Reference article: acp-2017-936

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

Erratum

Due to the continuous evaluation of the present data-set after the submission of this manuscript, an error in the calculation of the concentrations of NMHCs was found, resulting in an overestimation of ethane and ethylene (especially after December 2015). Propene and acetylene were also affected but not significantly (< 3%), while the remaining NMHCs were not affected at all. In particular, the correction decreased the levels of ethane and ethylene by 20 to 50% (from November 2015 to February 2016) and 17 to 38% (same period) respectively.

Although the levels of ethane and ethylene changed, the main conclusions of this manuscript were not affected. As a consequence, the figures were corrected and our answers to the reviewers are based on the corrected data. The co-authors would like to apologize for this inconvenience and they express their gratitude for the understanding.

In a summary, the following changes were done in the manuscript from this change in NMHCs levels:

- All the tables figures changed based on the new concentrations of the 4 compounds (ethane, ethylene, propene, acetylene). **The figures can be found before the replies section and the blue color indicates their numeration in the revised manuscript**.
- P5, L5: "The highest values 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."
- P7, L14: The phrase "Ethane, ethylene and acetylene were moderately (R^2 of 0.5–0.7) correlated with C4 or C5 compounds…." was changed with the "All NMHCs were well correlated ($R^2 > 0.81$) …".

- P7, L18: In the phrase “The strong correlation ($R^2 > 0.84$) of the hydrocarbons, except ethane, with BC_{ff} could imply stronger emission of NMHCs from fossil fuel combustion processes relatively to wood burning”, the term “except ethane” was removed.

- P8, L18: The phrase “For the nSP cases (Fig. 7 and S7) the concentrations of all compounds were very low (lower than the minimum of the SP periods) and almost equal, with the exception of ethane and acetylene that demonstrated higher concentrations in December by a factor of two (Fig. S7a,e).” was changed to the “NMHCs levels during the nSP periods in October and December 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.”.

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[a] 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			
NMHCs	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[b]	16 October 2015 - 15 February 2016, Athens, Greece			
	Patision (Urban)	Demokrirtos (Suburban)	Tatoi (Suburban)	Ancient Agora (urban)	Demokrirtos (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 (with 1-butene)	1.6	0.19 (with 1-butene)	2.1			1.5	3.6	1.8 - 2.6	2.6	1.3	0.1	15.2
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 (with 2-methyl-1-butene)	1.7	0.27 (with 2-methyl-1-butene)	4.2			0.3	0.5	0.4 - 0.7	1.1	0.6	0.1	9.3
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	1.0	0.1	13.7

a 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.

b Range estimated from Figure 1, included in Durana et al., 2006.

Table 2. 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
Ethane														
Ethylene	0.94													
Propane	0.92	0.94												
Propene	0.94	0.97	0.96											
i-Butane	0.82	0.90	0.95	0.92										
n-Butane	0.84	0.91	0.97	0.92	0.99									
Acetylene	0.89	0.91	0.90	0.91	0.88	0.88								
i-Pentane	0.73	0.85	0.88	0.85	0.96	0.95	0.81							
n-Pentane	0.74	0.85	0.90	0.88	0.97	0.96	0.84	0.96						
Benzene	0.87	0.95	0.93	0.96	0.91	0.92	0.89	0.87	0.89					
BC	0.93	0.95	0.92	0.96	0.88	0.89	0.90	0.84	0.85	0.93				
BCwb	0.91	0.87	0.81	0.89	0.70	0.72	0.77	0.65	0.64	0.83	0.91			
BCff	0.84	0.90	0.89	0.90	0.91	0.91	0.89	0.89	0.90	0.89	0.95	0.75		
CO	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	
NO	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

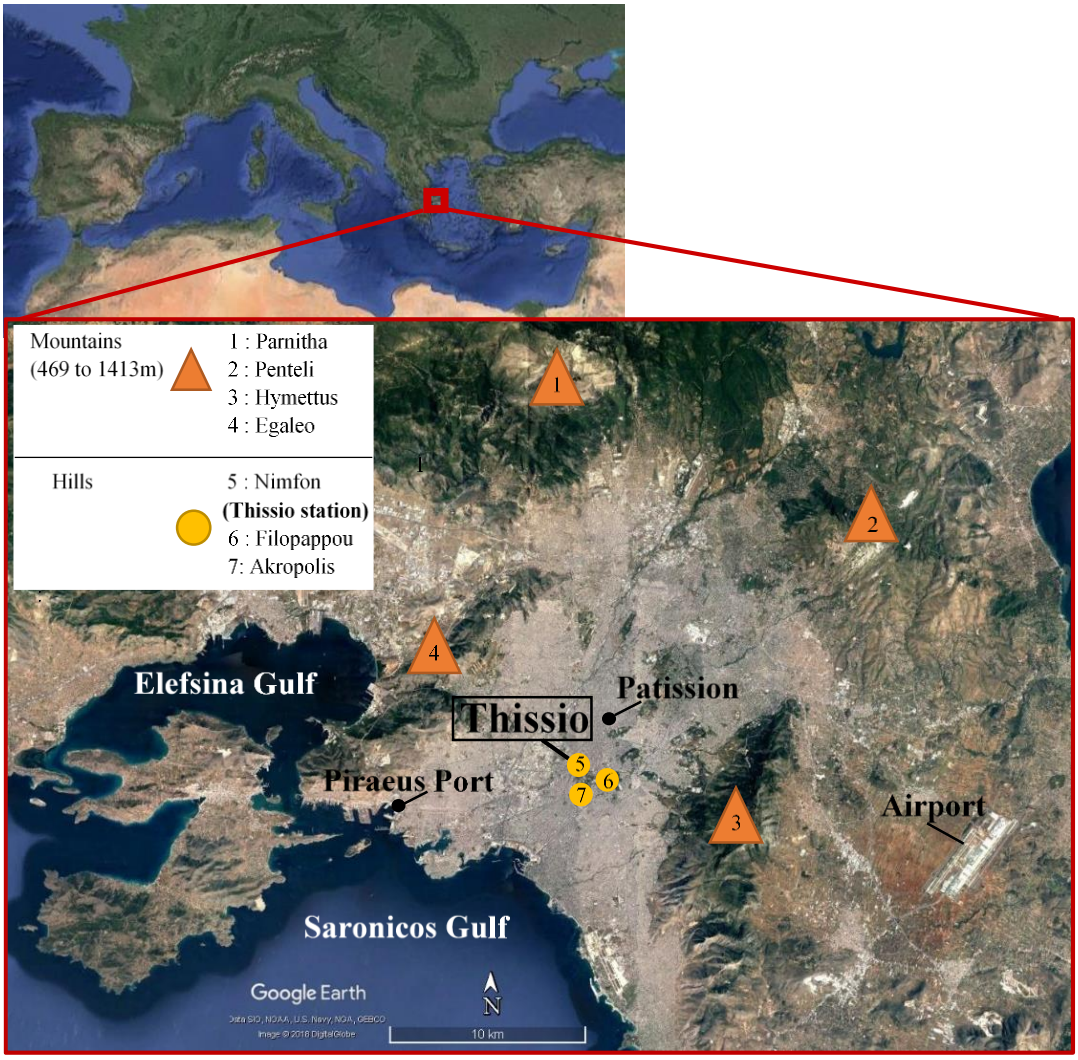

Figure 1. Map of the Greater Athens Area. The four mountains define the borders of the area.

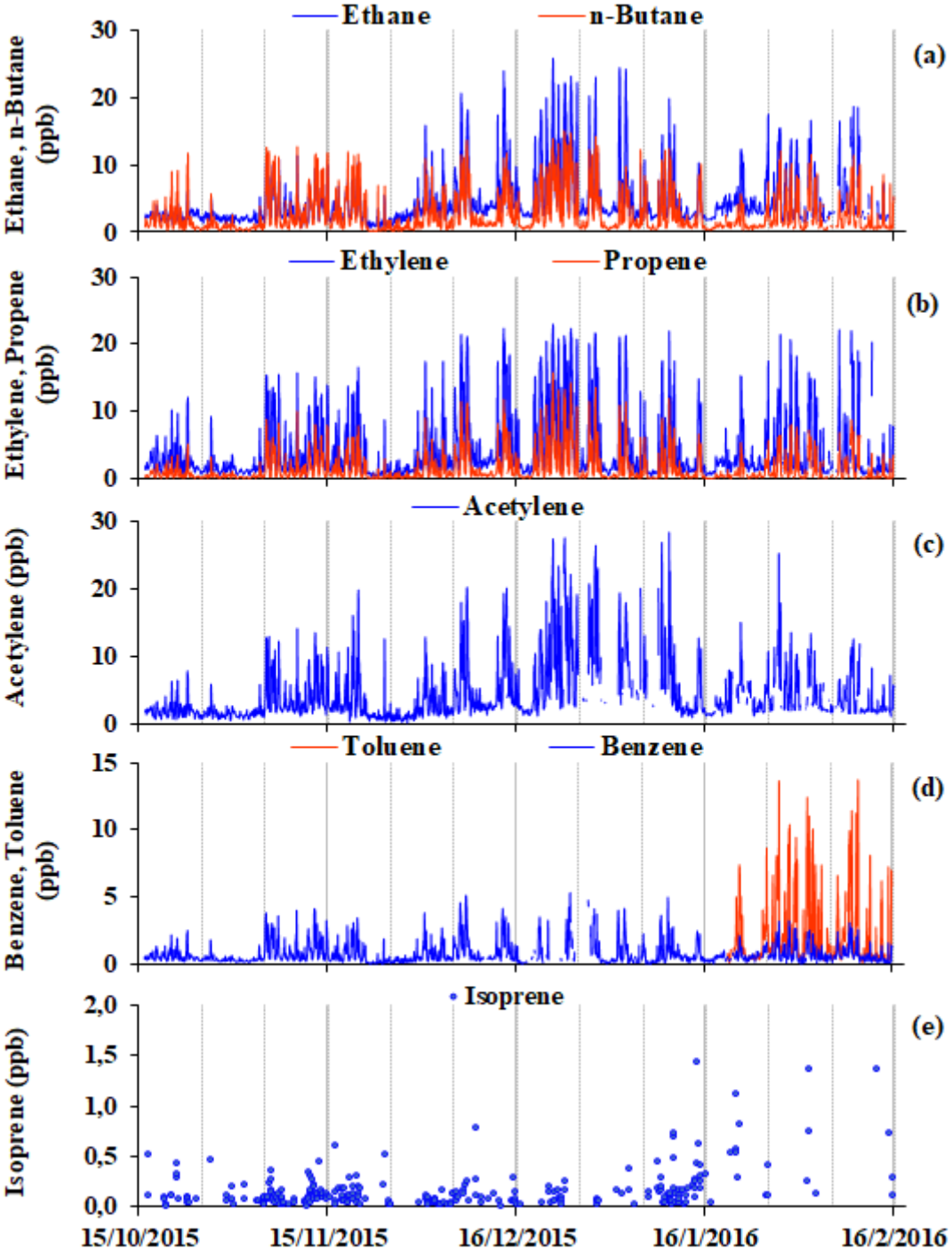

Figure 2. **Temporal variability of (a) ethane and n-butane, (b) ethylene and propene, (c) acetylene, (d) benzene and toluene and (e) isoprene, based on hourly averaged levels for the period 16 October 2015 - 15 February 2016, at NOA's urban background site in Thissio, downtown Athens.**

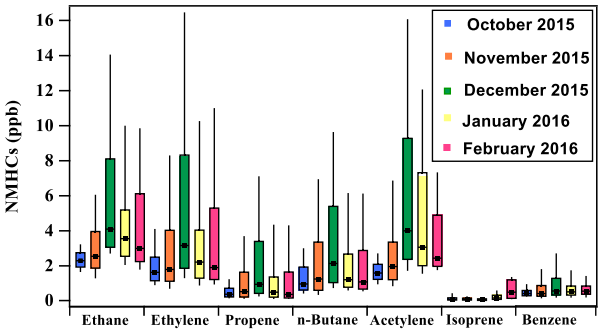

Figure 3. Monthly box plots for ethane, ethylene, propene, n-butane, acetylene, isoprene and benzene. The black dot represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1st and 3rd quartiles (i. e. Q1 and Q3). The whiskers correspond to the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

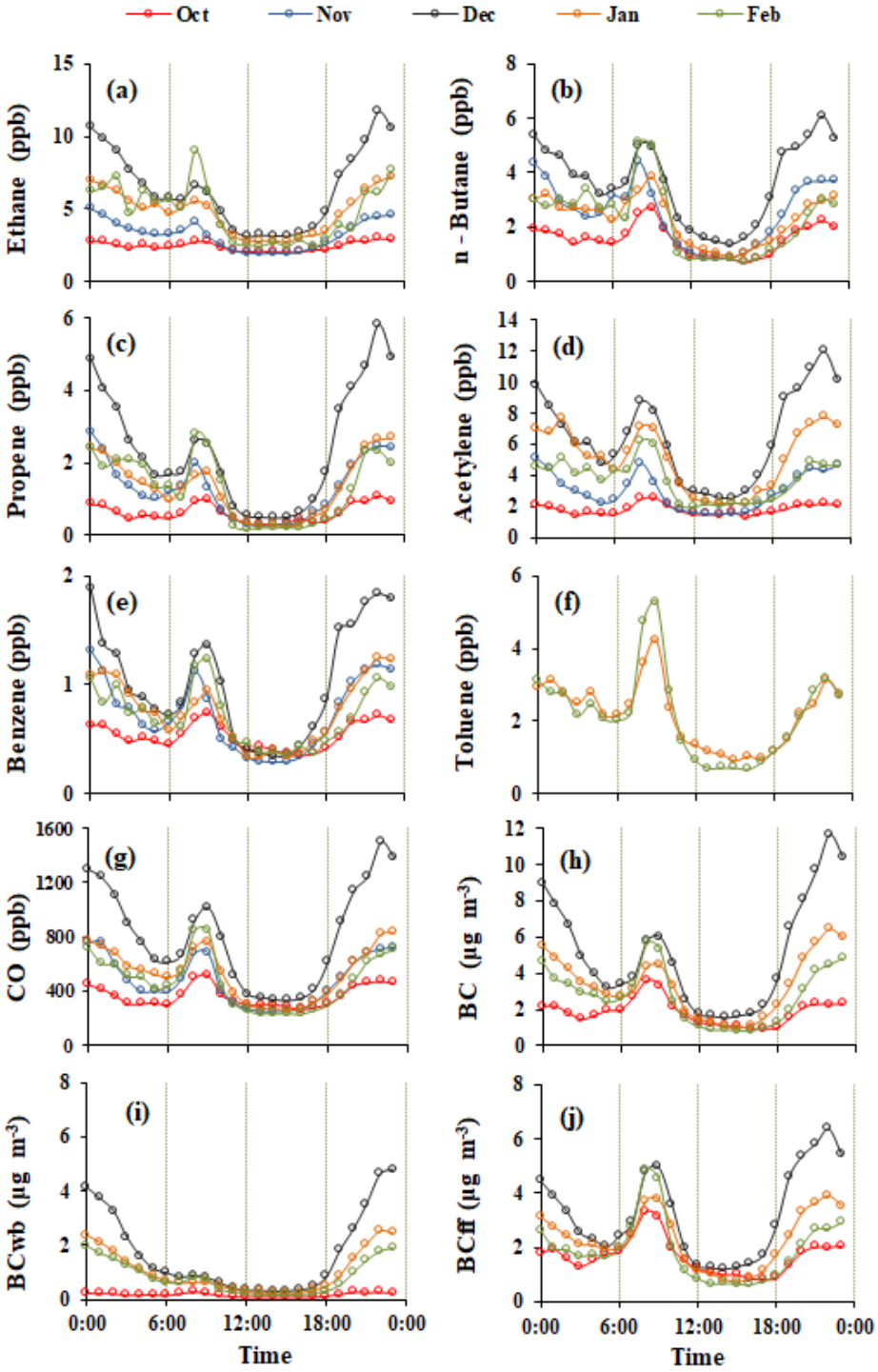

Figure 4. Monthly diurnal variability of (a) ethane, (b) n-butane, (c) propene, (d) acetylene, (e) benzene, (f) toluene, g) CO, h) BC, i) BC_{wb} and j) BC_{ff} based on hourly averaged values.

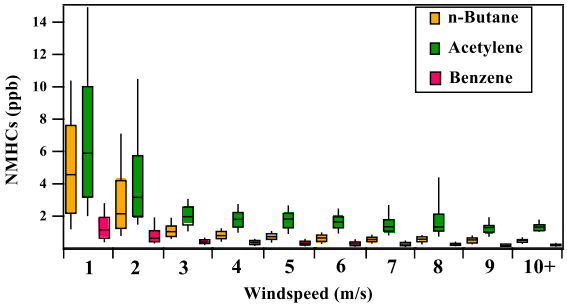

Figure 5. Boxplots for (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the period 16 October 2015 - 15 February 2016. The black line represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1st and 3rd quartiles (i. e.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

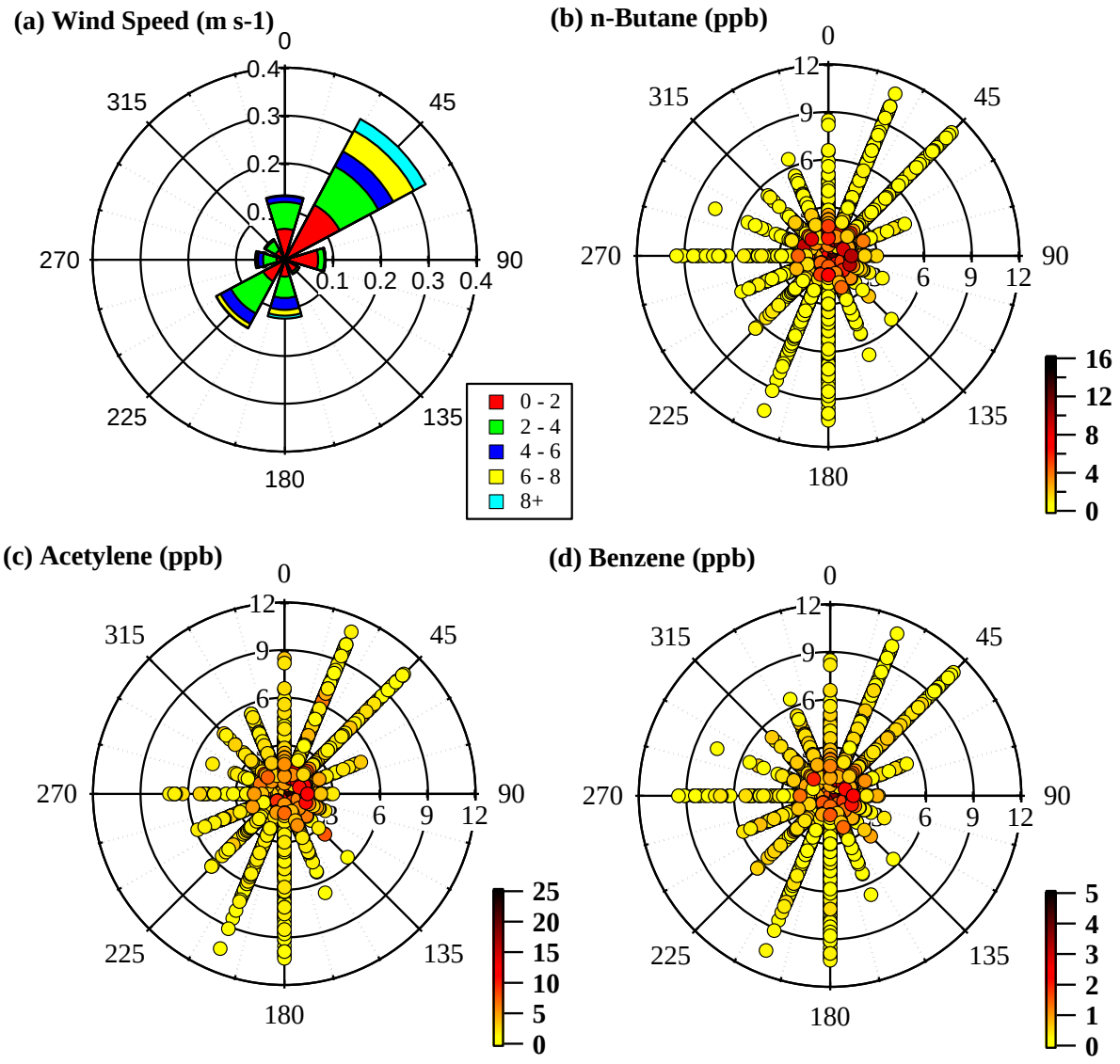

Figure 6. Wind rose (a) and concentration roses of (b) n-butane, (c) acetylene, and (d) benzene for the period 16 October 2015 to 15 February 2016.

