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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   **Abstract.** Long-term trends of wet deposition of inorganic ions are affected by

2   multiple factors, among which emission changes and climate conditions are dominant

3   ones. To assess the effectiveness of emission reductions on the wet deposition of

4   pollutants of interest, contributions from these factors to the long-term trends of wet

5   deposition must be isolated. For this purpose, a two-step approach for preprocessing

6   wet deposition data is presented herein. This new approach aims to reduce the impact

7   of climate anomalies on the trend analysis so that the impact of emission reductions on

8   the wet deposition can be revealed. This approach is applied to a two-decade wet

9   deposition dataset of sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) at rural

10   Canadian sites. Analysis results show that the approach allows for robustly identifying

11   inflection points on decreasing trends in the wet deposition fluxes of SO_4^{2-} and NO_3^- in

12   northern Ontario and Québec. The inflection points match well with the three-phase

13   mitigation of SO_2 emissions and two-phase mitigation of NOx emissions in Ontario.

14   Improved correlations between the wet deposition of ions and their precursors'

15   emissions were obtained after reducing the impact from climate anomalies.

16   Furthermore, decadal climate anomalies were identified as dominating the decreasing

17   trends in the wet deposition fluxes of SO_4^{2-} and NO_3^- at a western coastal site. Long-

18   term variations in NH_4^+ wet deposition showed no clear trends due to the compensating

19   effects between NH_3 emissions, climate anomalies, and chemistry associated with the

20   emission changes of sulfur and nitrogen.

21

1.   Introduction

23   To assess the long-term impacts of acidifying pollutants on the environment, the wet

24   deposition of sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+), among other

25   inorganic ions, has been measured for several decades through monitoring networks

26   such as the European Monitoring and Evaluation Programme (EMEP) (Fowler et al.,

27   2005, 2007; Rogora et al., 2004, 2016), the National Atmospheric Deposition

28   Program/National Trends Network in the U.S. (Baumgardner et al., 2002; Lehmann et

29   al., 2007; Sickles & Shadwick, 2015), and the Canadian Air and Precipitation

30   Monitoring Network (CAPMoN) (Vet et al., 2014; Zbieranowski and Aherne, 2011).

31   The high-quality data collected from these networks have been widely used to quantify

32   the atmospheric deposition of acidifying pollutants (Lajtha & Jones, 2013; Lynch et al.,

33   2000; Pihl Karlsson et al., 2011; Strock et al., 2014; Vet et al., 2014). The data have

34   also been utilized to identify trends in the atmospheric deposition of reactive nitrogen

35   (Fagerli & Aas, 2008; Fowler et al., 2007; Lehmann et al., 2007; Zbieranowski and

36   Aherne, 2011) and to examine the impacts of acid rain and the perturbation of the

37   natural nitrogen cycle on sensitive ecosystems (Wright et al., 2018). The long-term data

38   can also be used for assessing the effectiveness of environmental policies (Butler et al.,

39   2005; Li et al., 2016; Lloret & Valiela, 2016).

40

41   The wet deposition of SO_4^{2-}, NO_3^- and NH_4^+ is affected by not only their gaseous

42   precursors' emissions (Butler et al., 2005; Fowler et al., 2007; Li et al., 2016) but also

43   complex atmospheric processes (Cheng & Zhang, 2017; Yao & Zhang, 2012; Zhang et

44   al., 2012). Those atmospheric processes sometimes lead to extremely high wet

45   deposition fluxes of ions during a precipitation event or even throughout a particular

46   month. Furthermore, climate anomalies can alter the relative contributions of local

47   sources versus long-range transport to the total wet deposition amounts at reception

48   sites, thereby complicating the relationships between wet deposition and the emission

49   of air pollutants of interest (Lloret & Valiela, 2016; Monteith et al., 2016; Wetherbee

50   & Mast, 2016). The emissions of SO_2 and NOx have been decreasing substantially in

51 Europe and North America (Butler et al., 2005; Li et al., 2016; Pihl Karlsson et al.,

52 2011); coincidently, climate anomalies have also occurred more frequently in recent

53 decades (Burakowski et al., 2008; Lloret & Valiela, 2016; Wijngaard et al., 2003),

54 thereby leading to more complicated linkages between wet deposition and emission

55 trends on decadal scales.

