

Dear Prof. Yu (Editor):

We are submitting a revision of our paper (manuscript #acp-2016-918) entitled, “**Long-term air concentrations, wet deposition, and scavenging ratios of inorganic ions, HNO<sub>3</sub> and SO<sub>2</sub> and assessment of aerosol and precipitation acidity at Canadian rural locations**”, for further consideration in Atmospheric Chemistry and Physics. We have addressed all of the comments provided by the reviewers. The details can be found in our enclosed responses to the reviewers’ comments. For your convenience, a copy of the paper with track-changes is attached.

Thank you for taking care of the review process for this paper.

Sincerely,

Irene Cheng and Leiming Zhang

Air Quality Research Division  
Environment and Climate Change Canada

## Response to Reviewer 1

We thank the reviewer for the suggestions to improve our paper. Our point-by-point responses to each comment are shown in blue.

### General comments

The manuscript includes updated long-term data on concentrations, wet deposition, and scavenging ratios of atmospheric pollutants in Canadian sites. As outlined briefly in the introduction, there is, indeed, a need for keeping track of the recent evolution of atmospheric pollutants contributing to smog and acid rain, particularly in Canadian sites. Much of the information in the literature refers to datasets from the contiguous US or from European sites, two other regions where data from similar extensive monitoring networks have been available for decades, while Canadian sites have received relatively less attention. Observations of a recent decrease in precipitation acidity in North America (including Canada) and Europe have been accumulating, and have been the subject of many papers. The topic is not necessarily new. However, many aspects of the chemistry, transport, and deposition of these atmospheric pollutants are still not well-understood. Despite the inherent interest in reporting updated geographical patterns and temporal trends of atmospheric pollutants, much of the data presented here is not necessarily “new”, and similar reports and conclusions can be found in the literature. For example, a recent global assessment of precipitation chemistry and deposition of these substances already includes much of the information presented in the manuscript (Vet et al. 2014). The report from Vet et al. (2014) not only includes much of the data used here (data obtained from the same CAPMoN network in the same locations), but also allows to put the data into a regional context, and compare the observed geographical patterns and temporal trends with those of emissions. Surprisingly, the Vet et al. (2014) assessment was not mentioned in the manuscript. In my opinion further attention should have been paid to clarify, complement and update the information already existing in the literature.

Response: The global assessment study by Vet et al. (2014) has been discussed in the revised paper (sect. 3.2.1 and 3.2.3). Please note that our study has a different scope from that of Vet et al.; thus, the data and discussion are presented in very different ways. Our study includes the analysis of geographical and temporal trends of not only wet deposition, but also the atmospheric concentrations (sect. 3.1). This difference is an important to consider because the atmospheric concentrations of SO<sub>2</sub>, sulfate, and nitrate have stronger links to emissions changes than wet deposition of sulfate and nitrate. The latter is primarily affected by particle sizes, air concentrations, rainfall intensity, and precipitation and cloud types, which varies geographically. The way the air concentration and wet deposition trends were compared to those of emissions were very different. Our study plotted the annual air concentrations and annual emissions on the same graph in parallel as shown in Figures 2b, 3 and 4, whereas the emissions from two points in time were analyzed by Vet et al. The second major difference is that our study provides more detailed analysis of trends specifically for Canadian sites and regions, whereas a much broader (global) context of the trends were presented by Vet et al. over two three-year time periods (2000-2002 and 2005-2007). In this study, we compared the trends obtained from our study to those already existing in literature, e.g. Zbieranowski and Aherne (2011) for nitrogen measurements at Canadian sites and Lehmann et al. (2005, 2007) for U.S. sites. These two

studies were discussed in more detail with our results because we applied the same statistical method to analyze the long term temporal trends (Seasonal Kendall test and Mann-Kendall test).

I would recommend authors further efforts summarizing and presenting measurement data and trends in a clearer geographical/temporal context. According to the four objectives presented in the introduction some of the questions that needed to be answered in the manuscript were for example: as of 2011, how much have concentrations/deposition of the several substances decreased compared to a baseline year? Where? When? Are those changes parallel to emission reductions?

Response: We summarized the geographical and temporal trends as much as possible despite the vast amounts of data from the CAPMoN sites. Regarding geographical patterns, we reported the range in the median air concentration and range in annual wet deposition and then discussed reasons for the spatial variation (e.g. differences between coastal and continental sites, agricultural sites, and sites impacted by anthropogenic emissions). In terms of temporal trends, we reported the direction of the long-term trends found at most of the sites (increasing/decreasing) and the range in the magnitude of the trends for air concentrations and annual wet deposition. We then discussed the possible reasons (e.g. NH<sub>3</sub>, SO<sub>2</sub>, NO<sub>x</sub> emissions reductions) for particularly larger declines at southern Ontario and southern Quebec sites for atmospheric ammonium, sulfate and nitrate. This discussion was supported by showing a graph of the annual trends of air concentrations and emissions that are shown in parallel (Figures 2b, 3 and 4). The method for determining trends was not a comparison of the 2011 data with a baseline year. In our opinion, this method only gives a rough estimate of the change in the air concentrations or wet deposition between two points in time because it does not take into account the year-to-year variability or the statistical significance of the trends. Thus, in this study we examined the long-term trends using a well-established method for conducting statistical trends analysis (Seasonal Kendall test and Mann-Kendall test).

Much of the text is a never-ending compilation of ranges, averages, medians and percentiles of the various substances, sometimes referred as measured in site X or site Y (a non-Canadian reader must check supplementary Figure S1 constantly to figure out these locations), without a clear message being told. The reader gets usually overwhelmed by the amount of values, ranges and percentages presented in the text, much of which could just have been summarized in figures and tables, while getting very little or disperse information about the magnitude of changes that have taken place, and the spatial and temporal context of those changes.

Response: In terms of quantitative information, the text reported the range in the median air concentration and the range in annual wet deposition among the sites for the discussion on geographical variability. For temporal variability, the text reported only the range in the magnitude of the trends for air concentrations and annual wet deposition among the sites. Similarly only the range was reported for aerosol acidity, acid rain and the scavenging ratios. Considering the large amount of data analyzed, we feel that the statistics have already been minimized in the text. The detailed statistics for each site are provided in the tables and figures.

The text provided context on the spatial and temporal patterns and did not only refer to specific sites. For geographical patterns, we discussed that the spatial variation were attributed to sea salt

emissions from the ocean, agricultural activities, and anthropogenic emissions. We also mentioned the names of the sites belonging to these categories in case readers are interested in the detailed statistics for these sites in the tables and figures. For temporal trends, we discussed that the stronger declining trends at southern Ontario and southern Quebec sites for atmospheric ammonium, sulfate and nitrate were attributed to  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{NO}_x$  emissions reductions. We showed aerosol acidity was important to eastern Canada and central Ontario than other Canadian regions. We also discussed that acid rain impacts were more significant in southern Ontario and eastern Canada than western and central Canada. These examples show that the spatial and temporal trends were discussed in a broader, regional context in the paper, and not only referring to the individual sites.

In my opinion, the major contribution of the manuscript is the calculation of scavenging ratios and the development of an approach to estimate particulate and gaseous wet scavenging contributions to wet deposition at those sites. Again, issues arise regarding the way scavenging data is presented and contextualized. Is there any clear spatial pattern in scavenging ratios? Have those ratios change as concentrations decreased over the decades? Have the relative contributions of particulate and gaseous substances to deposition changed over time?

Response: The spatial patterns in scavenging ratios are discussed in the first paragraph of sect. 3.3.2. In this paragraph, we attributed the spatial variability in scavenging ratios to differences in the particle size distributions between coastal and inland sites.

We analyzed the long-term trends in the monthly scavenging ratios of  $\text{pSO}_4^{2-}$  and  $\text{SO}_2$  and  $\text{pNO}_3^-$  and  $\text{HNO}_3$  and their relative contributions to total wet deposition at eight sites representative of western/central Canada, southern Ontario and southern Quebec, and eastern Canada. Most of the trends were not statistically significant according to the Seasonal Kendall test. No consistent trends were found within each Canadian region either. Some statistically significant trends in scavenging ratios were found at a few locations and for some nitrogen and sulfur species. At Longwoods, there was a statistically significant declining trend in the scavenging ratio of  $\text{pNO}_3^-$ ; however the magnitude of the trend was only -6.3 (<1%) per year which is small compared to the scavenging ratio (values in the hundreds to thousands). At Algoma, a significant increasing trend in the scavenging ratio of  $\text{pSO}_4^{2-}$  was found with a slope of +11.4 per year. This suggests the atmospheric  $\text{pSO}_4^{2-}$  concentrations were decreasing at a slightly faster rate than the decrease in precipitation sulfate. This result is consistent with the emissions reductions having a greater impact on air concentrations than precipitation concentrations. Although the trend is statistically significant, the magnitude of the trend (11.4 or 1.4% per year) is again very small. At many of the sites, the lack of long-term trends in the scavenging ratios of sulfur and nitrogen species reflect the decreasing trends in both wet deposition and air concentrations (Table 2 and 4). There are also many factors that can affect the precipitation concentrations, such as particle sizes, air concentrations, rainfall intensity, and precipitation and cloud types, which vary geographically and could change over time. These uncertainties make it difficult to narrow down the reasons behind the long-term scavenging ratio trends.

We added the following paragraph in sect. 3.3.2 of the revised paper: “Most of the long-term scavenging ratio trends were not statistically significant according to the Seasonal Kendall test, but some statistically significant trends were found at a few locations and for some nitrogen and

sulfur species. At Longwoods, there was a statistically significant declining trend in the scavenging ratio of  $\text{pNO}_3^-$ ; however the magnitude of the trend was only  $-6.3$  ( $<1\%$ ) per year which is small compared to the scavenging ratio (values in the hundreds to thousands). At Algoma, a significant increasing trend in the scavenging ratio of  $\text{pSO}_4^{2-}$  was found with a slope of  $+11.4$  ( $1.4\%$ ) per year. At many of the sites, the lack of long-term trends in the scavenging ratios of sulfur and nitrogen species reflect the decreasing trends in both wet deposition and air concentrations (Table 2 and 4). There are also many factors that can affect the precipitation concentrations, such as particle sizes, air concentrations, rainfall intensity, and precipitation and cloud types, which vary geographically and could change over time.”

#### Specific comments

Please avoid including too much data (if any) in the abstract. The message is lost among the many references to substances, ranges, years

Response: The abstract has been revised by making it less quantitative. It now reads, “This study analyzed long-term air concentrations and annual wet deposition of inorganic ions and aerosol and precipitation acidity at 30 Canadian sites from 1983-2011. Scavenging ratios of inorganic ions and relative contributions of particulate- and gas-phase species to  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  wet deposition were determined. Geographical patterns of atmospheric  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  were similar to wet deposition and attributed to anthropogenic sources, sea-salt emissions, and agricultural emissions. Decreasing trends in atmospheric  $\text{NH}_4^+$  (1994-2010) and  $\text{SO}_4^{2-}$  (1983-2010) were prevalent. Atmospheric  $\text{NO}_3^-$  increased prior to 2001 and then declined afterwards. These results are consistent with  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{NH}_3$  emission trends in Canada and the U.S. Widespread declines in annual  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  wet deposition ranged from  $0.07$ - $1.0$   $\text{kg ha}^{-1} \text{a}^{-1}$  (1984-2011). Acidic aerosols and precipitation impacted southern and eastern Canada more than western Canada; however both trends have been decreasing since 1994. Scavenging ratios of particulate  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  differed from literature values by 22%, 44% and a factor of 6, respectively, because of the exclusion of gas scavenging in previous studies. Average gas and particle scavenging contributions to total wet deposition were estimated to be 72% for  $\text{HNO}_3$  and 28% for particulate  $\text{NO}_3^-$ , 37% for  $\text{SO}_2$  and 63% for particulate  $\text{SO}_4^{2-}$ , and 30% for  $\text{NH}_3$  and 70% for particulate  $\text{NH}_4^+$ .”

In section 2.1.4. authors stated that meteorological data was collected. Apart from precipitation, were these data included in the analyses? Are there any relationships between pollutants and wind, relative humidity or temperature data?

Response: Analysis of the relationships between the pollutants and temperature, relative humidity, and precipitation were discussed in the last paragraph of sect. 3.1.2 (p.10 ACPD version) and the correlation analysis results were shown in Table S1 of the supplementary material. We also showed the time-series trend of atmospheric  $\text{K}^+$  was similar to that of temperature for several agriculture/forested sites (Fig. S2a). In Fig. S2b, we showed the time-series trend of atmospheric ammonium was similar to that of temperature, and suggested that this was related to the formation of sulfate from the oxidation of sulfur dioxide based on the strong correlation between the sulfate/sulfur dioxide ratio and temperature. Relative humidity and precipitation had almost no influence on the temporal trends of particulate inorganic ions. For

wind direction data, we used it to confirm that the lower latitude sites (Longwoods, Egbert, Frelighsburg/Sutton) were impacted by transboundary emissions of SO<sub>2</sub> and NO<sub>x</sub> from the U.S. (p.8, lines 17-22 ACPD version). The wind direction data was also used to estimate the percentage frequency of winds from the ocean, which are contributing to atmospheric Na<sup>+</sup> and Cl<sup>-</sup> at coastal sites (Saturna, Kejimikujik) (p.8, lines 6-11 ACPD version).

Figure 1 is a very poor attempt to show the geographical and temporal changes in concentrations. First of all, the log scale makes it difficult to note the differences among sites or the changes between the two periods. Furthermore, what's the reason behind the two periods (1983-1996 and 1997-2010)? Is 1997 a "landmark" for Canadian emission regulations that would define a "before" and "after"? Why not comparing a year in the 1980's and a year at the end of the series (2011?) to actually show the decreases?

Response: Figure 1 has been revised; the log scale has been changed to a standard scale and box plots (similar to Fig. 6 for annual wet deposition) are used to show more statistics. We also created separate graphs for the 1983-1996 and 1997-2010 periods to show the differences in the geographical distributions of the air concentration. The air concentrations from 1983-2010 were analyzed in this study; 1997 is the halfway point in the data. We chose to divide the data at the halfway point to ensure consistency in the sample size when comparing data between two time periods. The emission changes in Canada and the U.S. did not occur in one particular year; thus 1997 should not be viewed as a landmark year for emission changes. As discussed on p. 9-10 ACPD version, ammonia emissions in Ontario and Quebec decreased only after 2002. NO<sub>x</sub> emissions in Canada began to decrease in 1997, while in the U.S. the decline was already occurring in 1994. From Fig. 4, SO<sub>2</sub> emissions in the U.S. have been declining since the early 1990s; however, in Canada only a larger decrease was observed after 2005. Given the vast amount of data analyzed in this study, there are numerous ways to analyze and present the data. Another way as the reviewer suggests is to compare the data from one year in the 1980s to another year in 2011. In our opinion, comparing one year to another year does not give very representative results. There may be year-to-year variability which is not considered when analyzing only two points in time. There also needs to strong justification on why the comparison was done specifically between year A and year B instead of other years.

In many cases (e.g. for NO<sub>3</sub>) the graphs show little changes or even increases, while in the text it has been clearly stated that concentrations of most substances have decreased. The case of NO<sub>3</sub> is particularly interesting. Figure 3 shows that averaged NO<sub>3</sub> concentrations and emissions started to decrease in 2001. Why not using that year to compare "before" and "after" concentrations for that substance?

Response: In the text, it states there was an even split in the number of sites with increasing and decreasing trends in NO<sub>3</sub><sup>-</sup> (p. 9, lines 30 onwards, ACPD version). We also reported that at 9 of 16 sites an increasing trend was found between 1991 and 2001 which was followed by a decreasing trend from 2001 to 2010 (p.10, lines 2-3). The increasing and decreasing trends in NO<sub>3</sub><sup>-</sup> were reflected in the Canadian NO<sub>x</sub> emissions data, which showed an increased from 1991 to 1997 and then decreased from 1997 to 2010 (Fig. 3). This shows the consistency between the graphs (Fig. 3) and the discussion in the text. In Fig. 3, we plotted the annual trends in NO<sub>3</sub><sup>-</sup> and

in  $\text{NO}_x$  emissions from 1991 to 2010, which clearly shows the change in the direction of the trends.

The multi-axis panels in Figure 5 are probably not the best option here. I would recommend to use cation/anion ratio data only for panel a (concentrations can be extracted from tables and text), and c/a ratio and pH data only for panel b (this time 2 Y axes can be used to highlight temporal trends).

Response: Figure 5 has been revised based on your suggestions. In the revised paper, Fig. 5a shows only the cation/anion (c/a) ratio, while Fig. 5b shows the c/a ratio and precipitation pH data. The cation and anion equivalent concentrations that were previously plotted in these figures have been summarized in Table S2.

As mentioned in the general comments, some of the most interesting contributions of the manuscript are in my opinion those regarding scavenging ratios. Much of that information is included as supplementary materials. Some of those graphs and tables could have been part of the main body text.

Response: There are already four large tables and ten figures in the main manuscript; thus there is not enough space to accommodate the tables of scavenging ratio statistics (in Table S2 and S3 of the supplementary material) or the large figure showing the monthly scavenging ratio variation (Fig. S5). Due to the different topics covered in this paper (including the geographical and temporal patterns of air concentrations, wet deposition, aerosol acidity, acid rain, scavenging ratios, and gas vs. particle wet scavenging), it is impossible to show all the results in the main manuscript.

## Response to Reviewer 2

We thank the reviewer for the suggestions to improve our paper. Our point-by-point responses to each comment are shown in blue.

This manuscript presents a detailed analysis of the trace gas concentrations and wet deposition fluxes measured at the Canadian Air and Precipitation Monitoring Network (CAPMoN) sites in the past thirty years (1983-2011). Long-term trends of aerosol ions and precipitation acidity at the Canadian sites are assessed from the aspect of acid deposition. The scavenging ratios for air pollutants as a measure of the wet scavenging efficiency are also estimated and compared with previous studies. The manuscript also presented a first attempt to quantify the relative contribution of gas and particle to measured wet deposition fluxes of ammonium, sulfate and nitrate.

Overall, the manuscript presents a very comprehensive summary of the air pollutant and wet deposition measurements at the Canadian network. While I also think that the manuscript can be difficult to follow due to the intense statistics reported in a parallel way, it is valuable to document the thirty-year dataset over Canada and the spatial and temporal patterns. The approach to estimate gas vs. aerosol contributions to wet deposition fluxes will be particularly helpful for model evaluation.

### Specific comments

1) Abstract, Page 1, Line 19: Suggest change “because of the exclusion of gas scavenging” to “because of the exclusion of gas scavenging in previous studies” to avoid confusion.

Response: Revised according to your suggestion.

2) Page 5, Line 10-13: This sentence is unclear. What is the difference between the Seasonal Kendall test and the Mann-Kendall test? Why are they inconsistent? Please clarify.

Response: The Seasonal Kendall test analyzes the temporal trend in the average air concentrations in each month separately and then aggregates the results to obtain the annual trend. In the Mann-Kendall test, the data are not split into twelve months before the temporal trend is analyzed (Gilbert, 1987). Therefore, the latter was used to obtain the annual total wet deposition trend. This has been clarified in sect. 2.2.1 of the revised paper.

3) Page 5, Line 13-14 Page 10, last paragraph: “The relationship between meteorological factors and temporal trends in air concentrations and wet deposition were also examined by correlation analysis”. As shown in Table S1 and discussed on Page 10, the correlation analysis was only applied to some particulate ions and trace gases, and not to wet deposition fluxes.

It is not convincing that we can use the correlation coefficients based on monthly averages to explain the long-term trends based on annual values. For example, the weak correlation between monthly K<sup>+</sup> concentration and precipitation may largely differ from their annual correlation, which is a better indicator for the descending trends in K<sup>+</sup> concentrations during 1993-2010.

Please clarify. Also please state in the title of Table S1 that the correlations are computed using monthly values.

Response: The air concentrations are more likely to be influenced by meteorological parameters (e.g. temperature, relative humidity, and precipitation) than wet deposition of pollutants. Wet deposition of the pollutants is predominantly affected by the air concentrations and the precipitation amount. Thus for wet deposition, we already discussed these correlation analysis results on p. 14 lines 16-32 of the ACPD version. To clarify, we revised the sentence before sect. 2.2.2 to, “Correlation analysis was performed between monthly averaged meteorological parameters and particulate ions and trace gases. For wet deposition of inorganic ions, the correlations with the precipitation amount and air concentrations were examined.” The caption for Table S1 was also revised to, “Pearson correlation coefficients between selected atmospheric ions and meteorological parameters (significant at  $p < 0.05$ ; otherwise non-significant (ns)). Note that the ion concentrations and meteorological parameters are monthly averages.”

Regarding the analysis of annual atmospheric  $K^+$  and annual precipitation amount, there was a statistically significant decreasing trend in atmospheric  $K^+$  for almost all the sites (Table 2, see the slope and C.I.); however, no statistically significant trends in the precipitation amount were found at the majority of the sites (Table 4, see the slope and C.I.). Note that it is important to consider the C.I. (90% confidence interval of the slope) to assess whether the trend is statistically significant. The results indicate the annual atmospheric  $K^+$  and annual precipitation trends were not the same.

4) Page 6, Line 7: Please clarify here how  $W(K/2)$  as the scavenging ratio for coastal site is calculated here. As half of  $W(K)$ ?

Response: Atmospheric  $K^+$  has a bimodal particle size distribution. It is predominantly associated with fine particles at inland locations, but also associated with coarse sea-salt aerosols at coastal locations. In our previous study (Cheng et al., 2015), we observed that the mean scavenging ratio of fine particles was 34 to 52% of that of coarse particles at inland locations, but was 80% at the coastal sites. Therefore, the fine scavenging ratio was reduced by about a factor of 2 at coastal locations to take into account that the  $K^+$  that may be associated with coarse aerosols. This explanation has been added to sect. 2.2.3 of the revised paper.

5) Page 7, Equ. (4)(5): Replace the \* with cross using the standard equation format.

Response: Equations 4 and 5 have been revised according to your suggestions.

6) Page 10, Figure 2-4: The manuscript concludes that the temporal trends in atmospheric inorganic concentrations are consistent with their emissions. Can you please also present the trends in percentage to discuss that to what extent the trends in pollutant concentrations reflect trends in emissions?

Response: The temporal trends expressed as percentages have been added to the captions of Fig. 2 to 4. In Fig. 2b between 2002 and 2010 (as discussed in the text), atmospheric ammonium at agricultural sites decreased by 6.3% while ammonia emissions in Ontario and Quebec decreased

by 2.4% and 1.1%, respectively. For atmospheric nitrate and NO<sub>x</sub> emissions (Fig. 3), the timing of the trends were not synchronized as discussed in the text. In Fig. 3 between 1991 and 2001 (as discussed in the text), atmospheric nitrate increased by 3.6%. However, the period of increasing NO<sub>x</sub> emissions in Canada was between 1991 and 1997 (at 8.5%). Then, from 2001 to 2010, atmospheric nitrate decreased by 6.5%. However, the period of decreasing NO<sub>x</sub> emissions in Canada was between 1997 and 2010 (at 25.8%). In Fig. 4 between 1990 and 2010 (as discussed in the text), atmospheric sulfate decreased by 4.5% at southern Ontario and Quebec sites and by 3.6% at other sites. Over the same period, SO<sub>2</sub> emissions decreased by 1.8% in Canada and 4.3% in the U.S. Note that the percentage change in pollutant concentrations may not be the same as the percentage change in emissions because the quantities are very different. However, it is clear that the direction of the trends is consistent.

7) Page 34, label of Figure 3: Please explain ‘Cdn’ in the caption. And ‘Nox’ should be ‘NO<sub>x</sub>’.

Response: Cdn is the abbreviation used for Canada. We have added this explanation in the captions for Fig. 3 and 4 and changed Nox to NO<sub>x</sub> in the legend.

8) Page 42, caption of Figure 10: Suggest change here (and a few places in the text, e.g., seasonal trend) “monthly trend” to “monthly variation” to avoid confusion with the long-term trend.

Response: In the revised paper, supplementary material and Fig. 10, we replaced “seasonal trend” or “monthly trend” with “seasonal variation” or “monthly variation”.

9) Supplement, Page S5, caption of Figure S4: “Five different months” should be “five different years”.

