Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Anthropogenic Secondary Organic Aerosols Contribute Substantially to Air Pollution Mortality" *by* Benjamin A. Nault et al.

Anonymous Referee #1

Received and published: 8 January 2021

This manuscript leverages an impressive breadth and diversity of data to shed light on a critical public health and environmental policy question: how many premature deaths can be avoided annually with reductions in emissions of organic compounds that humans have direct control over? The methods and approaches that are developed are generally sound, although far from perfect, for this kind of high-level endeavor. My main issues with the paper in its current form are the confusing organization and presentation of ideas, some slight misplaced focus on particular organic aerosol model updates, and the decision to ignore solid fuel burning in the model formulation. These and other issues below should be addressed before publication.

General Comments:

1. I think the main ideas in the paper are quite compelling: a) reconstruct measured SOA from in situ campaigns using correlations with likely predictors, b) incrementally improve a streamlined parameterization for SOA prediction (SIMPLE), c) integrate the SIMPLE predictions into a full-science CTM prediction of PM2.5 and use satellite data to further refine the predictions, d) feed those predictions to a premature death parameterization to quantify human health impact, and e) investigate key sensitivities. I would reorganize the entire paper so that the methods, results and discussion each flow in that order. Currently the introduction gives little clue about how the pieces will fit together or the goals of the paper, beyond showing that ASOA is important. Much of (b) above is discussed inappropriately in the current results section 4. Manuscript sections 3, 4 and 5 contain quite a lot of methods discussion that should be moved out to section 2. For example, equations rarely belong in a results section. I could even suggest that most of sections 2.2 and 2.4 be moved to SI. The details of the chemical mechanism used in 2.4 are a bit irrelevant once the SOA/R_BTEX enhancement ratio is confirmed for use in SIMPLE. If the mechanism were more sophisticated (e.g. HOM formation, carbon-conserving fragmentation to lower MW products, oligomerization, etc) then I think there would be more cause for focusing on it, but the schemes used here are relatively close to the SIMPLE approach in terms of one-way generation of SOA.

2. The authors repeatedly compare their updated approach including semivolatile POA to previous efforts to assess ASOA impacts on human health using nonvolatile POA assumptions. The implication here is that treating POA as semivolatile might be as important to getting ASOA correct as the dramatic increase in ASOA precursors. But one look at Fig. 6 shows that in most cases it's the way BTEX, IVOCs and Other Aromatics are treated (emissions, SOA yields, aging) that is really driving the ASOA formation. So while I think the update to semivolatile POA is a good one and it gives room for greater ASOA production, I think the authors focus on it too much in this

study (see specific comment #3 below and lines 572-581 for examples that should be addressed). Instead there should be much more focus in the budget section on how the parameters they have chosen for their VCP emissions and SOA chemistry scheme are driving larger IVOC and VOC contributions and how confident they are in those parameters. For the SIMPLE and GEOS-Chem sections, the key sensitivity is the SOA/R_BTEX ratio (see specific comment #7) and there should be more discussion on its impact. Also, the SIMPLE rate constant k is parameterized from the CalNex data, correct? Why was that not revisited and optimized for performance among all the measurement campaigns?

3. The authors spend some time in the discussion addressing the fact that solid fuel combustion emissions are missing from this study. I'm still very concerned that much of the global results they show are corrupted by this omission, not just in southern Asia and Africa. Large regions of Northern/Western Europe and North America will also be affected by residential wood fuel burning, especially in the winter. The authors should at least justify their omission of solid fuels for the measurement campaigns citing tracer analyses, for example. To address the global comparisons, can you add a reference to SOA/CO ratios for wood combustion and comment on their similarity or difference from what has gone into SIMPLE for this study?

4. Why does the SIMPLE model now rely on BTEX alone? It seems to be doing better overall than when it just relied on CO, but why not use more than one variable with BTEX to develop a multilinear fit for the SOAP emissions? For example, Seoul is likely a problematic point in the SOA vs. BTEX regression (see specific comment #7). It's driving down the ratio and thus probably leading to under-representing impacts in the Northeast US and LA. Taken together, Figs. 3 and 4 suggest that in Seoul there are SOA sources associated with CO emissions that are not as highly associated with BTEX. Using too many independent variables would surely end up overfitting, but why not add 1 or 2 key variables (like CO and POA) since you have a good idea that the relative contributions of sources (e.g. vehicles, VCPs, and solid fuel use) vary from city

to city?

