentrations of OC could mitigate these effects. Considering these potential effects on climate and the impact on glaciers, the sources, synoptic changes, and atmospheric processes that control EC and OC concentrations as well as the geochemical and climatic implications of changing carbonaceous aerosol burdens should receive special attention in future research.

Acknowledgements

This work was supported by the Ministry of Science and Technology of China (2005CB422004), the National Natural Science Foundation of China (40525001) and the project from Chinese Academy of Sciences (KZCX2-YW-148).

Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2009.06.023.

References

Andreae, M.O., 2007. Aerosols before pollution. Science 315, 50–51.
An, Zhisheng, Kutzbach, J.E., Prell, W., Porter, S.C., 2001. Evolution of Asian monsoons and phased uplift of the Himalaya-Tibetan plateau since Late Miocene times. Nature 411, 62–66.
Bonasoni, P., Laj, P., Angelini, F., Arduini, J., Bonafè, U., Calzolari, F., Cristofanelli, P., Decesari, S., Facchini, M.C., Fuzzi, S., Gobbi, G.P., Maione, M., Marinoni, A., Petzold, A., Villani, P., Vuillermoz, E., 2008. The ABC-pyramid atmospheric research observatory in Himalaya for aerosol, ozone and halocarbon measurements. Sci. Total Environ. 391 (2–3), 252–261.
Bond, T.C., Streets, D.G., Yarber, K.F., Nelson, S.M., Woo, J.-H., Klimont, Z., 2004. A technology-based global inventory of black and organic carbon emissions from combustion. J. Geophys. Res. 109, D14203. doi:10.1029/2003JD003697.
Cao, J.J., Lee, S.C., Ho, K.F., Zhang, X.Y., Zou, S.C., Fung, K.K., Chow, J.C., Watson, J.G., 2003. Characteristics of carbonaceous aerosol in Pearl River Delta region, China during 2001 winter period. Atmos. Environ. 37 (11), 1451–1460.
Cao, J.J., Lee, S.C., Zhang, X.Y., Chow, J.C., An, Z.S., Ho, K.F., Watson, J.G., Fung, K., Wang, Y.Q., Shen, Z.X., 2005. Characterization of airborne carbonate over a site on Asian Dust source regions during 2002 spring and its climatic and environmental significance. J. Geophys. Res. 110, D03203. doi:10.1029/2004JD005244.
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. doi:10.1029/2006JD008205.
Carrico, C.M., Bergin, M.H., Shrestha, A.B., Dibb, J.E., Gomes, L., Harris, J.M., 2003. The importance of carbon and mineral dust to seasonal aerosol properties in the Nepal Himalaya. Atmos. Environ. 37 (20), 2811–2824.
Chen, L.W., Moosmuller, H., Arnott, P.W., Chow, J.C., Watson, J.G., Susott, R.A., Babbitt, E.R., Wold, C.E., Lincoln, E.N., Hao, W.M., 2007. Emissions from laboratory combustion of wildland fuels: emission factors and source profiles. Environ. Sci. Technol. 41, 4317–4325.
Chow, J.C., Watson, J.G., Fujuta, E.M., Lu, Z., Lawson, D.R., 1994. Temporal and spatial variations of $PM_{2.5}$ and PM_{10} aerosol in the southern California air quality study. Atmos. Environ. 28, 2061–2080.
Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Frazier, C.A., Solomon, P.A., Thuillier, R.H., Magliano, K.L., 1996. Descriptive analysis of $PM_{2.5}$ and PM_{10} at regionally representative locations during SJVAQS/AUSPEX. Atmos. Environ. 30 (12), 2079–2112.
Chow, J.C., Watson, J.G., Chen, L.W.A., Arnott, W.P., Moosmüller, H., Fung, K.K., 2004. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. Environ. Sci. Technol. 38 (16), 4414–4422.
Clarke, A.D., Noone, K.J., 1985. Soot in Arctic snow: a cause for perturbations of radiative transfer. Atmos. Environ. 19, 2045–2053.
Davidson, C.I., Jaffrezo, J.L., Mosher, B.W., Dibb, J.E., Borys, R.D., Bodhaine, B.A., Rasmussen, R.A., Boutron, C.F., Gorlach, U., Cachier, H., Ducret, J., Colin, J.L., Heidam, N.Z., Kemp, K., Hillamo, R., 1993. Chemical constituents in the air and snow at Dye 3, Greenland: II. Analysis of Episodes in April 1989. Atmos. Environ. 27 (A), 2723–2738.
Duvall, R.M., Majestic, B.J., Shafer, M.M., Chuang, P.Y., Simoneit, B.R.T., Schauer, J.J., 2008. The water-soluble fraction of carbon, sulfur, and crustal elements in Asian aerosols and Asian soils. Atmos. Environ. 42, 5872–5884.
Flanner, M.G., Zender, C.S., Randerson, J.T., Rasch, P.J., 2007. Present-day climate forcing and response from black carbon in snow. J. Geophys. Res. 112, D11202. doi:10.1029/2006JD008003.

