

Response to reviewer #1

The authors thank reviewer #1 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.

Kahey et al. replace the hard-coded aqueous chemistry mechanism in CMAQ with a flexible chemical mechanism using the KPP solver. This allows a more general approach, with aspects such as mass transfer and H⁺ concentration now allowed to evolve dynamically. The authors demonstrate this method by first replicating the existing AQCHEM mechanism (AQCHEM-KMT), and then extending it with a more complete representation of organic chemistry (AQCHEM-KMTI). This demonstration shows little impact on the model representation of sulfur chemistry, but secondary organic aerosol is significantly affected. Their approach sidesteps some issues of the previous sulfur-focused implementation, such as the application of inappropriately long timesteps to the calculation of rapidly-evolving SOA concentrations, and delivers a useful tool for other groups to explore other aspects of aqueous phase chemistry.

This paper represents an incremental development in the representation of aqueous phase chemistry in a regional-scale model. However, such a development, especially in a model as widely used as CMAQ, is both overdue and welcome. The reapplication of KPP to solve aqueous phase chemistry seems natural and well implemented, and I am pleased to recommend this paper for publication in GMD, pending some minor revisions. I have outlined two general criticisms below, followed by a list of minor recommendations.

My first and most significant issue relates to the question of computational efficiency. The final paragraph of the conclusions is informative, evenly discussing the computational trade-offs associated with the new, more complete aqueous chemistry mechanism. However, it references timing data which has not been given previously. Section 2.1 or 2.2 would benefit significantly from a dedicated discussion of the execution time of AQCHEM in each of the scenarios in comparison to AQCHEM-KMT.

We have added the following text to section 2.2, p 9, line 13 (p 8, line 28 in original document):

It should be noted that by introducing the new solver and relaxing equilibrium assumptions that the computational requirements of AQCHEM-KMT significantly exceed those of AQCHEM, even before adding new chemical species or reactions. On average AQCHEM can simulate the scenarios of Table S5 with a runtime on the order of ~1 second, while AQCHEM-KMT requires ~65 seconds to model the scenario set. While cloud chemistry only accounts for a fraction of the computational time required by a three-dimensional chemical transport model like CMAQ, implementation of AQCHEM-KMT in a chemical transport model (CTM) will lead to an overall increase in CTM run time that will vary depending, in part, on the cloudiness of a modeled period. These requirements will likely increase as the chemical mechanism expands, and future efforts should be dedicated to investigating how to make the model more efficient, including revisiting equilibrium assumptions for certain processes or species.

It would also be useful to know the degree to which some of the assumptions previously used by AQCHEM were found to be inaccurate. For example, with AQCHEM-KMT, the authors can diagnose the (in)accuracy of the electroneutrality assumption previously forced on the aerosol.

We have added the following text to section 2.2, p 8, line 29 (p 8, line 23 in original document):

Additional box modeling investigations with a slightly expanded mechanism indicate that when one ignores aqueous diffusion limitations (for the default droplet diameter of 16 μm), assumes instantaneous equilibrium for ionic dissociation, and calculates pH assuming electroneutrality (but maintains the kinetic mass transfer treatment for transfer between the phases) that the predicted concentrations of SO₄²⁻, ORGC, and other major species are comparable to those predicted with the fully dynamic approach of AQCHEM-KMT. This indicates that the largest differences between AQCHEM-KMT and AQCHEM for the test scenarios are a result of using kinetic mass transfer coefficients to describe the transfer of species between the phases (i.e., not assuming instantaneous Henry's law equilibrium) and to a lesser extent the change in solvers.

My second issue regards operator splitting. Previous work has shown that splitting gas and aerosol-phase chemistry into two separate operations inevitably introduces errors, and that these errors can be quite large (Djouad and Michelangeli, 2004). This is especially pertinent now that mass transfer limitations are being explicitly considered. Unfortunately Kahey et al. do not state how their aqueous chemistry operator fits into CMAQ as a whole. My assumption is that it remains a separate operation from gas-phase chemistry, but without a clear explanation the reproducibility of the work is compromised. The paper would benefit from a description of the order of operation of AQCHEM-KMT with respect to the rest of the model operators.

The following text has been added to page 10, line 13 (p 9, line 19 in original document): “Note that in all CMAQ cases, cloud chemistry and gas phase chemistry are not solved simultaneously but are instead solved in separate operators. Following advection and diffusion, cloud processes (including cloud chemistry) are treated for resolved and sub-grid clouds. This is followed by gas phase chemistry (including heterogeneous chemistry on aerosols) and aerosol dynamics. Inevitably there are errors that can result from estimating the impacts of chemistry of different phases separately, and in the future, the feasibility of simultaneously solving chemistry across all phases will be investigated.”

