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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 #1

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General comments: This paper reports measurements and analysis of gas and particle-phase organics in suburban Paris, including seasonal variation, temporal evolution, and their sources. The most interesting part of the manuscript to me was the data on a few speciated IVOCs (C12-C16 normal alkanes) and the corresponding SOA analysis. IVOCs have been proposed to be an important class of SOA precursors. However, ambient IVOC concentrations are not routinely measured, therefore their SOA production is not well constrained. The few n-alkanes presented in this paper only account for a small fraction of total IVOCs emitted from primary sources, but they could still demonstrate the importance of IVOCs in SOA production. I support the publication of this paper in ACP after the following comments are addressed.

Specific comments:

My first major concern is the paper’s framing of IVOCs – The manuscript only considers 5 IVOCs (all n-alkanes) but it seems to equate them with “IVOCs”. For example, the abstract states that “10% (of the SOA is) explained by only C12-C16 IVOCs.” This statement is not correct. The only IVOCs that paper accounts for SOA formation from is C12 to C16 normal alkanes. That is a small subset of the IVOCs. There are likely many many more C12 to C16 IVOCs that were not measured that therefore not considered (branched, cyclic, PAH, etc.). This issue was mentioned in the discussion but statements like that given above in the abstract will likely confuse many readers because the text implies in many places that they are estimating the SOA from IVOCs not 5 n-alkanes. By only measuring a few compounds, the paper is likely only exploring the so called tip of the iceberg when it comes to SOA formation from IVOCs. For example, Fraser et al. (Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A., Air quality model evaluation data for organics. 4. C2-C36 non-aromatic hydrocarbons. Environ. Sci. Technol. 1997, 31, (8), 2356-2367) demonstrates that the vast majority of IVOC mass in Los Angeles is not n-alkanes (or simple aromatics, etc.). The paper needs to use more precise language to not confuse the reader into thinking it is provides a comprehensive estimate of SOA from IVOCs.

The second major point is that I have some problems with the SOA production estimates. The SOA yields for the IVOCs are taken from Lim and Ziemann. These experiments measured yields at very high concentrations (in excess of 500 ug/m3) in a smog chamber. These concentrations are substantially higher than the ambient concentration of 0.2∼9 ug/m3 in this study. This completely biases the gas particle partitioning and will cause the yields to be overestimated. This point is mentioned in the text, but the authors do not do any analysis to try to quantify the potential bias. Simply applying the yields of Lim and Ziemann to the atmosphere is completely unrealistic and will greatly overestimate the amount of SOA from these compounds. The authors need to quantitatively examine this bias. One way would be estimate the partitioning bias in the Lim and Ziemann data using other n-alkane yield parameterizations. Another would be to simply use the high-NOx yields for n-alkanes which were measured at atmospherically relevant concentrations of Presto et al. (2010). The bottomline is the SOA mass yields of C9-C16 are substantially overestimated if the effect of OA concentrations on SOA yields was not taken into account.

One consequence of using very high yields is that the few normal alkanes IVOC measured by this study contribute a surprising large fraction (10%) of the SOA. In diesel exhaust (likely the most important source of these normal alkanes) C12-C16 n-alkanes contribute less than 10% of the IVOC emissions (Schauer et al., 1999 EST). As a result, the amount of SOA formed solely by IVOCs could be greater than the measured SOA (without taking into account other processes such as aqueous reactions). Estimation of SOA production from the C12-C16 needs to be revisited.

There were a fair number of confusing statements with respect to SOA formation.

Page 4863 – In the same paragraph you say "SOA yields determined under low-NOx conditions were used when available (see Supplement, Sect. S3 for details)." But then two sentences later you say "However, for more consistency, only the SOA yields determined under high-NOx conditions are used here." Which is it?

"COA in chamber experiments is ten to hundred times higher than the ambient organic mass concentrations" This is true in some experiments (e.g. those of Lim and Ziemann) but that is not universally true.

Table 3 – I found the yields confusing. I realize these are yield to CO, but you are forcing the readers to do unit conversions to compare with the original sources. The authors should report the yields in the standard (and much more interpretable) units of mass SOA/mass precursor reacted.

CO as tracer for anthropogenic emissions, especially using VOC/CO ratios. CO (at

least in the US) is dominated by emissions from gasoline vehicles. I am not sure in Europe. Gasoline vehicles are only one class of anthropogenic source. How robust is it to use these ratios, especially for IVOCs which are likely emitted by other (non-gasoline vehicle sources)?

"The important use of diesel by light-duty cars in Europe, and more particularly in France, might explain the higher POA emission ratio determined at SIRTA, diesel being known to emit 13 times more organic particles than gasoline" It is not only that diesel emit more POA than gasoline powered cars, but they also likely emit less CO so one needs to consider both components in the OA/CO ratio.

Page 4868, line 13-14: "The I/VOC precursors explain 45% of the SOA measured at SIRTA". However, the SOA production from I/VOC was estimated using the integrated approach. This approach overestimates SOA production by assuming complete reaction of all precursors to form SOA. Since the time-resolved approach was also used in this study and better predict the actual SOA production in the atmosphere, the contributions of I/VOC precursors to SOA using this approach should be included in Fig. 6.

2) Page 4852, line 23-29 (also in abstract): The study reports a higher mixing ratio of C12-C16 in the summer than the winter. They speculate that this was due to gas/particle partitioning. I am skeptical of this claim. These are very volatile species – the least volatile (C16 normal alkane) has C* greater than 50,000 ug/m3. Therefore it seems extremely unlikely that appreciable amounts of any of these species would partition into the condensed under any atmospheric conditions. Furthermore, the modest summer-winter swing in temperature will only modestly change the vapor pressure (this change can easily be estimated with measured temperature and clausius claperyon). It seems much more likely that some other process (change in emissions, change in boundary layer height) is driving the seasonal changes in IVOC concentrations. If the authors want to argue that it is partitioning then they need to provide some quantitative evidence for it. The authors did cite some studies that suggest seasonal partitioning

effects – I looked up one of these references up (Bi et al. 2003). That study used filters followed by PUF. It is likely that the small amounts of IVOCs that they sampled in this carbon number range are simply sampling artifacts (adsorbed vapors on filters) as opposed to actual particle phase organics.

Abstract "including for the first time C12-C16 n-alkanes of intermediate volatility (IVOCs), suspected to be efficient precursors of secondary organic aerosol (SOA)." This statement is not true. In fact this paper cites some other studies that have measured IVOC n-alkanes. (Kadowaki, 1994; Bi et al., 2003; Guo et al., 2009). My favorite was not referenced – Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A., Air quality model evaluation data for organics. 4. C2-C36 non-aromatic hydrocarbons. Environ. Sci. Technol. 1997, 31, (8), 2356-2367. Previous models have also explicitly accounted for the large n-alkanes on SOA formation (see e.g. work of Havala Pye), chamber experiments to Jathar et al. (ACP 2012), etc.

The paper performed comprehensive speciation analysis of organic gases. Both speciated VOCs and NMOC were measured, it would be great to show the fraction of speciated VOCs are NMOC.

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