Han, Y.M., Han, Z.W., Cao, J.J., Chow, J.C., Watson, J.G., An, Z.S., Liu, S.X., 2008. Distribution and origin of carbonaceous aerosol over a rural high-mountain lake area, Northern China and its transport significance. Atmos. Environ. 42, 2405–2414.

Hansen, J., Nazarenko, L., 2004. Soot climate forcing via snow and ice albedoes. Proc. Natl. Acad. Sci. 101 (2), 423–428. doi:10.1073/pnas.2237157100.

Hatakeyama, S., 1993. Data of '91 IGAG/APARE/PEACAMPOT Survey. ISSN 1341-4356. National Institute for Environmental Studies (NIES), Japan.

Hatakeyama, S., 1995. Data of '93 IGAG/APARE/PEACAMPOT Survey. ISSN 1341-3651. National Institute for Environmental Studies (NIES), Japan.

Japar, S.M., Brachaczek, W.W., Grose, R.A., Norbeck, J.M., Pierson, W.R., 1986. The contribution of elemental carbon to the optical properties of rural atmospheric aerosols. Atmos. Environ. 20, 1281–1289.

Kim, Y.P., Moon, K.-C., Shim, S.-G., Lee, J.H., Kim, J.Y., Fung, K., Carmichael, G.R., Song, C.H., Kang, C.H., Kim, H.-K., Lee, C.B., 2000. Carbonaceous species in fine particles at the background sites in Korea between 1994 and 1999. Atmos. Environ. 34, 5053–5060.

Lavanchy, V.M.H., Gaggeler, H.W., Nyeki, S., Baltensperger, U., 1999. Elemental carbon (EC) and black carbon (BC) measurements with a thermal method and an aethalometer at the high-alpine research station Jungfraujoch. Atmos. Environ. 33, 2759–2769.

Li, X.X., Cao, J.J., Chow, J., Han, Y.M., Lee, S.C., Watson, J., 2008. Chemical characteristics of carbonaceous aerosols during dust storms over Xi'an in China. Adv. Atmos. Sci. 25, 847–855. 2008.

Liu, X.Q., Xu, B.Q., Yao, T.D., et al., 2008. Carbonaceous particles in Muztagh Ata ice core, west Kunlun mountains, China. Chin. Sci. Bull. 53, 2358–2364 (in Chinese).

Malm, W.C., Gebhart, K.A., Molenar, J., Cahill, T., Eldred, R., Huffman, D., 1994. Examining the relationship between atmospheric aerosols and light extinction at Mount Rainer and north Cascade National Parks. Atmos. Environ. 28, 347–360.

Mazzera, D.M., Lowenthal, D.H., Chow, J.C., Watson, J.G., Grubisic, V., 2001. PM_{10} measurements at McMurdo station, Antarctica. Atmos. Environ. 35, 1891–1902.

