Complex Natural Conditions Conditions

Concentration of Ammonia in the Erzgebirge and at the Anchor Station Melpitz – Estimation of N-Deposition over Grassland in Melpitz

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Objective

Vertical Transports under

Naturally and anthropogenically caused climate variations can influence the trace gas exchange at the lower border of This exchange the troposphere. is influenced bv meteorological parameters but also by trace aas concentrations as well as their respective ratios (codeposition). These effects can only be recognized. described and transferred to larger areas by long time The dry measurements at typical sites (anchor stations). deposition of N-containing gases (e.g. NO₂, HNO₃, HNO₂, NH₃) and particles (NH₄⁺, NO₃), together with the wet deposition of ammonium and nitrate, establishes a major sink for nitrogen in the troposphere and a source for different ecosystems. Here results for the N-Impact at the anchor station Melpitz for six years are presented und compared with model results. The results for 2002 were effected by a data lag of six weeks caused by a Flood. After them fluxes also calculated from parameters of a sonic anemometer. Ammonia is a basic trace gas mainly emitted from agriculture and due to its high deposition velocity the part of N-Impact is high. Therefore Ammonia measurements were done and compared for the three anchor stations Melpitz, Tharandter Wald and Oberbärenburg with different heights above see level.

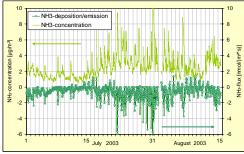


Figure 2: Example for NH₃-concentration measurement and calculated NH₃-flux using an bidirectional inferential model (parameters NH₃-concentration, R_a, R_b, global radiation, temperature and stomatal compensation point calculated for a concentration NH₄⁺ 200 µmol I⁻¹ and pH 6.3 for the leaf intercellular fluid, Γ = 400) for Melpitz in 2003.

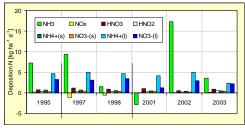


Figure 4: Estimation of yearly dry and wet deposition for N-species at Melpitz site (results for 2003 preliminary).

Results

In Figure 4 the estimated N-impact for the anchor station Melpitz is shown for six years (results from 1995, 97 and 98 are from an other project, Erismann et.al. 2001b). The Nimpact shows a high inter-annular variability between 5 and 27 kg N per hectare and year. The N-impact by wet deposition shows relatively constant amounts in the range about 7 kg throughout the year. In the dry summer 2003 the impact is lower. The strongest variability show the dry Nexchange caused by NH3, especially the year 2001 shows a singularity with a N-emission. Reasons can by found in the local sources of $\ensuremath{\mathsf{NH}}_3$ and in the possibility of an bidirectional flux influenced by meteorological conditions but also by different biological activities (Figure 2) . That means the grassland can be source or sink for NH3. The dry deposition of HNO_3 is in the range between 0.5 and 1 kg and depends on the concentration of HNO₃ (Figure 3). The deposition by particulate matter is less than 10 % of the dry N-Impact.

A comparison with results from a model for mapping total deposition loads (Gauger et al., 2002, Figure 6) for the available years shows a good agreement between experimental determined N-Impact and model calculation for grassland at Melpitz site. The calculated values for NH₃ and NH₄+ are lower for 1995 and 1997. NH₃-measurements were carried out with the 'AiRRminia'-system in summer and autumn in Melpitz and two stations in the Eastern Erzgebirge Mountains Tharandt (climate station Wildacker as open area in the forest) and Oberbärenburg (forest station). The three stations reflect a gradient in altitude in the VERTIKO target region.



Figure 1: View of the anchor station Melpitz (12°56' E, 51°32' N, 86 m above see level). Measurements for N-containing chemical species are highlighted.

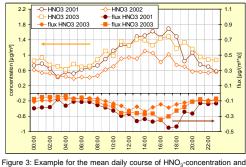


Figure 3: Example for the mean daily course of HNO₃-concentration and the calculeted HNO₃-flux using the HNO₃-deposition velocity calculated as $(R_a t R_b + R_b)^{-1}$ with $R_c = 0$. Number of measured daily courses for 2001: 30, for 2002: 38 and for 2003: 33. R_a atmospheric resistance, R_b laminar boundary-layer-restistance, R_c canopy resistance.

Table 1: Comparison of estimated N-Impacts for Melpitz with results of a model for mapping total deposition loads

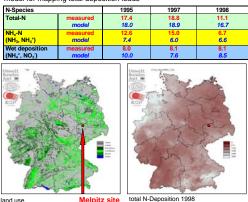


Figure 6: Example for land use and Total N-deposition from the model for mapping total deposition loads (the location of Melpitz site is highlighted) Figure 5 presents the results as average daily concentration courses). The half hourly means were calculated from 10minute means. The concentration measurements show different mean concentrations for the three sites. For Melpitz and Tharandt the $\rm NH_3$ -concentrations are higher as in Oberbärenburg. Mostly for Melpitz and Tharandt a typical pattern between day and night can be recognized. One reason could be that during times with higher temperatures (daytime) more NH₃ is in the gas phase. This emanates from evaporation of NH4NO3 from particles and from agriculture in the surroundings. For Melpitz the NH₃-concentration increase earlier as for Tharandt, one reason can by an earlier start of mixing of the boundary-layer for these flat grassland. For Oberbärenburg the mean NH3-concentration is more than two times lower than in Melpitz and shows only little variation. The mean NH3-concentrations decrease with increasing altitude and distance to sources.

