Responses to the Comments of the Reviewers

Reviewer 3

(1) This study incorporated aerosol water associated with secondary organic aerosol (SOAW) in a thermodynamic model and accounted for the influence of SOAW on the partitioning of inorganic species like sulfate, nitrate and ammonium. The updated thermodynamic model (ISORROPIA-lite) was integrated with a chemical transport model (PMCAMx) to evaluate the impact of SOAW on particulate matter (PM) concentration over the US. It was found that while SOAW significantly increased total aerosol water by 20-50%, the corresponding enhancement in PM mass concentration was mostly negligible (around or less than 2%). The study concluded that it was important to account for the influence of SOAW on PM due to changes in particle size and thus optical properties and deposition rate. Major revisions are suggested for the manuscript before acceptance for publication.

Our responses and corresponding changes to the manuscript (in blue) follow each comment of the reviewer (in black).

(2) This study was directed at addressing an important gap in the current modeling of PM by linking the thermodynamics of inorganic species and SOA. However, the manuscript missed key discussions that would serve as the basis for this study. Specifically, the manuscript did not explain the current inorganic aerosol formation pathways in ISORROPIA-lite and how much these pathways are expected to be influenced by enhanced aerosol water from SOA. Some novel aqueous pathways for inorganic aerosol formation and synergistic effects between different inorganic components have been found in recent studies (e.g., aqueous conversion of SO_2 to SO4 by dissolved NO2 and NH3,1 hydroxymethansulfonate formation,2 air-water interface catalyzed reactions,3 black carbon catalyzed reactions4 and etc). Therefore, it is important to describe what aqueous inorganic pathways ISORROPIA-lite accounts for, whether the novel pathways are relevant for the simulation over the US, and what the limitations are if some potentially important pathways are not accounted for. For now, the model sensitivity in PM mass to SOAW is not presented in context of these discussions.

We now clarify in the revised manuscript that ISORROPIA-lite is an aerosol thermodynamics model, therefore it focuses on the simulation of the thermodynamic equilibrium of atmospheric aerosol. Processes like the one mentioned by the reviewer (bulk aqueous-phase reactions, heterogeneous interface reactions, catalyzed reactions, etc.) are usually described in the corresponding chemical transport module (aqueous-phase chemistry, inorganic and organic aerosol chemistry, etc.) and not in the aerosol thermodynamics module. A brief description of the processes described by PMCAMx currently (e.g., the aqueous oxidation of SO_2 to sulfate by NO_2, the formation of hydroxymethansulfonate, etc.) has been added in the PMCAMx description section.

(3) Other suggestions include to discuss the potential impact of increased aerosol water on the radiative properties of PM over the US. Specifically, what is the change in direct radiative forcing due to more scattering caused by increased aerosol water?

A brief discussion of the expected magnitude of these effects has been added to the revised paper.

References

(1) Peng, J.; Hu, M.; Guo, S.; Du, Z.; Zheng, J.; Shang, D.; Levy Zamora, M.; Zeng, L.; Shao, M.; Wu, Y.-S.; Zheng, J.; Wang, Y.; Glen, C. R.; Collins, D. R.; Molina, M. J.; Zhang, R. Markedly Enhanced Absorption and Direct Radiative Forcing of Black Carbon under Polluted Urban Environments. Proc. Natl. Acad. Sci. U.S.A. 2016, 113 (16), 4266–4271. https://doi.org/10.1073/pnas.1602310113.

(2) Moch, J. M.; Dovrou, E.; Mickley, L. J.; Keutsch, F. N.; Cheng, Y.; Jacob, D. J.; Jiang, J.; Li, M.; Munger, J. W.; Qiao, X.; Zhang, Q. Contribution of Hydroxymethane Sulfonate to Ambient Particulate Matter: A Potential Explanation for High Particulate Sulfur During Severe Winter Haze in Beijing. Geophys. Res. Lett. 2018, 45 (21). https://doi.org/10.1029/2018GL079309.

(3) Hung, H.-M.; Hoffmann, M. R. Oxidation of Gas-Phase SO 2 on the Surfaces of Acidic Microdroplets: Implications for Sulfate and Sulfate Radical Anion Formation in the Atmospheric Liquid Phase. Environ. Sci. Technol. 2015, 49, 13768–13776. https://doi.org/10.1021/acs.est.5b01658.

