

**The authors want to thank both the editor and the reviewer for their helpful comments. All these comments have been considered in the revised version and below a point by point answer is presented. To facilitate their reading we decided to first summarize the main and significant changes performed in the new manuscript, before presenting the answers to the reviewer.**

### **Changes in the new manuscript**

- 10 On the new version of the manuscript the following major changes were performed according to the remarks of the reviewer and the editor:
- Our dataset was compared to previously reported values for the area not only arithmetically (as in the submitted version), but also by means of the emission ratios calculated using the same procedure presented in the work of Kourtidis et al., (1999), performed almost 20 years ago at the same street canyon (Patission). The comparison depicted evidence of changes on the emissions sources over time. To sum up, we use the same tools as the previous (and past) publications with VOC measurements in the same area of Athens.
  - Furthermore, an extra comparatively study with the past findings is made in the new version of the Supplement. We recall that in order to address the concerns of the reviewer about evaporative losses, we examined the ratio of Butanes-to-(C2 – C5)Alkanes (%) and Pentanes-to-(C2 – C5)Alkanes (%) relatively to temperature at the previously submitted version (as an answer in his/her 1st peer-review). Now, in the new version of the manuscript and the supplement, we complete the previous investigation by following the same methodology as in Kourtidis et al. (1999), thus we additionally examined the relationship of the normalized to OH reaction ratio of NMHC/benzene for the 15:00 and 07:00 to the boiling point of the selected NMHCs (as an answer to the updated suggestions of the reviewer to his/her 2nd peer-review). The latter is compared to the observations in Kourtidis et al. (1999).
  - The tunnel part was transferred to the Supplement and corrections on Figure 9 (comparison of morning profiles) were accordingly made. In addition, following his/her suggestions we added in the profile (Figure 9) results on xylenes and ethylbenzene. The reasons that could possibly lead to the differences between the tunnel and street canyon observations were already explained at the previous version and still exist at the supplementary material justifying our findings and our choice to maintain the tunnel part on our study.
- 30 In addition, we would like to point out (as indicated from the title and from the introduction) that the objective of this work is not VOC source apportionment in Athens, but the investigation of the contribution of traffic and heating to the observed levels.

## Answers to reviewer

5

We would like to thank the reviewer for his/her comments which help us to improve the submitted version. Below is a point by point reply to the comments. Changes on the manuscript (discussed on the authors reply) are indicated with italics. Furthermore, minor grammar and typo corrections were done on the manuscript on behalf of the authors.

10

The authors made considerable efforts to modify the paper. However, unfortunately, there are still multiple issues which have not been addressed in a satisfactory way. Still, the current state of the paper and the replies made by the authors do not warrant the publication of the paper in its current stage in ACP without additional discussion. Here I repeat those issues, which I believe need some additional clarification. First I list my initial review point, then I add my updated remark, denoted as "Reviewer Remark":

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.

### **Reviewer Remark:**

In their reply the authors did not really demonstrate the novelty of their work apart from the fact their measurements include C2-C3 data. However, including these NMHCs did not yield new knowledge about NMHC sources in Athens beyond the paper by Kaltsonoudis et al (2016). Kaltsonoudis et al (2016) even included detailed source apportionment for traffic and biomass burning for the Athens case, which the authors did not apply and did not address. What do we learn from this paper which has not yet been described earlier. Even worse, now the authors have removed the reference to Kourtidis et al (1999) who described temperature effects on traffic NMHCs emissions for the same city.

The authors argue: "However direct comparison with the work performed 20 years ago is difficult considering differences in sampling period (summer versus winter and thus different photochemistry), location, sampling method and analytical techniques." I cannot completely follow this argument. Emission studies can be done for nighttime periods minimizing photochemical effects, all the locations are within the GAA and sampling methods and analytical methods are similar. Even, if the suite of NMHCs may not be exactly the same, the application of source apportionment methods such as PMF would just require a few representative NMHC describing source profiles. There is not necessarily a "complete" suite of NMHCs necessary as it is also shown by the Kaltsonoudis et al (2016) paper, who applied a rather limited VOC dataset. Did the authors try at all to make comparisons? Again, in my opinion this would be feasible and would provide interesting insights.

10 ***Authors Reply:***

We would like to thank the reviewer for his/her comments and explanation. Here is a point-by-point answer to the previous statements:

- 15 a) The authors demonstrated clearly in the introduction the novelty of this work. This work report levels of C2 – C6 NMHC (mainly) in Athens for winter. These levels for winter (or cold) season were never reported again in the literature, with only two exceptions. Indeed, Kaltsonoudis et al., (2016) report winter levels of isoprene, benzene, toluene, xylenes and monoterpenes (C5 – C8 NMHC), however it is apparent that the only common species between that work and ours are isoprene and benzene (although there are references for toluene, ethylbenzene and o- / m- / p- xylenes in the new manuscript). Concerning previous ground-based measurements in Athens that were conducted more than 20 years ago, we have to take into account three facts: 1) they, indeed, report levels of C4 – C12 NMHC, which is a greater number of compounds compared to this work (however, it is already mentioned that there are no measurements of C2 and only one work for C3 NMHC), 2) the majority of these measurements were conducted in summer, in which the meteorology and dynamics are different from winter and 3) it was demonstrated in the introduction that between 20 years ago and today, changes in pollutant sources occurred in Athens, as a result of the environmental protection strategies that were employed for the emissions control. Consequently, there is missing information for C2 – C6 NMHC in Athens that reflects the current situation, while there is no information about these species for winter (with the exception of isoprene and benzene). In addition, in Athens a new source of pollutants arose, i.e. wood burning for residential heating in winter. From the literature we know that this source contributes more to light NMHC than heavier, so our work is trying to provide an insight of the contribution of this source to the observed levels.
- 25
- 30 b) The authors still argue that direct comparison with the works performed 20 years ago is difficult considering differences in sampling period (summer versus winter and thus different photochemistry), location, sampling method and analytical techniques (or analytical resolution to be more precise). Nevertheless, they do agree that a comparison of emission ratios between the past and today is possible. Consequently, in the new manuscript a paragraph with comparison of enhancement ratios for Thissio and Patisision station is now included.

c) The authors have indicated already from the title that the objective of this work is not VOC source apportionment in Athens, but the investigation of the contribution of traffic and heating to the observed levels. Consequently, the statement of the reviewer that "...including these NMHCs did not yield new knowledge about NMHC sources in Athens beyond the paper by Kaltsonoudis et al (2016)" is contradicting because, as it was mention previously, this paper is not dedicated to source apportionment and in addition, Kaltsonoudis et al (2016) did not include 9 out of the 11 NMHC that are reported in the current work. Thus, our work is yielding new knowledge for the two main NMHC **current** sources in Athens (traffic and heating), that is our focus.

d) The authors believe that the current state of the analysis of the measurements and the results are serving the goal of the paper and no PMF is needed. Based on their experience on PMF analysis, the authors are convinced that such an approach requires more species and a longer period in order to get more variability and contrast between factors (sources). Concerning the winter-time period under investigation, a more complete dataset is available only for a month. A PMF analysis would result in more than 2 factors, which would be certainly difficult to interpret due to a lack of robustness. That's why our current strategy is to focus first on these two wintertime sources (traffic and domestic heating) using specific ratios and additional tracers (e.g. BC wood burning and fossil fuel fractions) and in a second step in the near future to perform such PMF analysis using a one-year dataset.

Concerning the statement for the PMF that "Even, if the suite of NMHCs may not be exactly the same, the application of source apportionment methods such as PMF would just require a few representative NMHC describing source profiles. There is not necessarily a "complete" suite of NMHCs necessary as it is also shown by the Kaltsonoudis et al (2016) paper, who applied a rather limited VOC dataset", we would like to address here the "PMF overview" of the paper in question, Kaltsonoudis et al (2016), paragraph 5.4, page 14839: "In the present study the PMF analysis did not result in such separations since the VOC portfolio did not include light alkanes, which are usually included in datasets obtained by gas chromatographic (GC) techniques. The vehicular exhaust and LPG sources widely reported in the literature include a large fraction of these species; thus, such a separation was not favored by the PMF analysis.". Although in the current work are reported light alkanes, as we demonstrated before, we don't believe that a PMF analysis is suitable for the objectives of this paper.

**Abstract:**

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?

**Reviewer Remark:**

In general, the term microscale meteorology is fine. However, still this would rather describe specific condition for mixing processes observed at a given site, which may not necessarily be similar for a different location within the urban area. For instance, the built environment would have a significant impact on these exchange processes.

- 5 In addition, what about PBL variations, which are not included in the term microscale meteorology? Also, still I believe, that the temporal variability of NMHC emissions is an important factor. Just one example: a typical morning rush hour peak is not entirely explained by low winds that are often observed during the same time frame. I would believe that low a PBL height and increased traffic emission would be an important factor. I would still doubt that "Microscale meteorological conditions and especially wind speed seems to **control** the variability of NMHC levels...".

10

**Authors Reply:**

In general, we agree that depending on the location of the sampling station, the built environment could play a significant role to the observations. However, in our case, the station is situated on a hill, away from buildings and dense built environment and since the remark refers to the abstract we avoid clarifying further the microscale conditions. Nevertheless, given the structure of the current manuscript, we decided that this information could be included in Sect. 3.1 page 6 line 12 as follows: "...*Apart changes in emission sources and source strength during the last twenty years, differences in sampling period (summer versus winter), location and built environment (kerbside versus urban background), analytical resolution...*".

- 15 Furthermore, the role of PBL was not underestimated in the manuscript. In page 7 lines 14-18 there is a reference discussing the role of the diurnal variability of PBL that could trigger the observed winter-time enhancement of the NMHC levels. Furthermore, according to Kassomenos et al. (1995) the day-night difference on PBL is more pronounced during summer compared to winter, supported also by the recent work of Alexiou et al. (2018). Thus, the night-time accumulation of the pollutants during the winter months highlights essentially the impact of additional emission sources. This statement is added on the manuscript (page 7, lines 18 - 20) and the following additional comment about the PBL is also now included on the abstract (page 1, line 20 – 23) regarding its role synergistically to the wind speed impact on the winter-time enhancement of NMHCs levels: '*Microscale meteorological conditions and especially wind speed in combination with the PBL height, seem to contribute significantly on the variability of NMHC levels, with an increase up to a factor of 10 under low wind speed ( $<3 \text{ m s}^{-1}$ ), reflecting the impact of local sources rather than long range transport*'.

30

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?

**Reviewer Remark:**

Still, I have some trouble with the revised sentence. On one side the authors state that "For the night peak, the selected tracers and profiles clearly indicate contribution from both traffic and domestic heating..." and then continue that more specific tracers would be necessary for quantification of these sources. The latter statement contradicts the first statement: either the data set has tracers and profiles that clearly indicate these specific sources or not. Also, the authors emphasize the night peak. This implies that daytime emissions would be different. I would assume that domestic heating sources would become less, while traffic sources would increase and it seems the authors can differentiate this different behaviour in their data-set. Why would, for instance, a source apportionment method based on these specific tracers and profiles not be able to estimate relative source contributions?

10 ***Authors Reply:***

We disagree with the reviewer on his/her comment that the two above mentioned sentences contradict each other. We claim that the data set used and the selected tracers clearly indicate the presence of two different sources during night but we cannot accurately quantify the role of each. In other words, it is a question of quantification and not qualification. The diurnal variability of  $BC_{ff}$  and  $BC_{wb}$  clearly corroborate our hypothesis. However, to avoid any misunderstanding we removed the sentence indicated by the reviewer "However, the present data-set does not allow for quantification of each source due to the similarity of emissions, thus measurements of more specific tracers are needed for the better understanding of the contribution of these nocturnal VOC sources". We replace it by "*NMHCs slopes versus  $BC_{wb}$  are almost similar when compared to those versus  $BC_{ff}$  (slight difference for ethylene), indicating that NMHCs are probably equally produced by wood and oil fossil fuel burning*" (page 1, lines 30-31) which is in line with the similar levels of  $BC_{ff}$  and  $BC_{wb}$  observed during night. Nevertheless, the quantification of each emission source is not possible by means of the specific methodology.

25 **Introduction:**

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.

**Reviewer Remark:**

30 The reply given by the authors is not convincing. Still, it would be fair to mention the number of NMHCs measured in this range and the number of NMHCs in this range used in this study in order to make a precise statement here and avoid any speculation.

***Authors Reply:***

The text was corrected accordingly in page 3 lines 14-17: 'The current study presents, time-resolved data of 11 selected from 15 determined NMHCs with two to six carbon atoms, during a time span of several months (October 2015 to mid-February 2016) in the Great Athens Area (GAA). In addition, time-resolved data of toluene, ethylbenzene, m- /p- xylenes and o-xylene are used, which were monitored simultaneously from mid-January to mid-February 2016.'

5

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

**Reviewer Remark:**

10 There is still an issue: in order to perform an "...investigation of traffic and residential heating impact on the NMHC levels..." the authors would still need to verify and quantify any other potential NMHC source, regardless of its magnitude. Even, if there are no industrial sources as the authors point out, I still would think there are solvent and evaporative sources. Also, what about the port of Athens?

Otherwise, I am not sure what still needs to be investigated exactly for this task (3).

15

**Authors Reply:**

Great changes in Athens VOCs sources occurred the last 20 years such as significant decrease in industrial emissions around Athens (the 2 power plants were decommissioned), renewal of the cars fleet and since 2013 industrial activities were significantly reduced due to economic recession. Our suggestion for the existence of two main sources namely traffic and heating is in line with Kaltsonoudis et al (2016) who reported that wood burning and traffic consist the main winter-time emission sources in Athens, whereas the industrial impact is low. Regarding the reviewer suggestion to tackle the evaporative sources note that the *Section S.3. Investigation of the evaporation losses* of the manuscript was already presenting an approach for the investigation of the evaporation losses based on the ratio Butanes-to-(C2 – C5)Alkanes (%) and Pentanes-to-(C2 – C5)Alkanes (%) versus the temperature. For both cases low evaporation occurs under low temperatures, which is the winter case. The relationship of temperature and evaporation emission in Athens was previously investigated by Kourtidis et al (1999). Thus, in order to compare our findings with this past report, in the revised supplement (*Section S.3. Investigation of the evaporation losses*) a new graph based on the approach described in Kourtidis et al. (1999) is included. Finally, activities in the harbor are much linked to touristic activities and recreation which is significantly reduced in winter and the biggest part is related to traffic of heavy trucks for loading and unloading.

30 Nevertheless, since the remark concerns part of the introduction, there is no reason to justify in this sentence our choice to further investigate these two sources. Moreover, in the paragraph 3.4.3 of the Sect. 3 "*Results and Discussion*", we have demonstrated that we investigate specific SP samples (meaning certain hours) for the morning peak and the night-time enhancement period so (1) SP periods reflect the impact of local sources rather than long range transport and (2) based on the analysis and comparison with other pollutants, we can assume that we have minimal contribution of other sources than

traffic and heating. However, in order to better clarify our intentions, we decided to change the title of the paragraph 3.4 (page 9 line 1) from “*Identification of NMHC emission sources*” to “*Identification of NMHC emission sources with emphasis on traffic and heating*”.

5

#### **On line NMHC measurements**

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?

#### **Reviewer Remark:**

This appears cherry-picking to me. The authors state that they focus on C2-C6 NMHCs, then include a C7 compound from a different instrument, but exclude other NMHCs from that different instrument. The authors did not address my question whether the exclusion of these other NMHCs would introduce a bias in the data analysis. As the authors have a complete suite of NMHC measurements, it would be straight forward to include all NMHCs, and make a source apportionment analysis first, and not rely on a reference only (Vrekoussis et al., 2013), which did not include VOCs.

#### **Authors Reply:**

In order to better address the concerns of the reviewer, in the morning profile ethylbenzene and o-m-p xylenes are now additionally included in order to eliminate the bias into the data analysis. In the new figure 9 (morning profile) we observe the important contribution of the m/p – xylenes, however the general image of the profile didn’t change. Thus, Figure 9 is corrected as follows on the manuscript:



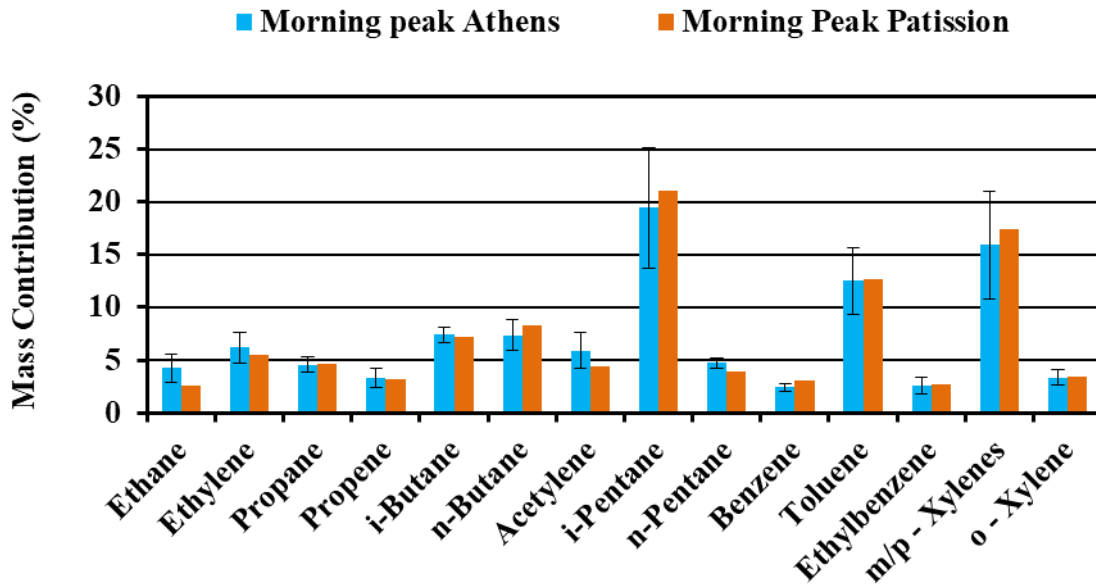


Figure 9. %Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00LT), median values in Thissio and mean values in Patission Monitoring Station.

5 The old figure 9 is transferred on the Supplement:

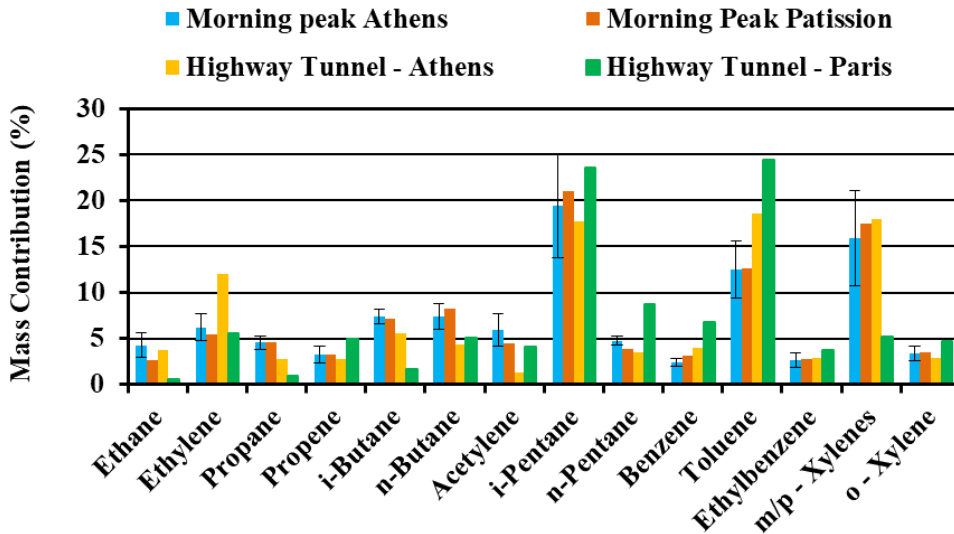


Figure 9. % Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00 LT), median values in Thissio, mean values in Patission Monitoring Station, in a highway tunnel in GAA and a highway tunnel close to Paris.

