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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.

Anonymous Referee #1

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This paper presents an analysis of hydrocarbon data collected at a ground site on the island of Crete. To my knowledge this is the first time the GCxGC technique has been applied to the in-situ analysis of air in a non-urban setting. The data are of interest to the atmospheric chemistry community for the novel measurements of several aromatic species and as an example of the potential analytical promise of the technique. The sequential model analysis and its application to aromatic oxidation products is interesting as is the general correlation between hydrocarbon mixing ratios and the 24 hour OH action integral. The paper is generally well written and the analysis sound with a couple of exceptions. The analysis of the benzeneacetaldehyde reactivity should be reworked to include a structure-activity based analysis. My major criticism is that there was a heavy a reliance on simple box model analysis to try to understand the factors controlling ambient variability and to calculate air mass age from changes in hydrocarbon concentrations. In one section the box model analysis does not lead to significant, defensible conclusions. The air mass age calculations are presented rather perfunctorily and deserve more comment and attention. These concerns and some minor comments are detailed below.

Specific Comments

section 2.2

Can you comment on the presence of octanal as an interferent in the 124-TMB measurement - is octanal a sampling artifact or is it present in the air?

As you mentioned in section 3.1 the o-xylene data look odd. o-Xylene has a high mean (as listed in Table 1) compared to toluene and m.p-xylene. Also its diel cycle shown in Figure 2 is not very pronounced compared to other aromatics. I would have expected a better correlation between o-xylene and m.p-xylene given that they have very similar emission sources and removal processes. Based on the GAA source region data, the o-xylene / toluene ratio at Finokalia to be less than 0.2 (due to atmospheric processing) while they observed ratio was 0.58. My experience with VOC data from urban areas (by GC-FID, GC-MS) is that the o-xylene / m,p-xylene ratio is around 0.4. This number is consistent with the GAA data. Is it possible there was an interfering compound in your o-xylene measurements or perhaps a local source?

It would be good to list the minimum and maximum mixing ratios in Table 1 as well. The observed dynamic range is as important as the mean.

Throughout the paper the concept of air mass age appears. It would be prudent to define what you mean by the age of an air mass in a dynamic fluid and how the ages shown in Table 1 would relate to chronological age one would get from back trajectory information. A plot of your Table 1 ages vs. Kho shows more or less the expected trend from such a chemical kinetic analysis - the more reactive species have the lower

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age. You should comment on how the emission footprints at different scales will affect the age calculation. For example the most reactive compounds will have very low mixing ratios by the time air masses arrive at your site from urban sources in Turkey / Greece. These species would be more susceptible to air mass contamination by sources on Crete than less reactive hydrocarbons whose concentrations are correspondingly higher - all else being equal. Mixing ratios of the very reactive species will thus appear higher than they should be relative to less reactive compounds and this will bias air mass age calculations. I suspect this situation is influencing your data and is interesting in its own right.

section 3.2.

The diel patterns shown suggest to me that the measurements were impacted by local emissions in the morning. It is hard for me to otherwise understand how a regular diel pattern would emerge for these species at a remote site. Mid-morning peaks of VOC mixing ratios are typically seen in urban / rural sampling sites. The maxima reflect morning vehicle emissions into shallow boundary layer, with mixing ratios decreasing as the mixed layer grows during the day. Is the diel VOC cycle correlated with the diurnal wind direction oscillation mentioned in section 3.1? You reference other analyses (Salisbury, 2003) that are concluding that air masses took 0.5 to 1 day to travel to the measurement site from the mainland. Is it possible for diel variations in the source region to propagate to the receptor region over this scale? Were similar diel cycles observed in other trace gas data such as PTR-MS based hydrocarbon measurements or in the CO data? More discussion is needed here to offer an explanation as to probable causes.

section 3.3

In part this section was used to analyze the causes of the diel cycle but the analyses and conclusions are not very informative. There is the risk here of presenting an over interpretation on an interpolated sub set of your data. The box model analysis is too simplistic to address these data. Since so little is concluded, I would suggest removing this section from the paper. The analysis of the data itself, through your treatments in section 3.4 and 3.5, are far more fair, informative, and interesting. Compared to these sections, section 3.3 detracts from the quality of the paper.

section 3.4

The relationship between ln{X} vs the 24 hr integrated OH concentration is interesting, however I don't understand the values of the x and y axes given the units in Figure 4: the y-axis values are negative and the x-axis values are fantastically low numbers. If I understand your intention, values of the OH action integral would be in the range of 8.64e(10) molec cm-3 s. The slope of figure 4 is far too large to be a bimolecular rate coefficient .

Since n-decane mixing ratios appear to be close to your detection limit would there be less scatter in Figure 4 if toluene was plotted instead? You should state up front that the 24 hour integration time gave the best fit which is consistent with the Salisbury reference that air masses arrived at Finokalia from mainland sources in about 1 day. Does this imply that local OH concentrations are representative of "regional OH"? This would seem to be an interesting point worth commenting upon.

Since you are trying to relate time series variability to VOC lifetimes why not use the approach of Jobson et al. [JGR : 1999, vol 104, 16091]? In this analysis the standard deviation of ln[X] is plotted as a function of average lifetime for species that have similar source sink relationships. This would apply to most of the species you measured (vehicle exhaust VOCs removed atmospherically by OH). The Jobson et al paper shows that for remote data the relationship follows an inverse square root dependence on lifetime. Furthermore, the analysis can reveal the influence of local emissions on VOC distributions through a weak lifetime dependence. Your Figure 5 is similar to the variability lifetime analysis. However the linear regression slopes you calculate for ln{X} vs. time integrated OH are a source of uncertainty (given the poor correlations) that will cause

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the data in Figure 5 to look scattered and obscure trends. A bivariate regression would be preferred for calculating slopes in Figure 4. There is no clear trend in Figure 5, which suggests that the slopes are weakly related to lifetime. The variability vs. lifetime analysis should at least be examined to see if that improves the information content of the data and to draw conclusions about the impact of local sources.

section 3.5

Benzeneacetaldehyde would also have a photolysis loss channel. This should be mentioned and figured into the analysis / commentary. Likely nothing is known about benzeneacetaldehyde photolysis given that very little seems to be known about benzaldehyde tropospheric photolysis rates.

You also state that given the observed [BA]/[EB] ratios that benzeneacetaldehyde (BA) is likely less reactive than ethylbenzene. Given the -CHO hydrogen, it's likely that BA is more reactive than ethylbenzene. For example the benzaldehyde + OH rate coefficient at room temp is about 1.29 x 10-11 cm3 molecule-1 s-1 (see Calvert reference). I would anticipate BA to be a bit more reactive than benzaldehyde. Since BA will also likely photolyze I think it's fair to assume it would have a shorter atmospheric lifetime than ethylbenzene, and a much shorter lifetime than acetophenone. The assumption that the acetophenone and benzeneacetaldehdye rate coefficients are close to each other appears to be in error, and you would therefore need to rethink the acetophenone and benzeneacetaldehdye yield discussion. A more thorough analysis of the relative OH rate coefficients and lifetimes of the ethylbenzene oxidation products is required, giving due consideration to structure- activity relationship to estimate rates constants.

Photochemical ages calculations - why not use the 24 hour time integrated OH values used in Figure 4? These values are an independent measure of photochemical age that can be compared to those you calculate from equation 11. This would be an interesting comparison. Your data from Figures 4 and 5 have shown that there is a weak chemical kinetic signature in the data. The question is whether the analysis of photo-

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chemical age from equation 11 would display a better correlation with the measured time integrated OH.

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