

# ***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 #3 This paper describes the implementation of the (State-wide Air Pollution Research Center) SAPRC-11 representation of BTEX mono-aromatic chemistry into the 9-02 version of the GEOS-Chem global chemical transport model. This is timely, given the importance of aromatic chemistry in the global atmosphere, with respect to air quality (i.e. ozone and other secondary photochemical pollutants) and secondary organic aerosol formation. Model evaluations have been carried out against a significant, wide ranging observational database (both long term ground and aircraft flight path measurements) of aromatics and ozone concentrations. Model

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Discussion paper



analysis of the effects of the new chemistry on the important model outputs of O<sub>3</sub>, NO<sub>x</sub> and HO<sub>x</sub> have been carried out and discussed with respect to global and regional biases. Overall, this paper is reasonably well written (although lacking in some detail, especially with respect to the specific aromatic chemistry implemented – see discussion) and will be useful to the global CTM community. It is in good scope for GMD. I recommend publication after the following comments have been addressed. We thank the reviewer for comments, which have been incorporated to improve the manuscript. (1) More detailed description of aromatic photochemistry implemented (base case and updated aromatic chemistry). It would be useful to the reader to have a more detailed description of the aromatic chemistry represented in the Base model as well as the SAPRC update. For example, a simplified schematic showing the structure of the different mono-aromatics and how reaction with OH leads to initial OH-adducts (and OH abstraction products from OH attack at the methyl groups) that can then convert to different ring retaining and ring opening products, though the representative RO<sub>2</sub> species formed from subsequent reactions with O<sub>2</sub> and NO, leading to significant O<sub>3</sub> production. This chemistry is briefly discussed in the text, and in a way that is only understandable from an experienced GEOS-Chem user (from the base case at least) but should be given in more detail as this important chemistry is the subject of this paper. Thanks for the comment from referee. We have described the aromatics chemistry of the base case in the introduction: “A simplified aromatic oxidation mechanism has previously been employed in GEOS-Chem (e.g., Fischer et al., 2014; Hu et al., 2015), which is still used in the latest version v12.0.0. In that simplified treatment, oxidation of benzene (B), toluene (T), and xylene (X) by OH (Atkinson et al., 2000) is assumed to produce first-generation oxidation products (xRO<sub>2</sub>, x = B, T, or X). And these products further react with hydrogen peroxide (HO<sub>2</sub>) or nitric oxide (NO) to produce LxRO<sub>2</sub>y (y = H or N), passive tracers which are excluded from tropospheric chemistry. Thus in the presence of NO<sub>x</sub>, the overall reaction is aromatic + OH + NO = inert tracer. While such a simplified treatment can suffice for budget analyses of the aromatic species themselves, it does not capture ozone production from aromatic

oxidation products.” In the revised text, we have taken toluene as an example to describe the SAPRC-11 aromatics chemistry: “As discussed by Carter (2010a, b), aromatic oxidation has two possible OH reaction pathways: OH radical addition and H-atom abstraction (Atkinson, 2000). 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 addition of aromatic rings. The OH-aromatic adduct is reaction with O<sub>2</sub> to form an OH-aromatic-O<sub>2</sub> adduct or HO<sub>2</sub> and a phenolic compound (further consumed by reactions with OH and NO<sub>3</sub> radicals). The OH-aromatic-O<sub>2</sub> adduct further undergoes two competing unimolecular reactions to ultimately form OH, HO<sub>2</sub>, an  $\alpha$ -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). Formed from the phenolic products, the SAPRC-11 mechanism includes species of cresols (CRES), phenol (PHEN), xylenols and alkyl phenols (XYNL), and catechols (CATL). Due to their different SOA and ozone formation potentials (Carter et al, 2012), these phenolic species are represented separately. Relatively high yields of catechol (CATL) have been observed in the reactions of OH radicals with phenolic compounds. Furthermore, their subsequent reactions are believed to be important for SOA and ozone formation (Carter et al, 2012).” Also, when discussing the SAPRC aromatic-ozone chemistry in Section 5.4, it would be useful to provide the basic photochemical ozone formation chemistry equations (including PAN formation) so that the discussion in the text can be followed more closely. In the revised text, we have referenced the basic chemistry equations: “From Base to SAPRC, modeled PAN has been enhanced in a global scale (Fig. 8 and 9) via reactions of aromatic-OH oxidation products with NO<sub>2</sub> (equation of BR13 in Table S2). In the SAPRC-11 aromatics chemical scheme the immediate precursor of PAN (peroxyacetyl radical) has five dominant photochemical precursors. They are acetone (CH<sub>3</sub>COCH<sub>3</sub>, model species:

ACET), methacrolein (MACR), biacetyl (BACL), methyl glyoxal (MGLY) and other ketones (e.g., PROD2, AFG1). These compounds explain the increased rate of PAN formation. For example, the SAPRC simulation has increased the concentration of MGLY by a factor of 2. 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 NO<sub>x</sub> in the remote regions, due to the re-release of NO<sub>x</sub> from organic nitrates (as opposed to removal by deposition). Due to such re-release of NO<sub>x</sub> from PAN-like compounds and also transport of NO<sub>x</sub>, NO<sub>x</sub> increases by up to 5% at the surface in most remote regions and by ~1% in the troposphere as a whole. This then leads to increased ozone due to the effectiveness of ozone formation in the free troposphere.” (2) Discussion of uncertainties in the aromatic chemistry and comparisons with other, more detailed mechanisms. There is little discussion about the development of the SAPRC chemical mechanisms, the uncertainties in the specific aromatic chemistry implemented and how the chemistry compares to other widely used detailed chemical schemes. SAPRC was originally developed in order to model one day photochemical smog episodes typical of, for example, Los Angeles and other North American urban centres. SAPRC is a highly efficient and compact chemical mechanism, therefore can be implementation into CTMs, but is based on lumped chemistry, which is partly optimised on empirical fitting to smog chamber experiments that are representative to US one day conditions. Therefore, some discussion should be made with respect to applications of this optimised chemistry outside these optimisation conditions – e.g. SH tropics. How does the SAPRC chemistry compare to more detailed chemical mechanisms, which are based upon more fundamental laboratory and theoretical data, which are used for policy and scientific modelling multi-day photochemical ozone formation that is experienced over Europe – e.g. the Master Chemical Mechanism? It is also clear from the literature and atmospheric chamber model-mechanism comparisons that aromatic chemistry is still far from being completely understood. For example, Bloss et al., (2005) show that for alkyl substituted mono-aromatics, comparisons to chamber

experiment over a range of VOC/NO<sub>x</sub> conditions that the chemistry under predictions the reactivity of the system but over predicts the amount of O<sub>3</sub> produced (model shows more NO to NO<sub>2</sub> conversion than on the experiments). How does the uncertainties in the fundamental aromatic chemistry effect the modelling shown here? 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 ~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) NO<sub>x</sub> experiments where O<sub>3</sub> 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 NO<sub>x</sub> 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/NO<sub>x</sub> conditions, the chemistry under predicts the reactivity of the system but over predicts the amount of O<sub>3</sub> formation (model shows more NO to NO<sub>2</sub> conversion than on the

experiments).” (3) Specific Comments References are not in alphabetical order We have reordered the references in alphabetical order. How much more computational effort does implementing SAPRC-11 chemistry add in terms of model simulation times? In the revised Sect. 5.4, we have added the information as: “Implementing SAPRC-11 aromatic chemistry would add ~3% more computational effort in terms of model simulation times.” Introduction – better referencing of the aromatic literature needed, e.g. Atkinson and Arey (2003) and Calvert et al., (2002). We have added this two references into the revised introduction. “Despite the potentially important influence of aromatic compounds on global atmospheric chemistry, their effect on tropospheric ozone formation in polluted urban areas remains largely unknown”. This statement is simply not true. There is a large amount of literature on this subject and original policy based emission reactivity indexes such as MIR (which is based on SAPRC) and POCP (which is based on MCM) show the importance of aromatic chemistry to ozone formation in the US and Europe respectively. We have revised this sentence as: “Despite the potentially important influence of aromatic compounds on global atmospheric chemistry, their effect on global tropospheric ozone formation in polluted urban areas is less analyzed with the model simulation.” “Current global CTMs reproduce much of the observed regional and seasonal variability in tropospheric ozone concentrations.” This is a broad statement and needs to be qualified. Surely the very reason that you are carrying out this study is that this is not true?! We have added further statement of model bias on ozone: “However, some systematic biases can occur, most commonly an overestimation over the northern hemisphere (Fiore et al., 2009; Reidmiller et al., 2009; Yan et al., 2016, 2018a, b; Ni et al., 2018)” “GEOS-Chem” needs to be defined in more detail. References to v9-02 and v11-02 need to be added. We have added more information of GEOS-Chem v9-02 in revised Sect. 2: “GEOS-Chem is a global 3-D chemical transport model for a wide range of atmospheric composition problems. It is driven by meteorological data provided from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office (GMAO). A detailed description of the GEOS-Chem

