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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Volatile and intermediate-volatility organic compounds in sub-urban Paris: variability, origin and importance for SOA formation" *by* W. Ait-Helal et al.

Anonymous Referee #2

Received and published: 9 April 2014

General Comments:

The paper presents measurements of I/VOC and uses two approaches (integrated and time resolved) to estimate SOA formation from measurements made during the MEGAPOLI campaign, near Paris. Estimated SOA are compared to measured OOA determined from PMF analysis of AMS measurements and the agreement is improved when compounds of intermediate volatility (in this case n-alkanes in the C12 – C16 range) are included. In general, the data collection and methodologies are sound and of good quality and the manuscript will be of interest to the atmospheric community. The text requires a little tightening up to improve the flow and readability but I support

publication once the following comments, outlined below, have been addressed.

Specific Comments:

Page 4848, Line 26: I am unclear what the abbreviation m a.g.l. is? Please define. Also it is not clear what the time resolution of the adsorbent cartridge measurements were, this needs to be stated for both the I/VOC and OVOCs. I think it would be really helpful to the reader to add the offline adsorbent cartridge measurements to Table 2, this table could have two parts one for the online measurements as already shown and another for the offline measurements.

Page 4854, Line 15: Why are the OM measurements averaged to 3 hours, the AMS has much higher time resolution? Is this the time resolution of the adsorbent cartridge samples?

Page 4852, Line 23: the authors describe the seasonal differences in the IVOCs (C12 – C16 alkanes) between winter and summer and say that the lower mixing ratios in winter may be due to gas-to-particle partitioning. I think that the difference between winter and summer should be explicit defined as difference in the gas phase mixing ratios. How are the particles being removed during the gas phase adsorbent cartridge measurements? Could the use of different sampling modules (SASS in summer and ACROSS in winter) be the source of any of these differences? In the conclusions section the authors state that 'the partitioning from the gas phase to the particulate phase dominates the variability and is enhanced in winter', in my opinion they have not shown this. Previous work (Williams, B. J.; Goldstein, A. H.; Kreisberg, N. M.; Hering, S. V., In situ measurements of gas/particle-phase transitions for atmospheric semivolatile organic compounds. Proceedings of the National Academy of Sciences of the United States of America 2010, 107, (15), 6676-6681.) showed that these n-alkanes are > 90 % in the particle phase (from measurements and Pankow theory) so I expect enhanced partitioning will only be able to explain a small change in winter/summer concentrations. The authors have everything they need to calculate the gas to particle partitioning of

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these alkanes using Pankow partitioning theory (Pankow, J.F. 1994, Atmospheric Environment, 28, 185-188). This needs to be done to support the stated conclusion. Does it explain the observations?

In section 3.2, the authors describe the PMF analysis of the AMS data and describe the two factor solution, HOA and OOA. The HOA factor having been further split in other work into HOA-traffic and COA (which I assume is cooking organic aerosol because it is not explicitly defined here). In many previous papers OOA is further split into two factors called SV-OOA (semi-volatile OOA) and LV-OOA (low volatility OOA), I am curious as to whether the authors thought about doing this? Typically SV-OOA represents fresher SOA which might be expected to form faster and be more associated with gas phase oxidation chemistry while LV-OOA is more aged. I would think that with the approach employed here that the authors would want to be comparing their results to SV-OOA as opposed to the total OOA.

The discussion of the use of an inert tracer for normalization (Page 4864) is very confusing and it is very unclear what was actually done. It seems like no normalization was done but I cannot be sure. This paragraph needs to be significantly reworded for clarity.

In Figure 5a, the datapoints are color coded by the O3/CO ratio as a proxy for photochemical processing, why was this ratio used and not the photochemical age using m,p-xylenes and ethyl benzene that was determined early in the paper? What's the justification for the use of this different photochemical aging metric used in this plot?

The Bahreini et al., (2012) citation is not correct for the statement being made (Page 4867, Line 19). A more appropriate reference is Dallmann, T. R.; Kirchstetter, T. W.; DeMartini, S. J.; Harley, R. A., Quantifying on-road emissions from gasoline-powered motor vehicles: Accounting for the presence of medium and heavy-duty diesel trucks. . Environmental Science and Technology 2013, 47, 13873−13881. Figure 3 in this paper clearly shows the emission differences for various pollutants including primary

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organic aerosol (POA). It should also be stated in the paper that this factor of 14 $\pm$ 5 is for heavy duty trucks and not passenger vehicles (they are very few diesel passenger vehicles in the US) which may differ in their emission characteristics.

In Section 5.2.2, Line 27 should add that the 8 excluded datapoints are shown as grey symbols in Figure 9. During event 5 ("Atlantic Polluted") there is a substantial overestimation of the SOA mass that is not discussed. Can the authors elaborate on the likely cause of this?

In Figure 9, the exclusion of the grey data points should be explained in the caption or at the very least the caption show direct the reader to the explanation in the text.

Supporting Information Line 77 – there is a missing citation here, recently Gentner et al., 2013 reported emission factors for VOCs and IVOCs for light duty gasoline vehicles from tunnel measurements. [Citation: D. R. Gentner, D. R. Worton, G. Isaacman, L. Davis, T. R. Dallmann, E. Wood, S. Herndon, A. H. Goldstein and R. A. Harley (2013). Chemically speciated emissions of gas-phase organic carbon from motor vehicles and implications for ozone production. Environmental Science and Technology, 47, 11837-11848.]