56

57 Many trend analysis studies in the literature simply examined annual or seasonal values

58 as the data inputs for two popular trend analysis tools, i.e., the Mann-Kendall (M-K)

59 and linear regression (LR) methods (Marchetto et al., 2013; Waldner et al., 2014 and

60 references therein). These studies focused on the detection of statistically significant

61 trends; for example, Waldner et al. (2014) conducted a comprehensive analysis on the

62 applicability of the techniques to different choices of length and temporal resolutions

63 of a data series. Regarding the resolved trend results, these approaches are not well

64 suited to separating the impact of air pollutants' mitigation from the perturbation by

65 climate anomalies. Large uncertainties thus existed in the studies interpreting the major

66 driving forces determining the extracted trends in the wet deposition of SO_4^{2-}, NO_3^- and

67 NH_4^+. Regarding that air pollutant's emission mitigation targets often vary in different

68 phases of the entire study period, inflection points may exist in the trends in the wet

69 deposition of ions. The inflection points were rarely studied, despite their importance

70 for assessing the effectiveness of environmental policies. An alternative would be to

71 use high time resolution data in the Ensemble Empirical Mode Decomposition (EEMD)

72 method (Wu & Huang, 2009); however, this method still suffers from the end effect in

73 certain scenarios, whereby the extracted trends cannot be explained (Yao & Zhang,

74 2016).

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76   A new approach is presented herein that aims to reduce the perturbations from climate

77   anomalies on data inputs so that robust trends can be elucidated for evaluating the

78   effectiveness of emission control policies. In this approach, raw data are preprocessed

79   to generate a new variable, which is then applied to M-K and LR methods. A piecewise

80   linear regression (PLR) is also used to extract trends for cases in presence of inflection

81   points. The extracted trends in the wet deposition data on a decadal scale are then

82   properly linked to major driving forces such as emission reductions and climate

83   anomalies. This new approach is first applied to the wet deposition data of SO_4^{2-}, NO_3^-

84   and NH_4^+ in Canada, as an example to demonstrate its capability and advantages over

85   the traditional approaches. The extracted trends in the wet deposition of ions are further

86   studied through correlation analysis with known emission trends of their respective

87   gaseous precursors (SO_2, NOx and NH_3) in Canada and the U.S. Major driving forces

88   for the trends of ion wet deposition and how the wet deposition ions responded to their

89   precursors' emissions in Canada are then revealed.

90

91   **2.   Methodology**

92   Wet   deposition   flux   (F_{wet})   data   were   obtained   from   CAPMoN

93   (https://www.canada.ca/en/environment-climate-change/services/air-

94   pollution/monitoring-networks-data/canadian-air-precipitation.html). Data from four

95   sites have been collected for over twenty years and were chosen herein to illustrate the

96   novel trend analysis method (Table S1). Site 1 is an inland forest site at Chapais in

97   Québec. Site 2 is situated in a coastal forest area at Saturna in British Columbia. Sites

98   3 and 4 are two inland forest sites at the Chalk River and at Algoma, respectively, in

99   northern Ontario. Details on data sampling, chemical analysis and quality control can

100   be found in previous studies (Cheng & Zhang, 2017; Vet & Ro, 2008; Vet et al., 2014).

101 The emissions data of gaseous precursors were downloaded from the Air Pollutant

102 Emission Inventory (APEI, https://pollution-waste.canada.ca/air-emission-inventory/)

103 in Canada and from the USEPA National Emissions Inventory (NEI,

104 https://www.epa.gov/air-emissions-inventories/air-emissions-sources) in the U.S.

105 These data were demarcated at a provincial level in Canada and at a state level in the

106 U.S. Data for the years of 1990 to 2011, which correspond to the period of selected F_{wet}

107 data, were used in this study.

108

109 The M-K method is a popular nonparametric statistical procedure that can yield

110 qualitative trend results, such as "an increasing/decreasing trend with a P value of

111 <0.05," "a probable increasing/decreasing trend with a P value of 0.05-0.1," "a stable

112 trend with a P value of >0.1, as well as a ratio of <1.0 between the standard deviation

113 and the mean of the dataset," and "a no trend for P>0.1 with all other conditions"

114 (Kampata et al., 2008; Marchetto et al., 2013). The LR method has also been widely

115 used to extract trends (Marchetto et al., 2013; Waldner et al., 2014). Zbieranowski and

116 Aherne (2011) used LR to extract trends by separating different phases because of the

117 presence of inflection points in the entire study period, and the approach is same as PLR

118 (Vieth, 1989). In this study, the three methods were employed to compute the trends

119 of ion wet deposition using software downloaded from https://www.gsi-

120 net.com/en/software/free-software/gsi-mann-kendall-toolkit.html and Excel 2016, first

121 using the annual F_{wet} directly as input data, then using a modified input data set, as

122 described below.

