

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 #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 SO<sub>4</sub> 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<sub>3</sub>, 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.”.

*p. 3, l. 24: “The trap was then heated rapidly to 22 °C...”*

*Is this a typo? Compounds won't desorb well (if at all) at these temperatures. Should this read 220°C?*

**Reply:** We agree with the remark; indeed, it is a typo. The text was corrected accordingly in the same page and line.

*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. “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.”

*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 at p.5, l. 5: "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."

*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  $\mu\text{g m}^{-3}$  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 C<sub>4</sub> (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. "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<sub>4</sub> (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<sub>2</sub> already reported by Kalabokas et al. (1999) and Gratsea et al. (2017), due to the air quality measures taken by the Greek government. 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.’”

*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 “.....the duration of the night peak is at least a factor of 2 larger, which could imply the impact of heating in 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.

*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). ”

*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*

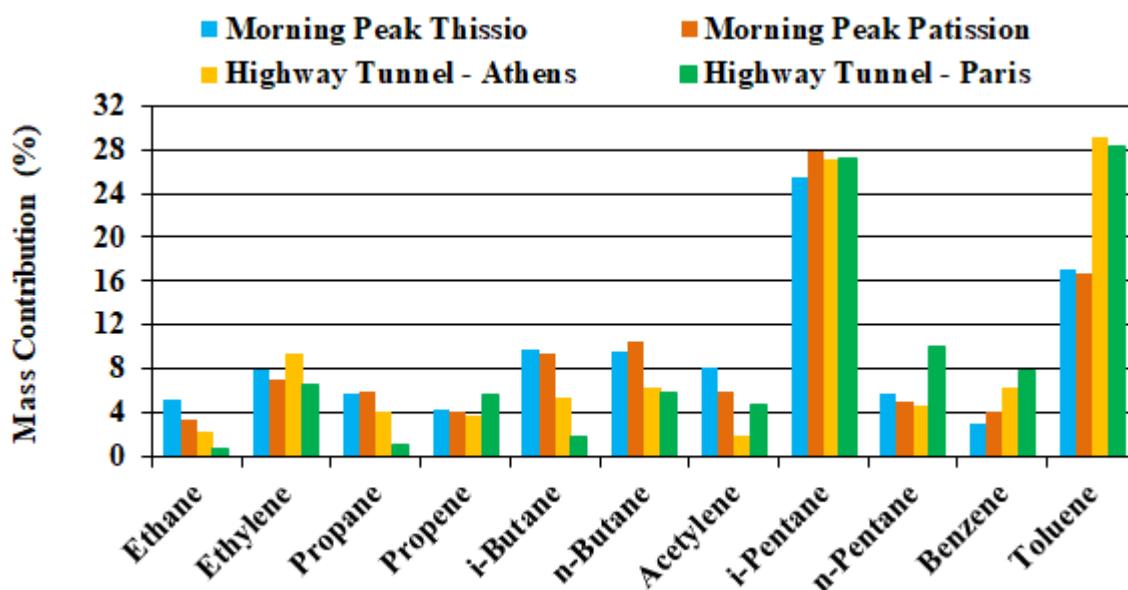
**Reply:** Following the reviewer's comment, the text was clarified as follows: “NMHCs levels during the nSP periods in October and December were equal (Fig. 8 and S8). Furthermore, the concentrations of all compounds during nSP were very low; even lower than the minimum values observed during mid-day during SP periods of the same months.”

*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:





**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.

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 Patisson 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 Patisson 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<sub>2</sub>-C<sub>4</sub> 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 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, 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.

## **References**

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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<sup>a</sup> for each compound determined on the current samples is included below the table.**

| Studies          | Rappenglück et al., 1998                      | Rappenglück et al. 1999               | Moschonas and Glavas, 1996                         | Kaltsonoudis et al. 2016   |                       | Baudic et al., 2016                         | Salameh et al., 2015                          | Durana et al., 2006   | Current work                                       |                            |     |      |      |
|------------------|---|---------------------------------------|--|--|-----------------------|---|---|---|--|----------------------------|-----|------|------|
| Analysis details | GC – FID<br>Every 20min                       | GC – FID<br>Every 20min               | GC – MS<br>60 min (morning sampling, 12 canisters) | PTR-MS<br>Every 10s/24h  |                       | GC – FID                                    | GC - FID                                      | GC - FID  | GC – FID<br>Every 30min                            |                            |     |      |      |
|                  | 20 August – 20 September 1994, Athens, Greece | 30 May – 16 June 1996, Athens, Greece | June 1993, May and July 1994, Athens, Greece       | 3- 26 July 2012 (Demokritos) & 9 January – 6 February 2013 (Thissio) |                       | 16 October – 22 November 2010 Paris, France | 28 January – 12 February 2012 Beirut, Lebanon | April-October 1998-2001<br>February-July 2004<br>Bilbao Spain** | 16 October 2015 - 15 February 2016, Athens, Greece |                            |     |      |      |
| NMHCs            | Patision (Urban)                              | Demokirtos (Suburban)                 | Tatoi (Suburban)                                   | Ancient Agora (urban)  | Demokirtos (Suburban) | Thissio (Urban background)                  | Les Halles station (Urban background)         | Saint Joseph University (Suburban)                              | Bilbao (Urban center)                              | Thissio (Urban background) |     |      |      |
|                  | ppbv  |                                       | ppbv   | ppbv   | ppb                   |   | ppb   | ppb   | ppbv   | ppb                        |     |      |      |
| Ethane           |   |                                       |  |  |                       |   | 3.8   | 2.8   | 2.5-3.5  | 4.5                        | 3.1 | 0.6  | 25.9 |
| Ethylene         |   |                                       |  |  |                       |   | 1.3   | 2.1   | 2-2.3  | 4.1                        | 2.2 | 0.3  | 22.9 |
| Propane          |   |                                       |  | 1.2  |                       |   | 1.6   | 3.0   | 1.7-2.5  | 3.1                        | 1.8 | 0.2  | 17.8 |
| Propene          |   |                                       |  | 3.9  |                       |   | 0.4   | 0.6   | 0.7-0.9  | 1.5                        | 0.6 | 0.02 | 15.7 |
| i-Butane         |   |                                       |  | 1.1  |                       |   | 0.9   | 1.9   | 0.7-2  | 2.3                        | 1.1 | 0.1  | 14.9 |
| n-Butane         | 12.4  | 1.6                                   | 0.19   |  |                       |   |   |   |  |                            |     |      |      |
|                  | (with 1-butene)                               |                                       | (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 |
|                  | 14.2  | 1.7                                   | 0.27   |  |                       |   |   |   |  |                            |     |      |      |
| n-Pentane        | (with 2-methyl-1-butene)                      |                                       | (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 |

