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

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Abstract. Non-methane hydrocarbons (NMHCs) play an important role in atmospheric chemistry, contributing to ozone and secondary organic aerosol formation. They can also serve as tracers for various sources such as traffic, solvents, heating and vegetation. The current work presents, for the first time to our knowledge, time-resolved, uninterrupted data of NMHCs, from two to six carbon atoms, during a period of five months (mid-October 2015 to mid-February 2016) in the Great Athens Area (GAA), Greece. The measured NMHC levels are among the highest reported in literature for the Mediterranean area and the majority of the compounds demonstrates a remarkable day to day variability. Their levels increase by up to factor of four from autumn (October-November) to winter (December-February). Local meteorology and especially wind speed seems to control the variability of NMHC levels, with an increase up to a factor of 10 occurring under low wind speed (<3 m s^{-1}), reflecting the impact of local sources rather than long range transport. All NMHCs demonstrated a pronounced bimodal, diurnal pattern with a morning peak followed by a second one before midnight. The amplitude (intensity) of both peaks is gradually increasing towards winter, respectively to autumn, by a factor of 3 to 6 and nicely follow that of carbon monoxide (CO), indicating contribution from additional sources e.g. heating. By comparing the NMHC diurnal variability with that of black carbon (BC), its fractions associated with wood burning (BC_{wb}) and fossil fuel combustion (BC_{ff}), as well as with source profiles we conclude that the morning peak is attributed to traffic while the night one mainly to heating. However, the present data set does not allow for quantification of the relative contribution of fossil fuel and wood burning for heating purposes, although tracers and source profiles clearly indicate the presence of both sources.

1 Introduction

Non-methane hydrocarbons (NMHCs) are key atmospheric constituents for atmospheric chemistry. In the presence of NOx, their oxidation leads to formation of tropospheric ozone and other species, such as peroxy radicals (RO_2) and peroxy acetyl

nitrate (PAN), thus affecting the oxidative capacity of the atmosphere (Atkinson, 2000 and references therein). NMHCs' oxidation contributes to the formation of secondary organic aerosols (SOA), which in turn affects light scattering, visibility and CCN formation (Tsigaridis and Kanakidou, 2003; Seinfeld and Pandis, 2016 and references therein). They mainly originate from anthropogenic sources such as traffic, solvents' use, residential heating, natural gas use, industrial activity, but also emit from natural sources such as vegetation (Guenther et al., 1995; Barletta et al., 2005; Kansal, 2009; Sauvage et al., 2009; Salameh et al., 2015; Baudic et al., 2016b; Jaimes-Palomera et al., 2016). Besides their key role as secondary pollutants precursors, NMHCs are of interest regarding their association with health issues (EEA report, N^{o} 28/2016, 2016). In particular and since 2013, atmospheric substances have been classified by the International Agency for Research on Cancer (WHO-IARC, 2013) in four major groups regarding their carcinogenicity to humans, with benzene and 1,3-butadiene among those NMHCs classified as potential carcinogens (IARC, 2012).

Athens, the capital of Greece and an important megacity, pollution-wise, in the Eastern Mediterranean, with almost five million of inhabitants, is frequently subjected to intense air-pollution episodes, leading to exceedance of the EU air quality limits. The driving processes and atmospheric dynamics of these episodes have been scrutinized during the last decades (Cvitas et al., 1985; Lalas et al., 1982, 1983, 1987; Mantis et al., 1992; Nester, 1995; Melas et al., 1998; Ziomas et al., 1998; Kanakidou et al., 2011). However, the measurement of pollution precursors is limited to ozone and nitrogen oxides, with almost no information on NMHC levels being available. The few existing NMHC measurements in Athens are based on non-continuous intervals with the use of canisters or sorbent tubes, performed just for a few days during summertime or autumn (Moschonas and Glavas, 1996; Klemm et al., 1998; Kourtidis et al., 1999; Moschonas et al., 2001; Giakoumi et al., 2009). Continuous measurements of NMHCs in Athens for a period of one month, have been conducted 20 years ago at three locations, two suburban and one urban, and were limited to compounds containing more than four atoms of carbon (Rappenglück et al., 1998, 1999). Since then significant changes have unambiguously occurred in NMHCs sources in Athens. For instance Gratsea et al. (2017) reported significantly decrease in carbon monoxide (CO) levels from traffic due to car fleet renewal, fuel improvement and metro line extension, while new sources of pollution emerged, especially after 2012, due to uncontrolled wood burning for domestic heating (Saffari et al., 2013; Paraskevopoulou et al., 2015; Kaltsonoudis et al., 2016a; Fourtziou et al., 2017). The latest work on Volatile Organic Compounds (VOCs) in Athens was performed by Kaltsonoudis et al. (2016) it was limited to one month monitoring during summer and winter also and contained no measurements of light compounds from the NMHCs group. The above demonstrate the increasing need for intensive measurement of NMHCs in Athens, to better understand their sources, temporal characteristics and role on smog formation, in the new conditions established during the economic crisis years, with competing traffic and wood burning.

The current study presents, time-resolved, uninterrupted data of NMHCs from two to six carbon atoms, during a time span of several months (October 2015 to mid-February 2016) in the Great Athens Area (GAA). The emphasis of this work is on: (1) the determination of the ambient levels of C2-C6 NMHCs, twenty years after their first measurements (especially for C2-C3, these are the first continuous measurements of NMHCs in Athens); (2) the study of their temporal characteristics and the determination of the factors controlling their variability, and (3) the investigation of traffic and heating impact on NMHCs

levels. Finally, to further shed light on the impact of biomass burning on NMHC levels during wintertime, an intensive campaign of 4 weeks duration was conducted from 15th of January to 15th of February 2016, when, in addition to C2-C6 measurements, a C6-C12 analyzer was also deployed and selected tracers were measured in parallel.

2 Experimental

2.1 Sampling site

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

2.2 On line NMHC measurements

Two portable gas chromatographs equipped with a flame ionization detector (GC-FID, Chromatotec, Saint Antoine, France) were used for the measurement of NMHCs in Athens. Specifically, the "airmoVOC C2-C6" (during the whole period, from October 2015 to February 2016) and the "airmoVOC C6-C12" Chromatrap GC (from mid-January until mid-February 2016) analyzers were used for the determination of C2-C6 and C6-C12 NMHCs respectively, collecting ambient air through collocated inlets at the rooftop of the station, 4 m above ground. The C2-C6 NMHC analyzer was set to sample on a 10 min basis and an analysis time of 20 min, while for the C6-C12 the respective timing was 20 min and 10 min. Therefore, the synchronized monitoring was performed with an overall 30 min time resolution, for both analyzers.

For the airmoVOC C2-C6 analyzer, 189 mL of air was drawn through a 0.315 mm diameter, 6 m-long stainless-steel line with a flow rate of 18.9 mL min^{-1}. Once sampled, ambient air was passed through a Nafion dryer (activated by gas nitrogen) to reduce the water content and then hydrocarbons were preconcentrated at -9 ^{0}C (Peltier cooling system), on a 2.25 mm internal diameter, 8 cm-long glass trap containing the following adsorbents: Carboxen 1000 (50 mg), Carbopack B (10 mg) and Carbotrap C (10 mg) all from Supelco Analytical, Bellefonte, PA, USA. The trap was then heated rapidly to 22 ^{0}C for 4 min and the pre-concentrated VOCs were thermally desorbed onto a Plot Column (Restek Corp., Bellefonte, PA, USA, Al_2O_3/Na_2SO_4), 25 m x 0.53 mm, 10 mm film thickness). 1 min prior to the analysis, the oven temperature was raised from 36 to 38 ^{0}C, followed by a constant heating rate of 15 ^{0}C min^{-1} to 200 ^{0}C by the end of the analysis. Details about the equipment technique and performances are provided by Gros et al. (2011). The overall estimated uncertainty of the measurement is 15%.

The airmoVOC C6-C12 analyzer was collecting 900 mL of air through a 0.315 mm diameter, 6 m-long stainless-steel line with a flow rate of 45 mL min^{-1}. The hydrocarbons were preconcentrated at ambient temperature on a glass trap containing

the adsorbent Carbotrap C. Then the trap was heated to 380 ^{0}C over 2 min to desorb the pre-concentrated VOCs into a separation column (MXT30CE, Restek Corp., 30 m x 0.28 mm, 1 mm film thickness). With one minute delay, the oven temperature was raised from 36 to 50 ^{0}C at a rate of 2 ^{0}C min^{-1}, followed by a second heating of 10 ^{0}C min^{-1} up to 80 ^{0}C. Finally, at a constant heating rate of 15 ^{0}C min^{-1} the temperature reached 200 ^{0}C and remained there until the end of the analysis. In the present work only toluene will be used from the C6-C12 GC data series.

Simultaneous calibration and identification of the compounds were performed by a certified National Physical Laboratory (NPL) standard of NMHC mixture (~4 ppb) containing: ethane, ethylene, propane, propene, i-butane, n-butane, acetylene, i-pentane, n-pentane, isoprene, benzene and 15 additional hydrocarbons.