Supporting information line 80, what is meant by American oil, does this refer to American gasoline? If so, are the differences between American and European gasoline known, where are they reported?

Technical Corrections:

Page 4844, Line 10: Reword 'If a high density of population characterizes the megacities, they are also remarkable by their. . ..' to read something like 'If a high population density characterizes a megacity, they are also defined by their. . . '.

Page 4845, Line 13: Replace 'qualified' with 'defined'.

Page 4845, Line 14: Replace 'any' with 'either'.

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Page 4848, Line 18: Add ‘n-alkanes’ after ‘their C*, C12-C16’.

Page 4848, Line 19: Replace ‘are’ with ‘were’.

Page 4850, Line 26: Replace ‘great’ with ‘high’.

Page 4851, Line 8: Too many significant figures are shown considering the uncertainties, round these to read ‘(440 $\pm$ 220 m and 1340 $\pm$ 610)’.

Page 4851, Line 13: Replace ‘which the’ with ‘these is’.

Page 4853, Line 9: Suggest rewording ‘suggesting their secondary origin’ to read ‘suggesting they were predominantly secondary in origin’.

Page 4854, Line 4: Add ‘only a’ before ‘few sunny days. . ..’

Page 4854, Lines 4-5: Remove ‘equal to’ from the sentence ‘average temperature was equal to 18.3 ($\pm$ 3.8) C’.

Page 4854, Line 7: Remove ‘equal to’ from the sentence ‘average wind speed was equal to 3.7 ($\pm$ 1.5) m s-1’.

Page 4854, Line 16: Replace ‘which is equal to’ with ‘of’.

Page 4855, Line 1: Replace ‘a’ with ‘one’.

Page 4855, Line 17: Add ‘predominately’ after ‘CO is’.

Page 4855, Line 19: The sentence ‘This may indicate that, during event 4, CO is of primary but also of secondary origin and/or issuing from long range transport, according to its long atmospheric lifetime which is about a month (Parrish et al., 1998). These assumptions are supported by. . ..’ does not make sense as written, this needs to be reworded for clarity.

Page 4856, Line 15: Remove ‘the’ before ‘megacities’.

Page 4863, Line 20: Add ‘the’ after ‘based on’.

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Page 4863, Line 21: Add ‘of’ after ‘downwind’.

Page 4863, Line 22: Remove ‘also’ after ‘Boynard et al., (2014)’ and replace ‘are’ with ‘were’.

Page 4863, Line 28: Replace ‘change’ with ‘have changed’.

Page 4864, Line 24: Replace ‘have’ with ‘had’.

Page 4865, Line 11: Replace ‘any of the two’ with ‘both the’.

Page 4865, Line 11: Replace ‘does not include the biogenic’ with ‘did not include any biogenic’.

Page 4865, Line 22: Reword ‘until now, estimations have only considered the SOA formation in dry conditions’ to read ‘typically estimations only consider SOA formation under dry conditions’.

Page 4865, Lines 25-26: Reword ‘Carlton et al., (2008) have improved the agreement between the observations and the prediction in the total mass concentrations and the variability,’ to read ‘Carlton et al., (2008) improved the agreement between observations and predictions of total mass concentrations and its variability,’.

Page 4866, Line 1: Add ‘likely’ after ‘also’ and replace ‘the’ with ‘an’.

Page 4866, Line 2: Remove ‘the’.

Page 4866, Line 14: Replace ‘consists in’ with ‘consists of’.

Page 4867, Line 4: Replace ‘is equal to’ with ‘was’.

Page 4867, Line 9: Replace ‘is equal to’ with ‘was’.

Page 4867, Line 19: Replace ‘Besides’ with ‘Also’.

Page 4868, Line 18: Rewrite ‘It can be seen that light alkanes, which have the highest emissions, exhibit a low or no SOA yield formation’ to read ‘It can be seen that the light

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alkanes, which have the highest emissions, exhibit low to no SOA formation potential'.

Page 4868, Line 19: Remove this 'Indeed, their emission in the gaseous phase is enhanced by their high-volatility'.

Page 4868, Line 24: Replace 'exceed' with 'exceeded'.

Page 4869, Line 4: Replace 'by considering VOCs and the sum of VOCs and IVOCs,' with 'by using VOCs or I/VOCs (sum of VOCs and IVOCs),'.

Page 4869, Line 1: Rewrite 'the SOA estimated' to read 'the estimated SOA'.

Page 4869, Line 21: Remove 'a' after 'characterized by'.

Page 4870, Line 7: Remove 'the' before 'SOA formation'.

Figures 2 and 3 captions: Replace 'The grey-shaded areas highlight the "Atlantic Polluted" wind regimes associated to stagnant conditions and corresponding to an OOA increase' with 'The grey-shaded areas highlight the "Atlantic Polluted" wind regimes associated with stagnant conditions and increased OOA'.

Figure 8 caption: This should include the definition of the gray boxes as previously defined in Figures 2 and 3. Add 'The grey-shaded areas highlight the "Atlantic Polluted" wind regimes associated with stagnant conditions and increased OOA'.

Figure 9 caption: Replace 'are' with 'were'.

Supporting Information, Line 56: Replace 'on' after represented with 'in'.

Supporting Information, Line 62: Change '. . ..significantly over the last decade at $\pm$30 %.' to read 'significantly ($\leq$ 30 %) over the last decade'.

Supporting Information, Line 63: Replace 'leaded' with 'led'.

Supporting Information, Line 75: Replace 'few' with 'little'.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 4841, 2014.