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The sensitivity of PM$_{2.5}$ acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites

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Abstract. 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 the equilibrium among acids and their conjugate bases. In practical terms, simultaneous measurements of at least one semivolatile constituent, e.g. NH$_3$ or HNO$_3$, are required to provide a constraint on the calculation of pH. Long-term records of aerosol pH are scarce due to the limited monitoring of NH$_3$ in conjunction with PM$_{2.5}$. In this study, 10-year (2007–2016) records of pH of PM$_{2.5}$ at six eastern Canadian sites were calculated using the E-AIM II model with the input of gaseous NH$_3$, gaseous HNO$_3$ and major water-soluble inorganic ions in PM$_{2.5}$ provided by Canada's National Air Pollution Surveillance (NAPS) Program. Clear seasonal cycles of aerosol pH were found with lower pH ($\sim$ 2) in summer and higher pH ($\sim$ 3) in winter consistently across all six sites, while the day-to-day variations of aerosol pH were higher in winter compared to summer. Tests of the sensitivity of aerosol pH to meteorological parameters demonstrate that the changes in ambient temperature largely drive the seasonal cycle of aerosol pH. The sensitivity of pH to chemical composition shows that pH has different responses to the changes in chemical composition in different seasons. During summertime, aerosol pH was mainly determined by temperature with limited impact from changes in NH$_x$ or sulfate concentrations. However, in wintertime, both meteorological parameters and chemical composition contribute to the variations in aerosol pH, resulting in the larger variation during wintertime. This study reveals that the sensitivity of aerosol pH to chemical composition is distinctly different under different meteorological conditions and needs to be carefully examined for any particular region.

1 Introduction

Aerosol acidity is among the most important parameters for atmospheric particulate chemistry as it has a large impact on both gas–particle partitioning of semi-volatile ionizable components and rates of many reactions occurring in aerosol liquid water (Seinfeld and Pandis, 2006; Losey et al., 2016; Guo et al., 2017a; Nah et al., 2018; Freedman et al., 2019). Laboratory and field studies have also shown that enhanced acidity in aerosol can increase the formation of secondary organic aerosol (Surratt et al., 2007; Zhang et al., 2007b), one of the major components responsible for particulate air pollution (Zhang et al., 2007a; Huang et al., 2014). Studies have shown that highly acidic particles can have adverse health effects related to respiratory diseases (Utell et al., 1983; Dockery et al., 1996). More acidic particles can enhance the solubility of several trace metals in fine particulate matter (PM$_{2.5}$) to induce oxidative potential inside the human body as an indirect health effect of acidic particles (Fang et al., 2017).

pH is the parameter frequently used to describe the acidity of the aerosol aqueous phase and is calculated as the negative logarithm of hydrogen ion activity. Few methods can directly measure the pH of aerosol (Rindelaub et al., 2016; Craig et al., 2018; Wei et al., 2018), so aerosol acidity is usually presented using indirect proxies such as ion balance (cation-to-anion ratio), neutralization ratio ([NH$_4^+$]/(2[SO$_4^{2-}$]) +

[NO$_3^-$]) and strong acidity (Σcation-Σanion) (Yao et al., 2006; Du et al., 2010; Zhou et al., 2017). However, these indirect methods can lead to substantial uncertainty in acidity assessment (Hennigan et al., 2015; Guo et al., 2016; Murphy et al., 2017). Calculation of pH through thermodynamic modelling such as E-AIM (Clegg et al., 1998) and ISORROPIA II (Fountoukis and Nenes, 2007), with the input of reliable chemical compositions of the aerosol and at least one semi-volatile gas and meteorological data, has been shown to be a more rigorous approach to calculate the pH of aerosol liquid water. Murphy et al. (2017) and Song et al. (2018) both showed that the constraint from phase partitioning of NH$_3$/NH$_4^+$ should be included in calculations using aerosol thermodynamic models to get reliable pH calculations, which indicates that NH$_3$ observation can greatly improve the reliability of the aerosol acidity assessment.

However, long-term observations of NH$_3$ with corresponding particulate matter composition measurements are very scarce. Some of the few long-term monitoring networks are NAMN in the UK, SEARCH in the US and NAPS in Canada. In the UK, 30 of the NAMN (National Ammonia Monitoring Network) sites have been providing monthly-integrated NH$_3$ and particulate inorganic ionic composition data since 2000 (Tang et al., 2018). SEARCH (Southeastern Aerosol Research and CHaracterization Network) is one long-term monitoring program of NH$_3$ in the United States, which has both 24 h average gas phase NH$_3$ and particle phase ionic species measurements at eight sites located in the southeastern United States with a 3 d sampling frequency. In Canada, the National Air Pollution Surveillance (NAPS) program is the only program employing the long-term measurement of 24 h average NH$_3$ concentrations with a 3 d sampling frequency at 12 monitoring sites where PM$_{2.5}$ constituents are also measured.

Several studies have examined the response of pH to changes in chemical composition with conceptual modelling. Weber et al. (2016) showed that in summertime, aerosol tends to remain highly acidic with the reduction of sulfate and the increase in the ammonia-to-sulfate ratio. The modelling results of Guo et al. (2017b) showed that for wintertime meteorological conditions aerosol pH has similar sensitivity to NH$_3$ concentrations in China and the eastern US under fixed temperature and relative humidity. These two sensitivity tests of aerosol pH suggest that aerosol pH seems to have weak response to chemical composition changes. However, these studies both carried out conceptual modelling or calculations under fixed meteorological parameters. The time series of aerosol pH in six regions within the United States calculated by Lawal et al. (2018) showed that pH has seasonal variation that depends on the region, suggesting that changes in meteorological conditions can also contribute to pH changes. Thus, the relative contributions of changes in meteorological conditions and chemical composition to variability in pH are still unclear and require systematic studies. As a result, in this study, we focus on the long-term variations

of aerosol pH at six eastern Canadian sites (four urban and two rural) along with conceptual modelling of the sensitivity of aerosol pH to meteorological parameters and chemical composition changes to assess the major factors determining aerosol pH, and its variability, in different sites and seasons.

