

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 #1

Received and published: 18 June 2007

The analysis presented by Arsene et al. uses similar methodology employed by Rudolph et al. [1997] for the indirect determination of OH and Cl levels in the Eastern Mediterranean. While conducting an analysis using similar methods employed by others is not necessarily an uncommon practice, in the case of the current manuscript the authors are re-hashing data analysis methods that are well over a decade old for the determination of Cl atom concentrations. Effectively, the manuscript is presenting “old” science which unfortunately brings nothing new to the debate over Cl atom concentrations in the troposphere/marine environment. In essence, the authors have used seven pairs of NMHCs using the “log-log” method to back out Cl and OH mixing ratios. Several recent manuscripts have used more innovative and robust methodologies for the determination of tropospheric Cl concentrations. In my opinion, the work presented

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here does not expand on previous analysis methodologies and does not provide any new insight on tropospheric Cl chemistry.

Comments on the Experimental Section

What is the difference between a “natural” and “rural” site? Is “natural” supposed to mean remote? If so, please state this.

P6332, L8: “...city of Crete, Heraklion, and is occasionally affected by emissions of the city.” Replace “of” with “from”

P6332, L10-12: If local influences are “important” why weren’t measurements made from other wind directions and speeds in order to compare and contrast the results and sort out the air mass composition between different sectors/conditions?

P6332, L14-16: During the summer 2006 intensive, why were measurements only conducted between 07:00 to 22:00 every day?

This brings up a critical issue regarding the author’s discussion of “seasonal and diurnal variations” in section 3.1. The fact that there were not samples collected for an 8 hour period overnight - the time period when the largest changes in diurnal patterns are expected - presents a fundamental problem with the discussion in section 3.1 because the statements made by the authors are unsubstantiated. There is ample evidence in a variety of published manuscripts which show diurnal variability, even in a marine environment.

The following concerns are raised because the authors have not included any references for the experimental details provided, which raises concern, because the details provided are vague and leave out important details which are fundamental to the methodology employed for the indirect determination of Cl and OH.

P6332, L18-20:

“For each analysis 990 ml of air were drawn from about 5m above the ground via a

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stainless steel inlet at a flow rate of 50 ml min⁻¹ (air sample integrated over 20 min)."

What were the dimensions (ID) of the stainless steel inlet? Was a filter used? Why was the flow rate through the inlet 50 ml/min? With such a slow flow rate through the inlet, were any experiments carried out to confirm that there were no losses/artifacts in the sample line?

As part of any sound experimental section, precise details are critical - the following should be revised:

"...the hydrocarbons were trapped on Tenax TA cooled at about -100 C."

Making the statement "about -100 C" is by no means quantitative - what was the range of the Tenax trap - was it +/- 10 C, 20C, etc? State this explicitly as breakthrough can occur for the light NMHCs on Tenax at these temperatures. Additionally, why was the sample first trapped on Tenax and then desorbed on to another trap filled with glass beads at -196 C? Was this to remove CO₂? If so, please state the rationale for this. Additionally, Tenax can be problematic regarding sample artifacts during desorption - particularly at high temperatures for alkenes. What was the desorption temperature? What are the sample loop sizes; mesh size of the Tenax and/or glass beads? How was the sample "transferred"? What was the desorb temp of the glass bead loop? Were any experiments conducted to ensure ozone-alkene reactions weren't a problem? Did the water trap have to be changed? If so, how often?

P6332, L26: "The column was initially kept at..." Replace "kept" with "held"

P6333, L2: "The total analysing time was 40 min." Replace "analyzing" with analysis or cycle

The following questions are raised regarding the fact that the authors used a PLOT column for NMHC measurements up to C₈ - which is not an ideal column choice for separation and quantification of NMHCs greater than C₇.

The authors state that a certified standard containing ethane, ethane, propane and

n-butane at 100 ppmv was used as the primary calibration standard. Who was the standard certified by and at what level (100 +/- ?? ppmv)/what calibration scale(s) are the measurements referenced? How were the compounds quantified that were not in the primary standard (C5-C8 NMHCs)? Was a uniform per-carbon response used? If so, how was this verified? Beyond the C5 region on some PLOT columns, the per-carbon response can decrease (and sometime significantly) with increasing carbon number. How was ethyne quantified? Was it assumed to have the same per-carbon response as the other C2 NMHCs (depending on the make-up gas flow rates to the FID, this isn't always a safe assumption)? If so, how was this verified?

