"A framework for expanding aqueous chemistry in the Community Multiscale Air Quality (CMAQ) model version 5.1" by Kathleen M. Fahey et al.

Response to reviewer #2

The authors thank reviewer #2 for their comments and suggested revisions. In the following, we restate the reviewer comments and follow with our response in "bold" font. Note that any references to page/line number are made for both the "updated" manuscript (with markup) and the original discussion paper.

Fahey et al. developed a new cloud chemistry mechanism (AQCHEM-KMT) for use in large-scale models and implemented it into CMAQ. AQCHEM-KMT allows for the investigation of aqueous-phase chemical reactions that could not be implemented into the aqueous-phase chemistry mechanism that is currently implemented in CMAQ (AQCHEM) because of its explicit consideration of processes such as mass transfer limitations. As most large-scale models use an aqueous-phase chemical mechanism similar to AQCHEM, this development represents a significant step forward in examining the influence of aqueous-phase chemical reactions on the chemical composition of the atmosphere in large-scale models. The paper is well written, and I recommend publication in GMD after some very minor issues are addressed.

The authors find much larger differences between AQCHEM-KMT and AQCHEM for sulfate than for SOA, but the reasons for this difference could be more explicitly discussed than they currently are. What other aqueous-phase reactions or types of reactions can now be implemented in AQCHEM-KMT that was not possible with AQCHEM?

AQCHEM-KMT would be well-suited to represent additional S(IV) oxidation chemistry as well as other species' chemistry (like oxidant or nitrogen chemistry) not currently represented in CMAQ cloud chemistry at all. A future application for AQCHEM-KMT will likely be to replace the "parameterized" in-cloud SOA production from glyoxal and methylglyoxal with an explicit/mechanistic representation of that chemistry. While in-cloud production of organic acids that remain in the aerosol phase after cloud droplet evaporation has been widely studied in laboratory and modeling experiments (e.g., Lim et al., 2010), implementation of an explicit representation of such a chemical mechanism is something that could not easily be done with AQCHEM and its forward Euler solver, in part due to the increased stiffness of the system (and thus the implementation of the simple parameterization of in-cloud SOA chemistry in AQCHEM in CMAQv4.7).

This parameterization typically predicts only low surface level concentrations of in-cloud SOA on average and may be more "episodic" in nature than SO_4^{2-}. While SO_4^{2-} production in-cloud is a major production pathway for atmospheric SO_4^{2-} (potentially dominating over gas phase production) and contributes significantly to predicted average surface SO_4^{2-} concentrations, in-cloud SOA will likely only be a small fraction of total SOA production on average, in part because of the "transient" nature of clouds as well as the fact that the only chemical pathways represented in the model for in-cloud SOA production are photochemically driven (and thus may only be important during only a fraction of the day or only certain seasons (e.g., summer)). As mentioned in section 3.1, in the parameterization for in-cloud SOA formation, aqueous phase OH concentrations are held constant during cloud processing, so there is a reduced sensitivity to mass transfer limitations for those reactions, because they do not consider mass transfer limitations for OH.

We have added some additional text to section 3.1 (new text is underlined)

Pate 12, line 19: "Absolute ORGC mass predictions are less impacted than SO_4^{2-}, but these tend to be low on average in the base case and may have limited sensitivity to changes in mass transfer treatment due in part to CMAQ's implementation of cloud SOA formation…"

Page 12, lines 22-29 (p 11, line 18 in original document): "The hydroxyl radical concentration is estimated at the start of cloud processing based on the initial gas phase concentration (Henry's law) and held constant for the duration of the "master" cloud time step (i.e., mass transfer limitations are not considered for OH). This was done in part to compensate for the lack of a more complete treatment of radical/organic chemistry in the aqueous phase, along with a relatively loose coupling between gas and aqueous chemistry in CMAQ. A constant oxidant concentration may cause an artificially high rate of consumption of the precursor species

and insensitivity of the reaction to droplet size and associated mass transfer limitations. In fact, it has been suggested that in-cloud oxidation of organic species by OH may be oxidant limited due in part to the effects of mass transfer limitations on aqueous OH concentrations (Ervens et al., 2014)...”

Are there other sulfate production mechanisms that are better suited for AQCHEM-KMT than AQCHEM that are not currently included in the model, or do the authors expect sulfate to almost always be similar for AQCHEM-KMT and AQCHEM on monthly time scales?

There are additional aqueous phase production pathways for SO_4^{2-} that are not included in AQCHEM that may be an important contributor to SO_4^{2-} concentrations in certain environments, such as the oxidation of SO_2 by HNO_4 (Leriche et al., 2003) or NO_2 or aqueous oxidation of SO_2 by OH (Seinfeld and Pandis, 2006). These may have an impact on the monthly average SO_4^{2-} values but would need to be implemented and investigated further to determine whether they either lead to a regional average increase or if they lead to more episodic changes and have limited impacts on average SO_4^{2-} predictions.

