

Characteristics of carbonaceous aerosol in a two-week campaign at Ny-Ålesund

Xie Zhouqing(谢周清)^{1,*}, Wang Xinming(王新明)², Sun Liguang(孙立广)¹, Long Nanye(龙楠焯)³ and Cheng Bangbo(程帮波)¹

1 Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

2 State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

3 School of Earth and Space Science, University of Science and Technology of China, Hefei 230026, China

Received July 15, 2005

Abstract The concentrations of organic carbon (OC) and elemental carbon (EC) in total suspended particle (TSP) were investigated at Ny-Ålesund, Svalbard in a two-week campaign. The levels of OC and EC are $0.86 \pm 0.27 \mu\text{g m}^{-3}$ (mean \pm standard deviation) and $0.19 \pm 0.10 \mu\text{g m}^{-3}$, respectively. Back trajectory analysis of air masses arriving at Ny-Ålesund reveals that long-range transport of polluted air play insignificant role in OC and EC levels, to which the potential influence of the local contamination were ascribed. The average OC/EC ratio is 5.41, suggesting the presence of the secondary organic aerosols. The estimated secondary organic carbon (SOC) in TSP is $0.59 \mu\text{g m}^{-3}$, accounting for 64% of the total organic carbon.

Key words Organic carbon (OC), Elemental carbon (EC), TSP, SOC, Ny-Ålesund.

1 Introduction

Atmospheric aerosol contains a significant fraction of carbonaceous material, which makes important role in the environmental, health and climate effects (Turpin and Huntzicker 1991; Holgate 1995). Commonly, carbonaceous aerosol is classified into two main fractions, elemental carbon (EC) and organic carbon (OC). Elemental carbon, also known as black carbon, has a graphic-like structure and is black. In a global-scale, EC plays significant role in global warming in terms of direct forcing (Jacobson 2001). In a regional-scale, EC can alter regional atmospheric stability and vertical motions via heating the air, and affect circulation and hydrologic cycle with significant regional climate effects (e. g. , China and India) (Menon *et al.* 2002). Particulate organic carbon is a mixture of hydrocarbons and oxygenates, containing

polycyclic aromatic hydrocarbon (PAH) and other compounds with possible mutagenic and carcinogenic effects (Pandis *et al.* 1992).

While black carbon is essentially a primary pollutant, emitted directly during the incomplete combustion of fossil and biomass carbonaceous fuels, organic carbon has both a primary and secondary origin (Castro *et al.* 1999). Primary particulate organic carbon is formed during combustion and emitted mainly as submicron particles (Castro 1999). The secondary origin of particulate organic carbon is from gas to particle conversion of volatile organic compounds (VOC) in the atmosphere (Pandis 1992). It is necessary to quantify primary and secondary sources for controlling particulate carbon pollution since reduction of direct emissions only affects primary particulate carbon constituents (Larson *et al.* 1989).

During the past three decades, there has been increasing interest in the presence of airborne pollutants in the Arctic region (AMAP 1998). However, quantitative information concerning the OC and EC in the ambient air, especially the importance of secondary organic carbon production, is scarce.

This study is aimed to investigate the levels of OC and EC at Ny-Ålesund, Svalbard, a high Arctic region, and obtain the information of secondary organic carbon production.

2 Sampling and analysis

2.1 Sample Collection

Aerosol sampling was conducted using a middle-volume bulk aerosol sampler (Tianhong Instruments, Wuhan, China) at Ny-Ålesund (78°55'N, 11°56'E), Svalbard which has been received intensive attention for its advantage in scientific research (e. g. , environmental change and atmospheric contamination). The sampler was placed about 2 m above the ground. The site was approximately 100 m southeast of the Chinese Arctic Yellow River Station (Fig. 1) and was operated during the First Chinese Arctic Station Research Expedition (3 August-18 August 2004). The sampling period spanned approximately 2-week. Total suspended particle (TSP) was collected on 90 mm diameter glass microfibre filters (Whatman GF/A glass filters, Cat. No. 1820 090) at a flow rate of 100 L/min. Sampler was not fitted with a wind direction controller, and therefore collected air samples only from prevailing wind directions. A continuous sampling period lasted 24h, except 2 samples, which only lasted 12 h, due to the weather. All filter samples were retrieved from the sampler with strict contamination control procedures as outlined by Gao *et al.* (1996). Filters were placed and sealed in clean plastic bags and kept at 4°C until lab analysis (Xie *et al.* 2002). A total of 15 samples were collected. The sampling information is listed in table 1. One of samples, namely, Ny-A03, is not used for analysis here because of electrical power supply failure for unclear reason during the sampling and the loss of automatically recorded data, such as sampling hours.