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

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

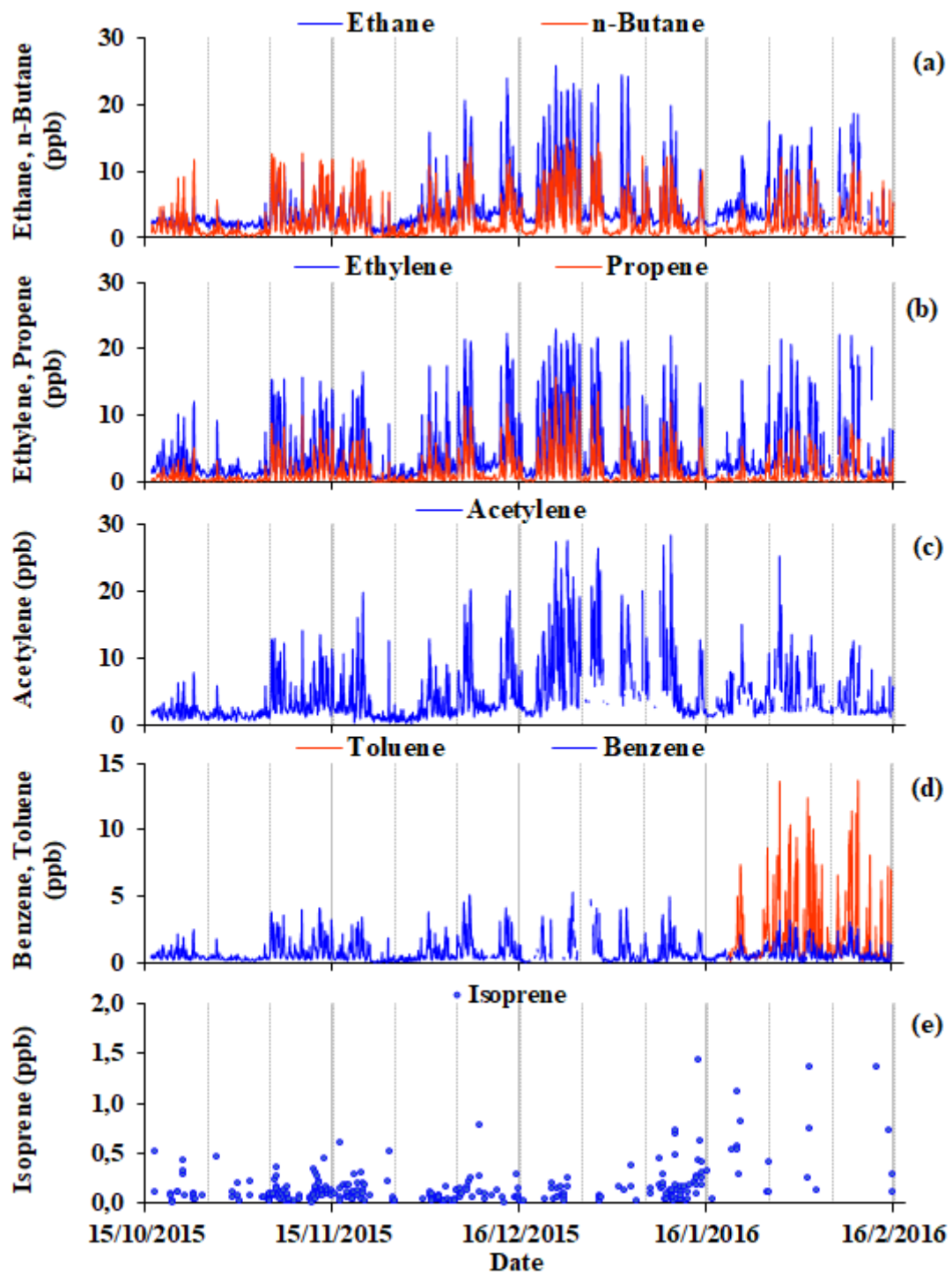


Figure 1: Temporal variability of (a) ethane and n-butane, (b) ethylene and propene, (c) acetylene, (d) benzene and toluene and (e) isoprene, based on hourly averaged levels for the period 16 October 2015 - 15 February 2016, at NOA's urban background site in Thissio, downtown Athens.

