Scientific paper

Black carbon and ionic species in the Arctic aerosol

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Abstract: Previous studies on Arctic aerosol characteristics have shown a pronounced winter-spring maximum and summer-autumn minimum in aerosol concentration. Measurements of black carbon concentration in the atmospheric aerosol were obtained by means of an aethalometer at the Zeppelinfjellet station Ny-Ålesund, Svalbard. Simultaneous 24 hour measurements of the concentration of key aerosol species like sulphate, ammonium and nitrate together with sulphur dioxide, conducted by NILU are presented and discussed in order to evaluate the transport processes governing their presence in the High Arctic. Large variations are seen to be superimposed on an overall trend that apparently exhibits higher values in winter than in late summer. Back trajectory analysis of the airmasses arriving at Zeppelin station, reveals that enhanced concentrations observed for black carbon and sulphate are associated with long range transport of polluted air from Eurasia. Black carbon, sulphur dioxide and sulphate concentrations are correlated well. Nitrate and ammonium display a rather poor association with the above species and between each other.

1. Introduction

The term Black Carbon (BC) is commonly used in the literature to describe the optically absorbing part of carbonaceous aerosols. It is produced during the incomplete combustion of fossil and other fuels as well as biomass burning. In remote regions the concentration of BC in the air is an excellent tracer of aerosol derived from anthropogenic emissions. Fossil fuel and biomass combustion is the only source of BC in the atmosphere and its concentration is dependent on transport and physical removal processes (see *e.g.* Penner and Eddleman, 1993). Its lifetime in the atmosphere is variable depending on its ability to: 1) mix with other aerosols (coagulation), 2) interact chemically with gaseous species and 3) become hygroscopic and absorb water. These processes are not yet fully understood but it is recognized that freshly emitted BC aerosol is a reducing agent in the atmosphere. Freshly emitted BC particles play an important role in heterogeneous chemical reactions due to its large surface area and the formation of functional groups (*e.g.* carboxylic) on its surface (Lary *et al.*, 1999). During its lifetime in the atmosphere, BC surface is chemically modified, it becomes hygroscopic and can be activated as CCN (Chughtai *et al.*, 1996). It gradually becomes "inert" as the aerosol ages in the atmosphere. Previous

studies on Arctic aerosol characteristics have shown a pronounced winter-spring maximum and summer-autumn minimum in aerosol concentration as a result of long-range transport from industrial regions and relatively inefficient atmospheric removal processes. The present work aims to comment on the transport and evolution processes of atmospheric aerosol in the Arctic, by studying the variation in concentration of key aerosol species. In the case of black carbon its mass is chemically conserved (affected only by physical removal processes) while other species namely SO_2 and SO_4, have their concentration governed by chemistry through gas to particle conversion as well as the physical removal processes. Apart from the fact that such measurements in the Arctic are lacking, they facilitate the study of aged aerosol properties by allowing the investigation of these species after long range transport in the absence of intermediate range sources.

2. Experimental

Measurements of BC concentration in the atmospheric aerosol were obtained by means of an aethalometer (Magee AE-9) at the Zeppelinfjellet station (474 m asl; 78°54'N, 11°53' E), Ny-Ålesund, Svalbard. Two intensive field campaigns were conducted in August 1998 and May 1999, and continuous measurements of BC occurred from the first campaign to June 1999. The aethalometer continuously monitors the attenuation of light through an aerosol loaded filter in comparison to a reference value from a particle-free section of the filter. The instrument is calibrated so that the BC mass is calculated from the relationship:

$$BC \text{ mass/filter unit area: } BC_m = ATN/\alpha_{API},$$

where $ATN = -100 \ln(I/I_0)$, I_0 = transmitted light intensity through a blank portion of filter material, I = transmitted light intensity through a portion of aerosol loaded filter material, and α_{API} is the absorption efficiency of BC aerosol on the filter.