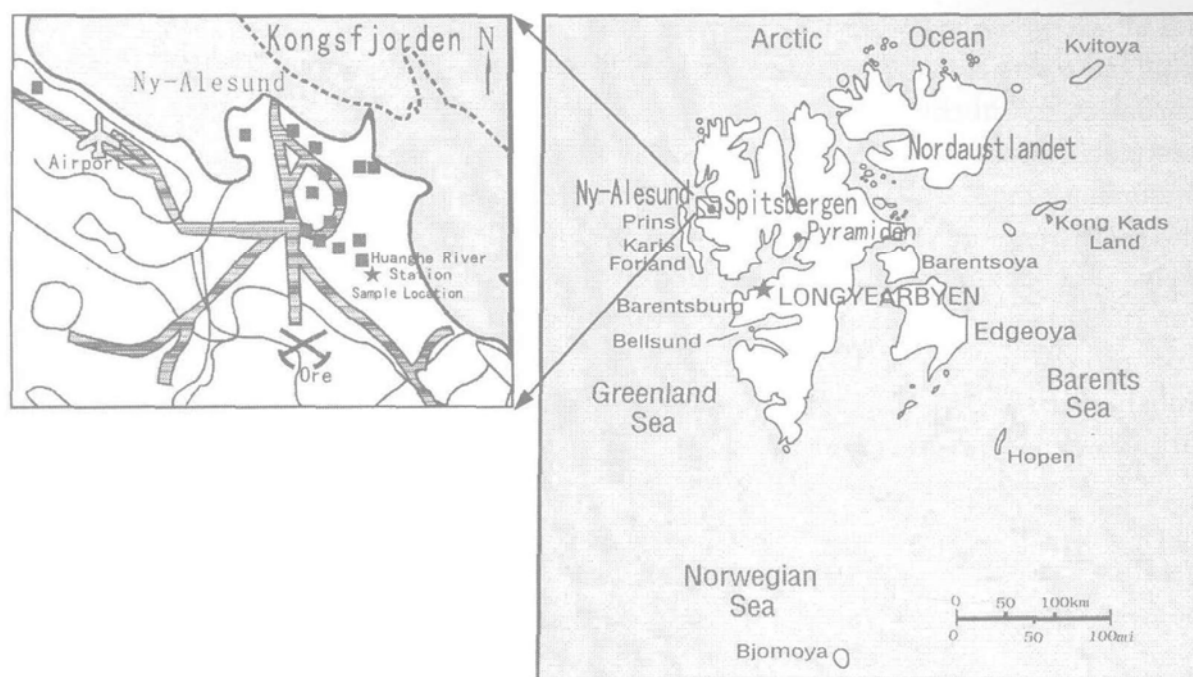


Fig. 1 The sketch map of sampling site

2.2 Carbonaceous aerosol analysis

The measurement procedure was reported in detail by Chen *et al.* (2005). Here it is briefly described. Portions of filter samples (1.5 cm²) were cut for analyzing organic and elemental carbon contents (OC and EC) by a thermal-optical carbon analyzer (Sunset Laboratory Inc., Forest Grove, OR) with a modified NIOSH (National Institute of Occupational Safety and Health) thermal-optical transmission (TOT) protocol. The punch aliquot of filter was heated stepwise at temperature of 310, 475, 575, and 650 °C in a pure helium atmosphere for detecting the OC fraction, and at temperatures of 550, 625, 700, 775, and 850 °C in an oxidizing atmosphere of 2% oxygen (by volume) in a balance of helium for detecting the EC fraction. The carbon evolved at each temperature was oxidized to carbon dioxide (CO₂) and then reduced to methane (CH₄) for quantification with a flame ionization detector (FID). Some of OC was pyrolyzed to EC with the temperature increases in inert helium and is subtracted from the elemental carbon amount according to the initial laser absorbance. At the end of every analysis, a fixed volume loop of methane is injected automatically as an internal standard to calculate the carbon results. The measurement was performed at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