Response: This has been corrected in the revised paper.

# Long-term air concentrations, wet deposition, and scavenging ratios of inorganic ions, HNO<sub>3</sub> and SO<sub>2</sub> and assessment of aerosol and precipitation acidity at Canadian rural locations

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**Abstract.** This study analyzed long-term air concentrations and annual wet deposition of inorganic ions and aerosol and precipitation acidity at 30 Canadian sites from 1983-2011. Scavenging ratios of inorganic ions and relative contributions of particulate- and gas-phase species to NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> wet deposition were determined. ~~Long-term median atmospheric NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> between sites ranged from 0.1-1.7, 0.03-2.0, and 0.6-3.5 μg m<sup>-3</sup>, respectively. Their median annual wet deposition varied from 0.2-5.8, 0.8-23.3, and 0.8-26.6 kg ha<sup>-1</sup> a<sup>-1</sup>.~~ Geographical patterns of atmospheric Ca<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> were similar to wet deposition and attributed to anthropogenic sources, sea-salt emissions, and agricultural emissions. Decreasing trends in atmospheric NH<sub>4</sub><sup>+</sup> (1994-2010) and SO<sub>4</sub><sup>2-</sup> (1983-2010) were prevalent. Atmospheric NO<sub>3</sub><sup>-</sup> increased ~~from 1991-2001~~ prior to 2001 and then declined ~~from 2001-2010~~ afterwards. These results are consistent with SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> emission trends in Canada and the U.S. Widespread declines in annual NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> wet deposition ranged from 0.07-1.0 kg ha<sup>-1</sup> a<sup>-1</sup> (1984-2011). Acidic aerosols and precipitation impacted southern and eastern Canada more than western Canada; however both trends have been decreasing since 1994. Scavenging ratios of particulate NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> differed from literature values by 22%, 44% and a factor of 6, respectively, because of the exclusion of gas scavenging in previous studies. Average gas and particle scavenging contributions to total ~~to~~ wet NO<sub>3</sub><sup>-</sup> deposition were estimated to be 72±23% for HNO<sub>3</sub> and 28±23% for particulate NO<sub>3</sub><sup>-</sup>. ~~SO<sub>2</sub> and particulate SO<sub>4</sub><sup>2-</sup> contributed 37±20% for SO<sub>2</sub> and 63±20% for particulate SO<sub>4</sub><sup>2-</sup>, and to wet SO<sub>4</sub><sup>2-</sup> deposition, respectively. NH<sub>3</sub> and particulate NH<sub>4</sub><sup>+</sup> contributed 30±19% for NH<sub>3</sub> and 70±19% for particulate NH<sub>4</sub><sup>+</sup> to wet NH<sub>4</sub><sup>+</sup> deposition.~~

## 1 Introduction

The Canadian Air and Precipitation Monitoring Network (CAPMoN) measures trace gas concentrations and particulate inorganic ion concentrations in air and precipitation at rural locations across Canada. Since 1983, the network has been collecting filter and precipitation samples and the number of sites has expanded to 33 as of 2010. CAPMoN was developed to monitor trends in atmospheric pollutants contributing to smog and acid rain, and the data was later used to assess the impacts of environmental policies in the Canada-U.S. Air Quality Agreement. This bilateral agreement signed in 1991 recognizes the impacts of transboundary pollution and sets objectives to reduce SO<sub>2</sub> and NO<sub>x</sub> emissions.

In this study, the focus is on the particulate base cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) and acidic anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>), nitric acid, and sulfur dioxide that have direct impacts on acid rain. Nitrates and sulfates in acid rain reduce soil quality by causing the depletion of base cations, which are plant nutrients and are also involved in neutralizing acids. Base cations in soil can be replenished by mineral weathering, deposition, wind erosion, agricultural tilling, and forest fires (Hedin et al., 1994; Driscoll et al., 2001). However, when acidic deposition exceeds the supply of base cations, soil acidification occurs. Soil acidity has consequently increased the leaching of inorganic aluminum (Al) monomers, which is a toxic form of Al to plants and animals (Driscoll et al., 2001). Trees (e.g., red spruces and sugar maples) experienced damage to foliage, decreased adaptability to cold climates, slower growth, and mortality during 1960s-1980s from direct and indirect impacts of acid rain (Driscoll et al., 2001; Watmough and Dillon, 2003). Acid rain and runoff of acidic soil also increased nitrates, sulfates and inorganic Al and reduced pH in surface waters of Atlantic Canada, southcentral Ontario, and northeastern U.S. (Clair et al., 2002; Driscoll et al., 2003; Jeffries et al., 2003). Lake acidification has led to detrimental effects including mortality on zooplankton and fish (Driscoll et al., 2001 and references therein). Terrestrial birds are also impacted because when calcium is depleted from soil, less calcium-rich insects are available for birds to consume (Hames et al., 2002). Calcium deficiency in birds can cause eggshell thinning and other reproductive consequences (Hames et al., 2002).

Assessments of lake acidification in the previous decade indicate declines in nitrates and sulfates in surface water, some improvements to pH and acid neutralizing capacity, and conversion to less toxic organic Al (Clair et al., 2002; Driscoll et al., 2003; Jeffries et al., 2003; Kothawala et al., 2011; Strock et al., 2014). Although nitrate and sulfate deposition have been decreasing, surface water conditions have not improved at the same rate because nitrates and sulfates that have accumulated in soil and wetlands over a long period of time is gradually releasing to surface waters (Stoddard et al., 1999; Driscoll et al., 2001; Clair et al., 2002; Jeffries et al., 2003). A recent assessment by Lawrence et al. (2015) indicates no additional soil acidification and that acid deposition effects on soil have started to diminish in northeastern U.S. and eastern Canada according to indicators, such as exchangeable Ca and Al, base cations, and pH levels. Considering the role of inorganic ions on acid deposition effects on biota, it is important to continually study the wet deposition of inorganic ions.

The wet deposition of particulate base cations and acidic anions depend on the particulate concentrations of these inorganic ions in air and some trace gases, such as nitric acid and sulfur dioxide. This simplified relationship is the premise behind the scavenging ratio, defined as a ratio of a pollutant's concentration in precipitation to that in air. In reality, wet deposition is a very complex process that involves an understanding of cloud and precipitation processes and aqueous phase chemistry, which are considered to be the major sources of uncertainty in wet deposition modeling (Tost et al., 2007; Kajino and Aikawa, 2015). Scavenging ratios can be considered a measure of the wet scavenging efficiency of air pollutants, since they have been used to compare the precipitation removal of different pollutants in previous studies (Galloway et al., 1993; Guerzoni et al., 1995; Tuncel and Ungör, 1996; Shrestha et al., 2002; Hicks et al., 2005; Kulshrestha et al., 2009; Bourcier et al., 2012; Zhang et al., 2015). These studies demonstrated that scavenging ratios vary according to particle size distribution similar to the particle size dependency of scavenging coefficients typically used in wet deposition modeling (Wang et al., 2014). Thus, scavenging ratios of particulate-phase pollutants have been used as a surrogate for other particulate-phase pollutants with similar particle sizes (Cadle et al., 1990; Sakata and Asakura, 2007; Cheng et al., 2015).

The objectives of this study were to (1) analyze long-term geographical patterns and temporal trends in nitric acid and sulfur dioxide concentrations and the air concentrations and wet deposition of base cations and acidic anions; (2) examine geographical and temporal trends in aerosol acidity and acid rain; (3) determine scavenging ratios for particulate inorganic ions using precipitation and air concentrations; and (4) develop an approach for estimating particulate and gaseous species wet scavenging contributions to total nitrate, ammonium and sulfate wet deposition and their scavenging ratios.

## **2 Methodology**

### **2.1 Data description**

#### **2.1.1 CAPMoN datasets**

24-hr integrated trace gas concentrations and particulate inorganic ion concentrations in air and precipitation are measured by CAPMoN at rural locations across Canada. This dataset was accessed online from the NAtChem database (Environment Canada, 2015a). The monitoring sites are located in various regions of Canada with the majority of the sites residing in the province of Ontario and Quebec (Fig. S1). Site elevations range from 14-707 m.a.s.l. The sites include continental and coastal sites, and the land use types of most CAPMoN sites are categorized as forested or agricultural sites (Table 1). Only the sites with long-term data ( $\geq 9$  years) were analyzed in this study. The measurement periods are not synchronized between all sites; therefore, some sites may have different starting and end dates.

#### **2.1.2 Air concentrations**

Non-size selective filters are used to collect air samples, which are analyzed for major inorganic ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) and  $\text{HNO}_3$  and  $\text{SO}_2$  trace gases. Teflon filters are used for the inorganic ions, while nylon and impregnated cellulose filters are used for  $\text{HNO}_3$  and  $\text{SO}_2$ , respectively. The filters are placed in a three stage filter pack, which samples air at 10 m above ground. Every 24 hr at 8:00 LT, the sequential sampler passes air through a different filter pack. The filters are retrieved and delivered to CAPMoN laboratories for chemical analysis. The collected mass for each species, blank values, and mass flow rates are used to determine the air concentrations in  $\mu\text{g m}^{-3}$ . Quality control of the data are performed using the Research Data Management and Quality Assurance System (RDMQ<sup>TM</sup>) software (McMillan et al., 2000), which processes and manages large amounts of data, applies quality control checks, and assigns validity flags to each data point. The standard data flags warn users of missing values, invalidated values, valid values below detection limit, valid estimated and interpolated values, non-conforming sampling periods, and valid values that have been replaced by the detection limit. In this study, valid air concentrations from 16 sites were analyzed. Available air measurements between 1983 and 2010 at the 16 sites are shown in Table 1.

### 2.1.3 Precipitation concentrations

Precipitation is sampled using a wet-only precipitation collector, which automatically opens when sensors detect precipitation. Precipitation is collected in a specially-designed plastic bag in the collector. The bags containing precipitation are retrieved each day between 8:00 and 9:00 LT and are sealed, weighed and then kept refrigerated. The 24-hr integrated precipitation samples are analyzed for  $\text{H}^+$  and major inorganic ions (described in Sect. 2.1.2) in concentrations of  $\text{mg l}^{-1}$ . Precipitation amount is also recorded daily at the precipitation monitoring sites for the determination of wet deposition flux. Standard data flags similar to the air data are applied to the precipitation data. In this study, valid precipitation concentrations from 30 sites were analyzed. Available precipitation measurements between 1984 and 2011 at the 30 sites (two collocated collectors at Egbert) are shown in Table 1.

### 2.1.4 Meteorological data

Hourly air temperature, relative humidity and wind direction data at collocated or nearby stations to CAPMoN sites were obtained from the Canadian Climate Data Archives (Environment Canada, 2015b). Hourly air temperature and relative humidity were averaged to daily values to correspond with the sampling intervals of the air and precipitation concentrations. Hourly wind direction data were used to determine the prevailing wind directions at each site.

## 2.2. Data analysis

### 2.2.1 Long-term patterns

Geographical patterns and temporal trends in air concentrations and wet deposition were examined. The geographical patterns in air concentrations were based on 24-hr integrated measurements. For wet deposition, geographical patterns in the

annual wet deposition flux were analyzed since annual wet deposition is typically reported in previous studies. Daily precipitation concentrations were multiplied by the corresponding daily precipitation amount above the rain gauge detection limit of 0.2 mm. The annual wet deposition flux was obtained by summing the daily wet deposition flux. Thus, only the years with complete wet deposition data are used to determine the annual wet deposition. Statistical analyses of temporal trends were performed using regression analysis of the annual average air concentrations and annual wet deposition for all years with complete data. The Mann-Kendall Test and Seasonal Kendall Test were also applied to the annual wet deposition and annual average air concentrations, respectively, to assess whether there was a statistically significant monotonic trend (Gilbert, 1987; Prestbo and Gay, 2009; Zbieranowski and Aherne, 2011; Cole et al., 2014). The Seasonal Kendall and Sen's estimator of slope provides the magnitude of the temporal trend on a per year basis. The Seasonal Kendall test analyzes the temporal trend in the average air concentrations in each month separately and then aggregates the results to obtain the annual trend. The Mann-Kendall test, except it analyzes the temporal trend in each month separately (Gilbert, 1987). The Mann-Kendall test was used to obtain the annual total wet deposition trend because the magnitude of the slope (trend) based on monthly total wet deposition (if the Seasonal Kendall test was applied) is inconsistent with that of the annual wet deposition trend since wet deposition depends on the precipitation amount. The relationship between meteorological factors and temporal trends in air concentrations and wet deposition were also examined by correlation analysis. Correlation analysis was performed between monthly averaged meteorological parameters and particulate ions and trace gases. For wet deposition of inorganic ions, the correlations with the precipitation amount and air concentrations were examined.

### 2.2.2 Aerosol acidity

The molar cation/anion charge equivalent ratio (c/a) (Hennigan et al., 2015) was used as a measure of H<sup>+</sup> and aerosol acidity for the air sampling sites. The ions associated with acidic aerosols are predominantly SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>; however there are also contributions from organic acids which have not been accounted for by the c/a (Kerminen et al., 2001). Base cations and NH<sub>4</sub><sup>+</sup> are involved in neutralizing acidic aerosols. A c/a near 1 indicates that the aerosols are generally neutral, whereas a lower ratio near 0.75 is indicative of acidic aerosols (Zhang et al., 2007; He et al., 2012). Daily c/a were determined only if all the ion measurements are available.

### 2.2.3 Scavenging ratio

In this study, monthly scavenging ratios (W) were first determined for ions existing only in the particulate phase (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and Cl<sup>-</sup>) using Eq. 1 (Kasper-Giebl et al., 1998; He and Balasubramanian, 2008):

$$W = \frac{C_{\text{prec}}}{C_{\text{air}}} \times \frac{\rho_a}{\rho_w}, \quad (1)$$

$C_{\text{prec}}$  and  $C_{\text{air}}$  are the precipitation and air concentrations, respectively. Surface air concentrations were used, even though in theory most of the scavenging occurs at the cloud height (Duce et al., 1991).  $\rho_a$  and  $\rho_w$  are the densities of air ( $1.2 \text{ kg m}^{-3}$ ) and water, respectively, which are used to convert the scavenging ratios to a mass basis. Scavenging ratios were determined on a monthly basis because they have less variability compared to daily (i.e. paired) or precipitation event scavenging ratios (Galloway et al., 1993) and consider the average air concentration during both precipitation and dry periods (Kasper-Giebl et al., 1998). For the calculation of monthly scavenging ratios in Eq. 1, monthly volume-weighted precipitation concentrations and monthly average air concentrations based on  $\geq 15$  daily measurements in each month were used. Only daily precipitation concentrations with at least 0.2 mm precipitation amount were included. If there is insufficient data in each month, the scavenging ratio is not calculated. To account for the dependence on particle size distribution, the scavenging ratio of coarse PM ( $W_{\text{cPM}}$ ) was determined by averaging  $W_{\text{Ca}}$ ,  $W_{\text{Mg}}$ , and  $W_{\text{Na}}$  since these base cations are predominantly in coarse PM (Cheng et al., 2015).  $W_{\text{K}}$  was used as a surrogate for the scavenging ratio of fine PM ( $W_{\text{fPM}}$ ) for inland sites, whereas  $W_{\text{K}/2}$  was assumed for coastal sites to take into account the  $\text{K}^+$  that may be associated with coarse aerosols following the methodology in (Cheng et al., (2015). Atmospheric  $\text{K}^+$  is predominantly associated with fine particles at inland locations, but also associated with coarse sea salt aerosols at coastal locations. In our previous study (Cheng et al., 2015), we observed that the mean  $W_{\text{fPM}}$  was 34 to 52% of that of  $W_{\text{cPM}}$  at inland locations, but was 80% at the coastal sites. Therefore, the fine scavenging ratio was reduced by about a factor of 2 at coastal locations. Scavenging ratios and wet scavenging in general are also affected by the chemical composition of aerosols, gas solubilities, temperature, precipitation amount and type, droplet size, nucleation efficiency, vertical concentration differences, and cloud type, which can contribute to the large variability in the scavenging ratios (Cadle et al., 1990; Duce et al., 1991; Galloway et al., 1993).

#### 2.2.4 Relative contributions and scavenging ratios of gaseous and particulate phases

CAPMoN sites measure total  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  in precipitation. However, wet deposition of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  can be attributed to the precipitation scavenging of particulates and gases, such as  $\text{pNO}_3^-$  and  $\text{HNO}_3$ ,  $\text{pSO}_4^{2-}$  and  $\text{SO}_2$ , and  $\text{pNH}_4^+$  and  $\text{NH}_3$  (Kajino and Aikawa, 2015). To determine their relative contributions and the scavenging ratios of gases, particulate wet scavenging is first determined using  $W_{\text{cPM}}$ ,  $W_{\text{fPM}}$ , particulate air concentration, and mass fractions in fine and coarse PM. The difference between the total wet scavenging and particulate wet scavenging is assumed to be due to the precipitation scavenging of gases. This assumption was also used in previous studies to estimate  $\text{NO}_3^-$ ,  $\text{HNO}_3$ ,  $\text{SO}_4^{2-}$ , and  $\text{SO}_2$  scavenging ratios (Cadle et al., 1990) and the wet scavenging contributions by gaseous oxidized mercury and particulate mercury (Sakata and Asakura, 2007; Cheng et al., 2015). Eq. 2 was used to determine the wet scavenging of  $\text{pNO}_3^-$ :

$$[\text{pNO}_3^-]_{\text{prec}} = W_{\text{fPM}} [\text{pNO}_3^-]_{\text{air}} P_f + W_{\text{cPM}} [\text{pNO}_3^-]_{\text{air}} (1-P_f), \quad (2)$$

$W_{\text{fPM}}$  and  $W_{\text{cPM}}$  are the monthly scavenging ratios of fine and coarse PM, respectively (Sect. 2.2.3).  $[\text{pNO}_3^-]_{\text{air}}$  is the monthly average  $\text{NO}_3^-$  air concentration.  $P_f$  is the mass fraction of  $\text{NO}_3^-$  in fine PM, which varies with air mass origins and tends to

form at lower temperatures (Zhang et al., 2008; Zhao and Gao, 2008). A  $P_f$  of 0.84 was assumed for the winter months (DJF), whereas 0.29 was used for all other months. These are average mass fractions observed at CAPMoN sites in a short-term field study (Zhang et al., 2008). Eq. 2 accounts for the different scavenging efficiencies of small and large particles.

The contribution of  $\text{HNO}_3$  to nitrate wet deposition was calculated using Eq. 3:

$$5 \quad [\text{HNO}_3]_{\text{prec}} = [\text{total NO}_3^-]_{\text{prec}} - [\text{pNO}_3^-]_{\text{prec}}, \quad (3)$$

$[\text{total NO}_3^-]_{\text{prec}}$  is the monthly volume-weighted  $\text{NO}_3^-$  precipitation concentration and  $[\text{pNO}_3^-]_{\text{prec}}$  is the wet scavenging of  $\text{pNO}_3^-$  calculated from Eq. 2. If  $[\text{HNO}_3]_{\text{prec}} < 0$ , it is assumed that only  $\text{pNO}_3^-$  contributed to total nitrate precipitation and no gas scavenging occurred. The relative contributions of particulate and gaseous species to  $\text{NO}_3^-$  wet deposition were determined using Eq. 4 and 5. Scavenging ratios of  $\text{pNO}_3^-$  and  $\text{HNO}_3$  were determined using Eq. 1.

$$10 \quad \% \text{pNO}_3^- = ([\text{pNO}_3^-]_{\text{prec}} / [\text{total NO}_3^-]_{\text{prec}}) \times 100\%, \quad (4)$$

$$\% \text{HNO}_3 = ([\text{HNO}_3]_{\text{prec}} / [\text{total NO}_3^-]_{\text{prec}}) \times 100\%, \quad (5)$$

Similarly, Eq. 2-5 were used to determine the relative contributions of  $\text{pSO}_4^{2-}$  and  $\text{SO}_2$  to total  $\text{SO}_4^{2-}$  wet deposition and  $\text{pNH}_4^+$  and  $\text{NH}_3$  to total  $\text{NH}_4^+$  wet deposition. A  $P_f$  of 0.94 for  $[\text{pSO}_4^{2-}]_{\text{air}}$  and  $P_f$  of 0.954 for  $[\text{pNH}_4^+]_{\text{air}}$  was used for all months because these were the average mass fractions observed at CAPMoN sites (Zhang et al., 2008).  $\text{pSO}_4^{2-}$  and  $\text{pNH}_4^+$  have similar  $P_f$  because they have similar particle size distributions and often exist together as  $(\text{NH}_4)_2\text{SO}_4$  in the atmosphere. Scavenging ratios for  $\text{NH}_3$  were not determined because  $\text{NH}_3$  air concentrations were not available.

### 3 Results and Discussion

#### 3.1 Air concentrations

##### 3.1.1 Geographical patterns

20 Air concentration statistics and geographical patterns of eight particulate inorganic ions,  $\text{SO}_2$ , and  $\text{HNO}_3$  are plotted in Fig. 1a and b. The data were divided into two time periods from 1983-1996 and 1997-2010 to examine potential changes in concentrations due to  $\text{NO}_x$  and  $\text{SO}_2$  emission changes. The range in concentrations (based on the 5<sup>th</sup> percentile to 95<sup>th</sup> percentile concentration) from all daily samples at all locations was 0.009-2.9  $\mu\text{g m}^{-3}$  for  $\text{Ca}^{2+}$ , 0.002-0.5  $\mu\text{g m}^{-3}$  for  $\text{Mg}^{2+}$ , and 0.006-0.2  $\mu\text{g m}^{-3}$  for  $\text{K}^+$ . Larger variability was observed in  $\text{Ca}^{2+}$  likely because of the variability of soil emissions  
 25 depending on land use and wind. Large variability is also expected for  $\text{Na}^+$  and  $\text{Cl}^-$  because coastal sites are more frequently impacted by sea-salt aerosols than continental sites. The  $\text{Na}^+$  and  $\text{Cl}^-$  air concentrations ranged from 0.005-1.4  $\mu\text{g m}^{-3}$  and 0.003-1.9  $\mu\text{g m}^{-3}$ , respectively. The range in concentrations were 0.018-5.8  $\mu\text{g m}^{-3}$  for  $\text{NH}_4^+$ , 0.009-8.7  $\mu\text{g m}^{-3}$  for  $\text{NO}_3^-$ , and

0.07-14.5  $\mu\text{g m}^{-3}$  for  $\text{SO}_4^{2-}$ .  $\text{HNO}_3$  and  $\text{SO}_2$  ranged from 0.014-5.0  $\mu\text{g m}^{-3}$  and 0.011-25.2  $\mu\text{g m}^{-3}$ , respectively. These ions and trace gases are likely to have larger variability in air concentrations than base cations because some sites may be impacted more by anthropogenic emissions, which form secondary pollutants such as  $\text{SO}_4^{2-}$ ,  $\text{HNO}_3$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$ , than other sites.

5 The geographical patterns in air concentrations were examined in greater detail based on the median concentration at each location. Long-term median  $\text{Ca}^{2+}$  concentrations among the sites ranged from 0.03-0.6  $\mu\text{g m}^{-3}$ . The highest median during both time periods were observed at Longwoods and Egbert, which are the lowest latitude and most inland air concentration sites. Longwoods and Egbert are also predominantly agriculture sites. The median  $\text{Mg}^{2+}$  concentrations ranged from 0.01-0.09  $\mu\text{g m}^{-3}$ . The highest median was also observed at Longwoods and Egbert. Higher median concentrations were also  
10 found at several western Canada sites including at Bratt's Lake, Esther and Saturna in the post-1997 period. The median concentrations ranged from 0.02-0.06  $\mu\text{g m}^{-3}$  for  $\text{K}^+$ , which is the ion with the least spatial variability in the air concentration. The highest concentrations were observed at Longwoods as well as at Bratt's Lake post-1997. The median  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations ranged from 0.02-0.5  $\mu\text{g m}^{-3}$  and 0.007-0.3  $\mu\text{g m}^{-3}$ , respectively. As expected, the highest median for both ions were observed at the two coastal locations, Saturna and Kejimikujik, due to the proximity to sea-salt aerosol emissions  
15 from the ocean. These two sites are the farthest west and east air sampling locations respectively.  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations at Saturna were larger and had greater variability than at Kejimikujik likely because of the higher frequency of marine airflows arriving at Saturna (68% of winds from N and W directions) than at Kejimikujik (31% of winds from E and S directions).

