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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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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*

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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 but we still point out the potential small interference by furan.

(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 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 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 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

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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 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 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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