

Interactive comment on “Deployment of a ground-based CIMS apparatus for the detection of organic gases in the boreal forest during the QUEST campaign” by K. Sellegri et al.

K. Sellegri et al.

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We wish to thank the three referees of this paper and T. Karl for their work and valuable comments.

A clear concern has been shown from T. Karl and referees #1 and #2 about the validity of our isoprene measurements. Indeed, both the fact that isoprene mixing ratios are 2 to 10 times higher than previously measured on the same site by Hakola et al. (2000) and that they show high concentrations after sunset are indicative of a possible contamination from another compound.

We believe that the high mixing ratios observed for mass 69 amu + hydrates do not necessarily evict isoprene from the candidates to this mass. First, the use of the on-line CIMS method might be more efficient than the previous terpenes measurement

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methods (storing on cartridges). For example, acetone, which has been now extensively measured with the CIMS method, and approved, also shows mixing ratios from 3 to 10 times higher than previously measured on the same site during august 2001 (Boy et al., 2003). Also, PTR-MS measurements of isoprene have previously shown higher concentrations than canister+GC samplings for low concentrations (Warneke et al., 2001). Moreover, during the QUEST measurement campaign, terpenes oxidation products have been found during warmer days to be surprisingly high in the particulate phase compared to august 2001 (Laaksonen et al., 2004). The presence of unfrozen parts of the ground was noticed early during the measurement campaign, and might be responsible for high levels of soil-emitted isoprene. The MVK+MaCR mixing ratios are very much correlated to the isoprene mixing ratios (thus also maximum around 21:00, with a slight delay compared to isoprene), which is neither contradictory nor unexpected.

However, we do not have any explanation of the increase of what would be isoprene until 2 hours after sunset. The median H₂O mixing ration daily variation shows a maximum during the day and not during the night. Water clustering of methanol should be minimum when the water vapor content drops after 18:00 UTC, and thus should not contribute to the isoprene concentration increase at this time. However, methanol mixing ratios at night reach 400 ppt and interference from methanol-water clustering with isoprene can not be excluded when isoprene is not present.

Consequently, as suggested by reviewers #1 and #2, we decided to remove mass 68 amu being identified as isoprene. Instead, because we believe that masse 68 amu + hydrates are dominantly linked to the biogenic VOC source (they are highly correlated to other terpenes), we will name mass 68 amu “isoprene + compound X”. This compound still needs to be identified, reporting its presence can help future investigations using CIMS or PTR-MS for the choice of on-line standards. It is difficult to investigate a posteriori what the interference with isoprene could have been. In-situ calibration tests have been done for isoprene but they do not insure that no interference took place.

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We believe that it is important that, if there is a biogenic compound interfering with isoprene measurements, it should be mentioned. Concerning the interference from MBO, it is true that during LBA-CLAIRE, the authors first suggested that the discrepancy between the PTR-MS and canister+GC measurements was due to MBO, but then concluded that this would be very unlikely. We also conclude that MBO is very unlikely contributing to isoprene concentrations.

As a whole, the measurements presented in this work show daily variations of biogenic compounds concentrations which are co-varying with independent measurements such as the aerosol surface, or CO concentrations. This is a good indication that the technique is analyzing VOCs with consistency. Identification of the compounds measured with the ground-based CIMS technique is the subject of this paper, in which, some candidates are proposed. We do not claim to have succeeded in identifying all compounds with certainty, but this work can help future analysis of this kind. Clearly, more in situ measurements are needed with an instrument such as a PTRMS or PITMAS to validate these results with fragmentation studies.

References Boy et al., ACPD, Vol 3, 3769-3831, 2003 Hakola et al., Atmos. Env. 34, 4971-4982, 2000. Laaksonen et al., proceedings of the 16th Conference on Nucleation and Atmospheric Aerosols, Kyoto, 190-193, 2004. Warneke et al, JAC, 38, 167-185, 2001.

Specific answers:

To Referee #1

Because of interferences with MVK+MaCR cis-3-hexenyl acetate analysis and resulting mixing ratios have been removed as well.

To Referee #2

Rigorous calibrations to determine humidity-dependent calibration factors have been performed for some of the species. However, calibrations do not prevent interferences

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from other unknown compounds during atmospheric sampling (isoprene is a good example to illustrate this). This is true for any analytical methods and especially for any mass spectrometric method. Even if you have calibrated mass X with the compound you think is standing for mass X, how do you know that in the field another compound with the same mass is not interfering? What should be done is a fragmentation study on site, more calibrations would not help. Specificity is more a problem, in this regard, we have been very clear. Interferences of methanol with isoprene has already been addressed. DMA concentrations are under detection limits, hence the eventual interference from NO_2^+ do not seem to be significant. $m/z=83$ amu can not be hexenol, hydration is too important in our system. Its contribution to masses 101 and 119 amu is small, from the high hydration observed for alcohols (see methanol).

As already mentioned, reporting the presence of these masses and attempting identification can help future investigations using CIMS or PTR-MS. Moreover, the overall daily variation of the organic compounds measured during this campaign give good indications of their implication in the growth of nucleated particles. They can also help in the comprehension of the nucleation and growth of newly formed particles.

To Referee #3

[1] Collision rate $2.3 \cdot 10^{-9}$ is used for all gases. This is better specified in the text.

[2] Reactions (1) and (2) as first approximation has been more explicitly stressed.

[3] Diffusion is indeed enhanced by 30 % for small ions compared to ions twice as large. It means that the underestimation of concentrations are higher for compounds of small masses.

[4] The reason for the water clustering of trace ions to be lower than 3 is that hydronium ions have hydration enthalpies larger than any other ion species (Keese et al., 1986), and H_2O exchange reactions are fast compared to the ion-molecule reactions with trace gases of interest. This is now properly explained in the text.

[5] Calibrations of acetonitrile, acetaldehyde, methanol, isoprene were performed from the same gas bottle standard mixture. Hence, the red calibration curve for the peak family 33 amu is standing for methanol and isoprene at the same time (with a ratio of 1:1). This is now clarified in the text. However, because methanol is highly hydrated, it is indeed possible that mass 105 amu is more representative of the tail of the methanol distribution ((H+methanol(H₂O)₄) than the isoprene contribution. This is now added to the text, and mass 87+hydrate now stands for isoprene+compound X.

[6] see answer to remark [4]

[7] Ref has been added

[8] Cis-3-hexenyl Acetate has been removed from the paper, and half of mass 143 amu has been taken into account in MVK/MaCR concentrations.

All technical corrections have been made. The legend on Figure 4 is 78/96 and 114/96.

References Keesee, R. and A. Castleman, "Thermodynamic data on gas-phase ion-molecule association and clustering reactions", J. Phys. Chem. Ref. Data, 15, 1011-1071, 1986.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 3835, 2004.

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