What is the measurement precision for each of the NMHCs? How is/was this determined? Again, this concern is raised because of the methodology employed for determining OH and Cl.

Why was the primary calibration standard only analyzed once per day? What was the day to day variability of its analysis (did the detector response change)?

What sample amount was analyzed for the 100 ppmv primary standard? How reproducible were the injections using the gas tight syringe? What was the matrix gas of the primary standard? Were there any differences in detector response as a result of different matrix gases and sample amounts (it's assumed that you didn't analyze 990 ml of the 100 ppmv std)? Was a calibration curve generated using the primary standard to ensure linearity? How is the calibration scale maintained over time?

How was the LOD determined? The manuscript states "about 5 pptv" - again, this is very vague and is not a good practice for quantitative scientific analysis. For example, was the LOD determined as 5 times the baseline noise? Moreover, does the LOD decrease with increasing carbon number? Please show explicitly how the LOD was determined as this is a significant concern regarding the butane analysis.

How was the absolute accuracy of the measurements determined? Again, the authors state "about 10%" - from what/where do these absolute calibration numbers emanate?

Accuracy estimates don't come from thin air, they are produced by a comprehensive statistical analysis of potential errors in preparing and analyzing the standards that comprise the calibration scale.

Results Section The authors state the following:

Figure 1 depicts the diurnal variability of relatively long lived (ethane, propane, Fig. 1a) and short lived (i-pentane, n-pentane, Fig. 1b) NMHCS, measured at Finokalia during the campaign in summer 2006.

First off, the authors can not state that Fig 1 shows the diurnal variability - or lack there of - because they do not have measurements during the 8-hour period which constitutes the "nighttime" period. Essentially, the authors have presented daytime measurements only and this should be clearly reflected in the text.

Both ethane and propane do not show any clear diurnal variability and changes in their patterns are mainly influenced by the long range transport due to their relatively long lifetimes toward OH radicals ($\tau_{\text{ethane}}=11.5$ days and $\tau_{\text{propane}}=2.9$ days, for a mean OH of 4×10^6 radicals cm^{-3}).

Again, there is no basis for the statement that ethane and propane do not show any clear diurnal variability as there are no measurements during the night to show how the diurnal profiles might be changing. Moreover, while ethane distributions can be influenced by long range transport and are not likely to exhibit much diurnal variability, it is highly unlikely that this is the case for propane during the summer! This is clearly an unsupported statement which must be substantiated.

On the opposite a clear diurnal variation is observed for the shorter lived NMHCS, i- and n-pentane, with minimum around 19:00, summer local time, especially during days when no significant changes occurred in the wind speed (Fig. 1b).

First - the beginning of the sentence needs to be revised from "On the opposite..." to something more like "In contrast to ethane and propane..." Additionally, I would dis-

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agree that a clear diurnal variation is observed for i- & n-pentane - there is a bit more variability in the measurements - which almost appears random - but the profiles look similar to that of propane.

In my opinion, there is insufficient data to support any of the discussion regarding the diurnal variability of the NMHCs and the authors should consider revising this section significantly.

While the ~3 days of measurements each month have captured the seasonality of the gases shown, I would be hesitant to use the phrase “distinct minimum during the warm season”, especially regarding i-pentane. While a minimum is observed for i-pentane, it can also be seen that the variability increases likely resulting from fuel evaporation and combustion. If a larger number of samples were collected during the summer months, would there in fact be a minimum in i-pentane? I would recommend addressing this further.

Additionally, the authors state the following:

“Based on NMHCS observations at both sites i-butane/n-butane ratio is plotted against n-butane (Figure 4a). As the ratio varies between 0.3 and 3 for the rural site and 0.6 and 3 for the natural site, this is clearly indicating the presence of Cl atoms in the area.”

How does this clearly indicate the presence of Cl atoms? This is an overstatement does not clearly indicate the presence of Cl atoms - at most, it infers that Cl atoms may be present.

