Geoscientific
Model Development
Discussions

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

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Anonymous Referee #1 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 NOx, OH,

and ozone, and show that there are small global impacts 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. We thank the reviewer for comments, which have been incorporated to improve the manuscript. 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). Thanks for the comment from referee. We have added the modeled spatial distributions of annual mean surface (revised Figure 12) and zonal average latitude-altitude distributions of annual mean (revised Figure 13) benzene, toluene, and xylene simulated in the Base case for the year 2005. Also shown in these figures are the respective changes from Base to SAPRC. These two figures show that the changes from Base to SAPRC in annual average surface aromatics and zonal average aromatics are less than 2% for individual species. The differences between Base and SAPRC is much smaller than the modeled bias in SAPRC compared to aromatics observations. Thus we have kept the ozone comparison with Base and SAPRC in Sect. 5.3 to show the effects from SAPRC on ozone simulation. 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. In the revised Table S1, we have identified new vs. existing species 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. In the revised Table S2, we have identified new vs. updated reactions by changing "new" to "relevant" in the table caption and adding a column for "New or Updated" to the table. The updated reaction is meant to update the rate parameters. 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: MO2 (not MEO2), CH2O (not HCHO), ALD2 (not CCHO), and many more. This work will be much more 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. The SI tables should be updated where relevant to match. We have updated the species list in Table S1 and Table S2 to match the GEOS-Chem conventions for existing species. 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: âĂć 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. We have added the information in the revised Sect. 3.1: "For comparison to the model results, we averaged the high temporal-spatial resolution observations to the model resolution." âĂć 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? We first averaged the measurements to the model output resolution. Then in comparison, we use annual means of observations and model data along the flight track. In the revised description, we have added the details: "To evaluate our results, measurements are averaged to the model output resolution. Vertically, results from GEOS-Chem model simulations at the 250 hPa level are used to compare with observations between 200–300 hPa. Then the annual means of observations and model data sampled along the flight tracks are used in the comparison." âĂć Why are monthly means used for EMEP comparisons but annual means used for EEA comparisons (pg 7, lines 11-12 and 21)? We used monthly means for EMEP comparisons but annual means for EEA comparisons, mainly because that the EEA measurements have much more missing data than the EMEP observations. âĂć 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)? Based on the comment from referee#2, in the revised text, we have removed the model evaluation with AQS ozone measurements, because that it is inappropriate to directly compare AQS ozone observations near the surface (âĹij 10 m) to GEOS-Chem ozone at 65 m height with 2x2.5 deg horizontal resolution. âĂć For KCMP, the paper specifies use of hourly observations (pg 7, line 26); are hourly model values also used? We averaged the hourly observations to monthly values and then compared to the monthly model results. We have added the information in the revised sentence: "We averaged the hourly observations of benzene, toluene and C8 (xylenes + ethylbenzene; here consistent with the model speciation) aromatics to monthly values and then used for our model evaluation." âĂć 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). We have added the information at the end of this paragraph: "Monthly mean simulations at the 990 hPa level (∼190 m) are used for comparison." âĂć Why are so many more EMEP sites used for ozone (130) than for aromatics (8-14) (Table 1)? It is because that aromatics

downloaded from EMEP (http://www.nilu.no/projects/ccc/emepdata.html) are much less than ozone measurements. âĂć 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. The sites and location information of aromatics data used here are described in detail in Cabrera-Perez et al., 2016 who download the raw data and provide the collated data. We have added this information in the revised text: "Further details of the sites and location information of EEA (and EMEP) used here are described in Cabrera-Perez et al., 2016." 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. We have added the modeled spatial distributions of annual mean surface (revised Figure 12) and zonal average latitude-altitude distributions of annual mean (revised Figure 13) benzene, toluene, and xylene simulated in the Base case for the year 2005. Also shown in these figures are the respective changes from Base to SAPRC. 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?). Thanks for the comment from referee. We have added discussion in the revised Sect. 4.1: "Anthropogenic aromatics emissions are reported to have significant changes in emissions and their distributions over the decade by EDGARv4.3.2 (Crippa et al., 2018; http://eccad.aeris-data.fr/#DatasetPlace:EDGARv4.3.2$DOI). It shows that the total aromatics emission from anthropogenic source are enhanced by 5% (2005) and

