acp-2015-920: Simulating secondary organic aerosol from missing diesel-related intermediate-volatility organic compound emissions during the Clean Air for London (ClearfLo) campaign

Response to Reviewer 2 comments

We thank this reviewer for their supportive and helpful comments. Below we respond to each comment individually.

The reviewer's comments are in italics and blue font, our responses in normal text.

In this paper, Ots et al. present an interesting method to account for the emissions of intermediate volatile organic compounds (IVOCs). They suggest that VOC emissions can be added proportionally to VOC emissions as opposed to the POA emissions which is the standard method used by current Volatility Basis Set (VBS) models. This approach can potentially pave the way for an accurate representation of IVOCs in the emission inventories which is proved to be a necessity for SOA models during the last decade. Overall, the manuscript is well written and scientifically sound. I recommend this study for publication after taking the following comments into account.

General comment:

> *The authors include additional diesel related IVOC emissions based on the VOC emissions from the transport sector. This resulted in a significant improvement of their model results which brought the predicted SOA close to measurements during winter, spring, and summer while it resulted in an overprediction during autumn (Fig. 17 of the manuscript). However, the transport sector consist only one of the ten sectors that their emission inventory includes. This raise the question of how much their model performance will change (towards overprediction) if they will add the missing IVOC emissions from the rest nine sectors. Do they have indications that the only important source of IVOCs is the transport sector? While I strongly support the suggested approach of deriving the IVOC emissions based on intermediate length alkanes (or naphthalene seen in other studies; Pye and Seinfeld, 2010) I am quite sceptic about the impact shown here by only one sector. I suggest adding a discussion on this matter, probably in section 4.*

Response: We thank the reviewer for this suggestion. The following text has now been added to the discussion:
"In our experiment of semivolatile POA (denoted 1.5volPOA), IVOCs were included from all source sectors. This experiment simulated substantially less ASOA than our addition of IVOCs associated with just the traffic source sector. This means that a combination of the POA-based and our addition of diesel-IVOCs proportionally to NMVOCs would not create a substantial overestimation of SOA concentrations compared to measurements. Nevertheless, further modelling studies (including different assumptions regarding ageing rates, fragmentation, and yields) as well as more measurements of IVOC emissions from different sources are clearly necessary."

Specific comments

1. *Page 2 line 20: Biomass burning OA (BBOA) is also a usual component that PMF can identify. Does SFOA correspond to BBOA? If so, you should use the latter since it is more commonly used by the AMS community. Furthermore, you should also report the oxygenated organic aerosol (OOA) which then can be split into LV-OOA and SV-OOA.*

Response: We have added OOA and BBOA to the list of PMF factors. We have also added a sentence explaining SFOA and BBOA: "The SFOA factor is a more general version of BBOA as it includes in addition to biomass other sources such as coal and charcoal."

2. *Page 2 lines 22-27: Since the main focus of the manuscript is the simulation of SOA, it would be good to add a sentence regarding the performance of the global models in terms of SOA (e.g.,Spracklen et al., 2011;Jathar et al., 2011;Jo et al., 2013;Mahmud and Barsanti, 2013;Shrivastava et al., 2015;Tsimpidi et al., 2016)*

Response: We have added the sentence:
"Global modelling studies of SOA specifically have demonstrated huge uncertainties (up to tenfold) in total simulated SOA budgets (Spracklen et al., 2011; Jathar et al., 2011)."

3. *Page 3 line 20: Please add recently developed models that follow the same assumption in order to indicate that the factor of 1.5 is widely used up to date (e.g.,Koo et al., 2014;Tsimpidi et al., 2014)*

Response: Thank you for these suggested additional references which have now been included. (Note that LatexDiff doesn't seem to handle differences in a long list of citations very well, so the line shoots off the paper border, but we assure you that all of the original references as well as the additional ones are in the revised manuscript.)

4. *Page 4: The line numbers here and in a number of the following pages are not correct. They should either restart in each page or continue throughout the text.*

Response: We believe this bug has been fixed in the latest Copernicus LaTex package (for the submission we used 4.0 updated on 14-Dec-2015, but the latest is 4.2 updated on 22-Jan-2016).

5. *Page 5 line 13: Do HOA and SFOA correspond to the fossil fuel combustion and domestic combustion of you emission inventory (EI)? Please clarify since it is not clear if you used these fractions to convert the OC from your EI to OA.*

Response: The splits applied to the national PM inventory included the total OM (HOA and SFOA) so we did not apply an additional conversion. We now realise how having this sentence right after the emission fractions is confusing, so we have moved this sentence into the next section (following the initial OM/OC ratios for the VBS species).

6. *Pages 5 line 28: Assuming that POA is treated as non-volatile will result in unrealistically high OA concentrations in the aerosol phase. This will favor the partitioning of your semivolatile compounds (e.g. oxidation products of IVOCs) into the aerosol phase resulting in an overestimation of SOA as well. On the contrary, if you do*

not assume that POA and SOA participate in the same solution during the phase partitioning, you should expect an underestimation of SOA. Please comment at this point on the implications of your assumption regarding the POA volatility.

