Reply to the comments and suggestions of reviewer #1

The study presented is very rich in data and analysis. However, some of the information could be summarized making the manuscript more readable, especially in the results section. Every sub-section of the results section has a summary after the description of the results, the summary is good but the text prior to it is overwhelming and unnecessary when having adequate figures/tables supporting the text. The figures and tables should be more carefully thought through, as it takes a lot of time to grasp the information.

Re: Following the suggestions from the reviewer and Tom Butler (Reviewer #2), we have substantially revised the text to make it more concise and readable. The graphs and tables have been rearranged, eg. Fig. 2 has been moved to Supplemental materials, and a more concise Fig. 2 (as suggested by the reviewer) has been added.

The reader might have issues to grasp what was done every single step of the way to obtain the results and the analysis, as the methodology is not really clear. This might be a consequence of not having a dedicated section for the methodology. Additionally, it might be challenging the reading when interchanging time periods and not giving a clear context, especially when trends and changes in concentrations are calculated based on different time period, and not really explained why.

Re: Following the suggestions of the reviewer in the detailed part of the review, we have substantially revised the text to have a clearer context in presenting the results, and explained, for example, why we calculated 10 and 25 years of changes. We also added a dedicated subsection “Statistical analysis and method” to explain how the analysis was carried out.

More information is needed to understand the levels of concentration behind the clusters, this might be due to emissions, meteorology, terrain, etc. It is important to know if one cluster can be more populated than others in terms of sources, and if that is still the case throughout the study period.

Re: The fundamental justifications for clustering of 4 regions are: (1) difference in emissions of SO_2, NO_x and NH_3; (2) the latitudinal gradient of the region, which affects the temperature and the solar radiation; (3) the prevailing atmospheric circulation due to mid-latitude Rossby waves. Regions 1 and 4 can be separated from Regions 2 and 3 because of the low emissions of SO_2, NO_x as well as NH_3, and also their low/high latitudes; Regions 2 and 3 can be separated from each other due to the large difference in NH_3 emissions. We used ambient concentration of SO_2 during the cold season to indicate the difference in SO_2 emissions; used NO_3 and RNO_3 during the cold season to indicate the difference in NH_3 emissions.

To support the justification of the clustering, we have added a table in Supplemental materials to show the correlation coefficients of the ambient annual concentration of each site vs. the regional averaged value for each species. For most site and species (except for NO_3), the correlation coefficients are larger than 0.95. Also as shown in the time series (Fig. S2), the annual concentrations of sites within each region are highly correlated, which is a demonstration that the clustering of sites is successful.

Responses to detailed comments:

Section 1

P2/L20: the reference to WHO fact sheets should be substituted by papers available describing the impact of air pollution on human health.

Re: We have substituted the web link by the journal paper references.

P3/L4-P4/L25: the authors appropriately describe how emissions have been evolving throughout the study period and the legislation to enforce such changes, but there is no single reference to corroborate the numbers. Please add the references grounding your narrative. Additionally, only the US situation was described, there is similar discourse for Canada. Please revise.

Re: References have been added, and the discussion for Canadian emissions has been added.

P5/L1-4: the authors describe trend analysis studies for other regions than US, and this might be misleading, even unnecessary. Please consider to remove.

Re: The mentioned part has been removed, and the text has been revised.

Section 2.1

P6/L25 Please add a reference describing the CASTNET network
The authors describe the temporal resolution of the measurements available for each network, but was never mentioned which resolution is actually taken for the analysis; this is mentioned in the abstract only.

Re: The references for CASTNET have been added. How annual means were derived was added in the new “Statistical analysis and method”.

Section 2.2
P7/L14: When referring to ‘mean concentration’, is it temporal mean and if so for which time period? Please describe this step.

Re: We have specified it was “3-years mean concentration of NO3 and SO2 of each site”.

P7/L24-25 Here the authors refer to clustering of data between 1989 and 1991. Please describe how was the clustering obtained and why these 3 years and not any other period.
Title for section 3 should only refer to results.

Re: The method of how to cluster the sub-regions was now clearly specified in the text; We also added an extra table (Table S.3) in Supplemental materials, showing the correlation coefficients of the annual concentration from each site *vs.* the averaged value of the cluster for each species. The text has been accordingly revised (P9 L18-24).

We have specified that we used the mean concentrations at the beginning of the period because SO2 was highest and it clearly separated regions 1 and 4 from regions 2 and 3.

Section 3.1
Please consider to add a table with the average values and STD for each region, this would improve readability for quick check and cross comparison and avoid a long text.

Re: It has been added in Supplemented materials as Table S.1 and S.2.

P8/L18 Consider to enumerate the species considered in this section.

Re: It has been revised accordingly (P10 L3-4).

P9/L4 Did the authors mean "spatially uniform"?

Re: We specifically mentioned "was spatially uniform".

P9/L16 Please add references to corroborate your assumption.
Re: References have been added, and more corroboration has been added. (P10 L24 – P11 L2)

P9/L8-13 There is a degree of repetition in this paragraph, suggestion that it would fit best at the beginning of the section, before going into detail about each region.

Section 3.2
P10/L16 Discrepancy between the time period described in the title and the introduction of the work.

Re: It was corrected.

P10/L19 Why was the year 2000 chosen for normalization?
P10/L20 Typically one would cluster the time series on the basis of similarity, usually comparing magnitude or time variation, but as referred before, nothing was told before how were the stations clustered.
Re: The text explaining why year 2000 was chosen for normalization was added (P12 L10-13). In the Section 2.3, we have substantially improved the justification of clustering. Essentially it was based on similarity (correlation coefficients, Table S.3) and magnitude of time variation.

A suggestion for Figure 2 to be moved to the Supplements, and have a figure with average across the region and its variation for both cold and warm. Note that it's hard to read a single plot and across. For figure 3 would be best to put cold and warm seasons together, helping the reader to analyze the results. There is a typo in the legend for SO_{42-}
Generally, the section lacks which figures the reader should be looking at while reading the results section.

Re: Fig. 2 has been removed to the Supplemental materials, and a new Fig. 2 (as suggested) has been added. Fig. 3 has been revised according to the suggestions. We also specified in the revised text the results presented in this section are mainly based on Fig. S3 and Fig. 3

Section 3.3 Generally, the section lacks which figures the reader should be looking at while reading the results section.
Re: We specified the results presented in Section 3.3 are summarized from Tables 2 and 3.

Table 3 There is a possible highlighting mistake for concentrations above 1.0 ug m-3, e.g. NO_{3-}
Re: The mistake was corrected.

P17/L10 Please explain why these years were chosen and how the averaging was calculated.
Re: The explanation has been added, and text has been revised accordingly (P19 L6-L14)

P19/L25-26 The last sentence ("the difference…") is importantly mentioned but the only discussion being written so far. To keep it consistent, it should be moved to the discussion.
Re: We have revised the text, and added two more references for the extra reduction of NOx during O3 season. Because of lack of emission data, it is difficult to have a more in-depth discussion.

P22/L18 How was the normalization of the annual means done? Is it related to the year 2000? Please describe.
Re: We explicitly mentioned that "The regressed trends are normalized to the regressed value of year 2000 as this is the turning point for the trend of NO3-".

Figure 4 does not describe which of the panels is depicted the pollutants.
Re: The mistake was corrected.

Figure 5 Please explain why NO3 shows a different pattern that the remaining species.
Re: In the caption of Fig. 5, we explicitly mentioned that "The dot lines link the annual concentrations from 1990 to 2016 for species except NO3- to show the temporal trends". The reason that we didn't use dot-line for NO3 is that NO3 during cold season in region 3 has no trend.

Section 4
P23/L2-3 here is explained why the year 2000 is chosen, please revise the structure so this information is prior to the results.
Re: It was revised accordingly.

Section 5
P23/L16 Please revise section title.
Re: The title has been revised to "4.1 RSO4 and correlations of RSO4 vs. SO2".

P23/L19 Why did the authors chose RSO2 instead of 1-RSO4?
Re: *We don't know why "Sickles and Shadwick (2015) chose RSO2. For us, because we are concerned about the fraction of SO2 being oxidized to SO4, so RSO4 is a more direct metrics than RSO2.*

Figure 8b has a typo in the legend, and displaying the R would be a good addition
Re: The typo has been corrected. R2 has been added in the graphs.

Section 6

The paper is already long, it does not need a summary. PL11-L20 is a section on their own, as there is no real description of the emission in the Eat-US and Canada.
Re: We have corrected it accordingly.

P30/L23 again inconsistency between periods.

Re: The inconsistency has been corrected.

We sincerely thank the reviewer for his/her exceptionally detailed, very careful, thoughtful, and constructive comments and suggestions. We thank the reviewer for putting time and effects and helping to improve the quality of the manuscript.

Reply to comments of Reviewer #2 (Tom Butler)

First, we would like to thank Tom Butler (the reviewer) sincerely for his very detailed, thoughtful and constructive review and comments. It helps to improve the quality of the manuscript significantly.

Answers to specific comments:

Comments 1-7: We have revised the manuscript accordingly.