Moreover, as it was already mentioned in the previous comment (for Page 2 L34 - page 3 L1) (1) PMF source apportionment is not an objective of this paper and (2) the chosen samples of the analysis are unlikely to be influenced by other sources than traffic and heating.

- 5 Furthermore, the reference to Vrekoussis et al., (2013) concerns the reduction on the industrial activity and is not connected with emission sources since it is used in order to support the scope of the study.

### **Tunnel measurements**

10

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

#### **Reviewer Remark:**

It seems the description of the tunnel is still missing in the manuscript. Also, the authors did not mention explicitly whether  
20 this tunnel contains all lanes for both driving directions or whether there were separated compartments for each driving direction. They did not mention either, whether there was any artificial ventilation or not.

#### **Authors Reply:**

The authors decided to transfer the tunnel measurements (experimental and figures) to the supplement in Sect. S.2a.  
25 Furthermore, in the description of the tunnel (now in the supplement) the additional information is added in page 12, lines 20 - 21 as follows: "*Each driving direction consist a separated compartment and a ventilation system was installed but not operated*".

### **30 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 there has been some interruption of NMHC data contrary to what the authors claim in the abstract of the paper.

**Reviewer Remark:**

- 5 The authors statement of 87% data availability would imply that the instrument did not work uninterrupted (again, I believe that such a species like ethane would always be above the detection limit, if the instrument is working properly). As a consequence I would recommend to replace the statement made in the abstract of the paper (page 1, L16) "...to our knowledge, time resolved, uninterrupted data of NMHCs..." by "...to our knowledge, time resolved data of NMHCs..."

10 **Authors Reply:**

We followed his/her suggestion and now in page 1, line 16 reads as follows: "*The current work presents, for the first time to our knowledge, time resolved data of NMHCs, from two to six carbon atoms.*".

- 15 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?

**Reviewer Remark:**

- 20 The authors did not change much. The authors still state that "...this decrease has to be seen with cautious considering differences in [...] sampling method 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?

**Authors Reply:**

- 25 The analytical techniques used in the past were reliable and all results are totally comparable in technical basis. Our statement about the techniques was mainly related to the sampling frequency and it is corrected to avoid any misunderstanding. Nevertheless, there are differences between the past and the current conditions that should be stated in order to be consistent with parameters could drive the observed changes. Measurements during cold or warm period definitely determine the levels of NMHCs due to changes on emission sources strength, dilution processes or photochemical rate. The levels of traffic related compounds on samples collected close to major street canyon could also be differentiated
- 30 by those in further distance. In the work of Moschonas and Glavas, (1996) performed close to our sampling site, the samples (n = 12) were collected during morning in summer, thus the comparison with the current results considering periods including the total day fraction could result into discrepancies. One more important parameter that should be taken into consideration is the reduction of the industrial activity in Athens and the close located areas during the last decade; and the increase of wood burning after 2012 as a consequence of the financial recession. Both processes and other antipollution

practices applied the last years as well, are clearly expected to differentiate the emissions into the atmosphere and possibly change the pollution profile in GAA. However, as it is already mentioned before, the authors agree with the reviewer for a comparison of emission ratios between past measurements and current results.

To summarize all the above, the authors firstly change the statement in question as follows (page 6, lines 10 - 16): *“This decreasing trend is in agreement with a decrease in primary pollutants CO, SO<sub>2</sub> already reported by Kalabokas et al. (1999) and Gratsea et al. (2017), due to the air quality measures taken by the Greek government and economic recession (since 2012). Apart changes in emission sources and source strength during the last twenty years, differences in sampling period (summer versus winter), location and built environment (kerbside versus urban background), analytical resolution (morning collected samples compared to continuously averaged levels) should be considered rendering the direct comparison between the present and past measurements quite difficult in the overall evaluation of the NMHCs decrease’.*

Secondly, investigation of enhancement ratios NMHC-to-NO<sub>x</sub> and NMHC-to-CO according to the methodology introduced by Kourtidis et al., (1999) was also included in the revised version. For the comparison with the NMHC-to-NO<sub>x</sub> enhancement ratios reported in Kourtidis et al., (1999), the weight/weight (w/w) ratios were re-converted in ppb/ppb ratios by dividing them with the ratio of the molecular weight of the NMHC to the molecular weight of NO<sub>x</sub> equal to 31.6. Thus, in the new manuscript the following paragraph in Sect. 3.1 page 6 line 16 will be added: *“However, in order to better investigate the observed decreasing trend and compare these results to past measurements, enhancement ratios are calculated for i – pentane, benzene, toluene, ethylbenzene and o – xylene to NO<sub>x</sub> (sum of NO and NO<sub>2</sub>), following the approach of Kourtidis et al., (1999) from the measurements performed in the street canyon (Patission) and presented at Table 2. In a summary, the enhancement ratios are the slopes of the x-y plots of the selected NMHC (in ppb) to NO<sub>x</sub> (or CO, both in ppb), and for which morning concentrations (07:00 to 10:00 LT) at wind speed lower than 2 m s<sup>-1</sup> and of SSW to SWW direction (206° to 237°) are used. The NO<sub>x</sub> and CO data for the Patission site are provided by the Hellenic Ministry of the Environment & Energy, Dept. of Air Quality. Additionally, the same enhancement ratios were calculated for Thissio station, for concentrations associated with wind speed lower than 2 m s<sup>-1</sup> (no distinction to wind direction), thus maximizing the local influence. Since the enhancement ratios are calculated during the time-window of the traffic rush hours, it is assumed that they are representatives of traffic emissions only. Both Thissio station and Patission street canyon demonstrate similar enhancement ratios with differences in the order of 15-30% and 20-35% relatively to NO<sub>x</sub> and CO respectively and great differences comparatively to the previously reported values. Enhancement ratios for i-pentane, toluene, ethylbenzene and o-xylene to NO<sub>x</sub> for the same station (Patission) show values which are lower by a factor of  $6 \pm 1$  compared to the ones reported in Kourtidis et al. (1999), whereas a factor of 12 is observed for benzene. The same stands for the present enhancement ratios of the selected NMHCs to CO with a decrease of 2 to 5 times. The lower enhancement ratios reveal the strong impact of the air quality measures to VOC emissions, while the high difference to benzene enhancement ratio is a direct outcome of the Directive n°2000/69/CE (now Directive n°2008/50/EC) of the European Union for the reduction of this compound, especially in fuels”.*

**Table 2:** Enhancement ratios of NMHC to NOx (ppb/ppb) and to CO (ppb/ppb), calculated from the present data-set for Thissio Station and the Street canyon measurements (Patisson station) for the time-window of the traffic rush hours. The enhancement ratios presented in the 3rd and 6th column are reported in Kourtidis et al., (1999) and they were calculated for the same station in the street canyon.

Ratios of NMHCs to:	NOx (ppb/ppb)			CO (ppb/ppb)		
	Thissio station (urban background)	Patisson station (traffic)	Patisson station (traffic), 1994*	Thissio station (urban background)	Patisson station (traffic)	Patisson station (traffic), 1994
	21 January - 15 February 2016	23 - 24 February 2017	20 August - 20 September 1994	21 January - 15 February 2016	23 - 24 February 2017	20 August - 20 September 1994
<b>i - Pentane</b>	0.0639	0.0490	0.2468	0.0072	0.0058	0.0098
<b>Benzene</b>	0.0095	0.0083	0.1042	0.0012	0.0009	0.00414
<b>Toluene</b>	0.0417	0.0320	0.1799	0.0056	0.0034	0.00715
<b>Ethylbenzene</b>	0.0073	0.0053	0.0338			
<b>o - Xylene</b>	0.0082	0.0059	0.0471			

5 \* The NMHC-to-NOx enhancement ratios given in w/w (weight/weight) were converted in ppb/ppb by dividing them with the ratio of the molecular weight of the NMHC to the molecular weight of NOx (equal to 31.6 according to Kourtidis et al., 1999).

10

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.

**Reviewer Remark:**

15 Why would it be important to note that Paris is located at the mid-latitude and in the northern hemisphere with regard to NMHC emissions? Would it be different for city at the same latitude, but in the southern hemisphere? For instance, would traffic emissions depend on the latitude?

There is not such a thing as oceanic continental climate; this does not exist! Apart from that the climate of Paris is definitely not continental! There are no cold winters in Paris! Also, in Paris, it can be pretty hot during summer time, which cannot be

considered "mild". I would rather use that term for the winter period in Paris. The authors want to check an appropriate climate description for Paris.

***Authors Reply:***

- 5 We thank the reviewer for the comment and we corrected the phrase as follows (page 7 line 7-9), since the emissions are not latitude depended: *“NMHC levels are also compared with those obtained in Paris, one of the European megacities, with more than 10 million inhabitants with relatively mild winters and warm summers. Again, the observed levels in Athens are significantly higher compared to those reported for Paris (Baudic et al., 2016).*

10

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

**Reviewer Remark:**

- 15 With regard to traffic related evaporative NMHC emissions the authors need to consider the work by Kourtidis et al. (1999) who specifically addressed the processes related to these emissions for the same city, Athens. The NMHC mixture might have changed, but not the underlying processes. Unfortunately, the authors removed this reference from the previous manuscript version.

***Authors Reply:***

- 20 The reference of Kourtidis et al. 1999 was erroneously removed from the revised version and now was included again. More specifically, to compare our observations for the relationship between temperature and VOC emissions from fuel evaporation with those of Kourtidis et al. (1999), we now included in the supplement a new graph presenting the ratio of NMHC/benzene for the 15:00 and 07:00 (normalized to the OH reaction) to the boiling point of the selected NMHC, following the approach described in Kourtidis et al (1999). Accordingly, in the manuscript page 11 line 13-17 was modified as follows: *“These*  
25 *observations are in agreement with the general behavior of the temperature dependency reported in Kourtidis et al., (1999) (Fig. S13 and Sect. S3), that performed an investigation of the dependence of the fractionation of NMHCs in evaporative emissions from temperature in Athens. Although the examined periods differ in ambient temperature (winter is colder than autumn), the exponential curve fitting of both datasets was similar.”*

- 30 The new figure for the supplement:

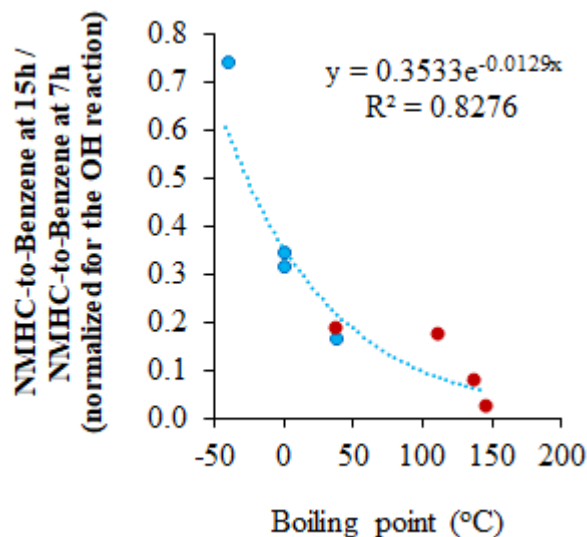


Figure S13. Ratios of the NMHC/benzene ratio for 15:00 (higher daily temperature) and 07:00 (lower daily temperature) to the boiling points of the selected NMHC, divided by the reaction rate constant of each species with OH. The plotted NMHC are propane, i-/n-butane, i-/n-pentane, toluene, ethylbenzene and o-xylene. The red cycles indicate compounds (not values) in common with the work of Kourtidis et al., (1999).

Page 6, L4-7: From Fig 3 I see that  $B_{ff}$  increases similarly to  $B_{wb}$  at night. Why can the authors make the statement that traffic would not be as important as heating?

10 **Reviewer Remark:**

The authors do not consider the nighttime variation of the PBL which would also contribute to a sustained higher level of pollutants, regardless of their origin.

**Authors Reply:**

15 From figure 4 it is obvious that  $BC_{ff}$  during the months with residential heating (November to February) is similar to  $BC_{wb}$ . Taking into account that  $BC_{ff}$  originates from both heating using fuel and traffic and that during October traffic contributes almost 50% of the  $BC_{ff}$  observed during the months with heating activities (November to February) one could deduce that heating from both fuel and wood burning is more important compared to the traffic. Regarding the reviewer comment on the role of PBL on NMHCs variability information is now added (page 7 line 30-32) 'Moreover, night-time emissions occur in a shallower boundary layer relatively to the mid-day, resulting into accumulation of pollutants (Alexiou et al., 2018).'

20

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.

**Reviewer Remark:**

I did not see the change the authors may have done in the text (mentioning the line would be helpful).

5

**Authors Reply:**

The statement for a higher morning PBL relatively to the night-time concerns the period after the sunrise, i.e around mid-day and morning was replaced by mid-day'. During the preparation of the second version of the manuscript the paragraph 3.2 *Diurnal variability of NMHCs* was rearranged and the PBL comment was removed. We add the comment again with the proper correction '*Moreover, night-time emissions occur in a shallower boundary layer relatively to the mid-day, resulting into accumulation of pollutants (Alexiou et al., 2018).*' in page 7 line 30-32.

10

15 **The role of meteorology on NMHC levels**

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.

20

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).

25

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?

**Reviewer Remark:**

As the x-axis of figure 5 shows discrete values, it would be good to have a clear definition of these ranges. Also, are calm wind situations considered, i.e. below the threshold of the wind sensor (both, in figures 5 and 6)?

30

**Authors Reply:** All wind speed values above the threshold of wind sensor are used on Figures 5 and 6. The lower monitored value is 0.4m/s. The x-axis is properly adjusted in order to depict the range of each bin as also noted in the figure caption.



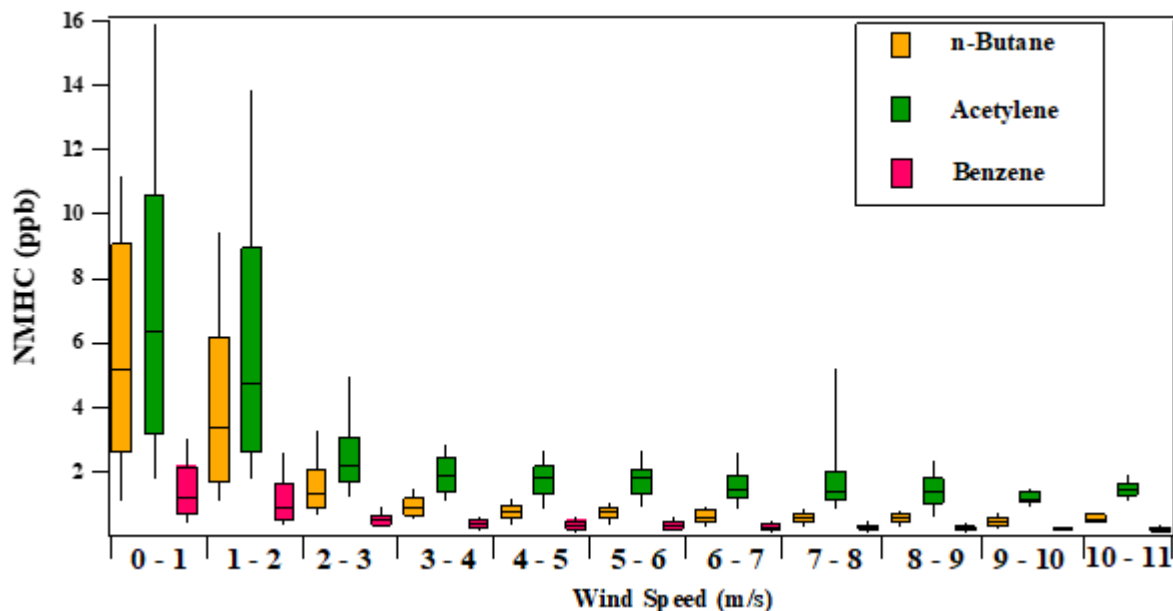


Figure 5. Boxplots for (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the period 16 October 2015 - 15 February 2016. The black line represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1<sup>st</sup> and 3<sup>rd</sup> quartiles (i. e. Q1 and Q3). The whiskers correspond to the 1<sup>st</sup> and the 9<sup>th</sup> deciles (i. e. D1 and D9). The range of each wind speed bin is depicted on x-axis.

#### Identification of NMHC emission sources

10

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

#### Reviewer Remark:

The authors should mention this limitation in the text.

15 *Authors Reply:*

Our reply is now mentioned in Sect. S.2a page 13 line 11-12 of the Supplement: '*Due to the small number of samples a baseline subtraction from the tunnel data was not possible*'.

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

#### Reviewer Remark:

There must be some dilution. A tunnel is not a closed box and it seems the length of the tunnel is only 200 m.

***Authors Reply:***

5 We agree with the reviewer on the potential dilution, especially for such a short tunnel and for that reason, the sampling was conducted in the middle of the tunnel in order to eliminate any transfer of air from the ambient environment. We have already justified our choice in Sect. S.2a page 12, line 21-22.

10 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.

**Reviewer Remark:**

15 I agree that the "Morning Peak Thissio" and "Morning Peak Patisson" profiles agree with each other within the uncertainties. Still their comparison with the tunnel measurements and both tunnel measurements among themselves are very different. The authors themselves make a reference to various papers which report important differences between tunnel measurements worldwide and also state that there is a possibility that the car-fleet in the tunnel is not representative for the GAA. Why then compare two consistent real-world street canyon measurements with tunnel measurements, whose data is  
20 questionable?

***Authors Reply:***

25 What we compare in our study is the profile at an urban background location (Thissio) with that of a street canyon (Patisson) and a tunnel and not two real-world street canyon measurements with tunnel as the reviewer states. Also, the tunnel measurements were now moved to the supplement (as Sect. S.2a). The profile of the morning peak at Thissio and Patisson are providing similarities, highlighting the common fuel type. The profile of the Athens tunnel is quite differentiated by the Paris one and the findings are in accordance with previous works elsewhere as stated in the manuscript. The investigation of the evaporative losses in the Supplement, indicates that the emission differences between the Athens tunnel and the other two locations could be attributed to the higher temperatures during the tunnel measurements in  
30 combination with the decreased car fleet relatively to the early morning compared to the two profiles obtained for the city (not possible to perform measurements in the tunnel on a 24h basis). Furthermore, the side effects of the financial recession are depicted through the avoidance of the tunnel due to the tolls.

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"?

**Reviewer Remark:**

See my Reviewer Remark above

5

**Authors Reply:**

See our answer above.

- 10 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?

**Reviewer Remark:**

- 15 The remarks made by the authors in the comments for P8, L31-32 were: "Moreover higher values of ethane, propane and butanes that are depicted in the morning hours at the urban sites relatively to the tunnel measurements, reflect the increased numbers of LPG powered vehicles in Athens and natural gas-powered buses". I deduce again, that the tunnel measurements were not representative for the GAA. For me, it does not make much sense to include the tunnel data then.

