Supporting Information

1) Comparative analysis of different approaches estimating m-value

Results from the new approach discussed in the main body of the paper (referred to as Approach C) are compared with those from two other approaches using data at Site 1 as an example. Note that Approach C (i) uses 24 month data (in every two calendar year) in each data array, (ii) rearranges the 24 elements from the smallest to the largest to form a data array, and (iii) removes the outliers from the data array. In comparison, Approach A only uses 12 month data (in each calendar year), and does not rearrange the data (simply following the sequence of January, February, etc.). Approach B also uses 12 month data in each calendar year, rearranges the data elements following the Approach C, but does not remove the outliers.

The m-values for each calendar year from using Approach A are shown for F_{wet} of SO_4^{2-} in Fig S1a-h. The values of R^2 from using Approach A were much lower than those from using Approach C, e.g., only 0.76 in 1988, 0.50 in 1989, 0.67 in 1990, 0.56 in 1994, 0.39 in 1995 and 0.14 in 1996. The low values of R^2 were primarily due to monthly scale climate anomalies, e.g., the time shift in rain, dry or snow seasons, which led to largely varying monthly F_{wet} of SO_4^{2-} during the 24 years. Under such low values of R^2, the calculated m-values mix with large perturbations from monthly scale climate anomalies, and are not suitable for extracting the long-term trend.

The m-values from using Approach B are shown in Fig S2a-h. In most cases, the values of R^2 from using Approach B were higher than those from using Approach A, but were substantially lower than those from using Approach C. The m-values calculated using Approach B also mix with larger perturbations to m-values from climate anomalies, leading to larger uncertainties in the interpretation of the extracted trends in terms of air pollutants' emissions and climate anomalies.

A linear regression analysis was then conducted, assuming zero interception and using the m-values calculated from Approach B against the annual F_{wet} data, and obtained the value of R^2 as high as 0.99 (not shown). 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.

To demonstrate if the two-year interval (24 month data) used in Approach C is long enough, an additional test (Approach D) is also conducted by using three-year interval to calculate the m-value. As expected, there were maximum monthly values of F_{wet} severely deviated from the general trend (Fig S3a-c). After excluding these outliers, the values of R^2 in each regression equation were almost the same as those obtained from Approach C. Thus, Approach C is believed to be the optimum approach among the methods discussed above.

