Source Attribution of Ozone and Precursors in the Northeast U.S. Using Multiple Photochemical Model Based Approaches (CMAQ v5.3.2 and beyond)

Qian Shu[1], Sergey L. Napelenok[1], William T. Hutzell[1], Kirk R. Baker[1], Benjamin Murphy[1], Christian Hogrefe[1], Barron H. Henderson[1]

[1]U.S. Environmental Protection Agency, Research Triangle Park, NC, 27711, USA.

Correspondence to: Sergey L Napelenok (sergey.napelenok@epa.gov)

Response to reviewer 2

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The ISAM is a powerful tool for source apportionment of O3 and PM2.5 in CMAQ. The authors have updated ISAM with more attribution options and compared the results with different options to those using OSAT or the brute force method. Generally, the manuscript is well written, and the work is worthy of publication. There are a few questions that need to be addressed:

It is not quite clear in what cases or on what purpose is each of the option the best one? For example, is ISAM-OP2 more suitable for RNOx attribution? The authors could elaborate more.

We have added more sentences and discussions in conclusion section to elaborate it as below.

Lines 531-538 "*After assigning products to sources emitting nitrogen reactants, the OP2 option can predict results of RNOx attributions that are more comparable to OSAT and BF. It demonstrated that the OP2 works better for RNOx because it makes it easier to find the original source and lessens the effect of other sources when these species are cycling quickly through an integrated chemical reaction system. Unlike O3 and RNOx, the VOC contribution for the majority of source categories depends very little on the ISAM option. We expect that the user will use OP5 for O3 and OP2 for RNOx, but this is not a firm suggestion. In turn, we give the user this flexibility so that ISAM can be used for a wide range of purposes*."

The CB6R3 and CB6R4 were used in CMAQ and CAMx, respectively. What are the impacts of using different chemical mechanisms?

Evaluating the accuracy of source apportionment model results is challenging because the source contribution of secondary pollutants such as ozone cannot be assessed independently based on observations. In this case, we use CAMx-OSAT and brute-force methods as alternative references. The primary objective of this paper is to document recent ISAM updates and demonstrate their impacts on source apportionment results for O3 and its precursors for added ISAM options. OSAT and ISAM are two different source apportionment methods, embedded in the two different parent models, CMAQ and CAMx. We are not making a strictly consistent

comparison because that is impossible, considering there are many differences in model formulations and data requirements. However, we have tried to make most configuration options as similar as possible. Chemical mechanism is one of the things that we can't resolve perfectly, as it is not feasible to use the same version of chemical mechanism between CMAQ v5.3.2 and CAMx v7.10. The most updated carbon bond mechanism in CMAQ v5.3.2 is CB6R3 (https://github.com/USEPA/CMAQ/blob/5.3.2/CCTM/src/MECHS/README.md) while CAMx v7.10 has CB6r2h and CB6r4/r5 as Table 5-1 in the CAMx user guide(https://camx.com/Files/CAMxUsersGuide_v7.10.pdf). CMAQ has an alternative chemical mechanism called "CB6R3m" that adds detailed halogen chemistry and DMS. Sarwar et al. (2015, 2019) demonstrated that updating CB6R3m is more beneficial in the hemispheric CMAQ model, where the influence on intercontinental transport over oceans is larger than over land. Model sensitivity runs were also completed with CB6R3 (without detailed halogen and DMS chemistry) and CB6R3m (with detailed halogen and DMS chemistry) over the Northern Hemisphere for three months in 2015 (October–December) by Sarwar. It reduces ozone by 3–14 ppb (Figure 1) over much of the ocean. It reduces ozone over land by much smaller margins than over sea water (https://github.com/USEPA/CMAQ/blob/5.3.2/DOCS/Release_Notes/detailed_halogen_and_DMS_chemistry.md).

For this study, as our focus was more on the regional domain over the Northeast U.S., CB6R3 was chosen for CMAQ-ISAM. It is noteworthy that the major updates for CB6R4 from CB6R3 are to (1) replace full marine halogen chemistry with a condensed iodine mechanism called "I-16," which could reduce ozone depletion over marine areas, and (2) add dimethyl sulfide (DMS) chemistry. Emery et al. (2016) demonstrated that the difference in ozone decrements between full halogen chemistry and I-16 is small and can be neglected over land. In this case, CB6R4 was chosen rather than CB6R2h and CB6R5. With these two chemical mechanism configurations, our study shows similar results to Sarwar et al. (2015, 2019) and Emery et al. (2016) when CMAQ predicted total MDA8 O3 compared to that of CAMx (Figure 6 in the paper). We have discussed these in Lines 390–396. Although we cannot eliminate the influence of different chemical mechanisms, just like other potential uncertainties, we tried to diminish the inevitable difference in this study. It is still valuable to show these intercomparisons between ISAM and OSAT at some levels. Future studies could be done when two models implement an identical chemical mechanism.