2 Data sources and analysis method

2.1 NAPS database and chosen study sites

All the PM$_{2.5}$ composition and trace gas data used in this study were downloaded from the NAPS program website (http://maps-cartes.ec.gc.ca/rnspa-naps/data.aspx, last access: 4 December 2018). The NAPS program provides long-term monitoring of air-quality-relevant pollutants at various sites across Canada. Altogether, there are 12 sites with comprehensive gas phase and particle phase composition measurements, including 4 coastal sites (Halifax, Saint John, Burnaby and Abbotsford), 1 central site (Edmonton) and 7 eastern sites (Toronto, Simcoe, Hamilton, Windsor, Ottawa, Montreal and St Anicet). Ambient samples of gaseous components (including NH$_3$ and HNO$_3$) and the dominant inorganic components of PM$_{2.5}$ were taken over 24 h from 00:00 to 24:00, generally every 3 d.

Six sites in the provinces of Ontario and Quebec were chosen for this study (Fig. 1), including Toronto (the largest city in Canada), Ottawa, two other metropolitan cities (Windsor and Montreal) and two sites in rural regions (Simcoe and St Anicet). The details of these monitoring sites including their longitudes and latitudes, NAPS monitoring station codes, and duration of the data record used for this study can be found in Table S1 in the Supplement. These sites were chosen because (1) they have long-term (at least 8-year) records of gaseous and PM$_{2.5}$ chemical components concentrations, and (2) they are located in the central region of North America with little influence of sea salt (Vet et al., 2014) and therefore the acidity of PM$_{2.5}$ is mainly dominated by the chemistry of sulfate, total nitrate and total ammonia (Young et al., 2013; Allen et al., 2015; Hennigan et al., 2015).

Measurements of 24 h average concentrations between 2007 and 2016 of alkaline and acidic gaseous components and major water-soluble inorganic ions in PM$_{2.5}$ were used in this study for pH calculation. Citric acid-coated denuders were used to collect gas phase NH$_3$ samples. Na$_2$CO$_3$-coated denuders were used to collect gas phase HNO$_3$ samples. After alkaline and acidic gases were removed by passing through the two denuders, PM$_{2.5}$ samples were captured by a filter pack consisting of a front Teflon filter and a backup Nylon filter. The benefit of a nylon filter is that it captures volatized nitrate during sampling as the artefact of the evaporation ammonium nitrate and corrects the data accordingly (Yu et al., 2006; Babich et al., 2011). All the extracts were measured by ion chromatography. Field blanks were routinely performed as the background corrections. The detailed

Figure 1. Six NAPS monitoring sites chosen for this study: Toronto, Ottawa, Windsor, Montreal, Simcoe and St Anicet.

protocol for ambient constituent measurements for the NAPS database can be seen in Dabek-Zlotorzynska et al. (2011). In total, there are 1067, 851, 711, 840, 713 and 742 sets of valid data used at the sites of Toronto, Ottawa, Windsor, Montreal, Simcoe and St Anicet, respectively.

Relevant historical meteorological data including hourly average temperature, relative humidity and atmospheric pressure were downloaded from http://climate.weather.gc.ca (last access: 22 April 2019). The closest stations with complete data recordings were chosen as the meteorological data source. The 24 h average values of meteorological parameters during each sampling time period were calculated and used as the input for E-AIM thermodynamic calculation. Specifically, the St Clair meteorological station was chosen as the meteorological data source for the Toronto NAPS site (0.9 km from sampling site), the Delhi CS station for the Simcoe site (21 km), the Windsor A station for the Windsor site (9 km), the Ottawa CDA RCS station for the Ottawa site (6 km), the McTavish station for the Montreal site (16 km) and the St-Anicet 1 station for the St Anicet site (0.1 km).

2.2 E-AIM thermodynamic modelling

The Extended AIM thermodynamic model (http://www.aim. env.uea.ac.uk/aim/aim.php, last access: 29 August 2018) was applied for the calculation of aerosol acidity as E-AIM relies on few assumptions during the calculation of aerosol inorganic components' behaviour and it can also calculate the activity coefficient of each ion, which is crucial for aerosol pH calculation (Wexler, 2002). Specifically, model II, which mainly focuses on the thermodynamic calculations of the H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O system (Clegg et al., 1998), was used in this study. Model II was chosen rather than model III or IV because it can deal with a wider range of

relative humidity and temperature, which gives more reliable information on the seasonal variation of aerosol acidity. The SNA (sulfate, nitrate and ammonium) components in PM$_{2.5}$ generally contributed more than 80 % of total measured charges in the particles. Temperature, relative humidity, total ammonia (summation of gas phase ammonia and ammonium in PM$_{2.5}$), total nitrate (summation of gas phase nitrate acid and nitrate in PM$_{2.5}$) and sulfate were used as the inputs for this model. Partitioning of both NH_3/NH_4^+ and HNO_3/NO_3^- allows for a strong constraint on the aerosol pH calculation (Murphy et al., 2017). Particles were forced to be metastable without any formation of salts or ice precipitation. Aerosol pH was calculated according to the following formula (Robinson and Stokes, 2002):

$$pH = -\log(a_H^+) = -\log(f_H^+ \times \chi_H^+ \times 55.509) \quad (1)$$

where a_H^+ is the activity of the hydrogen ion in aerosol liquid water, f_H^+ is the hydrogen ion's mole-fraction-based activity coefficient, χ_H^+ is the mole fraction of the hydrogen ion, and 55.509 is the conversion factor from a mole-based activity coefficient to a molality-based one. Model IV was also used to assess the influence from non-volatile cations.