2.3 Auxiliary measurements

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

2.4 Tunnel measurements

Measurements were conducted in a tunnel at the peripheral, highway of Athens, called Attiki Odos, on 12 May 2016 from 12:00 LT to 12:45 LT (LT = UTC+2) in order to identify the NMHCs fingerprint of traffic emissions in the frame of the source apportionment investigation. For this canisters were used and the sampling time ranged between 2 and 6 minutes. Four samples were collected in total and were analyzed via the GC-FID described in Sect. 2.2. Prior to the analysis the samples were diluted by a factor of two with zero-air, and then each canister was connected to the GC-FID system using a Teflon sampling line.

3 Results and discussion

3.1 Temporal variability of NMHCs

Figure 1 presents the temporal variability of selected NMHCs for five major groups of compounds: ethane and n-butane (for saturated hydrocarbons), propene and ethylene (for alkenes), acetylene (for alkynes), benzene and toluene (for aromatics) and isoprene (for potential biogenic compounds). Other measured NMHCs are presented in Fig. S1. During the reported period, the data coverage for all C2-C6 NMHCs was higher than 90% with the exception of isoprene (approximately 10%).

The latter led to difficulty to determine a representative diurnal variability for this compound, nevertheless, the significant night time levels (above 300 ppt in some cases) could be indicative of non-vegetation sources (Borbon et al., 2001, 2003).

The majority of the compounds showed a remarkable day to day variability throughout the study period and levels increasing by up to factor of four, from autumn (October-November) towards winter (December-February; Fig. 1 and S1). The highest concentrations ranged between 30 and 40 ppb for ethane and ethylene and were encountered in wintertime, while lower values were below 5 ppb for the whole period. During the period of intensive measurements, toluene exceeded 10 ppb, while benzene was below 6 ppb during the four month monitoring period. Benzene is the only NMHC included in the European air quality standards due to its possible adverse health effects (IARC, 2012). The average concentration of benzene during the studied period was 0.7 ppb (still not a full year), which is considerably below the EU average annual limit of 5 μg m^{-3} or 1.5 ppb (Directive 2008/50/EC of the European Parliament).

In Table 1, the measurements of this study are compared with those reported in the literature for Athens in the past and other selected areas worldwide. The comparison with those already published for the GAA, indicates an apparent decrease by a factor of 2 to 6 for the majority of the species lying above C4 (taking as reference the case of Ancient agora urban area in the close vicinity of the Thissio Station), always bearing in mind differences in sampling period (summer versus winter), location, sampling method and analytical techniques. Comparison with other Mediterranean or south European locations with long-term observations is possible only with Beirut (Salameh et al., 2015) and Bilbao (Durana et al., 2006). The levels observed in Athens are significantly higher even by more than 100%, with the exception of propane, butanes and toluene for Beirut and n-butane, benzene and toluene for Bilbao, which are quite similar to Athens. NMHC levels are also compared with those from Paris, the latter as representative of a mid-latitude, northern hemisphere (urban) location. Again the observed levels in Athens are significantly higher compared to those reported for Paris (Baudic et al., 2016). Furthermore, our findings for benzene and toluene, were significantly lower than the 12 hour day-time average levels reported for a Cairo rural background area , as reported by Khoder et al., 2007 (mean levels of 5.8 and 7.5 ppb respectively).

According to Fig. 1, a common pattern for all NMHC concentrations was their gradually increase from October to December, which reflects the transition from the warmer period to the colder one. This is better illustrated in Fig. 2, which depicts the monthly mean concentration for every NMHC presented in Fig. 1. The increase in NMHC levels during the cold period could be explained by the respective increase in their lifetime due to less photochemistry and the contribution from additional sources, such as heating. However, the role of atmospheric dynamics should not be neglected, since the decrease in the height of the planetary boundary layer (PBL) could also trigger the winter-time enhancement of the NMHC levels. Nevertheless, according to Kokkalis (personal communication) the winter-time decrease of PBL is in the range of 20%, thus the limited dilution couldn't be the only factor determining the enhancement of NMHCs level. Wind speed and direction have to be considered as well and will be discussed thereafter.

3.2 Diurnal variability of NMHCs

During the whole monitoring period, all hydrocarbons demonstrated a pronounced bimodal diurnal pattern (Fig. 3 and S2). A morning peak was observed lasting from 07:00LT to 10:00LT, followed by a second one before midnight. The amplitude (intensity) of both peaks is gradually increasing from October to winter time by a factor of 3 to 6 and nicely follow that of carbon monoxide (CO), indicating the possible contribution from additional sources, e.g. heating (Fig. 3g). By comparing the NMHC diurnal variability with that of BC, as well as its fractions associated with wood burning (BC_{wb}) and fossil fuel combustion (BC_{ff}), it is deduced that the morning peak could be mainly attributed to traffic and the late evening to heating processes, namely the combined use of heavy oil and wood burning. Although the amplitude of both peaks is almost similar (with the exception of December), the duration of the night peak is at least a factor of 2 larger, indicating the predominant role of heating in air quality during wintertime. Moreover, night-time emissions occur in a shallower boundary layer relatively to the morning, resulting into accumulation of pollutants.

3.3 The role of meteorology on NMHC levels

Once emitted in the atmosphere, NMHCs react mainly with OH and NO_3 radicals during day and night-time, respectively, and with ozone throughout the day (Crutzen 1995, Atkinson 2000). Still, in addition to chemistry, many other factors, such as the strength of the emission sources and the atmospheric dynamics (meteorology and boundary layer evolution), determine their abundance and diurnal variability. To investigate the role of wind speed and wind direction, the dependence of n-butane, acetylene and benzene, selected as representative of alkanes, alkynes and aromatics, against wind speed and direction, is depicted in Fig. 4 and 5 respectively (Fig. S3 and S4 include the rest of the compounds). For all studied NMHCs, the highest concentration occurred under low wind speed (< 3 m sec^{-1}) reflecting the critical role of local sources versus long range transport. On a monthly basis, the NMHC dependence on wind speed remains the same as for the total period (Fig. S5).

To investigate the impact of wind direction on NMHC levels, fig. 5 presents the distribution of wind sectors frequency of occurrence during the sampling period and that of wind speed per sector, as well as the variability of n-butane, acetylene and benzene levels as a function of wind direction. Enhanced levels of NMHCs are found under influence from air masses from northerly directions, still it should be noted the low frequency of occurrence of this sector (1%). During the whole sampling period, the NE sector, associated with relatively strong winds (u > 3 m sec^{-1}), was the most frequent, resulting to moderate levels of NMHCs. Overall, a similar distribution of NMHC levels is shown for the different compounds, indicating moderate to higher values from the N-NE-E-SE directions, and lower values from the extended NW-W-SW sector, the latter associated with high wind speeds. The exception is the NE sector which despite the higher wind speeds still shows moderate to high levels, as a result of local sources orientation upwind the measurement site. Indeed, the northern suburbs of GAA are characterized by increased number of fireplaces (Athanasopoulou et al., 2017) due to the age of the buildings, while the higher living standards of their inhabitants probably reflect the combined use of heating oil in central heating systems and the use of wood in fireplaces and/or woodstoves. The impact of the N sector on NMHCs levels can be also seen when

comparing October with December. Although a similar wind origin distribution was observed during these two periods (Fig. S6), a 2 to 3 times higher levels of NMHCs were observed on December under N winds influence compared to October.

The ambient temperature is another parameter which can influence NMHC levels, as high temperatures favor the evaporation of low volatility hydrocarbons and also trigger the production of some biogenic compounds, whereas lower temperatures could trigger the emission of NMHCs from increased heating demand, as other tracers as well (Athanasopoulou et al., 2017). The average monthly temperatures varied from 18 ^{0}C in October and November to 10-13 ^{0}C in December and late winter, respectively. When NMHCs are examined against temperature (not shown here), a clear tendency is not evident, although the highest levels occur at lower temperatures.

3.4 Identification of NMHC emission sources

3.4.1 Interspecies correlation

Table 2 shows the interspecies correlation of NMHCs for the total period of measurements, for the investigation of their common origin. Most NMHCs were highly correlated, with the exception of the light NMHCs (C2) with those heavier than C4 or C5 compounds. Ethane, ethylene and acetylene were moderately (R^2 of 0.5–0.7) correlated with C4 or C5 compounds, whereas isoprene was excluded from Table 2 since it wasn't correlated to any NMHC. The strong correlation of NMHCs with combustion tracers, such as CO, NO and BC, could indicate their common variability due to both dilution and common sources from combustion. The deconvolution of BC into its fossil fuel and biomass burning fractions enables further classification of NMHCs into groups that could possibly be emitted by those two distinct sources. The strong correlation (R^2 > 0.74) of the hydrocarbons, except ethane, with BC_{ff} could imply stronger emission of NMHCs from fossil fuel combustion processes relatively to wood burning. Finally, no change in the correlation coefficients and the resulting picture is observed when data sets are separated between day (6:00-18:00) and nighttime (18:00-6:00) time intervals. However the above analysis could give only a rough idea on the sources impacting NMHCs levels. More precise picture could emerge with comparison with source profiles and such discussion follows in the paragraph below.