20 **Authors Reply:**

As it is already mentioned, the tunnel measurements and discussion are now transferred to the supplement. However, the comparison with the street canyon measurement and the tunnel measurements remain in the main manuscript, a fact also justified in a previous comment (for Page 8, L31-32).

25

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 nighttime period?

- 30

**Reviewer Remark:**

The authors did not address the impact on wind direction. Background NMHC concentrations can critically change with wind direction, in particular at coastal locations. How can one minimum NMHC value observed during mid-day and

potentially under one distinct wind direction be representative for all potential wind direction conditions at nighttime from 18:00- 05:00 LT? Also, the authors neglect daytime photochemical degradation, albeit limited, but still present in those months.

5 **Authors Reply:**

Regarding the photochemistry, with regard to OH radicals, lifetimes in the range of 21h for propene to several days for the rest of NMHCs (e.g. 2.7d, 10d and 21d for ethylene, n-butane and propane, isoprene is excluded) occur under a typical day-time (12h) winter level of  $5 \times 10^5$  molecule  $\text{cm}^{-3}$  OH radicals. By considering that the changes of the local emission sources of traffic and heating spanning in the range of a few hours during morning and evening, the role of photochemical degradation could be omitted due to the dominance of the emissions. Considering the long lifetime of the NMHCs and the decreased photochemistry on winter-time the wind speed is of more importance than wind direction. The morning profile at Thissio station has been determined for smog conditions, i.e. low wind speed all directions included, reflecting local sources not related to NMHCs transported from different directions.

15

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

**Reviewer Remark:**

The statement made by the authors should be added in the manuscript.

20 **Authors Reply:**

The statement is added in the manuscript (page 11, line 34 – page 12, line 2) as follows: '*When these two profiles are compared (Fig. 11), the statistically significant at  $p < 0.01$  difference is obvious, with a smaller contribution from i-pentane (traffic source contributor) during December*'.

25

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

**Reviewer Remark:**

Still, the term "profile" does not make sense, as long as it is not defined (for instance, there are vertical temperature profiles).

30 **Authors Reply:**

The term profile was accordingly replaced by the most appropriate term '*conditions*' in page 12, line 31.

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

**Reviewer Remark:**

Still, the tunnel measurements would not support this as discussed earlier.

**Authors Reply:**

- 5 Any conclusions concerning the tunnel measurements are removed from the manuscript. Please refer to our answer previously for comments Page 8, L31-32 and Page 8, L1-3.

Table 1: Remove the term "worldwide" in the table caption, as Table 1 shows a few selected data from the  
10 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.

15 **Reviewer Remark:**

The authors should state explicitly that mean values are shown in the table.

**AuthorsReply:**

We disagree with the remark. Based on the Table 1 caption, the use of the mean values was already stated: '*Comparison of  
20 NMHCs mean levels between this study and already published works in Athens, Greek and other Mediterranean or European sites. Information about the analyzing or sampling techniques and data resolution are included when available. The number of measurements<sup>a</sup> for each compound determined on the current samples is included below the table*'. In order to be consistent, we also add the term 'mean' in the manuscript (page 6, line 7): '*In Table 1, the mean measurements of this study are compared with those reported in the literature for Athens in the past and other selected areas*'.

25

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%.

30 **Reviewer Remark:**

I did not argue the term "nighttime", I argued the term "peak", which does not make much sense for a time period of 11 hours.

**Authors Reply:**

The period 18:00-05:00 LT corresponds to the night-time enhancement of the observed levels based on Figure 8, whereas the night-time peak is encountered around midnight. Thus, we agree with the reviewer about the ‘peak’ and we correct accordingly the caption of figure 11 (first version Figure 10) by replacing the term ‘night peak’ by the more appropriate ‘*night-time enhancement period*’.

5

### References:

- Alexiou, D., Kokkalis, P., Papayannis, A., Rocadenbosch, F., Argyrouli, A., Tsaknakis, G. and Tzani, C.G.: Planetary boundary layer height variability over Athens, Greece, based on the synergy of Raman and Radiosonde data: Application of the Kalman filter and other techniques, EPJ Web of Conferences 176, 06007, doi.org/10.1051/epjconf/201817606007, 2018.
- 10
- Directive 2000/69/EC of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air.
- Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe.
- 15
- Klemm, O. and Ziomas I. C., Urban Emissions Measured with Aircraft, Journal of the Air & Waste Management Association, 48 (1), 16-25, doi:10.1080/10473289.1998.10463672, 1998
- Kassomenos, P., Kotroni, V., and Kallos, G.: Analysis of climatological 710 and air quality observations from Greater Athens Area, Atmos. Environ., 29, 3671-3688, doi.org/10.1016/1352-2310(94)00358-R, 1995.
- Kourtidis, K. A., Ziomas, I. C., Rappenglueck, B., Proyou, A. and Balis, D.: Evaporative traffic hydrocarbon emissions, traffic CO and speciated HC traffic emissions from the city of Athens, Atmos. Environ., 33(23), 3831–3842, doi:10.1016/S1352-2310(98)00395-1, 1999
- 20

# Non Methane Hydrocarbons variability in Athens during winter-time: The role of traffic and heating

Anastasia Panopoulou<sup>1,2,4</sup>, Eleni Liakakou<sup>2</sup>, Valérie Gros<sup>3</sup>, Stéphane Sauvage<sup>4</sup>, Nadine Locoge<sup>4</sup>, Bernard Bonsang<sup>3</sup>, Basil E. Psiloglou<sup>2</sup>, Evangelos Gerasopoulos<sup>2</sup>, Nikolaos Mihalopoulos<sup>1,2</sup>

5 <sup>1</sup>Chemistry Department, University of Crete, 71003 Heraklion, Crete, Greece

<sup>2</sup>National Observatory of Athens, Institute for Environmental Research and Sustainable Development, 15236 Palea Penteli, Greece.

<sup>3</sup>LSCE, Laboratoire des Sciences du Climat et de l'Environnement, Unité mixte CNRS-CEA-UVSQ, CEA/Orme des Merisiers, 91191 Gif sur Yvette Cedex, France.

10 <sup>4</sup>IMT Lille Douai, Univ. Lille, SAGE - Département Sciences de l'Atmosphère et Génie de l'Environnement, 59000 Lille, France

*Correspondence to:* Eleni Liakakou (liakakou@noa.gr)

**Abstract.** Non-methane hydrocarbons (NMHCs) play an important role in atmospheric chemistry, contributing to ozone and secondary organic aerosol formation. They can also serve as tracers for various sources such as traffic, solvents, heating and vegetation. The current work presents, for the first time to our knowledge, [time resolved, uninterrupted](#) data of NMHCs, from two to six carbon atoms, during a period of five months (mid-October 2015 to mid-February 2016) in the Great Athens Area (GAA), Greece. The measured NMHC levels are among the highest reported in literature for the Mediterranean area during winter months and the majority of the compounds demonstrate a remarkable day to day variability. Their levels increase by up to factor of four from autumn (October-November) to winter (December-February). Microscale meteorological conditions and especially wind speed [in combination with the PBL height, seem to contribute significantly on](#) ~~seems to control~~ the variability of NMHC levels, with an increase up to a factor of 10 ~~occurring~~ under low wind speed (<3 m s<sup>-1</sup>), reflecting the impact of local sources rather than long range transport. All NMHCs demonstrated a pronounced bimodal, diurnal pattern with a morning peak followed by a second one before midnight. The amplitude of both peaks is gradually increasing towards winter, respectively to autumn, by a factor of 3 to 6 and nicely follow that of carbon monoxide (CO), indicating contribution from sources other than traffic, related to combustion e.g. domestic heating (fuel or wood burning). By comparing the NMHC diurnal variability with that of black carbon (BC), its fractions associated with wood burning (BC<sub>wb</sub>) and fossil fuel combustion (BC<sub>ff</sub>), as well as with source profiles we conclude that the morning peak is attributed to traffic while the night one mainly to heating. For the night peak, the selected tracers and source profiles clearly indicate contribution from both traffic and domestic heating (fossil fuel and wood burning). [NMHCs slopes versus BC<sub>wb</sub> are almost similar when compared to those versus BC<sub>ff</sub> \(slight difference for ethylene\), indicating that NMHCs are probably equally produced by wood and oil fossil fuel burning. However, the present data set does not allow for quantification of each source due to the similarity of emissions, thus measurements of more specific tracers are needed for the better understanding of the contribution of these nocturnal VOC sources.](#)

## 1 Introduction

Non-methane hydrocarbons (NMHCs) are key atmospheric constituents for atmospheric chemistry. In the presence of NO<sub>x</sub>, their oxidation leads to formation of tropospheric ozone and other species, such as peroxy radicals (RO<sub>2</sub>) and peroxy acetyl nitrate (PAN), thus affecting the oxidative capacity of the atmosphere (Atkinson, 2000 and references therein). NMHC oxidation contributes to the formation of secondary organic aerosols (SOA), which in turn affects light scattering, visibility and CCN formation (Tsigaridis and Kanakidou, 2003; Seinfeld and Pandis, 2016 and references therein). In urban areas they mainly originate from anthropogenic sources such as traffic, solvent use, residential heating, natural gas use, industrial activity, but also from natural sources such as vegetation (Guenther et al., 1995; Barletta et al., 2005; Kansal, 2009; Sauvage et al., 2009; Salameh et al., 2015; Baudic et al., 2016; Jaimes-Palomera et al., 2016). Besides their key role as secondary pollutants precursors, NMHCs are of interest because of their association with health issues (EEA report, No 28/2016, 2016). In particular and since 2013, atmospheric substances have been classified by the International Agency for Research on Cancer (WHO-IARC, 2013) in four major groups regarding their carcinogenicity to humans, with benzene and 1,3-butadiene among those NMHCs classified as potential carcinogens (IARC, 2012).

Athens, the capital of Greece with almost five million of inhabitants, is frequently subjected to intense air-pollution episodes, leading to exceedance of the EU air quality limits. The driving processes and atmospheric dynamics of these episodes have been scrutinized during the last decades (Cvitas et al., 1985; Lalas et al., 1982, 1983, 1987; Mantis et al., 1992; Nester, 1995; Melas et al., 1998; Ziomas et al., 1995; Kanakidou et al., 2011). However, the measurements of pollution precursors are mostly limited to ozone and nitrogen oxides. The few existing and non-continuous NMHC measurements in Athens by means of canisters or sorbent tubes have been performed for short period (days) during summertime or autumn (Moschonas and Glavas, 1996; Klemm et al., 1998; Moschonas et al., 2001; Giakoumi et al., 2009). Continuous measurements of NMHCs in Athens for a period of one month have been conducted during summer 20 years ago at three locations, two suburban and one urban, reporting almost 50 C<sub>4</sub> – C<sub>12</sub> compounds (Rappenglück et al., 1998, 1999), and recently by Kaltsonoudis et al. (2016), for 1 month in winter 2013 at an urban location (Thissio) and one in summer 2012 at a suburban one (A. Paraskevi), reporting 11 oxygenated organic gaseous compounds and C<sub>5</sub> – C<sub>8</sub> NMHC. Meanwhile, significant changes in pollutant sources occurred in Athens the last 20 years, which lead to significant decreases in the annual concentrations of major pollutants such as CO, SO<sub>2</sub>, NO<sub>x</sub> (Gratsea et al., 2017; Kalabokas et al., 1999). As this trend was attributed to the car fleet renewal, fuel improvement, metro line extension and industrial emission controls, a decrease in NMHC levels originating from traffic and industrial emissions is also expected. However, after 2012, a new winter-time source of pollution emerged in Greece, due to uncontrolled wood burning for domestic heating (Saffari et al., 2013; Paraskevopoulou et al., 2015; Kaltsonoudis et al., 2016; Fourtziou et al., 2017; Gratsea et al., 2017). This is an important source of various pollutants such as particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), black carbon (BC) and CO (Gratsea et al., 2017; Hellén et al., 2008; Paraskevopoulou et al., 2015; Schauer et al., 2001 et references therein), while it can represent up to 50% of the mass of Volatile Organic Compounds (VOCs) during winter (case of Paris; Baudic et



al., 2016). Studies for the characterization of the VOC emissions from domestic wood burning based on emissions close to sources, in ambient air or in chambers are published, however, differences are observed in the emission rates or the emission profiles, that are attributed to the type of wood, stove, lightening material and the burning stages (Barrefors and Petersson, 1995; Baudic et al., 2016; Evtugina et al., 2014; Gaeggeler et al., 2008; Gustafson et al., 2007; Hellén et al., 2008; Liu et al., 2008; Schauer et al., 2001 and references therein). Moreover, the studies reporting light NMHC measurements from domestic wood burning are very few (Barrefors and Petersson, 1995; Baudic et al., 2016; Liu et al., 2008; Schauer et al., 2001) and present significant discrepancies. For example, the higher contribution of benzene relatively to acetylene in the residential wood burning profile reported by Baudic et al. (2016) was different from the profile of Liu et al. (2008). In addition, in their recent work, Kaltsonoudis et al. (2016) reported important contribution of wood burning to the wintertime night concentrations of aromatics and oxygenated VOCs. The above clearly demonstrates the increasing need for intensive measurements of NMHCs in Athens, which in turn will allow ~~to assess~~assessing the impact of future changes (fuel composition changes or other control strategies) on atmospheric composition. In other words, there is a need to establish a “current baseline” for Athens atmospheric composition in terms of NMHC levels.

The current study presents, time-resolved, ~~uninterrupted~~ data of 11 selected from 15 determined NMHCs with two to six carbon atoms, during a time span of several months (October 2015 to mid-February 2016) in the Great Athens Area (GAA). In addition, time-resolved data of toluene, ethylbenzene, m- /p- xylenes and o-xylene are used, which were monitored simultaneously from mid-January to mid-February 2016. The emphasis of this work is on: (1) the determination of the ambient levels of C2 – C6 NMHCs during autumn and winter, twenty years after their first summer-time measurements. Especially for C2 – C3, these are the first ever continuous measurements of NMHCs in Athens; (2) the study of the NMHC temporal characteristics and the determination of the factors controlling their variability, and (3) the investigation of traffic and residential heating impact on NMHC levels which are among the most important sources of air pollution in Athens, especially during the “crisis” period characterized by an important decline of industrial activity (Vrekoussis et al., 2013).

## 2 Experimental

### 2.1 Sampling site

Measurements were conducted from 16 October 2015 to 15 February 2016, at the urban background station of the National Observatory of Athens (NOA, 37.97° N, 23.72° E, 105 m a.s.l and about 50 m above the mean city level) at Thissio, considered as receptor of pollution plumes of different origins (Paraskevopoulou et al, 2015). The station is located in the historical center of Athens, on top of a hill (Lofos Nimfon), surrounded by a pedestrian zone, a residential area and by the Filopappou (108 m a.s.l) and Acropolis Hills (150 m a.s.l), which are located 500 m and 800 m away respectively (Fig. 1). More information about Athens' morphology, meteorology and dominant transport patterns can be found in Kanakidou et al. (2011), Melas et al. (1998) and references therein.

## 2.2 On line NMHC measurements

- Two portable gas chromatographs equipped with a flame ionization detector (GC – FID), Chromatotec, Saint Antoine, France) were used for the measurement of NMHCs in Athens. Specifically, the “airmoVOC C2 – C6” (during the whole period, from October 2015 to February 2016) and the “airmoVOC C6 – C12” Chromatrap GC (from mid-January until mid-
- 5 February 2016) analyzers were used for the determination of C2 – C6 and C6 – C12 NMHCs respectively, collecting ambient air through collocated inlets at the rooftop of the station, 4 m above ground. The C2 – C6 NMHC analyzer was set to sample ambient air on a 10 min basis followed by an analysis time of 20 min, while for the C6 – C12 the respective timing was 20 min and 20 min, with a total cycle of 30min (sampling and analysis). Therefore, the synchronized monitoring was performed with an overall 30 min time resolution, for both analyzers.
- 10 For the airmoVOC C2 – C6 analyzer, 189 mL of air was drawn through a 0.315 cm diameter, 6 m-long stainless-steel line with a filter of 4  $\mu\text{m}$  pore size at the sampling inlet, and a flow rate of 18.9 mL  $\text{min}^{-1}$ . Once sampled, ambient air was passed through a Nafion dryer (activated by gas nitrogen) to reduce the water content and then hydrocarbons were preconcentrated at  $-9\text{ }^{\circ}\text{C}$  (Peltier cooling system), on a 2.25 mm internal diameter, 8 cm-long glass trap containing the following adsorbents: Carboxen 1000 (50 mg), Carbopack B (10 mg) and Carbotrap C (10 mg) all from Supelco Analytical, Bellefonte, PA, USA.
- 15 The trap was then heated rapidly to  $220\text{ }^{\circ}\text{C}$  for 4 min and the pre-concentrated VOCs were thermally desorbed onto a Plot Column (Restek Corp., Bellefonte, PA, USA,  $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ ), 25 m x 0.53 mm, 10 mm film thickness). 1 min prior to the analysis, the oven temperature was raised from 36 to  $38\text{ }^{\circ}\text{C}$ , followed by a constant heating rate of  $15\text{ }^{\circ}\text{C min}^{-1}$  to  $200\text{ }^{\circ}\text{C}$  by the end of the analysis. Details about the equipment technique and performances, as well as the estimation of the uncertainty, are provided by Gros et al. (2011). The detection limit is in the range of 0.02 ppb (propene, n-pentane) to 0.05 ppb (propane),
- 20 while for ethane and ethylene is 0.1 ppb.
- The airmoVOC C6 – C12 analyzer was collecting 900 mL of air through a 0.315 cm diameter, 6 m-long stainless-steel line with a filter of 4  $\mu\text{m}$  pore size at the sampling inlet, and a flow rate of 45 mL  $\text{min}^{-1}$ . The hydrocarbons were preconcentrated at ambient temperature on a glass trap containing the adsorbent Carbotrap C. Then the trap was heated to  $380\text{ }^{\circ}\text{C}$  over 2 min to desorb the pre-concentrated VOCs into a separation column (MXT30CE, Restek Corp., 30 m x 0.28 mm, 1 mm film
- 25 thickness). With one minute delay, the oven temperature was raised from 36 to  $50\text{ }^{\circ}\text{C}$  at a rate of  $2\text{ }^{\circ}\text{C min}^{-1}$ , followed by a second heating of  $10\text{ }^{\circ}\text{C min}^{-1}$  up to  $80\text{ }^{\circ}\text{C}$ . Finally, at a constant heating rate of  $15\text{ }^{\circ}\text{C min}^{-1}$  the temperature reached  $200\text{ }^{\circ}\text{C}$  and remained there until the end of the analysis. In the present work, ~~only~~ [toluene, ethylbenzene, m-/p- xylenes and o-xylene \(TEX\)](#) will be used from the GC C6 – C12 data series. The uncertainty of the instrument is less than 20% and the detection limit of ~~the BTEXtoluene~~ [the BTEXtoluene](#) is 0.03 ppb.
- 30 Simultaneous calibration and identification of the compounds were performed by a certified National Physical Laboratory (NPL) standard of NMHC mixture ( $\sim 4$  ppb) containing: ethane, ethylene, propane, propene, i-butane, n-butane, acetylene, i-pentane, n-pentane, isoprene, benzene and 15 additional hydrocarbons.

