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 at the end of the replies section.
- 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.”.

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).

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."

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: "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).".

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."

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: "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)."

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).".

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: "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.

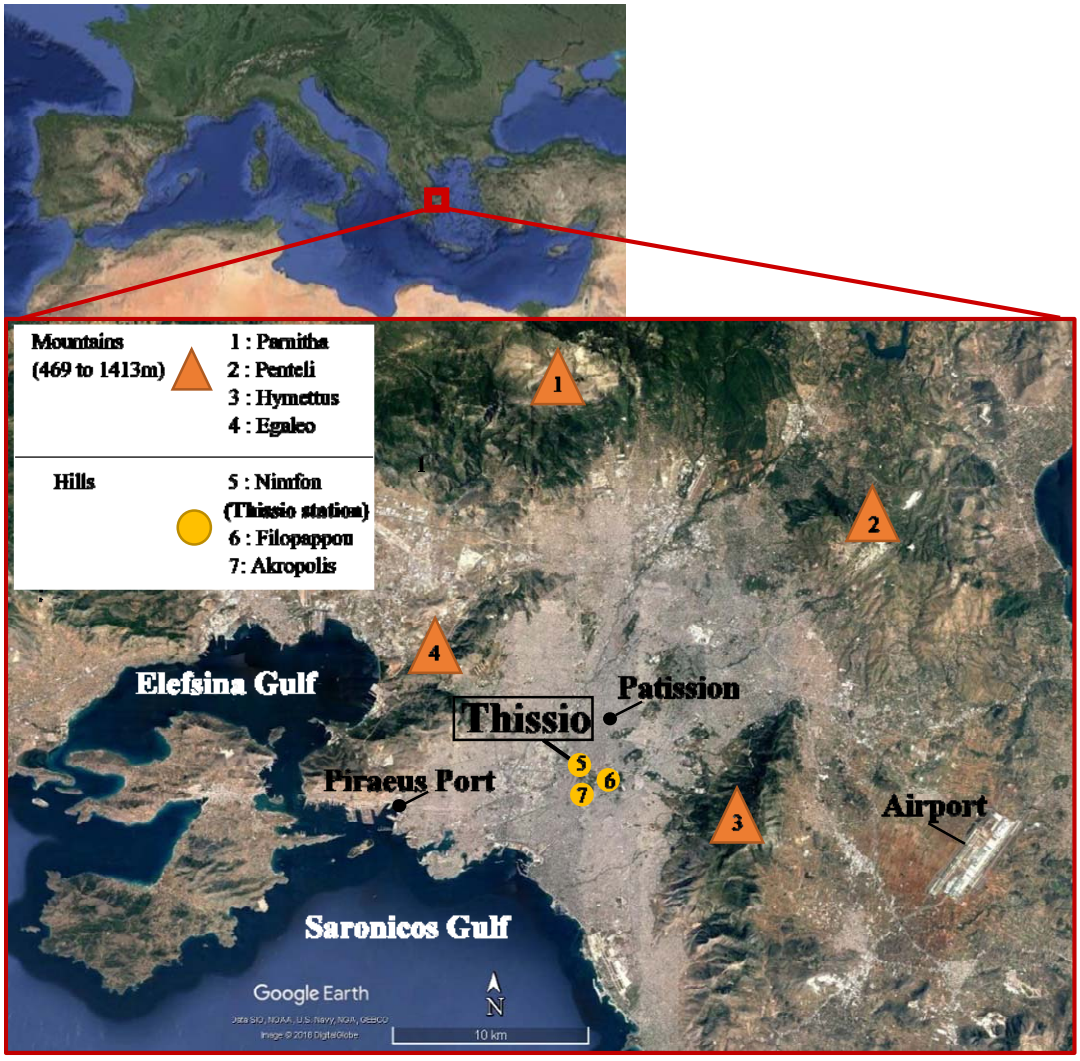
P 3, L3: Mention those selected tracers explicitly and mention what kind of sources those tracers are tracing.

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 XX: 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 "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 50m above

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.

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.

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: "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: "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.

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."

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). 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).

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."

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%)".

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: "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."

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: "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.

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.

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.

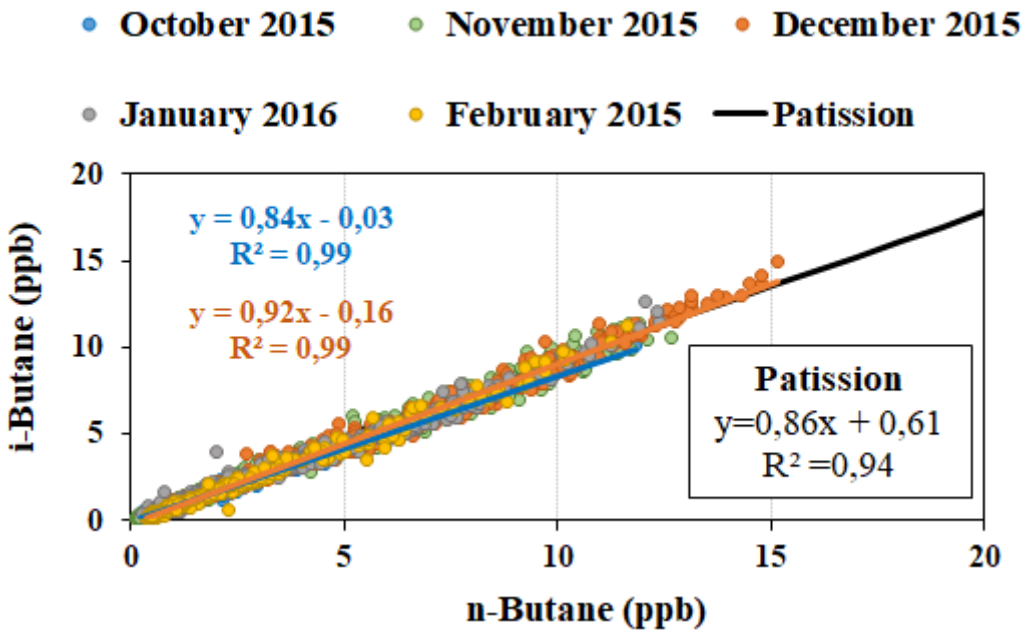


Figure S10. Scatter plots between i-butane relatively to n-butane for October 2015, November 2015, December 2015, January 2016 and February 2016 for the Thissio site. The black line corresponds to the Patission data regression.