123

124 The modified input data set was produced in two steps. The first step was an effort to

125 reduce the perturbation from the monthly climate anomalies to the input data. This was

126   done by creating a new variable that was defined as the slopes of the regression

127   equations of a series of study years against a climatology (base) year using monthly

128   F_{wet} data. Note that the monthly F_{wet} data were aggregated from daily raw data before

129   the regression analysis. To ensure the presence of enough data points in each regression

130   equation, the data corresponding to two-year periods (or 24 monthly F_{wet} values) were

131   grouped together, as detailed below. At a selected site and for a given chemical

132   component, monthly F_{wet} data were generated for the first two years and were grouped

133   together and rearranged from the smallest to the largest values to form an array of data

134   with 24 data points, i.e., A(i) with i=1 to 24. Repeating the above procedure for the

135   subsequent years using a two-year interval to eventually obtain a series of data arrays,

136   A(i) now becomes A(i, j) with i=1 to 24 and j=1 to N, where N is the total number of

137   data arrays. The climatology data array (CA(i)) was then defined as the average of all

138   of the arrays as follows:

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

140

141   LR with zero interception was applied for each individual data array against the

142   climatology data array. In cases where the maximum monthly deposition flux deviated

143   greatly from the general regression curve, the slopes (m-values) were calculated after

144   excluding the maximum monthly deposition flux, which is an approach that reduced

145   the perturbation to the m-values from the monthly scale climate anomalies. The second

146   step was to screen out the outliers in m-values, which reduced the perturbation to the

147   m-values from the annual-scale climate anomalies.

148

149   An analysis of Site 1 is used to illustrate the new approach and demonstrate its

150   advantages against the existing common approaches used in the literature. Twelve four-

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151   year periods of data (1988-1989, 1990-1991, etc.) are available from this site. The

152   regression of each data set against the climatology data set was first performed using

153   all of the monthly values to obtain an m-value (the slope) (Fig. 1a-d). For eight out of

154   the 12 data sets, the m-values were recalculated after excluding the maximum monthly

155   value of F_{wet}, which appeared to be an apparent outlier of the linear regression. The R^2

156   values, which are conventionally used in LR, were then significantly increased for these

157   eight sets, e.g., from the original values of 0.79-0.94 to the improved values of 0.92-

158   0.98. To demonstrate that the excluded maximum value was an outlier, the case of the

159   1990-1991 data set was taken as an example. The new regression equation (y=1.47x,

160   R^2=0.98, Fig. 1a) predicted a maximum value in the range of 330-368 mg m^{-2} month^{-1}

161   using three times the standard deviation (±3 SD, 0.08) at a 99% confidence level. The

162   actual observed maximum value of 532 mg m^{-2} month^{-1} was much larger than the upper

163   range of the predicted value and was thus believed to be caused by monthly scale

164   climate anomalies. The maximum value was treated as an outlier and excluded for

165   analysis. Using the similar procedure, all outliers in this study were identified. The

166   exclusion of the observed maximum value greatly reduced the perturbation of the short-

167   term climate anomalies to the calculated m-value in this two-year period, i.e., the m-

168   value decreased from 1.67 to 1.47, which in turn increased the relative contribution of

169   the air pollutants' emissions to the calculated m-value. In summary, this new approach

170   meets the objective of identifying outlier data points by applying the criteria of being

171   outside the boundaries of ±3 times the standard deviation of the general trend.

172

173   The revised m-values were further scrutinized by eliminating the outliers caused by the

174   annual-scale climate anomalies. For example, the m-value of 1.31 in 1998-1999 greatly

175   deviated from other m-values, narrowly oscillating approximately 0.96±0.07 (average

176 ± 1 SD) during the period of 1994-2005, even with the ±3 SD being considered (Fig.

177 1a-d). Using the value of 0.96 as the reference, climate anomalies likely increased the

178 F_{wet} of SO_4^{2-} by 37% in 1998-1999. The m-values were then calculated by shifting one

179 year in time to 1997-1998 (1.07) and to 1999-2000 (1.24). The F_{wet} in 1998 was less

180 affected by climate anomalies than that in 1999. Thus, the m-value in 1997-1998 was

181 within 0.96±0.21 (average ± 3 SD) and used to replace the m-value in 1998-1999 for

182 the trend analysis. Similar to the first step discussed above, this approach meets the

183 objective of identifying outlier m-values by applying the criteria of being outside the

184 range of ±3 SD plus the average m-value during a decade or a longer period.