14% (2011) compared to the year 2000. The model bias would be partly benefit from this emission increase with enhanced modeled mixing ratios of benzene and toluene." Specific Comments Pg 2, lines 17-18: can some references be provided to back this up? We have added the references of Lewis et al., 2013 and Cabrera-Perez et al., 2016. Pg 2, lines 29-30: is the overestimate global, or region-specific? We have revised this sentence: "However, some systematic biases can occur, most commonly an overestimation over the northern hemisphere" Pg 2, line 35: the introduction has jumped from models in general to GEOS-Chem specifically, so GEOS-Chem needs some introduction here We have revised this sentence: "Another motivation for the modeling comes from recent updates in halogen (bromine-chlorine) chemistry, which when implemented in GEOS-Chem, a global chemical transport model being used extensively for tropospheric chemistry and transport studies (Zhang and Wang, 2016; Yan et al., 2014; Shen et al., 2015; Lin et al., 2016), decrease the global burden of ozone significantly (by 14%; 2–10 ppb in the troposphere) (Schmidt et al., 2017)." 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). We have modified the version. 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) We have modified the equation as aromatic + OH + NO = inert tracer Pg 3, lines 31+: what model time step is used? We have added the time step information: "The chemistry time step is 0.5 h, while the transport time step is 15 min in the model." 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/NOx as they are the focus. We have removed the CO emission description and moved the NOx emission behind the NMVOC emission description. 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). We have added the species for the "aromatics" source and removed the "(71 Tg C)" in this sentence: "On a carbon basis, the global aromatics (benzene + toluene + xylenes) source accounts for $\sim$ 23% (16 TgC) of the total anthropogenic NMVOCs." 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? We have added some details of major updates in the SAPRC-11: "SAPRC-11 is an updated version of the SAPRC-07 mechanism (Carter and Heo, 2013) to give better simulations of recent environmental chamber experiments. The SAPRC-07 mechanism underpredicted NO oxidation and O3 formation rates observed in recent aromatic-NOx environmental chamber experiments. The new aromatics mechanism, designated SAPRC-11, is able to reproduce the ozone formation from aromatic oxidation that is observed in environmental chamber experiments (Carter and Heo, 2013)." 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. We have modified the description by taking toluene as an example: "In SAPRC-11, taking toluene as an example in Table S2, the reactions following abstraction lead to three different formation products: an aromatic aldehyde (represented as the BALD species in the model), a ketone (PROD2), and an aldehyde (RCHO). The largest yield of toluene oxidation is the reaction after OH addi- tion of aromatic rings. The OH-aromatic adduct is reaction with O2 either forming HO2 and a phenolic compound (further consumed by reactions with OH and NO3 radicals), or to form an OH-aromatic-O2 adduct. The OH-aromatic-O2 adduct further undergos two competing unimolecular reactions to ultimately form OH, HO2, an α-dicarbonyl (such as glyoxal (GLY), methylglyoxal (MGLY) or biacetyl (BACL)), a monounsaturated dicarbonyl co-product (AFG1, AFG2, the photoreactive products) and a di-unsaturated dicarbonyl product (AFG3, the non-photoreactive products) (Calvert et al., 2002)." 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 4âŮęx5âŮę spin-up run from Jan-Jun 2004 followed by a 2âŮęx2.5âŮę spin-up run for Jul-Dec 2004? We have revised these sentences: "Both simulations (Base and SAPRC) at 2.5° long. 2° lat. are conducted from July 2004 to December 2005, allowing for a 6-month spin-up for our focused analysis over the year of 2005 based on the available observations (Sect. 3). Initial conditions of chemicals are regridded from a simulation at 5° long. 4° lat. started from 2004 with another spin-up run from January to June 2004. For comparison with aromatics observations over the US in 2010–2011 (Sect. 3), we extend the simulations from July 2009 to December 2011 with July-December 2009 as the spin-up period." Pg 7, lines 13-14: The model speciation of xylenes should be clarified in the earlier section 2.2 about the mechanism. We have added the model speciation of xylenes in revised Sect. 2.1: "Here the model speciation of xylenes includes m-xylene, p-xylene, o-xylene and ethylbenzene (Hu et al., 2015)." Pg 8, lines 13-21: The model-observation difference would be a useful metric to include in Table 1. We have added the calculation of model-observation difference in revised Table 1. It is the MRB (relative bias of model results) defined as: (MMOD – MOBS)/MOBS. Pg 8, line 30: Why are these 6 sites the ones used? We have added the reason: "The sites are chosen as the first six stations with largest amount of data." Pg 9, lines 13, 19: what are the lifetimes for benzene and toluene? The lifetime of benzene is between several hours and several days, and toluene is between several days and several weeks irrespective of the time of year (http://www.nzdl.org/gsdlmod?a=p&p=home&l=en&w=utf-8). We have added the lifetime for toluene in the revised Sect. 4.2. 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? Thanks for this comment from referee. We have added the discussion in the revised Sect. 4.2: "The different profile shapes in the lower troposphere for benzene, toluene and C8 aromatics are mainly due to their different emissions and lifetime. The modeled overly rapid aromatics drop-off with altitude probably implies

