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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Simulating secondary organic aerosol from missing diesel-related intermediate-volatility organic compound emissions during the Clean Air for London (ClearfLo) campaign" *by* R. Ots et al.

Anonymous Referee #1

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This is an interesting and generally well-written paper which draws attention to another potentially important source of SOA in the atmosphere. The paper makes nice use of high-quality atmospheric data-sets, and uses not just OA measurements but also other gas and particle data to build confidence in the model. The main conclusions are important: that emissions of IVOC from diesel and their subsequent SOA formation might be much more important than previously assumed.

There are some issues however that I think the authors need to deal with before acceptance for ACP. The main issues I see are:

1. The paper begins (Fig.1, also Sect. 2.5) with an example of a so-called add1.5xPOA approach of illustrating the importance of the 1.5 x PM assumption for IVOC, contrasting with the new addDiesel approach used in this paper (Fig.2). We then see many results from the base and addDiesel cases, but have to wait until almost the very end before seeing some annual-average result from the add1.5xPOA case.

   The 1.5xPM approach used here though differs from that of previous authors, e.g.Robinson et al. (2007), Shrivastava et al. (2008) or even the Bergstrom et al. (2012) paper. In the add1.5xPOA used here, the authors still seem to assume the same inert POA emission as in the base-case, but add IVOC with a very high C* value. If correct, this is a significant deviation from the other studies, which added SVOC and IVOC across a range of volatilities. If the authors really did just use one IVOC component at C*=1.0e5, then this will lead to more POA close to sources and less downwind compared to e.g. Robinson.

   This begs the question, would a more 'traditional' (Robinson-like) add1.5xPOA scheme give results that might anyway have been better compared to observations than the Base-case used here? This would not mean that diesel-IVOC isn't important, but it might have qualified the relative importance. Of course, one is adding less IVOC and hence producing less SOA. On the other hand, an 1.5xPOA approach (with both SVOC and IVOC) would have generated a bigger gradient between London and the outlying sites, perhaps in better agreement with the observed gradients.

   Concluding, I think they could be better off either (i) re-running with the (dare-I-say) 'traditional' 1.5xPOA for SVOC+IVOC, or (ii) just skipping this test altogether.

2. Given that POA are assumed to be inert, this study likely overestimates OA close to sources. The statement that diesel IVOC can explain about 30% of the annual SOA around London would have to change if POA were allowed to evaporate and react in the atmosphere.

3. The results presented here make a strong case that most SOA is ASOA. This conclusion contrasts strongly with studies based upon radiocarbon and other tracers. Heal et al. (2011) for example suggest a much stronger component from BSOA in Birmingham, and state that this was consistent with other European studies. Can the authors explain this apparent discrepancy?

4. The mass yields for OH oxidation of the n-pentadecane IVOC products is ca. 0.8 for C* up to 10 ug/m3, after correcting for the assumed density, and the great majority of this is one bin, the 10 ug/m3 bin. The potential for much SOA formation is very clear, but I wonder if the authors are exaggerating the amounts. The mass yields are taken from Presto et al. (2010), but that paper suggested that the yields were the product of multi-generational aging, not of the first reaction step. I wonder if aging should have been ignored for these compounds?

Some smaller points follow:

Abstract: I found the first sentence rather vague (what is high-resolution?), and not so interesting (yet another model study). The abstract would make more impact if it began with a comment on the extent of new emissions which forms the basis for this study.

P2, L12. I don't think the results 'prove' that the model has good SOA prediction skill. Even if the comparison with measurements was impressive, there are too many unknowns regarding SOA formation and I don't think any model can claim good skill. I think that this phrase can be omitted.

P3, L64. You need to define the temperature at which these C* values apply.

P3, L76. Why mention AMS for organic PM? I don't think many European PM inventories make use of AMS data.

P4, L114. Define PMF. Also, which PMF method was used?

P5, L132. WRF can be set up in many different ways, with varying impacts on accuracy for air pollutant applications. Please give more details or a suitable reference.

P5, L137, specify anthropogenic emissions here.

P5, L138, specify aerodynamic diameter.

P5, L142. Why use a paragraph on an NFR system which is not used in this work? Delete.

P6, L156. The term SFOA is confusing, and wasn't used by Bergstrom et al as claimed here. If I understand right SFOA includes biomass burning (which is usually said to give BBOA), but also coal and charcoal.

P6, L173. It could be noted that the Jathar et al. (2014) study also suggested different ratios of IVOC to PM than those of Shrivastava et al.

P7, L191. 'under modeled SOA' - do you mean when comparing with observations?

P7, L200. Shouldn't you also mention aromatics and other compounds here.

P7, L207. Which GC x GC system? Explain what is meant.

P7, L209. Any reference for the number of studies providing that rate constant?

p8, L247. Biogenic emissions of what?

p9. Sect. 2.6 'Comparison with measurements': This section can be simply renamed 'Measurements, since that is what it deals with down to L288.

P9, L259. Why have references to Fig. 3? Give the references after the mention of each site, or add 'site details given in' or some such phrase.

P9, L274. Are you sure that European inventories don't include cooking OA? I think it may be underestimated, but am not sure it is ignored completely.