185

186 More justification of the new approach can be found in the Supporting Information,

187 including Figs. S1-3, wherein the statistical comparison between this and other

188 approaches was presented. Theoretically, the extracted trend using the data

189 preprocessed with the new approach is determined by the local emissions of air

190 pollutants, the regional transport of air pollutants, and a small portion of climate

191 anomalies that are unable to be removed by the new approach. It is assumed that the

192 extracted trend is less affected by microphysical/chemical processes, since two-year

193 data were used together to calculate the m-value.

194

195 In theory, if the data from different sites in the same region are grouped together for

196 trend analysis, the results may be better linked to the trends of the regional emissions

197 of related air pollutants. In the following sections, trend analysis results from individual

198 sites as well as those from grouped sites are discussed. Sites 1, 3 and 4 showed similar

199 trends in the wet deposition of SO_4^{2-} and NO_3^-, and these three sites were grouped

200 together.

201 **3. Results and discussion**

202 *3.1 Trends at Site 1 after reducing perturbations from climate anomalies*

203 Trends in the m-values shown in Fig. 2 represent the trends after removing the

204 perturbations from climate anomalies at Site 1 in northern Québec from 1988 to 2011.

205 SO_4^{2-} and NO_3^- showed decreasing trends from a LR analysis, with R^2 values of 0.81

206 and 0.71, respectively, and P values <0.01. The decreasing trends were also confirmed

207 by the M-K method analysis. NH_4^+ exhibited a stable trend from M-K analysis, as well

208 as no significant trend with P value >0.05 from LR analysis.

209

210 The m-values of SO_4^{2-} and NO_3^- also allowed for the identification of trends in different

211 phases. The inflection point for each phase is critical to a) link the annual F_{wet} of ions

212 and the emissions of the corresponding precursors and b) assess the effectiveness of

213 environmental policies. For example, the trends in the m-values of SO_4^{2-} can be clearly

214 classified into three phases. The m-values oscillated approximately 1.38±0.08 during

215 Phase 1 (1988 to 1993) and approximately 1.02±0.08 during Phase 2 (1994 to 2005),

216 with a significant difference between the two phases under the t-test (P value <0.01),

217 thereby implying an abrupt decrease of approximately 30% at the inflection point

218 between the two phases. In contrast, the m-values linearly decreased by approximately

219 20% every two years, starting from the end of Phase 2 to Phase 3 (2006-2011). Again,

220 a significant difference existed between Phase 2 and Phase 3 under the t-test (P value

221 <0.01). Overall, PLR should be applied separately for the different phases in the

222 presence of the inflection points, rather than LR for the entire period, and the result is

223 presented as:

224
$$\begin{cases} m-value = 1.38, 1988 \leq x < 1994 \\ m-value = 1.02, 1994 \leq x \leq 2004 \\ m-value = -0.185 * \left(\frac{x}{2} - 1001\right) + 1.15, 2004 < x \leq 2010 \end{cases}$$

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225   where x represent the calendar year from 1988 to 2010.

226

227   The trend in the m-values of NO_3^- can be classified into two phases, with the inflection

228   point at 2003, according to the t-test result, i.e., the values oscillated approximately

229   1.09±0.09 during the period from 1988 to 2003 and then exhibited a significant decrease

230   of approximately 50% overall afterwards, with P value <0.01. The PRL result is

231   expressed as below:

232
$$\begin{cases} m - value = 1.09, 1988 \leq x < 2004 \\ m - vlaue = -0.128 * \left(\dfrac{x}{2} - 1001\right) + 1.08, 2004 \leq x \leq 2010 \end{cases}$$

233   The m-value of NO_3^- in 1998-1999 was approximately 30% larger than the mean value

234   in 1988-2003 and exceeded the mean value plus 3 SD in 1998-2003, and thus was not

235   included in the trend analysis. The sharp increase in F_{wet} of NO_3^- occurred mainly in

236   1999, which was probably caused by a large perturbation from climate anomalies.