The value for α_{API} provided by the manufacturer is 19 m^2 g^{-1}. The data reported here are based on this value. However, it has been recognized that these settings are specific for a given sampling site and aerosol type. In remote areas this value is expected to be lower resulting in higher BC mass concentrations from those reported here for Ny-Ålesund (Petzold and Niessner, 1995). Thermal analyses of the filter samples are currently being performed, so that in future work a correction factor can be applied to presented data. The concentration of inorganic aerosol species and their gaseous precursors were obtained by measurements performed at Ny-Ålesund by NILU. Details about the methodology used, are found in Tørseth et al. (2000). Air is sampled on a 24 hour basis by a low volume sampler utilising a three stage filter pack. A teflon filter on the first stage collects the aerosol while the second and third stage consist of Whatman 40 filters impregnated with potassium hydroxide for acidic gas collection and oxalic acid for alkaline gas collection, respectively. Samples are analysed by Ion Chromatography for sulphate, nitrate and ammonium. Results allow the concentrations of particulate sulphate and gaseous sulphur dioxide to be determined. The sampler's configuration does not permit distinction between nitric acid and particulate nitrate or ammonia and particulate ammonium. The results for these species are expressed as total nitrate and total ammonium. Meteorological parameters like temperature, pressure and relative humidity are also monitored by NILU at Ny-Ålesund and are utilized in the present work. Back trajectory analysis was also performed on selected periods of

frequent pollution episodes identified by high BC concentrations (January to March). Back trajectories for Ny-Ålesund were calculated by means of the NOAA developed model (HYSPLIT4 model, 1997). The model can be used for trajectory and concentration calculations. It employs a hybrid method between Eulerian and Langrangian approaches, in that advection and diffusion are calculated in a Langrangian framework, whereas concentrations are calculated on a fixed grid. Advection and diffusion are modeled so that "particle" dispersion is employed in the vertical direction and puff dispersion in the horizontal. The model requires gridded meteorological data as input, which are mapped on an internally defined grid system. Map projections such as mercator or polar stereographic are employed. In the vertical, a terrain-following co-ordinate system is used. A library, containing gridded land use and roughness length data for the whole globe with a resolution of 1×1 degree, is incorporated in the calculations. The model also calculates vertical mixing and stability. The calculations performed here used the NFL meteorological data, available at the NOAA web site, which cover the whole globe and are interpolated from global measurements. The model was run for the Zeppelin station altitude (475 m a.s.l.) and for at least a 5 days period in time.

