ATMOSPHERIC CONCENTRATION VARIATIONS OF GASEOUS AND PARTICULATE NITRATE AT DIFFERENT SITES IN EUROPE

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INTRODUCTION

The relative importance of nitrogen oxides as atmospheric pollutants has increased markedly during the last years. An observed decrease in NO emissions could not be detected in the NO2 concentration network in Europe. NO2 is oxidised at an appreciable rate to a variety of inorganic and organic species (NOx). The long-range transport of nitric acid (one of the most important atmospheric photochemical reaction products) from polluted regions contribute to elevated levels in rural areas downwind. HNO3 may be converted to particulate nitrates (e.g., with ammonia to NH4NO3). Nitrate and nitric acid are of interest for the environmental topic of acid deposition and eutrophication.

METHODS

Research on the temporal variation in both composition and concentration and on the interaction of reactive gases and aerosols in the atmosphere required sampling and analysis systems for the simultaneously determination with high time resolution. An automated monitoring system, applicable for measurements at urban and rural sites and for both gases (e.g., HNO3, HNO2, HCl) and particulate matter (e.g., nitrate, nitrite, chloride, sulphate) was developed and used in different field experiments. This based on a wet denuder and a steam jet aerosol collector in combination with a quasi online ion chromatography unit (Acker et al., 2004). The system was operated with a very short teflon inlet at about 3 m above ground and an air flow of 10 l min⁻¹. The use of ultra-pure water as denuder liquid and the very short sample air residence time (< 0.5 s) will limit possible artefact reactions. Results from field studies at different European sites will be presented:

- site Villa ADA, Rome city centre (NITROCAT, late spring 2001)
- site Realto, about 30 km north of the urban environment of Marseille and east of the industrial centre Berre pond (ESCOMPTA, summer 2001)
- site Roskilde, about 30 km south of Strasbourg, Upper Rhine Valley (INTERREG III, summer 2003)
- site Goldhauter in the Thuringian Forest, Germany (FEBUKO, autumn 2001)

At present, available nitrate data for particulate matter (PM) are obtained mainly with the standard 24 h sampling by filtration and subsequent analysis of the chemical composition. Sampling of aerosol-nitrate can be problematic because of evaporative loss of the semi-volatile ammonium nitrate or adsorption of nitric acid gas. Artifacts occurring with the main filter types in use in Europe for aerosol nitrate sampling are discussed in Schnaup et al. (2002). Quartz fibre filters are recommended for routine particle sampling when mass concentration is determined by weighing. A Digital high volume sampler equipped with Munktell MK 360 quartz fibre filters (TSP inlet 3 m above ground, air flow 500 l min⁻¹) was operated in parallel to the above mentioned denuder/steam jet measurements to get more information about the aerosol phase and to compare the obtained nitrate data.

RESULTS

At the investigated sites a great variability in HNO3 and nitrate was found, mainly caused by differences in air pollution situation and meteorology. The chemistry in the urban atmosphere over Rome is determined by high NO and NO2 concentrations (up to 89 µg m⁻³), mainly caused by the heavy traffic. In the morning hours the partition between nitric acid and nitrate is in favour of nitrate (up to 12 µg m⁻³),
because much ammonia is available (emitted from catalytic converters). Later on mixing processes dilute the nitrate concentrations. For HNO₃ a daily maximum in the range of 2-3 µg m⁻³ was registered.

The petrol chemistry near Mannesfeld is the reason for a sulphur dominated atmospheric chemistry and often ten times more sulphate compared to nitrate was found in the aerosol. Daily peaks in HNO₃ were observed at noon (see Fig. 1) ranging between 0.6 µg m⁻³ under neutral conditions (15-19 June) and 12 µg m⁻³ in periods with very high photochemical activity (O₃ up to 250 µg m⁻³).

The simultaneously done aerosol nitrate measurements show that for some periods (T > 30 °C, weak wind) significantly higher nitrate concentrations were detected by the steam jet, indicating possible NH₄NO₃ losses by evaporation processes during filter sampling. Higher nitrate concentrations were observed in the Upper Khine valley as well at a station in the Thuringian Forest (Figs. 2, 3).

At both sites the nitrate values equals or little exceeds that of sulphate in the aerosol phase. On average at noon 5 µg m⁻³ HNO₃ were found as photochemical reaction product near Strasbourg. Because of nearly 100% relative humidity HNO₃ was very low at the site Goldhütte. Up to 30 times more nitrate was detected in the aerosol phase.

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