

Reviewer 2#

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 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.

[In this paper, we intend to mainly discuss the aerosol pH response to each factor by interpreting how these factors can influence the equilibrium: $\text{NH}_3(\text{g}) \leftrightarrow \text{NH}_3(\text{aq})$ and $\text{NH}_4^+ \leftrightarrow \text{NH}_3(\text{aq}) + \text{H}^+$. The theoretical derivative of aerosol pH from the above two equilibria gives: $\text{pH} = \log([\text{NH}_3]/[\text{NH}_4^+]) + \log[\text{ALW}] + \text{p}K_a + \log K_H$. The S curve of partitioning vs pH as mentioned by the reviewer mainly discuss how pH will respond to $[\text{NH}_3]/[\text{NH}_4^+]$, while our paper mainly talks about the influence on $\text{p}K_a$ and K_H . We mainly focus on the ten-year time series of pH and try to identify the major influencing factors for the seasonal oscillation pattern. One piece of strong evidence for the dominant influence of temperature on pH is Figure 4 showing that the seasonal pattern of aerosol pH variation can be reconstructed without changing chemical composition. We can also theoretically derive that about 26% increase in NH_3 concentration is required to off-set the effect of temperature decreasing 2 °C if RH and particle composition do not change. We agree that the change in chemical composition can also affect or even dominate pH variation if the concentration change is large enough. However, we do not intend to have too much quantitative discussion in this paper but mainly try to identify the most important factor.]

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 NO₃⁻/SO₄²⁻ 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 NO₃⁻ to TNO₃ 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 HNO₃ 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.

[We agree that the difference in nitrate to sulfate molar ratio can also affect the aerosol pH sensitivity to chemical composition, so we will put more relevant statement when discussing chemical composition effect. However, we also wish to point out that we found the impact of nitrate was limited in the regions we studied, and even in wintertime it is both lower NH₃ concentration and more nitrate that jointly lead to the greater pH variability. Higher nitrate in winter alone cannot explain the whole pattern, and this can also be seen from the site by site comparison that the sites with lower NH_x to sulfate molar ratio (as an indicator for lower NH₃) tended to have larger sensitivity to composition changes.]

“...During summer ammonium nitrate formation is unfavorable, while in wintertime ammonium nitrate can form very efficiently. As a result, in summertime, the aerosol liquid water content was mainly contributed by ammonium sulfate while in wintertime it was affected by both sulfate and nitrate. The effect of nitrate formation to aerosol pH will be further discussed in section 3.4.”

“...Apart from the effect of lower temperature, lower NH_x to sulfate molar ratio also made aerosol pH much more sensitive to chemical composition changes than the other seasons because it will make the $\log([\text{NH}_3]/[\text{NH}_4^+])$ part in equation 2 more sensitive to chemical component changes...”

“...However, the effect of the addition of total nitrate is more complicated. Based on equation [2], the added TNO₃ concentration can impact aerosol pH in two opposite ways. First, because ammonium nitrate is more hygroscopic than ammonium sulfate (Gysel et al., 2007), the particulate nitrate formation will raise the liquid water content [ALW] in aerosol, increasing the aerosol pH; however, nitrate formation will also scavenge NH₃ from gas phase, and the smaller value of $[\text{NH}_3]/[\text{NH}_4^+]$ will make aerosol more acidic. These two factors altogether contribute to the arc-shaped curve of the relationship between aerosol pH and nitrate shown in Figure 8(b). Figure S7 shows...”

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?

[We agree with this point and have changed this statement.]

“...calculate the aerosol water content and the H^+ concentration through the equilibrium among acids and their conjugate bases.”

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 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 constituent 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...).

[We agree that for the S curve there is a range of pH corresponding to sharp change in the phase partitioning of semi-volatile bases or acids. However, we'd like to make a point that the pH being insensitive to phase partitioning is not equivalent to pH being poorly constrained or less reliably calculated. Even gas phase (or particle phase) fraction does not fall into 20% to 80%, pH can still be reliably calculated as long as the measurement has enough accuracy. For example, if $Frac(NH_3) > 80\%$, aerosol pH can still be reliably calculated with the accurate input, while the difference is that pH is less sensitive to NH_3 concentration under higher $Frac(NH_3)$ conditions.]

Line 15, as noted above, measured NH_3/NH_4^+ constraint on pH only works when there is some fraction in each phase. If the particle pH is very low or high, then it is possible for the system to 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.

[We agree that there is an optimal range for NH_3/NH_4^+ constrained pH calculation. However, we wish to note that there is no clear boundary between whether it is NH_3/NH_4^+ affecting aerosol pH, or aerosol pH affecting NH_3/NH_4^+ phase partitioning. Especially for particles made mostly of ammonium salts, the equilibrium between NH_4^+ and H^+ is the strong constraint of aerosol acidity. Another way to look at it is through the interpretation of Figure 5, the largest aerosol pH gradient occurs in the regions where there is little free gas phase NH_3 . In these regions, a small change in gas phase NH_3 concentration will result in a large aerosol pH change. In this case, it is hard to tell whether it is the modelling that has the poor constraint or the aerosol pH itself actually dramatically changing.]

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.

[We have also now included these limitations in the discussion of aerosol pH calculation.]