237   Moreover, the monthly F_{wet} values of NO_3^- in March, April, July and August 1999 were

238   actually lower than the corresponding long-term averages in 1988-2003 (excluding

239   1999) (Fig. S4a). This outcome indicates that the large increase in annual F_{wet} of NO_3^-

240   in 1999 was unlikely to have been determined by the emissions of its gaseous

241   precursors. The same can be said for the large increase in F_{wet} of SO_4^{2-} in 1999 (Fig. 2a,

242   S4b).

243

244   The trends in the m-value of SO_4^{2-} at Site 1 (Fig. 2a) were clearly different from those

245   of the SO_2 emissions in Québec (Fig. 2c) but matched well to those in Ontario (Fig. 2c),

246   which is also supported by their Pearson correlation coefficients, e.g., no significant

247   correlation (r = 0.46 and P value >0.05) for the former case and a good correlation (r =

248   0.96 and P value <0.01) for the latter case. Note that r instead of R^2 is conventionally

249   used in correlation analysis and is therefore used here. Zhang et al. (2008) reported that

250   this remote area can receive the long-range transport of air pollutants from Ontario but

251   that transport is less likely from the intensive emission sources in Québec.

252

253   The trends in NOx emissions during 1990-2003 had similar bell-shape patterns in

254   Québec and Ontario, although with different magnitudes of emissions (Fig. 2f). A

255   different trend pattern was seen for the m-value of NO_3^- at Site 1 than for the

256   abovementioned provincial emissions during the same period (Fig. 2d), and there was

257   no significant correlation (r<0.41, with P value >0.05) between the m-value of NO_3^-

258   and the emissions of NOx in Québec or Ontario. Different results were found for the

259   period of 2002-2011 than those of 1990-2003 discussed above. In 2002-2011, the m-

260   value of NO_3^- decreased by ~50% and the NOx emissions decreased by ~40% in

261   Québec and Ontario; also, good correlations (r = 0.94-0.95 with P values <0.01) were

262   observed between m-values and emissions. The contrasting results between the two

263   different periods discussed above implied one possibility, i.e., that the perturbation

264   from climate anomalies, which was unable to be removed by the new approach,

265   overwhelmed the effect of NOx emissions on trends in m-values of NO_3^- in 1990-2003,

266   while the reverse was true in 2002-2011. However, other possibilities cannot be

267   excluded. F_{wet} of NO_3^- and precipitation depth exhibited only a weakly significant

268   correlation, with r = 0.58 and P<0.05 in 1988-2003 (the values in 1999 were excluded).

269   Annual precipitation varied by only ~20% during the fifteen years, and this factor alone

270   was unlikely to explain the ~100% interannual variation of F_{wet} of NO_3^- during that

271   period.

272

273   The m-values of NH_4^+ at Site 1 had no significant correlation (r = 0.21 and P value

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274 >0.05) with the emissions of NH_3 in Québec but exhibited a weakly significant

275 correlation (r = 0.60 and P value <0.05) with the emissions of NH_3 in Ontario. Nearly

276 all of the NH_4^+ was associated with SO_4^{2-} and NO_3^- in the atmosphere (Cheng and

277 Zhang, 2017; Teng et al., 2017; Tost et al., 2007; Zhang et al., 2012), and the trends in

278 the m-value of NH_4^+ could be affected by many other factors besides NH_3 emissions

279 and climate anomalies.

280

281 LR analysis of the annual F_{wet} of these ions revealed decreasing trends for SO_4^{2-} and

282 NO_3^- (second row in Fig. 2). The M-K method analysis also confirmed the decreasing

283 trends with annual F_{wet} as input. However, the three-phase trends in F_{wet} of SO_4^{2-} and

284 the two-phase trends in F_{wet} of NO_3^- and related inflection points, identified using the

285 m-values discussed above, were not identified by the t-test when simply using annual

286 F_{wet} data as input. The correlations between annual F_{wet} and emissions were 0.89 for

287 SO_4^{2-} vs. SO_2 in Ontario and 0.74-0.76 for NO_3^- vs. NO_x in Québec and Ontario (P

288 values <0.01), while the corresponding r values were as high as 0.95 and 0.84-0.85

289 between m-values and emissions. After reducing the perturbations from climatic factors

290 to the annual F_{wet}, stronger correlations were obtained between F_{wet} and emissions.

291

292 The stable trend in annual F_{wet} of NH_4^+ and the decreasing trend in annual F_{wet} of NO_3^-

293 gradually increased the relative contributions of reduced nitrogen in the total nitrogen

294 wet deposition budget, e.g., from 40% in 1998-1999 to 52% in 2010-2011. A similar

295 trend has also been recently reported in the U.S. (Li et al., 2016). Such a trend was

296 mostly due to the mitigation of NOx rather than climate anomalies.

