Phase Distribution of Oxidized and Reduced Nitrogen Species in the Ambient Air

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INTRODUCTION

Deposition fluxes of nitrate (NO_3^-), nitric acid (HNO_3), ammonium (NH_4^+), and ammonia (NH_3) play crucial roles in biogeochemical cycles in terrestrial ecosystems. Dynamic interactions between the gas and particulate phases lead to varying deposition mechanisms of these nitrogen species (**Fig. 1**). This reveals the importance of the phase distribution to determine atmospheric nitrogen input into ecosystems. We compare oxidized (HNO_3 and NO_3^-) and reduced (NH_3 and NH_4^+) nitrogen species in the gas and particulate phases, as measured in February and May 2000 at the BITÖK ecosystem research site "Waldstein" in the "Fichtelgebirge" mountain range, Germany (**Fig. 2**).

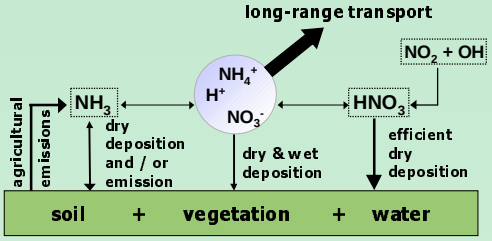

Fig. 1: Processes and pathways of atmospheric nitrogen species.

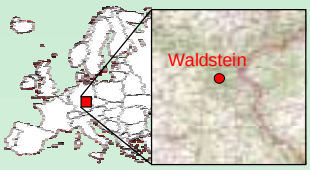

Fig. 2: Map of Europe and NE-Bavaria.

METHODS

For size-resolved particle collection, a 5-stage impactor was used, covering size ranges from 0.05 to 10 µm particle diameter. After sampling, NO_3^- was analyzed by ion chromatography, and NH_4^+ by using a flow injection analysis system.

Nitric acid (HNO_3) was determined using a modified wet annular denuder system after Keuken et al. (1988). Atmospheric NH_3 mixing ratios are measured continously at our site employing a horizontal continous-flow wet denuder (Wyers et al., 1993).

RESULTS

Fig. 3 displays median mixing ratios of HNO_3, NO_3^-, NH_3 and NH_4^+ as measured in February and May 2000. The two columns represent typical compositions of the atmospheric nitrogen budget during wintertime and summertime, respectively. We find considerably lower concentration of total reactive nitrogen (excluding NO_x) during winter (1.5 ppb) as compared to summer (4.4 ppb).

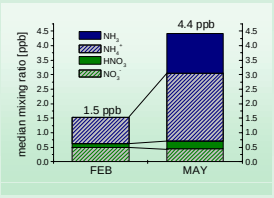

Fig. 3 Median mixing ratios of oxidized and reduced nitrogen.

The particulate species dominate the studied atmospheric nitrogen budget with an overall fraction of more than 90 % in winter and still more than 60 % in summer.
Clearly, oxidized nitrogen species are less important than reduced nitrogen species at our site, particularly in summer.

The difference in the phase partitioning of reduced and oxidized nitrogen during summer and winter (representing different micrometeorological conditions) is also reflected in the correlation of the gas/particle ratios with ambient temperature and humidity conditions, as presented in **Fig. 4**. The gas/particle ratios are shown on a molecular basis for reduced (circles) and oxidized (triangles) nitrogen. They both increase with increasing temperature (left panel), and decrease with increasing relative humidity (right panel). Hence, the importance of the gas phase increases with increasing temperature and decreasing relative humidity.

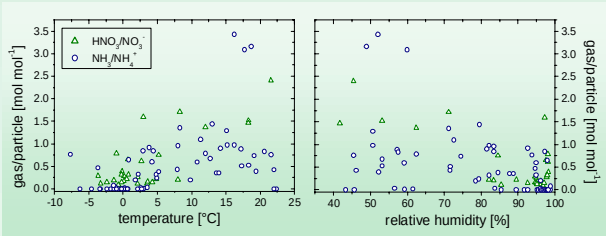

Fig. 4: Gas/Particle molar ratio vs. temperature and relative humidity.

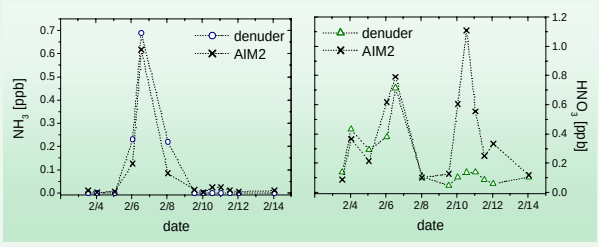

Fig. 5 Comparison of measured NH_3 and HNO_3 and AIM model calculations.

Taking into account the rural setting of our site, we expect that ambient aerosol particles are in equilibrium with the surrounding gas phase. **Fig. 5** shows a comparison of our gas phase measurements in February and the results of a thermodynamic equilibrium model (AIM2, Clegg et al., 1998). Mixing ratios of NH_3 (left panel) were usually very low, however, elevated levels could be observed from Feb 06 to 08. The HNO_3 pattern (right panel) is more variable, but still, the model curve imitates the measurements very well.

CONCLUSIONS

- At our site, reduced nitrogen is more important than oxidized nitrogen, indicating a prevailing influence of agricultural emissions as compared to photochemical oxidation processes.
- Phase partitioning of the studied nitrogen species exhibits a dependence on ambient temperature and humidity conditions. The gaseous species are more important in summertime than during winter.
- A thermodynamic equilibrium model is applicable and shows good agreement with our measurements. The particulate phase seems to be in equilibrium with the surrounding gas phase.
- The dominance of particulate species emphasizes the need for reliable methods to determine particulate dry deposition.

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