

Interactive comment on “Impact of Urban Emissions on a Biogenic Environment during the wet season: Explicit Modeling of the Manaus Plume Organic Chemistry with GECKO-A” by Camille Mouchel-Vallon et al.

Anonymous Referee #2

Received and published: 3 January 2020

Review of manuscript acp-2019-1024, "Impact of Urban Emissions on a Biogenic Environment during the wet season: Explicit Modeling of the Manaus Plume Organic Chemistry with GECKO-A"

The authors present an application of the GECKO-A model to GoAmazon2014/5 campaign to understand impacts of the Manaus plume on biogenic SOA, with a focus on the T3 site. Overall, I think it is valuable work, and continued investigation and application of the GECKO-A model stands to deepen our understanding of the "molecular view" of the atmosphere. However, I'm not sure the authors fully achieve their stated

C1

goals of improved understanding of the influence of the plume, which is used in this work primarily as a benchmark against which to test the model. Instead, I think their discussions of the model strengths and weaknesses are more enlightening, and an expansion of some of these discussions may further increase the scientific value of this application. In general, this work is important, and fitting for this journal, but I think there are some places that need major revision.

Major comment: (1) The focus on this work claims to be on anthropogenic influence, but one major result is the relative lack of skill GECKO-A has in capturing the impact of the Manaus plume on SOA production. This suggests to me that a major result might actually be just that the box model is poorly including anthropogenic emissions. SOA formation is underpredicted, OH concentrations are significantly over predicted, so perhaps there are just more or more reactive VOCs in the city than being included in the model. This is further exacerbated by the issue that the surrogate composition of the fuel emissions are known to not really accurately represent the true composition. The ability of the model to capture clean conditions, which with MEGAN and the PTR have reasonably well constrained emissions, speaks well of GECKO-A, and suggests just that the issue may be in the emissions being fed to the model.

(2) This paper is primarily an exploration of the strengths and weakness of GECKO-A, it doesn't do much to discuss the "Impact of Urban Emissions" as the title suggests. There is some discussion, but mostly it is a comparison of GECKO-A to other models (VBS, Shrivastava) and not really providing new information beyond a further exploration of GECKO-A. I think there are interesting results regarding GECKO-A, in particular the discussion of reduced complexity, which seems like a real place for GECKO-A to provide generalizable scientific insight (how complex do we really need models to be?), and that the weaker part of the work is the attempts to understand the Manaus plume (for which the emissions may not be correct, and aging may not be incorporated, and other issues). Potential issues in modeling the plume end up conflated with potential issues in the model, and instead I think perhaps some of the discussions about the

C2

model could instead be bolstered and thought about more deeply (e.g., I don't think the explanations for H/C discrepancies are likely complete).

Technical comments: Line 1. Missing "of" : "investigation of the"

Line 7. Not clear what it means for the model to "reproduce measured primary compounds" after tuning emissions. Aren't the primary compounds just the emissions, so you tune for this result, and it isn't really impacted by the skill of the model? Perhaps it will be more clear to me after a detailed reading.

Line 15. "particularly intense all year long" is a bit odd, perhaps the authors mean "more photochemically active than other regions throughout most of the year"?

Line 36-37. This mid-paragraph question is odd. "Would" in what case? Do the authors mean "Do"? Maybe just rephrase this without the use of this rhetorical question.

Line 50. The discussion of the "molecular view," while valuable, has some gaps or issues here. In particular, those citations of Koss et al. are an odd choice, as I believe they are just using a PTR, and if I'm not mistaken, there was a PTR run at T3 by the Martin group (some of the data of which is used in this work). Other groups (e.g. the Kroll group, and the CLOUD group) have tried to combine multiple spectrometers to actually capture the whole range of compounds, reaching more a molecular view. However, even still, this would be more reasonably considered a "formula view", as these instruments do not separate molecules out from their formulas. There were also several other instruments at T3 approaching a molecular view (I believe for instance the Goldstein group has collected and run GCxGC of filter samples, providing some molecular information), though perhaps not comprehensively. I would re-frame some of this discussion to more accurately capture the landscape and discuss what existing measurements can or can't provide (e.g., I agree the available instruments probably don't provide a comprehensive measurement to compare to models, particularly for gas-phase oxygenates).