the modelled aromatics lifetime is short." Pg 10, line 25: any comment on why winter shows an increase when the other seasons do not? We have added the discussion in the revised Sect. 5.1: "This winter increase versus decline in other seasons is probably attributed to the weaken photochemical reactions involving NOx in winter." 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. We have revised this sentence as: "The free tropospheric 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 NO2 but then it ends with "throughout the troposphere." We have revised this sentence as: "Figure 6 shows that simulated surface NO2 mixing ratios in the SAPRC scenario are enhanced over most locations across the globe". Pg 11, lines 1-3: Because of the different color scales, the overall NOx changes are not obvious in Figs 6 and 7. I'd suggest adding another panel to show the total NOx change. We have added the modeled spatial distributions of annual mean surface NOx (revised Figure 7) and zonal average latitude-altitude distributions of annual mean (revised Figure 8) NOx simulated in the Base case for the year 2005. Also shown in these figures are the respective changes from Base to SAPRC. Pg 11, lines 4-7: any comments on what is driving the NO3 global decreases and regional increases? We have added the discussion following this sentence: "The NO3 global decreases are mainly due to the consumption of NO3 by reaction with the aromatic oxidation products. However, the NO3 regional increases are probably caused by the enhanced regional atmospheric oxidation capacity." 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. Thanks for this comment from referee. We have kept the table in the revised manuscript, mainly because that the amount of data in Table 2 is large to be difficult presented as a figure and be also difficult to show the specific value in the bar charts. In the revised Table 2, we have removed the calculation results of species (H2O2 and

N2O5) that are not discussed in the text. Pg 11, lines 31: Might be useful for this discussion to include the OH/HO2 ratio in the table (or figure) We have included the OH/HO2 ratio in the revised Table 2. 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. Based on the recent data analysis, we cannot yet comment on why the ozone declines in regions dominated by biomass burning or biogenic emissions. We have revised this sentence to include the specific regions: "ozone declines in regions of South America, Central Africa, Australia and Indonesia over the tropics (30°S–30°N)." The reasons for the ozone decline are discussed below: "These decreases are probably related to the upward transport of aromatics by tropical convection processes. The aromatics transported to the upper troposphere may cause net consumption of tropospheric OH and NOx, which can further reduce ozone production." Pg 12, lines 13-22: The reasons for the ozone increases are described, but what is causing the ozone decreases? The reasons for the ozone decline are discussed below: "These decreases are probably related to the upward transport of aromatics by tropical convection processes. The aromatics transported to the upper troposphere may cause net consumption of tropospheric OH and NOx, which can further reduce ozone production." Pg 12, lines 27-28: Simulated production and loss rates could be used to test this. Thanks for this comment from referee. Regretfully, we did not output the modeled results of production and loss rates. 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? Based on the comment from referee#2, in the revised manuscript, we have removed the model evaluation with

