Nitrous Acid (HNO₂) Concentration Measurements and Estimation of Dry Deposition over Grassland in Eastern Germany

Guest contribution

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Introduction and results

The importance of nitrous acid in tropospheric chemistry has been recognised (Harrison and Kitto, 1994; Lammel and Cape, 1996). Its significance lies especially in its ability to undergo rapidly photolysis to form the hydroxyl radical (Eq. 1) (Platt et al., 1980).

\[ \text{HNO}_2 + \text{h}_v \rightarrow \text{NO} + \text{OH} \]  (1)

Measurements of the concentration of nitrous acid vapour by a wet annular denuder (Wyers et al., 1993) over grassland at the Melpitz research site (Spindler et al., 1996; Gnaauk et al., 1997) in Germany (Federal State of Saxony) were performed in 1995. For a comparison of the wet-annular denuder nitrous acid measurements with a simultaneous detection by a DOAS system at the same site see Ackermann et al., 1998. As an example of the results of measurements during one day per week, at 1.84 m above ground, annual mean concentrations are smaller than 0.4 µg/m² during daytime and up to 0.8 µg/m² in the night. The concentrations are generally smaller in summer than in winter. Similar studies have been performed by Slanina et al., 1990 and Wyers et al., 1994.

For gradient measurements, two denuders were placed at levels 0.76 and 4.53 m. The hourly samples of the stripping solution used (0.001 n Na₂CO₃) were analysed off-line as nitrite by ion chromatography. For two summer days (18th June, and 25th June, 1997) the concentration courses of HNO₂ at two levels above ground were registrated. The influence of radiation during day results in a concentration around 100 ppt HNO₂ (Neftel et al., 1996). Together with micrometeorological data from a sonic anemometer, the HNO₂ flux was
estimated for the daytime (8 a.m. to 5 p.m.) if the surface is dry and the wind velocity is noticeable for such calculations. Using a simple resistance model a maximal possible deposition velocity (\(v_d\max\)) can be estimated for \(R_c = 0\) (Eq. 2).

\[
v_d\max(z) = \frac{1}{R_a(z) + R_b + R_c}
\]  

Fig. 1 shows \(v_d\) in comparison to \(v_d\max\). \(v_d\) was calculated from the gradient measurements and falls in the range of \(v_d\max\) and sometimes \(v_d > v_d\max\). This may indicate an influence of the measured concentration profile from additional sinks for HNO\(_2\) (lower level) or sources of HNO\(_2\) (upper level), possible reactions are shown in reactions 3 and 4. Artefacts caused from concentration differences of NO\(_2\) in combination with traces of SO\(_2\) cannot explain this effect (Harrison and Peak, 1997).

\[
\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2 \\
2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3
\]

A simulated mean of a daily course of concentration for HNO\(_2\) and NO\(_x\) at the two levels above ground for 11 summer days is shown in Fig. 2. Clearly recognisable is the influence of the daily radiation to the HNO\(_2\) decline and its new formation in the evening after sunset (especially at the upper level). Febo \textit{et al.}, 1996 suggested reaction 3, which occurs on surfaces, as being
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responsible for an emission of HNO₂ from wet surfaces (for example from the ground at night). In this case the concentration has to increase towards the surface for an emission. From our vertical subdivided concentration measurements we see no significant evidence of a negative vertical gradient of HNO₂. This is in agreement with the results presented by Neftel et al., 1996 and usual for conditions with concentrations of NO₂ < 10 ppb. The significant smaller HNO₂ concentration at the lower level at night, especially in the morning must be a result of transport processes. This is probably because the relative surface wetness is higher in the morning.

Fig. 2: Eleven day averages of daily courses of concentration

The fact that in the morning more NO was found at the lower level is a strong hint of a temporary morning source witch is found in the federal highway from Leipzig to Torgau, north of the site. Simultaneously this is also an indirect indication that HNO₂ from cars is not a significant source in our investigations. The scatter plots (Figs. 3a and 3b) illustrate the interaction between NOₓ and HNO₂ concentration during the day and during the night. NO₂ has an influence of the net HNO₂ formation especially at night.
Fig. 3: Scatter between NO$_2$, NO and HNO$_2$ (0.75 m over ground); a) night, 18:00–06:00 h and b) day, 06:00–18:00 h.

Conclusions

For two days in summer (18th June, and 25th June, 1997) a mean HNO$_2$ deposition velocity of (2.43 ± 0.90) and (3.35 ± 0.66) cm/s during daytime was estimated using the gradient technique.

The calculated mean fluxes for both days are (0.0054 ± 0.0017) and (0.0076 ± 0.0013) µg/s m$^2$. This is a maximum N impact from HNO$_2$ of 0.6 kg/ha a, because the estimation is based on maximum values the real impact is smaller and can be neglected in comparison to other N inputs in the ecosystem.

The mean daily courses from 11 summer days in 1997 show a positive vertical concentration gradient of HNO$_2$ at all times investigated. It can thus be concluded that for the investigated time period there is no significant source of HNO$_2$ at ground level (grassland).

Acknowledgements

We wish to thank the European Commission (DG XI, 7221010) and the State Government of Saxony (4.7541.82-IfT/402) for sponsoring the project "Towards Development of a deposition monitoring network for air pollution of Europe" (Phase 1, 1994/1995 and 2 1997–1999) We are indebted to Mrs. A. Thomas for the IC analysis and for Mr. A. Grüner and J. Hanß for technical support.
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