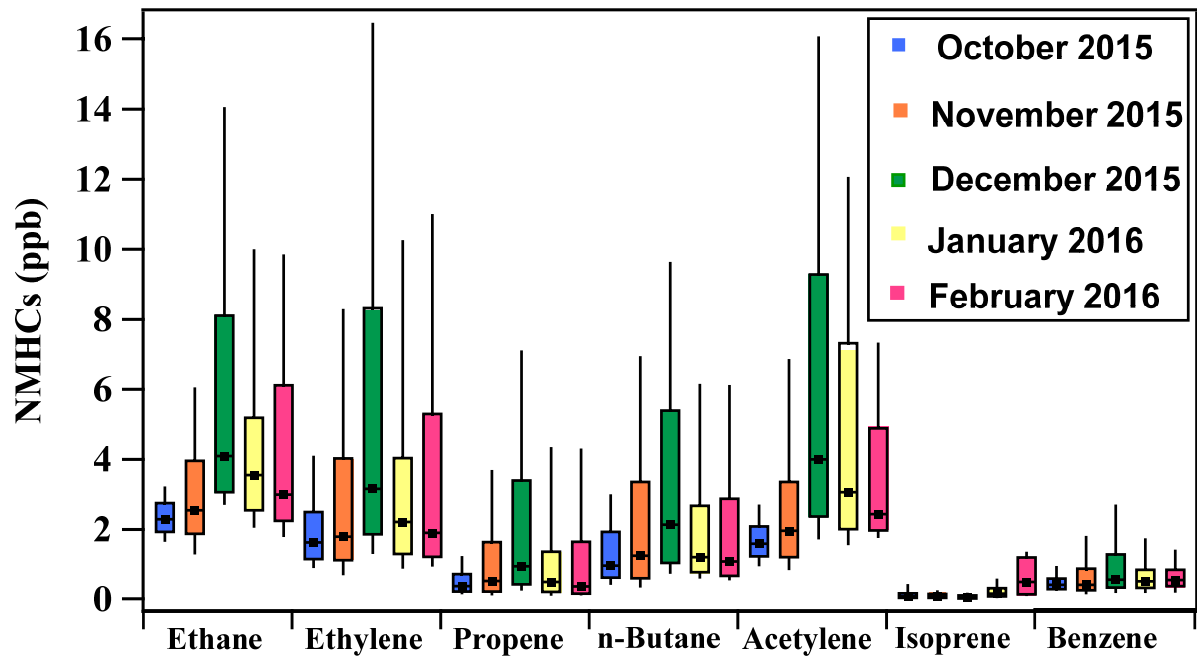


Figure 2. Monthly mean concentrations of ethane, ethylene, propene, n-butane, acetylene, isoprene and benzene. The black dot represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1<sup>st</sup> and 3<sup>rd</sup> quartiles (i. e. Q1 and Q3).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



