Response to the Comments of Reviewer 1

(1) *This manuscript describes air quality model simulations with PMCAMx of North America with focus on the U.S. The model simulations include ISORROPIA-lite to simulate aerosol liquid water not only from inorganic PM constituents, but with water uptake contributed from secondary organic aerosol (SOA) constituents. The authors investigate the amount and relative change in aerosol water, dry mass from nitrate, HCl, HNO_3, and ammonium due to this process. The authors find ubiquitous increase in predicted wet and dry PM_1 mass concentrations. The authors identify an important and interesting topic regarding interactions among water uptake, organic aerosol species formed in situ and the impacts on particle-phase chemical composition.*

We thank the reviewer for pointing out the importance of this study. Our responses and corresponding changes to the manuscript (in regular font) follow each comment of the reviewer (in italics).

(2) *There is no connection of model predictions to measurements and it is difficult to understand if the changes represent improved predictive skill. The authors generally provide little to no support for employed values (e.g., kappa, density) or the city selection. If statistical tests were performed, for example, to determine that the 1% difference in PM_1 dry mass is statistically significant – they are not discussed. Would such change be sufficient to be detected in an observational network or during a field campaign? I cannot support publication of this manuscript in its present form. Provided the comments below are addressed the manuscript may be publishable.*

We have done our best to address each comment of the reviewer and to improve the manuscript accordingly. Unfortunately, the most important predicted variable for the current simulations, the aerosol liquid water, is a challenge to measure – and for that reason no particle liquid water content measurements are thus available for the model evaluation. A detailed model performance evaluation for the rest of the $PM_{2.5}$ components has been provided by Skyllakou et al. (2021). Given the small changes in the average concentrations of the major $PM_{2.5}$ components when the secondary organic aerosol water is included in the simulation the performance of the model remained practically the same. It is considered good for the total $PM_{2.5}$ concentration and average for most of the components. This information has been added to the revised paper.

We have added explanations and the corresponding references for the employed values for the hygroscopicity parameter, density, etc. and also about our city selection. We now clarify in the paper that a 1% change in PM_1 is not important for all practical purposes. We now clarify that the change is very small and we just mention the exact number in parenthesis to avoid confusion about what we consider very small. That said, there are still cases where the changes are important, and we still keep those points in the revision – always noting conditions for which they occur.

Detailed Comments

(4) *This a 3-D modeling study, and authors make no connection to field observations. The title should reflect that. For example, "Effect of simulated …."*

Good point. We have added information about the model performance for total $PM_{2.5}$ and the concentrations of the major $PM_{2.5}$ components during the simulation. We have made the proposed change in the title of the paper.

(5) *The authors motivate their work with discussion of $PM_{2.5}$, and classify all of their results in terms of PM_1. Why the disconnect? Further, how was PM_1 calculated from model output? This is not described in main text or supplemental information.*

PMCAMx simulates the aerosol size/composition distribution using a sectional approach so it predicts PM_x where *x* can be among other choices 1, 2.5 and 10 μm. This is now explained in the model description. The disconnect is mainly due to the regulation of $PM_{2.5}$ and not PM_1. We agree with the point of the reviewer though and we have focused on PM_1 in our discussion in the revised paper.

(6) *Line 37: "Potassium levels can be significant … biomass burning" This sentence seems a little out of place, especially given the Cl discussion regarding biomass burning later in the manuscript (lines 171-173). Also, is the review paper by Pye et al, the best reference for this point?*

Good point. We have deleted this sentence from this point in the manuscript together with the corresponding reference.

(7) *The HCl hotspot in KS should be addressed. In the text, chlorine species are discussed primarily in relation to their presence due to biomass burning, which (I don't think) is happening in the KS hotspot.*

A brief discussion of the source of this rather low chloride concentration (~ 0.1 μg m^{-3}) in this area has been added to the paper.

(8) *Line 50: Does "a lot more hygroscopic" have a quantitative meaning?*

Indeed so, as on a per mass basis SOA can uptake multiple times (depending on source and ageing, a factor of 2-3) water compared to primary OA. We have rephrased the corresponding sentence to reflect this.

