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A lab above the clouds (II) Aerosol and trace gas measurements at the Sonnblick Observatory

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Abstract

Within the project "Backgroundmeasurements Sonnblick" major inorganic aerosol compounds as well as the trace gases sulphur dioxide, nitric acid and ammonia were collected with filterpacks at the Sonnblick Observatory (SBO). Daily samples were collected from Dec. 2002 until Oct. 2004.

The major inorganic aerosol compounds nitrate, sulphate and ammonia showed average concentrations ranging from 5,5 to 15 nmol/m³, while the trace gases nitric acid, sulphur dioxide and ammonia range from 2,9 to 19 nmol/m³. The calculations of summer to winter ratio represent the seasonal changes of the concentration values of the individual compounds. The highest ratio is found for ammonia, where differences between summer and winter concentrations are very pronounced. Sulphur dioxide, on the contrary does not present a marked seasonal cycle. Scavenging ratios were calculated to compare aerosol data with precipiation samples. The recent measurements were compared with a data set collected from 1991-1993 and we found good agreement between both series. Another comparison was performed for particulate sulphate determined with the Filter packs and a High-Volume at the same time at Sonnblick and showed good agreement.

Keywords

Aerosols, trace gases, Sonnblick, scavenging ratios, sulphate, nitrate, ammonium, sulphur dioxide, nitric acid, ammonia, oxalat

Introduction

The seasonal concentrations and the vertical distribution of atmospheric aerosols and trace gases depend on the strength and variability of their emission sources, their air chemistry behaviour and meteorological conditions. To get information about the vertical distribution of air constituents sampling sites at higher elevations are needed in addition to ground based measurements. These sampling platforms can either be airborne (e.g. airplane measurements) or they can be situated at mountain slopes or even mountain tops. As already mentioned before (A Lab above the clouds I) the SBO provides such a sampling platform.

Results

Seasonal cycles of aerosol compounds and trace gases

The trace gases nitric acid and ammonia as well as the aerosol components nitrate, sulphate, and ammonium, showed lower concentration values in the winter months (November till January), than during the summer months (June tili August). In comparison with previous measurements at Sonnblick (KASPER and PUXBAUM, 1998), the increase of nitric acid concentrations occurred slightly later and is less pronounced. The concentration values for sulphur dioxide do not show marked difference between winter and summer. Except for these differences, the results of the recent measurements correspond widely with the trends of the years 1991 till 1993. (Figures 1a and 1b). Basically, both the measured concentration range and the annual cycle are very similar, especially in the winter months. That is the time when Sonnblick is influenced by the free troposphere.

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The evaluation of trace gases showed major differences, although the basic trends remained. During both sampling periods sulphur dioxide showed only a weakly pronounced seasonal cycle. Elevated concentrations are not driven by the air status at the site (like it is the case for the aerosol compounds), but rather determined by long-distance transport and cloud events (TSCHERWENKA et al. 1998).