(4) Zhang, F.; Wang, Y.; Peng, J.; Chen, L.; Sun, Y.; Duan, L.; Ge, X.; Li, Y.; Zhao, J.; Liu, C.; Zhang, X.; Zhang, G.; Pan, Y.; Wang, Y.; Zhang, A. L.; Ji, Y.; Wang, G.; Hu, M.; Molina, M. J.; Zhang, R. An Unexpected Catalyst Dominates Formation and Radiative Forcing of Regional Haze. Proc. Natl. Acad. Sci. U.S.A. 2020, 117 (8), 3960–3966. https://doi.org/10.1073/pnas.1919343117.

Reviewer 4

(1) The manuscript simulated the SOAW and investigated its effects on inorganic species of PM1 over the US. It is revealed that SOAW can increase the average aerosol water by a factor of up to 2 and generally increase the partitioning of ammonium nitrate. This is an interesting topic and has important implications for understanding the role of the environmental effects of SOA. The manuscript is clearly written and ACP is an appropriate venue, but I do have some concerns regarding methods and data analysis that must be addressed before the paper can be considered for publication.

Our responses and corresponding changes to the manuscript (in blue) follow each comment of the reviewer (in black).

(2) The effects of SOAW on the partitioning of organic species were not considered. How would SOAW impact the partitioning of organic vapors? More importantly, what is the role of SOAW in aqueous phase chemistry?

ISORROPIA-lite is an aerosol thermodynamics model, therefore it focuses on the simulation of the thermodynamic equilibrium of atmospheric aerosol. For the simulation of organic aerosol the volatility basis set (VBS) approach is used. Therefore, partitioning of organic vapors is described in the corresponding chemical transport module and not in the inorganic aerosol thermodynamics module. A brief description of the organics species partitioning in PMCAMx has been added in the PMCAMx description section.

(3) The fractional bias of the total $PM_{2.5}$ and its major components of the PMCAMx was typically 30%. This is significantly higher than the 1% increase in PM levels induced by SOAW. The 1% difference is so small (within the uncertainty of the PM simulation) that it is not sound to compare the SOAW effects on the absolute changes of PM components across different regions. The authors should focus more on the fractional changes of PM induced by SOAW instead of the absolute changes. That said, for example, Figure 6 can be removed or go to the supplemental information.

Please note that the fractional bias was a lot lower. For example, it was 5% for the annual average $PM_{2.5}$ concentrations in more than 1000 measurement stations. The bias was 5% for OA, 17% for sulfate, 6% for EC, etc. The highest bias was for nitrate. We do believe that the absolute changes are important (e.g., for the estimation of the direct effect) as are the fractional changes suggested by the reviewer. In the revised paper we present both in most cases. We have followed the advice of the reviewer and moved Figure 6 to the Supplemental Information.

Specific comments

(4) Title: The paper discussed the effects of SOAW on PM1, not fine PM. Please clarify.

We have added the PM_1 to the title.

(5) Lines 92-94: It would be helpful to elaborate on the chosen values of SOA density and κ here.
A brief discussion and the corresponding references have been added.

(6) Lines 110-114: The four volatility bins of SOA only cover the SVOC range. Why were these bins selected for the simulation? LVOC should also be considered.
The LVOCs (and the ELVOCs) are implicitly included in the lowest volatility bin of this version of the VBS used in PMCAMx. These compounds are always in the particulate phase in these simulations and therefore the addition of lower bins increases the computational cost without changing the predicted organic aerosol concentration. A brief explanation of this choice has been added to the revised paper.

(7) Lines 122-124: This is confusing. Why were the model predictions more reliable for RH values above 95%?
We have rephrased this rather confusing statement.

(8) Lines 129-132: Why was κ=0.2 selected as the maximum value, not 0.3 given that the κ of SOA is 0.1-0.3?
The κ=0.3 represents an extreme case for the simulation of the average effects over the US. The two current simulations also provide a good estimate of the corresponding uncertainty. A brief explanation for our choice has been added to the paper.