(9) *Line 117 and Line 119: can justification be provided for the Kappa and SOA density values? Can the authors defend the use of the kappa values in the context of a regional simulation or evaluation focused on discussion of urban areas? In the simulations here, aromatic SOA has the same hygroscopic properties and density as 'aged' SOA? Why not pick a higher and lower bounds-0.3 to 0.05? Or better yet, why not apply k values based on chemical information of SOA species since the authors have that information from the model? Any which way, some reasoning for the chosen kappa values is needed.*

We have added a brief discussion of the hygroscopicity parameter values in the literature and provided justification of our choices in the revised paper. Given that our paper investigates the potential significance of this effect we have chosen to provide the results of two simulations one with relatively low and relatively high hygroscopicity of SOA, which bound the range of the

corresponding effects of the SOA water on particle water, mass and impacts on semi-volatile inorganic species partitioning. A more detailed treatment of the hygroscopicity parameter (e.g., assigning a different value to each OA component) is of course possible – and is left to be the topic of future work. We have also added a discussion of this point in the end of the paper.

(10) *Why were the particular cities selected? Why are they introduced in the end?*

Our intention is to look into more detail into the behavior of SOA water and its effects in selected locations in the domain. We have chosen one city from the West, one from the South, one from the Southeast and one from the Northeast. They are all in different environments with different major sources and climatological conditions. We explain our reasoning in the revised paper.

(11) *It is difficult to accurately measure RH above ~95%. Did the authors screen out any RH values when evaluating water mass predictions?*

This is a relevant point for the analysis of measurements. Given that the RH is predicted in this case and it does not suffer from the corresponding experimental challenges there was no need for screening of the few values above 95%. In fact, it points to the potential need for measurements at ultra-high RH – which is quite possible (e.g., https://acp.copernicus.org/articles/10/1329/2010/) but seldomly carried out by research groups. We will clarify these points in the revision.

(12) *The authors state "The model performance has been evaluated for fine PM and its components for the examined period by Skyllakou et al. (2021)." What did they find? For example, in these simulations there is a universal increase in PM_1 mass. Was such a one-way bias observed in Skyllakou? Does this model configuration address model bias in a way that enhances predictive skill? From my quick read of Skyllakou it appears there is often a positive bias (overprediction) of $PM_{2.5}$ mass concentrations. To what degree does this new model process exacerbate bias and error?*

Skyllakou et al. (2021) found that PMCAMx had a small fractional bias (5%) and fractional error (25%) for the annual average $PM_{2.5}$ concentrations of 1067 measurement stations in the US. Given that the effect of the extension of the model on the total fine PM mass is small (of the order of 1%), this does not result in any noticeable change in its already very good performance for dry fine PM. We do stress now in the revised paper that the major effect of including the SOA water in the simulations is the increase of the predicted aerosol water with implications that include its climatic effects (increase of the aerosol direct effect), visibility, atmospheric chemistry. The corresponding effects of the extension on reproducing the fine PM mass, at least in the area studied, are minor to negligible.

(13) *Starting at line 217: "Aerosol liquid water directly affects the PM sensitivity and dry deposition rates, with direct implications for emissions control policy." It reads awkwardly to introduce these new ideas in the last paragraph of the manuscript.*

We have deleted these sentences and focused the last paragraph on the significance of the SOA water for climate change, visibility and aerosol chemistry.

(14) *The finding that increasing the amount of liquid water increasing nitrate concentrations is an important finding in the spirt and context of this sentence – but the authors gloss over this.*

Thank you for this comment. The effects on predicted nitrate are discussed in the end of the first paragraph of the conclusions. We have extended that discussion and also added this point to the concluding paragraph of the manuscript.

(15) *Table S1: Can the authors provide quantitative meaning or context for "low", "high" and "modest"? How does RH change in these areas?*

We have replaced the qualitative metrics with predicted concentrations and added information about the RH in these areas.

(16) *Sacramento is listed as "low" SOA in Table S1. Sacramento is one of the top 20 most polluted cities in U.S. AMS studies in Davis, CA & Cool, CA (i.e., near Sacramento) are heavily organic dominated. Can the authors defend the choice to characterize Sacramento as 'low'?*

Following the advice of the reviewer (see also our response to Comment 15) we have replaced the qualifiers with quantitative metrics (concentrations). The predicted annual average SOA concentration in Sacramento by PMCAMx is now shown in the table.

Editorial

(17) *The months used for the seasonal definitions are not provided.*

We now state clearly the months used for the seasonal definitions (DJF for winter, MAM for spring, JJA for summer, and SON for fall).

(18) *The y-axis in the first row of Fig. S7 is log scale. Why? There should be a note in the Figure caption each time the axes differ.*

We have chosen a log scale here to show clearly both the relatively small average and the large range of high values. This is now noted in the corresponding figure caption.

(19) *The authors rely on some supplemental figures heavily, referring to them many times. They should probably be in the main text.*

We have followed the advice of the reviewer and moved Figures S2, S4 and S7 to the main text.