Dear Prof. Ding – co-editor of ACP,

Thank you very much for handling the review process of our manuscript (acp-2019-418) titled "Decoding long-term trends in the wet deposition of sulfate, nitrate and ammonium after reducing the perturbation from climate anomalies." We have carefully revised the paper and addressed all the comments provided by the reviewers. Our detailed replies are attached below.

For your and the reviewers' convenience to review the changes, a copy of the text with highlighted changes (from track changes) is also attached here.

We hope you and the reviewers will find the revised paper meets the standard of the journal.

Sincerely,

Xiaohong Yao and Leiming Zhang

Response to Referee #1

We greatly appreciate the reviewer for proving the constructive comments, which have helped us improve the paper quality. We have revised the paper accordingly as detailed in our point-by-point responses below.

RC- Reviewer's Comments; AR – Authors' Responses

RC: General comments

The objective of the study is to understand the effect of emission reduction on long term trends of wet deposition of inorganic ions. In that purpose, the effects of climate anomalies must be isolated to better highlight emission reduction effects. A two decade dataset of wet deposition of SO42-, NO3- and NH4+ is studied with a new approach at rural Canadian sites. A new method is applied to extract trends and inflection points, by pre processing the data sets and applying further common statistical tools such as M-K and L-R methods. The presentation of the new pre processing method based on slopes for monthly wet deposition fluxes during 2 year periods should be clarified and better explained to avoid losing the reader. Indeed, there are several explanations that would need to be better justified to highlight the true added value of this new method. The summary stipulated that more robust results are found with this new method, but this seems to be only true because some points are excluded from the correlation analysis. The robustness of the method needs further justification. This sentence on robustness in the abstract has to be removed, unless it is really justified. This analysis is based on the assumption that removing the maximum wet deposition flux corresponds to removing climate anomalies, based on a pre processing of the data: this is exactly the point that has to be better justified, because all the analysis of the results relies on that statement. When reaching the conclusion, the reader understands that the role of climate anomalies is also very important. The displayed purpose of the paper should be to highlight both the roles of climate anomalies and emission trends, rather than only focusing on emissions. The link with climate anomalies is also an interesting way in understanding the wet deposition flux trends. The statistical approach lacks from being scientifically justified in terms of geophysical variable influence. I recommend major revision for this study, especially concerning the climate anomalies justification. Indeed, if this part is not well justified, the rest of the study cannot follow. Generally, a table with a summary of different phases of trends for each site and each ion would help to better capture the results.

AR: In the revised paper, we have added more justification to support our analysis, in particular on the types of climate anomalies (e.g., precipitation depth, wind pattern at local and regional scales) that may cause the abnormality of wet deposition fluxes of ions on monthly and annual scales. We have added the geometric average concentration of ions in precipitation and precipitation depth to reveal the influence of geophysical variables on wet deposition. The two parameters clearly demonstrate that the maximum values of wet deposition fluxes of ions that deviated positively from the general trend were mainly caused by extreme precipitation events rather than abnormal increase or decrease in geometric average concentration of ions. However, the causes were yet to be identified for the maximum monthly value of Fwet that were negatively deviated from the general trend. This later case has also been stated in the revised paper.

Abnormal increase or decrease in wet deposition of ions associated with climate anomalies at one site does not necessarily mean that the abnormality also occur on a regional scale. This is the case when the data at three sites (Sites 1, 3 and 4 in the same region) were combined together. In such a circumstance, the abnormality identified at a particular site may be a local instead of a regional phenomenon. Thus, the maximum value of wet deposition that deviated substantially from the regression curve needs to be removed for identifying general trends caused by emission trends at one sampling site. Removing the abnormal maximum value of wet deposition would minimize the effects of climate anomalies on the calculated m-values and subsequently derived trend results, thus focusing on the effects of emission control policies. As demonstrated in the revised Supporting Information and revised paper, the new approach proposed in this study is indeed more robust than simply using annual F_{wet} as data input for trend analysis. Following the reviewer's recommendation we have replaced the world "robustly" with "statistically" in several places.

We should not overemphasize the effect of climate anomalies on wet deposition of ions when the data at one site was analyzed just in case it is only a local phenomenon. Moreover, abnormal increase (decrease) in wet deposition of ions due to climate anomalies at one site does not necessarily mean the abnormal increase (decrease) in the total deposition of ions (wet plus dry). Regarding the impacts of atmospheric deposition on eco-systems, the total deposition of ions (wet plus dry) should be more important than wet deposition alone. We prefer to focus on how to removing climate anomalies and to establish the relationship between wet deposition of ions and their corresponding emissions of air pollutants in this study. We agree with the reviewer that it is valuable to compare the effects of climate anomalies on wet deposition at different sites in a regional scale in terms of their similarity and differences, but such effort requires datasets larger than what is available in our study (and is out of the scope of the present study).

Several methods can be used to do PRL analysis in literature. The simplest one is to manually conduct piecewise regression, where inflection points are visibly recognized, and this method is also used in the present study. A few complex algorithms are also available in the literature to conduct PRL if with hundreds of data points (Ryan and Porth, 2007 and references cited there). The complex algorithms are, of course, seldom used to identify trends in annul wet deposition of ions because of the shorter data record history. The reference (Ryan and Porth, 2007) has been added in the revision.

A table summarizing phase classification for m-values of wet deposition of SO42- and NO3- at different sites has been added in the Supporting Information (Table S2).

RC: Introduction Wet deposition fluxes of sulfate, nitrate and ammonium are affected by emissions of precursors, atmospheric processes, and climate anomalies. A definition of complex atmospheric processes and climate anomalies that are specifically linked to this study would be useful. Moreover, some more details are expected to explain these three processes, references to literature are not sufficient.

AR: We have revised the second paragraph of Introduction to address this comment, which reads: "The wet deposition of SO_4^{2-}, NO_3^- and NH_4^+ is affected by not only their gaseous precursors' emissions (Butler et al., 2005; Fowler et al., 2007; Li et al., 2016) but also complex atmospheric processes such as long-range transport, chemical transformation, and dry and wet removal (Cheng & Zhang, 2017; Yao & Zhang, 2012; Zhang et al., 2012). These processes can be largely affected by climate anomalies. For example, climate anomalies can sometimes bring extreme precipitation amounts throughout a particular month, and subsequently lead to extremely high wet deposition fluxes of ions through enhanced wet removal rainout and washout of air pollutants."

RC: Methodology This paragraph should be separated into different sub-paragraphs, with 2.1 statistical methods (line 112), 2.2 Data sets (line127), 2.3 Filtering climate anomalies (or something like that, line 152).

AR: The section has been split into subsections: "2.1 Data sources, 2.2 statistical methods, 2.3 Filtering climate anomalies, 2.4 Example case for filtering, 2.5 Justification for the new approach."

RC: Line 125 and below: it is not clear why you use annual wet deposition fluxes as input data, whereas a modified dataset is based on monthly wet deposition fluxes. A figure would be useful to understand how this new dataset is built.

AR: Annual wet deposition fluxes are widely used as input data to derive the trend in literature. Annual wet deposition fluxes are the sum of monthly wet deposition fluxes. The newly developed approach in this study discards the simple sum of monthly wet deposition fluxes. Alternatively, we use monthly wet deposition fluxes to derive m-value by removing the abnormal maximum value for trend analysis. In fact, both annual wet deposition fluxes and m-values are based on monthly wet deposition fluxes.

To demonstrate the advantage of our newly developed approach against the conventional approach, we conducted a comparison of their performance in predicting the trend. The clarification has been added in the revised paper, which reads: "The annual Fwet is widely used for trend analysis and the trend results are thereby used to compare with those derived from the approach proposed in this study."

Our example case presents all details while adding new figure may be redundant. Please see our revised Supporting Information.

RC: Line 145, what is the scientific explanation of excluding the maximum deposition flux when it deviates from the general regression? You only give a statistical explanation, which does not help in understanding the underlying geophysical causes.

AR: Extreme precipitation depth led to the monthly maximum deposition fluxes of ions severely deviating from the general regression. In the revision, it reads as "The actual observed maximum value of 532 mg m^{-2} $month^{-1}$ was much larger than the upper range of the predicted value and was thus believed to be caused by monthly scale climate anomalies, i.e., the occurrence of extreme amount of precipitation. The maximum monthly deposition flux in 1990-1991 occurred in September 1990 when the monthly precipitation depth reached 294 mm, which was much higher than those in the same month of other years, e.g., 169, 68, 95 and 127 mm in 1988, 1989, 1991 and 1992, respectively. The maximum daily precipitation depth in September was also higher in 1990 (91 mm) than in other years (43.6, 12.2, 13.6 and 26.8 mm in 1988, 1989, 1991 and 1992, respectively). However, the monthly geometric average concentration of SO_4^{2-} in precipitation (1.8 mg L^{-1}) in September 1990 was close to the mean value (1.7±0.3 mg L^{-1}) in September 1988-1992 and was even smaller than that (2.9 mg L^{-1}) in August 1990. The maximum value was treated as an outlier and excluded for analysis."

RC: Line 154: do you mean twelve two year periods of data?

AR: corrected.

RC: Line159: again, you mention the exclusion of maximum values of wet deposition fluxes, which leads to an increase of the R2 values: this is obvious statistically, but the scientific justification of this exclusion must be clarified.

AR: Please see our response above to the comment on Line 145.

RC: The explanation line 167 that maximum values are believed to be caused by climate anomalies is just a hypothesis and not sufficient to prove that you can exclude this maximum. Furthermore, this paragraph about filtering and excluding values is a bit strange in the methodological section, as it presents results already.

AR: Please see our response above to the comment on Line 145. Without an example case for filtering data, it is difficult for readers to capture the exact procedure of the new approach. We prefer to keep this part in the Method section. In Results and discussion, we focus on the analysis of trend results.

RC: Line 190: Comparisons between this new approach (Approach C) and traditional approaches (A and B) are given in supporting information. Why a 12 month period is *used in approaches A and B, whereas a 24 month period is used in approach C?*

AR: The direct comparison between Approach C and the conventional method (using annual F_{wet}) is difficult to demonstrate which one is more robust. We thereby compare the results by using 12 month period (Approach A and B), 24 month period (Approach C) and 36 month period (Approach D).

A linear regression analysis result, assuming zero interception and using the m-values calculated from Approach B against the annual F_{wet} data, showed the value of R^2 as high as 0.99 (Fig. S4 added in the revision). Thus, the trend result derived from Approach B is exactly the same as that from using the annual wet deposition flux of ion. When we compare the m-values of Approach C with those of Approach B, the conclusion is applicable for the comparison between Approach C and the use of annual F_{wet}.

m-values derived from Approach C are more robust than those from Approach B. This is because the use of 24 month data in Approach C instead of 12 month in Approach B allows gaining high R^2 values and minimizing uncertainties of m-values. The trend results would be more robust by using m-values from Approach C than by using those from Approach B.

This has been clarified in Supporting Information. More summary of the comparison has also added in Supporting Information.

RC: Line 195: what do you mean by "a small portion of climate anomalies that are unable to be removed by the new approach"? This is not precise enough.

AR: This part has been revised to: "climate anomalies that are unable to be removed by the new approach".

RC: Results and discussion
Line 208: as mentioned in the general comment, all the analysis of results here relies on the assumption that removing maximum wet deposition fluxes are associated to climate anomalies, which has to be better justified in the methodological section.

AR: Please see our response to the comment on Line 145 above. In addition, we have also added more justification, which reads: "The abnormally increased Fwet of SO42- in 1999 was mainly because of the increased precipitation depth (1312 mm), which was the largest during 1998-2011 (the annual average precipitation depth excluding 1999 was 1067±86 mm). However, the geometric average concentration of SO42- in precipitation in 1999 (1.0 mg L-1) was close to those in the other years, e.g., 0.9 mg L-1 in 1997 and 1998, and 1.0 mg L-1 in 2000. "

RC: Line 210: please specify Fig 2a for SO42-, 2d for NO3- (and so on).

AR: The sentences have been revised to: "SO_4^{2-} and NO_3^- showed decreasing trends from a LR analysis, with R^2 values of 0.81 and 0.71, respectively, and P values <0.01 (Fig. 2a and 2d). The decreasing trends were also confirmed by the M-K method analysis. NH_4^+ exhibited a stable trend from M-K analysis (Fig. 2g), as well as no significant trend with P value >0.05 from LR analysis. The annual F_{wet} of these ions are also shown in Figs. 2b, 2e and 2f and annual emissions of SO_2, NO_x and NH_3 in Figs. 2c, 2f and 2i, respectively. These data were used to compare and facilitate analysis in terms of identifying inflection points and the advantage of using the m-value over the annual F_{wet}, as presented below. "

RC: Line 212: where can we check that NH4+ exhibits a stable trend from M-K analysis, in Fig 2? From line 215 and below, are you still commenting Fig 2? Please specify to facilitate the reading.

