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Atmospheric
Chemistry
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Discussions

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

Anonymous Referee #1

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1 GENERAL COMMENTS

The paper "Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland)" compares on a campaign base, three instruments for measuring NH3 concentrations in an intensively managed grassland, focussing especially on a new instrument: a modified PTR-MS. This paper is of great interest to the scientific community as NH3 is a pollutant of growing interest for atmospheric chemistry (as a major precursor of aerosols), as well as a critical species in the nitrogen biospheric cycle. As spotted by the authors, there is a lack of good datasets of NH3 fluxes and concentration, which mainly comes from the stickiness of

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NH3, which causes NH3 measurements to be difficult. The new technique PTR-MS is promising as it may be a concurrent method to the existing TDLAS and QCLAS for which inter-comparison campaigns are not fully convincing (e.g. see below reference Withehead et al., 2007).

The paper is very well organised, and written, and is therefore easy to read. The title and abstract reflects the content of the manuscript. The experiments have been very thoroughly conducted and are exposed in sufficient details so that the reader can have a critical view on the work, except for the NH4+ concentration which should be given.

This work shows that the three method compared (PTR-MS, AIRRMONIA, GRAEGOR) are well correlated providing that it is not raining. The PTR-MS and the AIRMONIA are correlated within 3% and the GRAEGOR is within 5% of the other two. During rain event, the PTR-MS gives substantially lower NH3 concentrations, which can be explained by dew condensation in the especially long sampling line used (17 m), under laminar conditions. Overall the comparison is very encouraging for the PTR-MS.

Although the paper is of great quality, it may be improved with the following suggestions:

• 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.

• 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.

• 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.

• 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.

• 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.

Provided the authors discuss the points mentioned above, I think this paper should be published.

2 DETAILED COMMENTS

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

Page 19804 Line 5-8: Unclear. Rephrase.

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

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

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

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

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

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 bellow). 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.

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.

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

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

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
AIRMONIA	2.1	470	112	0.02	1.2
GRAEGOR	5.5	3119	50	0.05	0.5

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PTR-MS 2.0 1765 447 8.6 0.3

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.

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