Comment 8: We agree with the reviewer that the Section 3.2 has too much detail on the description of year-to-year variations. We have done significant revisions to remove and skip the minor changes that don't address the overall patterns. We are very appreciate of the reviewer's suggestions.

Comments 9-18: We have revised the manuscript accordingly.

Comment 19: We agree that the original texts are not very clear, and can cause confusion to readers. We have revised the text to indicate that the correlations between SO4 and SO2 can be described by linear regressions for 1990-2010 and 2010-2016 respectively, but the correlation between SO4 and SO2 for the whole study period of 1990-2016 needs to be described by a power-law regression. This helps to explain why in the past some studies suggest that the relationship between SO4 and SO2 be linear, while others suggest that it be a power-law relationship.

Comments 20-29: We have revised the manuscript according to the suggestions.

Comment 30: We tried to combine the 2nd and 3rd graphs into one, but the lines cross over each other, and it is difficult to see each line, so we leave 2nd and 3rd graphs as separate ones.

General comments: We have taken the suggestions of the reviewer, and rounded up some percentage numbers with decimals to integers.

Air quality in the eastern United States and Eastern Canada for 1990-2015: 25 years of change in response to emission reductions of SO_2 and NO_x in the region

Jian Feng[1*], Elton Chan[2] and Robert Vet[1+]

[1]Air Quality Measurement and Analysis Research Section, Atmospheric Science and Technology Directorate, Environment and Climate Change Canada, Toronto, Canada

[2]Measurements, Modelling and Interpretation Section, Atmospheric Science and Technology Directorate, Environment and Climate Change Canada, Toronto, Canada

[*]*Correspondence to*: jian.feng@canada.ca

[+]*Retired from Environment and Climate Change Canada in 2018.*

Abstract

SO_2 and NO_x are precursors to form sulfate, nitrate and ammonium particles in the air, which account for more than 50% of PM2.5 mass in the eastern US (Bell et al., 2007), and are dominant components of PM2.5 during many smog events (Dabek-Zlotorzynska et al., 2011). H_2SO_4 and HNO_3, formed from oxidation of SO_2 and NO_x respectively, are the main sources of acid deposition through wet and dry depositions. NO_X is also a precursor to the formation of tropospheric O_3, which is an important atmospheric oxidant and is also essential for the formation of other atmospheric oxidants, such as OH and H_2O_2.

In the past 26 years from 1990 to 2015, emissions of SO_2 and NO_x in the US were significantly reduced from 23.1 and 25.2 million tons/year in 1990 to 3.7 and 11.5 million tons/year in 2015 respectively. In Canada, SO_2 and NO_x were reduced by 63% and 33% from 1990 to 2014. In response to the significant reductions of SO_2 and NO_x emissions, air quality in the eastern US and Eastern Canada improved tremendously during 1990-2015. In this study, we analyzed surface air concentrations of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3 and SO_2 measured weekly by the Clean Air Status and Trends Network (CASTNET) in the US and measured daily from the Canadian Air and Precipitation Monitoring Network (CAPMoN) in Canada to reveal the temporal and spatial changes of each species during the 25-year period. For the whole eastern US and Eastern Canada, the annual mean concentrations of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3, SO_2 and TNO_3 (NO_3^- + HNO_3, expressed as the mass of equivalent NO_3^-) were reduced by 73.3%, 29.1%, 67.4%, 65.8%, 87.6% and 52.6% respectively from 1990 to 2015. In terms of percentage, the reductions of all species except NO_3^- were spatially uniform. The reductions of SO_2 and HNO_3 were similar in the warm season (May-October) and the cold season (November-April), and the reductions of SO_4^{2-}, NO_3^- and NH_4^+ were more significant in the warm season than in the cold season. The reductions of SO_4^{2-} and SO_2 mainly occurred in 1990-1995 and 2007-2015 during the warm season, and in 1990-1995 and 2005-2015 during the cold season. The reduction of NO_3^- mainly occurred in the Midwest after 2000. Other than in the Midwest, NO_3^- exhibited very little change during the cold season for the period. The reduction of NH_4^+ generally followed the reduction trend of SO_4^{2-}, especially after 2000 the temporal trend of NH_4^+ was almost identical to that of SO_4^{2-}. The ratio of S in SO_4^{2-} to total S in SO_4^{2-} plus SO_2, as well as the ratio of NO_3^- to TNO_3 increased by more than 50% during the period. This indicates that a notable change in regional chemistry took place from the beginning to the end of the period with a higher percentage of SO_2 being oxidized to SO_4^{2-}, and a higher percentage of HNO_3 being neutralized to NH_4NO_3 near the end of the period.

1. Introduction

Gases and particulate matter released into the air through anthropogenic activities can pollute the air and deteriorate the air quality locally, regionally, and continentally. Air pollution, which can decrease lung function, causing the development of asthma, bronchitis and lung cancer (Kunzli et al, 2000; Heroux et al., 2015; WHO, 2006), is considered as a major environmental risk to human health by the World Health Organization (WHO). Air pollution is also linked to stroke and heart disease and improvement of air quality can significantly reduce the PM2.5- and O_3-related mortality burden (Zhang et al., 2018). When emitted gases and particulate matter or secondary pollutants formed in the air from emissions are brought to the Earth's surface through dry and/or wet deposition, they pose a risk to the established ecosystems through acid rain as well as excessive deposition of nitrogen and sulfur.

Air pollution also affects long term climate through scattering and absorption of solar radiation by directly emitted or secondarily formed aerosols in the air (Haywood and Shine, 1995; Yu et al., 2006). In some heavily polluted regions, even local weather can be affected due to the change of energy budgets in the atmosphere and at the Earth's surface (Kajino et al., 2017).

In order to control air pollution, the US passed the Clean Air Act (CAA) of 1963 (Kuklinska et al., 2015). Major amendments to the law were passed in 1970, 1977 and 1990 (Kuklinska et al, 2015). The Amendments to the CAA of 1990 addressed acid deposition, ozone depletion, and toxic air pollution (CAA, 1990). Specifically Title IV of the 1990 Amendments to the CAA, also known as acid deposition control, targeted emission reductions of two acid deposition precursors, SO_2 and NO_X, which along with CO, O_3, Pb and particulate matter, are among the 6 species designated as criteria pollutants by United States Environmental Protection Agency (US EPA). SO_2 and NO_x in the air can be oxidized to form acid H_2SO_4 and HNO_3, which in turn can react with NH_3 to form fine particulate matter (PM2.5), and with crustal material or sea salts to form coarse particles (Yoshizumi and Hoshi, 1985; Zhuang et al., 1999). NO_X, together with volatile organic compounds (VOCs), also participate in formation of tropospheric O_3, which is another criteria pollutant and an important atmospheric oxidant. Title IV of the Clear Air Act 1990 specifically targets SO_2 and NO_x emissions from stationary fuel combustion facilities. The first phase of the Title IV of the 1990 CAA Amendment, which was implemented on January 1, 1995, requires 110 power plants to reduce the SO_2 emissions to a level calculated as the product of an emissions rate of 2.5 lbs of SO_2/mmBtu times an average of their 1985-1987 fuel use (Lee, 1991). The second phase, which took effect on January 1, 2000, requires approximately 2000 utilities to reduce SO_2 emission to a level of 1.2 lbs of SO_2/mmBtu times the average of their 1985-1997 fuel use (Lee, 1991). Since 1990, the national emissions of SO_2 in the US decreased steadily from 23.1 million tons in 1990 to 21.3 million tons in 1994, and dropped significantly to 18.6 million tons in 1995 due to the first phase implementation of Title IV of the 1990 CAA Amendments (EPA 2016; EPA 2019). The SO_2 emissions underwent a small increase during 1996-1998 to 18.9 million tons in 1998, and then continued the steady decrease to 14.5 million tons in 2005. From 2005 to 2012, the decrease of the emissions was accelerated with an annual reduction rate of 1.34 million tons /year during the period. The emissions of SO_2 were leveled off during 2012-2015. In 1990, 87.9% of SO_2 emissions were from stationary fuel combustion facilities, 2% from on-road vehicles, and 2% from off-road mobile sources. By 2007, SO_2 emission from on-road vehicles was totally eliminated due to cleaner gasoline. In 2014, of the 4.9 million tons of total SO_2 emissions, stationary fuel combustion, off-road mobile, and industrial and other processes contributed 4.1, 0.1, and 0.7 million tons respectively (EPA 2016).

