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Poster Session I. Aerosol chemistry

EVIDENCE FOR HETEROGENEOUS FORMATION OF NITROUS ACID ON CLOUD DROPLETS

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INTRODUCTION

There is an increasing international interest (e.g., EU framework 5) in specific nitrogen compounds (e.g., HNO_3, HNO_2, organic nitrates) in view of the effects on health (ozone precursors, nitrosamines), on vegetation (acid deposition), building materials (corrosion) and climate (OH source). The heterogeneous conversion of NO_2 to HNO_2 on wet surfaces and its oxidation to HNO_3 will influence the oxidising capacity of the atmosphere especially in polluted air masses. A compilation of atmospheric observations of HNO_2 shows that despite higher HNO_2 concentrations in urban compared to rural areas (a factor of three, by average) the source strength when normalised to NO_2 levels is very similar in both environments (Lammel, 1999). At all sites where nitrous acid was observed over longer periods, it was found that the conversion efficiency is strongly variable. This can be explained partly by the influence of the second precursor which is water (vapour). The conversion rate is also strongly surface dependent, how laboratory and field studies have shown (e.g., Febo, 1999; Amman *et al.*, 1998, Kleffmann *et al.*, 1998). This implies the necessity to control the mixing height and the available surface area (surface-to-area ratio).

METHODS

Measurements were performed to investigate our expectation that the comparatively very great specific droplet surface in fog or clouds is place for a heterogeneous HNO_2 formation. The field studies were done during cloud events occured at the Mt. Brocken summit (1142 m a.s.l.; Harz Mountains, Germany). Nitrous acid can be determined in ambient air using spectroscopic methods (not suitable for measurements inside of clouds) or denuder systems. To avoid long sampling times and artefacts on conventional denuder surfaces the approach for a wet effluent diffusion denuder (Simon and Dasgupta, 1983; Tscherwenka, 1998; Zellweger *et al.*, 1999) was adopted. Continuously wetted denuder surfaces are always fresh for sorption reactions and allow in coupling with an ion chromatography unit and with beforehand preconcentration a quasi-continuously measurement of soluble trace gases (e.g., HNO_2, HNO_3). Via an 8-port high pressure valve two preconcentration columns were alternatively loaded with the analyte and rinsed with the eluent. An active cloud water collector (Winkler type) in front of the denuder unit was used to separate the cloud droplets from the interstitial air (Acker *et al.*, 1999). The airflow through the denuder is 10 L/min and using 15 min sampling time we are able to record atmospheric concentration of 15 ng/m^3 of HNO_2 and HNO_3 (corresponding to 5-7 ppt). An important finding of our Brocken site experiment, wherein first time simultaneous measurements of nitrogen acids and nitrogen oxides (Figure 1) in the presence of clouds (Figure 3) were done, was the first order relationship of HNO_2 with NO_2 in a cloud. The correlation is strong significant ($r^2 = 0.96$) between HNO_2 and NO_2 concentration (Figure 2). This result supports the idea of heterogeneous HNO_2 formation on water droplets. Using droplet spectra measurements (FSSP) the surface to volume ratio has been estimated during the cloud event being ~0.5, which is significant higher than that known for the Earth's surface and even aerosol. Also in the field measured nitrite concentrations in the cloud water samples of the investigated episodes were low (8 to 1 ng/m^3). At pH 4.7 to 2.9 most of the HNO_2 was observed in the gas phase (Figure 3), whereas most of the nitric acid was soluted in the cloud water.

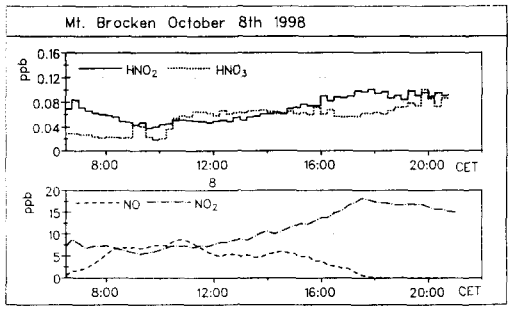

Fig. 1

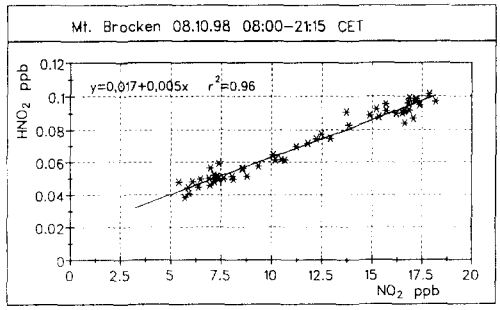

Fig. 2

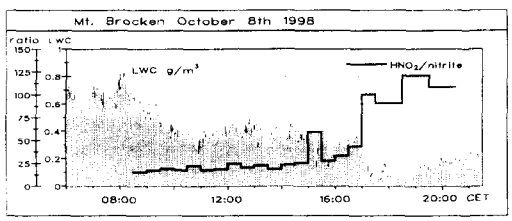

Fig. 3

Figure 1. Simultaneous measurements of nitrogen compounds inside cloud
Figure 2. Correlation between nitrous acid and the precursor nitrogen dioxide
Figure 3. Time series of liquid water content and of the HNO_2/nitrite ratio

CONCLUSION

Based on field studies we know that HNO_2 formation can occur through NO_2 reactivity on urban surfaces, vegetation, aerosol particles, soot and that wet surfaces are very efficient. Evidence was found for HNO_2 formation also on cloud droplets. However it is unknown, whether particular conditions are necessary in order to render these surfaces reactive for NO_x chemistry. The influence of the chemical composition of droplets (e.g., pH, trace metals) and its specific surface on the heterogeneous formation will be investigated in future studies.

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