3.4.2 Impact of various sources on the NMHC levels

To identify periods with differentiated impact from the different pollution sources (with emphasis on traffic and heating), the methodology described by Fourtziou et al. (2007) was applied. The criteria for this separation have been the wind speed not to exceed the threshold value of 3 m s^{-1} (light breeze conditions) and the presence of precipitation (on/off criterion). The role of wind speed was clearly seen at the Sect. 3.3 (Fig. 4). Based on these criteria, the first group (non-shaded in Fig. 6) corresponds to higher wind speeds and thus more efficient dispersion of locally emitted pollutants (ventilation), as well as the incidents of rain and is characterized as non-smog periods (nSP). The second group (shaded area in Fig. 6) refers to lower wind speeds, favoring accumulation of high pollution loads within the mixing layer and is henceforth referred to as smog periods (SP). The frequency of SP and nSP periods was 65% and 35% respectively. Note that the word "smog" is used

as a synonym to highlight cases of relatively high air pollution, as also indicated by the high levels of CO and BC encountered during the SP periods (Fig. 6).

The diurnal variability of all compounds was investigated separately for two distinct months, October and December, representative of non-heating and heating activities, respectively (Fig. 7 and S7, S8). Note that SP periods represent 55% of the considered time in October and 73% in December. According to previous findings (Paraskevopoulou et al. 2015; Kaltsonoudis et al. 2016; Fourtziou et al. 2017; Gratsea et al. 2017) wood burning for domestic heating has gained a marking role as a winter-time emission source in Greece, over the last years. Since wood burning is reported as emission source of specific organic compounds (Baudic et al., 2016; Gaeggeler et al., 2008; Gustafson et al., 2007; Hellén et al., 2008; Kaltsonoudis et al., 2016), it can be safely considered as a possible factor contributing to the winter time increase of NMHC levels in GAA. Thus the two selected months are expected to have different source profile. October, without or very limited heating demand, was used as a reference period, while December in south-central Greece is traditionally the beginning of the heating period. The low values of BC_{wb} recorded in October, even during the SP periods, validates the methodology followed for the separation (Fig. 7).

The levels of all measured NMHCs were significantly higher in December compared to October for the SP periods (Fig. 7 and S7). The most striking difference is related to the night and early morning peak, while during mid-day the difference is minimum. It is worth noting the level of NMHCs during the traffic related morning peak. Although higher mean levels were observed in December, the amplitude of the morning peak is almost similar in both examined months, denoting no important change in the traffic source between the heating and non-heating periods. For the nSP cases (Fig. 7 and S7) the concentrations of all compounds were very low (lower than the minimum of the SP periods) and almost equal, with the exception of ethane and acetylene that demonstrated higher concentrations in December by a factor of two (Fig. S7a,e). Accordingly, the diurnal variability of all investigated NMHCs was less pronounced compared to the SP periods with a slight increase during night in December, which could be attributed to a background contribution from heating sources. In Sect. 3.4.3 the origin of the morning and nights peaks related to NMHCs will be further investigated.

3.4.3 Impact of sources on morning and night peaks of NMHCs

Morning peak: As discussed in Sect. 3.2, the morning peak (07:00 – 10:00 LT) of NMHCs could be attributed mainly to traffic. Figure 8 presents the profile of this peak (% mass contribution of the measured NMHCs), during January and February when toluene data were available and compares it with the profile obtained into a tunnel in GAA. The profile of the morning peak was obtained for each NMHC by subtracting the baseline level from the maximum (more details on the calculations are provided in Sect. S2). Measurements into the tunnel allowed for the extraction of the profile of traffic related NMHCs, to be used as reference for identifying the signal of traffic in ambient conditions, assuming that tunnels receive or exchange no significant air mass portions with the outside environment. A very good agreement is observed between the two profiles regarding the dominant species, highlighting the importance of traffic in the morning values of NMHCs. It is interesting to note that the profiles, especially those derived from the morning peak, nicely fit with that reported for traffic by

Baudic et al. (2016) in Paris (when only the common NMHCs measured in this work have been used). Higher values of butanes are however be noted in the morning peak than in the tunnel experiments, it may reflect a higher proportion of the evaporative contribution from the traffic source in ambient air compared to air measured in a tunnel.

Toluene, an important contributor to the traffic profile (Fig. 8), was measured only for one month during winter. To obtain a better idea on the variability of the traffic source during the studied period, the variability of selected NMHCs (ethylene, i-pentane and benzene) relatively to BC_{ff}, the latter used as traffic source tracer, was also plotted for October and December (Fig. 9). Significant correlations are revealed with slopes remaining almost stable during both months, indicating similar emission ratios during the whole studied period, and probably equal contribution from traffic. The exception is ethylene (the most reactive compound measured after isoprene) which shows higher slope in December and could be attributed to enhanced photochemical decay in October compared to December.

Nighttime peak: During nighttime both BC_{ff} and BC_{wb} were maximized (e.g. Fig. 3 and 7), denoting significant contribution from both fossil fuel and wood burning (the contribution of the later was more evident during winter). Figure 10 presents the NMHC profile of the nighttime peak, which has been calculated by the subtraction of the background concentration (minimum value between 12:00 and 17:00LT) from the night maximum value, for both October and December. As already discussed, traffic is expected to be the main source of NMHCs during nighttime in October, whereas heating competes traffic during December. When these two profiles are compared (Fig. 10), the difference is obvious, with a smaller contribution from i-pentane (traffic source contributor) during December. In addition, enhanced contributions from C_2 (ethane, ethylene and acetylene) are apparent in December compared to October. These C_2 hydrocarbons have been reported as important contributors to the wood burning source profile by Baudic et al. (2016) in Paris. Preliminary data from a fireplace experiment (not part of this work) also confirm these findings; and are in line with our results reported in Fig. 7 indicating possible impact of wood burning during nighttime in winter months.

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

4 Conclusions

For the first time to our knowledge, continuous measurements of 11 Non Methane Hydrocarbons with two to six carbon atoms (C2-C6 NMHCs) were conducted for several months (mid-October 2015 to mid-February 2016) in the Great Athens

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

For the better understanding of the impact of sources on the NMHCs levels, the studied period was further separated into smog (SP) and no-smog (nSP) (period) periods, based on the absence of rainfall and low wind speed. October and December were chosen for further comparison due to different meteorological profiles and possible sources taking into account the already proved increased winter-time heating demand (Athanasopoulou et al., 2017). The comparison of morning maximum of NMHCs profile for the SP with those have been obtained by tunnel experiments in Athens and Paris further confirms the role of traffic in the observed morning NMHCs peak. The October and December SP NMHCs' night profiles depicted difference indicating attributed to heating. However, NMHCs slopes versus BC_{wb} are almost similar when compared to those versus BC_{ff} (slight difference for ethylene), indicating that NMHCs are probably equally produced by wood and oil fossil fuel burning. An extended dataset (future long term measurements) is needed in order to distinguish the contribution of different sources types and to further quantify their impact on the NMHCs levels.

5 Data availability

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

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References

Air quality in Europe — 2016 report, Eur. Environ. Agency [online] Available from: https://www.eea.europa.eu/publications/air-quality-in-europe-2016.

Athanasopoulou, E., Speyer, O., Brunner, D., Vogel, H., Vogel, B., Mihalopoulos, N. and Gerasopoulos, E.: Changes in domestic heating fuel use in Greece: effects on atmospheric chemistry and radiation, Atmos Chem Phys, 17(17), 10597–10618, doi:10.5194/acp-17-10597-2017, 2017.

Atkinson, R.: Atmospheric chemistry of VOCs and NOx, Atmos. Environ., 34(12), 2063–2101, doi:10.1016/S1352-2310(99)00460-4, 2000.

Barletta, B., Meinardi, S., Sherwood Rowland, F., Chan, C.-Y., Wang, X., Zou, S., Yin Chan, L. and Blake, D. R.: Volatile organic compounds in 43 Chinese cities, Atmos. Environ., 39(32), 5979–5990, doi:10.1016/j.atmosenv.2005.06.029, 2005.

Baudic, A., Gros, V., Sauvage, S., Locoge, N., Sanchez, O., Sarda-Estève, R., Kalogridis, C., Petit, J.-E., Bonnaire, N., Baisnée, D., Favez, O., Albinet, A., Sciare, J. and Bonsang, B.: Seasonal variability and source apportionment of volatile organic compounds (VOCs) in the Paris megacity (France), Atmos Chem Phys, 16(18), 11961–11989, doi:10.5194/acp-16-11961-2016, 2016b.

Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J. C. and Guillermo, R.: An investigation into the traffic-related fraction of isoprene at an urban location, Atmos. Environ., 35(22), 3749–3760, doi:10.1016/S1352-2310(01)00170-4, 2001.

Borbon, A., Fontaine, H., Locoge, N., Veillerot, M. and Galloo, J. C.: Developing receptor-oriented methods for non-methane hydrocarbon characterisation in urban air—Part I: source identification, Atmos. Environ., 37(29), 4051–4064, doi:10.1016/S1352-2310(03)00525-9, 2003.

Cvitas, T., Gusten, H., Heinrich, G., Klasinc, L., Lalas, D. and Petrakis, M.: Characteristics of summer air pollution in Athens, Greece, [online] Available from: http://agris.fao.org/agris-search/search.do?recordID=US8627593 (Accessed 3 October 2017), 1985.

Crutzen, Paul J.: Ozone in the troposphere. Composition, chemistry, and climate of the atmosphere, 349-393, 1995

Durana, N., Navazo, M., Gómez, M. C., Alonso, L., García, J. A., Ilardia, J. L., Gangoiti, G. and Iza, J.: Long term hourly measurement of 62 non-methane hydrocarbons in an urban area: Main results and contribution of non-traffic sources, Atmos. Environ., 40(16), 2860–2872, doi:10.1016/j.atmosenv.2006.01.005, 2006.

European Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations, Official Journal L 085 , 29/03/1999, p. 0001 – 0022

European Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, Official Journal L 152, 11/6/2008, p. 1-44

Fourtziou, L., Liakakou, E., Stavroulas, I., Theodosi, C., Zarmpas, P., Psiloglou, B., Sciare, J., Maggos, T., Bairachtari, K., Bougiatioti, A., Gerasopoulos, E., Sarda-Estève, R., Bonnaire, N. and Mihalopoulos, N.: Multi-tracer approach to

characterize domestic wood burning in Athens (Greece) during wintertime, Atmos. Environ., 148, 89–101, doi:10.1016/j.atmosenv.2016.10.011, 2017.

Gaeggeler, K., Prevot, A. S. H., Dommen, J., Legreid, G., Reimann, S. and Baltensperger, U.: Residential wood burning in an Alpine valley as a source for oxygenated volatile organic compounds, hydrocarbons and organic acids, Atmos. Environ., 42(35), 8278–8287, doi:10.1016/j.atmosenv.2008.07.038, 2008.

Giakoumi, A., Maggos, T., Michopoulos, J., Helmis, C. and Vasilakos, C.: PM2.5 and volatile organic compounds (VOCs) in ambient air: a focus on the effect of meteorology, Environ. Monit. Assess., 152(1–4), 83, doi:10.1007/s10661-008-0298-2, 2009.

Gratsea, M., Liakakou, E., Mihalopoulos, N., Adamopoulos, A., Tsilibari, E. and Gerasopoulos, E.: The combined effect of reduced fossil fuel consumption and increasing biomass combustion on Athens' air quality, as inferred from long term CO measurements, Sci. Total Environ., 592(Supplement C), 115–123, doi:10.1016/j.scitotenv.2017.03.045, 2017.

Gros, V., Gaimoz, C., Herrmann, F., Custer, T., Williams, J., Bonsang, B., Sauvage, S., Locoge, N., d'Argouges, O., Sarda-Estève, R. and Sciare, J.: Volatile organic compounds sources in Paris in spring 2007. Part I: qualitative analysis, Environ. Chem., 8(1), 74–90, doi:10.1071/EN10068, 2011.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res. Atmospheres, 100(D5), 8873–8892, doi:10.1029/94JD02950, 1995.

Gustafson, P., Barregard, L., Strandberg, B. and Sällsten, G.: The impact of domestic wood burning on personal, indoor and outdoor levels of 1,3-butadiene , benzene , formaldehyde and acetaldehyde, J. Environ. Monit., 9(1), 23–32, doi:10.1039/B614142K, 2007.

Hellén, H., Hakola, H., Haaparanta, S., Pietarila, H. and Kauhaniemi, M.: Influence of residential wood combustion on local air quality, Sci. Total Environ., 393(2–3), 283–290, doi:10.1016/j.scitotenv.2008.01.019, 2008.

Jaimes-Palomera, M., Retama, A., Elias-Castro, G., Neria-Hernández, A., Rivera-Hernández, O. and Velasco, E.: Non-methane hydrocarbons in the atmosphere of Mexico City: Results of the 2012 ozone-season campaign, Atmos. Environ., 132(Supplement C), 258–275, doi:10.1016/j.atmosenv.2016.02.047, 2016.

IARC, Chemical Agents and Related Occupations, Monographs on the Evaluation of Carcinogenic Risks to Humans, 2012, vol. 100F, 249-285; 309-333 http://monographs.iarc.fr/ENG/Monographs/vol100F/mono100F.pdf

Kaltsonoudis, C., Kostenidou, E., Florou, K., Psichoudaki, M. and Pandis, S. N.: Temporal variability and sources of VOCs in urban areas of the eastern Mediterranean, Atmos Chem Phys, 16(23), 14825–14842, doi:10.5194/acp-16-14825-2016, 2016a.

Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E., Dermitzaki, E., Unal, A., Koçak, M., Markakis, K., Melas, D., Kouvarakis, G., Youssef, A. F., Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojie, F., Wittrock, F., von Savigny, C., Burrows, J. P., Ladstaetter-Weissenmayer, A. and Moubasher, H.: Megacities as hot spots of air pollution in the East Mediterranean, Atmos. Environ., 45(6), 1223–1235, doi:10.1016/j.atmosenv.2010.11.048, 2011.

Kansal, A.: Sources and reactivity of NMHCs and VOCs in the atmosphere: A review, J. Hazard. Mater., 166(1), 17–26, doi:10.1016/j.jhazmat.2008.11.048, 2009.

Khoder, M. I.: Ambient levels of volatile organic compounds in the atmosphere of Greater Cairo, Atmos. Environ., 41(3), 554–566, doi:10.1016/j.atmosenv.2006.08.051, 2007.

Klemm, O., Ziomas, I. C., Balis, D., Suppan, P., Slemr, J., Romero, R. and Vyras, L. G.: A summer air-pollution study in Athens, Greece, Atmos. Environ., 32(12), 2071–2087, doi:10.1016/S1352-2310(97)00424-X, 1998.

Kourtidis, K. A., Ziomas, I. C., Rappenglueck, B., Proyou, A. and Balis, D.: Evaporative traffic hydrocarbon emissions, traffic CO and speciated HC traffic emissions from the city of Athens, Atmos. Environ., 33(23), 3831–3842, doi:10.1016/S1352-2310(98)00395-1, 1999.

Lalas, D. P., Veirs, V. R., Karras, G. and Kallos, G.: An analysis of the SO2 concentration levels in Athens, Greece, Atmospheric Environ. 1967, 16(3), 531–544, doi:10.1016/0004-6981(82)90162-7, 1982.

Lalas, D. P., Asimakopoulos, D. N., Deligiorgi, D. G. and Helmis, C. G.: Sea-breeze circulation and photochemical pollution in Athens, Greece, Atmospheric Environ. 1967, 17(9), 1621–1632, doi:10.1016/0004-6981(83)90171-3, 1983.

Lalas, D. P., Tombrou-Tsella, M., Petrakis, M., Asimakopoulos, D. N. and Helmis, C.: An experimental study of the horizontal and vertical distribution of ozone over Athens, Atmospheric Environ. 1967, 21(12), 2681–2693, doi:10.1016/0004-6981(87)90200-9, 1987.

Mantis, H. T., Repapis, C. C., Zerefos, C. S. and Ziomas, J. C.: Assessment of the Potential for Photochemical Air Pollution in Athens: A Comparison of Emissions and Air-Pollutant Levels in Athens with Those in Los Angeles, J. Appl. Meteorol., 31(12), 1467–1476, doi:10.1175/1520-0450(1992)031<1467:AOTPFP>2.0.CO;2, 1992.

Melas, D., Ziomas, I., Klemm, O. and Zerefos, C. S.: Anatomy of the sea-breeze circulation in Athens area under weak large-scale ambient winds, Atmos. Environ., 32(12), 2223–2237, doi:10.1016/S1352-2310(97)00420-2, 1998.

Moschonas, N. and Glavas, S.: C3□C10 hydrocarbons in the atmosphere of Athens, Greece, Atmos. Environ., 30(15), 2769–2772, doi:10.1016/1352-2310(95)00488-2, 1996.

Moschonas, N., Glavas, S. and Kouimtzis, T.: C3 to C9 hydrocarbon measurements in the two largest cities of Greece, Athens and Thessaloniki. Calculation of hydrocarbon emissions by species. Derivation of hydroxyl radical concentrations, Sci. Total Environ., 271(1), 117–133, doi:10.1016/S0048-9697(00)00838-X, 2001.