Acknowledgements

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Methods

The flux measurements took place at the anchor station Melpitz (IfT research station) situated near Torgau in the river Elbe valley (Figure 1). The station is located on a flat meadow. The grassland was fertilized only in spring with 70 kg N ha-1 and cut normally three times per year. Aerodynamic profile technique was used to determine the net fluxes of the gaseous compounds NO, NO2 (NOx) and NH3 (influences by reactions of NO with O3 during the gradient measurements are not considered). Concentrations of NO_x , NH_3 , HNO_2 and HNO_3 have been measured by chemiluminescence (NO_x) and wet annular denuder techniques (NH3: acidic coating 'AMANDAsystem'; HNO3 and HNO2: alkaline coating 'batch denuder'), respectively. The artefact formation for HNO2 in the denuder can be neglected because SO_2 concentration is low (Spindler et al. 2003). Dry deposition of HNO3 was estimated by resistance analogy (Figure 3), for HNO₂ a mean deposition velocity of 0.8 cm s⁻¹ is used. NO₃⁻ and NH4+ concentration of aerosol particles are determined from a low flow filter sampler (upstream impactors for PM1, PM2.5 and PM10). The size dependent deposition velocity was modeled on the basis of the friction velocities (Slinn, 1982). The N-input by precipitation (NO3-, NH4+) was quantified using a wet-only sampler (Brüggemann and Spindler, 1999). Alternatively the NH₃ concentration can be measured with the 'AiRRmonia' system (Figure 2 and 5). In principle this is a smaller version of the denuder system 'AMANDA' (Erisman et al. 2001a). The rotating wet annular denuder is replaced by a channel system positioned on a Teflon membrane, which is permeable for NH3. The absorption solution counter flows on the opposite side of the membrane. Ammonia passes the membrane completely and forms ammonium in the absorption solution. Fluxes of ammonia can be calculated using a inferential model for a bi-directional flux (Figure 2, Spindler et al., 2001). NH₃ concentration measurements were done also at anchor stations Tharandt and Oberbärenburg in the VERTIKOtarget area (Figure 5).

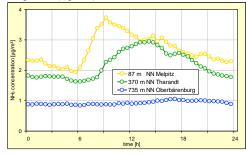


Figure 5: Average daily course of NH₃-concentration 2003 at Melpitz (29 days in July), Tharandt (32 days in May and June) and Oberbären burg (15 days in October).

References

Brüggemann, E.; Spindler, G. (1999) Wet and dry deposition of sulphur at the site Melpitz in East Germany. Water, air, and Soil Pollution **109**, 81-99.

Erisman, J.W.; Otjes, R.; Hensen, A.; Jongejan, P.; van den Bulk, P.; Khlystov, A.; Mols, A.; Slanina, S. (2001a) Instrument development and application in studies and monitoring of ambient ammonia. Atmos. Environ. 35, 1913-1922.

Erisman, J.W.; Hensen, A.; Fowler, D.; Flechard, C.R.; Gruener, A.; Spindler, G.; Duyzer, J.H. Westrate, H.; Römer, F.; Vonk, A.W.; Jaarsfield, H.V. (2001b) Dry Deposition Monitoring in Europe. Water, Air, and Soil Pollution: Focus 1, 17-27.

Gauger, Th.; Anshelm, F.; Schuster, H.; Erisman, J.W.; Vermeulen, A.T.; Draaijers, G.P.J.; Bleeker, A.; Nagel, H.-D. (2002) Mapping of ecosystem specific long-term trends in deposition loads and concentrations of air pollutants in Germany and their comparison with Critical Loads and Critical Levels. Unweitbundesamt und Institut für Navigation der Universität Stutgart, Final Report 299 42 210, part 1 207 pages, part 2 108 pages.

Slinn, W.G.N. (1982) Predictions for particle deposition to vegetative canopies. Atmos. Environ 16, 1785-1794.

Spindler, G.; Teichmann, U.; Sutton, M.A. (2011) Anmonia dry deposition over grassland – micrometeorological flux –gradient measurements and bidirectional flux calculations using an inferential model, Q.J.R. Meteorol. Soc. 127, 795-814.

Spindler, G.; Hesper, J.; Brüggemann, E.; Dubois, R.; Müller, Th.; Herrmann, H. (2003) Wet annular denuder measurements of nitrous acid: laboratory study of the antefact reaction of NO_2 with S(IV) in aquueous solution and comparison with field measurements. Atmos. Env. **37**, 2643-2662.

Specific Contributions to the General Objective of VERTIKO

- Fluxes for heat and trace gases are avialable for modeling in the VERTIKO data base.
- The complete N-impact was estimated for an anchor station in an agricultaral region (grassland) and
- compared with results of an total deposition model. NH₃ concentration measurements outside Melpitz (Oberbärenburg VERTIKO-TUBAF, TU-Freiberg and
- Tharandt VERTIKO-TUD, TU-Dresden).
- Tharandt VERTIKO-TUD, TU-Dresden).
 Validation and parametrization of SVAT.



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