

Interactive comment on “The sensitivity of PM_{2.5} acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites” by Ye Tao and Jennifer G. Murphy

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This paper determines particle pH over a 10-year period at a number of sites in eastern Canada. pH is reported to be higher in winter vs. summer by about one pH unit, similar to what has been reported in Atlanta, although the Atlanta aerosol pH is a bit lower in both seasons [Guo et al., 2015]. The authors conclude that the difference in pH is largely due to T. Another major finding is that pH is reported to be more variable in winter due to particle composition effects. The topic is appropriate for publication in ACP. The paper is an important contribution to the growing knowledge on fine particle

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pH.

There are a number of points the authors could consider.

1) Although it is concluded that T is the main driver of lower pH in summer, with minor influence by aerosol composition, ambient data did not seem to be used in the assessment. For example, maybe a comparison table could be made showing summer vs winter average concentrations of the main species involved (sulfate, ammonium and nitrate). (I would also suggest including the ratio of nitrate to sulfate, which may be important for the next point.) Note that Guo et al (2015) reported a role of higher ion concentrations (sulfate) in summer as a cause for their reported differences in summer and winter pHs, but did not do a detailed investigation specifically on the effect of temperature. This paper can address this issue in much more detail and provide a more definitive conclusion. As noted in this paper, some of the T effects result from the equilibrium constants (Henry's law and dissociation, K_a 's) depending on T. Guo et al (e.g., see [Guo et al., 2017] supplemental material: <https://www.atmos-chem-phys.net/17/5703/2017/acp-17-5703-2017-supplement.pdf>) has shown one way to look at T (and particle water effects) is through S curves of partitioning vs pH. I think this is a useful way to think of things and it may be useful here. Overall, I think more insight could be gained if the authors tried to remove or account for the T effects in their data and then look for other possible drivers of pH differences.

2) The contrast in particle chemical composition effect on pH could be explored further by investigating the role of particle nitrate, or with nitrate to sulfate ratios. The paper tends to hint at the role of nitrate on this effect, but maybe it is playing a very large role here. If so, the paper could be more precise than just stating composition effects. For example, in summer the nitrate levels are likely to be low because of the higher temperatures favoring the gas phase, resulting in low $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios. Particle water, in the summer, is then largely controlled by the main hygroscopic species, non-volatile sulfate (and T, RH). pH depends on the inverse of particle water concentration. In contrast, in winter, the $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio is likely much higher since nitrate partitioning to

the particle is more favored. (I.e., at lower T , there is a higher predicted fraction of NO_3^- to TNO_3 at a given pH; see LWC and T affect on nitrate partitioning vs pH S curves in Guo et al. (2017) supplemental material). Indeed, Fig S5 shows that based on this data set, a small fraction of nitrate partitions to the aerosol in summer, whereas a much larger fraction is in the particle phase in winter. This means that in winter liquid water is affected by both sulfate and nitrate, and possibly more so by nitrate. Nitrate is semi-volatile, which leads to feed backs [Guo et al., 2017]. The last figure shows part of this dependence; initially the uptake of nitrate leads to higher liquid water (nitrate is highly hygroscopic), which dilutes the H^+ and raises pH. If nitrate partitioning is in the sensitive part of the S curve then higher pH leads to more nitrate, which allows for more uptake of nitrate (see again S curves for nitrate partitioning and LWC effects). Hence the more partitioning of nitrate drives the pH higher (as seen in Fig 8b, although this is overwhelmed at some point apparently by the increase in H^+ from the dissociation of HNO_3 aq). Also, with high particle nitrate the system becomes more sensitive to T , and so overall it might simply be the higher nitrate levels in winter cause greater variability in winter pH.

Minor Comments.