3. Results

The results for BC, sulphate, sulphur dioxide, nitrate and ammonium are presented in Fig. 1. Sulphate and sulphur dioxide are presented as sulphur mass concentration while nitrate and ammonium are expressed as the sum of gaseous (HNO_3 and NH_3) and aerosol ionic component concentrations, respectively. The winter period of measurements between October and June is presented here in order to evaluate long range transport events. Large variations are seen to be superimposed on an overall trend of increasing concentrations from October to March, and decreasing from April to June. The mass concentration levels for BC and inorganic species are comparable to those reported by Worthy et al. (1994) and Jaeschke et al. (1999), respectively. Some distinct features for the presented aerosol species can be derived from Fig. 2 where 30-day running mean values of the concentrations are displayed together with the water-mixing ratio. It is observed that changes in the general trends of the concentrations of ammonium, sulphate and SO_2 occur when sunlight returns to the Arctic. Higher photochemical conversion rates of SO_2 to sulphate lead to the latter becoming the dominant sulphur component during spring in contrast to the dark period of the year. This is a general feature in the Arctic also observed at Alert (Sirois and Barrie, 1999). It has to be noted that the other oxidation path of SO_2 to sulphate through diffusion of SO_2 in aerosol droplets is continuously contributing to sulphate conversion to a certain extent. It is not clear how the increased ammonia/ammonium values during the same period are associated to the sulphur compounds. However, high ammonium concentrations associated with sulphate were linked by Jaeschke et al. (1999) to long range transported pollutants from Siberia. The water-mixing ratio was calculated from meteorological parameters. It is evident that low values of the examined species are associated with humid airmasses indicating increased aerosol washout. It has to be noted that aerosol in-cloud scavenging was observed at the measuring site on Zeppelin mountain to have the strongest effect on aerosol number concentration and BC mass concentration. Table 1 displays the correlation coefficients between the examined species. BC and sulphate concentrations are
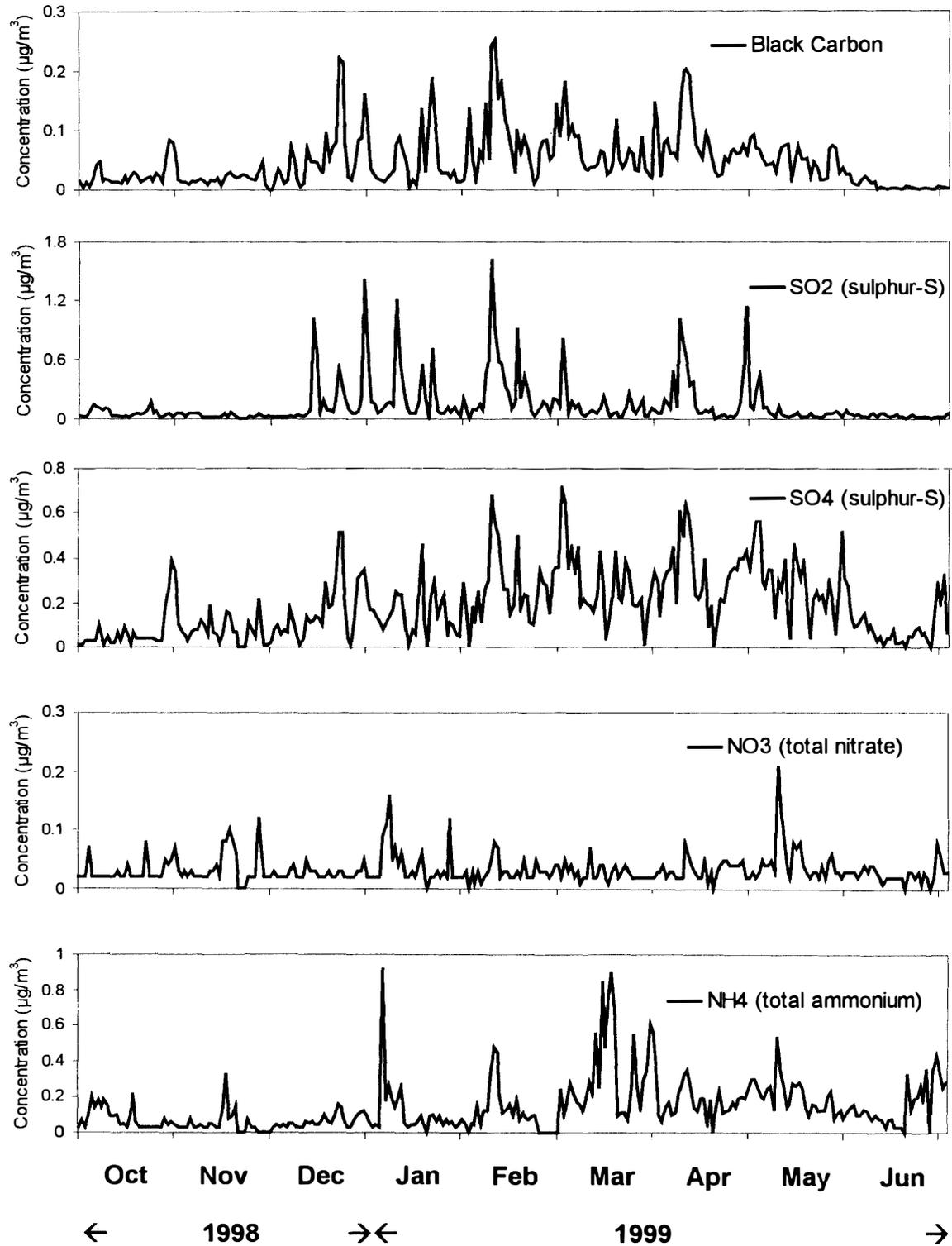
Fig. 1.   Time series of Black Carbon, sulphur dioxide, sulphate, total nitrate and total ammonium 24 hour mass concentration (μg m^{-3}) from October to June at Zeppelin station, Ny-Ålesund.