3 Results and discussion

3.1 Time series of pH at six Canadian sites

The 10-year time series of PM$_{2.5}$ pH values at the six sites is illustrated in Fig. 2. To our knowledge, this is the first long-term study of aerosol pH in Canada and provides one of the longest records for the evaluation of trends anywhere in the world. The reliability of the pH calculations depends on several assumptions, including that daily average values
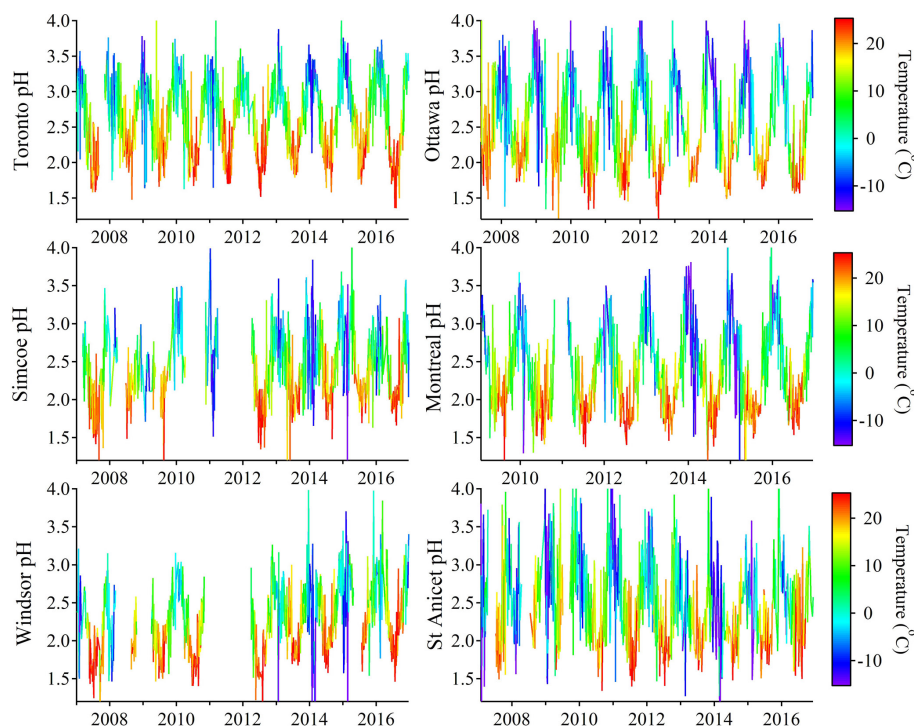
Figure 2. The time series of $PM_{2.5}$ pH at six sites coloured by ambient temperature.

are appropriate for the calculations, and that the gas and particle phases are equilibrated. The limitations of using the 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. The comparisons of modelled and measured gas phase fractions of total ammonia, denoted as $\text{Frac}(NH_3) = n(NH_3)/[n(NH_3) + n(NH_4^+)]$, are plotted in Fig. S2 in the Supplement, where the linear regressions were all close to 1:1 line with high R^2 (> 0.88), indicating that the E-AIM modelling results are consistent with the observed phase partitioning characteristics of NH_3/NH_4^+. The use of the phase partitioning of both NH_3/NH_4^+ and HNO_3/NO_3^- to constrain the aerosol pH helps to avoid significant over- or underpredictions (Murphy et al., 2017).

In Fig. 2, all the time series of aerosol pH show a strong seasonal oscillation pattern between 1.5 and 4.0. By colouring the pH values by ambient temperature, we can clearly see that particles were generally more acidic when ambient temperature was higher. This variation pattern is consistent in both spatial (six sites) and temporal (10-year) terms. In the long term, the seasonal variation of aerosol pH fits well with the variation of ambient temperature. However, larger variation of aerosol pH can be identified during wintertime. In some cases, the aerosol is very acidic, with pH < 2,

even when temperature $< 0\,^\circ\text{C}$. This variation pattern is more clearly illustrated in the box-and-whisker plots of pH in each month at six sites shown in Fig. 3. The pH values are lowest in the summer (July and August averages < 2) and highest in the winter (January and February averages > 2.5). The aerosol was consistently more acidic and had smaller pH variation in warmer months, and showed higher average (and median) pH values but exhibited larger variation in wintertime.