5. Lines 455-457: This observation about SVOCs is difficult to believe based on existing NMOG and POA profiles in the literature. I have yet to see a volatility profile for any source where the SVOC accounted for half of the total ASOA precursor, let alone 88%. Is there something unexpected going on with the CO normalization of POA vs. VOCs here? I confess this one catches me completely by surprise, and likewise the large influence of SVOCs in Fig. 3 looks strange as well. The authors have made an emphatic case for the dominant and growing role of VCPs. Wouldn't these be overwhelmingly VOCs and IVOCs? Cooking emissions are used to explain this to some degree, but if the Robinson et al. (2007) profile is used for the cooking emissions, I would expect a lot more 10^3 and 10^4 C* compounds. Regardless, SVOC should probably be included on Fig. 2 as a separate series like BTEX and IVOC. And I recommend adding more description about how SVOC emission ratios were derived.

Specific Comments:

1. Line 95-98: These generalities about IVOCs and SVOCs are perhaps useful as an introduction for those who may be unfamiliar but based on more current understanding of emissions sampling and speciation, they may be more confusing than helpful. Lu et al. (2018) show in their Fig. 1 that most of the IVOC would have missed the filters for the vehicles they studied, but much of the SVOC is expected to be captured by the filters. Even more SVOC would presumably be captured for stationary sources at conditions relevant for "condensable particulate matter" measurements (i.e. low dilution, cooled temperatures); see Morino et al. (2018). As for IVOCs, VBS profiles for biomass burning sources like those in May et al. (2013) show that IVOCs are probably included in many if not most PM emission factors measured for these sources if the emissions are not diluted enough. The authors here are not focused on wildfires, but certainly cooking/residential wood-burning PM emission factors may include these IVOCs. Admittedly, the problem is even more complicated by the fact that many countries report wood-burning PM emission factors at high temperature conditions, so they

may not actually be capturing the IVOCs. Still, it's highly uncertain to what extent they are already measured. I urge the authors to update their discussion of these classes of compounds to better reflect some of the nuances we now understand better.

2. Line 99-118: I encourage the authors to add residential wood burning/cookstoves to their list, and possibly also the recent work on asphalt emissions (Khare et al., 2020).

3. Line 119-132: I think the authors get somewhat stuck on the SVOC portion of the ASOA problem in this paragraph and would do well to keep the broad focus on both IVOC-SOA and SVOC-SOA they have been introducing so far. For one thing, I'm not sure how important revising the (terrible) assumption of POA nonvolatility is for connecting urban PM to health impacts in the context of annual mean guidelines. Of course it's important to know how much of the PM started as an SVOC vapor for the purposes of control. But meanwhile, if we think that a portion of the SOA mass was emitted in the particle phase and then evaporated, oxidized and recondensed after dilution, then how does updating our conceptual picture to consider that portion volatile necessarily help us control it better – we could still control it with particulate filters. To me, the important reasons to update the conceptual model from nonvolatile POA to semivolatile are to 1) better track the composition of the OA because maybe it has different toxicity or efficiencies for losses as it is oxidized, 2) sensitivity to temperature and concentration swings might have an impact on urban scale versus suburban or rural exposure or diurnal timing of concentration peaks and thus impacts on human exposure. Adding in the SVOC and IVOC vapors helps us achieve a total mass balance on the amount of carbon with the potential to make SOA and this is really a separate point. In short, the authors could make it more clear in this paragraph, at least qualitatively, which sources of uncertainty they are most concerned about in previous estimations of PM mortality. Is it a) poor traditional POA models, b) undersampled SVOC and IVOC emissions from known sources, c) underestimated yields (i.e. vapor wall-losses, etc), d) missing or unacknowledged sources of vapor precursors or e) something else. Right now, it seems like (a) is their chief concern.