297

298 *3.2 Decadal climate anomalies drove trends at Site 2*

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299   Fig. 3 shows the trend analysis results at Site 2. An obvious shift in the m-values and

300   annual F_{wet} occurred during 2001-2002, as detected by the t-test, i.e., the m-values of

301   SO_4^{2-} oscillated approximately 1.15±0.11 in 1990-2001 and 0.76±0.02 in 2002-2011

302   (or 0.83±0.12 if the value in 2006-2007 was included), but with a significant difference

303   between the two periods with P value <0.01. The annual F_{wet} of SO_4^{2-} oscillated

304   approximately 632±63 mg m^{-2} in 1990-2001 and 452±74 mg m^{-2} in 2002-2011, and the

305   values between the two periods showed significant differences. The shift led to the m-

306   values and annual F_{wet} of SO_4^{2-} exhibiting a consistent decreasing trend by ~40% overall

307   from 1990 to 2011 using the LR and the M-K method.

308

309   The emissions of SO_2 oscillated approximately 1.13±0.07 in 1990-2001 and 1.06±0.03

310   in 2002-2011 in British Columbia, which did not support the large decrease of

311   approximately 40% in wet deposition of SO_4^{2-} in 2002-2011. Statistically, no

312   correlation existed between annual F_{wet} of SO_4^{2-} and the emissions of SO_2 in British

313   Columbia, with r = 0.52 and P value >0.05. Although the transboundary transport of air

314   pollutants from the U.S. cannot be excluded, the almost constant m-values from 2002

315   to 2011 (excluding 2006-2007) at Site 2 were inconsistent with the approximately 70%

316   decrease in emissions of SO_2 in the state of Washington in the U.S. during that period

317   (not shown). Precipitation cannot explain the jump in wet deposition either, because

318   there was no corresponding jump in precipitation during 2001-2002 (Fig. 3b).

319

320   van Donkelaar et al. (2008) analyzed aircraft and satellite measurements from the

321   Intercontinental Chemical Transport Experiment and proposed the long-range transport

322   of sulfur from East Asia to the west coast of Canada. The average wind fields in 1990-

323   2011 at different altitudes also showed air masses primarily originating from the Pacific

14

324   Ocean in the west (Fig. 4a). However, the climate anomalies of wind fields in 1990-

325   2001 compared against 1990-2011 clearly showed a counterclockwise pattern in the

326   corresponding coastal area, including Site 2, while a clockwise pattern existed in 2002-

327   2011 against 1990-2011 (Fig. 4b, c). The decadal climate anomalies of wind fields in

328   2002-2011 very likely caused a large decrease in the contribution of air pollutants from

329   the eastern coast to Site 2, resulting in a distinct demarcation at 2002. This hypothesis

330   was also supported by a large rebound of the m-value in 2006-2007, due to the increase

331   in F_{wet} of SO_4^{2-} in 2007. The climate anomalies of wind fields in 2007 against 1990-

332   2011 showed a counterclockwise pattern in the north, while the clockwise pattern was

333   pushed to the south (Fig. 4d). A greater contribution of air pollutants from the eastern

334   coast to Site 2 might have led to the large increase in F_{wet} of SO_4^{2-} during a few month-

335   long periods in 2007.

336

337   The present study is the first one to identify the decreasing trend in the annual F_{wet} of

338   SO_4^{2-} as being very likely caused by decadal climate anomalies rather than by the

339   emission reductions of SO_2. The decadal climate anomalies may substantially alter the

340   long-range transport of air pollutants to the reception site. Note that the causes for the

341   decadal climate anomalies in this region are beyond the scope of the present study, but

342   some information can be found in the literature (Bond et al., 2003; Coopersmith et al.,

343   2014; Deng et al., 2014).

344

345   For the wet deposition of NO_3^-, the m-values also showed a clear shift, i.e., the m-values

346   oscillated approximately 1.09±0.14 in 1990-2001 and 0.88±0.06 in 2002-2011, with a

347   significant difference between the two periods under the t-test with P value <0.01. The

348   annual F_{wet} of NO_3^- varied substantially, and the shift could not be identified

349   statistically. However, the annual F_{wet} of NO_3^- exhibited a decreasing trend by M-K

350   method analysis. Similar to the case of SO_4^{2-}, no significant correlation (r = 0.49, P

351   value >0.05) existed between the annual F_{wet} of NO_3^- and the emissions of NOx in

352   British Columbia.

353

354   In addition to decadal climate anomalies, the interannual climate variability also

355   affected the trends in m-values and annual F_{wet} of NO_3^-. The perturbations from

356   interannual climate variability cannot be completely removed by the new approach, and

357   they complicate the relationship between the F_{wet} of NO_3^- and the emissions of NO_x in

358   British Columbia. For example, the m-values in 1990-1991, 1996-1997, 1998-1999 and

359   2000-2001 were nearly constant at 1.17±0.03. However, the NOx emissions in British

360   Columbia in 1998-1999 were 26% greater than those in 1990-1991. There was a sharp

361   decrease in the NOx emissions (by ~30%) from 2002 to 2011 in British Columbia.

