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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Oxygenated compounds in aged biomass burning plumes over the Eastern Mediterranean: evidence for strong secondary production of methanol and acetone" *by* R. Holzinger et al.

Anonymous Referee #1

Received and published: 9 November 2004

The manuscript by Holzinger et al presents airborne PTR-MS measurements conducted within the MINOS field project in the Mediterranean in August 2001. It focuses on measurements conducted in 10 biomass-burning plumes intercepted on 5 days between 14 and 24 August 2001. Based on normalized excess mixing ratios (NEMR) it is concluded that methanol and acetone are photochemically produced in aged (2-3 days) biomass-burning plumes, while CO is depleted. In addition, an analysis of the acetonitrile measurements performed during the campaign is presented. The authors present median mixing ratios and conclude that dry deposition over the land and/or the sea is the dominant atmospheric sink for acetonitrile.

The presented measurements contribute to the limited database on oxygenated carbonaceous compounds in biomass-burning plumes and the atmospheric burden of acetonitrile, and I recommend publication of these measurements. I do, however, have some comments on the data analysis and some of the conclusions drawn in the manuscript. In the following, I recommend some changes to the original manuscript that should be considered before final publication.

General remarks:

My main concerns are related to the following two points.

1) The method by which the NEMRs were calculated is not well described. I suggest correlating the measurements of the different compounds and reporting the slope of the correlation line (representing the NEMR) together with r^2 as a measure for the quality of the correlation. As shown in Figure 2 of the manuscript, the measurements are suited for this kind of analysis.

2) A more comprehensive evaluation and comparison of the NEMR determined here with available data from the literature should be conducted.

Specific remarks:

- page 6324, line 10: in a recent laboratory experiment [Christian et al., JGR, 2003], the acetone emission ratios were determined by substracting MVE emissions determined by FTIR from the emissions at mass 59 as measured by the PTR-MS due to possible interferences. Please comment why this interference can be excluded here.

- Page 6325, second paragraph: please include the integration time and the resulting time resolution of the measurements.

- Section 3.1, first paragraph: move the definition used to identify the biomass burning plumes from the end of the paragraph to the beginning.

- It is not well explained how the normalized excess mixing ratios (NEMR) were de-

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termined. Are the background values substracted from each in-plume value, and the resulting values than averaged to derive one value for the average excess mixing ratio for each plume? I suggest that the authors consider determining the NEMR's by correlating the measurements of methanol, acetone, PAN, and CO with acetonitrile and reporting the slope (representing the NEMR) together with r^2 (as a quality measure for the correlation). Also, the authors might consider using the more common term 'enhancement ratio' for the NEMR throughout the manuscript.

- Table 1: it would be interesting to add the enhancement ratios (as determined by the slope of the correlation lines) for methanol, acetone, and PAN with respect to CO in Table 1.

- Table 2: The manuscript would benefit from extending Table 2 by including more available data from the literature. In particular, since it is concluded that their high enhancement ratios for acetone and methanol are due to secondary production, the values should be put in perspective to other available data. For acetonitrile and acetone, corresponding tables have been presented in Jost et al., JGR, 2003, (Tables 3 and 4).

It appears that the value derived for the enhancement ratio of acetonitrile with respect to CO (2.0 mmol/mol) might also be interpreted as the emission ratio from high N-containing biomass fuel (as mentioned in the manscript), since comparable values have been found in fire emissions (e.g., Lobert et al., 1990, Jost et al., 2003). The interpretation of this high value as being caused by the OH oxidation of CO also seems 'plausible', especially considering the high OH concentration reported based on ground-based measurements. However, it is not the only possible explanation. While this is pointed out in Section 3.1, the abstract and the conclusion suggest that photochemical decay of CO was observed in the biomass-burning plumes. Based only on the PTR-MS measurements (without assuming the ground-based OH measurements being representative for the whole region) I believe this statement is too strong. However, certainly CO is oxidized over the course of some days and this should be taken

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into account in the analysis of measurements in aged biomass-burning plumes (as mentioned also by Mauzerall at al., 1998).

For acetone, available observations support the finding that aged plumes exhibit higher enhancement ratios of acetone with respect to CO than young plumes. Values on the order of the one reported here (18 mmol/mol) have been reported elsewhere as well (see Table 4 of Jost et al., 2003), and some more recent data could be added to Table 2 (e.g., 7.5 nmol/mol from Singh et al., 2004).

There are only few published measurements of the methanol enhancement ratio in biomass-burning plumes, and Table 2 should be extended by including the data available (e.g., 16.3 mmol/mol from Singh et al., 2004, 12.1 mmol/mol from Wisthaler et al., 2002). The observations of the methanol-acetonitrile-ratio mentioned in the comment from Thomas Karl should be mentioned as well. If the methanol-acetonitrile-ratio determined during MINOS compares well with emission ratios from biomass burning sources (even though it is not clear if Thomas Karl is referring to young or aged smoke plumes), it might imply that no significant photochemical production of methanol can be inferred from the present observations.

There are some measurements available in the literature for enhancement ratios between PAN and CO (e.g., Mauzerall et al., 1998, Singh et al., 2000, Singh et al., 2004), which should be added to Table 2 and referred to in the text.

Overall, the results presented in Table 2 represent the main result of the present manuscript related to biomass burning, and they should be discussed more thoroughly and set in context with values from the literature in the revised version of the manuscript.

- Please add the fact that a lower average than median mixing ratio indicates high variability at the beginning of section 3.2, maybe directly after the second sentence.

Technical comments: - page 6328, line 22: change ‘(Warnecke and de Gouw, 2001)’

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to ‘Warnecke and de Gouw (2001)’.

- Throughout the list of references: use ‘J. Geophys. Res.’ (instead of J. Geo. Res.)

- Please check the correct referencing for the following papers (sometimes the doi is not given in the list of reference, sometimes the issue is missing, the correct way to refer to the papers is usually given in the original paper): Christian et al., 2003, Heikes et al., 2002, Jacob et al., 2002, Jost et al., 2003, Singh et al., 2003, Singh et al., 2004.

- Page 6333, line 22: update the reference for Williams et al., 2004, which has been published in the meantime.

- Figure 1: add units to the axis of the figure.

- Figure 1, color scale, Figure 2, left plot, Figure 3: use km as the unit for altitude.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6321, 2004.