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°C to 25°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."

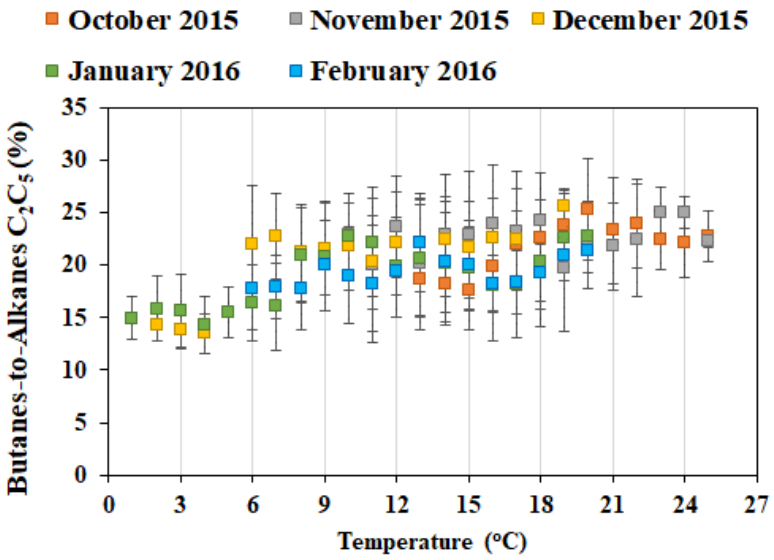


Figure S11. Scatter plots of the ratio Butanes-to-Alkanes C2C5 (%) to temperature for October 2015, November 2015, December 2015, January 2016 and February 2016.

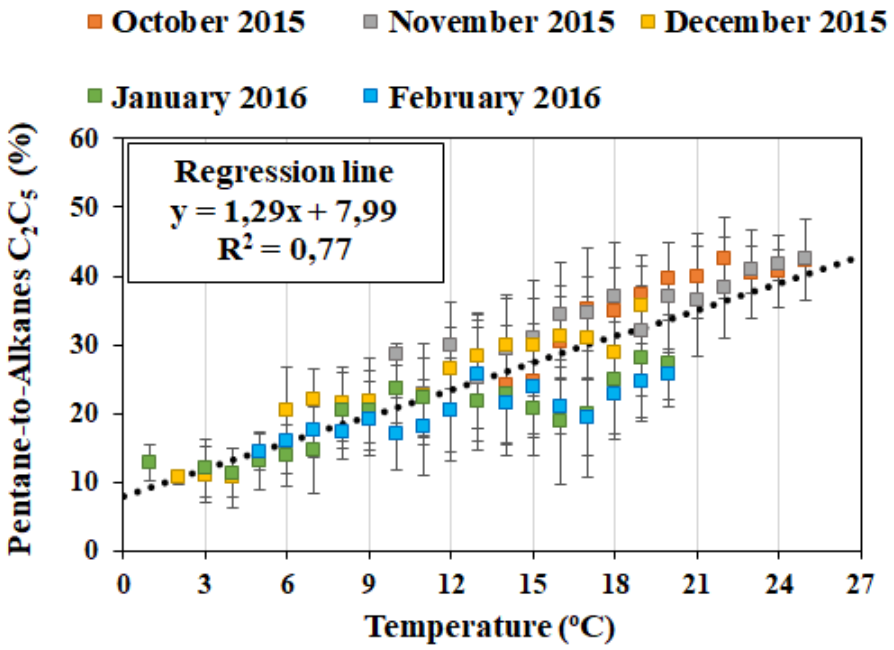


Figure S12. **Scatter plots of the ratio Pentanes-to-Alkanes C2C5 (%) to temperature for October 2015, November 2015, December 2015, January 2016 and February 2016.**

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).

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.'

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".

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: "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: "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 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.

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."

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

Reply: Based on the comment, the phrase was clarified as follows: "…..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: "….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)."

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, 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) 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: "……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: "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.

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.

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.

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**.**

Figure 8: Error bars should be included.

Reply: Error bars can be added only for the Thissio data.

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: 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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Table 1. Comparison of NMHC mean levels between this study and already published work 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