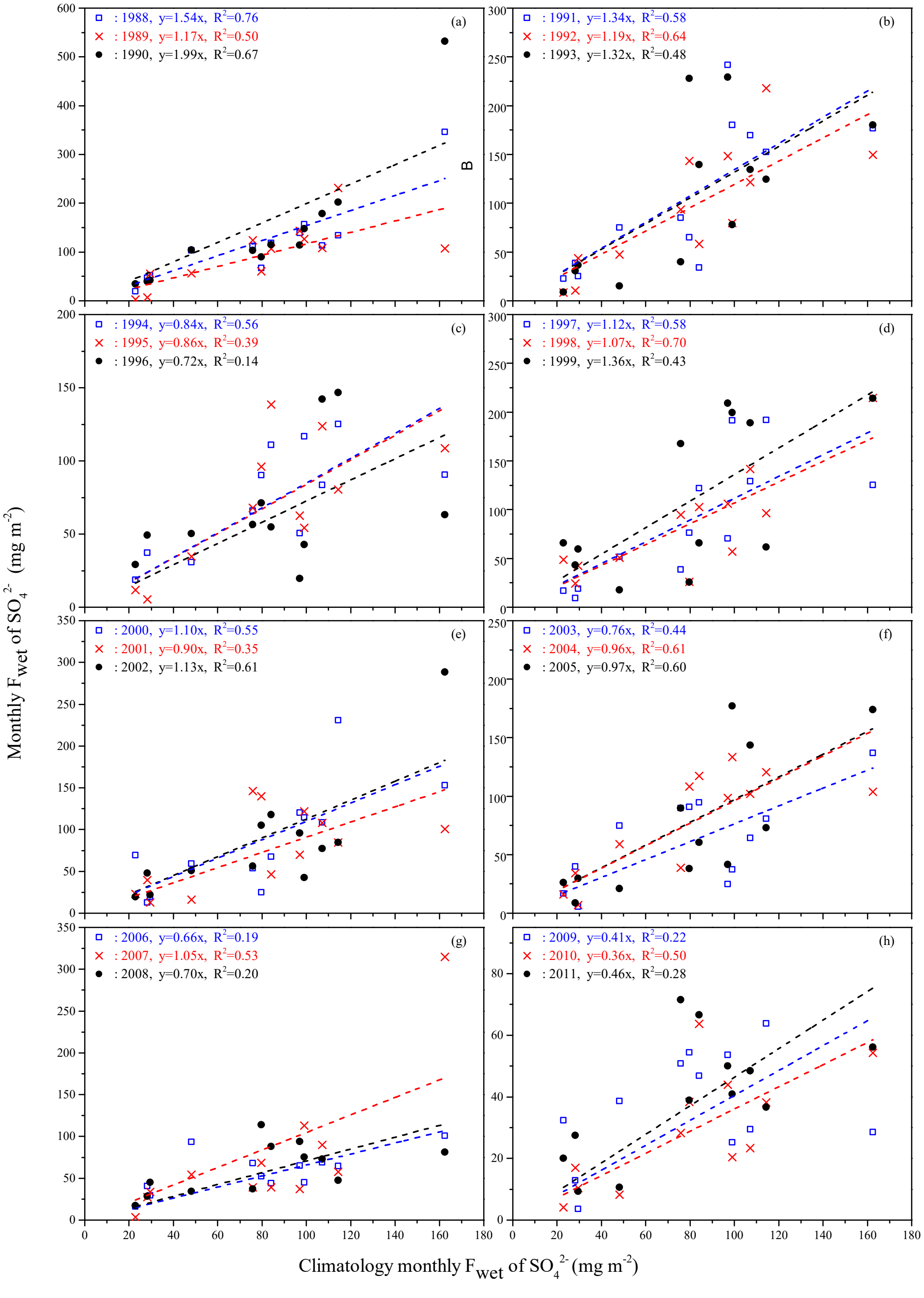

Fig S1. Fitting monthly F_{wet} of SO_4^{2-} against climatology values using LR with zero interception at Site 1 according to Approach A.