AR: The sentence has been revised as: "NH_4^+ exhibited a stable trend from M-K analysis (Fig. 2g), as well as no significant trend with P value >0.05 from LR analysis."

The sentence in Line 215 has been revised as: "The m-values of SO_4^{2-} and NO_3^- also allowed for statistical identification of trends in different phases supported by annual variations in emissions of SO_2 and NO_x (Figs. 2c and 2f) to some extent."

RC: Line 241: the sharp increase in NO3- wet deposition flux in 1999 is supposed to be due to a "probable large perturbation from climate anomalies": this is not sufficiently justified. A scientifically argument needs to be provided.

AR: The sentence has been revised to: "The sharp increase in F_{wet} of NO_3^- occurred mainly in 1999, which was probably due to largely increased annual precipitation depth as mentioned in Section 2.4. The analysis was also supported by the geometric average concentration of NO_3^- in precipitation, which was 1.1 mg L^{-1} in 1999, 5% lower than that in 1988 and only 5-10% higher than those in 1990-1991, 1993 and 2002. "

RC: Line 252: "Note that... here" should be declared in the method section, not in the results section. Moreover, R2 are written in the figures, and the text stipulates that R values will be used: this is not consistent.

AR: This sentence has been moved to the method section. It now reads: "Note that R^2 is conventionally used in LR and PRL. However, r instead of R^2 is used in correlation analysis. Thus, R^2 and r are used for the two types of analyses in this study, respectively."

It is consistent because LR is conducted for trend analysis. In the text, the correlation analysis of m-values with emissions is presented.

RC: Line 268: again, perturbations from climate anomalies unable to be removed by the new approach needs to be specified: what can they be exactly? What do they represent in terms of geophysical variables?

AR: We could not identify the exact cause despite extensive analysis. We thereby have revised the text to: "The contrasting correlation results between the two different periods discussed above implied the complex link between wet deposition of NO_3^- and emissions of NO_x. One might assume that the perturbation from climate anomalies might not be fully removed by the new approach for the period of 1990-2003, which overwhelmed the effects of NOx emissions on the trends in m-values of NO_3^-. Such a possibility is practically very low since the approach works well for the period of 2002-2011. The contrasting results between these two periods are yet to be explained."

RC: Line 282: please detail "many other factors" for describing NH4+ trends.

AR: The sentence has been revised to: "Nearly all of the NH_4^+ was associated with SO_4^{2-} and NO_3^- in the atmosphere (Cheng and Zhang, 2017; Teng et al., 2017; Tost et al., 2007; Zhang et al., 2012), and the trends in the m-value of NH_4^+ could be affected by many other factors besides NH_3 emissions and climate anomalies, e.g., gas-aerosol partitioning and different dry and wet removal efficiencies between NH_3 and NH_4^+, pH value of wet deposition."

RC: Line 293: after comparing m-values and annual deposition fluxes in the paragraph (lines 284-293), what is the interpretation of the statements? What do you want to highlight here?

AR: This part has been split into two parts in the revised paper. The first part reads: "In addition, LR analysis of the annual F_{wet} of SO_4^{2-} revealed a decreasing trend (second row in Fig. 2b). The M-K method analysis also confirmed the decreasing trend with annual F_{wet} as input. However, the three-phase trend in F_{wet} of SO_4^{2-} and related inflection points, identified using the m-values discussed above, were not identified by the t-test when simply using annual F_{wet} data as input. Identifying these inflection points are crucial to assess the effectiveness of environmental policies. The correlation between annual F_{wet} and emission was 0.89 for SO_4^{2-} vs. SO_2 in Ontario (P values <0.01), while the corresponding r value was as high as 0.96 between m-value and emission. After reducing the perturbations from climatic factors to the annual F_{wet}, a stronger correlation was obtained between F_{wet} and emission. The increased r further solidified the dominant contribution of the long-range transport of air pollutants from Ontario rather than Québec to the wet deposition of SO_4^{2-} at Site 1."

The second part reads: "LR analysis of the annual F_{wet} of NO_3^- revealed a decreasing trend (second row in Fig. 2e), confirmed by the M-K method analysis. However, the two-phase trend in F_{wet} of NO_3^- and related inflection point were not identified by the t-test when simply using annual F_{wet} data as input. The correlations between annual F_{wet}

and emission were 0.74-0.76 for NO_3^- vs. NO_x in Québec and Ontario (P values <0.01), while the corresponding r values increased to 0.84-0.85 between m-value and emission. Both the identified inflection point and the stronger correlation between m-value and emission demonstrated the advantage of using the m-value over annual F_{wet} of NO_3^- in trend analysis. ”

RC: Line 301: paragraph 3.2 should be separated into different sub paragraphs (based on ions for example).

AR: The section has been split into: “3.2.1 Trend in m-value of SO_4^{2-}, 3.2.2 Trend in m-value of NO_3^- and NH_4^+.

RC: Line 388: again, justify which climate anomalies you are talking about to remove m values

AR: This part has been revised to: “The three-phase trend in m-values of SO_4^{2-} and the two-phase trend in m-values of NO_3^- were also obtained at Sites 3 and 4 after excluding a few m-values that were caused by large perturbations from climate anomalies. For example, the annul precipitation depths of 1044 mm in 1987 and 905 mm in 1997 at Site 4 were evidently lower than the average value of 1299±124 mm (excluding 1987 and 1997) in 1985-1997 (Table S2). However, the geometric average concentration of SO_4^{2-} of 1.5 mg L^{-1} in 1997 was the same as the mean value of 1.5±0.2 mg L^{-1} in 1995-1999 (excluding 1997). The value of 1.6 mg L^{-1} in 1987 was also same as that in 1989. The lower annul precipitation depths in 1987 and 1997 than in the other years were very likely the dominant factor causing the abnormally lower m-values in 1986-1987 and 1996-1997.”

RC: Line 413: what is the reason of unrealistic emission inventory? It could be useful to recall here which emission inventory is used here.

AR: Real on-road emission factors of NOx measured from Transportation and Mobile Equipment in each year of 1990-2003 in Ontario and Quebec are needed to address this issues. Unfortunately, on-road emission factors of NOx are always adopted according to the values in literature rather than measured in different years. Without real on-road emission factors of NOx measured in different years, it is difficult to identify the exact causes. Discussion on emission inventory has been added, which reads: “inconsistent with the bell-shape profile of the NOx emissions mainly caused by annual variations in NOx emission from the sector of Transportation and Mobile Equipment in Ontario and Québec, which could be due to either the perturbation from climate anomalies or unrealistic emissions inventory from (APEI) in Canada.”

RC: Conclusions
Line456: this statement about the importance of climate anomaliesvs emission trends is really interesting but unfortunately it is not specified earlier as an objective of the

study: rather than removing climate anomalies, the purpose of the study could be to highlight the roles of both emission trends and climate anomalies, depending on the periods. The conclusion ends with results consideration that should be in the results section. The conclusion has to be more general and give some general clues for the interpretation of results that were presented. In the present state, it seems that the conclusion is not terminated.

AR: Please see our responses to the general comments. We have revised the conclusion accordingly, i.e., removing the detailed results in the second half of the last paragraph in the Conclusion section and make the conclusions more general, which reads: “The long-term variations in Fwet of NH4+ generally showed no clear long-term trends. Moreover, no apparent cause-effect relationships were found between the wet deposition of NH4+ and the emission of NH3. It can be reasonably inferred that additional key factors besides those discussed in this study also impact the trends of Fwet of NH4+. Thus, cautions should be taken to use wet deposition fluxes of NH4+ to extrapolate emissions of NH3.”

Response to Referee #2

We greatly appreciate the reviewer for proving the constructive comments, which have helped us improve the paper quality. We have revised the paper accordingly as detailed in our point-by-point responses below.

RC- Reviewer's Comments; AR – Authors' Responses

RC: General comments
This paper asserts that statistical trends analysis of the linkage between emissions changes and measured wet deposition is obscured by multiple factors including climate anomalies. The target analytes of wet deposition measurements (SO4-2, NO3-, NH4+) undergo complex atmospheric transformations from their emitted precursors and washout or entrainment in precipitation are dependent on the climate. The climate anomalies are not specifically identified, but evidence exists that they influence relationships between wet deposition and emission trends and are occurring more frequently. Thus, a need exists for a statistical analysis technique to reduce the impact of the climate anomalies and increase the time interval of comparisons as emission changes, especially those due to regulations, are phased in incrementally and are not linear. The authors propose a statistical method based on the development of an input dataset termed "climatology" (an average of 12 ranked 24-month wet deposition flux measurements) and trends analyses to produce regression slopes for each of the 12 individual 2-year periods considered and the averaged "climatology" dataset. The regressions used are based off the Mann-Kendall (M-K) method, linear regression (LR), and piecewise linear regression (PLR). The authors propose that the time-series of the derived regression slopes better reflects the trends in reported emissions of precursor gases, than the time-series of the annual wet deposition flux data itself.

The method is novel and them-value time-series relates better to emissions time-series than wet deposition flux (Fwet) time-series at Site 1 for SO4-2 and to a lesser degree for NO3. The m-value time-series appears to reflect inflection points in the emissions time-series that are not as easily observable in the wet deposition flux time-series. However, the method does not improve the relationship of m-values of NH4+ to NH3 emissions at site1. Furthermore, the method does not seem to show improved m-value correlation with emissions over the annual Fwet data any other location (at Sites 2, 3, and 4) or species. There is no direct comparison metrics to gauge the improvement of the m-values over the annual Fwet other than visual interpretation of plots. The m value time-series will obviously be visually "cleaner" since a) the m-value has outliers removed and b) the m-value represents 24 data points and the annual Fwet represents 12 data points.

AR: We have added the comparison at Sites 3 and 4 in the revised Supporting Information, which reads: "Using the m-values over the annual F_{wet} of SO_4^{2-} improves the r value from 0.73 to 0.87 at Site 3 and from 0.91 to 0.93 at Site 4. Using the m-values over annual F_{wet} of NO_3^- improves the r value from 0.81 to 0.87 at Site 3 and from 0.78 to 0.89 at Site 4." No significant correlation of m-value and F_{wet} with the corresponding emissions existed at Site 2 and the comparison is thereby not presented.

RC: The largest problem with the study is that that technique is not demonstrated to be robust. The method hinges on the stability of the m-values, but they are very susceptible to the large-value outliers (e.g. example described in text for '90-'91, causes a 0.2 change in m-value; shown in Fig 1). Moreover, for Site 1, the authors acknowledge that 8 of 12 (67%) of datasets needed to have an outlier removed, which from my interpretation greatly compromises the robustness of this technique and its applicability to different datasets.

AR: We originally only explained the method from a statistical analysis consideration, which may hinder the real advantage of the method. In the revised paper, we have made substantial revisions in several sections to clarify this point. For example, we have changed this sentence "The actual observed maximum value of 532 mg m^{-2} $month^{-1}$ was much larger than the upper range of the predicted value and was thus believed to be caused by monthly scale climate anomalies" to this: "The actual observed maximum value of 532 mg m^{-2} $month^{-1}$ was much larger than the upper range of the predicted value and was thus believed to be caused by monthly scale climate anomalies, i.e., the occurrence of extreme amount of precipitation. The maximum monthly deposition flux in 1990-1991 occurred in September 1990 when the monthly precipitation depth reached 294 mm, which was much higher than those in the same month of other years, e.g., 169, 68, 95 and 127 mm in 1988, 1989, 1991 and 1992, respectively. The maximum daily precipitation depth in September was also higher in 1990 (91 mm) than in other years (43.6, 12.2, 13.6 and 26.8 mm in 1988, 1989, 1991 and 1992, respectively). However, the monthly geometric average concentration of SO_4^{2-} in precipitation (1.8 mg L^{-1}) in September 1990 was close to the mean value (1.7±0.3 mg L^{-1}) in September 1988-1992 and was even smaller than that (2.9 mg L^{-1}) in August 1990." There are several other similar changes which can be found from the track change version of the paper.

In our approach, only the maximum value in 24 months severely deviated from the general trend was removed to calculate m-values. Thus, we have 95%-100%, i.e., 23/24 -24/24 monthly values, data to calculate m-value with high R^2 values (e.g., 0.92-0.98 at Site 1 for SO_4^{2-}). The calculated m-value would fully reflect the contribution from emissions of air pollutants since only 5% data are sometimes removed. When the data size is even larger, e.g., the group of Sites 1, 3 and 4, 100% data are used to calculate m-value. Using m-values calculated from Approach C is applicable for different datasets.

