Atmos. Chem. Phys. Discuss., 3, S1245–S1254, 2003
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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “GC x GC measurements of C_7-C_{11} aromatic and n-alkane hydrocarbons on Crete, in air from Eastern Europe during the MINOS campaign” *by* X. Xu et al.

X. Xu et al.

Received and published: 8 August 2003

We would like to thank both anonymous referees for reviewing our paper. We revised our paper based on their comments and suggestions.

Response to comments by referee #1

Section 2.2

Octanal is probably both present in air and a sampling artifact. Octanal and some other long-chain n-aldehydes at ppt-to-ppb levels have been observed in air samples collected at remote and urban sites (e.g. Yokouchi et al., 1990; Ciccioli et al., 1993; Greenberg et al., 1996; Grosjean et al., 1996; Helmig et al., 1996; Wedel et al., 1998; Bowman et al., 2003). In marine air or coastal areas, the observed concentration of

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these n-aldehydes exceed those of many NMHCs. Since these aldehydes are very reactive (Heike Plagens, 2001), it is suspected that they are at least partially produced in the sampling systems used (Greenberg et al., 1996; Helmig et al., 1996; Tanaka, 2000). However, some tests show that artifact production of these species is not significant (Helmig et al., 1996; Bowman et al., 2003). More recent laboratory study by Wildt et al. (2003) shows that these aldehydes are emitted from many plant species after exposure to ozone and/or insect attack. Ozonolysis of unsaturated fatty acid lipids is believed to be one of the potential sources of the long chain n-aldehydes at remote sites (Yokouchi et al., 1990; Helmig et al., 1996; Bowman et al., 2003). Since the lipids can also be present in the sampling systems, e.g., in the aerosols sticking on the inner wall or filters of the sampling system, production of the n-aldehydes within the systems cannot be ruled out, although its significance is unknown.

It is true that the o-xylene measurements are not consistent with data from the GAA and those of the other aromatics. This inconsistency cannot be explained by any local sources since local sources (if any) would have influenced measurements of other species as well. The possibility that o-xylene was interfered by other compounds cannot be excluded although GC$\times$GC-TOF-MS measurements of air samples collected at Finokalia did not reveal any peaks interfering with o-xylene (see Xu et al., 2003). To our knowledge, the most probable interfering compound is heptanal. Since the retention time of heptanal does not differ much from that of o-xylene (only about 4 i.u. in our first dimensional column), complete separation of these compounds cannot be achieved on our system if they are present at comparable and significant levels.

We have added to Table 1 a column containing the minimum and maximum mixing ratios for the listed components.

In the revised manuscript, we define our photochemical age and point out that the estimated photochemical ages do not represent the chronological age one would get from back trajectory information. Several methods can be used for estimating photochemical ages. They are usually applied to cases in which trace gases are emitted in

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distant source regions but not (or nearly not) emitted at the measurement site. If local sources do have a significant influence on the measured concentrations, the calculated air mass ages will bias toward lower values. The more reactive the species, the lower the calculated age, provided that local sources are similar to the distant sources. However, in summer the Finokalia site is hardly influenced by emissions from other parts of Crete due to the special local wind system (Mihalopoulos et al., 1997). During MINOS local emissions were restricted to a few cars per day passing by the site. GC×GC, GC-MS and PTR-MS measurements (Gros et al, 2003; Salisbury et al., 2003) do not suggest any significant local influences. Photochemical ages derived from GC×GC and PTR-MS data are inconsistent with local emissions. Therefore, the differences between the estimated ages shown in Table 1 should be attributed to other causes as mentioned in our paper.

