Reviewer 1#

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.

[Thanks. We have included this statement in the conclusion part.]

"…This study focused on a number of sites with relatively low ambient mass loadings of aerosol inorganic constituents dominated by sulfate-nitrate-ammonium system. Regions in which $PM_{2.5}$ is strongly influenced by dust or marine sources may have different sensitivities for chemical and meteorological factors. However, for places…"

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?

[In this sampling apparatus, a backup nylon filter is used to capture the volatilized nitrate from the Teflon filter and to correct for semi-volatile ammonium nitrate loss. The subsequent evaporation of nitrate from the nylon filter has been proved to be negligible by Yu et al. (2006).]

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, artic air influences many of the sites? The interpretation of pH under conditions with a low fraction of ALW seems questionable.

[In our pH calculation, aerosol is forced to be metastable with no solid formation allowed, as mentioned in section 2.4. Our data show that almost all sampling days had average RH higher than 40%, larger than the efflorescence relative humidity of ammonium sulfate, so the aerosol is likely to have deliquesced during the diurnal variation of RH and T. After selecting all the sampling events with RH<40%, as shown in the below figure, the predicted $F(NH_3)$ still has good agreement with the

measured F(NH$_3$) for most of the data points. As a result, this assumption does not have significant impact on our calculation.]
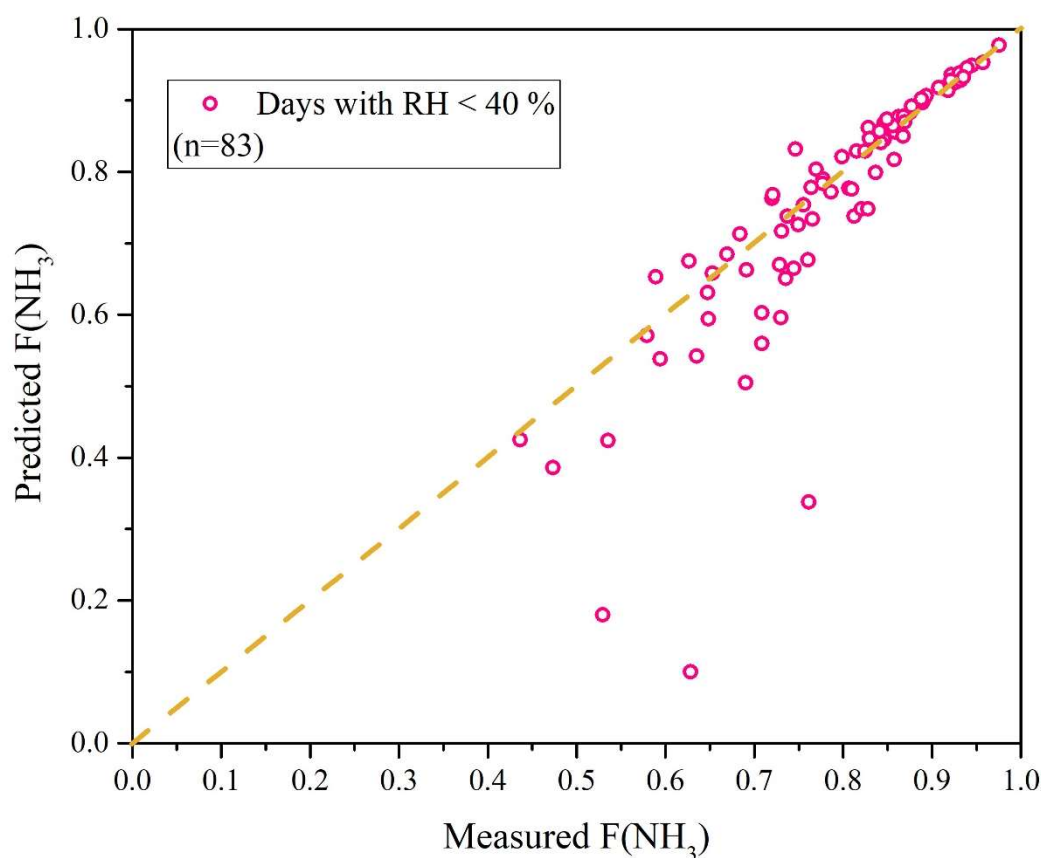
The authors should replicate Figure S2 with the predicted and measured ε(NO3).
[We put the comparison between predicted and measured ε(NO$_3$) in the graph below, which showed poor correlation. According to the results shown in Figure S5, for most of the model output, nitrate phase partitioning tended toward extreme values (ε(NO$_3$) <20 % or >80 %). In contrast, measured ε(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 ε(NO$_3$). We also have evidence to suggest that sometimes it's improper to use daily average concentration and meteorological parameters to calculate average ε(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.]

