

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 analysis of the effects of the new chemistry on the important model outputs of O₃, NO_x and HO_x 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.

(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 RO₂ species formed from subsequent reactions with O₂ and NO, leading to significant O₃ 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.

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.

(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 implemented 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_x conditions that the chemistry under predictions the reactivity of the system but over predicts the amount of O₃ produced (model shows more NO to NO₂ conversion than on the experiments). How does the uncertainties in the fundamental aromatic chemistry effect the modelling shown here?

(3) Specific Comments

References are not in alphabetical order

How much more computational effort does implementing SAPRC-11 chemistry add 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).

“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.

“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?!

“GEOS-Chem” needs to be defined in more detail. References to v9-02 and v11-02 need to be added.

“SAPRC-11” also needs better defining

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_x)

3.2 Aromatic Surface Measurements – where is the KCMP tower? Define.

5.1 NO_y Species – *“Combining the changes in NO...”* ???

5.2 OH and HO₂ – “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?

“In these locations, the peroxy radicals formed by aromatic oxidation react with NO₂ and HO₂” – surely NO and HO₂?

“This in turn influences OH, as the largest photochemical sources of OH are the photolysis of O₃ as well as the reaction of NO with HO₂” – largest photochemical sources of OH in the model.

“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?

5.3 Ozone – “The aromatics transported to the upper troposphere may cause net consumption of tropospheric OH and NO_x, which can further reduce ozone production”. How?

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_x, HCHO, PAN, Glyoxal and Methyl Glyoxal? These are all important tracers of active photochemistry.

References

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605–4638, <https://doi.org/10.1021/cr0206420>, 2003.

Bloss, C., Wagner, V., Bonzanini, A., Jenkin, M. E., Wirtz, K., Martin-Reviejo, M., and Pilling, M. J. Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data, Atmos. Chem. Phys., 5, 623-639, 2005.

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G.: The mechanisms of atmospheric oxidation of aromatic hydrocarbons, Oxford University Press, New York, 2002.