Atmos. Chem. Phys. Discuss., 6, S6772–S6777, 2007
www.atmos-chem-phys-discuss.net/6/S6772/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Boundary layer concentrations and landscape scale emissions of volatile organic compounds in early spring" *by* S. Haapanala et al.

S. Haapanala et al.

Received and published: 13 February 2007

The authors wish to thank Anonymous Referee 1 for valuable comments and suggestions to improve the manuscript. We have answered each of the specific comments below. Whenever the referee is cited, the text has been written inside quotation marks.

Introduction

"The authors argue that information on the distribution of VOCs throughout the boundary layer is important in the context of the particle formation events. This point should be extended and clarified - it sets the stage for a later discussion of the VOC results and their significance in relation to the particle formation (a discussion that unfortunately is not included in the manuscript yet, but should be added!)." This discussion is

now extended in the manuscript.

Materials and methods

“Figure 1: Indicate the location of SMEAR II on the map. Is Table 1 not giving the landuse information for the whole area shown in Fig.1. (km2 instead of m2)?” The location of SMEAR II is now indicated on the map with a white star. Table 1 gives the land use information from the whole area. There was a typo that is now corrected.

“P.10570, line 17: Please give information on the location of Juupajoki relative to SMEAR II.” Juupajoki meteorological station (61°50’N, 24°17’E, 153 m a.s.l.) is located about 500 m east from SMEAR II station. This is now indicated in the text, too.

“P.10571, line 10: Does this reference only describe the inlet system or the whole VOC analysis? It is also not clear whether the VOC sampling here is the same as the one described later for the sampling on the balloon. If not, a quick description of the VOC sampling on aircraft should be added.” This reference describes the sampling in the aircraft. Chemical analysis of samples is described in the manuscript and this is now indicated clearly.

“line 27f: Some evidence for a complete trapping with this setup should be presented, e.g. by including typical ratios of the concentrations in the second cartridge relative to those in the first cartridge.” Trapping ratios varied between samples and compounds, but about 90 percent of the measured total monoterpene concentration was trapped in the first cartridge. We believe this indicates fairly good trapping using this setup. This is now written in the manuscript.

“General comment to the description of the VOC analysis systems: A description of the accuracy and detection limits is required. Maybe adding this information in the form of a table would be helpful. As it stands now, it is hard to oversee the complexity of different sampling/analytical devices. The information presented later in table 2 is insufficient.” We added new Table 3 to summarize the different sampling procedures. Table 4 gives

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corresponding concentration detection limits and now also analytical uncertainties for different compounds.

“P. 10572, line 11 f: The assumptions should not only be mentioned but also be commented and discussed. For example, under what conditions is the assumption of balanced emissions and sinks reasonable? Is the 20negligence a general fact? It would be particularly important to include statements on what points are of particular interest when applying this method for conditions at this time of the year (implications of reduced mixing, possibly different lifetimes due to lower oxidant levels, etc.).” The principles of the mixed box method are well described in the literature cited and references therein. Flux underestimate due to entrainment negligence is discussed and analyzed in detail now. Differences in the lifetimes of the VOC compounds are included in the calculations of chemical sink.

“Lines 24f: A good estimate of the chemical losses is obviously the key for surface flux estimates with this method. Therefore, more details about the model used for calculating the OH concentrations must be included. Was the model driven by observations? Uncertainty estimates for the OH concentrations? Also, it is not clear from the description what O3 concentrations were used for the calculation of chemical losses, whether they were derived from measurements (what type, surface/airplane/balloon) or modelled.” It is true that correct values of O3 and OH concentrations are essential for flux estimates. However, some practical restrictions must be accepted for experimental works. Typical monthly averages of OH concentrations were adopted directly from Hakola et al. (2003). They used observational data from year 2000 to initialize the model. The spring of 2000 was quite typical for southern Finland, so we believe the [OH] data is usable for the present study. However, large uncertainties in the [OH] data must be assumed. One possible estimate is to compare values of consecutive months in the spring. This gives factor of about 3, which may be taken as the uncertainty estimate. Detailed description of the model runs can be found in the original paper (Hakola et al. 2003). OH concentrations are now discussed in greater detail in the manuscript.

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Ozone concentrations were measured at the top of the SMEAR II mast (page 10572, line 23). The accuracy of these measurements are good (order of 1 percent) but it must be noted that they actually represent only the lowest part of the boundary layer.