Moreover, when analyzing the butane ratios, a critical matter that must be addressed is how important are the measurements and their associated errors when placed in the context of using this ratio to infer Cl atom chemistry. While I suspect that the authors have inferred indirect evidence regarding the presence of Cl atoms, they have fallen short of explicitly illustrating this important fact to the reader. It is not necessarily uncommon to observe similar trends when plotting i-butane/n-butane vs n-butane; that

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is, exhibiting an increasing ratio as the mixing ratios decrease/approach the LODs. However, the measurement precision and as mixing ratios approach LODs can strongly influence this trend and lead to incorrect conclusions for “clearly indicating the presence of Cl atoms in the area” via indirect methods. The authors should carefully consider these issues in addition to other methods of determining Cl concentrations using VOC measurements.

For example, how would the results of this analysis change if a more rigorous approach, such as mass balance, were employed to determine Cl and OH concentrations? Would minimizing the residuals for the best fit to the observations using loss by reaction with OH, loss by reaction with Cl and mixing/dilution provide similar results? NMHC lifetime-variability relationships?

Additionally, the following statement strikes me as a bit odd:

“It is interesting to note the difference in Cl atom concentrations derived for summer time at the natural site (Finokalia, median of 2.3×10^4 , standard deviation of data, $s \approx 1.9 \times 10^4$ atoms cm^{-3}) and at the rural area (University campus, Heraklion, median of 4.5×10^4 , standard deviation of data, $s \approx 2.7 \times 10^4$ atoms cm^{-3}). Although influence from local anthropogenic sources could account for the higher values observed at the rural site, more work is clearly needed in order to examine this hypothesis.”

On a side note, it would be helpful to the reader to include a map including the sample locations showing the proximity of the two sites. However, this particular finding could be viewed as contradictory (again being able to see where the sampling locations reside is important for addressing this statement) - how would local anthropogenic sources facilitate the increased Cl concentrations observed inland, particularly since the authors state that only measurements were included that “avoided important local influences” and were performed when the prevailing winds were from the N-NW with wind speeds higher than 5 m/s. These results need to be flushed out in more detail with supporting evidence.

In its current form, I feel that the results presented in this manuscript essentially use “old” science regarding their data analysis and convey no new significant findings - only a new data set has been utilized for the indirect determination of Cl. From my perspective, I feel that this paper actually illustrates that NMHC measurements haven't improved over the last decade to provide any additional insight for the determination of Cl chemistry and that we are no better off regarding the debate of Cl chemistry than we were a decade ago - which is clearly not the case.

Some additional technical corrections:

The Cl atoms concentration has been estimated to range between 0.6×10^4 and 4.7×10^4 atom cm^{-3} , in good agreement with gaseous hydrochloric acid (HCl) observations in the area.

Should read - The Cl atom...

Most of the non-methane hydrocarbons (NMHCS) are recognized to play a central role in the oxidation capacity of the atmosphere by determining the concentration of the hydroxyl (OH) or hydro-peroxyl (HO₂) radicals.

Don't ozone, water vapor and sunlight determine the OH concentrations - I would rephrase this to state that OH is central to controlling the trace gas concentrations in the atmosphere.

A certified gas standard mixture containing 100 ppmv of ethane, ethylene, propane and n-butane was used as primary calibration standard and was daily injected with a pressure-lock syringe.

Should read - injected daily...

The chemistry model used to calculate the OH radical levels is a condensed chemical mechanism which, apart from the background O₃/NO_x/OH/CO and CH₄ chemistry, takes also into account the oxidation chemistry of C₁-C₅ NMHCS including isoprene and dimethyl sulphide.

C1 is methane, it is not a NMHC - NMHCs start at C2.

Ethylene and propylene are not IUPAC nomenclature and should be replaced with ethane and propene. It is remarkable to note that n-butane leads to much higher OH levels (almost a factor of 2 higher than the other NMHCS, Figure 3a) which can be explained by its higher kCl/kOH ratio than that of other studied NMHCS (further discussed in section 3.3).

Revise - remarkable is an overstatement; It is worth noting that...

3.3 Estimation of Cl atom levels from NMHCS variability NMHC variability, not NMHCS variability

3.3.1 The evidence of Cl atom presence Revise to something like the following: Evidence for Cl atom chemistry

An examination of i-butane/n-butane ratio versus n-butane levels indicates at a first glance the dominant radical chemistry acting on specific air masses.

Replace “indicates at a first glance” with illustrates

Hydrocarbons variability is interrelated with their reactivity toward OH radicals and Cl atoms through logarithmic approaches outlined here below.

Replace “Hydrocarbons variability...” with “Hydrocarbon variability...”

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 6329, 2007.

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