model is available at [http://acmg.seas.harvard.edu/geos/geos\\_chem\\_narrative.html](http://acmg.seas.harvard.edu/geos/geos_chem_narrative.html).” We have changed the recent version of v11-02 to v12.0.0 based on the comment from referee#1. “SAPRC-11” also needs better defining We have revised the introduction of SAPRC-11 in Sect. 2.2: “This work uses a more detailed and comprehensive aromatics oxidation mechanism: the State-wide Air Pollution Research Center version 11 (SAPRC-11) aromatics chemical mechanism. SAPRC-11 is an updated version of the SAPRC-07 mechanism (Carter and Heo, 2013) to give better simulations of recent environmental chamber experiments.” 2.2. Updated aromatic chemistry – “Moreover, SAPRC-11 is able to reproduce the ozone formation from aromatic oxidation that is observed in environmental chamber experiments”. Under what conditions? (VOC/NO<sub>x</sub>) We have added this information in revised Sect. 2.2: “The new aromatics mechanism, designated SAPRC-11, is able to reproduce the ozone formation from aromatic oxidation that is observed in almost all environmental chamber experiments, except for higher (>100 ppb) NO<sub>x</sub> (Carter and Heo, 2013).” 3.2 Aromatic Surface Measurements – where is the KCMP tower? Define. We have added the location of KCMP tower: “The KCMP tall tower measurements (at 44.69°N, 93.07°W, Minnesota, US) have been widely used for studies”. 5.1 NO<sub>y</sub> Species – “Combining the changes in NO...” ??? “Combining the changes in NO...” is to discuss the NO<sub>x</sub> (NO + NO<sub>2</sub>) changes here; following paragraphs discuss the other NO<sub>y</sub> species. 5.2 OH and HO<sub>2</sub> – “Compared to the Base simulation, OH increases slightly by 1.1% at the surface in the SAPRC simulation (Fig. 8 and Table 2).” Discussion of the observed decreases? We have added description of decreases in the revised sentence: “Compared to the Base simulation, OH increases slightly by 1.1% at the surface in the SAPRC simulation, with that declines over the tropics (30°S–30°N) are compensated by enhancements over other regions (Fig. 8 and Table 2).” “In these locations, the peroxy radicals formed by aromatic oxidation react with NO<sub>2</sub> and HO<sub>2</sub>” – surely NO and HO<sub>2</sub>? Have changed NO<sub>2</sub> to NO. “This in turn influences OH, as the largest photochemical sources of OH are the photolysis of O<sub>3</sub> as well as the reaction of NO with HO<sub>2</sub>” – largest photochemical sources of OH in the model. We have revised this sentence as: “This in

turn influences OH, as the largest photochemical sources of OH in the model are the photolysis of O<sub>3</sub> as well as the reaction of NO with HO<sub>2</sub>” “Seasonally, a few surface locations see OH concentration increases of more than 10% during April–August (not shown), including parts of the eastern US, central Europe, eastern Asia and Japan.” There seem to be a few points in the text where interesting model results are eluded to but “not shown”. Could some of these not be included in the supplementary? We have added a figure in the revised supplementary to show the modeled spatial distributions of surface OH during April–August simulated in the Base case for the year 2005. Also shown is the respective relative changes (%) from Base to SAPRC. 5.3 Ozone – “The aromatics transported to the upper troposphere may cause net consumption of tropospheric OH and NO<sub>x</sub>, which can further reduce ozone production”. How? By reactions of aromatics with OH and NO<sub>x</sub>. Could other atmospherically important species that are in aromatic chemistry be compared to the observations – specifically the detailed data sets from CALNEX – e.g. HO<sub>x</sub>, HCHO, PAN, Glyoxal and Methyl Glyoxal? These are all important tracers of active photochemistry. Thanks for the comment from referee. Regretfully, we have no measurements of species other than aromatics (Benzene, Toluene and C<sub>8</sub> aromatics) from CalNex.

Please also note the supplement to this comment:

<https://www.geosci-model-dev-discuss.net/gmd-2018-196/gmd-2018-196-AC3-supplement.pdf>

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