The median  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations ranged from 0.1-1.7  $\mu\text{g m}^{-3}$  and 0.03-2.0  $\mu\text{g m}^{-3}$ , respectively (Fig. 1a and b).  
20 Compared to pre-1997 period, the median concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were lower in the post-1997 period. The highest concentrations for both ions were observed at Longwoods and Egbert. Higher concentrations were also found at Sutton, Esther, and at Frelighsburg post-1997. The majority of these sites except for Sutton are agriculture sites located in southern Ontario and Quebec, which implies that higher ammonia emissions from agricultural regions may react with acidic gases in the atmosphere to form particulate ammonium (Pitchford et al. 2009). Acidic gases, such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , are produced  
25 from the oxidation of  $\text{SO}_2$  and  $\text{NO}_x$  respectively and are primarily emitted from industrial and urban areas. The proximity of these lower latitude air sampling sites to major industrial areas in Ohio and Pennsylvania, USA could result in higher acidic gas concentrations at these sites. This is evident in the air concentration plots for  $\text{HNO}_3$  that show higher concentrations of  $\text{HNO}_3$  at sites having higher  $\text{NO}_3^-$ . The median  $\text{HNO}_3$  concentrations ranged from 0.07-1.1  $\mu\text{g m}^{-3}$ . Southerly winds also impacted Longwoods, Egbert, and Frelighsburg/Sutton approximately 20%, 32%, and 34% of the time, respectively. The  
30 median  $\text{SO}_4^{2-}$  concentrations among the air sampling sites ranged from 0.6-3.5  $\mu\text{g m}^{-3}$ . The concentrations were lower during the post-1997 than during the pre-1997 period. The highest median concentration was observed at Longwoods. Higher median concentrations were found at several southern Ontario and Quebec sites including Egbert, Sutton, Frelighsburg, Sprucedale, and Chalk River. Larger variability in the concentrations was generally observed across sites in

southern and eastern Canada. This pattern is likely attributed to the proximity of the sites to combustion and industrial sources in southern Ontario and Quebec. The southern Canada and Atlantic Canada sites (e.g. Kejimikujik) are downwind of combustion and industrial areas in Ohio and Pennsylvania. In contrast,  $\text{SO}_4^{2-}$  concentrations at sites located in western and central Canada (e.g., Saturna, Esther, Cree Lake, Bratt's Lake, and ELA) were at or below the overall median concentration of all the sites and had smaller variability.

The median  $\text{SO}_2$  concentrations ranged from 0.4-6.4  $\mu\text{g m}^{-3}$  during the 1983-1996 period and from 0.6-2.3  $\mu\text{g m}^{-3}$  post-1997 (Fig. 1b). There was also a reduction in the variability of the concentrations in the post-1997 period. The lower latitude southern Ontario and Quebec sites had higher  $\text{SO}_2$  concentrations, whereas western and central Canada sites had much lower concentrations. This geographical pattern is similar to that of  $\text{SO}_4^{2-}$ . One exception was that the  $\text{SO}_2$  concentrations in eastern Canada were similar to or even lower than in western Canada, whereas  $\text{SO}_4^{2-}$  concentrations in eastern Canada were slightly higher than in western Canada. Eastern Canada sites including Montmorency, Lac Edouard, and Kejimikujik are remote sites; therefore  $\text{SO}_2$  concentrations are likely not elevated by the time it arrives at these remote locations since  $\text{SO}_2$  can undergo deposition or transform to  $\text{SO}_4^{2-}$  during transport. The slightly higher  $\text{SO}_4^{2-}$  in eastern Canada could be from sea-salt sulfate due to the proximity to the Atlantic Ocean.

### 3.1.2 Temporal patterns

The Kendall slopes and confidence interval in Table 2 shows the annual rate of change in the concentrations of particulate ions and trace gases at the air sampling sites for all years with available data. A significant temporal trend in  $\text{Ca}^{2+}$  was observed at 5 of 16 sites with no significant changes in the concentrations observed at the remaining sites. Decreasing trends were observed at Saturna, Longwoods, and Egbert, while increasing trends were observed at Esther and Kejimikujik. The largest decline in  $\text{Ca}^{2+}$  was  $-16 \text{ ng m}^{-3} \text{ a}^{-1}$  at Longwoods. Overall the temporal changes in  $\text{Ca}^{2+}$  are small. For  $\text{Mg}^{2+}$ , a significant decreasing trend was found at Saturna, Longwoods, Chalk River, and Kejimikujik. However, the rate of decline was very small ranging only from  $-0.5$  to  $-1.1 \text{ ng m}^{-3} \text{ a}^{-1}$ . The rate of decline for  $\text{K}^+$  ranged from  $-0.5$  to  $-3.8 \text{ ng m}^{-3} \text{ a}^{-1}$  and was observed at 14 of 16 sites. A plot of the annual average  $\text{K}^+$  for ten of the active air sampling sites are shown in Fig. 2a for the 1983-2010 period, which illustrates a gradual decline in  $\text{K}^+$ . Significant decreases in  $\text{Na}^+$  were found at 11 of 16 sites with magnitudes ranging from  $-0.3$  to  $-4.5 \text{ ng m}^{-3} \text{ a}^{-1}$ . The steepest decline was observed at a coastal site in western Canada. However, increasing trends were observed at two coastal sites in eastern Canada (Montmorency and Kejimikujik). For  $\text{Cl}^-$ , decreasing temporal trends were found at only 6 of 16 sites, suggesting that the temporal trends are not necessarily related to sea-salt emissions. The decline in  $\text{Cl}^-$ , ranging from  $-0.1$  to  $-0.8 \text{ ng m}^{-3} \text{ a}^{-1}$ , were found at sites in western and central Canada and at Algoma and Longwoods.

$\text{NH}_4^+$  concentrations have been decreasing at 12 of 16 air sampling sites (Table 2). This result is consistent with the widespread decrease in  $\text{NH}_4^+$  at CAPMoN sites during 1988-2007 (Zbieranowski and Aherne, 2011). The rate of decrease ranged from  $-4$  to  $-58 \text{ ng m}^{-3} \text{ a}^{-1}$ . The largest declines as shown in Fig. 2b were observed at Longwoods, Egbert, Sprucedale,

and Frelighsburg, which are agriculture sites located in southern Ontario and Quebec. The annual decrease was 7.3 times greater than other sites based on the linear regression slopes. The decreasing trend in  $\text{NH}_4^+$  corresponds to the decreasing trend in ammonia emissions in Ontario and Quebec particularly in the post-2002 period (Fig. 2b) (Environment Canada, 2014). Aside from its relationship to ammonia, the negative trend in  $\text{NH}_4^+$  was also strongly tied to trends in  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

5 There was an even split in the number of sites with increasing trends and decreasing trends in  $\text{NO}_3^-$ . The rate of increase ranged from 1.3-6.4  $\text{ng m}^{-3} \text{ a}^{-1}$  among active sites, whereas the annual trend was 6-40  $\text{ng m}^{-3} \text{ a}^{-1}$  among inactive sites (e.g. Esther, Sutton, Montmorency). The annual trend in  $\text{NO}_3^-$  decreased from -9.3 to -53  $\text{ng m}^{-3} \text{ a}^{-1}$  at other sites (Table 2). Larger declines were observed at the agriculture sites located in southern Ontario and Quebec. Differences in temporal trends were also observed during different time periods. At 9 of 16 sites, an increasing trend was found between 1991 and

10 2001 which was followed by a decreasing trend from 2001 to 2010 (Fig. 3). The difference in  $\text{NO}_3^-$  trends between the two decades was also reported in previous analysis of CAPMoN sites (Zbieranowski and Aherne, 2011). The change in  $\text{NO}_3^-$  temporal trends closely resembled that of  $\text{NO}_x$  emissions in Canada. Between 1991 and 1997,  $\text{NO}_x$  emissions in Canada increased annually and only began to decrease from 1997 to 2010 (Fig. 3) (Environment Canada, 2014). In the U.S.,  $\text{NO}_x$  emissions were constant over the 1991-1994 period and only began to decrease after 1994 (USEPA, 2015). Reductions in

15  $\text{NO}_x$  emissions were implemented following the introduction of the Canada-U.S. Air Quality Agreement and the U.S. Acid Rain Program and Clean Air Interstate Rule. The decrease in  $\text{NO}_x$  emissions were largely attributed to lower emissions from stationary fuel combustion and transportation sectors (Lloret and Valiela, 2016).

$\text{SO}_4^{2-}$  decreased at a rate of -28 to -109  $\text{ng m}^{-3} \text{ a}^{-1}$  depending on the location (Table 2). The steepest annual declines were observed in the southern Ontario and Quebec region as shown in Fig. 4. The slope of the linear regression equation for the

20 southern Ontario and Quebec sites in Fig. 4 was two times greater than that of other air sampling sites, which are coastal or higher latitude sites distant from major industrial and urban areas. The geographical patterns in the temporal trends of  $\text{SO}_4^{2-}$  were also similar to those of  $\text{SO}_2$  and  $\text{HNO}_3$ . The annual trends for  $\text{SO}_2$  and  $\text{HNO}_3$  in the southern Ontario and Quebec region declined 3.8 and 4.9 times faster, respectively, than other air sampling sites across Canada based on the linear regression slopes. Negative trends for  $\text{SO}_4^{2-}$  and  $\text{SO}_2$  concentrations followed the decreasing trend in  $\text{SO}_2$  emissions in both

25 Canada and U.S. since 1990 (Environment Canada, 2014; USEPA, 2015) (Fig. 4), corresponding to the period of the Canada-U.S. Air Quality Agreement and the U.S. Acid Rain Program and Clean Air Interstate Rule. Note the steeper decline in  $\text{SO}_2$  emissions in Ontario in recent years, which is potentially attributed to the phase-out of coal use in Ontario power plants beginning in 2005 (MOE, 2015).

The influence of meteorological parameters including temperature, relative humidity and precipitation rates on the temporal

30 trends of particulate ions and trace gases were also investigated by performing correlation analyses on the monthly averaged data. The descending trend in  $\text{K}^+$  between 1993 and 2010 at the majority of the sites was not strongly influenced by precipitation as evident by the weak correlation coefficients (Table S1). Higher correlation between monthly average  $\text{K}^+$  and temperature were found at Sprucedale, Frelighsburg and Lac Edouard ( $r = 0.52-0.69$ ,  $p < 0.05$ ). At these sites, the monthly

average  $K^+$  peaked in March-April and was at the minimum concentration during December-January, which resembled the seasonal temperature cycle (Fig. S2a). The higher  $K^+$  in the early spring could be attributed to increase soil emissions from agriculture operations and forest fires during springtime since the major sources of particulate  $K^+$  are from biomass and soil. Decreasing  $NH_4^+$  observed at most of the sites was only weakly correlated with monthly precipitation rates and relative humidity, implying these meteorological parameters had little influence on the long-term temporal trend. Higher correlation between monthly average  $NH_4^+$  and temperature was found at Kejimikujik ( $r = 0.63$ ,  $p < 0.05$ ). The maximum  $NH_4^+$  typically occurred during April-May and reached its lowest concentration during December-January (Fig. S2b). This seasonal trend is linked to the formation of  $SO_4^{2-}$  through  $SO_2$  oxidation, which tends to occur at higher temperatures because of increase production of atmospheric oxidants. This theory is consistent with the very high correlation between monthly average  $NH_4^+$  and  $SO_4^{2-}$  ( $r = 0.91$ ,  $p < 0.05$ ) at Kejimikujik. Overall, strong correlations between  $NH_4^+$  and  $SO_4^{2-}$  were observed at all the sites ( $r = 0.6-0.94$ ,  $p < 0.05$ ). The high correlation between  $SO_4^{2-}/SO_2$  ratio and temperature ( $r = 0.61-0.84$ ,  $p < 0.05$ ) suggests  $SO_4^{2-}$  formation from the gas-phase oxidation of  $SO_2$  (Yao et al., 2002). Besides the relationship between  $NH_4^+$  and  $SO_4^{2-}$ , three of the sites including Saturna, ELA and Egbert exhibited strong correlations between  $NH_4^+$  and  $NO_3^-$  ( $r = 0.52-0.7$ ,  $p < 0.05$ ) indicating that  $NH_4^+$  also followed the temporal trend of  $NO_3^-$  at some locations. In summary, precipitation and relative humidity had little impact on the long-term temporal patterns of particulate ions. Seasonal temperature trends is linked with the seasonal cycle of atmospheric oxidants which explains the short-term patterns in  $SO_4^{2-}$  and  $NH_4^+$ ; however, there is no clear evidence that long-term temperature changes impacted their long-term trends.

### 3.1.3 Aerosol acidity (c/a)

The median c/a ranged from 0.97-1.6 and an overall median c/a of 1.07 was observed across all sites (Fig. 5a). These values are based on inorganic ion contributions to aerosol acidity. Organic acids do not contribute significantly to aerosol acidity compared to the strong inorganic acids (Zhang et al., 2007; Ziemba et al., 2007; He et al., 2012); however, they have been included in the measure of aerosol acidity in some studies (Hennigan et al., 2015 and references therein). Among the sites, the highest aerosol acidity was observed at Kejimikujik because of the higher equivalent anion concentrations relative to cations (Table S2). Higher aerosol acidity was prevalent generally in eastern Canada and central Ontario regions. In contrast to Kejimikujik, the majority of the sites had higher cation than anion concentrations or near equivalent cation and anion concentrations (Table S2). Even though locations like Longwoods and Egbert had greater amount of anions than other locations due to higher  $NO_3^-$  and  $SO_4^{2-}$ , there were sufficient amounts of cations, mainly  $NH_4^+$ , to neutralize the acidic species. While the overall median c/a was close to 1 for all Canadian sites, more than half of the daily c/a data were below 1 at eight locations (Fig. 5a). This suggests there was a substantial amount of time between 1994 and 2010 when aerosols were acidic at some Canadian sites.

A significant increasing trend in the c/a was observed between 1994 and 2010, which indicates a widespread decline in aerosol acidity (Fig. 5b). The rate of decrease in aerosol acidity was small and fairly uniform spatially based on the Kendall

slope results. According to [Table S2](#) and Fig. 5b, the annual average cation and anion concentrations and c/a at most of the sites (data combined from 13 of 15 sites) were relatively constant between 1994 and 2000. Since 2001, the annual average cation and anion concentrations and aerosol acidity have been on a slight decline ([Table S2](#)). The decrease in cation concentrations appeared consistent with the declining trend in  $\text{NH}_4^+$  discussed earlier, since  $\text{NH}_4^+$  is the largest contributor to cation concentrations. For anions,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are the predominant ions. Thus, the decline in anions was also consistent with the decreasing rates for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . As mentioned earlier, the decreasing trends in  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were consistent with the reductions in ammonia,  $\text{NO}_x$  and  $\text{SO}_2$  emissions.

## 3.2 Wet deposition

### 3.2.1 Geographical patterns

The annual wet deposition statistics for the various ions at the 30 locations are shown in Fig. 6. The annual wet deposition was based on all years with complete data because the annual flux was determined by summing the daily fluxes. The range in the annual wet deposition based on the 5<sup>th</sup> and 95<sup>th</sup> percentile annual wet deposition rate ( $\text{kg ha}^{-1} \text{a}^{-1}$ ) was: 0.08-3.6 for  $\text{Ca}^{2+}$ , 0.02-1.6 for  $\text{Mg}^{2+}$ , 0.01-0.7 for  $\text{K}^+$ , 0.03-12.0 for  $\text{Na}^+$ , 0.06-23.0 for  $\text{Cl}^-$ , 0.1-6.4 for  $\text{NH}_4^+$ , 0.4-26.5 for  $\text{NO}_3^-$ , and 0.5-32.7 for  $\text{SO}_4^{2-}$ . The lowest annual wet deposition rates for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  were observed at Snare Rapids, which is a remote site in the Northwest Territories of Canada. The highest annual wet deposition recorded at the most eastern coastal site in Bay d'Espoir, Newfoundland were from ions related to sea-salt aerosols, including  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{Mg}^{2+}$ . For  $\text{Ca}^{2+}$  and ions derived from anthropogenic sources (e.g.,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ), the highest annual wet deposition rates were observed at Priceville and Longwoods, which are the two most southern wet deposition sites in Canada and closest to urban and industrial areas.

Long-term median annual wet deposition of  $\text{Ca}^{2+}$  ranged from 0.1-2.8  $\text{kg ha}^{-1} \text{a}^{-1}$  among the wet deposition sites. The highest annual wet deposition was observed at Priceville and Longwoods (Fig. 6). Higher median wet deposition was also found at Algoma, Egbert, and Warsaw Caves. The majority of these sites are agriculture sites. The lowest median wet deposition was observed at the western and eastern coastal sites. The median annual wet deposition of  $\text{Mg}^{2+}$  ranged from 0.03-1.0  $\text{kg ha}^{-1} \text{a}^{-1}$ . The highest wet deposition was found at the western and eastern coastal sites with the exception of Goose Bay, which is a higher latitude coastal site located in Labrador. It had the lowest annual precipitation amount among coastal sites in eastern Canada (Fig. S3). Annual  $\text{Mg}^{2+}$  wet deposition at inland sites was typically at or below the overall median wet deposition for all sites; however, they are slightly higher at Longwoods and Priceville. The median annual wet deposition of  $\text{K}^+$  ranged from 0.05-0.4  $\text{kg ha}^{-1} \text{a}^{-1}$ . Similar to  $\text{Mg}^{2+}$ , higher annual wet deposition of  $\text{K}^+$  was observed at eastern coastal locations with the exception of Goose Bay. Annual wet deposition for inland sites was around the overall median annual wet deposition for all sites except at Longwoods, Algoma and Priceville. The median annual wet deposition of  $\text{Na}^+$  and  $\text{Cl}^-$  ranged from 0.05-7.5  $\text{kg ha}^{-1} \text{a}^{-1}$  and 0.1-13.6  $\text{kg ha}^{-1} \text{a}^{-1}$ , respectively. The geographical patterns in the annual wet

deposition were similar between  $\text{Na}^+$  and  $\text{Cl}^-$ . Annual wet deposition at western and eastern coastal sites were higher and had greater variability than inland locations.

Median annual  $\text{NH}_4^+$  wet deposition ranged from 0.2-5.8  $\text{kg ha}^{-1} \text{a}^{-1}$  (Fig. 6). Higher annual wet deposition was observed at lower latitude continental sites. Higher latitude continental locations (e.g. Cree Lake, Island Lake, Pickle Lake, Bonner Lake, Chapais) and coastal locations were well below the overall median annual wet deposition. The median annual wet deposition ranged from 0.8-23.3  $\text{kg ha}^{-1} \text{a}^{-1}$  for  $\text{NO}_3^-$  and 0.8-26.6  $\text{kg ha}^{-1} \text{a}^{-1}$  for  $\text{SO}_4^{2-}$ . These two ions have similar spatial patterns in annual wet deposition. Higher median annual wet deposition occurred at southern Ontario and Quebec sites. Lower median annual wet deposition was observed in eastern Canada. The lowest median annual wet deposition for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , which were well below the overall median annual wet deposition for all sites, was recorded in western and central

Canada. These results are consistent with Vet et al. (2014), which observed higher sulfur wet deposition around Lake Ontario and Lake Erie and much lower sulfur wet deposition in western North America than eastern North America.

The geographical patterns in the wet deposition were predominantly affected by the air concentrations. For example, the higher  $\text{Na}^+$  and  $\text{Cl}^-$  wet deposition at coastal locations can be traced back to the higher  $\text{Na}^+$  and  $\text{Cl}^-$  air concentrations. Similarly, the higher  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  wet deposition occurring at southern Ontario and Quebec locations was consistent with the geographical patterns in the air concentrations. Although precipitation amount is used to determine wet deposition, only the wet deposition patterns of  $\text{Mg}^{2+}$  and  $\text{K}^+$  were potentially influenced by precipitation amount. As shown in Fig. S3, the annual precipitation amount generally increases from western to eastern sites. Only the  $\text{Mg}^{2+}$  and  $\text{K}^+$  wet deposition were higher at eastern Canada locations.

### 3.2.2 Temporal trends

Long-term temporal trends in the annual wet deposition of ions were analyzed using Sen's slope (Table 3 and 4) and linear regression analysis. The annual wet deposition of  $\text{Ca}^{2+}$  and  $\text{K}^+$  has not changed significantly at almost all locations. For  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , there were no significant changes in the annual wet deposition rate at most of the sites, while a very small statistically significant decline in the annual wet deposition was observed at other sites. Of these sites, the rate of decline ranged from -0.001 to -0.008  $\text{kg ha}^{-1} \text{a}^{-1}$  for  $\text{Mg}^{2+}$  and -0.002 to -0.02  $\text{kg ha}^{-1} \text{a}^{-1}$  for  $\text{Na}^+$ . Decline in base cations has been reported at other Canadian sites during the 1990s (Watmough et al., 2005). The small decrease or lack of change in base cation wet deposition is expected because the major source of base cations at rural Canadian sites are from natural emissions (Watmough et al., 2005). Monitoring the wet deposition  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  trends are important because these ions neutralize soil acidity and mitigate further harmful impacts to plants and wildlife. A declining trend in the  $\text{Cl}^-$  wet deposition was observed at 5 of 16 sites (Fig. 7a), and the magnitude ranged from -0.007 to -0.03  $\text{kg ha}^{-1} \text{a}^{-1}$  (Table 3).

Significant trends in the annual wet deposition of  $\text{NH}_4^+$  were observed at only 3 of 16 locations. There were two sites with increasing temporal trend (0.05  $\text{kg ha}^{-1} \text{a}^{-1}$ ), whereas a decreasing trend was found at one location (Table 4). A lack of an

overall consistent temporal trend in precipitation  $\text{NH}_4^+$  was also found in previous analysis of CAPMoN sites (Zbieranowski and Aherne, 2011). These trends were in contrast to those in the U.S., which has seen an increase in precipitation  $\text{NH}_4^+$  at 64% of the wet deposition sites between 1985 and 2004 (Lehmann et al., 2007). While increasing  $\text{NH}_4^+$  in precipitation helps to increase precipitation pH and promote plant growth, a counter-effect is that soils can become acidic when  $\text{NH}_4^+$  undergoes nitrification (Vogt et al., 2006).

Declining trends in  $\text{NO}_3^-$  wet deposition was observed at 10 of 16 sites (data combined in Fig. 7a), while no significant trend was found at other locations. The rate of decrease ranged from  $-0.07$  to  $-1.0 \text{ kg ha}^{-1} \text{ a}^{-1}$  and was largest at the southern Ontario and Quebec sites (Algoma, Longwoods, Egbert, Sprucedale, Frelighsburg, Lac Edouard). One exception was the non-significant trend at Sutton (Table 4) even though this site is only 15 km from Frelighsburg. The discrepancy in the temporal trends at these two sites can be partially attributed to the different measurement periods. Measurements of wet deposition at Sutton ended in 2002, whereas Frelighsburg has been actively measuring wet deposition since 2001. This suggests the rate of decrease in  $\text{NO}_3^-$  wet deposition was more rapid in the period after 2001 and corresponds with the decline in  $\text{NO}_3^-$  air concentrations over the same time period discussed earlier. In the U.S. northeast, the decline in precipitation  $\text{NO}_3^-$  was observed at only 25% of the sites in that region during 1985-2004 (Lehmann et al., 2005). A recent study of  $\text{NO}_3^-$  wet deposition from 1985-2011 across North America indicates a 40-50% decrease in eastern North America after 2000 (Lloret and Valiela, 2016). Similar to the air concentrations of  $\text{SO}_4^{2-}$ , decline in  $\text{SO}_4^{2-}$  wet deposition was also prevalent throughout Canadian sites. This finding is consistent with the decrease in precipitation  $\text{SO}_4^{2-}$  reported at other Canadian sites during the 1990s (Watmough et al., 2005) and at 89% of the wet deposition sites in the U.S. between 1985 and 2004 (Lehmann et al., 2007). Decreasing temporal trends in  $\text{SO}_4^{2-}$  wet deposition was found at 11 of 16 sites with magnitudes ranging from  $-0.1$  to  $-1.0 \text{ kg ha}^{-1} \text{ a}^{-1}$  depending on the location (Table 4). The overall rate of decline was  $\sim 2$  times higher at the southern Ontario and Quebec sites relative to other locations (Fig. 7b), which is consistent with the patterns in the air concentrations of  $\text{SO}_4^{2-}$  described earlier. The large declining trends in the wet deposition of nitrogen and sulfur-containing species in conjunction with the relatively smaller declines or lack of change in base cations indicate that acid rain has attenuated over time. This is largely attributed to policies controlling  $\text{NO}_x$  and  $\text{SO}_2$  emissions.

