

## ***Interactive comment on “Global tropospheric effects of aromatic chemistry with the SAPRC-11 mechanism implemented in GEOS-Chem” by Yingying Yan et al.***

### **Anonymous Referee #1**

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### **General Comments**

The manuscript by Yan et al. describes the implementation and impacts of an updated scheme for oxidation of aromatics (SAPRC-11) in the GEOS-Chem chemical transport model. The authors have provided a comprehensive overhaul to the previously very simplified benzene, toluene, and xylene chemistry. The updates are described in sufficient detail to allow reproducibility. The new simulation has been evaluated using both aircraft and surface observations and overall shows good agreement for aromatics and a reduction in model bias for ozone. The authors also quantify the impacts on related species including NO<sub>x</sub>, OH, and ozone, and show that there are small global impacts

C1

but significant regional impacts (especially over anthropogenic source regions).

Overall, the updated chemistry is a valuable and important addition to a widely used global chemical transport model. The paper is generally well written, well structured, and easy to follow. The content and presentation are well suited to GMD, and I recommend publication once the following comments have been addressed.

#### ***1. Model-observation comparisons should include the Base simulation***

Section 4 compares the SAPRC (updated) simulation to the observations and discusses differences and biases. However, the Base (original) simulation is never compared to the aromatics observations. There is a brief comparison to the ozone observations, although this is buried in Section 5.3. To clearly show the impacts of the new chemistry on the simulation, both the Base and SAPRC simulations should be compared to the observations in Section 4. The Base simulation should be added to Figures 2-5, and the discussion currently on Page 12 lines 29-39 should be moved to Section 4 (along with Table 3).

#### ***2. SI tables should clearly identify new vs. updated species/reactions and should be consistent with GEOS-Chem nomenclature.***

Table S1 states it provides a list of “new model species”, but several of these are existing species in GEOS-Chem. This should be clarified, and could be done by changing “new” to “relevant” in the table caption and adding a column for “New or Existing” to the table.

Similarly, Table S2 states it lists “new reactions and rate parameters”, but again some reactions are currently in GEOS-Chem (presumably the rate parameters have been updated). Clarity is needed around what is new in the mechanism.

Finally, the species names in the SI do not match the GEOS-Chem conventions for existing species. Just a few examples of what GEOS-Chem uses: MO<sub>2</sub> (not MEO<sub>2</sub>), CH<sub>2</sub>O (not HCHO), ALD<sub>2</sub> (not CCHO), and many more. This work will be much more

C2

usable by the GEOS-Chem community if the species list is updated to match. Existing species names are given at [http://wiki.seas.harvard.edu/geos-chem/index.php/Species\\_in\\_GEOS-Chem](http://wiki.seas.harvard.edu/geos-chem/index.php/Species_in_GEOS-Chem)

The SI tables should be updated where relevant to match.

### **3. More details are needed to understand and be able to reproduce the model-observation comparisons**

Section 3 describes the observations used and, to some extent, the method in which the model was sampled for the comparisons. Some details are missing here that would be necessary for one to reproduce this work. Specifically, I had the following questions:

- CALNEX observations are at 1 second / 100 m resolution (pg 6, lines 20-21). This is much higher resolution than the model (2x2.5 degrees, timestep on order of minutes). Have the aircraft data then been averaged to the model resolution? If not the statistics will be biased by comparing multiple observation points to a single model grid point, especially as there will not be equal observation points in a given gridbox / timestep.
- For CARIBIC comparisons model output is sampled along the flight track (pg 6, lines 31-33). If this is the case, then why are model annual means used for the comparison? Shouldn't these be treated in the same way as CALNEX?
- Why are monthly means used for EMEP comparisons but annual means used for EEA comparisons (pg 7, lines 11-12 and 21)?
- Why are urban and suburban sites excluded from EEA comparisons (pg 7 lines 18-19) but not excluded from AQS comparisons (pg 10, line 2)?
- For KCMP, the paper specifies use of hourly observations (pg 7, line 26); are hourly model values also used?