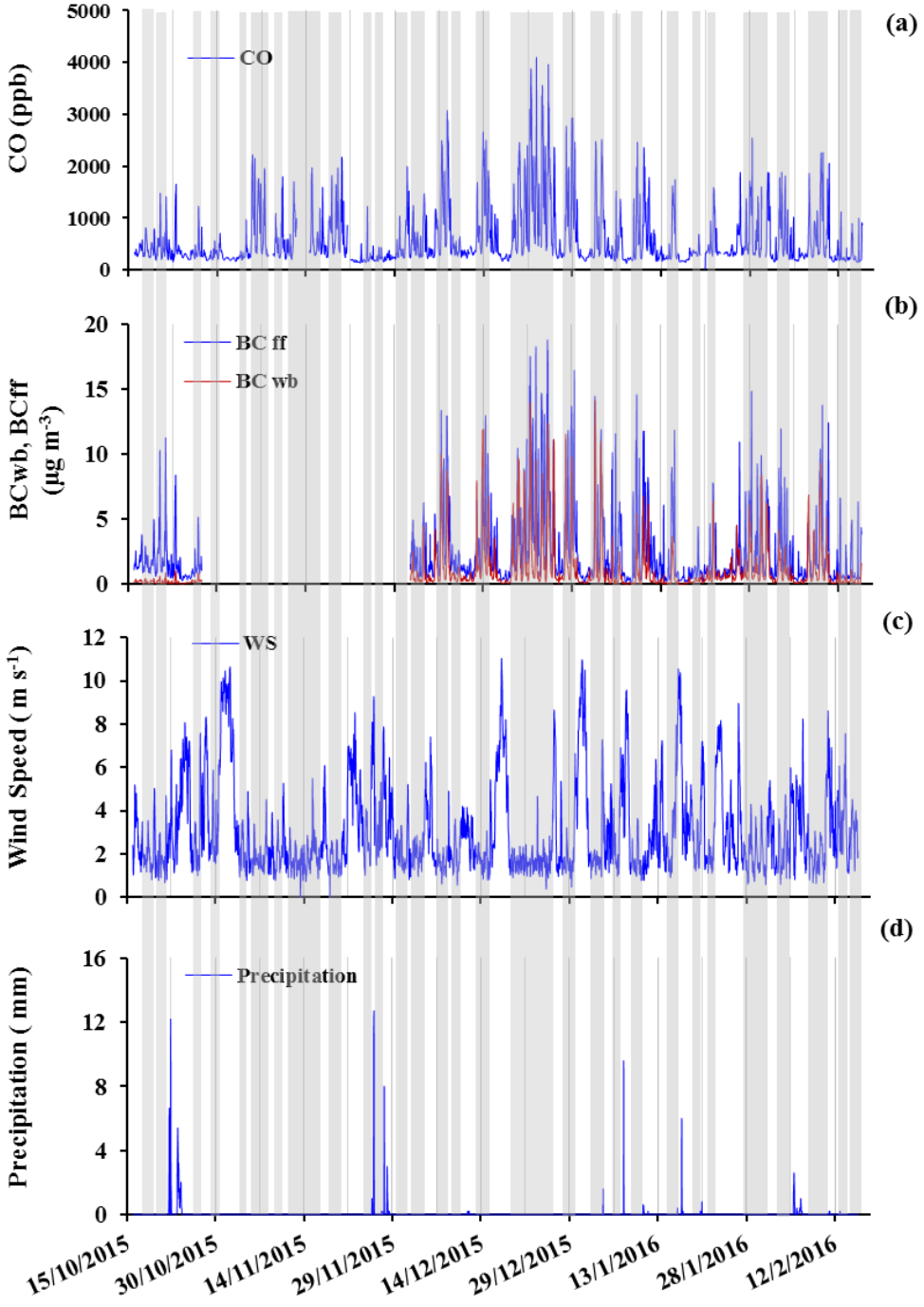

Figure 7. Temporal variability of (a) CO, (b) BC_{wb} and BC_{ff} fractions, (c) wind speed and (d) precipitation for the experimental period. Grey frames correspond to smog periods (SP), while the remaining part to non-smog periods (nSP).

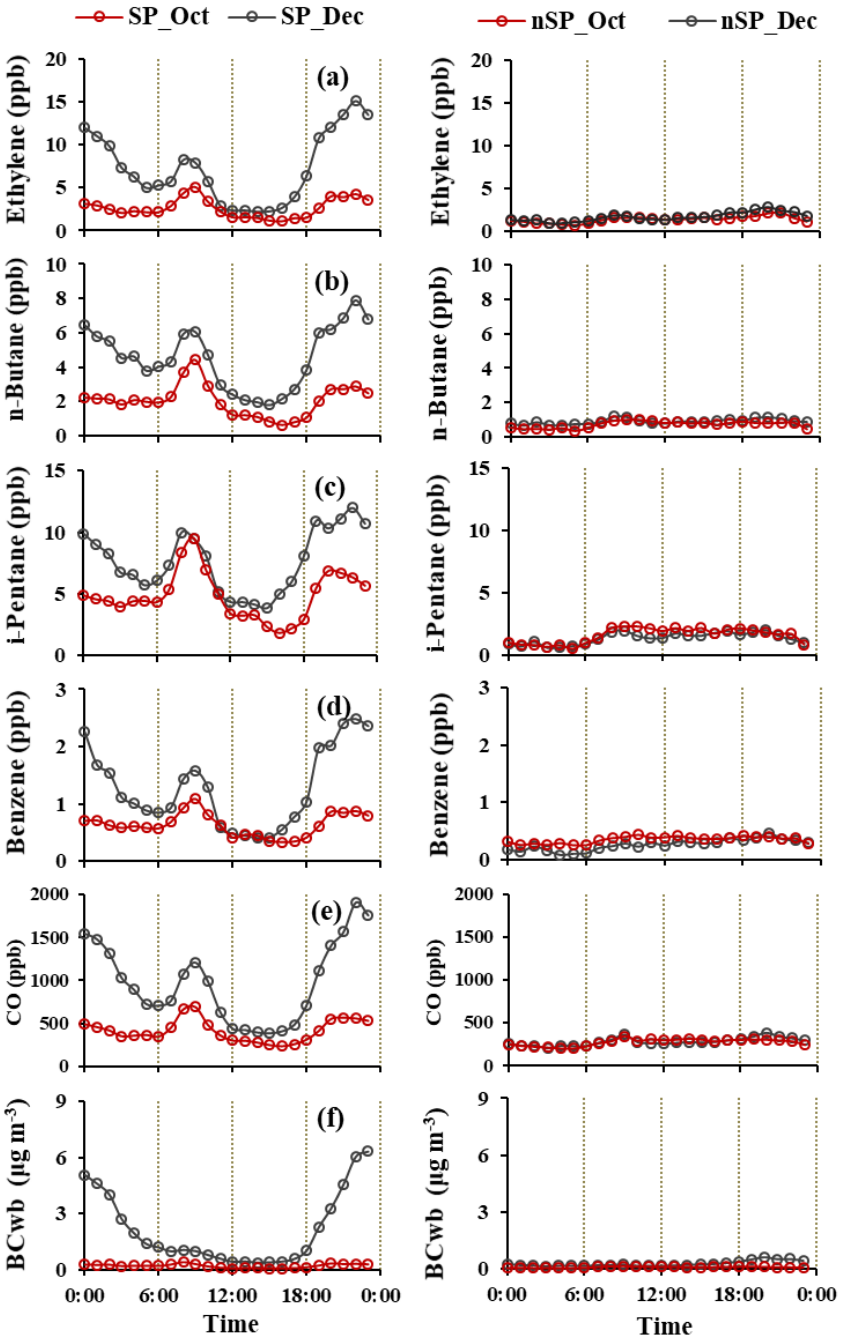

Figure 8. Diurnal patterns of (a) ethylene, (b) n-butane, (c) i-pentane, (d) benzene, (e) CO, (f) BC_{wb} during the SP (left column) and the nSP (right column) periods identified during October 2015 (red) and December 2015 (black) respectively. Note: SP periods are defined by wind-speed lower than 3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

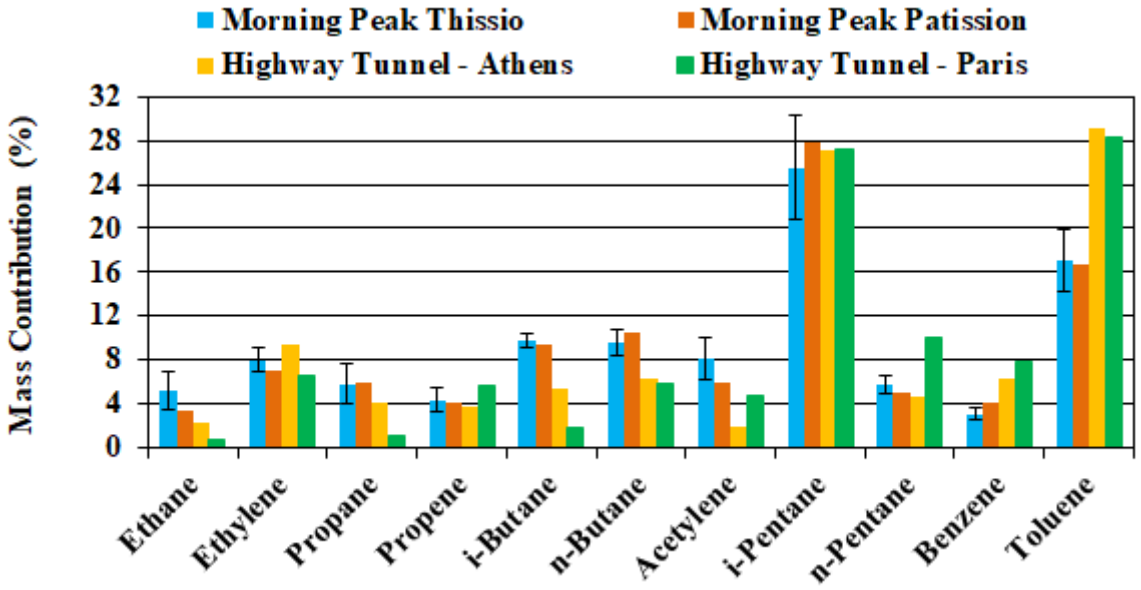

Figure 9. % Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00 LT), median values in Thissio, in Patission Monitoring Station, in a highway tunnel in GAA and a highway tunnel close to Paris.

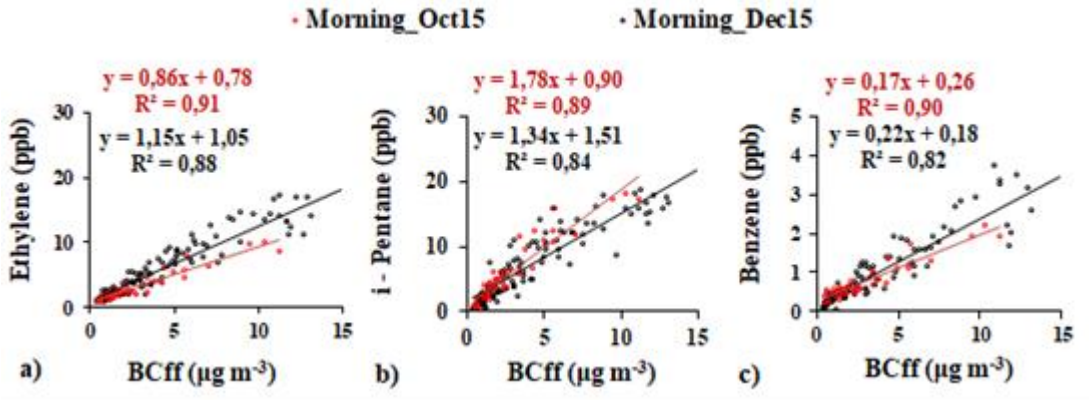

Figure 10. Regressions between ethylene, i-pentane, and benzene versus BC_{ff} (a-c) for the morning period (07:00 – 10:00LT) in October and December 2015.

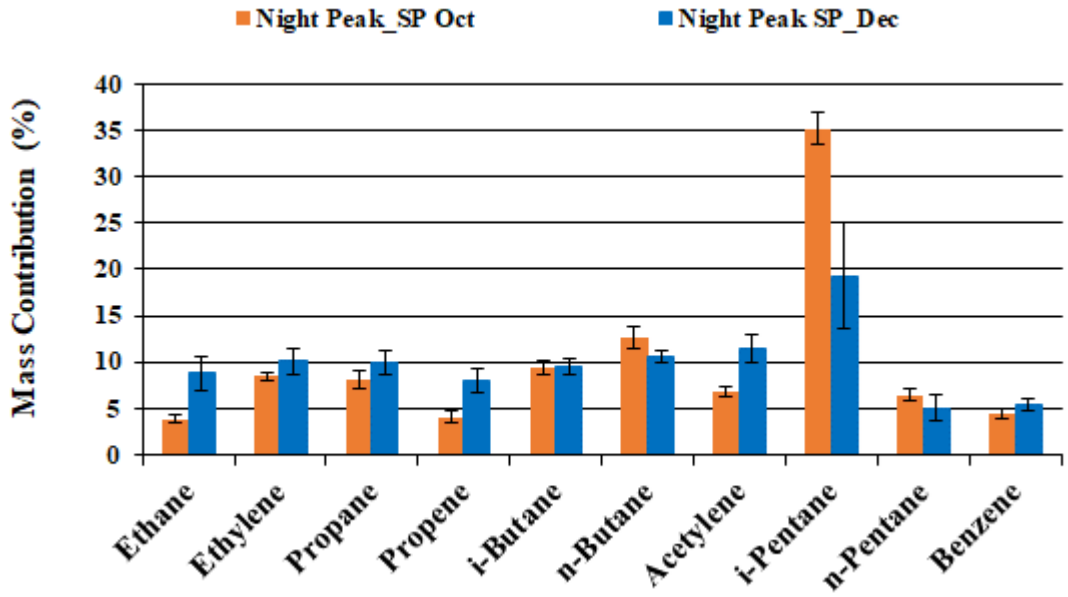

Figure 11. % Mass contribution of the measured NMHCs during the night peak (18:00 – 05:00LT) for the SP of October (orange) and the SP of December (black color).

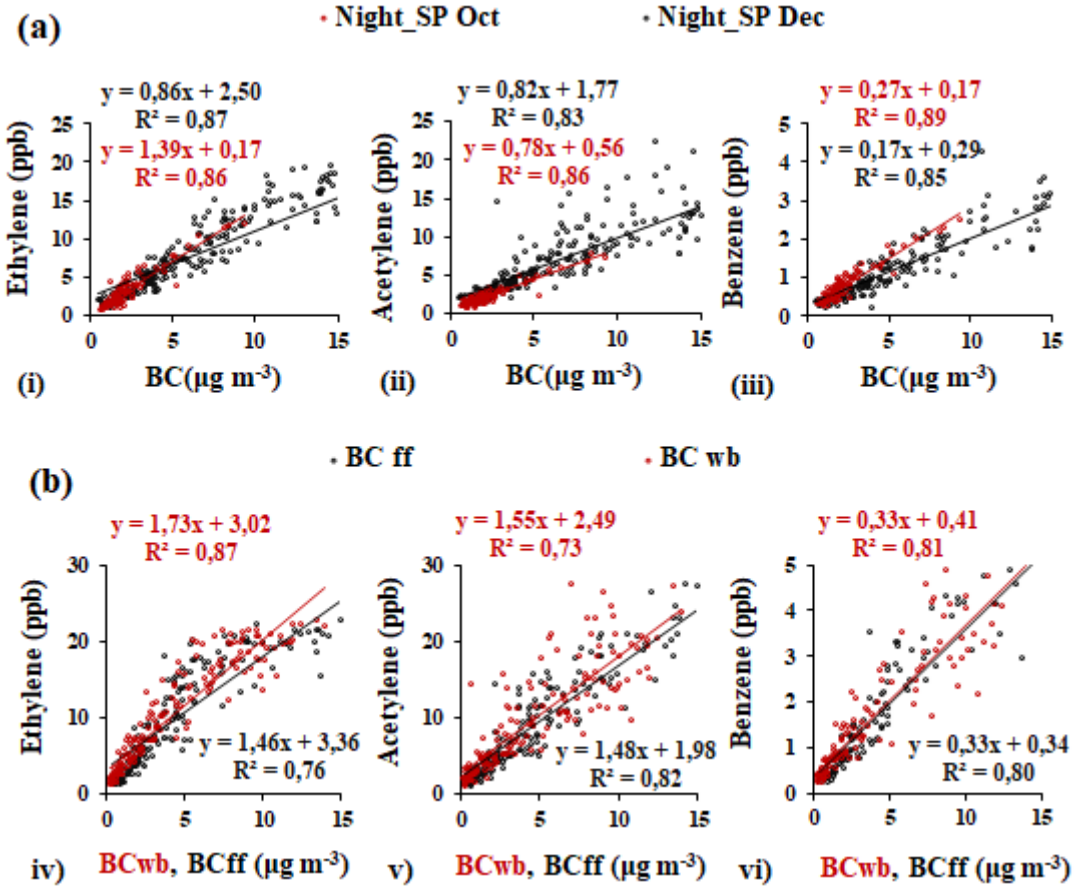

Figure 12. Regressions between ethylene, acetylene and benzene (a) against BC (i-iii) for the night period (18:00 – 05:00LT) of SP October and December 2015 and (b) against BC_{wb} (red) and BC_{ff} (black) for the night period (22:00 – 04:00LT) of SP December 2015.

Answers to reviewer

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 (the comments are in Italics). With blue color are noted the exact changes in the revised manuscript.

Reviewer #1:

1: "I do feel, however, that there is insufficient evidence presented here to support the authors' claim that the boundary layer height change between October and December is not the main cause of the observed increase in VOC mixing ratios. I would suggest the authors either re-phrase the sections relating to this (to include the possibility of meteorology playing a major role) or provide more evidence in support of this."

Reply: Unfortunately, we don't dispose detailed data of MBL variability not only for our site but for the whole GAA. We have however indications that support our statement on a minor role of MBL in explaining the significant increase of the NMHCs in winter relative to October (reference period).

1: If we examine the nighttime ratio (median value) of winter versus October for all NMHCs a great variability can be seen among the various compounds ranging from 1 or even lower to 2. For instance, the pentanes, compounds characteristic of traffic have a winter/October ratio during nighttime of 1, while other NMHCs emitted from wood burning in addition to traffic (e.g. benzene) have a ratio of 1.4. Same stands also for ethane, ethylene or acetylene compound also emitted by wood burning and depict a winter versus October ratio of 1.7, 1.5 and 2.7 respectively. The above information indicates that source impact is higher compared to MBL.

2: An additional indication corroborating with the above conclusion comes from SO4 diurnal variability measured at the same site and period using an ACSM, thus with similar time resolution with the NMHCs. Sulfate is a regional pollutant thus MBL changes are expected to dictate its diurnal profile rather than local sources. No significant diurnal variability can be seen for sulfate during the winter months (December 2015, January and February 2016), indicating also higher source impact compared

to MBL. For information, the NO_3, another regional pollutant but with significant local influence, maximizes during night compared to day indicative of impact from local sources especially wood burning (Theodosi C., personal communication).

Throughout the article: "C2-C6"

Should be written as C2 – C6

Reply: We follow his/her suggestion and it has been changed along the article with C6 – C12.

P 2, L 11: "Athens, the capital of Greece and an important megacity…."

Is Athens a megacity? Generally a megacity is considered as one with a population of more than 10 million. Further justification is required or this should be removed.

Reply: Indeed, Athens is not a megacity and the word "megacity" was removed.

P 2, L 27: Comment "The above demonstrate the increasing need for intensive measurement of NMHCs in Athens, to better understand their sources, temporal characteristics and role on smog formation, in the new conditions established during the economic crisis years, with competing traffic and wood burning." Perhaps more fundamentally there is need to observe the current atmospheric composition to allow for the impact of future changes (fuel composition changes or other control strategies) to be assessed. There is a need to establish a "current baseline" for Athens.

Reply: We thank the reviewer for his/her comment and the proposition was added to the manuscript: "Consequently, the above demonstrate the increasing need for intensive measurement of NMHCs in Athens, to observe the current atmospheric composition to allow for the impact of future changes (fuel composition changes or other control strategies) to be assessed. There is a need to establish a "current baseline" for Athens.".

In the revised manuscript: P.3 L.10 - "The above clearly demonstrates the increasing need for intensive measurements of NMHCs in Athens, which in turn will allow to assess 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.".

P. 3, L. 24: "The trap was then heated rapidly to 22 ^{o}C…"

Is this a typo? Compounds won't desorb well (if at all) at these temperatures. Should this read 220^{o}C?

Reply: We agree with the remark; indeed, it is a typo. The text was corrected accordingly in P.4 L.15.

P 3, L 28: "The overall estimated uncertainty of the measurement is 15%."

A more detailed discussion of the measurement uncertainty is required to understand how this value is derived. Which parameters are included within the uncertainty? Does the uncertainty vary with compound type? Is it dependent upon mixing ratio or constant across the measurement range? These are all important details which should be included here.

Reply: We thank the reviewer for his/her remark. As all this info is already reported in the literature and the following sentence is included in order to avoid repetitions: P.4 L.18 - "Details about the equipment technique and performances, as well as the estimation of the uncertainty, are provided by Gros et al. (2011).".

P 4, L 28: "…with the exception of isoprene (approximately 10%)."

Why was the data coverage for isoprene worse than others? Were there interferences? This is important to inform other potential users of this equipment for the measurement of VOCs and also needed to confirm that the data quality of the other VOC measurements wasn't impacted by these issues.

Reply: The low coverage of isoprene is mainly due to the very low activity of its normal sources (biogenic) for the studied period and not to instrument malfunction. To avoid misunderstanding the sentence was rephrased as follows: "The latter can be attributed to the low activity of its principal source, that is emissions from vegetation (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). Consequently, it is not possible to determine an accurate diurnal variability for this compound."

In the revised manuscript: P.5 L.30 - "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.".

P 5, L 1: "… the significant night time levels (above 300 ppt in some cases)."

Can this data be trusted given the aforementioned problems with the isoprene data coverage? Further discussion may be needed (unless this is covered in the explanations of the isoprene data coverage above).

Reply: The answer is included in the previous comment.

P 5, L 5: "… while lower values were below 5 ppb for the whole period."

I'm unsure what this statement means, clarification is needed. Does this relate to ethane and ethylene or the other VOCs measured?

Reply: It refers to ethane and ethylene and thus the sentence was corrected accordingly to the text in P.6 L.6: "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.".

P 5, L 8: "The average concentration of benzene during the studied period was 0.7 ppb (still not a full year), which is considerably below the EU average annual limit of 5 μg m^{-3} or 1.5 ppb (Directive 2008/50/EC of the European Parliament)."

The data presented here doesn't include summer time values where we'd expect lower mixing ratios. If these were included then presumably the value would fall well below the threshold. This should be

included here, it is of interest in- and of- itself, but also leads the reader to question whether the current directives are suitable and adequate?