Nester, K.: Influence of sea breeze flows on air pollution over the attica peninsula, Atmos. Environ., 29(24), 3655–3670, doi:10.1016/1352-2310(95)98468-N, 1995.

Paraskevopoulou, D., Liakakou, E., Gerasopoulos, E. and Mihalopoulos, N.: Sources of atmospheric aerosol from long-term measurements (5years) of chemical composition in Athens, Greece, Sci. Total Environ., 527(Supplement C), 165–178, doi:10.1016/j.scitotenv.2015.04.022, 2015.

Rappenglück, B., Fabian, P., Kalabokas, P., Viras, L. G. and Ziomas, I. C.: Quasi-continuous measurements of non-methane hydrocarbons (NMHC) in the Greater Athens area during medcaphot-trace, Atmos. Environ., 32(12), 2103–2121, doi:10.1016/S1352-2310(97)00430-5, 1998.

Rappenglück, B., Kourtidis, K., Melas, D. and Fabian, P.: Observations of biogenic and anthropogenic NMHC in the greater Athens area during the PAUR campaign, Phys. Chem. Earth Part B Hydrol. Oceans Atmosphere, 24(6), 717–724, doi:10.1016/S1464-1909(99)00071-4, 1999.

Saffari, A., Daher, N., Samara, C., Voutsa, D., Kouras, A., Manoli, E., Karagkiozidou, O., Vlachokostas, C., Moussiopoulos, N., Shafer, M. M., Schauer, J. J. and Sioutas, C.: Increased Biomass Burning Due to the Economic Crisis in Greece and Its Adverse Impact on Wintertime Air Quality in Thessaloniki, Environ. Sci. Technol., 47(23), 13313–13320, doi:10.1021/es403847h, 2013.

Salameh, T., Sauvage, S., Afif, C., Borbon, A., Léonardis, T., Brioude, J., Waked, A. and Locoge, N.: Exploring the seasonal NMHC distribution in an urban area of the Middle East during ECOCEM campaigns: very high loadings dominated by local emissions and dynamics, Environ. Chem., 12(3), 316–328, doi:10.1071/EN14154, 2015.

Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P. and Galloo, J. C.: Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas, Atmos. Environ., 43(15), 2430–2441, doi:10.1016/j.atmosenv.2009.02.001, 2009.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons., 2016.

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

Wiley: Composition Chemistry, and Climate of the Atmosphere - Hanwant B. Singh, [online] Available from: http://www.wiley.com/WileyCDA/WileyTitle/productCd-0471285145.html.

WHO - IARC: Outdoor air pollution a leading environmental cause of cancer deaths, Press Release n°221, **2013**

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

.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

Atmospheric Chemistry and Physics Discussions

Table 1. Comparisons of NMHC levels between this study and previous studies in Athens, Greece and worldwide. Monitoring/analyzing techniques and sampling frequency 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	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 samplin, 12 canisters)	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	16 October – 22 November 2010 Paris, France	28 January – 12 February 2012 Beirut, Libanon	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)	Les Halles station (Urban background)	Saint Joseph University (Suburban)	Bilbao (Urban centre)	Thissio (Urban background)			
								Mean	Median	Min	Max
	ppbv		ppbv	ppbv	ppb	ppb	ppbv	ppb			
Ethane					3.8	2.8	2.5-3.5	6.9	4.8	0.8	39.9
Ethylene					1.3	2.1	2-2.3	5.6	3.0	0.3	35.2
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	15.8
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	4.4	2.7	0.1	29.1
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)		0.1	0.1		0.2	0.1	0.01	1.43
Benzene	11.7	2.5	2.12	5.0	0.4	0.5	0.5 - 1	0.8	0.5	0	5.3
Toluene	21.2	6.7	1.15	14.3	0.8	2.2	2 – 2.6	2.2	1.0	0.1	13.7

[a] ethane N= 2848, ethylene N=2863, propane N=2866, propene N=2846, i-Butane N=2881, n-butane N=2884, acetylene N=2862, i-pentane N=2874, n-pentane N=2859, isoprene N=264, benzene N=2685, toluene N=637.

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

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

Atmospheric Chemistry and Physics Discussions

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

Total	Ethane	Ethylene	Propane	Propene	i-Butane	n-Butane	Acetylene	i-Pentane	n-Pentane	Benzene	Toluene	BC	BCwb	BCff	CO	NO
Ethane	1.00															
Ethylene	0.87	1.00														
Propane	0.78	0.87	1.00													
Propene	0.79	0.92	0.92	1.00												
i-Butane	0.59	0.78	0.91	0.84	1.00											
n-Butane	0.62	0.80	0.93	0.86	0.99	1.00										
Acetylene	0.72	0.77	0.76	0.78	0.71	0.72	1.00									
i-Pentane	0.44	0.67	0.78	0.73	0.92	0.91	0.59	1.00								
n-Pentane	0.46	0.67	0.80	0.77	0.94	0.92	0.64	0.92	1.00							
Benzene	0.65	0.85	0.86	0.93	0.83	0.85	0.71	0.75	0.79	1.00						
Toluene	0.66	0.80	0.78	0.83	0.86	0.85	0.58	0.87	0.84	0.78	1.00					
BC	0.82	0.88	0.84	0.92	0.78	0.79	0.75	0.71	0.72	0.86	0.82	1.00				
BCwb	0.78	0.75	0.66	0.79	0.49	0.52	0.55	0.42	0.41	0.69	0.52	0.83	1.00			
BCff	0.67	0.80	0.80	0.81	0.84	0.83	0.74	0.79	0.82	0.79	0.86	0.91	0.56	1.00		
CO	0.76	0.88	0.89	0.92	0.85	0.86	0.78	0.76	0.79	0.90	0.85	0.94	0.75	0.87	1.00	
NO	0.72	0.81	0.81	0.81	0.82	0.83	0.73	0.80	0.77	0.79	0.82	0.83	0.57	0.85	0.88	1.00

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

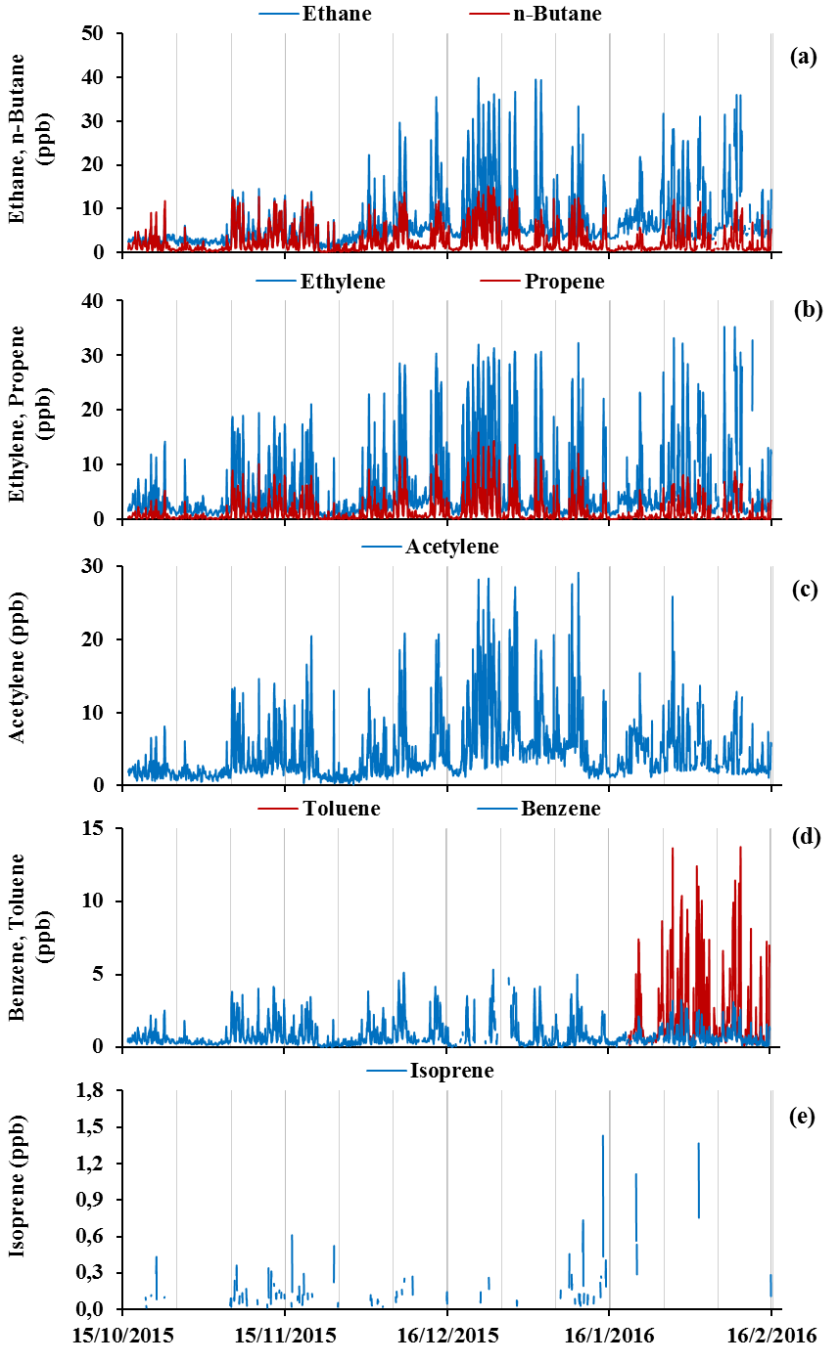

Figure 1: Temporal variability of (a) ethane and n-butane, (b) ethylene and propene, (c) acetylene, (d) benzene and toluene and (e) isoprene, based on hourly averaged levels for the period 16 October 2015 - 15 February 2016, at NOA's urban background site in Thissio, downtown Athens.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