Compared with the calculated m-values from Approach B using 12 month data, the use of 24 month data in each array in Approach C largely increased R^2 value and decreased uncertainties of the calculated m-values. However, a linear regression analysis result, assuming zero interception and using the m-values calculated from Approach B against the annual F_{wet} data, showed the value of R^2 as high as 0.99 (Fig. S4 added in the revision). This means that the trend analysis results would be the same regardless of using annual F_{wet} data or the m-values as input if Approach B is used. The extracted trends would include larger perturbations from climate anomalies in Approach B. Thus, it can be concluded that the trend analysis results derived from m-values calculated from Approach C would be more robust than those derived from m-values calculated from Approach B. It is also safe to say that the trend results derived from m-values calculated from Approach C are more robust than those derived from annual F_{wet} data.

From Comment 4 listed below, we realize that the original text may mislead the reviewer, i.e., 8/12 datasets needed to have an outlier removed because of the maximum F_{wet} being positively deviated from the general trend. This is of course impossible and may make the reviewer doubt the robustness of Approach C. We have therefore clarified this in the revised paper, which reads: "Three out of the 12 data sets showed the maximum F_{wet} being positively deviated from the general trend, five negatively deviated from the general trend, and four consistent with the general trend."

RC: There appears to be a m-value error analysis conducted with three different approaches in the Supplemental section (Approaches A through C), but no summary or assessment of m-value stability or uncertainty is given. This needs to be developed much more. Sources of uncertainty in the m-values are not discussed.

AR: We have added such analysis, and details can be found in section 1 of the revised Supporting Information.

RC: A reader will likely ask why are large Fwet values so frequently (the 8 of 12 datasets mentioned above) in disagreement with the rest of the monthly values? This question is not answered. What causes the large flux (other than climate anomaly?) Is this a high or low rain event month? Is this rain after a stagnation event?

AR: The large F_{wet} value was mainly caused by extreme precipitation depth in monthly scale. We have clarified the frequency of the large values (see the response to the comment above). The distribution result is quite normal. Although the maximum monthly value of F_{wet} positively deviated from the general trend was clearly attributed to extreme precipitation, the cause was yet to be identified for the maximum monthly value of F_{wet} negatively deviated from the general trend. This latter case has also been stated in the revised paper.

RC: There is too much assigning uncertainty to vague "Climateanomalies" and "interannual climate variability". These concepts are neither adequately defined nor is any impact that they might have on monthly wet deposition values identified. The section on "interannual climate variability" could be strengthened with local ambient concentrations which are possibly available.

AR: We have revised discussions where appropriate throughout the paper. For example, the secondary paragraph of Section 3.2.2 has been revised substantially, which now reads: "In addition to decadal anomalies of wind fields, the interannual climate variability such as precipitation depth, annual anomalies of wind fields in 2007, etc., (Fig. 3b) also affected the trends in m-values and annual F_{wet} of NO_3^-. The annual precipitation depth largely varied from 601 mm to 1054 mm in the two decades. The perturbations from interannual variability of precipitation depth cannot be completely removed by the new approach. For example, the calculated m-values in 1992-1993 and 1994-1995 were evidently lower than the m-values in 1990-2001. However, the annual geometric average concentrations of NO_3^- in 1992-1995 varied around 0.77±0.11 mg L^{-1} and were even larger than the values of 0.66±0.08 mg L^{-1} in 1990-2001 (excluding 1992-1995). The lower m-values were mainly attributed to the lower precipitation depth in 1992-1994 (Fig 3b) rather than lower emissions of NOx. Interannual climate variability including precipitation depth and annul anomalies of wind fields may complicate the relationship between the F_{wet} of NO_3^- and the emissions of NO_x in British Columbia." Also in the Conclusion section, the revised version on this point reads: "At this location, the decreasing trends in F_{wet} of SO_4^{2-} and NO_3^- were caused by the decadal anomalies of wind fields, as well as being affected by interannual climate variability including precipitation depth and annul anomalies of wind fields, etc., which overwhelmed the impact of the emission changes of the gaseous precursors in this province. This is the first study that has identified that decadal anomalies of wind fields can dominate trends in F_{wet} of SO_4^{2-} and NO_3^-."

RC: At the very least, some more detail and explanation describing the meaning of Fig 4 and how it was derived and its effect on sulfur could be provided.

AR: In Fig. 4, the re-analysis data are used. The re-analysis data have been constrained by observational data and the reference has been cited. We have also added more detailed discussion, which reads: "The wind vector and wind speed from the North American Regional Reanalysis (NARR), with a spatial resolution of 32 km by 32 km (Mesinger et al., 2006), were thereby analyzed to study the decadal changes in wind fields and associated potential impacts on the long-range transport of air pollutants over the western coastal Canada and U.S. The average wind fields including mean wind vector and speed (shading in Fig 4a-d) in 1990-2011 at 925 hPa showed air masses over the western coastal Canada and U.S. were primarily originated from the Pacific Ocean (Fig. 4a). However, the anomalies of wind fields in 1990-2001 relative to 1990-2009 clearly showed a counterclockwise pattern in the corresponding coastal area, including Site 2., while a clockwise pattern existed in 2002-2011 relative to 1990-2009 (Fig. 4b, c). The anomalies shown in Fig. 4c indicated the northwesterly wind being enhanced in 2002-2011 over the western coastal Canada and U.S., possibly reducing air pollutants being transported from the continent to Site 2. In contrast, the anomalies in Fig. 4b indicated that the northwesterly wind was reduced in 1990-2001. Consequently, more air pollutants might have been transported from the continent to Site 2, resulting in a distinct demarcation in 2002. This hypothesis was also supported by a large rebound of the m-value in 2006-2007, due to the increase in F_{wet} of SO_4^{2-} in 2007. The climate anomalies of wind fields in 2007 relative to 1990-2009 showed a counterclockwise pattern in the north, while the clockwise pattern was pushed to the south (Fig. 4d). With the northwesterly wind being reduced, a greater contribution of air pollutants from the coast of Canada and U.S. to Site 2 might have led to the large increase in F_{wet} of SO_4^{2-} during a few month-long periods in 2007."

RC: The reader will also pause as to why so much network-validated data is omitted. Most of the rationale appears to be statistically based (i.e. 'because it doesn't fit the trend'; see the ±3σ criteria presented online 173) which is insufficient without some scientific support (see the discussion on uncertainty of m-values above). More worrisome is the omission of the m-values (i.e. omission of 24 network-validated datapoints) in 1999 on the basis that they don't fit the expected emission trend and are "probably caused by a large perturbation in climate anomalies", but no real evidence is presented.

AR: The evidence has been added in the revision in a few places, (1) "The abnormally increased F_{wet} of SO_4^{2-} in 1999 was mainly because of the increased precipitation depth (1312 mm), which was the largest during 1998-2011 (the annual average precipitation depth excluding 1999 was 1067±86 mm). However, the geometric average concentration of SO_4^{2-} in precipitation in 1999 (1.0 mg L^{-1}) was close to those in the other years, e.g., 0.9 mg L^{-1} in 1997 and 1998 and 1.0 mg L^{-1} in 2000." (2) "The sharp increase in F_{wet} of NO_3^- occurred mainly in 1999, which was probably due to largely increased annual precipitation depth as mentioned in Section 2.4. The analysis was also supported by the geometric average concentration of NO_3^- in precipitation, which was 1.1 mg L^{-1} in 1999, 5% lower than that in 1988 and only 5-10% higher than those in 1990-1991, 1993 and 2002."

RC: Specific comments (Individual Science Q) On page 8, the authors state (line 172) which in turn increase the relative contribution of the air pollutants' emissions to the calculated value. I assume that the authors are presuming that a monthly change in emissions would not impact the Fwet as much as a large monthly change in precipitation depth or concentration in precipitations. This point should be stressed more in the discussion.

AR: Yes, monthly change in emissions should not impact the F_{wet} as much as large monthly changes in precipitation depth or concentration in precipitations. In the revision, we have added this statement: "Note that monthly changes in emissions may not impact the F_{wet} as much as does a large monthly change in precipitation depth or concentration in precipitation. For example, the monthly average concentrations of SO_2 were almost the same in May, September and October of 1990 (~0.7 µg m^{-3}) while the monthly F_{wet} of SO_4^{2-} varied significantly, e.g., 113, 179 and 532 mg m^{-2} $month^{-1}$, respectively in the same months. The monthly average concentration of SO_2 in February

(4.8 μg m^{-3}) was the largest among the twelve months of 1990, but the corresponding monthly F_{wet} of SO_4^{2-} was the smallest (34 mg m^{-2} $month^{-1}$).”

As show in the revised Fig S2c, the geometric average concentrations of SO_4^{2-} at Site 1 in six months of 1996, including February, April, May, June, September and November, narrowly varied around 0.63±0.05 mg L^{-1} (Fig. S2c). The six months were almost evenly distributed in 12 months of 1996. This also suggests that monthly change in emissions would not impact the monthly geometric average concentrations of SO_4^{2-}. However, the geometric averages largely oscillated from 0.27 mg L^{-1} to 1.77 mg L^{-1} in the other six months of 1996 at the site. Based on the narrow variation in the former six months, it can be inferred that the large oscillation in the latter six months were less likely due to monthly changes in emissions. For example, the value of 1.77 mg L^{-1} in March of 1996 was the largest and approximately two and half times of 0.68 mg L^{-1} in February of 1996. The monthly average concentrations of SO_2 in ambient air were close to each other, i.e., 2.6 μg m^{-3} in March and 2.4 μg m^{-3} in February of 1996. Thus, the large oscillation in the latter six months were very likely due to the effects of climate anomalies imposing on atmospheric processes. However, we cannot quantify what types of climate anomalies caused this. We have added clarification in the revised manuscript and Supporting Information on this point.

RC: The text does not adequately describe Fig 2 (lines 208 to 213). What is shown and why? I assume the objective of this plot is 1) to show the improvement of the fitted trend of the top row (m-value time-series) to the middle row (Fwet time-series). A metric (correlations with emissions?) is needed to demonstrate the advantage of the m-value over the annual Fwet. The secondary objective of Fig 2 is to show the incremental trends or “phases”. The plots do not currently accomplish this as Phase 1, 2, or 3 are not shown. Also, the PLR segments for Phase 1, 2, and 3 identified in the text are not described. The overall fits shown (e.g. R2 = 0.81 in 2a and R2 = 0.62 in 2b) are not significant in the analysis, but are shown on the plots. The PLR segments should be shown for the emissions as well (or at least compared with the 2a PLR segments). Considering both of these objectives, the strength in this technique appears to be that the PLR segments for the top-row more closely resemble the PLR segments for the bottom row and that the PLR segments for the middle row do not reflect this. Please reorganize the discussion and analysis to support this. For example, the lines from 283-293 describing the improvement of the m-values over the annual Fwet data should be elaborated on and moved up in the discussion.

AR: We have made a substantial revision by reorganizing the discussion and analysis in Section 3.1. Three phases have been labeled in Fig 2. The objectives of Fig. 2 have also been added in the context. We agree that the added objectives makes the part more readable.

The overall fits (e.g. $R^2 = 0.81$ in 2a and $R^2 = 0.62$ in 2b with $P<0.01$) shown here are significant, i.e., “SO_4^{2-} and NO_3^- showed decreasing trends from a LR analysis, with R^2

values of 0.81 and 0.71, respectively, and P values <0.01 (Fig. 2a and 2d)."

RC: I assume the phase year classification sproposed by the authors(Phase 1,2 nd 3) are derived from the emissions data patterns, but the logic behind the years of the phases is not specifically discussed (i.e. why 1988 to 1993 and not 1995?) Do the phases align with emissions regulation implementation? The PLR segments are often derived from a set of points as low as N=5 (e.g. Phase 1 from 1988 to 1993). Comparisons should state that this is a low N for comparison.

AR: The three phases of SO_4^{2-} and two phases of NO_3^- were firstly visibly identified by simple screening. We then confirmed the phase results by t-test statistically. This is the simplest way to do PRL analysis if the data size is not too large. The phases were supported by emissions of SO_2 and NOx to some extent, but a few inconsistences still existed, e.g., the almost constant m-value of NO_3^- in Phase 1 against the bell-shape distribution of NOx emission in the same Phase.

We don't think that emission data alone can allow classifying these phases of SO_4^{2-} and NO_3^-. It is well known that real emissions of air pollutants may not always align with emission regulation schedules. Emissions regulation implementation always needs to be examined by using long-term field measurements. However, emission data can facilitate the analysis of phase changes in m-values, since inflection points of different phases of m-values and emissions should be close to each other.

The m-values in 1988-1993 oscillated approximately 1.38±0.08 while the m-value in 1994-1995 largely decreased down to 0.91, the latter period was clearly related to Phase 2 (1994 to 2005) with m-values around 1.02±0.08. The statistical results confirmed the classification.