Reply: We agree with the reviewer and the sentence was removed.

P 5, L 12: "The comparison with those already published 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 the Thissio Station), always bearing in mind differences in sampling period (summer versus winter), location, sampling method and analytical techniques."

Is it possible to estimate of the actual decrease? This would be of interest here, despite the various caveats that must be included.

Reply: The following sentence was added in P.6 L.12: "The comparison with those already published for the GAA, indicates an apparent decrease by a factor of 2 to 6 for the majority of the species lying above C_4 (taking as reference the case of Ancient agora urban area in the close vicinity of the Thissio Station). This decreasing trend is in agreement with a decrease in primary pollutants CO, SO_2 already reported by Kalabokas et al. (1999) and Gratsea et al. (2017), due to the air quality measures taken by the Greek government. However, this decrease has to be seen with cautious considering differences in sampling period (summer versus winter), location, sampling method and analytical techniques.".

P 5, L 20: "Furthermore, our findings for benzene and toluene, were significantly lower than the 12 hour day-time average levels reported for a Cairo rural background area, as reported by Khoder et al., 2007 (mean levels of 5.8 and 7.5 ppb respectively)."I don't see the significance of this statement? It needs expanding to make its relevance clear.

Reply: The aim of this part is to compare our measurements with those reported in the literature for other Eastern Mediterranean locations. The text was rearranged in order to state the relevance of the comparison as follows: 'Furthermore, our measured benzene and toluene levels (Table 1), were significantly 7 and 3 times lower than the 12-hour day-time average levels reported for a Cairo rural area by Khoder et al. (2007), and equal to 5.8 and 7.5 ppb for benzene and toluene respectively."

In the revised manuscript the statement is removed.

P 5, L 23: "… pattern for all NMHC concentrations was their gradually increase from October:.."

Typo gradually to gradual

Reply: Based on the reviewer's comment the text was corrected accordingly.

P 5, L 29:"… according to Kokkalis (personal communication) the winter-time decrease of PBL is in the range of 20%, …"

This is an important statement in the context of this article and needs more detailed supporting evidence. Later figures and text attempt to reaffirm this statement to support the implication that source-changes define the changes in VOC composition. In its current format I don't see a convincing argument to support this. Either the authors need to include substantial supporting evidence for this or the text should be altered to include the possibility that the variations in VOC mixing ratios could be due to changes in Meteorology.

Reply: The remark was answered in another comment in the beginning of the answers part.

P 6, L 7: "Although the amplitude of both peaks is almost similar (with the exception of December), the duration of the night peak is at least a factor of 2 larger, indicating the predominant role of heating in air quality during wintertime."

This would also be conducive with boundary layer dynamics dictating the night time profile.

Reply: Although from the indications presented above, BL seems not to be the main factor, the sentence was corrected to tone down the impact of heating in P.7 L.11 "……..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.".

P 6, L 25: "… the most frequent, resulting to moderate levels of NMHCs."

Typo "to" to "in"

Reply: Based on the reviewer's comment the text was corrected accordingly.

P 7, L 2: "… 2 to 3 times higher levels of NMHCs were observed on December…"

Typo "on" to "in"

Reply: Based on the reviewer's comment the text was corrected accordingly.

P 7, L 7: "When NMHCs are examined against temperature (not shown here), a clear tendency is not evident, although the highest levels occur at lower temperatures."

A plot of this would be useful to be included here.

Reply: Following the reviewer's proposition the graph was added in the supplement as Fig. S7.

P 7, L 21: "More precise picture…"

Typo "More" to "A more"

Reply: Based on the reviewer's comment the text was corrected accordingly.

P 8, L 15: "The most striking difference is related to the night and early morning peak, while during mid-day the difference is Minimum."

This requires more detail. While the concentration rise is smaller at mid-day, the relative rise looks to be more or less the same for the early morning and mid-day periods (approximately double). Including the percentage increase would clarify this.

Reply: Based on the reviewer's comment, the text was corrected as follows: "The most striking difference is related to the extensive night peak, while during mid-day the difference is minimal. The night peak of the compounds in December (SP period) is 2 to 6 times higher than October's (SP period) with the highest values corresponding to 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). "

In the revised manuscript: P.9 L.20 - "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).".

P 8, L 16: "… while during mid-day the difference is minimum…"
Typo "minimum" to "minimal"
Reply. Based on the reviewer's comment the text was corrected accordingly.

P 8, L 18: "For the nSP cases (Fig. 7 and S7) the concentrations of all compounds were very low (lower than the minimum of the SP periods) and almost equal, with the exception of ethane and acetylene that demonstrated higher concentrations in December by a factor of two (Fig. S7a, e)."
I can't make sense of this sentence, it needs re-writing/re-phrasing for clarity
Reply: Following the reviewer's comment, the text was clarified as follows: **"**NMHCs levels during the nSP periods in October and December 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.**"**
In the revised manuscript: P.9 L.26 - "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.".

P 8, L 32: "It is interesting to note that the profiles, especially those derived from the morning peak, nicely fit with that reported for traffic by Baudic et al. (2016) in Paris (when only the common NMHCs measured in this work have been used)."
I don't see a "nice fit" they look different in magnitude and relative composition. Please provide more detail of what the authors are implying by this.
Reply: The entire "Morning Peak" paragraph of the Sect. 3.4.3 was re-written and figure 8 will be replaced by the following one (now Fig. 9):

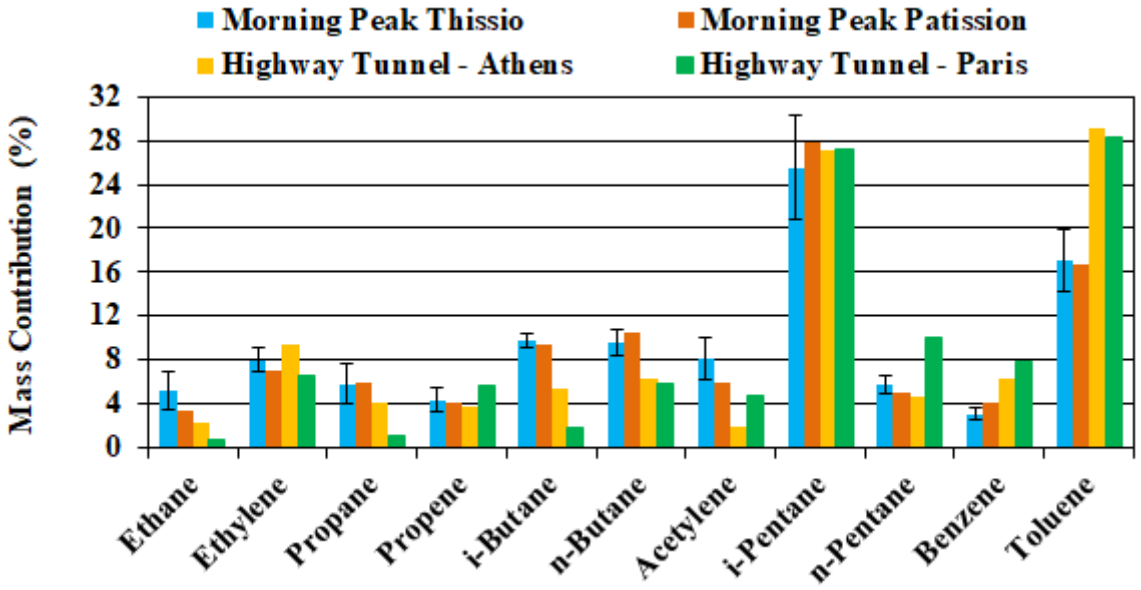

Figure 9. % Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00 LT), median values in Thissio, in Patission Monitoring Station, in a highway tunnel in GAA and a highway tunnel close to Paris.

The previous profiles had common dominant species (i-pentane and toluene) but indeed there were other discrepancies. For that reason we included measurements of an intensive campaign that was performed during the Athens campaign, at Patission Monitoring station of the Hellenic Ministry of Environment and Energy, a site located in a street canyon and significantly impacted by traffic conditions, thus better representing the traffic profile of the GAA. The two profiles of Patission and Thissio are fitting nicely, but differences are apparent if they are compared to tunnel profiles. The conclusion is that the observed discrepancies are attributed to the type of fuel of the vehicles.

In the revised manuscript, the corresponding paragraph will be re-written as follows:

"As discussed in Sect. 3.2, the morning peak (07:00 – 10:00 LT) of NMHCs could be attributed mainly to traffic. Figure 8 presents the profile of this peak (% mass contribution of the measured NMHCs), during January and February SP days when toluene data were available. Additionally, in the same figure the morning profile obtained from a 2 – days campaign conducted in Patission Monitoring Station (a street canyon located at the center of Athens) and the profiles of two tunnel measurements in G.A.A and Paris are reported. Details on the calculations for the morning profile for the two sites are provided in

Sect. S2. Patission profile reflects all types of traffic-related emissions due to the combination of the high number of vehicles and buses that cross this street, frequent traffic jam conditions, the variety of types of fuels, vehicles age and their maintenance etc.

The two morning profiles, although performed at sites with different impact of traffic, agrees quite well ($R^2 > 0.97$). Iso - pentane and toluene are the two main compounds contributing to the morning profiles accounting by about 44% of the total measured NMHCs at both locations, followed by n- and i-butane and ethylene accounting for almost 30%. Differences among the two morning profiles between these 5 main species are minimum (less than a factor of 1.5). Note also that the morning profile at Thissio is the mean of a whole month period compared to a campaign of two days in Patission which could explain the differences between the two profiles. The profiles obtained at the two tunnels although differ in terms of tunnel length, city, and period have a lot of common features. Again i-pentane and toluene are the two main compounds of the profile accounting by about 56% of the total measured NMHCs at both sites, followed by n -butane, ethylene and benzene accounting for almost 20% in total again at both sites. The most striking difference between the two sites concerns n-pentane (almost a factor of two higher in Paris compared to Athens). Despite the differences between the two tunnel studies the similarity is almost 80% ($R^2 > 0.91$). 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 Patission morning profiles and their difference from the Athens and Paris tunnel profiles, indicate the importance of the type of fuel used. The latter is also concluded in recent works (Ait-Helal et al., 2015; Q. Zhang et al., 2018; Y. Zhang et al., 2018), where important differences are reported between tunnel measurements worldwide, and attributed to the variance of the car-fleet (type of vehicle and fuel). 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 quite low. In any case, the prevalence of i-pentane and toluene in all profiles, indicate the continuing dominance of gasoline powered cars. Moreover, higher values of ethane, propane and butanes that are depicted in the morning peaks of 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). In fact, the connection of high levels of C_2-C_4

alkanes and the number of LPG-powered cars is highlighted in other tunnel works as well (Ait-Helal et al., 2015; Q. Zhang et al., 2018)."

In the revised manuscript: From P. 10 L.1

"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 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 (Patission Monitoring Station) and the profiles of two tunnel measurements in G.A.A and Paris are also reported. Details on the calculations for the morning profile for the two sites are provided in Sect. S2. Patission 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 ($R^2 > 0.97$). Iso - pentane and toluene are the two main compounds contributing to the morning profiles accounting by about 44% of the total measured NMHCs at both locations, followed by n- and i-butane and ethylene accounting for almost 30%. Differences between the two morning profiles regarding these 5 main species are weak (less than a factor of 1.5). Note also that the morning profile at Thissio is the mean of a whole month period compared to the two days campaign at Patission which could explain the small differences between the two profiles. 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. 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 Patission 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 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. S10 and S11 where the ratios of butanes and pentanes-to-total Alkanes C2 – C5 (%) 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. In addition, the above results could indicate why the Athens tunnel results performed in May differ from Patission 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. S12). 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 Patission 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)."

P 9, L 2: "… butanes are however be noted in the morning peak…"
Typo "be" needs to be removed

Reply: The corresponding paragraph was modified (answer of the previous comment).

P 9, L 4: "Toluene, an important contributor to the traffic profile (Fig. 8), was measured only for one month during winter."

Does this affect the plot? Is that why the toluene is lower than at other sites? This sentence needs expanding upon to clarify its effect, if any, upon the figure.

Reply: The short-term measurement of toluene has no effect on fig. 8 (now Fig. 9), because the morning profile derived from days that toluene data were available, so all the compounds have the same number of data.

P 9, L 12: "…(the contribution of the later was more evident during winter)."

Typo "latter" not "later"

Reply: The corresponding section was changed (previous comment).

Fig 7 caption: I suggest including the definition of SP and nSP within the figure caption

Reply: We agree with the reviewer and definition of SP and nSP was added in the figure caption (now Fig. 8).

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Reference article: acp-2017-936

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

Answers to reviewer

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 (the comments are in Italics). With blue color are noted the exact changes in the revised manuscript.

Reviewer #2:

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."

Reply: We agree with the reviewer that this work reports for the first time C2 and C3 data in Athens. Note that Kaltsonoudis et al., paper although report measurements during wintertime in GAA did not report any NMHC data below C5 and the only common compounds with this work is isoprene, benzene and toluene. **Consequently, this work reports for the first time to our knowledge C2-C5 NMHCs measurements in Athens during winter time and for the first time ever C2-C3 data in GAA.**

We agree also that since the last pioneering work by Rappenglück et al., performed in Athens 20 years ago a lot happened in Athens in terms of source evolution (see for instance Kalabokas et al., 1999; Gratsea et al., 2017). The above demonstrate, as reviewer 1 highlighted, the increasing need for intensive measurement of NMHCs in Athens, to observe the current atmospheric composition to allow for the impact of future changes (fuel composition changes or other control strategies) to be assessed. 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. For that reason, the introduction was changed to include all the above remarks and points raised by the reviewers:

"Non-methane hydrocarbons (NMHCs) are key atmospheric constituents for atmospheric chemistry. In the presence of NO_x, their oxidation leads to formation of tropospheric ozone and other species, such as peroxy radicals (RO_2) and peroxy acetyl nitrate (PAN), thus affecting the oxidative capacity of the atmosphere (Atkinson, 2000 and references therein). NMHCs' 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, solvents' use, residential heating, natural gas use, industrial activity, but also emit 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 regarding 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, pollution-wise, 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., 1998; Kanakidou et al., 2011). However, the measurements of pollution

precursors are mostly about ozone and nitrogen oxides. The few existing and non-continuous NMHC measurements in Athens by means of canisters or sorbent tubes, 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 20 years ago at three locations, two suburban and one urban, containing almost 50 $C_4 – C_{12}$ 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), containing 11 aromatic and oxygenated organic gaseous compounds (5 NMHCs). Meanwhile, significant changes in pollutant sources occurred in Athens the last 20 years, which inflicted important decreases in the annual concentrations of major pollutants such as CO, SO_2, NO_x (combustion marker) (Gratsea et al., 2017; Kalabokas et al., 1999). Because the latter trend is attributed to the car fleet renewal, fuel improvement, metro line extension and industrial emission controls, a decrease to the NMHCs 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). In general, there are some studies in a global scale for the characterization of the VOC emissions from domestic wood burning, however, differences are observed to the emission rates or the emission profiles of the VOCs, that are attributed to type of wood, stove, lightening material and the variety of emissions from the burning stages (Barrefors and Petersson, 1995; Baudic et al., 2016; Evtyugina 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). In contrast, the studies including light NMHCs are very few (Barrefors and Petersson, 1995; Baudic et al., 2016; Liu et al., 2008; Schauer et al., 2001) and present discrepancies. For example, the higher contribution of

benzene relatively to acetylene to the residential wood burning profile reported by Baudic et al. (2016) that is not depicted in the profile of Liu et al. (2008).

Nevertheless, the latest work on VOCs in Athens of Kaltsonoudis et al. (2016) gave a first insight about the positive effects of the Greek air pollution on aromatics and oxygenated VOC levels, pointing out the important contribution of wood burning to the wintertime night concentrations. Consequently, the above demonstrate the increasing need for intensive measurement of NMHCs in Athens, to observe the current atmospheric composition to allow for the impact of future changes (fuel composition changes or other control strategies) to be assessed. There is a need to establish a "current baseline" for Athens. In addition, it would be interesting to investigate the contribution of traffic and wood burning to the light NMHCs, which are two competitive sources with similar NMHC tracers that could lead to an overestimation of the first due to the contribution of the second (Schauer et al., 2001).

The current study presents, time-resolved, uninterrupted data of 11 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). 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 their temporal characteristics and the determination of the factors controlling their variability, and (3) the investigation of traffic and residential heating impact on NMHCs levels."

In the revised manuscript: From P. 2 - "Non-methane hydrocarbons (NMHCs) are key atmospheric constituents for atmospheric chemistry. In the presence of NO_x, their oxidation leads to formation of tropospheric ozone and other species, such as peroxy radicals (RO_2) and peroxy acetyl nitrate (PAN), thus affecting the oxidative capacity of the atmosphere (Atkinson, 2000 and references therein). NMHCs' 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, solvents' use, residential heating, natural gas use, industrial activity, but also emit 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 regarding 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, pollution-wise, 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., 1998; Kanakidou et al., 2011). However, the measurements of pollution precursors are mostly about ozone and nitrogen oxides. The few existing and non-continuous NMHC measurements in Athens by means of canisters or sorbent tubes, 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 20 years ago at three locations, two suburban and one urban, containing almost 50 C_4 – C_{12} 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), containing 11 aromatic and oxygenated organic gaseous compounds (5 NMHCs). Meanwhile, significant changes in pollutant sources occurred in Athens the last 20 years, which inflicted important decreases in the annual concentrations of major pollutants such as CO, SO_2, NO_x (combustion marker) (Gratsea et al., 2017; Kalabokas et al., 1999). Because the latter trend is attributed to the car fleet renewal, fuel improvement, metro line extension and industrial emission controls, a decrease to the NMHCs 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). In general, there are some studies in a global scale for the characterization of the VOC emissions from domestic wood burning, however, differences are observed to the emission rates or the emission profiles of the VOCs, that are attributed to type of wood, stove, lightening material and the variety of emissions from the burning stages (Barrefors and Petersson, 1995; Baudic et al., 2016; Evtyugina 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). In contrast, the studies including light NMHCs are very few (Barrefors and Petersson, 1995; Baudic et al., 2016; Liu et al., 2008; Schauer et al., 2001) and present discrepancies. For example, the higher contribution of benzene relatively to acetylene to the residential wood burning profile reported by Baudic et al. (2016) that is not depicted in the profile of Liu et al. (2008).

Nevertheless, the latest work on VOCs in Athens of Kaltsonoudis et al. (2016) gave a first insight about the positive effects of the Greek air pollution on aromatics and oxygenated VOC levels, pointing out the important contribution of wood burning to the wintertime night concentrations. Consequently, the above demonstrate the increasing need for intensive measurement of NMHCs in Athens, to observe the current atmospheric composition to allow for the impact of future changes (fuel composition changes or other control strategies) to be assessed. There is a need to establish a "current baseline" for Athens. In addition, it would be interesting to investigate the contribution of traffic and wood burning to the light NMHCs, which are two competitive sources with similar NMHC tracers that could lead to an overestimation of the first due to the contribution of the second (Schauer et al., 2001).

The current study presents, time-resolved, uninterrupted data of 11 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). 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 their temporal characteristics and the determination of the factors controlling their variability, and (3) the investigation of traffic and residential heating impact on NMHCs levels."

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

Reply: Based on the reviewer comments, the text was clarified as follows (P.1 L.18): "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."

P 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?

Reply: By local meteorology the authors mean the microscale meteorology. For that reason, the term "local meteorology" is replaced by "microscale meteorological conditions" in the manuscript. It is worthwhile noting that previous work performed in Athens on aerosols showed that during summer the majority of pollutants originate from regional sources outside Greece (more than 60%), whereas during winter local sources prevails (more than 80%) (Theodosi et al., 2011; Paraskevopoulou et al., 2015). Due to the financial crisis, industrial activities have been considerably decreased in Athens with most industries either closing or moved out Greece (Vrekoussis et al., 2013). Thus, traffic and heating can be considered as the main sources of pollutants in GAA during winter. Temporal variability of these sources is indeed an important factor controlling NMHCs levels and our analytical resolution of 1h captures quite well this temporal variability.

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

Reply: Based on the suggestion of the reviewer, the text was clarified as follows: "The amplitude (intensity) 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 traffic related to combustion e.g. domestic heating (fuel or wood burning).".

In the revised manuscript: P.1 L. 24 - "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).".

P 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?

Reply: This sentence at the abstract is based on the results presented in detail in the manuscript, where the reader can find all the necessary details. In any case latter the sentence in the abstract was rephrased as follows: "Following the same comparison for the night peak, the tracers and source profiles clearly indicate the presence of traffic and domestic combustion of fossil fuel and wood burning for heating purposes. However, the present data-set does not allow for quantification of each source due to the similarity of emissions, thus measurements of more specific compounds are needed for the better understanding of the contribution of these three nocturnal VOC sources."

In the revised manuscript: P.1 L.28 - "For the night peak, the selected tracers and source profiles clearly indicate contribution from both traffic and domestic heating (fossil fuel and wood 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."

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

Reply: Since the manuscript refers to urban measurements, the text is corrected as follows (P.2 L.6): "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).".

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

Reply: The typo was corrected accordingly.

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

Reply: The citation was corrected accordingly.

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

Reply: The citation was corrected accordingly.

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

Reply: The citation did not correspond to the statement of the phrase and it was removed.

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

Reply: We agree with the not properly use of the term "limited" and for that reason it was changed throughout the manuscript and also to the corresponding line: "Continuous measurements of NMHCs in Athens for a period of one month have been conducted 20 years ago at three locations, two suburban and one urban, containing almost 50 $C_4 – C_{12}$ compounds (Rappenglück et al., 1998, 1999), and recently by Kaltsonoudis et al. (2016), for 1 month in winter 2013 at an urban background location (Thissio) and one in summer 2012 at a suburban one (A. Paraskevi), containing 11 aromatic and oxygenated organic gaseous compounds in total (5 NMHCs)."

