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Chemical composition and sources of aerosol particles at Zeppelin Mountain (Ny Ålesund, Svalbard): An electron microscopy study

Stephan Weinbruch[a,*], David Wiesemann[a], Martin Ebert[a], Katharina Schütze[a], Roland Kallenborn[b,c], Johan Ström[d]

[a] Institute of Applied Geosciences, Technical University Darmstadt, Schnittspahnstr. 9, D-64287 Darmstadt, Germany
[b] Department of Chemistry, Biotechnology and Food Sciences (IKBM), Norwegian University of Life Sciences (UMB), NO-1432 Ås, Norway
[c] Norwegian Institute for Air Research (NILU), NO-2027 Kjeller, Norway
[d] Department of Applied Environmental Science (ITM), Stockholm University, Svante Arrhenius väg 8, S-109 61 Stockholm, Sweden

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ABSTRACT

Aerosol particles were collected at the Zeppelin Mountain Atmospheric Research Station (474 m asl) near Ny Ålesund (Svalbard, Norway) on 27 different days between July 2007 and December 2008. The size, morphology and chemical composition of 57,617 individual particles were studied by high-resolution scanning electron microscopy and energy-dispersive X-ray microanalysis. Based on chemical composition, morphology, mixing state and stability under electron bombardment, the particles were assigned to one of the following groups: sea salt, aged sea salt, Ca sulphates, Na sulphates, carbonates, soot, silicates, fly ashes, secondary aerosol, secondary aerosol plus sodium, secondary aerosol plus soot, mixed particles and others.

Sea salt, aged sea salt, silicates and mixed particles (mixtures of sea salt, silicates and Ca sulphates) are the most abundant groups for particles with aerodynamic diameters > 0.5 µm, secondary aerosol, mixed particles and secondary aerosol with soot inclusions below 0.5 µm. Silicate fly ashes (major source coal burning) and metal fly ashes (from metallurgical high temperature processes) occur only at very low number concentrations. In contrast to previous work, the fly ash abundance is not correlated with air masses that crossed industrialized regions in Central and Eastern Europe, Scandinavia or Russia. These observations indicate a significant reduction of long-range transport of heavy metals to Svalbard. Soot (external and internally mixed with secondary aerosol) shows a pronounced seasonal pattern with a much lower abundance during summer compared to spring, autumn and winter. The soot abundance is not correlated with the air mass back-trajectories. During summer (July and August), soot was only observed when cruise ships were present in the area around Ny Ålesund (Kongsfjorden). Pronounced seasonal patterns were observed for the abundance of the mineral dust component which is generally lower in summer compared to the other seasons. The observed seasonal dependence of anthropogenic primary particles (soot, fly ashes) is in good agreement with the Arctic circulation pattern.

1. Introduction

It is evident from numerous publications that inorganic (originating for example from coal burning or metallurgical processes) as well as organic pollutants are transported from industrialized regions in Europe, Russia, Northern America, and even the Asian industrialized regions, to the Arctic (e.g., Shaw, 1982; Pacyna et al., 1984, 1985; Pacyna and Ottar, 1985; Maenhaut et al., 1989; Shevchenko et al., 2003; Berg et al., 2004; Hirdman et al., 2010; Hung et al., 2010). According to Pacyna (1995), emissions from anthropogenic sources in Europe and Asia dominate the pollution during winter. During summer pollution episodes, emissions from sources in Europe are reported to be of higher importance than those from Russia (Pacyna, 1995). In recent studies, decreasing time trends were observed for Ni and some persistent organic compounds (Berg et al., 2004; Hung et al., 2010) as well as for black carbon (Eleftheriadis et al., 2009; Hirdman et al., 2010). According to Hirdman et al. (2010), changes in emissions in the source regions dominate the observed time trends.

The Zeppelin Mountain Atmospheric Research Station (474 m asl) near Ny Ålesund (Svalbard, Norway) is established as a background station and, thus, well suited to monitor long-range transport of

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* Corresponding author. Tel.: +49 6151 165280; fax: +49 6151 164021.
E-mail address: weinbruch@geo.tu-darmstadt.de (S. Weinbruch).

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pollutants into the Arctic (e.g., Beine et al., 1996; Ström et al., 2003; Berg et al., 2004; Hirdman et al., 2010). The inorganic aerosol composition at this location and in the settlement of Ny Ålesund was investigated by bulk chemical measurements during the past 30 years (Pacyna et al., 1984, 1985; Pacyna and Ottar, 1985; Maenhaut et al., 1989) as well as by single particle analysis (Anderson et al., 1992; Behrenfeldt et al., 2008; Geng et al., 2010). The previous single particle studies at this location were restricted to the time period of late spring to early summer (May–July). In contrast, a more complete coverage of the different seasons of a year is provided by the present study. As pronounced seasonal patterns in particle concentration and size distribution were observed (Ström et al., 2003), our study is aiming to contributing to a more complete characterization of the aerosol chemistry at Ny Ålesund.