3 Results and discussion

3.1 The levels of OC and EC; Local sources of contamination

A summary of the measurement results for the concentrations of OC, EC and TC

in TSP are given in Table 1. The average OC and EC concentrations are 0.86 and 0.19 $\mu\text{g}/\text{m}^3$, respectively and the average TC concentration is 1.05 $\mu\text{g}/\text{m}^3$. OC and EC concentrations in this study are similar to values of 0.40 $\mu\text{g}/\text{m}^3$ and 0.04 $\mu\text{g}/\text{m}^3$, respectively, found at Mace Head (Castro 1999), which is a remote site apart from contamination. The daily variations in the OC and EC concentrations were observed. The coefficients of variances (CVs) for OC and EC are 31.4% and 52.6%, respectively. The maximum values of OC and EC are 1.32 and 0.42 $\mu\text{g}/\text{m}^3$, approximately 3 or 10 times higher than the ones at Mace Head, indicating potential occasional events of atmospheric pollution occurred in summer at Ny-Ålesund. The pollution is probably ascribed to the long-range transport of anthropogenic aerosol from southern latitudes or local contamination.

Geographically, Ny-Ålesund lies in the Svalbard archipelago, which is situated approximately half-way between the North Cape of Norway and the North Pole and is therefore far removed from major sources of atmospheric pollution. However, since the first reports of 'Arctic haze' by Mitchell *et al.* (1956) studies have shown that significant long-range transport of atmospheric pollutants to Svalbard can occur and is thought to originate in the Kola/Karelia region of Russia, Western Europe, and North America (e. g. , Rahn and Shaw 1982; Beine *et al.* 1996; Burkow and Kallenborn 2000). Thus, deposition of atmospheric pollutants on Svalbard has been attributed to long-range sources.

To investigate the air mass origin during the sampling period, backward trajectories of air mass were calculated by means of the NOAA developed HYSPLIT4 model (Draxler and Rolph 2003). The calculations performed here used the NFL meteorological data, available at the NOAA web site, which cover the whole globe with $1^\circ \times 1^\circ$ resolution and are interpolated from global measurements. The model was run for a 120 h period in time. The results present that the sampling period was mainly characterized by air masses arriving from the polar region (Greenland or high Arctic Ocean) and the North Atlantic (Fig. 2), which is previously termed as background air with litter contamination (Eleftheriadis *et al.* 2004). Air mass origin from anthropogenic emission areas such as Kola Peninsula or Western Russia was not observed. The long-range transport of anthropogenic source was therefore presumed to play insignificant role in the EC or OC in summer at Ny-Ålesund.

In Svalbard, local mining industries have been presented since the turn of the century and coal-fired power stations in the Isfjord area (Longyearbyen, Barentsburg, and Pyramiden) have been operated for at least 40 years (Rose *et al.* 2004). Given the great distances from major sources in continental Europe or North America, these small, industrial point sources within Isfjord may combine to form a significant source of emission in this sensitive, low deposition area. Therefore, it may be that these local sources are not 'negligible' as has been suggested in previous studies (e. g. , Lannefors *et al.* 1983). It has found that these sources may account for elevated levels of contaminants (e. g. , PAHs, SCPs) in sediments within a radius of 60–70 km, which represents a land area of 7000–9500 km^2 receiving enhanced deposition (Rose *et al.* 2004). Spheroidal carbonaceous particles (SCPs), which are composed mainly of elemental carbon (EC), are produced from the high temperature

combustion of fossil-fuels and have no natural sources. In lake sediments SCPs provide an unambiguous record of industrially derived, atmospherically deposited pollution. Change in the levels of SCPs and PAHs (semi-volatile organic compounds) in lake sediments in Svalabrd associated with local contamination thus support this work findings that local sources pose mainly impact on the EC and OC in atmosphere at Ny-Ålesund in summer.