In the revised manuscript: P.2 L.20 - “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 C4 – C12 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 C5 – C8 NMHC.”.

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

Reply: We clarified the phrase as follows (P.2 L.28): “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).”.

P 2, L26: Again, as mentioned above the term "limited" is not properly chosen. The Kaltsonoudis et al paper actually reports VOCs, which are not measured by Panopoulou et al. Also, while it is true that the Athens winter campaign reported by Kaltsonoudis et al was shorter than the one reported by Panopoulou et al, it seems that Kaltsonoudis et al also report a summer campaign for Athens, which the Kaltsonoudis et al paper does not.

Reply: This remark was already addressed before (answer of the comment for P2 L20-21).

P 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.

Reply: In the NMHCs campaign from 16 October 2015 to 16 February 2016 15 NMHCs were measured, however we chose for this paper the 11 that are the most representative of the sources that the manuscript is dealing with. In the intensive campaign of January and February 2016, 15 additional NMHCs were measured, that will be evaluated for their publication in the future.

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

Reply: Based on the comment the text was corrected accordingly: "In addition, it is interesting to investigate the contribution of traffic and wood burning to the light NMHCs, which are two competitive sources with similar NMHC tracers that could lead to an overestimation of the first due to the contribution of the second (Schauer et al., 2001)."

As mentioned before traffic and heating are the two most important local sources of pollution in GAA during wintertime. There is no main industrial zone around Athens anymore.

In the revised manuscript: P.3 L.19 - "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).".

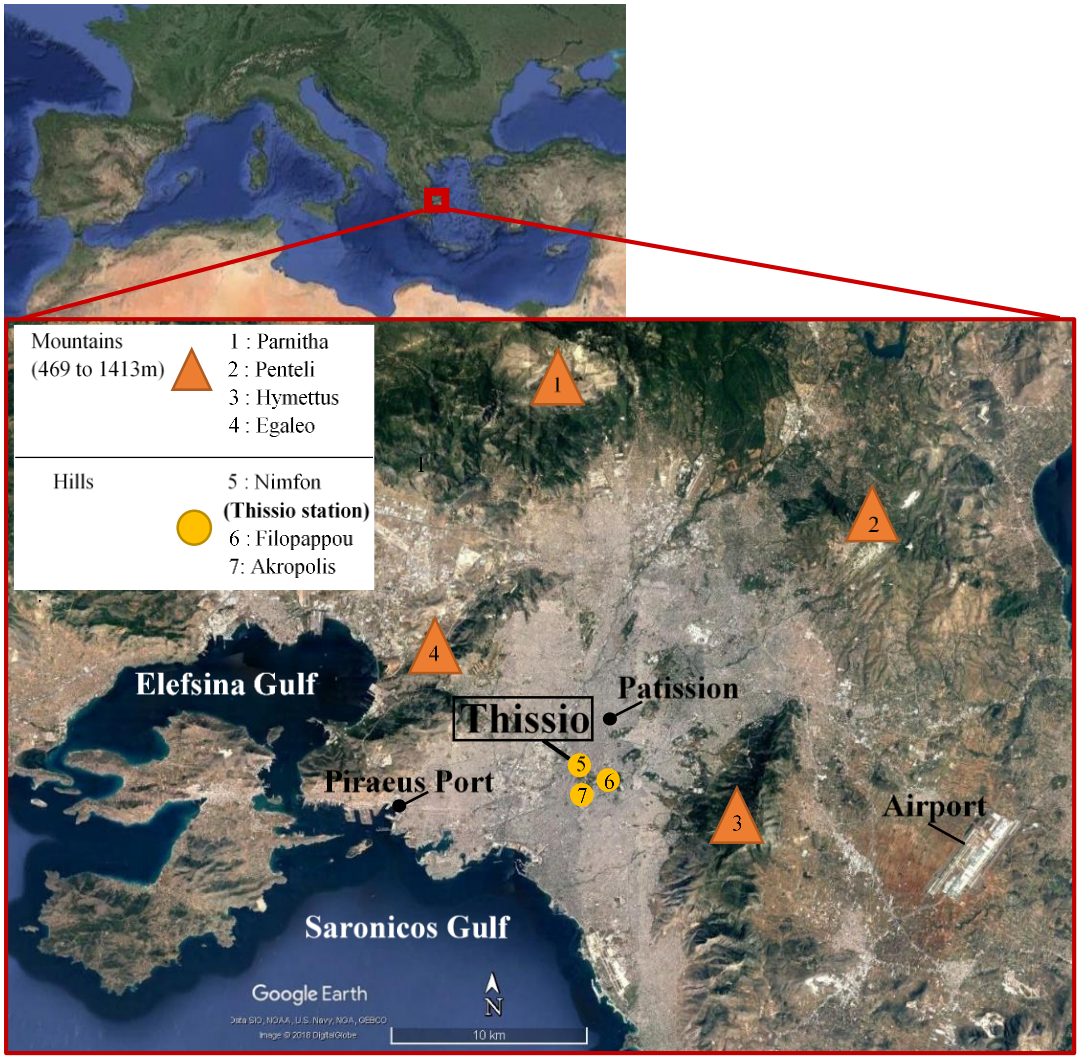
P 3, L3: Mention those selected tracers explicitly and mention what kind of sources those tracers are tracing.

Reply: The corresponding phrase was removed.

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

Reply: The following map will be included in the revised manuscript:

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



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

Reply: Based on the comment, the text was corrected accordingly (P.3 L.24): "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).” Note that GAA is not exactly a flat area thus for the information requested by the reviewer is not easy to give an accurate answer as a clear reference site is missing.

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

Reply: Based on the comment, the text was corrected accordingly: “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 (108m a.s.l) and Acropolis Hills (150m a.s.l), which are located 500m and 800m away respectively”. The site is indeed very specific as it holds the oldest meteorological station of Greece which provides continuous data since 1858.

In the revised manuscript: P.3 L.26 – “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).”

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

Reply: We refer to sampling time. The GC is continuously flushed with ambient air. Based on the comment, the text was corrected accordingly: “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 10 min.”

In the revised manuscript: P.4 L.6 – “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).”

P 3, L20: The sampling line has a pretty small diameter, which is very unusual. The authors should clarify why they chose that small diameter. Also, why did the authors use a stainless steel sampling line

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

Reply: The diameter of the sampling line is 0.315cm and not mm as was written. The typo was corrected accordingly.

We used a stainless-steel line for sampling following the recommendation by ACTRIS guidelines of 2014 for trace gases networking: Volatile organic compounds and nitrogen oxides (ACTRIS, Deliverable WP4 / D4.9 (42), 2014/09/30).

In general, the calibrations were made directly on the sampling port of the GC and the sampling line was checked for losses, by performing a number of calibrations the same day through the sampling line and also directly on the GC-FID, resulting in similar results.

There was a stainless-steel filter (screens) at the sampling inlet with a pore size of 4μm.

Part of these information will be included in the revised manuscript as follows (P.4 L.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 4μm pore size at the sampling inlet, and a flow rate of 18.9 mL min^{-1}.

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

Reply: Based on the reviewer's #1 comment, we have clarified the sentence as follows (P.4 L.18): "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 0.02ppb (propene, n-pentane) to 0.05ppb (propane), while for ethane and ethylene is 0.1ppb."

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

Reply: The remark was already addressed before for the comment of P3 L20 and the text will be corrected accordingly.

P 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?

Reply: The main part of the paper is focused on C2 – C6 NMHCs, from which we chose only the compounds dedicated to the scope of this paper (the role of traffic and heating on the winter levels of NMHCs, the two most important sources of pollution during wintertime in the area). Toluene was available only for one month at the end of the campaign, thus it was selected as an additional tool for our analysis. Moreover, it was only used for the interpretation of the morning profile of Thissio, for which we have subtracted a background concentration (described in the section S2 of the supplement) in order to compare with the traffic profiles available in the literature.

The uncertainty of the instrument is less than 20% and the detection limit of toluene is 0.026 ppb. These elements were introduced also in the manuscript (P.4 L.27).

Auxiliary measurements

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

Reply: Based on the comment, the Sect. 2.3 was modified as follows: "Real time monitoring of carbon monoxide (CO), black carbon (BC) and nitrogen oxides (NO_x = NO and NO_2) was also conducted during the reported period. For CO and NO_x, Horiba 360 Series Gas Analyzers of one-minute resolution were used and calibrated with certified standards. A seven wavelength Magee Scientific AE33 aethalometer (five minutes resolution) was operated for the measurement of BC; and its fractions associated with fossil fuel and wood burning (BC_{ff} and BC_{wb}, respectively) were calculated based on the biomass burning contribution derived automatically by the instrument software. Meteorological data were provided by NOA's meteorological station at Thissio premises."

In the revised manuscript: P.4 L.6 – "Real time monitoring of carbon monoxide (CO), black carbon (BC) and nitrogen oxides (NOx = NO and NO_2) was also conducted during the reported period. For CO and NOx 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_{ff} and BC_{wb}, respectively) derived automatically by the instrument software. Meteorological data were provided by NOA's meteorological station at Thissio premises.".

Tunnel measurements

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

Reply: The tunnel where the measurements are performed is at the periphery of GAA. Its length is 200m and measurements are performed at the middle of the tunnel. The tunnel is at a highway with toll and mainly used by private cars to avoid Athens center and consequently traffic jams. It has 3 lanes at each direction with no specific restrictions for heavy duty vehicles. Measurements at the tunnel were indeed performed a different period with the measurements and the idea was to obtain a NMHCs profile characteristic for traffic. Given the different period of the measurements and the fact that the toll could prevent buses and trucks to use it frequently, a campaign performed during wintertime at a street canyon in the center of Athens with heavy traffic was preferred to obtain a traffic profile (see new figure 8, now figure 9). Part of this information will be added at the revised manuscript (also in the answer for the comment of P4 L20 – 21).

P 4, L19: What type of canisters were used?

Reply: The canisters were Entech's Silonite (Silonite™ VS Summa). They have an internal Silonite™ coating that provides a high-quality, long-term sample storage solution. These canisters are certified to meet the technical specifications required for EPA methods TO-14a and TO-15. Part of these information will be added at the revised manuscript (also in the answer for the comment of P4 L20 – 21).

In the revised manuscript: P.5 L.16.

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

Reply: The canisters were evacuated prior sampling and the sampling procedure was held up to atmospheric pressure. To push the sample from the canister to the GC line, pressure higher than the atmospheric is needed and this is achieved by over-pressurizing the canister by an addition of a known volume of zero air into the container.

The Teflon line (PTFE) was used for the connection of the canister with the GC. The artifacts in the canisters and the sampling line were checked and no artifacts were found.

In order to better explain the sampling and analysis methods with canisters, the Sect. 2.4 was updated as follows:

"2.4 Street canyon and tunnel measurements

In order to identify the NMHCs fingerprint of traffic emissions, NMHCs measurements were conducted at a monitoring station belonging to the Hellenic Ministry of Environment and Energy, located at a street canyon downtown Athens with increased traffic and frequent traffic jams (Patission 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 200m and it has 3 lanes at each direction with no specific restrictions for heavy duty vehicles. The

measurements are performed at the middle of tunnel to avoid as possible the influence of ambient air from outside. Concerning the Patission campaign, samples were collected during the morning rush hour, every 1-hour from 06:55 LT to 10:15 LT (LT = UTC+2).

In both cases for the sampling were used 6L stainless steel – silonite canisters - and the sampling time ranged between 2 and 10 minutes. The analysis method is described elsewhere (Sauvage et al., 2009). In summary, before the analysis, the samples were diluted by a factor of two with zero-air, afterwards each canister was connected to the GC-FID system using a Teflon (PTFE) sampling line and finally analyzed by the same GC-FID method as described in Sect. 2.2. Before the 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."

In the revised manuscript: P.5 L.9 – "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 (Patission 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. The measurements are performed at the middle of the tunnel to avoid as possible the influence of ambient air from outside. Concerning the Patission street campaign, samples were collected every hour during the morning rush hour, from 06:55 LT to 10:15 LT (LT = UTC+2).

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."

Temporal variability of NMHCs

P 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.

Reply: Based on the comment, the phrase was corrected as follows: "During the reported period, the data availability (in comparison with the maximum potential data availability) for all C2-C6 NMHCs was higher than 87% with the exception of isoprene (approximately 10%)".

In the revised manuscript: P.5 L.28 – "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).".

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

Reply: Based on the comment, the term worldwide was removed.

P 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?

Reply: The sentence was re-phrased as follows (P.5 L.28): "The comparison with those already published for the GAA, indicates an apparent decrease by a factor of 2 to 6 for the majority of the species lying above C_4 (taking as reference the case of Ancient agora urban area in the close vicinity of the Thissio Station). This decreasing trend is in agreement with a decrease in primary pollutants CO, SO_2 already reported by Kalabokas et al. (1999) and Gratsea et al. (2017), due to the air quality measures taken by the Greek government. However, this decrease has to be seen with cautious considering differences in sampling period (summer versus winter), location, sampling method and analytical techniques."

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

Reply: Based on the comment, the text was rephrased, and a new sentence was added: "Comparison with other Mediterranean or south European locations with long-term winter observations is possible only with Beirut (Salameh et al., 2015) and Bilbao (Durana et al., 2006). Beirut, located in the Eastern Mediterranean basin (approximately 200Km SE of Greece, 230m above sea level), has a population of 2000000 citizens 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 of 400000 citizens in north Spain, located along a river delta in SE–NW direction, where two mountain ranges run 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. Furthermore, our measured benzene and toluene levels (Table 1), were significantly 7 and 3 times lower than the 12-hour day-time average levels reported for a Cairo rural area by Khoder et al. (2007), and equal to 5.8 and 7.5 ppb for benzene and toluene respectively."

In the revised manuscript: P.6 L.17 – "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.".

P 5, L18-20: The same comment as above applies here. As long as there is more elaborated comparison, the presentation of the data remains generic.

Reply: Based on the comment, the sentence was clarified (P.6 L.23): "NMHC levels are also compared with those from 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 population. The climate is both oceanic and continental, with cold winters (temperatures can be below 0°C) and mild but wet summers."

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

Reply: The remark was already addressed before for the comment of P5 L15-18.

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

Reply: We agree with the reviewer and the term background was removed.

In the revised manuscript the phrase was removed.

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

Reply: The remark was addressed previously for the comment of P 5, L15-18.

In the revised manuscript the phrase was removed.

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

Reply: As the present manuscript includes only the October 2015 to February 2016 data-set of NMHCs in order to provide information on winter-time sources, annual variability of the other NMHC sources could not be addressed. However, due to the variability of temperatures that have been encountered during October and November, we investigated the relationship between NMHCs levels and temperature. The corresponding section will be placed in the supplement (Sect. S3) as follows:

S.3 Investigation of evaporation losses (Sect. 3.4.3, Fig. 8).

In Sect. 3.4.3, the increased mass contribution of butanes and propane to the morning profiles of Thissio and Patission was attributed to LPG fuels, thus to fuel evaporation. To better investigate this possibility, the monthly variation of i-butane relatively to n-butane (Fig. S10) has been examined. The two compounds have linear relationship with no significant temporal differences on the slopes (only October and December equations are presented). In addition, the regression is similar to the one derived from the Patission measurements (depicted on the box on Fig. S10), thus enhancing our assumption that the observations of these compounds are traffic related.

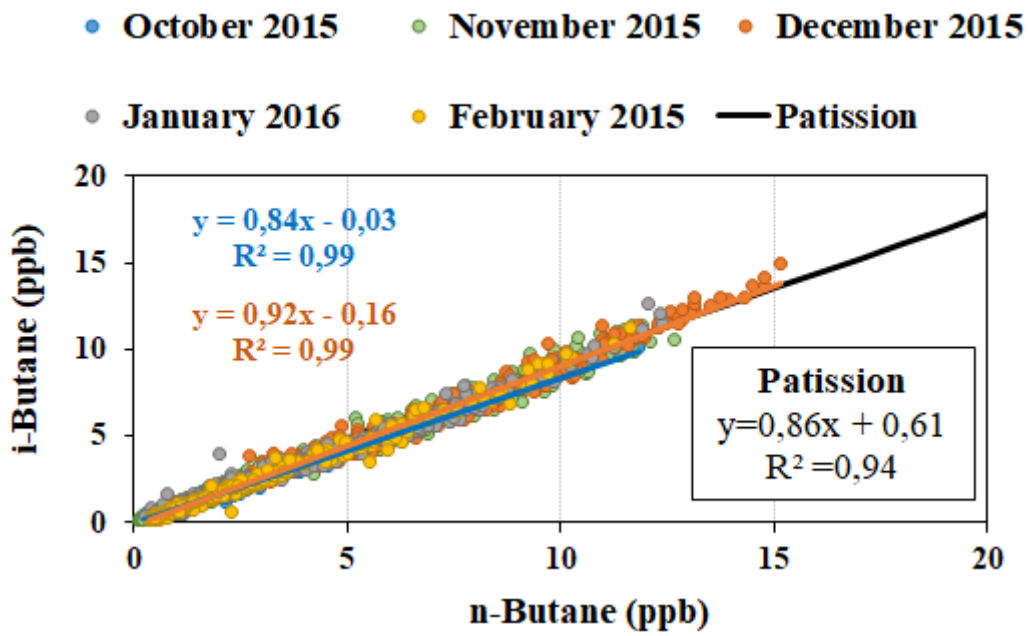


Figure S10. **Scatter plots between i-butane relatively to n-butane for October 2015, November 2015, December 2015, January 2016 and February 2016 for the Thissio site. The black line corresponds to the Patission data regression.**

Furthermore, a similar approach as Na and Kim (2001) proposed for Seoul (South Korea) has been applied, in order to investigate the relationship of the ratio Butanes-to-Alkanes C2 – C5 (%) and temperature for every month (Fig. S11). More specifically, the ratio of the sum of i-butane and n-butane versus the sum of ethane, propane, i-butane, n-butane, i-pentane and n-pentane for every sample was calculated. Ethylene, propene and acetylene are excluded from this ratio due to their reactivity. The mean and standard deviation values of the ratio were derived for the temperatures between 1^{o}C to 25^{o}C (minimum and maximum of the period respectively) and were plotted against the temperature for each month. The highest values of the ratio are observed for high temperatures and the lowest for low ambient temperature, although the standard deviation is considerable. It is interesting to note that the same pattern is observed when the ratio Pentanes-to-AlkanesC2 – C5 (%) versus the temperature is examined (Fig. S12). Taking into account the positive dependence of the two ratios to temperature, we can assume that fuel evaporation losses from cars are also an important source of NMHCs. In addition,

the above results could indicate why the Athens tunnel results performed in May differ from Patission and Thissio winter morning profiles."

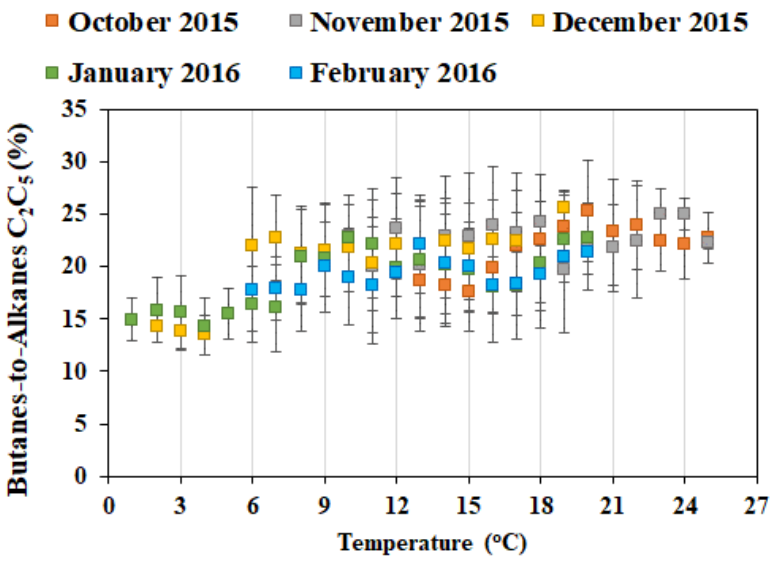


Figure S11. Scatter plots of the ratio Butanes-to-Alkanes C2C5 (%) to temperature for October 2015, November 2015, December 2015, January 2016 and February 2016.

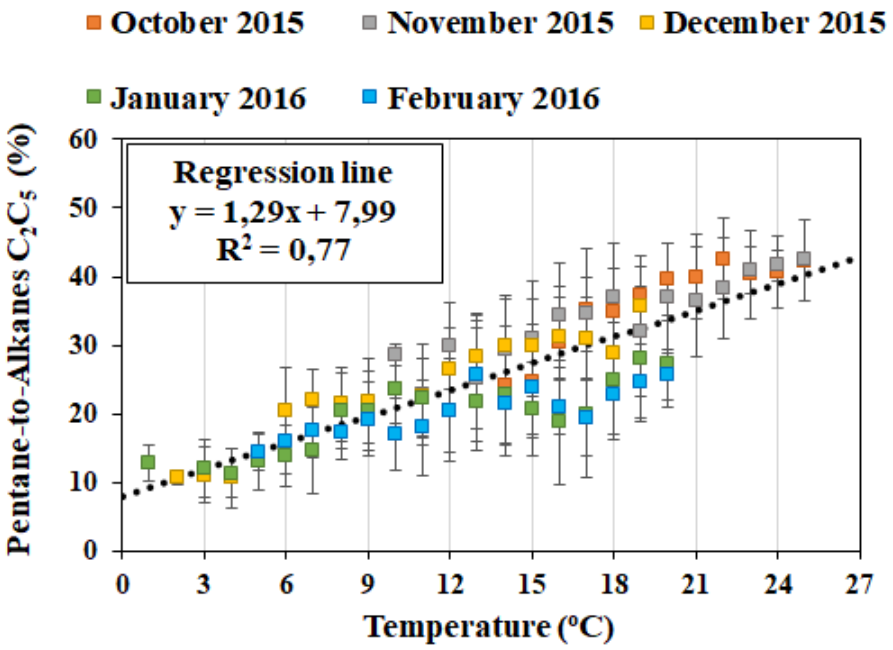


Figure S12. Scatter plots of the ratio Pentanes-to-Alkanes C2C5 (%) to temperature for October 2015, November 2015, December 2015, January 2016 and February 2016.

