Response to the Comments of Referee #1

General Comments:

(1) The paper by Kaltsonoudis et al. focuses on VOC composition measurements (performed using proton transfer reaction mass spectrometry) in Greece during the summer of 2012 and winter of 2013 and PMF source apportionment analyses using the measured datasets. The measurements in summer were conducted at two "background" sites in Patras (in June) and Athens (in July) during 2012, while the measurements in winter were conducted near the city centre of Athens in 2013. The paper is written well and nicely structured. The reported VOC data and analyses will be useful for the atmospheric chemistry community. I recommend publishing the paper in ACP after the following major concerns have been addressed by the authors.

We appreciate the constructive comments and suggestions by the referee. We have done our best to address all of them.

Major Concerns:

(2) Experimental details: Section 2.0. While the authors have done a good job in providing an overview of the measurements, I find the current version "sketchy" when it comes to critical details pertaining to the PTR-MS measurements. The authors should provide additional information and clarify certain issues related to the measured datasets.

We have added the requested experimental information related to the PTR-MS measurements. Specific details are provided below.

(i) What was the residence time of air in the Teflon inlets during each of the PTR-MS deployments? What was the dwell time per m/z when the PTR-MS was used in the mass scan mode? The authors should specify the mass range intervals that were monitored in the 10 s measurement cycle.

The residence times for air through the sampling lines prior to the PTR-MS were 10 s for the Patras summer campaign, 12 s for the Athens summer campaign, and 16 s for the Athens winter campaign. The reference to the mass scan mode is a typographic error. The measurements were conducted in the multiple ion detection (MID) mode. The dwell times for these MID mode measurements were in the range of 5-500 ms. A 200 ms dwell time was used for most of the reported m/z values. For some of the higher m/z values a dwell time of 500 ms was selected. The dwell time for the m/z values 21, 30, 32 and 37 were 200, 5, 5 and 10 ms respectively in all three campaigns. The rest time (up to the 10 s value) were made up by the pauses (pause cal. function of the PTR-MS) during the m/z selections of the quadrupole. We have corrected the typo and added the above information in the revised manuscript.

(ii) How often were the calibrations performed and did the sensitivities change over the course of the different deployments? Were humidity effects on the sensitivities of individual compounds considered during the calibration experiments? If not, how have these been addressed? The calculation of the concentrations for the calibrated compounds does not appear to have been normalized to the primary hydronium ion signal (that is cps/ppb appears to have been used instead of ncps /ppb). This could have a significant effect on the measurements depending on the difference in intensity of the primary ion signal between the calibration experiments and the ambient measurements. What are the detection limits for the compounds? The authors mention that for compounds where calibration was not possible, they used a value of k = 2 x

10^9 cm^3 s^{-1}. They should also provide the Equation used by them in this case or cite the work listing the Equation at this place.

Calibrations were performed once per week. The sensitivities for the reported compounds for all campaigns were in the range of 4.7 to 24 ncps. For example the sensitivity for acetonitrile for the three campaigns was 15.8-19.8 ncps, for benzene 9.5-13.3 ncps and for a-pinene 4.7-6.8 ncps. These values did not change significantly (less than 40%) during the measurements. The detection limits for the calibrated compounds based on Karl et al. (2003) were in the range of 34 to 97 ppt with the exception of methanol which ranged from 188 to 307 ppt for the three campaigns. Humidity effects on the sensitivities of the individual compounds were not considered during the calibrations. A precision calibrator (Teledyne, model 702) was used for the dilution of the VOC standard with VOC free air (using a Supelco filter). This calibrator type does not make adjustments for the humidity. The ratio of m/z 37 to m/z 19 was 0.039 ± 0.009 during the Patras summer campaign, 0.044 ± 0.012 during the Athens summer campaign, and 0.038 ± 0.008 during the Athens winter campaign. In all campaigns the m/z 37 to m/z 19 ratio was always less than 0.06 (typically ranging from 0.025 to 0.05). This ratio is considered low and stable, thus no corrections were applied for the $H_3O^+(H_2O)$ ion. The concentrations of all compounds were normalized to the primary hydronium ion signal (please see Equations 1 and 2 of the revised manuscript). For compounds for which calibration was not possible, the corresponding mixing ratios were estimated based on Equation 3 of Taipale et al. (2008). The above additional information and equations have been added to the revised manuscript.

(iii) It is mentioned that similar instrumentation was used for the winter deployment. Please clarify whether it was the same PTR-MS instrument?

It was the same PTR-MS instrument. This is now clarified in the revised paper.

(iv) PTR-MS instrumental background measurements: It is mentioned that "blanks" were measured by passing the air through a Supelco activated charcoal filter. The more widely used method in the measurement community is to use a heated Pt/Pd catalyst (or catalytic convertor) for generating the background air free of the relevant VOCs, as the activated charcoal filters are not good at removing oxygenated VOCs such as methanol. How did the authors ensure that they obtained good background measurements for such compounds (e.g. methanol). Note that humidity effects also affect the background of methanol strongly (see de Gouw and Warneke, 2007).

This is a valid concern. Unfortunately a catalytic convertor was not available for generating VOC-free air. Instead the activated charcoal filter (Supelco) was used as the final purification step of the "clean" air. This may not have been sufficient to generate methanol - free air and could have added additional uncertainty to our methanol measurements. Given that the methanol measurements are of secondary importance for the purposes of this manuscript we have not included them in the revised paper.

(v) The authors acknowledge that the m/z =69 signal is a mix of furan and isoprene. The diurnal variability of the signal does indicate most of it is likely isoprene for the summertime deployments. Recent work using a high mass resolution PTR-TOF-MS instrument in the Kathmandu Valley (Sarkar et al., 2016) and previous laboratory measurements of biomass fuel emissions (Akagi et al. 2011) have shown that in air influenced by biomass burning, furan is still the minor contributor (25-30%) only. The authors may like to include and discuss the above works which support their contention.

This is a good suggestion. Since the quadrupole of the PTR-MS cannot distinguish between the different species in several m/z values (including m/z 69) we have chosen to report most of the common atmospheric compounds detected in the corresponding m/z values. For the summer campaigns the m/z 69 diurnal profile indicates that isoprene is the dominant molecule for this m/z. For the Athens winter campaign where biomass burning had a strong influence on the reported concentrations of m/z 69 we both report the corresponding atmospheric compounds and also comment that isoprene is the predominant compound for m/z 69. We have added discussion of this point in the revised paper together with the corresponding references suggested by the reviewer.

(3) PMF analyses: The authors should mention whether mass concentrations of VOCs were used as input for the PMF model. If so, were temperature and pressure corrections taken into account? A sentence providing the correlation between the estimated total VOC concentrations (PMF) Vs the observed total VOC concentrations (on x axis) should be added.

Mixing ratios (ppb) were used as the input for the PMF model and therefore temperature and pressure corrections were not applied. We have added a figure (Figure S47) in the Supplementary Material showing the correlation between the total VOC concentrations estimated by the PMF model versus the measured ones for the three campaigns. The estimated concentrations of the PMF model correlated well (R^2 ranged from 0.994 to 0.999) with the measured values for the three campaigns. We have added a sentence with the correlation results and the corresponding figure to the revised manuscript.

(4) The PMF analyses should be improved by addition of conditional probability function analyses (see Fleming et al. 2012). This will yield potential wind direction dependence of sources and could be particularly useful for identifying strong point or area sources influencing the measurement site. During their summer deployments, the authors observed significantly higher methanol at one of the sites relative to the other. Some explanation regarding the possible cause/causes is required and this may help.

The origin of the air masses during the three campaigns has been investigated using FLEXPART and HYSPLIT. These data are available in the SI of Kostenidou et al. (2015) for the summer measurements in Patras and Athens and in Florou et al. (2016) for the winter measurements. The dependence of the PMF Factors on wind direction has been also investigated with rose plots. The corresponding rose plots have been included in the revised SI. We have added a paragraph discussing these results in the revised paper.

(5) The inclusion of isoprene in the o-BVOC factor does not seem reasonable as being a hydrocarbon, isoprene cannot possibly be produced by atmospheric oxidation. The authors should clarify the same in the discussion.

We clarify in the revised paper that the b-OVOC factor for the Patras summer campaign includes mainly products of the oxidation of biogenic VOCs, but also some primary VOCs. Approximately 70% of the measured isoprene during the Patras summer campaign was included by the PMF analysis in the BVOC factor (see also Figure S20 in the SI). The remaining 30% was included in other factors, with 15% in the b-OVOC factor. This small amount of isoprene assigned to this factor can be justified either as direct biogenic emissions that have originated far from the area close to the measurement site and have not yet reacted or it can be due to the uncertainties of the PMF analysis. The factor was named b-OVOC (biogenic oxygenated VOCs) due to the strong influence by formic acid, acetone and acetic acid. We have added the above clarifications to the paper.

(6) I am somewhat surprised by the absence of fuel evaporation as a source. Considering previous studies in Paris and several other urban sites, it is important for the authors to discuss the absence of such a source.
Most of the urban source apportionment VOC studies have separated the anthropogenic VOCs into several categories including fuel evaporation, industrial solvents, diesel exhaust emissions, etc. (Brown et al., 2007; Tolga et al., 2007; Badol et al., 2008; Leuchner and Rappengluck, 2010; Yurdakul et al., 2013; Boynard et al., 2014; Wang et al., 2014). In the present study the PMF analysis did not produce such factors since light alkanes were not measured, in contrast to the previous studies based on gas chromatography. The vehicular exhaust and LPG sources widely reported in the literature include a large fraction of these species, thus such a separation was not favored by the PMF analysis. We have included this important point in a new paragraph synthesizing the results of the PMF analysis.

(7) Table 4: Authors may want to compare their ERs and EFs with values reported for other types of fuels (see Yokelson et al. 2013 and Stockwell et al. 2015) in addition to the Warneke et al. study already considered. This would enable them to include more fuel types for comparison with their ERs and EFs.
We have followed the reviewer's suggestion and added the comparisons with the results of Yogelson et al. (2013) and Stockwell et al. (2015). Table 4 has been replaced by two new tables (one for emission ratios and one for emission factors) in the revised paper.

Suggestions:

(8) While the authors have done a really good job in comparing their measurements to other studies in the Mediterranean region, a global perspective in terms of a comparison of the VOC concentration rankings with other sites in the world in summer (see for e.g. Table 3 of Sinha et al., 2014) and winter (see for e.g Figure 5 of Sarkar et al., 2016) would add a global flavor. A new Figure or Table is not necessary but a few sentences comparing the concentration ranking of VOCs observed during their deployments in Greece with similar recent measurements reported from some of the other urban /suburban sites elsewhere in the world would certainly help provide a more general perspective on the relative source strengths and ambient VOC composition in summer and winter, which is one of the primary objectives of their work. For example, it is interesting to note that the relative concentration ranking of VOCs in the Kathmandu valley in winter is quite different from that in Athens.
We have extended our comparison to include other areas and comparisons with the results of Sinha et al. (2014) and Sarkar et al. (2016).

(9) Discussion related to the Traffic source: A recent work published in GRL (see Link et al. 2016) reports that precursor compounds emitted from diesel vehicles can photo-chemically produce isocyanic acid (a compound recently reported by Chandra and Sinha, 2016 and Sarkar et al. 2016 using the PTR-MS technique in ambient field studies after the first field observations reported by Roberts et al., 2011 using negative ion CIMS). As the authors operated their PTR-MS in mass scan mode, it would be interesting to know if they observed any detectable signal at m/z 44 and whether the signal showed any diurnal variability. As an extremely toxic compound that can be measured using the PTR-MS, this information would certainly be useful to the readers.

Unfortunately we only have limited mass scan mode measurements (see also our response to Comment 2i). During each campaign we used the mass scan mode for 10-15 min every 2-3 days in order to take a look beyond the normally measured m/z values. These data were not sufficient to reach any robust conclusion regarding isocyanic acid. For example, a mass scan measurement during the morning rush hour (10:00) in Athens during the winter gave concentrations for m/z 44 lower than 60-80 ppt, while there was 1.7 ppb of benzene and 3.9 ppb of toluene during the same period.

Minor comments:

(10) Line 1; Page 5: Rate constants are normally reported in italics and small letters.. ..so it should be “ *k*” instead of “K”.

We have replaced “K” with “*k*”.

(11) Line 20, Page 6: Why is the second traffic peak at 22:00 hr? This does not seem like the normal evening traffic rush hour period when office goers return home. Please clarify.

This evening traffic peak is a little after the closing of the various merchant shops in the summertime and is consistent with the increased traffic observed during these periods as both the customers and owners return home. Kostenidou et al. (2015) observed HOA and BC peaks during the same period in both Athens and Patras. We have added an explanation of this peak to the revised paper.

(12) Line 30 Page 6: Benzene/Toluene ratio as a clock: The authors need to be careful here as some biomass sources can emit more benzene relative to toluene rendering the use of the T/B ratios as the sole criteria for aged air masses invalid, in particular when transported air masses across large distances are a strong possibility.

During the Patras summer campaign we could not identify any significant biomass burning sources either close to the measurement site or transported from larger distances. The acetonitrile levels were low and there were no significant peaks indicating biomass buring sources. Additionally the AMS measurements (Kostenidou et al., 2015) did not show any biomass burning related factor in the PMF analysis. We have added however a qualifier that this analysis assumes no influence from biomass burning sources.

Responses to the Comments of Referee #2

This papers presents the results of VOC measurements using a PTRMS in two of the largest cities in Greece (Athens and Patra) during the summer and winter seasons. The paper presents a good overview of the most dominant VOCs observed and applies a standard PMF analysis to discuss the sources of VOCs. This is a well-organized and nicely written manuscript. These types of PMF analysis on gas phase measurements can be a powerful tool for understanding sources and is a generally underutilized tool. This paper provides a nice frame work for future PTR studies which will utilize PMF in a similar fashion.

General Comments

(1) In generally I find the manuscript to be quite complete considering the extent of the data set collected. I have a few technical comments that will follow. My biggest comment is that a summary figure similar in design to Figure S20 would be highly beneficial in the main text. This paper ultimately focuses on using PMF to determine the impact of the various sources on ambient VOCs. In this sense a summary figure using pie charts to summarize for each measurement location and season showing the relative impact of each factor would be a great way to relay the study's results in a compact manner that is easy to digest. The figures currently in the main text show the diurnal trends of the figures nicely, but that does nothing to show the relative impacts of each factor. Addition of a figure like this and a more distilled discussion of the results from that figure would really benefit to overall clarity of the analysis.
We have followed the reviewer's suggestion and transferred this figure summarizing the PMF results from the SI to the revised paper.

(2) In general, there is a lack of discussion as to the potential for misidentification of observed m/z. The case that is most obvious is the treatment of isoprene, where the authors appropriately initially identify the potential for furan detection but end the discussion at that point. I would imagine that after performing PMF analysis and retrieving a BBVOC factor containing isoprene that the authors should discuss this 'isoprene' as potentially signal due entirely to furan, or at least partially. Continuing to label this measurement as isoprene is somewhat misleading, considering the potential overlap.
A similar point was made by Reviewer 1 (see Comment 2v). We have added discussion of the potential contributions of isoprene and furan to the signal at m/z 69 arguing that it is mostly isoprene in all of our data sets based on its diurnal profile during the summer and the biomass burning VOC literature (citations have been added) during the winter. After this discussion, our use of the term isoprene is justified.

(3) Section 2.2 on the experimental details is lacking some details on the method that are useful to the reader to understand the robustness of the measurements. Things like how long were the inlets overall in the various studies? Were the entire inlets heated to 60 C or just a subsection where the PTRMS sampled. What has been done to correct the data for humidity effects? How was the normalization of the data done? How often were calibration performed?