To assess the potential influence of non-volatile cations including Na^+, K^+, Mg^{2+} and Ca^{2+} on the seasonal variation pattern of aerosol pH, aerosol pH was also calculated using the E-AIM model IV (Friese and Ebel, 2010) with the input of a Na^+ concentration representing the contributions of all non-volatile cations ($[Na^+]+[K^+]+2[Mg^{2+}]+2[Ca^{2+}]$). The pH calculation results are illustrated in Fig. S3. Because E-AIM IV deals with a narrower range of meteorological conditions ($T \geq 263.15\,\text{K}$, RH $\geq 60\,\%$), E-AIM IV calculations were only possible for a limited part of the data sets. However, shown in Fig. S3, E-AIM IV modelling results show similar time series compared to E-AIM II results. These results confirm that the aerosol pH seasonal variation pattern was not significantly affected by the non-volatile cations. The involvement of non-volatile cations typically increases pH values by less than 0.1, and the change is less than 0.4 for more than 90 % of data (shown in Fig. S4). Using Na^+ to replace other non-volatile cations does not account for the precipitation of $CaSO_4$, which has the same effect on
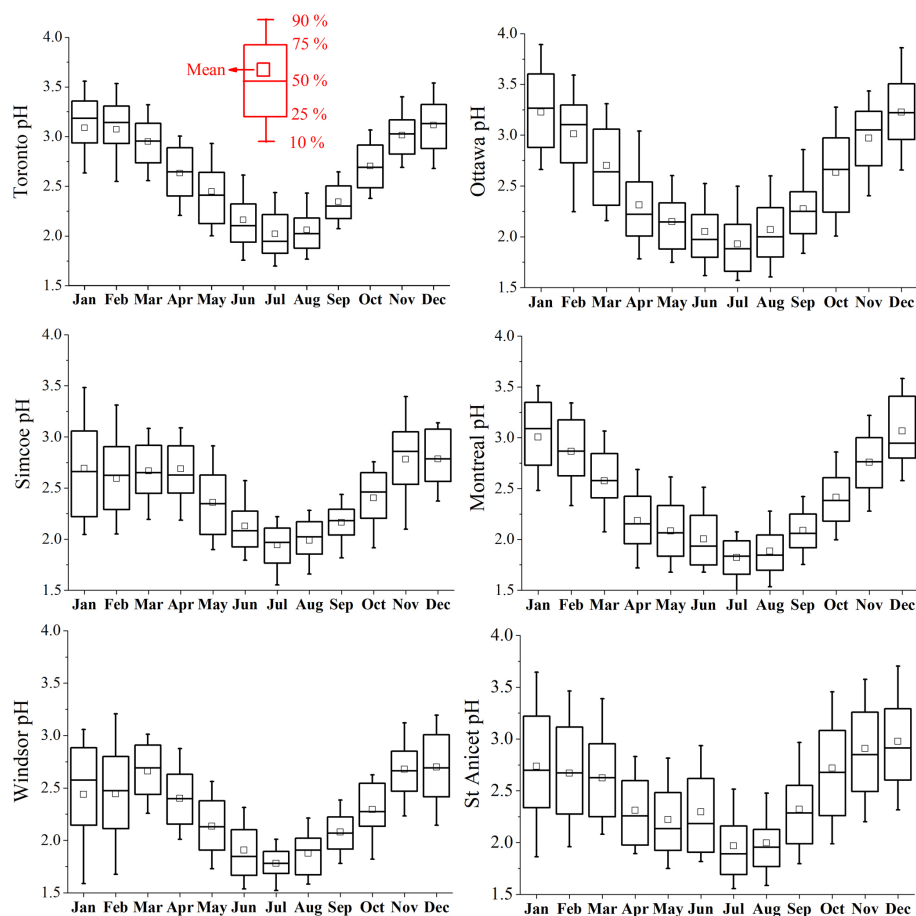
Figure 3. The box-and-whisker plot of aerosol pH in each month at six sites. In each box, the top, middle and bottom lines represent the 75th, 50th and 25th percentiles of statistical data, the upper and lower whiskers represent 90th and 10th percentiles, and the square marks represent the mean value.

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$_x$ (Fig. S2), suggesting that we are not missing substantial contributions to the ion balance in the particles by only considering ammonium sulfate.

The factors influencing aerosol pH can be roughly classified into two categories: meteorological parameters (including ambient temperature and relative humidity) and chemical composition (including gas phase and particle phase components). The following discussion will focus on the conceptual modelling of aerosol pH sensitivity to meteorological conditions in comparison to the impacts of changes in chemical composition.

3.2 Seasonal cycle of aerosol pH

To assess the sensitivity of aerosol pH to meteorological conditions and chemical composition changes individually,

we first examine the pH of aerosol with chemical composition held fixed at representative values under different meteorological conditions. Then we study the aerosol pH sensitivity to chemical composition changes under fixed typical meteorological conditions of each of the four seasons. Figure 4 displays the aerosol pH calculated under every combination of relative humidity from 30 % to 95 % and temperature from −10 to 30 °C with fixed chemical composition. The chosen concentrations for sulfate, TNO$_3$(= HNO$_3$ + pNO$_3$) and NH$_x$ are 15, 30 and 180 nmol m^{-3}, respectively, which are close to the 10-year average concentrations of chemical composition in the Toronto atmosphere (which were 17.6 nmol m^{-3} of sulfate, 34.2 nmol m^{-3} of TNO$_3$ and 188 nmol m^{-3} of NH$_x$).

It can be seen in Fig. 4 that particles tend to become more acidic at higher temperatures and lower relative humidity and become more neutralized when the temperature is lower or RH is higher. The square symbols in Fig. 4 are the monthly average values of ambient temperature and relative humidity in Toronto from 2007 to 2016 with standard deviations as error bars. The seasonal cycles of meteorological conditions at
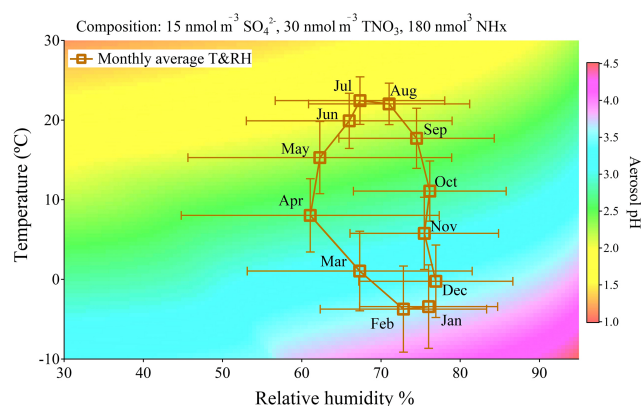
Figure 4. Plot of E-AIM calculated pH under different combinations of relative humidity (from 30 % to 95 %) and temperature (from −10 to 30 °C) with the fixed input chemical compositions (15 nmol m^{-3} sulfate, 30 nmol m^{-3} TNO$_3$ and 180 nmol m^{-3} NH$_x$). The square plots on the graph represent monthly averages of meteorological parameters in Toronto from 2007 to 2016 with standard deviations as error bars.

