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AMTD

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Interactive
Comment

Interactive comment on “Eddy covariance flux measurements of ammonia by electron transfer reaction-mass spectrometry” by J. Sintermann et al.

J. Sintermann et al.

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We thank the two anonymous reviewers for their helpful comments and appreciate their work. In the following we address the specific remarks individually.

Specific comments of anonymous referee#1:

anonymous referee#1: “The instrumental modifications seem to be minor compared to an earlier publication (Norman et al.) that demonstrated the feasibility of O₂⁺ chemistry to measure ammonia with a PTR-MS instrument. The authors create a new acronym - eTR-MS. While it seems an attractive marketing concept to create new acronyms sim-

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ilar to the 'iPAD, iPhone etc. mania world', my feeling is that the minimum requirement that warrants the creation of a new acronym in scientific technology should be the presentation of a truly novel concept or understanding of a mechanism that has not been published before.”

authors: We agree with the reviewer that our measurement system is based on a PTR-MS instrument. However, the reaction that is essential for the detection of m/z 17 (NH_3^+) is an electron transfer reaction while PTR stands for a proton transfer reaction. Therefore we keep the abbreviation (eTR-MS) to refer to the used measurement system in the manuscript. Norman et al. (2009) themselves stated that the "correct terminology of the instrument would be ETR-MS (Electron Transfer Reaction Mass Spectrometer), since it uses electron transfer instead of proton transfer as in the conventional PTR-MS". We had not the intention to establish a new brand, but we are convinced that the eTR-MS acronym can be used as long as it is clear for the reader that the instrument is based on modification and different application mode of the common PTR-MS. To avoid any misunderstandings we will remove the acronym "eTR-MS" in the abstract and will add "PTR-MS" in the article's keywords so that it is easy for the whole PTR-MS community to find the paper.

anonymous referee#1: "In the present case a thorough theoretical explanation and discussion describing the ion chemistry of O_2^+ in a flow-driftube (+possible side reactions) would be very valuable. For example is the theoretical reaction rate consistent with the obtained sensitivities?"

authors: We are convinced that a discussion of O_2^+ ion chemistry in the flow drift tube beyond what Norman et al. (2007) have described is not the scope of this article. We will clarify this aspect by adding the sentence "A detailed description of the ionisation detection scheme, the selectivity and sensitivity of the eTR-MS is given in Norman et al. (2007)". The experimental sensitivity in our case is within the uncertainty of the corresponding theoretically calculated sensitivity like shown by Norman et al. (2007). Using the theoretical reaction rate constant of $\text{O}_2^+ + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{O}_2$, $k = 2.6 \cdot 10^{\exp(-9)}$

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$\text{cm}^3 \text{s}^{-1}$ (Španěl and Smith, 1998), calculated reaction time $t = 101 \mu\text{s}$ and a relative mass discrimination $\text{NH}_3^+/\text{O}_2^+ = 0.42$ (experimentally determined like e.g. described by Ammann et al., 2004), the calculation (following de Gouw and Warneke, 2006) of the expected theoretical sensitivity yields $3.8 \text{ ncps ppb}^{-1}$. This is lower compared to the experimentally determined sensitivity of $5.73 \text{ ncps ppb}^{-1}$, but within the general uncertainty range of the theoretical sensitivity calculation: employing a theoretical sensitivity for field measurements can result in very inaccurate concentration calculations due to the uncertainty in e.g. reaction rate coefficient and transmission. Differences between calculated and experimentally determined sensitivities can amount to a factor of 2. It is therefore required to perform calibrations (de Gouw and Warneke, 2006).

anonymous referee#1: “What would be the consequence if more water vapor was present? It seems that there is still enough water to initiate H_3O^+ chemistry in the system, which is exploited to measure latent heat fluxes. What is the limit of water that can be present so that the detection of ammonia would not suffer?”