30 days running mean of 24h values


30 days running mean of 24h values
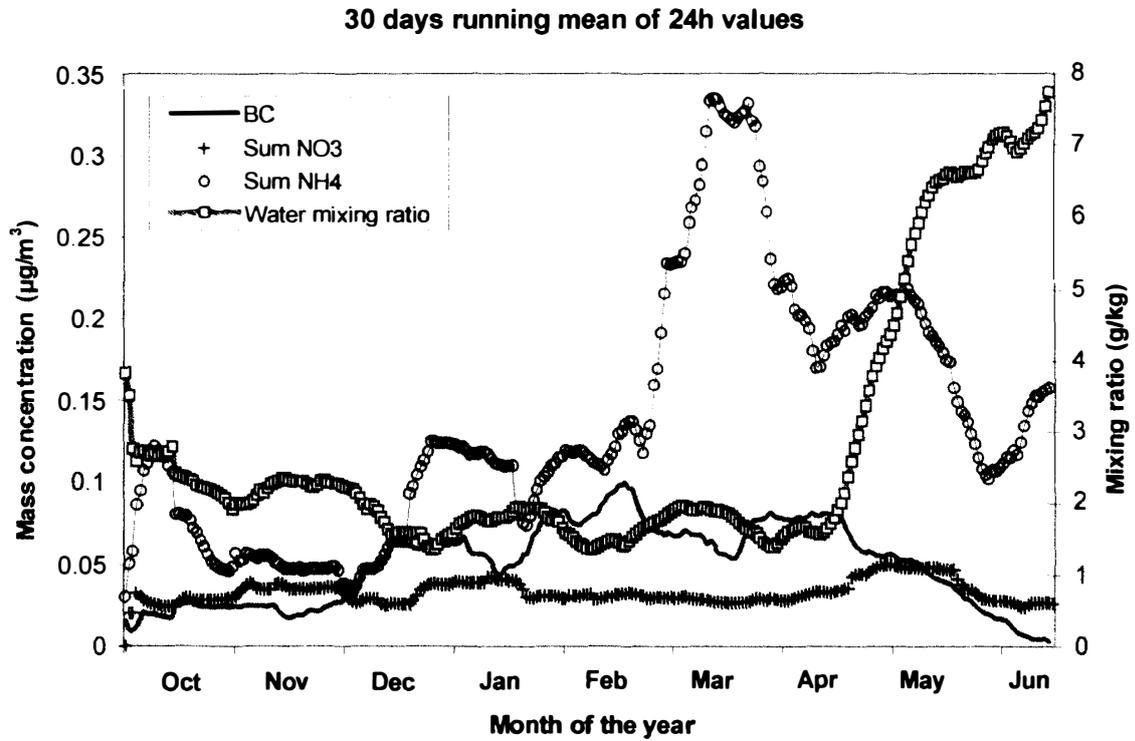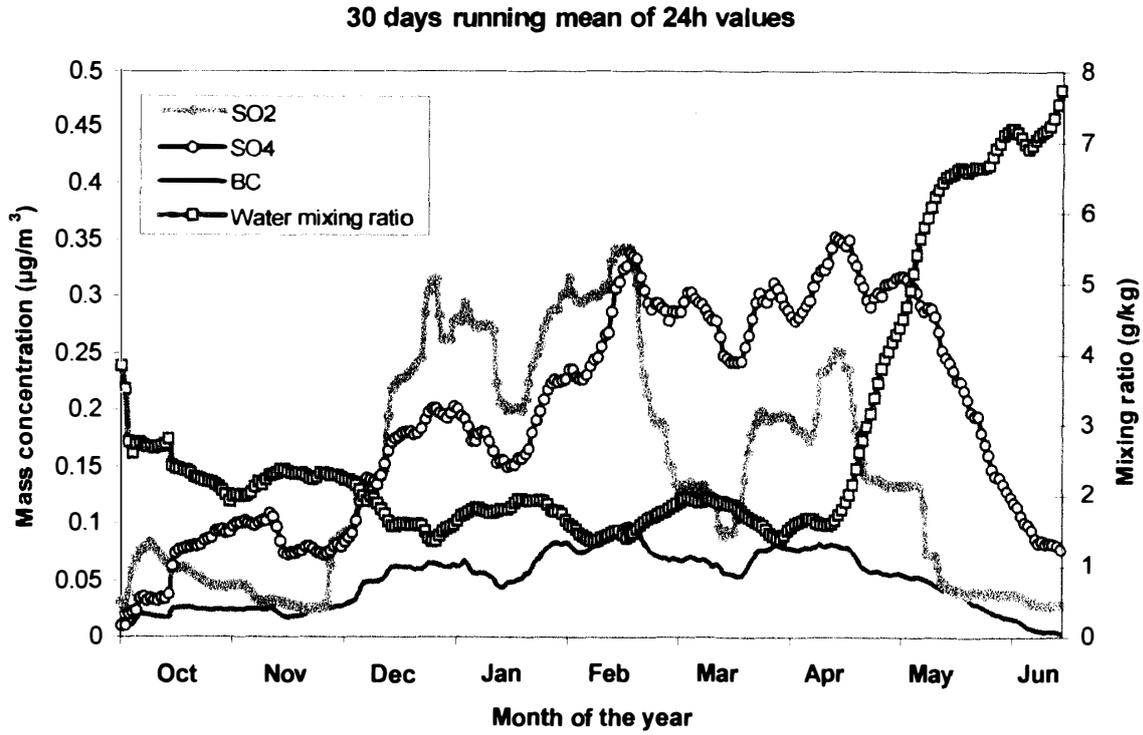
Fig. 2. Black Carbon, sulphur dioxide, sulphate, total nitrate and total ammonium running mean mass concentration ($\mu g\ m^{-3}$) for a 30 days time window, from October to June at Zeppelin station, Ny-Ålesund.