five other sites are listed in Table S2 and generally show similar seasonal cycling of RH and temperature. Even excluding changes in chemical composition, we find from Fig. 4 that we can explain the summer minimum and winter maximum in pH from Fig. 3. Temperature is the main factor driving the seasonal variation of aerosol pH while the changes due to RH variation are much smaller. 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 NH$_x \gg$ sulfate in chemical composition.

The temperature dependence of aerosol pH can be theoretically derived from the phase partitioning NH$_3$/NH$_4^+$ based on the equilibria NH$_3$(g) $\leftrightarrow$ NH$_3$(aq) and NH$_4^+$ $\leftrightarrow$ NH$_3$(aq) + H$^+$, which are governed by K_H and pKa, respectively (Hennigan et al., 2015). Under equilibrium, aerosol pH can be theoretically derived from the observed gas or particle concentration ratio of NH$_x$ and aerosol liquid water [ALW] as follows:

$$pH = \log([NH_3]/[NH_4^+]) + \log[ALW] + pKa + \log K_H, \quad (2)$$

which Hennigan et al. (2015) showed as 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 behaviour does not change. The partial derivative of aerosol pH dependence on temperature will give $\partial pH/\partial T = \partial(pKa + \log K_H)/\partial T \approx -0.05$ (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 Fig. 4 also illustrated that an approximately 10 °C increase of temperature is required for a 0.5 unit decrease in

aerosol pH under the same chemical composition and RH, which is consistent with the temperature sensitivity derived through the NH$_x$ phase partitioning method.

It is possible that the sensitivity of aerosol pH to chemical composition is different in different seasons. As a result, the sensitivity of aerosol pH to composition changes in each season is further studied through the conceptual modelling. In Fig. 5a–d the pH calculated under different combinations of NH$_x$ and sulfate concentrations under typical temperature and RH conditions in spring (April; $T =$ 10 °C, RH = 60 %), summer (July and August; $T = 25$ °C, RH = 70 %), fall (October; $T = 10$ °C, RH = 75 %) and winter (January and February; $T = -5$ °C, RH = 75 %) in the Toronto atmosphere are shown. Total nitrate concentrations were set to be 2 times larger than sulfate concentrations. This assumption is representative of the Toronto atmosphere as a 10-year average of sulfate concentration (17.6 nmol m^{-3}) is approximately half of the total nitrate molar concentration (34.2 nmol m^{-3}), though for any given day the ratio could be different. The corresponding calculation results of the particle phase fraction of nitrate ε(NO$_3^-$) in four seasons is shown in Fig. S5. During summer ammonium nitrate formation is unfavourable, 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 Sect. 3.4.

The markers in Fig. 5 represent the median and the range (from 10th percentile to 90th percentile) of NH$_x$ and sulfate concentrations in four seasons at six monitoring sites from 2007 to 2016. The three more westerly sites (Toronto, Windsor and Simcoe) tend to have higher sulfate in all seasons and Toronto has slightly higher NH$_x$. However, overall all six sites occupy regions of similar chemical sensitivity in the plots. The conceptual modelling of aerosol pH under summertime conditions, shown in Fig. 5b, suggests that the relatively low variability in summertime pH, shown in Fig. 3, results from the aerosol pH being insensitive to chemical composition changes under the corresponding meteorological conditions. Specifically, in summertime, pH was very constrained to the small range around 2 with little influence from the variation of chemical composition, even though the sulfate loadings were the most variable in the summer. Judging from the concentration ranges of sulfate and NH$_x$ shown in all six sites, in summertime even decreasing sulfate concentration by 1 order of magnitude does not significantly change the pH values, and this effect became more obvious with a higher NH$_x$: sulfate molar ratio.

