

## ***Interactive comment on “Gas-particle interactions above a Dutch heathland: I. Surface exchange fluxes of NH<sub>3</sub>, SO<sub>2</sub>, HNO<sub>3</sub> and HCl” by E. Nemitz et al.***

**E. Nemitz et al.**

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Many thanks to the anonymous reviewer for their insightful and very constructive comments on our manuscript, which we address in the order they were made.

### **General comments**

The referee notes that the NH<sub>3</sub> fluxes received more attention in the manuscript than the acid fluxes. We suspect this comment mainly concerns the modelling, which concentrated on NH<sub>3</sub>. Surface / atmosphere exchange is thought to be more complex for NH<sub>3</sub> compared with the acid gases, with a large regulatory component by the vegetation itself. By contrast, HNO<sub>3</sub> and HCl are thought to be deposited at  $V_{max}$ , controlled only by meteorological parameters. Although this was clearly not the case at Elspeet, the modelling of this effect, caused by chemical conversions on leaf surfaces and in the

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airspace, requires a very different modelling approach. A whole companion paper (Nemitz and Sutton, 2004) is devoted to the modelling of airborne gas/particle interactions, with additional discussion provided by Nemitz et al. (2004b).

### General comments

1. The results of the measurements at Elspeet are presented in a set of three papers and therefore the overall discussion of the measurements is distributed over these papers. However, we suggest adding the following text to the end of the discussions section to make the comparison more explicit: "The Elspeet experiment had been designed as a complementary study to the North Berwick experiment. At N. Berwick, under clean Scottish conditions, aerosol concentrations were much lower than at Elspeet. At both sites vapour concentrations were not in equilibrium with the aerosol phase. However, at N. Berwick aerosol evaporation was inhibited by large chemical time-scales and / or the absence of volatile aerosol components, and the impact on surface / atmosphere exchange fluxes was therefore negligible (Nemitz et al., 2000b)."

2. The findings of the other papers are mentioned in Section 5.5, but this was clearly not evident when reading Section 3.2. This is made clearer in a revised manuscript: "The validity of this assumption is discussed in Sect. 5.5 below and in more detail by Nemitz et al. (2004b)."

3. An emission potential of  $\Gamma = 2500$  is estimated for the previous measurements in Section 3.2, this is now repeated in Section 4.1. The presentation of the previous measurements is unfortunately insufficiently detailed to derive a range of values from the former measurements.

4. The spelling has been corrected.

5. The discussion and presentation of an alternative curve for an emission potential of 2000 has been removed from the text and Fig. 7. The referee asks if the influence of cuticular desorption may be confirmed in another way. Our approach to estimate  $\Gamma$

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seeks to minimize all non-stomatal exchange pathways. Hence we concentrate on very dry conditions. As mentioned elsewhere in the text there have been attempts to simulate desorption in leaf chemistry models (e.g. Flechard et al., 1999). However, these models need detailed data on event-based precipitation chemistry and the chemically resolved deposition of aerosols, which is even beyond this extensive dataset and would warrant a separate study.

6. The spelling has been corrected.

7. The grammar has been corrected.

8. The spelling has been corrected.

9. The spelling has been corrected.

10. The net flux of ammonia above the canopy is a result not only of  $R_w$ , but also of  $R_s$ ,  $\chi_s$  and the air concentration  $\chi_a$ . Although the  $RH$ -response curve of  $R_w$  appears to have been higher in 1996 than in 1990-92, the actual humidity (and therefore surface wetness) may have also been higher. In addition, the value of  $\chi_s$  was smaller. Overall, the measurements indicate that these effects balanced. We do not have enough (meteorological) data on the 1990-92 campaign to decide on the relative magnitude of all these effects.

11. The English has been corrected.

12. This is an interesting and counter-intuitive observation made by the referee. The distinction between dry and wet conditions was made using a conductivity-grid-type wetness sensor, which changes from wet signal to dry signal only when the last water has evaporated. Therefore, wet conditions included periods of drying out, during which most of the  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  volatilization and desorption would occur, while after leaf surfaces were fully dry little volatile material remained. Indeed all apparent emission fluxes were observed during the morning hours (06:00 – 11:00 hrs). A similar process would affect airborne chemical processes. A decrease in relative humidity

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would favour the evaporation of airborne aerosol down to the relative humidity of deliquescence beyond which a further decrease in  $RH$  does not have any further effect. By contrast, night-time conditions tend to include the transition from dry to wet canopies and here the difference between the two is not significant. Text has been added to clarify this issue. In response to this referee comment, we reanalyzed the data to compile a table similar to Table 3, using air  $RH$  for the distinction between dry and wet surfaces. Similar difficulties were encountered: the transition between the dry and wet canopy does not necessarily follow air  $RH$  either. For future studies, we recommend the use of leaf wetness sensors such as used by Klemm et al. (2002).

13. The capitalization has been changed in the text of Fig. 1.

14. Fig. 2 compares the  $NH_3$  concentration measured with three independent systems and the  $SO_2$  concentration measured with two systems. By contrast,  $HNO_3$  and  $HCl$  were measured with only one single system. Although the filter packs could have provided alternative estimates, these were not analysed for gas-phase  $NO_3^-$  and  $Cl^-$ . We are therefore not able to extend the comparison graphs to  $HNO_3$  and  $HCl$ . However, the control graph for  $SO_2$  should provide a good estimate of the performance for  $HNO_3$  and  $HCl$  also, since the three associated anions were measured by the same system, referenced to the same continuously added  $Br^-$  standard.

15. This has been done as suggested by the referee (see also reply to point 5 above).

Klemm, O., Milford, C., Sutton, M.A., Spindler, G., and van Putten, E. (2002): A climatology of leaf surface wetness. *Theoretical and Applied Climatology* 71(1-2), 107-117.

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