Section 3.2

The mean diel profiles shown in Fig. 2 represent average VOC diel cycles for the MINOS campaign. A similar diel cycle can be obtained from PTR-MS based benzene measurements, though the diel variation of benzene was not as strong as those shown in Fig. 2 (see Salisbury et al., 2003, for diel cycles of some other species and interpretations). The diel patterns do seem to suggest a significant local impact. However, as mentioned above, such local impact was absent during MINOS. There is a slight correlation between the VOC diel cycles and the diel wind direction oscillation. This correlation, however, does not suggest any local impact. Because of the coastal orography and sea-breeze oscillation the observed wind direction changed from southwest to northwest in the early morning and from northwest to southwest in the evening. The mid-morning peaks in the diel profiles coincide with the switch to northwest wind direction, which should suppress local influences. We may exclude that the observed diel patterns were caused by local emissions.

Now to the question “Is it possible for diel variations in the source region to propagate to the receptor region over this scale?" To answer this question one may need modelling, which is beyond the scope of this paper. We believe that the propagation of diel variations from the source region to the receptor region is not the only remaining explanation to the observed diel patterns. Let us first consider an extreme case, i.e., constant trace gas concentrations in the source region. If the trace gases are inert and the pollution plume is transported in the boundary layer of constant height, there should be no diel variations in the receptor region. However, the species we measured are not inert but very reactive. Photochemical reactions, which are highly dependent on the OH abundance and hence on the time of day, may cause strong variations of trace gas concentrations along the air mass trajectories. Consequently, even if there are no diel variations in the source region, diel variations may still be observed in the receptor region. The real situation is that the VOC concentrations in the source region have diel cycles as well. The patterns of the diel cycles are modified by photochemical reactions and other factors (e.g., variations of the boundary layer height and changes in mixing-in of more VOC depleted air) during horizontal advection. What we get at the measurement site is the modified and time-shifted diel cycles. Combining observations and modelling results, de Laat and Lelieveld (2000) showed that horizontal advection of air masses with different O_3 concentrations and photochemical processes are two important factors causing the typical diurnal O_3 cycle in the marine boundary layer. Although O_3 has much longer lifetime than those of the hydrocarbons we measured and experiences different photochemical reactions, the basic principles of their study are probably applicable to our observation.

We have added more discussion to this section.

Section 3.3

Indeed this section was used to analyze the causes of the observed diel cycles. Unfortunately, it seems not to be as successful as we hoped. Following the advice of both referees, we have removed this section.

Section 3.4

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Please note that in Fig. 4 the concentration unit for decane and OH is mol cm^{-3} (not molecule cm^{-3}). The mean concentrations of decane and OH are about 4.5$\times$10^{-16} and 7.5$\times$10^{-18} mol cm^{-3}, respectively. The y-axis values are negative because they are natural logarithm of values smaller than unity. The x-axis represents the integral of OH over 24 h (86400 s), therefore, the values are between 10^{-13} and 10^{-12} mol cm^{-3} s. The slope of Fig. 4 corresponds to k in cm^3 mol^{-1} s^{-1}. We have used cm^3 mol^{-1} s^{-1} instead of cm^3 molecule^{-1} s^{-1} because the former is used in the NIST database from which we got the literature k values.

We used the ln[decane]-Σ[OH]t correlation because it shows medium statistical significance (indicated by the correlation coefficient) among all the ln[X]-Σ[OH]t correlations. The ln[toluene]-Σ[OH]t plot is actually more scattered and hence shows less significant correlation. Nevertheless, we use this plot in the revised paper and add a table containing the correlation results for all species that are included in Fig. 5.

As for the issue of local OH vs “regional OH", our data do imply that local OH abundances are representative of regional OH. Although we do not mean to imply that the high-resolution measurements of OH represent the regional situation, we do believe that the daily averages or the 24-h integrals of local OH were probably representative of those of regional OH. As shown in Berresheim et al. (2003), OH concentrations observed at Finokalia during MINOS can be very well described by [OH]=aJ(O^{1}D)$^{0.68}$, with a = 1.4x10^{10}, 1.7x10^{10}, and 2.2x10^{10} s cm^{-3} for three OH measurement periods, respectively. This simple relationship explains 99% of the observed variance of OH. During MINOS clear sky conditions dominated over the Eastern Mediterranean, therefore it is likely that the J(O^{1}D) data from Finokalia are applicable to the Eastern Mediterranean region or are good approximations of J(O^{1}D) at other locations of the region. In addition, the pre-exponential factor a is related to boundary conditions, mainly mixing ratios of O_3, CO, CH_4. Since these species are less reactive, their temporal and spatial variations within individual periods were relatively small. In other words, both the chemical and radiative fields on which [OH] depended were probably fairly

