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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland)" *by* M. Norman et al.

M. Norman et al.

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The authors want to thank the two anonymous reviewers for good comments and suggestions that helped to improve the quality of the manuscript.

Anonymous Referee #1

The NH4+ concentration measured with the GRAEGOR should be showed in a graph (Figure 2) to allow the reader to make its own opinion on the observed differences between the three instruments. I also suggest to add the alternative GRAEGOR concentration on a graph like Figure 2 to better see the effect of the second calibration procedure mentioned in the text.

REPLY: The NH4+ concentration and the alternative GRAEGOR concentrations have been added to the revised version of the manuscript.

The paper (and especially the discussion) may be improved by making reference to the the paper of Whitehead et al. (2007) which compares TDLAS and QCLAS with AMANDA, and also studied the effects of tubing material on time response of NH3 analysis with QCLAS.

REPLY: This paper is in fact relevant and is now referred to in various parts of the revised text, including the introduction and the tubing material discussion .

One of the main question that arise from Figure 2 is why GRAEGOR gives higher NH3 concentrations in the morning peaks and lower concentrations in the afternoon? The authors should try to better discuss this point, although they have given some clues (effect of temperature on the calibration curve). This feature may well be due to both the PTR-MS and the AIRMONIA adsorbing NH3 in the early peak and desorbing NH3 later in the afternoon. This may well explain the 29 and 30 July patterns in particular, and is supported by the fact that the air is saturated with humidity when the GRAEGOR reads higher concentrations (Fig1 and Fig2). One question to ask here is also the potential for the three analysers to sample "fog water"; which may have been present during nights 28, 29 and 30 July.

REPLY: Regarding inlet designs, the AiRRmonia has similar if not less potential than GRAEGOR for absorption of NH3 on inlet walls. If absorption-desorption effects as suggested by the reviewer were important, we would expect differences between PTR-MS and GRAEGOR/AiRRmonia, rather than the observed differences between PTR-MS/AiRRmonia and GRAEGOR. Also, if the higher PTR-MS and AiRRmonia concentrations in the afternoon were due to desorption of previously absorbed ammonia, the higher afternoon concentrations should somewhat mirror the underestimate in the morning, but here the integral difference in the afternoon is larger than that of the preceding morning. Furthermore, several tests both in the laboratory and at the field site

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showed no losses in the PTR-MS inlet even at relative humidity of close to 100 %. Absorption was only observed when the tubing was cooled causing condensation on the inside tube wall. There is always the risk of sampling fog water for wet chemical samplers. The inlet to the PTR-MS instrument from the main inlet was designed so that only small particles might be able to pass into the instrument. The risk for sampling of fog droplets is therefore considered to be very small.

The authors should check that the GRAEGOR and the AIRPMONIA membrane blocks are different from those reported in Slanina et al. (2001). Their transfer efficiency should be of around 90% and theoretically less sensitive to temperature.

REPLY: The transfer efficiency of the AMFIA detector in GRAGOR is still 30%, which is different to the AMFIA detector in the AiRRmonia having a transfer efficiency of 90%. This might also be the reason that the GRAEGOR calibration was more dependent on temperature than the AiRRmonia calibration. Decuq et al., 2008 showed that although the sensor was improved, the signal still significantly depends on temperature.

An alternative way to avoid condensation problems in the inlet tube would be to increase the flow rate and the tube diameter to be in a well developed turbulent flow in the inlet of the PTR-MS (which would also be useful for flux EC measurements). Although laminar flow is better to avoid particle deposition to the wall, it favours temperature differences between the flow and the tube. The surface to volume ratio (4/d) should also be taken into account. Whitehead suggests using PE tubing may also be better.

REPLY: See our response to the detailed comments on the inlets below.

2 DETAILED COMMENTS Figure 1: why is there a whole in the wind speed dataset. Explain

REPLY: The missing wind data on 30.7.06 has been filled. No data are available due to instrumental failure in the morning of 28.07. As this period is not relevant for the results

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presented here, it is not further commented.

Page 19804 Line 5-8: Unclear. Rephrase.

REPLY: This has been rephrased in the revised version.

Page 19804 Line 10: "The r2 but would" Delete "but".