In the revised supplement the Sect. S3 is the following:

" **Section S.3. Investigation of the evaporation losses (Sect. 3.4.3, Fig. 8).**

In Sect. 3.4.3, the increased mass contribution of butanes and propane to the morning profiles of Thissio and Patission was attributed to LPG fuels, thus to fuel evaporation. To better investigate this possibility, we followed a similar approach as Na and Kim (2001) for Seoul (South Korea), in order to examine the relationship of the ratio Butanes-to-Alkanes$C_2 - C_5$ (%) and temperature for every month (Fig. S10). More specifically, the ratio of the sum of i-butane and n-butane versus the sum of ethane, propane, i-butane, n-butane, i-pentane and n-pentane for every sample was calculated. Ethylene, propene and acetylene are excluded from this ratio due to their reactivity. The mean and standard deviation values of the ratio were derived for the temperatures between 1ºC to 25ºC (minimum and maximum of the period respectively). These values were plotted against the temperature for each month. The highest values of

the ratio are observed for high temperatures and the lowest for low ambient temperature, although the standard deviation is considerable. It is interesting to note that the same pattern occurs when the ratio Pentanes-to-Alkanes$C_2 - C_5$ (%) versus the temperature is examined (Fig. S11). Taking into account the positive dependence of the two ratios to temperature, we can assume that fuel evaporation losses are also an important source of NMHCs. In addition, the above results could indicate why the Athens tunnel results performed in May differ from Patission and Thissio winter morning profiles.

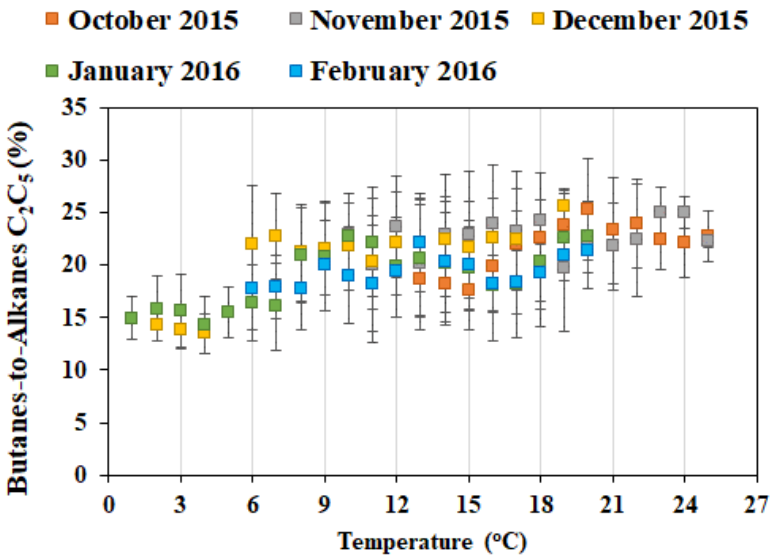


Figure S10. Scatter plots of the ratio Butanes-to-VOC C2C5 (%) to temperature for October 2015, November 2015, December 2015, January 2016 and February 2016.

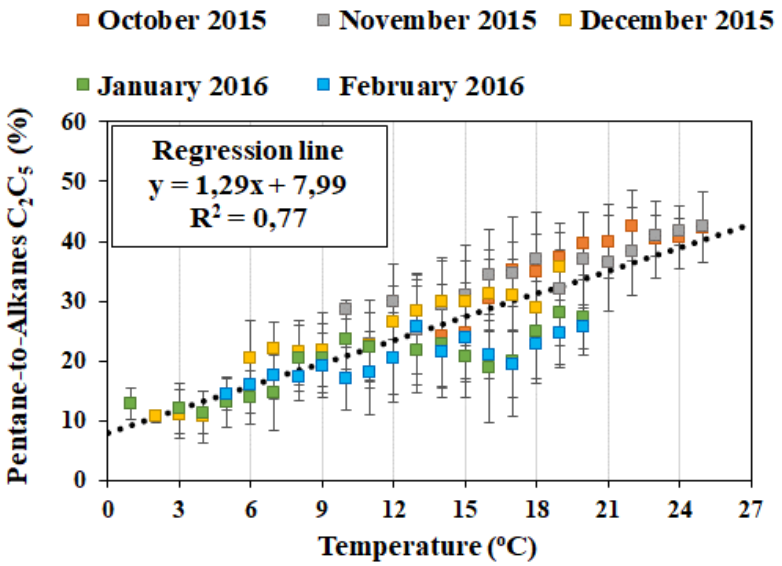


Figure S11. Scatter plots of the ratio Pentanes-to-VOC C2C5 (%) to temperature for October 2015, November 2015, December 2015, January 2016 and February 2016.

Furthermore, we examine the monthly variation of i-butane relatively to n-butane (Fig. S12). The two compounds have linear relationship with no significant temporal differences on the slopes (only October and December equations are presented). In addition, the regression is similar to the one derived from the Patission measurements (depicted on the box on Fig. S10), thus enhancing our assumption that the observations are traffic related.

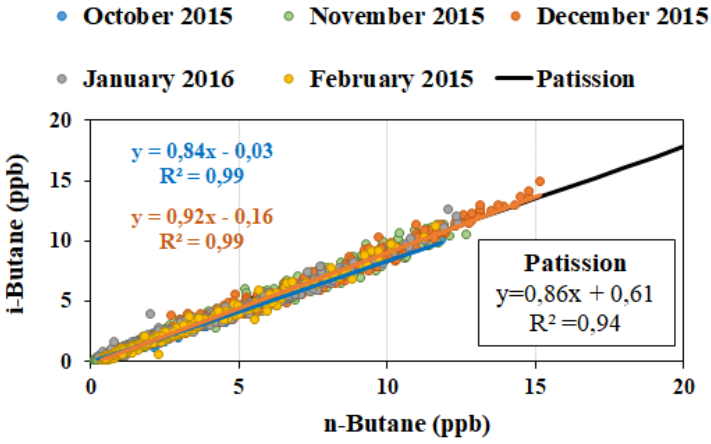


Figure S12. Scatter plots between i-butane relatively to n-butane for October 2015, November 2015, December 2015, January 2016 and February 2016 for the Thissio site. The black line corresponds to the Patission data regression.

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

Reply: We agree with the reviewer but his remark is valid only during nSP, as during the SP events are associated with low winds, i.e stagnant conditions, no frontal passages occur. Note also that in our manuscript the role of meteorology was highlighted (P.6, L.14).

In the revised manuscript: P.7 L.22.

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

Reply: This decrease by 20% refers to both day and night time and when the wintertime data is compared to the October (reference period). The sentence was corrected as follows: "Nevertheless, according to Kokkalis et al. (personal communication) the mean winter-time decrease of the PBL is in the range of 20% for both day and night period, thus the limited dilution couldn't be the only factor determining the enhancement of NMHCs level."

In the revised manuscript: P.6 L.34 - "Nevertheless, according to Kokkalis (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.".

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

Reply: Yes, the text will be changed by including the vertical dilution term.

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

Reply: See answer above for the role of dynamic meteorology during SP and nSP events (comment for P5 L27).

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

Reply: As we have seen before the impact of traffic remains almost unchanged from October to wintertime. Given also the fact that BDL change is within 20% from October to January then the increase in NMHCs could be related to an additional source during wintertime which is heating. Although the word heating is generic the contribution of electric heating is limited in Greece and the majority of the households used fuel for heating before the crisis. During the crisis and due to the increase in fuel and consequently in electricity most of the people used wood for burning. The increased role of wood for burning was clearly seen at the tracers used in this work (BC_{wb}). In addition, PMF analysis on aerosol data obtained before and after the crisis clearly showed the absence of wood burning as a source of pollution the years before 2012. Based on the comment, the sentence was clarified as follows: “The amplitude (intensity) 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), as well as BC and its fractions associated with wood burning (BC_{wb}) and fossil fuel combustion (BC_{ff}) (Fig. 3). 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 except traffic, e.g. domestic heating (petroleum oil or wood burning stoves). 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 by a factor of 2 larger, which could imply the predominant role of heating in air quality during wintertime. Consequently, these observations are indicative of the contribution of traffic and heating to the NMHCs levels".

In the revised manuscript: P.7 L.6 - "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. These observations are indicative of the contribution of traffic and heating to the NMHCs levels.".

P 6, L4-7: From Fig 3 I see that Bff increases similarily to Bwb at night. Why the authors make the statement that traffic would not be as important as heating?

Reply: The remark was also addressed before. Traffic is also a night-time emission source of NMHCs, however the increase in BC_{ff} during night is due both to traffic and fossil fuel used for heating. A comparison between the morning BC_{ff} peak which is exclusively due to traffic to that observed during night clearly shows that although amplitude could be similar the duration of the night peak is much longer (by almost a factor of 2). In addition, as it follows that of BC_{wb} emitted by wood burning for heating, indicates that heating rather than traffic is the main contributor of the BC_{ff} during night. However to avoid misinterpretation the phrase was changed into (P.7 L.13): "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 later from the combined use of heavy oil and wood burning."

P 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.

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".

The role of meteorology on NMHC levels

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

Reply: On the specific section only the major NMHCs reactions were considered, by taking into account that the Thissio site is located in an urban location. Nevertheless, the Cl role could be mentioned, since marine originated air masses could affect the area. Thus the text is changed into (P.7 L.18): "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 omitted, especially for coastal areas such as GAA (Arsene et al., 2007)."

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

Reply: We would like to thank the reviewer for this comment that helped us investigate this issue. For the better interpretation of the effect of wind speed and wind direction, the graphs of figure 5 (now figure 6) were changed. According to the figure 5, high concentrations of NMHCs are mainly depended on wind speed, since they occur only for wind speeds ranging from 1 to 3 m s^{-1} and independently on wind directions.

Furthermore, concerning the acetylene issue, we isolated the corresponding concentrations of the enhanced baseline levels based on the acetylene-to-CO ratio. After investigating the possible relationship of these levels with other compounds or meteorological factors, we found no specific relationship or trend for these values. For that reason, we examined the corresponding chromatograms and we found a slight moving of the peak of acetylene only, which is an indication of mis-identification of this compound. As it is not clear if the high values are due to an instrumental default or a co-elution with another compound, while there are indications that there is a link to the prolonged SP events that occurred in this period with the few nSP in-between, we decided to remove the values (293 values were removed out of 2862, i.e c.a 10% mainly from December and January).

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

Reply: We thank the reviewer for his/her comment that helped us investigate this matter. Due to an error in the calculation of the mean wind direction values, we re-plot the data by using hourly values and the new figure reveal increased contributions under the N sector (now figure 6).

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

Reply: The remark was addressed before for the comment of P6 L15-20 and P6 L21-22.

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

Reply: With the word "local" we refer not to immediate vicinity of Thissio but to the GAA in general as our site is considered as representative of a wider area in the GAA.

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

Reply: According to the demographic data of 2011, the population around the center of Athens is almost equal distributed (1 million citizens in the center and approximately 5 hundred thousand citizens in every sector around the center – North, West and South) which means that the population distribution couldn't be the only factor driving the emissions. Apart from the southern cleaner marine originated air masses but with population of low income, other factors could also affect the pollution sources of the city. The majority of the buildings in GAA have central heating systems regardless their age; while the residencies that have been constructed the last 20-30 years usually have both fire places and central heating, reflecting the combined use of several types of fuels such as wood, fuel, or other mixtures for heating purposes. The northern part of Athens has been mostly constructed based on this mixed heating systems pattern and in combination with the financial welfare of its residents relatively to areas close to the historic center of the city, south and west sectors, enhanced use of heating systems and thus increased emissions could be expected from this direction.

Based on the comment, we focused our investigation on morning and nights of October and December 2015 and it is apparent the contribution of the N to ESE sector to the December night concentrations especially at night. Consequently, the text was corrected accordingly: "The impact of the N to ESE

sector on NMHCs levels can be also seen when comparing the concentrations of the morning (07:00 – 09:00) and night (21:00 – 23:00) peak of October and December. The wind probability from N to ESE is similar for both months, however significantly higher concentrations are observed in the December night peak, that seem to affected by low wind speed (<2 m s^{-1}) that mainly originates from the N to NE sector."

In the revised manuscript: P.8 L.6 - "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 m s^{-1}) from the N to NE sector.".

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

Reply: Based on the comment, the phrase was clarified as follows (P.8 L.11): "…..also trigger the production of biogenic compounds, whereas……"

Identification of NMHC emission sources

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

Reply: Following the suggestion of the reviewer the term "locally" was removed.

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

Reply: Based on the comment, the sentence was clarified as follows (P.9 L.12): "….as emission source of specific organic compounds, such as ethane, ethylene, acetylene, benzene, methanol, acetaldehyde and acetonitrile…."

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

Reply: Due to the small number of samples a baseline subtraction from the tunnel data was not possible.

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

Reply: To avoid any dilution from outside air masses the tunnel measurements have been conducted in the middle.

P 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..

Reply: We would like to thank the reviewer for his detailed questions regarding our tunnel measurements. Indeed, our tunnel measurements were performed in May and temperature is different compared to winter-time. Note also that the tunnel experiments in Paris were performed in autumn that is a warmer period for Paris compared to winter.

To resolve the issue on the possible temperature influence, a campaign was conducted during winter time in Athens by collecting samples at Patission (a street canyon heavily influenced by traffic). Patission profile reflects all types of traffic-related emissions due to the combination of the high number of vehicles and buses that cross this street, the traffic jam, the variety of types of fuels, vehicles age and their maintenance etc. Samples were collected during the morning rush hours (from 6-10am) and reported together with the tunnel data at figure 8.

Several conclusions can be drawn from this figure. Firstly, the two morning profiles although performed at sites with different impact of traffic agrees quite well ($R^2 > 0.97$). Iso - pentane and toluene are the two main compounds contributing to the morning profiles accounting by about 44% of the total measured NMHCs at both locations, followed by n- and i-butane and ethylene accounting for almost

30%. Differences among the two morning profiles between these 5 main species are minimum (less than a factor of 1.5). Note also that the morning profile at Thissio is the mean of a whole month period compared to a campaign of two days in Patission which can explain the differences between the two profiles.

The profiles obtained at the two tunnels although differ in terms of tunnel length, city, and period have a lot of common features. Again i-pentane and toluene are the two main compounds of the profile accounting by about 56% of the total measured NMHCs at both sites, followed by n -butane, ethylene and benzene accounting for almost 20% again at both sites. The most striking difference between the two sites concerns n-pentane (almost a factor of two higher in Paris compared to Athens). Despite the differences between the two tunnel studies the similarity is almost 80% ($R^2 > 0.91$). 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 Patission morning profiles and their difference from the Athens tunnel profile, as well as the Paris tunnel profile, indicate the importance of the type of fuel used. The latter is also implied in recent works (Ait-Helal et al., 2015; Q. Zhang et al., 2018; Y. Zhang et al., 2018), where important differences are reported between tunnel measurements worldwide, attributed to the variance of the car-fleet (type of vehicle and fuel). In our case there is a possibility that the car-fleet in the tunnel is not representative for the GAA, since the existing tolls in short distance reduce the use of the tunnel due to financial issues. The latter scenario is further enhanced by the time of the measurements, since the traffic density is quite low at noon. In any case, the prevalence of i-pentane and toluene in all profiles, indicate the continuing dominance of gasoline powered cars. Moreover, higher values of ethane, propane and butanes that are depicted in the morning peaks of 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). In fact, the connection of high levels of C2-C4 alkanes and the number of LPG-powered cars is highlighted in other tunnel works as well (Ait-Helal et al., 2015; Q. Zhang et al., 2018).

In the revised manuscript, the corresponding paragraph will be re-written as follows:

"As discussed in Sect. 3.2, the morning peak (07:00 – 10:00 LT) of NMHCs could be attributed mainly to traffic. Figure 8 presents the profile of this peak (% mass contribution of the measured NMHCs),

during January and February SP days when toluene data were available. Additionally, in the same figure the morning profile obtained from a 2 – days campaign conducted in Patission Monitoring Station (a street canyon located at the center of Athens) and the profiles of two tunnel measurements in G.A.A and Paris are reported. Details on the calculations for the morning profile for the two sites are provided in Sect. S2. Patission profile reflects all types of traffic-related emissions due to the combination of the high number of vehicles and buses that cross this street, frequent traffic jam conditions, the variety of types of fuels, vehicles age and their maintenance etc.

The two morning profiles, although performed at sites with different impact of traffic, agrees quite well ($R^2 > 0.97$). Iso - pentane and toluene are the two main compounds contributing to the morning profiles accounting by about 44% of the total measured NMHCs at both locations, followed by n- and i-butane and ethylene accounting for almost 30%. Differences among the two morning profiles between these 5 main species are minimum (less than a factor of 1.5). Note also that the morning profile at Thissio is the mean of a whole month period compared to a campaign of two days in Patission which could explain the differences between the two profiles. The profiles obtained at the two tunnels although differ in terms of tunnel length, city, and period have a lot of common features. Again i-pentane and toluene are the two main compounds of the profile accounting by about 56% of the total measured NMHCs at both sites, followed by n -butane, ethylene and benzene accounting for almost 20% in total again at both sites. The most striking difference between the two sites concerns n-pentane (almost a factor of two higher in Paris compared to Athens). Despite the differences between the two tunnel studies the similarity is almost 80% ($R^2 > 0.91$). 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 Patission morning profiles and their difference from the Athens and Paris tunnel profiles, indicate the importance of the type of fuel used. The latter is also concluded in recent works (Ait-Helal et al., 2015; Q. Zhang et al., 2018; Y. Zhang et al., 2018), where important differences are reported between tunnel measurements worldwide, and attributed to the variance of the car-fleet (type of vehicle and fuel). 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 quite low. In any case, the prevalence of i-pentane and toluene

in all profiles, indicate the continuing dominance of gasoline powered cars. Moreover, higher values of ethane, propane and butanes that are depicted in the morning peaks of 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). In fact, the connection of high levels of C_2-C_4 alkanes and the number of LPG-powered cars is highlighted in other tunnel works as well (Ait-Helal et al., 2015; Q. Zhang et al., 2018)."

In the revised manuscript: P.10 L.1 – "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 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 (Patission Monitoring Station) and the profiles of two tunnel measurements in G.A.A and Paris are also reported. Details on the calculations for the morning profile for the two sites are provided in Sect. S2. Patission 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 ($R^2 > 0.97$). Iso - pentane and toluene are the two main compounds contributing to the morning profiles accounting by about 44% of the total measured NMHCs at both locations, followed by n- and i-butane and ethylene accounting for almost 30%. Differences between the two morning profiles regarding these 5 main species are weak (less than a factor of 1.5). Note also that the morning profile at Thissio is the mean of a whole month period compared to the two days campaign at Patission which could explain the small differences between the two profiles. 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. 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 Patission 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 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. S10 and S11 where the ratios of butanes and pentanes-to-total Alkanes C2 – C5 (%) 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. In addition, the above results could indicate why the Athens tunnel results performed in May differ from Patission 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. S12). 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 Patission 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).”.

P 8, L32 - P 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"?

Reply: The remark was addressed in the previous comment for P 8 L31-32.

P 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?

Reply: The remark was addressed before in the comment for P 8, L31-32.

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

Reply: We don't agree. At page 8, line 17 (now P.9 L.15), the results from two selected months are shown, not days.

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

Reply: First of all, after the correction of the ethylene concentrations, the slope of the graph changed. Based on the new graph, the December increase to the slope is 34%. Thus, given that also in all graphs the difference cases in slopes is within 30% we can assume that slopes remain almost stable during both months and the comment on ethylene was removed.

P 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?

Reply: As background value we use the minimum value observed during mid-day. For the morning and night profiles (Fig. 8 and 10, now Fig. 9 and 10) we used in the analysis only SP days, which means that wind speed is always less than 3m/s during all hours, and thus no major changes in wind speed, which is the most important parameter controlling NMHCs levels, are expected.

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

Reply: Yes differences are statistically significant ($p<0.01$).

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

Reply: This comment was already addressed before for P.6 L4-7.

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

Reply: Based on the comment, the sentence was clarified as follows (P.12 L.11): "……due to different temperature profiles….."

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

Reply: The discussion on the profile of the morning peak was changed as discussed in the earlier comments related to tunnel.

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

Reply: Based on the comment the sentence was clarified as follows (P.12 L.18): "An extended dataset of NMHCs and other organic tracers (future long-term measurements) is needed in order to distinguish the contribution of different sources types on seasonal basis and to further quantify their impact on the NMHCs levels".

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

Reply: The caption of Table 1 has respectively been corrected. Mean levels are used in the table. The second sentence referring to information about sampling or analysis and sampling frequency was replaced by data resolution. The results of Kaltsonoudis et al. (2016) are not listed on the table since datasets with numerous common compounds have been selected for the comparison. Nevertheless, the authors include now the compounds in common according to the suggestion of the reviewer.

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

Reply: The remark was addressed before for the comment of P6 L15 – 20.

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

Reply: A box-wisker plot was now used to better represent the NMHC data (now figure 2).

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

Reply: The data shown on the graphs are based on mean values, since part of this paper is focused on the elevated concentrations of the SP period. For that reason, we believe that they are better represented by mean than median values (now figure 4).

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

Reply: The graphs was re-made accordingly (now figure 5).

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

Reply: Figure 5 was replotted again with all data**.**

In the revised manuscript the figure 6 (previous figure 5) is in a pollution rose format.

Figure 8: Error bars should be included.

Reply: Error bars can be added only for the Thissio data (now figure 9).

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%.

