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

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1. Comparative analysis of different approaches estimating m-value

Results from the new approach discussed in the main body of the paper are referred to as Approach C. However, annual F_{wet} of ions are conventionally used to extract trends. m-values calculated by Approach C and annual F_{wet} of ions cannot be compared directly. Alternatively, two approaches, i.e., Approach A and B, are designed to calculate m-values to compare with Approach C. As presented below, the trend results derived from m-values calculated by Approach B would be exactly same as those derived from annual F_{wet} of ions. Thus, the comparison results between Approach C and Approach B would be applicable for those between Approach C and the use of annual F_{wet} of ions. Through analyzing the uncertainty sources of m-values in different approaches, which approach has the advantage can be better illustrated.

Approach C is compared with the other two 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 such as the time shift in rain, dry or snow seasons, etc., which led to largely varying monthly F_{wet} of SO_4^{2-} during the 24 years. For example, the lowest R^2 value of 0.14 in 1996 was mainly due to lower wet deposition fluxes in August and May-June than corresponding decade averages in 1988-1997 (Fig. S2a). These lower monthly fluxes in 1996 were evidently associated with lower monthly precipitation depths relative to those of decade averages (Fig S2ab). Moreover, the monthly geometric average concentrations in six months of 1996 narrowly varied around 0.63 ± 0.05 mg L^{-1} (Fig. S2c). Although the monthly precipitation depth in July of 1996 was even larger than the decade average in July of 1988-1997, the lower geometric average concentration of SO_4^{2-} in precipitation in July of 1996 (0.4 mg L^{-1}) overwhelmed the effect of precipitation depth and led to the lower monthly flux. Including July, the geometric averages largely oscillated from 0.27 mg L^{-1} to 1.77 mg L^{-1} in the other six months. 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 (not shown). Thus, the larger geometric average of SO_4^{2-} in March of 1996 was unlikely due to increases in monthly emissions of SO_2. Alternatively, atmospheric processes affected by unidentified climate anomalies very likely caused the larger geometric average value. The effects of the larger geometric average of SO_4^{2-} and the smaller precipitation depth in March canceled out each other, leading to the flux close to the decade average in that month.

The calculated m-value has a large standard deviation, i.e., approximately 60% of the m-value, with $R^2=0.14$ in 1996. With such a low value of R^2, the calculated m-values mixed with large perturbations from monthly scale climate anomalies are not suitable

for extracting the long-term trend.

The m-values from using Approach B are shown in Fig S3a-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. Also using the data in 1996 as an example, Approach B resulted in R^2 values of up to 0.77, which are still not high enough. The calculated m-value also had a large standard deviation, i.e., approximately 20% of the m-value. The large standard deviation was also very likely caused by those climate anomalies as mentioned above.

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 (Fig. S4). 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 a 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 S5a-c). After excluding these outliers, the values of R^2 in each regression equation were almost the same as those obtained from

Approach C.