By comparison, the pH calculated under spring and fall temperatures (10 °C) shown in Fig. 5a and c showed that pH became more sensitive to NH$_x$ variation but still remain quite insensitive to sulfate concentration changes within the relevant concentration range. In spring, the median concentrations of NH$_x$ at the sites of Toronto, Simcoe and Wind-
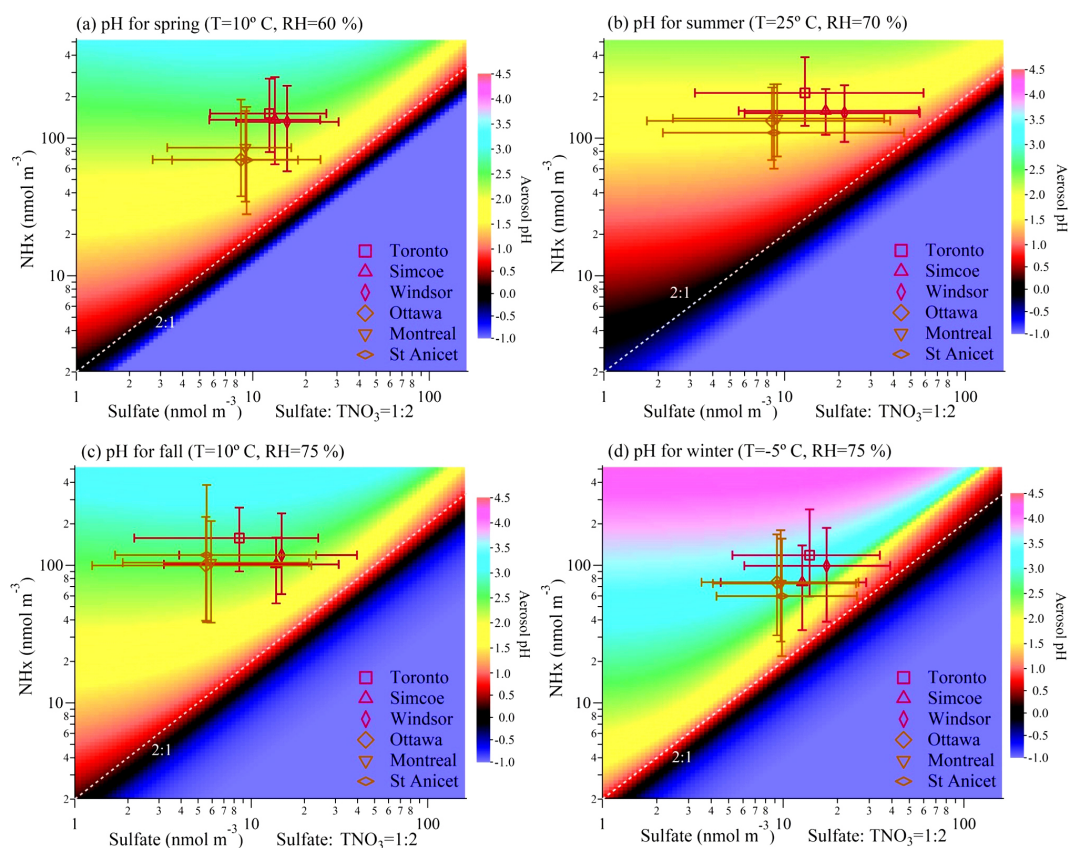
Figure 5. Aerosol pH calculated with fixed meteorological parameters (temperature and RH) under different combinations of NH$_x$ and sulfate concentrations. Total nitrate concentrations are set to be 2 times that of sulfate. The markers on the graph represent median summertime concentrations of NH$_x$ and sulfate at six sites from year 2007 to 2016 with error bars indicating the 10th percentile to 90th percentile. The fixed meteorological parameters chosen in panels **(a)**–**(d)** are representative of the conditions in spring (April), summer (July and August), fall (October) and winter (January and February) shown in Fig. 4.

sor were higher compared to the other three sites, leading to average April pH values in Toronto, Simcoe and Windsor (2.40–2.69) that were consistently higher than the other three sites (2.15–2.31). In October, NH$_x$ and sulfate concentrations had wider ranges of concentration, but we can conclude from Fig. 5c that the pH changes due to chemical composition were mainly driven by the variation of NH$_x$. The effect of relative humidity changes can be seen from the comparison between Fig. 5a and c, where it is shown that with fixed chemical composition, aerosol will be slightly less acidic at higher RH.

By comparison, under wintertime meteorological conditions, aerosol pH was higher in the region NH$_x$: sulfate > 2. Apart from the effect of lower temperatures, a lower concentration of NH$_x$ and 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([NH$_3$]/[NH$_4^+$]) part in Eq. (2) more sensitive to chemical component changes. This could contribute to the larger variation of wintertime aerosol pH shown in Figs. 2 and 3. In Simcoe, Windsor and St Anicet, the sites with lower

NH$_x$: sulfate molar ratios, wintertime pH values all exhibited significant variations. Under these conditions, not only the uncertainty in the SNA concentration measurements, but also the potential contributions from organic matter such as organic ammonium salts (Schlag et al., 2017; Tao and Murphy, 2018) or organosulfates (Vogel et al., 2016; Glasius et al., 2018), which current thermodynamic models do not fully consider, can contribute to uncertainty in aerosol pH calculation. These conceptual modelling results also provide insight into the challenges posed in the direct measurement of aerosol pH off-line as it is both strongly impacted by ambient environmental conditions and the NH$_3$ concentration equilibrated with the particle phase.

One key assumption in the above conceptual modelling is forcing the 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 a negligible influence on aerosol pH for samples from April to November but has a
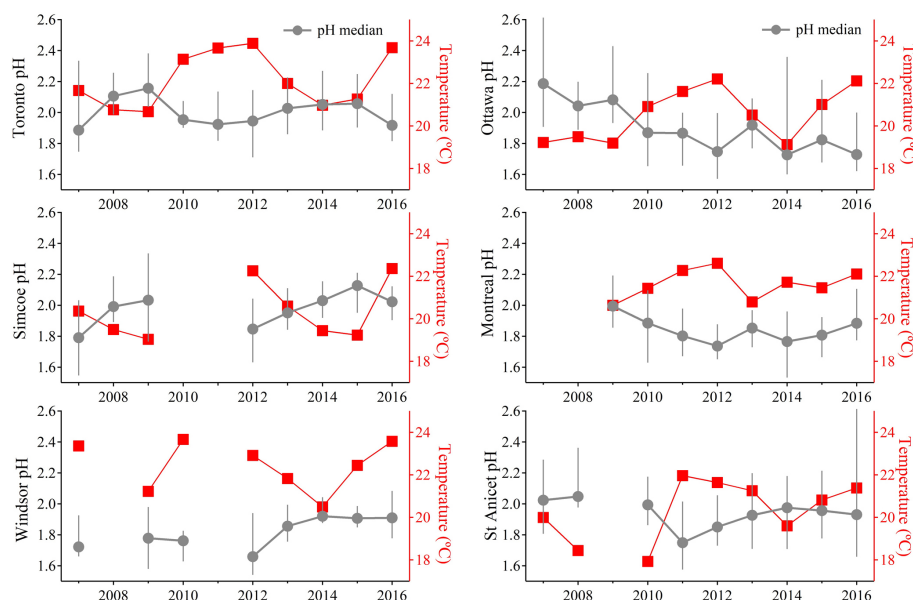
Figure 6. Median of aerosol pH in summertime (data on July and August) from year 2007 to 2016 at six monitoring sites. The error bars with median pH values represent the range from the 25th to 75th percentiles. Average ambient temperature in summertime (July and August) at each site is also plotted on right axis to illustrate the reverse trend of temperature with pH inter-annual variation.