A subsection (approximately 1 m) of the inlet live was heated to 60 ^{0}C. Sampling lines were 6-10 m long. The residence times for air through the sampling lines prior to the PTR-MS were 10 s for the Patras summer campaign, 12 s for the Athens summer campaign, and 16 s for the Athens winter campaign. Calibrations were performed once per week. The sensitivities for the reported compounds for all campaigns were in the range of 4.7 to 24 ncps. For example the sensitivity for acetonitrile for the three campaigns was 15.8-19.8 ncps, for benzene 9.5-13.3 ncps and for a-pinene 4.7-6.8 ncps. These values did not change significantly (less than 40%) during the measurements. The detection limits for the calibrated compounds based on Karl et al. (2003) were in the range of 34 to 97 ppt with the exception of methanol which ranged from 188 to 307 ppt for the three campaigns. Humidity effects on the sensitivities of the individual compounds were not considered during the calibrations. A precision calibrator (Teledyne, model 702) was used for the dilution of the VOC standard with VOC free air (using a Supelco filter). This calibrator type does not make adjustments for the humidity. The ratio of m/z 37 to m/z 19 was 0.039 ± 0.009 during the Patras summer campaign, 0.044 ± 0.012 during the Athens summer campaign, and 0.038 ± 0.008 during the Athens winter campaign. In all campaigns the m/z 37 to m/z 19 ratio was always less than 0.06 (typically ranging from 0.025 to 0.05). This ratio is considered low and stable, thus no corrections were applied for the $H_3O^+(H_2O)$ ion. The concentrations of all compounds were normalized to the primary hydronium ion signal (please see Equations 1 and 2 of the revised manuscript). For compounds for which calibration was not possible, the corresponding mixing ratios were estimated based on Equation 3 of Taipale et al. (2008). The above additional information and equations have been added to the revised manuscript.

Specific Comments

(4) In the first sentence of the abstract, the phrase "urban background sites" is used. This is not a commonly used term that requires some explanation. It may be best to simply state and urban site. Also in that first paragraph a sentence should be added introducing the winter season measurements. The last paragraph of the abstract launches into discussion of the results of winter measurements without first indicating that they were made.
We have deleted the term "background" given that the lack of major nearby sources (e.g., roads) is also mentioned in the site description. The last paragraph of the abstract has been rewritten explaining first when and where the measurements took place.

(5) Page 2, line 12, you need a new paragraph indent.
A new paragraph indent has been added at this point.

(6) Page 3, line 18, 'emissions' should be singular.
We have corrected the typo.

(7) Page 4, line 30. It is rather well known that activated charcoal filters induce changes in humidity. As the sensitivity of the PTRMS to various species, such as methanol, is dependent on RH, how well do the authors believe they have been able to capture the true instrument background?
This point was also raised by Referee #1 (see Comment 2iv). Unfortunately a catalytic convertor was not available for generating VOC-free air. Instead the activated

charcoal filter (Supelco) was used as the final purification step of the "clean" air. This may not have been sufficient to generate methanol - free air and could have added additional uncertainty to our methanol measurements. Given that the methanol measurements are of secondary importance for the purposes of this manuscript we have not included them in the revised paper.

(8) Page 7, line 14, the comment about elevated ozone levels being a result of long range transport seemly has no support in this manuscript. How do the authors know that? Were back trajectory analyses performed? This kind of a statement needs data to support it.
The importance of the long range transport can be seen in Figure S3 of the revised paper showing the ozone concentrations during this windy period. The maximum ozone concentration was actually observed a little before the midnight of June 18. This was actually the highest ozone level during the whole measurement period. This was in contrast to the low levels of NOx and BC observed during the same period. These results shown in Figure S3 strongly support the conclusion that the high levels of ozone were due to long range transport. Similar conclusions have been reached by Kouvarakis et al. (2002) reporting measurements performed onboard a cruise ship travelling on a regular basis in the area. They concluded that long range transport is the main factor contribution to high ozone levels in eastern Greece. We have added the above arguments and the reference to the work Kouvarakis et al. (2002) in the revised paper.

(9) Page 7, line 33, suggest editing the phrase "peaked during noon at concentrations" with 'peaked at noon with concentrations"
We have made the suggested correction.

(10) Page 8, line 2, suggest reversing the order of 'significantly' and 'influenced'
We have made the suggested correction.

(11) Page 8, line 6, what spikes are being referred to here?
This refers to the elevated monoterpene concentrations at around 7:00 seen in Figure 3b. We have replaced "spikes" with "elevated concentrations" to avoid confusion.

(12) Page 8, line 23, suggest reversing the order of 'traffic' and 'hour'.
We have made the change.

(13) Page 10, line 16-17, suggest rewriting to read "These periods (Table S2) occurred during the nighttime (18:00-06:00 LT) and were associated with acetonitrile"
We have rewritten this sentence.

(14) Page 10, Section 4, I would suggest that you reverse the order of the discussion in this section to first introduce the concept and equation for calculating EF, then discuss the results. Basically swap what is on page 11 with the text on page 10.
We have followed the suggestion of the reviewer and changed the order of these sections.

(15) Page 11, line 5, suggest editing to read "For the CO2 emission factor (EFCO2) a value of 1600".

We have made this suggested change.

(16) Page 11 line 27, why was the time period of two hours chosen here? Is there a basis for this time duration, was the correlation optimized at two hours, or is there a time shift that possibly induces a better correlation?
The correlation was optimized at two hours. We have added text here to clarify this point.

(17) Page 12, line 8, Edit beginning of sentence to read "The OVOC factor".
Done.

(18) Page 13, line 31, edit to read "Mixing ratios of OVOC-2 species were elevated during the night."
We have rephrased this sentence.

(19) Page 15, line 1-4, That do you suggest that the OVOC-1 factor is? In the next paragraph you state that the OVOC-2 factor is associated with the background of VOCs but no discussion here.
Factor OVOC-1 in the Athens winter campaign could not be associated with any specific potential source. We have added this explanation in the paper.

(20) Page16, line 12, Again to reiterate an above comment calling this isoprene in the biomass burning factor is likely misleading. If the authors make a change here, an update to the manuscript tables is likely necessary.
We have replaced "isoprene" with "m/z 69" at this point. The same has been made in the section discussing the wintertime measurements in Athens.

(21) Figures 2-4, I am not sure that the main text is the appropriate place for these figures. I would either move them into the supplemental or edit the figures to include only a few key species for all three measurement sites to compare the diurnals observed in each site/season.
We believe that these figures are quite useful for the reader of the paper as they summarize the behavior of some of the major species. We have followed the reviewer's suggestion and removed
the methanol and formic acid diurnal profiles from these three figures in the revised paper.

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Temporal variability and sources of VOCs in urban areas of Eastern Mediterranean

Christos Kaltsonoudis[1,2], Evangelia Kostenidou[1], Kalliopi Florou[1,2], Magda Psichoudaki[1,2], and Spyros N. Pandis[1,2,3]

[1]Institute of Chemical Engineering Sciences, ICE-HT, Patras, 26500, Greece
[2]Department of Chemical Engineering, University of Patras, Patras, 26504, Greece
[3]Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, 15213, USA

Correspondence to: Spyros N. Pandis (spyros@chemeng.upatras.gr)

Abstract. During the summer of 2012 volatile organic compounds (VOCs) were monitored by Proton Transfer Reaction – Mass Spectrometry (PTR-MS) in urban ~~backgrounds~~ sites, in Athens and Patras, two of the largest cities in Greece. Also during the winter of 2013 PTR-MS measurements were conducted in the center of the city of Athens. Positive matrix factorization (PMF) was applied to the VOC measurements to gain insights about their sources.

In summer most of the measured VOCs were due to biogenic and traffic emissions. Isoprene, monoterpenes and several oxygenated VOCs (oVOCs) originated mainly from vegetation either directly or as oxidation products. Isoprene average concentrations in Patras and Athens were 1 ppb and 0.7 ppb respectively while the monoterpene concentrations were 0.3 ppb and 0.9 ppb respectively. Traffic was the main source of aromatic compounds during summer. For Patras and Athens the average concentrations of benzene were 0.1 ppb and 0.2 ppb, of toluene 0.3 ppb and 0.8 ppb and of the xylenes 0.3 ppb and 0.7 ppb respectively.

Winter measurements in Athens revealed that biomass burning used for residential heating was a major VOC source contributing both aromatic VOCs and biogenic compounds such as ~~isoprene and the~~ mon~~oterpenes,~~ oterpenes~~and aromatic VOCs~~. Several episodes related to biomass burning were identified and emission ratios (ER) and emission factors (EF) were estimated.

1 Introduction

VOCs play an important role in atmospheric chemistry. Their reactions with hydroxyl (OH) radicals, ozone (O_3) and nitrate (NO_3) radicals produce secondary gas- and particulate-phase species (Atkinson, 2000; Hallquist et al., 2009). Many of the VOCs present in the atmosphere have adverse effects on human health (Kampa end Castanas, 2007) with exposure to compounds such as benzene, formaldehyde, and acetaldehyde having been related to cancer (Flesca et al., 1999). The European Commission has established an average annual limit of 1.5 ppb for benzene.

VOCs may originate from both natural and anthropogenic sources. Vegetation (Kesselmeier and Staudt, 1999; Goldstein and Galbally, 2007), volcanoes (Tassi et al., 2009; 2013) and marine emissions from the decay of organic matter (Kettle and Adreade, 2000; Meskhidze and Nenes, 2007; Colomb et al., 2008) are some of the natural sources that contribute significantly to the global VOC budget. Anthropogenic emissions originate mainly from the use and production of fossil fuels, industrial processes and biofuel combustion. Biomass burning also contributes substantially both at the regional and global scales (Crutzen and Andreae, 1990; Karl et al., 2007; Koppmann, 2007).

On-line measurement techniques with high resolution, can provide valuable information about the sources of atmospheric pollutants (Goldstein and Schade, 2000; Millet et al., 2005; Slowik et al., 2010). The PTR-MS, developed by Lindeger et al. (1998), can measure continuously the levels of a range of VOCs (DeGouw and Warneke, 2007).

Several campaigns focusing on VOC levels have been conducted in the Mediterranean basin. Holzinger et al. (2005b) reported secondary production of methanol and acetone in biomass burning plumes over the eastern Mediterranean during the MINOS campaign. PTR-MS measurements during summer in the background site of Finokalia (Crete, Greece) (Salisbury et al., 2003) indicated methanol, acetone, acetonitrile, benzene and toluene concentrations of 3.3-6.1, 2.9-4.5, 0.15-0.44, 0.13-0.38 and 0.04-0.08 ppb respectively. Davison et al. (2009) studied the concentration and fluxes of biogenic VOCs in a Mediterranean ecosystem in west Italy during May-June 2007. Median concentrations of 1.6-3.5 ppb for methanol, 0.4-1.3 ppb for acetaldehyde, 1.0-2.0 ppb for acetone, 0.1-0.14 ppb for isoprene and 0.2-0.3 ppb for the monoterpenes were reported. Seco et al. (2011) compared the summer and winter VOC concentrations in a forest site 50 km away from Barcelona. Aromatic VOCs showed small variations between the 2 periods while biogenic VOCs (bVOCs) and oxygenated VOCs (oVOCs), were elevated during summer mainly due to higher physiological activity and faster photochemistry.

In addition real-time measurements have been reported for urban or semi-urban environments in the Mediterranean. Filella and Penuelas (2006) studied the sources and variations of VOCs by PTR-MS at a semi urban site in Barcelona. Aromatic species such as toluene and benzene had diurnal patterns typical of traffic intensity. Their concentrations were higher during December and March. Biogenic species such as isoprene and monoterpenes had variable diurnal profiles during the four measurement periods. The isoprene diurnal cycle suggested considerable contribution from anthropogenic sources. Monoterpenes had higher concentrations at night, decreasing in the morning until midday and increasing again in the evening. For some periods a peak also occurred during morning hours (06:00-09:00 LT), which was attributed to temperature-dependent emissions. Methanol, acetone and acetaldehyde levels were influenced by biogenic sources during summer. In a study at two sites in the city of Athens Rappengluck et al. (1998) monitored VOCs continuously over a 30-day late summer period in 1994 by gas chromatography (GC). The C_4-C_{12} hydrocarbons measured were strongly related to traffic emissions.

Source apportionment analysis has been applied to VOC data sets in order to quantify the contributions of the different VOC sources (Millet et al., 2005; Brown et al., 2007; Vlasenko et al., 2009; Yuan et al., 2012). Slowick et al. (2010) performed PMF analysis of a PTR-MS dataset as well as a unified AMS/PTR-MS dataset over a two week period in Toronto Canada. PTR-MS data included ten mass to charge ratios (*m/z*). Factors related to traffic, long-range transport, local oxidation, and other sources were reported. Crippa et al. (2013) also performed PMF analysis on an AMS/PTR-MS unified dataset for the city of Paris during the MEGAPOLI project (summer 2009 and winter 2010 campaigns). The resulting common factors associated a large percentage of the aromatic VOCs with the hydrocarbon-like organic aerosol (HOA) during summer, while isoprene and the monoterpenes were mainly related with the semi-volatile oxygenated organic aerosol (SV-OOA). For the winter period wood burning also contributed to the levels of the above species. Yuan et al. (2012) reported that reactions interfere with the PMF analysis of VOCs, proposing that one source can yield several factors at different stages of photochemical processing.

Despite the previous efforts, little is known concerning the current VOC sources in urban areas of the eastern Mediterranean. Elevated PM concentrations have been detected in many urban areas (Pikridas et al., 2013) but the corresponding VOC emission~~s~~ and concentrations have not been quantified. Enhanced sunlight intensity, higher temperature and O_3 concentrations during summer promote the emissions and oxidation of several VOCs. The aim of this work is to provide insights about the current VOC composition and origin in urban areas in the Eastern Mediterranean during summer and winter. Another objective of the present study is to assess the impact of residential biomass burning for wintertime VOC levels in these urban areas.

2 Experimental

2.1 Sampling sites

Summer measurements in Patras (population 300,000) were conducted during 11 - 26 June 2012 in the Institute of Chemical Engineering Sciences (ICE-HT), located 8 km northeast of the city center (lat. 38.298, lon. 21.809, elevation 100 m). The area is surrounded by low vegetation and olive tree fields. The Athens (population 4 million) summer campaign was conducted between 3 and 26 July 2012 at the Demokritos National Center for Scientific Research in Athens (N.C.S.R.), which is located 8 km from the city center (lat. 37.995°, lon. 23.816°, elevation 280 m) at the foothills of a mountain covered with pine vegetation. For the Athens winter campaign, the National Observatory of Athens (N.O.A.) (lat. 37.973, lon. 23.718, elevation 110 m) was selected due to its proximity to the city centre (<1.5 km). The selected urban ~~background~~ site is located on top of a small hill away from major city roads. The Athens winter campaign took place from January 9 to February 6, 2013. The locations of all sampling sites are presented in Figure 1.

2.2 Experimental setup

Patras summer campaign: VOC concentrations were monitored by a PTR-MS (PTR-QMS 500, Ionicon Analytik). A High Resolution–Time of Flight–Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research) was used for the characterization of the aerosol composition. A Multi Angle Absorption Photometer (MAAP 5012, Thermo Scientific) monitored the black carbon (BC) concentration. A series of gas monitors was used for measuring nitrogen oxides (NO_x), O_3 and sulfur dioxide (SO_2)

(API Teledyne, models T201, 400E and 100EU respectively). A Scanning Mobility Particle Sizer (SMPS) provided the number size distributions (TSI, models 3080 and 3787). Meteorological variables and sunlight intensity were also measured. The sampling was conducted at approximately 15 m above ground. All gas species were sampled through Teflon (PTFE) tubing while all particulate species were sampled through 3/8 in copper tubing.

Athens summer campaign: The same instrumentation (PTR-MS and HR-ToF-AMS) was used for the Athens summer campaign. BC concentration was provided by an aethalometer operating at 880 nm (Magee Scientific, AE31). An SMPS measured the particulate number distributions (model 3022 TSI, custom DMA). A $PM_{2.5}$ cyclone and a silica drier were installed prior to the SMPS and the aethalometer. The PTR-MS and AMS were measuring from inside the mobile laboratory of the Laboratory of Air Quality Studies (LAQS) parked next the N.C.S.R. station. Sampling for these instruments was conducted at 6 m above ground. For the PTR-MS sampling 1/4 in PTFE tubing was used. For the AMS 3/8 in copper tubing was selected. O_3 and NO_x concentrations were measured by the Ministry of Environment, Energy and Climate Change at an adjacent (300 m away) station.

Athens winter campaign: The ~~instrumentation was similar to that of the~~same instrumentation used was the same as in the Patras summer campaign~~ was used~~. Additionally carbon monoxide (CO) and carbon dioxide (CO_2) were monitored (API Teledyne, models 300E and T360 respectively). A Horiba monitor (model APSA 365) was used for the SO_2 measurements. Meteorological data were obtained by the National Observatory of Athens. All sampling inlets were approximately 6 m above ground.