In summary, low R^2 values led to large uncertainties of calculated m-values when Approaches A and B were used. However, the same trend in wet deposition of ions would be gained regardless of using m-values calculated from Approach B or annual wet deposition fluxes. Compared with Approach B, Approach C largely increased R^2 values and thereby largely decreased uncertainties of calculated m-values. Compared with Approach D, the R^2 values from approach C were almost the same, but Approach C would generate more datasets for trend analysis. Overall, Approach C is the optimum approach among the methods discussed above.
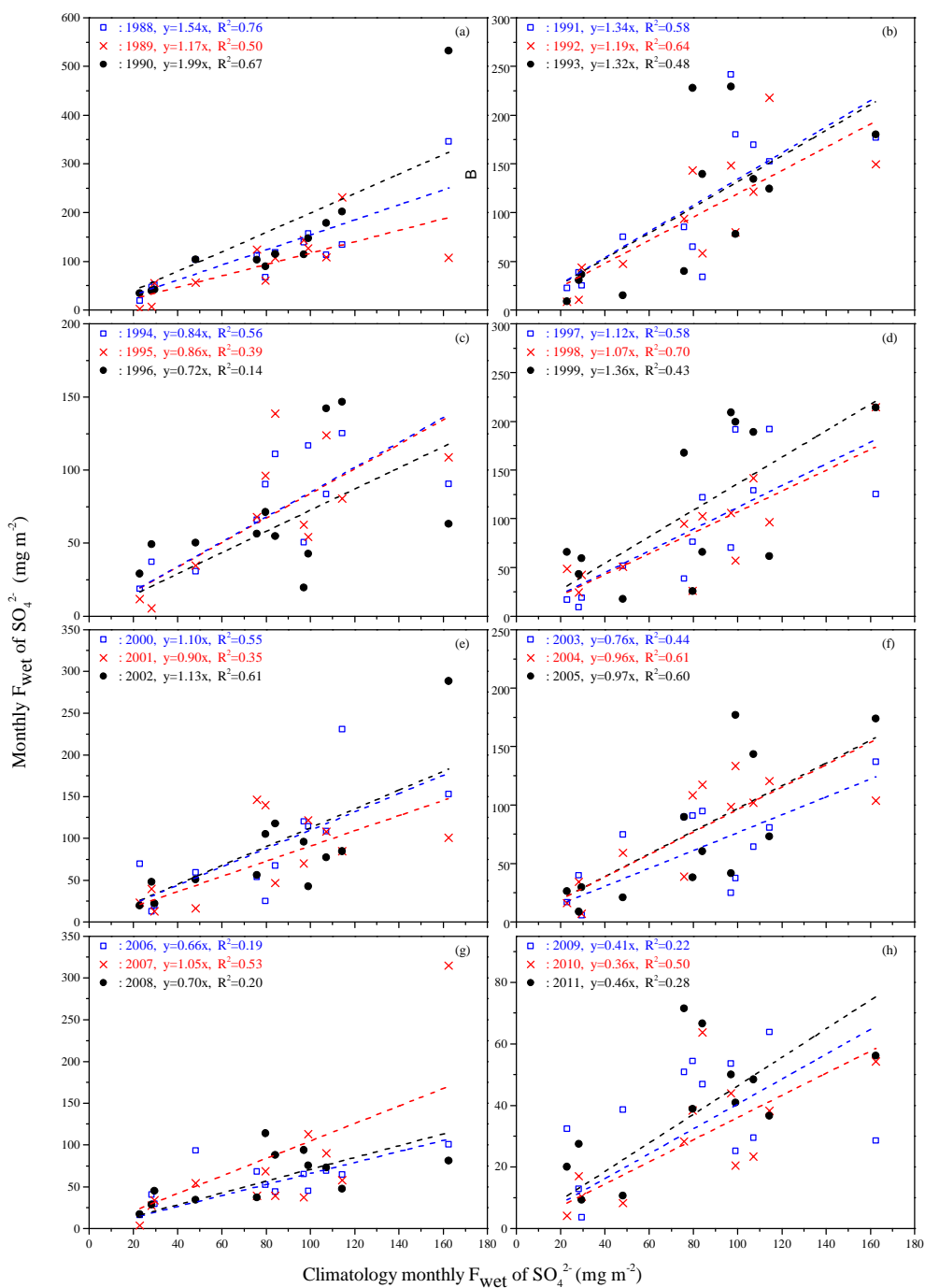