Ming, J., Cachier, H., Xiao, C., Qin, D., Kang, S., Hou, S., Xu, J., 2008. Black carbon record based on a shallow Himalayan ice core and its climatic implications. Atmos. Chem. Phys. 8 (5), 1343–1352.

Mueller, P.K., Mosley, R.W., Pierce, L.B., 1971. Carbonate and noncarbonated carbon in atmospheric particles. In: Englund, H.M., Beery, W.T. (Eds.), Proceedings of the Second International Clean Air Congress. Elsevier, New York, pp. 532–539.

Pant, P., Hegde, P., Dumka, U.C., Ram, S., Satheesh, S.K., Moorthy, K.K., Saha, A., Srivastava, M.K., 2006. Aerosol characteristics at a high-altitude location in central Himalayas: optical properties and radiative forcing. J. Geophys. Res. 111, D17206. doi:10.1029/2005JD006768.

Pereira, E.B., Evangelista, H., Pereira, K.C.D., 2006. Apportionment of black carbon in the south Shetland Islands, Antarctic Peninsula. J. Geophys. Res. 111, D03303. doi:10.1029/2005JD006086.

Polissar, A.V., Hopke, P.K., Malm, W.C., Sisler, J.F., 1998. Atmospheric aerosol over Alaska 1. Spatial and seasonal variability. J. Geophys. Res. 103, 19035–19044.

Qu, W., Zhang, X., Wang, Y., Wang, D., Li, Y., Cao, G., Zhao, Y., 2006. The physical and chemical characterization of carbonaceous aerosol at the atmospheric background site in Diqing, Yunnan. China Environ. Sci. 26, 266–270 (in Chinese).

Ramanathan, V., Chung, C., Kim, D., et al., 2005. Atmospheric brown clouds: impacts on South Asian climate and hydrological cycle. Proc. Natl. Acad. Sci. 102 (15), 5326–5333. doi:10.1073/pnas.0500656102.

Sagar, R., Kumar, B., Dumka, U.C., Moorthy, K.K., Pant, P., 2004. Characteristics of aerosol spectral optical depths over Manora Peak: a high-altitude station in the central Himalayas. J. Geophys. Res. 109, D06207. doi:10.1029/2003JD003954.

Salma, I., Chi, X.G., Maenhaut, W., 2004. Elemental and organic carbon in urban canyon and background environments in Budapest Hungary. Atmos. Environ. 38, 27–36.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics: from Air Pollution to Climate Change. John Wiley & Sons, Inc., New York, pp. 700.

Tanner, R.L., Bairai, S.T., Olszyna, K.J., Valente, M.L., Valente, R.J., 2005. Diurnal patterns in $PM_{2.5}$ mass and composition at a background, complex terrain site. Atmos. Environ. 39, 3865–3875.

Wang, Y.Q., Zhang, X.Y., Arimoto, R., Cao, J.J., Shen, Z.X., 2005. Characteristics of carbonate content and carbon and oxygen isotopic composition of north China soil and dust aerosol an its application to tracing dust sources. Atmos. Environ. 39, 2631–2642.

Wolff, E.W., Cachier, H., 1998. Concentrations and seasonal cycle of black carbon in aerosol at a coastal Antarctic station. J. Geophys. Res. 103, 11033–11041.

Wu, G.J., Yao, T.D., Xu, B.Q., Li, Z., Tian, L.D., Duan, K.Q., Wen, L.K., 2006. Grain size record of microparticles in the Muztagata ice core. Sci. China Ser. D-Earth 49, 10–17.

Xu, B.Q., Yao, T.D., Lu, A.X., Guo, X.J., Liu, X.Q., Li, Z., 2006. Variations of near-surface atmospheric CO_2 and H_2O concentrations during summer on Muztagata. Sci. China Ser. D-Earth 36 (1), 18–26.

Yu, W.S., Yao, T.D., Tian, L.D., Li, Z., Sun, W.Z., Wang, Y., 2006. Relationships between $\delta\ ^{18}O$ in summer precipitation and temperature and moisture trajectories at Muztagata, western China. Sci. China Ser. D-Earth 49, 27–35.