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Atmospheric
Chemistry
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Discussions

Interactive comment on "Tropospheric OH and Cl levels deduced from non-methane hydrocarbon measurements in a marine site" *by* C. Arsene et al.

Anonymous Referee #2

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The authors present an analysis of C2-C8 hydrocarbon data collected on the island of Crete to determine OH and Cl-atom concentrations. Overall the paper is well written and they have made some interesting comparisons of the estimated OH and Cl concentrations determined by hydrocarbon trends to photochemical box model calculations and through measurements of HCl (a source of Cl atoms from the HCl + HO reaction). The hydrocarbon data appear to be of good quality (more experimental detail is needed) but the analysis of the data could be much improved. The critical problem with the analysis is the simplistic assumption that a simple chemical kinetic model can be applied to the hydrocarbon trends to determine HO and Cl concentrations. While such treatments have been applied in the past a more critical examination of the data is warranted to understand atmospheric mixing effects on hydrocarbon trends. The state of the art is not in assuming kinetic behavior to calculate [HO] but in using the data to demonstrate kinetic behavior. The analysis and arguments presented are not convincing enough to really believe in the calculated HO and Cl concentrations and their associated uncertainties. This paper would be much stronger if the authors could better justify their analytical model and demonstrate to ACPD readers that mixing effects did not impact the observed hydrocarbon trends. Without demonstrating that the analytical model is reasonable there is no way to evaluate the uncertainty of the radical concentration calculations. The authors need to make an effort to address this point before this analysis paper is ready for publication.

Specific Comments

P6332. How far was the Finokalia site from the coast?

P6333. What was the sampling frequency at the University campus site (you state that at Finokalia samples were collected every hour.)

P6333. Who manufactured the certified gas standard and what was its stated accuracy?

P6333. How were responses of the NMHC determined from the certified standard? Do you use effective carbon number responses based on n-butane?

P6334. Remove the word “diurnal” from the description of Figure 1. Figure 1 displays the temporal variability over many days and nights.

P6334. It is very difficult to discern a diurnal trend in Figure 1B. To be more convincing I would suggest plotting the Figure 1 B data on a 24 hour clock as a new figure (Fig 1 C) so that the “diel” trend can be better visualized. To my eye it looks like propane and C5 alknes displays a similar trend. Why do NMHC mixing ratios go back up at night / early morning?

P6334. It’s surprising to me that there was no mixing height change observed at Finokalia when measurements were taken (07:00 to 22:00). Can you please elaborate this point. When did the sun come up and how rapidly did the nocturnal inversion layer break up and the full day time mixing height evolve? You predicate your box model analysis on the fact that mixing layer heights did not change over the course of the day. Please supply some evidence or some discussion on PBL height evolution at this site.

P6334. Figure 2. The bargraph style obscures the lower range of the “error bars”. Could this be re-plotted as symbols.

P6335. I’m confused by your use of “steady-state hypothesis”. Steady state of what? NMHC are decaying with time so they aren’t in steady state. Do you mean instead a box model and assume radical concentrations are at a fixed steady level?

A chemistry only box model is easy to propose and work with but you need to argue that it is a reasonable model. Why wouldn’t daytime exchange between the mixed layer and free troposphere reduce surface concentrations? The first step is to demonstrate that the data display chemical kinetic behaviour. For example, do plots of ln(n-hexane) vs ln(n-butane) yield slopes that are the ratio of their HO rate constants? What about other pairs? Is there a consistent pattern of descrepency between observed slopes and slopes caluated from HO rate constants? In many environments the slopes of these plots are a power law functions of the species lifetimes (c.f. Ehhalt, JGR, 1998; Jobson, JGR, 1999; Parrish, JGR, 2007). Deviations from kinetic trends are much more apparent if the kinetic slope is large. Do your data display such systematic deviations? Such an analysis would provide a test to determine how much of the diurnal change is due to chemistry and how much due to mixing. The important point here is determining if mixing effects are being confused with Cl-atom chemistry effects and to convince readers that this is not the case.

P6336. What data is being displayed in Figure 3a. Are these points hourly averages of all the data collected at Finokalia or just data from one particular day?

P6336. What is the averaging period for the 0-D box model [HO] shown in Table 1.

P6337. Can you please explain the “appropriate meteorological conditions” that yield chemical kinetic behavior? Are these similar to the conditions described for example in L.I. Kleinman et al., JGR, vol 108, no. D3, 2003 and S.A. McKeen et al., JGR, 95, 7493-7500, 1990?

P6337 L7. missing word “Apart from OH radicals. Ě”

P6337. The use of i-butane / n-butane ratios begs the question what is the natural variability of this ratio in the absence of Cl-chemistry? The data at large n-butane mixing ratios ($>$ 1000 pptv) display a constant ratio of ˜ 0.4. Why does the i-butane / n-butane only ratio increase for lower n-butane mixing ratios? Does Figure 4a simply imply that you are overestimating i-butane at low mixing ratios due to analytical uncertainties?

It would be instructive to show a plot of i-butane vs. n-butane on a log -log scale.

P6337. Do the data in Figure 4b imply that both HO and Cl chemistry are active in shaping these trends? You may want to draw in the HO kinetic line to compare the data against. Why should high insolation change the [Cl] / [HO] ratio compared to low insolation?

P6338. Again the chemical kinetic argument has been made but you need to justify it by demonstrating the data display chemical kinetic behavior (see Ehhalt et al., JGR, 1998; Jobson et al., JGR, 1999; Parrish et al. , JGR, 2007). Typically these slopes display square root dependence on HO rate constants but the dependency is a function of proximity to sources. Do your data display similar behavior? The calculation of the Cl-atom concentration by this approach has been done before. It completely ignores the effects of mixing. You need to do better than this to convince a more skeptical audience than Rudolph 1997 faced when he published his analysis.

P6339 and Table 2. What contributes to the large standard deviations associated with the calculated Cl concentrations?

P6340. For the night-time/daytime ratio method why did you use CO? Why not use another NMHC like benzene? Presumably there is a much better correlation between NMHCs than between NMHC and CO (which has other sources).

Table 3. The Cl + benzene rate constant appears to be in error (too large). It is not listed in reference A.

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