Table 1.   Correlation coefficients among the 24 h concentrations of aerosol and gaseous species measured at Ny-Ålesund from October to June.

Correlation coefficient	SO_2	SO_4	Sum NO_3	Sum NH_4	BC	H_2O Mixing ratio
SO_2	1.00					
SO_4	0.54	1.00				
Sum NO_3	0.11	0.26	1.00			
Sum NH_4	0.16	0.38	0.30	1.00		
BC	0.63	0.76	0.15	0.28	1.00	
H_2O Mixing ratio	−0.30	−0.15	0.12	−0.01	−0.29	1.00

Table 2.   Correlation coefficients among the 24 h concentrations of aerosol and gaseous species measured at Ny-Ålesund from October to June for the cases with BC concentrations above 50 ng/m^3.

Correlation coefficient	SO_2	SO_4	Sum NO_3	Sum NH_4	BC	H_2O Mixing ratio
SO_2	1.00					
SO_4	0.48	1.00				
Sum NO_3	0.02	0.15	1.00			
Sum NH_4	0.12	0.37	0.40	1.00		
BC	0.58	0.61	0.04	0.24	1.00	
H_2O Mixing ratio	−0.28	−0.20	0.27	0.07	−0.26	1.00

Table 3. Correlation coefficients among the 24 h concentrations of aerosol and gaseous species measured at Ny-Ålesund from October to June for the cases with BC concentrations below 50 ng/m^3.

Correlation coefficient	SO_2	SO_4	Sum NO_3	Sum NH_4	BC	H_2O Mixing ratio
SO_2	1.00					
SO_4	0.08	1.00				
Sum NO_3	0.06	0.21	1.00			
Sum NH_4	−0.01	0.27	0.16	1.00		
BC	0.31	0.59	0.15	0.23	1.00	
H_2O Mixing ratio	−0.12	0.15	−0.07	−0.02	−0.26	1.00

highly correlated. Sulphur dioxide shows a weaker correlation with BC and sulphate, while nitrate and ammonium display a rather poor association with BC and sulphate and between each other. Nitrate is the only component, which cannot be associated to any identified event of pollutant long-range transport. The effects of long range transport on the examined species are further explored by the correlation tests on polluted and background days. The limit of 50 ng/m^3 which is the average BC concentration of the whole data-set, is chosen as the criterion for this exercise (Tables 2 and 3). It is observed that the correlation coefficients calculated for the polluted days are very similar to those observed for the complete data-set. On the other hand, for the periods with background BC values they appear low for all species with the exception of the pair $BC-SO_4$. This indicates that the lifetime of these species is governed by the same atmospheric processes. Airmass back

