Atmospheric Measurement Techniques Discussions

Interactive comment on "Aerodynamic gradient measurements of the NH$_3$-HNO$_3$-NH$_4$NO$_3$ triad using a wet chemical instrument: an analysis of precision requirements and flux errors" *by* V. Wolff et al.

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We are grateful to the referees for taking time to carefully review the manuscript and help to improve it with their very useful comments. We will address the comments in order, quoting the comments in italic for convenience.

Anonymous Referee 1

Page 2426 Line 3: For a more complete discussion of the available instruments

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Interactive Discussion

Discussion Paper

please add e.g. after the sentence "To characterize the surface exchange of the NH3-HNO3-NH4NO3 triad, simultaneous measurements of NH3, HNO3, particulate NH4+ and NO3- are mandatory and they should be highly selective with respect to gaseous and particulate phases." a hint to the measurement system MARGA (ten Brink et al. 2007).

» The MARGA system, as it is described by ten Brink et al. (2007) is a (single height) monitoring system, which, in its sampling set-up (containing denuder-SJAC combinations), resembles the instrument used in this study, the GRAEGOR. However, it is not a gradient system and may therefore not be used for the determination of exchange fluxes. The present paper does not aim at giving a complete discussion of the availability for multi-component instruments, but scopes on the investigation of precision and errors associated with the determination of exchange fluxes making use of measurement of vertical concentration differences. It is therefore difficult to include a reference to the MARGA system in the introduction as suggested by the referee. However, we included the reference in section 2.1.3 where the measurement method is described.

Page 2427: The headline for section 2.1 (Site descriptions) in chapter 2 seems to be incomplete, because not only the site descriptions are given in 2.1.1 and 2.1.2 rather in 2.1.3 to 2.1.5 also the measurement-method, the calibration and determination of concentration difference errors are discussed. Therefore it seems to be better to give section 2.1 a more complex title e.g. "Site descriptions, measurement-method, calibration, and concentration difference error determination".

» The numbering of the chapters in Section 2 was corrected. A new section title 2.2 was introduced.

Page 2435: The description of formula 7 (line 19) "... where Sc and Pr are the Schmidt and Prandtl number ($\approx$ 0.72), respectively. Sc is a strong function of the molecular diffusivity of the trace gas (for HNO3 $\approx$ 1.25) ..." can be misunderstood because only for Pr a number is given in brackets. A better formulation can be the following: "...where Sc and Pr are the Schmidt and Prandtl number, respectively. Pr is $\approx$ 0.72 and Sc is a strong function of the molecular diffusivity of the trace gas (for HNO3 $\approx$ 1.25) ...".

» The text was corrected following the referee's suggestion.

E. Nemitz (Referee)

1. The authors acknowledge that above rough vegetation like forest, gradient measurements are conducted within the surface roughness layer, where, in general, site specific flux-gradient relationships need to be applied (end of Section 3.2). They then proceed by explaining that such analysis for the EGER site will be published elsewhere, and instead use the standard flux-gradient relationships to calculate approximate fluxes. This seems to be the wrong way round. If these site-specific relationships are being derived, they should be used in the revision of the manuscript and the other manuscript should be cited as 'in preparation'.

» We agree with the referee that the original formulation in the text was inappropriate. Unfortunately it was not possible to derive reliable site specific enhancement factors for scalar quantities within the present experiment. Therefore we made use of the conservative calculation approach not including the enhancement factor. It has to be noted that the use of directly measured u_* (with eddy covariance) already accounts for the enhancement of momentum flux in comparison to the original AGM method based on wind speed profiles (Garratt, 1992). Moreover, a systematic

enhancement factor would have little effect on the statistical significance of the derived fluxes as discussed here. We modified the paragraph in the text accordingly and, for a more logical order within the manuscript, we moved it to the methods section (2.3).

2. The problem with filtering fluxes for significance (e.g. page 2447, line 13) is that such tests tend to remove small fluxes. Extreme care has to be taken how the filtered dataset is used afterwards. For example, for the calculation of robust average fluxes, these periods smaller fluxes need to be intelligently gap filled in order not to bias the dataset.But even if the data are used to investigate processes, the removal of the smaller fluxes may in some instances bias the interpretation. In addition, if non-significant fluxes are averaged, the longer term average may become statistically significant. These aspects should be discussed in the revised manuscript.