NO_x forms in the air when nitrogen reacts with oxygen under high temperature. Anthropogenic emissions of NO_x are mainly due to stationary fuel combustion, on-road vehicles and off-road mobile operations. Nationwide in the US, they contributed 10.9, 9.6 and 3.8 million tons of the total 25.2 million tons of NO_x in 1990 (EPA 2016). Changes in NO_x emission during the 1990s were relatively small (Butler et al., 2003). Total NO_x emission remained generally constant from 1990 to 1998. From 1999 there was a decrease of NO_x emission from stationary fuel combustion, due to the implementation of Title IV of the 1990 CAA Amendment, which also stipulated the reduction of NO_x emissions from power plants, and took effect in 1996, as well as the implementation of the NO_x Budget Trading Program (NBP) that started in 2003 and was created to reduce NO_x emissions from power plants and other large combustion sources in the eastern US during warm months (https://www.epa.gov/airmarkets/nox-budget-trading-program). The NBP was replaced by the ozone season NO_x program under the Clean Air Interstate Rule in 2009. The NO_x emissions from stationary combustion facilities decreased steadily from 10.4 million tons in 1998 to 3.6 million tons in 2012, then remained relatively unchanged thereafter (EPA 2016). Emissions of NO_x from on-road vehicles declined slowly from 1990 until 2001, and there was a sharp increase in 2002. After 2002, on-road emissions of NO_x decreased continuously and steadily. The trend of NO_x emissions from off-road mobile was generally increased during the period from 1990-2002, up from 3.8 tons to 4.9 tons, but after that it was reduced gradually to 2.7 tons in 2014. Combining the emissions from stationary fuel combustion, on-road vehicles and off-road mobiles, the nationwide emissions of NO_x in the US changed little during 1990-1998, decreased during 1998-2001, increased in 2002, and then decreased steeply up to recent years.

In Canada, similar measures were adopted to reduce air pollutant emissions. SO_2 emissions in Canada were mainly from three major sectors: ore and mineral industries, oil and gas industry and electric utilities. For each sector, the annual SO_2 emissions were reduced from 1.5, 0.53 and 0.62 million tons in 1990 to 0.47, 0.28 and 0.27 million tons in 2015 (ECCC, 2019). Nationally, annual SO_2 emissions were reduced from 3.1 million tons in 1990 to 1.1 million tons in 2015 (ECCC, 2019). In 1990, the annual emissions of SO_2 from Eastern Canada accounted for 59% of the national annual emissions. NO_x emissions in Canada were mainly from transportation (43%) and oil and gas industries (14%) (ECCC, 2019). Nationally, annual emissions of NO_x were reduced by 25%, from 2.4 million tons in 1990 to 1.8 million tons in 2015. Specifically, annual emissions of NOx in Eastern Canada were reduced by close to 50%, from 1.2 million tons to 0.64 million tons.

Air quality trends during the past few decades, especially since 1990, are of great interests of both scientific communities and the general public. For the eastern part of US and Canada, trends of air quality after 1990 have been reported in previous studies for O_3 (Chan and Vet, 2010), O_3 and nitrate (Butler et al., 2011), particulate SO_4^{2-} (Hand et al., 2012) and air quality and atmospheric deposition (Sickles and Shadwick, 2007; Sickles and Shadwick, 2015, Cheng and Zhang, 2017). Sickles and Shadwick (2007, 2015) compared the 5-year averages of air quality and atmospheric deposition in the eastern US for 1990-2004 and 1990-2009. Cheng and Zhang (2017) reported the temporal trends of annual concentration of air pollutants from 31 Canadian rural locations, most of which were located in Eastern Canada. Aas et al. (2019) reported global and regional trends of atmospheric sulfur for 1990-2015, and found North America and East Asia had the largest reductions of sulfur emissions during the late part of the period. In this study, we analyze the surface air concentration data measured weekly by the CASTNET network in the US and measured daily from the CAPMoN network in Canada to reveal the detailed temporal and spatial trends of air quality from 1990-2015. These trends are not only important for the assessment of the improvement of air quality due to emissions reductions, but also are essential for the evaluations of chemical transportation models. The analysis will answer the following questions: (1) what are the trends of air pollutants over the eastern US and Eastern Canada following the significant reductions of SO_2 and NO_x emissions during 1990-2015; (2) what are the physical and chemical mechanisms responsible for the trends. We will look at the air concentrations of gases SO_2 and HNO_3, and particulates SO_4^{2-}, NO_3^-, and NH_4^+, which are either due to direct emissions of SO_2, or due to the oxidation of SO_2 and NO_x as well as reaction of these oxidants with NH_3.

2. Data and method

2.1 Networks of measurement: CASTNET and CAPMoN

The monitoring of background- and regional-level ambient pollutants is essential for assessing regional air quality. In the US and Canada, this long-term monitoring of air quality in rural and remote areas is fulfilled by the two monitoring networks: CASTNET and CAPMoN, respectively.

CASTNET is a monitoring network managed and operated by the US EPA in cooperation with several other federal, state and local partners (Clarke et al., 1997; Bloomer et al, 2010). The network was established under the 1990 CAA to assess the trends of acidic deposition due to emission reduction programs. The network makes weekly integrated measurements of gases (SO_2 and HNO_3) and particulates (SO_4^{2-}, NO_3^-, NH_4^+, Mg^{2+}, Ca^{2+}, Na^+, and Cl^-) using filter pack methods, as well as hourly measurements of O_3. At selected sites, it also measures hourly concentration of NO, reactive nitrogen (NO_y), SO_2, and CO.

CAPMoN is a monitoring network operated by Environment and Climate Change Canada (ECCC). The network began operation in 1983, although one of its two predecessor networks, the Air and Precipitation Network (APN), measured air concentrations as far back as in 1978. The network measures 24-hour integrated air concentrations of pollutants (from 08:00 AM to 08:00 AM, local time) through filter pack sampling, and 24-hour wet deposition by collection of precipitation samples at the ground level. The daily air concentration measurements by CAPMoN also include gases (SO_2 and HNO_3) and particulates (SO_4^{2-}, NO_3^{--}, NH_4^+, Mg^{2+}, Ca^{2+}, Na^+, and Cl^-), similar to CASTNET's weekly measurements. CAPMoN also measures hourly air concentration of O_3, NO_y, and gaseous Hg at selected sites. More details about the CAPMoN dataset can be found in Cheng and Zhang (2017).

2.2 Statistical analysis and method

As we focus on the long-term trends of air pollutants over the region, annual means for all, warm, and cold seasons were derived for each site from the weekly measurements of CASTNET and daily measurements of CAPMoM. In order to avoid the fluctuations of annual concentrations due to meteorology, 3-year averages were used to represent the mean concentrations at the beginning or the end of a period in calculating changes for that period.

The Mann-Kendall test (MKT) is a non-parametric test to detect the trend of a time series and it doesn't require the variable of the time series follows a normal distribution (Mann, 1945, Du et al., 2014). In this study, the MKT was used to detect if an increasing or decreasing trend exists when a time series generally looks flat. The p-value and tau coefficient are the two statistical parameters of the MKT, indicating the statistical significance and significance of a monotonic trend respectively.

To assess the changes of air pollutants in response to emission reductions of SO_2 and NO_x, we looked at the followings for species of SO_4^{2-}, SO_2, NH_4^+, NO_3^-, HNO_3 and TNO_3 (NO_3^- + HNO_3, expressed as equivalent NO_3^-) :

(1) temporal and spatial trends in the eastern US and Eastern Canada;
(2) 10-year and 25-year changes for the periods of 1990-2000 and 1990-2015;
(3) differences in trends in cold and warm seasons;
(4) time series of the annual regional means during the warm and cold seasons;
(5) long-term trends derived from polynomial regressions.

We also looked at correlations between SO_4^{2-} and SO_2, the ratio of sulfur (RSO_4) in SO_4^{2-} to total sulfur in SO_4^{2-} plus SO_2 in the air, the ratio of nitrogen (RNO_3) in NO_3^- to TNO_3, and their changes during the period, in order to explain the physical and chemical mechanisms responsible for the trends.

2.3 Region-clustering of CASTNET and CAPMoN sites in the eastern US and Eastern Canada

In the eastern US (EUS) and Eastern Canada (EC), there are significant spatial differences in emissions of SO_2, NO_x and NH_3. This results in distinctive regional patterns of air concentration of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3 and SO_2. In this study, we used the cold season (November to April) 3-year mean concentrations of NO_3^- and SO_2 of each site, supplemented with the ratio of RNO_3, as the criteria to cluster the CASTNET and CAPMoN sites into 4 different regions. The reasons for selecting the cold season are: (1) NO_3^- is mainly in form of NH_4NO_3 (Zhang et al., 2008), and it is much more thermodynamically stable in the cold season than in the warm season; (2) the oxidation rate of SO_2 is much lower in the cold season than in the warm season, therefore the air concentration of SO_2 more reflects the SO_2 emission rate of the region; (3) because NH_4NO_3 is much more thermodynamically stable and much less affected by ambient temperature, RNO_3 is mainly determined by the availability of NH_3 over the region; therefore RNO_3 during the cold season is an indicator of the abundance of NH_3 to form NH_4NO_3. To avoid the yearly fluctuation of annual concentrations, 3-year averages were taken to represent the mean concentrations of the beginning or the end of a period. The mean concentrations at the beginning of the period were used to cluster the sites as the emission rate of SO2 was highest.

