Atmos. Chem. Phys. Discuss., 3, S897–S907, 2003
www.atmos-chem-phys.org/acpd/3/S897/

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.

G. Salisbury et al.

Received and published: 27 June 2003

We would like to thank the anonymous referees and Thomas Karl for their thoughtful readings of our paper, and their useful and constructive comments and criticisms.

Referee #1

Major points

1. With regard to pinpointing the location of the fires, we would argue that the global MATCH model is not the best tool for the job. We are not using the model to argue the case for high biomass-burning influence in Period 3. As shown in Fig. 4c, the back trajectories were very consistent for this period. There was a great deal of agricultural burning occurring in Eastern Europe at the time of the MINOS campaign, and we have

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

now included a link to a satellite picture of fires on the 10th August 2001 in the Sea of Azov area to back up this point (Section 3.1.3). The elevated acetonitrile levels in this Period represent unambiguous evidence of biomass-burning activity (see Section 3.1.1 and references therein).

The referee is correct to suggest that the MATCH model uses a fire climatology. So although the modelled CO peak in Period 3 is likely due to climatological fires, the correspondence with measurements should not be over-interpreted. The text has been amended in Section 3.3.2 to read "The general levels of the measurements, the relatively high levels in Period˜1, and the relatively low levels in Period˜2 are all captured well by the MATCH-MPIC model. These features represent good evidence that the meteorology in the model was functioning well, and provides a solid basis for comparison of the MATCH acetone and methanol data with the measurements. The model CO also shows a pronounced peak in Period 3. However, the MATCH model uses a climatological fire scheme, so that this peak (much shorter and sharper than that seen in the measurements) will not represent the actual fires burning at that time." It follows, therefore, that no attempt is made to locate fires using the model.

The last paragraph of Section 3.2.2 and Table 3 have been omitted in the revised draft, in order to play down the importance of the acetone and methanol model-measurement comparison for Period 3.

2. The point the referee makes about Table 4 is based on a misreading of the paper, as Table 4 refers only to Period 1 of the campaign, where biomass-burning influence was at a minimum. The legend to this table has been revised to reiterate this point: "Fitting coefficients obtained in the multiple regression analysis performed on the acetone data in Period 1 of MINOS (29 July-2 August 2001), where biomass-burning influence was at its minumum." Note that this Table becomes Table 3 in the revised paper.

The extent to which the model captures the biomass-burning plume has been dealt with in point 1 above. To reiterate, we do not wish to over-interpret the model results

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

for Period 3. However, the measured acetone and methanol enhancements relative to CO are certainly of interest, as the referee suggests. This is now considered in more detail in Section 3.2.2, as follows: "Looking at the data in a different way, we note that the enhancements in the mixing ratios for CO, acetone and methanol from Period 1 to Period 3 were 42.4, 1.66, and 2.79 ppbv, respectively, based on the averages given in Table 1. If we assume that these enhancements were entirely due to biomass burning, we obtain the 'biomass-burning' methanol:CO and acetone:CO ratios 6.5 and 3.9%, respectively. Clearly these ratios are much higher than the PTR-MS lab measurements and literature values of the emission ratios, and may indicate secondary production of both species in the biomass-burning plume (see for example Reiner et al., 2001; Jacob et al., 2002), and/or that the observed enhancements were not simply due to biomass burning (see Section 4.1)." The model enhancements in acetone and methanol are not considered, for the reason given previously.

3. Further details of the secondary sources of acetone included in the MATCH model are now given in Section 3.3.1, Introduction to the model: "Photochemical production of acetone in the model occurs explicitly solely from propane; higher iso-alkanes do not represent a source of acetone, since n-butane chemistry, which is used as a pool for higher alkanes, does not produce acetone. Acetone from oxidation of terpenes is not explicitly included, but is parameterized from the biogenic emissions, assuming a 50% yield of acetone from 60 Tg yr-1 of monoterpene emissions using the GEIA distribution. This figure is likely too low in the light of the review by Jacob et al. (2002), but is nevertheless higher than in earlier modelling studies."

4. We have added an exploration of this suggestion in Section 3.3.2: "This conclusion is supported by the comparison of MINOS propane measurements with MATCH output propane data presented by Gros et al. (2003); MATCH was found to underestimate propane (a significant precursor of acetone) by a factor of 1.5-3. This deficiency in propane is, however, not sufficient to explain the shortfall in acetone. Even assuming 100% yield of acetone from OH-oxidation of propane, the MINOS campaign mean

propane mixing ratio of 235 pmol/mol implies an upper limit to the "missing" acetone of ca. 0.8 nmol/mol, taking into account the different lifetimes of the two species. Since the actual mean acetone deficit over the whole MINOS campaign (excluding the short biomass-burning peaks in Period 4) was 2.9 nmol/mol, we can conclude that a maximum of ca. 30% of the shortfall in acetone mixing ratios in the MATCH results can be accounted for by deficiencies in propane emissions in the model."