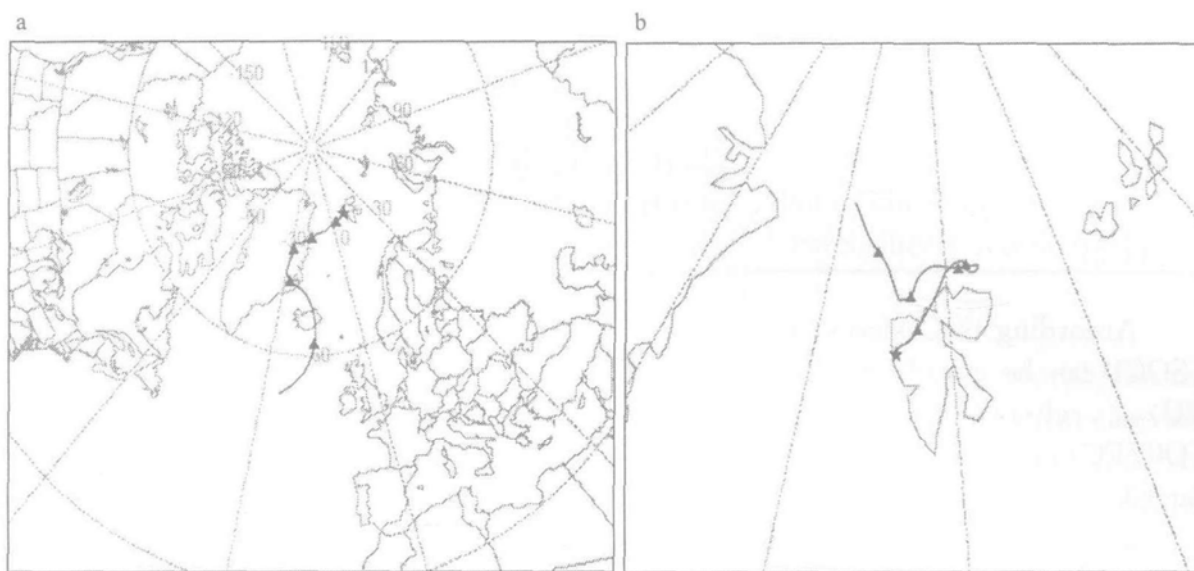


Fig. 2 Backward trajectories of air mass transport to Ny-Ålesund during sampling period. Trajectories have been calculated for the point of beginning sampling NyA01(a) and NyA15(b)

3.2 Estimation of secondary organic carbon concentrations

The ratio of OC over EC concentrations has been used to study emission and transformation characteristics of carbonaceous aerosol. In general, the values exceeding 2.0 have been used to indicate the presence of secondary organic aerosols (Gray *et al.* 1986; Chow *et al.* 1996).

In this study, the OC/EC ratios vary between 1.38 and 8.50 with an overall average of 5.41 (Table 1). There are only two samples with low values than 2.0. The minimum OC/EC ratio is comparable to the previous results observed at the rural sites during summer season (e. g. , 1.5 at the Anadia and Tabua rural sites). 86% of samples have OC/EC values higher than 2.0 (Table 1), indicating that the presence of secondary carbon in the Ny-Ålesund atmosphere is common in summer season. High OC/EC ratio in the Ny-Ålesund atmosphere can be explained by a greater incorporation of secondary organic carbon as a result of chemical transformation during long-range transport from the sea, which is revealed by backward trajectories in Fig. 2.

