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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #3

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General Comment:

This article describes the measurement of a series of volatile organic compounds by means of the CIMS technique in a boreal coniferous forest. In general the article is well structured, considerable effort has been made to assign the product ions observed and the results are compared with available literature data.

It is clear that the analysis of the measurements is hampered by extensive hydration and that some product ion assignments are speculative, indicating that calibration standards should be used whenever possible and that more laboratory measurements are needed to describe the complex chemistry involved. Some results are contradicted by literature data.

However, the authors sufficiently stress in their manuscript the uncertainties and the "weak points" of their measurements and analysis. As a first attempt to interpret the spectra obtained with their CIMS technique, I recommend publication in ACP, with the following revisions:

Specific comments:

[1] equation (3) page 3840: It is not clear from the text which values for the rate constants k in equation (3) are used? The same value for all trace gases, 2.3 10-9 cm3 s-1 (line 23 page 3839), or different values for each trace gas? Are laboratory measurements of these rate constants available? If so, in what range do they vary? References?

[2] Reactions (1), (2) page 3839 , equation (3) page 3840: It should be stressed more explicitly that this is a first approximation of the complex chemistry involved (see for example your remark on page 3843 line 29, P. Spanel and D. Smith, J. Phys. Chem. 99 (1995) 15551,...)

[3] page 3840 line 8: You mention that reverse reactions, mass discrimination, sticking of the gases are not taken into account in equation (3). Perhaps diffusion enhancement should be added to above mentioned list (less diffusion for heavy ions (for example ions resulting from the monoterpenes (m/z=137,155,173), ions resulting from pinonaldehyde (m/z= 169,187),...) with respect to the smaller ions. Or is diffusion enhancement negligible at 12mbar?

[4] Page 3841, line 14: You note: "Since hydration of compounds is dependent on their proton affinity, other atmospheric species, with lower proton affinity than H2O, should have a maximum count rate for clusters with n lower than 3". It is not clear what is meant here. According to Table 2, all trace gases studied have proton affinities larger than the one of H2O. You also note page 3839 line 10: "Then atmospheric gases X with proton affinities larger than that of H2O react in the flow tube reactor with reactant ions H3O+(H2O)n" This is contradictory.

[5] End of page 3841, beginning of page 3842, night time maximum isoprene: Calculations of methanol are based on masses 51, 69, 87 and the calculations for candidate isoprene on masses 105,123 and 141. However I suppose that the red calibration curve in the plot "33 amu" in Fig 3, is the calibration curve of methanol, since its lowest datapoint is at m/z=33. If so, the count rate at m/z=105 nearly equals the one at m/z=87. So, I do not understand why datapoints at m/z=105 are used for the calculation of isoprene instead of methanol. Could this explain the unexpected night time maximum of isoprene? Methanol clearly shows a night time maximum. Is it possible that the use of datapoint at m/z=105 for isoprene instead of methanol results in the unexpected night time maximum of isoprene? Perhaps it would be useful to also plot the calibration curve of isoprene. I think this paragraph needs some clarification.

[6] Page 3842, line 5: "In fact, mass 141 ...". It is not clear what is meant here. Why must cluster n=4 be smaller than cluster n=3? Does that relate to my previous remark [4], page 3841 line 14?

[7] Page 3845, line 14: Reference "P. Spanel, J.M. Van Doren, D. Smith, Int. J. Mass Spectrom. 213 (2002) 163" can be included. These authors also observe in their SIFT study poor hydration of saturated aldehydes (mainly monohydrates, see page 171 of this article).

[8] Table 3: ions at m/z=143 have been used for the calculation of MVK/MaCR and also for Cis-3-hexenyl Acetate. What are the implications on the resulting mixing ratios?

Technical corrections:

- Abstract, line 10: 32 instead of 33

- Page 3837, line 6: ... by the dynamics of the boundary layer

- Page 3837, line 11: ... at the site by means of adsorbent

- Page 3842, line 16: ... show a maximum count rate at 114 amu

- Page 3843, line 7: ... to mass 96 is subtracted from the measured count rate of mass 96 in order to obtain the contribution of TMA to this mass
- Page 3843, line 16: ... after mass 81 amu (Fig 3), indicating that a compound
- Page 3843, line 28: candidates
- Page 3845, line 27: At last
- Page 3847, line 3: ... measured for calibrated compounds
- Page 3851, line 11: Figure 6a shows that
- Page 3851, line 22: ... the following yield (?), bad structured sentence
- Page 3852, line 29: times
- Page 3854, line 14: include monoterpenes after MVK/MaCR
- Page 3854, line 15-16: "68 and 86" for isoprene; "and 86" is somewhat confusing.
- Page 3857, line 17: ... of its contribution
- Table 2: structural formula for formic and acetic acid is wrong
- Fig 4: legend in plot of this figure should be 96/78 and 96/114 instead of 78/96 and 114/96
- Fig 6.a and 6.b: Y-axis label of two last plots in Fig 6.a and 6.b should be ratio instead of mixing ratio

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