Response Letter to Reviewers for:

Reactive Organic Carbon Emissions from Volatile Chemical Products

Karl M. Seltzer[1], Elyse Pennington[2,3], Venkatesh Rao[4], Benjamin N. Murphy[5], Madeleine Strum[4], Kristin K. Isaacs[5], Havala O.T. Pye[5]

[1]Oak Ridge Institute for Science and Education Postdoctoral Fellow in the Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC 27711
[2]Oak Ridge Institute for Science and Education Fellow in the Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC 27711
[3]California Institute of Technology, Pasadena, CA 91125
[4]Office of Air and Radiation, US Environmental Protection Agency, Research Triangle Park, NC 27711
[5]Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC 27711

Correspondence to: Havala O.T. Pye (Pye.Havala@epa.gov)

Thank you to the editor and reviewers for taking the time to consider our manuscript and provide helpful comments. These comments significantly improved the rigor and quality of our manuscript, and your time and efforts are much appreciated. All reviewer comments are addressed individually below, point-by-point, with the original comments featured in bold text and our response followed in non-bold text.

All updates to the original submission were tracked in the revised submission.

Anonymous Referee #1:

One of the main conclusions the authors make is that this new framework includes spatial allocation to regional and local scales. Have you compared this to current surrogates provided with the 2017 NEI, CARB surrogates or published work such as "Improving spatial surrogates for area source emissions inventories in California" by Li et al. 2020? How do the regional and local distributions vary with this approach? What is the level of resolution the census data is applied to? County/census block? Possibly adding a difference plot comparing to current estimates would be helpful.

We used the same spatial allocation methods as the 2017 NEI. This largely includes population and employment-based allocation, as outlined in Table S6 of the SI. For employment-based allocation, we match the employment NAICS codes used by the 2017 NEI, as outlined in the Technical Source Documentation of the inventory.

In addition, we are familiar with Li et al. 2020 and cite the paper in our manuscript. However, there is a key difference in their analysis and our applications. Namely, application of their spatial surrogates is at the sub-County level for photochemical modeling purposes, whereas we use spatial proxies only to downscale national-level emissions to the county-level.

Comparing possible inventory differences due to variable spatial surrogates, especially at the sub-County level, was outside the scope of this analysis. Nonetheless, leveraging the results from Li et al. 2020 would certainly be considered for those types of applications.

Figure 5c shows a high amount of emissions per capita in Colusa, CA – what is the driver behind this in a relatively small county?

Colusa County is sparsely populated, but relative to their population, features high agricultural pesticide usage. As a result, while small in magnitude (see Colusa County in Fig. 5b), their per-capita emissions are quite high.

Since observed data is available to do comparison, it would be beneficial to show a range of predicted VCP emissions for LA county of the 30 reported species. It is noted that the observed total is 0.259 g while the inventory total is 0.226g; can you add uncertainty to the inventory value based on the discussions from sector 3.6 and 4?

It would be difficult to confidently show a range of predicted individual compounds for the evaluation since the uncertainty associated with the evaporative organic composition of individual product types is not known or provided by the source data. Our uncertainty analysis using Monte Carlo simulations focused on the total emission magnitude and did not perturb the relative abundance of an individual species in a product composition. For example, we do not know the uncertainty associated with the assignment of x% of toluene within a product type. One sentence regarding this limitation has been added to Section 2.2 and are included below:

Furthermore, the uncertainty associated with the evaporative organic composition of individual product types is not known or provided by the source data.

Additional emissions that could result from the discussion in Section 3.6 would not yield a change to the inventory evaluation. Since the evaluation is exclusive to 30 compounds, and these compounds are not influenced by the volatility (or emission) of the organics that are assumed to be non-evaporative, the predicted 0.226 g (g CO)$^{-1}$ would not change. As for the uncertainties discussed in Section 4, these would be difficult to translate without (1) incorporation of a two-box model into the framework to account for indoor loss, which is planned for future work or (2) localized post-use control status, which was outside the scope of this analysis.

In Section 5. on line 562 "The 95% confidence interval for the national level emissions from the complete sector for 2016 is 2.68 – 3.60 Tg (1.81 – 2.42 TgC). This is consistent with the 2017 National Emission Inventory and half the emissions magnitude reported elsewhere (McDonald et al., 2018)." Can the authors provide the 2017 NEI values that are being compared? It would also be helpful to add a national difference plot showing the variability between this new method and 2017 NEI totals for the three panels on figure 5 (state, county, county/capita).

We have added 2017 NEI values (2.84 Tg) for comparative purposes to both Section 5 and Section 3.2. We also direct the referee to Figure S4c in the SI for a county-level per-capita difference plot between the VCPy inventory and the 2017 NEI.

Anonymous Referee #2:

What is the role of disposal in this framework? If VCPs that are used on a short timescale but are disposed of using open methods, is that included in the framework? For example, VCPs could enter wastewater treatment plants and enter the atmosphere.

In this framework, disposal is treated as a permanent sequestration of organics. Research does suggest that organics entering a wastewater treatment plant are largely removed through biodegradation or sorption to sludge (Shin et al. 2015). However, there is significant aeration at such plants, providing opportunity for air release. The NEI does report emissions from Publicly Owned Treatment Works, but given the massive quantity of organics that feature this down-the-drain fate (organics from shampoos, soaps, conditioners, detergents), even marginal changes in the emission of organics from VCPs through this route could have notable impacts.