The sentence has been revised as: "The m-values of SO_4^{2-} and NO_3^- also allowed for the visible and statistical identification of trends in different phases in support by annual variations in emissions of SO_2 and NO_x (Fig. 2c and 2f) to some extent."

In the revision, we have also added: "The three phases generally aligned with the three-phase regulated SO_2 emissions in Ontario. It should be stated that Phase 1 and Phase 3 each covered only six years (N=6), respectively. Cautions should be taken to explain the trend result in each phase in relation to precursors' emissions."

RC: On lines 348 -354; the m-value time-series for Site 2 NO3- (Fig 3d) is interpreted to support the decadal shift hypothesis. However, strictly observing the data, without the hypothesis in mind, it is clear that the fourm-values from 1990 and '96-'00 are elevated, while the values from '92 and '94 are similar to values observed after the decadal shift has taken place. This is acknowledged in the text, but no support given other than it is attributable to climate anomalies.

AR: In the revision, we have added this statement: “For example, the calculated m-values in 1992-1993 and 1994-1995 were evidently lower than the m-values in 1990-2001. However, the annual geometric average concentrations of NO_3^- in 1992-1995 varied around 0.77±0.11 mg L^{-1} and were even larger than the values of 0.66±0.08 mg L^{-1} in 1990-2001 (excluding 1992-1995). The lower m-values were mainly attributed to the lower precipitation depth in 1992-1994 (Fig 3b) rather than lower emissions of NOx.”

*RC: TECHNICAL COMMENTS 1. Figures need descriptive captions and local explanations. 2. Labels on Fig 2 (title incorrect) 3. line 223: “in contrast”. Suggest removal, not really in contrast. 4. line 237: Vlaue should read value 5. For Figure 1, distinguish the outlier point removed for each plot (as done in Fig 2) also specify which fit (R2 and p-value applies to the modified fit (I believe it is *, but it is not labeled).*

AR: Figure captions and labels have all been revised as suggested.

Decoding long-term trends in the wet deposition of sulfate, nitrate and ammonium after reducing the perturbation from climate anomalies

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Abstract. Long-term trends of wet deposition of inorganic ions are affected by multiple factors, among which emission changes and climate conditions are dominant ones. To assess the effectiveness of emission reductions on the wet deposition of pollutants of interest, contributions from these factors to the long-term trends of wet deposition must be isolated. For this purpose, a two-step approach for preprocessing wet deposition data is presented herein. This new approach aims to reduce the impact of climate anomalies on the trend analysis so that the impact of emission reductions on the wet deposition can be revealed. This approach is applied to a two-decade wet deposition dataset of sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) at rural Canadian sites. Analysis results show that the approach allows for ~~robustly~~ statistically identifying inflection points on decreasing trends in the wet deposition fluxes of SO_4^{2-} and NO_3^- in northern Ontario and Québec. The inflection points match well with the three-phase mitigation of SO_2 emissions and two-phase mitigation of NOx emissions in Ontario. Improved correlations between the wet deposition of ions and their precursors' emissions were obtained after reducing the impact from climate anomalies. Furthermore, decadal climate anomalies were identified as dominating the decreasing trends in the wet deposition fluxes of SO_4^{2-} and NO_3^- at a western coastal site. Long-term variations in NH_4^+ wet deposition showed no clear trends due to the compensating effects between NH_3 emissions, climate anomalies, and chemistry associated with the emission changes of sulfur and nitrogen.

1. Introduction

To assess the long-term impacts of acidifying pollutants on the environment, the wet deposition of sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+), among other inorganic ions, has been measured for several decades through monitoring networks such as the European Monitoring and Evaluation Programme (EMEP) (Fowler et al., 2005, 2007; Rogora et al., 2004, 2016), the National Atmospheric Deposition Program/National Trends Network in the U.S. (Baumgardner et al., 2002; Lehmann et al., 2007; Sickles & Shadwick, 2015), and the Canadian Air and Precipitation Monitoring Network (CAPMoN) (Vet et al., 2014; Zbieranowski and Aherne, 2011). The high-quality data collected from these networks have been widely used to quantify the atmospheric deposition of acidifying pollutants (Lajtha & Jones, 2013; Lynch et al., 2000; Pihl Karlsson et al., 2011; Strock et al., 2014; Vet et al., 2014). The data have also been utilized to identify trends in the atmospheric deposition of reactive nitrogen (Fagerli & Aas, 2008; Fowler et al., 2007; Lehmann et al., 2007; Zbieranowski and Aherne, 2011) and to examine the impacts of acid rain and the perturbation of the natural nitrogen cycle on sensitive ecosystems (Wright et al., 2018). The long-term data can also be used for assessing the effectiveness of environmental policies (Butler et al., 2005; Li et al., 2016; Lloret & Valiela, 2016).

The wet deposition of SO_4^{2-}, NO_3^- and NH_4^+ is affected by not only their gaseous precursors' emissions (Butler et al., 2005; Fowler et al., 2007; Li et al., 2016) but also complex atmospheric processes such as long-range transport, chemical transformation, and dry and wet removal (Cheng & Zhang, 2017; Yao & Zhang, 2012; Zhang et al., 2012). These processes can be largely affected by ~~C~~climate anomalies. ~~largely affect the processes, e.g.,~~For example, climate anomalies can sometimes bring extreme precipitation amounts in~~throughout~~ a particular month~~,~~ and subsequently lead to extremely high wet deposition fluxes of ions through enhanced wet removal~~rainout and washout~~ of air pollutants.~~(Cheng & Zhang, 2017; Yao & Zhang, 2012; Zhang et al., 2012). Those atmospheric processes sometimes lead to extremely high wet deposition~~

~~fluxes of ions during a precipitation event or even throughout a particular month~~. Furthermore, climate anomalies can alter the relative contributions of local sources versus long-range transport to the total wet deposition amounts at reception sites, thereby complicating the relationships between wet deposition and the emission of air pollutants of interest (Lloret & Valiela, 2016; Monteith et al., 2016; Pleijel et al., 2016; Wetherbee & Mast, 2016). The emissions of SO_2 and NOx have been decreasing substantially in Europe and North America (Butler et al., 2005; Li et al., 2016; Pihl Karlsson et al., 2011); coincidentally, climate anomalies have also occurred more frequently in the recent decades (Burakowski et al., 2008; Lloret & Valiela, 2016; Wijngaard et al., 2003), thereby leading to more complicated linkages between wet deposition and emission trends on decadal scales.

Many trend analysis studies in the literature simply examined annual or seasonal values as the data inputs for two popular trend analysis tools, i.e., the Mann-Kendall (M-K) and linear regression (LR) methods (Marchetto et al., 2013; Waldner et al., 2014 and references therein). These studies focused on the detection of statistically significant trends; for example, Waldner et al. (2014) conducted a comprehensive analysis on the applicability of the techniques to different choices of length and temporal resolutions of a data series. Regarding the resolved trend results, these approaches are not well suited to separating the impact of air pollutants' mitigation from the perturbation by climate anomalies. Large uncertainties thus existed in the studies interpreting the major driving forces determining the extracted trends in the wet deposition of SO_4^{2-}, NO_3^- and NH_4^+. Regarding that air pollutant's emission mitigation targets often vary in different phases of the entire study period, inflection points may exist in the trends in the wet deposition of ions. The inflection points were rarely studied, despite their importance for assessing the effectiveness of environmental policies. An alternative would be to use high time resolution data in the Ensemble Empirical Mode Decomposition (EEMD) method (Wu & Huang, 2009); however, this method still suffers from the end effect in certain scenarios, whereby the extracted trends cannot be explained (Yao & Zhang, 2016).

A new approach is presented herein that aims to reduce the perturbations from climate anomalies on data inputs so that robust trends can be elucidated for evaluating the effectiveness of emission control policies. In this approach, raw data are preprocessed to generate a new variable, which is then applied to M-K and LR methods. A piecewise linear regression (PLR) is also used to extract trends for cases in presence of inflection points. The extracted trends in the wet deposition data on a decadal scale are then properly linked to major driving forces such as emission reductions and climate anomalies. This new approach is first applied to the wet deposition data of SO_4^{2-}, NO_3^- and NH_4^+ in Canada, as an example to demonstrate its capability and advantages over the traditional approaches. The extracted trends in the wet deposition of ions are further studied through correlation analysis with known emission trends of their respective gaseous precursors (SO_2, NOx and NH_3) in Canada and the U.S. Major driving forces for the trends of ion wet deposition and how the wet deposition ions responded to their precursors' emissions in Canada are then revealed.

2. Methodology

2.1 Data sources

Wet deposition flux (F_{wet}) data were obtained from CAPMoN (https://www.canada.ca/en/environment-climate-change/services/air-pollution/monitoring-networks-data/canadian-air-precipitation.html). Data from four sites have been collected for over twenty years and were chosen herein to illustrate the novel trend analysis method (Table S1). Site 1 is an inland forest site at Chapais in Québec. Site 2 is situated in a coastal forest area at Saturna in British Columbia. Sites 3 and 4 are two inland forest sites at the Chalk River and at Algoma, respectively, in northern Ontario. Details on data sampling, chemical analysis and quality control can be found in previous studies (Cheng & Zhang, 2017; Vet & Ro, 2008; Vet et al., 2014). The emissions data of gaseous precursors were downloaded from the Air Pollutant Emission Inventory (APEI, https://pollution-waste.canada.ca/air-emission-inventory/) in Canada and from the USEPA National Emissions Inventory (NEI, https://www.epa.gov/air-emissions-inventories/air-emissions-sources) in the U.S. These data were demarcated at a provincial level in Canada and at a state level in the U.S. Data for the years of 1990 to 2011, which correspond to the period of selected F_{wet} data, were used in this study.

2.2 Statistical methods

The M-K method is a popular nonparametric statistical procedure that can yield qualitative trend results, such as "an increasing/decreasing trend with a P value of <0.05," "a probable increasing/decreasing trend with a P value of 0.05-0.1," "a stable trend with a P value of >0.1, as well as a ratio of <1.0 between the standard deviation and the mean of the dataset," and "a no trend for P>0.1 with all other conditions" (Kampata et al., 2008; Marchetto et al., 2013). The LR method has also been widely used to extract trends (Marchetto et al., 2013; Waldner et al., 2014). Zbieranowski and Aherne (2011) used LR to extract trends by separating different phases because of the presence of inflection points in the entire study period, and the approach is same as PLR

(Vieth, 1989). In this study, the three methods were employed to compute the trends of ion wet deposition using software downloaded from https://www.gsi-net.com/en/software/free-software/gsi-mann-kendall-toolkit.html and Excel 2016, first using the annual F_{wet} directly as input data, then using a modified input data set, as described in Section 2.3.

The annual F_{wet} is widely used for trend analysis and the trend results are thereby used to compare with those derived from the approach proposed in this study. Note that R^2 is conventionally used in LR and PRL. However, r instead of R^2 is used in correlation analysis. Thus, R^2 and r are ~~therefore~~ used for the two types of analyses in this study, respectively~~below.~~ Moreover, several methods can be used to do PRL in classical statistics literature. The simplest one is to manually conduct piecewise regression~~,~~ where inflection points are visible to be recognized, and this approach is used in this study. ~~A few~~More complex algorithms are also available in ~~the~~ literature to conduct PRL for datasets with hundreds of ~~data~~ points (Ryan and Porth, 2007 and references ~~cited~~ therein). The complex algorithms ~~are, of course, unnecessarily~~have seldom been used to identify trends in annul wet deposition of ions because of the short~~er~~ data record ~~history~~.

2.3 Filtering climate anomalies

The modified input data set was produced in two steps. The first step was an effort to reduce the perturbation from the monthly climate anomalies to the input data. This was done by creating a new variable that was defined as the slopes of the regression equations of a series of study years against a climatology (base) year using monthly F_{wet} data. Note that the monthly F_{wet} data were aggregated from daily raw data before the regression analysis. To ensure the presence of enough data points in each regression equation, the data corresponding to two-year periods (or 24 monthly F_{wet} values) were grouped together, as detailed below. At a selected site and for a given chemical component, monthly F_{wet} data were generated for the first two years and were grouped together and rearranged from the smallest to the largest values to form an array of data with 24 data points, i.e., A(i) with i=1 to 24. Repeating the above procedure for the subsequent years using a two-year interval to eventually obtain a series of data arrays, A(i) now becomes A(i, j) with i=1 to 24 and j=1 to N, where N is the total number of data arrays. The climatology data array (CA(i)) was then defined as the average of all of the arrays as follows:

$$CA(i) = \frac{1}{N}\sum_{j=1}^{N} \quad A(i,j),\ i = 1\ to\ 24.$$

LR with zero interception was applied for each individual data array against the climatology data array. In cases where the maximum monthly deposition flux deviated greatly from the general regression curve, the slopes (m-values) were calculated after excluding the maximum monthly deposition flux, which is an approach that reduced the perturbation to the m-values from the monthly scale climate anomalies. The second step was to screen out the outliers in m-values, which reduced the perturbation to the m-values from the annual-scale climate anomalies.