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homogeneous over the Eastern Mediterranean region during the MINOS campaign. Consequently, the 24-h integrals derived from local OH measurements may be close to those one would obtain from OH values along the back trajectories. We have added additional comments to address this issue.

Our ln[X]-Σ[OH]t relationship as shown in Fig. 4 and the S_{lnX}-τ^b relationship of Jobson et al. (1999) are two different approaches for describing a common phenomenon, i.e., the variation driven by reactions of atmospheric VOCs. While the approach of Jobson et al. has been successfully applied to VOCs less reactive than C_6 hydrocarbons, it may encounter difficulties when applied to very reactive species such as those studied in our paper. One of the problem is that the full dynamic ranges of the reactive species are not quantified because the levels of these species often fall below the detection limits. Consequently, the calculated variabilities of these species are lower than the real variabilities, as already mentioned by Jobson et al. (1998). Since this problem affected many of the species we measured, it is not very suitable to analyze our data using the approach of Jobson et al. In the paper of Gros et al. (2003) the variability-lifetime relationship for the Finokalia site is studied based on GC-MS measurements of medium reactive and long-lived species. Our data follow the general trend shown in their S_{lnX} versus lifetime plot. However, if those data are added to the plot, the correlation will degrade due to the larger scattering of data points associated with the reactive species. We believe that in the future the application of the Jobson et al. method may be extended to the short-lived species when the detection limits for the reactive VOCs are significantly improved.

Besides the above problem, there are two other reasons that we use the ln[X]-Σ[OH]t approach instead of the approach of Jobson et al. First, the ln[X]-Σ[OH]t relationship is a phenomenon we observed during MINOS. We believe that the phenomenon may be of common interest and hence worthy of report. Second, the variations of reactive species and those of less reactive species are dominated by different mechanisms. Study of McKeen et al. (1996) suggests that dilution process is more important for less

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reactive species and photochemical oxidation for more reactive species. They found both processes were equally important for the variation of n-butane during PEM-WEST A. Most species we measured are much more reactive than n-butane, suggesting that their variations are dominated by photochemical reaction. Measurements of highly reactive VOCs and the availability of in-situ measurements of OH have made a good opportunity of testing some different data interpretation methods, such as the one we have used.

Section 3.5

We mention the photolysis of benzeneacetaldehyde in the revised paper.

Although the use of the structure-reactivity relationship is a good idea, it does not lead to more conclusive results. The main problem here is the large uncertainty in the estimated k values. The estimated k values for 12 aromatic compounds agree at best to a factor of 2 with the observations (Kwok and Atkinson, 1995). For example, the estimated k for acetophenone is 7.4x10^{-13} cm^3 molecule^{-1} s^{-1}, while the observed value is 2.74x10^{-12} cm^3 molecule^{-1} s^{-1}, about a factor of 4 disagreement. To estimate the rate constant for benzeneacetaldehyde, the electrophilic substituent constant ($\Sigma\sigma$+) for -CH_2CHO is needed. This constant is unfortunately not available. Since H abstraction by OH seems to be the main pathway for the benzeneacetaldehyde + OH reaction, we can neglect the contribution of OH addition to aromatic ring to obtain a lower limit estimate of the k value for benzeneacetaldehyde. Without OH addition to aromatic ring, the estimated k value is 2.2x10^{-11} cm^3 molecule^{-1} s^{-1}. This value is about 30 times of the estimated k value for acetophenone and 3 times of the k value for ethylbenzene. If this estimated k value for benzeneacetaldehyde is realistic and there is no other benzeneacetaldehyde source, the [BA]/[EB] ratio should be smaller than unity. However, about one fifth of the observed [BA]/[EB] ratios are larger than unity, implying that either benzeneacetaldehyde is less reactive than ethylbenzene or there are significant unknown chemical sources of benzeneacetaldehyde. Since the SAR results are highly uncertain and no additional chemical sources contributing sig-

