**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

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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Received and published: 12 October 2006

This paper expands on earlier attempts to derive the OH-radical concentrations from observed variability of atmospheric trace species. The novel issues here are: 1. The new 2D measurement techniques enables the measurement of more VOC species. 2. Shorter lived VOCs are taken into account 3. By separating day and night values, an estimate of the night-time concentration of NO3 is attempted.

The idea to correlate variability to lifetime is attractive, especially for experimentalists.

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Without the interference of a model, a data-only technique can be applied to a set of measurements. The authors show good insight in the factors that determine the variability of the measured VOCs. Boundary layer dynamics, turbulence, advection from nearby forests and anthropogenic sources, are all properly discussed. The only assumption the authors have to make in their analysis is that the VOCs have a common source area. With this assumption they are able to come up with a reasonable concentration for OH, and even for NO3. So the suggestion is made that this simple procedure can be used to estimate the concentrations of oxidizing compounds in the atmosphere. However, in my opinion the authors should provide a more careful analysis of the data. To stimulate discussion, I will raise a number of issues that came up while reading this well-written paper.

1. To measure compounds with a lifetime of one hour or less (sabinine) with a measurement technique that takes 60 minutes per sample (top page 8163) will never produce a reliable estimate of the true variability.

It turns out that the variability of the short-lived sabinene plays a pivotal role in the analysis. Is it not strange that if sabinene is not considered, no significant slope can be determined for the short-lived biogenic VOC and variability does not depend on the chemical lifetime anymore (page 8169)?

2. There are many disturbing factors that are not considered. For instance, OH changes considerably during a diurnal cycle.

Days with clouds and clear days are analyzed together, while the OH is probably much lower on cloudy days. Also, the diurnal cycle of short-lived compounds induced by OH variations during the day is something completely different than variability induced by 'transport time differences' (page 8158). Also, co-variation of emissions and OH (light dependent emissions) may interfere with the analysis. When switching to VOCs with a very short lifetime, these details become important and are mostly ignored in this study.

3. A value of b=0.75 (page 8167), that is outside the range between 0 (chemistry has

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had no time to act on the air parcels) and 0.5 (variability is significantly influenced by chemistry) signals problems with the measured variability (sabinene?)

My verdict (to be discussed) would therefore be: It is not possible to use the measured variability of short-lived VOCs to determine OH (and NO3) in a reliable way at the moment. Main problem is a reliable measurement of variability of short-lived compounds.

Some more technical remarks:

Page 8157: the remark behind GCxGC seems to be intermingled with another sentence. Intuitively, we may expectĚ..I do not see why you need intuition if you explain later that the explanation is in the transport time differences.

Section 3.4: Estimation of HO radical concentrations. The procedure is not totally clear to me. If we start from figure 6, a change in the HO concentration (or O3, NO3) will change the position of the points on the x-axis, since the lifetime is influenced. Is that what is done? The chi-squared value that is minimized, how is it defined? Is it the horizontal distance or the vertical distance between the line and the individual points? Since there are no units to chi-square, I assume the vertical distance. I suggest to graphically illustrate the procedure. If you modify OH, some points will move 'faster' than others on the x-axis? I was also puzzled by the fact that sometimes no minimum is found (top page 8169, table 4 does not give a clue, and contains values in the wrong column). Also, it seems that the error in the analysis is quite small. For instance, an NO3 concentration of 1.47 +/- 0.2x10ˆ8 seems quite accurate. What if you leave out species one-by-one? Why do the different methodologies in table 4 lead to differences that are much larger than the error estimates?

Units are expressed in pmol/mol and molecules/cm3, except for figure 2 (ppt). Also the conversion between the units seems to use something like 2.3x10ˆ19 molecules of air/cm3, which seems a bit a high number for an altitude of 1000m?

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