authors: The potential drawback of (unwanted) H_2O ion chemistry on NH_3 detection is twofold. a) Products of proton transfer reactions might interfere with the detection of electron transfer related ions. In case of NH_3 , m/z 17 can be solely attributed to NH_3^+ which is the unique product of the electron transfer reaction and has no interference with other masses. In addition, competing secondary reactions of H_3O^+ with NH_3 in the drift tube might influence the sensitivity of NH_3 detection under varying H_2O concentration. As mentioned in the manuscript (pp. 4715, l. 4-5) this has been investigated in the lab and the effect could be neglected. As well, Norman et al. (2007) stated that they found no influence of secondary H_3O^+ reactions at E/N below around 120 Td. Also for that reason we operated the eTR-MS at a drift tube voltage of 400 V to achieve a ratio E/N close to that threshold (since E/N is temperature dependent – see below, it was difficult to achieve ratios very much lower than around 120 Td in the high temperature configuration that was applied). b) As discussed in Section 4.3 the second drawback is the potential for NH_3 creation inside the instrument when H_2O

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originating from ambient sample gas diffuses back into the ion source. We investigated the influence of H₂O concentrations in a range of 0 to 30 mmol mol⁻¹ thus covering the ambient water vapour concentration under field conditions (for example, the highest H₂O concentration encountered in the presented field study was around 21 mmol mol⁻¹ and the highest H₂O concentration in Oensingen monitored over the whole year 2009 was about 27 mmol mol⁻¹). Thus under field conditions we are able to correct for the small water influence on the ammonia concentration and EC fluxes, but we must emphasise that the described water interference is an important issue in characterising the flux detection limit under background conditions.

anonymous referee#1: “Could H₃O⁺ and O₂⁺ chemistry be operated at the same time for selected VOCs and ammonia?”

authors: In the first place, it is in principle possible to measure NH₃ and selected VOCs at the same time using O₂⁺ chemistry only. The target compound has to have a lower ionisation energy than O₂ to be ionised by the electron transfer. It would also be important to know the fragmentation occurring with both charge transfer agents. In our case, only O₂ is supplied as source gas and the presence of H₃O⁺ primary ions depends on ambient H₂O concentration of which only a small fraction is potentially protonated by diffusing back into the ion source. The resulting H₃O⁺ ions have a much lower (i.e. < 10% of O₂⁺) and varying abundance than O₂⁺ ions. Therefore it may become complicated to routinely use both primary ions simultaneously for measurements of VOCs.

anonymous referee#1: “Page 4713: The T_d calculation seems to be wrong: 400V drift pressure and 2.13 mbar drift pressure does not give 120 T_d! It should be more like 83 T_d.”

authors: In the manuscript, we presented the drift tube E/N calculated for the applied conditions, i.e. for the operating temperature of 180°C. For 25°C drift tube temperature E/N would be around 81 T_d. Considering 180°C, E/N is close to 124 T_d:

$E = U / l_{\text{drift tube}} = 400 \text{ V} / 9.5 \text{ cm} = 42,1 \text{ V cm}^{-1}$; $N = 6 \exp^{23} * 2.13 / (22400 * 1013) = 5,63 \exp^{16}$ at 0°C and $N = 5.63 \exp^{16} * (273.15) / (273.15 + 180) = 3.4 \exp^{16}$ at 180°C
 $E / N = 1.238 \exp(-15) \text{ V cm}^2 \approx 123.8 \text{ Td}$ [1 Td = $1 \exp(-17) \text{ V cm}^2$]

In the manuscript, we will state the E/N ratio more precisely.

Specific comments of anonymous referee #2:

anonymous referee#2: Introduction “Lines 23-24 appear to be a typo or misprint.”

authors: We simplified the somewhat long sentence to have a clearer statement: “Ammonia (NH₃) is one of the least understood compounds among the important components in today’s terrestrial nitrogen cycle. It accounts for a major proportion of environmentally harmful effects of high nitrogen loads (Erismann et al., 2007).”

anonymous referee#2: Methods “2.1.3 page 4714 lines 21-22 Was there any loss of NH₃ from the standard in running it through the mass flow controller? Was the mixing ratio coming out of the mass flow controller calibrated or verified as the output of the permeation system as described on page 4175 lines 34-35? I understand that the system was until the signals stabilized but value could be less than calculated by the dilution if NH₃ was lost to the surfaces in the mass flow controller.”

authors: The setup to generate NH₃ containing air in the lab was checked in the same way like described on page 4175 lines 34-35 but this was done 3 weeks prior to that particular time response experiment. However, for comparing the time responses an approximate knowledge (e.g. $\pm 15\%$) of the NH₃ concentration was sufficient, since the relative influence of heating the drift tube was investigated. The revised text includes a statement that the 150 ppb of NH₃ used in this experiment was only approximate, for clarification. Before switching between high and low concentration, we waited long enough until the NH₃ concentration reaching the eTR-MS had stabilised. With a stable concentration over time, there should be no ongoing NH₃ retention by the mass flow controller and the complete setup was designed in a way that kept the flow of NH₃