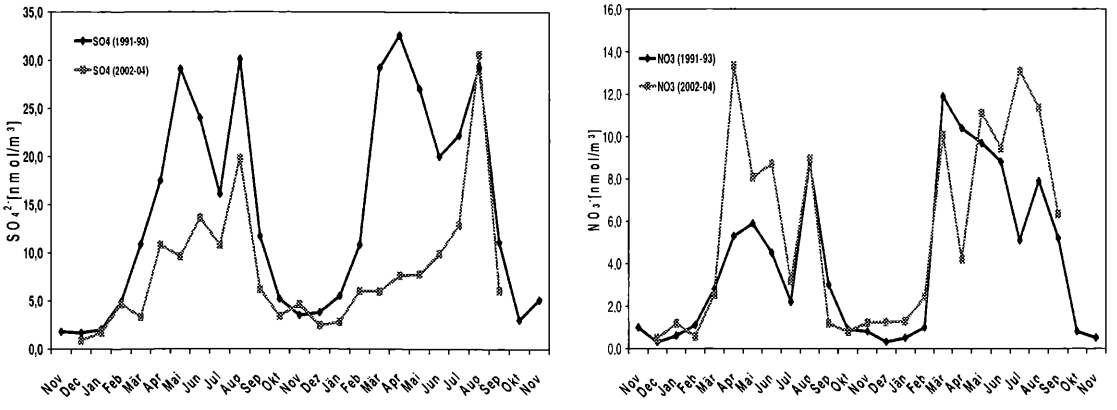

Fig. 1a and 1b: Comparison between aerosol measurements in 1991-93 and 2002-2004 for particulate sulphate and nitrate

Comparison of oxalate and sulphate concentrations

In attempting to characterize the organic aerosol fraction as well the determination of oxalate was included in the sampling program. Organic acids represent a significant contribution to the organic aerosol, in the range of 10% (LIMBECK and PUXBAUM 2000). Oxalic acid, a dicarboxilic acid that is very water soluble, is most frequently found in aerosol samples and often shows elevated concentration values. With respect to oxalic acid formation in the atmosphere, different mechanisms were discussed in the literature. The biomass combustion represents an emission source, whereas both the direct emission and the photochemical formation of this acid in an exhaust-gas plume are possible. Also anthropogenic sources are considered for the oxalic acid emission, whereas here the photochemical formation from hydrocarbon of antecedence is important.

Figure 2 compares the seasonal cycle of sulphate and oxalate at Sonnblick. The annual cycles of both compounds show good agreement, although oxalate concentrations are generally more than one order of magnitude lower than sulphate concentrations.

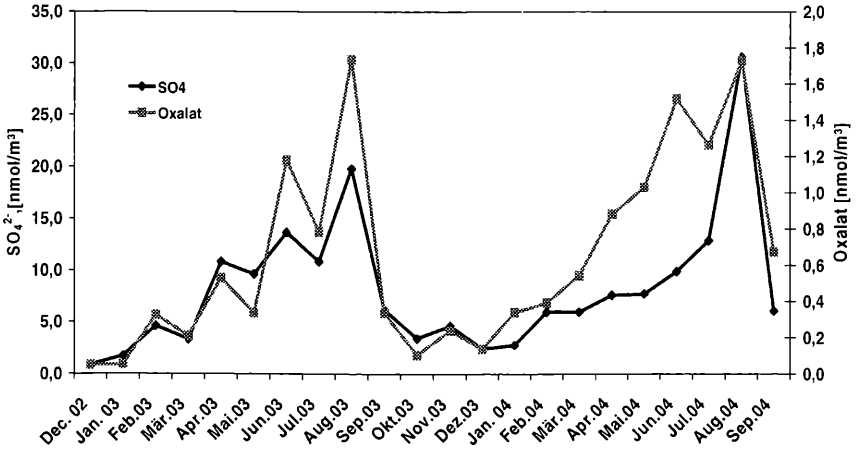

Fig. 2: Comparison between sulphate and oxalat concentrations

Comparison of aerosol data and gas phase concentrations and precipitation data

The collection of precipitation samples on a daily basis are carried out routinely since 1987 in cooperation with the Local Authority of Salzburg.

The concept of scavenging ratios is based on the simplified assumption that the concentration of a component in precipitation is related to the concentration of the respective compound in the air. Using this approach it has to be held in mind that the transfer of airborne compounds into the liquid phase and further to snow or rain is extremely complex (Slinn, 1984). Aerosol particles can act primarily as condensation nuclei. Thus they are already included in the cloud water drops when they form. Furthermore aerosol particles can be collected by the existing droplets via both, impaction and diffusion processes. Trace gases can also be dissolved in droplets. Especially nitric acid is very well soluble and reactive. In case of sulphur dioxide the uptake in the liquid phase does not depend only on the compound concentration in the gas and liquid phase, but also on another reaction partners (e.g. oxidation of sulphite to sulphate by hydrogen peroxide).