Fig. S1. Fitting monthly F_{wet} of SO_4^{2-} against climatology values using LR with zero interception at Site 1 according to Approach A (x, y and R^2 in legend represent climatology monthly F_{wet}, monthly F_{wet} in every year and the coefficient of determination in LR analysis, respectively)
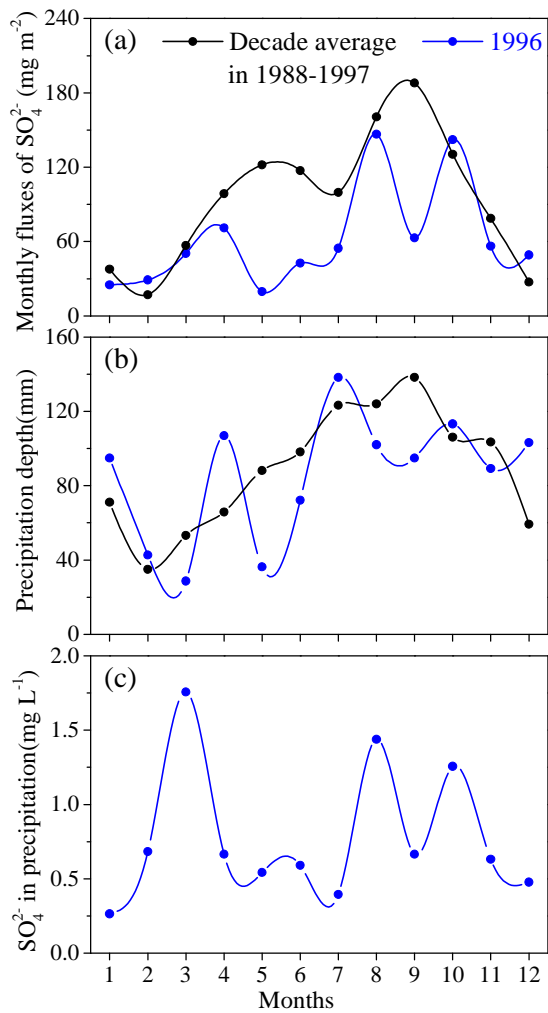
Fig. S2. Monthly variations in fluxes of SO_4^{2-}, precipitation depth and concentrations of SO_4^{2-} in precipitation (decade average fluxes of SO_4^{2-} and the values in 1996 are shown in a); decade average precipitation depth and the values in 1996 are shown in b); the monthly geometrically averaged concentrations of SO_4^{2-} in 1996 are shown in c).

