Response to Referee #1

Thank you for the insightful comments. Below are the referee comments in black, my responses to each point in red and changes made to the manuscript in blue.

This manuscript systematically investigated the water uptake potentials of a large library of the inorganic salts of amines with various functional groups (alkylamines, guanidinos, and amino acids), by computing the water activities of their aqueous solutions, as well as ternary mixtures of the salts, water and atmospheric-relevant organic proxies (either water soluble or water in-soluble). The author employed the Conductor-like Screening Model for Real Solvents (COSMO-RS) program with three parameterization methods (TZVP, FINE and ELYTE), depending on the specific cation in question. Based on the computational results, the water uptake potentials of amine salts depend more strongly on their cation chemical structures (eg, more substituents and more amino groups will enhance the water uptake of amine sulfates); but the anions may also affect such difference (eg, all bisulfate salts showed little difference in their aqueous solutions). Using an isoprene derived epoxydiol IEPOX as a proxy for water-soluble organics, the author showed that water soluble organics may enhance the water uptake of amine salts significantly, depending on the chemical structure of the salt. On the contrary, water in-soluble organics may simply become phase separated from the aqueous solutions to exert appreciable effects on the hygroscopicity of the salts.

While the manuscript has presented a thorough and comprehensive study on atmospheric-relevant amine salts in settings related to atmospheric chemical processes, I noticed a few items that may clarify some questions and further improve the structure and presentation of the manuscript:

1. Introduction. What are the (semi-)quantitative differences in water activity estimations using COSMOtherm program when compared with other methods (eg, the group attribution methods)? How about the differences in computational time, resource requirements, etc?

   Author response: It would be interesting to compare water activities from COSMOtherm and other models. Unfortunately it is not possible to calculate water activities in solutions containing aminium salts using group-contribution methods, because none of the group-contribution methods have been parametrized with experiments of aminium salts. This is why COSMOtherm is the only option for computing properties of aminium salts. For example, the commonly used AIOMFAC contains only NH$_4^+$ out of the studied cations. See fig. R1 below for a comparison between AIOMFAC- and COSMOtherm-derived water activities in aqueous ammonium salt solutions.
**Figure R1.** Comparison between COSMO*therm*- and AIOMFAC-derived water activities in the ammonium salts available in AIOMFAC.

Changes in manuscript (line 33): Though COSMO-RS calculations are much slower (several hours) than group-contribution methods (~ 1 second), mainly due to the quantum chemistry input needed for the COSMO-RS calculations, COSMO-RS is currently the only method capable of estimating water activities in aminium salts.

2. Methodology. Clearly it was difficult to find an “one-size-fit-all” computational method to address the complex research questions discussed here, and the manuscript states that FINE parameterization method was chosen for the amine salts and ELYTE for ammonium salts. However, when examining the Figs S1&S2, one could argue that the FINE may also be suitable for smaller amine salts. How was the “proper” parameterization method chose here? I think a more convincing approach is to calculate representative small amines using both FINE and ELYTE to see if the results are converging.

Author response: The ELYTE parametrization was selected for only ammonium sulfate, not all ammonium salts. This was mentioned in line 78 of the manuscript "The FINE parametrization is therefore used for all of the studied salts, with the exception of ammonium sulfate, which is calculated using the ELYTE parametrization." The ELYTE parametrization is only meant for calculations involving ionic species and should not be used for charge neutral systems. The FINE parametrization uses the higher level of theory (DFT) input, while TZVP and ELYTE use the lower level of theory input. For both neutral and ionic systems, the two levels of theory (BP/TZVP and BP/TZVPD) lead to different water activities, though the differences
between the parametrizations are larger in ionic systems than in neutral systems. Generally, the FINE parametrization should lead to more accurate results than the lower level TZVP parametrization and that is why it was chosen for the calculations here. These points were clarified in the manuscript.

Changes in manuscript (line 73): Based on these recommendations, the use of ELYTE should be limited to systems for which it was developed, unless the calculated values can be corroborated by experiments.

(line 78): Additionally, the current electrolyte parametrization is only available for the lower level of theory BP/TZVP cosmo files and not for the higher level of theory BP/TZVPD cosmo files, corresponding to the FINE parametrization. In case there are systematic errors within the different parametrizations or levels of theory, the comparison of the different salts is more reliable when the same parametrization is used in all calculations.

3. Results & Discussion. The point above also brings up another major question: what is the estimated uncertainty in the computational results presented in the manuscript? Some of the traces in the figures were quite close to each other and the lack of error bars was making it difficult to judge if the difference was within the uncertainties of the methods.

Author response: Thank you for the question. It is difficult to quantify the uncertainty of COSMOtherm calculations, because the performance of the model depends on the compound.

Changes in manuscript (line 126): Due to uncertainties in the calculated values, it is possible that there are no real differences between the water activities of the different aminium bisulfate solutions.

(line 102): Unfortunately, determining reliable error estimates of water activities in these salts is not possible due to lack of experimental data of similar salts. However, the errors are likely to be systematic for similar compounds, such as aminium ions. The order of the cations may therefore be more reliable than the order of the anions.

4. Results & Discussion. This study was very comprehensive with a lot of results, which leads to, in my opinion, very dense figures that are difficult to read and comprehend. I would like to recommend major reorganizations of the results for better presentations and support for the flow of the discussion. For example, some panels of Fig. 1 can go into supplementary, but others can be split into less busy ones (eg, Fig.1a may be divided into three panels, one for each amine group to highlight the differences).

Author response: Thank you for the suggestion. I have made a new figure that better highlights the differences between both anions and cations. The original Figure 1 was moved to the Supplement.

Changes in manuscript (line 101): Figure 1 shows COSMOtherm-derived water activities in selected salt solutions at 298.15 K.
Figure 1. COSMOtherm-derived water activities ($a_w$) in aqueous (a) amine, (b) guanidino and (c) amino acid bisulfate solutions, as well as selected (d) sulfate, (e) methylsulfonate and (f) nitrate solutions at 298.15 K. Activities were calculated in 0.01 intervals of salt mole fraction ($x_{salt}$) and plotted as lines for clarity. The black line represents ideality $a_w = x_w$. 