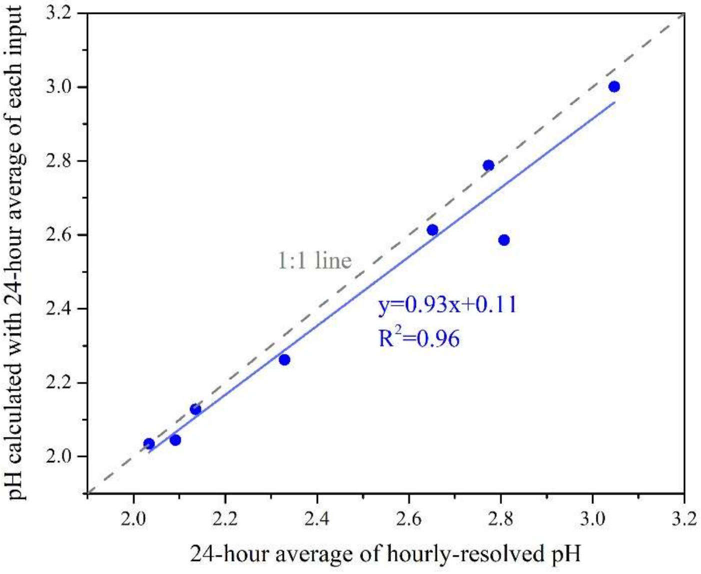
Reviewer 4#

Overall, the paper is well written and contributes meaningful analysis to the community. The authors could further justify their approach (general comment 1) and provide more supporting information (specific comment 2).

General comments: 1. Given the importance of meteorological drivers of pH (RH and T) indicated by the analysis, how did the authors justify the use of daily average RH, T, and composition led to the appropriate average pH? How important are diurnal variations in RH, T, and composition in dictating daily average pH?

[This is an important question given that many monitoring datasets available for aerosol pH calculation provide only 24-hour observation of chemical composition. The diurnal changes of RH and T can also drive diurnal variation in aerosol pH, just as they do on a seasonal scale. If both chemical composition and meteorological factors are changing within the 24-hour sampling period, the definition of the "average pH" of these particles are crucial for the justification of the calculation. Here we simply define the average pH of aerosol as pH calculated under 24-hour average concentrations and meteorological parameters, and evaluate how well this can successfully reconstruct the phase partitioning of NHx. The degree to which the diurnal variation of pH can deviate from this average value cannot be determined with the 24-hour average data, but is related to the sensitivity to each factor, which is partially addressed by this paper. For example, we have shown that $\partial pH/\partial T \approx -0.05$ (K^{-1}), so this rule will also hold for the diurnal pH variation. The graph below shows the comparison of summertime Toronto aerosol pH calculated with the 24-hour average values of meteorological parameters and chemical composition and the daily average of the hourly pH values (the data are from VandenBoer et al. (2011)), which showed high consistency. This result indicates that using daily average parameters to calculate aerosol pH is reliable.]



2. The manuscript presents evidence that long-term changes in pH are driven by changes in RH and T (Fig 6-7), however, sulfate likely correlates with T. St. Anicet and Toronto do not have statistically significant changes in sulfate over the time period. Is pH at those sites related to sulfate?

[On Figure 6 and 7, if we select data of Toronto and St Anicet sites from year 2013 to 2016, we can see that sulfate concentrations were continuously decreasing but aerosol pH at these two sites both showed minimum values in year 2014 due to the highest temperature at that year. This pattern indicates that aerosol pH was more significantly affected by temperature than by sulfate.]

Specific comments:

1. In a couple place, the authors mention "ion balance" which could imply they used a charge balance. I suggest rewording on page 1, line 9 and page 4, line 21. Page 4, line 21 indicates SNA contributed more than 80% of total charges. What is the remaining 20%? Salts (NaCl) and NVC are neglected. Are they important?

[We have reworded these two sentences. We also have assessed the influence of NVC by comparing the pH calculated with E-AIM II and E-AIM IV model, suggesting that the NVC will not affect the pH significantly. We also have added more discussion about this result in the response to Reviewer 2# comment.]

"…the H^+ concentration through the equilibrium among acids and their conjugate bases…"
"…more than 80% of total measured charges in the particles…"
"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 NHx calculated from the output of the thermodynamic model matches very closely with the measured gas fraction of NHx (Figure S2), suggesting that we are not missing substantial contributions to the ion balance in the particles by only considering ammonium sulfate."

2. At a minimum, tabulated pH values should be provided in the SI. The authors should consider providing additional data and/or model inputs/outputs for data documentation purposes.

[We will upload our dataset about chemical composition and pH calculation in the supplement excel file of this paper.]

VandenBoer, T. C., Petroff, A., Markovic, M. Z., and Murphy, J. G.: Size distribution of alkyl amines in continental particulate matter and their online detection in the gas and particle phase, Atmospheric Chemistry and Physics, 11, 4319-4332, 10.5194/acp-11-4319-2011, 2011.