Daily wet deposition of ions was correlated with their respective daily particulate matter concentrations and daily precipitation amount to gain insight into factors influencing the temporal trends in wet deposition. Moderate correlations ( $r = 0.38-0.41$ ,  $p < 0.05$ ) between daily wet deposition and particulate matter concentration were found for  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$ , whereas only weak correlations were found for other ions. This result partly explains the prevalent decline in wet deposition of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ . Decreasing  $\text{NO}_3^-$  wet deposition was also widespread; however it did not strongly correlate with particulate  $\text{NO}_3^-$  concentrations ( $r = 0.21$ ,  $p < 0.05$ ). This is potentially because both gaseous and particulate nitrogen species can contribute to  $\text{NO}_3^-$  wet deposition. This is supported by the slightly higher correlation ( $r = 0.33$ ,  $p < 0.05$ ) between daily  $\text{NO}_3^-$  wet deposition and  $\text{HNO}_3$ . For  $\text{SO}_4^{2-}$  wet deposition which can be attributed to the precipitation scavenging of particulate  $\text{SO}_4^{2-}$  and  $\text{SO}_2$ , only a weak correlation was found between daily  $\text{SO}_4^{2-}$  wet deposition and  $\text{SO}_2$  ( $r = 0.13$ ,  $p < 0.05$ ). Further

analysis on the relative contributions of gaseous and particulate species to  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  wet deposition will be discussed in Sect. 3.4. Moderate correlations between daily wet deposition and daily precipitation were found for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ( $r=0.50-0.56$ ,  $p<0.05$ ), while weaker correlations were found for other ions. Some correlation was expected because wet deposition is determined from precipitation concentration and precipitation amount. On an annual basis, there has been no significant change to the annual precipitation amount at most of the sites, except for significant increases at Bratt's Lake, ELA, Chalk River, and Kejimikujik (Table 4). The lack of change to the annual precipitation is inconsistent with the decreasing trends in  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  annual wet deposition found at the majority of the sites. Thus, long-term wet deposition of ions was not strongly influenced by long-term precipitation trends between 1983 and 2010.

### 3.2.3 Acid rain

The geographical patterns in acid rain as measured by precipitation pH are shown in Fig. 8. Precipitation pH is slightly acidic by nature due to the presence of carbonic acid formed by the dissolution of  $\text{CO}_2$ . A pH below 5 is considered to be acidic precipitation (Lehmann et al., 2007). According to Fig. 8, the median pH in daily precipitation samples across the sites ranged from 4.4-5.7. Between 1983 and 2011, acidic precipitation was observed in more than 50% of the daily precipitation samples at 19 of 31 or 61% of the sites. Acidic precipitation was prevalent in southern Ontario and some parts of eastern Canada, whereas pH was above 5 in western and central Canada. Similarly in regions close to southern Ontario and eastern Canada, higher occurrences of acid rain have been observed in the U.S. northeast region during the 1994-1996 and 2002-2004 periods (Lehmann et al., 2007). Acid rain has contributed to the acidification of soil and lakes (Stoddard et al., 1999; Driscoll et al., 2001; Clair et al., 2002; 2003; Jeffries et al., 2003; Watmough and Dillon, 2003). In the southern Ontario and eastern Canada region, the acid deposition effects are more concerning because the soil is slightly acidic naturally and shallow and the underlying bedrock provides insufficient acid buffering capacity (Clair et al., 2002; Watmough and Dillon, 2003). The geographical patterns in precipitation pH were consistent with those of aerosol acidity discussed earlier. The correlation between the median pH and aerosol acidity (as measured by c/a ratio) among 15 locations was 0.68, which suggests acidic particles partially contributed to acid rain at various Canadian sites.

Between 1983 and 2011, an increasing trend in pH was observed at 13 of 16 sites, while no significant change in pH was found at the remaining three sites (Table 4). The overall decline in acidic precipitation in Canada is consistent with the trends in the U.S. (Lehmann et al., 2007) [and  \$\text{H}^+\$  wet deposition trends between 2000-2002 and 2005-2007 periods over most of North America, Europe and Africa \(Vet et al., 2014\)](#). The rate of increase in pH was slightly higher at southern Ontario and Quebec sites (Table 4). Recent studies indicate there has been a gradual improvement to soil and surface water conditions due to decreases in  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  wet deposition; however, this recovery has been outpaced by the rate of decline in acidic wet deposition (Strock et al., 2014; Lawrence et al., 2015). The increasing temporal trends in pH can be partially attributed to aerosol acidity. A correlation of 0.29 between daily pH and c/a was found in this study. Based on the

annual trend between the 1994 and 2010 period, the annual average pH and c/a (data combined at 13 of 15 sites) had very similar trends (Fig. 5b) and the correlation coefficient improved to 0.86.

### 3.3 Scavenging ratios

#### 3.3.1 General statistics and comparisons with literature

5 A summary of the monthly average scavenging ratio ( $W$ ) (on a mass basis) statistics for the inorganic ions and trace gases are provided in Table [S2S3](#). Monthly  $W_{Ca}$  ranged from 120-14338. The minimum and maximum values were found at Egbert and Algoma, respectively.  $W_{Mg}$  ranged from 131-11243. The lowest  $W$  was recorded at Chapais, while the highest  $W$  was recorded at Kejimikujik.  $W_{Na}$  ranged from 76-12165. The lowest  $W$  was recorded at Chapais, while the highest  $W$  was recorded at Kejimikujik similar to  $Mg^{2+}$ . The  $W_K$  ranged from 69-5565 and had lower values compared to  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  because  $K^+$  is predominantly in fine particulate matter except for an additional coarse mode found at coastal locations (Zhang et al., 2008). For this reason, it is assumed that the  $W$  of fine PM ( $W_{fPM}$ ) was equivalent to the  $W_K$  for inland sites, while  $W_{K/2}$  was assumed for coastal sites. The minimum and maximum  $W_K$  were found at Montmorency and Kejimikujik, respectively. Since  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$  are mainly associated with coarse particulate matter, the average  $W$  of these ions was used as an estimate of the  $W$  of coarse particles ( $W_{cPM}$ ). The range of  $W_{cPM}$  was 83-12165. The minimum and maximum values were found at Chapais and Kejimikujik, respectively. The  $W_{Cl}$  ranged from 210-35521. The minimum and maximum values were found at Chapais and Algoma, respectively. Compared to other ions,  $W_{Cl}$  were larger and had greater variability. Overall, the range in the average  $W$  for these ions among the 13 sites was within the average  $W$  from previous studies (Table [S3S4](#)).

20 Monthly scavenging ratios were determined for particulate  $NO_3^-$  ( $pNO_3^-$ ) and  $HNO_3$  separately because both gaseous and particulate forms can contribute to  $NO_3^-$  wet deposition. Monthly  $W$  ranged from 135-4272 for  $pNO_3^-$  and 7-16658 for  $HNO_3$ . Based on the average scavenging ratio,  $W_{HNO_3}$  were greater than  $W_{pNO_3}$ . The average  $W_{pNO_3}$  from 13 sites were within the range of literature values in Table [S3S4](#); however the majority of the  $W_{pNO_3}$  in the literature are determined from total nitrate in precipitation and  $pNO_3^-$  in air. Thus, most of the  $W_{pNO_3}$  are overestimated. Scavenging ratios of  $pNO_3^-$  based on total nitrate in precipitation are higher by a factor of 1.4-18 depending on the site (average: factor of 6).

25 In this study, the average  $W_{HNO_3}$  at some sites were higher than those in Table [S3S4](#); however, they were most comparable to the average determined by Cadle et al. (1990) likely because of the similarity in the methods of determining  $W_{HNO_3}$ . The method first calculates the  $pNO_3^-$  scavenged and then the difference between the total  $NO_3^-$  and the  $pNO_3^-$  scavenged is assumed to be contributed by  $HNO_3$  scavenging. One major difference in the approach was that Cadle et al. (1990) used  $W_K$  as a surrogate for  $W_{pNO_3}$  to estimate the  $pNO_3^-$  scavenged, whereas in this study  $W_{pNO_3}$  considered the seasonal particle size distribution of  $pNO_3^-$ . The average  $W_{HNO_3}$  at some sites in this study were different than those determined by Hicks (2005) (Table [S3S4](#)), who assumed only  $HNO_3$  contributed to  $NO_3^-$  wet deposition. The values were also different from that of

Kasper-Giebl et al. (1998), who used a multiple linear regression (MLR) approach. For comparison purposes,  $W_{pNO_3}$  and  $W_{HNO_3}$  derived from MLR are also shown in Table S3-S4 and S4S5. The MLR results show  $W_{HNO_3} > W_{pNO_3}$ . However, this empirical method generated higher  $W_{pNO_3}$  and lower  $W_{HNO_3}$  at some locations compared to the method used in this study. Table S4-S5 indicates that the MLR model fit was considered weak to moderate ( $R^2 = 0.15-0.34$ ) depending on the site.

5 Monthly  $W_{pNH_4}$  ranged from 63-4356. The lowest  $W$  was recorded at Egbert, while the highest  $W$  was recorded at Algoma. Scavenging ratios of  $NH_3$  were undetermined because  $NH_3$  air concentrations were not available. Average  $W_{pNH_4}$  were also lower than some of the values in the literature (Table S3S4), which are likely overestimated because the values were based on the total  $NH_4^+$  precipitation concentrations, instead of  $pNH_4^+$  scavenged by precipitation. Comparison of these two methods of calculation indicates that the use of total  $NH_4^+$  precipitation concentration overestimated the scavenging ratios by 10 4-48% (average: 22%) depending on the location. Despite the coexistence of  $NH_4^+$  and  $SO_4^{2-}$  in the atmosphere, the difference between the average scavenging ratios of these ions can vary by 4-98% (average: 32%). The range of monthly scavenging ratios for  $pSO_4^{2-}$  and  $SO_2$  were 75-3146 and 0.3-12068, respectively. The average  $W_{pSO_4}$  among the sites in this study were lower than some of the literature values in Table S3S4. Most of the studies excluded the wet scavenging of  $SO_2$  because  $pSO_4^{2-}$  was assumed to be the dominant contributor to  $SO_4^{2-}$  wet deposition. This method overestimates the 15 scavenging ratio of  $pSO_4^{2-}$  by 18-85% (average: 44%) compared to the method used in this study. According to the limited number of  $W_{SO_2}$  estimates (Table S3S4), the precipitation scavenging of  $SO_2$  is less important compared to  $pSO_4^{2-}$  because of the lower  $W_{SO_2}$ . In this study,  $SO_2$  and  $pSO_4^{2-}$  can be equally important at times in terms of scavenging ratios. The average  $W_{SO_2}$  at more than half of the sites in this study were greater than literature averages. This is potentially due to the different methodologies for calculating  $W_{SO_2}$  and precipitation type. The MLR method yielded higher  $W_{pSO_4}$  and lower  $W_{SO_2}$  at some 20 locations compared to the method used in this study (Table S3-S4 and S4S5). The approach used in this study was similar to Cadle et al. (1990); however, that study used  $W_{NH_4}$  as a surrogate for  $W_{pSO_4}$  based on the assumption these ions are typically found in the same aerosols. There are however large uncertainties with  $W_{NH_4}$  because of the scavenging by both  $pNH_4^+$  and  $NH_3$ . As mentioned earlier, most of the  $W_{NH_4}$  in literature are overestimated because of the exclusion of  $NH_3$ . Use of these values could lead to a high bias in  $W_{pSO_4}$  and subsequently lower  $W_{SO_2}$ . Aside from the methodology, the scavenging ratios 25 determined by Cadle et al. (1990) were based on snowfall events, which favor the scavenging of particles over gases (Hicks, 2005; Zhang et al., 2013; 2015).

The variability in scavenging ratios among different ions and trace gases within the same month is shown in Fig. S4. The range in scavenging ratios can be quite large. This is expected because the different physical and chemical properties of the pollutants affect their wet scavenging efficiencies. For particulate matter, coarse particles (e.g.,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+$ ) are 30 scavenged more efficiently than fine particles (e.g.  $K^+$ ) (Galloway et al., 1993; Guerzoni et al., 1995; Tuncel and Ungör, 1996). The different solubilities of gaseous pollutants ( $HNO_3$  and  $SO_2$ ) can also explain the differences in scavenging ratios for different pollutants.  $W_{HNO_3}$  were 1.4 to 6 times higher than those of  $W_{SO_2}$  depending on the location (Table S2S3), which

is consistent with the higher solubility of HNO<sub>3</sub> compared to SO<sub>2</sub> ( $H = 2.1 \times 10^5 \text{ M atm}^{-1}$  vs.  $1.2 \text{ M atm}^{-1}$ ; Zhang et al., 2006; Sander, 2015).

### 3.3.2 Patterns-Variations in scavenging ratios

Although the monthly scavenging ratios of most ions span a wide range, the average scavenging ratios of particulate ions were within a factor of 1.6-4.5 among the 13 sites (Table [S2S3](#)). The average scavenging ratios of Na<sup>+</sup>, Cl<sup>-</sup> and Ca<sup>2+</sup> have larger spatial variability than other particulate ions. This may reflect the different precipitation scavenging efficiencies of particles in the marine boundary layer and continental atmospheres as hypothesized by Galloway et al. (1993). One related theory is that the higher relative humidity in marine environments is conducive to the hygroscopic growth of sea-salt aerosols which increases its scavenging efficiency (Hennigan et al., 2008). The average scavenging ratios ranged from 497-996 for fine particles (factor of 2 spatial variability) and 666-2077 for coarse particles (factor of 3 spatial variability). Larger scavenging ratios of fine particles were found at inland sites, where soil and biomass emissions are sources of K<sup>+</sup>. For coarse particles, the larger scavenging ratios at coastal sites (Table [S2S3](#)) were likely attributed to oceanic source of Na<sup>+</sup> and Mg<sup>2+</sup>. The greatest spatial variability was in the scavenging ratios of gases including HNO<sub>3</sub> and SO<sub>2</sub>. The average scavenging ratios varied by a factor 7.4 and 10.7, respectively. The large variability in scavenging ratios between sites is expected because the air and precipitation concentrations and precipitation type and amounts among other factors can also vary with location.

A pronounced seasonal variation can be seen in the monthly average scavenging ratios. The average scavenging ratio of most of the ions and HNO<sub>3</sub> were lowest during July or August (Fig. S5), which resembles the monthly NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> ~~trends-variations~~ in a previous study (Kasper-Giebl et al., 1998). There were two periods when the average scavenging ratios peaked: one peak during April-May and a second peak during September-October were observed for most of the ions and HNO<sub>3</sub>. A similar pattern was obtained for W<sub>pNO3</sub> when MLR was used to generate monthly scavenging ratios. However, different patterns were obtained for W<sub>HNO3</sub> and W<sub>pSO4</sub> derived from MLR, as shown by the higher values during winter and lower values in the warm seasons (Fig. S5 and Table [S5S6](#)).

Monthly patterns-variations in W<sub>SO2</sub> were different from those of other ions and HNO<sub>3</sub>. The average W<sub>SO2</sub> were lower during winter and peaked in the summer, and is supported by the MLR results as well (Fig. S5 and Table [S5S6](#)). This result is also consistent with the seasonal W<sub>SO2</sub> patterns from multiple U.S. sites (Hicks, 2005) and other studies suggesting the inefficient scavenging of SO<sub>2</sub> by snow (Kasper-Giebl et al., 1998 and references therein). However, limited field measurements of dissolved SO<sub>2</sub> (measured as sulfite) in precipitation samples indicate that the highest precipitation concentrations were found in the colder months, which is consistent with solubility theory (Hales and Dana, 1979; Dana, 1980). This finding does not necessarily contradict the results from this study because W<sub>SO2</sub> also depend on the air concentration. The higher ambient SO<sub>2</sub> likely due to higher combustion emissions associated with winter heating (Fig. S6) resulted in lower scavenging ratios,

and vice-versa during warmer months. Besides temperature effects on solubility, precipitation pH and the presence of  $\text{NH}_3$  and  $\text{H}_2\text{O}_2$  could also affect  $\text{SO}_2$  wet scavenging (Zhang et al., 2006).

Most of the long-term scavenging ratio trends were not statistically significant according to the Seasonal Kendall test, but some statistically significant trends were found at a few locations and for some nitrogen and sulfur species. At Longwoods, there was a statistically significant declining trend in the scavenging ratio of  $\text{pNO}_3^-$ ; however the magnitude of the trend was only -6.3 (<1%) per year which is small compared to the scavenging ratio (values in the hundreds to thousands). At Algoma, a significant increasing trend in the scavenging ratio of  $\text{pSO}_4^{2-}$  was found with a slope of +11.4 (1.4%) per year. At many of the sites, the lack of long-term trends in the scavenging ratios of sulfur and nitrogen species reflect the decreasing trends in both wet deposition and air concentrations (Table 2 and 4). There are also many factors that can affect the precipitation concentrations, such as particle sizes, air concentrations, rainfall intensity, and precipitation and cloud types, which vary geographically and could change over time.

### 3.4 Relative contributions of particulates and gases to nitrate, ammonium and sulfate wet deposition

In the previous section, scavenging ratios were determined for particulate ( $\text{pNO}_3^-$ ,  $\text{pNH}_4^+$ ,  $\text{pSO}_4^{2-}$ ) and gaseous ( $\text{HNO}_3$  and  $\text{SO}_2$ ) species. In this section, the relative percent contributions of these particulate and gaseous species to nitrate, ammonium, and sulfate wet deposition are determined. The average  $\pm 1\sigma$  of  $\text{pNO}_3^-$  contributions to nitrate wet scavenging ( $\%\text{pNO}_3^-$ ) was  $28\pm 23\%$  for all years of data at the 13 locations. Percent  $\text{HNO}_3$  contributions to nitrate wet scavenging ( $\%\text{HNO}_3$ ) was  $72\pm 23\%$ . Based on the average,  $\%\text{HNO}_3$  dominated  $\%\text{pNO}_3^-$  at most of the sites (Fig. 9a). Geographical variations were observed in the  $\%\text{pNO}_3^-$  and  $\%\text{HNO}_3$ . Average  $\%\text{pNO}_3^-$  were higher at the two lowest latitude sites and coastal sites (Fig. 9a). One reason is because of the higher  $\text{pNO}_3^-$  air concentrations at the lower latitude locations (Longwoods and Egbert) discussed in Sect. 3.1.1.  $\%\text{pNO}_3^-$  were also higher at the coastal locations (Saturna and Kejimikujik) likely because of the partitioning of  $\text{HNO}_3$  to sea-salt aerosols (Pryor and Sørensen, 2000; Fischer et al., 2006), which are typically coarse particles and hygroscopic and hence more efficiently removed by precipitation. In contrast,  $\%\text{HNO}_3$  were greater at the higher latitude continental locations (Fig. 9a). Relative contributions of  $\text{pNH}_4^+$  and  $\text{NH}_3$  were  $70\pm 19\%$  and  $30\pm 19\%$ , respectively. Precipitation scavenging of  $\text{pNH}_4^+$  was greater than  $\text{NH}_3$  at all sites (Fig. 9b). The percent  $\text{pSO}_4^{2-}$  contributions to sulfate wet scavenging ( $\%\text{pSO}_4^{2-}$ ) was  $63\pm 20\%$ , while percent  $\text{SO}_2$  contributions to sulfate wet scavenging ( $\%\text{SO}_2$ ) was  $37\pm 20\%$ . Average  $\%\text{pSO}_4^{2-}$  were greater than that of  $\%\text{SO}_2$  at most of the sites (Fig. 9c). No pronounced geographical patterns were observed in the relative contributions of gases and particulates to ammonium or sulfate wet deposition. Knowledge of the relative scavenging contributions of gases and particles may improve the wet deposition modeling of nitrate, ammonium, and sulfate, which continues to show discrepancies between model and observations (Appel et al., 2011; Zhang et al., 2012; Kajino and Aikawa, 2015; Qiao et al., 2015). Furthermore, gas- and particulate-phase pollutants may not come from the same source, since particulate matter can be re-emitted from natural sources and human activity. Aerosol formation is modeled separately in chemical transport models and the wet deposition of

particles and gases use different parameterizations in these models. The scavenging coefficient of gases in models depends on Henry's law constant or gas diffusivity and reactivity, whereas the scavenging coefficient of particles is a function of particle size distribution and collection efficiency among other factors (Gong et al., 2011). Studies also suggest different efficiencies between rainout and washout scavenging mechanisms for gases and aerosols (Gong et al., 2011; Kajino and Aikawa, 2015). These parameterizations can differ between different chemical transport models as well leading to large uncertainties in the wet deposition estimates (Tost et al., 2007). Gas/aerosol wet scavenging observations can also be used to evaluate those from wet deposition simulations (Kajino and Aikawa, 2015).

A seasonal eyele-variation was observed in the relative contributions of gases and particulates to nitrate, ammonium, and sulfate wet deposition. The contributions by particulates to nitrate, ammonium, and sulfate wet scavenging were greater during cold months and lower during summer (Fig. 10). This pattern is consistent with studies suggesting that particle scavenging by snow is more efficient than the scavenging by rain for an equivalent amount of precipitation (Zhang et al., 2013, 2015). Based on scavenging ratios, Zhang et al. (2015) found that snow scavenging can be 10 times more efficient than the rain scavenging of polycyclic aromatic compounds (PAC), and that snow scavenging of particulate-phase PAC can exceed that of gas-phase PAC by a similar magnitude. In contrast to particle scavenging, greater precipitation scavenging of gases was observed in the warm seasons (Fig. 10). This inverse relationship between particle and gas wet scavenging resulted because of Eq. 3, which assumes that the precipitation scavenging in excess of particle wet scavenging was due to gas scavenging. This assumption needs to be validated by independently deriving the gas scavenging contributions; however, the results based on the assumption are consistent with precipitation scavenging theories.

In terms of nitrate scavenging, the largest difference between gas and particulate wet scavenging were observed during warm months (factor of 4 higher for  $\text{HNO}_3$ ), whereas smaller differences were seen during cold months (Fig. 10a). The large contribution by  $\text{HNO}_3$  is expected because it is one of the most soluble gases and is effectively scavenged by rainout (Chang, 1984; Garrett et al., 2006).  $\%\text{HNO}_3$  were also fairly high during the cold months because of higher solubility at lower temperatures and the high absorption and retention of  $\text{HNO}_3$  and other strong acids on ice crystals (Diehl et al., 1995; Clegg and Abbatt, 2001). Snow scavenging of  $\text{HNO}_3$  can also exceed below-cloud rain scavenging of  $\text{HNO}_3$  for an equivalent precipitation rate (Chang, 1984).

Particle wet scavenging exceeded gas scavenging contributions to ammonium wet deposition in most months by a factor of 2.6 except during May-June (Fig. 10b). For sulfate scavenging, larger differences between gas and particulate wet scavenging were found during cold months (factor of 2 higher for  $\text{pSO}_4^-$ ), while small differences were observed during warm months (Fig. 10c). The greater scavenging of  $\text{pSO}_4^-$  during colder months is likely attributed to the effectiveness of particle scavenging by snow as discussed earlier. Another explanation for the large disparity between particle and gas scavenging in the cold months could be the low absorption of  $\text{SO}_2$  by ice crystals especially on low pH ice surfaces (Clegg and Abbatt, 2001). As for the smaller difference between particle and gas scavenging during warm months, experiments

suggest that snow scavenging of  $\text{SO}_2$  can be increased by the presence of  $\text{H}_2\text{O}_2$  and relatively higher temperatures of  $\sim 0^\circ\text{C}$  (Mitra et al., 1990). The latter conditions are conducive to the formation of a quasi-liquid layer on the ice surface, which may increase the dissolution of  $\text{SO}_2$  (Clegg and Abbatt, 2001).