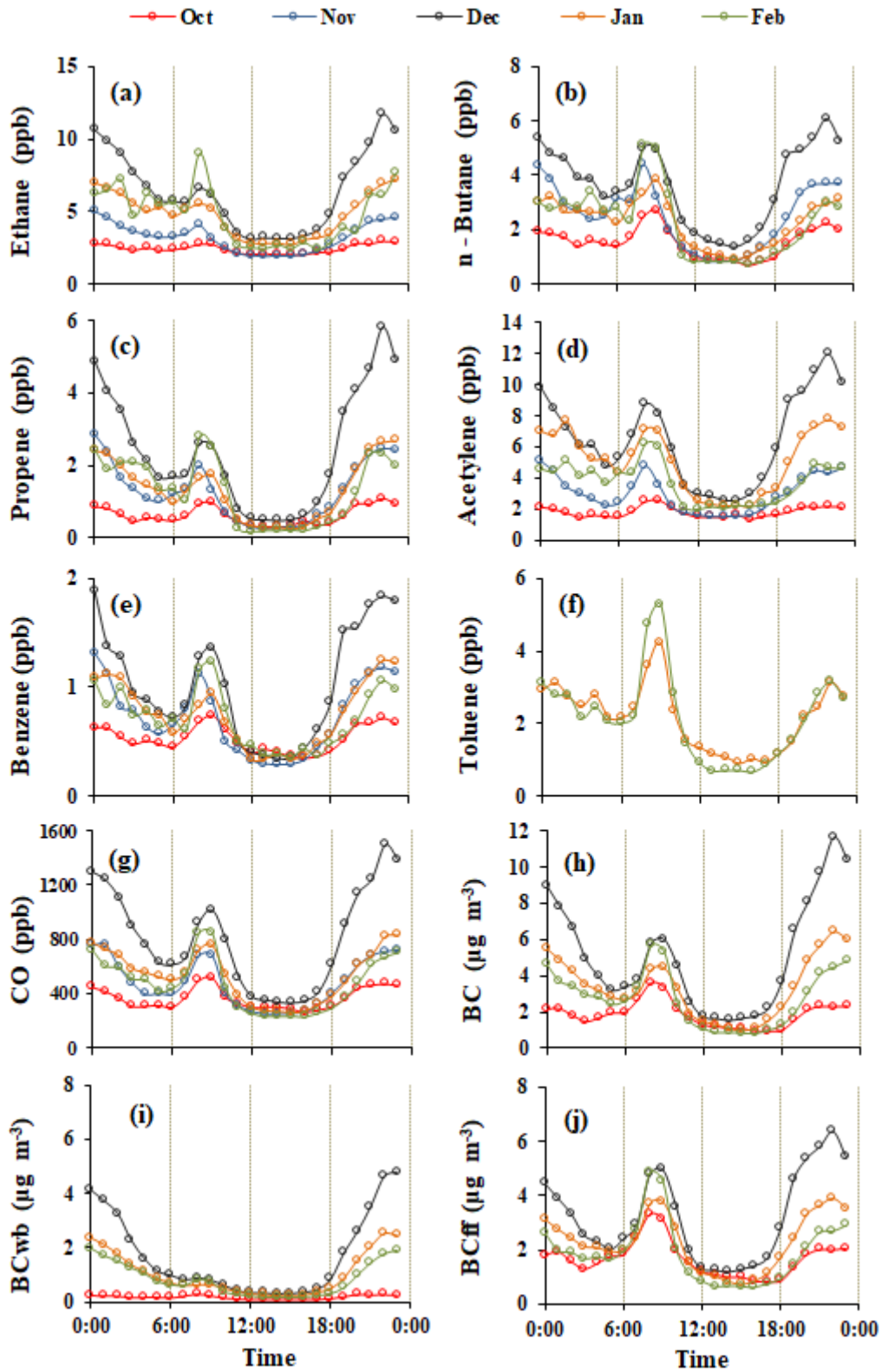


Figure 3. Monthly diurnal variability of (a) ethane, (b) n-butane, (c) propene, (d) acetylene, (e) benzene, (f) toluene, (g) CO, (h) BC, (i)  $BC_{wb}$  and (j)  $BC_{ff}$  based on hourly averaged values.

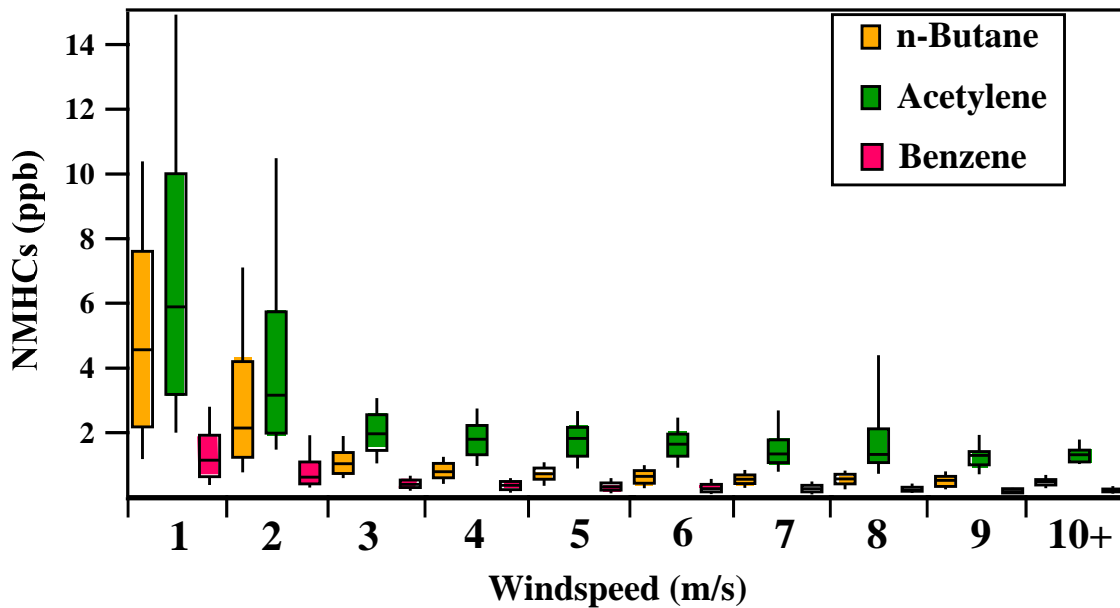


Figure 4. Box-whisker plots of (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the period 16 October 2015 - 15 February 2016. The black line represents the median value and the box shows the interquartile range. The bottom and the top of the box depict the 1<sup>st</sup> and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

