

## General Comments:

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:

## Major Concerns:

### 1) 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.

- 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.
- 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  $k = 2 \times 10^9 \text{ cm}^3 \text{ s}^{-1}$ . They should also provide the Equation used by them in this case or cite the work listing the Equation at this place.
- iii) It is mentioned that similar instrumentation was used for the winter deployment. Please clarify whether it was the same PTR-MS instrument?
- 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).

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.

2) 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.

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 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.

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.

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.

### **Suggestions:**

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.

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.

#### **MINOR comments:**

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

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.

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.

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