Based on the spatial patterns of mean air concentration of NO_3^- and SO_2, and RNO_3 during the cold season of 1989-1991, which are shown in Table S1.b and Fig. S1.b, 4 regions in the EUS and EC were clustered:

- Region 1: sites located north of latitude 40°, and with concentration of SO_2 less than 6.4 μg m^{-3} in the cold season.
- Region 2: sites with mean concentration of NO_3^- greater than 2.5 μg m^{-3}. Except for site ARE128 at 2.1 μg m^{-3}, the highest air concentration of NO_3^- of all other sites was 1.9 μg m^{-3}. For sites in region 2, RNO_3 was greater than 54%, which was higher than any CASTNET and CAPMoN sites in other regions.
- Region 3: sites excluded from regions 1 and 2, and with an air concentration of SO_2 greater than 15.0 μg m^{-3} during the cold season.
- Region 4: all other sites excluded from regions 1, 2 and 3. The highest mean SO_2 of sites in region 4 during the cold season was less than 11.7 μg m^{-3}.

The clustering of sites is shown in Fig. 1 with site names. Regions 2, 3, and 4 roughly correspond to the Midwest, Mid-Atlantic, and Southeast regions participating in the NBP (Butler et al., 2011). The site SND152 had a characteristic of region 2, but it is geologically located in region 4; therefore the site SND152 was not included in the study. Characteristics of each region are listed in Table 1. After grouping the sites into each cluster appropriately, annual concentrations of each species from each site within the cluster show high correlations with the averaged values of the cluster, as shown in Fig. S3 and Table S3. For example, as shown in Table S3 for region 2, the averaged correlation coefficients of the annual concentrations of each site *vs.* the averaged values of the cluster during the cold season are 0.98, 0.95, 0.98, 0.97, 0.98 and 0.98 for SO_4^{2-}, NO_3^-, NH_4^+, HNO_3, SO_2 and TNO_3, respectively. For all seasons, the corresponding averaged correlation coefficients are 0.97-0.99, 0.59-0.91, 0.93-0.98, 0.94-0.99, 0.96-0.99 and 0.86-0.98 for regions 1-4.

3. Results

3.1 Air quality in the eastern US and Eastern Canada at the beginning of the study period: 1989-1991

Three-year averages of air concentrations of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3, SO_2 and TNO_3, as well as RSO4 and RNO3 from 1989-1991 are used to describe the air quality at the beginning of the study period, and are shown in Table S1.a and b for the warm and cold seasons. Mapping of 3-year average for each species is also provided as Fig. S1 in the Supplement. Among the 4 regions and both the warm and cold seasons, region 1 had the lowest air concentration of all species with mean NO_3^-, HNO_3 and NH_4^+ concentrations of less than 1.0 $\mu g\ m^{-3}$. The mean air concentration of NO_3^- during the warm season was only 0.14 $\mu g\ m^{-3}$. Mean SO_4^{2-} concentrations were 2.9 and 2.3 $\mu g\ m^{-3}$ during the warm and cold seasons respectively, and SO_2 was 1.6 and 3.6 $\mu g\ m^{-3}$ correspondingly.

For regions 2-4, SO_4^{2-} was highest in region 3 and lowest in region 4 for both seasons, varying from 7.6 to 8.2 $\mu g\ m^{-3}$ during the warm season and 3.6 to 4.2 $\mu g\ m^{-3}$ during the cold season. The difference in the regional mean of SO_4^{2-} between region 2 and 3 was less than 0.1 $\mu g\ m^{-3}$ during the cold season. Generally SO_4^{2-} in regions 2-4 was spatially uniform. For each region SO_4^{2-} during the warm season was about double that during the cold season. Same as SO_4^{2-}, SO_2 was also highest in region 3 and lowest in region 4 for regions 2-4, but SO_2 in region 3 was much higher and was about 2.5 times that in region 4. SO_2 in regions 3 and 2 during the cold season, being 19.2 and 13.7 $\mu g\ m^{-3}$ respectively, were the two highest concentrations and the only two concentrations greater than 10.0 $\mu g\ m^{-3}$ among all species in 4 regions and during the warm and cold seasons. The difference in SO_2 between region 3 and 2 was less than 1.0 μg m^{-3} during the warm season, but was more than 5.0 μg m^{-3} during the cold season. Despite significant differences in SO_2 for regions 2-4, the corresponding differences in SO_4^{2-} were small. As an example, during the cold season, the annual concentration of SO_2 in region 3 was higher than that in region 4 by 10.0 μg m^{-3}, but the corresponding difference in SO_4^{2-} was only 0.7 μg m^{-3}. This can be attributed to the fact that the lifetime of SO_4^{2-} (~ 5-7 days) in the air is much longer than that of SO_2 (~ 2 days) (Penner et al. 2001; Pitari et al, 2016). Lee et al. (2011) estimated that the mean SO_2 lifetime in the eastern US is 19 ± 7 h in summer and 58 ± 20 h in winter. Comparing SO_2 in the cold season to that in the warm season, it was about 2 times higher in region 3 and 4, and 59% higher in region 2. In contrast to the pattern of SO_4^{2-}, NO_3^- in regions 2-4 was significantly different from region to region. Region 2 had the highest concentration of NO_3^- at 1.5 μg m^{-3} during the warm season and 3.6 μg m^{-3} during the cold season, which were about triple the value in region 3, which was the second highest. Region 4 had the lowest NO_3^- concentrations among regions 2-4, being 0.3 and 0.6 μg m^{-3} for the warm and cold seasons respectively. The lowest value for stations in region 2 during the cold season was 2.5 μg m^{-3} at ALH157, higher than the highest value of 2.1 μg m^{-3} at BEL116 in region 3. During the warm season, HNO_3 ranged from 1.7 μg m^{-3} in region 4 to 2.8 and 2.9 μg m^{-3} in regions 3 and 2. During the cold season, the highest concentration of HNO_3 was in region 3, and the lowest in region 2, with values of 2.3 and 1.8 μg m^{-3}, respectively. Considering both seasons, region 3 had the highest concentration of HNO_3 among the four regions. Region 2 had the lowest concentration of HNO_3 among regions 2-4 during the cold season due to the fact that a large portion of HNO_3 was neutralized by NH_3 to form NH_4NO_3. For TNO_3, in both seasons, region 2 had the highest concentration, being 4.3 and 5.3 μg m^{-3} in the warm and cold seasons, mainly because of the significantly higher concentration of NO_3^- than other regions. TNO_3 was 3.2 and 3.5 μg m^{-3} for region 3, and 2.0 and 2.3 μg m^{-3} for region 4 during the warm and cold seasons. NH_4^+ in regions 2-4 varied from 1.9 to 2.7 μg m^{-3} during the warm season, and 1.1 to 2.3 μg m^{-3} during the cold season, with the highest concentrations in region 2 and the lowest concentrations in region 4 for both seasons. NH_4^+

was higher in the warm season than in the cold season for all regions, as much more $(NH_4)_2SO_4$ formed in the warm season than in the cold season.

In general, region 1 had the lowest concentration of all species among the 4 regions, and region 4 had the second lowest except HNO_3 which was slightly more than in region 2 during the cold season. Regions 2 and 3 were the two most polluted regions in the EUS and ECA. Region 3 had the highest regional concentration of SO_2 in both seasons, more than double that in region 1 and 4; Region 2 had the highest concentration of NO_3^- and TNO_3. In both seasons, NO_3^- in region 2 was more than 4 times higher than that in regions 1 and 4, and TNO_3 was more than double that in regions 1 and 4.

3.2 Time series of annual concentrations of SO_4^{2-}, SO_2, NO_3^-, HNO_3, TNO_3 and NH_4^+ during 1990-2015

Time series of annual concentrations of SO_4^{2-}, SO_2, NO_3^-, HNO_3, TNO_3 and NH_4^+ for each region as well as each site of the region are shown in Fig. S3.a for the cold season and Fig. S3.b for the warm season. As an example, time series of regional averaged annual concentrations in regions 2 and 4 are shown in Fig. 2.a and b for the cold and warm seasons. Time series of regional averages for regions 1-4 normalized to year 2000 are presented in Fig. 3.a and 3.b for the warm and cold seasons. Year 2000 was chosen for normalization because: (1) emissions of NO_x changed little during the first 10 years; (2) 10 and 25 years of change of annual concentrations of each species will be discussed in Section 3.3. As shown in Fig. S3, the time series for the stations within each region were very highly correlated when the stations are properly grouped into 4 regions. The discussion in this section is based on the time series of annual concentrations presented in Fig. S3 as well as Fig. 3.