## 2.3 Auxiliary measurements

Real time monitoring of carbon monoxide (CO), black carbon (BC) and nitrogen oxides (NO<sub>x</sub> = NO and NO<sub>2</sub>) was also conducted during the reported period. For CO and NO<sub>x</sub> measurements, Horiba 360 Series Gas Analyzers of one-minute resolution were used which were calibrated with certified standards. A seven wavelength Magee Scientific AE33 aethalometer (one minute resolution) was operated for the measurement of BC and its fractions associated with fossil fuel and wood burning (BC<sub>ff</sub> and BC<sub>wb</sub>, respectively) derived automatically by the instrument software. Meteorological data were provided by NOAA's meteorological station at Thissio premises.

## 2.4 Street canyon ~~and tunnel~~ measurements

To identify the NMHCs fingerprint of traffic emissions, NMHCs measurements were conducted at a monitoring station belonging to the air quality agency of Athens and located at a street canyon downtown Athens with increased traffic and frequent traffic jams (Patisision street) on 22 to 24 February 2017 (37.99°N, 23.73°E) ~~as well as in a tunnel at the peripheral highway of Athens, (Attiki Odos), on 12 May 2016 from 12:00 LT to 12:45 LT (LT = UTC+2). The tunnel's length is 200 m with 3 lanes at each direction and no specific restrictions for heavy duty vehicles. Each driving direction consist a separated compartment and a ventilation system was installed but not operated. The measurements are performed at the middle of the tunnel to avoid as possible the influence of ambient air from outside. Concerning the Patisision street campaign, samples were collected every hour during the morning rush hour, from 06:55 LT to 10:15 LT (LT = UTC+2), in 6L stainless steel – silonite canisters.~~ ~~In both cases, 6L stainless steel – silonite canisters were used for the sampling and the sampling time ranged between 2 and 10 minutes.~~ The sampling method for ambient air is described in detail elsewhere (Sauvage et al., 2009). Before the analysis, the cylinders were pressurized by adding a known amount of zero-air resulting in a sample dilution by a factor of two. Afterwards each canister was connected to the GC-FID system using a Teflon (PTFE) sampling line and analyzed by the method described in Sect. 2.2. Before sampling, the canisters were cleaned by filling them up with zero air and re-evacuated, at least three times. The content of the cylinders was then analyzed by the GC-FID system to verify the efficiency of the cleaning procedure. The canisters were evacuated a few days prior to the analysis and they were analyzed maximum 1 day after the sampling.

## 3 Results and discussion

### 3.1 Temporal variability of NMHCs

Figure 2 presents the temporal variability of selected NMHCs for five major groups of compounds: ethane and n-butane (for saturated hydrocarbons), propene and ethylene (for alkenes), acetylene (for alkynes), benzene and toluene (for aromatics) and isoprene (for potential biogenic compounds). Other measured NMHCs are presented in Fig. S1. During the reported

period, the data availability (in comparison with the maximum potential data availability) for all C2–C6 NMHCs was higher than 87%. Most of the data for isoprene are below the limit of detection due to the low vegetation activity at this period of the year (Fuentes et al., 2000; Guenther et al., 1995). Moreover, the significant night time levels (above 300 ppt in some cases) could be indicative of non-vegetation sources, like traffic or domestic wood burning (Borbon et al., 2001, 2003; Gaeggeler et al., 2008; Kaltsonoudis et al., 2016). However due to the low data coverage, it is not possible to determine an accurate diurnal variability for this compound.

The majority of the compounds showed a remarkable day to day variability throughout the study period and levels increasing by up to factor of four, from autumn (October-November) towards winter (December-February; Fig. 2 and S1). The highest values which have been observed for ethane and ethylene ranged mostly between 26 and 23 ppb, and were encountered in wintertime. For these compounds, the lower values were above 0.3 ppb for the whole period. During the period of intensive measurements, toluene exceeded 10 ppb, while benzene was below 6 ppb during the four-month monitoring period. Benzene is the only NMHC included in the European air quality standards due to its possible adverse health effects (IARC, 2012).

In Table 1, the [mean values of the](#) measurements of this study are compared with those reported in the literature for Athens in the past and other selected areas. The comparison with those already published data for the GAA, indicates an apparent decrease by a factor of 2 to 6 for the majority of the species lying above C4 (taking as reference the case of Ancient agora urban area in the close vicinity of Thissio Station). ~~This decreasing trend is in agreement with a decrease in primary pollutants CO, SO<sub>2</sub> already reported by Kalabokas et al. (1999) and Gratsea et al. (2017), due to the air quality measures taken by the Greek government.~~ [This decreasing trend is in agreement with a decrease in primary pollutants CO, SO<sub>2</sub> already reported by Kalabokas et al. \(1999\) and Gratsea et al. \(2017\), due to the air quality measures taken by the Greek government and economic recession \(since 2012\). Apart changes in emission sources and source strength during the last twenty years, differences in sampling period \(summer versus winter\), location and built environment \(kerbside versus urban background\), analytical resolution \(morning collected samples compared to continuously averaged levels\) should be considered, rendering the direct comparison between the present and past measurements quite difficult in the overall evaluation of the NMHCs decrease.](#) ~~However, this decrease has to be seen with cautious considering differences in sampling period (summer versus winter), location, sampling method and analytical techniques.~~ [However, in order to better investigate the observed decreasing trend and compare these results to past measurements, enhancement ratios are calculated for i – pentane, benzene, toluene, ethylbenzene and o – xylene to NO<sub>x</sub> \(sum of NO and NO<sub>2</sub>\), following the approach of Kourtidis et al., \(1999\) from the measurements performed in the street canyon \(Patisision\) and presented at Table 2. In a summary, the enhancement ratios are the slopes of the x-y plots of the selected NMHC \(in ppb\) to NO<sub>x</sub> \(or CO, both in ppb\), and for which morning concentrations \(07:00 to 10:00 LT\) at wind speed lower than 2 m s<sup>-1</sup> and of SSW to SWW direction \(206° to 237°\) are used. The NO<sub>x</sub> and CO data for the Patisision site are provided by the Hellenic Ministry of the Environment & Energy, Dept. of Air Quality. Additionally, the same enhancement ratios were calculated for Thissio station, for concentrations associated with wind speed lower than 2 m s<sup>-1</sup> \(no distinction to wind direction\), thus maximizing the local influence. Since the enhancement ratios are calculated during the time-window of the traffic rush hours, it is assumed that they are](#)

representatives of traffic emissions only. Both Thissio station and Patisson street canyon demonstrate similar enhancement ratios with differences in the order of 15-30% and 20-35% relatively to NO<sub>x</sub> and CO respectively and great differences comparatively to the previously reported values. Enhancement ratios for i-pentane, toluene, ethylbenzene and o-xylene to NO<sub>x</sub> for the same station (Patisson) show values which are lower by a factor of  $6 \pm 1$  compared to the ones reported in Kourtidis et al. (1999), whereas a factor of 12 is observed for benzene. The same stands for the present enhancement ratios of the selected NMHCs to CO with a decrease of 2 to 5 times. The lower enhancement ratios reveal the strong impact of the air quality measures to VOC emissions, while the high difference to benzene enhancement ratio is a direct outcome of the Directive n°2000/69/CE (now Directive n°2008/50/EC) of the European Union for the reduction of this compound, especially in fuels.

Beirut, located in the Eastern Mediterranean basin (approximately 200 Km SE of Greece, 230 m above sea level), has a population of 2000000 inhabitants and a typical Mediterranean climate with mild winter and hot summer (Salameh et al., 2015). On the contrary Bilbao is an urban and industrial city with 400000 inhabitants in northern Spain, located along a river delta in SE–NW direction, with two mountain ranges in parallel to the river (Ibarra-Berastegi et al., 2008). Due to their location, both cities experience intense sea breeze cycles. The levels of NMHCs observed in Athens are higher, almost by a factor of two, with the exception of propane, butanes and toluene for Beirut and n-butane, benzene and toluene for Bilbao, which are quite similar to Athens. NMHC levels are also compared with those obtained in Paris, one of the European megacities, with more than 10 million inhabitants with relatively mild winters and warm summers. Again, the observed levels in Athens are significantly higher compared to those reported for Paris (Baudic et al., 2016). ~~NMHC levels are also compared with those obtained in Paris, the latter as representative of a mid latitude, northern hemisphere (urban) location. It is one of the European megacities, with more than 10 million inhabitants. The climate is both oceanic and continental, with cold winters (temperatures can be below 0 °C) and mild but wet summers. Again, the observed levels in Athens are significantly higher compared to those reported for Paris (Baudic et al., 2016).~~

According to Fig. 2, a common pattern for all NMHC concentrations was their gradual increase from October to December, which reflects the transition from the warmer period to the colder one. This is better illustrated in Fig. 3, which depicts the monthly mean concentration for every NMHC presented in Fig. 2. The increase in NMHC levels during the cold period could be explained by the respective increase in their lifetime due to less photochemistry and the contribution from additional sources, such as heating. However, the role of atmospheric dynamics should not be neglected, since the decrease in the height of the planetary boundary layer (PBL) could also trigger the observed winter-time enhancement of the NMHC levels. Nevertheless, according to ~~Kokkalis (Alexiou et al., (2018)) personal communication~~ the mean winter-time decrease of PBL compared to autumn is in the range of 20% for both day and night periods, thus changes in PBL couldn't be the only factor determining the enhancement of NMHCs level observed during wintertime. Furthermore, according to Kassomenos et al. (1995) the day-night difference on PBL is more pronounced during summer. Thus, the night-time accumulation of the pollutants during winter relatively to summer highlights essentially the impact of additional emission sources.

Meteorological conditions such as wind speed and direction have to be also considered and their respective role will be discussed thereafter.

### 3.2 Diurnal variability of NMHCs

During the whole monitoring period, all hydrocarbons demonstrated a pronounced bimodal diurnal pattern (Fig. 4 and S2). A morning peak was observed lasting from 07:00LT to 10:00LT, followed by a second one before midnight. The amplitude of both peaks is gradually increasing from October to winter time by a factor of 3 to 6 and nicely follows that of carbon monoxide (CO), BC and its fractions associated with wood burning ( $BC_{wb}$ ) and fossil fuel combustion ( $BC_{ff}$ ) (Fig. 4). As it was noted in Gratsea et al. (2017), the morning maximum of CO is attributed to morning traffic, while the winter night-time increase to additional sources such as domestic heating (fossil fuel or wood burning). Although the amplitude of both CO peaks (morning and night) is almost similar (with the exception of December), the duration of the night peak is at least a factor of 2 larger, which could imply the impact of heating on air quality during wintertime. [Moreover, night-time emissions occur in a shallower boundary layer relatively to the mid-day, resulting into accumulation of pollutants \(Alexiou et al., 2018\).](#) These observations are indicative of the contribution of traffic and heating to the NMHCs levels. By comparing the NMHC diurnal variability with that of BC, as well as its fractions associated with wood burning ( $BC_{wb}$ ) and fossil fuel combustion ( $BC_{ff}$ ), it is deduced that the morning peak could be mainly attributed to traffic and the late evening to ~~both~~ [traffic](#) and heating, the latter from the combined use of heavy oil and wood burning.

### 3.3 The role of meteorology on NMHC levels

Once emitted in the atmosphere, NMHCs react mainly with OH and  $NO_3$  radicals during day and night-time, respectively, and with ozone throughout the day (Crutzen 1995, Atkinson 2000), whereas the role of Cl could not be omitted, especially for coastal areas [\(Arsene et al., 2007\).](#) ~~such as the GAA (Arsene et al., 2007).~~ Still, in addition to chemistry, many other factors, such as the strength of the emission sources and the atmospheric dynamics (meteorology and boundary layer evolution), determine their abundance and diurnal variability. To investigate the role of wind speed and wind direction, the dependence of n-butane, acetylene and benzene, selected as representative of alkanes, alkynes and aromatics, against wind speed and direction, is depicted in Fig. 5 and 6 respectively (Fig. S3 and S4 include the rest of the compounds). For all studied NMHCs, the highest concentration occurred under low wind speed ( $< 3 \text{ m s}^{-1}$ ) reflecting the critical role of local sources versus long range transport. On a monthly basis, the NMHC dependence on wind speed remains the same for the total examined period (Fig. S5).

To investigate the impact of wind direction on NMHC levels, fig. 6 presents the distribution of wind sectors frequency of occurrence during the sampling period and that of wind speed per sector. In addition, the variability of n-butane, acetylene and benzene levels as a function of wind direction is also depicted. – Enhanced levels of NMHCs are found under the influence of air masses from all directions, especially under low wind speed. During the sampling period, the NE sector

associated with relatively strong winds ( $u > 3 \text{ m s}^{-1}$ ), was the most frequent one, resulting in moderate levels of NMHCs. Overall, a similar distribution was found for all NMHCs, indicating moderate to higher values under the N-NE-E-SE directions, and lower levels under the NW-W-SW sector, the latter associated with high wind speeds. The influence of the N to SE sector to the enhanced NMHCs levels is probably related to the northern suburbs of GAA, that are characterized by increased number of fireplaces, while the higher living standards of their inhabitants allow the combined use of heating oil in central heating systems and wood in fireplaces and/or woodstoves. The impact of the N to ESE sector on NMHC levels can be also seen when comparing the concentrations of the morning (07:00 – 09:00) and night (21:00 – 23:00) peaks in October and December (Fig. S6). The wind probability from N to ESE is similar for both months, however significantly higher concentrations are observed during nighttime in December affected by low wind speed ( $< 2 \text{ m s}^{-1}$ ) from the N to NE sector.

The ambient temperature is another parameter which can influence NMHC levels, as high temperatures favor the evaporation of low volatility hydrocarbons and also trigger the production of biogenic compounds, whereas lower temperatures could trigger the emission of NMHCs from increased heating demand, as other tracers as well (Athanasopoulou et al., 2017). The average monthly temperatures varied from  $18 \text{ }^{\circ}\text{C}$  in October and November to  $10 - 13 \text{ }^{\circ}\text{C}$  in December and late winter, respectively. ~~By examining When~~ NMHCs ~~are examined~~ against temperature (Fig. S7), a clear tendency is not evident, although the highest levels are observed at lower temperatures.

### 3.4 Identification of NMHC emission sources with emphasis on traffic and heating

#### 3.4.1 Interspecies correlation

Table 32 shows the interspecies correlation of NMHCs for the total period of measurements. All NMHCs were well correlated ( $R^2 > 0.81$ ), with the exception of isoprene which as seen before, had only few data above the LoD and thus was excluded from Table 32. Note also the excellent correlation of toluene with ethylbenzene, m-/p- xylenes and o-xylene ( $R^2$  from 0.92 to 0.93), during the common measured period (from mid-January until mid-February 2016) highlighting their common origin. The strong correlation of NMHCs with combustion tracers, such as CO, NO and BC, could indicate their common ~~origin~~ emission sources and variability. The deconvolution of BC into its fossil fuel and biomass burning fractions enables further classification of NMHCs into groups that could possibly be emitted by those two distinct sources. The stronger correlation ( $R^2 > 0.84$ ) of the hydrocarbons with  $\text{BC}_{\text{ff}}$  compared to  $\text{BC}_{\text{wb}}$  ( $R^2 > 0.64$ ) could imply stronger emission of NMHCs from fossil fuel combustion processes relatively to wood burning. Finally, no change in the correlation coefficients is observed when data sets are separated between day (6:00-18:00) and nighttime (18:00-6:00) time intervals. However, the above analysis could give only a rough idea on the sources impacting NMHCs levels. A more precise picture could emerge with comparison with source profiles and such discussion follows in the paragraph below.

### 3.4.2 Impact of various sources on the NMHC levels

To identify periods with differentiated impact from the different pollution sources (with emphasis on traffic and heating), the methodology described by Fourtziou et al. (2017) was applied. The criteria for this separation have been the wind speed not to exceed the threshold value of  $3 \text{ m s}^{-1}$  (light breeze conditions) and the presence of precipitation (on/off criterion). The role of wind speed was clearly seen at the Sect. 3.3 (Fig. 5). Based on these criteria, the first group (non-shaded in Fig. 7) corresponds to higher wind speeds and thus more efficient dispersion of emitted pollutants (ventilation), as well as the incidents of rain and is characterized as non-smog periods (nSP). The second group (shaded area in Fig. 7) refers to lower wind speeds, favoring accumulation of high pollution loads within the mixing layer and is henceforth referred to as smog periods (SP). The frequency of SP and nSP periods was 65% and 35% respectively. Note that the word "smog" is used as a synonym to highlight cases of relatively high air pollution, as also indicated by the high levels of CO and BC encountered during the SP periods (Fig. 7).

The diurnal variability of all compounds was investigated separately for two distinct months, October and December, representative periods of non-heating and heating activities, respectively (Fig. 8 and S8). Note that SP periods represent 55% of the considered time in October and 73% in December. According to previous findings (Paraskevopoulou et al. 2015; Kaltsonoudis et al. 2016; Fourtziou et al. 2017; Gratsea et al. 2017) wood burning for domestic heating has gained a marking role as a winter-time emission source in Greece, over the last years. Since wood burning is reported as emission source of specific organic compounds such as ethane, ethylene, acetylene, benzene, methanol, acetaldehyde and acetonitrile (Baudic et al., 2016; Gaeggeler et al., 2008; Gustafson et al., 2007; Hellén et al., 2008; Kaltsonoudis et al., 2016), it can be safely considered as a possible factor contributing to the winter time increase of NMHC levels in GAA. Thus, the two selected months are expected to have different source profile. October, without or very limited heating demand, was used as a reference period, while December in south-central Greece is traditionally the beginning of the heating period. The low values of  $\text{BC}_{\text{wb}}$  recorded in October, even during the SP periods, supports the methodology followed for the separation (Fig. 8).

The levels of all measured NMHCs were significantly higher in December compared to October for the SP periods (Fig. 8 and S8). The most striking difference is related to the night peak, while during mid-day the difference is minimal. For all compounds examined in this work, the night peak in December (SP period) is 2 to 6 times higher compared to October's (SP period) with the highest differences found for ethane, ethylene, propene and acetylene. On the other hand, the December to October ratio during mid-day is ranged between 2.6 (for propene and acetylene) to 0.9 (for benzene). It is worth noting the levels of NMHCs during the traffic related morning peak. Although higher mean levels were observed in December, the amplitude of the morning peak is almost similar in both examined months, denoting no important change in the traffic source between the heating and non-heating periods. In contrast, during the nSP periods in October and December NMHCs levels were equal (Fig. 8 and S8). Furthermore, the concentrations of all compounds during nSP were very low; even lower than the minimum values observed during mid-day during SP periods of the same months. Accordingly, the diurnal variability of all investigated NMHCs was less pronounced compared to the SP periods with a slight increase during night in December,



which could be attributed to a background contribution from heating sources. In Sect. 3.4.3 the origin of the morning and nights peaks related to NMHCs will be further investigated.

### 3.4.3 Impact of sources on morning and night peaks of NMHCs

#### *Morning peak:*

5 As discussed in Sect. 3.2, the morning peak (07:00 – 10:00 LT) of NMHCs could be mainly attributed to traffic. Fig. 9 presents the profile of this peak (% mass contribution of the measured NMHCs), during January and February SP days when toluene, [ethylbenzene](#), [m-/p- xylenes](#) and [o-xylene](#) data were also available. Additionally, in the same figure the morning profile obtained during the 2 – days campaign conducted in the street canyon located at the center of Athens (Patisson Monitoring Station) ~~is and the profiles of two tunnel measurements in G.A.A and Paris are~~ also reported. Details on the  
10 calculations for the morning profile for the two sites ~~are~~ provided in Sect. S2. Patisson profile reflects all types of traffic-related emissions due to the combination of the high number of vehicles and buses driving on this street, frequent traffic jam conditions, variety of types of fuels (gasoil, diesel, natural gas), vehicles age, maintenance etc.