Table 1. Concentrations of organic carbon (OC), elemental carbon (EC), total carbon (TC) ($\mu\text{g}/\text{m}^3$) and OC/EC

	Start Date	Duration (h)	OC	EC	TC	OC/EC
Ny-A01	03/08	24	1.28	0.19	1.47	6.77
Ny-A02	04/08	24	0.60	0.42	1.02	1.43
Ny-A04	06/08	12	1.32	0.22	1.54	5.96
Ny-A05	07/08	24	0.98	0.11	1.09	8.50
Ny-A06	08/08	24	0.75	0.15	0.91	4.89
Ny-A07	09/08	24	0.63	0.10	0.73	6.17
Ny-A08	10/08	24	0.44	0.32	0.75	1.38
Ny-A09	11/08	24	0.91	0.11	1.02	8.24
Ny-A10	12/08	24	0.75	0.28	1.03	2.64
Ny-A11	13/08	24	0.74	0.13	0.87	5.76
Ny-A12	14/08	12	1.21	0.21	1.42	5.71
Ny-A13	15/08	24	0.60	0.10	0.70	5.91
Ny-A14	16/08	24	0.97	0.24	1.21	3.98
Ny-A15	17/08	24	0.89	0.11	0.99	8.38
Average			0.86	0.19	1.05	5.41
STD			0.27	0.10	0.27	2.35
CV(%)			31.4	52.6	25.7	43.4

According to Castro *et al.* (1999), the production of secondary organic carbon (SOC) can be calculated from the following equation: $\text{OC}_{\text{sec}} = \text{OC}_{\text{tot}} - \text{EC} \times (\text{OC}/\text{EC})_{\text{min}}$, where OC_{sec} is the secondary OC (SOC), OC_{tot} is the total OC (TOC), and $(\text{OC}/\text{EC})_{\text{min}}$ is the minimum ratio observed. In this study, the $(\text{OC}/\text{EC})_{\text{min}}$ ratio, referred to the average value of the two ratios, is lower than 2.0.

The estimated SOC ranges between 0.00 and 1.04 $\mu\text{g}/\text{m}^3$ with an average value of 0.59 $\mu\text{g}/\text{m}^3$, accounting for 64% of organic carbon concentrations (Table 2). This implied SOC is an important component of organic particle material (PM). The range of 47–83% of SOC in organic carbon is comparable to the range of 41–78% observed in rural or remote sites during summer in Castro's study (1999).

Table 2 Levels of secondary organic carbon (SOC) estimated from minimum OC/EC ratios, primary organic aerosols (OC_{prim}) and the percentage of SOC in organic carbon

	SOC($\mu\text{g}/\text{m}^3$)	OC _{prim} ($\mu\text{g}/\text{m}^3$)	Percentage (SOC/OC, %)
Ny-A01	1.02	0.27	0.79
Ny-A02	0.00	0.59	0.00
Ny-A04	1.00	0.31	0.76
Ny-A05	0.81	0.16	0.83
Ny-A06	0.54	0.22	0.71
Ny-A07	0.48	0.14	0.77
Ny-A08	0.00	0.45	0.00
Ny-A09	0.75	0.16	0.83
Ny-A10	0.35	0.40	0.47
Ny-A11	0.56	0.18	0.76
Ny-A12	0.91	0.30	0.75
Ny-A13	0.46	0.14	0.76
Ny-A14	0.62	0.34	0.65
Ny-A15	0.74	0.15	0.83
Average	0.59	0.27	0.64
STD	0.32	0.14	0.29
CV(%)	54.2	51.9	45.3

4 Summary and outlook

Total Suspended Particle (TSP) samples were collected at Ny-Ålesund, Svalbard in a two-week campaign during the 2004 summer period. The concentrations of organic carbon (OC) and elemental carbon (EC) in TSP were measured. The average OC and EC concentrations in TSP were very low and comparable with the previous report at the remote or rural areas. Backward trajectories of air mass transport to the sampling sites indicate that long-range transport of anthropogenic source do not influence the EC or OC levels during sampling period in summer, which are mainly impacted by local source. Almost all of the samples have OC/EC ratios higher than 2.0, suggesting the presence of the secondary organic carbon, the amount of which is estimated to account for about 64% of the organic carbon. The findings provide an opportunity to understand the source of pollution and atmospheric secondary pollution in the high Arctic region.