C3

Line 54. I'm a big fan of GECKO-A, but maybe not everyone will agree that it is "the ideal tool". "an excellent tool" perhaps?

Line 171. The authors discuss the fact that n-alkanes are perhaps not a good surrogate for diesel fuel and gasoline IVOCs, which are mostly branched and cyclic. However, they do not explain why their estimates are less branched than other work has suggested, and importantly they do not discuss the impacts of these structural differences. They acknowledge that almost none of diesel fuel is comprised of the compounds they are using as surrogates, but do not further discuss this issue. Gentner et al. attempt to put estimates on the impact of branching and rings on SOA, so estimating this uncertainty shouldn't be too difficult.

Figure 5. The measurement of benzene and toluene at T3 are fairly poor constraints on these species as they catch only the tail end of the decay (and even still don't really agree with the toluene model). Is there no aircraft data or VOC measurements at T1 or T2 near Manaus to better constrain these?

Line 260. Again, are there T1 or T2 measurements that could help constrain VOCs in the city? Also, to what extent does model include residual biogenic VOCs present in the city? Presumably there are VOCs present in the city other than just the vehicle emissions, like biogenics from the surrounding forest (or volatile chemical products?), are those captured by the model? Is there a spin up time to allow the city emissions to have some equilibrium concentration of VOCs that would help suppress OH concentrations?

Figure 8. It would be helpful to add Glasius OS measurements to the figure as a dashed line.

Line 300-314. I'm not sure the explanations provided for the H/C disparity can really close the gap and it warrants further discussion. The examples the authors provide of oligomerization and fragmentation provide relatively modest decreases in H/C and also change the O/C. A huge fraction of the compounds would need to be oligomers or

C4

fragments for this to reconcile H/C, and this would likely shift the O/C. In the examples they provide, dimers still have H/C ratios well above the observed average. If, for instance, all of the C10 compounds were actually dimers, wouldn't this just bring the average down to 1.5 or 1.6? How do you get down to 1.3? What sorts of compounds can push H/C this far down? Trimers? Tetramers? And would the whole mass need to be comprised of these? The authors could play some games with their data to explore this, for instance assume all compounds are actually dimers or fragments and estimate the average H/C and O/C. This might further be scientifically interesting by putting some constraints on accretion products.

Line 316. How do the anthropogenic emissions used by Shrivastava compare to those used here?

Line 322. I don't fully understand the aging parameterization, could the authors provide more detail?

Line 362. The authors point out the importance of aging in capturing the polluted SOA, which the GECKO-A model does not really capture. Is this due to a lack of aging in the GECKO-A model? Maybe I missed it, but is the GECKO-A model only oxidizing the gas phase and not aging the particle? Considering the importance of aging on reproducing the SOA mass (Figure 7), could the authors include a parameterization of aging in the GECKO model? This might also address the H/C and O/C issues.

Line 367-368. Why is it unclear? It seems to capture polluted periods better than biogenic periods (Figure 7).

Line 400-402. The ideas of reducing complexity discussed in this section are very interesting. It's not completely clear to me that some of the conclusions aren't overextended. In particular, the conclusion that "diversity represents the number of species that would be needed to reproduce the same informational content regarding the composition of SOA." The parameter D is based solely on mass fraction, not their physicochemical properties, so it might not capture other properties such as oxygenation or volatility.

C5

Imagine a scenario where a small fraction of highly oxygenated compounds drive up O/C - this might still impact hygroscopicity but would this complexity be captured by D? Or a small fraction of more volatile components might partition between the gas- and particle-phase and drive oxidation of particle mass. While the exact mechanism of implementing such a reduction is out of scope of this manuscript, the overall point is that it's not to me that either of the diversity parameters really capture the complexity. Would it be possible to implement a variant of D for parameters of interest? For instance minimum number of components needed to describe O/C within 10% while capture some fraction of the mass? I'm not sure the best parameters, but the idea would be something that captures some of the properties beyond simply mass.

Line 403-405. Isn't it not only possible but certain that an effective species is not an individual species but rather a combination of explicit species? Otherwise D would be more similar to the other metric, or equal to N. The very nature of the parameter D is to be a mathematical descriptor, not an individual species, correct?

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-1024>, 2019.

C6