6 to 11 of February, BC > 100 ng/m3, max 300 ng/m3

NOAA AIR RESOURCES LABORATORY

Observed SO₂ / BC ratio: 6.69

NOAA AIR RESOURCES LABORATORY

Observed SO₂ / BC ratio: 5.41
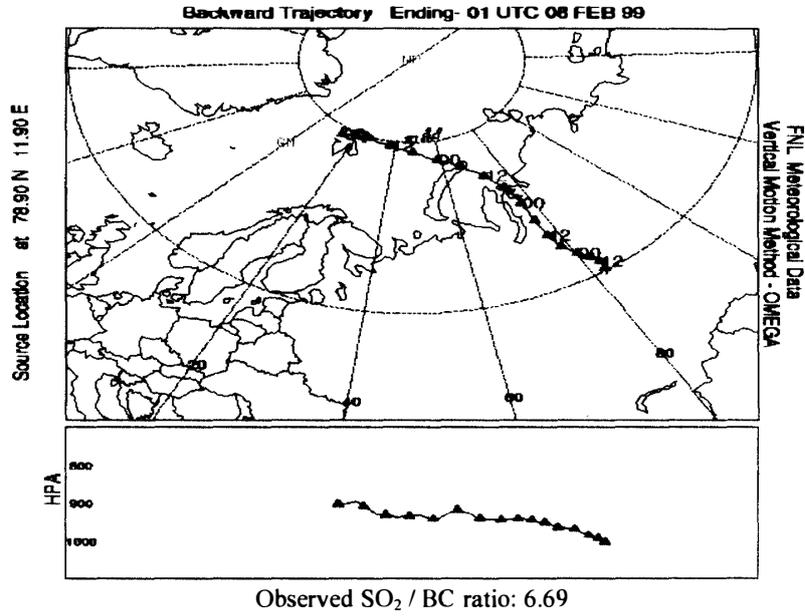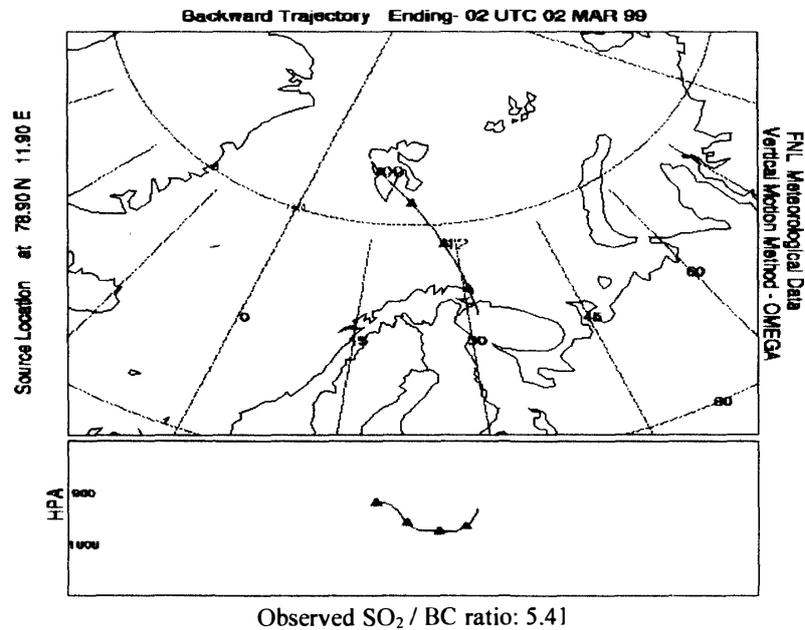
Fig. 3. Examples of airmass back trajectories associated with high BC concentrations at Ny-Ålesund, coinciding with the two main air pollution sources for the High Arctic, the industrial complexes at Norilsk and Kola peninsula of Russia. Back trajectories performed by means of the NOAA Hysplit model through their network service.