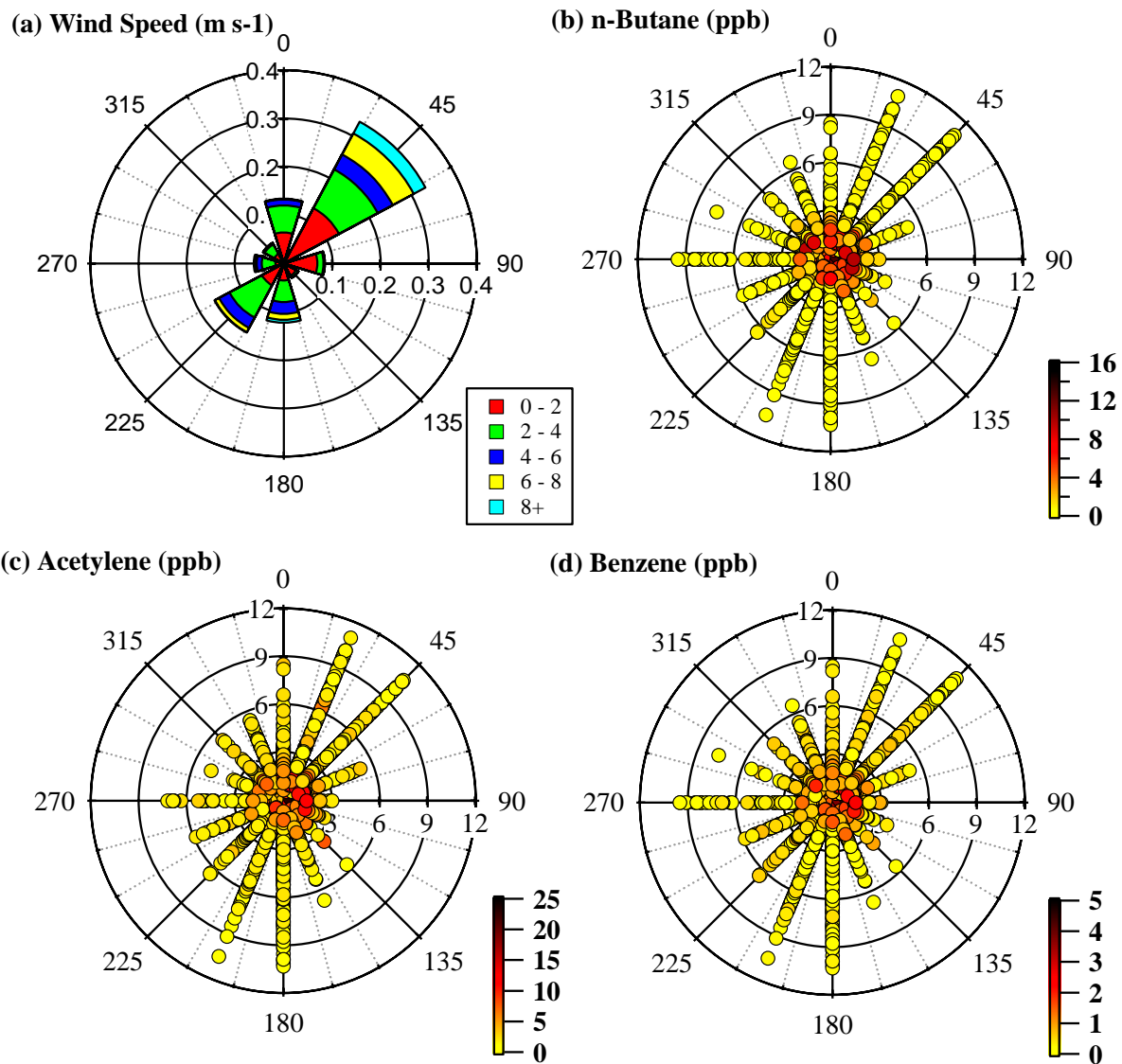


Figure 5. Wind roses of (a) Probability of wind speed, (b) n-butane, (c) acetylene, and (d) benzene for the period 16 October 2015 to 15 February 2016. The angle corresponds to wind directions, the radius to wind speed and the color-scale to the concentration levels.