#### 4 Conclusions

5 Long-term air concentrations, wet deposition, and scavenging ratios of inorganic ions were analyzed using CAPMoN data. Geographical variability in the air concentrations of inorganic ions can be attributed to proximity of the sites to anthropogenic sources, oceanic sea-salt emissions, and agricultural emissions. Annual wet deposition geographical patterns for  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  were similar to those in air. Widespread declines were observed for  $\text{NH}_4^+$  (1994-2010) and  $\text{SO}_4^{2-}$  (1983-2010) in air, which was attributed to decreases in  $\text{SO}_2$ ,  $\text{NO}_x$ , and local  $\text{NH}_3$  emissions.  $\text{NO}_3^-$  air  
10 concentrations increased from 1991-2001 and then decreased from 2001-2010, consistent with the trends in  $\text{NO}_x$  emissions in Canada over these two decades and in the U.S. over the last decade. However, widespread declines in annual wet deposition were only found for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  from 1984-2011.  $\text{SO}_4^{2-}$  air concentrations and annual wet deposition declined  $\sim 2$  times faster in southern Ontario and southern Quebec than other locations because of the proximity of the sites to industrial emission sources. Aerosol acidity and acid rain had greater impacts to southern and eastern Canada than western  
15 Canada. Temporal trends show aerosol acidity and acid rain have been decreasing simultaneously from 1994-2010, consistent with large declines in nitrate and sulfur species and slight declines or lack of change in base cations.

Scavenging ratios of particulate  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in literature may be overestimated on average by 22%, 44% and a factor of 6, respectively, because the wet scavenging of gases were excluded. The wet scavenging of  $\text{HNO}_3$  dominated particulate  $\text{NO}_3^-$  at most locations, while the wet scavenging of particulate  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  were more efficient than  $\text{NH}_3$  and  
20  $\text{SO}_2$ , respectively. The wet scavenging of particles was more efficient in the cold months likely because of the scavenging by snow. Greater gas scavenging was found in the warm months opposite in trend to particulate wet scavenging.

Long-term trends in inorganic ions provide greater insight into which Canadian regions are still susceptible to or likely recovering from acid rain impacts, and the effectiveness of environmental policies at mitigating acid rain. Particulate inorganic ions and trace gas scavenging ratios provide a measure of the wet scavenging efficiencies and are potentially  
25 useful surrogates for the wet scavenging of other pollutants provided that they have similar physicochemical properties (e.g. solubility, particle sizes, etc.). These results can be considered in future wet deposition modeling to improve the prediction of nitrate, ammonium, and sulfate wet deposition. Scavenging ratios can potentially be used to obtain a rough first order estimate of the wet deposition at other locations considering the uncertainties in both the scavenging ratios and in wet deposition modeling.

## Data availability

The datasets used in this study can be accessed from the websites in the reference list or by contacting the corresponding author.

## Competing interests

- 5 The authors declare that they have no conflict of interest.

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Table 1: Site and data descriptions. NA indicates no available data. Short-term data were not analyzed. Refer to Fig. S1 for a map of the sites.

Site name	Province	Latitude	Longitude	Elevation (m)	Coastal/inland	Land use	Air data	Wet deposition data
Saturna	BC	48.78	-123.13	178	Coastal	Forest	Dec 1990-Dec 2010	Jan 1990-Dec 2011
Snare Rapids	NT	63.52	-116.00	240	Inland	Forest	NA	Jan 1989-Dec 2011
Esther	AB	51.67	-110.20	707	Inland	Agricultural	Oct 1991-Mar 2003	Jan 1987-Dec 2002, Jan 2009-Dec 2011
Cree Lake	SK	57.35	-107.13	499	Inland	Forest	Jul 1982-May 1993	Jan 1984-Dec 1992
Bratt's Lake	SK	50.20	-104.71	600	Inland	NA	Aug 2001-Dec 2010	Jan 2001-Dec 2011
McCreary	MB	50.71	-99.53	335	Inland	Agricultural	NA	Jan 1984-Dec 1995
Island Lake	MB	53.87	-94.67	245	Inland	Forest	NA	Jan 1984-Dec 1997
Experimental Lakes Area (ELA)	ON	49.66	-93.72	369	Inland	Forest	Jan 1979-Dec 2010	Jan 1984-Dec 2011
Pickle Lake B	ON	51.45	-90.22	370	Inland	Forest	NA	Jan 2003-Dec 2011
Algoma	ON	47.04	-84.38	411	Inland	Forest	Oct 1980-Dec 2010	Jan 1985-Dec 2011
Burnt Island	ON	45.82	-82.95	185	Inland	Forest	NA	Jan 1992-Dec 2011
Bonner Lake	ON	49.39	-82.12	245	Inland	Forest	short-term	Jun 1985-Dec 2011
Longwoods	ON	42.88	-81.48	239	Inland	Agricultural	Jan 1983-Dec 2010	Jan 1984-Dec 2011
Priceville	ON	44.17	-80.66	475	Inland	Agricultural	NA	Jan 1985-Dec 1994
Egbert	ON	44.23	-79.78	253	Inland	Agricultural	Jul 1988-Dec 2010	Jan 1989-Dec 2011
Egbert-2	ON	44.23	-79.78	253	Inland	Agricultural	short-term	Jan 1997-Dec 2011
Sprucedale	ON	45.42	-79.49	350	Inland	Agricultural	May 2002-Dec 2010	Jan 2003-Dec 2011
Warsaw Caves	ON	44.46	-78.13	230	Inland	Agricultural	NA	Jan 1986-Dec 2011
Chalk River	ON	46.06	-77.41	184	Inland	Forest	Jan 1979-Dec 2010	Jan 1984-Dec 2011
Chapais	QC	49.82	-74.98	381	Inland	Forest	Jun 1988-Dec 2010	Jan 1988-Dec 2011
Frelighsburg	QC	45.05	-72.86	203	Inland	Agricultural	Nov 2001-Dec 2010	Jan 2002-Dec 2011
Sutton	QC	45.08	-72.68	243	Inland	Forest	Jan 1986-Mar 2002	Jan 1984-Dec 2001
Lac Edouard	QC	47.68	-72.44	243	Inland	Forest	Jan 2002-Dec 2010	Jan 2002-Dec 2011
Montmorency	QC	47.32	-71.15	640	Coastal	Forest	Dec 1980-Jan 1997	Jan 1984-Dec 1996
Harcourt	NB	46.50	-65.27	37	Coastal	Forest	NA	Jan 1984-Dec 2011
Kejimikujik	NS	44.43	-65.21	127	Coastal	Forest	May 1979-Dec 2010	Jan 1984-Dec 2011
Mingan	QC	50.27	-64.22	14	Coastal	Forest	short-term	Jan 1994-Dec 2011
Jackson	NS	45.59	-63.84	90	Coastal	Forest	NA	Jan 1984-Dec 2011
Goose Bay	NL	53.31	-60.36	39	Coastal	Forest	NA	Jan 1984-Dec 2011
Goose Bay B	NL	53.29	-60.39	39	Coastal	Forest	NA	Jan 1989-Dec 2007
Bay d'Espoir	NL	47.99	-55.81	190	Coastal	Forest	short-term	Jan 1984-Dec 2011

Table 2: Rate of change in annual air concentrations. Slope refers to the Seasonal Kendall slope ( $\text{ng m}^{-3} \text{a}^{-1}$ ); C.I. refers to the 90% confidence interval of the slope; ns indicates no significant trend; na indicates no available data.

Site	$\text{Ca}^{2+}$		$\text{Mg}^{2+}$		$\text{K}^+$		$\text{Na}^+$		$\text{Cl}^-$	
	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.
Saturna	-0.9	-1.3 to -0.6	-0.8	-1.1 to -0.4	-0.7	-1 to -0.5	-4.5	-6.5 to -1.8	1.0	ns
Esther	9.9	4.8 to 15.8	1.5	0.9 to 2.5	1.3	0.8 to 1.8	2.1	0.8 to 3.6	-0.4	-0.7 to 0
Cree Lake	na	na	na	na	-1.3	-2 to -0.5	0.5	ns	-0.5	-1 to -0.1
Bratt's Lake	5.5	ns	2.4	ns	-3.8	-5.3 to -2.4	-2.4	-4.2 to -1.3	-0.6	-1.3 to -0.2
ELA	0.5	ns	-0.2	ns	-0.5	-0.6 to -0.3	-0.7	-0.8 to -0.5	-0.2	-0.4 to -0.2
Algoma	-0.3	ns	-0.2	-0.5 to 0	-0.6	-0.8 to -0.5	-0.3	-0.5 to -0.2	-0.1	-0.2 to 0
Longwoods	-15.9	-21.1 to -10	-1.1	-2.1 to -0.4	-0.6	-0.9 to -0.3	-0.5	-0.8 to -0.2	-0.8	-1 to -0.5
Egbert	-9.7	-14.8 to -3.6	0.1	ns	0.02	ns	-0.2	ns	0.2	ns
Sprucedale	-2.7	ns	-0.9	ns	-1.2	-1.8 to -0.6	-1.3	-1.9 to -0.4	-0.2	ns
Chalk River	-0.3	ns	-0.6	-0.8 to -0.4	-0.8	-1 to -0.6	-0.5	-0.8 to -0.3	0.03	ns
Chapais	0.4	ns	-0.03	ns	-0.5	-0.6 to -0.4	-0.9	-1.2 to -0.7	0.3	0 to 0.6
Frelighsburg	-0.8	ns	0.3	ns	-1.1	-1.8 to -0.7	-2.6	-4.4 to -0.7	-0.01	ns
Sutton	1.5	ns	0.2	ns	-1.8	-2.3 to -1.4	-1.8	-2.3 to -1.4	-0.2	ns
Lac Edouard	-0.01	ns	-0.2	ns	-1.0	-1.4 to -0.6	-1.4	-2.1 to -0.5	-0.4	ns
Montmorency	na	na	na	na	-0.6	-1.1 to 0	1.4	0.8 to 2.1	0.1	ns
Kejimikujik	0.4	0 to 0.8	-0.5	-0.8 to -0.1	-0.5	-0.7 to -0.4	1.8	0.4 to 3	4.9	3.7 to 6.6

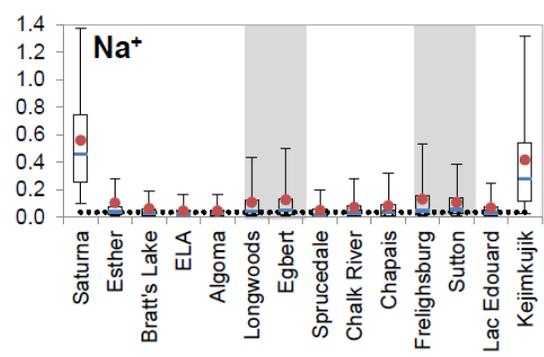
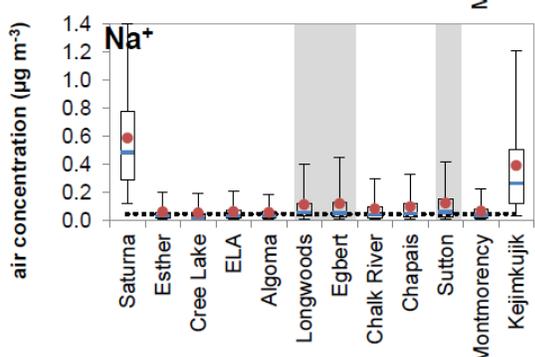
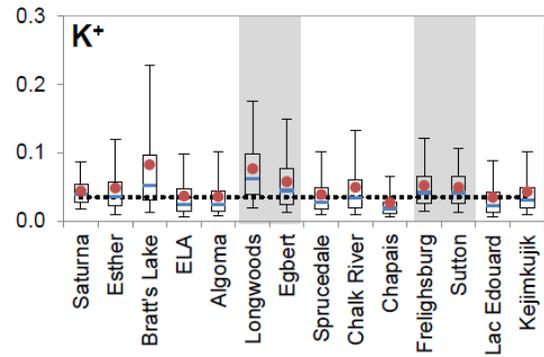
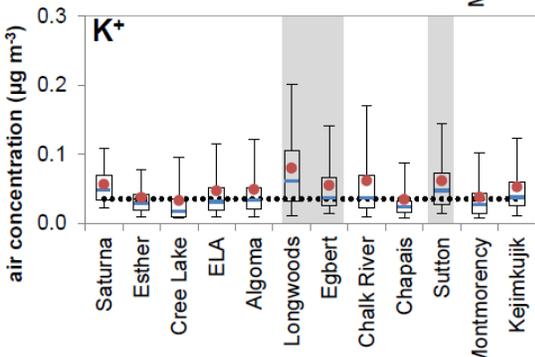
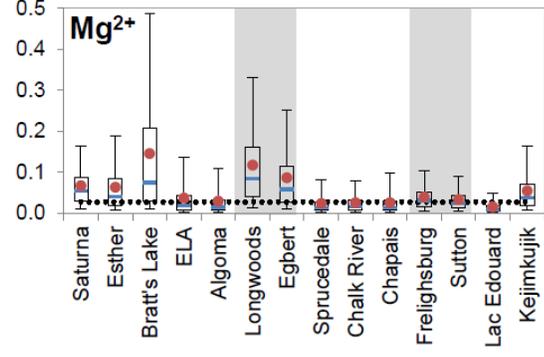
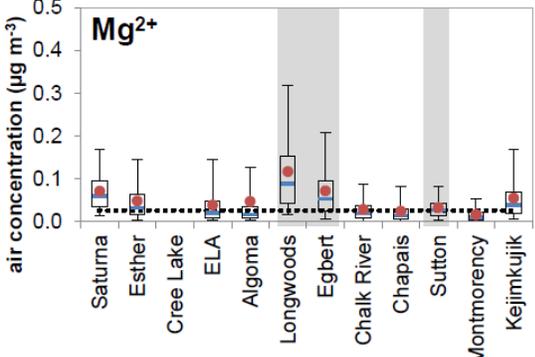
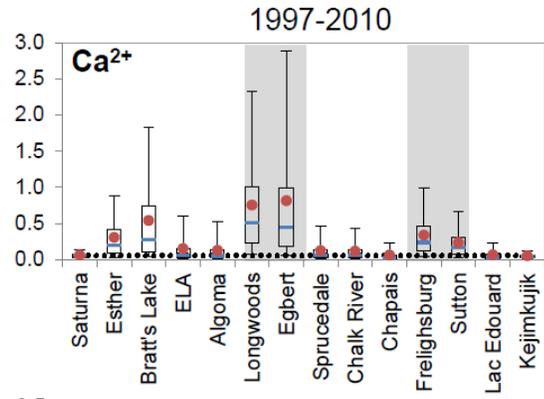
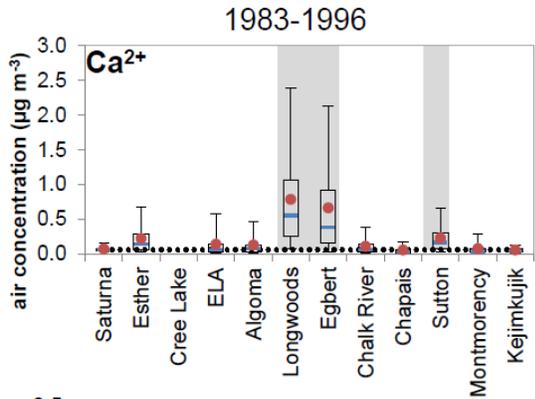
Site	$\text{NH}_4^+$		$\text{NO}_3^-$		$\text{SO}_4^{2-}$		$\text{SO}_2$		$\text{HNO}_3$	
	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.
Saturna	-7.6	-9.1 to -6.2	-9.3	-12.8 to -5.6	-28.8	-32.6 to -25.2	-62.6	-72.5 to -52.5	-17.1	-20.7 to -13.6
Esther	7.9	2 to 15.6	40.1	32.6 to 50.4	7.0	ns	-6.5	ns	12.0	2.2 to 21.8
Cree Lake	3.7	1.1 to 6.2	-1.1	ns	0.0	ns	8.4	ns	8.9	6 to 11.4
Bratt's Lake	-16.5	-23.4 to -9.7	-21.4	-34.3 to -10.5	-30.4	-51.1 to -11.8	1.6	ns	-19.4	-27.3 to -13.3
ELA	-4.4	-6 to -2.6	3.5	1.7 to 5.2	-28.4	-32.1 to -24.4	-14.6	-17.7 to -12.2	-2.3	-3.7 to -0.8
Algoma	-7.0	-9.9 to -3.7	6.4	4.4 to 8.4	-46.8	-55 to -39	-77.4	-87.2 to -67.3	-3.8	-7.1 to -0.9
Longwoods	-28.8	-34.4 to -23.1	-15.2	-22.9 to -6.5	-97.4	-110.2 to -87.4	-221.5	-240.2 to -202.1	-27.6	-32.7 to -23.3
Egbert	-41.8	-49.3 to -35.5	-34.2	-43.2 to -23.6	-93.9	-108.9 to -81.5	-199.4	-221.6 to -177.3	-25.1	-31.2 to -19.5
Sprucedale	-32.8	-52.4 to -12.6	-29.5	-39.9 to -16.6	-99.0	-150.5 to -36.8	-140.0	-188.7 to -97.2	-54.4	-74.5 to -36.3
Chalk River	-8.8	-11.6 to -6.4	2.8	1.5 to 4.3	-59.8	-66.9 to -52.1	-104.7	-115.3 to -94.1	-8.2	-10.8 to -5.7
Chapais	-5.7	-7 to -4.2	1.3	0.8 to 2	-41.3	-46.3 to -36	-45.5	-52.3 to -39.6	-4.3	-5.8 to -3.1
Frelighsburg	-58.2	-69 to -45.4	-53.4	-68.6 to -38.9	-108.6	-139.5 to -84	-160.8	-206 to -119.7	-81.7	-91.2 to -68.9
Sutton	-4.6	ns	18.8	13.9 to 24.2	-64.2	-80.4 to -51.2	-90.1	-112.8 to -67.3	-12.7	-18.9 to -4
Lac Edouard	-20.3	-27.9 to -13.1	-11.0	-14.3 to -6.4	-64.8	-88 to -47.6	-55.8	-76.2 to -34.1	-35.9	-42.4 to -27.1
Montmorency	9.6	6.1 to 14.6	5.9	4.5 to 8.2	-1.0	ns	-20.1	-40 to -3.2	21.0	14.9 to 29
Kejimikujik	-5.3	-6.5 to -4	2.5	1.4 to 3.8	-53.1	-59 to -47.5	-35.9	-41.2 to -30	-6.5	-7.9 to -4.8

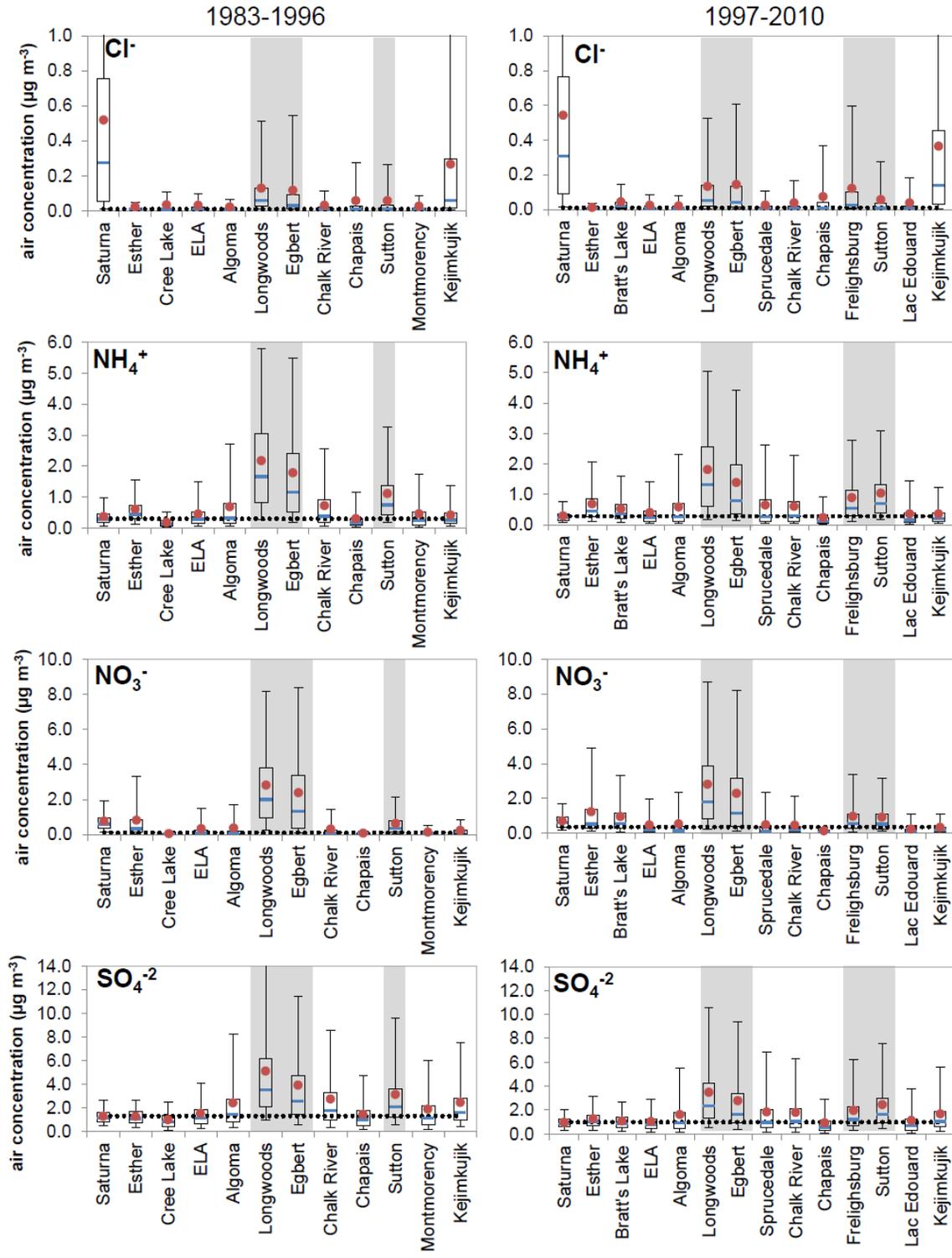
Table 3: Rate of change in annual wet deposition of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and Cl<sup>-</sup>. Slope refers to the Sen's slope (kg ha<sup>-1</sup> a<sup>-1</sup>); C.I. refers to the 90% confidence interval of the slope; ns indicates no significant trend.