2.4 Example case for data filtering

An analysis of Site 1 is used to illustrate the new approach and demonstrate its advantages against the existing common approaches used in the literature. Twelve ~~four~~two-year periods of data (1988-1989, 1990-1991, etc.) are available from this site. The regression of each data set against the climatology data set was first performed using all of the monthly values to obtain an m-value (the slope) (Fig. 1a-d). For eight out of the 12 data sets, the m-values were recalculated after excluding the maximum monthly value of F_{wet}, which appeared to be an apparent outlier of the linear regression. Three ~~(five)~~ out of the 12 data sets showed the maximum F_{wet} being positively ~~(negatively)~~ deviated from the general trend, five negatively deviated from the general trend, ~~while~~and four ~~out of the 12 data sets showed the maximum F_{wet}~~ consistent with the general trend. The R^2 values~~, which are conventionally used in LR,~~ were then significantly increased for these eight sets, e.g., from the original values of 0.79-0.94 to the improved values of 0.92-0.98. To demonstrate that the excluded maximum value was an outlier, the case of the 1990-1991 data set was taken as an example. The new regression equation ($y=1.47x$, $R^2=0.98$, Fig. 1a) predicted a maximum value in the range of 330-368 mg m^{-2} month^{-1} using three times the standard deviation (±3 SD, 0.08) at a 99% confidence level. The actual observed maximum value of 532 mg m^{-2} month^{-1} was much larger than the upper range of the predicted value and was thus believed to be caused by monthly scale climate anomalies, i.e., the occurrence of extreme amount of precipitation. The maximum monthly ~~maximum~~ deposition flux in 1990-1991 occurred in September ~~of~~ 1990 when the monthly precipitation depth reached~~of~~ 294 mm, which was much ~~larger~~higher than those in the same month of other years, e.g., 169~~ mm~~, 68~~ mm~~, 95~~ mm~~ and 127 mm ~~in the same month~~ in 1988, 1989, 1991 and 1992, respectively. ~~The same can be said for t~~The maximum daily precipitation depth in September was also higher~~, i.e., 91 mm~~ in 1990 (91 mm) than in other years~~against~~ (43.6~~ mm in 1988~~, 12.2~~ mm in 1989~~, 13.6~~ mm in 1991~~ and 26.8 mm in 1988, 1989, 1991 and 1992, respectively). However, the monthly geometric average concentration of SO_4^{2-} in precipitation ~~of~~ (1.8 mg L^{-1}-) in September ~~of~~ 1990 was close to the mean value (1.7±0.3 mg L^{-1}-) in September ~~of~~ 1988-1992~~.~~ and was even smaller than that ~~of~~

(2.9 mg L^{-1}) in August ~~of~~ 1990. The maximum value was treated as an outlier and excluded for analysis.

Using the similar procedure, all outliers in this study were identified. The exclusion of the observed maximum value greatly reduced the perturbation of the short-term climate anomalies to the calculated m-value in this two-year period, i.e., the m-value decreased from 1.67 to 1.47, which in turn increased the relative contribution of the air pollutants' emissions to the calculated m-value. Note that monthly changes in emissions may not impact the F$_{wet}$ as much as does a large monthly change in precipitation depth or concentration in precipitation~~s~~. For example, the monthly average concentrations of SO$_2$ were almost the same in May, September and October of 1990 (~0.7 µg m^{-3} ~~not shown~~) while the monthly F$_{wet}$ of SO$_4^{2-}$ ~~largely~~ varied significantly, e.g., 113 ~~mg m^{-2} month^{-1} in May~~, 179 ~~mg m^{-2} month^{-1}~~ and 532 mg m^{-2} month^{-1} ~~in September~~, respectively in the same months. The monthly average concentration of SO$_2$ in February (4.8 µg m^{-3} ~~not shown~~) was the largest among~~in~~ the twelve months of 1990, but the corresponding monthly F$_{wet}$ of SO$_4^{2-}$ was the smallest (34 mg m^{-2} month^{-1}).

Even~~ly~~ through comprehensive analysis, any single~~signal~~ climate factor alone, including monthly precipitation depth, was apparently unable to explain the negative deviation of the maximum monthly value of F$_{wet}$ ~~negatively deviated~~ from the general trend.~~, leaving that t~~The causes of such a~~the~~ negative deviation ~~wa~~is yet to be identified. In summary, the~~is~~ new approach proposed above ~~meets the objective of identifying outlier data points~~ by applying the criteria of being outside the boundaries of ±3 times the standard deviation of the general trend meets the objective of identifying outlier data points.

The revised m-values were further scrutinized by eliminating the outliers caused by the annual-scale climate anomalies. For example, the m-value of 1.31 in 1998-1999 greatly deviated from other m-values, narrowly oscillating approximately 0.96±0.07 (average ± 1 SD) during the period of 1994-2005, even with the ±3 SD being considered (Fig. 1a-d). Using the value of 0.96 as the reference, climate anomalies likely increased the F_{wet} of SO_4^{2-} by 37% in 1998-1999. The m-values were then calculated by shifting one year in time to 1997-1998 (1.07) and to 1999-2000 (1.24). The F_{wet} in 1998 was less affected by climate anomalies than that in 1999. Thus, the m-value in 1997-1998 was within 0.96±0.21 (average ± 3 SD) and used to replace the m-value in 1998-1999 for the trend analysis. Similar to the first step discussed above, this approach meets the objective of identifying outlier m-values by applying the criteria of being outside the range of ±3 SD plus the average m-value during a decade or a longer period. The abnormally increased F_{wet} of SO_4^{2-} in 1999 was mainly because of the increased precipitation depth (1312 mm), which was the largest ~~in~~during 1998-2011 (the annual average precipitation depth excluding 1999 ~~equal to~~was 1067±86 mm). However, the geometric average concentration of SO_4^{2-} ~~(1.0 mg L^{-1})~~ in precipitation in 1999 (1.0 mg L^{-1}) was close to those in the other years, e.g., 0.9 mg L^{-1} in 1997 and 1998~~,~~ and 1.0 mg L^{-1} in 2000.

2.5 Justification for the new approach

More justification of the new approach can be found in the Supporting Information, including Figs. S1-~~3~~6, wherein the statistical comparison between this and other approaches was presented. Theoretically, the extracted trend using the data preprocessed with the new approach is determined by the local emissions of air pollutants, the regional transport of air pollutants, and ~~a small portion of~~ climate anomalies that are unable to be removed by the new approach. It is assumed that the extracted trend is less affected by microphysical/chemical processes, since two-year data were used together to calculate the m-value.

In theory, if the data from different sites in the same region are grouped together for trend analysis, the results may be better linked to the trends of the regional emissions of related air pollutants. In the following sections, trend analysis results from individual sites as well as those from grouped sites are discussed. Sites 1, 3 and 4 showed similar trends in the wet deposition of SO_4^{2-} and NO_3^-, and these three sites were grouped together.

3. Results and discussion

3.1 Trends at Site 1 after reducing perturbations from climate anomalies

Trends in the m-values shown in Fig. 2 represent the trends after removing the perturbations from climate anomalies at Site 1 in northern Québec from 1988 to 2011. SO_4^{2-} and NO_3^- showed decreasing trends from a LR analysis, with R^2 values of 0.81 and 0.71, respectively, and P values <0.01 (Fig. 2a and 2d). The decreasing trends were also confirmed by the M-K method analysis. NH_4^+ exhibited a stable trend from M-K analysis (Fig. 2g), as well as no significant trend with P value >0.05 from LR analysis. The annual F_{wet} of these ions ~~we~~are also shown in Figs. 2b, 2e and 2f and annual emissions of SO_2, NO_x and NH_3 ~~were shown~~ in Figs. 2c, 2f and 2i,~~.~~ respectively. These data were used to compare and facilitate analysis in terms of identifying~~ication of~~ inflection points~~pitons~~ and the advantage of using the m-value over the annual F_{wet}, as presented below.

The m-values of SO_4^{2-} and NO_3^- also allowed for ~~the visible and~~ statistical identification of trends in different phases ~~in~~ supported by annual variations in emissions of SO_2 and NO_x (Figs. 2c and 2f) to some extent. The inflection point for each phase is critical to a) link the annual F_{wet} of ions and the emissions of the corresponding precursors, and b) assess the effectiveness of environmental policies. For example, the trends in the m-values of SO_4^{2-} can be clearly classified into three phases (Fig. 2a). Therefore~~Overall~~, PLR should be applied separately for the different phases in the presence of the inflection points, rather than LR for the entire period, and the result is presented as:

$$\begin{cases} m - value = 1.38, 1988 \leq x < 1994 \\ m - value = 1.02, 1994 \leq x \leq 20045 \\ m - value = -0.185 * \left(\frac{x}{2} - 1001\right) + 1.15, 20045 < x \leq 2010 \end{cases}$$

where x represents the calendar year from 1988 to 2010.

The m-values oscillated approximately 1.38±0.08 during Phase 1 (1988 to 1993) and approximately 1.02±0.08 during Phase 2 (1994 to 2005), with a significant difference between the two phases under the t-test (P value <0.01), thereby implying an abrupt decrease of approximately 30% at the inflection point between the two phases. ~~In contrast, t~~The m-values linearly decreased by approximately 20% every two years, starting from the end of Phase 2 to Phase 3 (2006-2011). Again, a significant difference existed between Phase 2 and Phase 3 under the t-test (P value <0.01). The three phases generally aligned with the three-phase regulated SO_2 emissions in Ontario. It should be stated that Phase 1 and Phase 3 each covered only six years (N=6)~~, respectively~~. Cautions should be taken to explain the trend result in each phase in relation to precursors' emissions.

The PRL result of NO_3^- is expressed as~~ below~~:

$$\begin{cases} m - value = 1.09, 1988 \le x < 2004 \\ m - value = -0.128 * \left(\frac{x}{2} - 1001\right) + 1.08, 2004 \le x \le 2010 \end{cases}$$

The trend in the m-values of NO_3^- can be classified into two phases~~,~~ with the inflection point at 2003, which was confirmed by ~~according to~~ the t-test result, i.e., the values oscillated approximately 1.09±0.09 during the period from 1988 to 2003 and then exhibited a significant decrease of approximately 50% overall afterwards, with P value <0.01. ~~The PRL result is expressed as below:~~

~~$\begin{cases} m - value = 1.09, 1988 \le x < 2004 \\ m - vlaue = -0.128 * \left(\frac{x}{2} - 1001\right) + 1.08, 2004 \le x \le 2010 \end{cases}$~~

The m-value of NO_3^- in 1998-1999 was approximately 30% larger than the mean value in 1988-2003 and exceeded the mean value plus 3 SD in 1998-2003, and thus was not included in the trend analysis. The sharp increase in F_{wet} of NO_3^- occurred mainly in 1999, which was probably due to largely increased annual precipitation depth as mentioned in Section 2.4. The analysis was also supported by the geometric average concentration of NO_3^- in precipitation, which was ~~(~~1.1 mg L^{-1}~~) in precipitation~~ in 1999, ~~to be even~~ 5% lower~~smaller~~ than that~~the corresponding value~~ in 1988~~,~~ and only 5-10% ~~larger~~higher than those~~the corresponding values~~ in 1990-1991, 1993 and 2002. ~~caused by a large perturbation from climate anomalies.~~ Moreover, the monthly F_{wet} values of NO_3^- in March, April, July and August 1999 were actually lower than the corresponding long-term averages in 1988-2003 (excluding 1999) (Fig. ~~S4a~~S6a). This outcome indicates that the large increase in annual F_{wet} of NO_3^- in 1999 was unlikely to have been determined by the emissions of its gaseous precursors. The same can be said for the large increase in F_{wet} of SO_4^{2-} in 1999 (Fig. 2a, ~~S4b~~S6b).

To demonstrate the advantage of using the m-values in trend analysis, m-values were correlated to the reported emissions of concerned air pollutants. The trends in the m-value of SO_4^{2-} at Site 1 (Fig. 2a) were clearly different from those of the SO_2 emissions in Québec (Fig. 2c) but matched well to those in Ontario (Fig. 2c), which is also supported by their Pearson correlation coefficients, e.g., no significant correlation (r = 0.46 and P value >0.05) for the former case and a good correlation (r = 0.96 and P value <0.01) for the latter case. ~~Note that r instead of R^2 is conventionally used in correlation analysis and is therefore used here.~~ Zhang et al. (2008) reported that this remote area can receive the long-range transport of air pollutants from Ontario but that transport is less likely from the intensive emission sources in Québec.