Response: In our simulations, POA and SOA do participate in the same solution during the phase partitioning, but the over- or underestimation of POA does not have a significant effect on the absorptive partitioning of SOA (Figure A; the POA units are in μg m^{-3}, note the nonlinear scale of the colours, Part. means particulate – i.e. the amount that is in condensed phase).

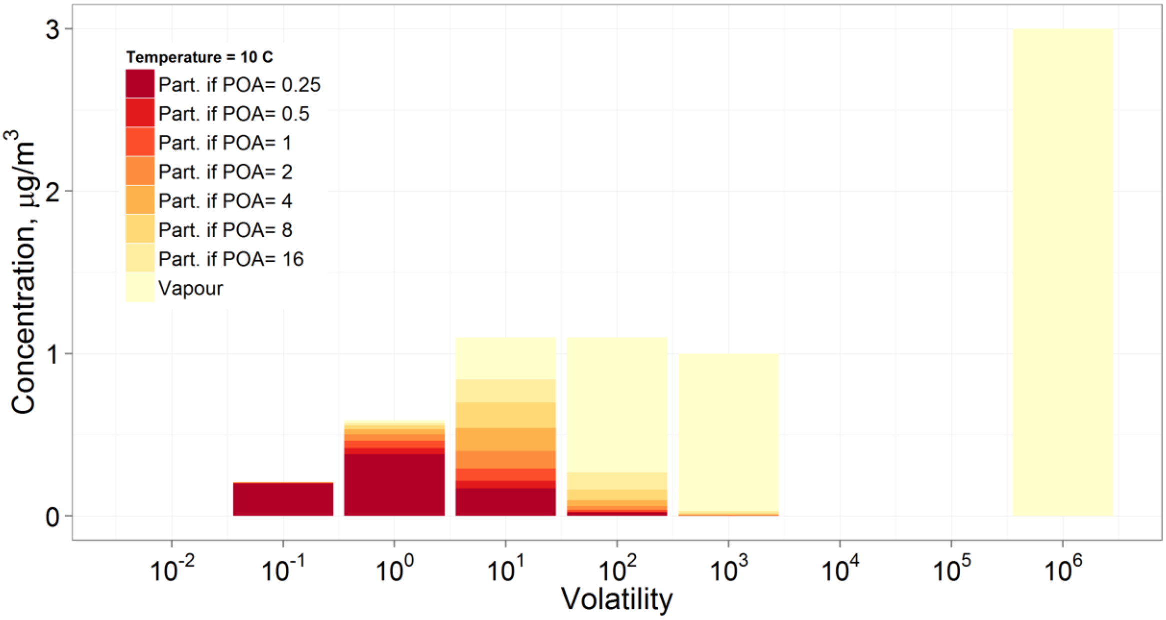

Figure A. Annual average concentrations of SVOCs and IVOCs in the volatility bins modelled with the addDiesel experiment at the North Kensington measurements site with their gas-particle partitions coloured yellow or orange-red, respectively (at an ambient temperature of 10 °C).

7. Page 6 line 2: Tsimpidi et al. (2010) used 4 volatility bins to distribute the oxidation products of VOCs. Can you please report the aerosol yields for the 5th volatility bin that you are using (C=0.1) and add a reference for them as well?*

Response: There are no initial yields for this bin from the VOCs, but VBS species will move into that bin via ageing. We have now changed the first sentence of this paragraph, as well as added a note about the lowest bin, to read: "Five volatility bins (C* = 0.1, 1, 10, 100, 1000 μg m^{-3}) are used for SOA production and ageing. The SOA yields for alkanes, alkenes, aromatics, isoprene and terpenes under high and low NOx conditions were taken from Tsimpidi et al. (2010). Note that Tsimpidi et al. (2010) reported yields for the four VBS bins between 1 and 1000 μg m^{-3}. In this work, the lowest VBS bin (0.1 μg m^{-3}) is used for the ageing reactions, as well as for SOA from the additional diesel IVOCs (explained in the next section)."

