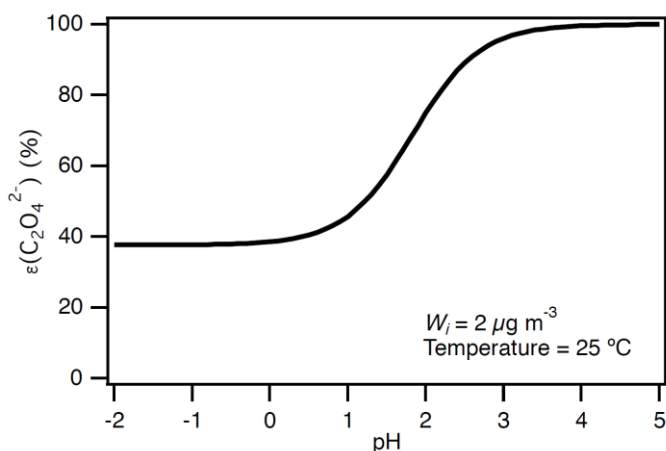


**Comment on Wang et al. (by A.Nenes, R.Weber, H.Guo, A.Russell, and P.Vasilakos)**

We feel that the manuscript contains conceptual issues that need to be addressed. Below is what we consider the main ones.

- The authors claim that thermodynamic models cannot be applied to ambient aerosol, because the system is “too complicated” due to the presence of organics. This discredits decades of research and aerosol model development and the extensive literature to evaluate them, without much proof on behalf of the authors. Instead, the authors chose, without supporting evidence, to come up with a much simpler (and considerably less accurate and evaluated) **conceptual model** of aerosol acidity, one that presumably uses the presence of aerosol oxalate as the “smoking gun” of aerosol neutrality, and the proposed NO<sub>2</sub>-enhanced sulfate production mechanism of Wang et al. (2016). This conceptual model, a fundamental premise of the paper, is incorrect; one can show (using the approach of Meskhidze et al. 2003 and Guo et al. 2016) that a considerable fraction of oxalic acid can partition to strongly acidic aerosol (see figure below). In a manuscript we have just submitted to ACPD (Nah et al., submitted), we use comprehensive field data to verify that the semivolatile partitioning of oxalic acid follows thermodynamic predictions just like for semivolatile inorganic ions, **and is in agreement with modeled pH.**



**Figure:** Fraction of total Oxalic acid (particle/[particle+gas]) that partitions to the aerosol phase as a function of aerosol pH. Note that there is always some oxalate in the aerosol phase, even at very low pH (where it is undissociated), due to the high solubility (Henry's Law constant) of oxalate. Calculations based on Nah et al. (submitted).

- Noteworthy is that Song et al (2018) carried out pH calculations (with the E-AIM model) for Beijing conditions and found that oxalic acid does not modulate aerosol pH considerably. This is in part because oxalate ion constitutes a relatively small fraction of the total ions in solution. The data presented in Wang et al. also shows that relatively minor amounts of oxalate are in the aerosol, so pH cannot be strongly affected. Regarding the discussion on the other effects of organics on pH predictions (such as liquid-liquid phase separation effects and water uptake), please also refer to Pye et al. (2018) and the relevant discussion of Guo et al. (2015).
- *Partitioning calculations for evaluating pH predictions:* The authors raise issues with the use of comparisons between predicted and measured partitioning of semivolatile species as a way to assess the thermodynamic model performance. Here we attempt to clarify the issue.

1. **At high RH**, it is expected that the aerosol is **fully deliquesced**. If this is the case, then all of the measured aerosol ammonium, nitrate and chloride are dissolved in water and in equilibrium with the gas phase. Errors in  $H^+$  therefore directly affect the measured inorganic aerosol species and their partitioning. This is when the comparison of predicted vs. measured partitioning most strongly constrains aerosol pH. The published body of evidence (e.g., Guo et al., 2015; Liu et al., 2017a; Song et al., 2018) shows that modeled pH values *are* reliable and representative of the aerosol acidity.
2. **At low RH**, the situation is less straightforward as the aerosol **may still be deliquesced (metastable mode) or be partially in solid state (stable mode)** so not all of the measured aerosol ammonium, nitrate and chloride may be dissolved. In this case, **liquid water content measurements are necessary** for constraining the amount of liquid phase. Guo et al. (2015) did this when supporting their calculations for the SE US; in the case of China, particle bounce measurements by Liu et al., (2017b) show particles are in the liquid state down to low humidity and Wu et al. (2018) found ISORROPIA metastable-predicted liquid water in good agreement with H-TDMA inferred liquid water during winter haze condition in Beijing. All this supports the metastable state for the haze fine particles.

When aerosol water measurements *are not* available, one can still use the RH history of the air mass to assess whether metastable aerosol is favored based on established knowledge of the efflorescence of the major salts that form in the aerosol; in China, the metastable assumption is expected to hold for a wide range of RH, as you rarely go below the efflorescence RH of pure ammonium sulfate (~35%) after exposure – usually during nighttime - to high RH (above 80%, the deliquescence RH of ammonium sulfate); if one considers the large amounts of nitrate that coexist – which effloresces at a *much lower* RH than ammonium sulfate – then you expect the metastable state to dominate for an even wider range of RH, certainly for the humidity levels experienced during intense haze events (e.g., supplementary material of Wang et al., 2016).

Song et al. (2018) finally show that the difference in pH between stable and metastable states may not significantly differ when the two solutions drastically differ in their predicted liquid water (one still requires however evaluation of the pH against partitioning measurements to believe them!). Therefore, asserting that uncertainty in which phase state is assumed invalidates the pH prediction is without merit.

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