REPLY: This has been deleted in the revised version.

Page 19804 Line 19: change to Figure 4a to 4e.

REPLY: This has been changed in the revised version.

Page 19804 Line 22: change to "in more details";

REPLY: This has been changed in the revised version.

Page 19806 section 4.2: The discussion would benefit from including a Figure with NH4+ concentration as a function of time.

REPLY: The NH4+ concentration have been added in a separate figure in the revised version of the manuscript.

Page 19806 and Page 19807 section 4.3: this section would benefit from referencing to Whitehead et al. 2007.

REPLY: This paper is included in the discussion in the revised version of the manuscript.

Page 19807 Line 1-3. This may not be fully true that the AIRMONIA has the best inlet system. Although the inlet is the shortest, the flow rate is also small and the Re is very low (See Table below). Although a low Reynolds avoids aerosol deposition, it favours temperature gradient between the flow and the tube hence favouring adsorption/ desorption of water. The surface to volume ratio should also be taken in to account. A larger surface to volume ratio favouring adsorption problems.

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REPLY: Part of the reviewers doubts obviously stem from our unprecise information on the AiRRmonia inlet which now is clarified in the revised manuscript. Using the correct inner diameter of 1.7 mm improves flow speed and residence time by roughly a factor of three compared to the reviewers calculation. As the inlet is not temperature-controlled, we do not see the potential of creating significant temperature gradients and thus adsorption/desorption of water in this short inlet. High-frequent temperature changes due to turbulent heat transport are thinkable, but they would only result in a damping, but not act as an ammonia removal process that could affect the concentration measurements at a time resolution of several minutes.

Page 19807 Line 11-12: This sentence is not true. This work does not prove that the PFA tubing did not absorb NH3 under such conditions. May be the AIRMONIA also adsorbs NH3 in a same way.

REPLY: It is true that this cannot be proven from these results. But the identical behaviour of all these inlets despite their very different characteristics like residence time and flow regimes represents strong evidence that no adsorption occurred. The statement is rephrased in the revised manuscript.

Figure 2: symbols for AIRRMONIA and PTR-MS are hard to distinguish. Change.

REPLY: This is changed in the revised manuscript.

Figure 4: Axis label are hard to read. Enlarge.

REPLY: This is changed in the revised manuscript.

TABLE. The following table shows an estimate of the tube residence time and a very rough estimate of the aerodynamic resistance from the centre of the tube to the walls estimated assuming linear wind profile for laminar conditions (with nu_air as diffusivity) and assuming a logarithmic profile for turbulent conditions (Re $>$ 2000). U= average air speed in the tube (ms-1), Re=Reynolds, Ra = Aerodynamic Resistance (sm-1), t = residence time in the tube (s), a = surface to volume ratio (mm-1). U Re Ra t a

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AIRMONIA 2.1 470 112 0.02 1.2 GRAEGOR 5.5 3119 50 0.05 0.5 PTR-MS 2.0 1765 447 8.6 0.3

REPLY: This is indeed important information. An additional table with information about the inlet characteristics has been included in the revised manuscript. The discussion regarding inlets and humidity dependence (section 4.3) has also been extended.

3 REFERENCES TO ADD IN THE PAPER Whitehead, J. D., M. Twigg, et al. (2008). "Evaluation of laser absorption spectroscopic techniques for eddy covariance flux measurements of ammonia." Environmental Science & Technology 42(6): 2041-2046.

REPLY: This paper was added to the reference list in the revised manuscript.

Anonymous Referee #2

Introduction The introduction is does a nice job of briefly summarizing previous NH3 intercomparisons in the literature. However, two recent ones, Schwab et al., "A Laboratory Intercomparison of Real-Time Gaseous Ammonia Measurement Methods", Environmental Science & Technology, 41 (24), 8412-8419, 2007 and Whitehead et al., "Evaluation of Laser Absorption Spectroscopic Techniques for Eddy Covariance Flux Measurements of Ammonia", Environmental Science & Technology, 42 (6), 2041-2046, 2008, are not cited or summarized.

REPLY: Both these papers have been added as references in the revised version of the manuscript.