PTR-MS operation: In all three campaigns, H_3O^+ was used as the reaction reagent for the PTR-MS. The drift tube was operated at a pressure of 2.2-2.3 mbar and its voltage was 600 V. The inlet flow was 0.5 L min^{-1} and the inlet tube and reaction chamber were heated to 60 ^{0}C. The residence times ~~for air~~ in~~through~~ the sampling lines prior to the PTR-MS ~~wer~~was~~e~~ 10 s for the Patras summer campaign, 12 s for the Athens summer campaign, and 16 s for the Athens winter campaign. –The corresponding ratio of the electric field strength to the gas number density was approximately 126 Td (1 Td = 10^{-17} V cm^2). Blanks were obtained at regular intervals through an activated carbon filter (Supelpure HC, Supelco). A teflon filter was installed before the sampling inlet. Concentrations were monitored in the ~~mass scan~~

~~mode~~ multiple ion detection (MID) mode with a total cycle time of 10 s. -The dwell times were in the range of 5-500 ms. A 200 ms dwell time was used for most of the reported *m*/*z* values. For some of the higher *m*/*z* values a dwell time of 500 ms was selected. The dwell times for ~~*the*~~ *m*/*z* ~~values~~ 21, 30, 32 and 37 were 200, 5, 5 and 10 ms respectively in all three campaigns.

Calibrations were performed once per week. The sensitivities for the reported compounds for all campaigns were in the range of 4.7 to 24 ncps. These values did not change significantly (less than 40%) during the three deployments. The detection limits for the calibrated compounds based on Karl et al. (2003) were in the range of 34 to 97 ppt. Humidity effects on the sensitivities of the individual compounds were not considered during the calibrations. A precision calibrator (Teledyne, model 702) was used for the dilution of the VOC standard with VOC-~~-~~free air (using a Supelco filter). This calibrator type does not make adjustments for the humidity. The ratio of *m*/*z* 37 to *m*/*z* 19 was 0.039 ± 0.009 during the Patras summer campaign, 0.044 ± 0.012 during the Athens summer campaign, and 0.038 ± 0.008 during the Athens winter campaign. In all campaigns the *m*/*z* 37 to *m*/*z* 19 ratio was always less than 0.06 (typically ranging from 0.025 to 0.05). This ratio is considered low and stable, thus no corrections were applied for the $H_3O^+(H_2O)$ ion. The concentrations of all compounds were normalized to the primary hydronium ion signal ~~(please see Equations 1 and 2 of the revised manuscript)~~. For compounds for which calibration was not possible, the corresponding mixing ratios were estimated based on Equation 3 of Taipale et al. (2008).~~A calibration standard for the VOCs (Ionicon Analytik) was used.~~ Concentrations are calculated based on:

[VOC] = CF~~voc~~ ~~Cvoc~~ RH^+/ ~~C_{H3O+}~~H_3O^+ (1)

where, CF~~VOC~~ is the calibration factor for each VOC and ~~C_{VOC}~~-RH^+ and ~~C_{H3O+}~~H_3O^+ are the counts per second for the corresponding VOC and the primary ion respectively. The concentrations reported for the non calibrated *m/z*'s are calculated for a reaction rate of ~~K~~k=2.0x10^{-9} cm^3 s^{-1} (2).

-Table S1 in the Supplementary Material summarizes the VOCs measured during the three campaigns. Formaldehyde (*m/z* 31) was not excluded in~~from~~ this dataset due to issues related to the humidity dependence of the measurements and its low proton affinity (deGouw and Warneke, 2007). Methanol was also excluded due to the difficulty of~~in~~ obtaining methanol-free air for the background measurements with the activated carbon filter. Acetaldehyde (*m/z* 45) was also excluded from the dataset due to negative values, probably resulting from CO_2 interferences (DeGouw and Warneke, 2007). Finally acrolein (*m/z* 57) and *m/z* 41 were ~~excluded~~ not included due to spikes associated ~~to~~ with butanol emissions from the SMPS instruments. Details for the rest of the instrumentation used in the campaigns can be found elsewhere (Kostenidou et al., 2015; Florou et al., 2016).

2.3 PMF analysis

The PMF technique (Paatero and Tapper, 1994; Lanz et al., 2007) was used for the deconvolution of the PTR-MS data into factors. The analysis was performed using the PMF evaluation tool (Ulbrich et al., 2009) with Igor Pro 6.22A (Wavemetrics). The uncertainties were calculated based on Poisson ion counting statistics (de Gouw et al., 2003) and the measured background concentrations. The overall uncertainty is described by (DeGouw et al., 2003; Slowik et al., 2010):

$$\Delta(I-I_b)=\sqrt{\frac{I}{\tau}+\frac{I_b}{\tau_b}} \tag{2}$$

where, I is the signal of the main measurements, I_b is the signal from the background measurements, $\Delta(I\text{-}I_b)$ is the overall uncertainty, τ is the dwell time of the main sampling and τ_b is the dwell time of the background sampling. A total of 29 *m/z* values (~~all the *m/z* values in~~ Table S1 ~~but methanol~~) were used for the PMF analysis. Mixing ratios (ppb) were used as input for the PMF model. Solutions with up to 10 factors were examined with an f_{peak} ranging from -2.0 to 2.0 with a step of 0.2. The averaging time used was 5 minutes. The optimum solution for each measurement period was selected by evaluation of the model residuals, the mass spectra composition, and the correlations of the factor time-series with other measured pollutants. The estimated concentrations by the PMF correlated very well (R^2 ranged from 0.994 to 0.999, Figure S47) with the measured values for all three campaigns.

3 VOC concentrations and diurnal profiles

3.1 Patras summer 2012

The overall measurement period can be divided into three sub-periods based on the prevailing meteorology, namely June 11 – 15, 16 – 22 and 23 – 26. During the first period SW winds prevailed with an average temperature of 24.4 ^{o}C, a wind speed of 3 m s^{-1} and 58% relative humidity. The second period was characterized by higher temperatures (28.4 °C) and stronger (5.3 m s^{-1}) E-NE winds. The average relative humidity was 29%. The final period had SW winds mainly during the day and E-NE winds during the night. The average temperature was 27.2 °C and the average relative humidity was 49%. Average wind speed decreased during this period to 2.4 m s^{-1}. There was no precipitation during the campaign. Additional information about the meteorological conditions and solar radiation can be found in the supplementary information (Figure S1). Back trajectory FLEXPART (Stohl et al., 2005) and Hysplit analysis (*Draxler and Rolph, 2013*) was performed (Kostenidou et al., 2015). The air masses were influenced mostly by the marine environment during the first period and by continental Greece during the second and third period.

Table 1 summarizes the average, median, upper and lower quartile of the concentrations for the ~~calibrated~~ some of the VOCs along with other gas and particulate species. ~~Methanol was the most abundant VOC with an average concentration of 10.2 ppb while acetone~~ Acetone was the ~~second~~ most abundant VOC with an average concentration of ~~with~~ 2.9 ppb. Acetic acid had a mean concentration of 2.2 ppb. The *m/z* 69, reported here as isoprene had an average concentration of 1 ppb. Throughout the campaign, the acetonitrile levels were on average 0.1 ppb with a flat diurnal profile, suggesting that biomass burning was not an important VOC source. Timeseries for the reported VOCs are presented in the SI (Figure S2). Maximum values for the aromatic compounds were in the range of 1 ppb for toluene and the xylenes while benzene concentrations up to 0.4 ppb were measured. Isoprene and the monoterpenes had peak concentrations up to 3 ppb and 1 ppb respectively at noon.

The average diurnal profiles for some of the VOCs measured are shown in Figure 2. The concentrations of isoprene, the monoterpenes, methyl vinyl ketone (MVK) and methacrolein (MACR) were low during nighttime (Figures 2a-2c) and increased in the afternoon with a maximum at 15:00 LT– 16:00 LT. Other compounds of mainly biogenic origin such as methyl ethyl ketone (MEK) (Figure 2d) displayed a similar diurnal pattern, having two additional small peaks at 09:00 LT and 22:00, something that shows either the influence of anthropogenic sources or the contribution of other molecules to the *m/z* 73 signal, reported here as MEK. Most of the biogenic VOCs had higher concentrations during the second and third period. During these periods the air masses reaching the site passed over continental Greece where there are mountains with forests.

Aromatic VOCs, like benzene, toluene and xylenes displayed diurnal cycles (Figures 2e, 2f, 2g) characteristic of traffic emissions, with a peak during the morning rush hour at 08:00 LT and one peak in the evening at 22:00 LT. This evening peak can be justified by the local lifestyle~~timetables~~, espec~~t~~ially the closing of the market at 21:00.~~,~~ Higher concentrations were observed during the first period and during daytime for the third period (Figure S2). This is consistent with significant local aromatic sources. The toluene to benzene ratio for the overall period was 2.5. During the three periods, the toluene to benzene ratio was 2.3, 2.0 and 2.6 respectively. Most of the reported toluene to benzene ratios in the literature are in the range of 1 or less (for aged air masses) to 4 (associated with fresh emissions measured in tunnels) (Roberts et al., 1984; Salisbury et al.; 2003, Kristensson et al., 2004). Assuming no influence from biomass burning sources ~~takes place~~ (~~no significant~~ the aceto~~ro~~nitrile levels ~~findings~~were low~~found~~) ~~Since~~ this ratio ~~is~~ can be considered ~~to be~~as a photochemical clock (Roberts et al., 1984), thus the sampled air during the second period was on average more aged. During this period the air masses sampled were less influenced by the city of Patras and the surrounding areas.

~~Methanol levels (Figure 2i) were affected by both anthropogenic and biogenic sources with higher values observed during the third period. Methanol's diurnal cycle had peaks during morning and evening rush hours.~~ Acetone's concentrations were marginally elevated during daytime from 13:00 LT– 22:00 LT (Figure ~~2j~~2i). Several oVOCs had a diurnal pattern similar to the biogenic VOCs. The diurnal profile~~s of formic acid/ethanol (Figure 2k) and~~ of acetic acid (Figure ~~2l~~2j) peaked at approximately 17:00 LT. Higher values of the oVOCs were observed during the second period (SI-Section 2, Figure S2) suggesting strong biogenic influence.

NO_x and BC concentrations displayed diurnal profiles (Figures S3 and S4) similar to those of the aromatic species, typical of traffic emissions. Higher values were observed for both species during the first and third periods, while for the second period lower values were measured due to the strong E-NE winds. The average concentration for NO_x was 5.1 ppb, while for BC a mean value of 0.5 μg m^{-3} was measured. SO_2 concentrations were elevated during the day. A peak during morning rush hour, similar to the aromatic VOCs, was observed but no peak was evident during evening rush hour. This can be explained by the low activity of heavy trucks during these hours (22:00-23:00 LT). A mean value of 1.3 ppb was found for SO_2. Ozone concentrations were elevated during the second period exceeding 60 ppb (8 h average) during the night of the 17 to 18 of July. These elevated O_3 levels were the result of long range transport from continental Greece and the Balkans~~.~~ The importance of the long range transport can be seen in Figure S3 ~~of the revised paper~~ showing the ozone concentrations during this windy period. The maximum ozone concentration was actually observed a little before the midnight of June 18. This was actually the highest ozone level during the ~~whole~~ measurement period. This was in contrast to the low levels of NO_x and BC observed during the same period. These results shown in Figure S3 strongly support the conclusion that the high levels of ozone were due to long range transport. Similar conclusions have been reached by Kouvarakis et al. (2002) reporting measurements performed onboard a cruise ship travelling on a regular basis in the area. They concluded that long range transport is the main factor contributi~~o~~ng to high ozone levels in eastern Greece. During these two days an average value of 55 ppb was measured. Diurnally averaged O_3 concentrations for the overall measurement period started to increase at 9:00 LT with a maximum of 58 ppb during 15:00-16:00 LT. During the night (21:00-7:00 LT) O_3 concentrations were in the range of 45 ppb.

3.2 Athens summer 2012

The Athens summer campaign was characterized by a prolonged heat wave with temperatures reaching up to 40 ^{o}C. The average temperature was 29.6 ^{o}C and the corresponding relative humidity was 40%. Local topography dictated the wind patterns, with the wind having mainly a E-SE direction. The wind direction varied especially during the morning hours (08:00-11:00 LT) with wind shifts bringing air masses from the N or E of the site. The average wind speed was 1.7 m s^{-1} with very low values during the night. No precipitation occurred throughout the campaign. More information concerning the meteorological conditions is included in the SI (Figure S5).

~~Methanol~~ Acetone was the most abundant VOC with an average value of ~~6.7 ppb (Table 2). The second most abundant was acetone with a mean concentration of~~ 4.3 ppb (Table 2), significantly higher than in Patras. Throughout the campaign the acetonitrile concentrations were on average 0.2 ppb with a flat diurnal profile, suggesting the lack of biomass burning sources. Figure S6 includes all the VOC time series for the Athens summer campaign. Toluene and the xylenes peaked during the morning hours at concentrations in the range of 3 ppb, while benzene had typical maximum values around 1 ppb during these hours. Isoprene and the monoterpenes peaked ~~during~~ at noon ~~at~~ with concentrations in the range of 1 and 2 ppb respectively.

The average isoprene concentration was 0.7 ppb with a diurnal profile (Figure 3a) similar to Patras. Local sources significantly influenced ~~significantly~~ the monoterpene concentrations (Figure 3b) with a peak during the morning hours (from 06:30 to 08:30) followed by several hours of elevated levels with a maximum at approximately 15:00-16:00 LT. This behavior is similar to that reported by Filella and Penuelas (2006) for the Barcelona semi-urban site. Nighttime stagnation conditions followed by morning N or NE winds caused these ~~spikes~~ elevated concentrations by transporting to the site nighttime emissions from the adjacent pine forest. MVK and MACR (Figure 3c) had a similar diurnal cycle to that of isoprene, while MEK (Figure 3d) peaked at 11:00-12:00 LT and had one more peak at 22:00, something seen also in the Patras summer campaign.

In Athens, higher aromatic concentrations were observed compared to the Patras summer campaign.. These species had similar diurnal cycles (Figures 3e, 3f, 3g) characteristic of traffic emissions, with a peak during the morning rush hour at 8:00-9:00 LT and one wide peak during the evening from 19:30 to 1:00 LT. The toluene to benzene ratio for the Athens summer campaign was 3.4, a value similar to that of fresh traffic emissions (Kristensson et al., 2004). Rappenglueck et al. (1998) reported a toluene to benzene ratio of 2.3 for the Demokritos site during August-September 1994. The correlation coefficients between the aromatic species (benzene, toluene, xylenes, C9 and C10 aromatics) were high (R^2 ranging from 0.92 to 0.96) suggesting a single source related to traffic emissions.

The diurnal profiles of most oVOCs, suggest anthropogenic influence (Figures 3i and~~,~~ 3j~~, 3k and 3l~~). ~~Methanol had a similar pattern to that of the aromatic species with peaks at 08:00 LT and 22:00 LT.~~ Acetone concentrations were elevated during the day with additional peaks during morning rush hour and during night (24:00 LT). ~~Formic acid/ethanol peaked during the afternoon hours, at 15:00-16:00 LT, similar to the biogenic VOCs.~~ Acetic acid concentrations were lower during the day with a peak at 22:00-23:00 LT and elevated concentrations during night hours. Morning rush ~~traffic~~ hour had a very small effect on acetic acid's levels. This compound appears to be associated mainly with regional sources.

~~Comparing the finding of the two summer campaigns with other works (Sinha et al., (2014) shows that in most cases lower~~The measured ~~–~~concentrations of~~for~~ acetonitrile, acetone, benzene and toluene in~~were seen for~~ Patras and Athens were lower than ~~compared with~~ summer measurements from Paris, Beijing, Mexico C~~c~~ity, Tokyo, Houston, London and Mohali (Sinha et al., 2014). Isoprene concentrations though were comparable with the findings from the above cities.