362   However, the m-values oscillated approximately 0.88±0.06 and showed no clear trend

363   based on either the M-K method or LR analysis. The interannual climate variability

364   apparently negated the impact of reduced emissions during these periods.

365

366   The m-values and the annual F_{wet} of NH_4^+ oscillated approximately 0.99±0.13 and

367   81±16 mg m^{-3}, respectively, in the period of 1990-2011, and showed no trend (Fig. 3).

368   Neither the m-values nor annual F_{wet} of NH_4^+ showed the two-period distribution

369   pattern or had any significant correlation with the emissions of NH_3 in British Columbia

370   at a 95% confidence level. Similarly to Site 1, the annual variation in F_{wet} of NH_4^+ at

371   Site 2 cannot be simply explained by known emission trends.

372

373   In summary, decadal climate anomalies overwhelmingly determined the long-term

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374   trends in the wet deposition of SO_4^{2-} and NO_3^-, with the perturbation from monthly and

375   annual climate anomalies removed at Site 2. The interannual climate variability further

376   complicated the trends, resulting in undetectable influences of the emission trends on

377   the deposition trends. Since the decrease in F_{wet} of NO_3^- appeared to be primarily caused

378   by climate anomalies, the relative contributions of NH_4^+ and NO_3^- in the total N wet

379   deposition varied little, i.e., 33% versus 67% in 2010-2011 and 31% versus 69% in

380   1990-1991.

381

382   *3.3 Regional trends in wet deposition in northern Ontario and Québec*

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

384   Ontario were generally similar to those found at Site 1 (Fig. S5 and S6). For example,

385   the three-phase trend in m-values of SO_4^{2-} and the two-phase trend in m-values of NO_3^-

386   were also obtained at Sites 3 and 4 after excluding a few m-values that were caused by

387   large perturbations from climate anomalies. Thus, Sites 1, 3 and 4 were combined

388   together to study regional trends in the northern areas of Ontario and Québec (Fig. 5a-

389   c). Similar to those found at the individual sites, the temporal profile of regional m-

390   values of SO_4^{2-} can be clearly classified into three phases (Fig. 5a) as follows: Phase 1

391   from 1988 to 1993 with m-values oscillating approximately 1.31±0.08, Phase 2 from

392   1994 to 2003 with near-constant m-values of 1.05±0.04, and Phase 3 for 2004 onward

393   with a decreasing trend by an overall ~50%. Significant differences of m-values existed

394   between any two of the three phases, based on the t-test results (P value <0.01). The

395   PRL result is expressed as below:

396
$$\begin{cases} m-value = 1.31, 1988 \leq x < 1994 \\ m-value = 1.05, 1994 \leq x < 2004 \\ m-value = -0.129 * \left(\frac{x}{2} - 1001\right) + 1.03, 2004 \leq x \leq 2010 \end{cases}$$

397   The three-phase pattern of m-values matched well with the three-phase emission profile

398   of SO_2 in Ontario. Statistically, an ~70% decrease in m-value and an ~70% decrease in

399   emissions were found from 1990 to 2011, with a correlation of r = 0.95 (P value <0.01).

400

401   The profile of the regional m-values of NO_3^- also clearly exhibited two phases,

402   according to the following t-test results between them: Phase 1 from 1988 to 2003, with

403   m-values narrowly varying approximately 1.11±0.05 and Phase 2 from 2004 to 2011,

404   with a decreasing trend by an overall ~40% against that in 2002-2003 (Fig. 5b). The

405   PRL result is expressed as below:

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

407   From 2002 to 2011, the m-value had a moderately good correlation with the NOx

408   emission in Ontario (r = 0.91, P<0.01), and the two variables decreased by 30-40% in

409   this period. From 1990 to 2003, the near constant m-value was, however, inconsistent

410   with the bell-shape profile of the NOx emissions in Ontario and Québec, which could

411   be due to either the perturbation from climate anomalies or unrealistic emissions

412   inventory. Considering that the first possibility was minimal over a large regional scale,

413   especially when the consistency was determined in a different time frame (2002-2011)

414   in the same region, it is thus doubtful that the bell-shape profile of the NOx emissions

415   in 1990-2003 was realistic.