C3

- For KCMP sampling at 185m (pg 7, line 25), what box is the model sampled from, and how does that model layer compare to the 185m sampling height? I presume it wouldn't be the lowest model layer, since that is centred at 65m (pg 7 line 36).
- Why are so many more EMEP sites used for ozone (130) than for aromatics (8-14) (Table 1)?
- It would be useful to include a table providing sites and location information in the SI, especially since some stations have been excluded. This is probably not feasible for the large number of ozone sites, but would be for the aromatics data.

### **4. Difference maps should be included for benzene, toluene, and xylene**

Although they are the focus of the paper, no maps of the aromatics spatial distribution are shown (except emissions), although they are hinted at on pg 11, lines 25-27. It seems to me critical to include figures analogous to Fig. 6 and 7 but for benzene, toluene, and xylene.

### **5. Some comments are needed on the likely impact of changing aromatic emissions**

Anthropogenic aromatics emissions are from the Year 2000, while simulations and observations are for 2005 and 2010-2011. There are likely to have been significant changes in emissions and their distributions over the decade (briefly noted by authors on pg 8, lines 20-21). This is not a problem per se, but the paper would benefit from discussion of the likely changes and how they would benefit the results shown here (i.e. have aromatics gone up, in which case this work provides an upper limit? or the opposite?).

#### **Specific Comments**

Pg 2, lines 17-18: can some references be provided to back this up?

Pg 2, lines 29-30: is the overestimate global, or region-specific?

C4

Pg 2, line 35: the introduction has jumped from models in general to GEOS-Chem specifically, so GEOS-Chem needs some introduction here

Pg 3, line 4: It would be better to use the updated GEOS-Chem versioning, which would make this version 12.0.0 rather than 11-02 (although technically the same).

Pg 3, line 9: I feel the equation would be easier to understand as aromatic + OH + NO = inert tracer (rather than “-NO” on the right-hand side)

Pg 3, lines 31+: what model time step is used?

Pg 4, lines 10-17: unclear why CO emissions are discussed here when CO is not a focus of the paper (and never shown later). If included here, would need to also include non-anthro CO sources (e.g. chemical production). Also, emissions from ships and aircraft missing. It might make sense to start this section with the NMVOC emissions rather than CO/NO<sub>x</sub> as they are the focus.

Pg 4, line 28: please specify species for the “aromatics” source – is this just benzene + toluene + xylene, or are other species included? Also “(71 Tg C)” can be deleted as it is given in the previous sentence (line 27).

Pg 5, line 15: “. . . which is consistent with the recent literature.” More details are needed. What specifically does the SAPRC-11 mechanism reconcile that is/was missing from other mechanisms?

Pg 5, lines 21-33: I find this description hard to follow and hard to relate to what is in the tables in the SI. I think it would be helpful to give an example that traces the oxidation of one aromatic through these different production pathways.

Pg 6, lines 7-12: This is a little confusing and would suggest rephrasing. Is there a separate 6-month spin-up for each scenario (Base and SAPRC)? Is July-December 2009 also a spin-up period? For the sentence about initial conditions, does this mean that there is a 4°x5° spin-up run from Jan-Jun 2004 followed by a 2°x2.5° spin-up run for Jul-Dec 2004?

C5

Pg 7, lines 13-14: The model speciation of xylenes should be clarified in the earlier section 2.2 about the mechanism.

Pg 8, lines 13-21: The model-observation difference would be a useful metric to include in Table 1.

Pg 8, line 30: Why are these 6 sites the ones used?

Pg 9, lines 13, 19: what are the lifetimes for benzene and toluene?

Pg 9, lines 23-34: any comment about the different profile shapes in the lower troposphere? What about the overly rapid benzene drop-off with altitude? Does that imply the modelled benzene lifetime is too short?

Pg 9, line 25: any comment on why winter shows an increase when the other seasons do not?

Pg 10, line 28: “The free tropospheric increases are largest in the remote northern regions” – I don’t see this in Fig. 7. Instead it looks like the NO increases are about the same from 30S-90N.

Pg 10, lines 31-32: Rephrase this sentence as the start suggests it is about the surface NO<sub>2</sub> but then it ends with “throughout the troposphere.”