larger influence on wintertime aerosol, indicating that wintertime aerosol is more sensitive to nitrate concentration (the statistical summary is shown in Fig. S6). The influence of nitrate on wintertime aerosol pH will be further discussed in Sect. 3.4.

3.3 Long-term trends of pH in summertime

The above time series analysis and conceptual modelling of aerosol pH suggest that in the study region during summertime, aerosol pH is strongly impacted by ambient temperature with much weaker response to the other factors, while during wintertime aerosol pH is affected by both temperature and chemical composition. Figure 6 shows the summertime (data from July and August) median aerosol pH in each year at the six monitoring sites. A summertime average temperature was also plotted on the right axes in each graph. The clear anti-correlation indicates that interannual variability in summer temperatures causes interannual variability in aerosol pH. Another application of this result can be found in Battaglia et al. (2017), who showed that urban aerosol in US cities tended to be more acidic than rural aerosol due to the urban heat island effect, consistent with the important role of temperature in aerosol pH determination.

The study conducted by Weber et al. (2016) found that in summertime, aerosol remained highly acidic even with a significant reduction of sulfate in the US. A similar conclusion could be drawn for conditions in Canada, where we found the role of temperature to be more significant than variations in chemical composition for trends in aerosol pH. Significant changes in the particle phase sulfate have been observed dur-

ing the summers of 2007–2016. Figure 7 displays the summertime average (data from July and August) concentrations of PM$_{2.5}$ sulfate at the six sites. Linear regressions are used to show the annual reductions in fine particulate sulfate. Significant decreasing trends (p value of linear regressions < 0.05) of sulfate have been observed at five out of six sites (excluding the St Anicet site where large inter-annual variation was found). Specifically, sulfate concentrations have experienced 61 %, 56 %, 62 % and 67 % reductions in Toronto, Simcoe, Windsor and Ottawa, respectively, over the decade from 2007 to 2016. There is no statistically significant long-term trend in the NH$_x$ values at any of these sites. Summertime aerosol pH is not decreasing with the decreasing trend of sulfate but is mainly influenced by the inter-annual variation of meteorological conditions.

3.4 pH trends in wintertime

To assess the effect of chemical composition changes on aerosol pH in winter meteorological conditions, wintertime average concentrations of sulfate and NH$_x$ in each year at each site were plotted in Fig. 8a with the colour representing the corresponding average pH values. The background colour in Fig. 8a represents pH calculated under different combinations of sulfate and NH$_x$ concentrations with fixed temperature ($-5\,^\circ$C), RH (75 %) and sulfate-to-TNO$_3$ molar ratio (1 : 2), the same as Fig. 5d but with a different scale and focused on a smaller range of chemical conditions. The figure clearly shows that changes in chemical composition under wintertime meteorological conditions can lead to significant changes in aerosol pH. Changes of 20 nmol m^{-3} in
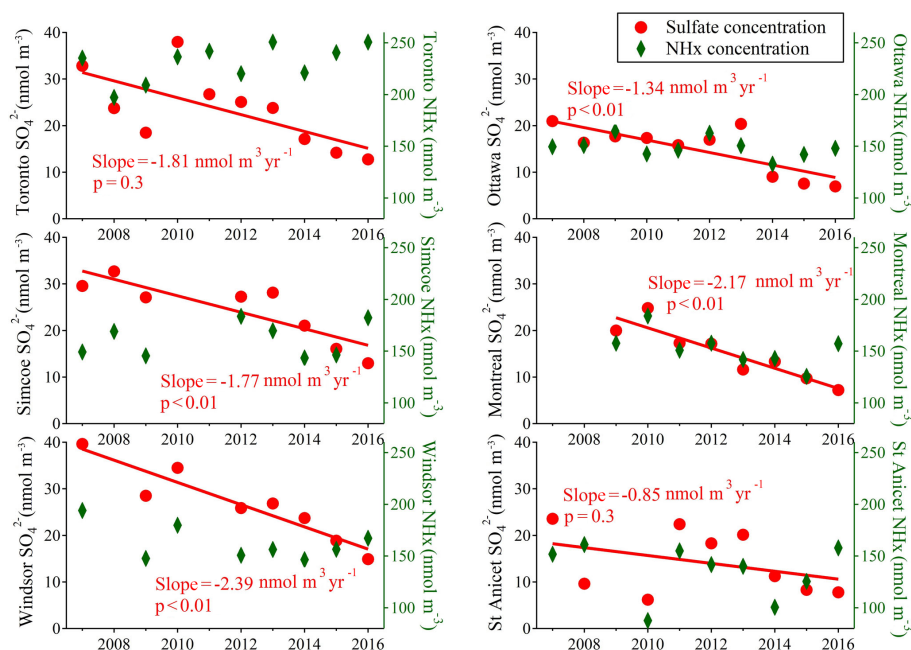
Figure 7. 10-year trends of summertime average concentrations of sulfate and NH$_x$ at each site. Linear regressions of sulfate were illustrated on each graph to represent the reduction of particulate sulfate from 2007 to 2016.

either NH$_x$ or sulfate can change aerosol pH by more than 0.5 units for some cases. Also, although most of the wintertime average pH values calculated for the actual chemical composition at each site (colours of the markers) generally agree with the pH calculated as the conceptual model (colours of the same position in the background), some of the data points were slightly more acidic than the background value, and this is likely the result of our simplified assumption of a fixed sulfate-to-TNO$_3$ molar ratio during the calculation in the conceptual modelling.

