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Atmospheric
Chemistry
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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 #1

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The manuscript by Salisbury and co-workers provides significant new information about the atmospheric chemistry of acetonitrile, acetone and methanol in a relatively unexplored region of the atmosphere, and as such deserves to be published. The analysis of the results is very detailed, but can be improved in a few places. The paper should be published after the authors take into consideration the following questions and comments:

1. The authors observe a significant enhancement of CO, acetonitrile and other species in period 3 and attribute these findings to biomass burning. The MATCH-MPIC model reproduces the enhancement; however, this part of the analysis can be improved and should allow the conclusions to be drawn with more confidence. First, does the model

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indeed attribute the enhancements to biomass burning? Figure 6 would be more convincing if it were shown that the enhancement in CO is indeed related to biomass burning CO. Also, the model can be used to pinpoint the location of the forest fires. Was the region responsible for the enhancement indeed near the Sea of Azov as suggested by the back-trajectories and the satellite images? The evidence from satellite data, cited in the abstract, is hardly described in the text. The model probably uses a fire climatology and the question whether or not the predicted fires were active should be addressed.

2. The authors suggest that at least part of the methanol and acetone observed during period 3 was released from biomass burning. Further down in Table 4 it is suggested that only 3.5% of the acetone was released from biomass burning which seems inconsistent. In any case, the question should be addressed if the observed enhancements of methanol and acetone versus CO were consistent with emission ratios from the literature. If yes, how was biomass burning methanol parameterized in the model and why does it not agree with the observations if the proper emission ratios were used? The modeled enhancements of acetone (0.5 ppbv) and methanol (0.9 ppbv) during period 3 seem small as compared with the observed enhancement of acetonitrile (0.3 ppbv), i.e. from the emission ratios one would expect more enhancement of acetone and methanol.

3. With regard to the MATCH-MPIC model: it would be good to indicate if secondary formation of acetone is included in the chemistry scheme and, if yes, from which precursors. Formation of acetone from monoterpenes could be significant in the Mediterranean region and may not be included in the model.

4. Parallel work has shown that the MATCH-MPIC model underestimates propane by a factor of three. The authors should explore the question whether or not this explains a significant part of the discrepancy between measured and modeled acetone.

5. In the multiple regression analysis discussed on pages 22 and 23: one wonders how

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background concentrations should be taken into account. For the long-lived species in Equation (5), one has to subtract the background mixing ratio from the different parameters prior to the fitting. Due to the absence of a figure it is very difficult to judge the usefulness of the multiple regression analysis. I recommend adding a figure that shows the agreement between the measured and fitted acetone. The authors only mention that the slope of such a figure is 1.0 and the offset is 0.0, which is no surprise, since it is imposed by the fitting procedure. Furthermore, the fitting coefficients in Table 4 should be discussed in more detail. In principle one would expect the fitting coefficients to be similar to the emission ratios, but this seems not to be the case. The biomass burning contribution of acetone, for example, was found to be smaller than that of acetonitrile, whereas the emission ratio is much higher.

6. The section ŞSummary and conclusionsŤ is unnecessarily long and just repeats most of the paper in detail.

Minor comments:

1. Page 6: rate coefficients are used to calculate the response of the PTR-MS, and the authors mention that the rate coefficients are derived using standard mixtures. The PTR-MS is not a good instrument to measure rate coefficients for ion-molecule reactions accurately. If indeed standard mixtures were used, there is no reason to derive rate coefficients first and subsequently the calibration factors. It is recommended to just derive empirical calibration factors from the standard mixtures and to use these factors to calibrate the data.

2. Page 11, section 3.2.2: can other sources be consistent with the observation that the methanol to acetone ratio is higher in the period with enhanced acetonitrile? For acetone it is shown further down in Table 4 that biomass burning was only a minor source.

3. Page 13, section 3.3.2: maybe it is good to indicate, for example in Figure 4, which areas are regarded as western and eastern Europe.

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4. Page 14: the discussion of diurnal variations in the model and measurements is not very convincing. The claim Şthat the model captured well the dynamic and chemical behavior of both speciesŤ is hard to maintain given the dissimilarities between the modeled and measured timelines in Figure 6.

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