Pg 11, lines 1-3: Because of the different color scales, the overall NO<sub>x</sub> changes are not obvious in Figs 6 and 7. I’d suggest adding another panel to show the total NO<sub>x</sub> change.

Pg 11, lines 4-7: any comments on what is driving the NO<sub>3</sub> global decreases and regional increases?

Pg 11, lines 8-11: Table 2 and the associated discussion in the text would be easier to follow if it were presented as a figure (e.g. a set of bar charts) rather than a densely packed table. Also, at the moment it includes species that are not discussed elsewhere in the text.

C6

Pg 11, lines 31: Might be useful for this discussion to include the OH/HO<sub>2</sub> ratio in the table (or figure)

Pg 12, lines 10-11: Please comment on why the ozone declines in biomass burning regions. Why have these changed in ways that are different from anthropogenic dominated regions? How can you tell that the changes are induced by biomass burning dominance rather than biogenic emissions dominance? If the former, I'm surprised not to see the same effects in boreal regions and in southern Africa.

Pg 12, lines 13-22: The reasons for the ozone increases are described, but what is causing the ozone decreases?

Pg 12, lines 27-28: Simulated production and loss rates could be used to test this.

Pg 12, lines 37-39: I think the conclusion here is that the halogen chemistry would bring the US ozone back down to the point that addition of aromatics would be a net improvement. If that's so, please make that point explicit. It also left me wondering what the impacts of the halogens would be outside of the US, where the biases shown in this work are already negative – would they become worse?

Pg 13, lines 6-9: It would be worth adding a panel to Figs. 8 and 9 to show the changes to the odd oxygen family. A panel for PAN would also be useful for the subsequent discussion.

Pg 13, line 25: which "organic nitrates" are referred to here? Is this PAN and analogues (PBZN)? Or does this refer to other organic nitrates like alkyl nitrates? It is not clear where in Table S2 one is meant to look for the chemistry of these nitrates.

Pg 13, lines 26-29: what NO<sub>x</sub> recycling is assumed in the model? Is this an effect that the authors have looked at (if so, can it be shown or described in more detail?), or does this refer to knowledge from existing literature (if so, references are needed...)?

Figure 2: Would be easier to interpret if common sites were aligned for the 3 species. (e.g. Zingst common between benzene and xylene, so move to upper left for xylene to

C7

match location for benzene, etc.)

### Technical Comments

Title: GMD requires specifying model version number in addition to name ("GEOS-Chem version 9-02")

Pg 5, line 5: suggest changing "true" to "the case"

Pg 5, line 6: change "v11-02" to "12.0.0" if changed above

Pg 5, line 10 (and elsewhere): the Carter and Heo (2013) reference is missing from the reference list

Pg 5, line 35: change "xylenols, phenols (XYNL)" to "xylenols and phenols (XYNL)" since XYNL represents both species.

Pg 6, line 8: suggest changing "based on the available observations" to "for comparison to the available observations"

Pg 6, line 18: suggest deleting "over the US" – this is too broad and already clear from the mention of California in the previous line.

Pg 7, line 7: change "though" to "through"

Pg 7, line 8: suggest changing "boundaries" to "geographic boundaries" (to clarify that this is not flux through e.g. air-land boundaries)

Pg 7, line 8: suggest changing to "locates measurement sites in locations where there are minimal..."

Pg 7, line 21: change "site" to "sites"

Pg 7, line 22: would be useful to add the location for the KCMP tall tower (e.g. US state?). Also does KCMP stand for something? Acronym is not defined.

Pg 8, line 2: suggest changing "part" to "section"

C8

Pg 8, line 5: suggest changing “To do” to “For”

Pg 10, line 1: suggest deleting “relatively”

Pg 13, line 33: suggest changing “give” to “provide”

Figure 7: caption error; missing reference to NO<sub>3</sub> and to middle plots

Figures 6-9: are these annual means? Which model year?

Table S1: Benzene, Toluene, and Xylene missing from species list

Table S2: What does “#” refer to?

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Interactive comment on Geosci. Model Dev. Discuss., <https://doi.org/10.5194/gmd-2018-196>, 2018.