NO_x and BC concentrations displayed diurnal profiles similar to those of the aromatic species, typical of traffic emissions (Figures S7 and S8). The average concentration of NO_x was 7.3 ppb, while BC had an average value of 0.7 $\mu g\ m^{-3}$. Increased solar radiation along with the availability of O_3 precursors resulted in high O_3 exceeding the EU 60 ppb 8-hour limit in 4 days during the 13 day period. The O_3 average diurnal pattern was similar to that of Patras during the summer with a maximum of 60 ppb during 15:00-16:00 LT. During the night concentrations of 50 ppb were measured.

3.3 Athens winter 2013

Due to the recent economic crisis and the increasing prices of heating oil at the time, a significant percentage of the population in Greece has been using wood for residential heating during the winter. During the winter of 2012-2013, extreme episodes of atmospheric pollution occurred in Athens, with hourly PM_1 levels reaching values up to 140 $\mu g\ m^{-3}$ (Florou et al., 2016). The average temperature, humidity, and wind speed during the Athens winter campaign were 11.9 ^{o}C, 70%, and 3.4 $m\ s^{-1}$ respectively. The wind direction patterns favored mainly S-SW winds and occasionally N-NE winds. Minimum night temperatures ranged from 3.3 ^{o}C to 15 ^{o}C. Precipitation occurred during January 11, 16, 18, 24, 25 and 26. Meteorological data are included in the SI (Figures S9 and S10).

Table 3 summarizes the average, median, lower and upper quartiles of the concentrations for some of the measured VOCs. The substantial difference between the median and average values for most species is due to periods with significant residential wood burning and corresponding high concentrations. ~~Extreme concentrations were measured with methanol reaching up to 90 ppb,~~Concentrations of~~for~~ acetone and acetic acid reached~~ing~~ 15 ppb while ~~, and~~ isoprene levels were as high as ~~reaching~~ 9 ppb~~ were measured~~. ~~Methanol,~~A~~ a~~cetone, acetic acid and toluene had ~~concentrations~~ mixin~~i~~g ratios with median values ~~ranging from 2.4 to~~in the range of 1.~~3~~ 5 ppb. ~~Methanol and acetone~~Acetone levels were significantly lower compared to the summer campaign. Formic acid/ethanol and acetic acid had similar concentrations with the summer. The time series of~~for~~ the measured VOCs is shown in Figure S11 in the SI.

Most of the VOCs (Figure 4) had higher average concentrations during the night and during the morning rush hour (peak at 09:00 LT). Evening concentrations started to increase at 19:00 LT. Very high concentration periods were detected for most of the measured VOCs. Aromatics increased during the morning rush hour together with formic acid and acetone. The toluene to benzene ratio for the campaign was 2.1 suggesting the importance of other sources in contrast to the summer ratio (3.4) when traffic dominated.

Isoprene and the monoterpenes had elevated concentrations during the morning but also during the evening (18:00-23:00 LT) (Figures 4a and 4b) mainly due to biomass burning. MVK, MACR and MEK were also produced by biomass burning sources (Figures 4c and 4 d). Although these compounds dominate their specific *m/z* values (*m/z*: 69, 71, 73) in typical rural environments, other compounds may be present in these *m/z* values during the Athens winter campaign. Karl et al. (2007) reported furan and other alkenes being detected at *m/z* 69, crotonaldehyde and other alkenes for *m/z* 71 and methyl propanal for *m/z* 73 during the burning of tropical biofuels. Akagi et al. (2011) and Yogelson et al. (2013) reported furan emissions factors higher than isoprene for some biomass fuel types. Based on reported emissions from various biofuel types, furan contributes around~~is in the range of~~ 30% of the *m/z* 69 in most cases (Stockwell et al., 2015, Sarkar et al., 2016). ~~Akagi et al., (2011) and Yogelson et al., (2013) reported furan emissions factors higher than isoprene for some biomass fuel types.~~ For the Athens winter campaign isoprene is believed to be the major component of *m/z* 69.

~~Comparing the above (Table 3) average values with other works (Sarkar et al., 2016) shows that~~ T~~t~~he VOC concentrations in Athens during winter are ~~in general~~ lower than those in Kathmandu or ~~the~~ Karachi (Sarkar et al., 2016) findings. Acetonitrile, acetone, benzene and toluene~~,~~ levels are similar to those measured in ~~resemble the~~ London, Paris and Barcelona~~, findings~~ while the isoprene concentration is higher and ~~(~~closer to the Kathmandu and Karachi values~~finings)~~.

NO$_x$, BC and CO had similar time series and average diurnal profiles (Figures S12 and S13) as the majority of the VOCs with peaks at morning rush hour and during the evening (18:00-23:00 LT). Their median values were 11.3 ppb, 1.0 μg m^{-3} and 100 ppb respectively. SO$_2$ concentrations were elevated mainly during the morning rush hour. During night lower SO_2 values were observed with some peaks around 23:00 LT that can be attributed to traffic and residential heating using diesel fuel. A median value of 1.1 ppb was observed. O_3 levels were reduced during the biomass burning periods to almost zero. For periods with stronger winds and low gas and particulate pollutant levels, the O_3 concentrations reached 30 to 40 ppb. The average O_3 diurnal pattern had a peak at 15:00 LT and a median value of 25 ppb for the campaign.

Acenonitrile (*m/z* 42) and levoglucosan's tracer (*m/z* 60 of the AMS) were used as markers in order to identify periods where wood burning had a substantial contribution to the VOC and particulate levels. The concentration of these two species (Section S4.1) had a relatively high correlation ($R^2=0.78$). In both cases elevated concentrations were observed mainly during the night, but also during the morning having a peak at 9:00 LT. These morning peaks can be attributed to residential heating at these hours but also can be a result of vertical mixing of the atmosphere. The acetonitrile's relative increase is higher than of the levoglucosan tracer (Figure 5) during the morning rush hour. Recently Dunne et al. (2012) reported interferences at PTR-MS *m/z* 42 under the H_3O^+ reaction when measuring in polluted urban environments. These interferences were attributed to the ^{13}C isotopologues of $C_3H_5^+$ and the product ion $C_3H_6^+$ formed by reactions with NO^+ and O_2^+ that exist in trace amounts in the reagent gas (H_3O^+). This leads to the conclusion that even though an increase due to biomass burning is apparent during the morning hours (increase in levoglucosan's tracer from the AMS), a fraction of *m/z* 42 concentration is due to species other than acetonitrile. During the morning, traffic appears to contribute significantly to the *m/z* 42 increase.

A set of criteria was established in order to select periods during which residential heating dominated the gas and particulate composition of ambient air. These periods (Table S2) ~~were~~ occurred during the nighttime (18:00-06:00 LT) and ~~had~~ were ~~assosiated~~associated with acetonitrile (concentrations exceeding 0.25 ppb). During these periods NW winds dominated bringing air masses from the northern parts of Athens to the site (Figure S10b). The average concentrations for these periods are shown in Table 3.

Excluding the above biomass burning periods from the campaign dataset resulted in a decrease of the average values of the measured species by 11-34%. Namely the average values decreased by ~~34% for methanol,~~ 26% for acetonitrile, 11% for formic acid and ethanol, 17% for acetone, 16% for acetic acid, 23% for isoprene, 25% for MVK and MACR, 17% for MEK, 23% for benzene, 18% for toluene, 22% for the xylenes and 24% for the monoterpenes.

4 Biomass burning emissions

Emission factors (EF) were calculated based on:

$$EF_i = \frac{(C_i)_{plume} - (C_i)_{back}}{(CO_2)_{plume} - (CO_2)_{back}} EF_{CO_2} \qquad (3)$$

~~$EF_i = \frac{(C_i)_{plume} - (C_i)_{background}}{(CO_2)_{plume} - (CO_2)_{background}} EF_{CO_2}$ (3)~~

where $(C_i)_{plume}$ and $(C_i)_{back}$~~ground~~ were the concentrations for species i, during the burning and the reference periods (background) respectively and $(CO_2)_{plume}$ and $(CO_2)_{back}$~~ground~~ are the concentrations of CO_2 during the biomass burning and the reference periods. For the CO_2 emission factor (EF_{CO2} ~~EF_{CO_2}~~) a value of 1600 g kg^{-1} was used. This value was selected based on the typical values reported in the literature for several fuel types. The estimated EFs for the measured species are shown in Table 4.

Emission ratios (Table 5) for the gas and particulate species were calculated as Δ[Species]/ΔCO (Table 4) where Δ[Species] is the difference in the concentration, of each compound, between the burning period and an adjacent reference period. This reference period was selected based on the lower acetonitrile, CO, and CO_2 concentrations at adjacent time periods (prior or later) to the period identified as biomass burning. The estimated ratios are given in Table 4. Emission ratios for toluene, xylenes, C9 and C10 aromatics seem to be greater than various SE, SW and pine spruce fuels (Warneke et al., 2011). Acetic acid's and acetonitriles's emission ratios were lower than the values reported by Warneke et al. (2011). ~~++++~~The modified combustion efficiency (MCE) calculated for these biomass burning periods was high (0.975 – 0.983) indicating low contribution from smoldering phase burning. ~~Emission factors (EF) were calculated based on:~~

~~$EF_i = \frac{(C_i)_{plume} - (C_i)_{background}}{(CO_2)_{plume} - (CO_2)_{background}} EF_{CO_2}$ (3)~~

~~where $(C_i)_{plume}$ and $(C_i)_{background}$ were the concentrations for species i, during the burning and the reference periods respectively and $(CO_2)_{plume}$ and $(CO_2)_{background}$ are the concentrations of CO_2 during the biomass burning and the reference periods. For the emission factor of EF_{CO_2} a value of 1600 g kg^{-1} was used. This value was selected based on the typical values reported in the literature for several fuel types. The estimated EFs for the measured species are shown in Table 4.~~

5 VOC sources

5.1 Patras summer 2012 - PMF

For the Patras PMF analysis of the PTR-MS data a four factor solution was selected. This choice is further discussed in the SI (Sections 5.1 and 5.2). An f_{peak} of zero was chosen based on the *m/z* composition of the factors and the correlations of the factors to known external (BC and NO_x) and internal (aromatic VOCs, biogenic VOCs) tracers (SI - Section 5.3). Solutions in the f_{peak} range from -0.4 to 0.2 have only minor differences. Other solutions deriving from different f_{peak} selections are also presented in the SI. The factors obtained were attributed to biogenic emissions (factor bVOC), traffic emissions (factor TRAF), oxygenated VOCs (factor OVOC) and oxygenated VOCs of biogenic origin (factor b-OVOC).

The bVOC factor included mainly isoprene (*m/z* 69) and the monoterpenes (*m/z* 137) (Figure 6). There were small contributions by *m/z* values 71, 81, 87 and 101. The factor average diurnal pattern has a peak at 15:00 LT. The factor showed weak correlations with the biogenic oxygenated organic aerosol (b-OOA) and the moderately oxygenated OA (M-OOA) (R^2=0.20 and 0.22 respectively) as obtained by the PMF analysis of the AMS data (Kostenidou et al., 2015). This weak correlation is due the fact that the b-OOA has been at least partially produced away from the measurement site. This highlights the challenges of combining gas and particulate phase measurements during source apportionment applications. Sunlight intensity had also a weak correlation (R^2 = 0.24) with the bVOC factor. The factor also showed weak correlation (R^2 = 0.29) with ambient temperature. These ~~Optimum~~ correlations improved to 0.28 and 0.35 respectively ~~was seen by~~after ~~Shifting~~ shifting the time series of the factor earlier by two hours. This~~,~~ ~~marginally improved this correlation (R^2 = 0.35) with temperature and with sunlight intensity (R^2 = 0.28)~~ suggests ~~ing. This~~

~~suggests~~ that some of the biogenic components included in this factor are transported emissions to the site from nearby areas. Wind roses indicate that the higher concentrations (above the 75% percentile) are com~~m~~ing from E-NE (Figure S24).

Factor TRAF included the aromatic species (*m/z* values 79, 93, 107, 121 and 135) as well as *m/z* values 43, 59, 61 and 69 (Figure 6). Some contribution by *m/z* values 71 and 73 was also observed. Its diurnal profile as expected is similar to that of the aromatic species (Figure 2) with one peak at 09:00 LT and one at 22:00 LT. The toluene to benzene ratio of the factor was 2.6 the same as the ratio for the third period. Correlations between this factor and BC were relatively high (R^2 = 0.66). The two hydrocarbon-like OA factors (HOA-1 and HOA-2) reported by Kostenidou et al. (2015) showed R^2 of 0.49 and 0.43 with this factor respectively. The PM_1 organonitrate calculated for the AMS measurements based on Farmer et al. (2010) also correlates well (R^2 = 0.59) with the TRAF factor. The main source of this factor based on the diurnal profiles and the correlations seen is traffic in the city of Patras and the surrounding areas. This is ~~further seen by~~consistent with the wind rose for this factor (Figure S24) that points out that the higher ~~greater~~ emissions are ~~coming from~~located to the W-SW of the site where the ~~(~~city of Patras is located~~)~~. Other sources such as cooking emissions, ships, etc., might contribute to this factor to some extent.

The ~~Factor~~ OVOC factor mainly included acetone. Other *m/z* values contributing to this factor were 43, 47 and 61 (Figure 6). A weak correlation between the factor and the AMS's b-OOA (R^2=0.29) was observed. Additionally low correlations were observed with particulate sulfate and nitrate (R^2 of 0.23 and 0.18 respectively). The factor's diurnal pattern (Figure 6) reveals elevated concentrations during the night and a minimum at 15:00 LT. The factor seems to be affected by mixing height changes and from long range transport.

The last factor, (b-OVOC) included oxygenated molecules (acetic acid, acetone and formic acid/ethanol). Other *m/z* values contributing to this factor were *m/z* 43, 69, 71, and 73 (Figure 6). This factor includes mainly products of the oxidation of biogenic VOCs, but also some primary VOCs. Approximately 70% of the measured isoprene during the Patras summer campaign was included by the PMF analysis in the BVOC factor (see also Figure S20 in the SI). The remaining 30% was included in other factors, with 15% in the b-OVOC factor. This small amount of isoprene assigned to this factor can be justified either as direct biogenic emissions that have originated far from the area close to the measurement site and have not yet reacted or it can be due to the uncertainties of the PMF analysis. The factor was named b-OVOC (biogenic oxygenated VOCs) due to the ~~strong influence by~~ formic acid, acetone and acetic acid that it includes. The b-OVOC diurnal cycle is similar to that of the bVOC factor shifted by approximately 2 hours. Based on this diurnal cycle,~~, these b-OVOC species~~ the OVOC species that ~~predominantly~~ contribute to this factor are~~can be considered as~~ either products of the oxidation of biogenic molecules or direct biogenic emissions. Ambient temperature and sunlight intensity ~~data~~ had a mild correlation with the b-OVOC with R^2 of 0.35 and 0.32 respectively. A weak correlation (R^2 = 0.27) of this factor was seen with the moderately oxygenated (M-OOA) by the AMS and no correlation (R^2 = 0.08) was observed with the b-OOA. As in the bVOC factor, the greater concentrations of the b-OVOC factor are coming from the E-NE (Figure S24). This supports the explanation that the b-OVOC factor is mostly oxidation products of local biogenic VOCs as well as temperature sensitive emissions.

The contribution of each factor to the various VOC species is presented in Figure ~~S21~~7. 81% of isoprene (*m/z* 69) is included in the biogenic factors bVOC and b-OVOC. Monoterpene *m/z* values (137 and 81) were mainly assigned by the PMF to the bVOC factor (73% and 63% respectively) and at smaller percentages to factor b-OVOC (9% and 6% respectively). Factor TRAF included the majority of the aromatic species (73 – 91 %). The rest of the aromatic species are assigned by the PMF to other factors. This is probably due to the combination of the low concentrations of most of the aromatics and the uncertainties of the PMF analysis. These values also provide an estimate of the uncertainty of these results. Patras summer PMF analysis demonstrates the importance of biogenic sources to the VOC budget of urban areas during summer.

5.2 Athens summer 2012 - PMF

After the evaluation of various solutions, five factors were selected for this period with an f_{peak} equal to zero (SI - Sections 6.1, 6.2, 6.3). The factors were attributed to monoterpene species (factor TERP), other biogenic emissions (factor bVOC), traffic emissions (factor TRAF) and two oxygenated VOC factors (factor OVOC-1 and OVOC-2).