In addition, LR analysis of the annual F_{wet} of SO_4^{2-} revealed a decreasing trend (second row in Fig. 2b). The M-K method analysis also confirmed the decreasing trend with annual F_{wet} as input. However, the three-phase trend in F_{wet} of SO_4^{2-} and related inflection points, identified using the m-values discussed above, were not identified by the t-test when simply using annual F_{wet} data as input. ~~Recall, the~~Identifying these inflection points is~~are~~ crucial to assess the effectiveness of environmental policies. The correlation between annual F_{wet} and emission~~s~~ was 0.89 for SO_4^{2-} vs. SO_2 in Ontario (P values <0.01), while the corresponding r value was as high as 0.96 between m-values and emission~~s~~. After reducing the perturbations from climatic factors to the annual F_{wet}, a stronger correlation~~s~~ was~~ere~~ obtained between F_{wet} and emission~~s~~. The increased r further solidified the dominant contribution of the long-range transport of air pollutants from Ontario rather than ~~those from~~ Québec to the wet deposition of SO_4^{2-} at Site 1.

The trends in NOx emissions during 1990-2003 had similar bell-shape patterns in Québec and Ontario, although with different magnitudes of emissions (Fig. 2f). A different trend pattern was seen for the m-value of NO_3^- at Site 1 than for the abovementioned provincial emissions during the same period (Fig. 2d), and there was no significant correlation ($r<0.41$, with P value >0.05) between the m-value of NO_3^- and the emissions of NOx in Québec or Ontario. Different results were found for the period of 2002-2011 than those of 1990-2003 discussed above. In 2002-2011, the m-value of NO_3^- decreased by ~50% and the NOx emissions decreased by ~40% in Québec and Ontario; also, good correlations ($r = 0.94$-0.95 with P values <0.01) were observed between m-values and emissions. The contrasting correlation results between the two different periods discussed above implied the complex link between wet deposition of NO_3^- and emissions of NO_x. ~~It can be speculated~~One might assume that the perturbation from climate anomalies~~, which was~~ might not~~ unable to~~ be fully removed by the new approach for the period of 1990-2003, which ~~-~~overwhelmed the effects of NOx emissions on the trends in m-values of NO_3^-~~-~~.~~in 1990-2003, while the reverse was true in 2002-2011. However, the~~ Such a possibility ~~wa~~is practically very low since the approach works well for the period of 2002-2011.~~, leaving~~ ~~t~~The contrasting results between these two periods are~~to be~~ yet to be explained.~~The contrasting results between the two different periods discussed above implied one possibility, i.e., that the perturbation from climate anomalies, which was unable to be removed by the new approach, overwhelmed the effect of NOx emissions on trends in m-values of NO_3^- in 1990-2003, while the reverse was true in 2002-2011. However, other possibilities cannot be excluded.~~ F_{wet} of NO_3^- and precipitation depth exhibited only a weakly significant correlation, with $r = 0.58$ and $P<0.05$ in 1988-2003 (the values in 1999 were excluded). Annual precipitation varied by only ~20% during the fifteen years, and this factor alone was unlikely to explain the ~100% interannual variation of F_{wet} of NO_3^- during that period.

LR analysis of the annual F_{wet} of NO_3^- revealed a decreasing trend (second row in Fig. 2e), confirmed by the M-K method analysis. However, the two-phase trend in F_{wet} of NO_3^- and related inflection point were not identified by the t-test when simply using annual F_{wet} data as input. The correlations between annual F_{wet} and emission~~s~~ were 0.74-0.76 for NO_3^- vs. NO_x in Québec and Ontario (P values <0.01), while the corresponding r values increased to 0.84-0.85 between m-value~~s~~ and emission~~s~~. Both the identified inflection point and the stronger correlation between m-value~~s~~ and emission~~s~~ demonstrated the advantage of using the m-value~~s~~ over annual F_{wet} of NO_3^- in trend analysis.

The m-value~~s~~ of NH_4^+ at Site 1 had no significant correlation (r = 0.21 and P value >0.05) with the emission~~s~~ of NH_3 in Québec but exhibited a weakly significant correlation (r = 0.60 and P value <0.05) with the emission~~s~~ of NH_3 in Ontario. Nearly all of the NH_4^+ was associated with SO_4^{2-} and NO_3^- in the atmosphere (Cheng and Zhang, 2017; Teng et al., 2017; Tost et al., 2007; Zhang et al., 2012)~~, e.g., gas-aerosol partitioning of NH_3/NH_4^+, scavenging efficiency of NH_3 and NH_4^+, pH value of wet deposition, etc.~~, and the trends in the m-value of NH_4^+ could be affected by many other factors besides NH_3 emissions and climate anomalies, e.g., gas-aerosol partitioning and different dry and wet removal efficiencies between NH_3 and NH_4^+, pH value of wet deposition.

~~LR analysis of the annual F_{wet} of these ions revealed decreasing trends for SO_4^{2-} and NO_3^- (second row in Fig. 2). The M-K method analysis also confirmed the decreasing trends with annual F_{wet} as input. However, the three-phase trends in F_{wet} of SO_4^{2-} and~~

~~the two-phase trends in F_{wet} of NO_3^- and related inflection points, identified using the m-values discussed above, were not identified by the t-test when simply using annual F_{wet} data as input. The correlations between annual F_{wet} and emissions were 0.89 for SO_4^{2-} vs. SO_2 in Ontario and 0.74-0.76 for NO_3^- vs. NO_x in Québec and Ontario (P values <0.01), while the corresponding r values were as high as 0.95 and 0.84-0.85 between m-values and emissions. After reducing the perturbations from climatic factors to the annual F_{wet}, stronger correlations were obtained between F_{wet} and emissions.~~

The stable trend in annual F_{wet} of NH_4^+ and the decreasing trend in annual F_{wet} of NO_3^- gradually increased the relative contributions of reduced nitrogen in the total nitrogen wet deposition budget, e.g., from 40% in 1998-1999 to 52% in 2010-2011. A similar trend has also been recently reported in the U.S. (Li et al., 2016). Such a trend was mostly due to the mitigation of NOx rather than climate anomalies.

3.2 Decadal climate anomalies drove trends at Site 2

3.2.1 Trends in m-value of SO_4^{2-}

Fig. 3 shows the trend analysis results at Site 2. An obvious shift in the m-values and annual F_{wet} occurred during 2001-2002, as detected by the t-test, i.e., the m-values of SO_4^{2-} oscillated approximately 1.15±0.11 in 1990-2001 and 0.76±0.02 in 2002-2011 (or 0.83±0.12 if the value in 2006-2007 was included), but with a significant difference between the two periods with P value <0.01. The annual F_{wet} of SO_4^{2-} oscillated approximately 632±63 mg m^{-2} in 1990-2001 and 452±74 mg m^{-2} in 2002-2011, and the values between the two periods showed significant differences. The shift led to the m-values and annual F_{wet} of SO_4^{2-} exhibiting a consistent decreasing trend by ~40% overall from 1990 to 2011 using the LR and the M-K method.

The emissions of SO_2 oscillated approximately 1.13±0.07 in 1990-2001 and 1.06±0.03 in 2002-2011 in British Columbia, which did not support the large decrease of approximately 40% in wet deposition of SO_4^{2-} in 2002-2011. Statistically, no correlation existed between annual F_{wet} of SO_4^{2-} and the emissions of SO_2 in British Columbia, with r = 0.52 and P value >0.05. Although the transboundary transport of air pollutants from the U.S. cannot be excluded, the almost constant m-values from 2002 to 2011 (excluding 2006-2007) at Site 2 were inconsistent with the approximately 70% decrease in emissions of SO_2 in the state of Washington in the U.S. during that period (not shown). Precipitation cannot explain the jump in wet deposition either, because there was no corresponding jump in precipitation during 2001-2002 (Fig. 3b).

van Donkelaar et al. (2008) analyzed aircraft and satellite measurements from the Intercontinental Chemical Transport Experiment and proposed the long-range transport of sulfur from East Asia to the west coast of Canada. The wind vector and wind speed from the North American Regional Reanalysis (NARR), with a spatial resolution of 32 km by 32 km (Mesinger et al., 2006), were~~as~~ thereby analyzed to study the decadale changes in wind fields and associated potential impacts on the long-range transport of air pollutants over the western coastal Canada and U.S. The average wind fields including mean wind vector and speed (shading in Fig 4a-d) in 1990-2011 at ~~different altitudes~~925 hPa ~~also~~ showed air masses over the western coastal Canada and U.S. were primarily originated~~ing~~ from the Pacific Ocean ~~in the west~~ (Fig. 4a). However, the ~~climate~~ anomalies of wind fields in 1990-2001 ~~compared against~~relative to 1990-~~2011~~ 2009 clearly showed a counterclockwise pattern in the corresponding coastal area, including Site 2., while a clockwise pattern existed in 2002-2011 ~~against~~ relative to

1990-~~2011~~ 2009 (Fig. 4b, c). The anomalies shown in Fig. 4c indicated the northwesterly wind ~~to~~ being enhanced in 2002-2011 over the western coastal Canada and U.S., possibly reducing air pollutants being transported from the continent~~al~~ to Site 2. In contrast, the anomalies in Fig. 4b indicated that the northwesterly wind was reduced in 1990-2001. Consequently,~~T~~ ~~he decadal climate anomalies of wind fields in 2002-2011 very likely caused a large decrease in the contribution of~~ more air pollutants ~~can~~might have been transported from the continent ~~eastern coast~~ to Site 2, resulting in a distinct demarcation in~~at~~ 2002. This hypothesis was also supported by a large rebound of the m-value in 2006-2007, due to the increase in F_{wet} of SO_4^{2-} in 2007. The climate anomalies of wind fields in 2007 ~~against 1990-2011~~relative to 1990-2009 showed a counterclockwise pattern in the north, while the clockwise pattern was pushed to the south (Fig. 4d). With the northwesterly wind ~~to~~ being reduced, ~~A~~ a greater contribution of air pollutants from the ~~eastern~~ coast of Canada and U.S. to Site 2 might have led to the large increase in F_{wet} of SO_4^{2-} during a few month-long periods in 2007.

The present study is the first one ~~to~~ identifying the decreasing trend in the annual F_{wet} of SO_4^{2-} as being very likely caused by decadal climate anomalies, i.e., ~~-~~wind fields, rather than by the emission reductions of SO_2. The decadal ~~climate~~ anomalies of wind fields may substantially alter the long-range transport of air pollutants to the reception site. Note that the causes for the decadal ~~climate~~ anomalies of wind fields in this region are beyond the scope of the present study, but some information can be found in the literature (Bond et al., 2003; Coopersmith et al., 2014; Deng et al., 2014).

3.2.2 Trends in m-values of NO_3^- and NH_4^+

For the wet deposition of NO_3^-, the m-values also showed a clear shift, i.e., the m-values oscillated approximately 1.09±0.14 in 1990-2001 and 0.88±0.06 in 2002-2011, with a significant difference between the two periods under the t-test with P value <0.01. The annual F_{wet} of NO_3^- varied substantially, and the shift could not be identified statistically. However, the annual F_{wet} of NO_3^- exhibited a decreasing trend by M-K method analysis. Similar to the case of SO_4^{2-}, no significant correlation ($r = 0.49$, P value >0.05) existed between the annual F_{wet} of NO_3^- and the emissions of NOx in British Columbia.

In addition to decadal ~~climate~~ anomalies of wind fields, the interannual climate variability such as precipitation depth, annual anomalies of wind fields in 2007, etc., (Fig. 3b) also affected the trends in m-values and annual F_{wet} of NO_3^-. The annual precipitation depth~~s~~ largely varied from 601 mm to 1054 mm in the two decades. The perturbations from interannual ~~climate~~ variability of precipitation depth cannot be completely removed by the new approach. For example,~~,~~ the calculated m-values in 1992-1993 and 1994-1995 were evidently lower than ~~other~~the m-values in 1990-2001. However, the annual geometric average concentrations of NO_3^- in 1992-1995 varied around 0.77±0.11 mg L^{-1} and were even larger than the values of 0.66±0.08 mg L^{-1} in 1990-2001 (excluding 1992-1995). The lower m-values were mainly attributed to the lower precipitation depth in 1992-1994 (Fig 3b) rather than lower emissions of NOx. Interannual climate variability including precipitation depth and annul anomalies of wind fields~~, etc.,~~ may ~~and they~~ complicate the relationship between the F_{wet} of NO_3^- and the emissions of NO_x in British Columbia. For example, the m-values in 1990-1991, 1996-1997, 1998-1999 and 2000-2001 were nearly constant at 1.17±0.03;~~:~~ ~~H~~however, the NOx emissions in British Columbia in 1998-1999 were 26% greater than those in 1990-1991. Moreover, t~~T~~here was a sharp decrease in the NOx emissions (by ~30%) from 2002 to 2011 in British Columbia. However, the m-values oscillated approximately 0.88±0.06 and showed no clear trend based on either the M-K method or LR analysis. The interannual climate variability apparently negated the impact of reduced emissions during these periods.