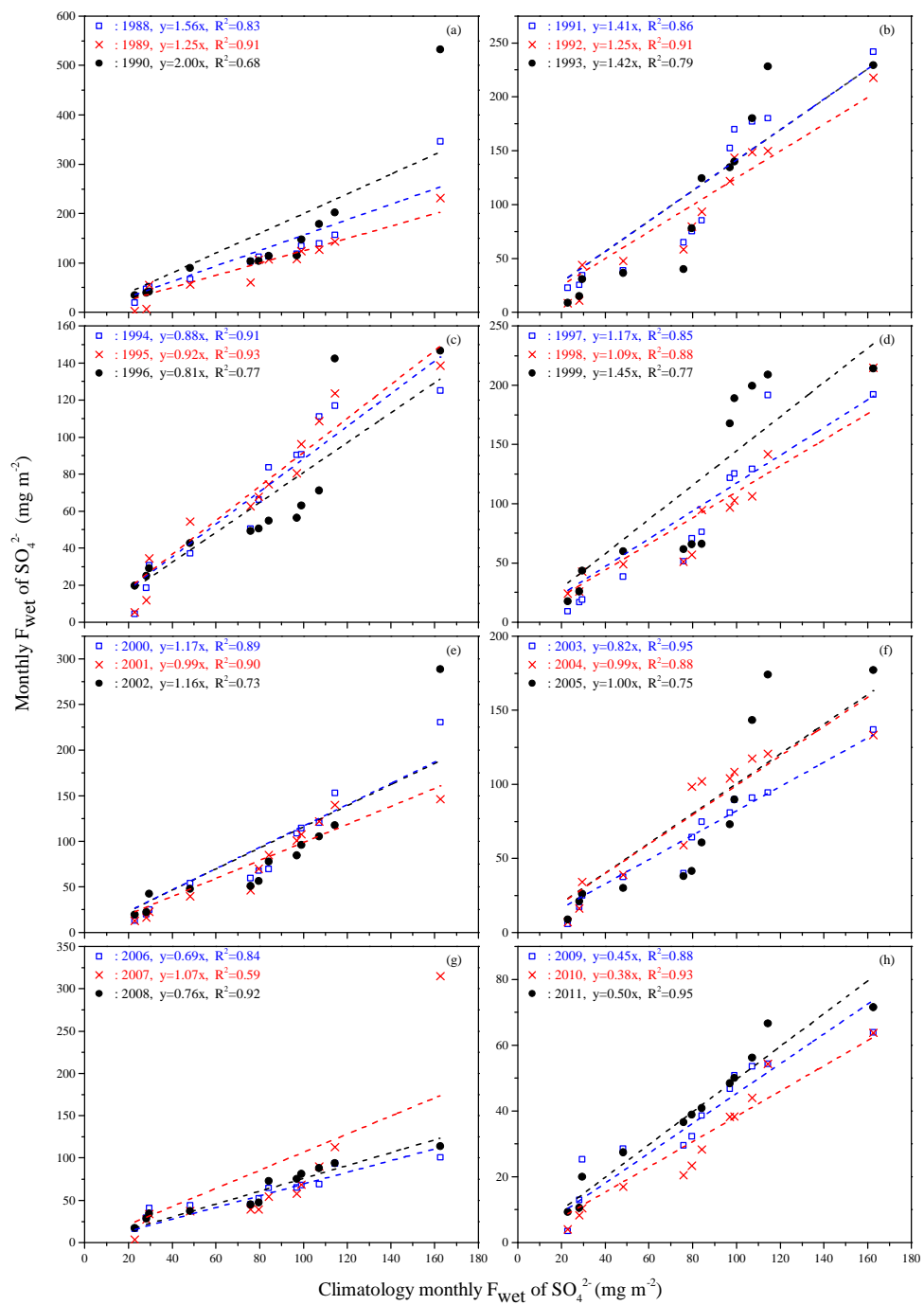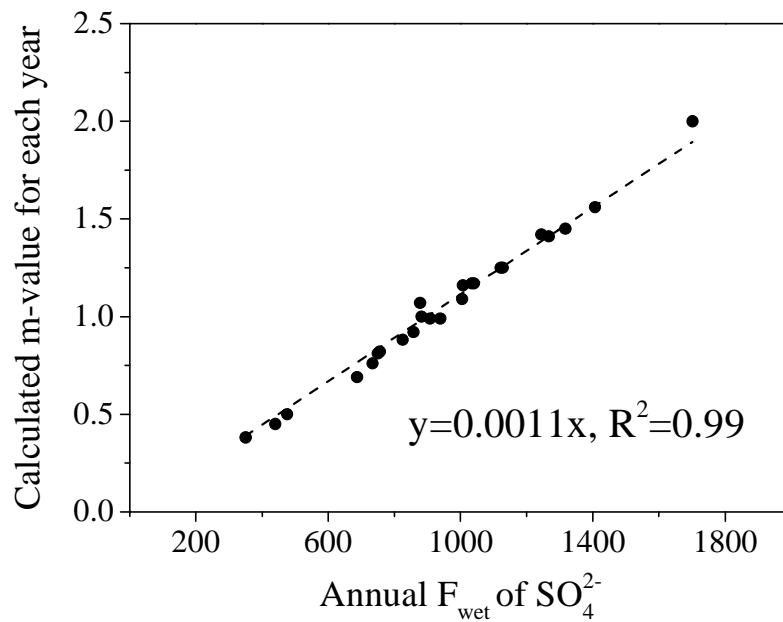Fig. S3. Same as in Figure S1 except for using Approach B.