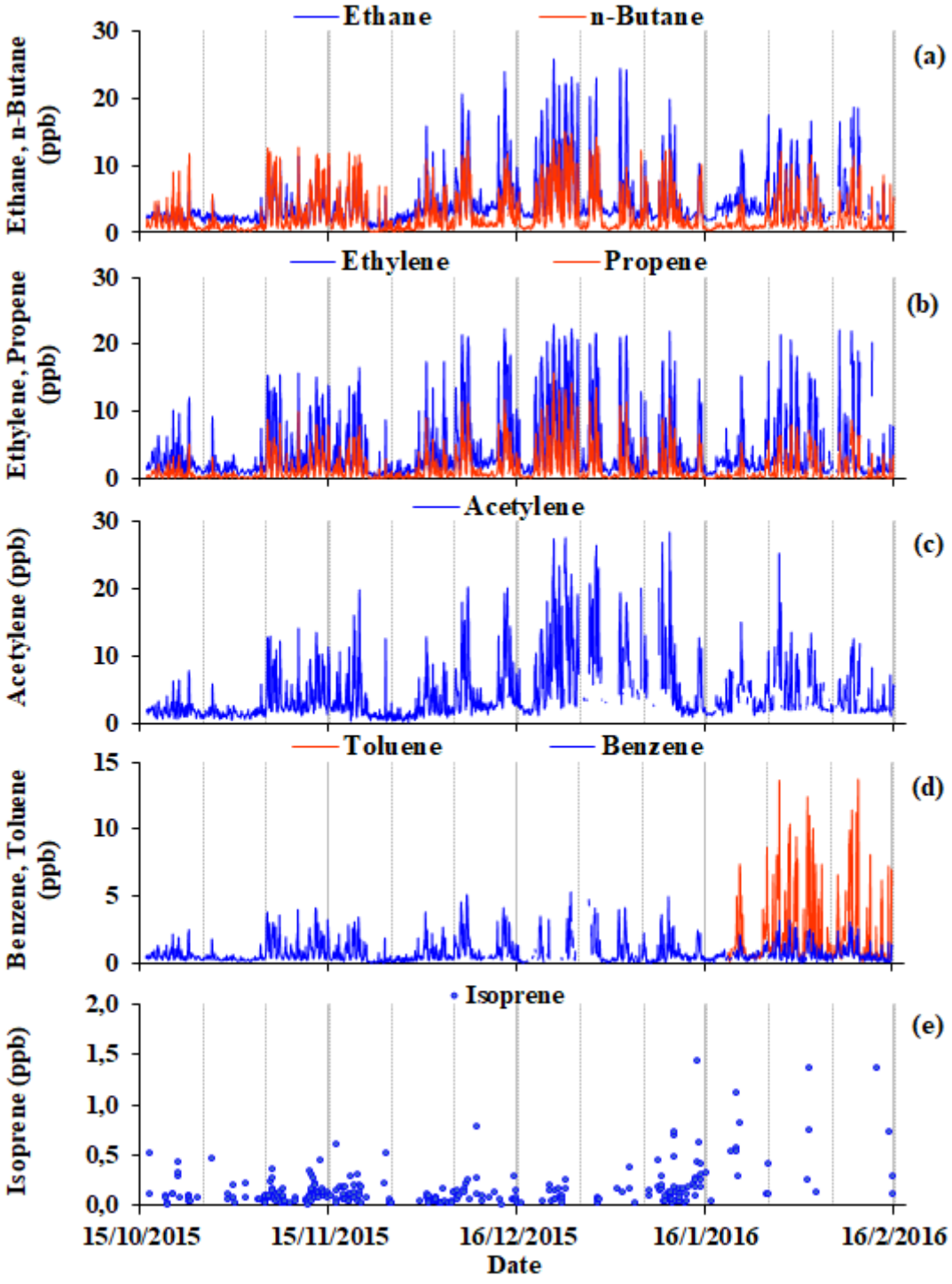

Figure 1: Temporal variability of (a) ethane and n-butane, (b) ethylene and propene, (c) acetylene, (d) benzene and toluene and (e) isoprene, based on hourly averaged levels for the period 16 October 2015 - 15 February 2016, at NOA's urban background site in Thissio, downtown Athens.

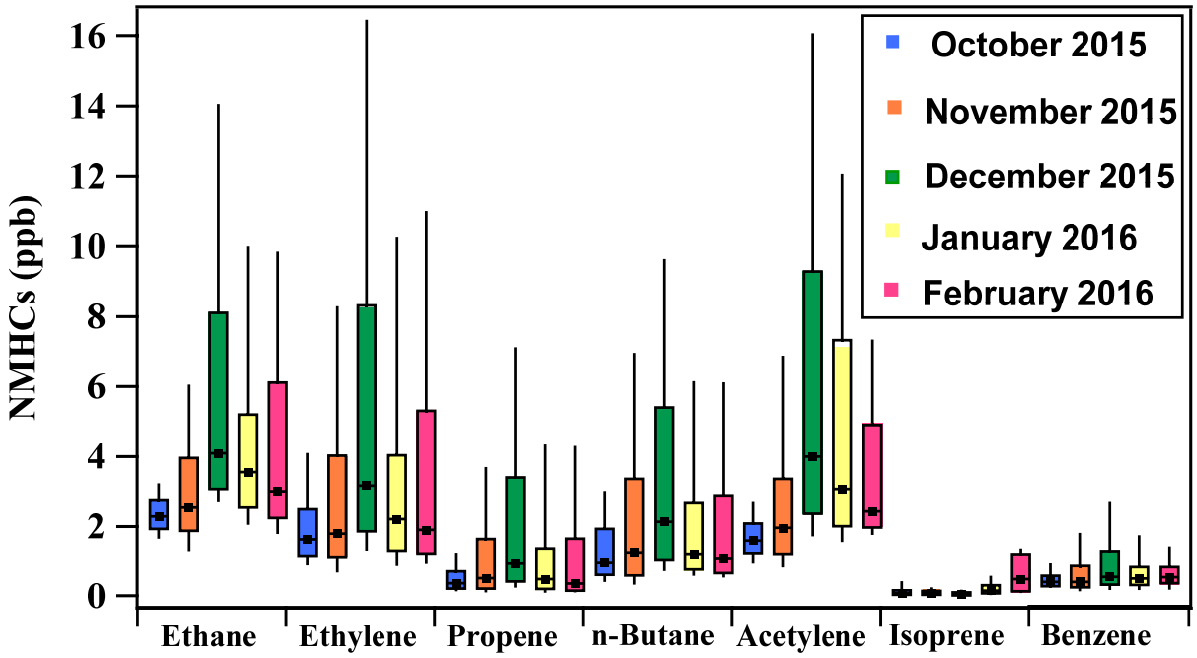

Figure 2. Monthly mean concentrations of ethane, ethylene, propene, n-butane, acetylene, isoprene and benzene. The black dot represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1st and 3rd quartiles (i. e. Q1 and Q3). The end of the whiskers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

