



A study of the sea-salt chemistry using size-segregated aerosol measurements at coastal Antarctic station Neumayer



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HIGHLIGHTS

- Size-segregated aerosol measurements were made at coastal site, Antarctica.
- Concentration of sea salt aerosol varied largely during the year.
- Sea salt contribution to particle mass smaller than 0.2 μm was negligible.
- Physico-chemical processes had modified sea salt aerosol.

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ABSTRACT

Aerosol chemical and physical properties were measured in 2010 at Neumayer research station, Antarctica. Samples for chemical analysis (ion chromatography) were collected using a Teflon/Nylon filter combination (TNY) sampler, and with a multi stage low pressure impactor (SDI). Particle number concentration was measured continuously with a Grimm OPC optical particle counter. Total particle number concentration varied largely throughout the year, and the highest number concentrations for particles larger than 0.3 μm were observed simultaneously with the highest sea salt concentrations. About 50% of the sea salt aerosol mass was found in the submicron size range. Below 0.2 μm of particle aerodynamic diameter the contribution of sea salt aerosols was negligible. Further analysis showed that sea salt aerosols had undergone physico-chemical processes, either during the transportation, or during their formation. High degree of chloride depletion was observed during austral summer, when the presence of acidic gases exhibit their characteristic seasonal maximum. Apart from chloride depletion, excess chloride relating to sodium was also detected in one SDI sample, indicating actually a sodium depletion by mirabilite formation on freshly formed sea ice areas. Analysis of selected episodes showed that the concentration of sea salt particles, their modal structure, and their chemical composition is connected with their source areas, their formation mechanisms, and local transport history.

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1. Introduction

Antarctica is geographically isolated from anthropogenic particle sources, therefore, the majority of measured particulate matter is of natural origin. Minor local anthropogenic sources comprise some emissions from research stations associated transportation. Excluding minor areas free of snow and ice occasionally producing crustal particles, the majority of particulate matter is originated

from the nearby ocean (Wagenbach et al., 1998; Minikin et al., 1998; Rankin and Wolff, 2003; Weller and Wagenbach, 2007). Primary sea salt aerosol is the major particulate matter (in mass) most time of the year (Weller et al., 2011). During austral summer secondary sulphate aerosol produced from biogenic precursor gases from the nearby ocean makes a substantial contribution to the particulate mass, and in the submicron size range sulphate aerosol is even the dominant one (Weller et al., 2011; Rankin and Wolff, 2003). While sulphate particles produced via gas to particle conversion are mainly found in the submicron size range, sea salt particles are spread over the size spectrum from 0.1 μm up to 10 μm .

Sea salt particles are produced mechanically either over ice free ocean by bubble bursting, or over freshly formed sea ice (Wolff et al., 2003; Rankin et al., 2000; Hall and Wolff, 1998).

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The chemical composition of aerosol particles produced from sea spray is similar to the sea water composition. On the contrary, the physico-chemical processes forming frost flowers over the freshly formed sea ice alter the chemical composition of sea salt particles. Most important of these processes is the depletion of sulphate, and to lesser extent the depletion of sodium compared to the sea water composition (Hall and Wolff, 1998). Once formed the sea salt particles further undergo physical and chemical processes during their transportation. The sea salt mass size distribution alters during the transport process due to the deposition of larger sea salt particles. The most important chemical process, which especially aged sea salt particles have undergone, is the reaction of sodium chloride with acidic gases, including HNO_3 and H_2SO_4 , which release HCl to the air and is the cause of chloride depletion in sea salt particles (Kerminen et al., 2000; Minikin et al., 1998; Wagenbach et al., 1998).

Using bulk filter samples impedes assessing the extent of different physico-chemical processes modifying sea salt particles. For example, sulphate measured from filter samples may have originated from secondary sulphate particles externally mixed with sea salt, or may be secondary sulphate produced on sea salt particles.

The sulphate content of sea salt particles also alters due to their formation processes. In addition to the sulphate depletion, a minor amount of sodium may have also been depleted when sea salt particles are formed on the sea ice (Wolff et al., 2003; Rankin et al., 2000; Hall and Wolff, 1998).

Chloride depletion typically takes place throughout the year, but the degree of chloride depletion varies largely throughout the year, and over particle size. During austral summer, when production of acidic gases is enhanced, chloride depletion is in its maximum. Chloride depletion may also take place for collected particles on the filter, which may lead to overestimation of chloride depletion.

Cascade impactors size segregate the sampled particles onto collection substrates where their exposure to acidic gases is minimized and are, hence, the method of choice (Pakkanen and Hillamo, 2002).

Earlier studies of sea salt chemistry from bulk filter measurements include (Weller et al., 2008; Weller and Wagenbach, 2007; Hara et al., 2005, 2004; Wagenbach et al., 1998; Wolff et al., 1998), and from size-segregated aerosol measurements (Jourdain et al., 2008; Virkkula et al., 2006; Rankin and Wolff, 2003; Jourdain and Legrand, 2002; Kerminen et al., 2000; Teinilä et al., 2000; Hillamo et al., 1998). Here we present results from size-segregated aerosol measurements at the coastal Antarctic station Neumayer (NM), and address the different physico-chemical processes altering particle composition. We will focus on sea salt particles, discussing the seasonality of the observed size distributions, and especially aim at assessing the size dependence sea salt chemistry. Further analysis of the size distributions of methane sulphonate (MSA^-) and nitrate have been excluded due to possible artefacts in the SDI and TNY samplers.

