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Atmospheric
Chemistry
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Discussions

Interactive comment on “In-situ measurement of reactive hydrocarbons at Hohenpeissenberg with comprehensive gas chromatography (GCxGC-FID): use in estimating HO and NO_3” *by* S. Bartenbach et al.

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We thank referee M. Krol for his useful comments on our paper. The technical and typographical points will be corrected in the revised version, the major points of discussion are addressed below:

1. We agree with referee M. Krol that the slow sampling time of our technique limits the time frequency with which we can determine HO or even NO_3. With the instrument described in this paper we cannot derive monoterpene concentrations on timescales similar to the lifetimes of these species. The long inherent integration time of this technique should not affect the relative variabilities of the species measured since all are

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integrated for the same time. i.e. a more reactive species should remain the most variable. Because of the sampling time of our technique we can, from this dataset, only attempt to determine campaign averages for such species. We argue that this information useful as currently the influence of NO3 in the atmosphere is poorly understood and any technique which permits estimation of its concentrations is of interest for atmospheric chemists. The exact effect of signal averaging on variability determination would be interesting to test with virtual species in a highly resolved mesoscale model which can take into account mixing of various scales. This however is beyond the scope of this paper which presents an instrument intercomparison, campaign interpretation and a potential novel use of VOC compounds. We agree with Referee M. Krol that in order to be able to derive time dependent NO_3 and OH data with this method the terpenes should be quantified specifically and rapidly (sub 1 minute). Unfortunately no such instrument exists to date which can do this. Recent reports show the potential of Proton-Transfer Reaction-TOFMS (PTR-TOFMS) systems, which still have a too low sensitivity to analyse e.g. monoterpenes in the atmosphere (see Blake et al., 2004; Inomata et al., 2006), this we have added at the end of paragraph 3.4.

2. The referee M. Krol is correct with his observation that the variability on cloudy days and clear days is different and that also the diurnal HO cycles can differ significantly from day to day. However, we do not have enough data to make further subsections of the dataset. With this paper we wanted to point out the possibility of determining atmospheric radical concentrations if no measurements are available on site. With larger datasets, i.e. accomplished by fast measurements, it may be possible to calculate diel HO concentrations and consider the weather conditions.

3. Jobson et al. (1999) found b values in the range of 0-0.5 for compounds with lifetimes between 2 and 30 days. This however is the first attempt of plotting the variability-lifetime relationship with fast reacting organic compounds and shows the potential of the technique.

Comments on the technical remarks:

2. To section 3.4: We have added a new figure (Fig. 7) and new text to illustrate the procedure of the radical concentration and the calculation of X^2. We have also examined the error estimate for the NO_3 concentration. If the species are left out one by one and we sum up the errors, we get an uncertainty of 74%. The overall result is then $1.47 \pm 1.0 \times 10^8$ molecules cm^{-3}.

3. Units: We have corrected the units from ppt to pmol/mol both in Figure 2 and 3.

References

Blake, R. S., Whyte, C., Hughes, C. O., Ellis, A. M., and Monks, P. S.: Demonstration of Proton-Transfer Reaction Time-of-Flight Mass Spectrometry for real-time analysis of trace volatile organic compounds, Anal. Chem., 76, 3841–3845, 2004.

Inomata, S., Tanimoto, H., Nobuyuki, A., Hirokawa, J., and Sadanaga, Y.: A novel discharge source of hydronium ions for proton-transfer reaction ionization: design, characterization, and performance. Rapid Comm. Mass Spectr., 20, 1025–1029, 2006.

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

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