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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Influence of aromatics on tropospheric gas-phase composition" *by* Domenico Taraborrelli et al.

Anonymous Referee #1

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Description:

This manuscript describes the changes in trace gas concentrations that occur when emissions of monocyclic aromatic compounds are included in a global general circulation / atmospheric chemistry model. Many recent studies have pointed out the strong influence of aromatic compounds on local and regional air quality, especially in East Asia, which makes this manuscript a timely assessment of their treatment in models and their global impacts. Here, the authors incorporate the MECCA mechanism into EMAC and diagnose the implications of aromatic chemistry by comparing a simulation with aromatic emissions turned on to one with aromatic emissions turned off. Unsurprisingly, they find that aromatic compounds contribute substantially to the global budgets of glyoxal and methylglyoxal – two of their main oxidation products and important

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SOA precursors – while their contributions to the budgets of smaller and more ubiquitous carbon-containing compounds, such as HCHO and CO, are smaller relative to the background. For budgets of HOx, NOx, and ozone, the effects are more complex; while aromatic emissions have small global effects (which, intriguingly, sometimes contradict those found by previous studies), their local effects can be moderately substantial and can vary in sign depending on local chemistry.

General comments:

The manuscript is straightforwardly written, well laid-out, and presents its findings clearly. Furthermore, because the authors use a highly comprehensive mechanism based on MCM, the chemical outcomes of aromatic oxidation are likely more robust than previous studies. However, it appears from looking more closely at the mechanism that some of the larger aromatic species (e.g. xylene and ethylbenzene) are not actually treated explicitly, but are oxidized in pathways identical to those of toluene with a "LCARBON" counter species denoting the carbon imbalance that arises from this treatment. This should be more explicitly described in the manuscript, which appears to imply that all aromatic species are treated independently by providing their individual emissions.

Another general concern is that in many places model outcomes are simply described without sufficient discussion of their causal pathways, which strongly diminishes the usefulness of these findings. Further, many of the important effects of these model outcomes are only touched on without any quantitative discussion – e.g., the changes to methane lifetime and SOA formation from glyoxal and methylglyoxal. Specific instances are pointed out in the comments below.

Finally, while the short discussion of uncertainties in Section 4 is a particularly useful addition to this manuscript, it does not go far enough to provide the reader with either quantitative or qualitative bounds on the model outcomes described herein. Of particular note, more attention should be paid to: (a) the effects of grid resolution –

given that there's a lot of spatial heterogeneity in model outcomes, and the effects even change sign depending on local conditions, is 1.875ËŽÂăsquare enough to resolve this chemistry? What outcomes might be masked by the artificial mixing that occurs in such large-scale grid boxes? (b) uncertainties in chemical mechanisms, especially the newly implemented ones described in the bullet point list in Section 2 – while there is some discussion in Section 4 of the uncertainty in the phenoxy + O3 reaction, it should be put into a larger context and more explicitly tied to the uncertainty bounds of model outcomes that might be expected given the uncertainties in the chemical mechanism; and lastly (c) uncertainties in emissions – while these are also discussed briefly in Section 4, the scope of the discussion is very limited and does not leave readers with any quantitative understanding of how well the emission totals are known, what their overall interannual variability might be, and how this could affect the model outcomes described in Section 3. I am not trying to argue that the authors need to perform additional sensitivity simulations, but the uncertainties merit a more lengthy, detailed, and quantitative description than is provided here. Additional (more specific) questions about uncertainty are given below.

Specific comments:

L 19 - Does the 200-300 Tg/yr refer to Tg O3?

L 69-72 - Because the primary findings of this paper rely so heavily on the magnitude of these emissions, some small discussion of their uncertainty is warranted. Do the sources from which the inventories were derived describe the range of plausible emission amounts? Do different anthropogenic or biomass burning inventories give different emission amounts? EDIT - I see this is partially addressed in Section 4 (though it would be useful here to direct the reader to the later discussion of uncertainties). However, the short paragraph about emissions uncertainties still lacks quantitative detail, and most of the questions above still remain unanswered. Also, can a numerical range of inter-annual variability of total pyrogenic aromatic emissions be provided?

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L 75 - It would be helpful here to give detail not only on the additions that have been to the mechanism, but also on generally what simplifications were made to MCM to arrive at MECCA. I realize that's available in Cabrera-Perez et al. 2016, but the reader should be able to get a sense of the methodology here without having to fully read another paper. In particular, it is problematic that this manuscript implies a full detailed mechanism for the suite of aromatics shown in Table 1 when in fact many of them just use the same oxidation schemes.