C5

4. Line 141: A complete introduction or general description of the modeling approach is needed to begin the methods section. Before the authors get into the extreme details (e.g. how data were averaged), we readers would do well to learn what the basic idea of the study is going to be (i.e. parameterize ASOA in cities using campaign data, replace ASOA in GEOS-Chem with these results, plug new PM2.5 into relative risk and premature death parameterizations, assess the impact, and explore some key sensitivities). For example, on line 142, I'm not sure what 'values' are being discussed, how they were measured, or how they will be used.

5. Figures are introduced out of order in the methods section.

6. It looks to me like the emission ratio in Tables S5-S8 that were calculated with Eq. 3 are in most (though not all) cases well outside the range of measured emission ratios from other campaigns. For example, o-xylene in Table S5 is all as high or higher than the maximum observations, propene in Table S7 as well. The values for London in Table S8 are either below the minimum observed or above the maximum, depending on the species. Are these predictions expected by the authors? Can they be explained by variations among cities? I recommend calculating and reporting the performance of the Eq. 3 model in reproducing the observed values in Tables S5-S8. Also, what values of t were used to calculate the emission ratios in Eq. 3? I assume many values used and then all averaged together? Or were the values for each daily averaged and then a campaign average derived from that? What is the spread in the intermediate emission ratio values? I think this paragraph (lines 150-161) could be written more clearly to better describe the multiple levels of averaging and error analysis taking place here.

7. Lines 181-188: I appreciate the spirit of the leave-one-out sensitivity study and the results presented in Table S10. However, I do not think it accomplishes what the authors intend, which is to justify their regressed slope of 24.8. The reference to 95% confidence intervals seems misleading, perhaps because a clear null hypothesis is not stated. I'm not sure I've seen confidence intervals used to prove two slopes are statistically similar before, but I'd be interested to learn if the authors can show their

C6

work. A conventional leave-one-out would calculate the error in predicting the removed point and then average the errors across all trials. I'm not sure how knowing this error statistic would be helpful either though, except to perhaps compare among similar leave-one-out analyses for the other slopes in Fig. 5. In my opinion, a better analysis would involve an assessment of the degree to which the Seoul data point is influencing the slope parameter. For example, the Cook's distance is commonly used in regression approaches to flag highly influential data points. If the point is determined to be influential, then the authors need to discuss what impact the change in slope from 24.8 to 34.0 has on the conclusions of the paper.

8. The SIMPLE model relies on having an accurate BTEX field for input. So how consistent were the HTAPv2 emission inputs with each of the measurement campaigns, allowing for expected deviations for year to year trends?

9. Why not add a supplemental figure showing the average spatial distribution of CO and R_btex emissions so readers can get a sense for which is driving the SIMPLE predictions in the various countries? I recommend at least plotting this as country averages, if not both country averages and grid cells. 10. Consider adding to the conclusions the ASOA-associated premature death estimates that you are most confident in.

Minor Comments:

1. Line 60: Rewrite "anthropogenic reactivity of specific volatile organic compounds" to "reactivity of specific anthropogenic volatile organic compounds" ?

2. Line 66: "results in up to. . ."

3. Line 67: "extrapolation" of what data specifically? Is it more informative to say "extrapolation from regions where detailed emission inventory data are available to other regions where uncertainties in emissions are larger." ?

4. Line 68: I agree that comprehensive air quality campaigns are certainly helpful and

possibly necessary, but it seems that robust national-scale institutions (government, academic, or private) are absolutely necessary to accurately catalogue emission factors and activity data to the level required to reduce the uncertainties discussed in this manuscript. Perhaps this sentence could be broadened to something like: "In addition to further development of institutional air quality management infrastructure, comprehensive air quality campaigns. . ."

5. Lines 104-106: Suggest rewriting: "Biogenic SOA (BSOA) in urban areas typically results from advection of regional background concentrations rather than processing of locally emitted biogenic VOCs."

6. Lines 116-118: Seltzer et al. (2020) is currently finalizing discussion in ACPD and presents a detailed VCP emission inventory for the U.S. Based on this, the authors may want to update this sentence to include that step forward, but it's their choice.

