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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.

S. Bartenbach et al.

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We appreciate the referee's comments and ideas and we have addressed all points raised in the revised manuscript. The technical comments will be changed in the revised form of the manuscript.

1. We agree with Referee 1 that generally breakthrough is a potential danger if the VOCs are sampled at a temperature of 25°C. The technical support data sheet for thermal desorption of Markes Ltd. (UK) indicated possible problems for compounds with a molecular weight lower than hexane. However in this study we focus on semi-volatile organic compounds, in particular the monoterpenes. We do not humidify the standard

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mixture prior to analysis as questioned by Referee 1. Because of the observed good agreement with the GC-MS data of the Meteorological Observatory Hohenpeissenberg we conclude that neither of these possible problems has effected the measurements significantly. This is now noted in the text.

2. In order to keep the instrumental description concise we limited details on the GC×GC in the initial text. However, since Referee 1 requested more details we gladly included more background details on GC×GC.

3. Referee 1 asks for details of the variability lifetime plot separated by day and night. We now give the A and b coefficients for the day and night data separately at the end of paragraph 3.3 in the revised paper.

4. Referee 1 is correct. The determination of the OH and NO₃ in this study relies on the biogenic species to give an optimum. One important assumption made however is that the source region of these compounds is similar. Since anthropogenic alkenes would not be from the same source we cannot include them in this plot since they would have experienced a different average OH/NO₃ field than the biogenics. The emphasis here was the quantification of the monoterpenes and their application to variability/lifetime analysis.

5. For clarity regarding the radical estimation, the first sentence of the last paragraph on page 8168, line 25, was changed to: “To calculate the daytime OH mixing ratio with a minimised influence of changes in the boundary layer height, the dataset was divided according to time in two sections (10:00 and 19:30 CEST day; 22:00 and 05:30 CEST night).”

The value of 5.3×10^6 in Table 4 is placed now in the correct column of the Table, and as requested by Referee 1, we have included the ‘day and night’ values from Table 4 in the revised text. The result of the HO radical estimation (page 8169, line 21) is for the biogenic dataset and is clarified now.

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6. Referee 1 is correct to point out that sabinene is important in the determination, we have also made this clear in the text (e.g. page 8166, line 11). Sabinene is the most variable of the monoterpenes measured, an observation which is consistent with its reaction rate with OH, O₃, and NO₃. Certainly more speciated monoterpene measurements would be helpful here in defining the line. We have accordingly inserted additional text to reflect this discussion.

7. The low concentrations of terpenes at night will not increase the errors in the calculation, since the measurements remain above the conservatively estimated detection limits for all compounds. The variability measured is therefore overwhelmingly attributable to atmospheric effects. Referee 1 also asks about the possibility of non-local sources (presumably of monoterpenes) playing a role in the determination of the nocturnal NO₃. We estimate that depending on the nocturnal wind speed we may have had small influences of VOCs originating from sources up to 50 kilometers away, assuming the boundary layer has not developed due to high wind speeds and hence mixing (assuming a VOCs lifetime of 2 hours and a wind speed of 15 km/h). If the inversion has formed, which was the case in most of the nights, then for an influence to occur the wind must pass over a hilltop that is also above the inversion, in the right direction relative to the wind and within 50 km of the site. Thus it is very unlikely that the site was affected by monoterpenes from other regions.

Comment on Figure 5: The colour scheme is changed in the revised version.

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

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