For the Athens summer campaign, the local monoterpene emissions were separated by the PMF from the rest of the biogenic emissions creating a new factor named TERP. The *m/z* values 137 and 81 were the main components of this factor and its diurnal profile (Figure ~~7~~8) has an early morning peak similar to that of the monoterpenes in this site (Figure 3). Other *m/z* values contributing to this factor were 43, 47, 59, 61, 69, 71, 73, 75, 77, and 93 (Figure ~~7~~8). No correlations ($R^2 < 0.05$) were found between this factor and measured particulate species. These monoterpene emissions were due to local pine vegetation and their concentrations were affected by local mixing phenomena.

Factor bVOC was mainly composed of isoprene (*m/z* 69) and isoprene hyperoxides (*m/z* 101). Also a fraction of *m/z* values 43, 47, 59, 71, 73, 75, 87, 93, and 121 was included. Its diurnal profile (Figure ~~7~~8) peaked at 15:00 LT, similar to the bVOC factor for the Patras summer campaign. This factor had a weak correlation ($R^2=0.15$) with the very oxygenated OA factor (V-OOA) obtained by the PMF analysis of the AMS data (Kostenidou et al., 2015). No correlation existed with the AMS M-OOA factor.

Factor TRAF included the aromatic species (*m/z* values 79, 93, 107, 121 and 135). Also *m/z* values 43, 47, 59, 61 and 73 contributed to this factor (Figure ~~7~~8). The diurnal profile is similar to that of the aromatic compounds (Figure 3) with one peak at 09:00 LT and one at 22:00 LT. The toluene to benzene ratio of the factor was 3.1 indicating relatively fresh traffic emissions. Factor TRAF had moderate to high correlations with most of the species emitted by transportation sources: NO_x ($R^2=0.69$), BC ($R^2=0.45$), AMS nitrate ($R^2=0.64$) and AMS HOA-2 ($R^2=0.58$). The factor's correlation with AMS HOA-1 was surprisingly weak ($R^2=0.16$). This inconsistency is believed to derive from the inhomogeneity of the source distribution around the sampling site along with the shifting wind directions (Kostenidou et al., 2015). The highest concentrations (upper quartile) ~~The wind rose for the greater concentrations (above the 75% percentile)~~ of this factor were observed during periods when the wind came from ~~show that they are coming from the~~ N-NE (Figure S34). Particulate organonitrates (AMS) showed good correlation with factor TRAF ($R^2=0.65$).

Factor OVOC-1 was dominated by acetone. Other *m/z* values contributing to this factor were 43, 47 and 61 (Figure ~~7~~8). No correlation ($R^2 <0.08$) was found between this factor and other species. Its concentration had a modest afternoon peak.

This factor is considered a mix of contributions by long range transport and various anthropogenic and biogenic sources.

The ~~last factor (~~OVOC-2~~)~~ factor included mainly acetone (*m/z* 59) and acetic acid (*m/z* 61). The *m/z* 43 and 47 also contributed (Figure ~~7~~8). The factors concentrations were elevated during the night. The factor had correlations with PM_1 nitrate (R^2=0.49), HOA-1, and HOA-2 (R^2 equal to 0.18 and 0.22 respectively) and also with V-OOA (R^2=0.34) and PM_1 sulfate (R^2=0.32). Due to these correlations and its diurnal profile, this factor is believed to be linked to a mix of urban sources as well as long range transport.

The fraction of some selected VOC species attributed to each factor is shown in Figure ~~S31~~ 9~~(SI)~~. The majority (58%) of isoprene is assigned to factor bVOC and smaller percentages to factors OVOC-1, TERP and TRAF (14, 20 and 7% respectively). Monoterpenes, *m/z* values 137 and 81, are almost exclusively included in factor TERP (84 and 76% respectively). The majority (55 to 73 %) of the aromatic species (*m/z* values 79, 93, 121 and 135) are part of factor TRAF.

5.3 Athens winter 2013 - PMF

A five factor solution and an f_{peak} equal to zero were selected for the Athens winter campaign (SI sections 7.1, 7.2 and 7.4). One factor was related to emissions originating from biomass burning (BBVOC). A factor for traffic emissions (factor TRAF) was identified and also one factor that was attributed mainly to industrial sources (factor IND). Finally two oxygenated VOC factors (OVOC-1 and OVOC-2) were found. The measurement period that was selected for this PMF analysis did not include the first day of the measurements of the Athens winter campaign. Including the first day in the Athens winter campaign in the PMF analysis~~,~~ resulted in the separation of the biomass burning source into two or more factors for solutions with 4 or more number of factors (SI Section 7.3). No distinct variation was seen for the favored wind direction between those BBVOC. Their time_series (Figure ~~S42~~S41) though similar showed significant differences for the first day of the campaign (Jan. 9 and Jan. 10) where lower temperatures were recorded.

Factor BBVOC correlated strongly with the AMS *m/z* 60 (R^2=0.92) linked to levoglucosan and also with acetonitrile (R^2=0.80). It also had a high correlation (R^2=0.84) with the AMS BBOA factor (Florou et al., 2016) and with other species emitted by biomass burning sources such as CO (R^2=0.59) and BC (R^2=0.63). The factor mainly included acetone, isoprene, MVK and MACR, MEK, benzene, xylenes, C9 aromatics and monoterpenes (Figure ~~8~~10). Due to the acetonitrile presence along with the high correlations obtained with known species of biomass burning origin (BBOA, AMS *m/z*60, CO, BC), this factor was considered to derive from emissions of biomass burning. The diurnal profile (Figure ~~8~~10) of the factor is characteristic of residential heating use: mild use during the early morning hours and high use during the night (from 18:00-24:00 LT). Wind roses (Figure S46) indicate that the higher concentrations for this factor were~~are~~ com~~m~~ing from N-NE of~~from~~ the site.

Factor TRAF has the same *m/z* values as in the summer campaigns and is mainly linked to traffic. The aromatics are the main VOCs contributing to this factor. Other *m/z* values that are present in considerable amounts are: 43 and 59 (Figure ~~8~~10). The toluene to benzene ratio for this factor is 3.0, similar to the value (3.1) of the same factor during the summer campaign in Athens. Its diurnal profile includes one large peak corresponding to the morning rush hour and a smaller peak at approximately 19:00 LT (Figure ~~8~~10). The three factors related to traffic (factors named TRAF for the three studied campaigns) had a ~~quite~~ consistent *m/z* spectrum with R^2 values ranging from 0.68 to 0.90.

Factor IND mainly includes toluene and acetone (Figure ~~8~~10). Its diurnal pattern is relatively flat with slightly elevated concentrations during the night. A weak minimum is observed at 09:00 LT. Due to the presence of toluene this factor is considered of anthropogenic origin, probably related to industrial activities far from the site.

Factor OVOC-1 includes mainly formic acid (*m/z* 47) and some isoprene. The factor's diurnal profile (Figure ~~8~~10) was characterized by higher values during the early morning hours, peaking at 8:00 LT. After a significant decline in the morning it slowly increased during the rest of the day. No significant correlations were found between this factor and other measured species. Factor OVOC-1 could not be ~~assosiated~~associated with any potential source. Wind roses (Figure S46) indicate that the higher concentrations we~~a~~re coming from the N-NE (city center) and that this factor is probably influenced by~~of~~ anthropogenic ~~influence~~sources.

The last factor (OVOC-2) includes *m/z* 43 and acetic acid. The diurnal profile had elevated values during the night hours and was slowly decreasing through the day. It is ~~believed to be~~ probably associated with background concentrations of several VOCs (Figure ~~8~~10).

For this measur~~in~~ement~~g~~ period, over 35% of benzene, 14% of the xylenes, 13% of the C9 aromatics and 14% of the C10 aromatics is estimated to be due to residential biomass burning (Figure 11). Additionally traditionally biogenic species such as ~~isoprene~~ m/z 69 and the monoterpenes were originating mainly (46 and 36% respectively) from residential biomass burning during this winter period. The Athens winter PMF analysis highlights the importance of biomass burning during winter for the VOC budget. Biomass burning and traffic were the major sources for the majority of the VOCs that were measured. On the contrary biogenic sources had a limited contribution to the VOC budget.

5.3 PMF overview

Most of the urban source apportionment VOC studies separate the anthropogenic VOCs into several categories related to vehicle exhaust emissions, the evaporation of fuel, industrial solvents, diesel exhaust emissions, etc. (Brown et al., 2007; Tolga et al., 2007; Badol et al., 2008; Leuchner and Rappengluck, 2010; Yurdakul et al., 2013; Boynard et al., 2014; Wang et al., 2014). In the present study the PMF analysis did not ~~conclude~~result in such separations since the VOC portfolio did not include light alkanes which are usually included in datasets obtained by ~~measurements as it is usually done by~~ gas chromatographic techniques (GC). The vehicular exhaust and LPG sources widely reported in the literature include a large fraction of these species, thus such a separation was not ~~favored~~favoured by the PMF analysis.

6 Conclusions

On-line measurements of VOCs and other gas and particulate species were performed in background urban sites of Greece during the summer and winter of 2012 and 2013. For the summer campaigns in Patras and Athens, the isoprene concentration was on average 1.0 and 0.7 ppb respectively. The corresponding values for the monoterpenes were 0.3 and 0.9 ppb with the elevated Athens concentrations originating mainly from local emissions. Typically the isoprene concentrations peaked during the day with values up to 2 ppb, while during the night the concentrations were lower (<0.5 ppb). Benzene, toluene and the xylenes average concentrations were 0.12, 0.28 and 0.25 ppb for Patras and 0.22, 0.81 and 0.67 ppb for Athens respectively.

These differences are considered modest if the population difference (one order of magnitude) is taken into account. During the morning rush hour aromatic compounds such as toluene, peaked up to 5 ppb for Athens during the summer and 1 ppb for Patras. Analogous concentrations were seen for the xylenes, while benzene values during rush hour were in the range of 1 ppb for Athens and 0.3 ppb for Patras.

During winter in Athens the average concentrations for isoprene and the monoterpenes were similar to the summer values (1.1 ppb for isoprene and 0.4 ppb for the monoterpenes) indicating the importance of biomass burning sources of these compounds. Benzene, toluene and the xylenes concentrations were elevated during winter (1.0 ppb, 2.3 ppb and 1.7 ppb respectively) compared to summer, something attributed to the lower mixing height and the presence of additional sources. Concentrations up to ~~90 ppb for methanol and up to~~ 15 ppb for acetic acid, toluene and the xylenes were measured. For the majority of the measured species elevated concentrations were observed during night signifying the importance of biomass burning, which was enhanced by the lower mixing heights.

PMF analysis showed that traffic was the major aromatic VOC source in all three campaigns. A traffic related factor was identified including more than 60% of benzene, 60% of toluene, 70% of the xylenes and 70% of the C9 aromatics. Especially during summer traffic dominated the above aromatic budget by contributing 73% of benzene for Patras and Athens, and 80% and 62% of toluene for Patras and Athens respectively. 85% of the xylenes in Patras and 70% in Athens were also apportioned to traffic.

The recent economic crisis along with the higher prices of fossil fuels has led to increased use of biomass burning for residential heating. Biomass burning emission ratios (ER) and emission factors (EF) due to residential heating were estimated. PMF analysis showed that the emissions of the aromatics by biomass burning were comparable to traffic emissions. Approximately 35% of benzene was due to biomass burning during the Athens winter campaign. Additionally during winter, the ‘traditional’ biogenic species, such as ~~*isoprene*~~*m/z* 69, the monoterpenes, MVK and MACR were originating mainly from biomass burning processes. During summer these biogenic species were almost exclusively linked to emissions from vegetation. During summer several oVOCs such as acetic acid, formic acid and ethanol were also linked to biogenic emissions either directly or as secondary products.

Acknowledgements

We thank Prof. Argyriou (Department of Physics - University of Patras) for providing the meteorological data, Dr. Elef~~u~~theriadis (N.C.S.R. "Demokritos") for providing the facilities for the Athens summer campaign, Dr. Gerasopoulos (National Observatory of Athens - N.O.A) for providing the facilities for the Athens winter campaign. This research was co-financed by Greece and the European Union through the education and lifelong learning operational program Thales: "Sources and physicochemical properties of fine and ultrafine aerosol particles that affect the regional climate of Greece". This research was also supported by the European Research Council Project ATMOPACS (Atmospheric Organic Particulate Matter, Air Quality and Climate studies) (Grant Agreement 267099) in coordination with project PEGASOS.

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Table 1: Concentrations (5 minute averages) of VOCs and other pollutants during the Patras summer campaign.

		Lower quartile	**Median**	**Average**	**Upper quartile**
VOCs	***m/z***	Concentration (ppb)			
~~Methanol~~	~~33~~	~~7.01~~	~~8.34~~	~~10.18~~	~~10.67~~
Acetonitrile	42	0.08	0.10	0.12	0.14
Formic acid, Ethanol	47	0.40	0.86	0.89	1.35
Acetone	59	2.05	2.44	2.93	3.23
Acetic acid	61	1.16	1.88	2.15	2.90
Isoprene	69	0.32	0.85	1.01	1.46
MVK+MACR	71	0.16	0.24	0.30	0.38
MEK	73	0.18	0.25	0.30	0.42
Benzene	79	0.06	0.09	0.12	0.17
Toluene	93	0.10	0.19	0.28	0.43
Xylenes	107	0.09	0.15	0.25	0.37
Monoterpenes	137	0.09	0.19	0.33	0.50
Other species	**Units**				
Black carbon (BC)	μg m^{-3}	0.27	0.44	0.49	0.67
Sulfur dioxide (SO_2)	ppb	0.98	1.15	1.25	1.41
Nitrogen oxides (NO_x)	ppb	1.8	3.7	5.1	6.4
Ozone (O_3)	ppb	41.2	49.2	48.7	56.4

Table 2: Concentrations (5 minute averages) of VOCs and other pollutants during the Athens summer campaign.

		Lower quartile	**Median**	**Average**	**Upper quartile**
VOCs	***m/z***	Concentration (ppb)			
~~Methanol~~	~~33~~	~~5.26~~	~~6.13~~	~~6.72~~	~~8.13~~
Acetonitrile	42	0.16	0.19	0.20	0.23
Formic acid, Ethanol	47	1.12	1.51	1.52	1.87
Acetone	59	3.27	4.09	4.28	4.92
Acetic acid	61	1.53	2.04	2.17	2.65
Isoprene	69	0.46	0.72	0.73	0.93
MVK+MACR	71	0.20	0.32	0.35	0.47
MEK	73	0.32	0.45	0.50	0.59
Benzene	79	0.12	0.16	0.22	0.24
Toluene	93	0.48	0.62	0.81	0.82
Xylenes	107	0.35	0.51	0.67	0.77
Monoterpenes	137	0.54	0.88	0.92	1.22
Other species	**Units**				
Black carbon (BC)	µg m^{-3}	0.43	0.60	0.72	0.89
Nitrogen oxides (NO$_x$)	ppb	5.1	5.6	7.3	7.5
Ozone (O$_3$)	ppb	49.6	55.5	54.1	59.1

Table 3: Concentrations (5 minute averages) of VOCs and other pollutants during the Athens winter campaign. Values are shown for the overall period and for the biomass burning periods.