7. Line 119: "uncertainty on the (burden of -or- emissions of) ASOA precursors. . ."

8. Eq. 3: Recommend adding an exp subscript to [OH] here to make it clear that it is calculated from Eq. 2.

9. Table S10. Please indicate which slope is being shown here (delta_SOA/R_BTEX)

10. Line 201: Many of the BTEX values are modeled with equation 3 right? Please make this clear.

11. Line 213: C* range is not consistent with how IVOCs are usually defined.

12. Line 209-210: Based on the reference, it appears the authors are specifically referring to underestimation of IVOCs in the ambient. Please make that more clear in the sentence.

13. Line 214-216: It's unclear to me how the IVOCs and unspeciated SOA precursors relate to each other here. Are the authors saying they used SOA yields from Jathar et al (2014) to define the IVOC SOA yields uniformly for all C* bins? Please clarify.

For example, a clearer way of making that point might be, "SOA yields from IVOC oxidation were parameterized with data from n-tridecane for gasoline engines and n-pentadecane for diesel engines (Jathar et al., 2014)."

14. Lines 216-218: Should VOCs be IVOCs here? Again, aren't all the IVOCs in this study unspeciated? If so, why make the distinction?

15. Line 224: Why was the Huffman et al. (2009) distribution not used for the cooking VBS distribution?

16. Table S9: What is the HOA and Other POA mass normalized to? Shouldn't these also be normalized to CO, or is POA a separate variable in the inventories? POA is never mentioned in the SI in the discussion of the inventory development.

17. SI Line 70: The emission ratios are small, or the range is small?

18. Lines 250-273: Is the TSI parameterization acting simultaneously with the Ma parameterization or are they different cases that are explored? It seems like Ma et al. (2017) is used for IVOC SOA yields instead of Jathar et al. (2014). There are a lot of parameterizations, precursors classes and products in this model approach. I strongly recommend adding a table(s) explicitly specifying all of the SOA yields and the corresponding precursors used in this study.

19. Line 273: Recommend rephrasing "increase in mass of 0.99" to "change in mass of 0.99" or "decrease in mass of 1%".

20. Line 276-281: This opening sentence is overly dense and meandering. What is the point of the appositive, "for ASOA apportionment (Fig. 1)"? It seems redundant. Should the second "apportionment" be "attribution"? The last portion of the sentence, after the GEOS-Chem reference should be broken off into its own sentence.

21. Line 335: Recommend presenting Eq. 4 as the summation of premature deaths among all considered causes.

22. Lines 363-376: This discussion belongs before the introduction of the premature death and RR parameterizations. The reader will follow along better if the discussion of GEOS-Chem ends with how the hybrid PM2.5 will be estimated so that it can be fed into the health eqns.

23. Line 448-449: Is BTEX meant to be here twice?

24. Throughout paper: USOA (urban SOA?) should be replaced with ASOA. It especially shows up in figures.

25. Line 536: Are the bottom-up ASOA predictions from GEOS-Chem just replaced with the SIMPLE post-processed predictions? If so, please state this clearer. What happens to the nonvolatile POA from GEOS-Chem that I think is included in the PM2.5 (line 289)? I presume the authors consider absorptive partitioning artifacts to be less important than other uncertainties in this study?

26. Fig. 9: Australia is white in panel a. Does that indicate less than 1 death per year due to ASOA?

27. Section 4 title is incomplete

References

Khare, Peeyush, et al. "Asphalt-related emissions are a major missing nontraditional source of secondary organic aerosol precursors." Science advances 6.36 (2020): eabb9785.

Lu, Quanyang, Yunliang Zhao, and Allen L. Robinson. "Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions." Atmospheric Chemistry & Physics 18.23 (2018).

May, Andrew A., et al. "Gas–particle partitioning of primary organic aerosol emissions: 3. Biomass burning." Journal of Geophysical Research: Atmospheres 118.19

(2013): 11-327.

Morino, Yu, et al. "Contributions of condensable particulate matter to atmospheric organic aerosol over Japan." Environmental science & technology 52.15 (2018): 8456-8466.

Seltzer, Karl M., et al. "Reactive Organic Carbon Emissions from Volatile Chemical Products." Atmospheric Chemistry and Physics Discussions (2020): 1-33.