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nificantly to the [BA]/[EB] ratio have been reported, we have assumed a more realistic case (i.e., benzeneacetaldehyde is less reactive than ethylbenzene and there is no additional contribution from other chemical sources of benzeneacetaldehyde). However, we cannot completely rule out that benzeneacetaldehyde is actually more reactive than ethylbenzene. At present, this issue cannot be settled due to the lack of measured kinetic data for the benzeneacetaldehyde + OH reaction. We have included the SAR results and pointed out potential errors in our interpretations.

It is a good idea to compare the estimated photochemical ages with the time integrated OH values shown in Fig. 4. Indeed there is a positive correlation between the photochemical ages and the integrated OH values. The correlation coefficient is 0.68, which is better than those of most ln[X]-Σ[OH]t correlations. The fact that the photochemical ages are positively correlated with the integrated OH values supports the idea that different intensities in photochemical reactions result in different [AP]/[EB] values, from which the photochemical ages are derived. Since the correlation provides no extra information, it is not shown in the revised paper.

Response to comments by referee #2

Section 3.1

We have included acetonitrile data in Fig. 1.

Table 1

Comments of the measurement techniques for the GAA data are already included in the published ACPD version. There is no doubt that the GAA data shown in Table 1 are less representative of the real situation of MINOS. However, data that are temporally and spatially more suitable are lacking. Air mass trajectories shown in Salisbury et al. (2003) for the periods 1-3 suggest that data from western Turkey would be more suitable for the comparison. Some trajectories from the last couple of days of the campaign (Salisbury, unpublished data) do indicate potential influences of the GAA. Only

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a few measurements might have been influenced by emissions from the GAA. Filtering the Finokalia data using the trajectory information does not result in substantially different results.

Interferences to o-xylene cannot be ruled out. Details see the response to comments by referee #1.

A column containing estimated photochemical ages is already included in the published ACPD version.

The superscripted 'e's are footnote marks linked to a same footnote. All other errors are already corrected in the published ACPD version.

Section 3.2

Fig. 2. shows average diel profiles derived from the entire campaign data. There are some day-to-day variations in the diel patterns, as implied by the error bars in Fig. 2. However, the average diel cycles do show patterns that may be related to some general dynamic and chemical causes. Although different air mass types have been identified based on data of acetonitrile and back trajectories (Salisbury et al., 2003), there were few substantial differences between trajectories for the last 1-2 transport days, which are more relevant to the reactive hydrocarbons. For this reason, we believed that not differences in transport times but photochemical reactions played an important role in forming the observed diel patterns. More discussion about the diel cycles can be found in our response to comments by referee #1.

Section 3.3

Following referee #1's suggestion, we have removed the original Section 3.3.

Section 3.4

The OH integral is calculated from the local OH measured by Berresheim et al. (2003). We agree that the local OH can be strongly influenced by local chemistry and dynamics,

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but we believe that due to the special situations during MINOS the 24-h integrals of local OH were probably representative of those of regional OH. Our arguments are given in the response to comments by referee #1. We show now toluene instead of n-decane in the ln[X]-Σ[OH]t plot. We also have added an additional table (Table 2) with results from all ln[X]-Σ[OH]t correlations.

Section 3.5

Results from analysis using SAR as well as comments about benzeneacetaldehyde photolysis are now included. We hope these can make our conclusions more robust.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 1477, 2003.

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