416

417   The regional m-values of NH_4^+ largely oscillated from 1988 to 2003 (Fig. 5c). The m-

418   values of NH_4^+, however, decreased by ~30% from 2002 to 2011, leading to a probable

419   decreasing trend in m-value from 1988 to 2011. No correlation was found between the

420   m-values of NH_4^+ and the emissions of NH_3 in Ontario, which is consistent with the

421   findings at the individual sites discussed above.

422 Since the decrease in F_{wet} values of NO_3^- at Sites 3 and 4 were very likely due to the

423 mitigation of NOx in Ontario, the decrease also changed the relative contributions

424 between NH_4^+ and NO_3^- in the total N wet deposition budget. For example, NH_4^+ and

425 NO_3^- contributed 52% and 48%, respectively, to the total budget in 2010-2011 and 34%

426 and 66%, respectively, in 1984-1985 at Site 3. The corresponding numbers at Site 4

427 were 58% and 42% in 2010-2011 and 47% and 53% in 1985-1986.

428

429 **4 *Conclusions***

430 Climate anomalies during the two-decade period resulted in annual F_{wet} of SO_4^{2-} and/or

431 NO_3^- deviating from the normal value by up to ~40% at the rural Canadian sites. The

432 new approach of rearranging and screening F_{wet} data can largely reduce the impact of

433 climate anomalies when used for generating the decadal trends of F_{wet}. With the climate

434 perturbation being reduced, F_{wet} of SO_4^{2-} exhibited a three-phase decreasing trend at

435 every individual site, as well as on a regional scale in northern Ontario and Québec.

436 The three-phase pattern of the decreasing trend in F_{wet} of SO_4^{2-} matches well with the

437 emission trends of SO_2 in Ontario, as supported by the good correlation between wet

438 deposition and emission, with r ≥ 0.95 and P<0.01. F_{wet} of NO_3^- exhibited a two-phase

439 decreasing trend, but only during the second phase F_{wet} of NO_3^-, and the emissions of

440 NOx in Ontario and Québec matched well, with a good correlation of r ≥ 0.91 and

441 P<0.01. Compared to the results obtained without applying the new approach, it is

442 concluded that, after reducing the perturbation from climate anomalies, 1) better

443 correlation was obtained between F_{wet} of ions and the emission of the corresponding

444 gaseous precursors in northern Ontario and Québec, and 2) the inflection points in the

445 decreasing trends of F_{wet} of SO_4^{2-} and NO_3^- were clearly identified.

446

447 However, the new approach cannot completely remove the perturbations from climate

448 anomalies, especially when this is the dominant factor and/or on long timescales, as

449 was the case at a coastal site of Saturna in British Columbia. At this location, the

450 decreasing trends in F_{wet} of SO_4^{2-} and NO_3^- were caused by the decadal climate

451 anomalies, as well as being affected by interannual climate variability, which

452 overwhelmed the impact of the emission changes of the gaseous precursors in this

453 province. This is the first study that has identified that decadal climate anomalies can

454 dominate trends in F_{wet} of SO_4^{2-} and NO_3^-.

455

456 The long-term variations in F_{wet} of NH_4^+ generally showed no clear long-term trends.

457 Moreover, no apparent cause-effect relationships were found between the wet

458 deposition of NH_4^+ and the emission of NH_3. This outcome is not surprising because

459 additional key factors besides those discussed in this study also impact the trends of

460 F_{wet} of NH_4^+. For example, NH_4^+ may be more greatly impacted by changes in SO_2 and

461 NOx than are NH_3 emissions in NH_3-rich scenarios. It should be noted that F_{wet} of N

462 via NH_4^+ exceeded those via NO_3^- in 2010 and 2011 in northern Ontario and Québec,

463 where the decrease in F_{wet} of NO_3^- was associated with decreasing NOx emissions. In

464 contrast, F_{wet} of NH_4^+ did not exceed F_{wet} of NO_3^- in 2010 and 2011 in the coastal area

465 in British Columbia, where the decreasing trends of F_{wet} of NO_3^- were determined to

466 result mainly from the perturbation by climate anomalies.

467

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

469 *Supplement*. The supplement materials are available online.

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

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

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475

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Figure 2. m-values and annual F_{wet} extracted trends at Site 1, and the annual emissions of air pollutants in Québec and Ontario, Canada. Full and empty markers in blue in (a), (b) 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.

Figure 3. Identical to Fig. 1, 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.

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