

Review of "Optimization of Sulfate Aerosol Hygroscopicity Parameter in WRF-Chem version (3.8.1)" by Kim et al.

The manuscript describes a new method for parameterizing the hygroscopicity of sulfate aerosols within WRF-Chem that accounts for whether the sulfate exists as neutralized ammonium sulfate or as sulfuric acid. A simple mixing rule is proposed based on the ratio of ammonium to sulfate ions, and multiple simulations are conducted assuming constant values for the hygroscopicity of each aerosol species. Model results are shown for southeast Asia and are compared to airborne observations from the KORUS-AQ field campaign. The model suggests that the sulfate aerosols over land are fully neutralized by ammonium ions, while the molar ratio of ammonium to sulfate is lower over coastal waters. This gives rise to significant changes in the hygroscopicity parameter over the water as well as notable changes in CCN, cloud droplet number, and cloud radiative effect over the entire domain. The comparisons to KORUS-AQ data show that the model captures the observed variability in aerosol mass; although, sulfate is significantly overpredicted during many time periods (Figure 1). The observed CCN-active aerosol fraction also tends to exceed model predictions, even when using the new parameterization (Figure 4). Overall, the manuscript is fairly well-written and the topic is interesting. A significant omission is not considering partial neutralization of the sulfate to form ammonium bisulfate. In addition, it is not well discussed how additional nitrate, sodium, or organic species from either continental or marine sources may impact the aerosol ion balance and acidity. I also note that the assumed hygroscopicity values do not appear consistent with what would be expected based on thermodynamic (Köhler) theory for CCN activation. Finally, some of the major conclusions about the "reliability" of the new parameterization need to be better supported by the results/discussion. The manuscript may be publishable, but only after the following comments are satisfactorily addressed.

### Specific comments:

1. It seems appropriate to also consider ammonium bisulfate using simple mole balance mixing rules following Nenes et al. (1998) and Moore et al. (2011, 2012). Using the molar ratio of ammonium to sulfate ions,  $R = n_{\text{NH}_4}/n_{\text{SO}_4}$ ,

For  $R \leq 1$ ,

$$n_{(\text{NH}_4)_2\text{SO}_4} = 0$$

$$n_{\text{NH}_4\text{HSO}_4} = n_{\text{NH}_4}$$

$$n_{\text{H}_2\text{SO}_4} = n_{\text{SO}_4} - n_{\text{NH}_4}$$

For  $1 < R < 2$ ,

$$n_{(\text{NH}_4)_2\text{SO}_4} = n_{\text{NH}_4} - n_{\text{SO}_4}$$

$$n_{\text{NH}_4\text{HSO}_4} = 2n_{\text{SO}_4} - n_{\text{NH}_4}$$

$$n_{\text{H}_2\text{SO}_4} = 0$$

For  $R \geq 2$ ,

$$n_{(\text{NH}_4)_2\text{SO}_4} = n_{\text{SO}_4}$$

$$n_{\text{NH}_4\text{HSO}_4} = 0$$

$$n_{\text{H}_2\text{SO}_4} = 0$$

where  $n_{(\text{NH}_4)_2\text{SO}_4}$ ,  $n_{\text{NH}_4\text{HSO}_4}$ , and  $n_{\text{H}_2\text{SO}_4}$  are the moles of ammonium sulfate, ammonium bisulfate, and sulfuric acid, respectively.

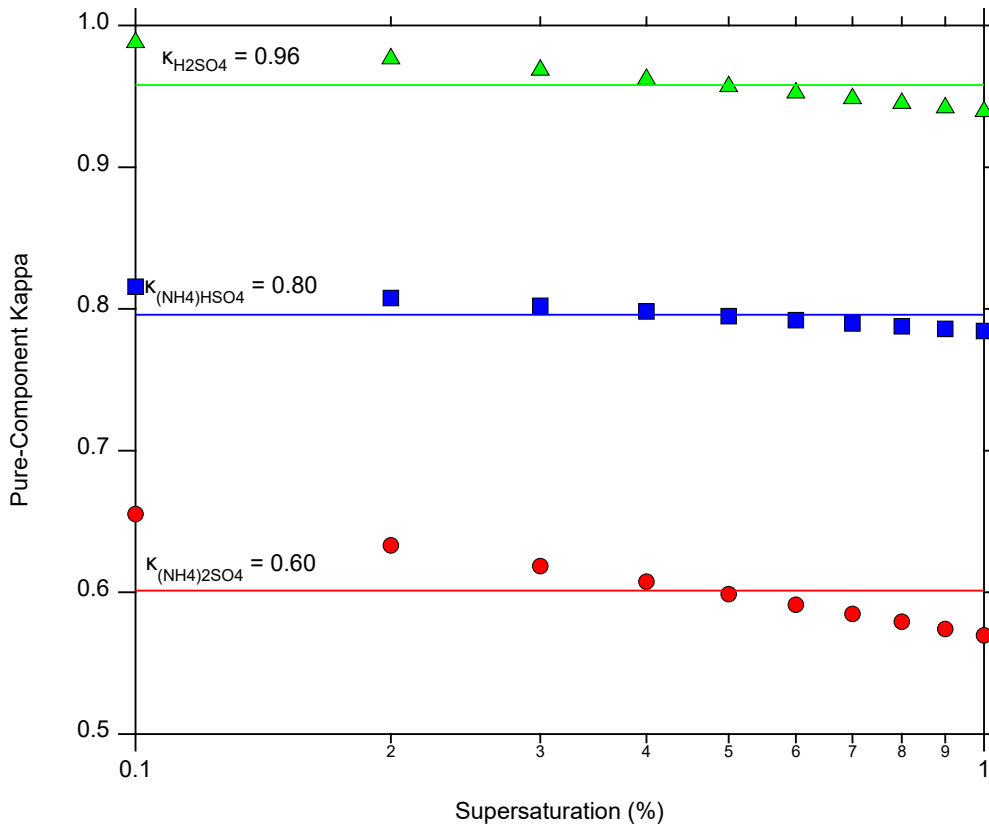
- The chosen  $\kappa$  values of 0.53 and 1.19 for ammonium sulfate and sulfuric acid that are reported on Line 95 do not seem correct to me. From the Köhler Theory equations given by Seinfeld and Pandis (2016) and the approximation for  $\kappa$  given in Petters and Kreidenweis (2007), we know that