P9, L276. This sentence was confusing. I can see that two instruments can disagree, but what does it mean if there is just one instrument? Can an AMS and its PMF disagree, or what?

P9, L284 .... what period/site/analysis are these sentences and statistics referring to?

P9, L289 on. This small section on statistical metrics has nothing to do with the discussion of AMS etc which it follows, and could be set in a small section of its own.

P9, L291. I don't think correlation coefficient needs a reference to Carslaw and Ropkins; 'r' has been used for many many years before that paper was written. Actually, NMGE might need more explanation. All these could usefully be defined in supplementary.

P10, equation (1): explain what i and n are.

P10, L298. Re-phrase - it sounds as though the measurement mean is better at capturing the variation in measurements than the model.

P10, L303. This bit about WRF could be moved to Sect. 2.1.

P11, around L35. All these numbers for NMB, etc. could be tabulated for easier comparison.

P12, L364. This refers to Fig. 12a,b, but there are no a,b labels in Fig.12

P12, L389. Re-phrase (or omit). It is obvious from the plots that this background OA is an overestimate for some days at least.

P13, L405 on. The whole discussion here is in terms of SOA and IVOC. But, how did the model perform for NOx and CO for these 'difficult' periods - maybe the problem is dispersion rather than IVOC? Or maybe the model's enthalpy values are wrong, and don't respond to cold temperatures as they should. I don't see why problems are blamed on domestic sources either. Wouldn't for example cold-starts for vehicles also produce more POA/IVOC, or commercial premises use more fuel in cold conditions? Are wood-burning emissions really an issue in London?

P15, L475. The title says comparison to previous (IVOC=1.5xPOA) approach, but as noted above, the method used here seems to be unique; not that of earlier papers.

P15-P16. The authors make various policy recommendations, e.g. (P15, L500) 'refinements should be reported to CEIP' and a very specific recommendation for PM1, PM1-2.5 and PM2.5-10 on P16, L533. Why not just suggest submission of size-distributions? Why no mention of volatility - the VBS approach almost begs for people to submit emissions in different volatility classes. And since this paper is really exploring IVOC and not PM emissions per se, why didnt the authors focus on those?

Actually, I suggest that the authors don't try to tell countries what to do, but rather discuss any scientific insights into emission reporting that this study on IVOC reveals.

P16, L509. Can't small changes in SOA (or any pollutant) also be a reflection of long-range transport? Not all pollution is formed at short time-scales close to source.

P16, L520. Where did the value 4.0e(-12) come from for ASOA and BSOA oxidation?

P16, L520 on. This section offers a few 'tuning' suggestions, but there are always any number of these in the field of SOA formation. For example, recent studies have suggested that SOA formation should be much greater than previously assumed, perhaps by a factor of four or so (Zhang et al., 2014).

P16, L527. I would say that this paper illustrates the potential for a significant contribution, rather than that they can quantify the relative impact. To do the latter, one would need to be sure that all relative impacts are reasonably well known, and that clearly isn't the case.

P17, Sect.5. The first paragraph simply repeats sentences from Sect. Don't do that.

This section should also mention the results for other pollutants (NOx, O3, etc.), which are the main reason one can have some confidence in the basic modeling system. (Use of such data is one of the strengths of this paper I think.)

P17, L563. imported from where?

P17, last paragraph. The interpretation of what contributes to the 90-th percentile is not so easy I think. And I certainly don't think one can state that 40% is due to missing diesel precursors. SOA is too complex for such simple statements.

P20, L635. Expand/explain CEIP. Is this the name of a report, or just a web side?

P21, L665, EEA, Entec - these references are too short for readers to understand or find. Give proper references, with addresses as necessary.

P29, Fig. 1. The caption should state early that this is PM25 *and* SVOC/IVOC gases. (The issue of IVOC or SVOC+IVOC is discussed above, but it complicates this figure.)

P31. Fig. 5. Explain 'Base' as used in legend.

P31. Fig. 6(a). NOx is a the sum of both NO and NO2. Were they really summed with own molecular weights, or is this as NO2? (ppb would have been easier to interpret!). Also, in the captions, add the superscript ion-labels too.

P33, Fig. 9. This Figure looks very fine on-screen, but when printing out it looks very different - much of the black seems to be over-written with green and/or blue. Please use a different figure format, and check the printout.

P34, Figs. 11-12. We don't really need these since Fig. 10 has made the point about gradients well. Move to Supplementary.

P35, Fig. 14. Why use log-log plots? Wouldn't a simple liner plot better display the range of data?

P36, Fig. 16. Here the addDiesel statistics look worse than the base-results. Are these really consistent with data presented in Table 4?

Figs and color schemes. The colors used for ASOA, addDiesel, etc seem to vary randomly from figure to figure (e.g. green is addDiesel in Fig.9 but observed SOA in Fig. 17. Please harmonize.

ADDITIONAL REFERENCES:

Heal, MR et al. Application of 14C analyses to source apportionment of carbonaceous PM2.5 in the UK, Atmos. Environ., 45, 2341-2348, 2011

Zhang, X., et al., Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, PNAS, 111, no. 16, 5802-5807, 2014

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