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Interactive comment on "Temporal variability and sources of VOCs in urban areas of Eastern Mediterranean" *by* Christos Kaltsonoudis et al.

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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. Details are provided below.

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 $k = 2 \times 10^9$ 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 percent) 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

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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 percent) only. The*

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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 percent 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 percent was included in other factors, with 15 percent 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 photochemically 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.

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