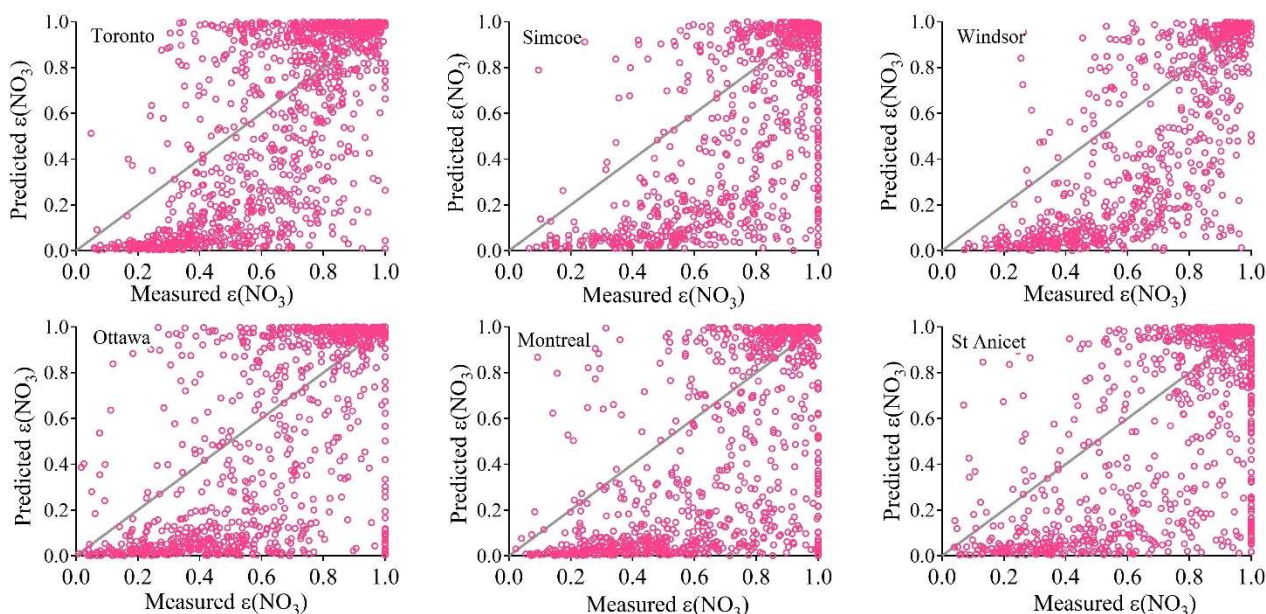
“... The reliability of the pH calculations depends on several assumptions, including that daily average values are appropriate for the calculations, and that the gas and particles phases are equilibrated. The limitations of using E-AIM II model also include the lack of consideration of non-volatile cations, aerosol liquid water contributed by organic species or possible phase separation etc. One rigorous method to evaluate the reliability of the calculated pH is to compare the input (measured) and output (modelled) gas-particle partitioning of semi-volatile species...”

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.

[In the final published version of Murphy et al. 2017 Faraday Disc paper, the pH is calculated with the molality-based activity, which is consistent with our current paper. The values of aerosol pH calculated in the two papers fall within the approximately same range.]

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.

[We put the comparison between predicted and measured $\epsilon(\text{NO}_3)$ in the graph below, which showed poor correlation. According to the results shown in Figure S5, for most of the model output, nitrate phase partitioning tended toward extreme values ($\epsilon(\text{NO}_3) < 20\%$ or $> 80\%$). In contrast, measured $\epsilon(\text{NO}_3)$ are distributed more evenly. Combined with the low concentration levels at these sites, both the measurement uncertainties and the presence of non-volatile cations drive large uncertainties in $\epsilon(\text{NO}_3)$. We also have evidence to suggest that sometimes it's improper to use daily average concentration and meteorological parameters to calculate average $\epsilon(\text{NO}_3)$, and it is also questionable to involve all non-volatile cations in predicting nitrate phase partitioning. We intend to address this issue more fully in a separate study.]



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 nonvolatile 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^+ .

[We have now added more discussion about how this assumption will affect the prediction results in this paragraph.]

“Using Na^+ to replace other non-volatile cations does not account for the precipitation of CaSO_4 , which has the same effect on aerosol pH of reducing sulfate. The substitution also does not perfectly reflect the impact on aerosol liquid water content, which may indirectly affect the pH. In general, the gas fraction of NH_x calculated from the output of the thermodynamic model matches very closely with the measured gas fraction of NH_x (Figure S2), suggesting that we are not missing substantial contributions to the ion balance in the particles by only considering ammonium sulfate.”

Pg 6 Line 26 typo.

[We have corrected this sentence.]

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).

[Thanks for providing another way to interpret this phenomenon. In this paper, we tend to focus on the effect the NH_x phase partitioning on the aerosol pH and wish to maintain consistent throughout the discussion. Figure 5(b) shows that for summertime aerosol that has little influence from nitrate, we can still see that aerosol pH becomes more sensitive to chemical composition when NH_x :sulfate is closer to 2; similarly, in wintertime aerosol pH becomes less sensitive to chemical composition in regions with higher NH_x :sulfate ratio.]

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?

[We added the explanation in this part that is focused on the potential influence from NH_x phase partitioning.]

“...made aerosol pH much more sensitive to chemical composition changes than the other seasons because these will make the $\log([\text{NH}_3]/[\text{NH}_4^+])$ part in equation 2 more sensitive to chemical component changes.”

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Guo, H., A. P. Sullivan, P. Campuzano-Jost, J. C. Schroder, F. D. Lopez-Hilfiker, J. E. Dibb, J. L. Jimenez, J. A. Thornton, S. S. Brown, A. Nenes, and R. J. Weber (2016), Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States, *J. Geophys. Res. Atmos.*, 121(17), 10,355-310,376.

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