

The lab above the clouds Aerosol chemistry at the Sonnblick Observatory

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Introduction

Atmospheric aerosols (particulate matter) play an important role in terms of health issues as well as climate. Especially during the cold season reports on aerosols and related health issues have become an important topic. Air quality standards set for particulate matter in ambient air (PM₁₀; particulate matter smaller than 10 µm a.d.) are exceeded in many regions in Europe. It has been shown (PUXBAUM et al. 2004) that at least in a number of cases these limit violations are already driven by elevated background concentration levels, which leave little tolerance for emissions in source regions, e.g. densely populated cities. Conditions at the Sonnblick Observatory (SBO) are definitely not the ones which can be attributed to possible violations of limit values of PM₁₀. On the contrary, the sampling site in the remote mountainous region of the Alps offers the opportunity for the determination of background concentrations. These results can also be used for assessing the influence of background concentrations of aerosol particles on climate issues.

Here we summarize the experimental setup and selected results of a two year sampling campaign of atmospheric aerosols at the Sonnblick Observatory.

Methods

Sampling was performed between 2005 and 2008 with a Digital High Volume sampler on quartz fiber filters (Pallflex, 150 mm). Sampling intervalls were one week to assure sufficient filter loadings.

Water soluble inorganic anions (chloride, nitrate, sulfate) and cations (sodium, ammonium, potassium, calcium, magnesium) were determined by ion chromatography. Analysis was performed by standard procedures using Dionex equipment. To determine short chain organic acids gradient anion analysis was carried out as well.

For determination of Total carbon (TC) aliquots of the filters were combusted at 1000 °C in an oxygen stream. The evolving carbon dioxide is detected with a NDIR monitor (Maihak SIFOR 200). To determine elemental carbon (EC) aliquots of the filters are precombusted in an oven at 340 °C in an oxygen atmosphere for two hours to remove all organic material. The remaining carbon is quantified as described above for TC. Organic carbon (OC) is calculated by subtracting EC from TC. Carbonate carbon (CC) is calculated based on the calcium content determined by ion chromatography.

Additionally the EC/OC split was estimated by a thermo-optical method for a limited number of samples. Therefore the sample is heated from room temperature to 800 °C with a rate of 20 °C /min. The evolving carbon dioxide is detected with a NDIR monitor. To account for charring the transmission of the filter is monitored by a laser. Thus it is possible to observe the beginning of carbonisation and the combustion of EC.

Selected filters were also analysed for anhydrosugars (e.g. levoglucosan – a tracer for wood burning) using liquid chromatography and pulsed amperometric detection (CASEIRO et al. 2007) and cellulose (tracer for plant debris) by enzymatical analysis followed by photometrical detection.

Aerosol mass is determined by weighing the filters prior and after sampling according to EN12341.

Results

Annual cycles determined for the major ions as well as TC, OC and EC showed low values during summer and elevated concentrations in the warm season. During winter the influence of the free troposphere is more pronounced, while the influence of boundary layer air becomes more important during summer and a modified mixing layer is formed. In case of major ions this was already seen during earlier measurements starting in 1991 and 2002. (e.g. KASPER & PUXBAUM 1998). Regarding the present measurements sulfate concentrations range from 0.2 to 2 $\mu\text{g}/\text{m}^3$ (related to 0°C and 1013 mbar) in summer and 0.1 to 1 $\mu\text{g}/\text{m}^3$ in winter. Based on the available data the summer to winter ratio between the concentrations of the major components is about 5. Results of TC are 0.2 to 2.5 $\mu\text{g}/\text{m}^3$ in summer and around 0.3 $\mu\text{g}/\text{m}^3$ in winter. The average ratio for TC/SO₄ is about 2.5. Monthly averages of the TC/SO₄ ratio range from 0.9 to 3 with no specific trend observed throughout the seasons.

Gravimetric analysis of the aerosol mass indicated an annual average from 5 $\mu\text{g}/\text{m}^3$. During an event of long range transport of Saharan dust the aerosol concentration increased strongly. This event was also characterised by thermo-optical analysis and calculation of backward trajectories.

The analysis of a limited number of samples showed small amounts of levoglucosan, 4 to 26 ng/m³. These concentrations contribute to 3 to 19 % of OC. Cellulose concentrations determined for a small set of samples come up to 25 to 85 ng/m³, which equals 6 to 22 % of OC. Earlier measurements of these tracer compounds are given in PUXBAUM et al. (2007) and SANCHEZ-OCHOA et al. (2007).

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