3.2.1 SO_4^{2-} and SO_2

3.2.1.1 SO_4^{2-} and SO_2 during the cold season

As seen from the time series of the annual concentrations in Fig. S3, SO_4^{2-} in region 1 had a steady decreasing trend from 1989 to 2000, then a relatively slower decreasing trend from 2001 to 2016. SO_4^{2-} in region 2 had a decreasing trend during 1989-1995 and a slow decreasing trend during 1995-2005. From 2005 to 2016, there was a straight decreasing trend with only small increases in 2008 and 2014. SO_4^{2-} in region 3 generally decreased significantly for the period 1989-1999 and was followed by a slow decreasing period from 2000-2008. There was a smooth decreasing trend from 2008 to 2016, and the drop of the annual concentration was significant in 2008-2011 and 2014-2016. SO_4^{2-} in region 4 had a peak in 1989 for 1988-1990, which was followed by three relatively constant periods of 1990-1993, 1994-2001 and 2002-2007 with the averages of the annual concentrations of SO_4^{2-} during the periods being 3.4 $\mu g\ m^{-3}$, 3.1 $\mu g\ m^{-3}$, and 2.8 $\mu g\ m^{-3}$ respectively. There were only two major drops between the periods, in 1994 and 2002 respectively. From 2007 to 2016, SO_4^{2-} in region 4 had a steep drop, and the concentration was reduced from 2.7 $\mu g\ m^{-3}$ in 2007 to 1.1 $\mu g\ m^{-3}$ in 2016. In general, SO_4^{2-} in the EUS and EC during the cold season can be described by two fast decreasing periods of 1989-1995 and 2005-2016, and a slow decreasing period of 1995-2005. The annual reduction rates during the three periods were 0.14, 0.03, and 0.05 $\mu g\ m^{-3} yr^{-1}$ in region 1; 0.16, 0.04, and 0.13 $\mu g\ m^{-3} yr^{-1}$ in region 2; 0.15, 0.05, and 0.15 $\mu g\ m^{-3} yr^{-1}$ in region 3; and 0.10, 0.04 and 0.14 $\mu g\ m^{-3} yr^{-1}$ in region 4. The decreasing rates in regions 2 and 3 were close. If all sites within regions 1-4 were combined, the corresponding rates were 0.14, 0.04, and 0.12 $\mu g\ m^{-3} yr^{-1}$ for the three periods.

SO_2 in regions 2-4 during the cold season had a significant drop in 1989-1995 with a temporary increase in 1993 and 1994. From 1995 to 2005 the decreasing trend was slow, and then there was a very steep reduction from 2005 to 2012. The trend from 2012 to 2016 was relatively flat. The trend of SO_2 in region 1 was similar except that there was no obvious increase in 1993- 1994.

SO_2 exhibited an annual reduction rate of 0.28, 0.06, and 0.12 $\mu g\ m^{-3} yr^{-1}$ in region 1; 0.83, 0.09, and 0.73 $\mu g\ m^{-3} yr^{-1}$ in region 2; 1.13, 0.22, 1.13 $\mu g\ m^{-3} yr^{-1}$ in region 3; 0.32, 0.08, and 0.49 $\mu g\ m^{-3} yr^{-1}$ in region 4 for the periods of 1989-1995, 1995-2005, and 2005-2012. For regions 1-4 combined, the corresponding reduction rates were 0.72, 0.16 and 0.48 μg $m^{-3}yr^{-1}$. For the third period, if we only consider 2005-2012, the annual reduction rate was 0.61 μg $m^{-3}yr^{-1}$. Although the trend of SO_2 during 2012-2016 was generally flat, the decrease of SO_4^{2-} during the period was still significantly, especially in terms of percentage.

3.2.1.2 SO_4^{2-} and SO_2 during the warm season

SO_4^{2-} in region 1 had a significant decrease from 1989 to 1996, followed by a levelling off until 2005 and a decreasing trend from 2005-2016. After a significant peak in 1989, SO_4^{2-} in region 2 had a large drop from 1989 to 1993. There was a steady decreasing trend for 1994-2004, followed by a significant peak in 2005 which was captured by all measurement sites within the region. This was followed by a smooth decreasing trend for 2005-2016, with major drops in 2005-2006, 2007-2009, 2012, and 2013-2016. Unlike region 2, SO_4^{2-} in region 3 had no significant peak in 1989, and had a decreasing trend during 1989-1999. There was a levelling off for 1999-2005, and it was followed by a significant decreasing trend for 2005-2016 with steep drops in 2005-2006, 2007-2009, and 2011-2016. SO_4^{2-} in region 4 had a decreasing trend in 1989-1994 and a slow decreasing trend in 1994-2000. After a drop in 2001, it had another levelling off in 2001-2007 with a peak in 2005. There was a significant straight decreasing trend for 2007-2016 with a major drop during 2007-2009. SO_4^{2-} in all stations converged to the regional average after 2009. In general, the trend of SO_4^{2-} during the warm season can be characterized by two fast reduction periods of 1989-1995 and 2007-2016, and a slow period of 1995-2007. For the three periods, SO_4^{2-} had a reduction rate of 0.17, 0.01 and 0.14 μg $m^{-3}yr^{-1}$ for region 1; 0.39, 0.03 and 0.43 μg $m^{-3}yr^{-1}$ for region 2; 0.28, 0.01 and 0.52 μg $m^{-3}yr^{-1}$ for region 3; and 0.24, 0.04 and 0.50 μg $m^{-3}yr^{-1}$ for region 4. For regions 3 and 4, the most significant decrease occurred in 2007-2009.

SO_2 concentrations during the warm season was quite low during 1990-2015 in region 1. There was a slow decreasing trend from 1990 to 2007, a relatively large decreasing trend in 2007-2009, and a level-off at very low concentration (< 1.0 μg m^{-3}) in 2009-2016. SO_2 during the warm season in regions 2-4 had similar trends: (1) a fast decreasing period of 1989-1995, with a levelling off period of 1992-1994 in region 2 and a peak in 1993 in regions 3 and 4; (2) a slowly decreasing period of 1995-2007 with an initial slow increase in 1995-1999 in region 2, and an initial steep increase in 1996-1998 in region 3 and 4; (3) a fast decreasing period of 2007-2016 with very steep decreases in 2007-2009. SO_2 had annual reduction rates of 0.12, 0.03 and 0.04 μg $m^{-3}yr^{-1}$ for region 1; 0.55, 0.08, and 0.43 μg $m^{-3}yr^{-1}$ for region 2; 0.46, 0.11 and 0.48 μg $m^{-3}yr^{-1}$ for region 3; 0.13, 0.05 and 0.22 μg $m^{-3}yr^{-1}$ for region 4. For the whole region, the annual reduction rates during the warm season were 0.31, 0.04 and 0.38 μg $m^{-3}yr^{-1}$ for SO_4^{2-}, and 0.34, 0.08, and 0.30 μg $m^{-3}yr^{-1}$ for SO_2 for the periods of 1989-1995, 1995-2007, and 2007-2016.

3.2.2 NO_3^-, HNO_3 and TNO_3

3.2.2.1 NO_3^-, HNO_3 and TNO_3 during the cold season

NO_3^- in EUS and EC during the cold season was dominated by NO_3^- in region 2, which was much higher than NO_3^- in other regions. As the trends of NO_3^- during the cold season were not as obvious as other species, the MKT was applied to detect if a monotonic (increasing or decreasing) trend existed. The MKT indicated that: (1) NO_3^- in region 2 had no obvious trend in the period of 1989-2001 ($p = 0.45$, tau $= 0.18$), but there was a decreasing trend for the period 2001-2016 ($p < 0.001$, tau $= -0.70$); the trends of NO_3^- in regions 1, 3 and 4 over the whole study period were pretty flat ($p = 0.17$-0.40, $|tau| < 0.2$).

Excluding a peak of 1.9 μg m^{-3} in 1993, the trend of HNO_3 in region 2 in the 1990s is flat. From 2003 to 2013, there was a decreasing trend, then a slow increasing trend for 2013-2016 in region 2. HNO_3 in region 3 showed a general declining trend by 21.7% (2004-2005 *vs.* 1989-1990) during 1989-2005. The declining trend of HNO_3 in the 1990s was consistent with the increasing trend of NO_3^- during the period, as more HNO_3 was neutralized by additional NH_3 made available from decreasing SO_4^{2-}. HNO_3 decreased markedly from 2005 to 2009 in region 3, then exhibited a slower decreasing trend for 2009-2016. HNO_3 in region 4 had an initial decrease from 1989 to 1991, then an increasing trend of 21.1% (1999-2000 *vs.* 1991-1992) for 1991-2000. The region then showed a slow decrease in 2000-2005, a fast decrease in 2005-2009, and a slow decrease in 2009-2016.

TNO_3 in the cold seasons over region 2, 3 and 4 had similar trends. For 1990-2001, the general trend of TNO_3 over the regions was from roughly constant to slowly increasing. This is consistent with the NO_x emission trend during the period. For 2001-2016, there was a significant decrease of TNO_3 over the three regions. For region 3, it occurred mainly during the period 2001-2009.