A more recent and appropriate reference for the CIMS instrument listed on p. 19794 line 4 would be Nowak, J. B., J. A. Neuman, K. Kozai, L. G. Huey, D. J. Tanner, J. S. Holloway, T. B. Ryerson, G. J. Frost, S. A. McKeen, and F. C. Fehsenfeld (2007), A chemical ionization mass spectrometry technique for airborne measurements of ammonia, J. Geophys. Res., 112, D10S02, doi:10.1029/2006JD007589.

REPLY: This has been changed in the revised manuscript

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Experimental p. 19796 lines 9-10 Were the instruments places in the center of the field minimizing any wind direction dependence on observed NH3 levels?

REPLY: The instruments were placed in the centre of the field. The field orientation along the prevailing wind directions at this site also helped to avoid significant disturbances due to different footprints of the instruments. This information is added in the revised text.

p. 19799 lines 1-2 How is the ambient background determined for GRAEGOR? How is the mean response time then determined? I realize a submitted paper is referenced but from the text I do not fully understand what that 55 min means.

REPLY: The sentence “The ambient background e-folding mean response time (1/e2 decay) is 55 min (cf. Thomas et al., An Automated Analyzer to Measure Surface-Atmosphere Exchange Fluxes of Water Soluble Inorganic Aerosol Compounds and Reactive Trace Gases, submitted to Environmental Science & Technology, July 2008).” is misleading and has been changed in the revised manuscript.

Results p. 19083 lines 3-10 This paragraph discusses changes in the regression parameters resulting in application of the different calibration to the GRAEGOR instrument. The authors show this nicely in separate panels of figure 4. They should also consider showing two traces for GRAEGOR in figure 2, allowing the reader to see how this affects the time series.

REPLY: An additional figure with both GREAGOR data sets has been added to the revised manuscript.

Discussion p. 19806 lines 1-19 This section discusses possible particle interference with the sampling methods used by each instrument. Since the GRAEGOR instrument measured aerosol NH4+ during the intercomparison this data should be shown in figure 2 or separately. An earlier section mentioned that anion data, i.e., NO3- in particular, are not included in this study. Were the anion data recorded and not included in this

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paper? If so, I hope the authors are considering a follow up paper to more closely examine the partitioning between the gas and aerosol phases.

REPLY: see above for answer to reviewer #1. The recorded anion data and gas-aerosol partitioning will be published elsewhere.

p. 19806 line 20 In the Inlets and humidity dependence section the following reference, Shah et al.,"Ammonia adsorption in five types of flexible tubing materials", Applied Engineering in Agriculture, 22 (6), 919-923, 2006, might add to the discussion.

REPLY: The work by Shah et al. also confirmed PFA to be among the most suitable materials for ammonia sampling. This references was added to the revised version of the manuscript. See also comments to reviewer #1.

References I cannot seem to find the following items in the reference list in the text: Gang, 2002 and Genfa et al., 2003. On the other hand, Williams et al., 1992 referred to in the text is not in the reference list.

REPLY: This was already corrected during the proofreading and is corrected in the revised version of the manuscript

Table 1 For consistency the authors should consider using cm instead of inches in describing the tubing (here and elsewhere in the text). Do 1/8 and ½ refer to inner or outer diameter of the tubing? The terms time resolution and time response are easily confused. Here I think the authors are using time resolution as referring to a data acquisition rate or sampling time, not instrument performance.

REPLY: Description of the inlets was changed to inner diameter and centimeters in the revised version of the manuscript. The paper uses the term time resolution for sampling times, not covering the instrumental response time. This is changed to sampling time in the revised version of the manuscript.

Figure 1 What happens to the wind speed data on July 30th?

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Interactive Comment

REPLY: The missing wind data on 30.7.06 has been filled. See further comments under reviewer #1

Figure 2 I find this figure cluttered. It is difficult to distinguish between the PTR-MS and AiRRMonia data. As mentioned earlier, I think the authors should consider showing two traces corresponding to the different calibrations used in Figure 4 for the GRAEGOR instrument.

REPLY: Figure 2 has been changed in order to visualize it better. An additional figure with both time series of the GRAEGOR data has been added to the revised manuscript.

Figure 4 The axis labels on each panel are very difficult to read and should be enlarged.

REPLY: This has been changed in the revised version of the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19791, 2008.