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**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.

**C. Warneke et al.**

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Both reviewers have made very insightful and constructive comments, which we have all taken into account and as a result improved the manuscript.

Reply to Reviewer 1:

*1) All the analytical details and procedures described in the manuscript have been previously described in the literature. Jordan et al. (2009) reported the improved analytical performance of High Sensitivity PTR-MS instruments which typically achieve similar signal intensities as the NOAA instrument. Veres et al. (2010) described the use of MOCCS system for HCHO calibration. Vlasenko et al. (2010) characterized the strong humidity-dependence of HCHO calibration factors and described the use of the m/z 37 to m/z 19 ratio as an intrinsic measure for humidity. Steinbacher et al. (2001) pointed out the need to subtract the m/z 31 background signal arising from the natural isotope of NO+. Results from measurement comparisons in the field were presented by Steinbacher et al. (2001), Karl et al. (2003), Inomata et al. (2008) and Vlasenko et al. (2010). Strictly judging, the paper does thus not present any novel concepts, ideas or tools. The available scientific information is, however, synthesized and put in the context of a new application, i.e., the deployment of the instrument on an airborne platform. I personally find this sufficient to merit publication but I invite other reviewers and the Editor to further evaluate this aspect.*

We agree with the reviewer that most analytical details and procedures for the HCHO detection with PTR-MS have been described in the literature before, but here we discuss the first aircraft measurements of HCHO with PTR-MS. Aircraft measurements present the most challengingconditions so that all the analytical procedures(instrument improvement, HCHO calibration, humidity dependence, background subtraction and inter-comparison), each previously described in a separate paper, have to be all used together to produce high-quality data. We therefore think,just as the reviewer himself/herself, that this manuscript is a significant advance in analytical analysis and procedures that merits publication.

*2) The authors make the ambitious claim that they "show that PTR-MS is capable of RELIABLY measuring HCHO on board an aircraft" (page 4634, line 23). I would argue that this paper adds to the long list of EXPLORATORY studies on the use of PTR-MS for HCHO measurements. The interference on m/z 31 from other compounds, methyl hydroperoxide (MHP) being a prominent candidate, still remains a major uncertainty. MHP levels up to 1 ppb are not uncommon for California (unpublished data by the Wennberg group) which contradicts the authors' statement that MHP levels are negligible compared to HCHO concentrations. The obtained intercomparison data (Fig. 7)* *do indeed suggest a positive bias in the PTR-MS data. Most certainly, a comparison of 14 data points (which, in addition, were sampled on non-identical air masses) is not sufficient to validate the reliability of an analytical method. It is not my intention to question the high analytical quality of the performed work. Nonetheless, the authors should clearly state the exploratory character of their measurements (in the abstract, in the conclusions and perhaps even in the title) and demand further validation work.*

The reviewer is correct that the inter-comparison is not detailed enough that a small possible interference cannot be ruled out. We have therefore taken the suggestions and added a sentence to the abstract and the conclusion stating that more inter-comparisons are needed and changed the sentence mentioned above to "further explore the capability of PTR-MS to measure HCHO".

Minor comments:

*1 Introduction: - include DFGAS (Difference Frequency Generation Absorption Spectrometer) in the list of instruments/techniques.*

We have included the DFGAS in the list of instruments and added a reference.

*2.1 PTR-MS instrument and HCHO detection - report drift tube temperature and E/N - specify the relative and absolute amount of the O2+ signal (which will react by electron transfer and eventually produce m31 from other compounds)*

We have added the drift tube temperature, E/N and the O2+ signal to the text.

*3.1 Interference test with GC-PTR-MS - sentence on MHP interference is repeated atend of paragraph, remove*

We have removed that sentence.

*3.2 Laboratory calibration - I assume the authors did not measure m19 and m37, but their isotopes m21 and m39. This should be stated and explained. - report precision (1 s integration, 1 sigma) of the measurements at 1 ppb (for typical continental BL*

*conditions) - Can the humidity dependence of the BG signal entirely be explained by the humidity-dependent change of NO+ and its isotope ?*

We have added a sentence explaining that we measure m21 and m39.

A more detailed discussion about the precision of the PTR-MSwas added: see comments by reviewer 2.

*Figure 1 - report S/N used for DL calculation (in figure caption)*

We added the S/N.

*Figure 5a: - consider plotting m31 vs. m37/m19 (color-coded in inlet-flow)*

In Figure 5a we want to show a "typical" calibration curve: signal versus inlet flow. Figure 5b basically shows what the reviewer suggests but in normalized signal, so we have decided to leave Figure 5 unchanged.

Reply to Reviewer 2:

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

We have added a sentence explaining that the background signal cannot complete be explained by the NO+ isotope.

*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 togenerate formaldehyde.*

We have used PEEK instead of PFAtubing for many years now, because it is at least as inert as PFA for almost all VOCs we have investigated (e.g. for PFA: Northway et al 2004), less permeable and blocks out light. We have not done any specific test for

HCHO production from ozonebut nothing in our standard tests suggests any issues with the PEEK tubing.

*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.*

The catalyst, as any other heated metal surface at that temperature,will remove ozone. We think it very unlikely that HCHO can be produced in our inlet in any significant amount, because of the short residence time (<1s) and low pressure (120mbar).We have added to the text that the catalyst removes ozone.