Fig. S4. LR analysis of annual F_{wet} of SO_4^{2-} and m-values of SO_4^{2-} calculated by Approach B at Site 1 (x, y and R^2 in legend represent annual F_{wet} of SO_4^{2-}, m-values calculated by Approach B and the coefficient of determination in LR analysis, respectively).

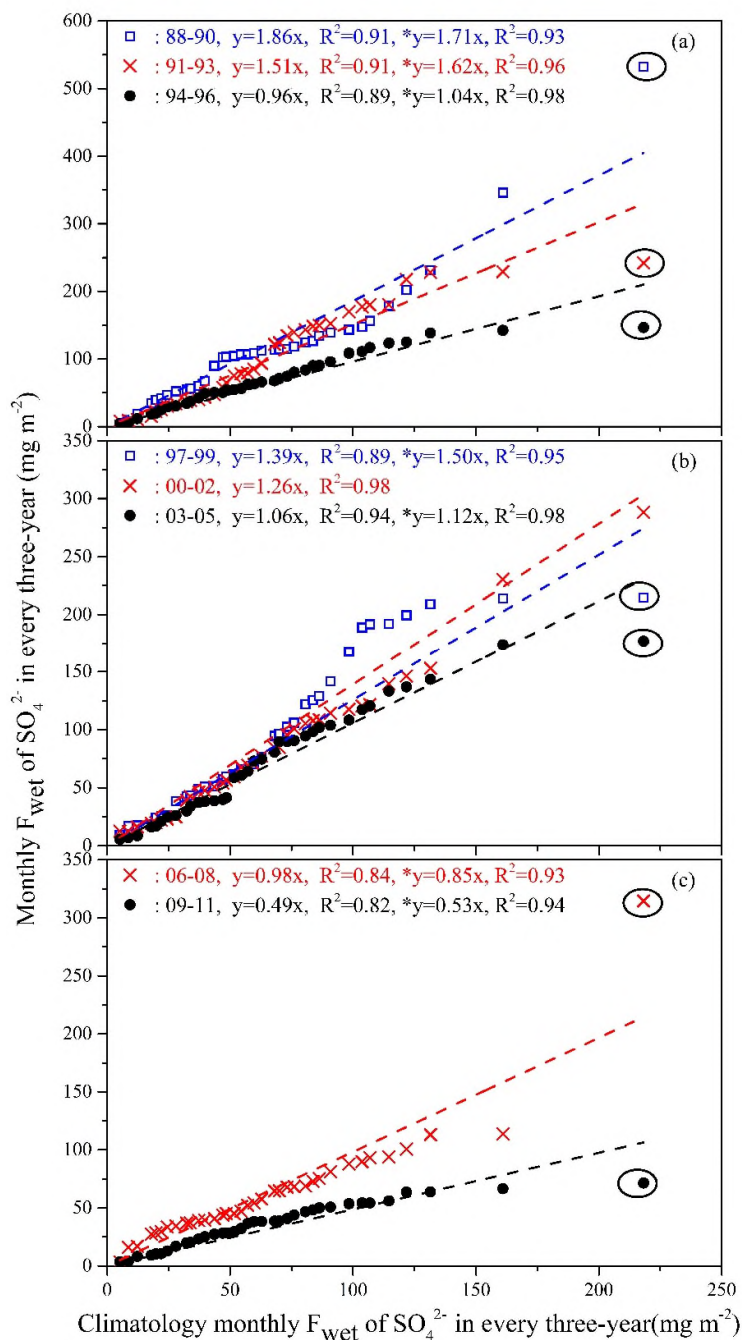Fig. S5. Fitting monthly F_{wet} of SO_4^{2-} against climatology values using LR with zero interception at Site 1 according to Approach D (x, y