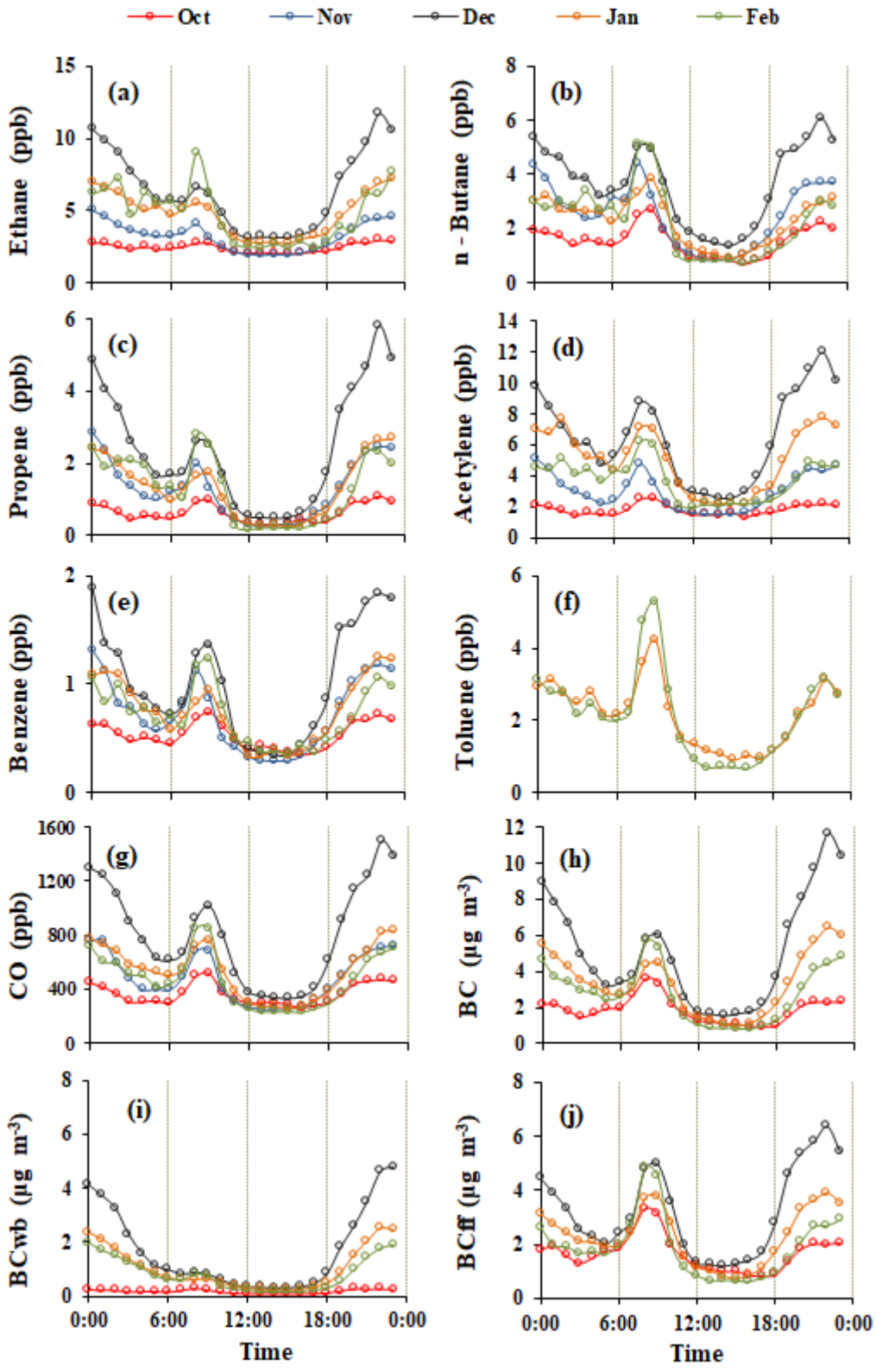

Figure 3. Monthly diurnal variability of (a) ethane, (b) n-butane, (c) propene, (d) acetylene, (e) benzene, (f) toluene, g) CO, h) BC, i) BC_{wb} and j) BC_{ff} based on hourly averaged values.

