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Atmospheric Chemistry and Physics Discussions

Interactive comment on "PTR-MS measurements of non-methane volatile organic compounds during an intensive field campaign at the summit of Mount Tai, China, in June 2006" *by* S. Inomata et al.

Anonymous Referee #3

Received and published: 5 February 2010

General comments:

This manuscript reported VOC measurements using PTR-MS during an intensive field campaign at a Central East China mountain site, in June 2006. OVOCs were found to be the major component of VOCs during this campaign. Emission ratios of VOCs with respect to CO were analyzed and found comparable to literature values.

The subject of this manuscript is within the scope of ACP and the VOC observations could be valuable to the atmospheric chemistry community. However, there are two po-

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tential issues that could compromise the data quality. First, the sensitivity of PTR-MS was affected by ambient humidity level due to its working principle, thus the background checks should be conducted without changing sample air humidity. For the same reason, the PTR-MS should also be calibrated at the same humidity level as the ambient air. As indicated by Inomata et al. (2008), PTR-MS was calibrated in this work with water concentration ranging from merely a few to 30 ppmv, which was much less than the ambient water concentration. Second, inter-comparisons between PTR-MS and GC based methods can definitely help to validate the PTR-MS data, but the results shown in Fig. 2, especially in the cases of m/e 69 and m/e 137, cannot convince the reviewer the two instruments were reporting the same concentration. Therefore, the reviewer cannot recommend publication of this manuscript in its current form. The reviewer suggests the author conduct extra tests on the PTR-MS performance under ambient conditions and substantially revise the manuscript before resubmission, especially after addressing the following comments.

Specific Comments:

1. Instruments described in the second paragraph of section 2.1 can be summarized into a table including instrument name, model number, working principle, species measured, sensitivity, and detection limit.

2. Although NOy was not the focus of this work, it might compromise the VOC data analysis. The author may want to find out if the NOy inlet also collected aerosol nitrate? If so, how efficiently was aerosol nitrate detected and how much did the aerosol nitrate contribute to the NOy signal?

3. Section 2.2 is very much the same as the experimental part of Inomata et al. (2008). The reviewer suggests the author substantially reduce the length of this part by using a table to summarize the PTR-MS operating parameters.

4. Page 26702, Line 23: The author stated that a commercial zero-air supply (Thermo Environmental Instrument Inc., Model 111) was used to determine the background sig-

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nals. The reviewer does not recommend this method because a charcoal filter was used inside this particular zero-air supply. Charcoal can significantly adsorb water vapor from the ambient air sample thus would affect the m/e 37 concentration significantly. The reviewer believes the sensitivity of the PTR-MS will differ substantially with/without the charcoal filter. In addition, the efficiency of this zero-air supply in removing VOCs was also questionable. Table 1 showed that the detection limit obtained from this work was as low as 10 pptv. Then, what was the magnitude of background signal? The reviewer strongly suggests the author re-check the background level and run calibrations with a catalytic converter specified by de Gouw et al. (2003).

5. Inomata et al. (2008) conducted an intensive research on the humidity dependence of PTR-MS response to HCHO. However, the water vapor concentration used in Inomata et al. (2008) was less than 30 ppmv, much less than the typical ambient level. The reviewer suggests the author conduct more calibrations within the RH range encountered in this work.

6. Fig. 2 d shows very good correlation coefficient (r2 = 0.92), but this might be just because of the single point at about 1.5 ppbv. If this point was removed, the data set would show much more scattering. In the case of Fig. 2 e, it is hard to find any correlation between the two data sets at all (r2 = 0.08).

7. Page 26706, Line 10: Since n-nonanal and n-decanal were also measured by other techniques, the reviewer suggests the author show an inter-comparison plot. Thus, the PTR-MS data can be validated.

8. Page 26708, Line 14: The author claimed that “This value is . . . the observed O3 increase”. This statement was very superficial. The observed O3 profile (Fig. 3b) was the result of both in-situ photochemical production and physical mixing of different air masses. A box model was not sophisticated enough to explain the observed O3 profile.

9. The reviewer suggests the author include a plot of NOz/NOy in Fig. 3 so that any injection of fresh NOx emission into the aged plume can be identified.

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Technical Comments:

1. Annotations in Fig. 3 a b c and Fig. 8 a b are not clear. The arrows should point to the traces.

2. Page 26706, Line 6: “The peaks at m/e 129. . .in this study.” is confusing.

3. Page 26708, Line 5: “bserved” should be “observed”.

4. Page 26708, Line 18: suggest change “is likely to have been controlled” to “was likely controlled”.

5. Page 26711, Line 5: This line is confusing.

References:

de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., and Fall, R.: Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, Int. J. Mass spectrom., 223, 365-382, Pii S1387-3806(02)00926-0, 2003.

Inomata, S., Tanimoto, H., Kameyama, S., Tsunogai, U., Irie, H., Kanaya, Y., and Wang, Z.: Technical note: Determination of formaldehyde mixing ratios in air with ptr-ms: Laboratory experiments and field measurements, Atmos. Chem. Phys., 8, 273-284, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 26697, 2009.