

Response to Reviewer 1

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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 SO₂, 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. NH₃, SO₂, NO_x 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 NH_3 , SO_2 , 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 pSO_4^{2-} and SO_2 and pNO_3^- and 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 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 pSO_4^{2-} was found with a slope of +11.4 per year. This suggests the atmospheric 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 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 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 NH_4^+ , NO_3^- , and SO_4^{2-} wet deposition were determined. Geographical patterns of atmospheric Ca^{2+} , Na^+ , Cl^- , NH_4^+ , NO_3^- , and SO_4^{2-} were similar to wet deposition and attributed to anthropogenic sources, sea-salt emissions, and agricultural emissions. Decreasing trends in atmospheric NH_4^+ (1994-2010) and SO_4^{2-} (1983-2010) were prevalent. Atmospheric NO_3^- increased prior to 2001 and then declined afterwards. These results are consistent with SO_2 , NO_x and NH_3 emission trends in Canada and the U.S. Widespread declines in annual NO_3^- and 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 NH_4^+ , SO_4^{2-} and 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 HNO_3 and 28% for particulate NO_3^- , 37% for SO_2 and 63% for particulate SO_4^{2-} , and 30% for NH_3 and 70% for particulate 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 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 SO₂ and NO_x 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⁺ and Cl⁻ 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_x emissions in Canada began to decrease in 1997, while in the U.S. the decline was already occurring in 1994. From Fig. 4, SO₂ 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 NO₃) 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 NO₃ is particularly interesting. Figure 3 shows that averaged NO₃ 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 NO₃⁻ (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 NO₃⁻ were reflected in the Canadian NO_x 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 NO₃⁻ and

in 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.