The two morning profiles, although performed at sites with different impact of traffic, agrees quite well ( $R^2 > 0.987$ ). Iso - pentane, ~~and~~ toluene [and m-/p- xylenes](#) are the ~~two-three~~ main compounds contributing to the morning profiles accounting  
15 by about ~~44~~<sup>50</sup>% of the total measured NMHCs at both locations, followed by n- and i-butane and ethylene accounting for almost ~~21~~<sup>30</sup>%. Differences between the two morning profiles regarding these 5 main species are weak (less than a factor of 1.~~25~~). Note also that the morning profile at Thissio is the mean of a whole month period compared to the two days campaign at Patisson which could explain the small differences between the two profiles. [In addition, a comparison with a tunnel study in Athens is made in the supplement \(Sect. 2a.\), in which similarities are seen for most of the main compounds \(i-](#)  
20 [pentane, m- / p- xylenes, ethylbenzene, o-xylene, benzene, n-pentane, i-butane, propene and ethane\), but with the exception of acetylene and toluene that they are lower by a factor of 4 and 1.5 respectively. Regarding the tunnel experiments, despite the different conditions associated with their profiles \(Paris versus Athens, tunnel length, season etc\), they present a a lot of common features \( \$R^2 > 0.91\$ \). Again i pentane and toluene are the two main compounds of the profiles accounting for about 56% of the total measured NMHCs, followed by n butane, ethylene and benzene accounting for almost 20% at both sites.](#)  
25 ~~The most striking difference between the two sites concerns n pentane (almost a factor of two higher in Paris compared to Athens). The biggest difference between the two Athens morning peaks and tunnels concerns acetylene (factor of 4), benzene and toluene (factor of 2).~~The similarity of Thissio and Patisson morning profiles and their difference from the Athens ~~and Paris~~ tunnel profiles probably indicates the importance of the type of fuel used. The latter is also observed in recent works (Ait-Helal et al., 2015; Zhang Q. et al., 2018; Zhang Y. et al., 2018), where important differences have been  
30 reported between tunnel measurements, and attributed to various typologies of the car-fleets (type of vehicles and fuels). In our case there is a possibility that the car-fleet in the tunnel is not representative for the GAA, since the existing tolls reduce the use of the tunnel due to financial issues. Also, measurements are performed during noon when the traffic density is relatively low compared to the morning peak. In any case, the prevalence of i-pentane and toluene in all profiles, indicates

the continuing dominance of gasoline powered cars and evaporative losses. The importance of evaporative losses can be seen in Fig. S110 and S121 where the ratios of butanes and pentanes-to- $(C_2 - C_5)_{total}$ -Alkanes- $C_2 - C_5$  (%) versus the temperature are respectively examined. Taking into account the positive dependence of the two ratios, especially that of pentanes, to temperature, we can assume that fuel evaporation losses are also an important source of NMHCs. [These observations are in agreement with the general behavior of the temperature dependency reported in Kourtidis et al., \(1999\) \(Fig. S13 and Sect. S3\), that performed an investigation of the dependence of the fractionation of NMHCs in evaporative emissions from temperature in Athens. Although the examined periods differ in ambient temperature \(winter is colder than autumn\), the exponential curve fitting of both datasets was similar.](#) In addition, the above results could indicate why the Athens tunnel results performed in May differ from Patisson and Thissio winter morning profiles. Moreover, the higher values of ~~ethane~~, propane and butanes that are depicted in the morning peaks at the urban sites relatively to the tunnel measurements, reflect the increased number of LPG powered vehicles in Athens and natural gas-powered buses (Fameli and Assimakopoulos, 2016). This is further highlighted when the monthly variation of i-butane relatively to n-butane is examined (Fig. S1432). The two compounds have linear relationship with no significant temporal differences on the slopes between the various months. Furthermore, the regression is similar to the one derived from the Patisson measurements, thus enhancing our assumption that butanes emissions are traffic related. Moreover, the relation between the high levels of C2 – C4 alkanes and the number of LPG-powered cars was highlighted in other tunnel works as well (Ait-Helal et al., 2015; Zhang Q. et al., 2018).

~~Toluene, an important contributor to the traffic profile (Fig. 9), was measured only for one month during winter.~~ To obtain a better idea on the variability of the traffic source during the studied period, the variability of selected NMHCs (ethylene, i-pentane and benzene) relatively to  $BC_{ff}$ , the latter used as traffic source tracer, was also plotted for October and December (Fig. 10). Significant correlations are revealed with slopes remaining almost stable (within 30%) during both months, indicating similar emission ratios during the whole studied period, and probably equal contribution from traffic.

*Night-time enhancement period*~~time peak~~: During nighttime both  $BC_{ff}$  and  $BC_{wb}$  were maximized (e.g. Fig. 4 and 8), denoting significant contribution from both fossil fuel and wood burning (the contribution of the latter was more evident during winter). Figure 11 presents the NMHC profile of the [night-time enhancement period for October and December SP nights \(details for the calculations are given in S.4\).](#) ~~nighttime peak, which has been calculated by the subtraction of the background concentration (minimum value between 12:00 and 17:00LT) from the night maximum value, for both October and December.~~ As already discussed, traffic is expected to be the main source of NMHCs during nighttime in October, whereas heating competes traffic during December. When these two profiles are compared (Fig. 11), the [statistically significant at  \$p < 0.01\$](#)  difference is obvious, with a smaller contribution from i-pentane (traffic source contributor) during December. In addition, enhanced contributions from C2 (ethane, ethylene and acetylene) are apparent in December compared to October. These C2 hydrocarbons have been reported as important contributors to the wood burning source profile by Baudic et al. (2016) in Paris. Preliminary data from a fireplace experiment (not part of this work) also confirm

these findings; and are in line with our results reported in Fig. 8 indicating impact of wood burning during nighttime in winter months.

Figure 12a (i-iii) presents the relation of ethylene, acetylene and benzene, main contributors of the wood burning profile (Baudic et al., 2016), to BC during the SP night-time periods (18:00 – 05:00 LT), in October and December. During both months, significant correlations were revealed for all examined NMHCs and the slopes remained relatively stable, indicating almost equivalent emission ratios from both traffic and heating sources. To better tackle with possible difference in NMHCs emissions from traffic and residential heating, these NMHCs were also plotted against  $BC_{wb}$  and  $BC_{ff}$  during the SP periods in December, from 22:00 to 04:00 LT, i.e. the time frame when traffic is quite limited (Fig. 12b, iv-vi). NMHC slopes versus  $BC_{wb}$  are almost similar when compared to those versus  $BC_{ff}$  (slight difference for ethylene), with a contribution of  $BC_{wb}$  and  $BC_{ff}$  to BC of 43% ( $\pm 10\%$ ) and 55% ( $\pm 11\%$ ) respectively, indicating that the studied NMHCs are probably equally produced by wood and fossil fuel burning.

#### 4 Conclusions

For the first time to our knowledge, ~~time resolved~~~~continuous~~ measurements of 11 Non Methane Hydrocarbons with two to six carbon atoms (C2 – C6 NMHCs) were conducted for several months (mid-October 2015 to mid-February 2016) in the Great Athens Area (GAA) by means of an automatic chromatograph, in parallel with monitoring of major pollutants and meteorological parameters. The temporal variability of NMHCs presented an increasing trend from October to December, due to changes in type and strength of sources, and atmospheric dynamics. In comparison with other works, higher concentrations are reported for the majority of NMHCs, indicating an air quality issue in Athens. With the exception of isoprene, all NMHCs presented a bimodal diurnal pattern with morning and a broader night-time maxima, whereas the lower concentrations were observed early in the afternoon. Typical indicators of combustion processes such as CO and BC, which was further deconvoluted into  $BC_{ff}$  and  $BC_{wb}$ , presented similar seasonal and diurnal variability relatively to the NMHCs, providing the opportunity to investigate their possible emission sources. Thus, the morning maximum, which follows the  $BC_{ff}$  tendency, was attributed to traffic, while the second one during night which maximized on December and coincides with those of  $BC_{wb}$  and  $BC_{ff}$  was attributed mainly to heating by both fossil fuel and wood burning.

For the better understanding of the impact of sources on the NMHCs levels, the studied period was further separated into smog (SP) and no-smog (nSP) periods, based on the absence of rainfall and low wind speed. October and December were chosen for further comparison due to different temperature ~~profiles-conditions~~ and possible sources taking into account the already proved increased winter-time heating demand (Athanasopoulou et al., 2017). The comparison of the morning maximum of NMHCs profile during SP days with those obtained at a street canyon of Athens (Patisson) ~~and tunnel experiments in Athens and Paris~~, further confirms the role of traffic in the observed morning NMHCs peak. The October and December SP NMHCs' night profiles depicted difference attributed mainly to heating. However, NMHCs slopes versus  $BC_{wb}$  are almost similar when compared to those versus  $BC_{ff}$  (slight difference for ethylene), indicating that NMHCs are probably equally produced by wood and oil fossil fuel burning. An extended dataset of NMHCs and other organic tracers

(future long-term measurements) is needed to apportion different sources types on seasonal basis and quantify their impact on the NMHCs levels.

## 5 Data availability

5 All the data presented in this paper are available upon request. For further information, please contact [Dr. Eleni Liakakou](mailto:liakakou@noa.gr) (liakakou@noa.gr).

## Acknowledgements

Support from CEA, CNRS and the Charmex program are acknowledged. We thank F. Dulac and E. Hamonou for the successful management of the Charmex program, D. Baisnée and T. Leonardis for technical support with the GCs, [the editor](#) 10 and the two anonymous reviewers for their comments which greatly improved the submitted version. The authors also acknowledge the Hellenic Ministry of the Environment & Energy, Dept. of Air Quality ~~and the Attiki Odos~~, for the access at the Patisson Station [and their database](#) for the purposes of the short intensive campaign; and [the Attiki Odos](#) for the access [to the tunnel](#) ~~respectively~~.

## References

- 15 Ait-Helal, W., Beeldens, A., Boonen, E., Borbon, A., Boréave, A., Cazaunau, M., Chen, H., Daële, V., Dupart, Y., Gaimoz, C., Gallus, M., George, C., Grand, N., Grosselin, B., Herrmann, H., Ifang, S., Kurtenbach, R., Maille, M., Marjanovic, I., Mellouki, A., Miet, K., Mothes, F., Poulain, L., Rabe, R., Zapf, P., Kleffmann, J. and Doussin, J.-F.: On-road measurements of NMVOCs and NO<sub>x</sub>: Determination of light-duty vehicles emission factors from tunnel studies in Brussels city center, Atmos. Environ., 122, 799–807, doi:10.1016/j.atmosenv.2015.09.066, 2015.
- 20 [Alexiou, D., Kokkalis, P., Papayannis, A., Rocadenbosch, F., Argyrouli, A., Tsaknakis, G. and Tzanis, C.G.: Planetary boundary layer height variability over Athens, Greece, based on the synergy of Raman and Radiosonde data: Application of the Kalman filter and other techniques, EPJ Web of Conferences 176, 06007, doi.org/10.1051/epjconf/201817606007, 2018](#)
- Arsene, C., Bougiatioti, A., Kanakidou, M., Bonsang, B. and Mihalopoulos, N.: Tropospheric OH and Cl levels deduced from non-methane hydrocarbon measurements in a marine site, Atmos Chem Phys, 7(17), 4661–4673, doi:10.5194/acp-7-4661-2007, 2007.
- Athanasopoulou, E., Speyer, O., Brunner, D., Vogel, H., Vogel, B., Mihalopoulos, N. and Gerasopoulos, E.: Changes in domestic heating fuel use in Greece: effects on atmospheric chemistry and radiation, Atmos Chem Phys, 17(17), 10597–10618, doi:10.5194/acp-17-10597-2017, 2017.
- Atkinson, R.: Atmospheric chemistry of VOCs and NO<sub>x</sub>, Atmos. Environ., 34(12), 2063–2101, doi:10.1016/S1352-30 2310(99)00460-4, 2000.

- Barrefors, G. and Petersson, G.: Volatile hydrocarbons from domestic wood burning, *Chemosphere*, 30(8), 1551–1556, doi:10.1016/0045-6535(95)00048-D, 1995.
- Barletta, B., Meinardi, S., Sherwood Rowland, F., Chan, C.-Y., Wang, X., Zou, S., Yin Chan, L. and Blake, D. R.: Volatile organic compounds in 43 Chinese cities, *Atmos. Environ.*, 39(32), 5979–5990, doi:10.1016/j.atmosenv.2005.06.029, 2005.
- 5 Baudic, A., Gros, V., Sauvage, S., Locoge, N., Sanchez, O., Sarda-Estève, R., Kalogridis, C., Petit, J.-E., Bonnaire, N., Baisnée, D., Favez, O., Albinet, A., Sciare, J. and Bonsang, B.: Seasonal variability and source apportionment of volatile organic compounds (VOCs) in the Paris megacity (France), *Atmos Chem Phys*, 16(18), 11961–11989, doi:10.5194/acp-16-11961-2016, 2016.
- 10 Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J. C. and Guillermo, R.: An investigation into the traffic-related fraction of isoprene at an urban location, *Atmos. Environ.*, 35(22), 3749–3760, doi:10.1016/S1352-2310(01)00170-4, 2001.
- Borbon, A., Fontaine, H., Locoge, N., Veillerot, M. and Galloo, J. C.: Developing receptor-oriented methods for non-methane hydrocarbon characterisation in urban air—Part I: source identification, *Atmos. Environ.*, 37(29), 4051–4064, doi:10.1016/S1352-2310(03)00525-9, 2003.
- 15 Cvitas, T., Gusten, H., Heinrich, G., Klasinc, L., Lalas, D. and Petrakis, M.: Characteristics of summer air pollution during the summer in Athens, Greece, *Staub - Reinhalt Luft*, 45(6), 297-301, 1985.
- Crutzen, Paul J.: *Ozone in the troposphere. Composition, chemistry, and climate of the atmosphere*, 349-393, 1995
- [Directive 2000/69/EC of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air.](#)
- [Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe.](#)
- 20 Durana, N., Navazo, M., Gómez, M. C., Alonso, L., García, J. A., Ilardia, J. L., Gangoiti, G. and Iza, J.: Long term hourly measurement of 62 non-methane hydrocarbons in an urban area: Main results and contribution of non-traffic sources, *Atmos. Environ.*, 40(16), 2860–2872, doi:10.1016/j.atmosenv.2006.01.005, 2006.
- European Environmental Agency (EEA): *Air quality in Europe — 2016 report (N<sup>o</sup> 28)*, <https://www.eea.europa.eu/publications/air-quality-in-europe-2016>
- 25 Evtugina, M., Alves, C., Calvo, A., Nunes, T., Tarelho, L., Duarte, M., Prozil, S. O., Evtugin, D. V. and Pio, C.: VOC emissions from residential combustion of Southern and mid-European woods, *Atmos. Environ.*, 83, 90–98, doi:10.1016/j.atmosenv.2013.10.050, 2014.
- 30 Fameli, K.-M. and Assimakopoulos, V. D.: The new open Flexible Emission Inventory for Greece and the Greater Athens Area (FEI-GREGAA): Account of pollutant sources and their importance from 2006 to 2012, *Atmos. Environ.*, 137, 17–37, 2016.
- Fourtziou, L., Liakakou, E., Stavroulas, I., Theodosi, C., Zarmpas, P., Psiloglou, B., Sciare, J., Maggos, T., Bairachtari, K., Bougiatioti, A., Gerasopoulos, E., Sarda-Estève, R., Bonnaire, N. and Mihalopoulos, N.: Multi-tracer approach to

- characterize domestic wood burning in Athens (Greece) during wintertime, *Atmos. Environ.*, 148, 89–101, doi:10.1016/j.atmosenv.2016.10.011, 2017.
- Fuentes, J. D., Gu, L., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J., Ciccioli, P., Lamb, B., Geron, C. and Guenther, A.: Biogenic hydrocarbons in the atmospheric boundary layer: a review, *Bull. Am. Meteorol. Soc.*, 81(7), 1537–1575, 2000.
- Gaeggeler, K., Prevot, A. S. H., Dommen, J., Legreid, G., Reimann, S. and Baltensperger, U.: Residential wood burning in an Alpine valley as a source for oxygenated volatile organic compounds, hydrocarbons and organic acids, *Atmos. Environ.*, 42(35), 8278–8287, doi:10.1016/j.atmosenv.2008.07.038, 2008.
- Giakoumi, A., Maggos, T., Michopoulos, J., Helmis, C. and Vasilakos, C.: PM<sub>2.5</sub> and volatile organic compounds (VOCs) in ambient air: a focus on the effect of meteorology, *Environ. Monit. Assess.*, 152(1–4), 83, doi:10.1007/s10661-008-0298-2, 2009.
- Gratsea, M., Liakakou, E., Mihalopoulos, N., Adamopoulos, A., Tsilibari, E. and Gerasopoulos, E.: The combined effect of reduced fossil fuel consumption and increasing biomass combustion on Athens' air quality, as inferred from long term CO measurements, *Sci. Total Environ.*, 592(Supplement C), 115–123, doi:10.1016/j.scitotenv.2017.03.045, 2017.
- Gros, V., Gaimoz, C., Herrmann, F., Custer, T., Williams, J., Bonsang, B., Sauvage, S., Locoge, N., d'Argouges, O., Sarda-Estève, R. and Sciare, J.: Volatile organic compounds sources in Paris in spring 2007. Part I: qualitative analysis, *Environ. Chem.*, 8(1), 74–90, doi:10.1071/EN10068, 2011.
- Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P.: A global model of natural volatile organic compound emissions, *J. Geophys. Res. Atmospheres*, 100(D5), 8873–8892, doi:10.1029/94JD02950, 1995.
- Gustafson, P., Barregard, L., Strandberg, B. and Sällsten, G.: The impact of domestic wood burning on personal, indoor and outdoor levels of 1,3-butadiene, benzene, formaldehyde and acetaldehyde, *J. Environ. Monit.*, 9(1), 23–32, doi:10.1039/B614142K, 2007.
- Hellén, H., Hakola, H., Haaparanta, S., Pietarila, H. and Kauhaniemi, M.: Influence of residential wood combustion on local air quality, *Sci. Total Environ.*, 393(2–3), 283–290, doi:10.1016/j.scitotenv.2008.01.019, 2008.
- Ibarra-Berastegi, G., Elias, A., Barona, A., Saenz, J., Ezcurra, A. and Diaz de Argandoña, J.: From diagnosis to prognosis for forecasting air pollution using neural networks: Air pollution monitoring in Bilbao, *Environ. Model. Softw.*, 23(5), 622–637, doi:10.1016/j.envsoft.2007.09.003, 2008.
- Jaimes-Palomera, M., Retama, A., Elias-Castro, G., Neria-Hernández, A., Rivera-Hernández, O. and Velasco, E.: Non-methane hydrocarbons in the atmosphere of Mexico City: Results of the 2012 ozone-season campaign, *Atmos. Environ.*, 132(Supplement C), 258–275, doi:10.1016/j.atmosenv.2016.02.047, 2016.
- IARC, Chemical Agents and Related Occupations, Monographs on the Evaluation of Carcinogenic Risks to Humans, 2012, vol. 100F, 249-285; 309-333 <http://monographs.iarc.fr/ENG/Monographs/vol100F/mono100F.pdf>