		Overall measurement period				**Biomass burning periods**			
		Lower quartile	**Median**	**Average**	**Upper quartile**	**Lower quartile**	**Median**	**Average**	**Upper quartile**
VOCs	***m/z***	Concentration (ppb)							
~~Methanol~~	~~33~~	~~1.23~~	~~2.42~~	~~6.07~~	~~5.91~~	~~13.78~~	~~19.68~~	~~25.65~~	~~30.51~~
Acetonitrile	42	0.05	0.08	0.16	0.18	0.34	0.45	0.55	2.70
Formic acid, Ethanol	47	0.95	1.33	1.80	2.01	2.31	3.13	3.69	4.57
Acetone	59	1.10	1.52	2.24	2.48	4.05	5.04	5.76	6.74
Acetic acid	61	0.95	1.38	2.11	2.42	2.65	4.02	5.26	6.22
Isoprene	69	0.41	0.60	1.05	1.07	1.92	2.56	3.25	3.91
MVK+MACR	71	0.13	0.21	0.41	0.43	0.79	1.05	1.35	1.58
MEK	73	0.28	0.41	0.59	0.67	1.00	1.29	1.52	1.82
Benzene	79	0.29	0.55	1.00	1.10	1.94	2.58	3.18	3.70
Toluene	93	0.94	1.34	2.34	2.72	4.23	5.49	6.25	7.06
Xylenes	107	0.43	0.83	1.69	1.94	3.32	4.28	5.09	5.68
Monoterpenes	137	0.15	0.23	0.43	0.46	0.87	1.22	1.37	1.71
Other species	**Units**								
Black carbon (BC)	µg m^{-3}	0.46	1.00	2.02	2.35	5.78	7.63	7.98	9.54
Sulfur dioxide (SO_2)	Ppb	0.7	1.1	1.6	1.9	1.1	1.8	2.3	3.0
Nitrogen oxides (NO_x)	Ppb	5.9	1.3	24.6	26.5	51.8	70.3	79.7	93.1
Ozone (O_3)	ppb	8.7	25.9	21.6	32.6	1.8	2.7	3.5	4.3
Carbon monoxide (CO)	ppm	0	0.1	0.3	0.4	1.0	1.2	1.4	1.7
Carbon dioxide (CO_2)	ppm	380	388	390	402	420	429	432	441

Table 4. Emission factors (g Kg^{-1}) for VOCs and other species during ~~the~~ biomass burning. ~~of biomass for residential heating. Comparison with reported emission factors from various biomass fuels.~~

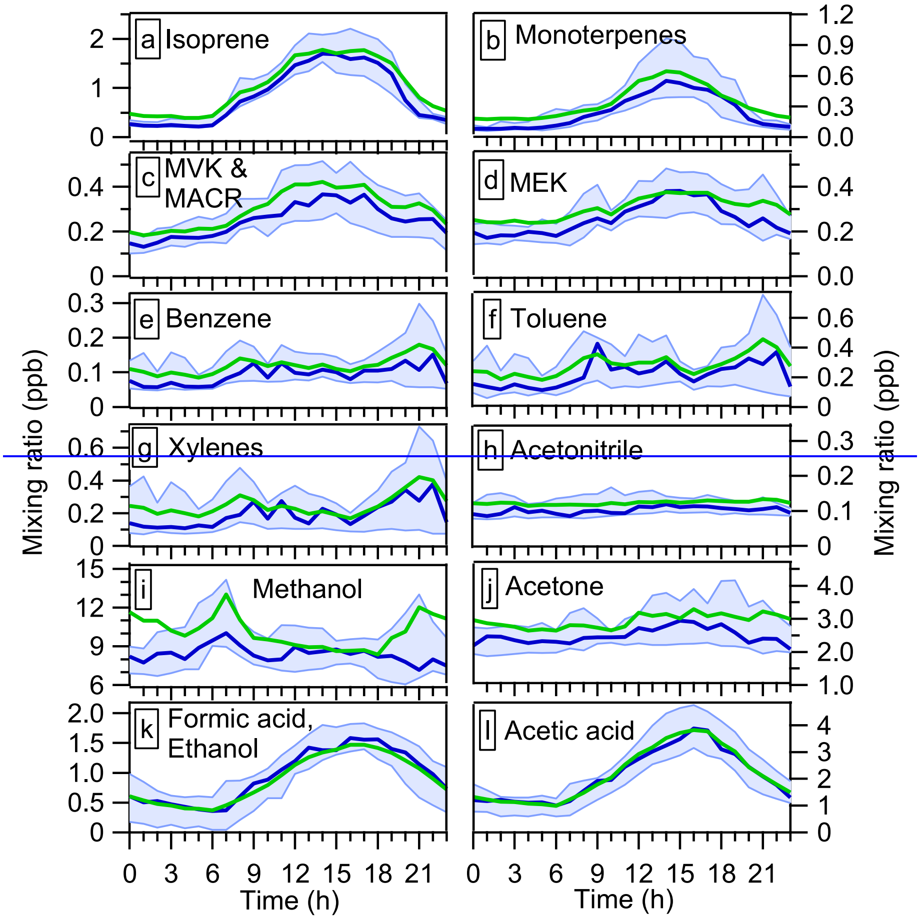
	Emission Factors g Kg^{-1} of fuel								
Species	Residential heating (This work)	Savanna fires (Sinha et al., 2003)	Yucatan Mexico (Yokelson et al., 2009)	Pine-forest Understory (Yokelson et al., 2013)	Coniferous Canopy (Yokelson et al., 2013)	African grass (Stockwell et al., 2015)	Alfalfa (Stockwell et al., 2015)	Black spruce (Stockwell et al., 2015)	Ponderosa pine (Stockwell et al., 2015)
CO_2	1600	1700 ±60	1641 ±40	1668 ±72	1670 ±128	1565 ±14	1352 ±55	1724 ±35	1594 ±109
SO_2	0.02 ±0.02	0.43 ±0.30	3.16 ±2.02	1.06 ±0.39	1.06 ±0.41	0.95 ±0.28	1.2 ±0.6	0.93 ±0.01	0.88 ±0.27
NO_x (as NO)	1.6 ±0.2	3.3 ±0.6	4.19 ±3.33	2.55 ±0.41	2.40 ±1.47	2.10	3.41	3.42	2.97
CO	22.2 ±2.8	68 ±30	80.2 ±19.4	72.2 ±26	85.3 ±38.3	22.6 ±4.8	76.5 ±7.3	46.5 ±8.7	95.3 ±27
Acetonitrile	0.01 ±0.002		0.5	0.13 ±0.09	0.14 ±0.06	0.02 ±0.02	0.67 ±0.11	0.05 ±0.02	0.20 ±0.11
Formic acid Ethanol	0.05 ±0.01	0.62 ±0.18	1.53 ±1.11	0.09 ±0.09 0.16 ±0.23	0.22 ±0.18 0.04 ±0.02	0.06 ±0.04	0.14 ±0.16	0.33 ±0.17	0.96 ±0.45
Acetone	0.14 ±0.02		1.10	0.35 ±0.29	0.37 ±0.2	0.09 ±0.07	0.82 ±0.11	0.72 ±0.78	0.82 ±0.49
Acetic acid	0.11 ±0.04	2.4 ±0.9	4.04 ±3.13	1.33 ±1.27	1.19 ±0.98	0.72 ±0.47	5.5 ±6.9	1.6 ±0.9	5.6 ±3.5
Isoprene furan	0.09 ±0.02	0.04 ±0.02		0.07 ±0.06 0.20 ±0.21	0.10 ±0.09 0.16 ±0.07	0.02 ±0.02 0.06 ±0.04	0.43 ±0.03 0.22 ±0.12	0.44 ±0.25 0.12 ±0.04	1.5 ±1.0 0.41 ±0.30
MACR MVK	0.04 ±0.006			0.05 ±0.04 0.22 ±0.17	0.08 ±0.07 0.30 ±0.20	0.07 ±0.07	0.30 ±0.03	0.23 ±0.12	0.61 ±0.35
MEK	0.04 ±0.006		0.62	0.12 ±0.11	0.12 ±0.06	0.02 ±0.02	0.29 ±0.06	0.06 ±0.04	0.21 ±0.14
Benzene	0.12 ±0.01	0.18 ±0.09	0.76	0.18 ±0.17	0.62 ±0.59	0.04 ±0.03	0.53 ±0.26	0.59 ±0.25	1.29 ±0.90
Toluene	0.26 ±0.03	0.13 ±0.10		0.14 ±0.12	0.25 ±0.12	0.03 ±0.02	0.46 ±0.06	2.4 ±1.2	3.0 ±2.1
Xylenes	0.26 ±0.03			0.17[*]	0.18[*]	0.006 ±0.005[*]	0.15 ±0.02[*]	0.19 ±0.09[*]	0.18 ±0.08[*]
Monoterpenes	0.08 ±0.02			0.25 ±0.24	0.62 ±0.46	0.005 ±0.004	0.12 ±0.02	0.10 ±0.04	0.22 ±0.16

[*] sum of m-, p-, o--xylene, and ethyl benzene

Table 5: Emission ratios for biomass burning due to residential heating. Comparison with reported emission ratios from various biomass fuels types.

Species	Emission Ratios (Δspecies/ΔCO, ppb/ppm)							
	Residential heating (This work)	SW fuels (Warneke et al., 2011)	SE fuels (Warneke et al., 2011)	Pine spruce (Warneke et al., 2011)	African grass (Stockwell et al., 2015)	Alfalfa (Stockwell et al., 2015)	Black spruce (Stockwell et al., 2015)	Ponderosa pine (Stockwell et al., 2015)
SO_2	0.4 ± 0.5	-	-	-	18.8±5.4	6.4±3.7	10±2	4.6±1.4
NO_x	52.7± 9	-	-	-	88	42	70	32
Acetonitrile	0.32 ± 0.05	0.56	1.03	1.05	0.50±0.39	6.0±0.9	0.73±0.17	1.4±0.6
Formic acid Ethanol	1.3 ± 0.3	0.77	1.08	1.0	1.65±0.81	1.08±1.29	4.1±1.5	5.9±1.1
Acetone	2.9 ± 0.5	0.84	1.93	1.94	1.19±1.42	5.2±0.5	8.9±11	3.9±1.1
Acetic acid	2.0 ± 1.0	4.84	13.61	8.19	13.2±6.8	31±40	15.6±6.4	25.4±8.1
Isoprene furan	1.6 ± 0.22	0.53	1.38	1.57	0.33±0.27 1.1±0.76	2.3±0.1 1.2±0.6	3.7±1.6 1.1±0.3	6.2±2.1 1.6±0.65
MVK+MACR	0.7 ± 0.1	0.43	1.08	1.32	1.11±0.94	1.6±0.3	1.9±0.7	2.5±0.7
MEK	0.7 ± 0.2	0.41	1.28	1.17	0.26±0.22	1.5±0.3	0.5±0.3	1.8±0.5
Benzene	1.8 ± 0.2	0.86	0.83	2.29	0.57±0.3	2.5±1.1	4.5±1.2	4.6±1.8
Toluene	3.3 ± 0.8	0.30	0.48	0.81	0.3±0.2	1.8±0.1	14.8±5.5	9.0±3.5
Xylenes	2.8 ± 0.6	0.19	0.35	0.60	0.07±0.04	0.5±0.04	1.0±0.3	1.0±0.4
Monoterpenes	0.7 ± 0.2	0.16	0.55	1.25	0.004±0.002	0.33±0.03	0.42±0.13	0.46±0.19

Figure 1: Maps of Greece, Athens and Patras together with the locations of the measurement sites used during the three campaigns.


a Isoprene
b Monoterpenes
c MVK & MACR
d MEK
e Benzene
f Toluene
g Xylenes
h Acetonitrile
i Methanol
j Acetone
k Formic acid, Ethanol
l Acetic acid
Mixing ratio (ppb)
Mixing ratio (ppb)
0 1 2
0.0 0.3 0.6 0.9 1.2
0 0.2 0.4
0.0 0.2 0.4
0 0.1 0.2 0.3
0 0.2 0.4 0.6
0 0.2 0.4 0.6
0 0.1 0.2 0.3
6 9 12 15
1.0 2.0 3.0 4.0
0 0.5 1.0 1.5 2.0
0 1 2 3 4
0 3 6 9 12 15 18 21
Time (h)
0 3 6 9 12 15 18 21
Time (h)

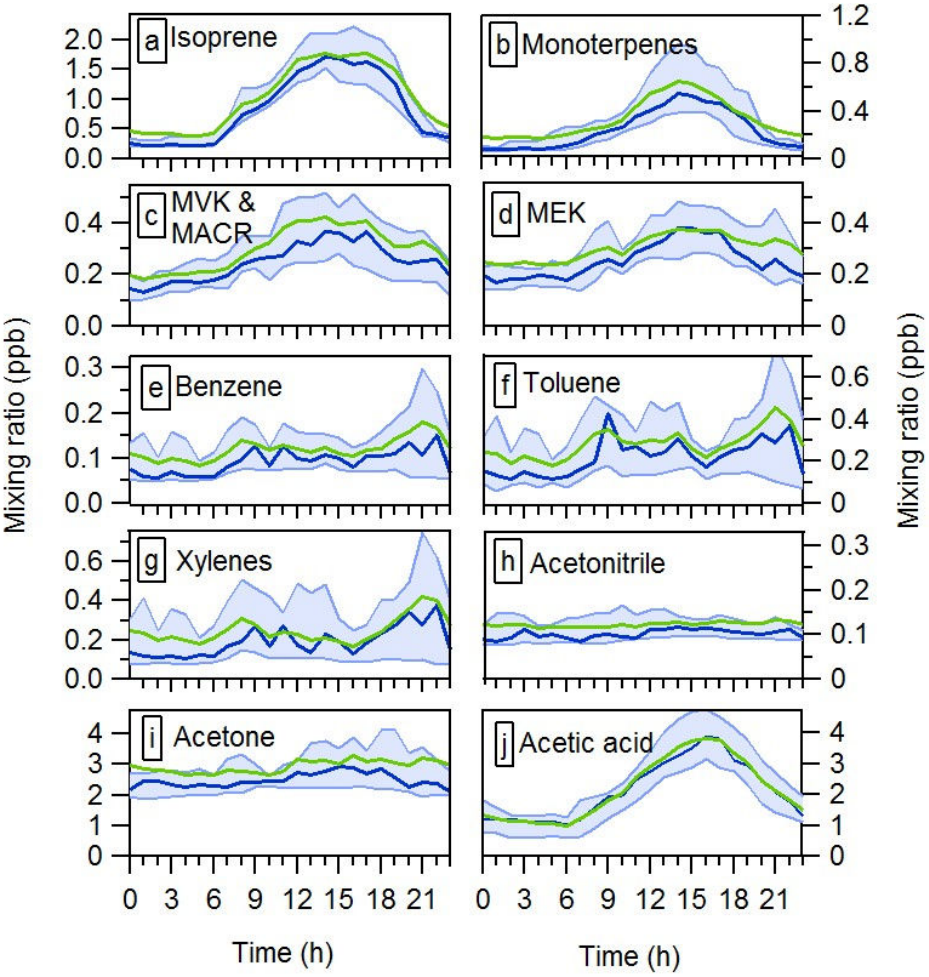
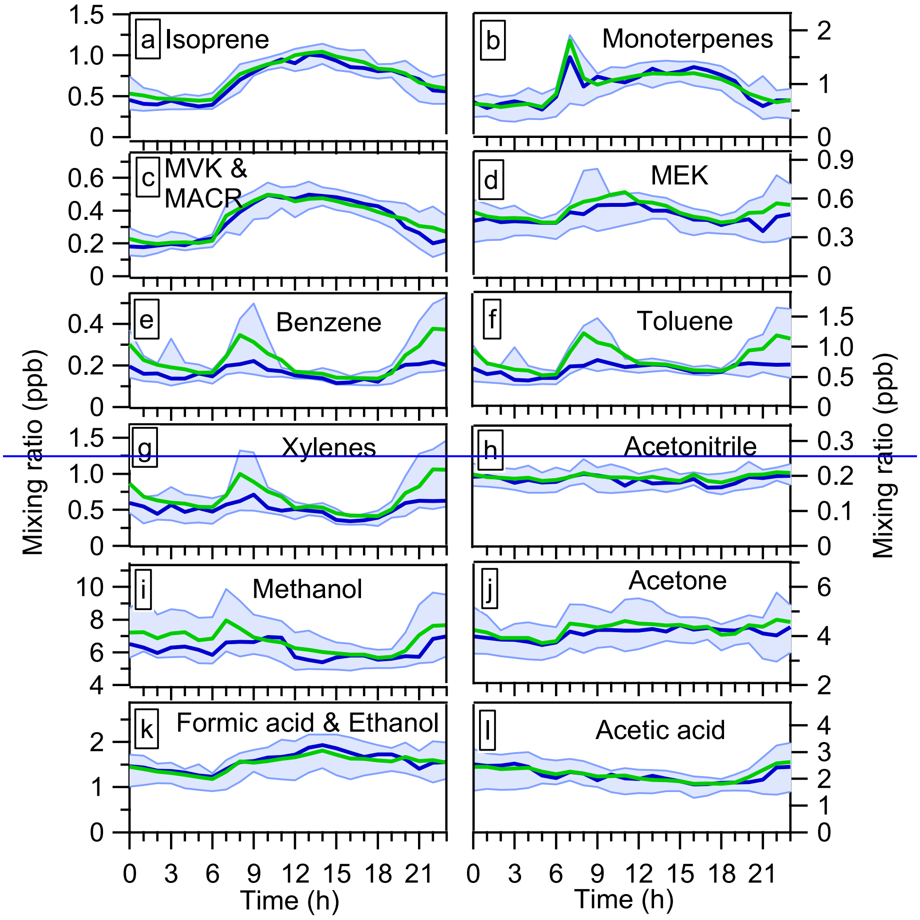

a Isoprene
b Monoterpenes
c MVK & MACR
d MEK
e Benzene
f Toluene
g Xylenes
h Acetonitrile
i Acetone
j Acetic acid
Mixing ratio (ppb)
Mixing ratio (ppb)
0.0 0.5 1.0 1.5 2.0
0 0.4 0.8 1.2
0.0 0.2 0.4
0 0.2 0.4
0.0 0.1 0.2 0.3
0 0.2 0.4 0.6
0.0 0.2 0.4 0.6
0 0.1 0.2 0.3
0 1 2 3 4
0 1 2 3 4
0 3 6 9 12 15 18 21
Time (h)
0 3 6 9 12 15 18 21
Time (h)