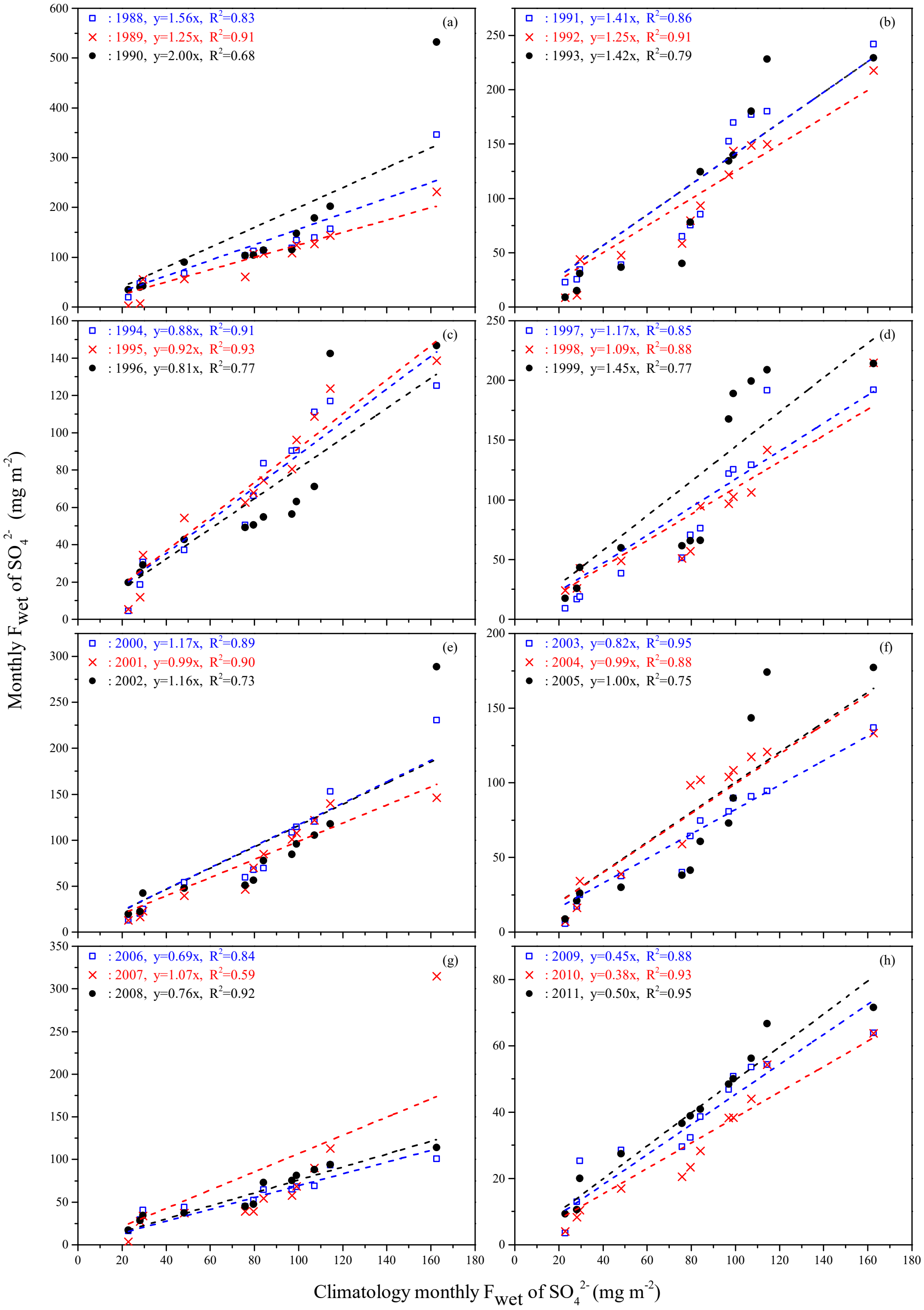

Fig S2. Same as in Figure S1 except using Approach B.

