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Atmospheric
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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 #2

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The Paper presents a detailed dataset of aromatics and higher n-alkanes obtained during the MINOS project at a ground site on Crete. Previous studies using this technique (GCxGC) have focussed on the urban environment and kinetic studies, this is the first paper where GCxGC has been used at a rural/semi-rural location. Much recent interest has attempted to tackle the problem of atmospheric hydrocarbon analysis in the isomerically complex area above the ’lightweight family’ of hydrocarbons (C1 - C7) particularly aromatic components which are both numerous and key precursors of both tropospheric ozone and secondary organic aerosol (SOA). Data is analysed with relation to reactivity towards the hydroxyl radical (OH) and chemical climatology. The paper is well written and the results presented in a clear and concise way.

There are techniques which can be applied to estimate hydroxyl oxidation rates such as structure activity relationships (SAR) (Kwok & Atkinson, 1995). The paper would benefit from the inclusion of such calculations, addressing any observed deviation from predicted rates. There are a lot of new measurements coming out of the experiments being conducted using the EUPHORE chamber and these will prove very useful in this type of interpretation.

Perhaps a comment on the ability of the method described to allow a more definitive method of positively identifying analytes whereas other previously employed methods namely GC-FID and GC-MS suffer as the sample matrix becomes more populated. Modern time-of-flight mass spectrometers with high data acquisition rates (such as the instrument employed for the peak identification) do allow for significant deconvolution of overlapping peaks when coupled to a standard single dimensional separation, these instruments are currently bulky and as such do not lend themselves to field deployments beyond the research laboratories where they are used. Currently the method adopted here (FID in field and TOF comparison to sample in research lab) is the closest we can get.

Better use of air mass classifications and back trajectory analysis in addition to the SAR calculations mentioned above will make this a good article.

SPECIFIC COMMENTS

Section 3.1

The Aegean area is prone to airmasses which have been influenced by biomass burning activities, this is referred to in the text citing Salisbury et al (2003) on numerous occasions, it would be clearer to include the acetonitrile data in the article, after all the data sets are from the same group.

Table 1

There is no comment of the measurement techniques, derivation and error in the GAA

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NMHC measurements, there are nearly 10 years old! There has been considerable efforts in Athens to reduce pollution levels before the city plays host to the Olympics in 2004, this may have lead to significant reductions in industrial areas in addition to road transport sources. Air mass patterns have been produced (Salisbury et al, 2003) yet the Finokalia data not been filtered using this information, this would have given a stronger argument of the comparison.

The mean concentration of o-xylene shown appears to be high, this suggests to me an interfering compound, since there are few industrial processes which use o-xylene as distinct from mixed xylenes.

A column showing OH lifetime or estimated photochemical age would prove useful in interpreting the text, there is ample space for such a column.

There are TWO superscripted 'e's, compounds m & p-xylene are di-methylbenzene and NOT methyl-ethylbenzene as noted in comments remove the notation on the p-/m-xylene subject line.

Section 3.2

The diel cycles presented are not typical of a remote site, one would expect such cycles close to an urban/industrial source but following transport times of 1-2 days it would be expected that this pattern would be very faint. This is especially true since Figure 2 if the entire campaign data combined and the strength of the diurnal signal would also suggest a very similar transport time for all air masses between exposure to urban emissions and arrival at the monitoring site. Earlier in the article (section 3.1) comments are made about the differing air mass types yet the diel variation suggests near identical air mass types with very similar transport times. At remote sites such as used in this study the collapse of the boundary layer at night usually is indicated by increases in concentration of trace species, this is seen here to some degree but the maximum daily concentrations appear to be centred on solar noon.

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Section 3.3

This section covers well known and much documented ideas on the processes affecting tracer levels during transport between source and observing station, whilst perfectly valid, perhaps inclusion in Section 3.1 would be better than a separate section.

Section 3.4

Is the 24hr integral calculated from the local OH, if this is the case then surely the OH as mentioned is strongly influenced by local chemistry and dynamics which casts doubt on the validity of this approach. Maybe other chemical tracers, photolysis fields etc along the path may be of use in this calculation. Back trajectories can assign a transport time and from this an integrated OH field can be derived. Why was n-decane used? There are other compounds with a higher mean/LOD ratio which may prove to provide more persuasive results, and given the kinetics data available this analysis could have been conducted on the other species and tabulated with one plot as an example of the technique.

Section 3.5

This is a good method of analysing the data collected, with solid underlying science given a number of assumptions but this is common in this sort of field data. However in this case there are unknowns in addition to the assumptions and much is inferred from these. Has the oxidation rate for benzeneacetaldehyde been estimated using SAR techniques, this would add to the comment made regarding the slow rate suggested for benzeneacetaldehyde from Figure 7. As noted by Referee 1 there is not doubt a photolysis channel for benzeneacetaldehyde and the strength of this is unknown, there should be a comment addressing this fact.

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

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