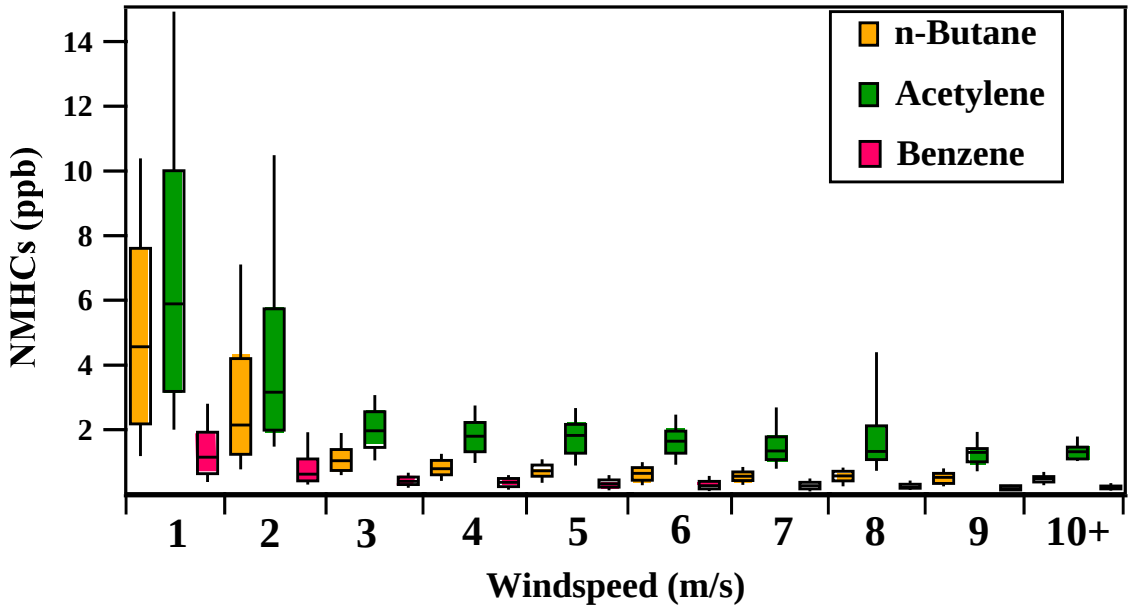

Figure 4. Box-whisker plots of (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the period 16 October 2015 - 15 February 2016. The black line represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1st and 3rd quartiles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

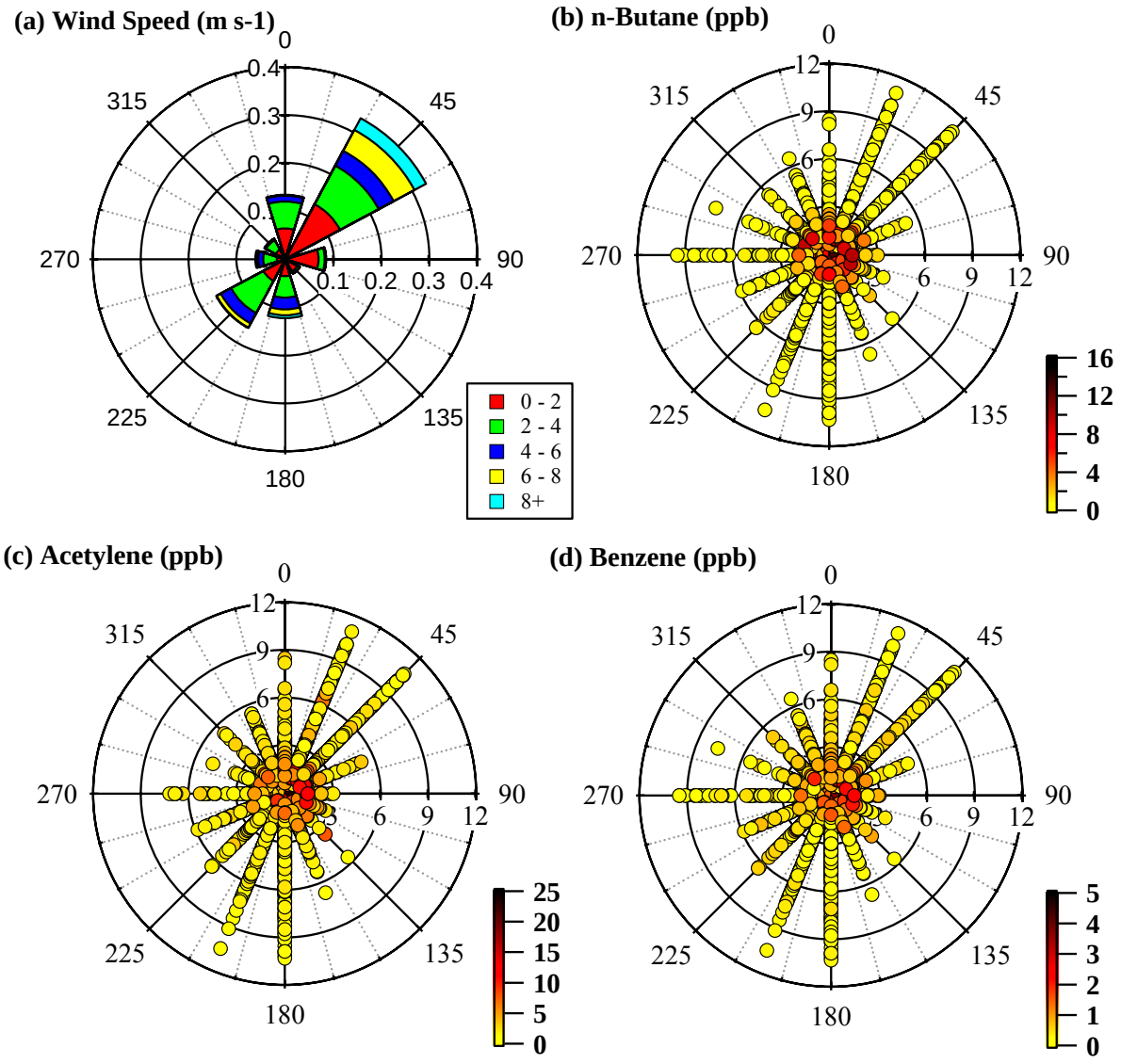

Figure 5. Wind roses of (a) Probability of wind speed, (b) n-butane, (c) acetylene, and (d) benzene for the period 16 October 2015 to 15 February 2016. The angle corresponds to wind directions, the radius to wind speed and the color-scale to the concentration levels.

