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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Large Contributions from Biogenic Monoterpenes and Sesquiterpenes to Organic Aerosol in the Southeastern United States" *by* Lu Xu et al.

Anonymous Referee #1

Received and published: 30 January 2018

This paper shows some interesting results from a novel experiment involving taking ambient air in an urban environment and conducting a chamber experiment after enhancing the concentrations of VOCs. The main emphasis of this paper is the use of α-pinene and β-caryophylene, the characterisation of the SOA produced using aerosol mass spectrometry and inferences are drawn regarding their contribution to particulate concentrations in the region.

Overall, this is a nice piece of work and well within the journal's remit. However, I do think that the significance is a little overblown in places and the authors need to express more caution in how they interpret some of the results. In spite of their statements otherwise, this is not a true simulation of atmospheric processes (see below), there are a few PMF-specific subtleties that aren't taken account of and how reliably this can be projected onto the wider world is open to question on a number of levels. But in spite of these issues, the conclusions are largely sound and this deserves to get published. I therefore recommend publication with minor revisions.

General Comments:

This paper makes the assumption of α-pinene and β-caryophylene being representative of monoterpenes and sesquiterpenes respectively. While these are common assumptions made in the community and the VOCs are both very well studied, their overall representativeness is in question because the level of oxidation in SOA from different precursors are known to vary substantially between compounds (Alfarra et al., Atmos. Chem. Phys., 13, 11769-11789, 10.5194/acp-13-11769-2013, 2013). This is especially true of the sesquiterpenes, as difficulties in working with a number of these compounds means that we lack data on a large subset of these. This should be discussed and any evidence to support this assumption properly cited.

Throughout the manuscript, there is a general tendency to treat LO-OOA and MO-OOA as defined chemical entities, whereas the truth is that these represent reductions of highly complex chemical systems and the exact factors reported are known to vary dataset to dataset. While common trends have been noted in terms of behaviour and mass spectral profile, their exact mass spectral nature depends on the measurement location and season and in many cases (particular in the wintertime), PMF will fail to separate them at all, instead returning a single OOA factor. This must be discussed in a meaningful manner in the introduction and discussion because it adds an extra layer of nuance to the results.

Related to the above point, there seems to be a general assumption that PMF had adequately accounted for the new SOA being formed, but in my mind, the decrease in MO-OOA in response to the β-caryophylene experiments in particular raises a number of red flags because this implies that the data model didn't hold and the factorisation wasn't sound. The authors need to pay much closer attention to whether the factorisations 'worked' or not; a good starting point would be inspecting the residuals (e.g. Q/Qexp) as a function of time over the course of the experiments and if they positively correlate at all with the amount of additional SOA, this would imply that PMF has failed to capture the chemistry perfectly.

The modelling work presented in section 3.6 left me slightly confused as to what the authors were trying to achieve and how. The text in the main article would suggest that an updated scheme is being compared with a very old one, but the supplement seems to say that specific mechanisms have been added here. This must be clarified. Also, as pointed out later in this section, this work does not directly preclude that other precursors may be contributing and the discussion dealing with this relies heavily on inferences drawn from the literature, so this work isn't really that dramatic a result in how it is presented now. I would suggest a more defined modelling experiment is constructed around a clear working hypothesis. This could just be a case of making the work shown here clearer and moving material from the supplement to the main article.

More generally, I noted a very odd tendency to leave certain pertinent (and in many cases interesting) details in the supplement that maybe should have been given more prominence or at least linked to the main article better. For example, the box modelling described in section S6 was very interesting, but it wasn't clear at all how this fit into the narrative of the main article. I also had a hard time reconciling the information about the CMAQ runs in the main article and the supplement as well (see above). I would revise what information goes where, using the main article for the discussions relating to the scientific arguments and making sure the material in the supplement is purely technical detail in support of this.

Specific comments:

Line 95: When saying ‘representative urban’, please be specific about what type of urban site this (e.g. background) and how you qualify this statement.

Line 115: What counts as ‘too much’ SOA and why?

Line 265: It has long been shown that α-pinene SOA produced in chambers produces a mass spectrum that is similar to LO-OOA and given that this mass spectral profile is also seen in the presence of strong emitters of this VOC (e.g. temperate and boreal forests), the case for α-pinene SOA being a strong contributor to LO-OOA has never really been in doubt in this reviewer’s opinion. Why is the evidence presented here any more ‘direct’ than those published previous? While the perturbation experiment does indeed produce LO-OOA as retrieved using PMF, this retrieval is still based solely on mass spectral similarity, so I would contend that this does not really present any new evidence to this effect.

Line 280: The fact that the oxidation rate of VOCs is dependent on oxidant concentration is very well established in kinetics. The discussion regarding this observation would be considered pointing out the obvious to many. It would be far more useful if a quantitative relationship with ozone concentration could be reported here.

Line 286: An alternative explanation here is that the experimental set-up here was not conducive to HOM formation for whatever reason. This should be added as a caveat.

Line 309: There is a major problem with this statement; the results indicate that the β-caryophylene SOA spectrum to be represented by PMF as a combination of the LO-OOA and COA mass spectra, but it would be a mistake to imply in any way that it is producing two ‘types’ of OA (this is clarified later in the manuscript but it is ambiguous here). Issues about the quality of the PMF retrieval aside (see above), in the hypothetical situation that there is an environment with a mixture of cooking and biogenic SOA, PMF will likely still separate these because it determines factors not just by mass spectral profile but by temporal profile, so would still return factors corresponding to cooking and an average of biogenic SOA from all sources. The only situation I could

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think where this would be a problem is if monoterpene and sesquiterpene SOA formation were not well matched temporally, in which case I could see how the COA-like component of sesquiterpene SOA would manifest as ‘mixing’ between the cooking and biogenic SOA factors, but this would be evident in the temporal profiles.

Line 350: How much more ‘realistic’ is this? While this would give a more life-like oxidant and NOx background, given that the chamber walls will act as a sink of VOCs, radicals and particles, I would still expect that the precursor perturbations would have to be higher than typical atmospheric concentrations to achieve realistic SOA concentrations and consequently have a higher VOC:NOx ratio. This must be discussed in an objective manner and while some of this is touched on in the supplement, it’s kind of glossed over in the main article.

Figure 6: The caption of this figure is excessively long.

Line S477: This doesn’t make sense. Why would the solver reduce the concentration of MO-OOA because it had been added to? I find it more likely that there was a breakdown in the data model and mass was being erroneously rotated out of the factor. This is undesirable, but also feeds into the discussion above regarding the relationship with COA.

Line S480: What other studies?

Technical comments:

Line 113: Please be more specific over which VOCs are anthropogenic vs biogenic. The word ‘respectively’ does not work when four are listed.

Line 179: Why not saturated fatty acids?

Line 119: Correct ‘concentration’ to ‘concentrations’.

Line 184: What are the oxidation states in each instance?

Section 2.2: Please specify the materials used for the aerosol and gas sampling lines.

Was the gas sampling line filtered or heated?

Line 200: The CMAQ grid cell depends on the exact model set-up being used. Is this referring to the activity specified in section 2.6? If so, this should be stated here.

Section 2.6: Please provide references or web links for the various inventories used.

Line S909: Pearson's R is not dependent on any numerical fitting method; it is merely a comparison between the two datasets.

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