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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.

Anonymous Referee #1

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This manuscript describes the analytical set-up and procedures to conduct airborne measurement of formaldehyde (HCHO) with a conventionally operated PTR-MS instrument. The authors characterize the instrumental operating parameters and performance characteristics of their instrument and describe the inlet and calibration system for HCHO measurements. Results from interference tests are presented along with humidity-dependent calibration and zeroing data from both the laboratory and the field. Exemplary raw and treated data from a CalNex 2010 flight are shown and results are compared to ground-based measurements with established techniques. Ultimately, application examples (regression analyses in different air masses) of the presented

method are given.

The paper is excellently structured and written, and its topic fits well within the scope of AMT. I do recommend publication in AMT but I would like to raise two major points of criticism:

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.

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.

Minor comments:

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

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)

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

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 ?

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

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

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