Specific comments and technical corrections

The following minor issues should be addressed:

- Page 5, line 18: The sentence beginning “While in AQCHEM...” is confusing and would benefit from a rewrite.

The sentence now reads as follows: “While instantaneous Henry’s Law equilibrium is assumed for all species in AQCHEM, in actuality, the distribution of a species between the gas and aqueous phases may deviate significantly from equilibrium”

- Page 8, line 13: Suggest that “Figures 2 b and d” is changed to “Figures 2b and 2d”

“Figures 2 b and d” has been changed to “Figures 2b and 2d”

- Page 11, line 7: The phrasing “At least a couple micrograms per meter” is rather vague.

Changed “concentrations can be at least a couple micrograms per cubic meter in magnitude” to “concentrations often exceed 2 micrograms per cubic meter in magnitude”

- Page 11, first paragraph: Some sense should be given of the relative impact of implementing AQCHEM-KMT. With only absolute differences given, it is difficult to tell if the changes are ever significant. Suggest the authors state what the maximum and average percentage change in the given grid cell is. Similarly, Figures 3 and 4 would benefit from an additional panel showing the “baseline” (AQCHEM) concentrations in January and July. Without this, it is difficult to tell the significance of AQCHEM-KMT’s changes.

Figures 3 and 4 have been updated to include the average “baseline” AQCHEM concentrations of SO_4^{2-} and ORGC for January and July. Figure captions have been updated to reflect the additional AQCHEM concentration plots. Section 3.1 has been updated due to the change to the figures as follows (additions/updates are underlined):

Page 11, line 26 (p 10, line 26 in original document) is now “Figures 3 and 4 show the average baseline (AQCHEM) concentrations and difference in predictions between AQCHEM (base)...”

Page 11, lines 27-28 (p 10, line 27 in original document): “In addition to a map of the average baseline concentrations (a,d), the figures include a map of monthly average (b,e) and maximum hourly (c,f) differences for January (top) and July (bottom) 2011”

The following text has also been added on page 12 lines 6-9 (p 11, line 5 in original document) (new text underlined) “The figures also include modeled total liquid water content values. While monthly average SO_4^{2-} predicted with AQCHEM-KMT is only 5.2% and 6.5% lower than the base in the cell selected for January and July respectively, when the maximum hourly difference is observed, AQCHEM-KMT predicts

35% less SO₄²⁻ at cell (264,54) and 15% less SO₄²⁻ at cell (183,213) compared to AOCHEM. For most hours,...

- Figure 1a: The caption is unclear. Specifically, it should be stated exactly what is varying between different points for the same solver (ie that different tolerances are being tested, and over what range). It would also be helpful to point out explicitly what is changing between the different plateaus - it appears that SDA is more sensitive to relative tolerance than to absolute tolerance, based on the clustering behavior.

The Figure 1 caption has been changed to read as follows: “Figure 1: Significant digits of accuracy (SDA) for the CMAQ species with the maximum error for (a) different variants of Rosenbrock solvers and (b) the Rodas3 solver at different combinations of relative and absolute tolerance. Each point in figure 1a represents a different relative and absolute tolerance combination. The absolute tolerances tested were 10⁻⁴, 10⁻², 10⁰, 10², and 10⁴ molecules/cm³ air for relative tolerances = 10⁻⁴, 10⁻³, 10⁻², and 10⁻¹. Each “plateau” visible for certain solvers in Figure 1a represents a different relative tolerance setting, with tighter tolerances leading to higher SDAs.”

- All of the figures showing land area should have axis markers (latitude and longitude, if possible, or at least the X and Y dimension indices). Once these are in place, the grid index given on page 11, line 5 should be changed to match the dimensions used for the figures, so that the reader can identify which point on the grid is being discussed.

Grid cell coordinates have been added to figures 3, 4, 6, and 10. Cell coordinates for plots in figure 5 are now referenced on page 12, lines 5-6 (p 11, line 4 in original document)

- Table 2: There are some typesetting issues here, particularly where a subscript should or should not have been used. Note, for example, the “Other information” entry for wet deposition.

In Table 2, under Wet deposition “Other information” the unit “(s)” is no longer a subscript

References

Djouad, R. and Michelangeli, D. V.: Investigation of splitting gas and aqueous operators in atmospheric multiphase box models, Atmos. Res., 71(4), 253–263, 2004.