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and zero air in contact with mass flow controller and the tubes constant even when switching between concentration and zero air.

anonymous referee#2: “2.2.2 It is unclear to me if the whole 23 m sample was ever calibrated by adding NH₃ at the tip”

authors: The calibration of the eTR-MS took place through the instrumental PEEK inlet tube without the larger 23 m $\frac{1}{2}$ ” bypass flow tube. Supplying calibration air with a well defined NH₃ concentration to the inlet line flushed with the high flow rate of 100 STP L min⁻¹ would become technically very complex. In Section 2.1.3 (pp. 4715, l. 27 ff.) the sentence is modified: “Calibrations were performed at the field site shortly before the slurry applications by guiding the calibration gas with an effective mixing ratio of 68 ppb NH₃ directly to the PEEK inlet of the eTR-MS”.

anonymous referee#2: “and the reevaluating the time response and if not why not? This should be stated clearly in the text as not to confuse the reader with the characterization of the PEEK instrument inlet.”

authors: We decided to empirically determine the high-frequency loss of the complete measurement system under ambient conditions in the field as discussed in Section 4.2. There are indications that NH₃ concentration step changes show varying temporal behaviour in tubes depending on the magnitude of the step and air humidity (Ellis et al., 2010). A lab experiment with the long tube and high sampling flow would be technically difficult and would probably not reflect the circumstances (humidity, ageing of tube surfaces, etc.) encountered in the field.

anonymous referee#2: “While reading the description of the 23 m sample line I became very concerned about the influence of ammonium nitrate decomposition affecting the measurements. The potential of this is discussed nicely in section 4.4 but a line stating that the potential of affects of ammonium nitrate decomposition is discussed in detail in section 4.4 would be appropriate and helpful to the reader.”

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authors: With regards to the potential of aerosol ammonium dissociation in the heated inlet line, we add a reference to the respective discussion section as suggested by the reviewer: pp. 4717, l. 20: “A side effect of heating the entire sampling tube and the eTR-MS is the potential to dissociate some of the aerosol particulate matter which could release NH₃. This aspect will be discussed in Section 4.4.”

anonymous referee#2: Results “3.1 page 4721 and Fig. 4 The curves in Fig 4 appear to be just connecting the dots. The actual fits to equation 5 should be plotted instead.”

authors: Figure 4 was modified accordingly and figure caption now is: “Fig. 4. Improvement of eTR-MS time response by heating of the new prototype PEEK drift tube: switches from ~150 ppb to 0 ppb NH₃; symbols show measurement data and solid lines represent the respective fits according to Eq. 5.” In that respect we realised that the numbers originally given for the coefficients in Eq. 5 were originating from a preliminary, erroneous fit. The correct values have been inserted in the text of Section 3.1 (pp. 4721, l. 14-18). For 100°C they are: $\tau_1 = 1.96$ s, $\tau_2 = 38.23$ s with a relative weight of the first, fast exponential function of 68%. For 180°C they are: $\tau_1 = 0.77$ s, $\tau_2 = 23.06$ s with a relative weight of the first, fast exponential function of 77%. For both temperatures the time constants of the fits have become a little bit faster than stated before. However, the statements and conclusions in the manuscript remained valid despite the minor change in values.

anonymous referee#2: Figures “Fig. 4. As mentioned before I think the fits to the equation 5 should be plotted.”

authors: see above

anonymous referee#2: “Fig. 5. Which H₂O is plotted?”

authors: Figure caption now says: “Fig. 5. Exemplary 20 Hz time series of w , T , NH₃ and H₂O obtained from sonic anemometer and eTR-MS measurements on (a) 4 August 2009, 13:20–13:30 and (b) 15 August 2009, 13:30–13:40.”

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anonymous referee#2: “Fig. 12. What are the tick increments on the positive side of the NH₃ flux axis? Are the major ticks increments of 20 as with the negative side of the axis or are they in increments of 5 as the opposite axis?”

authors: The left axis always shows NH₃ flux and right axis H₂O flux. The ticks in the figure are edited to improve the visualisation.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 4707, 2010.

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