2. Experimental

2.1. Sampling

Particle sampling was performed at the Zeppelin Mountain Atmospheric Research Station (474 m asl) near Ny Ålesund (Svalbard, Norway). Sampling took place on 27 different days between July 2007 and December 2008. Particles were collected on nickel grids covered with Formvar foil (fine fraction) or on copper foils (coarse fraction) using a two-stage micro inertial cascade impactor (50 % cut of diameters: 0.1–0.5 μm and 0.5–10 μm). Due to experimental problems (rupture of the Formvar foil for the fine fraction or insufficient number of particles for the coarse fraction) not all samples were suited for electron microscopy. The sampling date and time, samples suited for electron microscopy, weather conditions and average particle number concentration (diameter ≥ 3 nm) during sampling are summarized in the supplementary data (Table S1).

2.2. Electron microscopy

The size, morphology, mixing state and chemical composition of 57,617 particles on 64 samples were studied by high-resolution scanning electron microscopy and energy-dispersive X-ray microanalysis. All measurements were carried out with a field emission gun environmental scanning electron microscope (FEI ESEM Quanta 200 FEG, Eindhoven, The Netherlands) operated at 20 kV accelerating voltage. The size (equivalent projected area diameter) of the individual particles was obtained from secondary electron images. The chemical composition (elements with $Z \geq 5$) of the particles was determined by energy-dispersive X-ray microanalysis using a Si(Li) detector (EDAX, Tilburg, The Netherlands). The particles were studied without coating in the high vacuum mode of the instrument ($\approx 5 \times 10^{-6}$ mbar sample chamber pressure). The particles on the coarse stage were investigated by automated analysis, whereas the characterization of particles on the fine stage was carried out operator-controlled. Special emphasis was placed on detection of the element nitrogen in secondary aerosol particles. For this purpose, the beam was moved across a particle during analysis in order to minimize evaporation of nitrogen-containing phases (nitrates and/or ammonium compounds), which are often unstable under electron bombardment.

Based on the chemical composition, morphology, mixing state and stability under electron bombardment, the particles were assigned to thirteen different groups. The particle classification was performed with net X-ray count rates, i.e., matrix and geometric effects were not corrected for. Criteria for the definition of the particle groups are given in the supplementary data (Table S2). It should be emphasized here, that net X-ray count rates are sufficient for classification of particles into the different groups. Quantification of the particle composition prior to classification would not lead to different particle groups.

2.3. Particle number concentrations

Number concentrations of particles with diameters ≥ 3 nm were measured using a condensation particle counter (TSI model 3025, Shoreview, Minnesota, USA).

2.4. Back-trajectories

Air mass back-trajectories were calculated using the FLEXTRA trajectory model (Stohl et al., 1995; Stohl and Seibert, 1998) provided by the Norwegian Institute for Air Research (www.nilu.no/trajectories).

3. Results

The absolute number abundance of the different particle groups is shown in Table 1, the relative number abundance in Figs. 1 and 2. As the aerosol composition, particle number concentrations, weather conditions and air mass back-trajectories (Table 2) were quite similar during a given day, different samples of the same day are merged.

Sea salt, aged sea salt, silicates and mixed particles (mixtures of sea salt, silicates and Ca sulphates) are the most abundant particle groups in the coarse fraction. All four groups can be readily identified from the X-ray spectra. The coarse fraction is dominated by sea salt and aged sea salt on most sampling days (Fig. 1). The higher relative abundance of mixed particles in the coarse fraction on a few days is neither correlated with the weather conditions (local wind speed, local wind direction) nor the air mass back-trajectories.

In the fine fraction, secondary aerosol, mixed particles (mixtures of sea salt, silicates and Ca sulphates), and secondary aerosol with soot inclusions are the most abundant particle groups (Fig. 2). External soot and secondary aerosol plus sodium occur at minor abundance. The secondary aerosol is a complex mixture of sulphates, nitrates and organic material. The sulphate component can be recognized unambiguously from the presence of strong S–K$_\alpha$ and O–K$_\alpha$ peaks in the X-ray spectrum. The presence of nitrates and/or ammonium can be deduced from the N–K$_\alpha$ peak. High carbon concentrations in secondary aerosol particles indicate the presence of organic material or soot inclusions. The Formvar foil used as substrate for the fine particle fraction may lead to a small carbon signal in the X-ray spectrum. However, most secondary aerosol particles show much stronger carbon peaks indicating the presence of carbon within the particle. Soot inclusions within secondary particles can be identified from their typical morphology (agglomerates of primary particles with fractal-like geometry) after the secondary component is evaporated by electron bombardment. Soot occurs either as chain-like agglomerates (Fig. 3a) or as compacted agglomerates (Fig. 3b) of primary particles with grain sizes between 40 and 120 nm. In all samples, more than 99% of the soot agglomerates have chain-like structures for both, external and internally mixed agglomerates. If no soot inclusions are detected in secondary aerosol particles with high carbon content, it is concluded that organic material is present. Fly ash particles can be easily recognized from their morphology (spheres). They are present at minor abundance during most sampling days in autumn, winter and spring, and are practically absent during summer (July and August). Fly ash particles are usually internally mixed with secondary aerosol. Only 201 out of 57,617 particles were fly ashes with about $^3/_4$ having silicate and ¼ metal compositions. The metallic fly ashes consist of iron as major element and sometimes significant Ni, Cr, or Zn concentrations.