5.We agree with the referee that it is difficult to know how best to take background mixing ratios into account in the multivariate analysis, as they are not so easily quantified. We have added the following comment in the text: ŞIn this analysis, no attempt was made to define and substract background mixing ratios for the longer-lived tracers prior to the fitting procedure, because of the paucity of atmospheric measurements available in this region. Tests showed that subtraction of constant values from individual tracers made no difference to the fit achieved, but merely served to raise the value of the constant, background term in the resulting analysis."

We have added a Figure (Figure 9) showing the agreement between measured and fitted acetone.

The referee's last point in this paragraph is again based on the misunderstanding that Table 4 (now Table 3) has something to do with biomass burning (Period 3), which is, as discussed previously, not the case.

6. This section has been reduced by around 40% in the revised ms, and now concentrates on the sources of methanol and acetone, which is the main thrust of the paper.

Minor comments

1. The referee details here very closely the actual procedure we used! This section has been reworded to describe more accurately our calibration procedure.

2. As noted in major point #2 above, biomass-burning methanol emission appears to be consistently greater than acetone emission; a higher methanol/acetone ratio (given the

other way round in Table 2) is therefore to be expected in Period 3, where acetonitrile is elevated. Also as noted previously, Table 4 of the original ACPD manuscript (now Table 3) refers only to Period 1 of the campaign, where biomass-burning influence was at its minimum.

3. The W and E European source regions used in the model are defined in Fig. 4 of the revised ms.

4. A new section and figure are added in the revised ACPD manuscript to discuss the diel cycles of various species in more detail (Section 3.2.3; new Fig. 6). Much less emphasis is now placed on the model comparison, and Fig.7 of the original paper has been dropped. This point is answered more fully in the reply to Referee 2, below.

Referee #2

General comment

We assume that the referee's comment on under-interpretation refers in large part to the diel cycling (specific point 1). This is dealt with below. With regard to the MATCH model, we brought in this model comparison to see if the emissions currently used for Eastern Europe are realistic. This is now more clearly explained in the Introduction: "In this paper, the sources of acetone and methanol are examined in the light of results from the 3D global chemistry-meteorology model MATCH-MPIC (Model of Atmospheric Transport and Chemistry - Max Planck Institute for Chemistry version). Although the resolution of this model is necessarily coarse, the general lack of measurements of reactive organic species in the Eastern Mediterranean means that the MINOS campaign represented a unique opportunity to test the performance of a global atmospheric chemistry model in a relatively unexplored region, in atmospheric chemistry terms. Of particular interest is whether the GEIA organic emissions scheme used in the MATCH-MPIC model is realistic (see also Gros et al., 2003)." Indeed our results, as well as those of Gros et al. (see paper refs) show that there is still work to be done in this area. We concur that the model-measurement comparison may be over-interpreted in the original submitted paper, and as a consequence of the refereeŠs report the model results are interpreted more circumspectly, particularly regarding the diel cycling, in the revised manuscript.

Specific points

1. The diel cycles to which the referee refers are now discussed in a new section and figure, where we have made every effort to incorporate the referee's ideas and suggestions. The new text is reproduced in full here:

"Figs 2 and 3 show that pronounced diel cycles were observed both in the PTR-MS measurements and in the CO measurements during MINOS. The mean diel cycles for methanol, acetone, acetonitrile, CO, ozone and wind direction are given for Periods 1 and 3 in Figure 6. The first point to note when considering Fig.6 is that the averaged cycles shown represent less than four complete days in each case. Nevertheless, without over-interpreting the data, several interesting points can be made from this analysis. First, it may be noted that none of the trace gases were strongly correlated or anti-correlated with changes in local wind direction for either campaign period (bottom panels of Fig.6), with the possible exception of ozone in Period 3. This supports our assertion that local emissions and orographic features at the Finokalia site did not affect the PTR-MS measurements to any significant degree. Second, while in Period 3 there was a clear daytime peak of ozone, suggestive of local photochemical ozone production, the ozone diel cycle in Period 1 was more complex, and clearly involved the interplay of chemical and dynamical effects. Since inspection of Fig. 6 shows also that none of the other trace gases correlated strongly with ozone during either period, we can be confident that the other diel cycles observed, in particular for the purposes of the present work those of methanol and acetone, were not simply owing to local photochemistry. To check this conclusion, the trajectories obtained for Period 1 were used to calculate approximate hours of daylight experienced by the air en route to Finokalia from the Turkish coast. Although the peaks in ozone were found to correspond approximately to the calculated peaks in the number of daylight hours en route to the measurement site, no correlation, either positive or negative, was observed between either methanol or acetone and the number of daylight hours in this manner. Moreover, in Period 1, general decreases in methanol, acetone and CO were observed between ca. 08:00 and 18:00 local time, although it must be noted that the acetone diel cycle in Period 1 was much weaker than the the other two, and might not be significant. The acetonitrile profile shows that the degree of biomass-burning influence at this time was small and variable, although clearly non-zero. Acetonitrile was not correlated with any other parameter, and was likely controlled by the emission rates from distant sources.