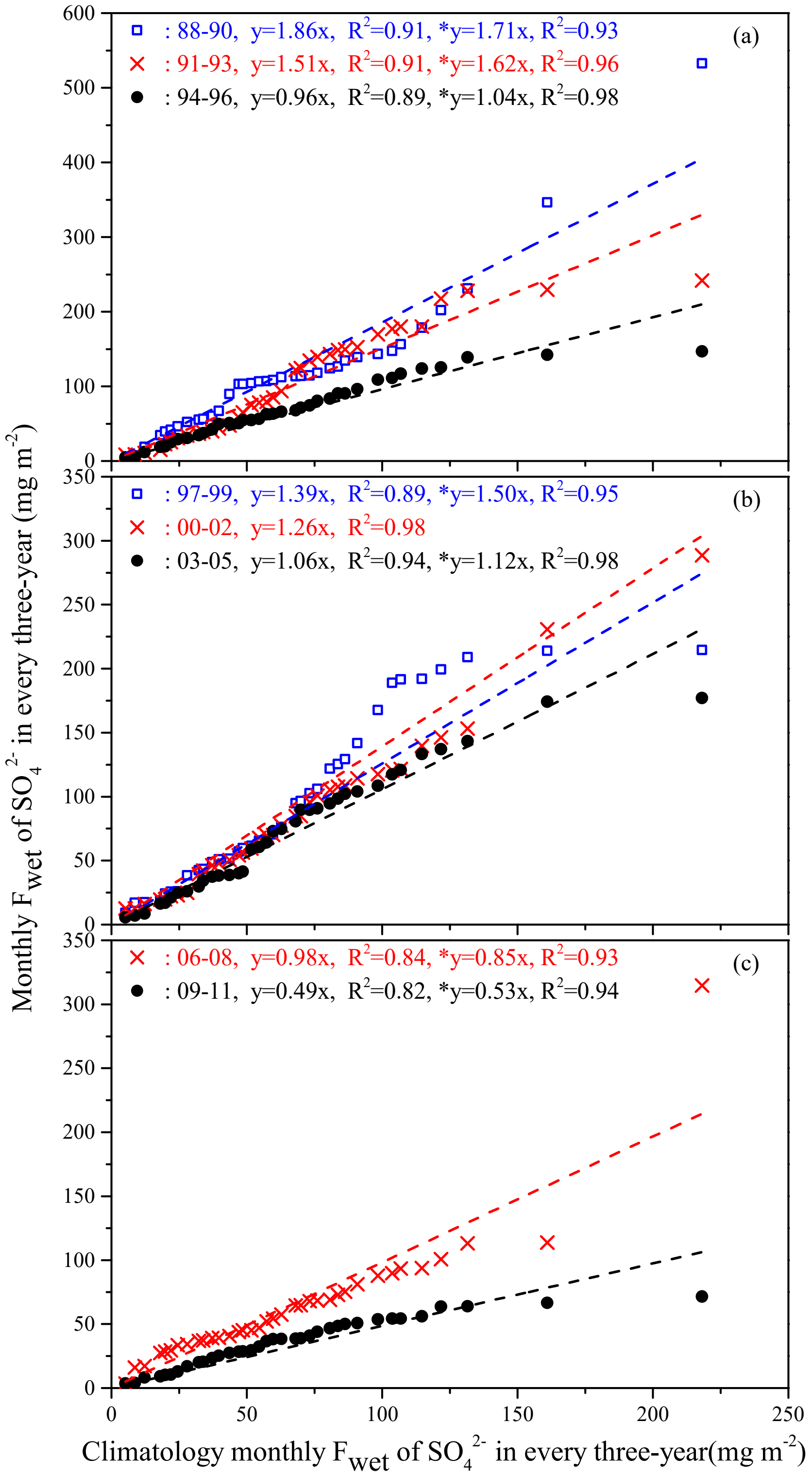

Fig S3. Fitting monthly F_{wet} of SO_4^{2-} against climatology values using LR with zero interception at Site 1 according to Approach D (* reflects the maximum value being excluded for LR analysis with zero interception).