Reply: (Now figure 11) As there is no light during this period and this is the period that heating starts, for simplicity it is considered as nighttime. Also, as discussed before this is the best way to consider the evening/night maximum which is quite broad (more than 8h).

Error bars have been included. Finally, by adding-up the values the sum is almost 100%. Differences are too small.

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Reference article: acp-2017-936

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

Summary of corrections

In the list below is a summary of the general changes to the revised manuscript.

In the text

- Corrections of typing and grammar errors.
- Rephrasing and re-writing of the text when necessary (see answers for the reviewers above).
- There is a new Introduction.
- The Sect. 3.4.3 was re-written, with new elements for discussion.

In the figures

- All the figures changed due to error described in the erratum.
- Error bars were included in Fig. 9 and 11 (see comments and answers for the reviewers above).
- The type of graph of the Fig. 3, 5 and 6 changed (see comments and answers for the reviewers above).

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

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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~~s~~ a remarkable day to day variability. Their levels increase by up to factor of four from autumn (October-November) to winter (December-February). ~~Local meteorology~~ Microscale meteorological conditions and especially wind speed 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~~ec~~$^{-1}$), 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 ~~(intensity)~~ 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 ~~additional~~ 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_{wb}) and fossil fuel combustion (BC_{ff}), as well as with source profiles we conclude that the morning peak is attributed to traffic while the night one mainly to heating. ~~However, the present data-set does not allow for quantification of the relative contribution of fossil fuel and wood burning for heating purposes, although tracers and source profiles clearly indicate the presence of both sources. Following the same comparison f~~For the night peak, the selected tracers and source profiles clearly indicate contribution from both ~~the presence of~~ traffic and domestic ~~combustion~~heating (~~of~~ fossil fuel and wood burning~~-~~)~~for heating purposes~~. However, the present data-set does not allow for quantification of each source due to the similarity of emissions,

thus measurements of more specific ~~compound~~tracers are needed for the better understanding of the contribution of these ~~three~~ nocturnal VOC sources.

1 Introduction

~~Non-methane hydrocarbons (NMHCs) are key atmospheric constituents for atmospheric chemistry. In the presence of NOx, their oxidation leads to formation of tropospheric ozone and other species, such as peroxy radicals (RO_2) and peroxy acetyl nitrate (PAN), thus affecting the oxidative capacity of the atmosphere (Atkinson, 2000 and references therein). NMHCs' 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). They mainly originate from anthropogenic sources such as traffic, solvents' use, residential heating, natural gas use, industrial activity, but also emit 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., 2016b; Jaimes-Palomera et al., 2016). Besides their key role as secondary pollutants precursors, NMHCs are of interest regarding their association with health issues (EEA report, N° 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 and an important megacity, pollution-wise, in the Eastern Mediterranean, 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., 1998; Kanakidou et al., 2011). However, the measurement of pollution precursors is limited to ozone and nitrogen oxides, with almost no information on NMHC levels being available. The few existing NMHC measurements in Athens are based on non-continuous intervals with the use of canisters or sorbent tubes, performed just for a few days during summertime or autumn (Moschonas and Glavas, 1996; Klemm et al., 1998; Kourtidis et al., 1999; Moschonas et al., 2001; Giakoumi et al., 2009). Continuous measurements of NMHCs in Athens for a period of one month, have been conducted 20 years ago at three locations, two suburban and one urban, and were limited to compounds containing more than four atoms of carbon (Rappenglück et al., 1998, 1999). Since then significant changes have unambiguously occurred in NMHCs sources in Athens. For instance Gratsea et al. (2017) reported significantly decrease in carbon monoxide (CO) levels from traffic due to car fleet renewal, fuel improvement and metro line extension, while new sources of pollution emerged, especially after 2012, due to uncontrolled wood burning for domestic heating (Saffari et al., 2013; Paraskevopoulou et al., 2015; Kaltsonoudis et al., 2016a; Fourtziou et al., 2017). The latest work on Volatile Organic Compounds (VOCs) in Athens was performed by Kaltsonoudis et al. (2016) it was limited to one month monitoring during summer and winter also and contained no measurements of light compounds from the NMHCs group. The above demonstrate the increasing need for intensive~~

measurement of NMHCs in Athens, to better understand their sources, temporal characteristics and role on smog formation, in the new conditions established during the economic crisis years, with competing traffic and wood burning.

The current study presents, time-resolved, uninterrupted data of NMHCs from two to six carbon atoms, during a time span of several months (October 2015 to mid-February 2016) in the Great Athens Area (GAA). The emphasis of this work is on: (1) the determination of the ambient levels of C2-C6 NMHCs, twenty years after their first measurements (especially for C2-C3, these are the first continuous measurements of NMHCs in Athens); (2) the study of their temporal characteristics and the determination of the factors controlling their variability, and (3) the investigation of traffic and heating impact on NMHCs levels. Finally, to further shed light on the impact of biomass burning on NMHC levels during wintertime, an intensive campaign of 4 weeks duration was conducted from 15th of January to 15th of February 2016, when, in addition to C2-C6 measurements, a C6-C12 analyzer was also deployed and selected tracers were measured in parallel.

Non-methane hydrocarbons (NMHCs) are key atmospheric constituents for atmospheric chemistry. In the presence of NOx, their oxidation leads to formation of tropospheric ozone and other species, such as peroxy radicals (RO_2) and peroxy acetyl nitrate (PAN), thus affecting the oxidative capacity of the atmosphere (Atkinson, 2000 and references therein). NMHCs' 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, solvents' use, residential heating, natural gas use, industrial activity, but also emit 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 regardingbecause 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 , pollution-wise, 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., 19958; Kanakidou et al., 2011). However, the measurements of pollution precursors are mostly limited ontoabout 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, containing reporting almost 50 C4 – C12 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, containing 11 aromatic and 11 oxygenated organic gaseous compounds and (5 C5 – C8 NMHCs from C5-C82). Meanwhile, significant changes in pollutant sources occurred in

Athens the last 20 years, which ~~inflicted important~~lead to significant decreases in the annual concentrations of major pollutants such as CO, SO_2, NOx ~~(combustion marker)~~ (Gratsea et al., 2017; Kalabokas et al., 1999). ~~Because the latter~~As this ~~-~~trend wa~~i~~s attributed to the car fleet renewal, fuel improvement, metro line extension and industrial emission controls, a decrease in NMHC~~s~~ 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). ~~In the literature, there are some s~~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 ~~to~~in the emission rates or the emission profiles ~~of the VOCs~~, that are attributed to the type of wood, stove, lightening material and ~~the variety of emissions from~~ the burning stages (Barrefors and Petersson, 1995; Baudic et al., 2016; Evtyugina 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 ~~-including~~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 ~~to~~in the residential wood burning profile reported by Baudic et al. (2016) ~~that is not depicted~~was ~~not confirmed~~different from ~~in~~ the profile of Liu et al. (2008).

~~Nevertheless, t~~In addition, in their ~~latest~~recent work, ~~on VOCs in Athens of~~ Kaltsonoudis et al. (2016) reported ~~gave a~~ important contribution of wood burning to the wintertime night concentrations ~~first insight about the positive effects of the Greek air pollution on~~of aromatics and oxygenated VOCs. ~~levels, pointing out the important contribution of wood burning to the wintertime night concentrations. Consequently, t~~The above clearly demonstrates the increasing need for intensive measurements of NMHCs in Athens, ~~, to observe the current atmospheric composition~~ which in turn will ~~to~~ allow to assess ~~for~~ the impact of future changes (fuel composition changes or other control strategies) on atmospheric composition ~~to be assessed~~. In other words, t~~T~~here is a need to establish a "current baseline" for Athens atmospheric composition in terms of NMHC~~s~~ levels. ~~In addition, it would be interesting to investigate the contribution of traffic and wood burning to the light NMHCs, which are two competitive sources with similar NMHC tracers that could lead to an overestimation of the first due to the contribution of the second (Schauer et al., 2001).~~

The current study presents, time-resolved, uninterrupted data of 11 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). 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. E~~(e~~specially for C2 – C3, these are the first ever continuous measurements of NMHCs in Athens~~)~~; (2) the study of th~~ei~~e NMHC~~sr~~ temporal characteristics and the determination of the factors controlling their

variability, and (3) the investigation of traffic and residential heating impact on NMHCs 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 FID), Chromatotec, Saint Antoine, France) were used for the measurement of NMHCs in Athens. Specifically, the "airmoVOC C2 – C6 C6" (during the whole period, from October 2015 to February 2016) and the "airmoVOC C6 – C12 C12" Chromatrap GC (from mid-January until mid-February 2016) analyzers were used for the determination of C2 – C6 C6 and C6 – C12 C12 NMHCs respectively, collecting ambient air through collocated inlets at the rooftop of the station, 4 m above ground. The C2 – C6 C6 NMHC analyzer was set to sample ambient air on a 10 min basis followed by and an analysis time of 20 min, while for the C6 – C12 C12 the respective timing was 20 min and 10 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.

For the airmoVOC C2 – C6 C6 analyzer, 189 mL of air was drawn through a 0.315 cm mm diameter, 6 m-long stainless-steel line with a filter of 4 μm pore size at the sampling inlet, and a flow rate of 18.9 mL 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 ^{0}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. The trap was then heated rapidly to 220 ^{0}C for 4 min and the pre-concentrated VOCs were thermally desorbed onto a Plot Column (Restek Corp., Bellefonte, PA, USA, Al_2O_3/Na_2SO_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 ^{0}C, followed by a constant heating rate of 15 ^{0}C min^{-1} to 200 ^{0}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), while for ethane and ethylene is 0.1 ppb. ~~The overall estimated uncertainty of the measurement is 15%.~~

The airmoVOC C6 – C12 ~~C12~~ analyzer was collecting 900 mL of air through a 0.315 cm ~~mm~~ diameter, 6 m-long stainless-steel line with a filter of 4 μm pore size at the sampling inlet, and a flow rate of 45 mL 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 ^{0}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 thickness). With one minute delay, the oven temperature was raised from 36 to 50 ^{0}C at a rate of 2 ^{0}C min^{-1}, followed by a second heating of 10 ^{0}C min^{-1} up to 80 ^{0}C. Finally, at a constant heating rate of 15 ^{0}C min^{-1} the temperature reached 200 ^{0}C and remained there until the end of the analysis. In the present work only toluene will be used from the GC C6 – C12 ~~C12~~ ~~GC~~ data series. The uncertainty of the instrument is less than 20% and the detection limit of toluene is 0.03 ppb.

Simultaneous calibration and identification of the compounds were performed by a certified National Physical Laboratory (NPL) standard of NMHC mixture (~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) and black carbon (BC) was also taking place during the reported period. For CO, Horiba 360 Series Gas Analyzer was used, calibrated with certified standard. More details for CO measurements can be found in Fourtziou et al. (2017). A seven wavelength Magee Scientific AE33 aethalometer was operated for the measurement of BC, and its fractions assiociated with fossil fuel and wood burning (BC_{ff} and BC_{wb}, respectively) were automatically derived from the instrument software. Meteorological data were collected from NOA's meteorological station at Thissio premises.~~

Real time monitoring of carbon monoxide (CO), black carbon (BC) and nitrogen oxides (NOx = NO and NO_2) was also conducted during the reported period. For CO and NOx measurements, ~~,~~ Horiba 360 Series Gas Analyzers of one-minute resolution were used which ~~and~~ 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_{ff} and BC_{wb}, respectively) ~~were calculated based on the biomass burning contribution~~ derived automatically by the instrument software. Meteorological data were provided by NOA's meteorological station at Thissio premises.

2.4 ~~Tunnel measurements~~ Street canyon and tunnel measurements

~~Measurements were conducted in a tunnel at the peripheral, highway of Athens, called Attiki Odos, on 12 May 2016 from 12:00 LT to 12:45 LT (LT = UTC+2) in order to identify the NMHCs fingerprint of traffic emissions in the frame of the source apportionment investigation. For this canisters were used and the sampling time ranged between 2 and 6 minutes.~~

~~Four samples were collected in total and were analyzed via the GC-FID described in Sect. 2.2. Prior to the analysis the samples were diluted by a factor of two with zero-air, and then each canister was connected to the GC-FID system using a Teflon sampling line.~~

T~~In order t~~o identify the NMHCs fingerprint of traffic emissions, NMHCs measurements were conducted at a monitoring station belonging to the air quality agency of Athens and~~Hellenic Ministry of Environment and Energy,~~ located at a street canyon downtown Athens with increased traffic and frequent traffic jams (Patission 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 ~~and it has~~with 3 lanes at each direction ~~with~~and no specific restrictions for heavy duty vehicles. The measurements are performed at the middle of the tunnel to avoid as possible the influence of ambient air from outside. Concerning the Patission street campaign, samples were collected every hour during the morning rush hour, ~~every 1 hour~~ from 06:55 LT to 10:15 LT (LT = UTC+2).

In both cases, 6L stainless steel – silonite canisters ~~for the sampling~~ were used ~~6L stainless steel – silonite canisters –~~for the sampling and the sampling time ranged between 2 and 10 minutes. The sampling ~~–and –~~method for ambient air is ~~detailed~~ 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~~dilution ~~samples were diluted~~ by a factor of two. A~~ with zero air, a~~fterwards each canister was connected to the GC-FID system using a Teflon (PTFE) sampling line and ~~finally~~ analyzed by the ~~same GC-FID~~ method ~~as~~ described in Sect. 2.2. Before ~~the~~ 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~~1~~ 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 coverage for all C2-C6 NMHCs was higher than 90% with the exception of isoprene (approximately 10%). The latter led to difficulty to determine a representative diurnal variability for this compound, nevertheless, the significant night-time levels (above 300 ppt in some cases) could be indicative of non-vegetation sources (Borbon et al., 2001, 2003).~~ During the reported period, the data availability (in comparison with the maximum potential data availability) for all C2-C6 NMHCs was higher than 87%~~ with the exception of isoprene (approximately 10%)~~. Most of the data for isoprene are below the limit of detection due ~~The latter can be attributed~~ to the low vegetation activity at this period of ~~its principal source, that is emissions from~~namely the vegetationthe 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~~Consequently~~, 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~~1~~ and S1). ~~The highest concentrations ranged between 30 and 40 ppb for ethane and ethylene and were encountered in wintertime, while lower values were below 5 ppb for the whole period.~~ 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~~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). ~~The average concentration of benzene during the studied period was 0.7 ppb (still not a full year), which is considerably below the EU average annual limit of 5 μg m^{-3} or 1.5 ppb (Directive 2008/50/EC of the European Parliament).~~

In Table 1, the measurements of this study are compared with those reported in the literature for Athens in the past and other selected areas~~ worldwide~~. ~~The comparison with those already published 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 the Thissio Station), always bearing in mind differences in sampling period (summer versus winter), location, sampling method and analytical techniques.~~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~~ the~~ Thissio Station). This decreasing trend is in agreement with a decrease in primary pollutants CO, SO_2 already reported by Kalabokas et al. (1999) and Gratsea et al. (2017), due to the air quality measures taken by the Greek government. However, this decrease has to be seen with cautious considering differences in sampling period (summer versus winter), location, sampling method and analytical techniques. ~~Comparison with other Mediterranean or south European locations with long term observations is possible only with Beirut (Salameh et al., 2015) and Bilbao (Durana et al., 2006). The levels observed in Athens are significantly higher even by more than 100%, 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 from Paris, the latter as representative of a mid latitude, northern hemisphere (urban) location. Again the observed levels in Athens are significantly higher compared to those reported for Paris (Baudic et al., 2016). Furthermore, our findings for benzene and toluene, were significantly lower than the 12 hour day time average levels reported for a Cairo rural background area , as reported by Khoder et al., 2007 (mean levels of 5.8 and 7.5 ppb respectively).~~Beirut, located in the Eastern Mediterranean basin (approximately 200 Km SE of Greece, 230 m above sea level), has a population of 2000000 inhabitants ~~citizens~~ 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 ~~of~~with 400000

inhabitants~~citizens~~ in northern Spain, located along a river delta in SE–NW direction, ~~where~~with two mountain ranges ~~run~~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. ~~Furthermore, our measured benzene and toluene levels (Table 1), were significantly 7 and 3 times lower than the 12-hour day-time average levels reported for a Cairo rural area, by Khoder et al. (2007) and equal to 5.8 and 7.5 ppb for benzene and toluene respectively.~~ NMHC levels are also compared with those ~~from~~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 ~~population~~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~~1~~, a common pattern for all NMHC concentrations was their gradual~~ly~~ increase from October to December, which reflects the transition from the warmer period to the colder one. This is better illustrated in Fig. 3~~2~~, which depicts the monthly mean concentration for every NMHC presented in Fig. 2~~1~~. 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 (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 ~~the limited vertical dilution~~changes in PBL couldn't be the only factor determining the enhancement of NMHCs level observed during wintertime. Meteorological conditions such as w~~W~~ind speed and direction have to be also considered ~~as well~~ 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~~3~~ 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), ~~as well as~~ 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 ~~exceptin addition to traffic~~ such as ~~, e.g.~~ domestic heating (fossil fuel or wood burning~~petroleum oil or wood burning stoves~~). 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 ~~in~~on air quality during wintertime. T~~Consequently, t~~hese 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. ~~The amplitude (intensity) of both peaks is gradually increasing from October to winter time by a factor of 3 to 6 and nicely follow that of carbon monoxide (CO), indicating the possible contribution from additional sources, e.g. heating (Fig. 3g). 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 heating processes, namely the combined use of heavy oil and wood burning. Although the amplitude of both peaks is almost similar (with the exception of December), the duration of the night peak is at least a factor of 2 larger, indicating the predominant role of heating in air quality during wintertime. Moreover, night-time emissions occur in a shallower boundary layer relatively to the mid-day morning, resulting into accumulation of pollutants.~~

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).~~ 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 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~~4~~ and 6~~5~~ respectively (Fig. S3 and S4 include the rest of the compounds). For all studied NMHCs, the highest concentration occurred under low wind speed (< 3 m s~~ec~~$^{-1}$) reflecting the critical role of local sources versus long range transport. On a monthly basis, the NMHC dependence on wind speed remains the same ~~as~~ for the total examined period (Fig. S5).

To investigate the impact of wind direction on NMHC levels, fig. 6~~5~~ presents the distribution of wind sectors frequency of occurrence during the sampling period and that of wind speed per sector. In addition,~~, as well as~~ 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 ~~from~~ of air masses from all directions, especially ~~the weaker northerly ones~~under low wind speed. ~~directions. , still it should be noted the low frequency of occurrence of this sector (1%).~~ During the ~~whole~~ sampling period, the NE sector~~,~~ associated with relatively strong winds (u > 3 m s~~ec~~$^{-1}$), was the most frequent one, resulting in~~to~~ moderate levels of NMHCs. Overall, a similar distribution ~~of NMHC levels is shown for the different compounds~~was found for all NMHCs, indicating moderate to higher values ~~from~~ under the N-NE-E-SE directions, and lower level~~values~~s ~~from~~ under the ~~extended~~ NW-W-SW sector, the latter associated with high wind speeds. ~~The exception is the NE sector which despite the higher wind speeds still shows moderate to high levels, as a result of local sources orientation upwind the measurement site.~~ The influence of the N to SE sector to the enhanced NMHCs levels is probably related ~~with~~to ~~Indeed,~~ the northern suburbs of GAA, that are

characterized by increased number of fireplaces ~~(Athanasopoulou et al., 2017) due to the age of the buildings~~, while the higher living standards of their inhabitants ~~probably reflect~~ allow the combined use of heating oil in central heating systems and ~~the use of~~ wood in fireplaces and/or woodstoves. ~~The impact of the N sector on NMHCs levels can be also seen when comparing October with December. Although a similar wind origin distribution was observed during these two periods (Fig. S6), a 2 to 3 times higher levels of NMHCs were observed on December under N winds influence compared to October.~~ The impact of the N to ESE sector on NMHC~~s~~ levels can be also seen when comparing the concentrations of the morning (07:00 – 09:00) and night (21:00 – 23:00) peaks in~~of~~ 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 ~~the~~ December ~~night peak, that seem to~~ affected by low wind speed (< 2 m s~~ec~~$^{-1}$) ~~that mainly originates~~ 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 ~~some~~ 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 ^{0}C in October and November to 10 - 13 ^{0}C in December and late winter, respectively. When NMHCs are examined against temperature (Fig. S7~~not shown here~~), a clear tendency is not evident, although the highest levels ~~occur~~ are observed at lower temperatures.

3.4 Identification of NMHC emission sources

3.4.1 Interspecies correlation

Table 2 shows the interspecies correlation of NMHCs for the total period of measurements~~, for the investigation of their common origin~~. ~~Most NMHCs were highly correlated, with the exception of the light NMHCs (C2) with those heavier than C4 or C5 compounds. Ethane, ethylene and acetylene were moderately (R^2 of 0.5–0.7) correlated with C4 or C5 compounds,~~ All NMHCs were well correlated (R^2 > 0.81), with the exception of ~~whereas~~ isoprene which as seen before, had only ~~Two~~ few data above the LoD ~~a much lower data coverage~~ and thus was excluded from Table 2 ~~since it wasn't correlated to any NMHC~~. The strong correlation of NMHCs with combustion tracers, such as CO, NO and BC, could indicate their common origin and variability ~~due to both dilution and common sources from combustion~~. 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~~74~~) of the hydrocarbons~~, except ethane,~~ with BC_{ff} compared to BC_{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 ~~and the resulting picture~~ 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 m~~M~~ore 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. (2010~~7~~) was applied. The criteria for this separation have been the wind speed not to exceed the threshold value of 3 m s~~ec~~$^{-1}$ (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~~4~~). Based on these criteria, the first group (non-shaded in Fig. 7~~6~~) corresponds to higher wind speeds and thus more efficient dispersion of ~~locally~~ 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~~6~~) 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~~6~~).