2. Experimental

Aerosol measurements were made at the Air Chemistry Observatory, NM Station ($70^\circ 39'S$, $8^\circ 15'W$) between February 16 and December 8, 2010. Particle number concentration was measured using a Grimm Optical Particle Counter (OPC, model 1.108). The flow rate of the Grimm OPC is 1.2 L min^{-1} , and the detection wavelength is 685 nm. The Grimm OPC measures particles in 15 size bins between 0.3 and $20 \mu\text{m}$. Averaging time of the Grimm OPC measurements was 10 min.

Size-segregated aerosol samples for chemical analysis were collected using a small deposit area impactor (SDI, Maenhaut et al. (1996)). Polycarbonate films coated with Apiezon-L vacuum grease

were used as particle impaction substrates (poreless film from Nuclepore Inc., thickness $10 \mu\text{m}$) in the SDI. The SDI has 12 collecting stages over the particle diameter range $0.045\text{--}20 \mu\text{m}$. At the pressure of 1013 mbar, and at the temperature of 23°C , the aerodynamic cut-off diameters of the individual SDI stages are equal to 0.045, 0.086, 0.153, 0.231, 0.343, 0.591, 0.796, 1.06, 1.66, 2.68, 4.08, and $8.50 \mu\text{m}$. The flow rate of the SDI impactor is 11 L min^{-1} . For chemical analysis particles were collected also on a Teflon/Nylon filter combination, (TNY, Jones et al. (1999)). The air samples for the SDI and TNY were taken directly from the common inlet duct. The cut-off of the inlet depends on the wind velocity. The tests with a TSI-APS 3321 showed that the cut-off is broadly around $7 \mu\text{m}$. The SDI and TNY filter sampling systems were housed within the NM Air Chemistry Observatory (for a detailed description of the sampling site, meteorological conditions, contamination free sampling, and analysis of the samples we refer to Wagenbach et al. (1988), König-Langlo et al. (1998) and Weller et al. (2008)). With a two-stage filter system including an upstream teflon (Millipore, 47 mm diameter, $1 \mu\text{m}$ pore size), and a downstream nylon filter (Gelman Nylasorb, 47 mm diameter, $1 \mu\text{m}$ pore size), roughly 60 m^3 of air was typically sampled over a 24 h collection period. The teflon filter collects all particulate compounds with efficiencies higher than 95%, but allows gaseous (acidic) species like HCl and HNO_3 to pass through as becoming partly adsorbed on the nylon filter (Piel et al., 2006). Note, however, that we did not analyse teflon and nylon filters separately, but refer to total concentrations of these species.

Sampling time for the SDI samples were typically 7–8 days, but there were long breaks for the SDI samplings during September and October. The collection time for the TNY samples were typically 24 h (sometimes 2 days), and the sampling usually started near midday. Total of 29 SDI samples were collected during the measurement campaign, but four of them were discarded from later analyses due to problems during the samplings.

Meteorological parameters like temperature, pressure, relative humidity, wind speed, and direction were available from the meteorological weather station. Ten day backward trajectories (arrival time 12:00) were calculated using a HYSPLIT4 model (Draxler and Hess, 1998). Used meteorological data was GDAS, 1° resolution, and three dimensional calculation was made using vertical wind velocities. Starting height of the calculations was 500 m above sea level.

The samplings were controlled in case of contamination from station activities by wind velocity, wind speed, and by the condensation particle counter (Weller et al., 2008). In case of contamination the samplings were interrupted. Aerosol samplings were switched off also during harsh weather condition like blizzards and drifting snow in order to avoid snow entering the inlet.

Collected SDI samples were analysed in the Finnish Meteorological Institute (FMI) aerosol laboratory. SDI substrates were dissolved into 5 mL of deionized water and stirred about 10 min. The anions and cations were analysed simultaneously with two Dionex ICS-2000 ion chromatograph systems. The anion analysis was made using AG17/AS17 columns with an ARS-300 suppressor and a KOH eluent generator (gradient run, $1\text{--}25 \text{ mmol L}^{-1}$). The cation analysis was made using CG12A/CS12A columns with a CSRS-300 suppressor and a methane sulphonate eluent generator (isocratic run, 25 mmol L^{-1}). Detection of the ions were made using a conductivity detector. The run time was 14 min. Analysed ions were MSA^- (methanesulphonate), Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} . Analytical accuracy of the measured ions is typically around $\pm 10\%$, and with low analytical concentrations between ± 20 and 25%.

The procedure for analysing the daily TNY filter samples, which was done at the Alfred-Wegener Institute, included wetting of the filters by $100 \mu\text{l}$ 2-propanol, soaking and shaking in 20 ml milliQ

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