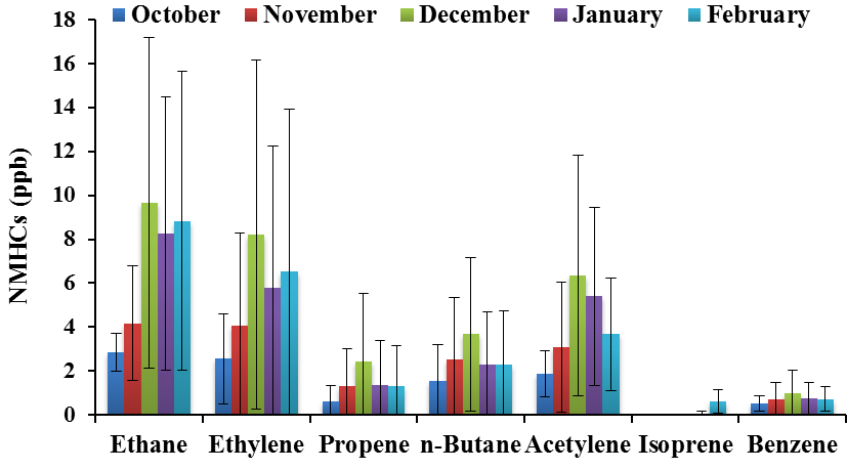

Figure 2. Monthly mean concentrations of ethane, ethylene, propene, n-butane, acetylene, isoprene and benzene. The bars stand for standard deviations.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

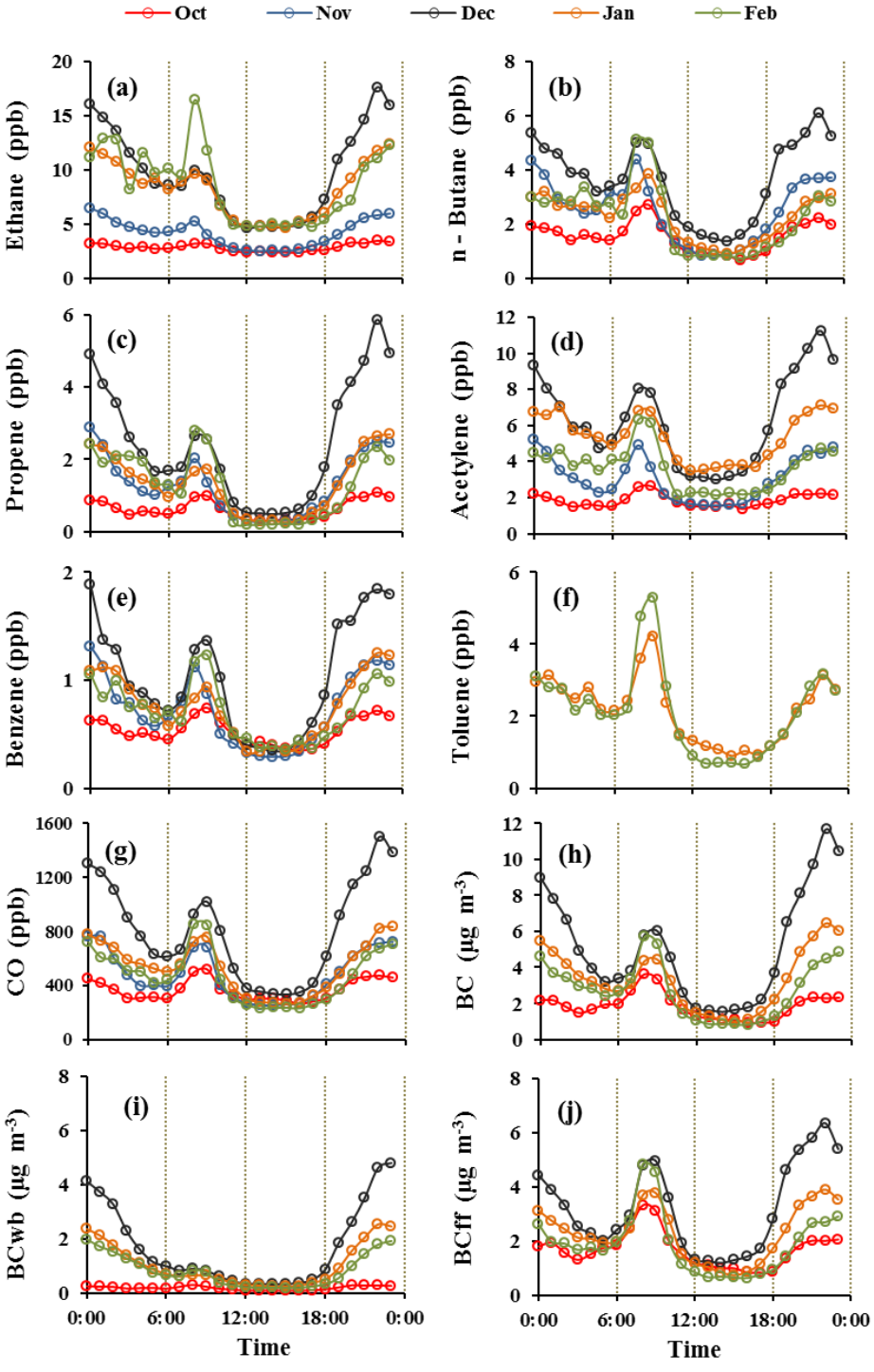

Figure 3. Monthly diurnal variability of (a) ethane, (b) n-butane, (c) propene, (d) acetylene, (e) benzene, (f) toluene, g) CO, h) BC, i) BC_{wb} and j) BC_{ff} based on hourly averaged values.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

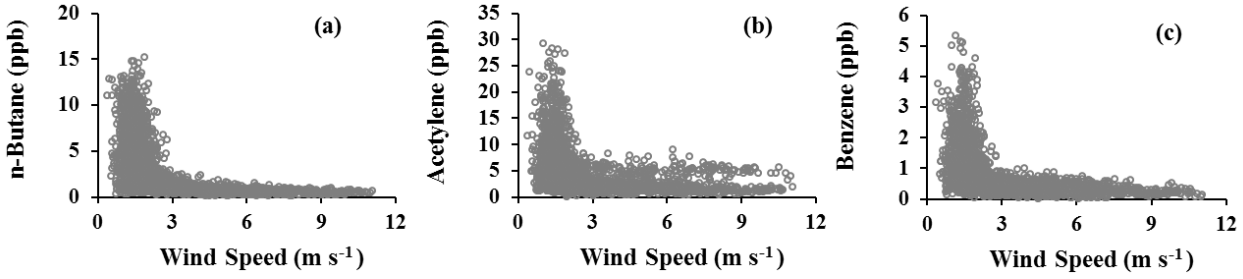

Figure 4. Variability of (a) n-butane, (b) acetylene and (c) benzene relatively to wind speed for the total period of measurements.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