AQS ozone measurements and the discussion of halogen chemistry, because that it is inappropriate to directly compare urban and suburban AQS ozone observations near the surface (âĹij 10 m) to GEOS-Chem ozone at 65 m height with 2x2.5 deg horizontal resolution. 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. We have added the modeled spatial distributions of annual mean surface PAN (revised Figure 7) and zonal average latitude-altitude distributions of annual mean PAN (revised Figure 8) simulated in the Base case for the year 2005. Also shown in these figures are the respective changes from Base to SAPRC. For the odd oxygen family (Ox), they are shown in revised Figure 10 and Figure 11. 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. We have added the specific species and the referred reactions shown in Table S2 in the revised sentence: "In addition, production of organic nitrates (PBZN (reactions of BR30 and BR31 in Table S2) and RNO3 (PO36)) in the model with SAPRC aromatics chemistry". Pg 13, lines 26-29: what NOx 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. . .)? We have changed the "recycling of NOx" to "such re-release of NOx" in the revised sentence. The re-release of NOx process have described in the former sentence: "In addition, production of organic nitrates (PBZN (reactions of BR30 and BR31 in Table S2) and RNO3 (PO36)) in the model with SAPRC aromatics chemistry may also explain the increase in ambient NOx in the remote regions, due to the re-release of NOx from organic nitrates (as opposed to removal by deposition)." 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 match location for benzene, etc.) We have moved the common sites to be aligned for the three species in the revised Figure 2. Technical Comments Title: GMD requires

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specifying model version number in addition to name ("GEOSChem version 9-02") We have added the model version into the title. Pg 5, line 5: suggest changing "true" to "the case" Have changed. Pg 5, line 6: change "v11-02" to "12.0.0" if changed above Have changed. Pg 5, line 10 (and elsewhere): the Carter and Heo (2013) reference is missing from the reference list We have added the Carter and Heo (2013) reference in the reference list. Pg 5, line 35: change "xylenols, phenols (XYNL)" to "xylenols and phenols (XYNL)" since XYNL represents both species. Have changed. Pg 6, line 8: suggest changing "based on the available observations" to "for comparison to the available observations" Have changed. 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. Have deleted "over the US". Pg 7, line 7: change "though" to "through" Have changed. Pg 7, line 8: suggest changing "boundaries" to "geographic boundaries" (to clarify that this is not flux through e.g. air-land boundaries) Thanks for comment from referee. We have changed. Pg 7, line 8: suggest changing to "locates measurement sites in locations where there are minimal. . ." Have changed. Pg 7, line 21: change "site" to "sites" Have changed. 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. We have added the location in the revised sentence: "The KCMP tall tower measurements (at 44.69°N, 93.07°W, Minnesota, US) have been widely used for studies". The the KCMP is the current Minnesota Public Radio. Pg 8, line 2: suggest changing "part" to "section" Have changed. Pg 8, line 5: suggest changing "To do" to "For" Have changed. Pg 10, line 1: suggest deleting "relatively" Have deleted. Pg 13, line 33: suggest changing "give" to "provide" Have changed. Figure 7: caption error; missing reference to NO3 and to middle plots We have added the reference to NO3 and to middle plots in caption of Figure 7. Figures 6-9: are these annual means? Which model year? Yes, they are annual means and for the year 2005. We have added the information in the captions. Table S1: Benzene, Toluene, and Xylene missing from species list We have added these three species in the revised Table S1. Table S2: What does "#" refer to? It is referred to zero. We have added this information

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in Table S2.

Please also note the supplement to this comment:
https://www.geosci-model-dev-discuss.net/gmd-2018-196/gmd-2018-196-AC1-supplement.pdf

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

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