

Interactive comment on “Calibration and intercomparison of acetic acid measurements using proton transfer reaction mass spectrometry (PTR-MS)” by K. B. Haase et al.

K. B. Haase et al.

khaase@usgs.gov

Received and published: 12 October 2012

Thank you for investing time and effort in reviewing our manuscript. It is much appreciated and has improved the quality of the paper. Responses to your comments are inline below.

1. p. 4638, line 9: The authors state that estimated acetic acid sinks exceed the estimated sources by about 24 Tg C yr⁻¹, but without giving the context of the magnitude of the estimated sinks and sources. It would be generous to the reader to include those values here to put a relative importance to the overesti-

C2506

mation.

-We agree with the reviewer's comment and have revised the introduction to provide discussion of the lifetime and estimated global source and sink magnitudes, along with a note that there are many situations where measurements exceed predictions by a large margin.

2. p. 4645, line 12: State the value from the study by de Gouw et al. that compares well. I know it is in Table 1, but again, to be generous to the reader it could be given here as well. Then the authors can be quantitative about how well it actually does compare.

-As suggested, this statement has been updated to note that the response for PTR-MS-1 (SS) is about 1 ncps/ppbv lower than that found by de Gouw et al. (2003) by fitting their signal through external acetic acid measurements.

3. p. 4648, line 24: Is the measured range of acetic acid concentrations reported here from the PTR-MS measurements or the MC/IC measurements? I'm guessing it is from the former, but since both measurements were discussed, it would be appropriate to be specific. Also, is the max mixing ratio of 3.555 ± 0.327 ppbv shown in Fig. 4 a single measurement, (along with all data points shown in Fig. 4a), or are these averaged in any way?

-The discussion of chemistry during the ICARTT campaign was based on individual acetic acid measurements when comparing with other compounds measured by PTR-MS and 1 hour averages when comparing to results obtained by GC analysis. This paragraph has been revised to indicate that the statistics are based on individual measurements, and the 1 hour PTR-MS averages are now mentioned in the discussion of the GC data.

C2507

4. One of the things that seems to be lacking from the paper is a justification for the usefulness of the PTR-MS measurement over the MC/IC measurement during the ICARTT deployment. Presumably, since the PTR-MS is a higher-rate measurement, short time periods when mixing ratios of acetic acid (and other measured compounds) are elevated can be quantified by the PTR-MS, and not with the slower-rate mist chamber. This seems like a detail that should be at least suggested, and possibly explored with actual data showing a short time period with changing air masses.

- Indeed, there are several justifications for calibrating the PTR-MS for acetic acid measurements. While high measurement frequency is the headline feature, online analysis without preconcentration and commercial availability are also features that make the PTR-MS an attractive approach. The individual PTR-MS measurements have been overlaid on Figure 2 in order to provide a better demonstration of the details captured by high time resolution measurements compared with 2-hour average measurements. Additionally, a brief discussion highlighting the greater time resolution compared to the MC/IC has been added into the discussion in section 3.4.

5. p. 4649, line 5: I'm not fond of the phrase "tracked those". Corresponded to? Correlated with?

-This sentence has been modified to state "...correlated with...".

6. A quantified estimate of the impact of the sum of the potential interferences for the m/z 61 and the m/z 43 fragments would be useful to justify that they are not impacting the intercomparison, rather than simply dismissing that they aren't important in the rural troposphere. Individually they may not be important, but together they may comprise a significant sum when anthropogenic tracers are elevated.

C2508

-Having some kind of estimate of the impact from other compounds would be useful and would certainly strengthen the paper. Generally, the ambient mixing ratios of ethyl acetate and peroxyacetic acid in rural atmospheres are low relative to acetic acid due to rapid photochemical and depositional losses, so they are not likely to be major contributors in this study. The longer-lived propanols appear to be present in low to mid parts-per-trillion levels even in airmasses that are of urban origin. Glycolaldehyde has been reported to reach levels of 1-2 ppbv within a pine forest, but measurements elsewhere are limited. Simultaneous measurements of acetic acid with propanols and glycolaldehyde are not available, making it hard to develop a credible interference budget. Additionally, many of these compounds were not measured (not reported) at Appledore or the surrounding region during ICARTT, excluding a direct estimate. It would be very interesting (perhaps by applying a PTR-TOF-MS) to help tease out the degree of possible interference (although some isobaric and isomeric interferences would still require an external technique). The discussion of the intercomparison between the PTR-MS and the MC/IC has been revised to consider the possibility of chemical interferences.

Technical Corrections: 1. p. 4639, line 14: I believe it is customary to use cm³ molec⁻¹ s⁻¹ or cm³ molecule⁻¹ s⁻¹.

2. p. 4640, line 10: The text should read "Lee et al. (2006b) calibrated their instrument..."

3. p. 4640, lines 12: The text should read "Chemical Ionization Reaction Time-of-Flight..."

4. p. 4642, lines 6-7: The sentence starting "The primary ion (H₃O⁺)..." seems to be a sentence fragment, or is missing a word somewhere.

5. p. 4644, line 11: Be specific about the section (Sect. 3.?) detailing the calibration experiments.

C2509

6. p. 4647, line 10: The word “the” is missing from “consistent with result from. . .”

7. p. 4647, line 27: A full stop (period) is missing from the end of the sentence ending “. . .reaction with H₃O⁺(H₂O). And similar to 2 above, the next sentence should read: “Hartungen et al. (2004) detected the presence...”

8. p. 4648, Section heading for 3.4: Appledore Island should be capitalized.

9. Table 3: The footnotes “4” are used in the header, but are not given below. I’m guessing they should be “2s”. Also, it may be favorable to use alphabetized footnotes rather than numerals, as numerals can be confused with exponents. This applies to Table 1 as well.

10. Fig. 3: It would be useful to show the 1:1 line for comparison.

Thank you for such careful reading of the manuscript. All the issues noted have been corrected.

References: de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, *J. Geophys. Res.*, 108, 4682-4700, doi: 10.1029/2003jd003863, 2003.

Interactive comment on *Atmos. Meas. Tech. Discuss.*, 5, 4635, 2012.