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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 #2 This paper reported an excellent timely effort updating aromatic VOC chemistry in GEOS-Chem, a widely used global chemistry model. The effort is very useful for the community given the importance of aromatics in regional and global chemistry and the potential limitation of the existing chemical mechanism included in GEOS-Chem. The paper describes the motivation, methodology in a very clear fashion. The key model results (e.g., NOx, HOx, ozone) are selected appropriately and discussed thoroughly, and are interpreted carefully by recognizing both the strengths and the potential limitations of the model setup and input data. A

very comprehensive model evaluation has been carried out using data from multiple global and regional networks/programs. I recommend publication after my following comments are considered. We thank the reviewer for comments, which have been incorporated to improve the manuscript. Major comments - The use of AQS ozone data in model evaluation is inappropriate and should be removed It is simply 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. The model evaluation results using AQS data is not only meaningless but also misleading, especially when these results are discussed along with other networks in remote environments, where the model evaluation is actually appropriate and meaningful. Thus, I strongly suggest the authors remove the model evaluation with AQS ozone and focus on using networks over rural and clean environments. Thanks for the comment from referee. In the revised manuscript, we have removed the model evaluation with AQS ozone measurements. - The adoption of SAPRC-11 and uncertainties in knowledge of aromatic chemistry The paper describes the SAPRC-11 mechanism itself in detail and the method to include it into GEOS-Chem clearly. However, it is yet to be more clear why it is chosen instead of other options, such as the condensed MCM mechanism. One thing about SAPRC is the use of maximum ozone formation as a primary metric in the chamber experiment benchmark, and the mechanism has been primarily used and evaluated in regional CTMs such as CMAQ and CAMx, at much finer resolution (i.e., a few kilometers). I think the present paper is the first to use it in a global model. Therefore, the authors should have some words justifying the approach. Also, are there other considerations behind the simplified GEOS-Chem aromatic chemistry, in addition to minimizing the number of reactions? Moreover, it should be noted that our knowledge about the very complex aromatic chemistry itself is not complete. For instance, how would the uncertainties in the yields of di-carbonyls and radical recycling affect the mechanism and the model simulations? The simplified chemistry in GEOS-Chem does not have radical cycling, but are there any assumptions/uncertainties in SAPRC-11 about radical cycling that

might have impact on the results too? Adding some discussions on these above questions would make the paper even stronger. Thanks for the comment from referee. We have added discussion in the revised Sect. 5.4: "SAPRC is a highly efficient and compact chemical mechanism with the use of maximum ozone formation as a primary metric in the chamber experiment benchmark. The mechanism has been primarily used and evaluated in regional CTMs such as CMAQ and CAMx, at much finer resolution (i.e., a few kilometers). Our study has significant application to use it in a global model. Implementing SAPRC-11 aromatic chemistry would add $\sim$3% more computational effort in terms of model simulation times. SAPRC is based on lumped chemistry, which is partly optimized on empirical fitting to smog chamber experiments that are representative to one-day photochemical smog episodes typical of, for example, Los Angeles and other US urban centers. However, SAPRC-11 gives better simulations of ozone formation in almost all conditions, except for higher (>100 ppb) NOx experiments where O3 formation rates are consistently over predicted (Carter and Heo, 2013). This over prediction can be corrected if the aromatics mechanism is parameterized to include a new NOx dependence on photoreactive product yields, but that parameterization is not incorporated in SAPRC-11 because it is inconsistent with available laboratory data. Other option, such as the condensed MCM mechanism, which are based upon more fundamental laboratory and theoretical data and used for policy and scientific modelling multi-day photochemical ozone formation, is experienced over Europe by Cabrera-Perez. (2016). Our results are consistent with the simulation of EMAC model implemented with a reduced version of the MCM aromatic chemistry. Moreover, aromatic chemistry is still far from being completely understood. For example, Bloss et al., (2005) show that for alkyl substituted mono-aromatics, when comparisons to chamber experiment over a range of VOC/NOx conditions, the chemistry under predicts the reactivity of the system but over predicts the amount of O3 formation (model shows more NO to NO2 conversion than on the experiments)." Minor comments P2, L19-L21: "Despite the potentially important influence of aromatic compounds on global atmospheric chemistry, their effect on tropospheric ozone forma-

tion in polluted urban areas remains largely unknown." "Unknown" is an overstatement of the issue to me. Aromatic VOCs have long been recognized as a key player in urban photochemistry, forming PAN and ozone, and SOA, despite the uncertainties with the chemistry (and emissions). We have revised this sentence as: "Despite the potentially important influence of aromatic compounds on global atmospheric chemistry, their effect on tropospheric ozone formation in polluted urban areas is less analyzed with the model simulation." P2, L21-L22: "The main source and sink processes of tropospheric ozone are photochemical production and loss, respectively (Yan et al., 2016)" Other references such as textbook by Seinfeld and Pandis (2006) would be more appropriate in this sentence. We have added two more references of Seinfeld and Pandis (2006) and Monks et al. (2015) in the revised text. P2, L33: ". . . including the parameterization of small-scale processes and their feedbacks to global-scale chemistry (Yan et al., 2014; Yan et al., 2016)." Other references should be added in addition to these two. We have added two more references of Chen et al. (2009) and Krol et al. (2005) in the revised text. P5, L27: "The OH-aromatic adduct is reaction with O2. . ." This sentence needs rephrase. We have revised this sentence as: "The OH-aromatic adduct is reaction with O2 to form an OH-aromatic-O2 adduct or HO2 and a phenolic compound (further consumed by reactions with OH and NO3 radicals)." P6, L13: Have the authors considered evaluating species other than ozone and aromatics, such as aircraft measurements of HOx (CalNex probably has some HOx measurements)? Thanks for the comment from referee. Regretfully, we have no measurements of HOx from CalNex. P7, L32: Data download link does not work (last access 9/26/18) http://aqsdr1.epa.gov/aqsweb/aqstmp/airdata/download_files.html We have removed the AQS ozone data analysis based on the first major comment above. P7, L36: see my first major comment. Thanks for the comment from referee. We have removed the model evaluation with AQS ozone measurements. P12, L30: The discussions at AQS sites should be removed. Have removed. P13, Section 5.4: See my second major comment. I suggest adding discussions of uncertainty in knowledge of aromatic chemistry and the considerations and assumptions in SAPRC-11. We

have added discussion in the revised Sect. 5.4. Please see details in the response of major comment 2. Table 2: I suggest add numbers for NH and SH We have added in the revised Table 2.

Please also note the supplement to this comment:
https://www.geosci-model-dev-discuss.net/gmd-2018-196/gmd-2018-196-AC2-supplement.pdf

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