

Review of “The sensitivity of PM_{2.5} acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites” by Tao and Murphy

General Comments:

This paper presents aerosol pH predictions at six Canadian sites based on long-term aerosol composition and NH₃ monitoring data. The authors characterize temporal trends in aerosol pH and seasonal averages at each site. Using the observational data, the authors characterize the sensitivity of pH to meteorology (Temp and RH) and composition (sulfate-nitrate-ammonium). The authors find that pH has a distinct seasonal profile at all of the sites, with summertime pH systematically lower than wintertime pH. During summer, aerosol pH is much less sensitive to perturbations in composition than it is to the met parameters. During winter, aerosol pH is still quite sensitive to meteorology, but is more sensitive to compositional changes than during summer. Overall, these results are novel and likely to be of interest to many in the atmospheric chemistry community. The topic is certainly relevant for *ACP*. The writing is clear, and the conclusions are robustly supported by the measurements and modeling results. I strongly endorse the manuscript for publication after the following specific concerns are addressed.

Specific Comments:

It is important that the authors state that their findings only apply to the sulfate-nitrate-ammonium system. Locations with dust and/or marine influence may exhibit very different trends and sensitivities to meteorology and composition.

The authors should discuss possible sampling artifacts as a function of temperature and season. The discussion on Pg. 4, lines 1-2 is presented in a way that assumes no sampling artifact, but studies (including the Yu et al. (2006) study that the authors cited) show evaporation of NH₄NO₃ from nylon filters. There is a temperature and RH-dependence to these losses, which are often greatest in summer. How would even small sampling artifacts during summer influence these results?

How were solids treated (prohibited or allowed?) in the model runs? How were data points with very low RH and ALW treated? Presumably, there were more of these points during winter, when dry, arctic air influences many of the sites? The interpretation of pH under conditions with a low fraction of ALW seems questionable.

The authors should replicate Figure S2 with the predicted and measured $\epsilon(\text{NO}_3)$.

While the authors find only minor effects of non-volatile cations (NVC) in their analysis, the limitations of this analysis need to be discussed. For example, Ca and Mg salts are typically much less soluble than analogous Na salts – replacing Ca and Mg with equivalent Na therefore does not account for potential precipitation, which may have a more pronounced effect on pH. Na is also more hygroscopic, which will affect the predicted ALW. Also, a brief discussion on the effects of NVC on pH (see Fig. 4c of Guo et al., 2018) should be included in the intro where composition effects on pH are discussed.

Temperature and RH are strongly linked in the atmosphere: discussing them as if they are independent parameters is not correct. A missing element from this manuscript is the role and trends in ALW, which is also closely connected to T and RH. Nguyen et al. (2016) show strong seasonal trends in ALW in the Northeast USA (see Fig. 2d), which would presumably have similar behavior to the Canadian sites analyzed in the present manuscript. If the Canadian sites do indeed show similar behavior (ALW maxima in summer), then it would imply the more acidic summertime particles occur despite the diluting effect of the ALW enhancement. This would be a very interesting contrast to the results of Guo et al. (2015) and Battaglia et al. (2017), who both show that aerosol pH decreases with increasing T. In their studies, the increase in T (and decrease in RH) that happen in the afternoon lead to decreasing ALW and a concentrating effect on H^+ (hence, decreasing pH). Clearly, the seasonal changes in composition would be an important factor that also contributes to these observations.

I found the explanation of Fig. 8b (pg. 9, line 12-24) to be quite confusing.

I completely disagree with the first sentence in the Abstract. Even if the chemical composition of an aerosol is known precisely, it is not possible to calculate the pH from an ion balance due to the buffering effects the HSO_4^-/SO_4^{2-} equilibrium (similar effect for organic acids, as well). Further in the manuscript – pg. 2 line 12 – the authors cite several studies which also contradict this statement. To my knowledge, there has never been a study which demonstrated a good connection between the ion balance and pH, so I think it is a mistake to lead the manuscript with this idea.

Technical Corrections:

Pg. 1, line 10 “constitute” or “constituent”?

Pg. 2, line 7: say “aerosol aqueous phase” instead of “aerosol liquid water”

Pg. 2, line 8: suggest deleting “very”

Pg. 6, line 26-28: this seems important - explain the derivation of this theoretical relation. Also, can the authors compare the prediction to their data?

Pg. 7, line 29 (pg. 9, line 14): I suggest alternate wording (“aerosol was more neutralized”) – because the pH is still quite acidic, suggest using “aerosol pH was higher” or similar.

Pg. 10, line 6-7; why would aerosol loading affect the results?

The role of organosulfates (mentioned pg. 8, line 5 and pg. 9, line 23) in aerosol pH is not clear? Can the authors add clarification?

The color scale on Figures 4, 5, and 8 can be difficult to distinguish certain levels – the color scale used with Fig. 2 is much easier to discern.

Address grammar and/or awkward phrasing in the following places: pg. 6, line 26; pg. 7 line 28; pg. 7 line 30.

References:

Battaglia, M. A., Douglas, S., and Hennigan, C. J.: Effect of the Urban Heat Island on Aerosol pH, *Environmental Science & Technology*, 51, 13095-13103, 10.1021/acs.est.7b02786, 2017.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, *Atmos Chem Phys*, 15, 5211-5228, 2015.

Guo, H., Nenes, A., and Weber, R. J.: The underappreciated role of nonvolatile cations in aerosol ammonium-sulfate molar ratios, *Atmos. Chem. Phys.*, 18, 17307-17323, 2018.

Nguyen, T. K. V., V. P. Ghate, and A. G. Carlton (2016), Reconciling satellite aerosol optical thickness and surface fine particle mass through aerosol liquid water, *Geophys. Res. Lett.*, 43, doi:10.1002/2016GL070994.

Yu, X. Y., Lee, T., Ayres, B., Kreidenweis, S. M., Malm, W., and Collett, J. L.: Loss of fine particle ammonium from denuded nylon filters, *Atmospheric Environment*, 40, 4797-4807, 10.1016/j.atmosenv.2006.03.061, 2006.