Reviewer 3#

The paper used E-AIM model to calculate the pH of six Canadian cities over the course of 10 years. The paper states that (1) summer pH is about 1 unit lower than winter aerosol pH; (2) the pH is dependent more on meteorological conditions in the summertime. In winter time both chemical composition and meteorological conditions influence the pH.

This paper is written clearly with a dataset that is suitable to be published in ACP. As the author stated, this paper is probably "the first long-term aerosol pH study in Canada" and provides the "longest records for evaluation of trends in the world". I enjoyed reading the paper and suggest the authors consider the following before having the manuscript published.

The author made a conclusion on the effects of temperature on aerosol pH in page 6, line 20-22: "This result suggests the central role of meteorological conditions, especially temperature, in the determination of aerosol pH seasonal cycle in mid- and high-latitude regions. "Despite that the evidence raised by the author did support this argument, I think extending the 6 cities dataset to all "mid- and high-latitude regions" is a bit too strong. For instance, what if there are farmland areas where ammonia emissions have a strong seasonal cycle. Then the temperature factor may not be the only dominant factor. I would advise the author to make some restrictions on this sentence.

[We agree to this point. Our conclusion stands when the chemical composition has NHx>> sulfate, as it will be discussed in the later section that lower NHx:sulfate molar ratio will lead to larger sensitivity to composition changes, so we have revised this sentence to a more rigorous description.]

"This result suggests the central role of meteorological conditions, especially temperature, in the determination of aerosol pH seasonal cycle in mid- and high-latitude regions with NHx >> sulfate in chemical composition."

One of the key assumptions in Figure 5 and 8(a) is that the sulfate:TNO3 ratio is 1:2. The author backed up this assumption in the text because in Toronto the average ratio of sulfate:TNO3 over the course of 10 years is about 1:2. However, since figure 5 examines the effects of chemical composition and temperature on pH from a seasonal perspective, is the sulfate:TNO3 ratio still 1:2 for each season? The author should show seasonal averaged information of sulfate:TNO3 to support that the ratio is still ~1:2, otherwise a sensitivity study of how sulfate:TNO3 influences the pH should be shown in the manuscript. Figure 5 should also simulate each season based on the actual sulfate:TNO3 ratios.

[We added the calculation showing the influence of this assumption to aerosol pH in each month in each sampling site.]

"One key assumption in the above conceptual modelling is forcing total nitrate to sulfate molar ratio to be 2. To test the effect of this assumption on the aerosol pH, we calculate the pH of aerosol on each sampling day assuming total nitrate to sulfate molar ratio to be 2 and compare with the pH calculated with the measured total nitrate. The results show that this assumption has negligible influence on aerosol pH for samples from April to November but has larger influence on wintertime aerosol, indicating that wintertime aerosol is more sensitive to nitrate concentration (the statistical summary is shown in Figure S6). The influence of nitrate to wintertime aerosol pH will be further discussed in section 3.4."

The authors stated that "Noticeably, when aerosol pH shows a decreasing trend with TNO3 concentration, there is still excess NH3 in the gas phase" in page 9, line 17. Theoretically, there will always be some level of NH3 in the gas phase, despite the absolute value might be small. Therefore, the author should define what "excess NH3" means here. Maybe a plot of NH3 concentration as a function of TNO3 concentration should be shown in Figure 8 as well to show that the NH3 concentration does not change too much with increasing TNO3 values. Maybe the authors could also add a couple of sentences to clarify why a decreasing pH would still lead to an excess NH3 concentration.

[We have rewritten this part to focus on the effect of ammonium nitrate formation on aerosol pH.]

"…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…"

Besides the typos mentioned by the previous reviewers, another typo I noticed is that the state "Vermont" is misspelled in Figure 1.

[Thanks for pointing out. We have corrected this typo.]

References:

Weber, R. J., et al. (2016). "High Aerosol Acidity Despite Declining Atmospheric Sulfate Concentrations over the Past 15 Years." Nature Geosci 9(4): 282-285.

Guo, H., et al. (2015). "Fine-Particle Water and Ph in the Southeastern United States." Atmos. Chem. Phys. 15(9): 5211-5228.