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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.

Anonymous Referee #2

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

General Comments: This contribution shows some more, urgently needed measurements of oxygenated VOCs at a non-urban, coastal location and compares them to a model of atmospheric transport and chemistry. While the paper contains interesting and important data, and is written concisely, it appears to under-interpret some of its findings while over-interpreting others. A good example for the latter is the detailed comparison to the MATCH-MPIC model, while, in its coarse resolution, it does not appear to be suitable for the described measurement situation. I believe the paper can be much improved by some minor modifications, a closer look at the actual data, and an

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Interactive Discussion
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even more careful interpretation of the model data as currently seen in the manuscript.

Specific comments: 1. It is surprising to me that the authors do not comment more on the obvious, large short-term cycling of methanol and acetone, and CO, seen in Figure 2 and later Figures. The variation is diurnal, can be seen throughout almost the complete data set, and is stronger for methanol than for acetone (Note: I assume that this is NOT an effect of instrument temperature for either VOCs or CO). An association with CO could indicate a local or regional pollution source (note that acetonitrile seems to show this variation as well). The brief "explanation" on pages 922/923 using the model results is clearly insufficient. The model results are hardly able to explain this finding even if the model were of sufficient resolution. I suggest to look into a correlation with daylight/temperature and a local land-sea breeze (page 913) phenomenon to support the argument of photochemistry, likely in conjunction with an ocean reservoir system and/or a low nighttime boundary layer. As the authors have not labeled what are the day- and nighttimes, further judgments cannot be made.

2. A look at the map in Figure 1 confirms that Crete is within one grid cell (2.5°, latitude/longitude should be labeled nonetheless ...) of Turkey, the assumed last major input of the investigated trace gases. Hence, it comes to no surprise that a model with a resolution of 2.8° (page 921) cannot capture the variability observed at Finokalia. The authors state at length the shortcomings of the model regarding absolute values and its adequacy regarding relative values. However, more important would be whether the coarse resolution model would be able to catch the measured variations at all even if the input data (emissions inventory) were correct ...

3. The authors should explain whether the OH number densities given in section 4.1 are day/night averages or measured daytime only data that were adjusted for the calculation, as these numbers appear high.

4. I have trouble following the argumentation in section 4.2. Previous measurements in the boundary layer over land have always shown good acetone-methanol correlations,

ACPD

3, S207–S209, 2003

Interactive Comment

mostly with higher methanol (>3:1). A coastal site showing less well-correlated values and less methanol is therefore of special interest regarding the role of the ocean, because, based on the short transport time from the continent, an initially high correlation appears unlikely to degrade that much if the ocean were a completely passive medium. A similar argument holds for correlations with CO. I cannot follow the argument that methanol has no significant anthropogenic sources. Such a statement can also not be found in the referred to paper by Galbally and Kirstine (2002). On the contrary, they do list several sources. Additionally, Schade and Goldstein (2001) found a significant correlation between an anthropogenic tracer and methanol, estimating that on average 20% of the measured mixing ratio was from anthropogenic sources (the authors do not cite that work). Thus, the author's notion that anthropogenic sources are insignificant at Finokalia does not hold in my eyes. Also, the production of methanol from methane oxidation could be evaluated further based on the onsite NOx measurements. It appears that a large fraction of the "missing" methanol in the model could be from methane oxidation (i.e. background), while any additional production since passing over land is likely lower.

5. As the judgment of methanol being the biogenic tracer is doubtful, the multiple regression analysis outcome that suggests very low anthropogenic contribution gets doubtful as well. Furthermore, the high contribution of the constant term not only signifies a more remote station, but, together with the actual acetone background value (an unusually high 1.7 ppbv), that a significant part of the tracer signals were lost before reaching Finokalia.

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