In Period 3, methanol, CO and acetonitrile all showed clear decreases between ca. 09:00 and 19:00 local time. One possible explanation for these observations is that the increasing radiation-induced turbulence during the daytime mixed less polluted free tropospheric air into the boundary layer. If this were the case, the overlying air must have been rather less influenced by biomass burning, to judge from the acetonitrile diel cycle. The acetone diel cycle does not fit this pattern, however, and it seems clear from Fig.6 that photochemical production of acetone was also occurring at this time, presumably due to higher levels of photochemical precursors than those observed in Period 1 of the campaign. It may be noted that acetone began to rise at ca. 04:00 local time, i.e. before sunrise and long before ozone started to rise (ca. 08:00), which would indicate that the photochemical acetone production observed was not occurring locally. The combination of diel cycling in the importance of the biomass-burning influence (cf. the methanol diel cycle) and regional photochemical production of acetone ensured that the averaged acetone peak did not coincide with those of either ozone or acetonitrile.

The diel cycle of methanol in Period 3 is particularly striking, and since methanol is highly water-soluble, a possible role of the ocean, either through uptake, emission or possibly both, cannot be ruled out. Indeed, the amplitude of the diel variation (defined as {90th percentile-10th percentile}/mean mixing ratio) for methanol was much greater in both periods (35 and 41%, respectively) than for acetone (8 and 17%, respectively).

In summary, consideration of Fig.6 provides evidence that the diel cycles observed during MINOS were mainly as a result of advection to the site and/or vertical mixing, with evidence of photochemical production only seen in the cases of ozone (possibly in both periods) and acetone in Period 3."

The temperature diel cycles for both periods were similar, with a sharp rise at ca 08:00 and a sharp fall at ca 20:00, and remaining roughly on a plateau in between. We did not feel that showing these profiles added enough to the discussion to merit their inclusion in Fig. 6.

In conclusion, we argue against the importance of local photochemistry for Period 1, where biomass-burning influence is at a minimum, and we hope that the new Section 3.2.3 strengthens our case to the satisfaction of the referee. This is also the reason why local day/night periods are not marked in the figures. The interpretation of Period 3 is more difficult owing to the large biomass-burning influence, which is why the model/measurement comparison of diel cycling was restricted to Period 1 in the submitted paper. This discussion has been much reduced in the new draft, to avoid the risk of over-interpreting the results from the global model, and the old Fig. 7 has been dropped.

2. Lat and long have now been labelled in Fig. 1.

Regarding the model, we believe that the results show that the model captures rather well the overall trends in the measurements, despite its coarse resolution. We include this comparison because we believe it is of scientific interest. As stated in the reply to the referee's 'general' comment, the introduction to the model comparison has now been reworded, and the comparison of detailed trends in Period 1 of the campaign Ű which we agree was probably pushing the interpretation too far originally Ű has been curtailed in the revised ms.

3. The figures used are 24-hr averages, which is now added in the text. See Berresheim et al., Atmos. Chem. Phys. Discuss., 3, 1183-1212, 2003, for more on

the OH measurements during MINOS.

4. As the referee does not cite which ’previous measurements’ are meant, it is difficult to judge how our MINOS measurements compare. The point of Fig. 8 is to show that methanol and acetone measurements were indeed quite well correlated for much of the campaign. We cannot of course rule out a role of the ocean, particularly in the case of methanol, but we see no definite evidence for it either. Indeed, it is difficult to see how a possible role of the ocean could be investigated from a series of measurements at one fixed point only. Nevertheless, this point is now discussed briefly in the new Section 3.2.3, as reproduced above.