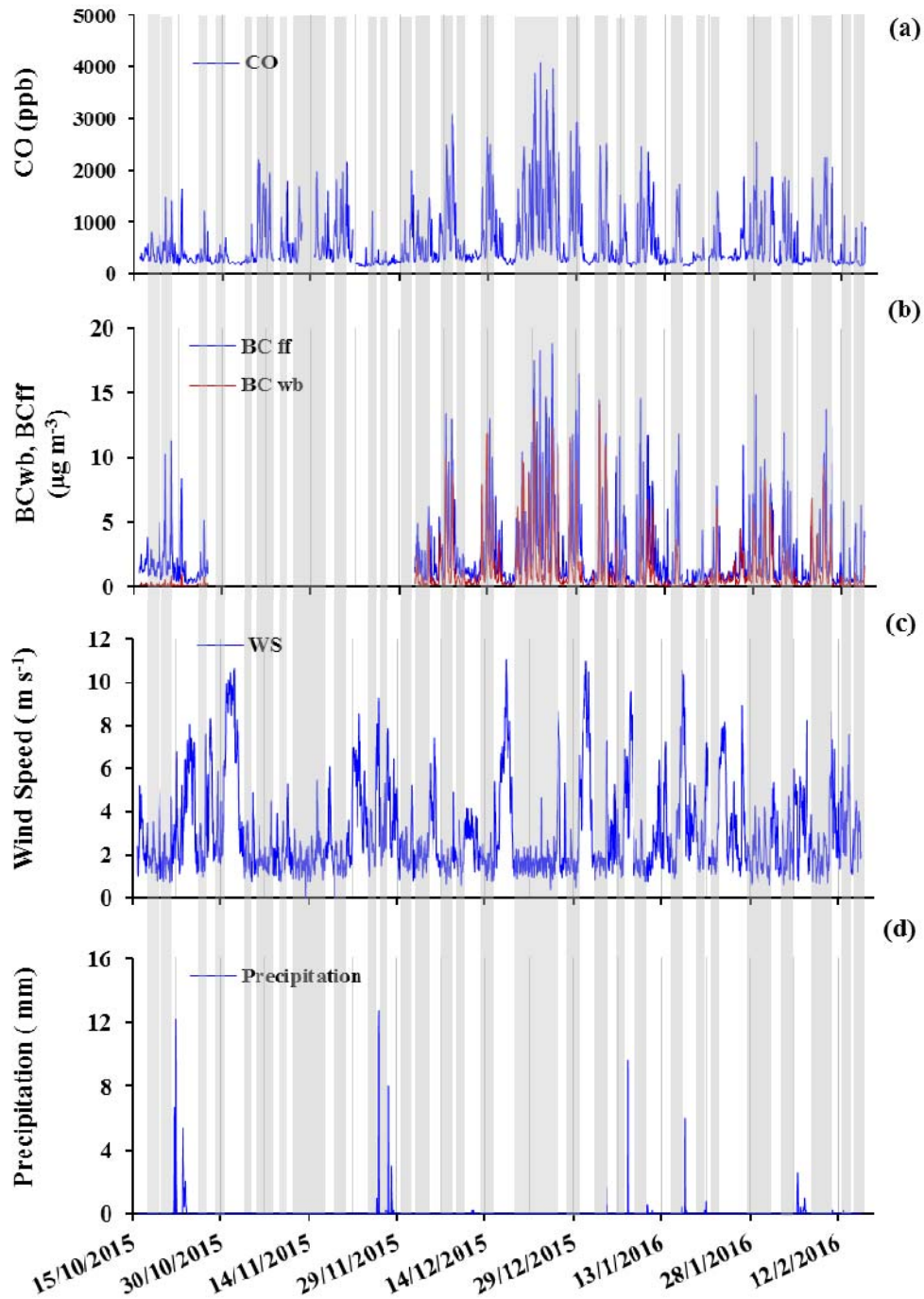


Figure 6. Temporal variability of (a) CO , (b) BC<sub>wb</sub> and BC<sub>ff</sub> fractions, (c) wind speed and (d) precipitation for the experimental period. Grey frames correspond to smog periods (SP), while the remaining part to non-smog periods (nSP).