Toronto Simcoe Windsor Ottawa Montreal St Anicet

Predicted ε(NO₃) vs Measured ε(NO₃)
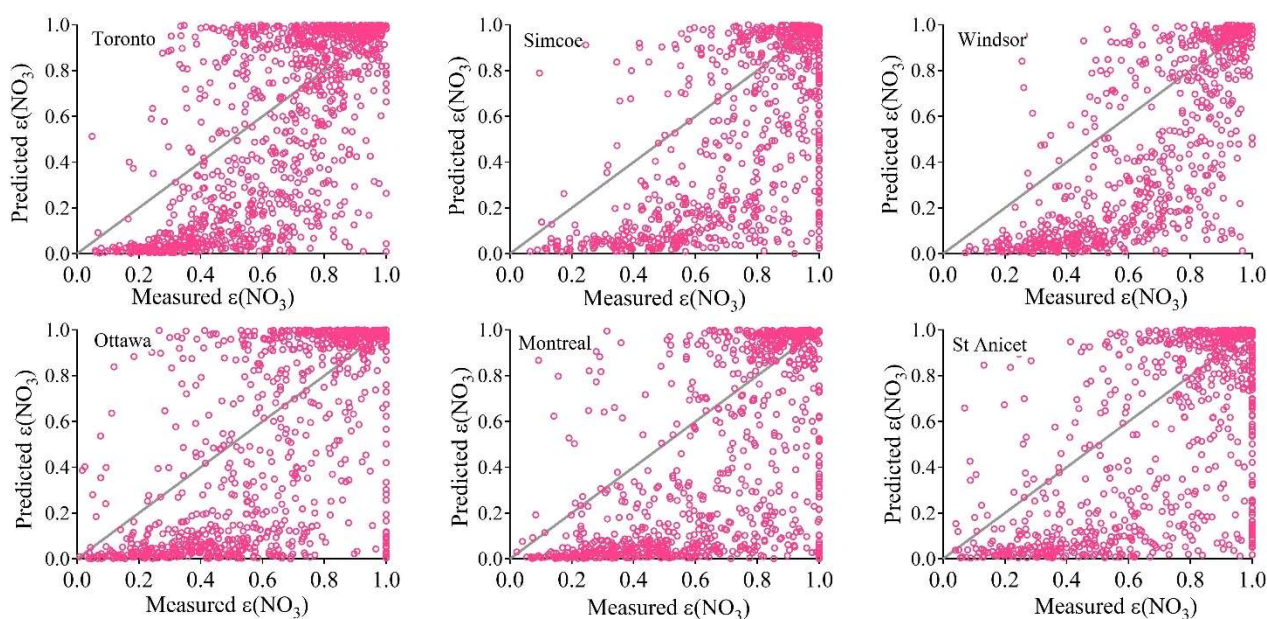
While the authors find only minor effects of non-volatile cations (NVC) in their analysis, the limitations of this analysis need to be discussed. For example, Ca and Mg salts are typically much less soluble than analogous Na salts – replacing Ca and Mg with equivalent Na therefore does not account for 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.

[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."

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.

[The plot of daily average RH and T shows very poor correlation (as shown in the figure below for the Toronto site, the other five sites all have similar pattern), suggesting that we do not need to be concerned about this as a confounding factor in our interpretation of the dominant cause of the seasonal variation pattern of aerosol pH. Based on our conceptual modelling of aerosol pH sensitivity to RH and T in Figure 4, it can be seen that under fixed chemical composition and temperature, the effect of changing relative humidity in changing pH is relatively small compared to temperature. Changing relative humidity from 40% to 90% generally can change aerosol pH within 0.5 unit, while the seasonal variation of temperature can drive aerosol pH oscillating between 2 and 4.]
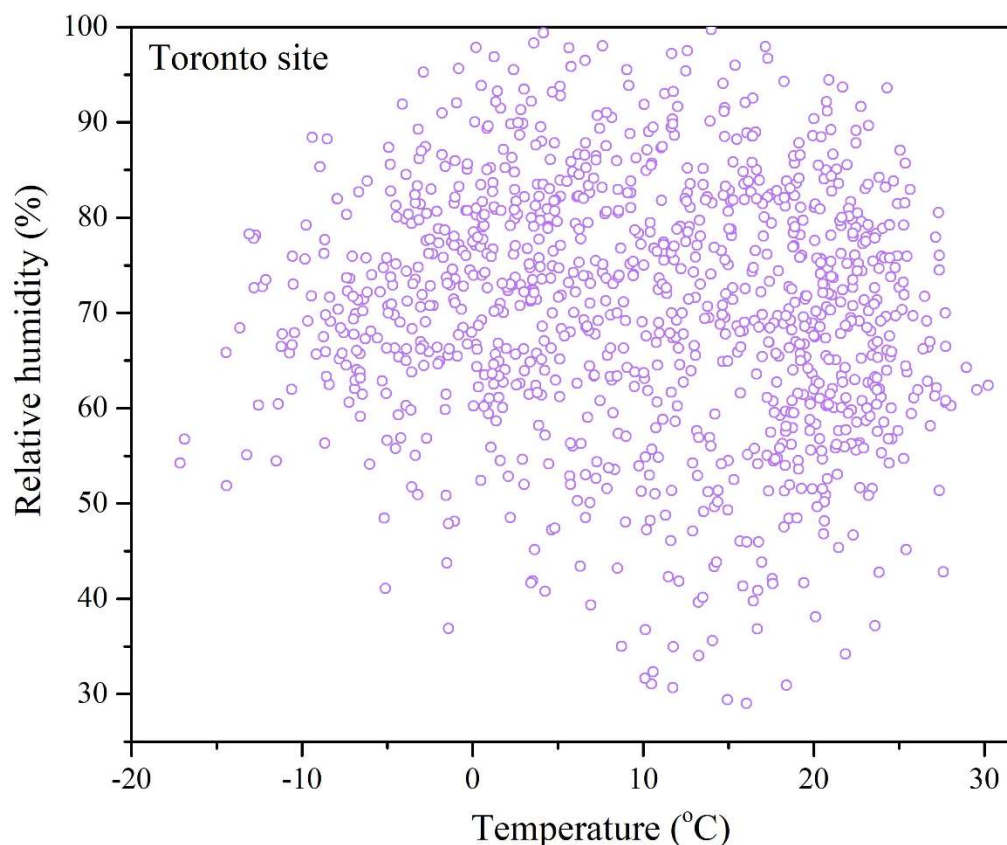
I found the explanation of Fig. 8b (pg. 9, line 12-24) to be quite confusing.