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~~7~~ and ~~S7,~~ 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 BC_{wb} recorded in October, even during the SP periods, ~~validates~~ supports the methodology followed for the separation (Fig. 8~~7~~).

The levels of all measured NMHCs were significantly higher in December compared to October for the SP periods (Fig. 8~~7~~ and S8~~7~~). ~~The most striking difference is related to the night and early morning peak, while during mid-day the difference is minimum.~~ The most striking difference is related to the ~~extensive~~ night peak, while during mid-day the difference is minimal. For all compounds examined in this work, t~~T~~he night peak ~~of the compounds~~ in December (SP period) is 2 to 6 times higher ~~than~~compared to October's (SP period) with the highest ~~values corresponding~~differences found for~~to~~ 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. ~~For the nSP cases (Fig. 7 and S7) the concentrations of all compounds were very low (lower than the minimum of the SP periods)~~

~~and almost equal, with the exception of ethane and acetylene that demonstrated higher concentrations in December by a factor of two (Fig. S7a,e). NMHCs levels dOn the other hand~~ 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: ~~As discussed in Sect. 3.2, the morning peak (07:00 – 10:00 LT) of NMHCs could be attributed mainly to traffic. Figure 8 presents the profile of this peak (% mass contribution of the measured NMHCs), during January and February when toluene data were available and compares it with the profile obtained into a tunnel in GAA. The profile of the morning peak was obtained for each NMHC by subtracting the baseline level from the maximum (more details on the calculations are provided in Sect. S2). Measurements into the tunnel allowed for the extraction of the profile of traffic related NMHCs, to be used as reference for identifying the signal of traffic in ambient conditions, assuming that tunnels receive or exchange no significant air mass portions with the outside environment. A very good agreement is observed between the two profiles regarding the dominant species, highlighting the importance of traffic in the morning values of NMHCs. It is interesting to note that the profiles, especially those derived from the morning peak, nicely fit with that reported for traffic by Baudic et al. (2016) in Paris (when only the common NMHCs measured in this work have been used). Higher values of butanes are however be noted in the morning peak than in the tunnel experiments, it may reflect a higher proportion of the evaporative contribution from the traffic source in ambient air compared to air measured in a tunnel.~~

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

The two morning profiles, although performed at sites with different impact of traffic, agrees quite well ($R^2 > 0.97$). Iso - pentane and toluene are the two main compounds contributing to the morning profiles accounting by about 44% of the total measured NMHCs at both locations, followed by n- and i-butane and ethylene accounting for almost 30%. Differences ~~among~~between the two morning profiles ~~between~~regarding these 5 main species are ~~minimum~~weak (less than a factor of

1.5). Note also that the morning profile at Thissio is the mean of a whole month period compared to the two days ~~a~~campaign ~~of two days in~~at Patission which could explain the small differences between the two profiles. Regarding the tunnel experiments, d~~D~~espite the different conditions associated with their ~~tunnel~~ profiles (Paris versus Athens, tunnel length, season etc~~…~~), they present a ~~The profiles obtained at the two tunnels although differ in terms of tunnel length, city, and period, have~~ a lot of common features ($R^2 > 0.91$)~~.~~. Again i-pentane and toluene are the two main compounds of the profiles accounting ~~by~~for about 56% of the total measured NMHCs~~ at both sites~~, followed by n -butane, ethylene and benzene accounting for almost 20% ~~in total again~~at both sites. The most striking difference between the two sites concerns n-pentane (almost a factor of two higher in Paris compared to Athens). ~~Despite the differences between the two tunnel studies the similarity is almost 80% ($R^2 > 0.91$).~~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 Patission morning profiles and their difference from the Athens and Paris tunnel ~~profiles,~~profiles probably indicates the importance of the type of fuel used. The latter is also ~~concluded~~observed in recent works (Ait-Helal et al., 2015; Zhang Q. et al., 2018; Zhang Y. et al., 2018), where important differences have been reported~~are reported~~ between tunnel measurements~~ worldwide~~, and attributed to ~~the variance of the~~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 ~~quite~~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.~~figures~~ S10 and S11 where the ratios of butanes and pentanes-to-total Alkanes ~~(~~C2 – C5 (%) 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. In addition, the above results could indicate why the Athens tunnel results performed in May differ from Patission and Thissio winter morning profiles. Moreover, the ~~,~~higher~~er~~ values of ethane, propane and butanes that are depicted in the morning peaks ~~of~~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. S12). The two compounds have linear relationship with no significant temporal differences on the slopes between the various months. Furthermore~~In addition~~, the regression is similar to the one derived from the Patission measurements, thus enhancing our assumption that butanes emissions are traffic related. Moreover~~addition~~, the ~~connection~~relation between the~~ of~~ high levels of C2 – C4 alkanes and the number of LPG-powered cars wa~~i~~s 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~~8~~), 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~~9~~). 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. ~~The exception is ethylene (the most reactive compound measured after isoprene) which shows higher slope in December and could be attributed to enhanced photochemical decay in October compared to December.~~

Nighttime peak: During nighttime both BC_{ff} and BC_{wb} were maximized (e.g. Fig. 4~~3~~ and 8~~7~~), denoting significant contribution from both fossil fuel and wood burning (the contribution of the latter was more evident during winter). Figure 11~~0~~ presents the NMHC profile of the 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~~0~~), the 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~~2~~ 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~~7~~ indicating ~~possible~~ impact of wood burning during nighttime in winter months.

Figure 12~~1~~a (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. 12~~1~~b, 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% (± 10%) and 55% (± 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, continuous measurements of 11 Non Methane Hydrocarbons with two to six carbon atoms (C2 – C6~~-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)~~ (period)~~ periods, based on the absence of rainfall and low wind speed. October and December were chosen for further comparison due to different temperature ~~meteorological~~ profiles 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 ~~for~~during~~the~~ SP days with those ~~have been~~ obtained ~~by~~ at a street canyon of Athens (Patission) 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 ~~indicating~~ 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 (future long-term measurements) is needed in order to distinguish the contribution of different sources types and to further quantify their impact on the NMHCs levels.~~ An extended dataset of NMHCs and other organic tracers (future long-term measurements) is needed ~~in order~~ to ~~distinguish the contribution of~~apportion different sources types on seasonal basis and ~~to further~~ quantify their impact on the NMHCs levels.

5 Data availability

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

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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[a] 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			
NMHCs	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[b]	16 October 2015 - 15 February 2016, Athens, Greece			
	Patision (Urban)	Demokrirtos (Suburban)	Tatoi (Suburban)	Ancient Agora (urban)	Demokrirtos (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 (with 1-butene)	1.6	0.19 (with 1-butene)	2.1			1.5	3.6	1.8 - 2.6	2.6	1.3	0.1	15.2
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 (with 2-methyl-1-butene)	1.7	0.27 (with 2-methyl-1-butene)	4.2			0.3	0.5	0.4 - 0.7	1.1	0.6	0.1	9.3
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	1.0	0.1	13.7

a 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.

b Range estimated from Figure 1, included in Durana et al., 2006.

Table 2. 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
Ethane														
Ethylene	0.94													
Propane	0.92	0.94												
Propene	0.94	0.97	0.96											
i-Butane	0.82	0.90	0.95	0.92										
n-Butane	0.84	0.91	0.97	0.92	0.99									
Acetylene	0.89	0.91	0.90	0.91	0.88	0.88								
i-Pentane	0.73	0.85	0.88	0.85	0.96	0.95	0.81							
n-Pentane	0.74	0.85	0.90	0.88	0.97	0.96	0.84	0.96						
Benzene	0.87	0.95	0.93	0.96	0.91	0.92	0.89	0.87	0.89					
BC	0.93	0.95	0.92	0.96	0.88	0.89	0.90	0.84	0.85	0.93				
BCwb	0.91	0.87	0.81	0.89	0.70	0.72	0.77	0.65	0.64	0.83	0.91			
BCff	0.84	0.90	0.89	0.90	0.91	0.91	0.89	0.89	0.90	0.89	0.95	0.75		
CO	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	
NO	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

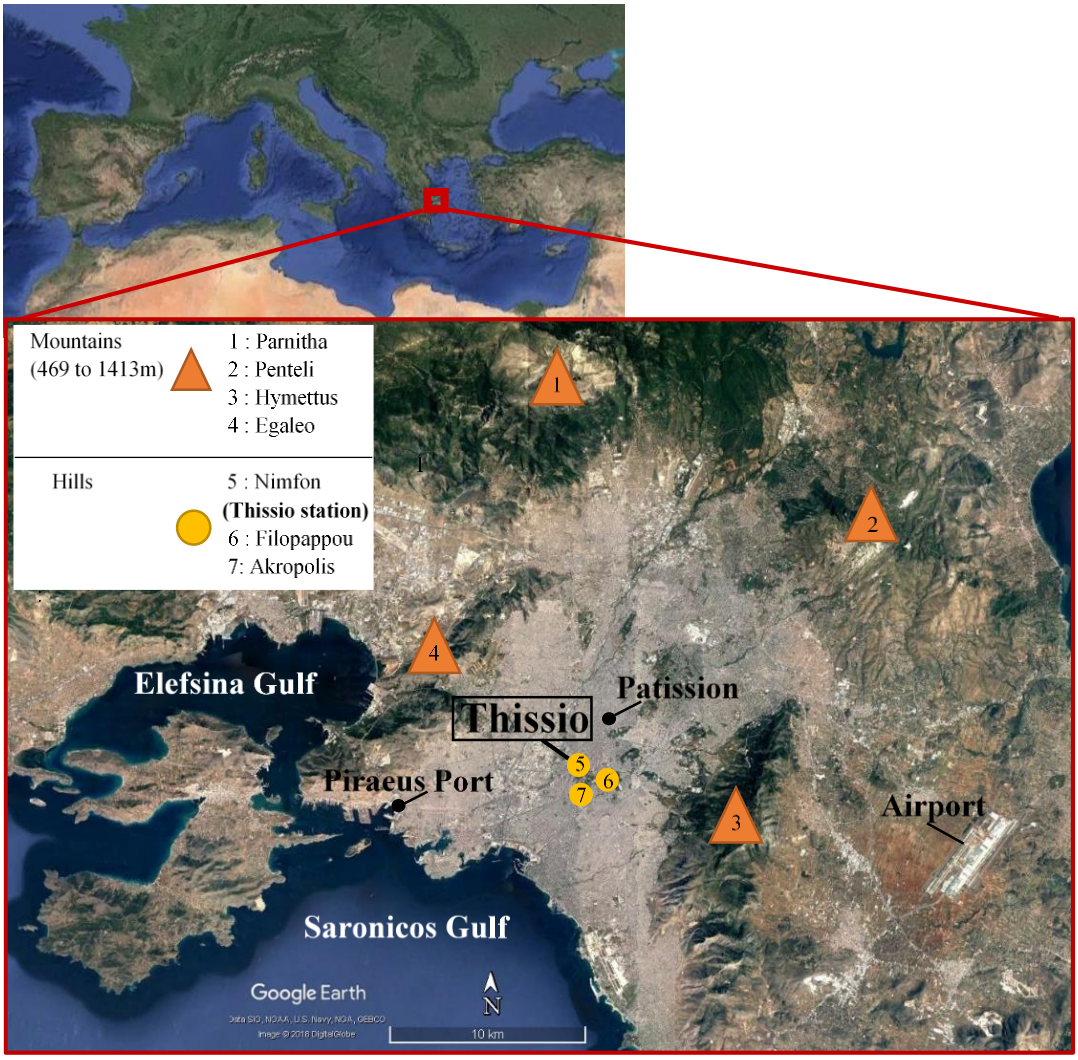

Figure 1. Map of the Greater Athens Area. The four mountains define the borders of the area.

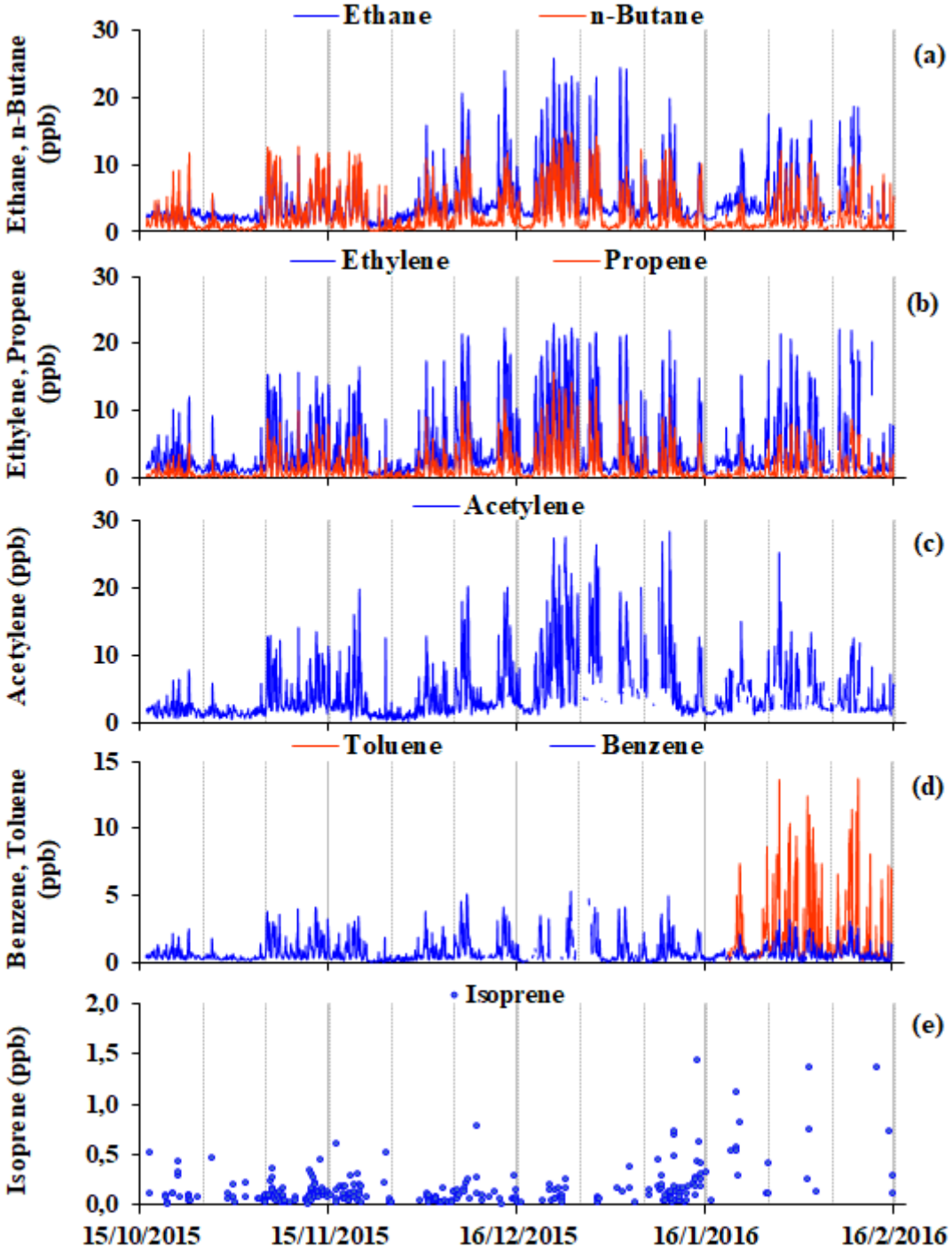

Figure ~~1~~2.~~:~~ Temporal variability of (a) ethane and n-butane, (b) ethylene and propene, (c) acetylene, (d) benzene and toluene and (e) isoprene, based on hourly averaged levels for the period 16 October 2015 - 15 February 2016, at NOA's urban background site in Thissio, downtown Athens.

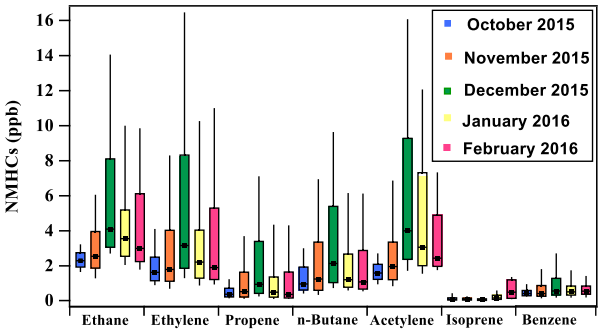

Figure 3~~2~~. ~~Monthly mean concentrations~~Monthly box plots for~~of~~ ethane, ethylene, propene, n-butane, acetylene, isoprene and benzene. The black dot represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1st and 3rd quartiles (i. e. Q1 and Q3). The ~~end of the~~ whiskers correspond to the 1st and the 9th deciles (i. e. D1 and D9). ~~Monthly mean concentrations of ethane, ethylene, propene, n-butane, acetylene, isoprene and benzene. The bars stand for standard deviations.~~

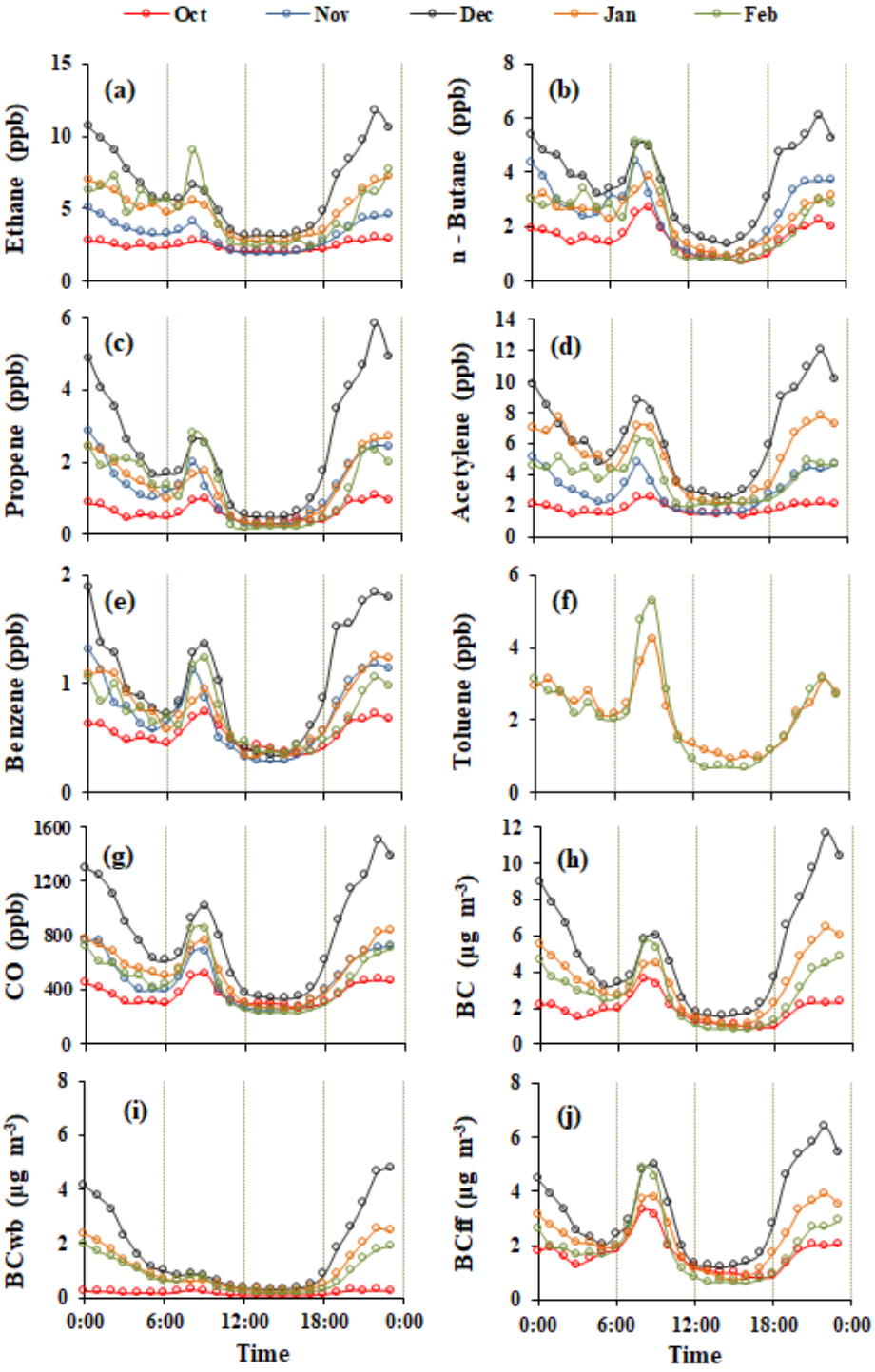

Figure 4~~3~~. Monthly diurnal variability of (a) ethane, (b) n-butane, (c) propene, (d) acetylene, (e) benzene, (f) toluene, g) CO, h) BC, i) BC_{wb} and j) BC_{ff} based on hourly averaged values.