8. Page 6 line 6: According to Lane et al. (2008) the use of aging reactions improved their results compared to measurements from urban areas but resulted in a strong overprediction over rural areas. They attributed this discrepancy to a potential balancing of decomposition to smaller more volatile products (fragmentation) and production of more substituted less volatile products (functionalization) during the

> *photochemical aging of biogenic SOA. This was also confirmed by laboratory studies (Ng et al., 2006). Therefore they suggested that no ageing of biogenic SOA should be considered. Furthermore, the use of an ageing rate constant of 4.0 x 10-12 cm3 molecule-1 s-1 is kind of conservative compared to what is used lately by most models (i.e. 1.0 x 10-11 cm3 molecule-1 s-1; Fountoukis et al. 2014). According to the above, I suggest either changing your scenarios by using 1.0 x 10-11 cm3 molecule-1 s-1 as a rate constant and assume no ageing of biogenic compounds or to make a sensitivity test and investigate the effect of these assumptions on your results (especially regarding the rate constant).*

Response: We address these issues of uncertainty with ageing rates in the Discussion:
"We use an ageing rate of 4.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for both ASOA and BSOA (Lane et al., 2008). This is slower than has been used in some other studies (for example, Tsimpidi et al. (2010) uses 4.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} : 10 times faster, or Fountoukis et al. (2011) uses $1.0{\times}10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}: 2.5 times faster). A combination of lower initial SOA yields, but slightly higher ageing rates could possibly flatten the diurnal cycle of our modelled SOA, matching the measurements better. Therefore, an improvement for the detailed, hourly, evolution could be achieved by a sensitivity study of these yields and ageing rates. This does not, however, change the main scope and results of this paper which illustrate the relative impact of the diesel-IVOCs on SOA formation."

> *9. Page 6 line 10: What is the saturation concentration of this "background OA" compound? Is this considered nonvolatile since it is very aged and highly oxygenated? Furthermore, please provide a reference for assigning a value of 0.4 μg m-3 to this compound. Does this value based on measurements?*

Response: Yes, the background OA is considered nonvolatile since it is very aged and highly oxygenated. We have now added this information to the sentence where it is first mentioned. We have also added a reference to Bergström et al. 2014, where this value is set based on measurements at background sites. The relevant text now reads: "A constant background OA of 0.4 μgm^{-3} is used to represent the contribution of OA sources not explicitly included in the model (e.g., oceanic sources or spores; Bergström et al. (2014)). This background OA is assumed to be highly oxygenated and is therefore included under modelled SOA when comparing with observations (with an OM/OC ratio of 2.0 it is also assumed to be nonvolatile)."

> *10. Page 7 line 35 (on the top of the page): What is the SOA mass yield that you used for the 1000 μg m-3 volatility bin? Please provide a reference as well.*

Response: Presto et al. 2010 did not report yields from this reaction to the 1000 μg m^{-3} volatility bin. We have now added a note about this: "For the oxidation products of $C_{15}H_{32}$, SOA mass yields were taken from Presto et al. (2010): 0.044, 0.071, 0.41, 0.30 for the 0.1, 1, 10, 100 μg m^{-3} bins, respectively (Presto et al. (2010) did not report a yield for the 1000 μg m^{-3} bin)."

11. Page 7 lines 28-29: A more fair comparison between the two approaches would be to add IVOCs proportionally to POA from sector 7 only as you did on your addDiesel scenario. Can you investigate this additional scenario as well?

Response: Adding IVOCs from all sectors maximises the potential effect of this approach of adding more emissions. It also makes the experiment with that approach directly comparable to what has been done in previous studies: Shrivastava 2008 for example. Furthermore, the effect of even including all sectors for SOA in the 1.5volPOA addition is much lower than for our addDiesel experiment, thus doing a finer addition would not change our conclusion that diesel IVOCs are a much bigger source than previously thought.

12. Page 9 Section 3.1: Since POA are assumed to be nonvolatile you would expect to overpredict their concentrations. Are the emissions so severely underestimated? Please report that the presented underprediction will be even more significant if you add the semivolatile character of POA.

Response: See our substantive response to Reviewer 1 Major Comment 1 on this point, and for the statement of modifications made to Methods and Results Sect.3.6.

13. Page 9 line 20: Please replace the "secondary pollutants" with "secondary inorganic pollutants"

Response: Done.

14. Page 10 lines 7-8: Add a reference to Fig. 7

Response: Added.

15. Page 13 line 30 (on the top of the page): How you calculated the 40%?

Response: The value was calculated as follows:
relative difference = (addDiesel-Base)/addDiesel.
We have added the following extra explanation into the manuscript: "… is 40% (calculated as the difference between SOA modelled with addDiesel and Base, relative to addDiesel: (addDiesel-Base)/addDiesel)."

16. Page 15 lines 4-5 (or 33-34): Pye and Seinfeld (2010) have used a naphthalene-like surrogate specie to describe IVOCs instead of the traditional "POA" method. Please refer to this work as well (maybe in the introduction).

Response: We have added a reference to Pye and Seinfeld (2010) where we mention global SOA budgets, but it is our understanding that they used CO emissions to derive a spatial distribution for naphthalene emission and then scaled their naphtalene up to include all IVOCs (using similar values as the Shrivastava et al.'s 2008 POA based approach). It is not completely different to the POA based approach (but different enough not to be mentioned in our list of 1.5xPOA). We have changed the sentence "To our knowledge, this is the first study where

IVOC emissions are added proportionally to VOC emissions” to “This is one of the very few studies where IVOC emissions are added proportionally to VOC emissions.”

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