Acknowledgements This research was supported by grants from the National Natural Science Foundation of China (Project No. 40306001) and the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (Grant No. 200354) from Ministry of Education of China and Chinese Academy of Sciences. Fieldwork was supported by the Chinese Arctic and Antarctic Administration. We thank teammates of the First Chinese Arctic Station Research Expedition for assisting in sampling aerosols and the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (<http://www.arl.noaa.gov/ready.html>) used in this publication.

References

- AMAP, assessment report (1998): Arctic pollution issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.
- Beine HJ, Engardt M, Jaffe DA *et al.* (1996): Measurements of NO_x and aerosol particles at the Ny-Ålesund Zeppelin mountain station on Svalbard; influence of regional and local pollution sources. *Atmos. Environ.* 30:1067 - 1079.
- Burkow IC and Kallenborn R (2000): Sources and transport of persistent pollutants to the Arctic. *Toxicol. Lett.* 112 - 113; 87 - 92.
- Castro LM, Pio CA, Harrison RM (1999): Carbonaceous aerosol in urban and rural European atmospheres; estimation of secondary organic carbon concentrations. *Atmos. Environ.* 33:2771 - 2781.
- Chen YJ, Sheng G, Bi XH *et al.* (2005): Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environ. Sci. Technol.* 39:1861 - 1867.
- Chow JC, Watson JG, Lu Z *et al.* (1996): Descriptive analysis of PM_{2.5} and PM₁₀ at regionally representative locations during SJVAQS/AUSPEX. *Atmos. Environ.* 30:2079 - 2112.
- Draxler RR and Rolph GD (2003): HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY, Website (<http://www.arl.noaa.gov/ready/hysplit4.html>). NOAA Air Resources Laboratory, Silver Spring, MD.
- Eleftheriadis K, Nyeki S, Psomiadou C *et al.* (2004): Background aerosol properties in the European Arctic. *Water, Air, and Soil Pollu.* 4:23 - 30.

- Gao Y, Arimoto R, Duce RA *et al.* (1996): Atmospheric non-sea-salt sulfate, nitrate and methanesulfonate over the China Sea. *J. Geophys. Res.* , 101:12601 - 12611.
- Gray HA, Cass GR, Huntzicker JJ *et al.* (1986): Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles. *Environ. Sci. Technol.* , 20:580 - 589.
- Holgate S (1995): Non-biological particles and health. Department of Health, HMSO, London, 87 - 124.
- Jacobson MZ (2001): Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, 409:695 - 697.
- Lannefors H, Heintzenberg J, Hansson HCh (1983): A comprehensive study of physical and chemical parameters of the Arctic summer aerosol; results from the Swedish expedition Ymer-80. *Tellus* 35B: 40 - 54.
- Larson SM, Cass RG, Gray HA *et al.* (1989): Atmospheric carbon particles and the Los Angeles visibility problem. *Aerosol Sci. Technol.* , 10:118 - 130.
- Menon S, Hansen J, Nazarenko L, Luo YF (2002): Climate effects of black carbon aerosols in China and India. *Science* 297:2250 - 2253.
- Mitchell M (1956): Visual range in the polar regions with particular reference to the Alaskan Arctic. *J. Atmos. Terr. Phys.* , Special Suppl. ; 195 - 211.
- Pandis SN, Harley RA, Cass GR *et al.* (1992): Secondary organic aerosol formation and transport. *Atmos. Environ.* , 26A:2269 - 2282.
- Rahn KA and Shaw GE (1982): Sources and transport of Arctic pollution aerosols; a chronicle of six years of ONR research. *Naval Res. Rev.* March, S2 - S26.
- Rose NL, Rose CL and Boyle JF *et al.* (2004): Lake-sediment evidence for local and remote sources of atmospherically deposited pollutants on Svalbard. *J. Paleolimnol.* , 31:499 - 513.
- Turpin BJ and Huntzicker JJ (1991): Secondary formation of organic aerosol in the Los Angeles Basin; a descriptive analysis of organic and elemental carbon concentrations. *Atmos. Environ.* , 25A:207 - 215.
- Xie ZQ, Sun LG, Wang JJ *et al.* (2002): A potential source of atmospheric sulfur from penguin colony emissions. *J. Geophys. Res.* , 107; doi:10.1029/2002JD002114.