Figure 2: Average VOC diurnal profiles during the Patras summer campaign. Green lines present the average values. The median value is shown with blue. The blue area corresponds to the interquartile range.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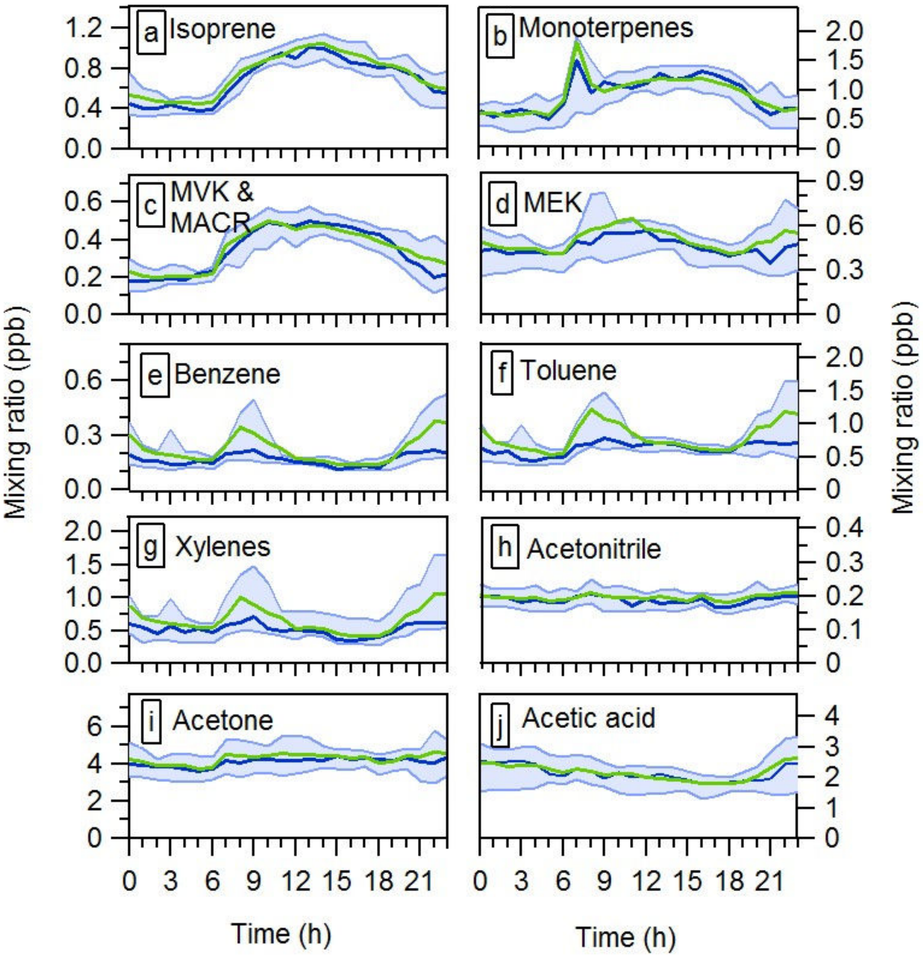
b Monoterpenes
c MVK & MACR
d MEK
e Benzene
f Toluene
g Xylenes
h Acetonitrile
i Methanol
j Acetone
k Formic acid & Ethanol
l Acetic acid
Mixing ratio (ppb)
Mixing ratio (ppb)
0 3 6 9 12 15 18 21
Time (h)
Time (h)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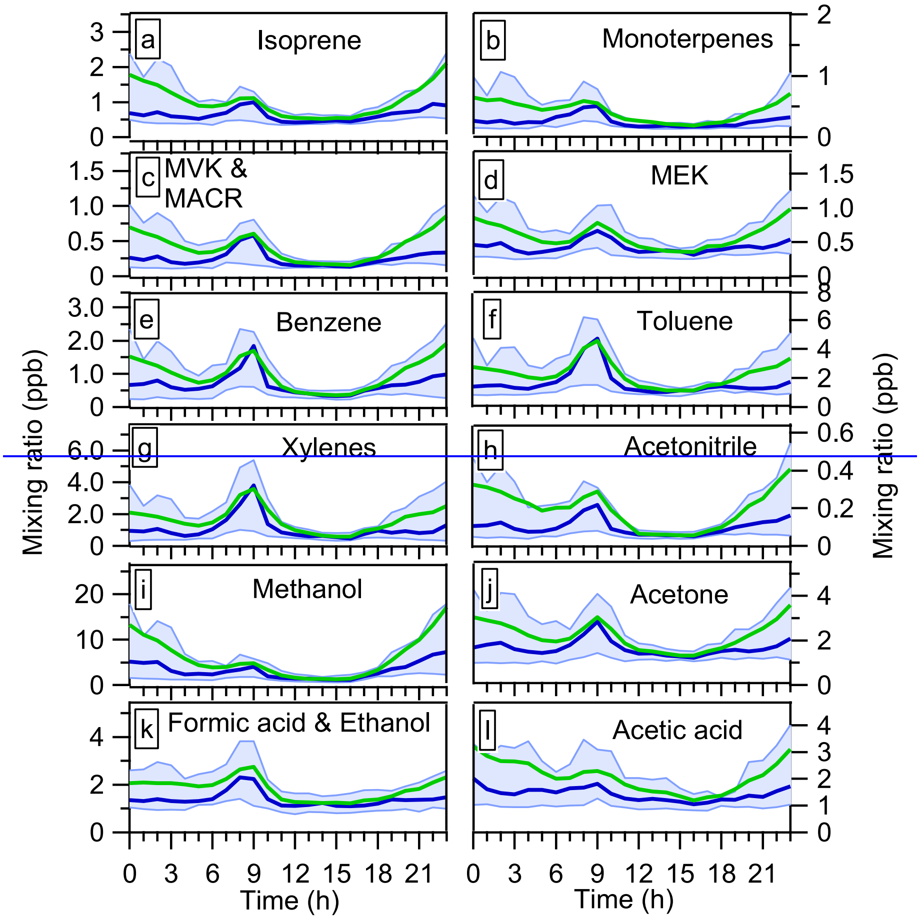
b Monoterpenes
c MVK & MACR
d MEK
e Benzene
f Toluene
g Xylenes
h Acetonitrile
i Acetone
j Acetic acid
Mixing ratio (ppb)
Mixing ratio (ppb)
0 3 6 9 12 15 18 21
Time (h)
Time (h)

Figure 3: Average VOC diurnal profiles during the Athens summer campaign. Green lines present the average values. The median value is shown with blue. The blue area corresponds to the interquartile range.


a Isoprene
b Monoterpenes
c MVK & MACR
d MEK
e Benzene
f Toluene
g Xylenes
h Acetonitrile
i Methanol
j Acetone
k Formic acid & Ethanol
l Acetic acid
Mixing ratio (ppb)
Mixing ratio (ppb)
0 3 6 9 12 15 18 21
Time (h)
0 3 6 9 12 15 18 21
Time (h)

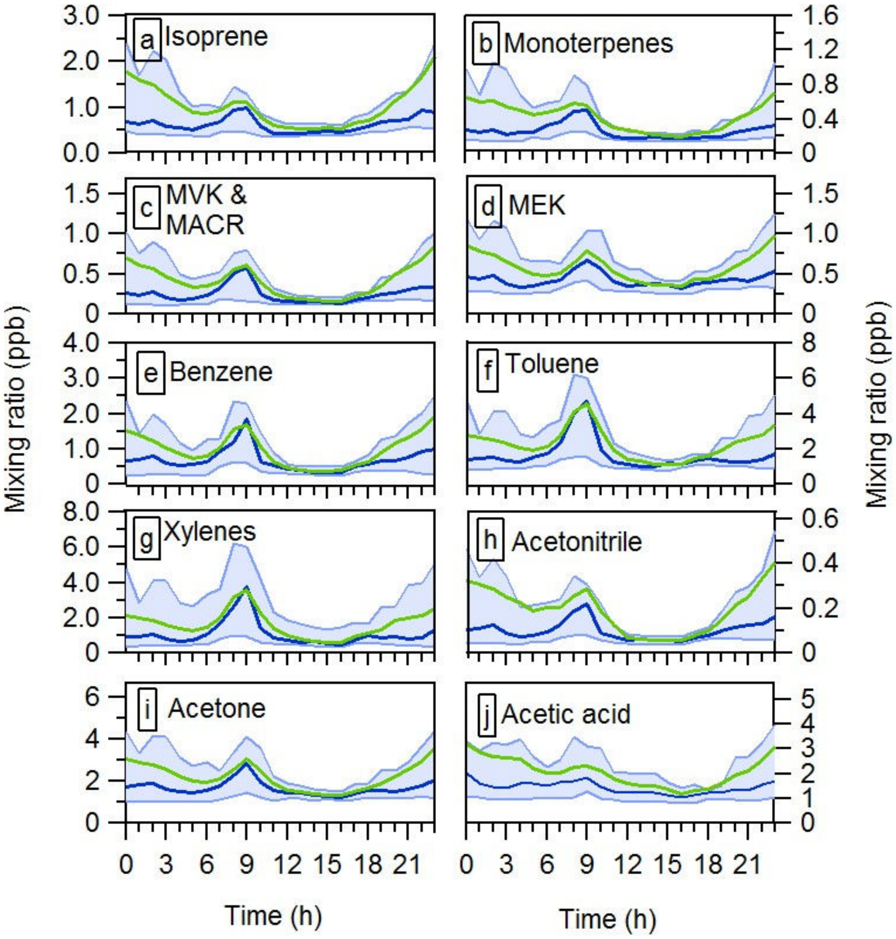
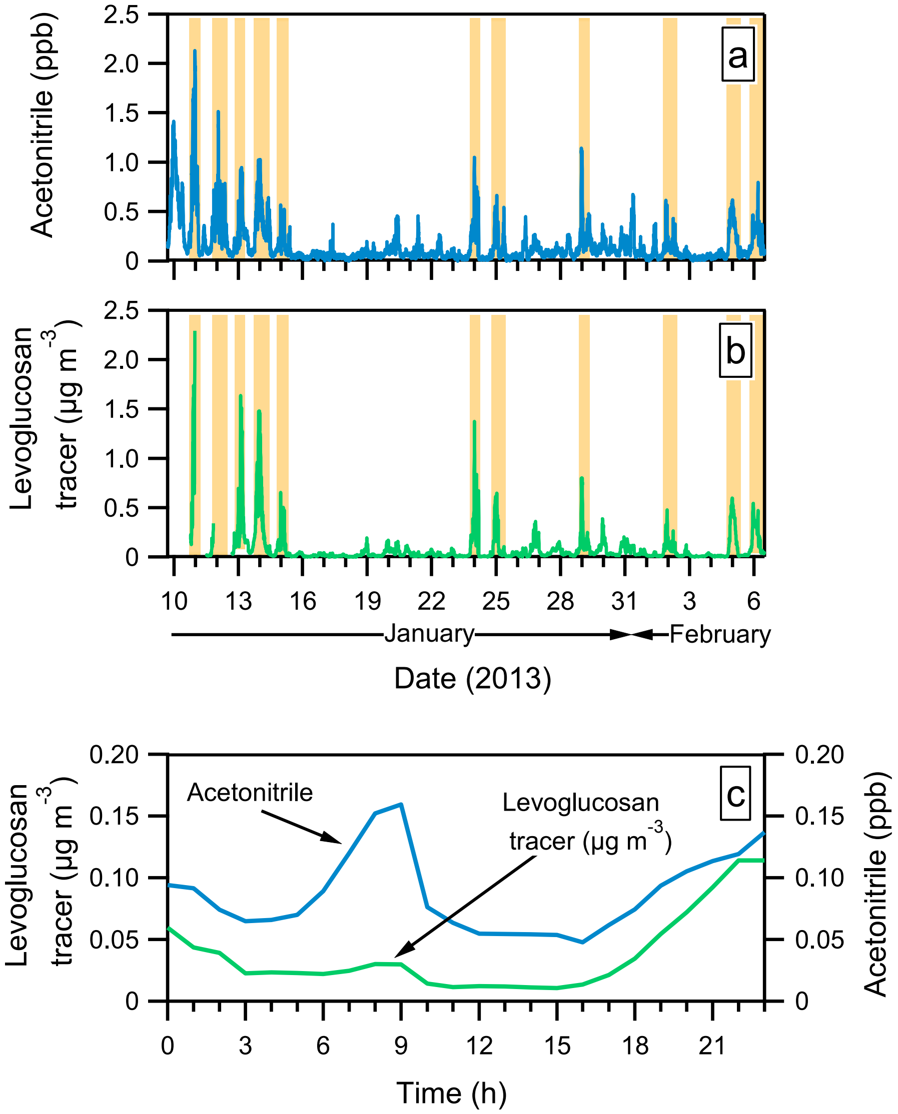

a Isoprene
b Monoterpenes
c MVK & MACR
d MEK
e Benzene
f Toluene
g Xylenes
h Acetonitrile
i Acetone
j Acetic acid
Mixing ratio (ppb)
Mixing ratio (ppb)
0 3 6 9 12 15 18 21
Time (h)
0 3 6 9 12 15 18 21
Time (h)

Figure 4: Average VOC diurnal profiles during the Athens winter campaign. Green lines present the average values. The median value is shown with blue. The blue area corresponds to the interquartile range.



5 **Figure 5:** Time series of (a) AMS levoglucosan tracer (*m/z* 60 of the AMS) and (b) acetonitrile for the Athens winter campaign. Light brown indicates periods where wood burning contributed substantially to the total VOC and particulate levels. Also shown (c) their average diurnal profiles.