The m-values and the annual F_{wet} of NH_4^+ oscillated approximately 0.99±0.13 and 81±16 mg m^{-3}, respectively, in the period of 1990-2011, and showed no trend (Fig. 3). Neither the m-values nor annual F_{wet} of NH_4^+ showed the two-period distribution pattern or had any significant correlation with the emissions of NH_3 in British Columbia at a 95% confidence level. Similarly to Site 1, the annual variation in F_{wet} of NH_4^+ at Site 2 cannot be simply explained by known emission trends.

In summary, decadal ~~climate~~ anomalies of wind fields overwhelmingly determined the long-term trends in the wet deposition of SO_4^{2-} and NO_3^-, with the perturbation from monthly and annual climate anomalies removed at Site 2. The interannual climate variability including precipitation depth, annual anomalies of wind fields, etc., further complicated the trends, resulting in undetectable influences of the emission trends on the deposition trends. Since the decrease in F_{wet} of NO_3^- appeared to be primarily caused by decadale climate anomalies of wind fields, the relative contributions of NH_4^+ and NO_3^- in the total N wet deposition varied little, i.e., 33% versus 67% in 2010-2011 and 31% versus 69% in 1990-1991.

3.3 Regional trends in wet deposition in northern Ontario and Québec

Trends in the m-values or annual F_{wet} of ions at Sites 3 and 4 in the northern regions of

Ontario were generally similar to those found at Site 1 (Fig. S5 and S6). The three-phase trend in m-values of SO_4^{2-} and the two-phase trend in m-values of NO_3^- were also obtained at Sites 3 and 4 after excluding a few m-values that were caused by large perturbations from climate anomalies. For example, the annul precipitation depths of 1044 mm in 1987 and 905 mm in 1997 at Site 4 were evidently lower than the average value of 1299±124 mm (excluding 1987 and 1997) in 1985-1997 (Table S2)~~For example, the three-phase trend in m-values of SO_4^{2-} and the two-phase trend in m-values of NO_3^- were also obtained at Sites 3 and 4 after excluding a few m-values that were caused by large perturbations from climate anomalies~~. However, the geometric average concentration of SO_4^{2-} of ~~1.6 mg L^{-1} in 1987 was same as that in 1989 and the value of~~ 1.5 mg L^{-1} in 1997 was ~~also~~ the same as the mean value of 1.5±0.2 mg L^{-1} in 1995-1999 (excluding 1997). The value of 1.6 mg L^{-1} in 1987 was also same as that in 1989. The lower annul precipitation depths in 1987 and 1997 than in the other years were very likely the dominant factor causing the~~overwhelmed to determine~~ abnormally lower m-values in 1986-1987 and 1996-1997~~ relative to those before and after~~. Thus, Sites 1, 3 and 4 were combined together to study regional trends in the northern areas of Ontario and Québec (Fig. 5a-c). Similar to those found at the individual sites, the temporal profile of regional m-values of SO_4^{2-} can be clearly classified into three phases (Fig. 5a) as follows: Phase 1 from 1988 to 1993 with m-values oscillating approximately 1.31±0.08, Phase 2 from 1994 to 2003 with near-constant m-values of 1.05±0.04, and Phase 3 for 2004 onward with a decreasing trend by an overall ~50%. Significant differences of m-values existed between any two of the three phases, based on the t-test results (P value <0.01). The PRL result is expressed as below:

$$\begin{cases} m-value = 1.31, 1988 \leq x < 1994 \\ m-value = 1.05, 1994 \leq x < 2004 \\ m-value = -0.129 * \left(\frac{x}{2} - 1001\right) + 1.03, 2004 \leq x \leq 2010 \end{cases}$$

The three-phase pattern of m-values matched well with the three-phase emission profile of SO_2 in Ontario. Statistically, a~~n~~ ~70% decrease in m-value and a~~n~~ ~70% decrease in emissions were found from 1990 to 2011, with a correlation of $r = 0.95$ (P value <0.01).

The profile of the regional m-values of NO_3^- also clearly exhibited two phases, according to the following t-test results~~ between them~~: Phase 1 from 1988 to 2003, with m-values narrowly varying approximately 1.11±0.05, and Phase 2 from 2004 to 2011~~,~~ with a decreasing trend by an overall ~40% against that in 2002-2003 (Fig. 5b). The PRL result is expressed as below:

$$\begin{cases} m - value = 1.11, 1988 \leq x < 2004 \\ m - value = -0.11 * \left(\frac{x}{2} - 1001\right) + 1.03, 2004 \leq x \leq 2010 \end{cases}$$

From 2002 to 2011, the m-value had a moderately good correlation with the NOx emission in Ontario ($r = 0.91$, $P<0.01$), and the two variables decreased by 30-40% in this period. From 1990 to 2003, the near constant m-value was, however, inconsistent with the bell-shape profile of the NOx emissions mainly caused by annual variations in NOx emission from the sector of Transportation and Mobile Equipment in Ontario and Québec~~in Ontario and Québec~~, which could be due to either the perturbation from climate anomalies or unrealistic emissions inventory from (APEI) in Canada. Considering that the first possibility was minimal over a large regional scale, especially when the consistency was determined in a different time frame (2002-2011) in the same region, it is thus doubtful that the bell-shape profile of the NOx emissions in 1990-2003 was realistic.

The regional m-values of NH_4^+ largely oscillated from 1988 to 2003 (Fig. 5c). The m-values of NH_4^+, however, decreased by ~30% from 2002 to 2011, leading to a probable decreasing trend in m-value from 1988 to 2011. No correlation was found between the m-values of NH_4^+ and the emissions of NH_3 in Ontario, which is consistent with the findings at the individual sites discussed above.

Since the decrease in F_{wet} values of NO_3^- at Sites 3 and 4 were very likely due to the mitigation of NOx in Ontario, the decrease also changed the relative contributions between NH_4^+ and NO_3^- in the total N wet deposition budget. For example, NH_4^+ and NO_3^- contributed 52% and 48%, respectively, to the total budget in 2010-2011 and 34% and 66%, respectively, in 1984-1985 at Site 3. The corresponding numbers at Site 4 were 58% and 42% in 2010-2011 and 47% and 53% in 1985-1986.

4 *Conclusions*

Climate anomalies during the two-decade period resulted in annual F_{wet} of SO_4^{2-} and/or NO_3^- deviating from the normal value by up to ~40% at the rural Canadian sites. The new approach of rearranging and screening F_{wet} data can largely reduce the impact of climate anomalies when used for generating the decadal trends of F_{wet}. With the climate perturbation being reduced, F_{wet} of SO_4^{2-} exhibited a three-phase decreasing trend at every individual site, as well as on a regional scale in northern Ontario and Québec. The three-phase pattern of the decreasing trend in F_{wet} of SO_4^{2-} matches well with the emission trends of SO_2 in Ontario, as supported by the good correlation between wet deposition and emission, with $r \geq 0.95$ and $P<0.01$. F_{wet} of NO_3^- exhibited a two-phase decreasing trend, but only during the second phase F_{wet} of NO_3^-, and the emissions of NOx in Ontario and Québec matched well, with a good correlation of $r \geq 0.91$ and $P<0.01$. Compared to the results obtained without applying the new approach, it is concluded that, after reducing the perturbation from climate anomalies, 1) better correlation was obtained between F_{wet} of ions and the emission of the corresponding gaseous precursors in northern Ontario and Québec, and 2) the inflection points in the decreasing trends of F_{wet} of SO_4^{2-} and NO_3^- were ~~clearly~~ visibly and statistically identified.

However, the new approach cannot completely remove the perturbations from climate anomalies, especially when this is the dominant factor and/or on long timescales, as was the case at a coastal site of Saturna in British Columbia. At this location, the decreasing trends in F_{wet} of SO_4^{2-} and NO_3^- were caused by the decadal ~~climate~~ anomalies of wind fields, as well as being affected by interannual climate variability including precipitation depth and annul anomalies of wind fields, etc., which overwhelmed the impact of the emission changes of the gaseous precursors in this province. This is the first study that has identified that decadal ~~climate~~ anomalies of wind fields can dominate trends in F_{wet} of SO_4^{2-} and NO_3^-. The new findings will stimulate more studies on the impacts of decadal~~e~~ climate anomalies on atmospheric deposition of concerned air pollutants~~chemicals~~.

The long-term variations in F_{wet} of NH_4^+ generally showed no clear long-term trends. Moreover, no apparent cause-effect relationships were found between the wet deposition of NH_4^+ and the emission of NH_3. It can be reasonably inferred that~~This outcome is not surprising because~~ additional key factors besides those discussed in this study also impact the trends of F_{wet} of NH_4^+. Thus, cautions should be taken to use wet deposition fluxes of NH_4^+ to extrapolate emissions of NH_3. ~~For example, NH_4^+ may be more greatly impacted by changes in SO_2 and NOx than are NH_3 emissions in NH_3-rich scenarios. It should be noted that F_{wet} of N via NH_4^+ exceeded those via NO_3^- in 2010~~

~~and 2011 in northern Ontario and Québec, where the decrease in F_{wet} of NO_3^- was associated with decreasing NOx emissions. In contrast, F_{wet} of NH_4^+ did not exceed F_{wet} of NO_3^- in 2010 and 2011 in the coastal area in British Columbia, where the decreasing trends of F_{wet} of NO_3^- were determined to result mainly from the perturbation by climate anomalies.~~

Data availability. Data used in this study are available from the corresponding authors.

Supplement. The supplement materials are available online.

Author contribution. X. Y. and L. Z. designed the study, analyzed he data and prepared the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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References

Baumgardner, R.E., Lavery, T.F., Rogers, C.M., and Isil, S.S.: Estimates of the Atmospheric Deposition of Sulfur and Nitrogen Species: Clean Air Status and Trends Network, 1990−2000, Environ. Sci. & Technol., 36, 2614-2629. https://doi.org/10.1021/es011146g, 2002.

Bond, N. A., Overland, J. E., Spillane, M., and Stabeno, P.: Recent shifts in the state of the North Pacific, Geophys. Res. Lett., 30, 2183, https://doi.org/10.1029/2003GL018597, 2003.

Burakowski, E. A., Wake, C. P., Braswell, B., and Brown, D. P.: Trends in wintertime climate in the northeastern United States: 1965-2005, J. Geophys Res. Atmos., 113, 1–12. https://doi.org/10.1029/2008JD009870, 2008.

Butler, T. J., Likens, G. E., Vermeylen, F. M., and Stunder, B. J. B.: The impact of changing nitrogen oxide emissions on wet and dry nitrogen deposition in the northeastern USA, Atmos. Environ., 39, 4851–4862, https://doi.org/10.1016/j.atmosenv.2005.04.031, 2005.

Cheng, I. and Zhang, L. Long-term air concentrations, wet deposition, and scavenging ratios of inorganic ions, HNO_3, and SO_2 and assessment of aerosol and precipitation acidity at Canadian rural locations, Atmos. Chem Phys., 17, 4711–4730, https://doi.org/10.5194/acp-17-4711-2017(2017).

Coopersmith, E. J., Minsker, B. S., and Sivapalan, M.: Patterns of regional hydroclimatic shifts: An analysis of changing hydrologic regimes, Water Resour. Res., *50*, 1960–1983. https://doi.org/10.1002/2012WR013320, 2014

Deng, Y., Gao, T., Gao, H., Yao, X., and Xie, L.: Regional precipitation variability in East Asia related to climate and environmental factors during 1979-2012, Scientific Reports, *4*, 5693. https://doi.org/10.1038/srep05693, 2014.

Fagerli, H., and Aas, W.: Trends of nitrogen in air and precipitation: model results and observations at EMEP sites in Europe, 1980-2003, Environ. Pollut. *154*, 448–461. https://doi.org/10.1016/j.envpol.2008.01.024, 2008

Fowler, D., Smith, R., Muller, J., Cape, J. N., Sutton, M., Erisman, J. W., and Fagerli, H.: Long Term Trends in Sulphur and Nitrogen Deposition in Europe and the Cause of Non-linearities, Water Air Soil Pollut., 7, 41–47. https://doi.org/10.1007/s11267-006-9102-x, 2007.

Fowler, D., Smith, R. I., Muller, J. B. A., Hayman, G., and Vincent, K. J.: Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001, Environ. Pollut., 137, 15–25,https://doi.org/10.1016/j.envpol.2004.12.028, 2005.

Kampata, J. M., Parida, B. P., and Moalafhi, D. B.: Trend analysis of rainfall in the headstreams of the Zambezi River Basin in Zambia, Phys. Chem. Earth, *33*, 621–625, https://doi.org/10.1016/j.pce.2008.06.012, 2008.

