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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Ground-based PTR-MS measurements of reactive organic compounds during the MINOS campaign in Crete, July-August 2001" *by* G. Salisbury et al.

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This manuscript presents a very interesting, robust dataset on oxygenated VOCs and their abundancy during the MINOS campaign. Reading through the paper and reviewer's response, I wanted to add some comments on methanol and acetone:

The authors base their arguments about potential methanol sources primarily on a recently published paper by Galbally and Kirstine (2002) and seem to ignore the fact that Heikes et al. (JGR, 2002) give a more conservative assessment of our current knowledge of the methanol budget. The review by Heikes et al. includes an updated summary of methanol measurements performed over the past years. Even though there is evidence that biogenic sources comprise a major part of the methanol budget,



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Heikes et al. point out that the best estimate of the global source strength of methanol is still poorly constrained and can range between 50 and >280+ Tg/y. This uncertainty mainly reflects the fact that only very limited sets of methanol data (especially in the tropics, but also in temperate ecosystems) are currently available. Taking the current uncertainty of the biogenic source of methanol, it appears that the anthropogenic portion could be anything between less than 1% and up to 20% (which for the latter case would not be neglectible anymore).

Page 928: 'The only other known route to photochemical production of methanol in the atmosphere is the photolysis of glycolaldehyde, derived from isoprene oxidation, with an estimated yield based on isoprene of ca. 2 to 3% (G. Moortgat, personal communication, 2002).' What about methane oxidation, which was estimated to account for as much as 30 Tg/y methanol (Bey et al., 2001)? Taking methane oxidation into account, how would this change the regression presented on page 929 ff using the linear model?

The multiple regression analysis seems to be interesting, however I agree with the reviewer's comment that it deserves more explanation/evaluation. Table 2 summarizes the calculated tracer ratios for various VOCs. It is argued that for period 1 methanol and acetone are of biogenic origin with a slope of 0.88. On the other hand the multiple regression suggests that in total 35% of acetone is due to biogenic influence. Does this mean that the 'effective' tracer ratio of the biogenic signature between acetone/methanol would be 0.88 x 0.35 = 0.30? Our data from a seasonal flux study at the Prophet site (deciduous forest, MI, USA) in the past year suggests a rather constant average acetone/methanol mixing ratio over the seasons ranging from 0.25 (spring/summer) to 0.31 (fall)). The ratio between fluxes varies much stronger with 1.14 in fall and 0.33 in spring/summer. The lower values in spring are due to rapid leaf expansion and pectin demethylation as cell walls grow; the higher ratios in fall argue for a substantial source of acetone due to senescing vegetation. In addition, given the fact that individual species in the tropics have different senescence patterns, the recent



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inverse modeling study by Jacob et al., reporting that leaf decomposition/senescence plays a relatively smaller role than suggested by Warneke et al (1999), might not be representative for many terrestrial ecosystems. Overall the flux data from the deciduous forest in MI strongly support the conclusion drawn on pages 930/932, arguing that the biogenic portion of the acetone budget seems to be underestimated by recent studies (Singh et al. 2000 and Jacob et al. 2002).

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Interactive comment on Atmos. Chem. Phys. Discuss., 3, 911, 2003.