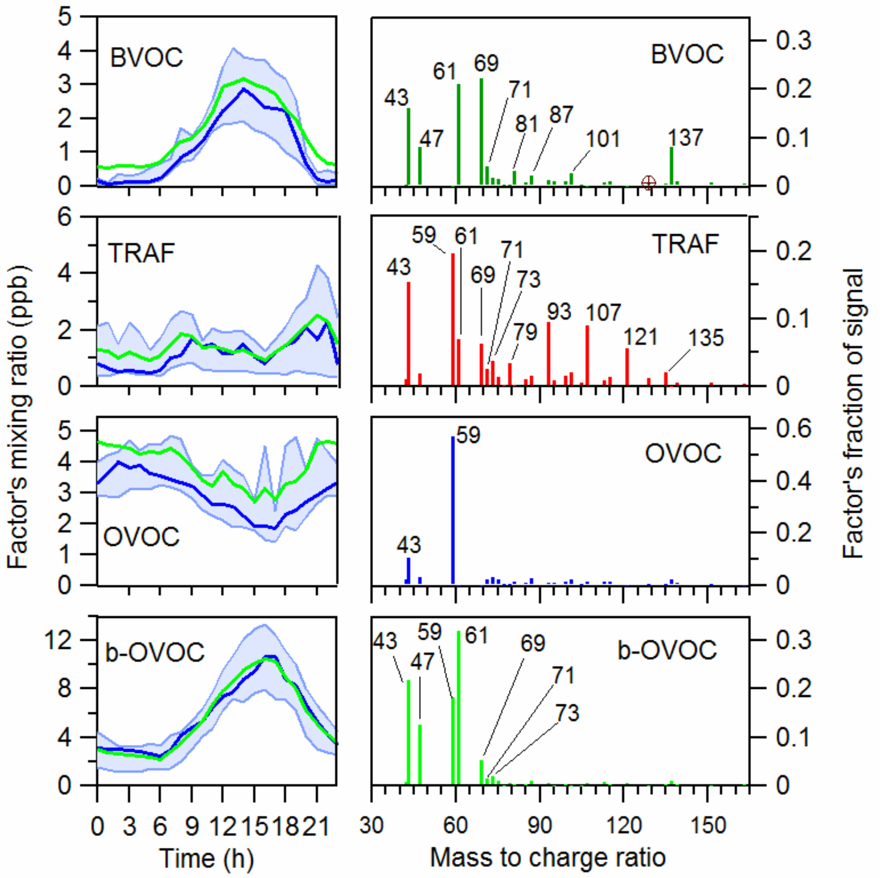


Figure 6: Results of Patras summer campaign PMF analysis. The left side shows the diurnal profiles of the factors. Green lines present the average values. The median value is shown with blue. The blue area is the interquartile range. The right side presents the *m/z* composition of each factor as a fraction of signal for each *m/z*. 5

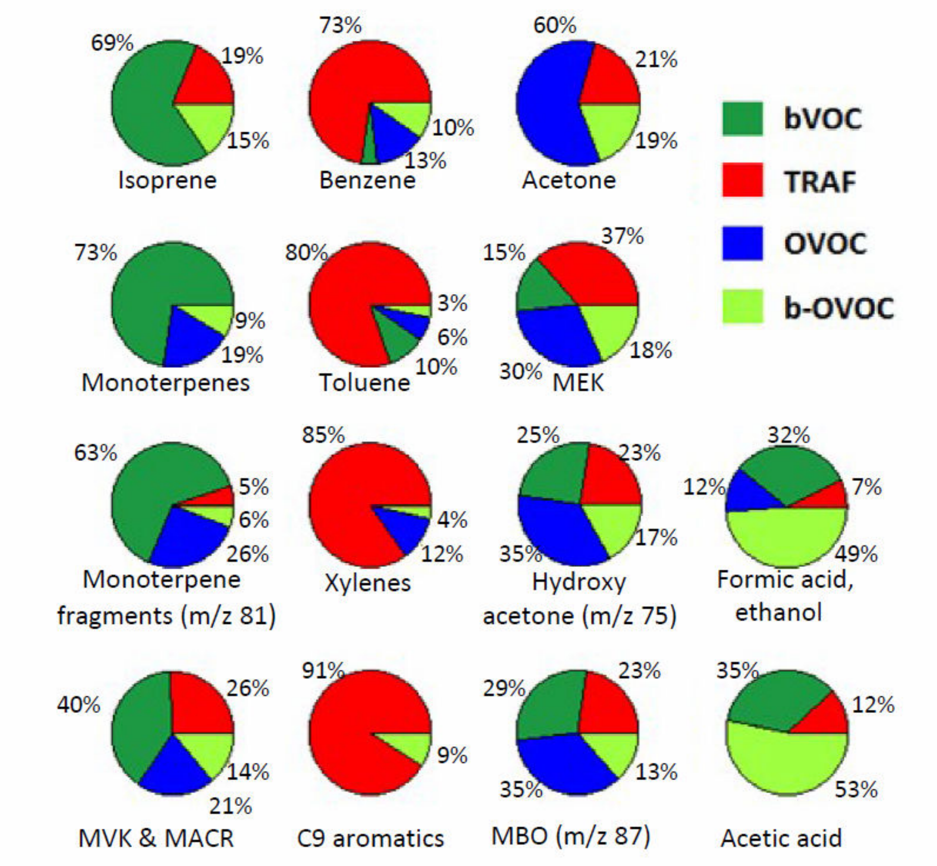


Figure 7. Species percentage (%) attributed to the various PMF factors for the Patras summer campaign.

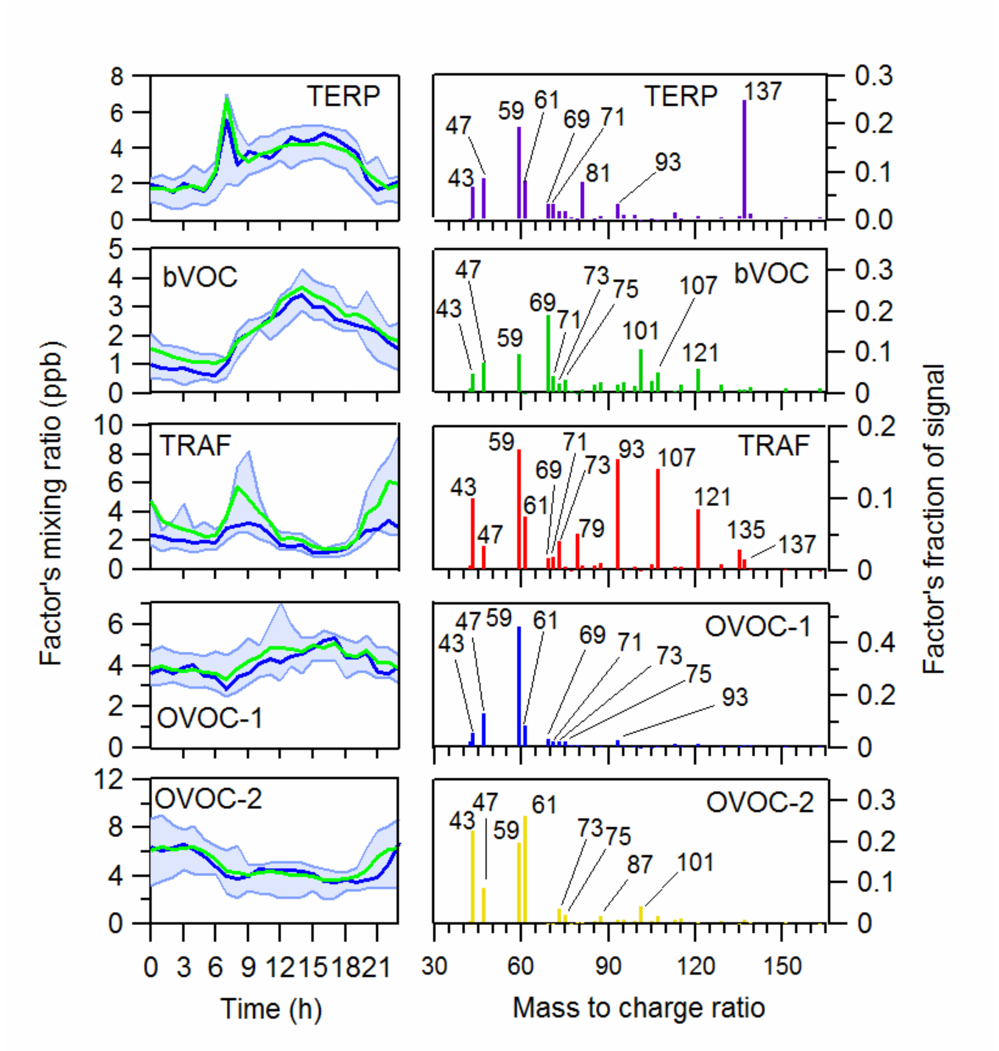


Figure ~~7~~8: Results of Athens summer campaign PMF analysis. The left side shows the diurnal profiles of the factors. Green lines present the average values. The median value is shown with blue. The blue area is the interquartile range. The right side presents the *m/z* composition of each factor as a fraction of signal for each *m/z*.

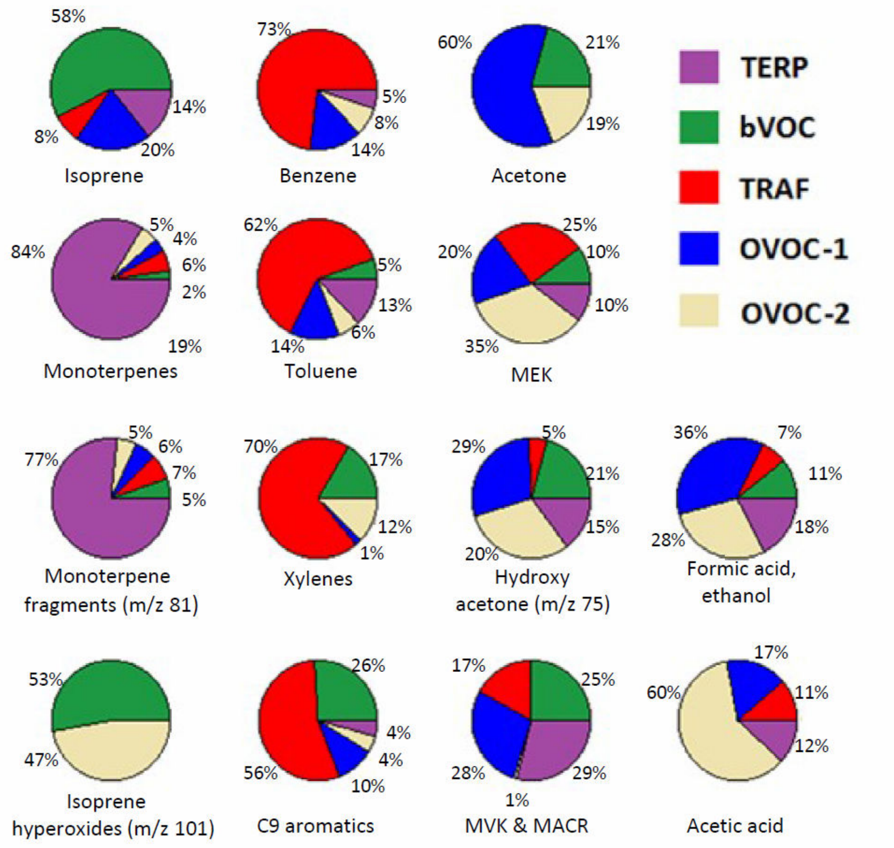


Figure 9. Species percentage (%) attributed to the PMF factors for the Athens summer campaign.

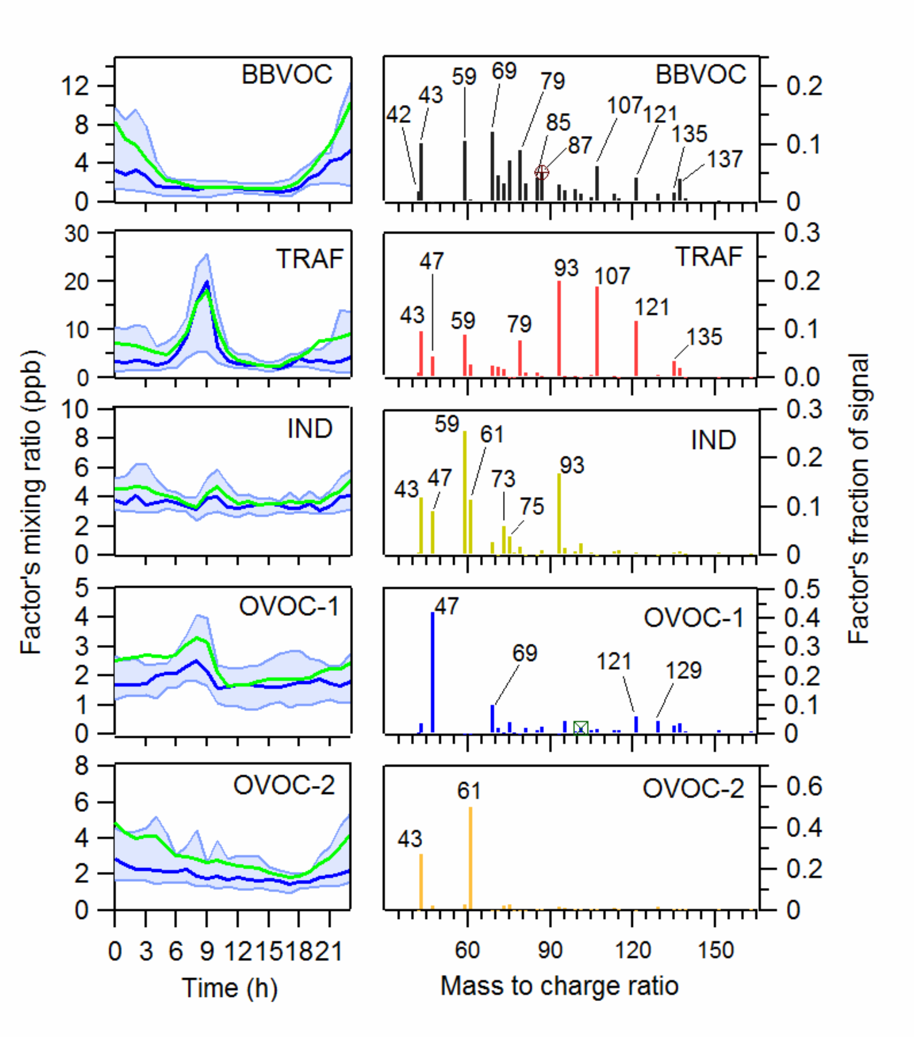


Figure ~~8~~10: Results of Athens winter campaign PMF analysis. The left side shows the diurnal profiles of the factors. Green lines present the average values. The median value is shown with blue. The blue area is the interquartile range. The right side presents the *m/z* composition of each factor as a fraction of signal for each *m/z*.

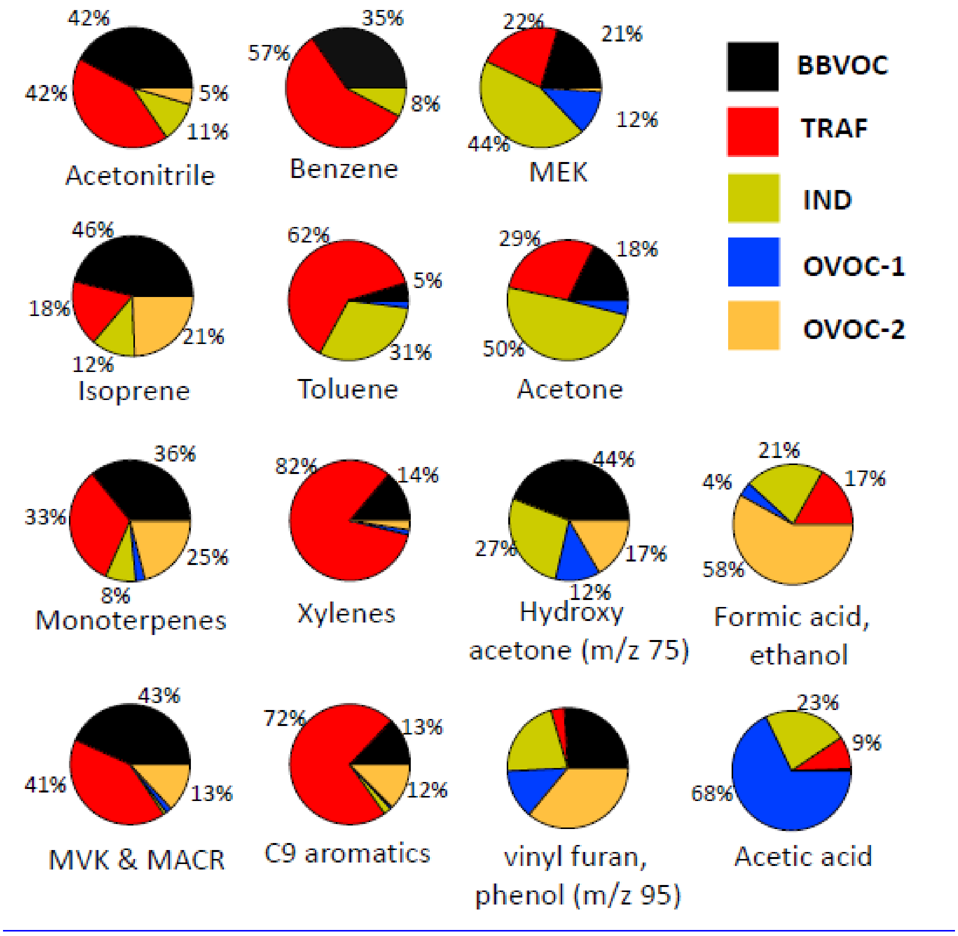


Figure 11. Species percentage (%) attributed to the PMF factors for the Athens winter campaign for the 5 factor solution.