- Kalabokas, P., Viras, L. and Repapis, C.: Analysis of the 11-year record (1987–1997) of air pollution measurements in Athens, Greece. Part I: Primary air pollutants, *Glob. Nest Int. J.*, 1(3), 157–168, 1999.
- Kaltsonoudis, C., Kostenidou, E., Florou, K., Psychoudaki, M. and Pandis, S. N.: Temporal variability and sources of VOCs in urban areas of the eastern Mediterranean, *Atmos Chem Phys*, 16(23), 14825–14842, doi:10.5194/acp-16-14825-2016, 2016.
- Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E., Dermizaki, E., Unal, A., Koçak, M., Markakis, K., Melas, D., Kouvarakis, G., Youssef, A. F., Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojie, F., Wittrock, F., von Savigny, C., Burrows, J. P., Ladstaetter-Weissenmayer, A. and Moubasher, H.: Megacities as hot spots of air pollution in the East Mediterranean, *Atmos. Environ.*, 45(6), 1223–1235, doi:10.1016/j.atmosenv.2010.11.048, 2011.
- Kansal, A.: Sources and reactivity of NMHCs and VOCs in the atmosphere: A review, *J. Hazard. Mater.*, 166(1), 17–26, doi:10.1016/j.jhazmat.2008.11.048, 2009.
- [Kassomenos, P., Kotroni, V., and Kallos, G.: Analysis of climatological 710 and air quality observations from Greater Athens Area, \*Atmos. Environ.\*, 29, 3671-3688, doi.org/10.1016/1352-2310\(94\)00358-R, 1995.](#)
- Klemm, O., Ziomas, I. C., Balis, D., Suppan, P., Slemr, J., Romero, R. and Vyras, L. G.: A summer air-pollution study in Athens, Greece, *Atmos. Environ.*, 32(12), 2071–2087, doi:10.1016/S1352-2310(97)00424-X, 1998.
- [Kourtidis, K. A., Ziomas, I. C., Rappenglueck, B., Proyou, A. and Balis, D.: Evaporative traffic hydrocarbon emissions, traffic CO and speciated HC traffic emissions from the city of Athens, \*Atmos. Environ.\*, 33\(23\), 3831–3842, doi:10.1016/S1352-2310\(98\)00395-1, 1999.](#)
- Lalas, D. P., Veirs, V. R., Karras, G. and Kallos, G.: An analysis of the SO<sub>2</sub> concentration levels in Athens, Greece, *Atmospheric Environ.* 1967, 16(3), 531–544, doi:10.1016/0004-6981(82)90162-7, 1982.
- Lalas, D. P., Asimakopoulos, D. N., Deligiorgi, D. G. and Helmis, C. G.: Sea-breeze circulation and photochemical pollution in Athens, Greece, *Atmospheric Environ.* 1967, 17(9), 1621–1632, doi:10.1016/0004-6981(83)90171-3, 1983.
- Lalas, D. P., Tombrou-Tsella, M., Petrakis, M., Asimakopoulos, D. N. and Helmis, C.: An experimental study of the horizontal and vertical distribution of ozone over Athens, *Atmospheric Environ.* 1967, 21(12), 2681–2693, doi:10.1016/0004-6981(87)90200-9, 1987.
- Liu, Y., Shao, M., Lu, S., Chang, C., Wang, J.-L. and Chen, G.: Volatile organic compound (VOC) measurements in the Pearl River Delta (PRD) region, China, *Atmospheric Chem. Phys.*, 8(6), 1531–1545, 2008.
- Mantis, H. T., Repapis, C. C., Zerefos, C. S. and Ziomas, J. C.: Assessment of the Potential for Photochemical Air Pollution in Athens: A Comparison of Emissions and Air-Pollutant Levels in Athens with Those in Los Angeles, *J. Appl. Meteorol.*, 31(12), 1467–1476, doi:10.1175/1520-0450(1992)031<1467:AOTPPF>2.0.CO;2, 1992.
- Melas, D., Ziomas, I., Klemm, O. and Zerefos, C. S.: Anatomy of the sea-breeze circulation in Athens area under weak large-scale ambient winds, *Atmos. Environ.*, 32(12), 2223–2237, doi:10.1016/S1352-2310(97)00420-2, 1998.

- Moschonas, N. and Glavas, S.: C3-C10 hydrocarbons in the atmosphere of Athens, Greece, *Atmos. Environ.*, 30(15), 2769–2772, doi:10.1016/1352-2310(95)00488-2, 1996.
- Moschonas, N., Glavas, S. and Kouimtzi, T.: C3 to C9 hydrocarbon measurements in the two largest cities of Greece, Athens and Thessaloniki. Calculation of hydrocarbon emissions by species. Derivation of hydroxyl radical concentrations, *Sci. Total Environ.*, 271(1), 117–133, doi:10.1016/S0048-9697(00)00838-X, 2001.
- 5 Nester, K.: Influence of sea breeze flows on air pollution over the Attica peninsula, *Atmos. Environ.*, 29(24), 3655–3670, doi:10.1016/1352-2310(95)98468-N, 1995.
- Paraskevopoulou, D., Liakakou, E., Gerasopoulos, E. and Mihalopoulos, N.: Sources of atmospheric aerosol from long-term measurements (5 years) of chemical composition in Athens, Greece, *Sci. Total Environ.*, 527(Supplement C), 165–178, doi:10.1016/j.scitotenv.2015.04.022, 2015.
- 10 Rappenglück, B., Fabian, P., Kalabokas, P., Viras, L. G. and Ziomas, I. C.: Quasi-continuous measurements of non-methane hydrocarbons (NMHC) in the Greater Athens area during MedCaphot-trace, *Atmos. Environ.*, 32(12), 2103–2121, doi:10.1016/S1352-2310(97)00430-5, 1998.
- Rappenglück, B., Kourtidis, K., Melas, D. and Fabian, P.: Observations of biogenic and anthropogenic NMHC in the greater Athens area during the PAUR campaign, *Phys. Chem. Earth Part B Hydrol. Oceans Atmosphere*, 24(6), 717–724, doi:10.1016/S1464-1909(99)00071-4, 1999.
- 15 Saffari, A., Daher, N., Samara, C., Voutsas, D., Kouras, A., Manoli, E., Karagkiozidou, O., Vlachokostas, C., Moussiopoulos, N., Shafer, M. M., Schauer, J. J. and Sioutas, C.: Increased Biomass Burning Due to the Economic Crisis in Greece and Its Adverse Impact on Wintertime Air Quality in Thessaloniki, *Environ. Sci. Technol.*, 47(23), 13313–13320, doi:10.1021/es403847h, 2013.
- 20 Salameh, T., Sauvage, S., Afif, C., Borbon, A., Léonardis, T., Brioude, J., Waked, A. and Locoge, N.: Exploring the seasonal NMHC distribution in an urban area of the Middle East during ECOCEM campaigns: very high loadings dominated by local emissions and dynamics, *Environ. Chem.*, 12(3), 316–328, doi:10.1071/EN14154, 2015.
- Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P. and Galloo, J. C.: Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas, *Atmos. Environ.*, 43(15), 2430–2441, doi:10.1016/j.atmosenv.2009.02.001, 2009.
- 25 Schauer, J. J., Kleeman, M. J., Cass, G. R. and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 3. C1–C29 Organic Compounds from Fireplace Combustion of Wood, *Environ. Sci. Technol.*, 35(9), 1716–1728, doi:10.1021/es001331e, 2001.
- 30 Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons., 2016.
- Theodosi, C., Grivas, G., Zampas, P., Chaloulakou, A. and Mihalopoulos, N.: Mass and chemical composition of size-segregated aerosols (PM1, PM2.5, PM10) over Athens, Greece: local versus regional sources, *Atmos Chem Phys*, 11(22), 11895–11911, doi:10.5194/acp-11-11895-2011, 2011.



Tsigaridis, K. and Kanakidou, M.: Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis, *Atmos Chem Phys*, 3(5), 1849–1869, doi:10.5194/acp-3-1849-2003, 2003.

Vrekoussis, M., Richter, A., Hilboll, A., Burrows, J. P., Gerasopoulos, E., Lelieveld, J., Barrie, L., Zerefos, C. and Mihalopoulos, N.: Economic crisis detected from space: Air quality observations over Athens/Greece, *Geophys. Res. Lett.*, 5 40(2), 458–463, doi:10.1002/grl.50118, 2013.

WHO - IARC: Outdoor air pollution a leading environmental cause of cancer deaths, Press Release no221, 2013.

Zhang, Q., Wu, L., Fang, X., Liu, M., Zhang, J., Shao, M., Lu, S. and Mao, H.: Emission factors of volatile organic compounds (VOCs) based on the detailed vehicle classification in a tunnel study, *Sci. Total Environ.*, 624, 878–886, doi:10.1016/j.scitotenv.2017.12.171, 2018.

10 Zhang, Y., Yang, W., Simpson, I., Huang, X., Yu, J., Huang, Z., Wang, Z., Zhang, Z., Liu, D., Huang, Z., Wang, Y., Pei, C., Shao, M., Blake, D. R., Zheng, J., Huang, Z. and Wang, X.: Decadal changes in emissions of volatile organic compounds (VOCs) from on-road vehicles with intensified automobile pollution control: Case study in a busy urban tunnel in south China, *Environ. Pollut.*, 233, 806–819, doi:10.1016/j.envpol.2017.10.133, 2018.

15 Ziomas, I. C., Suppan, P., Rappengluck, B., Balis, D., Tzoumaka, P., Melas, D., Papayiannis, D., Fabian, P., and Zerefos, C. S.: A contribution to the study of photochemical smog in the greater Athens area. *Beitrage zur Physik der Atmosphäre-Contributions to Atmospheric Physics*, 68(3), 191-204, 1995.

20

25

**Table 1. Comparison of NMHCs mean levels between this study and already published works in Athens, Greek and other Mediterranean or European sites. Information about the analyzing or sampling techniques and data resolution are included when available. The number of measurements<sup>a</sup> for each compound determined on the current samples is included below the table.**

Studies	Rappenglück et al., 1998		Rappenglück et al. 1999	Moschonas and Glavas, 1996	Kaltsonoudis et al. 2016		Baudic et al., 2016	Salameh et al., 2015	Durana et al., 2006	Current work			
Analysis details	GC – FID Every 20min		GC – FID Every 20min	GC – MS 60 min (morning sampling, 12 canisters)	PTR-MS Every 10s/24h		GC – FID	GC - FID	GC - FID	GC – FID Every 30min			
	20 August – 20 September 1994, Athens, Greece		30 May – 16 June 1996, Athens, Greece	June 1993, May and July 1994, Athens, Greece	3- 26 July 2012 (Demokritos) & 9 January – 6 February 2013 (Thissio)		16 October – 22 November 2010 Paris, France	28 January – 12 February 2012 Beirut, Lebanon	April-October 1998-2001 February-July 2004 Bilbao Spain <sup>b</sup>	16 October 2015 - 15 February 2016, Athens, Greece			
NMHCs	Patision (Urban)	Demokritos (Suburban)	Tatoi (Suburban)	Ancient Agora (urban)	Demokritos (Suburban)	Thissio (Urban background)	Les Halles station (Urban background)	Saint Joseph University (Suburban)	Bilbao (Urban center)	Thissio (Urban background)			
										Mean	Median	Min	Max
	ppbv		ppbv	ppbv	ppb		ppb	ppb	ppbv	ppb			
Ethane							3.8	2.8	2.5 - 3.5	4.5	3.1	0.6	25.9
Ethylene							1.3	2.1	2 - 2.3	4.1	2.2	0.3	22.9
Propane				1.2			1.6	3.0	1.7 - 2.5	3.1	1.8	0.2	17.8
Propene				3.9			0.4	0.6	0.7-0.9	1.5	0.6	0.02	15.7
i-Butane				1.1			0.9	1.9	0.7-2	2.3	1.1	0.1	14.9
n-Butane	12.4	1.6	0.19	2.1			1.5	3.6	1.8 - 2.6	2.6	1.3	0.1	15.2
	(with 1-butene)		(with 1-butene)										
Acetylene							0.5	2.2	1.5 - 2.7	4.2	2.4	0.1	28.5
i-Pentane	26.3	3.2	0.93	11.7			0.7	2.4	1 - 1.7	4.7	2.6	0.2	23.8
n-Pentane	14.2	1.7	0.27	4.2			0.3	0.5	0.4 - 0.7	1.1	0.6	0.1	9.3
	(with 2-methyl-1-butene)		(with 2-methyl-1-butene)										
Isoprene			3.18(with trans-2-pentene & cis-2-pentene)		0.7	1.1	0.1	0.1		0.2	0.1	0.01	1.4
Benzene	11.7	2.5	2.12	5.0	0.2	1.0	0.4	0.5	0.5 - 1	0.8	0.5	0.02	5.3
Toluene	21.2	6.7	1.15	14.3	0.8	2.3	0.8	2.2	2 - 2.6	2.2 <sup>d</sup>	1.0 <sup>d</sup>	0.1 <sup>d</sup>	13.7 <sup>d</sup>
Ethylbenzene	4.0	1.3	0.20	2.7				0.3	0.6 – 0.8	0.4 <sup>d</sup>	0.2 <sup>d</sup>	0.03 <sup>d</sup>	2.7 <sup>d</sup>
m-/p- Xylenes	11.3 <sup>c</sup>	3.2 <sup>c</sup>	0.63 <sup>c</sup>	12.1				0.4	2.0 – 2.4	1.2 <sup>d</sup>	0.5 <sup>d</sup>	0.03 <sup>d</sup>	8.3 <sup>d</sup>
o- Xylene	5.5	1.5	0.3	3.7				0.3	0.4 – 0.5	0.4 <sup>d</sup>	0.2 <sup>d</sup>	0.03 <sup>d</sup>	3.1 <sup>d</sup>

<sup>a</sup> ethane N= 2848, ethylene N=2859, propane N=2861, propene N=2842, i-Butane N=2876, n-butane N=2879, acetylene N=2565, i-pentane N=2874, n-pentane N=2859, isoprene N=264, benzene N=2683, toluene N=637.

5 | <sup>b</sup> Range estimated from Figure 1, included in Durana et al., 2006.

<sup>c</sup> Sum of the reported mean value for m – Xylene and p – Xylene.

<sup>d</sup> Only from 20 January 2016 to 15 February 2016

**Table 2: Enhancement ratios of NMHC to NOx (ppb/ppb) and to CO (ppb/ppb), calculated from the present data-set for Thissio Station and the Street canyon measurements (Patisson station) for the time-window of the traffic rush hours. The enhancement ratios presented in the 3rd and 6th column are reported in Kourtidis et al., (1999) and they were calculated for the same station in the street canyon.**

<b><u>Ratios of NMHCs to:</u></b>	<b><u>NOx (ppb/ppb)</u></b>			<b><u>CO (ppb/ppb)</u></b>		
	<b><u>Thissio station (urban background)</u></b>	<b><u>Patisson station (traffic)</u></b>	<b><u>Patisson station (traffic), 1994*</u></b>	<b><u>Thissio station (urban background)</u></b>	<b><u>Patisson station (traffic)</u></b>	<b><u>Patisson station (traffic), 1994</u></b>
	<b><u>21 January - 15 February 2016</u></b>	<b><u>23 - 24 February 2017</u></b>	<b><u>20 August - 20 September 1994</u></b>	<b><u>21 January - 15 February 2016</u></b>	<b><u>23 - 24 February 2017</u></b>	<b><u>20 August - 20 September 1994</u></b>
<b><u>i - Pentane</u></b>	<b><u>0.0639</u></b>	<b><u>0.0490</u></b>	<b><u>0.2468</u></b>	<b><u>0.0072</u></b>	<b><u>0.0058</u></b>	<b><u>0.0098</u></b>
<b><u>Benzene</u></b>	<b><u>0.0095</u></b>	<b><u>0.0083</u></b>	<b><u>0.1042</u></b>	<b><u>0.0012</u></b>	<b><u>0.0009</u></b>	<b><u>0.00414</u></b>
<b><u>Toluene</u></b>	<b><u>0.0417</u></b>	<b><u>0.0320</u></b>	<b><u>0.1799</u></b>	<b><u>0.0056</u></b>	<b><u>0.0034</u></b>	<b><u>0.00715</u></b>
<b><u>Ethylbenzene</u></b>	<b><u>0.0073</u></b>	<b><u>0.0053</u></b>	<b><u>0.0338</u></b>			
<b><u>o - Xylene</u></b>	<b><u>0.0082</u></b>	<b><u>0.0059</u></b>	<b><u>0.0471</u></b>			

\*The NMHC-to-NOx enhancement ratios given in w/w (weight/weight) were converted in ppb/ppb by dividing them with the ratio of the molecular weight of the NMHC to the molecular weight of NOx (equal to 31.6 according to Kourtidis et al., 1999).