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

We constantly perform leak tests in the aircraft and PEEK is much less permeable than Teflon, which is the main reason we are using PEEK. But problems like this could always influence any measurement, especially on aircrafts, where constant vibrations can loosen fittings, but we are confident that this was not a significant problem during CalNex, because it would influence all the compounds measured and correlations of VOCs with other instruments would diminish, which was not observed.

*5) The values for the background that are subtracted judged by figure 6 are verysmooth. However, during the actual background determinations, e.g. just after20:30, the background looks much noisier. How is this treated in the error propagation/uncertainty estimate of the reported formaldehyde concentrations. Is it reasonableto report a 1 sec time, if the background used for subtraction results from time averaging?*

The background is measured periodically with fiveindividual data points, which are

then averaged, so that each individual background measurement has a high precision. The background points are interpolated using the measured humidity dependence of the HCHO background, so that the background is accurately enough known and not too variable on a 1-s time base throughout the flight so that 1-s measurements are meaningful. See also next comment.

*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 mentionedthat the uncertainty of the calibration is 30% and that PTR-MS and DOAS andHantzsch agree within uncertainty (of measurement or calibration?). I believe it wouldhelp 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 uncertaintyvaries during the flight. For example, right before 20:00 the background is lowwhereas directly before 21:30 the background and total signal are quite similar. Hencethe uncertainty in % must be much larger for the latter?*

The reviewer points out that we did not define the uncertainty of the HCHO measurement well enough and we agree. We now have clearly explained that the uncertainty of the in-flight calibration causes an accuracy of 30%, which is independent of the mixing ratio. The precision of the HCHO measurements is shown in a new Figure 6. The precision is strongly dependent on the actual signal in Hz, which is dependent on the instrument background, the mixing ratio and for HCHO also on the humidity. This is shown in Figure 6. Furthermore, the precision also depends on how accurate the background can be determined. This is now also explained in the text.

This Figure adds more detail than the reviewer asked for, butwe think that it is a very useful addition to the manuscript as the topic of PTR-MS precision and accuracy has rarely been discussed in the PTR-MS literature in enough detail.

*7) In figure 5 it appears as if in essence two calibration curves exist, the lab data and2010/04/21 and a second one consisting of 2010/06/18 and 2010/04/20. Can this* *bediscussed more in detail?*

We do not know, why there were such differences in the calibration curves, which is the main reason for the accuracy to be 30%, which is not as good as can be expected from PTR-MS calibrations using the MOCCS system. We now state that more clearly in the text.

*8) As the intercomparison is an important aspect of the paper, I suggest changingfigure 7: I realize showing the diurnal traces is a common practice. However, a) thereare only 14 PTR-MS data points on this, which is the focus of this work, and b) foran intercomparison scatter plots like the inset are more useful, as diurnal traces donot convey much, especially nothing quantitative as required for an intercomparison. Iwould suggest to instead show individual scatter plots of DOAS vs. PTR-MS, Hantzschvs. PTR-MS, and Hantzsch vs. DOAS (or the other way around), and I believe at leastthe PTR-MS data should have error bars on it.*

We agree with the reviewer that for an inter-comparison the most important figure is the scatter plot, which we are showing in Figure 7. The time series gives lots of extra information about diurnal and long-term variations of the ground site data that a scatter plot cannot show and even though it is not strictly necessary for the purpose of the inter-comparison, we feel that we would loose important information, if we don't show the time series and have therefore decided to leave the plot unchanged.

*9) The same for the acetaldehyde data. If I understand correctly the PIT-MS and GCM-Swere both at the ground site but show large differences, e.g. 5/31/10. I believethat the quality of agreement is again expressed better as a scatter plot of PTR-MS vsGC-MS, etc. and Rˆ2 values etc.*

The main point of showing the acetaldehyde data is to demonstrate that at night the aircraft and the ground site are not necessarily in the same airmass. This is best done with the time series and we would therefore like to keep this time series as well, but we have added the slope and the R-coefficient to the text.

Specific/technical comments;

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

We have added the reference.

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

We have added the detection limit.

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

We have added the reference.

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

We have added the instrument to the list and the reference.

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

We have added the reference.

*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?*

We have specified that we are looking at secondary production of HCHO during the plume evolution.

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

We have added the reference.

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

We have added the reference.

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

The catalyst removes ozone. See comment earlier.

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

Formic and acetic acid were measured with PTR-MS. This was added to the text.

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

The humidity is not dependent on the inlet flow. The humidity in the atmosphere usually decreases with altitude and the inlet flow is dependent on the altitude, so they always change together in the aircraft, but are actually not dependent on each other. This is now better explained in the text.

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

We have added that to the text.

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

We have added the accuracy of the instruments to this part of the text as well and changed the text to say: PTR-MS and Hantzsch agree to just outside the stated uncertainties.

*Figure 1: What is the definition of detection limit?*

The S/N=3 was added to the caption.

*Figure 2: Please add a legend for CC*

The legend was added.

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

We have added the color code to the legend.

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

We added extra coloring to the FT and BL data points.

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

We have moved the labels to better positions.

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

We have changed the legend.

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Interactive comment on Atmos. Meas. Tech. Discuss., 4, 4631, 2011.