Figure 8b shows the effects that temperature, relative humidity and TNO$_3$ concentrations can have on the pH of aerosol with 10 nmol m^{-3} sulfate under wintertime meteorological conditions. Generally, a lower temperature and higher relative humidity will make aerosol pH higher. However, the effect of the addition of total nitrate is more complicated. Based on Eq. (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 the gas phase, and the smaller value of [NH$_3$]/[NH$_4^+$] will make the aerosol more acidic. These two factors altogether contribute to the arc-shaped curve of the relationship between aerosol pH and nitrate shown in Fig. 8b. Figure S7 shows the box-and-whisker plots of wintertime average molar ratio of TNO$_3$ to sulfate concentration in each year at each sampling site, where it shows that the molar concentration of TNO$_3$ was generally more than 2 times higher than the

sulfate concentration, which could contribute to wintertime aerosol being more acidic than the value calculated using the forcing sulfate : TNO$_3$ = 1 : 2. As a result, during wintertime, both chemical composition and meteorological conditions can have significant impacts on aerosol pH without a clear dominant factor. As a corollary, the uncertainty in measurements of particle composition, the influence of non-volatile cations and the potential contribution from organic acids or organosulfates (the error caused by misrepresenting organosulfates as inorganic sulfate) will also have a more significant impact on the determination of aerosol pH in winter by potentially over- or underestimating the sulfate or nitrate that is balancing the ammonium.

4   Conclusion

The pH values of fine particulate matter at six eastern Canadian sites, including Toronto, Windsor, Simcoe, Ottawa, Montreal, and St Anicet from 2007 to 2016 were calculated by the E-AIM model constrained by input from the NAPS database and meteorological data. Strong seasonal cycles of aerosol pH were found at all six sites over the 10 years. A consistent pattern of aerosol pH fluctuation from acidic (pH < 2) in summer to higher pH around 3 in winter was found at all six sites. Ambient temperature proved to be mainly responsible for the seasonal cycle of aerosol pH. The sensitivity tests of pH to chemical composition shows aerosol pH has different sensitivity to chemical composition changes in different seasons. During summertime, aerosol pH was
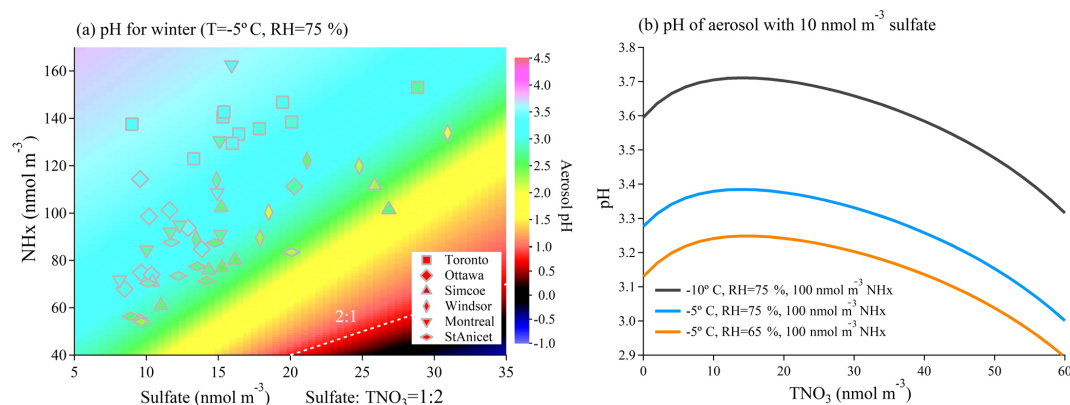
Figure 8. (a) The plot of aerosol pH under wintertime meteorological conditions ($-5\,^{\circ}$C, RH $= 75\,\%$) under different combinations of sulfate and NH$_x$ with more focused region compared to Fig. 5d. The markers on the graph represents the average wintertime (data from January and February) sulfate and NH$_x$ concentrations in each year in each sampling site with colour indicating average pH value. **(b)** pH of aerosol with 10 nmol m^{-3} sulfate under different combinations of temperature and relative humidity as the function of TNO$_3$ in the system.

mainly controlled by ambient temperature while the fluctuation of NH$_x$ and sulfate concentrations did not contribute significantly to the inter-annual variation of aerosol pH. In comparison, in wintertime, aerosol pH can be greatly influenced by both chemical compositions and meteorological conditions. When temperatures are low, aerosol pH at these six sites are very sensitive to all the changes in NH$_x$, sulfate and TNO$_3$ concentrations, leading to the higher variation of aerosol pH in wintertime compared to that in summertime. This study focused on a number of sites with relatively low ambient mass loadings of aerosol inorganic constituents dominated by a 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 with high particulate pollution and different concentration levels of NH$_3$, similar approaches can also be applied to assess the aerosol pH sensitivity to chemical composition and meteorological parameters to assess the generalizability of our findings.

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