3.2.2.2 NO_3^-, HNO_3 and TNO_3 during the warm season

NO_3^- in region 1 had an increasing trend in 1990-2000, a decreasing trend in 2000-2007, and a flat trend in 2007-2016. Linear regression of annual NO_3^- concentration in region 2 during the warm season from 1990 to 1999 showed a slow increasing trend for NO_3^- in the 1990s. After 2002, there was a straight decline of NO_3^- concentration until 2009, and a steady decreasing from 2011-2016. Linear regression of NO_3^- in region 3 shows a flat trend during 1989-2000 and a weakly increasing trend during 1990-1999. Between 2000 and 2005, NO_3^- in region 3 exhibited a clearly declining trend. From 2005 to 2016, the trend was generally flat. Annual concentration of NO_3^- in region 4 had a weakly increasing trend for 1992-2000, followed by a decreasing trend for 2000-2005 and a slow increasing trend for 2005-2016. In general, NO_3^- during the warm season had a flat-to-weakly-increasing trend for 1990-2000 and a strong decreasing trend for 2000-2005 for regions 2-4. For 2005-2016, there was a decreasing trend for region 2, a flat trend for region 3, and a weakly increasing trend for region 4.

HNO_3 in region 1 was very low (< 1.0 μg m^{-3}) in general during the whole study period. There was flat trend in 1990 to 2001, a slow decreasing trend in 2001 to 2009, and a flat trend again in 2009 to 2016. HNO_3 in regions 2-4 can be characterized by three periods: a flat (regions 2 and 3) or a week increasing (region 4) trend for 1989-1999, a significant decreasing trend for 1999-2009, and a generally flat trend for 2009-2016.

HNO_3 dominated over NO_3^- in TNO_3 during the warm season for all regions, and especially in regions 3 and 4, where the ratio of NO_3^- to TNO_3 was usually less than 20%. Therefore, the trend of TNO_3 generally followed that of HNO_3 during the warm season. In the 1990s (1990-1999) the trend of TNO_3 in the warm season over regions 2 and 3 was very flat, and there was a very weakly increasing trend over region 4. The turning point of the trend was in 1999. For the period 1999-2009, all three regions showed significant decreasing trends. For 2009-2016, the trends in the three regions were generally flat.

3.2.3 NH_4^+

3.2.3.1 NH_4^+ during the cold season

NH_4^+ during the cold season in region 1 had a flat trend in 1990-1999, a very slow decreasing trend in 1999-2009, followed by a generally flat trend in 2009-2015. The trend of NH_4^+ in region 2 during the cold season was affected by both SO_4^{2-} and NO_3^-. It had a near-linear decreasing trend from 1991 to 2009, and was followed by another steeper declining trend for 2009-2016. NH_4^+ in region 3 had a steep decrease in 1989-1994, and was followed by a weak decrease and a steep decrease in 1994-2009 and 2009-2016 respectively. NH_4^+ in region 4 remained unchanged during 1990-2001. After 2001, NH_4^+ decreased steadily until 2016.

3.2.3.2 NH_4^+ during the warm season

NH_4^+ in region 1 changed little in 1990-2005 and 2009-2015 during the warm season, but there was a decreasing trend in 2005-2009. Excluding the two significant peaks in 1989 and 2005, NH_4^+ in region 2 showed a consistent and steady decreasing trend from 1990 to 2016. Fig. 3 shows that the trend of NH_4^+ in region 3 generally followed that of SO_4^{2-} closely because NH_4^+ in region 3 was dominantly associated with SO_4^{2-} during the warm season. The two trends were almost identical after 2000. From 1995-2005, the trend of NH_4^+ in region 3 was almost flat. There was a major decrease of NH_4^+ in region 3 in 2005-2009 when it decreased by almost 50% in 4 years. NH_4^+ in region 4 changed little from 1990-2000. Although during the same period SO_4^{2-} had an obvious decreasing trend, its impact on NH_4^+ was offset by the increasing trend of NO_3^- during this period. After a drop in 2000-2001, NH_4^+ had a flat trend for 2001-2007, a dramatic decrease in 2007-2009, and a steady decreasing trend for 2010-2016.

3.3 10 and 25 years of changes of ambient SO_4^{2-}, SO_2, NH_4^+, NO_3^-, HNO_3 and TNO$_3$ in the EUS and EC for 1990-2015

As mentioned in Section 1, emissions of NO_x changed little during the 1990s in the EUS. Correspondingly, the time series of TNO$_3$ in regions 2-4 during the 1990s didn't decrease or even increased, as shown in Section 3.2. Also, some important metrics, such as RSO$_4$ during the cold season and RNO$_3$ during the warm and cold seasons, only started to have significant changes after the first 10 years. In order to capture how ambient air pollutants responded to emission reductions of SO_2 and NO_x temporarily, 10 and 25 years of change of ambient SO_4^{2-}, SO_2, NH_4^+, NO_3^-, HNO_3, and TNO$_3$ during 1990-2015 are presented in Tables 2 and 3, and are summarized in Sections 3.3.1 and 3.3.2. To avoid the fluctuation of annual ambient concentrations due to the variation of meteorology, the changes are calculated based on 3-year averages centered on 1990, 2000, and 2015.

3.3.1 10 years of changes for the period 1990-2000

During the 10-year period of 1990-2015, air quality in the EUS and EC underwent a number of major changes which are summarized as follows:

1. During the first 10 years, SO_2 concentrations declined in all regions and seasons by more than 25.0% except for region 4, which had a reduction of 15.5% during the warm season and 23.8% during the cold season.
2. SO_4^{2-} showed a similar but less significant decreasing trend as SO_2. The reduction was more than 20% in all regions except for region 4 during the cold season. Region 4 during the warm season had a similar reduction rate to region 3 despite the significant difference in the reduction rates of SO_2 in the two regions.
3. NO_3^- increased between 6.6% and 40.0% during the cold season for regions 1-4. Changes of NO_3^- during the warm season in regions 3 and 4 were very small, and only had a significant reduction of 9.6% in region 2.
4. TNO_3 increased little in region 1, by 0.09 and 0.02 $\mu g\ m^{-3}$ for the cold and warm seasons respectively. TNO_3 in regions 2 and 3 changed very little during the cold season, and had a 9.4% and 11.8% reduction during the warm season. TNO_3 in region 4 increased by 3.9% during the warm season, and by 14.2% during the cold season.
5. NH_4^+ declined by 12% to 29.8% during both seasons, except for a negligible change in region 4 during the cold season.
6. In summary, over the first ten-year period of 1990-2010, SO_2, SO_4^{2-} and NH_4^+ declined by 31.6%, 26.7% and 18.5% respectively in the EUS and EC. HNO_3 reduced in regions 1-3. NO_3^- increased in regions 1-4 during the cold season, and changed very little (< 0.15 $\mu g\ m^{-3}$) during the warm season. Considering both seasons and all regions, NO_3^- increased by 12.7%, HNO_3 declined by 5.6%, and

the change of TNO_3 was negligible with the mean concentration being 3.02 μg m^{-3} for 1989-1990 *vs.* 3.05 μg m^{-3} for 1999-2001.

3.3.2 25 years of changes for the period 1990-2015

During the 25-year period of 1990-2005, air quality in the EUS and EC changed significantly, and are summarized as follows:

1. Among all species, the most significant reduction during the period was SO_2. The reduction of SO_2 in regions 2-4 was similar in percentage, from 83.9% in the warm season for region 4 to 91.2% in the warm season for region 3. There were no major differences between the warm and cold seasons in terms of percentage reduction. In terms of absolute value, the biggest reduction was for SO_2 in region 3 during the cold season, and the 3-year-averaged annual concentration was reduced from 19.2 μg m^{-3} to 2.2 μg m^{-3}.
2. The reduction in SO_4^{2-} concentrations during the cold season was relatively uniform in terms of percentage, ranging from 60.1% in region 2 to 62.5% in region 3. The reduction was more significant during the warm season than during the cold season, ranging from 72.7% in region 1 to 78.7% in region 4. The reductions in regions 2, 3, and 4 were similar in terms of values in both seasons. The reduction of SO_4^{2-} in terms of percentage was much smaller than SO_2 in all regions during both seasons except for SO_4^{2-} during the warm season in region 1.
3. During the warm season, the reduction of NO_3^- was seen in all 4 regions, ranging from 14.3% and 15.6% in regions 1 and 4, to 36.2% and 57.5% in regions 3 and 2. The reduction of NO_3^- during the cold season was only observed in region 2 (30.4%). Although TNO_3 was reduced during the cold season in regions 3 and 4, a higher percentage of HNO_3 was converted to NO_3^- as more excess NH_3 was available to form NH_4NO_3 due to the reduction of SO_4^{2-}. As a result, the trend of NO_3^- in the two regions during the cold season changed very little. Unlike regions 3

and 4, region 2 did observe a significant reduction of NO_3^- in the cold season, following a 38.3% reduction of TNO_3. This can be explained as region 2 is an NH_3-rich region. Formation of NH_4NO_3 during the cold season in the region is less sensitive to the excess NH_3 made available from SO_4^{2-} reduction than in regions 3 and 4. This can also be demonstrated by the least reduction of HNO_3 (in terms of percentage) in region 2 during the cold season as well as the correlations of RNO_3 *vs.* SO_4^{2-} shown in Section 5.4.