$$\ln^2 S_c = \frac{4A^3}{27\kappa D_d^3} = \frac{4A^3 \rho_w M_s}{27\nu \rho_s M_w D_d^3}$$

which yields

$$\kappa = \left(\frac{M_w}{\rho_w}\right) \left(\frac{\rho_s}{M_s}\right) \nu$$

where  $M_w$  and  $\rho_w$  are the molar mass and density of water, respectively;  $M_s$  and  $\rho_s$  are the molar mass and density of water of the dry solute, respectively; and  $\nu$  is the van't Hoff factor that represents incomplete solute dissociation. Fortunately, these parameters are known for the sulfate-ammonium salts studied in this work, and the pure component van't Hoff factor can be calculated using a suitable thermodynamic model (e.g., the Pitzer model) to account for the supersaturation-dependent change in solute molality at the point of CCN activation.



Neglecting the supersaturation-dependence and taking an average of the calculated kappas over the 0.1-1% supersaturation range yields estimates for kappa of 0.60, 0.80, and 0.96 for ammonium sulfate, ammonium bisulfate, and sulfuric acid, respectively. These values are in reasonable agreement with the CCN-derived values reported by Petters and Kreidenweis (2007) of 0.61 and 0.90 for ammonium sulfate and sulfuric acid, respectively, and significantly different from the values reported in this manuscript.

3. On Line 90, it is stated that the upper bound of kappa is around 1.40, but this is not a theoretical limit. Rather, Petters and Kreidenweis (2007) note that this is the upper end of the range of typical hygroscopic species of atmospheric relevance. Please clarify or strike this sentence.
4. The first part of Equation 3 suggests that R could be negative, which is non-physical.
5. The discussion on Page 5 and the kappa values for land and sea assumed on Line 144 also seem unrealistic, especially for the coastal region studied here that is susceptible to significant transport of continental emissions. This line of reasoning seems to suggest that the source of aerosol SO<sub>4</sub> is decoupled from ammonia for the marine atmosphere and that there is a significant local marine source of SO<sub>4</sub>. What is the contribution of SO<sub>4</sub> over the sea that is due to local sources versus transport?
6. How often is the ammonium data not available, and does this land-sea kappa parameterization differ notably from the R-based parameterization during periods where ammonium data are available?
7. On Line 193, it is stated that marine aerosols consist of mostly hydrophilic substances, which I'd suggest be revised to say "hygroscopic substances".
8. The citation for Park et al., 2020 that is referenced on Line 207 does not appear to be in the reference list.
9. For Figure 4 and related discussion on Lines 209-219, please also show the CCN and aerosol number concentration in cm<sup>-3</sup> in addition to the CCN-active fractions. How well do the AS, SA, RA, and LO simulations capture the observed variability in CCN and aerosol number concentrations measured during KORUS-AQ?
10. It's hard to see the differences in Figure 4 that accompany the discussion on Lines 220-227 that the new simulations outperform the AS simulation. The clearest discrepancies between the orange, yellow, and green curves appear during the May 22 – May 30 time period when the comparison is made over the ocean. Is this period driving the error metrics, and is the difference due to the model computed R values or because of the imposed land-sea kappas? Please add a table with the calculated error metrics that underpin these conclusions.
11. The statement on Lines 286-287 that the new parameterizations "could produce more reliable aerosol and CCN concentrations than the previous method" (and again on Line 300) is not currently well supported by the manuscript. First, the aerosol and CCN concentration simulation results need to be added to the manuscript (as requested in the comment above), and second, it's not clear that the results

are more or less reliable. The model results do seem to show significant differences across the simulations, but there needs to be more quantitative discussion about why one or the other simulation would be “more reliable”.

12. What is the support for the statement on Lines 289-290 that the increased CDNCs “suppress local precipitation, prolong cloud lifetime, and consequently reflect more sunlight”? I agree that these processes may be plausible explanations for the simulated changes in CRE, but I don’t think that the manuscript establishes a clear causal link to these processes.
13. What is the contribution of aerosol nitrate and sodium ions to the observations and simulations? How does the presence of these additional aerosol constituents impact the results shown here?

#### **References Cited:**

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