**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "Airborne formaldehyde measurements using PTR-MS: calibration, humidity dependence, inter-comparison and initial results" *by* C. Warneke et al.

Anonymous Referee #2

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This paper details airborne measurements of formaldehyde during the CalNex campaign on board the NOAA WP3 aircraft via Proton Transfer-Mass Spectrometry. The authors perform interference tests for a wide variety of VOCs, none of which were found to interfere significantly, and characterize the water interference for humidity conditions ranging from those in the free troposphere to those in the marine boundary layer. The authors then present formaldehyde measurements from the CalNex field campaign, which agree within error with ground measurements at the Pasadena site. This work demonstrates how PTR-MS can be used to measure HCHO, although perhaps not under all scenarios. As PTR-MS is increasingly used this represents an important

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Interactive Discussion

Discussion Paper

contribution.

Overall, this paper is well written and contains important contributions, and I recommend it for publication after addressing the following comments.

My primary concerns are with the zeroing/background method.

1) What does the background signal correspond to? The authors state that part of it comes from a NO+ isotopologue. If this is the case, can they quantify this part from the major isotopologue? I understand if its origin cannot be determined.

2) Some types of tubing, e.g., polyethylene tubing can result in formaldehyde generation, especially in the presence of sunlight. I have not heard of any inlet studies performed with PEEK. Did the authors investigate whether PEEK reacts with ozone to generate formaldehyde.

3) It is not mentioned whether the catalyst for zeroing removes ozone along with VOCs. If it does, this may result in an interference not accounted for in the background measurement (as it would not contain ozone), i.e. formaldehyde generation from ozone.

4) A second concern is permeation of formaldehyde from the cabin through the inlet walls or small leaks. If the cabin has elevated formaldehyde, either permeation through the inlet tube or small leaks could contribute to a background, and it would have a water dependence. This might be entirely irrelevant, but were tests conducted to see whether this could be the case?

5) The values for the background that are subtracted judged by figure 6 are very smooth. However, during the actual background determinations, e.g. just after 20:30, the background looks much noisier. How is this treated in the error propagation/uncertainty estimate of the reported formaldehyde concentrations. Is it reasonable to report a 1 sec time, if the background used for subtraction results from time averaging?

6) I am a little confused about the detection limit and uncertainty. It is discussed that

the detection limit depends on relative humidity, which is reasonable. It is also mentioned that the uncertainty of the calibration is 30% and that PTR-MS and DOAS and Hantzsch agree within uncertainty (of measurement or calibration?). I believe it would help clarify: a) What is the uncertainty of the PTR-MS formaldehyde measurement? b) Should it not also depend on conditions. From Figure 6, I would guess that the uncertainty varies during the flight. For example, right before 20:00 the background is low whereas directly before 21:30 the background and total signal are quite similar. Hence the uncertainty in % must be much larger for the latter?

7) In figure 5 it appears as if in essence two calibration curves exist, the lab data and 2010/04/21 and a second one consisting of 2010/06/18 and 2010/04/20. Can this be discussed more in detail?

8) As the intercomparison is an important aspect of the paper, I suggest changing figure 7: I realize showing the diurnal traces is a common practice. However, a) there are only 14 PTR-MS data points on this, which is the focus of this work, and b) for an intercomparison scatter plots like the inset are more useful, as diurnal traces do not convey much, especially nothing quantitative as required for an intercomparison. I would suggest to instead show individual scatter plots of DOAS vs. PTR-MS, Hantzsch vs. PTR-MS, and Hantzsch vs. DOAS (or the other way around), and I believe at least the PTR-MS data should have error bars on it.

9) The same for the acetaldehyde data. If I understand correctly the PIT-MS and GC-MS were both at the ground site but show large differences, e.g. 5/31/10. I believe that the quality of agreement is again expressed better as a scatter plot of PTR-MS vs GC-MS, etc. and R^2 values etc.

Specific/technical comments;

P4632, line 6: Please define or give a reference for "normal operating mode".

P4632, line 10-11: Please define detection limit here. I believe later it is defined as 3

sigma?

P4633, line 13-14: Please add a reference for these lifetime estimates, and clarify whether photolysis or OH are more important.

P4633, line 19-29: Recently LIF detection has been demonstrated (e.g., Hottle et al., ES&T, 2008).

P4634, line 27: Please define or give a reference for "standard instrument settings".

P4635, line 2-3: "a plume study was used to show the atmospheric HCHO production" What does this statement mean, specifically "to show the atmospheric production?"- HCHO not from primary emission?

P4636, line 7-8: Please define or give a reference for "standard PTR-MS conditions"

P4637, line 5: Please refer to (Wert et al., JGR-Atmos., 2002) for PFA transmission of formaldehyde under various conditions

P4637, line 13-15: Does the catalyst also remove ozone, as I would be concerned over the reaction of PEEK with ozone to generate formaldehyde. Were any tests performed to determine whether this may be the case?

P4641, line 1: Please state how formic acid and acetic acid were detected?

P4643, line 8: The cause for the humidity dependence on the inlet flow is confusing to me. Is the inlet flow diluted with flow from the reagent ion source?

P4643, line 18-19: Please clarify the text to reflect that this was the laboratory calibration line, as it is ambiguous here what the "solid red line" refers to.

P4646, line 3-5: Please state the uncertainty of PTR-MS, DOAS and Hantzsch as otherwise the statements cannot be evaluated. PTR-MS is nearly twice Hantzsch, which is a large difference. I think this deserves more discussion.

Figure 1: What is the definition of detection limit?

Figure 2: Please add a legend for CC

Figure 7c: Please clarify in either words or the legend the color code for the PTR-MS measurements.

Figure 8: It is unclear which of the raw data points belong to LA or the FT. I recommend four individual plots for clarity.

Figure 9a: Would it be possible to move the plume crossing labels to a less obstructive position?

Figure 9c: Please clarify "acal" as acetaldehyde and make consistent with the rest of the paper and the caption.

References:

Wert, B.P., Fried, A., Henry, B., Cartier, S., Evaluation of inlets used for the airborne measurement of formaldehyde. J. Geosphys. Res. 107 (D13), doi:10.1029/2001JD001072 (2002).

Hottle, J.R., Huisman, A.J., Digangi, J.P., Kammrath, A., Galloway, M.M., Coens, K.L., Ketusch, F.N., 2009. A Laser Induced Fluorescence-Based Instrument for In-Situ Measurements of Atmospheric Formaldehyde. Environ. Sci. & Techn. 43, 790-795.

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