and R^2 in legend represent climatology monthly F_{wet}, monthly F_{wet} in every three-year and the coefficient of determination in LR analysis, respectively; and all P values <0.01; * reflects the maximum value (cycled marker) excluded for LR analysis.)
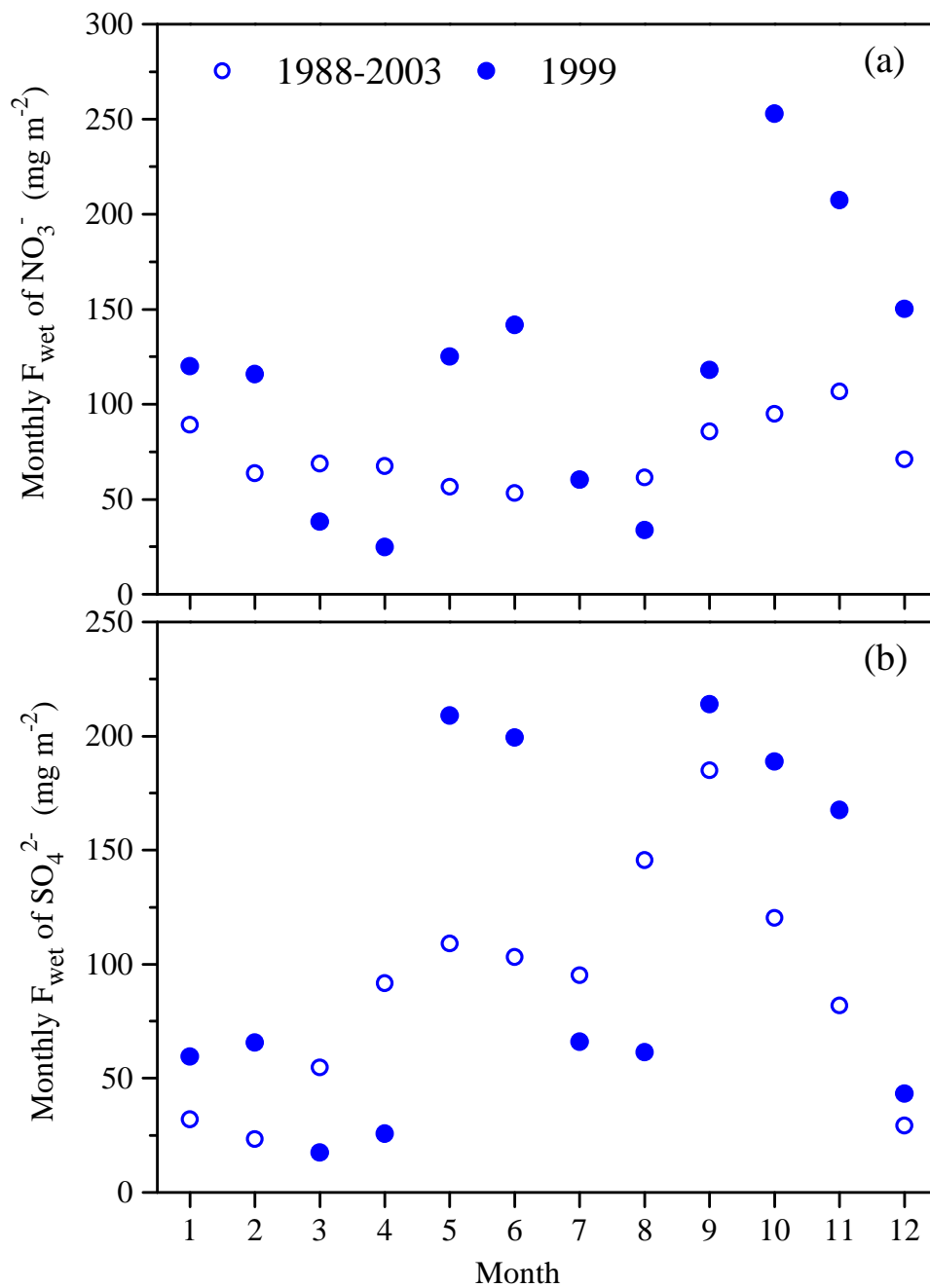
Fig. S6. Monthly variations in F_{wet} of NO_3^- and SO_4^{2-} at Site 1 in 1999 and corresponding long-term averaged monthly variations in 1988-2003 excluding 1999.