**Table 32. Correlation coefficients ( $R^2$ ) of NMHCs and major gaseous pollutants for the total period of measurements (all significant at  $p < 0.01$ ).**

	Ethane	Ethylene	Propane	Propene	i-Butane	n-Butane	Acetylene	i-Pentane	n-Pentane	Benzene	BC	BCwb	BCff	CO
<b>Ethane</b>														
<b>Ethylene</b>	0.94													
<b>Propane</b>	0.92	0.94												
<b>Propene</b>	0.94	0.97	0.96											
<b>i-Butane</b>	0.82	0.90	0.95	0.92										
<b>n-Butane</b>	0.84	0.91	0.97	0.92	0.99									
<b>Acetylene</b>	0.89	0.91	0.90	0.91	0.88	0.88								
<b>i-Pentane</b>	0.73	0.85	0.88	0.85	0.96	0.95	0.81							
<b>n-Pentane</b>	0.74	0.85	0.90	0.88	0.97	0.96	0.84	0.96						
<b>Benzene</b>	0.87	0.95	0.93	0.96	0.91	0.92	0.89	0.87	0.89					
<b>BC</b>	0.93	0.95	0.92	0.96	0.88	0.89	0.90	0.84	0.85	0.93				
<b>BCwb</b>	0.91	0.87	0.81	0.89	0.70	0.72	0.77	0.65	0.64	0.83	0.91			
<b>BCff</b>	0.84	0.90	0.89	0.90	0.91	0.91	0.89	0.89	0.90	0.89	0.95	0.75		
<b>CO</b>	0.91	0.95	0.94	0.96	0.92	0.93	0.92	0.87	0.89	0.95	0.97	0.87	0.93	
<b>NO</b>	0.86	0.90	0.90	0.90	0.90	0.91	0.89	0.90	0.88	0.89	0.91	0.76	0.92	0.94

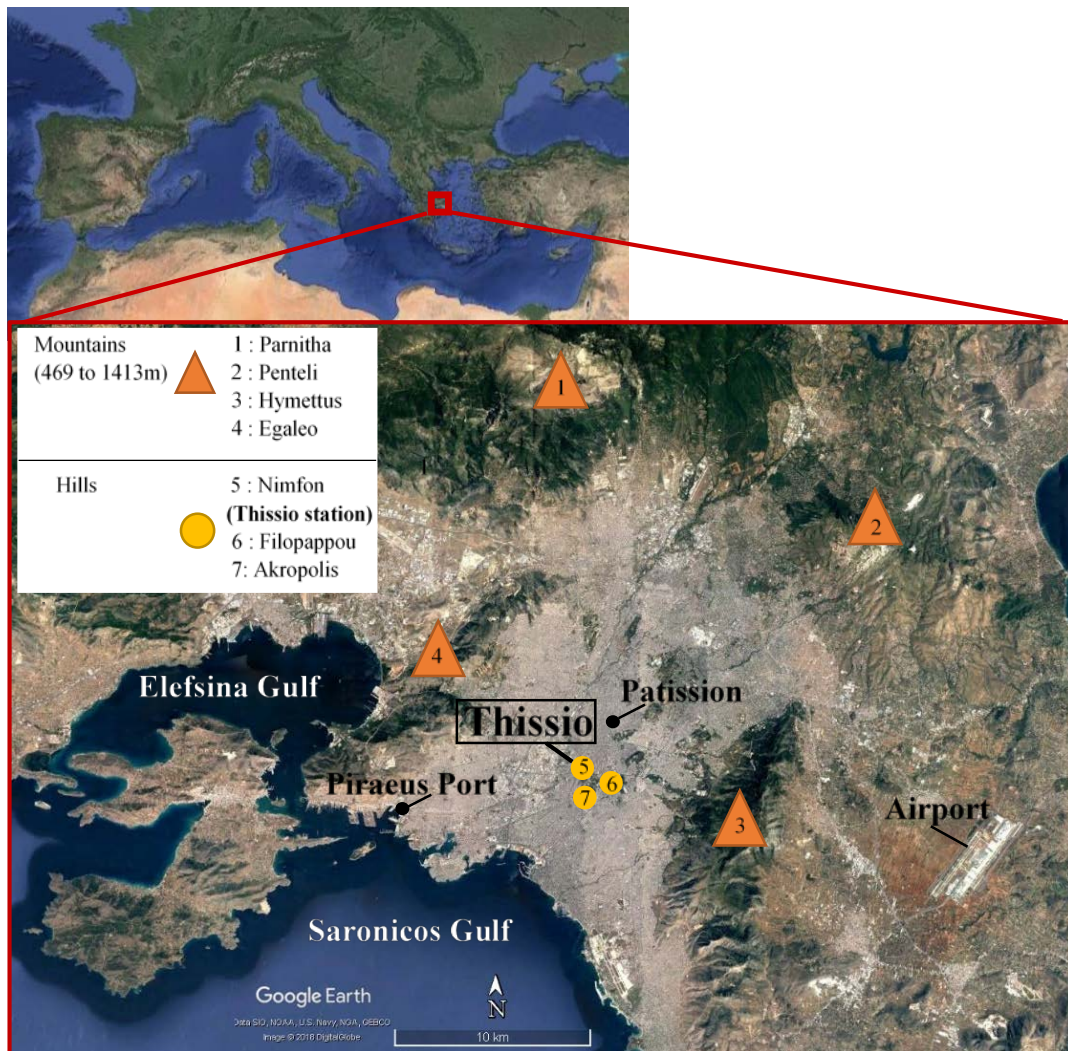


Figure 1. Map of the Greater Athens Area. The four mountains define the borders of the area.

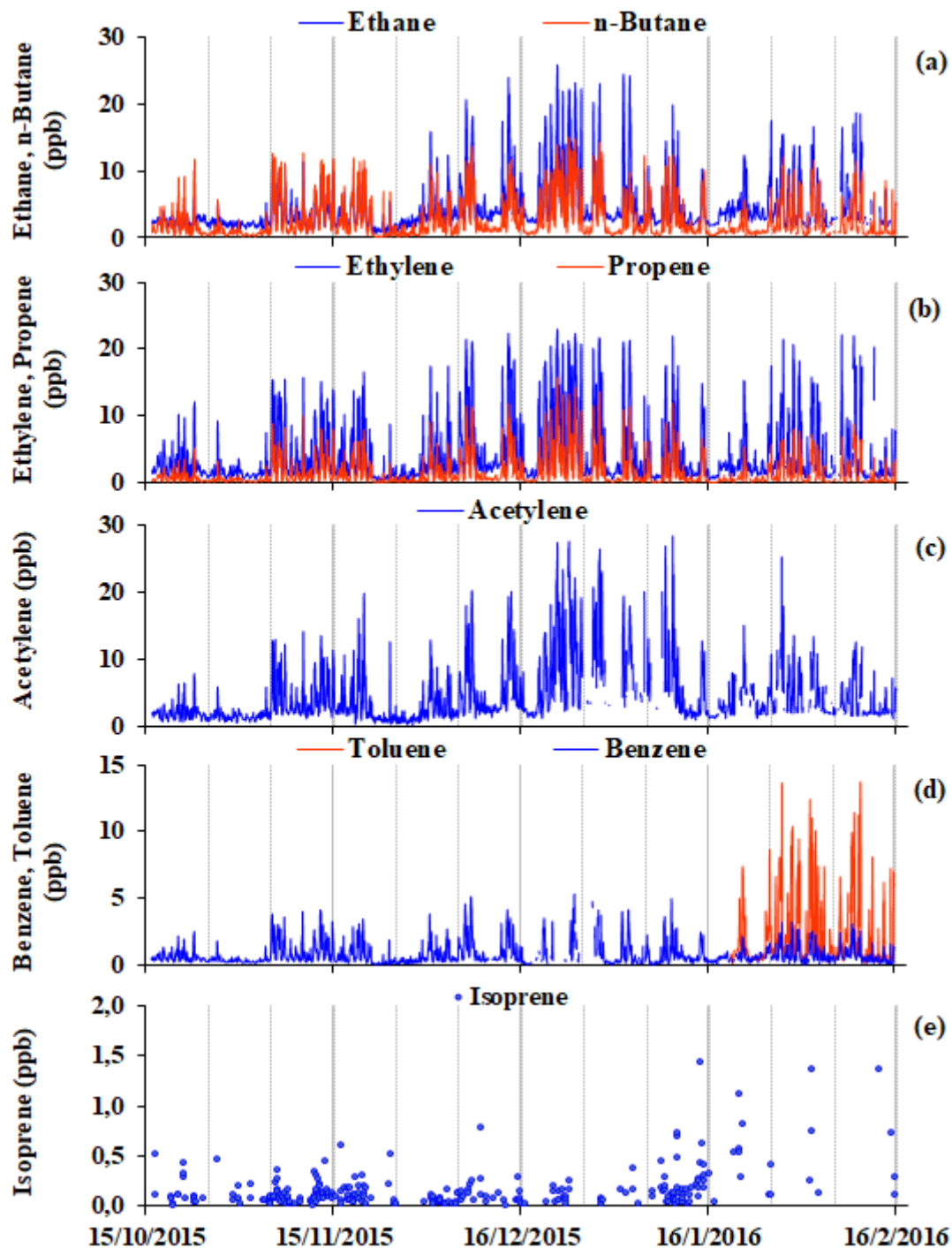


Figure 2. Temporal variability of (a) ethane and n-butane, (b) ethylene and propene, (c) acetylene, (d) benzene and toluene and (e) isoprene, based on hourly averaged levels for the period 16 October 2015 - 15 February 2016, at NOA's urban background site in Thissio, downtown Athens.

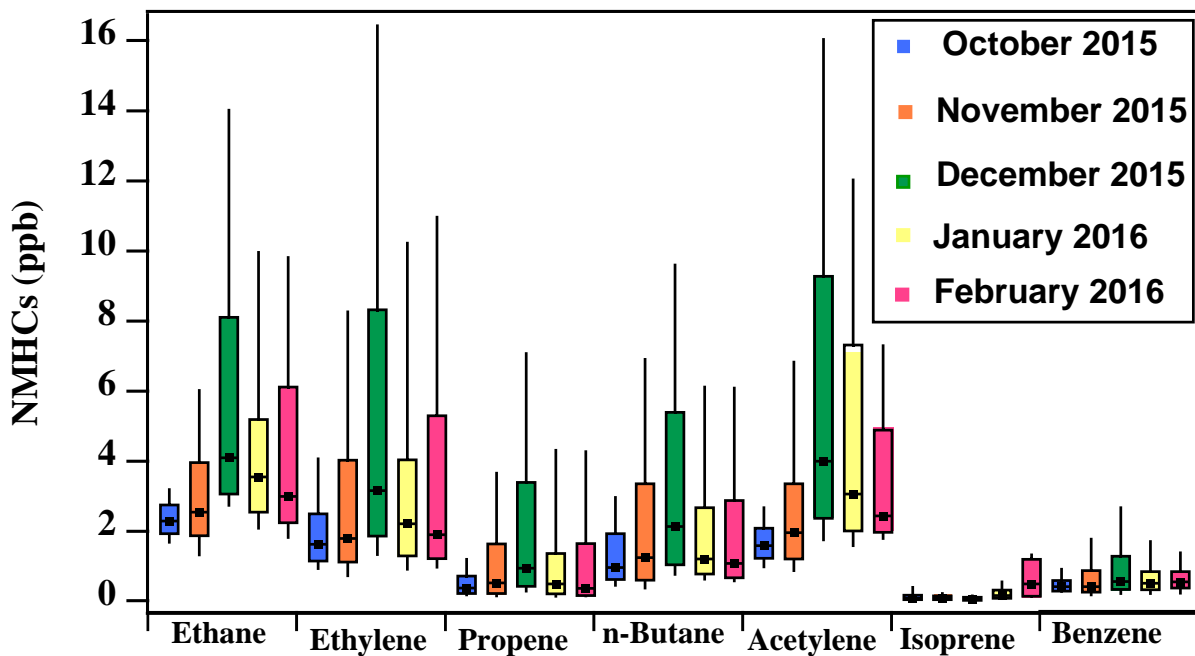


Figure 3. Monthly box plots for ethane, ethylene, propene, n-butane, acetylene, isoprene and benzene. The black dot represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1<sup>st</sup> and 3<sup>rd</sup> quartiles (i. e. Q1 and Q3). The whiskers correspond to the 1<sup>st</sup> and the 9<sup>th</sup> deciles (i. e. D1 and D9).

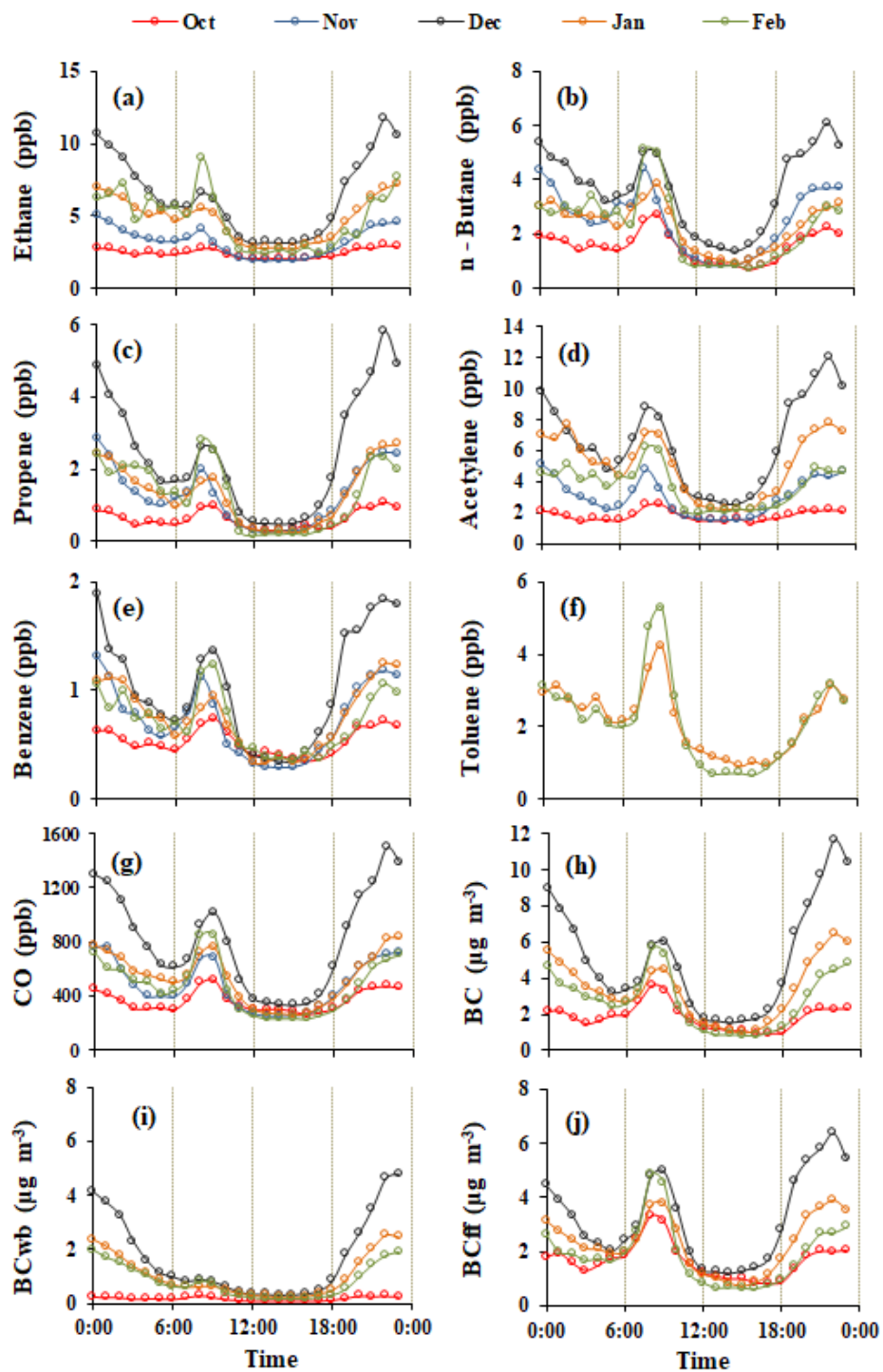


Figure 4. Monthly diurnal variability of (a) ethane, (b) n-butane, (c) propene, (d) acetylene, (e) benzene, (f) toluene, (g) CO, (h) BC, (i)  $BC_{wb}$  and (j)  $BC_{ff}$  based on hourly averaged values.



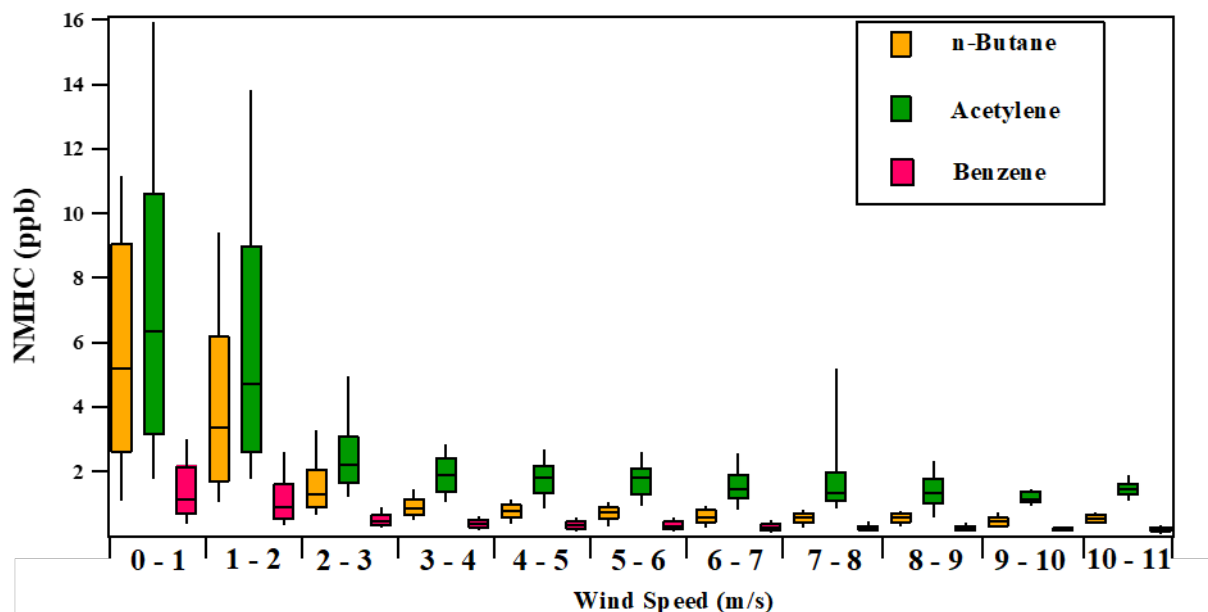


Figure 5. Boxplots for (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the period 16 October 2015 – 15 February 2016. The black line represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1<sup>st</sup> and 3<sup>rd</sup> quartiles (i. e. Q1 and Q3). The whiskers correspond to the 1<sup>st</sup> and the 9<sup>th</sup> deciles (i. e. D1 and D9).

Figure 5. Boxplots for (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the period 16 October 2015 - 15 February 2016. The black line represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1st and 3rd quartiles (i. e. Q1 and Q3). The whiskers correspond to the 1st and the 9th deciles (i. e. D1 and D9). The range of each wind speed bin is depicted on x-axis.