[We have rewritten this part to describe the process in more detail.]

"…However, the effect of the addition of total nitrate is more complicated. Based on equation [2], the added TNO_3 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 NH_3 from gas phase, and the smaller value of $[NH_3]/[NH_4^+]$ 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…"

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 HSO4-/SO42- 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.
[Thanks for pointing that out. We have changed this description.]

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

Technical Corrections:
Pg. 1, line 10 "constitute" or "constituent"?
[We have made the change.]

Pg. 2, line 7: say "aerosol aqueous phase" instead of "aerosol liquid water"
[We have made the change.]

Pg. 2, line 8: suggest deleting "very"
[We have made the change.]

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?
[We have extended this part for detailed explanation.]

"…Under equilibrium, aerosol pH can be theoretically derived from the observed gas/particle concentration ratio of NHx and aerosol liquid water [ALW] as: $pH = log([NH_3]/[NH_4^+])+log[ALW]+pKa+logK_H$, which Hennigan et al. (2015) showed having good agreement with E-AIM modelling results. Because both K_H and pKa have strong temperature dependencies (Chameides, 1984; Bell et al., 2007), aerosol pH is going to be temperature-dependent even if liquid water content or NH_3/NH_4^+ partitioning behavior does not change. The partial derivative of aerosol pH dependence on temperature will give $\partial pH/\partial T=\partial(pKa+logK_H)/\partial T\approx-0.05$ (K^{-1}), which corresponds to 0.1 unit increase (decrease) of aerosol pH if temperature decreases (increases) by 2 °C. The pH gradient shown in Figure 4 also illustrated that approximately 10 °C increase of temperature is required for 0.5 unit decrease in aerosol pH under the same chemical composition and RH, which is consistent with the temperature sensitivity derived through NHx phase partitioning method."

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.
[We have made the change.]

Pg. 10, line 6-7; why would aerosol loading affect the results?
[We will rephrase this sentence with more accurate description. According to the aerosol pH calculated under different chemical composition shown in Figure 5, it's both the concentration of particulate chemical composition and gas phase NH_3 that determine the aerosol pH sensitivity.]

"…for places with high particulate pollution and different concentration level of NH₃, similar approaches can also be applied…"

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?
[We intend to make a point that there is a possibility of misrepresenting organosulfates as inorganic sulfate. We have added this explanation in the main text]

"…the potential contribution from organic acids or organosulfates (the error caused by misrepresenting organosulfates as inorganic sulfate) will also have a more significant impact…"

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.
[We have refined the color used for plotting these figures.]

Address grammar and/or awkward phrasing in the following places: pg. 6, line 26; pg. 7 line 28; pg. 7 line 30.
[We have rephrased these sentences.]

"…aerosol pH is going to be temperature-dependent even if…"
"…where it shows that with fixed chemical composition, aerosol will be slightly less acidic at higher RH."
"…Apart from the effect of lower temperature, lower concentration of NHx and lower NHx to sulfate molar ratio also made aerosol pH much more sensitive to chemical composition changes…"

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.
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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.