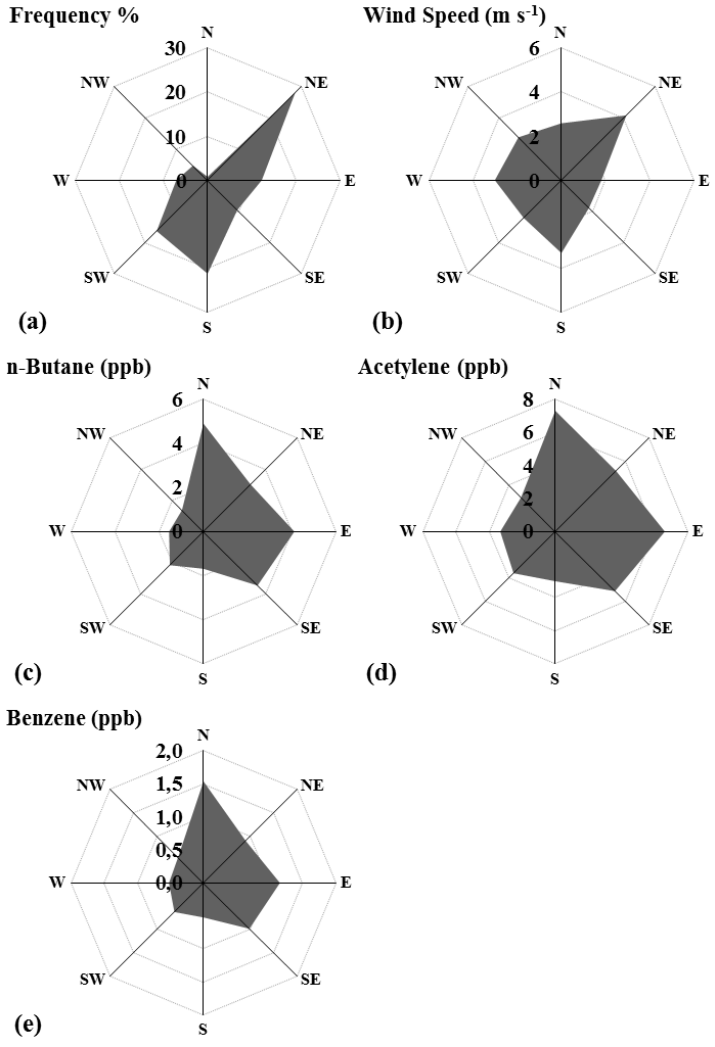

Figure 5. Variability of (a) wind sector frequency of occurrence and (b) wind speed of air masses reaching the Thissio site; and (c) n-butane, (d) acetylene and (e) benzene concentrations, relatively to wind direction for the total period of measurements.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

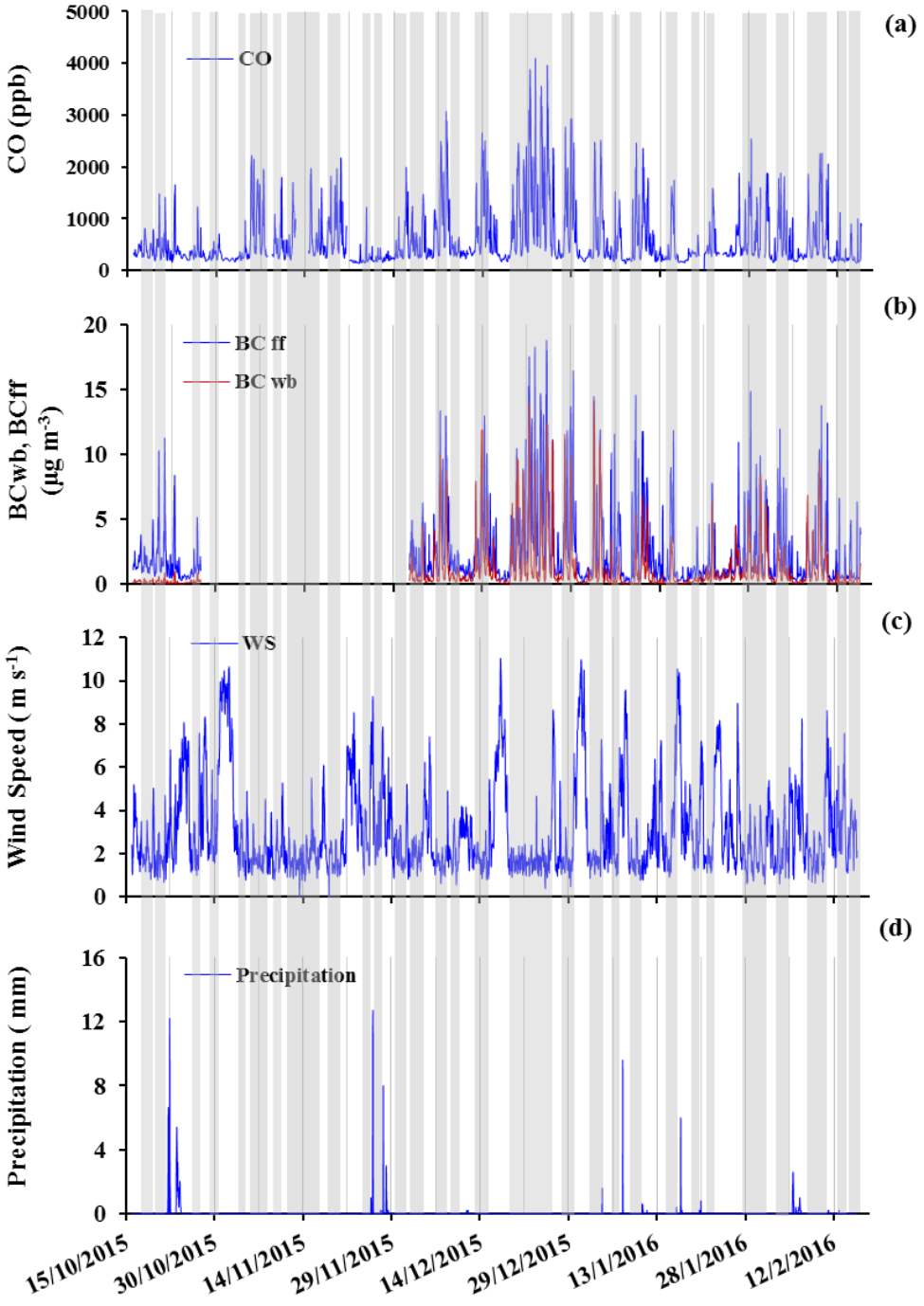

Figure 6. Temporal variability of (a) CO , (b) BC_{wb} and BC_{ff} fractions, (c) wind speed and (d) precipitation for the experimental period. Grey frames correspond to smog periods (SP), while the remaining part to non-smog periods (nSP).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

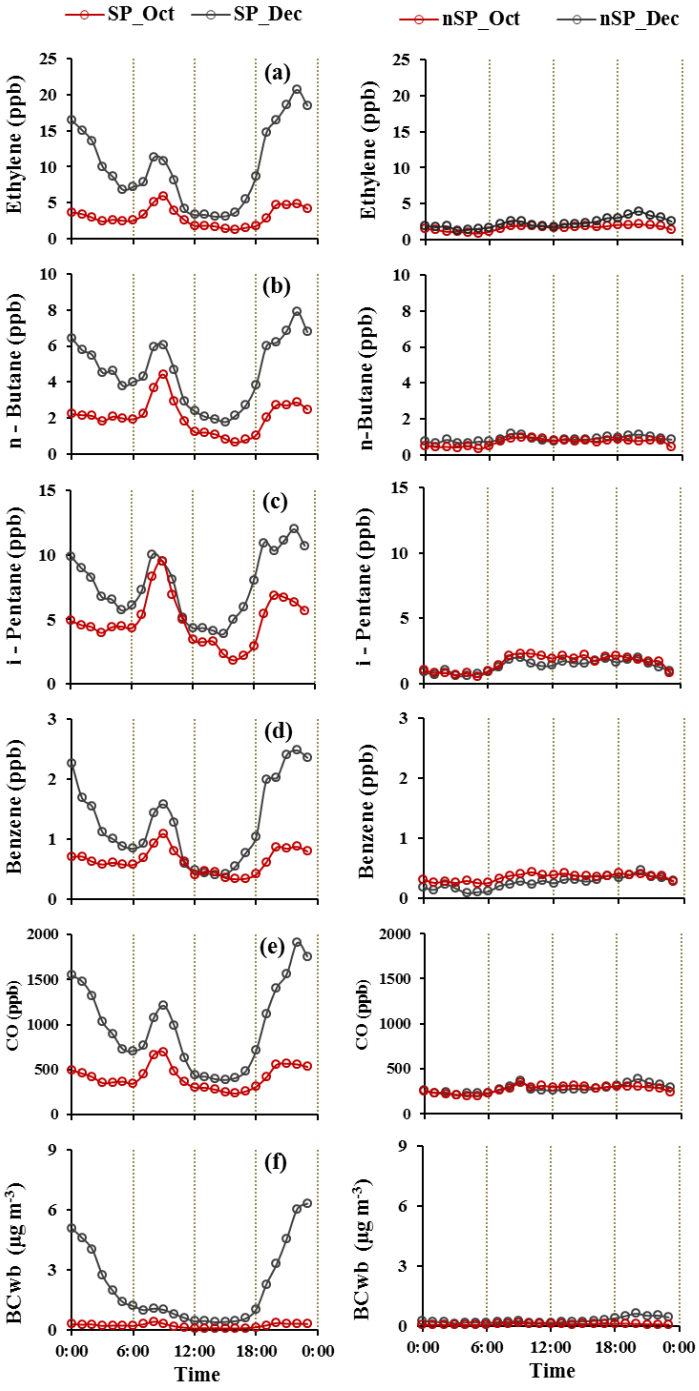

Figure 7. Diurnal patterns of (a) ethylene, (b) n-butane, (c) i-pentane, (d) benzene, (e) CO, (f) BC_{wb} during the SP (left column) and the nSP (right column) periods identified during October 2015 (red) and December 2015 (black) respectively.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 22 November 2017