The Monte Carlo analysis is focused on the uncertainty in the total emissions per capita as the primary outcome. The assumption here is the uncertainty lies primarily in the model inputs, and the outcome is deterministic. I expect this assumption to be valid for total emission per capita as the primary outcome, but may not be so if we examine the composition instead. For example, how does uncertainty in the composition profile affect the emissions?

We do partially include uncertainty in the composition of VCPs in our Monte Carlo assumptions. This is accomplished by assigning uncertainty in the evaporative organic proportions of each sub-PUC, as noted in Section 2.2. However, due to data limitations, we do not assign uncertainty to the composition of evaporative organics. Nonetheless, changes in the organic composition of the evaporative organics would result in changes in the volatility distribution of the organics, which is implicitly accounted for via assigned uncertainty to the characteristic evaporation timescale.

Similarly, for the input variables that were examined (e.g. uncertainty in v_e, depth), what is the uncertainty in the composition of emissions? E.g. what is the uncertainty in median c*? I expect that if v_e increases, it might increase emissions of lower volatility compounds more than it increases those of higher volatility ones.

This is a great question. With available data, the uncertainty associated with the composition of the emissions would be extremely difficult to determine. For example, we do not know the uncertainty associated with the assignment of x% of toluene within a product type. However, we can test the second question. Our median log(C*) for the emissions from the complete sector is 7.6 and the 95% uncertainty associated with that number due to the model inputs we can perturb (including v_e) is 7.5 – 7.8. This is certainly an underestimate in the uncertainty since, again, we do not know how the uncertainty associated with the composition of individual product types.

As for v_e, if this variable were increased, the characteristic evaporation timescale of all components would increase, assuming all other variables are held constant. If this were to happen, all compounds that are already predicted to evaporate (i.e. higher volatility ones) would still evaporate. However, as the reviewer points out, this could have notable impacts on lower volatility compounds that were previously predicted to not evaporate.

For many of the water-based VCPs, I would expect that evaporation will be based more on K_AW (or Henry's Law constant) rather than K_OA. How much would that change the estimates?

When using the QSAR predicted K_{OA} and K_{OW} and equation 3.4 of Weschler and Nazaroff (2008) for two compounds (propylene glycol and PCBTF), we yield a calculated K_{WA} that is larger for one (propylene glycol), indicating less partitioning to air, and one that is smaller (PCBTF), indicating more partitioning to air. However, the change in the subsequent characteristic evaporation timescale from such changes seems to be only relevant for VCPs that would feature small to medium use timescales (e.g. < 1 day). For VCPs with a long use timescale (e.g. architectural coatings), this change would not yield a different conclusion regarding the proportion of emissions.

What is the fraction of VCPs that are based on fossil-carbon vs modern carbon? Is that something that can be estimated?

This is difficult to determine. Some compounds emitted from VCPs (e.g. ethanol, many fragrances) are likely dominated by modern carbon, whereas others (e.g. mineral spirits) are likely dominated by fossil-carbon. However, it is our understanding that the demand for "green" solvents has and continues to grow. According to an industry study (The Freedonia Group, 2016), approximately 15% of functional solvent usage is derived from natural or renewable resources.

Lines 296-297: For 4 PUCs, employment statistics were used for the spatial allocation of commercial VCP emissions. I am wondering that regarding the automation considerations, the number of employees might underestimate the VCP emissions from those sites and sales allocation or GDP of the production sector distribution might be better tools for that purpose.

Since emission more likely occurs at or near the time of use, we prefer employment (for industrial sub-PUCs) as a spatial downscaling proxy over production sector statistics. In addition, larger production facilities are more likely to have add-on controls. While we did not consider add-on controls in this manuscript, emissions from these sources are likely non-linear with production volume.

It is not surprising that regional and localized differences are significant. For many of the compounds, the atmospheric lifetimes could be long enough that these differences probably do not matter too much. This might also depend on the scale of air quality modeling.

We agree.

In Lines 25-27 (abstract) and in Section 3.3, when comparing to 2017 NEI, the terms "increase" and "decrease" are misleading, since they can be confused with year-to year increase/decrease. I suggest using terms like "overestimate" or "underestimate", or just "higher" or "lower".

We adjusted both the text in the abstract and Section 3.3 to help alleviate this confusion. The two relevant sentences in the abstract now reads:

VCPy predicts more VCP emissions than the NEI for approximately half of all counties, with 5% of all counties featuring emissions more than 55% higher. Categorically, VCPy reports higher emissions for personal care products (150%) and paints/coatings (25%) when compared to the NEI, whereas pesticides (-54%) and printing inks (-13%) feature lower emissions.

Line 80: there are two references for Li et al. 2018.

We believe this is a mistake on the part of the reviewer. We refer to the first reference as "Li et al., 2018" in the text and the second reference as "Li and Cocker 2018," since there are only two authors of that manuscript.

Figure 6: what does X stand for?

The "X" represents each compound in the figure. A clarification has been added to the Fig. 6 caption.

<u>Additional edits:</u>

Following submission, we learned of more recent sales proportions for water vs. solvent-based architectural coatings in a California Air Resource Board survey. As a result, we updated the water vs. solvent-based proportions from 88/12% to 94/6% (i.e. the proportion of water-based coatings to total architectural coatings increased). These changes had marginal impacts on the complete inventory (~2%) and modest impacts on the architectural coatings sub-PUC (~25%).