First line of Abstract that states: Aerosol pH is difficult to measure directly but can be calculated if the chemical composition is known with sufficient accuracy and precision to calculate the aerosol water content and the H^+ concentration through ion balance. Strictly speaking this is true, but in practical terms can it be done. For example, there is the issue of measurement uncertainty and propagation of those errors, leading to high uncertainty in H^+ . One must also measure all ions at actual ambient aerosol liquid water concentrations, eg, one would have to measure bisulfate and sulfate levels that exist in the ambient aerosol accurately. Given that ion balances have been used in the past to incorrectly infer acidity, I suggest removing this sentence to avoid perpetuating this idea? Second line of Abstract that states: In practical terms, simultaneous measurements of at least one semi-volatile constituent, e.g. NH_3 or HNO_3 , are required to

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provide a constraint on the calculation of pH. Is this strictly true as a general rule? Consider the sigmoid curves for the fractional partitioning of a semi-volatile species vs pH (see Guo et al. 2017 supplemental material). For a given set of conditions, there is only about a 1.5 to 2 pH range that partitioning is sensitive to pH, outside this range there is very little sensitivity (e.g., either all is in gas or all in particle phases). This line in the text could be clarified by stating that the semi-volatile constitute used to constrain the pH calculations should be in both the particle and gas phase, e.g., $\epsilon = p/(g+p)$ or $g/(g+p)$ between say 20 and 80%. It then raises the question of how one actually goes about solving for a final pH given missing species (i.e., does one iterate, is for how many times. . .). Line 15, as noted above, measured $\text{NH}_3/\text{NH}_4^+$ constraint on pH only works when there is some fraction in each phase. If the the particle pH is very low or high, then it is possible for the system of have practically no gas phase NH_3 present or no particle phase NH_4^+ present, in which case the observed concentrations of these species do not provide a good constraint on pH. Section 2.4: Some things to consider briefly discussing regarding the model and its assumptions: Lack of consideration of other species by E-AIM (e.g., non-volatile cations, which is discussed later in the paper), specific RH range data in this study (can one believe the predictions down to 30% and greater than 90% RH – why not test with comparison of observed/measured NH_3 partitioning?), no consideration of organic species influence on LWC, and no consideration of possible phase separations (ie, more important at lower RH). Some of these issues are noted at the very end of the paper, it might be worth point them out when the thermodynamic model is discussed.

This paper often refers to an earlier paper by Murphy et al. 2017 Faraday Disc. In that paper the pH was calculated differently; there is a difference of a factor of 55.509, the conversion from mole-based to molality-based activity. Does this account for the generally higher pH reported in Murphy et al of 2.5 to 5.5 for a similar region as discussed in this paper (ie, that paper reported molarity based pH, whereas this paper molality based pH)? Also see [Jia et al.]. I think the difference in pH calculations (and results) between these two papers should be noted.

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Page 5 and Fig S2. The comparisons between measured and predicted NH_3 and NH_4^+ are very useful, but why not show a similar set of plots in the supplementary for HNO_3 and NO_3^- . This would provide a more complete assessment of the model predictions and a useful contrast to what has been reported in a number of other papers which show that ammonia/ammonium partitioning is much better predicted by thermodynamic models than nitrate partitioning [Guo et al., 2017; Guo et al., 2016], [Guo et al., 2018] supplemental material, and [Nah et al., 2018] supplemental material.

Bottom of page 5 and on. It should be discussed that there is an important limitation in assessing the effect of non-volatile cations on pH using an equivalent Na^+ . Some non-volatile cations, such as Ca^{2+} and Mg^{2+} , have greater nonlinear effects on activity than Na^+ such that they can behave very differently than Na^+ (e.g., CaSO_4 can precipitate out). Because this is not considered, the effect of these cations may be greater than anticipated from the results based on an analysis using equivalent Na^+ .

Pg 6 Line 26 typo.

Pg 7 line 20 As noted above, one may want to point out this is due to LWC is controlled by non-volatile sulfate in the summer (which is likely not true in winter) and NH_4^+ volatility acts to buffer the pH of this system when there is little nitrate (Weber et al, 2017).

Pg 7 line 30 to Pg 8 line 2. Can a physical explanation be given to support the statement that lower NH_x and lower NH_x to sulfate molar ratio is the reason? Maybe it is nitrate that is playing a role here also?

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