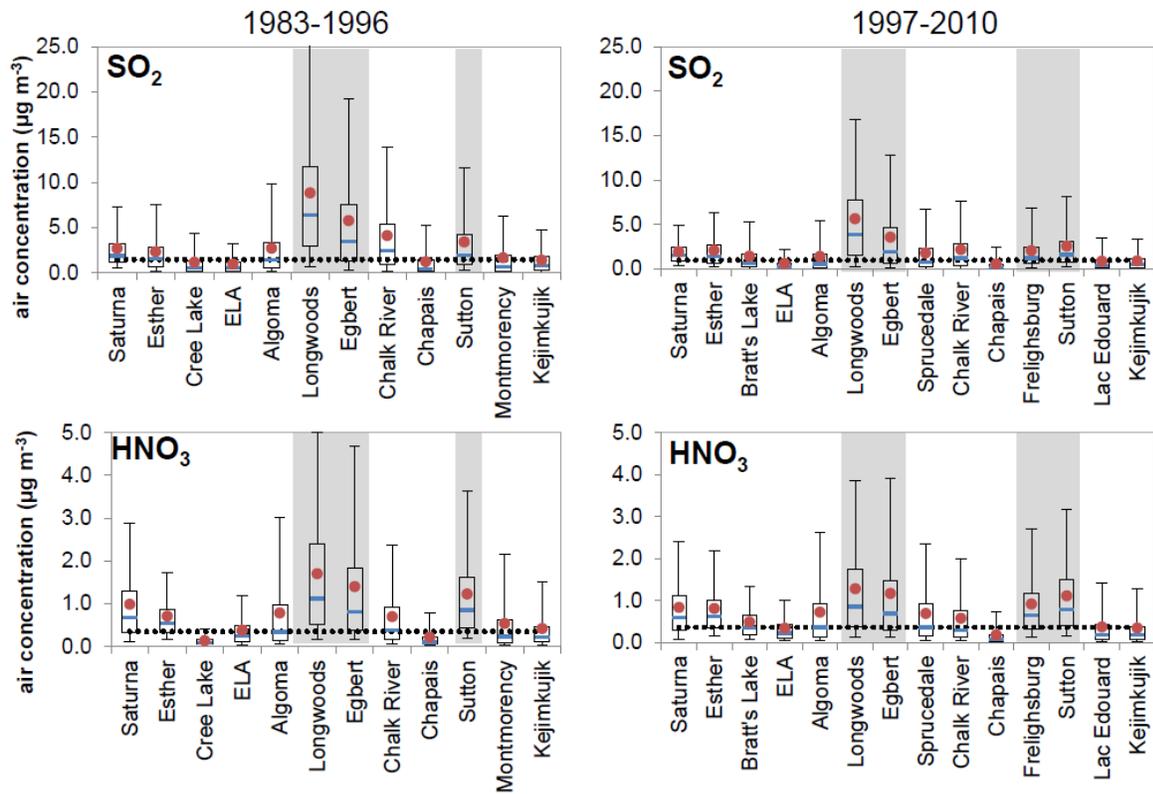
Site	Ca <sup>2+</sup>		Mg <sup>2+</sup>		K <sup>+</sup>		Na <sup>+</sup>		Cl <sup>-</sup>	
	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.
Saturna	0.001	ns	-0.0003	ns	-0.0002	ns	0.001	ns	0.002	ns
Esther	0.010	ns	0.003	ns	0.002	ns	0.002	ns	-0.001	ns
Cree Lake	-0.014	ns	-0.001	ns	-0.003	ns	0.001	ns	-0.002	ns
Bratt's Lake	0.036	ns	0.009	ns	0.005	ns	0.002	ns	0.001	ns
ELA	0.008	ns	0.002	ns	0.002	ns	-0.002	-0.004 to -0.0002	-0.001	ns
Algoma	-0.009	ns	-0.003	-0.0064 to -0.0005	-0.003	-0.0059 to -0.0003	-0.004	ns	-0.015	-0.025 to -0.01
Longwoods	-0.017	ns	-0.002	ns	0.006	0.003 to 0.011	0.004	ns	-0.013	-0.023 to -0.003
Egbert	0.003	ns	-0.001	ns	-0.0005	ns	0.004	0.002 to 0.009	-0.008	ns
Sprucedale	-0.024	ns	-0.008	-0.015 to -0.003	-0.002	ns	-0.005	ns	-0.037	ns
Chalk River	0.001	ns	-0.001	ns	-0.001	ns	0.001	ns	-0.008	-0.013 to -0.004
Chapais	0.004	ns	-0.001	-0.0022 to -0.0003	-0.0002	ns	-0.003	-0.006 to -0.001	-0.007	-0.012 to -0.002
Frelighsburg	0.020	ns	0.001	ns	0.001	ns	0.002	ns	-0.012	ns
Sutton	-0.029	-0.058 to -0.005	-0.002	ns	-0.001	ns	0.002	ns	-0.006	ns
Lac Edouard	-0.004	ns	-0.002	ns	-0.002	ns	-0.014	-0.022 to -0.001	-0.025	-0.046 to -0.008
Montmorency	-0.023	ns	-0.002	ns	0.001	ns	0.009	0.0009 to 0.016	0.006	ns
Kejimikujik	0.007	ns	0.003	ns	-0.0003	ns	0.024	ns	0.056	ns

Table 4: Rate of change in annual wet deposition of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , nss- $\text{SO}_4^{2-}$ , precipitation amount and pH. Slope refers to the Sen's slope ( $\text{kg ha}^{-1} \text{ a}^{-1}$ ); C.I. refers to the 90% confidence interval of the slope; ns indicates no significant trend; na indicates no available data.

Site	$\text{NH}_4^+$		$\text{NO}_3^-$		$\text{SO}_4^{2-}$		nss- $\text{SO}_4^{2-}$		Annual precip ( $\text{mm a}^{-1}$ )		pH ( $\text{a}^{-1}$ )	
	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.	Slope	C.I.
Saturna	-0.01	ns	-0.07	-0.13 to -0.01	-0.13	-0.17 to -0.06	-0.12	-0.16 to -0.07	-1.5	ns	0.012	0.009 to 0.016
Esther	0.02	ns	0.04	ns	-0.02	ns	na	na	-1.4	ns	-0.012	ns
Cree Lake	-0.02	ns	-0.05	ns	-0.09	ns	na	na	-2.0	ns	-0.010	ns
Bratt's Lake	0.07	ns	0.02	ns	0.10	ns	na	na	25.9	ns	-0.009	ns
ELA	0.05	0.03 to 0.07	0.02	ns	-0.04	ns	na	na	6.0	ns	0.009	0.003 to 0.014
Algoma	-0.06	-0.09 to -0.02	-0.38	-0.51 to -0.26	-0.60	-0.71 to -0.47	na	na	-7.8	-14.5 to -2.7	0.020	0.016 to 0.025
Longwoods	0.03	ns	-0.33	-0.48 to -0.17	-0.55	-0.7 to -0.36	na	na	3.9	ns	0.023	0.019 to 0.028
Egbert	-0.001	ns	-0.31	-0.45 to -0.18	-0.45	-0.57 to -0.33	na	na	3.8	ns	0.027	0.022 to 0.03
Sprucedale	-0.03	ns	-1.01	-1.4 to -0.48	-1.00	-1.46 to -0.36	na	na	9.1	ns	0.030	0.018 to 0.042
Chalk River	0.01	ns	-0.19	-0.24 to -0.11	-0.36	-0.43 to -0.29	na	na	5.3	2.1 to 8.3	0.020	0.018 to 0.022
Chapais	-0.01	ns	-0.21	-0.28 to -0.11	-0.34	-0.45 to -0.25	na	na	-0.9	ns	0.015	0.013 to 0.018
Frelighsburg	-0.02	ns	-0.93	-1.29 to -0.64	-0.93	-1.57 to -0.16	na	na	13.5	ns	0.056	0.036 to 0.069
Sutton	0.05	0.01 to 0.09	0.01	ns	-0.57	-0.9 to -0.23	na	na	4.0	ns	0.017	0.01 to 0.026
Lac Edouard	-0.07	ns	-0.69	-0.91 to -0.38	-0.46	-0.77 to -0.23	na	na	14.6	ns	0.027	0.018 to 0.045
Montmorency	0.05	ns	0.20	ns	-0.27	ns	-0.27	ns	27.8	6.1 to 45.7	0.008	0.001 to 0.014
Kejimikujik	0.01	ns	-0.12	-0.18 to -0.06	-0.27	-0.37 to -0.2	-0.28	-0.36 to -0.2	10.9	3 to 17.2	0.014	0.011 to 0.017







**Figure 1: Geographical patterns of particulate inorganic ions and trace gas concentrations. Sites are arranged in order from western to eastern Canada. Grey shaded regions correspond to southern Ontario or southern Quebec sites. The blue line indicates the median; the red dot indicates the mean; the box and whiskers include the interquartile range and the 5<sup>th</sup> to 95<sup>th</sup> percentile range, respectively; the dotted line is the overall median among the sites.**

**Geographical patterns of base cations,  $\text{Cl}^-$  and  $\text{NH}_4^+$  (a) and  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HNO}_3$  and  $\text{SO}_2$  (b) for the 1983-1996 and 1997-2010 periods. Sites are arranged in order from western to eastern Canada. Bars indicate the median concentration. Error bars indicate the 95<sup>th</sup> percentile concentration. Diamonds indicate the mean concentration. Grey shaded regions correspond to southern Ontario or southern Quebec sites.**

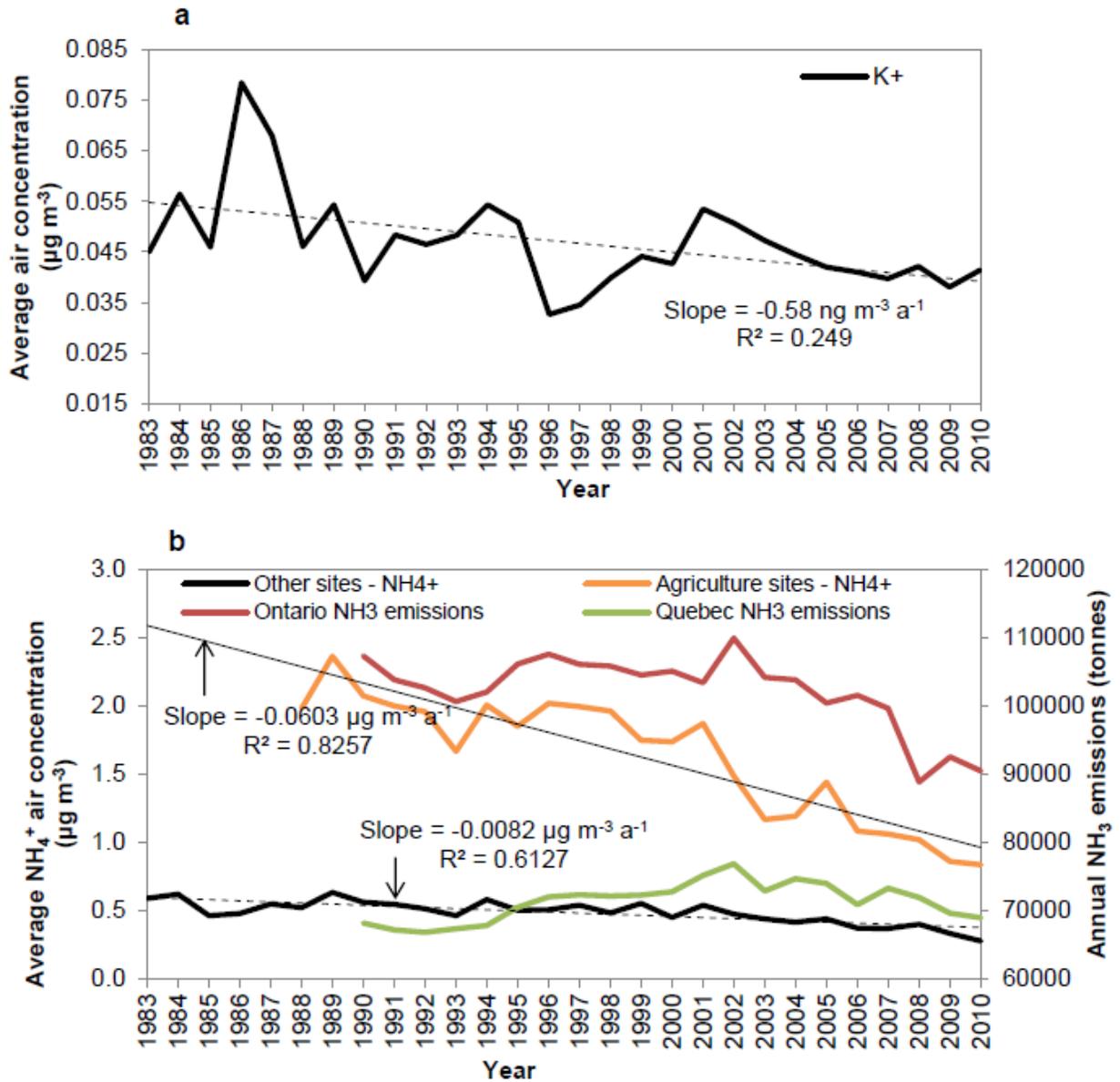


Figure 2: Temporal trends of annual average atmospheric  $K^+$  (a) and atmospheric  $NH_4^+$  and annual ammonia emissions (b). In (b) between 2002 and 2010, atmospheric  $NH_4^+$  at agricultural sites decreased by 6.3% while ammonia emissions in Ontario and Quebec decreased by 2.4% and 1.1%, respectively.

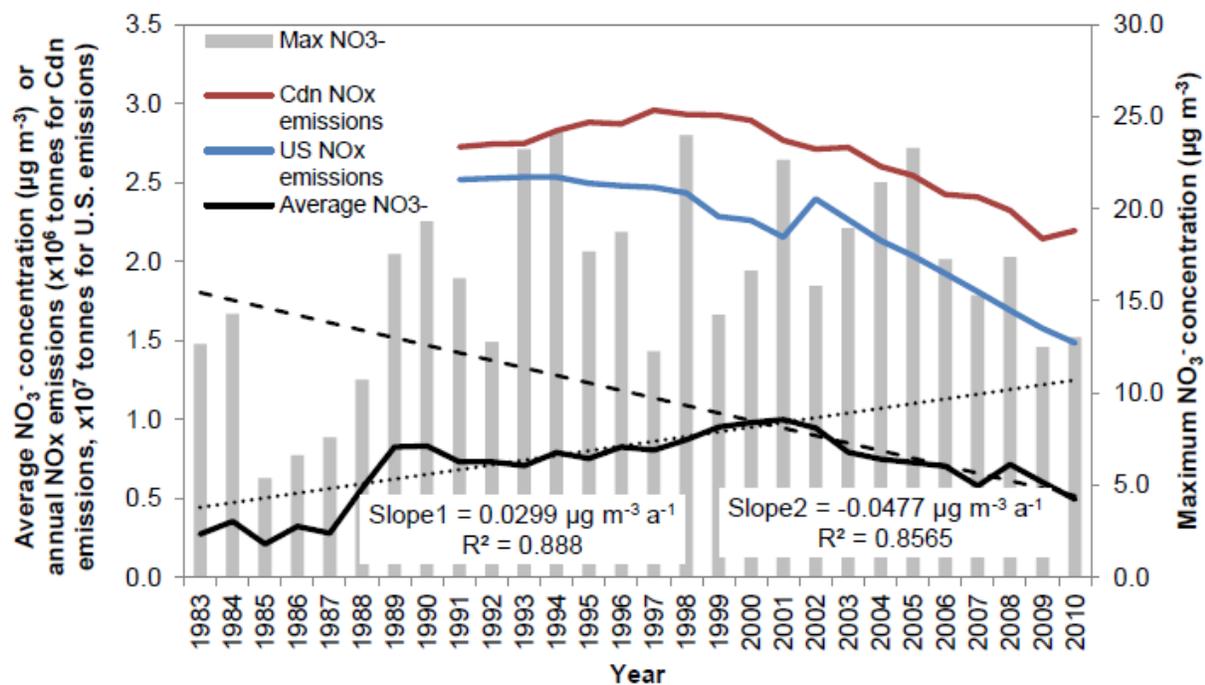


Figure 3: Temporal trends of annual atmospheric NO<sub>3</sub><sup>-</sup> and annual NO<sub>x</sub> emissions. Slope1 refers to the regression line for NO<sub>3</sub><sup>-</sup> between 1991 and 2001 (positive trend, 3.6% increase), while Slope2 is for the period between 2001 and 2010 (negative trend, 6.5% decrease). Between 1991 and 1997, NO<sub>x</sub> emissions in Canada (Cdn) increased by 8.5%. Between 1997 and 2010, Cdn NO<sub>x</sub> emissions decreased by 25.8%.

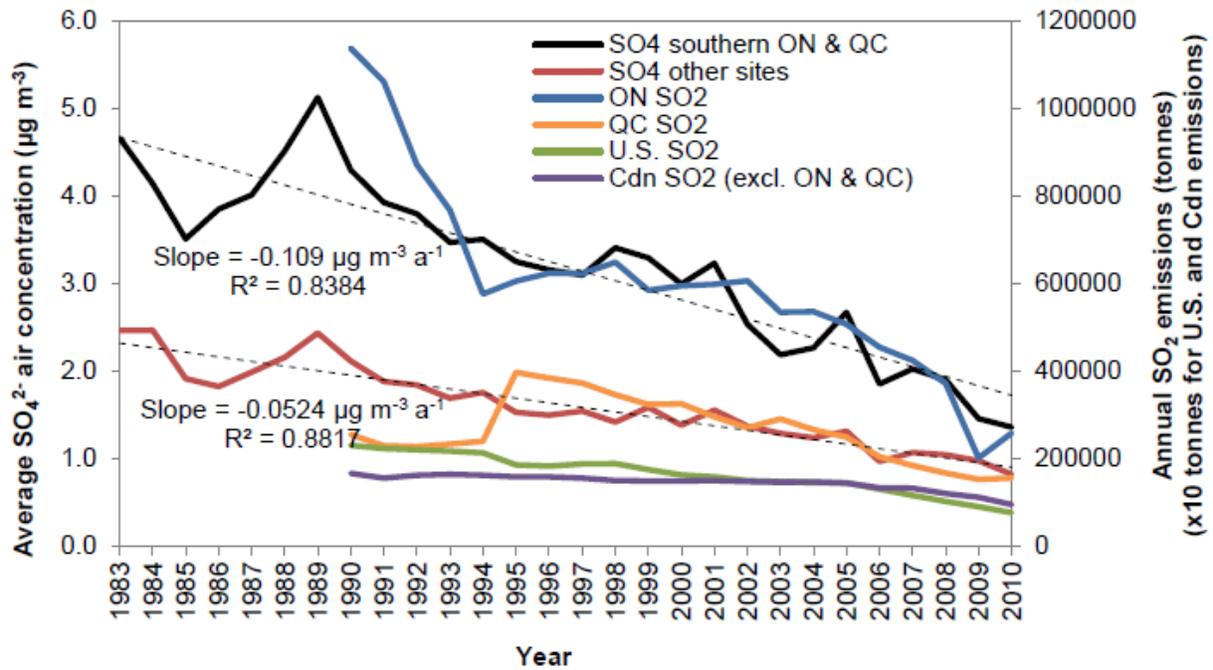


Figure 4: Temporal trends of annual average atmospheric SO<sub>4</sub><sup>2-</sup> and annual SO<sub>2</sub> emissions. ON and QC refer to the province of Ontario and Quebec, respectively. Between 1990 and 2010, atmospheric SO<sub>4</sub><sup>2-</sup> decreased by 4.5% at southern Ontario (ON) and Quebec (QC) sites and by 3.6% at other sites. Over the same period, SO<sub>2</sub> emissions decreased by 1.8% in Canada (Cdn) and 4.3% in the U.S.

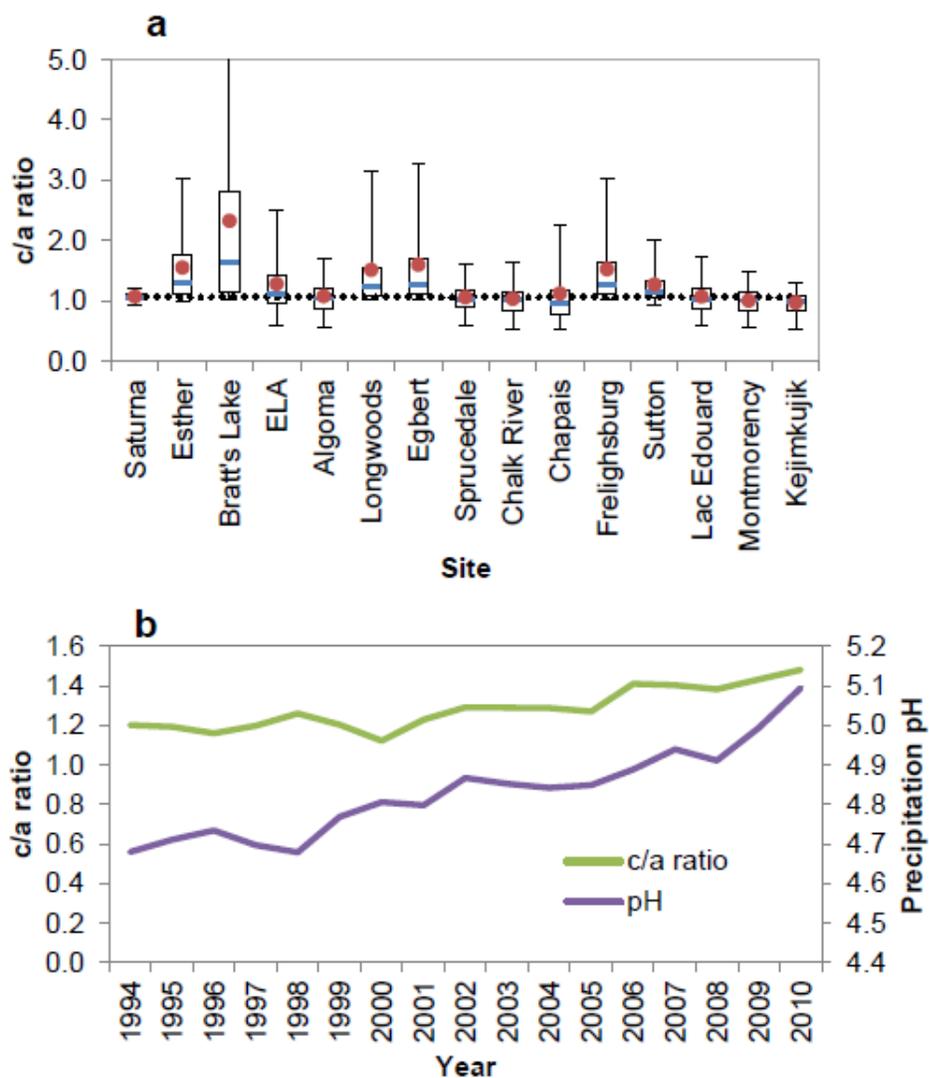
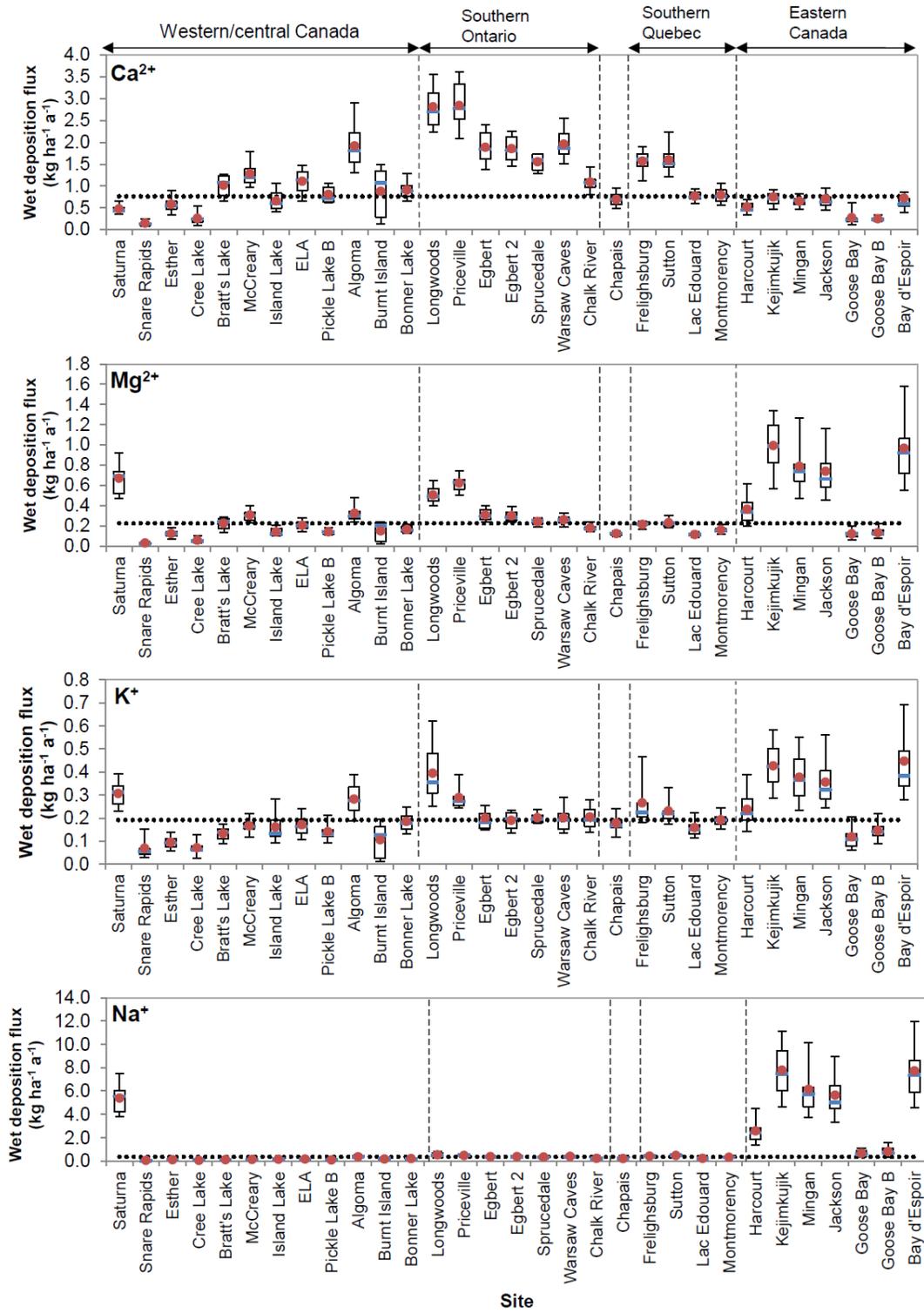
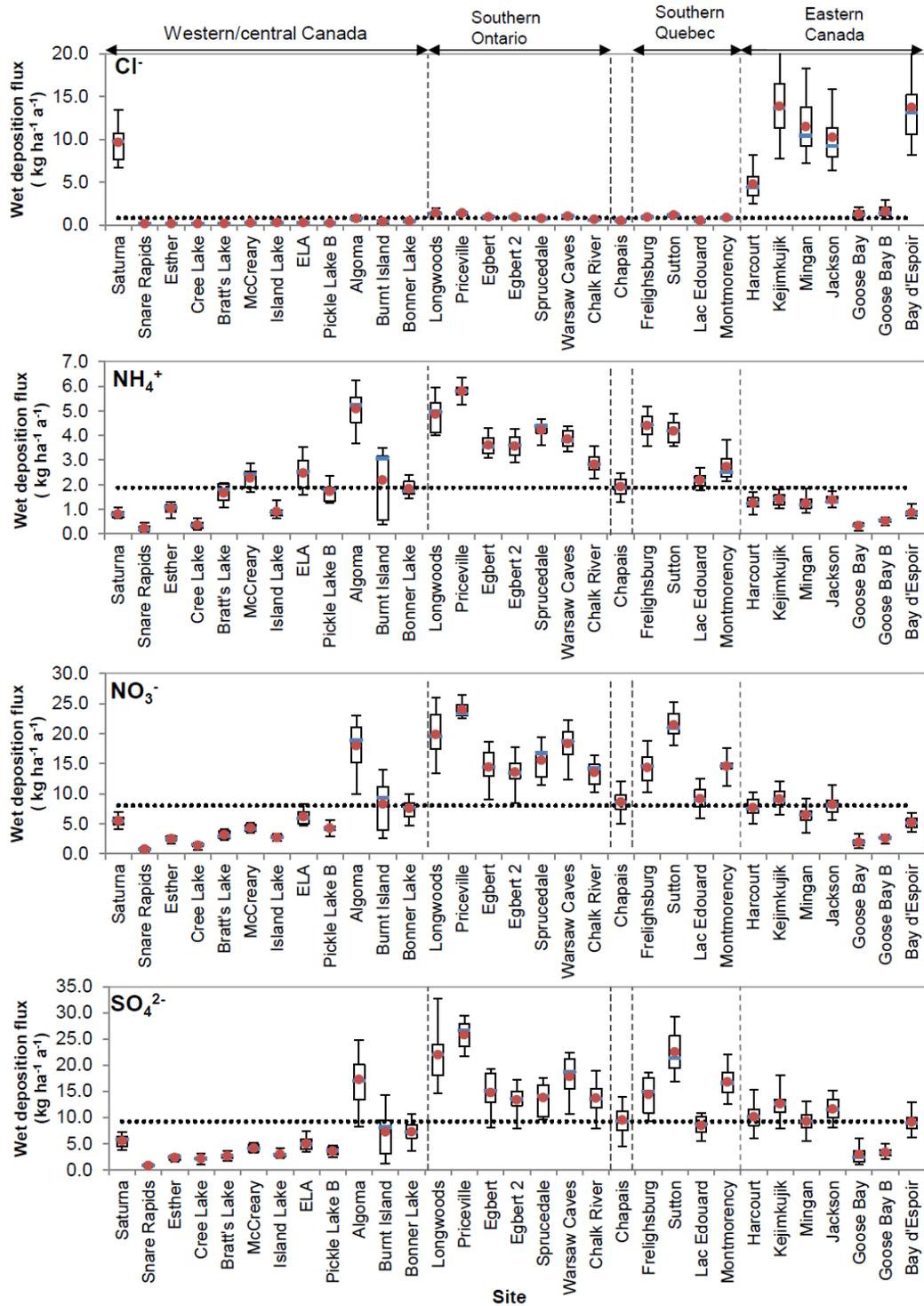