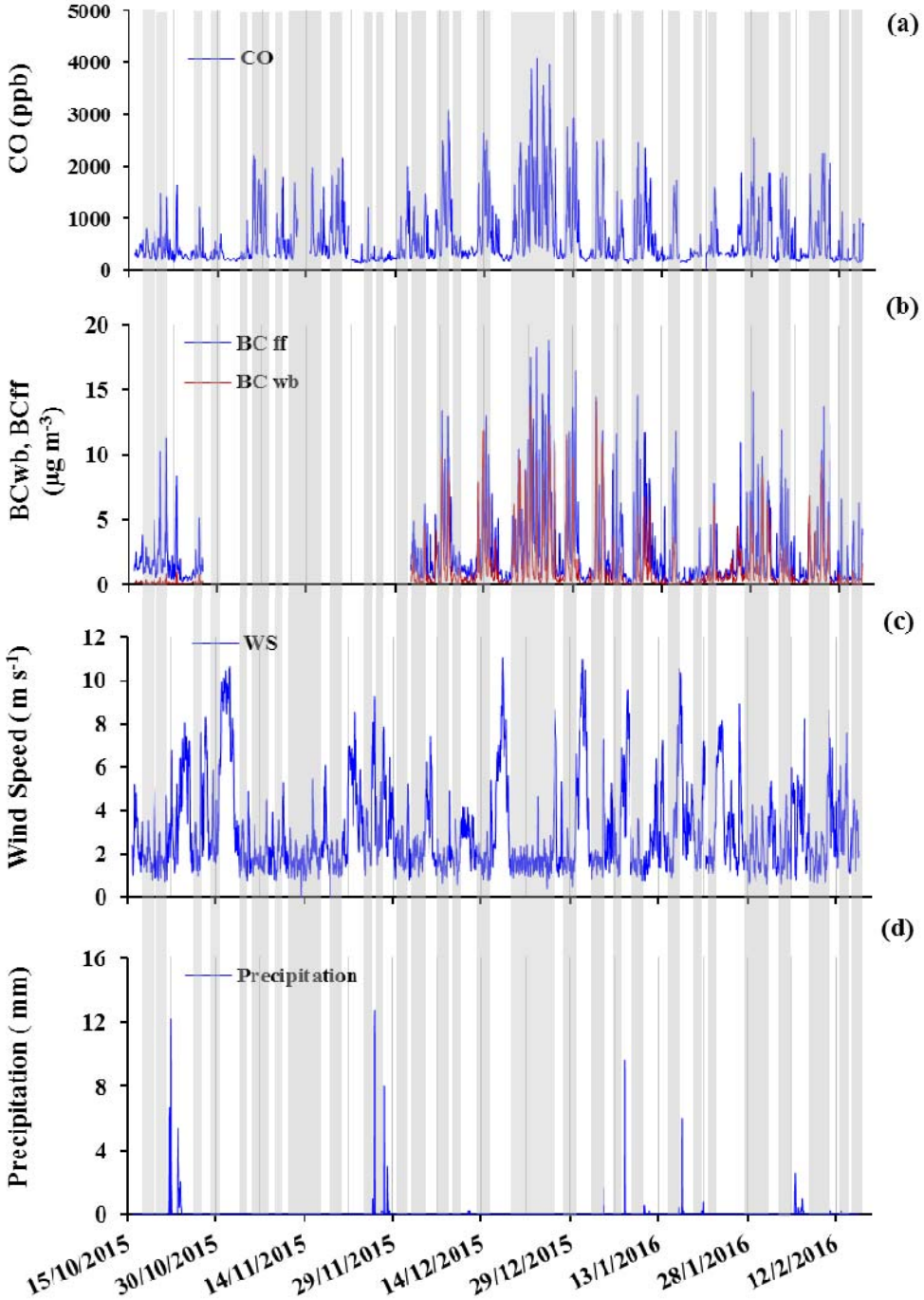

Figure 6. Temporal variability of (a) CO , (b) BC_{wb} and BC_{ff} fractions, (c) wind speed and (d) precipitation for the experimental period. Grey frames correspond to smog periods (SP), while the remaining part to non-smog periods (nSP).