In the introduction, it would be good to specify that when you refer to the aqueous phase you are referring specifically to cloud droplets and not liquid water associated with aerosols

Page 2, line 8-9: Changed “aqueous phase production of SO_4^{2-} dominates” to “aqueous phase production of SO_4^{2-} in cloud and fog droplets dominates”

Page 2, lines 10 and 11: Changed “aqueous” to “in-cloud”

Page 2, Lines 13-14: Changed “potentially significant role that aqueous pathways may have on the formation” to “potentially significant role that aqueous pathways (in cloud droplets and wet aerosols) may have on the formation”

Page 3, line 31 (p 3, line 28 in original document): Changed “mass transfer between the gas and aqueous phases” to “mass transfer between the gas phase and cloud droplets”

Page 3, line 34 (p 3, lines 30-31 in original document): Changed “these additional aqueous-phase chemistry options” to “these additional in-cloud aqueous-phase chemistry options”

Page 4, line 3 (p 3, line 33 in original document): Changed “updated aqueous chemistry options” to “updated cloud chemistry options”

Page 4, line 9 (p 4, line 6 in original document): Specified that we are applying KPP to the “in-cloud” aqueous phase chemical mechanism
.
Page 3 line 13: Refer to Table S3 so one can readily find the seven oxidation reactions, or list them here.

We have added the following sentence after referring to the seven oxidation reactions on page 3: “The seven reactions represented are the oxidation of aqueous SO_2 by hydrogen peroxide, ozone, oxygen (catalyzed by iron and manganese), methylhydroxyperoxide, and peroxyacetic acid as well as two reactions that parameterize SOA formation from glyoxal and methylglyoxal.”

Many abbreviations/acronyms in the text and tables are not defined (e.g., MPAN). Perhaps add a table of abbreviations/acronyms in the SI.

We have attempted to find all the abbreviations/acronyms in the text and define them (at least) at their first mention. These include the following updates:

On page 1, line 30: Changed “during the SOAS field campaign period” to “during the Southern Oxidant and Aerosol Study (SOAS) period”

On page 2, line 18 (p 2, line 17 in original document): Changed "more than half of the total PM$_{2.5}$ concentration" to "more than half of the total fine particulate matter (PM$_{2.5}$) concentration"

On page 3, line 14: Changed S(VI) to "sulfate"

On page 3, line 18 (p 3, line 16 in original document): Changed "stiff systems of ODEs" to "stiff systems of ordinary differential equations (ODEs)"

On page 4 line 21 (p 4, line 18 in original document): Changed S(VI) to SO$_4^{2-}$

On page 6, line 8 (p 6, line 4 in original document): Changed "i.e., IEPOX/MAE" to "i.e., isoprene epoxydiol/methacrylic acid epoxide chemistry"

On page 6, line 22 (p 6, line 18 in original document): Changed "as a successor to LSODE" to "as a successor to the Livermore Solver for Ordinary Differential Equations (LSODE)"

On page 11, line 1 (p 10, line 4 in original document): Changed "formation from IEPOX and MPAN products" to "formation from IEPOX and methacryloylperoxynitrate (MPAN) products"

On page 11, line 11 (p 10, line 12 in original document): changed "2013-specific EGU continuous…" to "2013-specific electric generating unit (EGU) continuous…"

On page 11, line 12 (p 10, line 13 in original document): changed "with BELD4 land cover" to "with Biogenic Emissions Land Use Database (BELD4) land cover"

On page 14, lines 7-8 (p 13, line 1 in original document): changed "ΔSOA$_{IEPOX/MPAN}$, ΔSOA$_{2-MG}$" to "change in total SOA from the IEPOX/MPAN pathways (ΔSOA$_{IEPOX/MPAN}$), change in 2-MG (ΔSOA$_{2-MG}$)"

References:

Leriche, M., Deguillaume, L., and N. Chaumerliac (2003) Modeling study of strong acids formation and partitioning in a polluted cloud during wintertime. J. Geophys. Res., 108(D14), doi:10.1029/2002JD002950

Lim, Y.B., Tan, Y., Perri, M.J., Seitzinger, S.P., and B.J. Turpin (2010) Aqueous chemistry and its role in secondary organic aerosol (SOA) formation. Atmos. Chem. Phys., 10, 10521-10539.

Seinfeld, J. and S. N. Pandis (2006) Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd ed. John Wiley and Sons, Inc.