We have also added some lines to clarify it. Lines 232-236 "*It is noteworthy that the major updates for CB6R4 from CB6R3 are to (1) replace full marine halogen chemistry with a condensed iodine mechanism called "I-16," which could reduce O_3 depletion over marine areas, and (2) add dimethyl sulfide (DMS) chemistry. Emery et al. (2016) demonstrated that the difference in O_3 decrements between full halogen chemistry and I-16 is small and can be neglected over land.*"

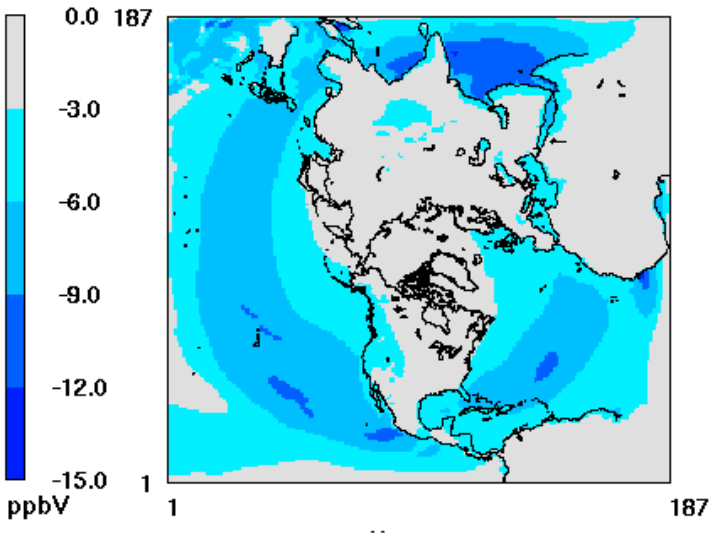

Figure 1: Impact of halogen chemistry on ozone (three-month average).

Table 5-1. Gas-phase chemical mechanisms currently implemented in CAMx v7.1.

Mechanism ID	Description
CB05	Carbon Bond 2005 (Yarwood et al., 2005b). 156 reactions among 51 species (38 state gases, 13 radicals).
CB6r2h	Carbon Bond v6, "Revision 2" (Yarwood et al., 2010; Yarwood et al., 2012a; Hildebrandt Ruiz and Yarwood, 2013), with updates to include reactions involving oceanic halogen compounds (Yarwood et al., 2014). 304 reactions among 115 species (88 state gases, 27 radicals).
CB6r4	Carbon Bond v6, "Revision 4" adds temperature- and pressure-dependent NO_2-organic nitrate branching from CB6r3 (Emery et al., 2015), a condensed set of reactions involving ocean-borne inorganic iodine (Emery et al., 2016a), and DMS oxidation reactions (Emery et al., 2019). 233 reactions among 87 species (62 state gases, 25 radicals).
CB6r5	Carbon Bond v6, "Revision 5" incorporates recent updates to chemical reaction data from IUPAC (Atkinson et al., 2004; IUPAC, 2019) and NASA (Burkholder et al., 2015) for inorganic and simple organic species that play a role in ozone formation. Same number of reactions and species as CB6r4.
SAPRC07TC	The Statewide Air Pollution Research Center 2007 mechanism that includes updates to support toxics and numerical expressions of rate constants to support the current chemistry mechanism compiler (SAPRC07TC; Carter, 2010; Hutzell et al., 2012). 565 reactions among 117 species (72 state gases, 45 radicals).
MECH10	A user-defined simple chemistry mechanism can be developed for any gas and/or particulate species, which is defined by a "Mechanism 10" parameters file and solved within a user-supplied subroutine called "chem10.f."

Some mistakes in the manuscript. For example, lines 76-77: "when the ratio (PH2O2/PHNO3) is below 0.35, the formation is classified as NOx-limited…"; lines 199-

200: “when the ratio of PH2O2/PHNO3 exceeds 0.35, the produced O3 is attributed to VOC emissions…”

We have corrected all similar errors.

References

1. Ramboll Environ. CAMx user guide v7.10. https://camx.com/Files/CAMxUsersGuide_v7.10.pdf
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4. Emery, C., Liu, Z., Koo, B., Yarwood, G. 2016. Improved Halogen Chemistry for CAMx Modeling. Final report for Texas Commission on Environmental Quality WO 582-16-61842-13, May 2016, available at https://www.tceq.texas.gov/airquality/airmod/project/pj_report_pm.html (last accessed 13 December 2019).