Sulphate, nitrate and ammonium determined in precipitation samples can be related to aerosol phase sulphur, nitrate and ammonium (aerosol scavenging) and to the trace gases sulphur dioxide, nitric acid and ammonia (gas phase scavenging).

Figure 3 show the annual cycle of concentrations in gas phase and in precipitation. Unfortunately, between November 2003 and May 2004 there was a longer loss of precipitation measurements because of a failure of the instrument for collection of precipitation. Even so, the regular trend of the concentration values in aerosol and in snow can be recognized.

Comparison between Filter packs and High-Volume

During the period of October 2002 untill September 2004 the SBO was one of six sampling sites operated within the EU project 'CARBOSOL'. In this project weekly aerosol samples were collected with a High-Volume Sampler $PM_{2,5}$ on quartz fiber glass filters. Figure 4 shows an intercomparison of the seasonal trend of sulphate measured with both methods, filter packs and High-Volume sampling. The results agree very well and can be taken as a starting point for further aerosol measurements at SBO based on High Volume sampling.

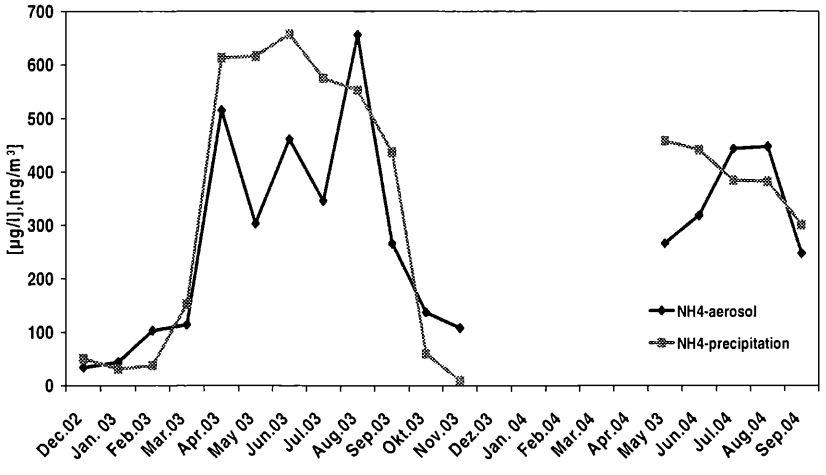

Fig. 3: Comparison aerosol and precipitation data for NH_4^+

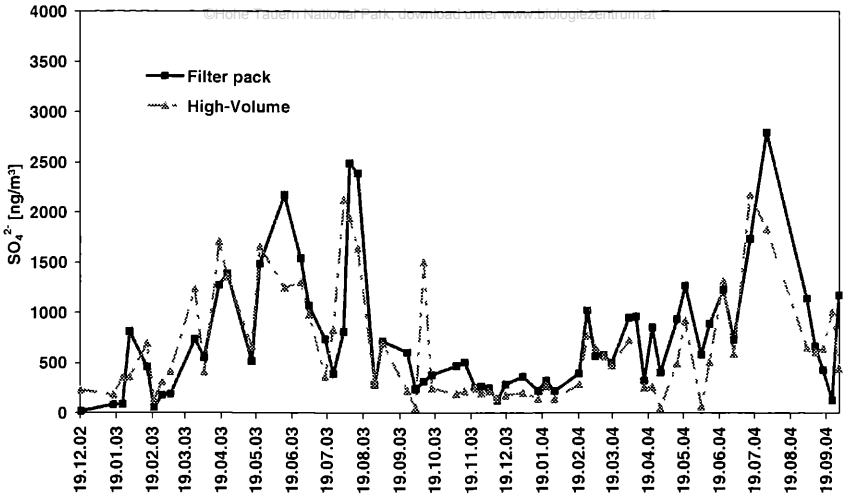

Fig. 4: Comparison between Filter pack and High-Volume for SO_4^{2-}

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