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Interactive comment on “In-situ measurement of reactive hydrocarbons at Hohenpeissenberg with comprehensive gas chromatography (GCxGC-FID): use in estimating HO and NO₃” by S. Bartenbach et al.

Anonymous Referee #1

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Referee Comment

This paper describes the analysis of VOCs at the Meteorological Observatory Hohenpeissenberg using comprehensive two-dimensional gas chromatography during a field study. The authors show that the technique provides quantitative data through comparison with an existing, validated method, which has not been presented before for atmospheric samples. The variability of concentrations of VOCs obtained during a field study, were used to derive a mean OH radical concentration which was compared to the measured value and this analysis extended to NO₃ concentrations at night. This

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paper presents the use of hydrocarbon measurements obtained by a relatively new technique in an interesting and novel way and I recommend publication of this article in ACP after some minor changes. The paper has been well written and is presented in a clear and concise way.

General Remarks

1. The trapping of hydrocarbons at 25 C can be prone to breakthrough if large volumes are sampled. Have the authors undertaken breakthrough testing prior to the campaign? Do you humidify the standard mixture prior to analysis to ensure that the sample and standard are analysed at similar RH?
2. The details of the modulator are very limited. More details are required in the text for general interest.
3. When determining the values for A and b from the variability - lifetime plots, the authors have presented the entire data (i.e. day and night) only. Later, when estimating OH concentrations the data is split into day and night. It would be interesting to see what the variability - lifetime plots look like when split into day and night. The values of A and b for the two time periods would also be very interesting. Does b tend towards 0 when the station is above the boundary layer?
4. The authors use the 13 compounds specified to estimate the OH radical concentrations. The choice of anthropogenic compounds (alkanes and aromatics) which have negligible reactivity towards ozone means they surely do not have any relevance when trying to determine the best fit. It is not surprising that a best fit cannot be calculated using the whole data set. It would be more appropriate to use anthropogenic compounds which also react with ozone, such as styrene or alkenes. Were no measurements of these compounds available from the GCXGC?
5. The section regarding the OH radical estimation is confusing. At the start of page 8169, you should state explicitly that you are talking about the daytime measurements

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only. The value of 5.3×10^6 , is in the wrong place in table 4 (i.e. is placed under the total column rather than the biogenic only column). Also the “day and night” values are given in table 4 but they are not referred to in the text. On line 21, the results from the simultaneous variation of O₃ and OH are given. Are these for the biogenic only or the whole data set?

6. When sabinene is removed from the data, the authors could not determine a suitable slope for the short lived biogenics and found that variability does not depend on chemical lifetime. What do the authors think are the causes of variability of the other terpenes? Transport only? In this case, the sabinene seems to be distorting the overall biogenic picture.

7. For the calculation of NO₃ concentrations, do the very low concentrations of terpenes at night increase errors in the calculation? Also, the observatory is above the BL at night and in the free troposphere. Are the sources of terpenes therefore a combination of local night-time emissions and other longer-range transport to the site (or are they too reactive)? The authors should indicate how relevant non-local sources are to the calculated NO₃ concentrations.

Technical comments

1. Throughout the paper, acronyms are used without being explained first. All acronyms should be explained on first use, especially in the abstract.
2. GCXGC should be given its full title at the start i.e. comprehensive two-dimensional gas chromatography
3. page 8157, line 3: Formation of secondary organic aerosol is also a loss route of oxygenated VOCs.
4. page 8157, line 9: Replace “or” with “of”. Line 13: Remove “biogenic VOCs are compared”
5. page 8157, line 12: the observatory is called MOHp in the abstract and then the

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GAW observatory here. I realise these are the same place but it need clarifying

6. page 8159: line 2: Change “to develop” to “developing. Line 23; Replace “is under-going” with “undergoes”

7. Page 8162, line 15: Remove (Max-Planck Institute)

8. Table 4: The 5.3 value appears to be in the wrong place.

9. Figure 5: It is difficult to see the difference in the blue colours in this graph. I suggest the colour scheme is changed.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 8155, 2006.

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