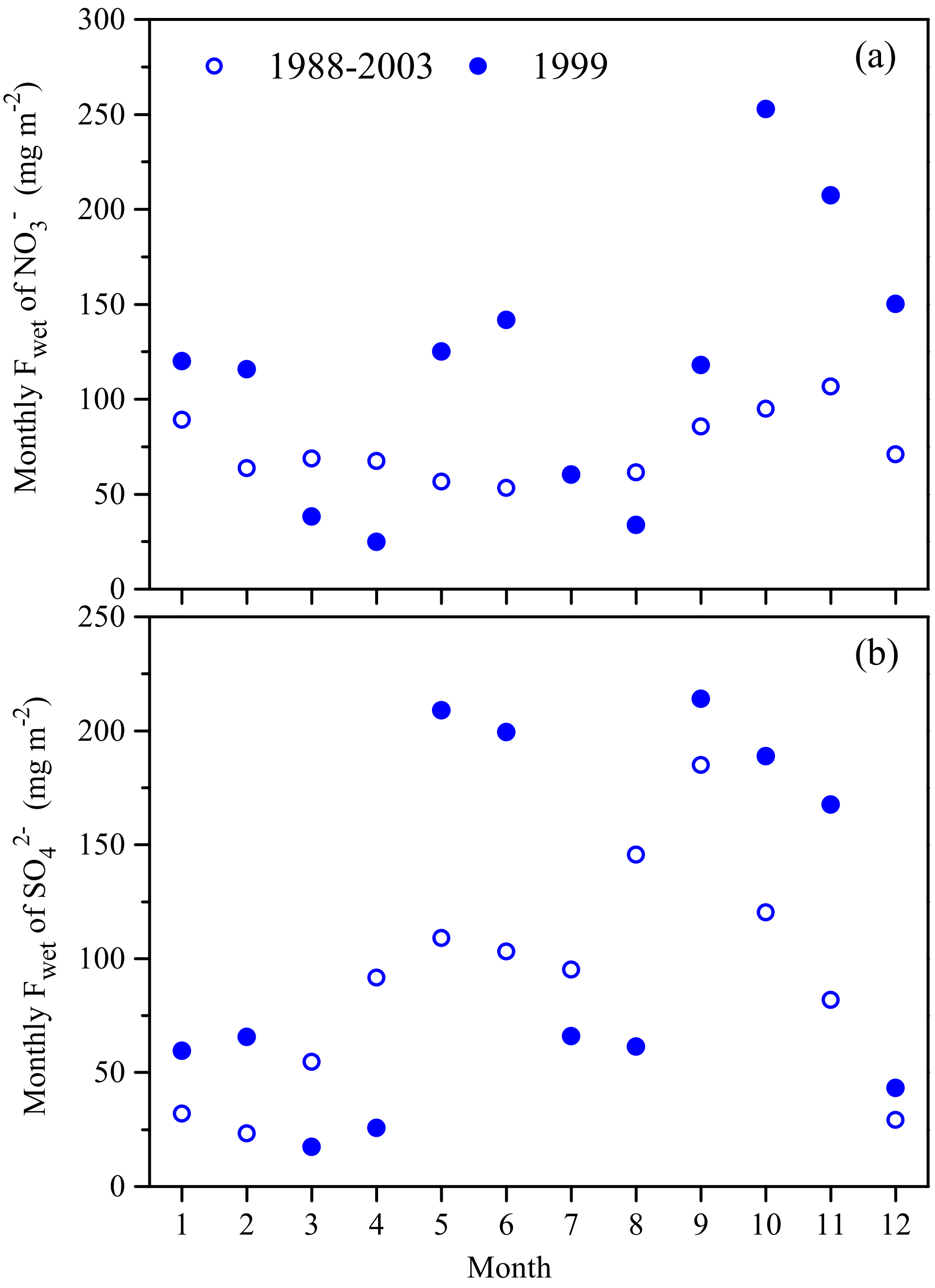

Fig S4. Monthly variations in F_{wet} of NO_3^- and SO_4^{2-} at Site 1 in 1988-2003 excluding 1999 and those in 1999.

2) Summary for trends in the wet deposition of SO_4^{2-}, NO_3^- and NH_4^+ at Sites 3 and 4

At Site 3 located in northern Ontario, SO_4^{2-} and NO_3^- showed decreasing trends from 1984 to 2011 with R^2 of 0.86 and 0.56 ($P<0.01$), respectively, from LR analysis. The decreasing trends were also confirmed by M-K method analysis. NH_4^+ exhibited no trend from M-K analysis and no significant trend from LR analysis.

The trends in the m-values of SO_4^{2-} also exhibited the three-phase pattern, i.e., with the values decreased by approximately 30% from 1984-1985 (the start of in Phase 1 covering 1984-1991) to 1992-1993 (the start of Phase 2 covering 1992 to 2003) and narrowly oscillated around 0.99±0.05 during Phase 2. The values linearly decreased by approximately 10% every two-year staring from the end of Phase 2 to Phase 3 in 2004-2011.

The trends in the m-values of NO_3^- reproduced the two-phase pattern similar to those at Site 1, i.e., the values oscillated around 1.08±0.07 from 1984 to 2003 in Phase 1, and the values non-lineally decreased by approximately 40% from the end of Phase 1 to the end of Phase 2 in 2004-2011.

The annual F_{wet} of SO_4^{2-} and NO_3^- also exhibited decreasing trends as revealed by LR analysis and M-K method analysis at Site 3. However, the three-phase trends in F_{wet} of SO_4^{2-} and related inflection points, as have been identified by the m-value, were not identified by directly applying F_{wet} values.

Similar results to those at Site 3 were also identified at Site 4 (Fig S6). For example, the three-phase pattern of m-value of SO_4^{2-} and the two-phase pattern of m-value of NO_3^- can also be clearly identified at Site 4. However, it is not the case for annual F_{wet} of SO_4^{2-} and NO_3^-. In addition, large decreases in m-values and annual F_{wet} of NH_4^+ occurred from 2000 to 2011 at Site 4, leading to an overall decreasing trend in m-value with two outliers being excluded and a probable decreasing trend in annual F_{wet} of NH_4^+. However, the annual emissions of NH_3 in Ontario were almost constant during 1990-2007, e.g., at the level of $1.03 \pm 0.03 * 10^5$ T per year, which cannot explain ~40% variation in m-value and ~90% variation in annual F_{wet} during that period. Actually, no significant correlation existed with $P<0.05$ between the annual F_{wet} of NH_4^+ at Site 4 and the annual emissions of NH_3 in Ontario during the period of 1990-2011.