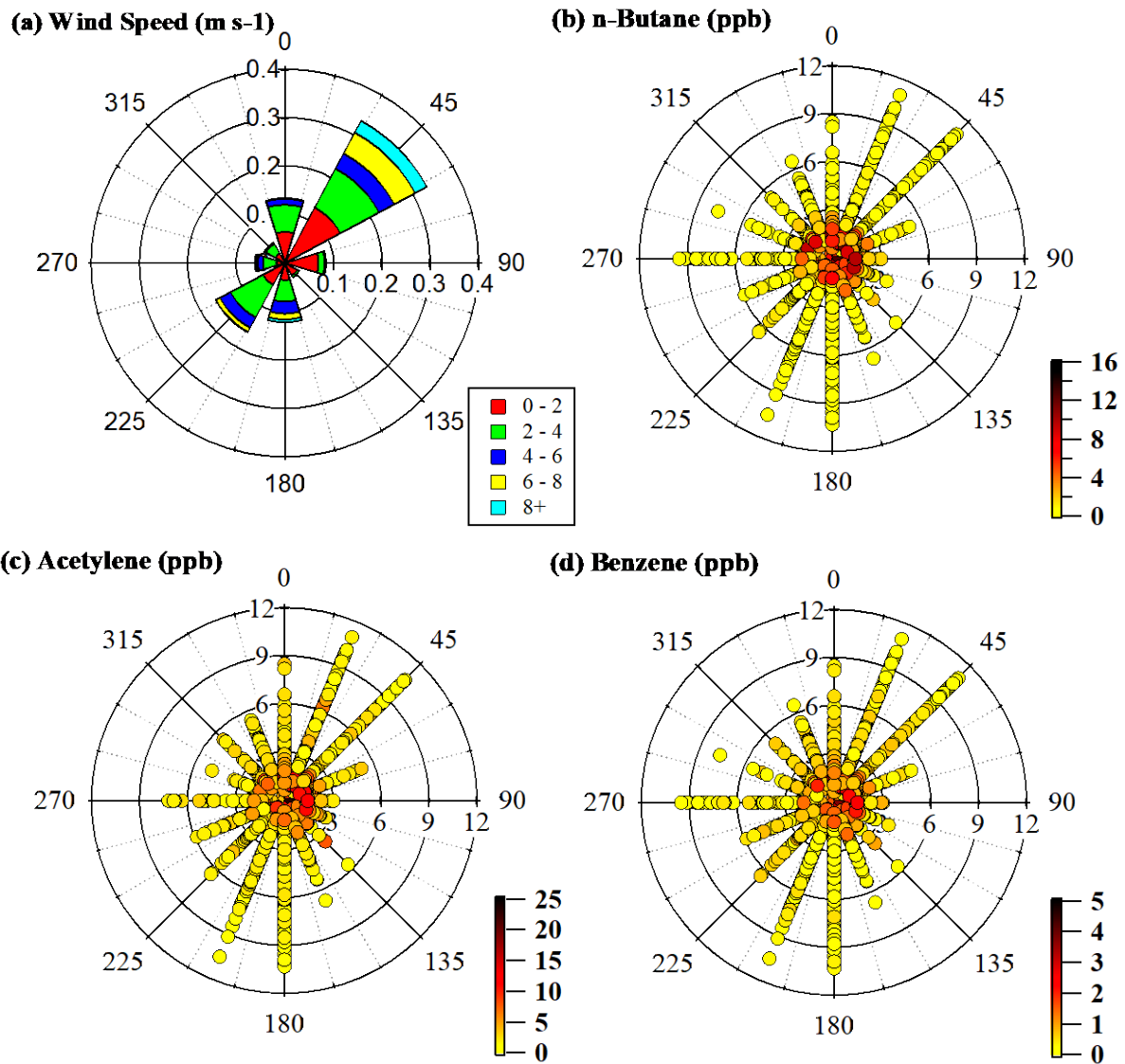
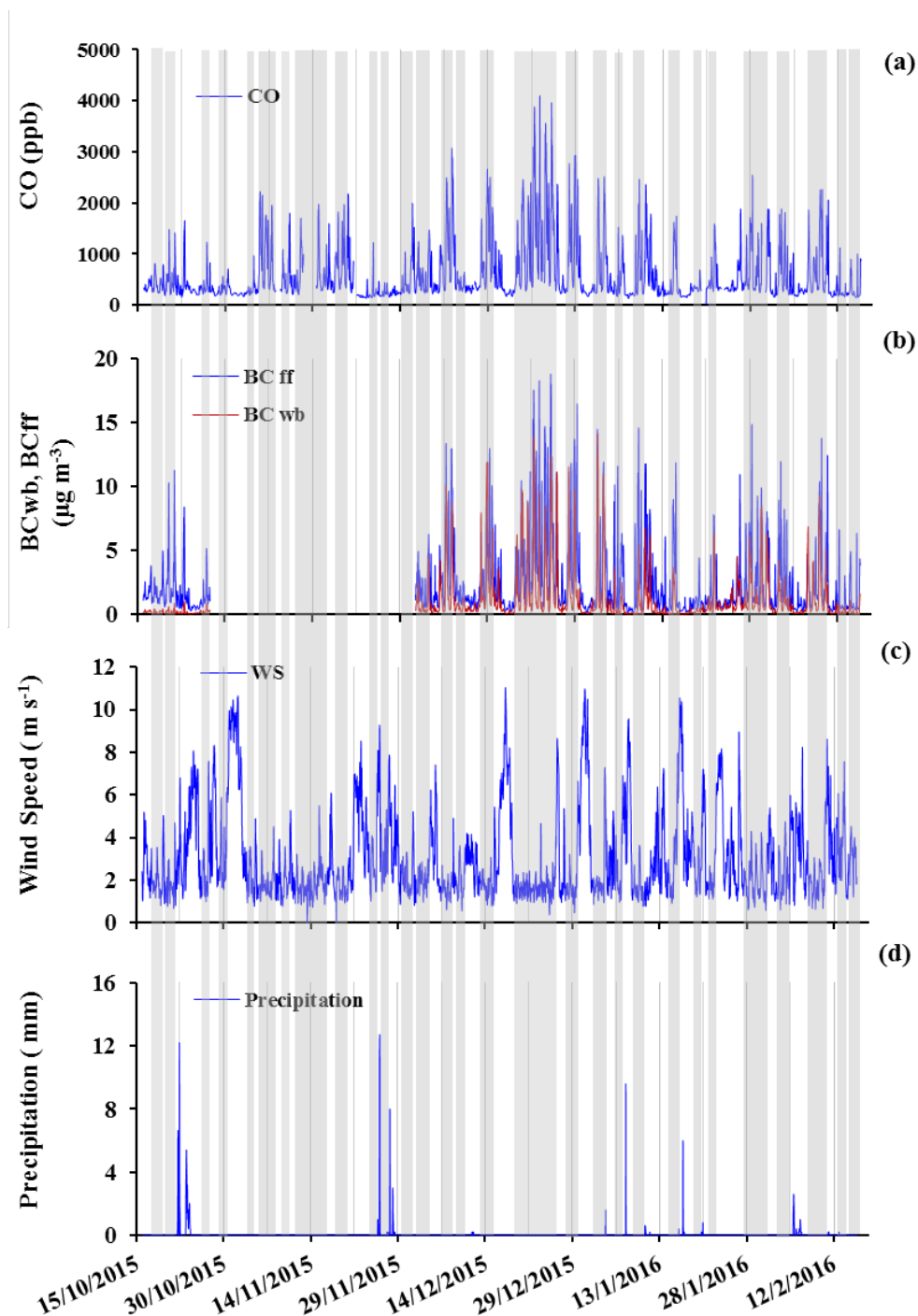


Figure 6. Wind rose (a) and concentration roses of (b) n-butane, (c) acetylene, and (d) benzene for the period 16 October 2015 to 15 February 2016.



**Figure 7. Temporal variability of (a) CO, (b) BC<sub>wb</sub> and BC<sub>ff</sub> fractions, (c) wind speed and (d) precipitation for the experimental period. Grey frames correspond to smog periods (SP), while the remaining part to non-smog periods (nSP).**

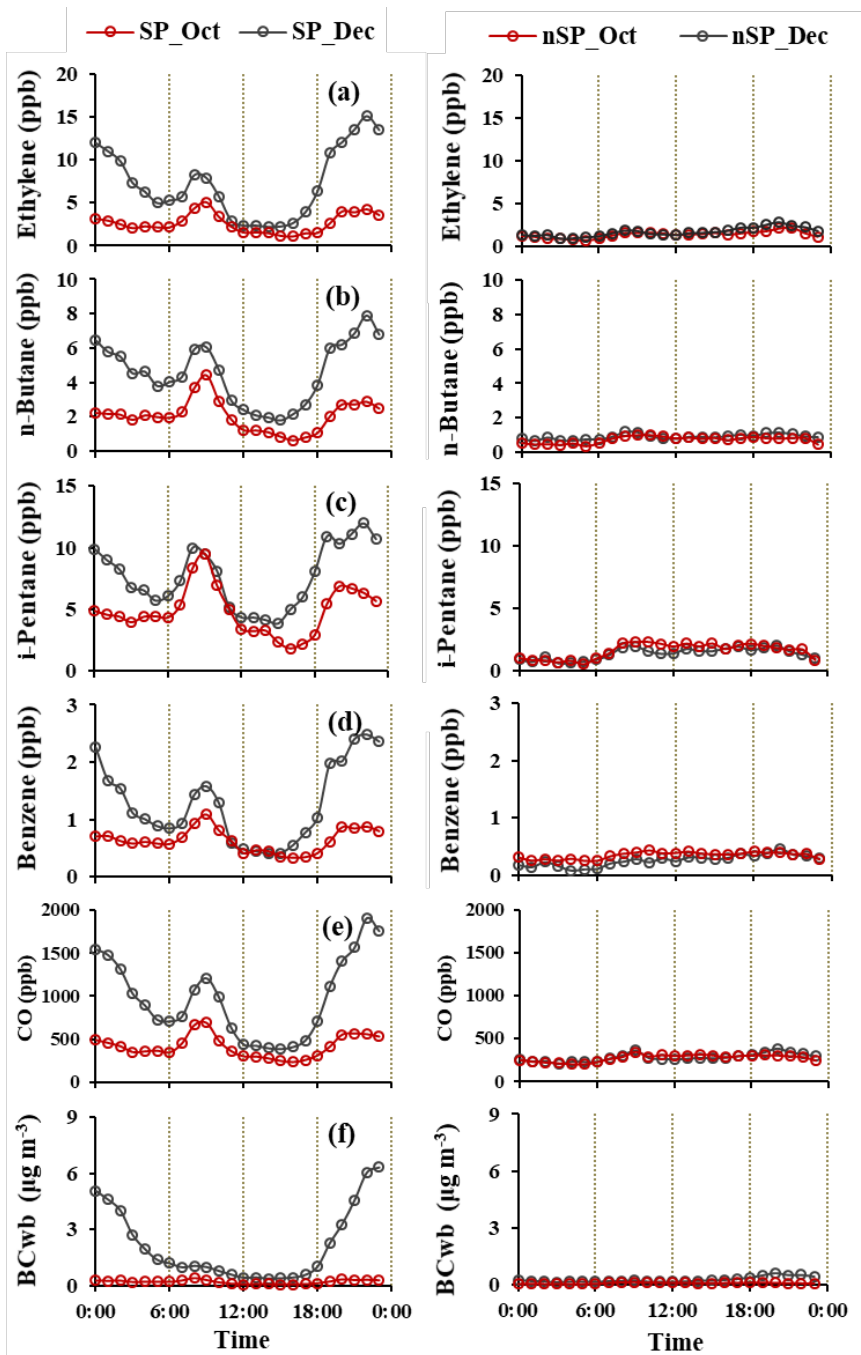
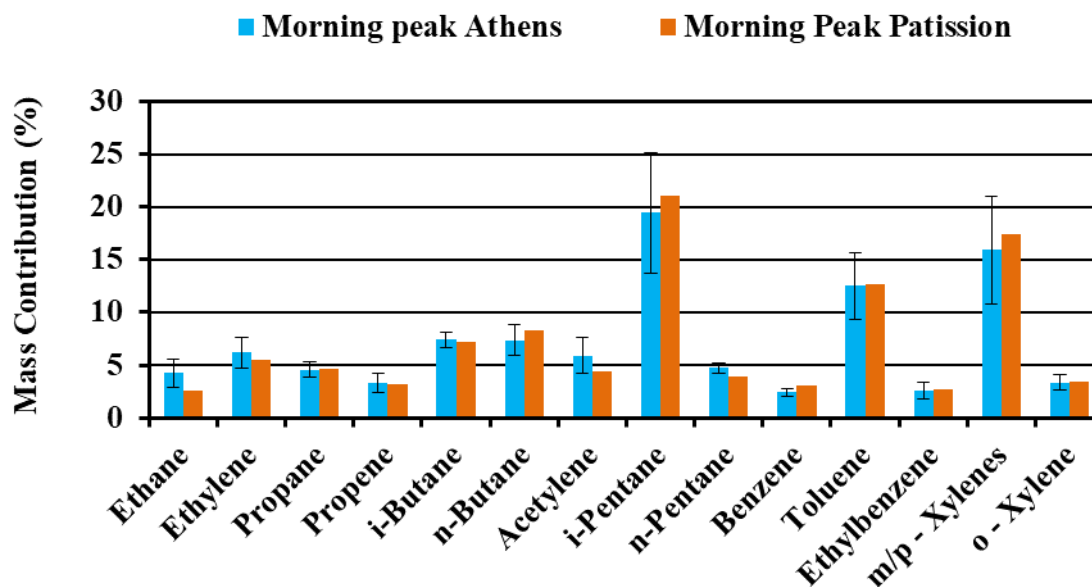


Figure 8. Diurnal patterns of (a) ethylene, (b) n-butane, (c) i-pentane, (d) benzene, (e) CO, (f)  $BC_{wb}$  during the SP (left column) and the nSP (right column) periods identified during October 2015 (red) and December 2015 (black) respectively. Note: SP periods are defined by wind-speed lower than  $3 \text{ m s}^{-1}$  and absence of rainfall, while nSP periods are defined by winds-speeds higher than  $3 \text{ m s}^{-1}$ .

5



**Figure 9. % Mass contribution of the measured NMHCs during the morning peak (07:00—10:00 LT), median values in Thissio, in Patission Monitoring Station, in a highway tunnel in GAA and a highway tunnel close to Paris.**

5 **Figure 9. %Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00LT), median values in Thissio and mean values in Patission Monitoring Station.**

10

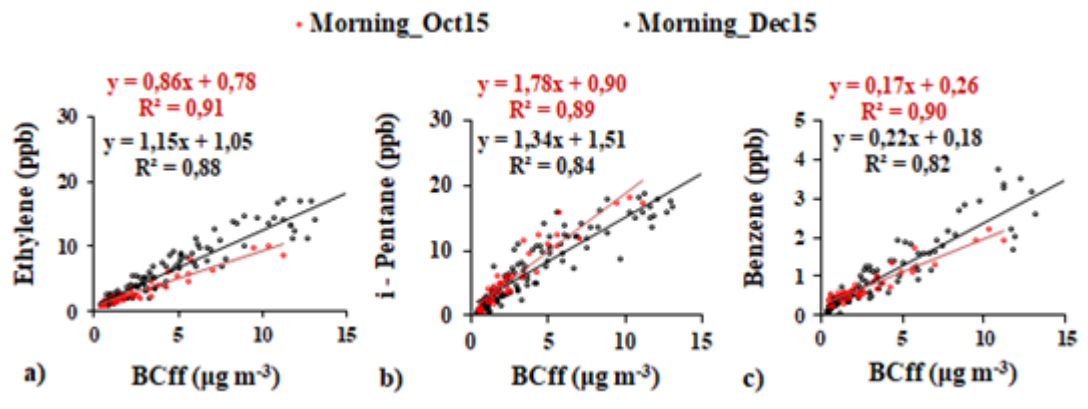


Figure 10. Regressions between ethylene, i-pentane, and benzene versus  $BC_{fr}$  (a-c) for the morning period (07:00 – 10:00LT) in October and December 2015.

5

10

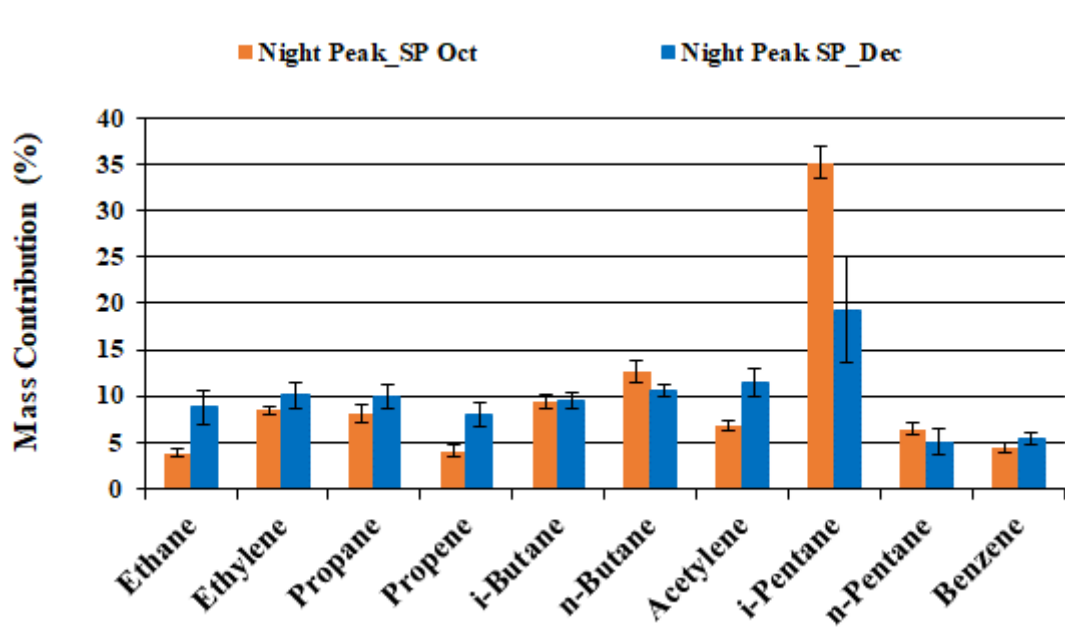


Figure 11. % Mass contribution of the measured NMHCs during the night-time enhancement period peak (18:00 – 05:00LT) for the SP of October (orange) and the SP of December (black color).

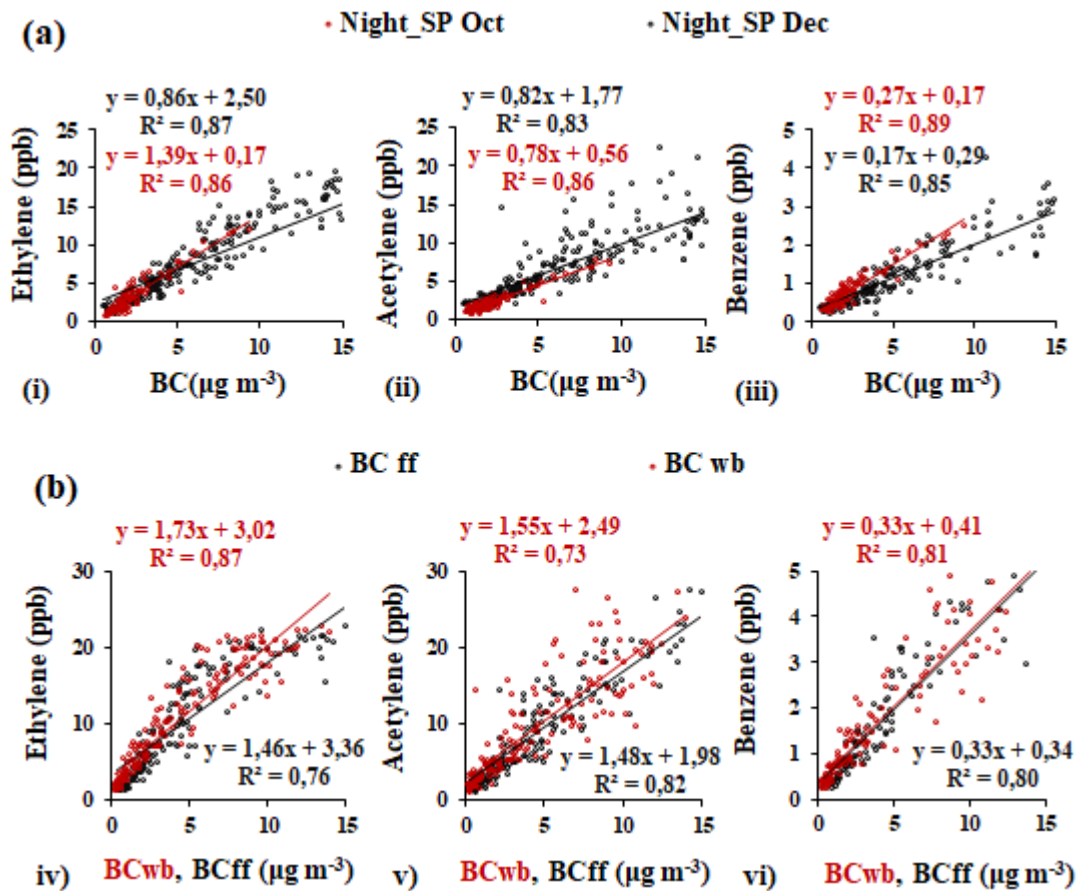


Figure 12. Regressions between ethylene, acetylene and benzene (a) against BC (i-iii) for the night period (18:00 – 05:00LT) of SP October and December 2015 and (b) against BC<sub>wb</sub> (red) and BC<sub>ff</sub> (black) for the night period (22:00 – 04:00LT) of SP December 2015.

5

10