L 122-124 - This is not a complete explanation of the OH increase in high-NOx regions. It is stated that the increased OH is "caused by the reaction of NO with HO2", but it was also stated two lines previously that NO decreases in these regions. Does HO2 increase enough as to offset both the NO decrease and the OH decrease through direct reaction with aromatics? What causes such a pronounced HO2 increase? Further, Figures 4 and 5 are not particularly useful to the reader without an explanation of why these effects occur. What causes the seasonal variability in the effects of aromatics on OH? Why are they strongest in the upper troposphere?

L 123 - Is this "positive correlation" a quantitative effect, diagnosed by some sort of regression analysis (across time? or just regions?), and if so, can it be explained in more detail here? If this "positive correlation" is just meant to say that including anthropogenic emissions causes an increase in OH, then this phrasing is misleading – better just to state simply that OH is higher in AROM than NOAROM in these regions. Also, are these correlations really diagnosed from anthropogenic emissions in particular, or from the inclusion of all aromatic emissions (including biogenic and pyrogenic)?

L 132 - The increased methane lifetime is likely to be of great interest to readers. Can it be quantified?

L 138-140 - The same comment above (L 123) applies here to the "correlation" phrasing.

L 141 - It appears Figure 9 is discussed here in the text before Figures 7 (L 143) and 8

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(L 157)

L 141-145 - The same comment above (L 122-124) applies here; why do these seasonal and zonal patterns arise?

L 153 - Can some more quantitative description of the variation with tropopause definition (and a description of the definition itself) be included here? What specifically is meant by "robust"? Figure 7 makes it look instead like there are large absolute differences right at the tropopause, which would imply that the definition might be highly important.

L 154 - What is meant by "these changes", and why does the explanation provided here differ from those above (L 134-136)?

L 159 - Extra close-parentheses.

L 143-164 - This paragraph is long and covers a wide range of different topics; consider splitting it up? Also, the sentences around L 156-160 seem to be in an odd order; the sentence beginning "However, with aromatics" seems like it should be followed by the sentence beginning "Ozone is known to react", while the two intervening sentences seem like a non sequitur.

L 161-164 - How well is this chemistry known? The cited study describes the reactions of the phenoxy radical with O3 and with other phenoxy radicals, but presumably this is also in competition with many other reactions, including possible unimolecular rearrangements or decomposition. Have competitive studies been reported? If not, can some estimate of competing reactions rates be used along with the uncertainty bounds of the phenoxy + ozone reaction rate to determine some level of certainty for this discussion here? Considering how strong the simulated effect is, and how its catalytic nature under some conditions could magnify even small errors, some discussion of uncertainty is warranted. EDIT - I see this is partially addressed below in section 4 (it'd be nice to have some parenthetical here directing the reader to the later discussion on

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uncertainties). Some questions remain, though – most notably why the rate constant "has to be regarded as a lower limit" (L 227) and whether competing reactions might also be uncertain.

L 164 - No period (assuming this is the end of the sentence).

L 173-174 - How does nitrophenol photolysis come into play here for the phenoxy radicals? R1 implies either that nitrophenol photolysis does not form phenoxy radicals or that the mechanism skips the phenoxy radical step and goes directly to decomposition products.

L 186-187 - This phrasing does not make it particularly clear which simulation has the higher NO3 concentrations.

L 188 - Why does this effect occur in places with pyrogenic aromatic emissions, while the HOx and O3 effects described previously are more strongly associated with anthropogenic emissions? The same question applies to the HONO increase on L 191.

L 198-200 - What is the explanation for these findings?

L 208-209 - Was the effect on the SOA budget quantified here? It seems this effect would be of great interest to some readers.

L 218 - It seems odd that so much detail is shown in the many other figures for other species discussed in this manuscript, but this interesting finding for CO is not shown. Can a CO figure be added, and can an explanation be given for these spatial effects?

L 230-231 - It was earlier implied (L 173-174) that the model *does* account for the effects of photolysis of nitrophenols. Can this be clarified?

Table 5 is cut off by the end of the page.

Can the OH mixing ratios in Figures 3-5 be expressed instead in the more commonly used concentration units?

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Figure 4 is very confusing. What are the units on the left plot? Why are there two very close blue and red lines in the left plot? Why does the caption reference solid and dashed lines in the right plot when only solid lines exist? The same questions apply to Figure 9.

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