Results and discussion

"P. 10573, line 11: It is not clear what the averages represent. Please indicate whether they are means over several flights(indicate number!) or even flights on various days." This is now indicated in the text and table caption.

"lines 13f: Please clarify the reasoning for the very low isoprene concentrations. It would be interesting whether light/temperature conditions alone are sufficient to explain these low concentrations or if an additional seasonal variation of the emission factors is necessary." This discussion is now extended.

"line 27: When comparing to the data of Hakola et al., temperature conditions during 2001 should be mentioned." Average temperature was -5°C and this is now indicated in the text.

"P10573/4: I am missing a summarizing, concluding remark after this paragraph. The MT concentrations measured here during spring time were of similar magnitude and of the same distribution. Is this according to/contradicting to expectations (based on knowledge about seasonal variations of emissions)?" This paragraph is now partly re-written and hopefully better.

"Lines 9f: Here and in several other instances it is not evident whether the profiles originate from airplane or balloon measurements. For interpreting the shape of the profiles, it may be important to distinguish between the results of different platforms. Also, details about the flight patterns of the light aircraft need to be included somewhere." Aircraft routes are now described in the text. We have now also tried to make it clear what part of the data originates from aircraft and what part of the data from balloon flights.

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"Lines 15f: I agree that the uncertainty derived from a 2h sampling must be a lower bound estimate for the airborne measurements. Still, some more reasoning about the use of the uncertainty of a surface measurement for qualifying the airborne measurements should be added. This type of questions hopefully become obsolete if the description of the sampling/analytical systems in the M+M section is clarified and extended." Unfortunately, we don't have other methods to qualify the measurements and we believe that the uncertainties derived from ordinary 2h samples are close enough to be used with airborne measurements.

"P.10575. Flux estimates: It is not clear what kind of flux values are presented here. Is it the range of fluxes derived from individual profiles or from certain averages? An estimate of the uncertainties of the fluxes should be presented. The authors mention analytical uncertainties, but the boundary layer heights and the modelled OH concentrations in particular seem to be at least as important for the overall uncertainty of the estimates." The flux values presented in the text are averages over the whole campaigns. Uncertainty estimates are presented in the text and shown in the Figure 8 (Figure 9 in the improved manuscript). These estimates include uncertainties of boundary layer height, measured VOC concentrations, O3 and OH concentrations and reaction rate constants. These are now mentioned in the manuscript.

"More details on the modelled VOC emissions should be given. It is not clear whether a seasonal dependence of emission factors was accounted for. Please clarify the discussion about landscape vs ecosystem scale emissions. The flux estimates presented here obviously represent the landscape scale, and the emission model, too, no? If the discrepancy between modelled and estimated landscape fluxes holds even after a careful uncertainty estimate of the flux estimates, it needs to be discussed in more detail. Is there enough evidence to conclude that emission models for this area do not adequately describe the real emissions? Is it true for this season only?" Springtime emission factors were used when available. Emission model was originally developed using leaf scale emission data. However, the same algorithm is widely applied

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to ecosystem and even landscape scale. Some more discussion on the discrepancy is added.

Conclusions

"The conclusions should be significantly extended. It now reads like a mixture of summarizing results and single non-structured interpreting statements. Despite cold weather, boundary layer concentrations of monoterpenes were not lower than during summer - this calls for a conclusion. Do the authors want to make a point that even though emissions are lower in spring, the resulting concentrations of (condensable) vapours might be of the same magnitude as in summer due to the reduced mixing, enhanced lifetime of the compounds? Line 19f: It should be discussed earlier why gradient methods were not applicable in this case. It also should be discussed why the mixed box technique was still applicable - e.g. in the discussion of assumptions for this method in chapter 2. As the original point of this work is the performance of measurements in this particular season, an extended discussion (and conclusions) on whether and under what conditions these methods are still applicable, would be of high interest. The conclusion on the preference of aircraft vs. balloon platforms needs to be explained further, it is not evident from the results presented here. For example, one could argue that the more stationary balloon platform is advantageous because it has a constant footprint whereas the aircraft measurements imply a varying footprint. Again, a clear distinction of airplane and balloon results in the previous section and information on the flight pattern will help to follow this interpretation.Finally, after mentioning the significance of biogenic VOCs on particle formation in the introduction, a statement or comment on the implication of the results presented here on this topic would be valuable." Conclusions are now mostly re-written and we have tried to address the comments presented by the referees.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10567, 2006.