Black Carbon and sulphur species
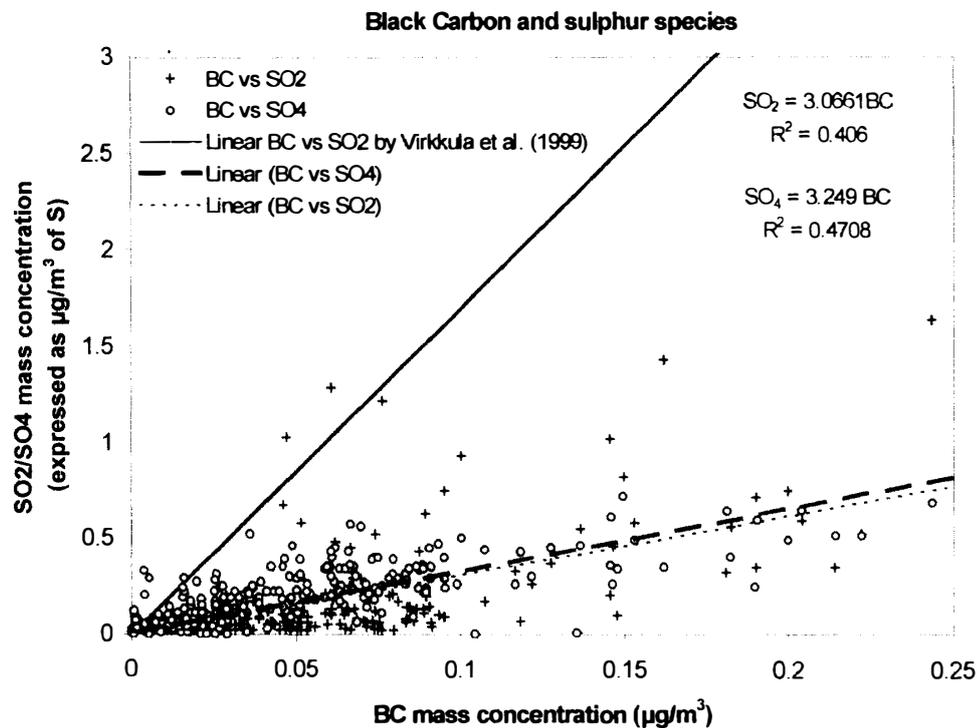
Fig. 4. Linear regression results for the pairs BC-SO_2 and BC-SO_4. The relationship between BC-SO_2 based on the measured BC data and the SO_2 calculated from their ratio observed near the emission sources at the Kola peninsula is also presented.

trajectory analysis for Zeppelin station, reveals the expected association of enhanced concentrations observed for BC and sulphate with long range transport of polluted air from Eurasia. A simplified approach for estimation of air mass origin was followed for the months with highest BC concentrations observed (December–April). The origin of an air mass was classified according to major geographical sectors, when 75% of the trajectory points fall within a sector. These sectors were selected as follows (defined by the region between longitude intervals): Russian ($30°E$–$130°E$), North Pacific ($130°E$–$130°W$), American ($130°W$–$60°W$), Atlantic ($60°W$–$5°W$), European ($5°W$–$30°E$). An additional sector, the Polar Oceanic region, was defined as the area north of $80°$. It was found that the dominant sectors was the Polar Oceanic region which accounted for 40% of the trajectories and the Russian sector with 31%. All other sectors contributed less than 12%, while 18% of the trajectories were of mixed origin. It is concluded that the high BC concentration events during this period originate almost exclusively from the Russian sector. Two examples of major long range transport events identified during this study are shown in Fig. 3. The relationship between the two sulphur species and BC is explored in the graph of Fig. 4. The graph also includes the estimated BC mass concentration for the measured SO_2 concentrations when the ratio SO_2/BC, reported by Virkkula *et al.* (1999) and found equal to 16 at Sevettijarvi near the industrialised Kola peninsula, is utilised. There is lack of other such measurements near the Russian pollution source areas. Penner and Eddleman (1993), have constructed a model for BC global concentration estimates based on the BC/SO_2 ratio. For

the whole of Russia they assume this ratio to be equal to 3. The average SO_2/BC ratio derived from Fig. 4 is very close to this figure. Long term measurements of BC concentration along with that of the sulphur species at Ny-Ålesund are needed in order to explore the significance of this ratio as a characteristic feature of the arctic aerosol.

Acknowledgments

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