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.”