~~Pihl-Karlsson, G., Akselsson, C., Hellsten, S., and Karlsson, P. E.: Reduced European emissions of S and N – Effects on air concentrations, deposition and soil water chemistry in Swedish forests, Environ. Pollut., *159*(12), 3571–3582,https://doi.org/10.1016/j.envpol.2011.08.007, 2011.~~

Lajtha, K., and Jones, J.: Trends in cation, nitrogen, sulfate and hydrogen ion concentrations in precipitation in the United States and Europe from 1978 to 2010: a new look at an old problem, Biogeochemistry, 116, 303–334. https://doi.org/10.1007/s10533-013-9860-2, 2013.

Lehmann, C. M. B., Bowersox, V. C., Larson, R. S., and Larson, S. M.: Monitoring Long-term Trends in Sulfate and Ammonium in US Precipitation: Results from the National Atmospheric Deposition Program/National Trends Network, Water Air Soil Pollut., 7, 59–66. https://doi.org/10.1007/s11267-006-9100-z, 2007.

Li, Y., Schichtel, B. A., Walker, J. T., Schwede, D. B., Chen, X., Lehmann, C. M. B., Puchalski, M.A., Gay, D.A., and Collett, J. L.: Increasing importance of deposition of reduced nitrogen in the United States, Proc. Natl. Acad. Sci. U.S.A., *113*, 5876-5879, https://doi.org/10.1073/pnas.1525736113, 2016.

Lloret, J., and Valiela, I.: Unprecedented decrease in deposition of nitrogen oxides over North America: the relative effects of emission controls and prevailing air-mass trajectories. Biogeochemistry, 129, 165–180. https://doi.org/10.1007/s10533-016-0225-5, 2016.

Lynch, J. A., Bowersox, V. C., and Grimm, J. W.: Acid rain reduced in Eastern United States, Environ. Sci. Technol., 34, 940–949. https://doi.org/10.1021/es9901258, 2000.

Marchetto, A., Rogora, M., and Arisci, S.: Trend analysis of atmospheric deposition data: A comparison of statistical approaches, Atmos. Environ., 64, 95–102, https://doi.org/10.1016/j.atmosenv.2012.08.020, 2013.

Mesinger, F., DiMego, G., Kalnay, E., Mitchell, K. and Coauthors, 2006: North American Regional Reanalysis. Bulletin of the American Meteorological Society, 87, 343–360, doi:10.1175/BAMS-87-3-343.

Monteith, D., Henrys, P., Banin, L., Smith, R., Morecroft, M., Scott, T., Andrew, C. Beaumont, D., Benham, S., Bowmaker, V., Corbet, S., Dick, J., Dod, B., Dodd, N., McKenna, C., McMillan, S., Pallett, D., Pereira, M.G., Poskitt, J., Rennie, S., Rose, R., Schäfer, S., Sherrin, L., Tang, S., Turner, A., and Watson, H.: Trends and variability in weather and atmospheric deposition at UK Environmental Change Network sites (1993–2012), Ecol. Indic., 68, 21–35. https://doi.org/10.1016/j.ecolind.2016.01.061, 2016.

Pihl Karlsson, G., Akselsson, C., Hellsten, S., and Karlsson, P. E.: Reduced European emissions of S and N – Effects on air concentrations, deposition and soil water chemistry in Swedish forests, Environ. Pollut., *159*(12), 3571–3582,https://doi.org/10.1016/j.envpol.2011.08.007, 2011.

Rogora, M., Colombo, L., Marchetto, A., Mosello, R., and Steingruber, S.: Temporal and spatial patterns in the chemistry of wet deposition in Southern Alps, Atmos. Environ., *146*, 44–54. https://doi.org/10.1016/j.atmosenv.2016.06.025, 2016.

Rogora, M., Mosello, R., and Marchetto, A.: Long-term trends in the chemistry of atmospheric deposition in Northwestern Italy: The role of increasing Saharan dust deposition. Tellus B Chem. Phys. Meteorol., *56*, 426–434. https://doi.org/10.1111/j.1600-0889.2004.00114.x, 2004.

Ryan, S.E. and Porth, L.S.: A tutorial on the piecewise regression approach applied to bedload transport data, General Technical Report RMRS-GTR-189, https://www.fs.fed.us/rm/pubs/rmrs_gtr189.pdf, 2007.

Sickles II, J. E., and Shadwick, D. S.: Air quality and atmospheric deposition in the eastern US: 20 years of change, Atmos. Chem. Phys., *15*, 173–197. https://doi.org/10.5194/acp-15-173-2015, 2015.

Strock, K. E., Nelson, S. J., Kahl, J. S., Saros, J. E., and McDowell, W. H.: Decadal Trends Reveal Recent Acceleration in the Rate of Recovery from Acidification in the Northeastern U.S., Environ. Sci. Technol., *48*, 4681–4689. https://doi.org/10.1021/es404772n, 2014.

Teng, X., Hu, Q., Zhang, L.M., Qi, J., Shi, J., Xie, H., Gao, H.W., and Yao, X.H.: Identification of major sources of stmospheric NH_3 in an urban environment in northern China during wintertime, Environ. Sci. Technol., 51, 6839–6848, https:// 10.1021/acs.est.7b00328, 2017.

van Donkelaar, A., R. V. Martin, R. Leaitch, A. M. Macdonald, T. W. Walker, D. Streets, Q. Zhang, E. J. Dunlea, J. Jimenez-Palacios, J. Dibb, L. G. Huey, R. Weber, and M. O. Andreae.: Analysis of aircraft and satellite measurements from the Intercontinental Chemical Transport Experiment (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada, Atmos. Chem. Phys., 8, 2999-3014, https://doi:10.5194/acp-8-2999-2008, 2008.

Vet, R., Artz, R. S., Carou, S., Shaw, M., Ro, C.-U., Aas, W., Baker, A., Bowersox, V.C., Dentener, F., Galy-Lacaux, C., Hou, A., Pienaar, J.J., Gilletti, R., Forti, C., Gromov, S., Hara, H., Khodzher, T., Mahowald, N.M., Nickovic, S., Rao, P.S.P., and Reid, N. W. A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus, Atmos. Environ., 93, 3–100. https://doi.org/10.1016/j.atmosenv.2013.10.060, 2014.

Vet, R., and Ro, C.-U.: Contribution of Canada–United States transboundary transport to wet deposition of sulphur and nitrogen oxides—A mass balance approach, Atmos. Environ., *42*, 2518–2529. https://doi.org/10.1016/j.atmosenv.2007.12.034, 2008.

Waldner, P., Marchetto, A., Thimonier, A., Schmitt, M., Rogora, M., Granke, O., Mues, V., Hansen, K., Pihl Karlsson, G., Zlindra, D., Clarke, N., Verstraeten, A., Lazdins, A., Schimming, C., Iacoban, C., Lindroos, A-J, Vanguelova, E., Benham, S., Meesenburg, H., Nicolas, M., Kowalska, A., Apuhtin, V., Napa, U., Lachmanova, Z., Kristoefel, F., Bleeker, A., Ingerslev, M., Vesterdal, L., Molina, J., Fischer, U., Seidling, W., Jonard, M., O'Dea, P., Johnson, J., Fischer, R., and Lorenz, M.: Detection of temporal trends in atmospheric deposition of inorganic nitrogen and sulphate to forests in Europe, Atmos. Environ., 95, 363-37. http://dx.doi.org/10.1016/j.atmosenv.2014.06.054, 2014.

Wetherbee, G. A., and Mast, M. A.: Annual variations in wet-deposition chemistry related to changes in climate, Clim. Dynam., 47, 3141–3155, https://doi.org/10.1007/s00382-016-3017-7, 2016.

Wijngaard, J. B., Tank, A. M. G. K., and Können, G. P.: Homogeneity of 20th century European daily temperature and precipitation series. Int. J. Climatol., 23, 679–692, https://doi.org/10.1002/joc.906, 2003.

Wright L.P., Zhang L., Cheng I., Aherne J., and Wentworth G.R.: Impacts and effects indicators of atmospheric deposition of major pollutants to various ecosystems – A review. Aerosol Air Qual. Res., 18, 1953-1992, doi: 10.4209/aaqr.2018.03.0107, 2018

Wu, Z., and Huang, N. E.: Ensemble empirical mode decomposition: a noise-assisted data analysis method. Advances in Adaptive Data Analysis, 1, 1–41, https://doi.org/10.1142/S1793536909000047, 2009

Vieth, E.: Fitting piecewise linear regression functions to biological responses, J. Appl. Physiol., 67, 390–396, doi:10.1152/jappl.1989.67.1.390, 1989.

Yao, X. H., and Zhang, L. Supermicron modes of ammonium ions related to fog in rural atmosphere, Atmos. Chem. Phys., 12, 11165–11178, https://doi.org/10.5194/acp-12-11165-2012, 2012

Yao, X., and Zhang, L. Trends in atmospheric ammonia at urban, rural, and remote sites across North America, Atmos. Chem. Phys., 16, 11465–11475, https://doi.org/10.5194/acp-16-11465-2016, 2016.

Zbieranowski, A.L. and Aherne, J.: Long-term trends in atmospheric reactive nitrogen across Canada: 1988–2007, Atmos. Environ., 45, 5853-5862, https://doi.org/10.1016/j.atmosenv.2011.06.080, 2011.

Zhang, L., Jacob, D. J., Knipping, E. M., Kumar, N., Munger, J. W., Carouge, C. C., van Donkelaar, A., Wang, Y.X., and Chen, D.: Nitrogen deposition to the United States: Distribution, sources, and processes, Atmos. Chem. Phys., 12, 4539–4554, https://doi.org/10.5194/acp-12-4539-2012, 2012.

Zhang, L., Vet, R., Wiebe, A., and Mihele, C.: Characterization of the size-segregated water-soluble inorganic ions at eight Canadian rural sites, Atmos. Chem. Phys., 8, 7133–7151, https://doi.org/10.5194/acp-8-7133-2008, 2008.

List of Figures

Figure 1. Fitting monthly F_{wet} of SO_4^{2-} against the climatology values from every two years using LR with zero interception at Site 1, according to the new approach described in Section 2. ~~* reflects the maximum value excluded for LR analysis.~~ Fitted lines represent the LR function with zero interception using 24 elements~~;~~. x, y and R^2 in the legend represent climatology monthly F_{wet}, monthly F_{wet} in every two-year and the coefficient of determination in LR analysis, respectively.~~;~~ * reflects the maximum value (cycled markers) excluded for LR analysis and all P values <0.01.

Figure 2. m-values and annual F_{wet} of SO_4^{2-}, NO_3^- and NH_4^+ ~~extracted trends~~in 1988-2011 at Site 1, and the annual emissions of ~~air pollutants~~SO_2 and NO_x in 1990-2011 in Québec and Ontario, Canada. Full and empty markers in blue in (a), (~~b~~d) and (g) represent the calculation of m-values without and with the outlier, respectively. Empty markers in red represent the outliers in m-values and are excluded for trend analysis, as detailed in Section 2. R^2 reflects the coefficient of determination of a variable against the calendar year from LR analysis, and the fitted lines represent the LR function.~~;~~ M-K results are shown~~include~~ in (a-b), (d-e) and (g-h). Phases 1, 2 and 3 in (a) and (c), Phases 1 and 2 in (d) and (f) were gained from PLR presented in Section 3.1.

Figure 3. ~~Identical to~~Same as in Fig. ~~1~~2, except for Site 2, and the annual precipitation and annual emissions in British Columbia, Canada. Horizontal dashes in (b) represent precipitation, and the fitted lines represent the LR function.

Figure 4. ~~Average wind fields in 1990-2011 (a) and anomalies at 925 hpa in 1990-2001 (b), 2002-2011 (excluding 2007) (c), and 2007 (d) in western coastal Canada and the U.S.~~ The mean wind vector and speed (shading area) during 1990-2011 (a), the anomalies of wind vector and wind speed (shading area) during 1990-2001 (b), 2002-2011 (c) and 2007 (d) at 925 hPa over the western coastal Canada and U.S. (~~T~~the anomalies in b,c,d were conducted relative to the 20-year period of 1990-2009 and the wind vector and wind speed were from the North American Regional Reanalysis (NARR), with a spatial resolution of 32 km by 32 km~~.~~).

Figure 5. Regional m-values at Sites 1, 3 and 4: (a): SO_4^{2-}, (b): NO_3^-, and (c): NH_4^+. R^2 reflects the coefficient of determination of a variable against the calendar year from LR analysis, and the fitted lines represent the LR function.~~;~~ M-K results are shown~~include~~ in (a-c).~~;~~ Phases 1, 2 and 3 are shown in (a) and (c).~~,~~ Phases 1 and 2 in (a) and (b) were gained from PLR presented in Section 3.3.