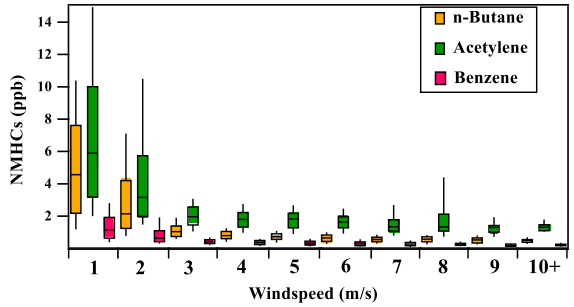

Figure 5~~4~~. ~~Box-whisker~~Boxplots ~~plots of~~for (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the period 16 October 2015 - 15 February 2016. The black line represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1st and 3rd quartiles (i. e. Q1 and Q3). The ~~end of the~~ whiskers correspond to the 1st and the 9th deciles (i. e. D1 and D9). ~~Variability of (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the total period of measurements.~~

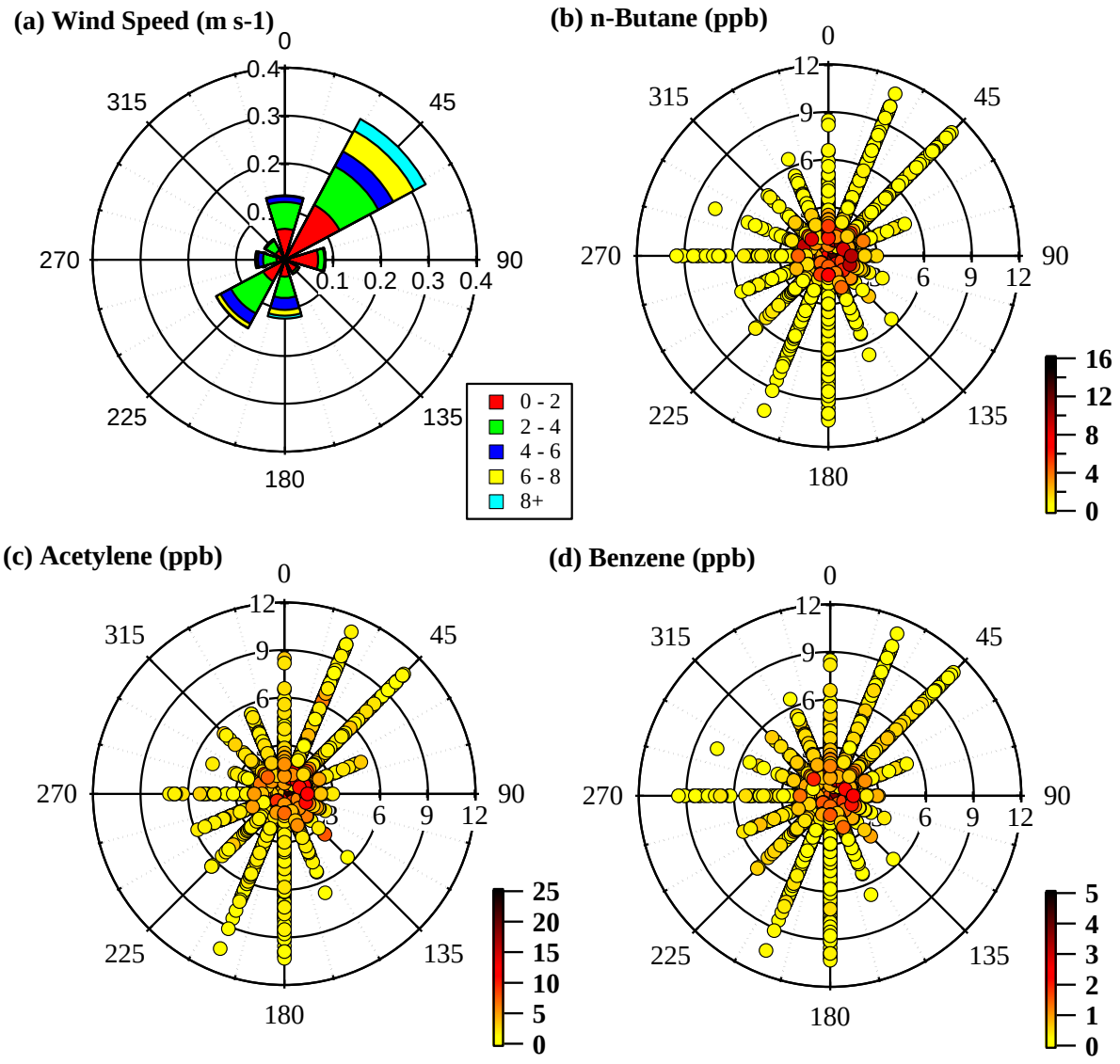

Figure 6~~5~~. Wind rose (a) and concentration roses of ~~Probability of ,~~ (b) n-butane, (c) acetylene, and (d) benzene for the period 16 October 2015 to 15 February 2016. ~~The angle corresponds to wind directions, the radius to wind speed and the color-scale to the concentration levels.~~

~~**Variability of (a) wind sector frequency of occurrence and (b) wind speed of air masses reaching the Thissio site; and (c) n-butane, (d) acetylene and (e) benzene concentrations, relatively to wind direction for the total period of measurements.**~~

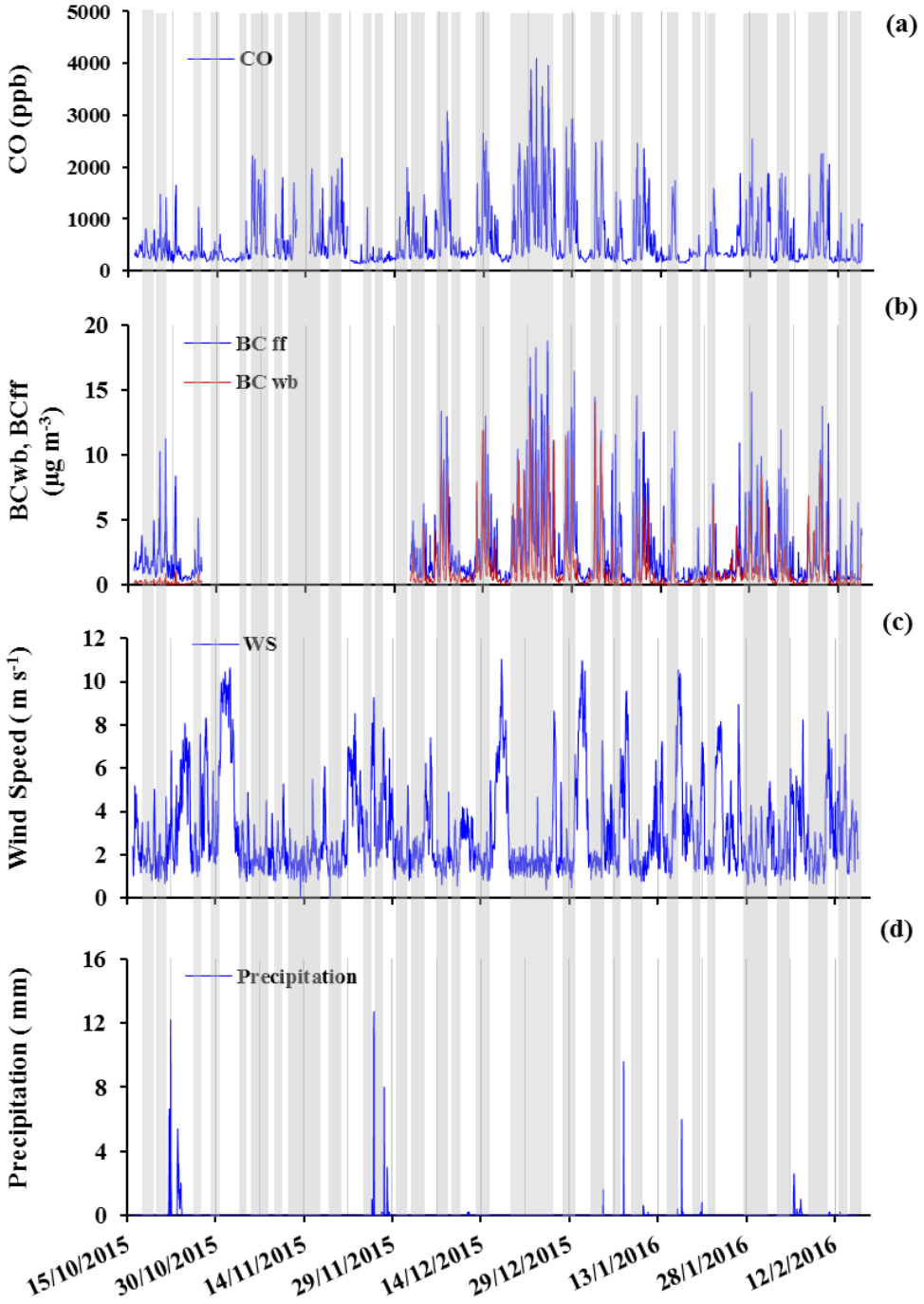

Figure 7~~6~~. Temporal variability of (a) CO~~=~~, (b) BC_{wb} and BC_{ff} fractions, (c) wind speed and (d) precipitation for the experimental period. Grey frames correspond to smog periods (SP), while the remaining part to non-smog periods (nSP).

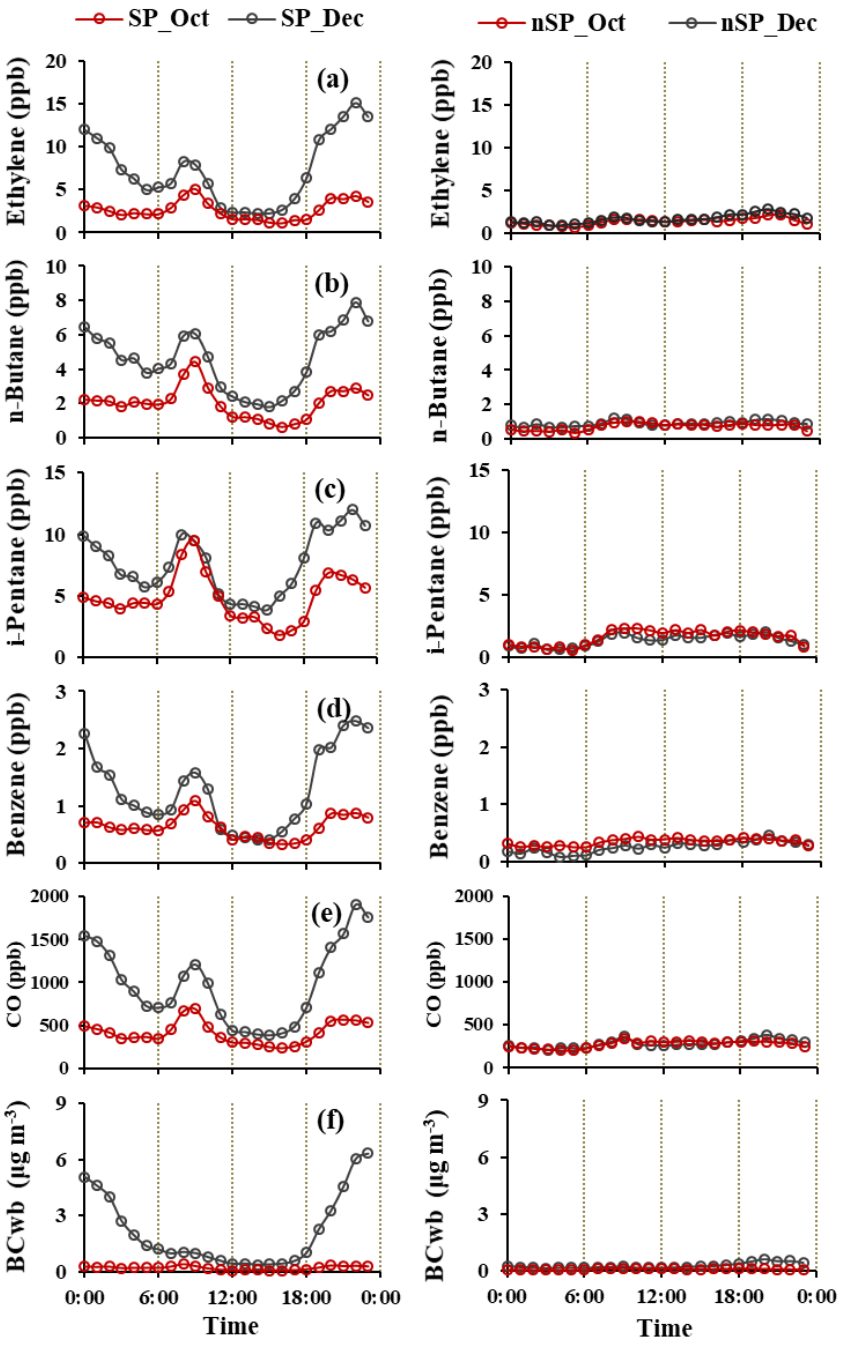

Figure 8~~7~~. Diurnal patterns of (a) ethylene, (b) n-butane, (c) i-pentane, (d) benzene, (e) CO, (f) BC_{wb} during the SP (left column) and the nSP (right column) periods identified during October 2015 (red) and December 2015 (black) respectively. Note: SP periods are defined by wind-speed lower than 3 m ~~.~~s~~ec~~$^{-1}$ and absence of rainfall, while nSP periods are defined by winds-speeds higher than 3 m ~~.~~s~~ec~~$^{-1}$.

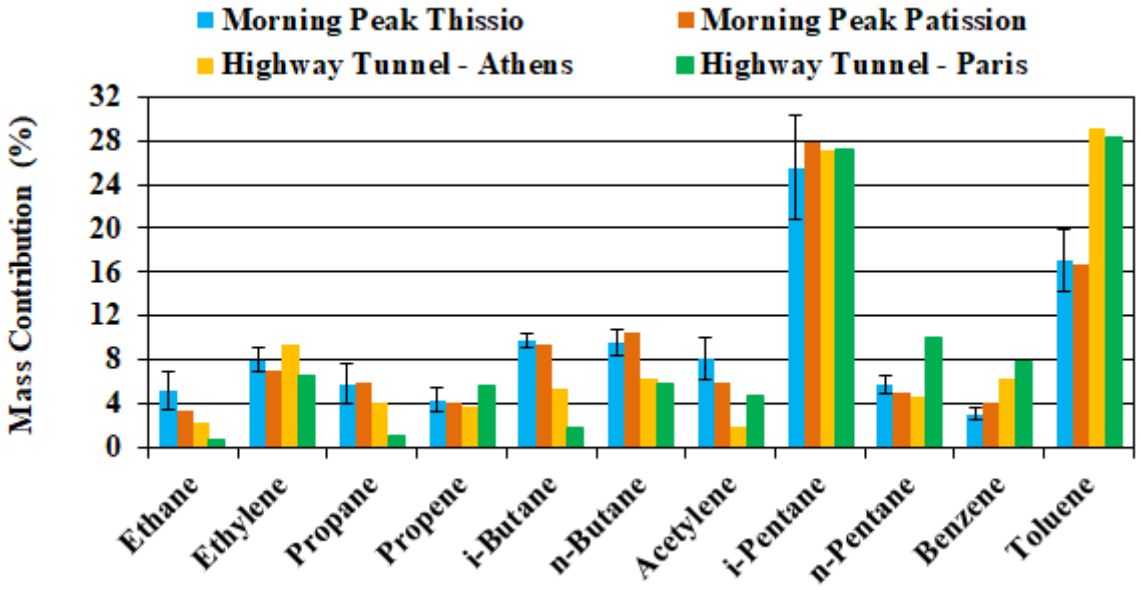

Figure 9~~8~~. % ~~Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00LT, median values, blue color), in a highway tunnel in GAA (orange color) and a highway tunnel close to Paris (yellow color).~~

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.

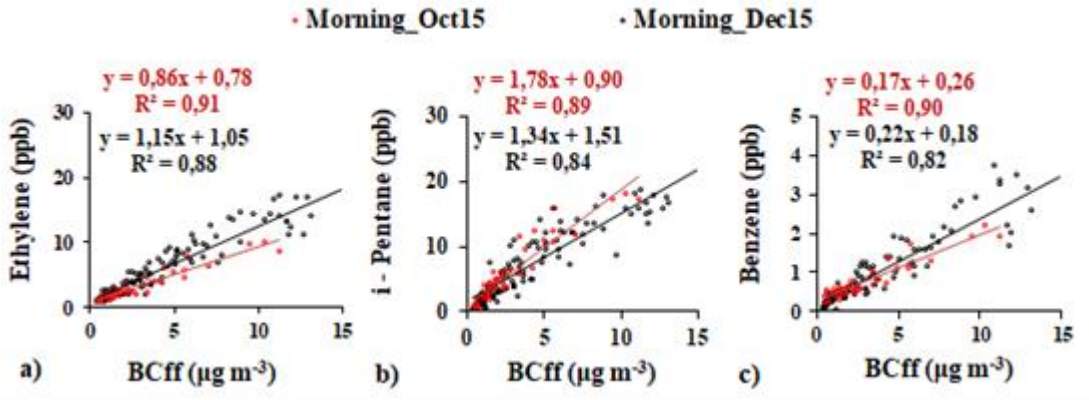

Figure 10~~9~~. Regressions between ethylene, i-pentane, and benzene versus BC_{ff} (a-c) for the morning period (07:00 – 10:00LT) in October and December 2015.

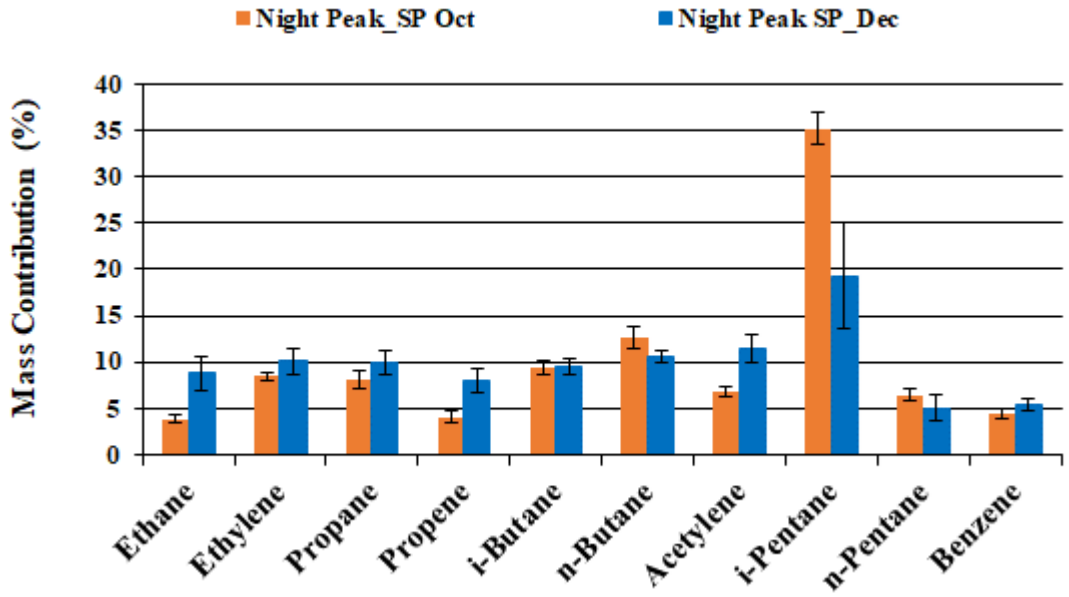

Figure 11~~0~~. % Mass contribution of the measured NMHCs during the night peak (18:00 – 05:00LT) for the SP of October (orange~~yellow~~) and the SP of December (black color).

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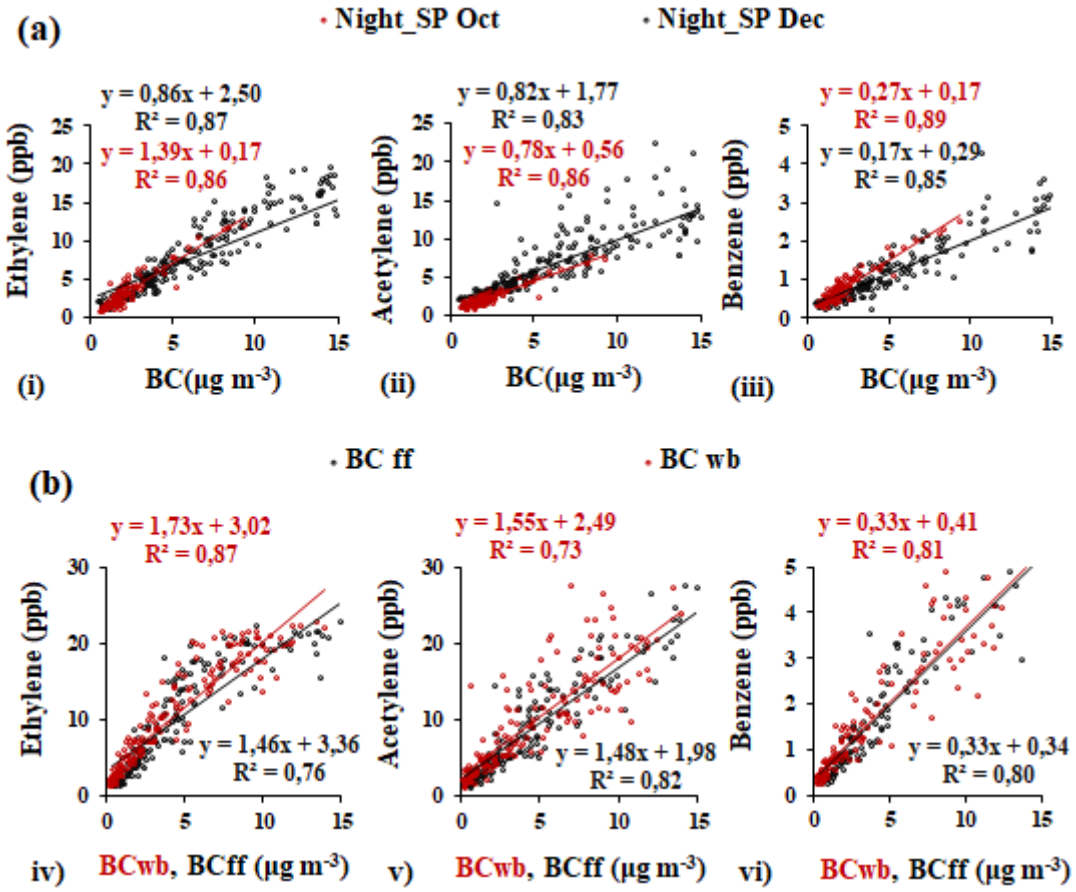

Figure 12~~1~~. Regressions between ethylene, acetylene and benzene (a) against BC (i-iii) for the night period (18:00 – 05:00LT) of SP October and December 2015 and (b) against BC_{wb} (red) and BC_{ff} (black) for the night period (22:00 – 04:00LT) of SP December 2015.