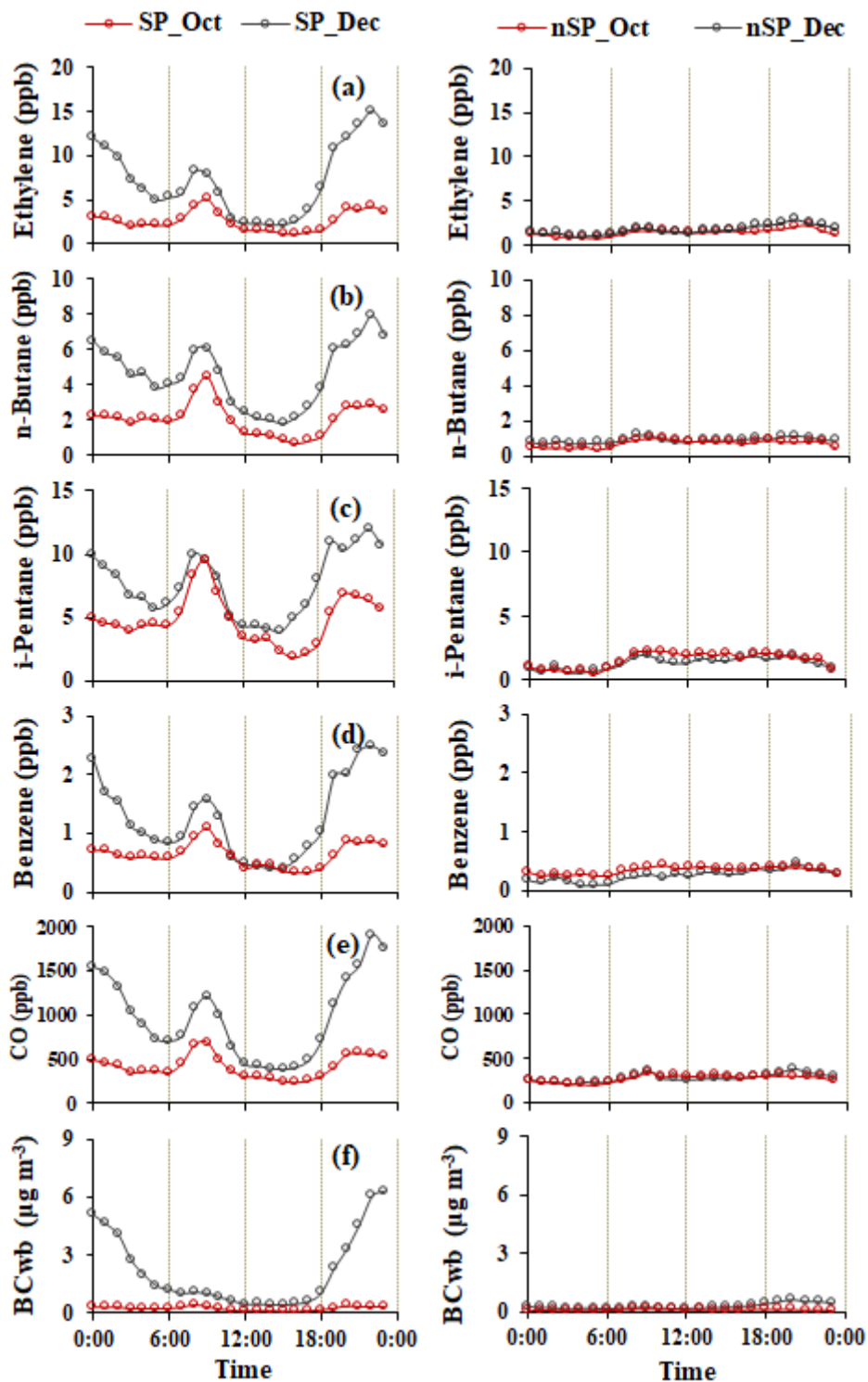


Figure 7. Diurnal patterns of (a) ethylene, (b) n-butane, (c) i-pentane, (d) benzene, (e) CO, (f)  $\text{BC}_{\text{wb}}$  during the SP (left column) and the nSP (right column) periods identified during October 2015 (red) and December 2015 (black) respectively. Note: SP periods are defined by wind-speed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

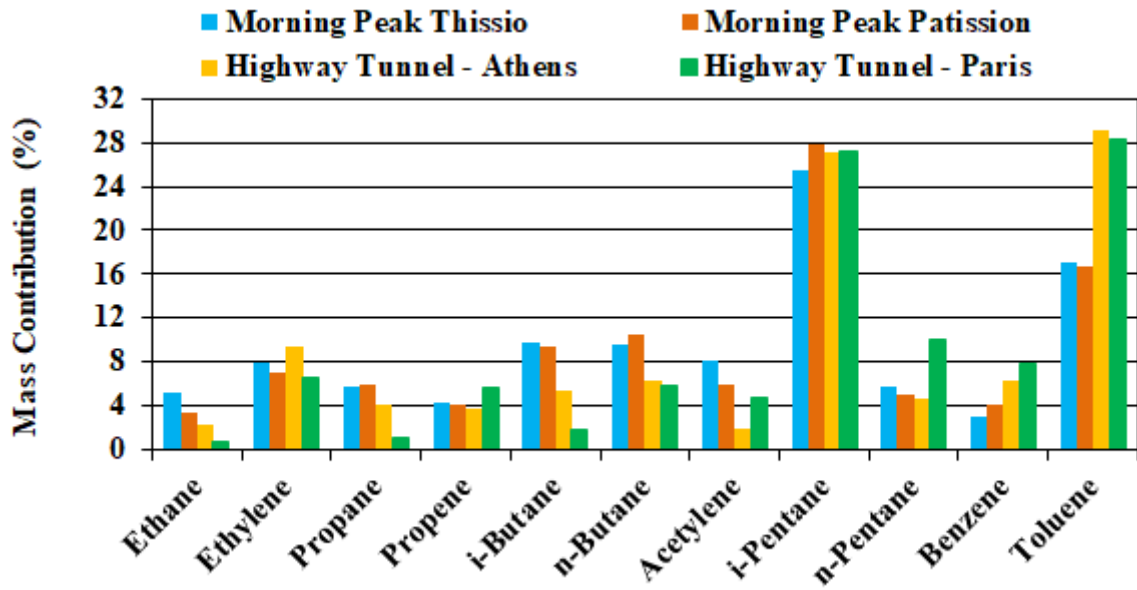


Figure 8. % Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00LT, median values in Thissio, in Patission Monitoring Station, in a highway tunnel in GAA and a highway tunnel close to Paris.

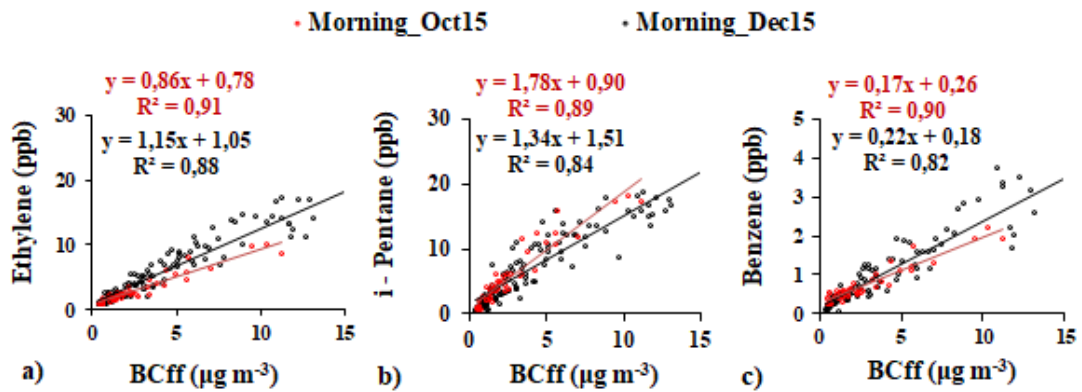


Figure 9. Regressions between ethylene, i-pentane, and benzene versus  $BC_{ff}$  (a-c) for the morning period (07:00 – 10:00LT) in October and December 2015.

