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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 #2

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Review of Holzinger et al.: "Oxygenated compounds in aged biomass burning plumes over the Eastern Mediterranean: evidence for strong secondary production of methanol and acetone" ACPD 4-6321

General Comments: The authors explore a subset of data of VOC and CO measurements from airborne measurements over the Mediterranean during the MINOS campaign to extrapolate secondary production of oxygenated VOCs in biomass burning plumes. They also analyze their acetonitrile data more closely, which, however, is not reflected in the title of the manuscript. The paper is otherwise well presented and worth publishing both with regards to the data the title focuses on, and the acetonitrile anal-

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ysis. I encourage the authors to expand on the manuscript. I suggest publication after some minor revisions, especially with regards to some of the conclusions.

Specific comments:

Experimental

the authors should state the parent ion signal counts used during flights

a comparison with a gravimetrically prepared standard from Dan Riemer and Eric Apel is mentioned, but not the results of the comparison

it is stated that the detection limit of methanol was 0.5 ppb. However, Figure 2 contains methanol data below that level, unless the plotted values are “excess” mixing ratios, which they do not seem to be

Biomass Burning plumes:

the NEMR calculations are somewhat unclear: is the NEMR calculated from the slope of background corrected VOC/acetonitrile ? how about the confusing Table 2 footnote numbers?

Page 6326, lines 22ff.: There is quite a bit speculation in this paragraph. First, the assumption that OH abundances are as high as 4.5E06 throughout the Mediterranean region (at all altitudes ?!) is correct seems unlikely. The authors themselves suggest that an alternative explanation for the high NEMR of acetonitrile compared to CO is a higher nitrogen content of the biomass burning fuel, based on results presented by Christian et al. (2003). If the assumption that agricultural waste burning contributed a lot to the observed plumes is correct, that may as well have provided such a fuel. So this explanation appears more likely.

The authors make no attempt to explain why they observed elevated methanol and acetone abundances when compared to emission ratios from biomass burning other than saying that secondary production must have occurred. Assuming that this is cor-

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rect (note that there is no direct evidence even for this assumption), they move on to state that this must mean that biomass burning in general must result in higher total acetone and methanol emissions to the atmosphere then previously measured, and extrapolate new values from their data. Wow! Hold on: Singh et al. (2004) also measured excess acetone and methanol in numerous aged Asian biomass burning plumes and did not find such high values (the authors refer to these data). A possible explanation for this large discrepancy may lie in the authors' PAN data: There appears to be a much higher PAN abundance in the Mediterranean than over the Pacific (Singh et al., 2004), pointing to a higher NOx abundance (and more intense chemistry) closer to the place off biomass burning. It is conceivable that higher NOx (and probably also ozone and OH) levels in the Mediterranean have led to increased secondary production. I encourage the authors to explore this hypothesis by analyzing the richer MINOS data set. The current conclusions are a bit too bold, meaning the authors' results should be generalized in the way done.

the comparison to the Salisbury paper may be revised based on the above critique. It does not seem that the MATCH-MPIC model could be made to match the Finokalia data by inputting higher BB emissions. Its background was much too low, more likely resulting from a too low green plant emissions input.

Acetonitrile VMRs:

this compilation of the MINOS measurements is not part of the title, but the data seems rich and interesting. Possibly the authors could compare to more previous data sets to strengthen their arguments. As the Williams et al. (2004) data have not yet appeared in the literature, maybe the authors would want to include some of them here?

I suggest to give the manuscript a new title to reflect this interesting analysis

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