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

At Site 3 located in northern Ontario, m-values of 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 (Fig S7). 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 S8). 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 $1.03\pm0.03 *10^5$ 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.

In order to examine the advantage of m-values over F_{wet}, the two parameters were correlated to emissions of air pollutants, respectively. Using 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 m-values over annual Fwet 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.
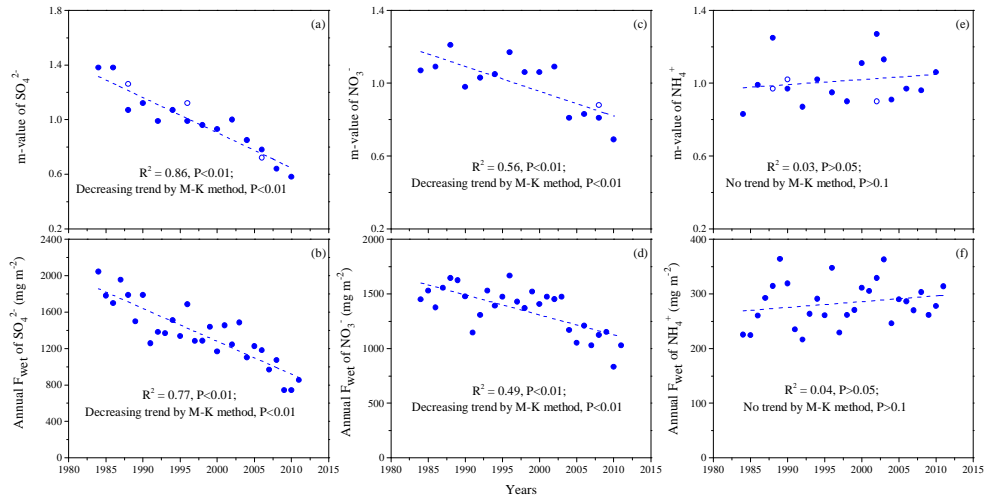
Fig. S7. m-values and annual F_{wet} extracted trends at Site 3. a, c and e: full and empty markers represent the calculated m-values without and with the outlier, respectively, as detailed in Section 2; R^2 reflects coefficient of determination of variable with calendar year from LR analysis; M-K analysis results are shown in (a-f).
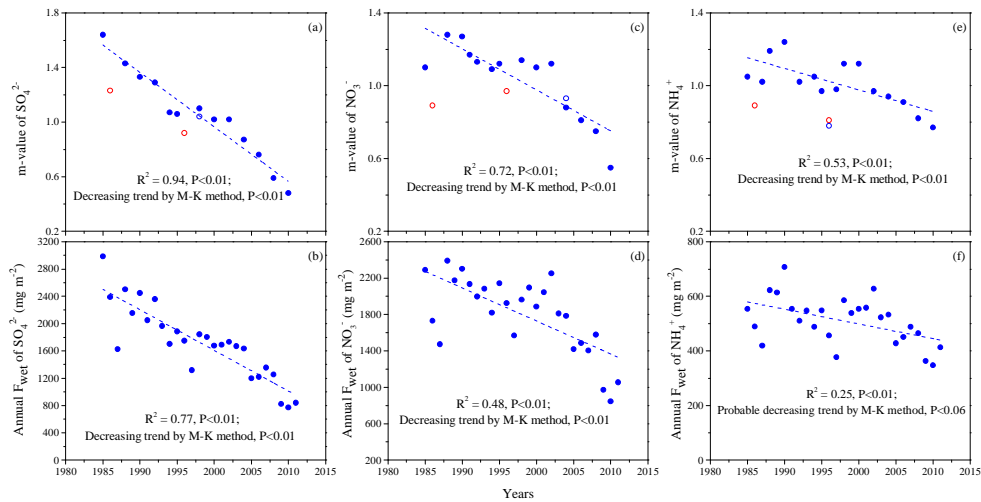
Fig. S8. m-values and annual F_{wet} extracted trends at Site 4. a, c and e: full and empty markers in blue represent the calculated m-values without and with the outlier, respectively; empty marker in red represents abnormal m-value and is excluded from trend analysis as detailed in Section 2; R^2 reflects coefficient of determination of variable with calendar year from LR analysis; M-K analysis results are shown in (a-f).

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

Table S2. Phase classification for m-values of wet deposition SO_4^{2-} and NO_3^- at different sites.

Site ID and location	m-values of wet deposition SO_4^{2-}	m-values of wet deposition NO_3^-
Site 1 at Chapais	Phase 1:1998-1993, Phase 2:1994-2005, Phase 3:2006-2011	Phase 1:1988-2003, Phase 2:2004-2011
Site 2 at Saturna	Phase 1:1990-2001: Phase 2002-2011	Phase 1:1990-2001: Phase 2002-2011
Site 3 at Chalk River	Phase 1:1984-1991, Phase 2:1992-2003, Phase 3:2004-2011	Phase 1:1984-2003, Phase 2:2004-2011
Site 4 at Algoma	Phase 1:1985-1993, Phase 2:1994-2003, Phase 3:2004-2011	Phase 1:1985-2003, Phase 2:2004-2011