Figure 5: Geographical patterns of cation/anion (c/a) ratio and cation and anion concentrations (a) and temporal trends of annual average c/a ratio, cation and anion concentrations, and precipitation pH (b). In (a), the blue line indicates the median; the red dot indicates the mean; the box and whiskers include the interquartile range and the 5<sup>th</sup> to 95<sup>th</sup> percentile range, respectively; the dotted line is the overall median among the sites.





**Figure 6: Geographical patterns of the annual wet deposition of ions.** Sites are arranged in order from western to eastern Canada. The blue line indicates the median; the red dot indicates the mean; the box and whiskers include the interquartile range and the 5<sup>th</sup> to 95<sup>th</sup> percentile range, respectively; the dotted line is the overall median among the sites.

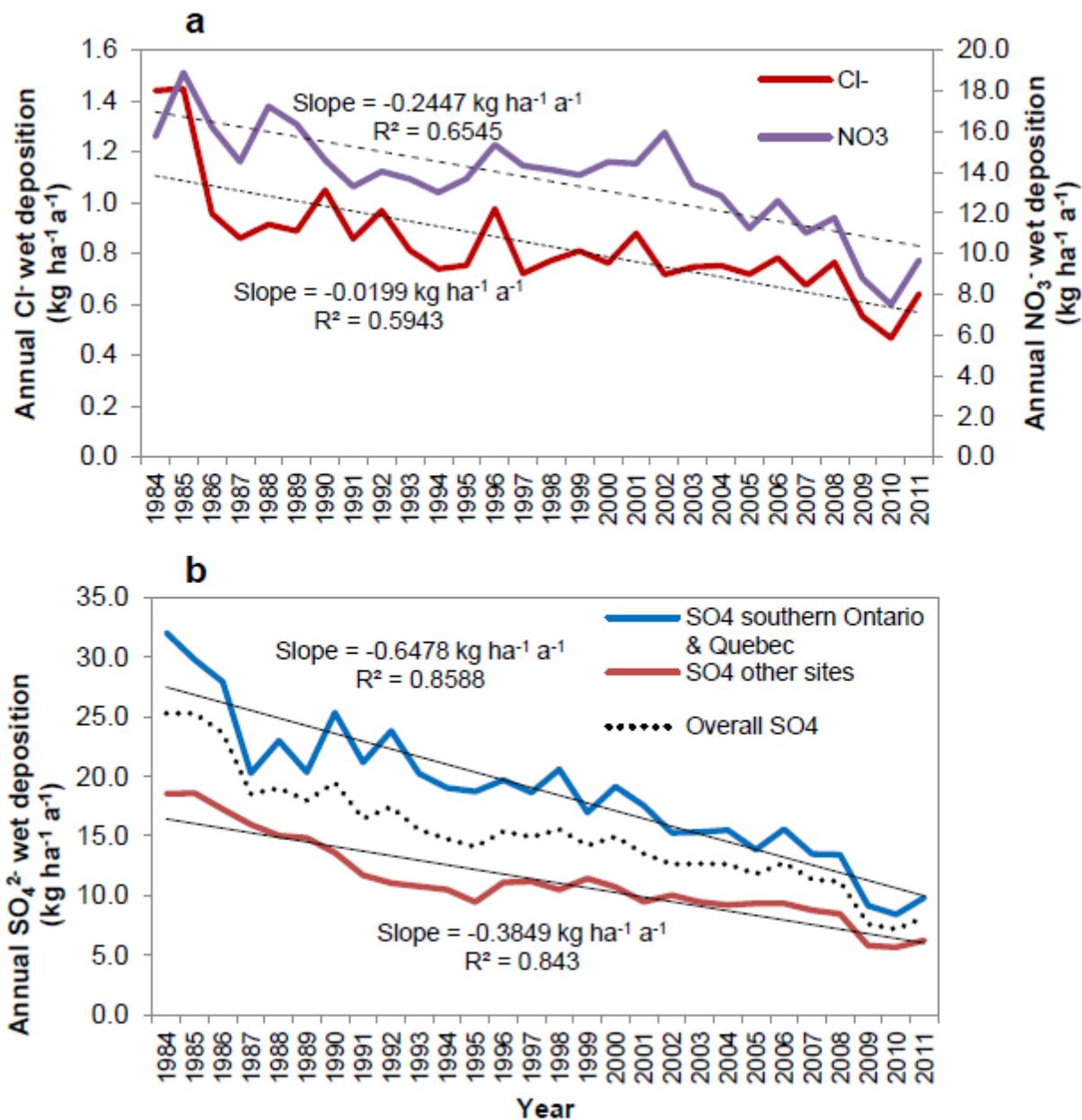


Figure 7: Temporal trends of annual wet deposition of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> (a) and SO<sub>4</sub><sup>2-</sup> (b).

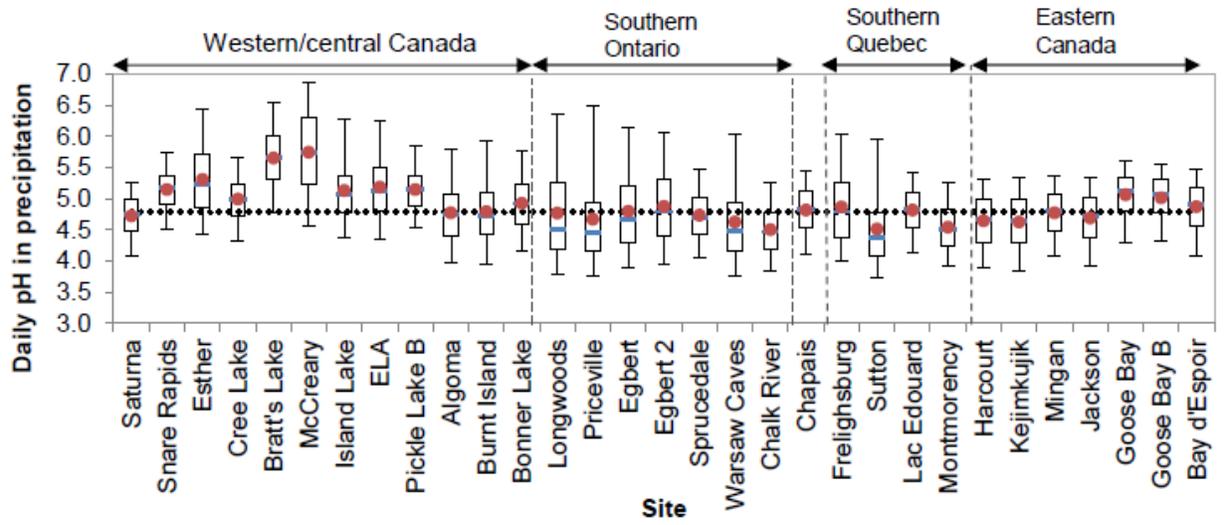
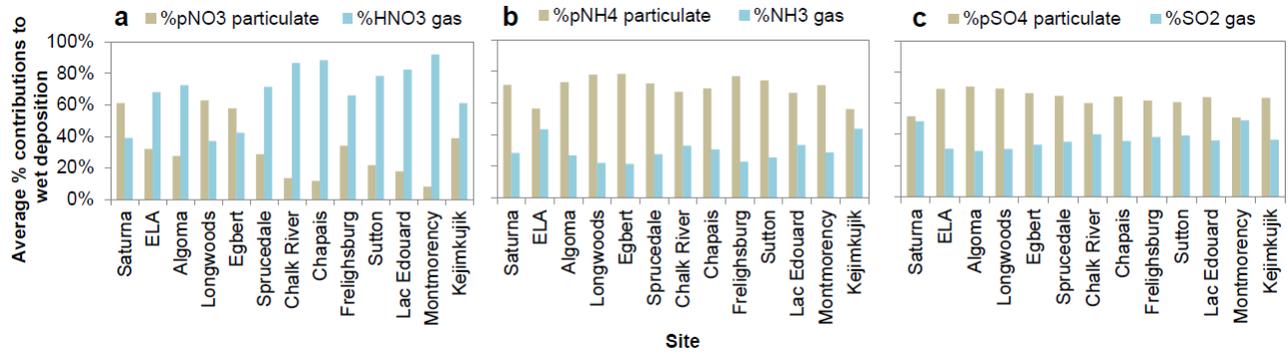


Figure 8: Geographical patterns of precipitation pH. See Fig. 6 caption.



**Figure 9: Average percent contributions of gas and particulate-phase species to nitrate (a), ammonium (b), and sulfate (c) wet deposition.**

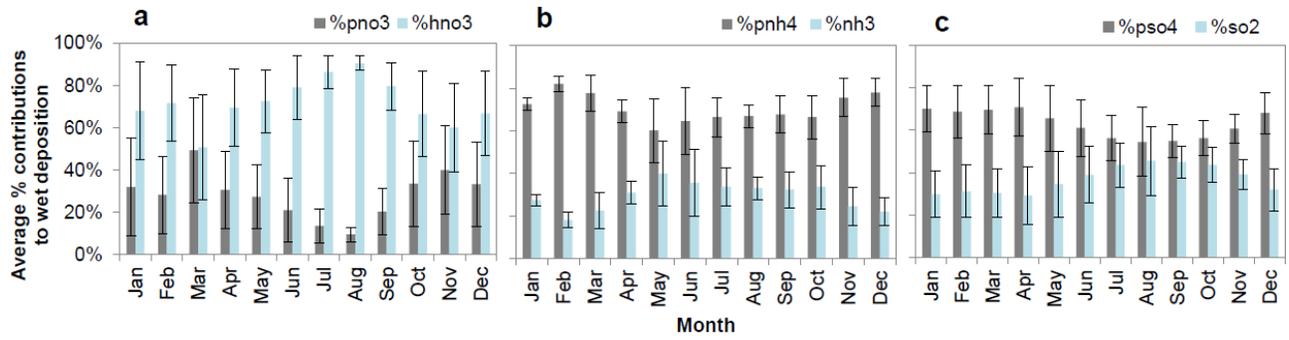


Figure 10: Monthly trend-variation in the contributions of gas and particulate-phase species to nitrate (a), ammonium (b), and sulfate (c) wet deposition. Error bars represent the standard deviation of the percent contributions by gas and particulate-phase species between sites.

## *Supplementary Material*

### **Long-term air concentrations, wet deposition, and scavenging ratios of inorganic ions, HNO<sub>3</sub> and SO<sub>2</sub> and assessment of aerosol and precipitation acidity at Canadian rural locations**

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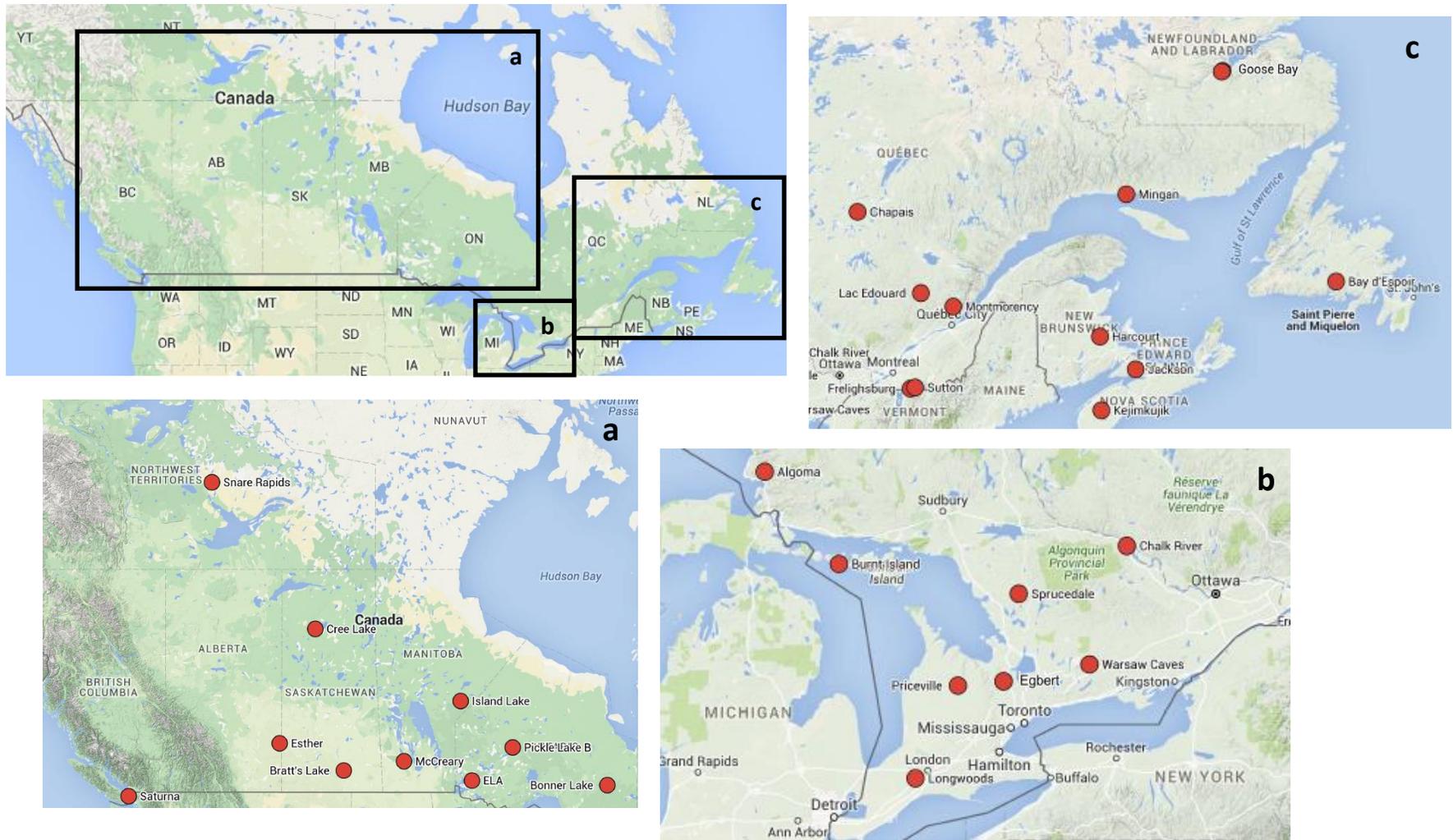
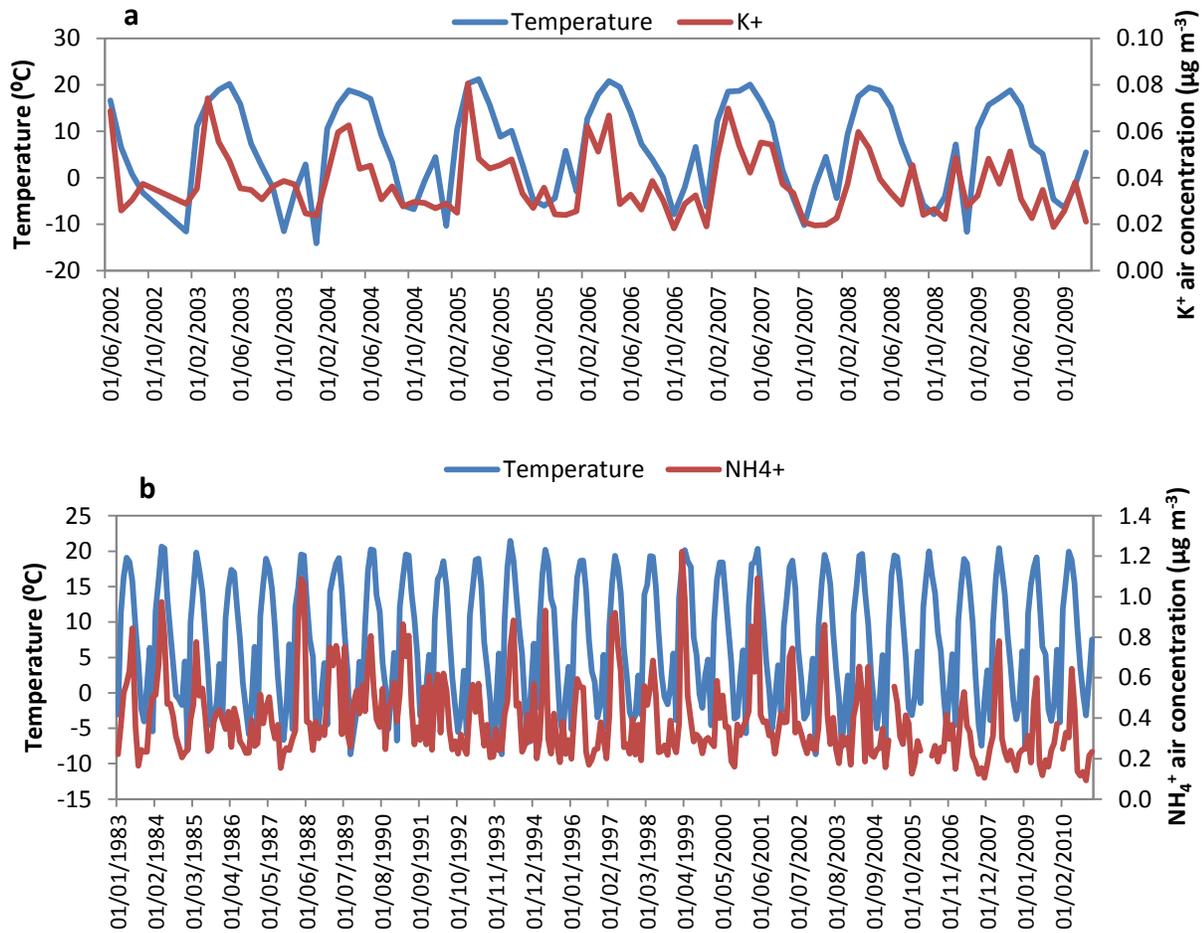


Figure S1: Map of 30 CAPMoN sites in western/central Canada (a), southern Ontario (b), and Quebec and eastern Canada (c).



**Figure S2: Time-series plots of monthly average air temperature and atmospheric K<sup>+</sup> from Sprucedale, Frelighsburg and Lac Edouard (combined) (a) and monthly average air temperature and atmospheric NH<sub>4</sub><sup>+</sup> at Kejimikujik (b).**

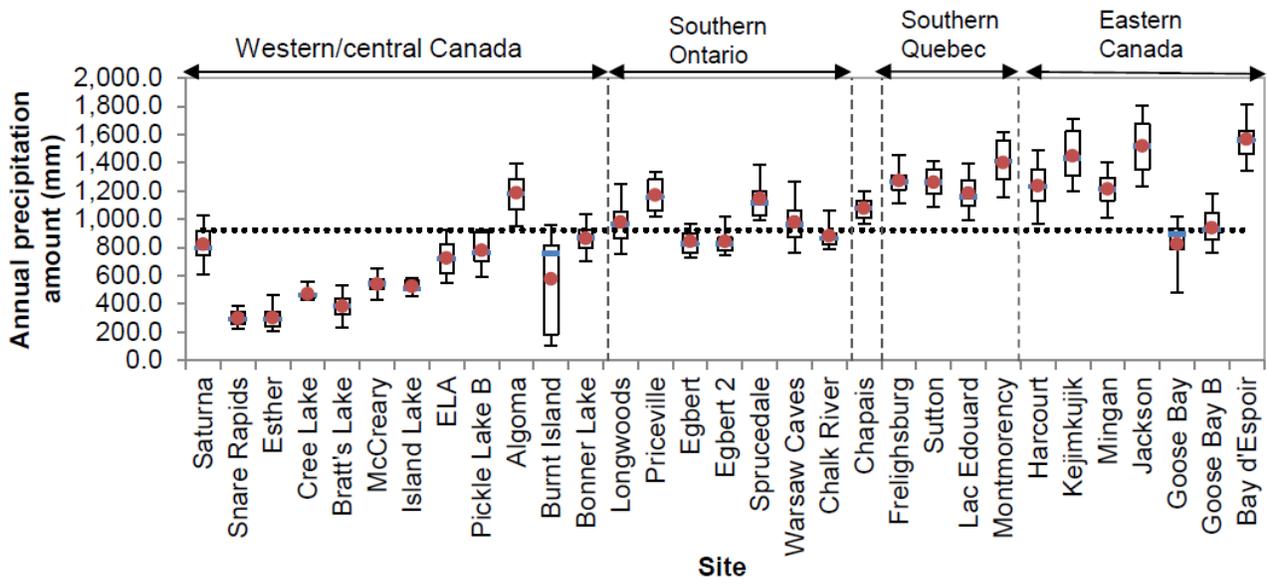


Figure S3: Geographical pattern of the annual precipitation amount. The blue line indicates the median; the red dot indicates the mean; the box and whiskers include the interquartile range and the 5<sup>th</sup> to 95<sup>th</sup> percentile range, respectively; the dotted line is the overall median among the sites.