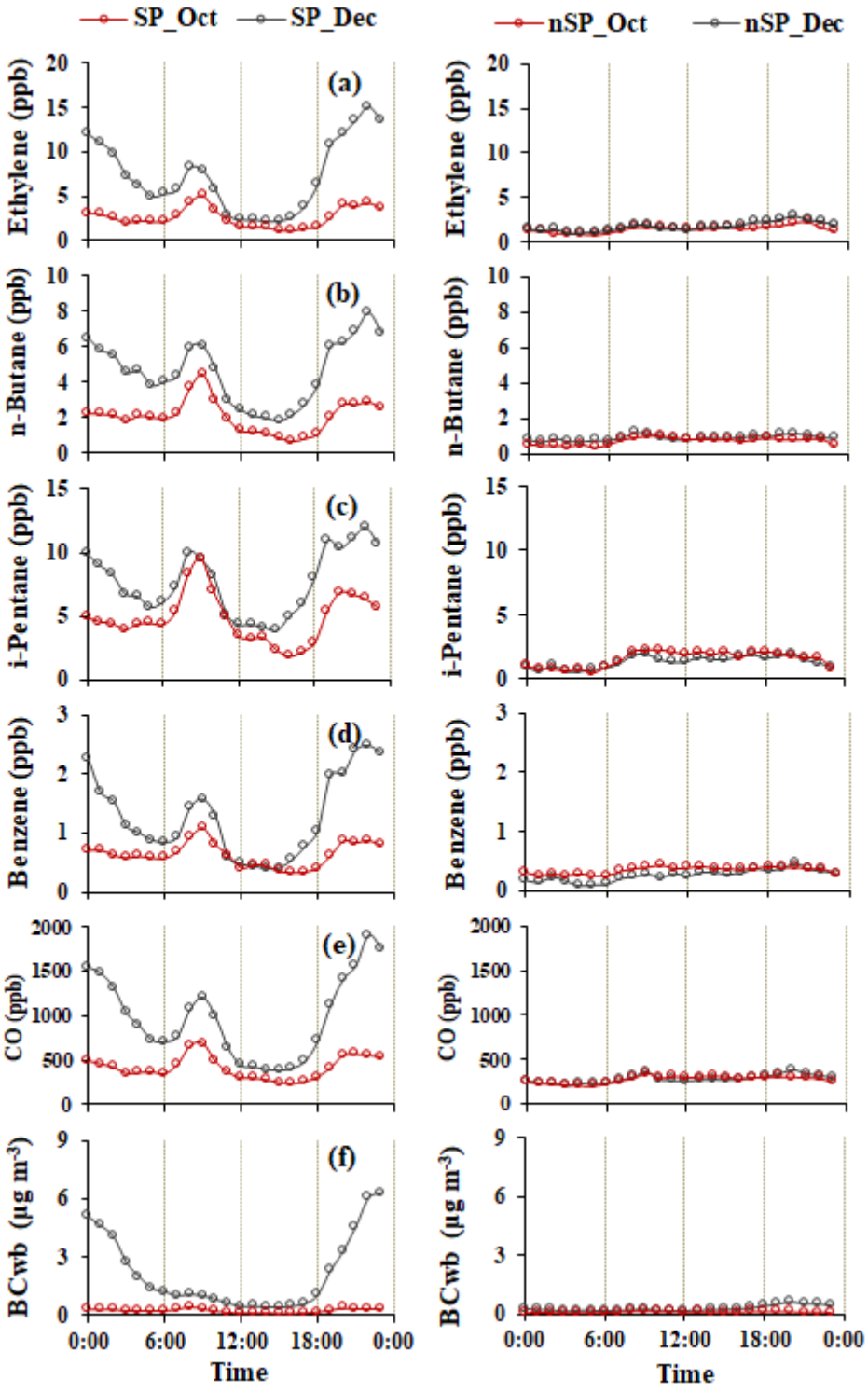

Figure 7. Diurnal patterns of (a) ethylene, (b) n-butane, (c) i-pentane, (d) benzene, (e) CO, (f) BC_{wb} during the SP (left column) and the nSP (right column) periods identified during October 2015 (red) and December 2015 (black) respectively. Note: SP periods are defined by wind-speed lower than 3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

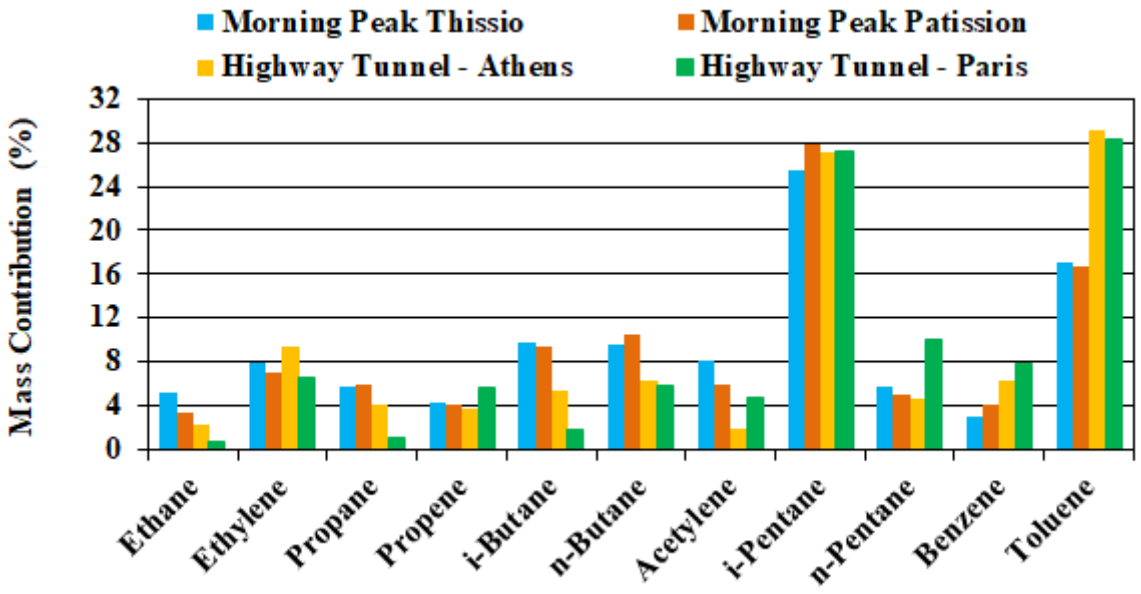

Figure 8. % Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00LT, median values in Thissio, in Patission Monitoring Station, in a highway tunnel in GAA and a highway tunnel close to Paris.

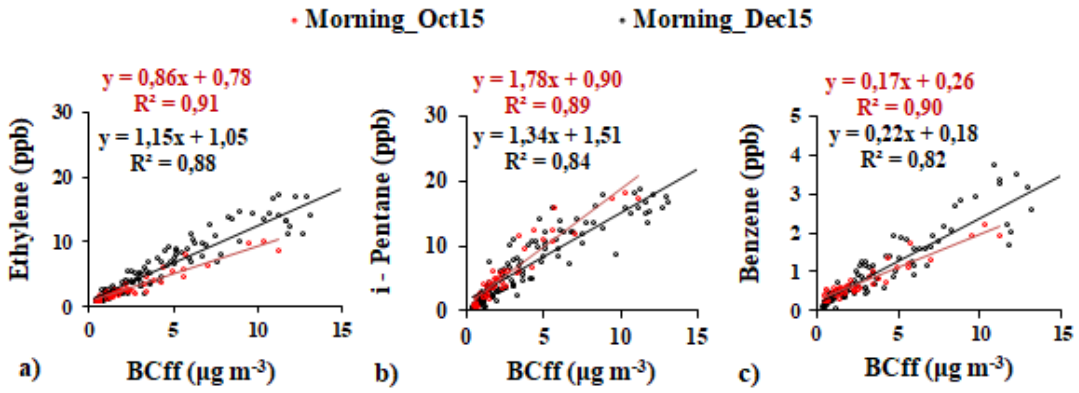

Figure 9. Regressions between ethylene, i-pentane, and benzene versus BC_{ff} (a-c) for the morning period (07:00 – 10:00LT) in October and December 2015.