4. The reduction of HNO_3 was similar in all four regions during the warm season, ranging from 63.1% to 68.8%. During the cold season, region 2 had the lowest percentage reduction at 56.0%, and region 1 had the highest at 63.5%. The reduction of HNO_3 can be through two paths: a reduction of NO_x emissions and an increased neutralization of HNO_3 by more excess NH_3 due to lower amount of formation of $(NH_4)_2SO_4$ and NH_4HSO_4. In terms of percentage, the reduction of HNO_3 was more significant than TNO_3 during the cold season, ranging from 14.4% more in region 4 to 28.0% more in region 1.
5. TNO_3 had a reduction rate ranging from 35.5% for the cold season in region 1, to 64% during the warm season in region 3. The reduction during the warm season was much higher than in the cold season, ranging from 11.4% higher in region 4 to 23.9% higher in region 3. The difference was partially due to extra reductions of NO_x emissions from power plants and other large combustion sources during the ozone season (May – September) required by the NBP that began in 2003 and the Clean Air Interstate Rule that started in 2009 (Napolitano et al., 2007; Butler et al., 2011; Sickles and Shadwick, 2015).
6. The reduction of NH_4^+ was similar in regions 2, 3, and 4, ranging from 48.9% to 53.2% in the cold season, and from 74.0% to 75.7% in the warm season. The reduction of NH_4^+ during the warm season was more significant than in the cold season, over 20% more in regions 2-4. The reduction of NH_4^+ generally followed the trends of SO_4^{2-}, but the reduction rate was much lower than that of SO_4^{2-} during the cold season because a certain percentage of NH_4^+ was associated with NO_3^- and the reduction of NO_3^- was not as significant as SO_4^{2-} during the cold

season. Region 2 exhibited the largest reduction of NH_4^+ (75.7%) during the warm season, contributed by a 76.8% reduction of SO_4^{2-} as well as a 57.5% reduction of NO_3^-.

7. RSO_4 increased the most in region 3 during the cold season at 166.3%, and the least in region 1 during the warm season at 0.6%. During the warm season, RSO_4 increased by 54.9% and 58.4% in regions 2 and 3, respectively. The increase of RSO_4 during the cold season was much higher than in the warm season in terms of percentage, ranging from 48.6% in region 1 to 166.3 % in region 3.
8. RNO_3 increased significantly in regions 1, 3, and 4 in both seasons, ranging from 73.9% to 94.9%, but RNO_3 only increased by 8.0% and 12.8% in the warm and cold seasons for region 2, which was rich in NH_3.
9. As presented in Table 3, for the whole region: (1) among the 5 species of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3 and SO_2, only SO_4^{2-} and SO_2 still had regionally-averaged annual concentrations exceeding 1.0 $\mu g\ m^{-3}$ at the end of the study period. (2) SO_4^{2-} was reduced by 73.3% for the whole region during the study period, and it was reduced about 15% more in the warm season than in the cold season in terms of percentage; (3) NH_4^+ was reduced more in the warm season than in the cold season, in terms of both percentage and absolute value; (4) NO_3^- was reduced by 29.1% for the whole region. The reduction during the cold season occurred only in region 2, and the reduction during the warm season mainly occurred in regions 2 and 3. The reduction of NO_3^- for the whole region was mainly due to the reductions in region 2 during the warm and cold seasons; (5) RSO_4 increased by 97.7% in the cold season, much higher than 26.2% in the warm season. RSO_4 increased the most in region 3 during the cold season, in terms of both absolute value and percentage.

3.4 Air quality at the end of the study period: 2014-2016

3-year-averaged air concentrations for 2014-2016 are used to describe the air quality at the end of the study period, and are presented in Table S2 and Fig. S2. The air concentration mentioned in this Section refers to the 3-year-averaged air concentration for each species, either for the warm or the cold seasons.

As at the beginning of the period, region 1 had the cleanest air among all regions with the lowest air concentrations, being less than 1.0 μg m^{-3}, for all species and for both the warm and cold seasons. Unlike at the beginning of the period that SO_4^{2-} during the warm season was about double that during the cold season in regions 2-4, SO_4^{2-} at the end of the period had no significant differences between the two seasons. The air concentrations of SO_4^{2-} were less than 2.0 μg m^{-3} in all regions and both seasons. For regions 2-4 the regional averages ranged from 1.6 to 1.8 μg m^{-3} during the warm season, and from 1.4 to 1.7 μg m^{-3} during the cold season. SO_2 during the warm season was only from 0.6 to 1.0 μg m^{-3} for regions 2-4. In the cold season, SO_2 in regions 2 and 3 was the same at 2.2 μg m^{-3}, and was only 1.1 μg m^{-3} in region 4. NH_4^+ during the warm season varied from 0.5 to 0.7 μg m^{-3} for regions 2-4. During the cold season, it was 0.5 and 0.8 μg m^{-3} in regions 4 and 3 respectively, and it was much higher in region 2 with the value of 1.2 μg m^{-3}. The air concentration of NO_3^- during the warm season was very low in regions 3 and 4 with values of 0.3 μg m^{-3}, and it was doubled in region 2, being 0.6 μg m^{-3}. During the cold season, NO_3^- was much higher than during the warm season, being 2.5, 1.3 and 0.5 μg m^{-3} for regions 2, 3, and 4 respectively. HNO_3 in regions 2-4 varied from 0.6 μg m^{-3} in region 4 to 1.1 μg m^{-3} in region 2 during the warm season, and from 0.7 μg m^{-3} in region 4 to 0.9 μg m^{-3} in region 3 during the cold season. There was little difference between the warm and cold seasons in regions 3 and 4. TNO_3 was highest in region 2 in both seasons, being 1.7 and 3.2 μg m^{-3} for the warm and cold seasons respectively. Region 3 had the second highest TNO_3 with values of 1.2 μg m^{-3} and 2.1 μg m^{-3} for the warm and cold seasons, and the corresponding values for region 4 were 0.9 μg m^{-3} and 1.3 μg m^{-3}.

In summary, for species of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3 and SO_2, region 1 had air concentrations of less than 1.0 μg m^{-3} for all species in both seasons. For regions 2-4, NO_3^- was less than 1.0 μg m^{-3} for all regions and both seasons except regions 2 and 3 during the cold season, for which the air concentrations of NO_3^- were 2.5 and 1.3 μg m^{-3} respectively; HNO_3 was less than 1.0 μg m^{-3} except region 2 during the warm season with a value of 1.1 μg m^{-3}; NH_4^+ was less than 1.0 μg m^{-3} for all regions except region 2 during the cold season at 1.2 μg m^{-3}; SO_4^{2-} was greater than 1.0 but less than 2.0 μg m^{-3} for regions 2-4 and both seasons; SO_2 was greater than 1.0 but less than 2.5 μg m^{-3} for regions 2-4 and both seasons, except regions 3 and 4 during the warm season being 0.8 and 0.6 μg m^{-3}. Among 4 regions, region 2 had the highest air concentration for all species except HNO_3 during the cold season. Especially NO_3^- in region 2 was double the second highest value in region 3 in both seasons. Also NO_3^- in region 2 had the highest in value (at 2.5 μg m^{-3}) among all species in 4 regions and both seasons, although it has significantly decreased from 3.6 μg m^{-3} at the beginning of the study period.

3.5 The Long-term trends derived with polynomial regressions

Through trial and error, we found that polynomial regressions can reasonably describe the long-term trends of species for the period. Through these regressions, we can eliminate the relative-short-term variations due to meteorology. The 4th order polynomial regressions were applied to the normalized annual means of SO_4^{2-}, SO_2 and NH_4^+ during the cold and warm seasons. For NO_3^-, HNO_3 and TNO_3, we applied the 5th polynomial regressions to better capture the trends. The regressed trends are normalized to the regressed values of year 2000 as this was the turning point for the trends of NO_3^-. Examples of the regression for SO_4^{2-} and SO_2 in region 3 during the cold season are shown in Fig. 4. Fig. 5 shows the comparisons between the normalized annual means during the cold season in region 3 and the corresponding regressed values.

The regressed trends for SO_4^{2-}, SO_2, NH_4^+, NO_3^-, HNO_3 and TNO_3 for the 4 regions during the cold and warm seasons are shown in Fig. 6.a. The regressed trends for regions 1-4 clearly show: (1) the most significant reduction of all species was SO_2; (2) There were significant disparities of the reduction rates between SO_4^{2-} and SO_2 during the cold season. There were also disparities during the warm season in regions 1-3, but much less significant than the cold season; (3) among all species, the least significant reduction was for NO_3^- during the period. Fig 6.b shows the regressed trends for each species during the cold and warm seasons for different regions. For SO_4^{2-} and SO_2, there were large differences for the trends during 1990-2000 between regions 1 and 4. The trends of NH_4^+ were different for the 4 regions during 1990-2000 in both seasons, and during 2000-2016 in the cold season. In the warm season, the trends of NO_3^- were similar for regions 2-4 during 1990-2000, but were different during 2000-2016. The trends of HNO_3 and TNO_3 were different for 1990-2000 during the warm season, but were similar during 2000-2016.