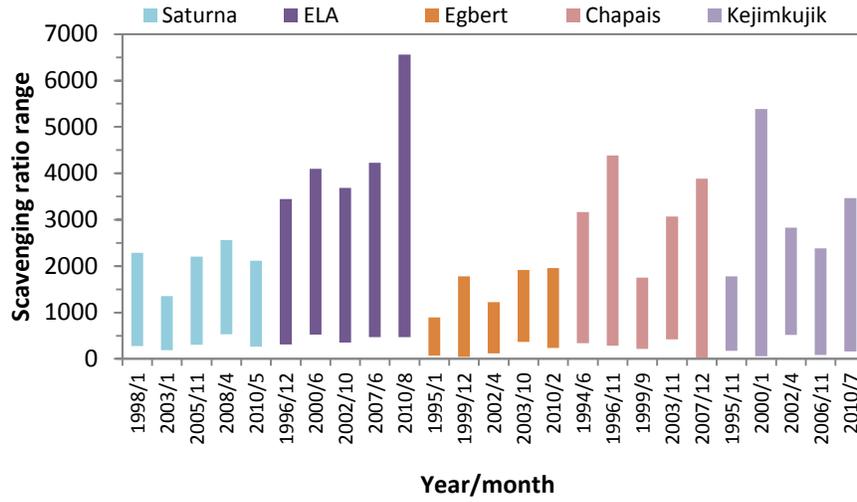


Figure S4: Variability in scavenging ratios among different inorganic ions and trace gases within the same month for five different ~~months~~ years at five of the sites.

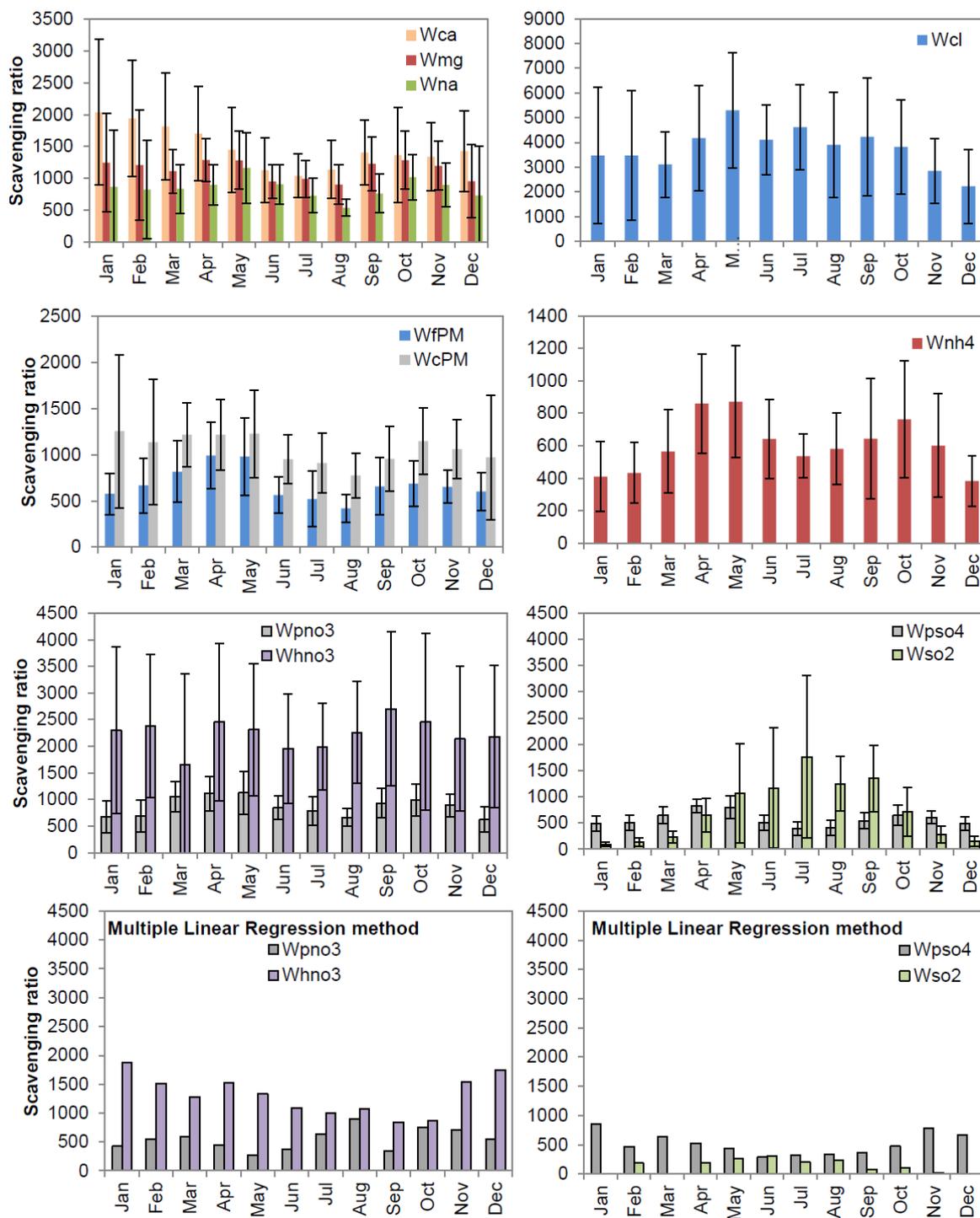


Figure S5: Monthly ~~variation trend~~ in scavenging ratios among 13 sites. Error bars represent the standard deviation of scavenging ratios between sites.  $W_{fPM}$  and  $W_{cPM}$  are the fine and coarse particle scavenging ratios, respectively.

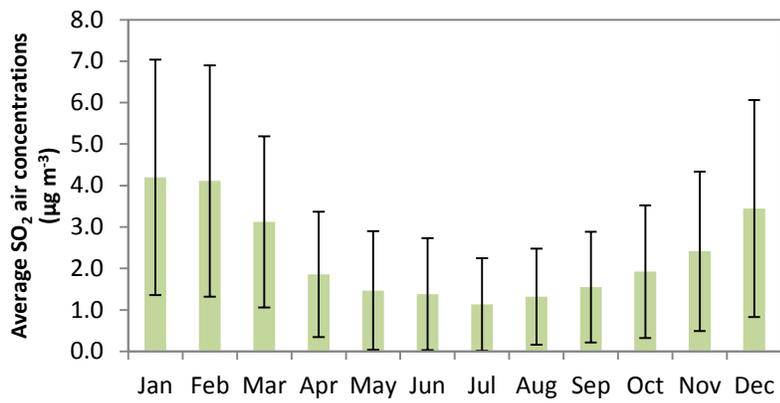


Figure S6. Monthly trend-variation in SO<sub>2</sub> air concentrations. Error bars represent the standard deviation between sites.

Table S1: Pearson correlation coefficients between selected ions and meteorological parameters (significant at  $p < 0.05$ ; otherwise non-significant (ns)). Note that the ion concentrations and meteorological parameters are monthly averages.

Site	K <sup>+</sup>			NH <sub>4</sub> <sup>+</sup>					SO <sub>4</sub> <sup>2-</sup> /SO <sub>2</sub>
	Temp	RH	Precip	Temp	RH	Precip	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Temp
Saturna	-0.20	0.18	0.18	-0.04 <sup>ns</sup>	-0.23	-0.17	0.67	0.60	0.61
Bratt's Lake	0.09 <sup>ns</sup>	-0.20	-0.25						
ELA	0.20	-0.03 <sup>ns</sup>	0.12	-0.26	0.13	-0.22	0.70	0.78	0.75
Algoma	0.42	-0.07 <sup>ns</sup>	-0.04 <sup>ns</sup>	0.36	0.10	-0.17	0.23	0.87	0.73
Longwoods				-0.05 <sup>ns</sup>	0.20	-0.06 <sup>ns</sup>	0.44	0.68	0.81
Egbert				-0.07 <sup>ns</sup>	0.03 <sup>ns</sup>	-0.21	0.52	0.75	0.77
Sprucedale	0.69	0.05 <sup>ns</sup>	-0.14 <sup>ns</sup>	0.30	0.06 <sup>ns</sup>	-0.23	0.20 <sup>ns</sup>	0.92	0.73
Chalk River	0.31	-0.005 <sup>ns</sup>	0.05 <sup>ns</sup>	0.37	0.09	0.02 <sup>ns</sup>	0.10 <sup>ns</sup>	0.85	0.64
Chapais	0.41	-0.17	0.18	0.38	-0.21	0.04 <sup>ns</sup>	0.23	0.85	0.77
Frelighsburg	0.53	0.08 <sup>ns</sup>	0.13 <sup>ns</sup>	0.11 <sup>ns</sup>	0.13 <sup>ns</sup>	-0.13 <sup>ns</sup>	0.36	0.86	0.84
Lac Edouard	0.52	-0.15 <sup>ns</sup>	0.21	0.34	0.01 <sup>ns</sup>	0.11 <sup>ns</sup>	0.23	0.94	0.76
Kejimkujik	0.31	-0.17	-0.15	0.63	-0.30	-0.32	-0.16	0.91	0.83

Table S2: Average cation and anion concentrations (neq m<sup>-3</sup>) in particulate matter by site and year

<u>Site</u>	<u>Cation</u>	<u>Anion</u>		<u>Year</u>	<u>Cation</u>	<u>Anion</u>
<u>Saturna</u>	<u>0.047</u>	<u>0.045</u>		<u>1994</u>	<u>0.074</u>	<u>0.066</u>
<u>Esther</u>	<u>0.052</u>	<u>0.033</u>		<u>1995</u>	<u>0.071</u>	<u>0.063</u>
<u>Bratt's Lake</u>	<u>0.060</u>	<u>0.031</u>		<u>1996</u>	<u>0.073</u>	<u>0.063</u>
<u>ELA</u>	<u>0.024</u>	<u>0.024</u>		<u>1997</u>	<u>0.073</u>	<u>0.063</u>
<u>Algoma</u>	<u>0.024</u>	<u>0.028</u>		<u>1998</u>	<u>0.076</u>	<u>0.064</u>
<u>Longwoods</u>	<u>0.133</u>	<u>0.108</u>		<u>1999</u>	<u>0.075</u>	<u>0.066</u>
<u>Egbert</u>	<u>0.096</u>	<u>0.072</u>		<u>2000</u>	<u>0.067</u>	<u>0.062</u>
<u>Sprucedale</u>	<u>0.024</u>	<u>0.024</u>		<u>2001</u>	<u>0.078</u>	<u>0.068</u>
<u>Chalk River</u>	<u>0.028</u>	<u>0.034</u>		<u>2002</u>	<u>0.073</u>	<u>0.061</u>
<u>Chapais</u>	<u>0.016</u>	<u>0.019</u>		<u>2003</u>	<u>0.065</u>	<u>0.055</u>
<u>Freighsburg</u>	<u>0.060</u>	<u>0.043</u>		<u>2004</u>	<u>0.063</u>	<u>0.054</u>
<u>Sutton</u>	<u>0.062</u>	<u>0.054</u>		<u>2005</u>	<u>0.069</u>	<u>0.059</u>
<u>Lac Edouard</u>	<u>0.016</u>	<u>0.018</u>		<u>2006</u>	<u>0.058</u>	<u>0.046</u>
<u>Montmorency</u>	<u>0.023</u>	<u>0.026</u>		<u>2007</u>	<u>0.058</u>	<u>0.048</u>
<u>Kejimkujik</u>	<u>0.035</u>	<u>0.041</u>		<u>2008</u>	<u>0.060</u>	<u>0.048</u>
				<u>2009</u>	<u>0.052</u>	<u>0.041</u>
				<u>2010</u>	<u>0.048</u>	<u>0.037</u>

Table S2S3: Scavenging ratio (W) statistics from this study (mass basis). na indicates no available data. “C” indicates coastal locations.

Site	W <sub>Ca2+</sub>	W <sub>Mg2+</sub>	W <sub>Na+</sub>	W <sub>coarsePM</sub>	W <sub>finePM = W<sub>k</sub></sub>	W <sub>Cl</sub>	W <sub>NH4</sub>	W <sub>pNO3</sub>	W <sub>HNO3</sub>	W <sub>pSO4</sub>	W <sub>SO2</sub>
<b>Mean</b>											
Saturna <sup>C</sup>	1671	1493	1390	1505	567	2103	445	897	776	602	233
ELA	1893	1347	1208	1496	885	3519	848	1224	3079	696	1247
Algoma	2413	1510	1002	1426	911	5779	762	1204	2064	734	330
Longwoods	911	901	865	881	996	2011	303	657	749	601	125
Egbert	625	748	713	697	554	1914	283	583	982	473	181
Sprucedale	1822	1299	905	1342	611	4278	577	998	2012	611	445
Chalk River	na	na	666	666	580	5065	466	632	3005	547	560
Chapais	2077	899	475	1043	758	1855	625	932	5527	661	1291
Freighsburg	852	838	647	781	553	2554	411	642	1375	471	414
Sutton	1010	936	594	753	497	4377	350	631	1616	473	396
Lac Edouard	1702	1105	577	1128	512	3192	465	842	2398	496	771
Montmorency	1200	1148	599	742	607	4969	406	697	2201	471	1222
Kejimkujik <sup>C</sup>	1729	1980	2120	2077	702	4959	303	1120	1842	571	1339
Max avg/min avg ratio	3.9	2.6	4.5	3.1	2.0	3.1	3.0	2.1	7.4	1.6	10.7
<b>Median</b>											
Saturna <sup>C</sup>	1552	1404	1245	1430	502	1934	416	796	650	533	208
ELA	1395	1141	993	1358	765	3235	726	1151	2711	628	1141
Algoma	1946	1266	816	1272	769	4532	655	1046	1880	698	203
Longwoods	840	832	775	802	682	1684	252	601	857	531	60
Egbert	535	693	585	635	440	1355	245	521	829	428	127
Sprucedale	1504	1238	765	1218	556	3872	582	945	1906	582	204

Chalk River	na	na	531	531	437	4321	401	526	2568	449	284
Chapais	1743	712	363	883	640	1216	544	787	4914	578	828
Frelighsburg	774	754	540	742	438	1788	405	599	1322	442	251
Sutton	968	888	549	706	445	2972	314	562	1452	435	241
Lac Edouard	1483	1015	497	1023	450	2480	380	780	2077	404	453
Montmorency	1130	833	474	623	432	3633	347	559	2173	386	809
Kejimkujik <sup>C</sup>	1482	1416	1447	1452	541	3511	279	926	1571	488	461
Max median/min median ratio	3.6	2.0	4.0	2.7	1.8	3.7	3.0	2.2	7.6	1.8	19.0
<b>Standard deviation</b>											
Saturna <sup>C</sup>	798	727	734	655	271	1001	217	381	547	276	123
ELA	1684	810	1016	990	483	2159	476	680	1636	336	880
Algoma	1869	1061	661	973	653	5161	517	753	1017	284	372
Longwoods	439	398	362	312	869	1331	159	233	453	273	142
Egbert	373	317	427	322	501	1547	170	307	647	214	180
Sprucedale	1039	634	637	597	286	2940	253	504	840	259	523
Chalk River	na	na	450	450	417	3763	313	392	1629	352	681
Chapais	1273	668	349	641	407	1969	328	529	2654	339	1373
Frelighsburg	415	367	382	331	514	2288	157	311	523	170	438
Sutton	374	371	254	302	321	3320	155	284	618	234	445
Lac Edouard	1003	597	361	517	281	2188	257	412	1195	260	843
Montmorency	628	783	354	441	478	4489	231	425	960	324	1151
Kejimkujik <sup>C</sup>	1134	1643	1942	1823	671	4723	154	687	1172	391	2245

Table S3S4: Scavenging ratios from literature (mass basis). \* Most literature values excluded gas scavenging except where indicated;  
<sup>1</sup>Derived from multiple linear regression; <sup>2</sup>W<sub>pNO<sub>3</sub></sub> based on sum of pNO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> in air; <sup>3</sup>W<sub>pSO<sub>4</sub></sub> based on sum of pSO<sub>4</sub><sup>2-</sup> and SO<sub>2</sub> in air;  
<sup>4</sup>Snow events only.

Location	W <sub>Ca<sup>2+</sup></sub>	W <sub>Mg<sup>2+</sup></sub>	W <sub>Na<sup>+</sup></sub>	W <sub>K<sup>+</sup></sub>	W <sub>Cl</sub>	*W <sub>NH<sub>4</sub></sub>	*W <sub>pNO<sub>3</sub></sub>	*W <sub>pSO<sub>4</sub></sub>	W <sub>HNO<sub>3</sub></sub>	W <sub>SO<sub>2</sub></sub>	Reference
CAPMoN sites, Canada	625-2413	748-1980	475-2120	497-996	1855-5779	283-848	583-1224	471-734	749-5527	125-1339	This study
							523-1776	391-903	722-2848	31-409	This study <sup>1</sup>
Eastern Canada							832-2950	831-1550			Barrie et al. (1985) <sup>2</sup>
NADP/CASTNET sites, U.S.	860-2526	656-2011	798-7409	265-885	1430- 22950						Cheng et al. (2015)
NADP/AIRMoN sites, U.S.						96-3050		216-2710	300-1700		Hicks (2005) <sup>3</sup>
Northern Michigan				80-4600		40-2200	500	60-2280	3500- 4550	219-355	Cadle et al. (1990) <sup>4</sup>
Barbados			578-869				336-409	264-315			Galloway et al. (1993)
Bermuda			560-749				273-447	182-242			Galloway et al. (1993)
Ireland			1692-5800				535-1258	321-734			Galloway et al. (1993)
Vitoria, Spain	3983		3625	1151	3030	1739	2303	2830			Encinas et al. (2004)
Central France				20000- 250000		500-8500	4500- 16500	750-5250			Bourcier et al. (2012)
Sardinia, Italy	3459-4605	1013-1524	1708-1815	1630- 1845	2085-2419		754-1062	1728-2173			Guerzoni et al. (1995)
Turkey	1649±466		789±176	619±138		624±147	612±228	1177±301			Tuncel and Ungör (1996)
Mt. Sonnblick, Austria						2160	3120	1680			Kasper-Giebl et al. (1998) <sup>2</sup>
							1104	1056	3480	96	Kasper-Giebl et al. (1998) <sup>1</sup>
Hyderabad, India	2265	877	517	723	109	389	317	160			Kulshrestha et al. (2009)
Bay of Bengal	582	5039	5282	58	16085	336	3591	426			Kulshrestha et al. (2009)
Nepal	1805±1873	2580±2277	1393±1593	2436±20 92	2582±1870	1811±23 51	2502±2007	487±326			Shrestha et al. (2002)
Singapore	697±376	318±201	500±180	744±590	2624±1129	1660±12 84	2134±1671	2596±2076			He and Balasubramanian (2008)
Maldives	470-1200	500	1000-1100	140-220	1100-1200	530-600	930-2000	490-580			Granat et al. (2010)

Table S4S5: Gas and particle scavenging ratios for nitrate and sulfate derived from multiple linear regression [ $C_{\text{prec}} = \text{constant} + W_{\text{gas}}C_{\text{gas,air}} + W_{\text{part}}C_{\text{part,air}}$ ].  $C_{\text{prec}}$  is the total precipitation concentration of nitrate or sulfate;  $W_{\text{gas}}$  and  $W_{\text{part}}$  are the gas and particle scavenging ratios, respectively;  $C_{\text{gas,air}}$  and  $C_{\text{part,air}}$  are the air concentrations of  $\text{HNO}_3$  or  $\text{SO}_2$  and  $\text{pNO}_3^-$  or  $\text{pSO}_4^{2-}$ , respectively.  $R^2$  is the coefficient of determination and r-part is the partial correlation. ns indicates not significant coefficients ( $p > 0.05$ ).

Site	$W_{\text{pNO}_3}$	$W_{\text{HNO}_3}$	$R^2$	r-part $\text{pNO}_3^-$	r-part $\text{HNO}_3$		$W_{\text{pSO}_4}$	$W_{\text{SO}_2}$	$R^2$	r-part $\text{pSO}_4^{2-}$	r-part $\text{SO}_2$
Saturna	910	1175	0.20	0.22	0.33		903	45	0.14	0.31	0.06
Bratt's Lake	694	1359	0.16	0.29	0.25				<0.1		
Algoma	1121	1253	0.24	0.25	0.28		434	85	0.17	0.33	0.08
Longwoods	544	776	0.14	0.28	0.21		393	ns	0.12	0.33	-0.01
Egbert	523	722	0.18	0.30	0.20		391	ns	0.16	0.37	0.01
Sprucedale	882	1308	0.21	0.21	0.26		505	ns	0.13	0.35	-0.02
Chalk River	786	1510	0.17	0.15	0.28		487	ns	0.14	0.36	-0.01
Chapais	1776	2848	0.25	0.16	0.39		623	409	0.20	0.41	-0.04
Sutton	944	1241	0.15	0.19	0.25		535	31	0.17	0.39	0.03
Lac Edouard	1532	1289	0.33	0.25	0.22		482	80	0.19	0.37	0.06
Frelighsburg	958	1470	0.26	0.28	0.29		526	104	0.13	0.32	0.08
Montmorency	1470	1493	0.34	0.16	0.45		481	ns	0.22	0.46	-0.03
Kejimkujik	1561	2382	0.19	0.22	0.33				<0.1		
<i>Overall</i>	570	1253	0.21	0.22	0.29		489	32	0.20	0.38	0.04

Table S5S6: Monthly gas and particle scavenging ratios for nitrate and sulfate derived from multiple linear regression (similar to Table S4S5)

Month	$W_{pNO_3}$	$W_{HNO_3}$	$R^2$	r-part $pNO_3^-$	r-part $HNO_3$		$W_{pSO_4}$	$W_{SO_2}$	$R^2$	r-part $pSO_4^{2-}$	r-part $SO_2$
Jan	425	1871	0.23	0.16	0.37		851	ns	0.25	0.40	-0.06
Feb	548	1511	0.27	0.24	0.35		467	184	0.20	0.34	0.00
Mar	583	1283	0.26	0.26	0.31		633	ns	0.18	0.32	0.02
Apr	442	1518	0.21	0.18	0.30		525	195	0.22	0.28	0.09
May	270	1332	0.18	0.10	0.31		434	257	0.19	0.22	0.13
Jun	373	1093	0.22	0.11	0.31		284	307	0.22	0.22	0.17
Jul	636	1005	0.19	0.13	0.29		317	204	0.21	0.26	0.09
Aug	894	1065	0.24	0.17	0.30		333	230	0.20	0.26	0.09
Sep	345	842	0.11	0.08	0.20		362	77	0.17	0.29	0.05
Oct	749	862	0.17	0.24	0.19		472	107	0.24	0.28	0.11
Nov	712	1543	0.20	0.28	0.24		780	21	0.21	0.35	0.03
Dec	554	1741	0.24	0.25	0.33		670	ns	0.19	0.32	0.00