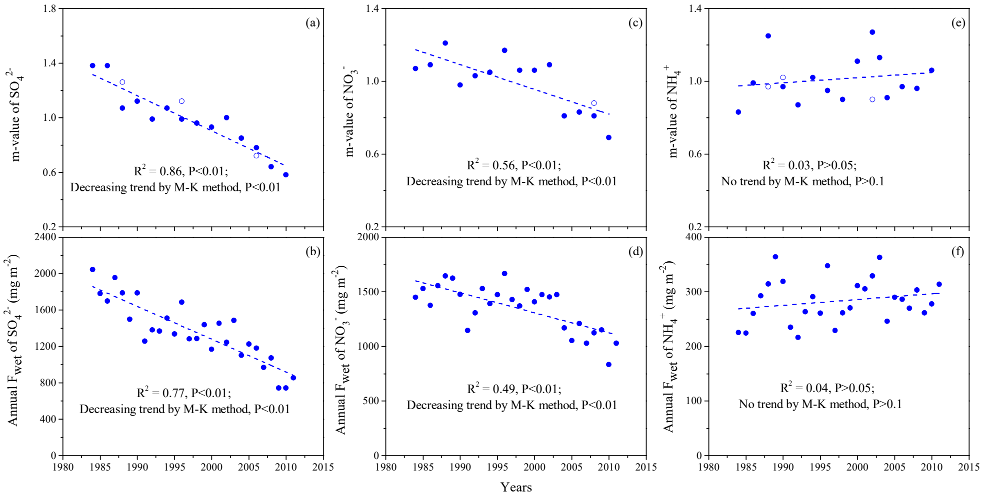

Fig S5. m-values and annual F_{wet} extracted trends at Site 3. a, c and e: full and empty markers represent the calculated m-values without and with the outlier, respectively, as detailed in Section 2; R^2 reflects coefficient of determination of variable with calendar year from LR analysis.

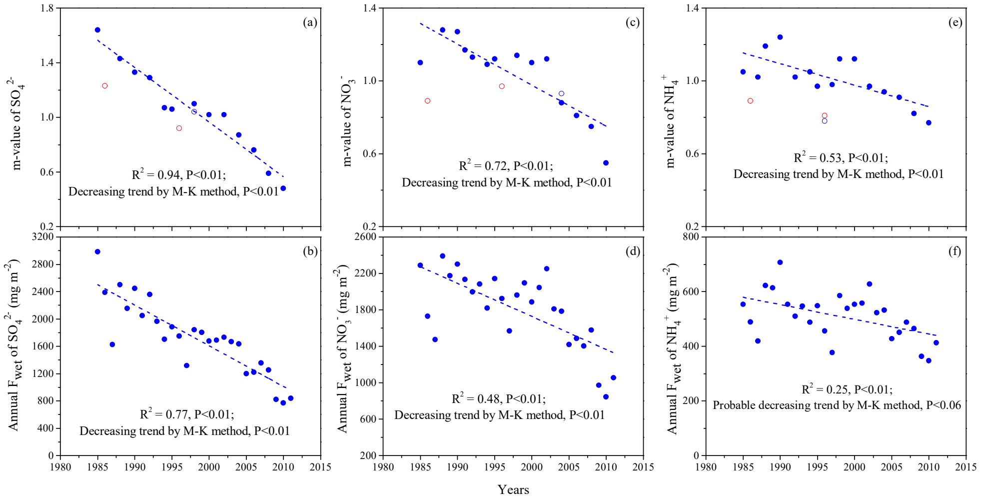

Fig S6. m-values and annual F_{wet} extracted trends at Site 4. a, c and e: full and empty markers in blue represent the calculated m-values without and with the outlier, respectively; empty marker in red represents abnormal m-value and is excluded for trend analysis as detailed in Section 2; R^2 reflects coefficient of determination of variable with calendar year from LR analysis.

Table S1. Sites and data descriptions.

Site ID and location	Province	Latitude	Longitude	Elevation (m)	Coastal/ inland use	Wet deposition data
Site 1 at Chapais	Québec	49.82	74.98	381	Inland Forest	Jan 1988–Dec 2011
Site 2 at Saturna	British Columbia	48.78	123.13	178	Coastal Forest	Jan 1990–Dec 2011
Site 3 at Chalk River	Ontario	46.06	77.41	184	Inland Forest	Jan 1984–Dec 2011
Site 4 at Algoma	Ontario	47.04	84.38	411	Inland Forest	Jan 1985–Dec 2011