» We agree with the reviewer that selection/filtering of non-significant flux data is a critical issue and has to be performed with care. Depending on the further use of the data, all data (including non-significant values) or only significant values should be selected. We want to point out that we did not apply such a filtering except for the specific evaluation in Figs. 14 and 15. For the larger part of the manuscript we included all data (significant and non-significant) and showed the respective uncertainties (e.g. Figs. 7, 8, 12, 13). We fully agree that for longer-term averaging of fluxes (including gap-filling algorithms), the full dataset should be used.

In the last part of the manuscript we did a detail evaluation of the uncertainty distribution. For this purpose, the relative amounts of significant concentration differences (uncertainty < 100%) is listed in Table 5. Finally the flux uncertainty distribution for the sub-group of significantly resolvable concentration differences is presented in Figs. 14 and 15. In order to make this clearer to the reader we added a corresponding explanation in Section 4.5.

3. The scope of Table 6 is unclear. It appears to contain both measurements of several compounds and estimates of single compounds. If the latter is to be included, the table is grossly incomplete. Many more continuous/semi-continuous measurements of NH3 fluxes exist with and without error estimates.

» Table 6 aims at giving an overview for a comparison with other multi-component measurements; only a few single compound measurements were included. We added an explanation about this when introducing the table in section 5.2.1.

4. In several previous studies, errors were derived in terms of statistical errors on the gradient derived from multi-point measurements. This applies in particular to gradient measurements with filter packs at 5 heights or more (e.g. Sutton et al., 1993a, b; Nemitz et al., 2004a). This is an alternative approach to considering the error on the flux, which clearly an only works if measurements at more than two heights are available. This could be mentioned and discussed in the revised manuscript.

» We followed the reviewer's suggestion and included this alternative approach to determine a random error of a concentration gradient for multi-point measurements in section 5.2.1.

5. Why are the uncertainty ranges for NO3- fluxes constant with time, while the others change (Fig. 12)?

» For NO3- we could not determine a relation between $\sigma \triangle C$ and C in the EGER experiment and used the Laplace standard deviation as a constant error range (see Fig. 11). We slightly modified the text in Sect. 4.3 to make this clearer.

6. How does Ra calculated by Eq. (6) compare with the alternative formulation of $Ra = u/u_*2 - (psi_H - psi_M)/(ku_*)$? The difference is that Eq. (6) is based on an average relationship between u and u* (as expressed by an average z0), while the other formulation uses the relationship between u and u* actually measured for each period.

» We agree with the reviewer, that our calculation of Ra is based on an average relationship between u and u* and thus on an average z0 value. We consider this approach as more reliable than using individual values for u and u* for each half hour. It was found that half-hourly values of u and u* were often affected by (random) errors that lead to a large implausible variability in the values of z0. Within the observation periods z0 of the forest canopy was assumed to remain relatively constant. For the grassland site, average empirical z0 values were related to the growing canopy height (see explanation in Sect. 2.2).

7. The height/fetch rule of 1:100 (page 2437, line 18) is only a rule-of-thumb. The exact fetch requirement depends on atmospheric stability. I am sure the authors are aware of this. The 1:100 rule is only cited to develop the argument that above forest, it cannot easily be avoided that flux measurements are made in the surface roughness layer. However, the effect of stability should probably be mentioned in order not to mislead the reader.

» The respective paragraph in section 3.2 was modified following the referee's suggestion.

8. How do the authors explain the relatively large deviations from the 1:1 line for the side-by-side intercomparison for NH4+ and NH3?

» In contrast to NH3, HNO3, and NO3-, the slope of the orthogonal fitted line through the NH4+ data shows a large deviation from the 1:1 line. We discussed findings for the PILS instrument, where the sampling efficiency was found to be different for different ionic species and was largest for NH4+. Additionally we included in the revised manuscript a hypothesis on bacterial grows and NH4+ consumption in the SAJC as it has been observed for the MARGA instrument (Otjes, 2009, personal communication).

9. I agree that as u* becomes smaller, the relative error increases (e.g. Nemitz et al., 2009) as mentioned on page 2444, line 2. What are the implications for the error calculations presented here?

» We agree with the referee that the statement at the end of section 4.4 was incomplete and therefore misleading. We added another sentence to explain our point.

References

Garratt, J. R.: The Atmospheric Boundary Layer, Cambridge University Press, 1992.