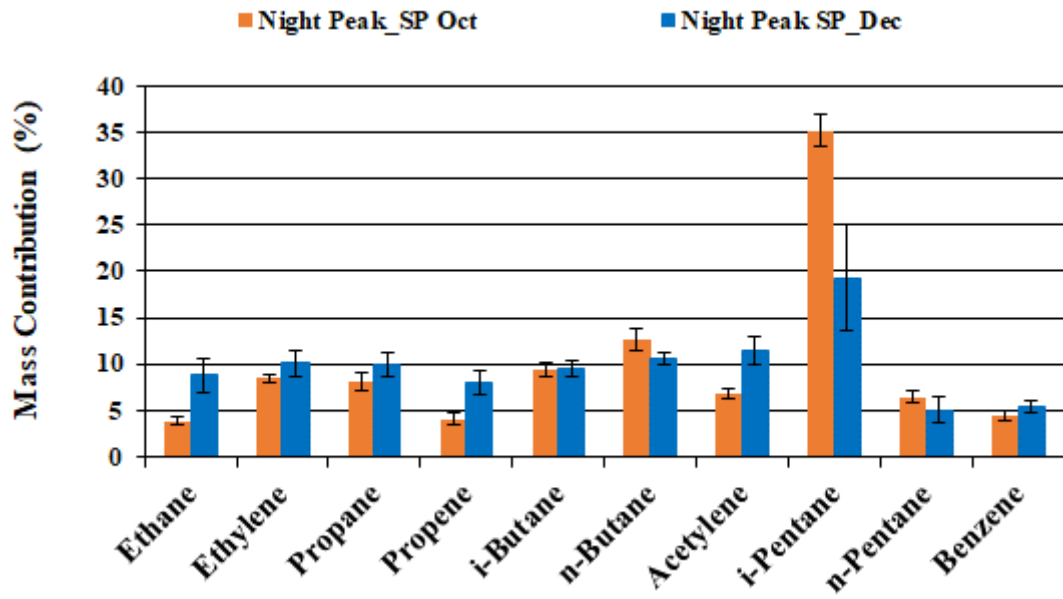


Figure 10. % Mass contribution of the measured NMHCs during the night peak (18:00 – 05:00LT) for the SP of October (orange) and the SP of December (black color).

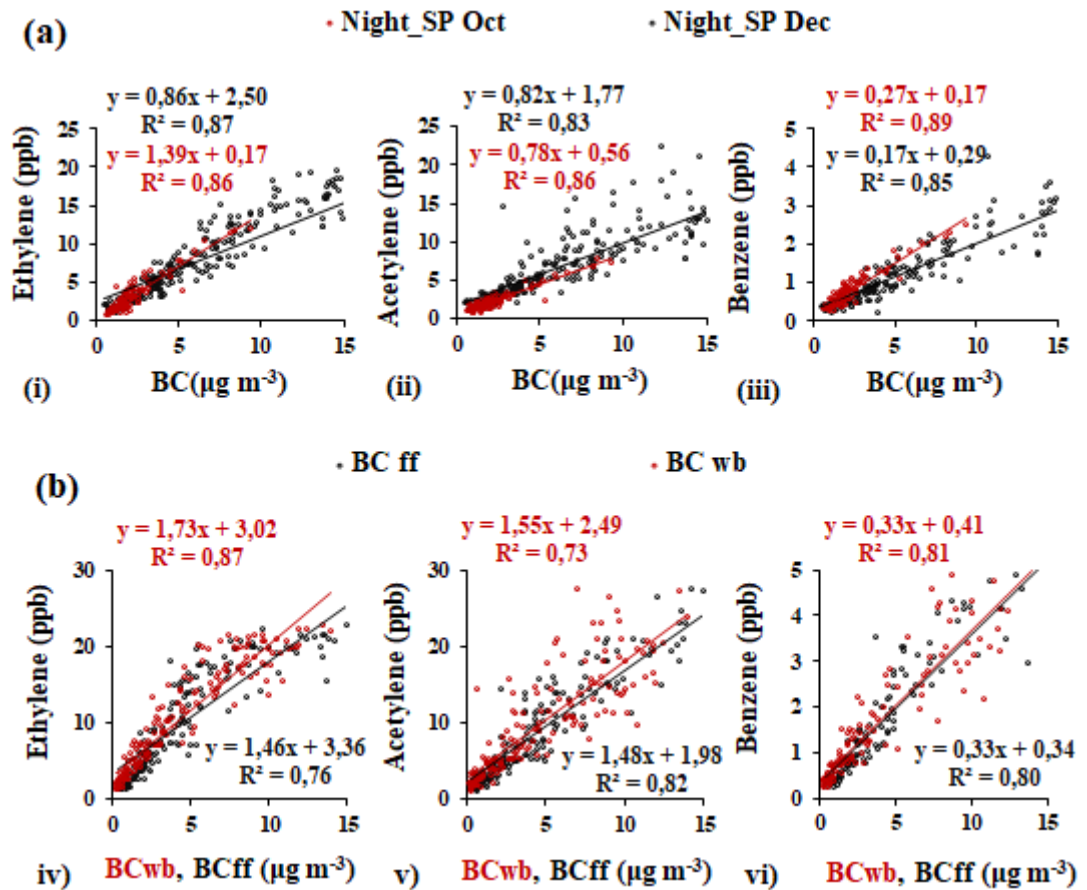


Figure 11. Regressions between ethylene, acetylene and benzene (a) against BC (i-iii) for the night period (18:00 – 05:00LT) of SP October and December 2015 and (b) against BC<sub>wb</sub> (red) and BC<sub>ff</sub> (black) for the night period (22:00 – 04:00LT) of SP December 2015.