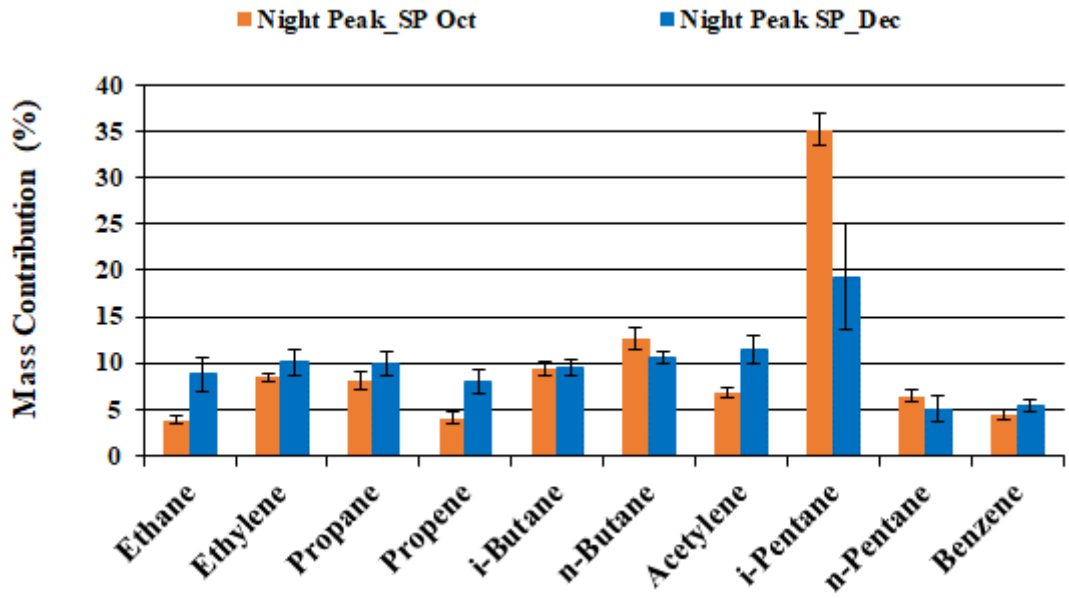

Figure 10. % Mass contribution of the measured NMHCs during the night peak (18:00 – 05:00LT) for the SP of October (orange) and the SP of December (black color).

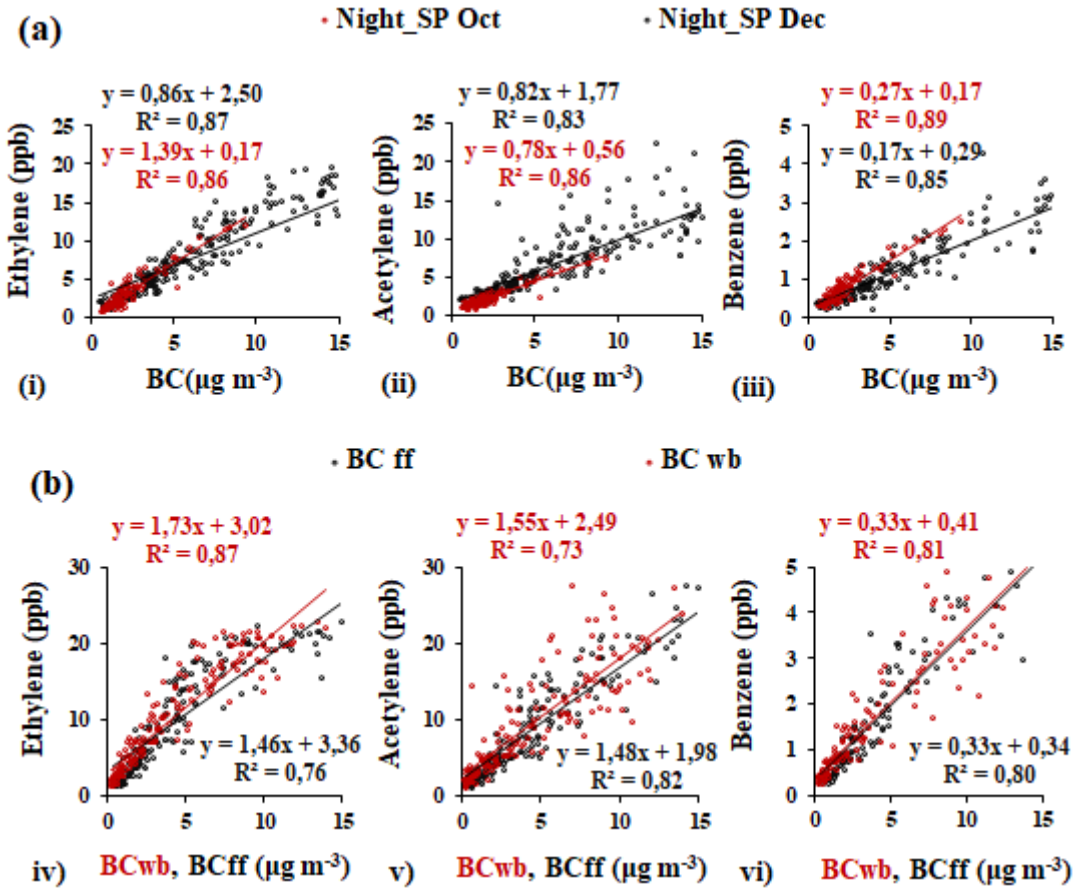

Figure 11. Regressions between ethylene, acetylene and benzene (a) against BC (i-iii) for the night period (18:00 – 05:00LT) of SP October and December 2015 and (b) against BC_{wb} (red) and BC_{ff} (black) for the night period (22:00 – 04:00LT) of SP December 2015.