Geoscientific
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Interactive comment on "**Photochemical grid model implementation of VOC, NO$_x$, and O$_3$ source apportionment**" *by* **R. H. F. Kwok et al.**

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Anonymous Referee #1

Summary: The authors have implemented and applied ozone "source apportionment" in the Community Multi-scale Air Quality model (CMAQ). Implementation is a significant effort that provides important capabilities to CMAQ that are relevant to scientific exploration and regulatory application. Application and evaluation showed results that would be expected from implementation in similar models.

The paper would be improved by addressing three things. 1) The weaknesses inherent sensitivity metric application, particularly with respect to biogenic VOCs. 2) Discussion different ozone endpoint for results. 3) Minor comments.

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We appreciate the suggestions from the reviewer on how to improve the presentation of our work. Below, we outline how we addressed each of the three areas suggested.

1 Sensitivity Metrics:

The source apportionment technique relies on the PH2O2/PHNO3 indicator that has been extensively used for Carbon Bond IV. The PH2O2/PHNO3 ratio, often referred to as the Sillman ratio, is a simplification of a more complex relationship (Sillman, 1995, A5 (PH2O2+PROOH)/PHNO3). The Carbon Bond IV mechanism lacks an organic peroxide (ROOH), which requires the simplification of based on the ratio of PROOH/PH2O2 in a 1995 Lack Michigan simulation. Though Dennis and Tonnesen showed its robustness, I am not aware of a published comparison to the robustness of (PH2O2+PROOH)/PHNO3. The poor performance of biogenic zero out could be related to ROOH production. The speciation of VOCs are important in determining the PH2O2/PROOH ratio in the presence/absence of NOx. The PH2O2/PROOH dependence could suggest that biogenic VOC sensitivity would be mischaracterized by PH2O2/PHNO3. Though the explanation of non-linearity is suggestive, it is not definitive. In fact, the first order sensitivity shows better performance for BIOG for both the slope and correlation. At least some discussion of the metric is warranted, as well as more discussion of the fundamental issues with applying a binary metric.

It is correct that the apportionment technique relies on the PH2O2/PHNO3 indicator ratio in the current implementation. However, we had spent a substantial amount of time prior to settling on this ratio testing and comparing nine other ozone regime indicators including (PH2O2+PROOH)/PHNO3. At one point, the code even offered users a choice for selecting the indicator they wanted or an ensemble estimated from all of them. However, we moved away from this option as it offered little change in the performance of the attribution estimates and offered little additional information in the results. Specifically, the underestimation of biogenic VOC attribution was evident in the simulations using each ratio and was identical in the results using the Sillman ratio with and without the ROOH production term.

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To clarify this point in the manuscript, we have added the following text to section 3.1:

Ozone production is attributed to either VOC or NOx emissions sources based on the ozone chemical formation regime that is estimated using the PH2O2/PHNO3 indicator ratio, similar to the implementation in CAMx. Other indicator ratios were also explored including H2O2/(O3+NO2), O3/NOZ, HCHO/NOY, and (PH2O2+PROOH)/PHNO3, but these offered no additional gain in model performance.

The concern that biogenic VOC attribution is underestimated is certainly troublesome and we are currently investigating the issue in more detail. The nonlinearity in the interaction is the most likely cause, because performance of 2nd order DDM estimate is substantially better than 1st order DDM estimate. The fact 1st order DDM performance is better than ISAM for this metric is due to different model formulation and does not really offer any explanation for poor ISAM biogenic attribution.

2 Ozone Endpoint:

The authors show only daytime-average for most results and all-hour averages for ISAM/DDM. I suspect that the choice to average was based on the autocorrelation of hourly results, but this is not discussed. Averaging, however, removes variability. An alternative metric that would be more relevant, would be maximum daily 1-hour average or maximum daily 8-hour average. The 8-hour average would still have some reduction in variability, but would be more relevant to the regulatory application that is likely to use this tool. Thus, the brute-force evaluation of 1- or 8-hour average would be more interesting. In addition, why do some results use all-hour and others daytime only?

The choice for showing the results for daytime hours for ozone was made keeping in mind the typical use of the tool. Inline apportionment tools, like ISAM, by design, do not account for sensitivity to ozone titration, which often occurs outside of daylight hours. This is actually evident if figure 5 (zero-out comparison with DDM and ISAM), where ISAM is never less than zero, while DDM shows negative sensitivities that match with

zero-out. Choosing all hours or daytime hours for other species depended on the goal of specific figures and metrics – either diagnostic or demonstrative.

The results are generally not further averaged. All the statistics and figures show all of the hours provided in the model output (aside from excluding nighttime hours for some species), so no further variability is lost. We had considered evaluating 1-hr max and 8-hr max ozone quantities, but decided against it due to the loss in variability that the reviewer notes.

To clarify these decision in the manuscript, the following text was added at first mention of excluding nighttime hours in section 4.1:

The CMAQ model performed well this day with an O3 bias of 4.7ppb and average error of 9ppb across the domain during daytime hours. Nighttime hours were excluded from ozone analysis, because ISAM was not designed to predict titration events that often occur at night in areas of large NOx emissions.

3 Minor comments:

Page 5802, line 23-24 - add some more detail than just a hanging line.

We have added the following text to further describe the deposition processes:

ISAM apportions CMAQ-calculated wet and dry deposition O3, NOx, and all VOC species into individual sources as done in the previous PM2.5 ISAM code. Both of these processes follow simple linear algorithms where the mass removed is a function of existing mass and a removal coefficient and thus did not require additional consideration for the ozone implementation.

Page 5803, line 5 - is J = J*something?

We appreciate the reviewer noticing the awkward phrasing and have changed the text to state:

. . . J the Jacobian matrix calculated based on the average of bulk concentrations before

and after any gas-phase solver for CB05 model species . . .

Page 5803, line 11 - The effect on accuracy will likely depend on the time of day, as sensitivity typically shifts with time. During the PH2O2/PHNO3 transition, this could be important if the synchronization time step is not controlled. Some discussion is warranted.

This implementation is similar to what is currently used in implementation of DDM in both CMAQ and CAMx. It was demonstrated that there is minimal loss of accuracy from solving during the middle of model synchronization time step during all hours including regime transitions. This was noted in more detail in the text and reference was provide for further information to the reader:

The solution is obtained only once for every model synchronization time step Δt instead of incremental chemical time steps to increase computational efficiency at little expense to accuracy as was previously shown in the original implementation of the CMAQ decoupled direct method (DDM) (Hakami, 2004) .

Page 5803, 5804 - consider harmonizing subscripts in equation 7 with 8 and 9.

The species subscript for VOCs was changed in equation 7 to s in order to match equations 8 and 9.

Page 5812, line 2-5 - reword.

The awkward phrasing was changed to the following:

In general, correlations between ISAM/zero-out estimates are high for both ambient concentration and deposition of O3 for the major emissions sectors. ISAM estimates of NOx are higher than nitrogen-out in most sectors except boundary condition. And ISAM VOC estimates are similar when compared to VOC-out in most sectors except EGU and MARINE.

Page 5812, line 11 - consider splitting this paragraph to help distinguish between what

I believe are very distinct points.

A paragraph break was added to better distinguish the discussion between the two points.

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