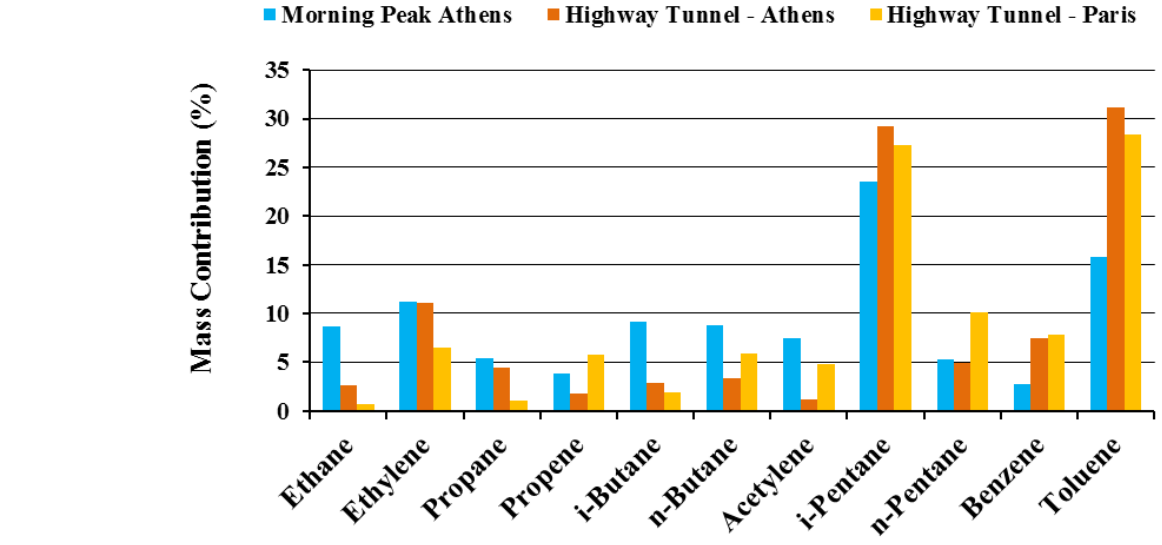

Figure 8. % Mass contribution of the measured NMHCs during the morning peak (07:00 – 10:00LT, median values, blue color), in a highway tunnel in GAA (orange color) and a highway tunnel close to Paris (yellow color).

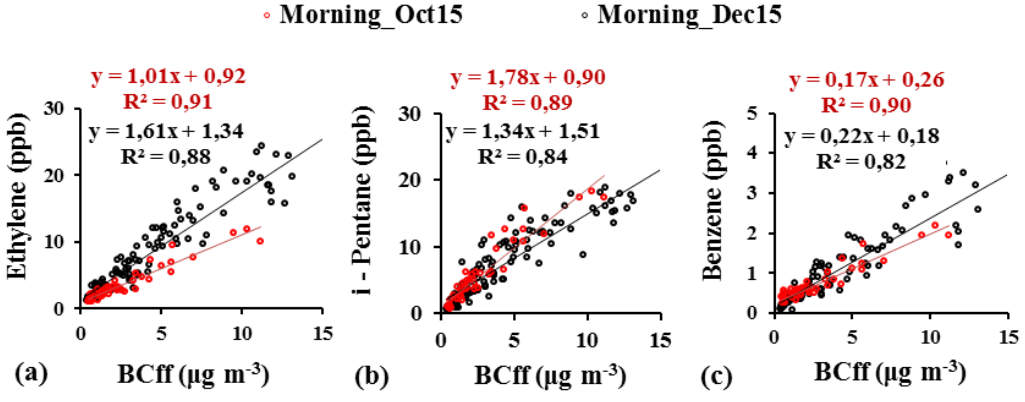

Figure 9. Regressions between ethylene, i-pentane, and benzene versus BC_{ff} (a-c) for the morning period (07:00 – 10:00LT) in October and December 2015.

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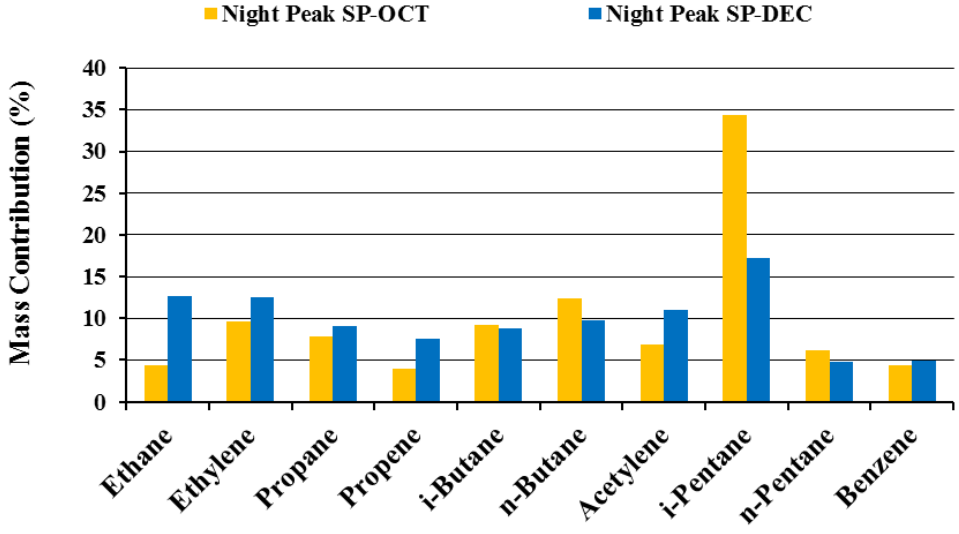

Figure 10. % Mass contribution of the measured NMHCs during the night peak (18:00 – 05:00LT) for the SP of October (yellow) and the SP of December (black color).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-936
Manuscript under review for journal Atmos. Chem. Phys.
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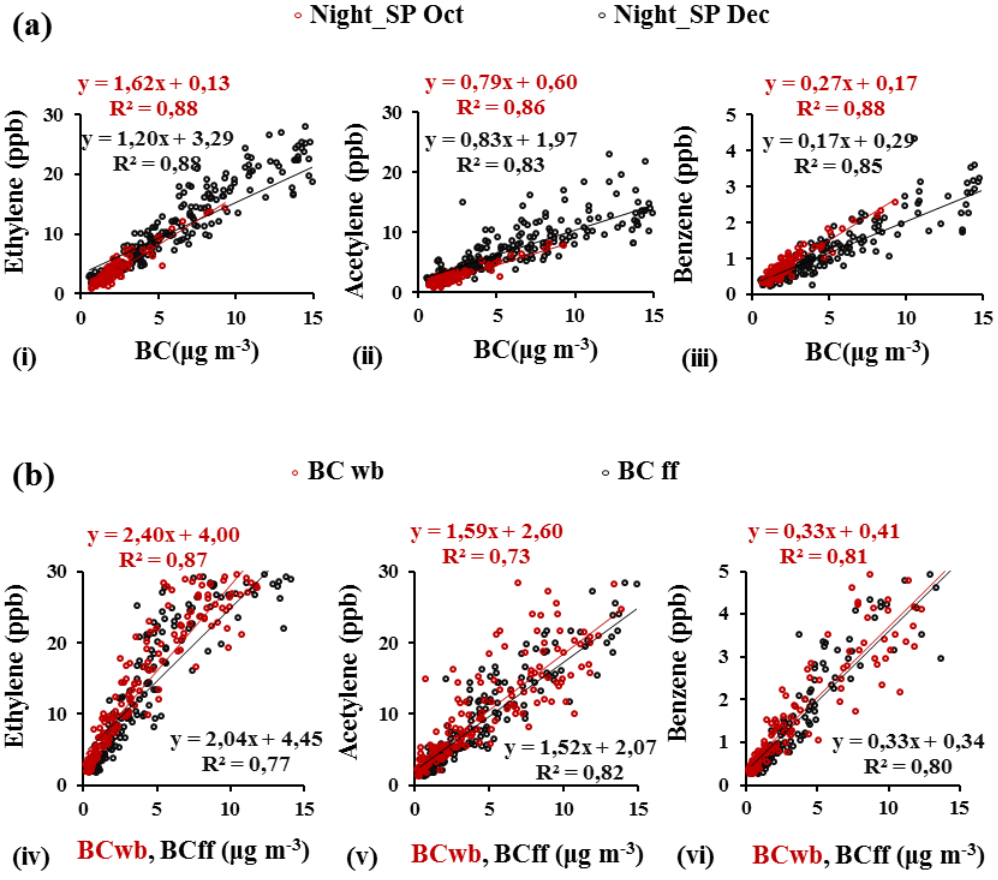

Figure 11. Regressions between ethylene, acetylene and benzene (a) against BC (i-iii) for the night period (18:00 – 05:00LT) of SP October and December 2015 and (b) against BC_{wb} (red) and BC_{ff} (black) for the night period (22:00 – 04:00LT) of SP December 2015.