As regards anthropogenic sources of methanol, we agree that we worded this point too strongly in the original ms. The Schade and Goldstein (2001) paper is now cited in Section 4.2.1, as well as the Heikes review noted by T. Karl in his short comment. Even taking into account these works, it still seems true to us that biogenic sources of methanol dominate, so that the thread of our argument, and the multivariate analysis in Section 4.2.2, remain intact. This paragraph now reads:

"The lack of good correlation between CO and acetone suggests that the second and/or third of these explanations may be the most likely. Moreover, recent reviews of the global methanol budget (Galbally and Kirstine, 2002; Heikes et al. 2002) suggest that the global anthropogenic source of methanol may be relatively small. Galbally and Kirstine (2002) estimate a global anthropogenic source of methanol in the range 3-5 Tg yr-1. The total source estimate they derive is 83-260 Tg yr-1, which implies a maximum estimated anthropogenic contribution of ca. 6%. Heikes et al. (2002) estimate an anthropogenic methanol source term of 5-11 Tg yr-1, with a total source of 90-490 Tg yr-1. These figures imply a maximum anthropogenic contribution to methanol of ca. 12%. A rather higher anthropogenic contribution to methanol mixing ratios (20%) was derived by Schade and Goldstein (2001) based on measurements made in a ponderosa pine plantation in the Sierra Nevada mountains, although the authors stress that this figure should be treated as an upper limit (Section 3.2, p.3115). Even assuming that up to 20% of the methanol observed during MINOS was of anthropogenic origin, we propose that only strong biogenic emissions are realistically able to explain the high methanol mixing ratios observed during Period 1 of MINOS, where biomass-burning influence was at a minimum. The correlation of methanol with benzene, a well-known anthropogenic tracer, for Period 1 gave a correlation coefficient (r2 value) of just 0.08. Moreover, methanol production from methane is very slow, and only likely to occur to any appreciable extent where NOx is very low. In fact, assuming a rather high 24-h mean CH3O2 mixing ratio of 20 pmol/mol, and that the yield of methanol from the methylperoxy self-reaction is 100%, which is far from the case, we calculated a methanol production rate of just 29 pmol/mol/d using the latest IUPAC recommended rate data (available at http://www.iupac-kinetic.ch.cam.ac.uk/). This amount is clearly far too small to be a significant factor in the form of the methanol diel cycle observed during MINOS. 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. 2-3% (G. Moortgat, personal communication, 2002), and biomass burning (Christian et al., 2003, and references therein). The importance of this source in the absence of biomass burning is difficult to quantify, but this does not in itself affect the argument made here, since this process too represents a biogenic source of methanol."

It should also be noted that methanol production from methane oxidation is already in the model, and so this cannot be the reason for 'missing' methanol in the model results.

5. The wording of the introductory paragraph of Section 4.2.2 has been altered slightly to demonstrate that we understand that methanol is not a perfect biogenic tracer, but may still be useful as one, "to a first approximation".

The possibility that not all the methanol may have been of biogenic origin has been incorporated into the discussion of the multivariate analysis as follows: "The use of methanol as a tracer for direct biogenic emissions suggests that 20% of the acetone observed in Period 1 of MINOS derived from this source. It is worth noting that even if

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

we assume that 20% of the methanol observed was actually of anthropogenic origin, the results presented in Table 3 are little affected: 20% of 20% implies an extra 4% of anthropogenic acetone, making ca. 6% in total - still a very small figure."

We cannot follow the referee's reasoning that a high background acetone figure implies that "a significant part of the tracer signals were lost before reaching Finokalia." However, the point that the high constant term implies a more remote station has been incorporated into the text at this point (Section 4.2.2).

Short comment by T. Karl

We 'seem to ignore' the Heikes review paper because it wasn't published when this paper was submitted! We cite it now, in the Introduction and in the discussion on methanol sources in Section 4.2.

The possibility that up to 20% of the methanol observed might be of anthropogenic origin has now been incorporated into Section 4.2; see reply to Referee #2 above.

Page 928: methane oxidation is already discussed in the text. The revised text in Section 4.2 (see reply to Referee #2, point 4 above) shows that the rate of methanol production from the methylperoxy self-reaction is far too small to explain the levels of methanol we observed during MINOS.

Last paragraph: the ratio acetone:methanol for Period 1 was 0.88 (not the slope); see Table 2. We do not argue that acetone was purely biogenic at any stage of the paper, but merely that the two compounds clearly have some common sources other than biomass burning. (See opening paragraph of Section 4.2.1.) Section 4.2.2 is an attempt to quantify the biogenic component of acetone for Period 1, and it is certainly very interesting that the 'biogenic ratio' acetone:methanol of 0.30 derived by T. Karl from our data is in concordance with his own measurements, although the very different location leads us to be wary of over-interpreting this ratio.

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

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper