Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-936-RC2, 2018


Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Non Methane Hydrocarbons variability in Athens during winter-time: The role of traffic and heating" *by* Anastasia Panopoulou et al.

**Anonymous Referee #2**

Received and published: 4 January 2018

The authors present an analysis of a continuous time series for selected C2-C7 NMHCs for a site in Athens, Greece, during wintertime 2015/16 and investigate this data with respect to the contribution of traffic and heating to the observed ambient NMHC levels. They also include speciation of BC data, which is either related to wood burning (BCwb) or fossil fuel combustion (BCff). They also include NO and CO data. While I see the value of this larger online NMHC data set, I am disappointed to see how this data has been presented and analyzed. Unfortunately, there are three major points, which - in my opinion - do not warrant its publication in its current stage in ACP without critical major revisions:



Printer-friendly version

Discussion paper

1) On the background of existing literature I am not sure what the real novelty of this paper in terms of methods and results is. While I agree that C2 and C3 measurements have not yet been done before in Athens, it seems the inclusion of these does not yield more findings than already reported by Kaltsonoudis et al (2016). On the other hand, the Panopoulou et al paper makes same sketchy description of meteorological impacts on NMHCs, but lacks some elaborate analysis similar to those presented in Rappengluck et al (1998) for transport effects and also Kourtidis et al (1999) for temperature effects for Athens. As the authors make an important point on page 2, L27-29, that there have been new conditions during the economic crisis years (i.e. competing traffic vs wood burning emissions) it would be actually meaningful to perform a comparative analysis between the data sets reported 20 years ago and the ones reported by Panopoulou et al. It seems both studies include continuous NMHC measurements and PMF source apportionment analysis would be feasible and would provide interesting insights.

2) It seems that for many statements made in this paper, statements can be made in contrast to the statements made by the authors.

3) Many statements and presentations were made in a negligent way.

Some more detailled review below:

Abstract:

Page 1 L18: "..among the highest in literature for the Mediterranean area..." It should be clarified if this refers to the same season or not. It is known that many primarily emitted pollutants reach higher values in wintertime.

Page 1 L20-21: What do the authors exactly mean by local meteorology, as this term is quite unusual? Its connotation would mean that it is not representative for a larger fetch. I disagree that "local" meteorology would control the variability of NMHC levels alone. What about the temporal variability of NMHC emissions?





Printer-friendly version

Discussion paper

Page 1 L24-25: Why would the fact that NMHCs nicely follow CO hint towards additional sources e.g. heating? This can also be true in the case of traffic emissions. Also, heating is a very general term. For instance electric heating would not emit CO and NMHCs locally (just to name one kind of heating)?

Page 1 L27-29: Why does the present data not allow for the quantification of the relative contribution of fossil fuel and wood burning for heating purposes?

Introduction:

Page 2 L3-4: This is only true for urban areas!

Page 2 L6: replace "Baudic et al., 2016b" by "Baudic et al., 2016".

Page 2 L7: This EEA report is not properly cited in the list of references.

Page 2 L14: The "Cvitas et al paper" should be properly cited as its primary appearance is in a journal.

Page 2 L14: As far as I understand it, the Kourtidis et al paper analysed online NMHC data contrary to what the authors state.

Page 2 L20-21: The term "limited" is not properly chosen, as it seems the range of the NMHC data and the number of NMHCs reported by Panopoulou et al. is also limited. It would be fair to mention the entire C range of those earlier measurements which Panopoulou et al cite in order to properly put them into perspective. Also, it looks to me that those measurements contained significantly more speciated NMHCs, and according to table 1 these earlier NMHC measurements include NMHCs with four C atoms contrary to what the authors state here ("...containing more than four atoms of carbon...").

Page 2, L24: The Saffari et al paper is on the Thessaloniki case, not on the Athens case.

Page 2, L26: Again, as mentioned above the term "limited" is not properly chosen.

The Kaltsonoudis et al paper actually reports VOCs, which are not measured by Panopoulou et al. Also, while it is true that the Athens winter campaign reported by Kaltsonoudis et al was shorter than the one reported by Panopoulou et al, it seems that Kaltsonoudis et al also report a summer campaign for Athens, which the Kaltsonoudis et al paper does not.

Page 2 L30: It would be fair to mention how many NMHCs were actually measured as it seems that the paper does not report some important NMHCs such as 1,3-butadiene and others, for instance.

Page 2 L34 - page 3 L1: The authors should mention why the analysis is restricted towards traffic and heating impact on NMHC levels.

Page 3 L3: Mention those selected tracers explicitly and mention what kind of sources those tracers are tracing.

Sampling site

In general: I suggest to include a map here. Not everyone is familiar with Athens

Page 3, L7: Actually, more important than the altitude above sea level would be the altitude of the hill site above the surrounding area.

Page 3 L9: How far away from the site are the Filopappou and Acropolis hills and how high are those? Again, a map would be helpful. It is not sufficient to refer to other publications here, as it seems the site the authors are talking about is a very specific one.

On line NMHC measurements

Page 3, L7-8: What do the authors mean by " ...was set to sample on a 10 min basis..."? Do they refer to the sampling time or sampling frequency? Is the GC continuously flushed with ambient air?

Page 3, L20: The sampling line has a pretty small diameter, which is very unusual. The

authors should clarify why they chose that small diameter. Also, why did the authors use a stainless-steel sampling line and not a glass line, which will have the least interaction with the sample, in particular when considering this very long line (6 m)? Did the authors check the sampling line for any potential losses of NMHCs, e.g. through looking into any deviations of the C-response? Did the authors make calibrations directly to the GC or through the sampling line? Did the authors use any filter at the sampling inlet?

Page 3, L28-29: Is this uncertainty true for all VOCs? Usually, it would be class specific. What are the detection limits?

Page 3, L30: Same as mentioned above with regard to the sampling line.

Page 4, L5: Why is only toluene used? Why not at least ethylbenzene and the xylenes in addition? Would the exclusion of these NMHCs not introduce a bias into the data analysis, as important tracers for solvent emissions are excluded? What are the uncertainties and the detection limits for this GC?

Auxiliary measurements

In general: The authors also report NO measurements at some point in the paper, but neglect to mention the instrumental description here.

Tunnel measurements

Page 4 L16: The authors should mention the length of the tunnel, whether lanes were for both directions (there could also be dedicated tunnels for one direction only), if there was any artificial ventilation and if there might have been any limitations on traffic through this tunnel (in some cases heavy duty traffic is not allowed). In any case an estimate of the traffic fleet composition (e.g. heavy duty vs light duty vehicles) would be helpful. All these factors have an impact on the NMHCs levels. At what location of the tunnel did the authors make the measurements exactly? I see the measurements were taken on 12 May 2016, which is different from wintertime. Wouldn't the temperature





Printer-friendly version

Discussion paper

be different from wintertime and wouldn't this have an enhanced impact on NMHC emissions through evaporation, for instance?

Page 4 L19: What type of canisters were used?

Page 4 L20-21: Why was it needed to dilute the sample by a factor of two? Why was a Teflon transfer line used? What kind of Teflon in particular? Did the authors check any NMHC artifacts in the canisters and the sampling path (i.e. Teflon line)?

Temporal variability of NMHCs

Page 4 L28: I do not understand the concept of data coverage here, as it is not explained. It could refer to the percentage of data above the detection limit vs maximum available data, but this does not make complete sense, as I doubt there were any data of ethane below the detection limit, for instance. However, it cannot be true either that it refers to the data availability vs maximum potential data availability during the time period reflecting instrumental potential instrumental malfunctions and/or failure. This should be clarified. The only thing I understand is that the there has been some interruption of NMHC data contrary to what the authors claim in the abstract of the paper.

Page 5, L12: Remove the term "worldwide" as Table 1 shows data from the Mediterranean/European area at the most.

Page 5, L15: The authors should clarify why the reader should bear in mind differences in sampling methods and analytical techniques. Are some of the sampling methods and/or analytical techniques and associated results listed suspicious and cannot be compared to each other?

Page 5, L15-18: While I agree that the authors choose Bilbao and Beirut since long-term NMHC measurements were reported for both sites, the authors neglect to describe similarities and differences among those sites in terms of urban size, morphology and climatological conditions.

Page 5, L18-20: The same comment as above applies here. As long as there is no

more elaborated comparison, the presentation of the data remains generic.

Page 5, L21: How much does "significantly" really mean here?

Page 5, L21-22: I am confused about the term "...Cairo rural background area...". It looks like a contradiction to me.

Page 5, L22: It is not clear what the two values of 5.8 and 7.5 ppb refer to. Do they refer to benzene and toluene, or do they refer to benzene (or toluene?) from Athens and Cairo?

Page 5, L25-27: The authors neglect to mention the annual variability of other NMHC sources, e.g. evaporation losses.

Page 5, L27: The authors neglect to mention that "atmospheric dynamics" would not only include PBL variations, but also synoptic meteorology. In many cases this would imply enhanced ventilation during wintertime (e.g. through frontal passages).

Page 5, L29: The authors mention that "...the winter-time decrease of the PBL is in the range of 20%....". Does this value refer to the maximum daily PBL height, an average daily PBL height or to the daytime or nighttime PBL height? This may all make a difference.

Page 5, L30: I think the authors only refer to vertical dilution only, here.

Page 5, L30-31: Those are very generic statements here, as it is well-known that dynamic meteorology plays a major role in the distribution and dilution of atmospheric trace gases and it would be rather surprising that "only one factor" would be important.

Page 6, L3-4: I reiterate my comment made above: Why would the fact that NMHCs nicely follow CO hint towards additional sources e.g. heating? This can also be true in the case of traffic emissions. Also, heating is a very general term. For instance electric heating would not emit CO and NMHCs locally (just to name one kind of heating)?

Page 6, L4-7: From Fig 3 I see that Bff increases similarily to Bwb at night. Why can

the authors make the statement that traffic would not be as important as heating?

Page 6 L9-10: I disagree. Usually, PBL heights are at a minimum during morning hours before sunrise, unless the authors can show other evidences for their statement.

The role of meteorology on NMHC levels

Page 6 L12: Some NMHCs also react with Cl. The latter potentially important for coastal areas. Also, in principle all reactions occur throughout the entire day. It just depends on the availability of reacting compounds.

Page 6 L15-20: This is a pretty generic description. It is well-known that the concentration of primarily emitted gaseous pollutants will decrease due to dilution regardless of their chemical class. However, windspeeds < 3 m/s alone would not indicate the presence of local sources. This would only be true for calm winds. From the plots it seems like these are skewed distributions with maximum concentration values around 2 m/s or so. This would rather indicate some regional flow impacts, which the authors neglected to consider. It seems a more elaborate analysis of windspeeds and their effect on NMHC levels in the Athens area has already been presented in Rappengluck et al (1998). With regard to potential long-range transport it is actually interesting to see that there is some acetylene data still around 5 ppb or so at windspeeds around 9 m/s and higher. In fact, those are very high acetylene values despite strong dilution. What is the reason for this?

Page 6 L21-22: In Fig 5a it is quite surprising to see that the minimum occurrence (north; 1% occurence) is just side-by-side with the maximum occurrence (northeast; I would guess 27% occurence). What is the reason for this quite unusual wind direction occurrence distribution?

Page 6 L24-29: Large part of the discussion here contradicts the authors' statement on the dependence of NMHC on windspeed made earlier. For instance, it looks to me that strongest wind speeds (e.g. NE) would not necessarily be associated with

lowest concentrations, while lowest wind speeds (e.g. SE) would not necessarily be associated with highest concentrations.

Page 6, L29: Those sources cannot be defined as local sources any more, as they are not located in the immediate vicinity of the Thissio site.

Page 6, L30-32: I do not understand this sentence. On the one hand the authors mention increased number of fireplaces, on the other hand the authors mention central heating systems (wouldn't central heating systems decrease the number of individual fireplaces?). Also, the authors state that the higher NMHC values to the N sector is due to the age of the buildings. Isn't another (potentially more) important factor that a higher fraction of Athens' population may be located north of Thissio than towards other directions? Also, wouldn't southerly winds bring in cleaner marine air, making the S-N difference in the NMHC concentration not even more drastic? If the authors want to point out heating sources, wouldn't it make sense to distinguish between day- and nighttime?

Page 7, L4: What biogenic compounds are not triggered by temperature?

Identification of NMHC emission sources

Page 7, L28: Remove "locally", as dispersion acts on all airborne compounds and is not confined to locally emitted pollutants.

Page 8, L8: Mention the NMHC tracers for wood burning exactly.

Page 8, L28-30: Did the authors also apply the baseline subtraction for the tunnel measurements?

Page 8, L30-31: How can the authors justify that their tunnel measurements are not influenced by outside air masses?

Page 8, L31-32: I completely disagree on the authors' statement. The authors neglect to mention what they consider "dominant species", however just looking into NMHCs

such as acetylene, benzene, and toluene, the two profiles "Morning Peak Athens" and "Highway Tunnel - Athens" are completely different: while acetylene for the "Morning Peak Athens" is about 6-7 times higher than for the case "Highway Tunnel - Athens", benzene and toluene values are about 2-3 times lower at the same time.

Page 8, L32 - Page 9, L1: I disagree here again! I do not see that profiles fit nicely. Instead, there are a lot of significant differences. Also, what do the authors consider "common NMHCs"?

Page 8, L1-3: Why should there be higher traffic related butane fraction due to evaporation in ambient air than in the tunnel? Even more surprising, as the tunnel measurements were taken in May, which presumably has warmer temperatures than wintertime. Also, when butanes should be related to evaporation why does propane, another prominent tracer for evaporation, show pretty similar values in the tunnel measurements compared to the "Morning Peak Athens" data?

Page 8, L7: "...during both months...". I disagree with this statement, as only results from two selected days are shown.

Page 8, L8-10: If this justification is true for ethylene, why would it be different for i-pentane? Still, photochemical decay should also be more active for i-pentane in October than in December. However, i-pentane shows a lower slope in December than in October contrary to ethylene. Also, could a difference in solar radiation energy in October vs December in the 7:00-10:00 LT time frame explain an increase in the slope of ethylene by about 60%?

Page 8, L12-14: The definition of the background concentration appears odd. How can the minimum value between 12:00-17:00LT be representative for the nighttime period 18:00-05:00LT? Both are pretty long periods (5 and 11 hours, respectively). From Figs. 4 and 5 we learnt that the NMHC concentration critically depends on wind speed and wind direction. How can the authors make sure that such changes in wind speed and/or wind direction would neither occur during the daytime reference period nor during the





Printer-friendly version

Discussion paper

nighttime period?

Page 8, L16-19: Are these differences statistically significant?

Page 10, L9-10: Not sure, how the authors know that BCff at night is due to fossil fuel heating only, and not also impacted by traffic.

Page 10, L13: What were those "different meteorological profiles"?

Page 10, L14-16: This is not supported by the data presented in the paper!

Page 10, L19-20: There are already 4 months of continuous NHMC measurement available. Why is there a longer data set needed to distinguish different source types?

Table 1: Remove the term "worldwide" in the table caption, as Table 1 shows a few selected data from the Mediterranean/European area at the most. What does the second sentence of the table caption refer to? What quantities are compared in this table: means or medians or ....? What do the authors mean by "sampling" frequency: sampling duration or measurement cycle? There is no information given for "sampling frequency" for Baudic et al., Salameh et al., and Durana et al.. Why are the results for the summer 2012 and winter 2013 Athens campaigns reported by Kaltsonoudis et al (2016) not listed in this table? At least, results for isoprene, benzene, and toluene would be comparable.

Figure 1: There is a quite unusual long-term baseline increase of acetylene starting about 1 ppb at the end of November until early January, when it reaches a bit more than 5 ppb (which is pretty high for an urban background site!). Then it abruptly decreases. This feature is not seen in other NMHCs shown in this plot. What is driving (a) this continuous increase and (b) its abrupt decrease?

Figure 2: Why is the mean and not the median shown, as Fig 1 clearly shows that NMHC data is not normally distributed?

Figure 3: Is the data shown based on mean or median hourly averaged values? It

should be median values.

Figure 4: The figure should be better shown with Box-Whisker plots for designated windspeed classes, as the data cloud in Figure 4 could be misleading, as the number of overlapping data points might differ significantly.

Figure 5: What quantity for the NMHC data is shown: mean or median data? Standard deviation bars should be included.

Figure 8: Error bars should be included.

Figure 10, figure caption: I disagree that such a long time period (18:00-05:00 LT; 11 hours!) can be considered a nighttime "peak". Error bars should be included. I do not see that the values shown in the figure add up to 100%.

---

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936, 2017.



Printer-friendly version

Discussion paper