4. Discussions

4.1 RSO_4 and correlations of RSO_4 *vs.* SO_2

RSO_4 is a metric describing how much sulfur in the air is oxidized from gas SO_2 to particulate SO_4^{2-}. The similar metric, the ratio of SO_2 mass oxidized below 2 km to SO_2 mass emitted, was used by Shah et al (2018). RSO_2, which is 1 - RSO_4, was used by Sickles and Shadwick (2015). RSO_4 is also an indicator of gas-particle partition ratio for sulfur in the air as SO_2 and SO_4^{2-} exist in the air as gas and particle respectively. This metrics depends on a number of factors: the oxidation capacity of the air, the local emission rate of SO_2, the transportation of SO_2 and SO_4^{2-} from upwind regions, and the time it takes to bring upwind SO_2 and SO_4^{2-} to a local site. Generally the longer it takes to transport an upwind air parcel, the more percentage of SO_2 is oxidized into SO_4^{2-} and the more SO_2 is dry-deposited than SO_4^{2-}, so the higher RSO_4; also the less percentage of SO_2 is emitted locally and the higher the atmospheric oxidation capacity, the higher RSO_4. RSO_4 for 1989-1991 and 2014-2016, and the changes of RSO_4 between 1989-1991 and 2014-2016 during the warm and cold seasons are presented in Fig. S4. During the warm season, because more solar photons are available to produce O_3 from NO_x and VOCs, RSO_4 was much higher in the warm season than cold season. At the beginning of the period, RSO_4 in the warm season was about double that in the cold season in regions 1, 2 and 4, and around triple in region 3. RSO_4 was much higher in regions 4 and 1 than in regions 2 and 3 because the local emissions of SO_2 were much higher in regions 2 and 3. The “freshly” emitted SO_2 made RSO_4 in regions 2 and 3 relatively smaller. RSO_4 in region 3 during the cold season was only 13.1% in 1989-1991, indicating a very low sulfur gas-particle partitioning ratio. Fig. S4 shows that during the cold season, RSO_4 increased by more than 40% at all sites except for VPI120, which increased by 18.7%. During the warm season, RSO_4 increased at all sites except for VPI120, ASH135 and WST109, which decreased by 25.0%, 12.5% and 3.9% respectively. The most significant increase of RSO_4 was in region 3 during the cold season, with a regional average of 166.3%.

Fig. 7 shows that RSO_4 increased with year linearly for region 1 and quadratically for regions 2-4 for both seasons. RSO_4 increased significantly after 2005 in regions 2-4. Fig. 8 shows the correlations of RSO_4 *vs.* SO_2 for regions 2-4 and it is clearly that RSO_4 increased with the decrease of SO_2. The increase of RSO_4 was relatively slow when the concentration of SO_2 was greater than 5 $\mu g\ m^{-3}$ in the cold season, and 7.5 $\mu g\ m^{-3}$ in the warm season. RSO_4 soared when SO_2 was less than 5 $\mu g\ m^{-3}$ in the cold season in regions 2-4, and less than 3 $\mu g\ m^{-3}$ in the warm season in regions 2 and 3. The increase of RSO_4 with the decrease of SO_2 can be explained as follows: (1) the atmospheric oxidants didn't decrease as much as SO_2 emissions did. For example, the daily maximum 8 hour average O_3 only decreased by 14% for the EUS during the May-September ozone season from 1997 to 2008 (Butler et al., 2011), and decreased by 4-15% during 1997-2006 for region 2, 3, and 4 (Chan, 2009). No decreasing trend was found for the EUS during the cold season for 1997-2006 (Chan, 2009). Sickles and Shadwick (2015) found that O_3 in the EUS increased during the cold season for 1990-2010. O_3 is an atmospheric oxidant, and is a precursor to the formation of other atmospheric oxidants, such as OH and H_2O_2. Therefore, relative to the significantly reduced SO_2, more atmospheric oxidants were available to oxidize SO_2, and RSO_4 increased significantly during the period. (2) NH_3 was relatively unchanged during the period, and even increased in some regions (Yao and Zhang, 2016). The decrease of SO_2 caused the decrease of H_2SO_4 formation. Together this made cloud or rain droplets or snow particles less acid, which was beneficial to the oxidation of SO_2 by H_2O_2 in aqueous phase (Makar et al., 2009; Jones and Harrison, 2011).

The disparity of the reduction of SO_4^{2-} and SO_4^{2-} in responses to emission reductions of SO_2, namely the reduction rate of SO_2 was faster than SO_4^{2-}, has been reported and discussed in some previous studies (Lövblad et al., 2004; Reid et al. 2001; Sickles II and Shadwick, 2015; Shah et al., 2018; Aas et al., 2019). The time series of the normalized regional concentrations of SO_4^{2-} and SO_2 in Fig. 3 have clearly shown the disparity during the period of 1990-2015. The significant increase of RSO_4 during the period, especially during the cold season, explains why the reduction rate of SO_2 was much higher than that of SO_4^{2-}. The reduction of SO_2 was due to not only the emission reductions, but also more faction of SO_2 was converted to SO_4^{2-}. Faster reduction of SO_2 was observed for all 4 regions during the cold season, both before and after year 2000, and it was more significant after 2000. This can be explained by the fact that the increase of RSO_4 with time was nonlinear. As shown in Table 2, in the first 10 years of the study period, the increase of RSO_4 was relatively limited. During the cold season, it was only increased by 7.3% in region 4 to 16.5% in region 3. It was in the last 10 years from 2005-2015 when SO_2 was further reduced that RSO_4 increased dramatically. As shown in Tables 2 and 3, during the cold season in region 3, RSO_4 was only increased by 16.5% in the first 10 years from 1990-2000, but it was increased by 149.8% for the last 15 years of 2000-2015. During the warm season, the disparity of reduction between SO_2 and SO_4^{2-} was much less, as clearly shown in Fig. 3. This is because the increase of RSO_4 during the warm season was much less significant than during the cold season (Table 4). In the first 10 years, RSO_4 changed from -4.1% in region 4 to 7.7% in region 1. For the period of 1990-2015, RSO_4 only increased by 0.6% and 12.4% percentage in regions 1 and 4. The disparity of the reduction rate of SO_2 *vs.* SO_4^{2-} for these two regions was only 1.7% and 5.2% during the warm season respectively. This is expected, and can be explained as follows: (1) in the warm season more atmospheric oxidants are produced due to more solar photons available than in the cold season, so oxidation of SO_2 is less limited by the availability of atmospheric oxidants in the warm season; (2) in the cold season, limited atmospheric oxidants are available for the oxidation of SO_2. The reduction of the SO_2 emissions to the air will make more atmospheric oxidants available to each SO_2 molecule, increase the oxidation rate of SO_2, and result in an increase of RSO_4; (3) furthermore, in the EUS, the annual mean O3 concentration decreased in the warm season and increased in the cold season for the study period (Sickles and Shadwick; 2015). This made the overall oxidation capacity of the lower atmosphere in the EUS higher in the cold season and lower in the warm season.

4.2 Correlations of SO_4^{2-} *vs.* SO_2

Correlations between SO_4^{2-} and SO_2 are presented in Fig. 9 for regions 1-4 and for the warm and cold seasons. The SO_4^{2-}-SO_2 relationships can be described by linear regressions for the period of 1990-2010 with R = 0.87 - 0.98 during the warm season, and R = 0.96 - 0.99 during the cold season. During the cold season, region 1 had the highest slope, and it was followed by regions 4, 2, and 3. During the warm season, the slopes for regions 1 and 4 were similar, and were higher than slopes for regions 2 and 3. A linear relationship between the annual concentrations of SO_4^{2-} and SO_2 indicates that there exists a linear relationship between the concentration of SO_4^{2-} and the emission of SO_2. This is consistent with the relationship of the SO_4^{2-} concentration and the SO_2 emission rate from the early 1990s through 2010 revealed in the study of Hand et al. (2012). As RSO_4 significantly increased when SO_2 was further reduced during 2010-2016, as seen in Fig. 8, the slopes of the linear regression for

2010-2016 were much higher than those for 1990-2010. A power law regression, which bends a linear regression with a gentle slope to a linear regression with a steep slope, described the SO_4^{2-}-SO_2 relationships very well with R= 0.97-0.98 during the cold season, and R=0.94-0.99 during the warm season, as shown in Fig. 10. In some previous studies (e.g., Jones and Harrison, 2011), nonlinear power-law relationships have been found for observations at different sites and seasons, and for different periods. Our results indicate that a linear relationship between SO_4^{2-} and SO_2 exists for a relatively short period, but generally the correlation of SO_4^{2-} *vs.* SO_2 is a power-law relationship.

4.3 RNO$_3$

Similar to RSO$_4$ being a gas-particle partition indicator for sulfur in the air, RNO$_3$ is a metric indicating the fraction of gas HNO_3 is aerosolized (Sickles and Shadwick, 2015). In the air, the emitted NO_x is oxidized to gas HNO_3, which can be aerosolized through two paths: (1) reaction with NH_3 to form NH_4NO_3; (2) reaction with existing aerosols such as seal salts and crustal materials to form NaNO3, $Ca(NO_3)_2$, $Mg(NO_3)_2$ et al. The ratio is significantly sensitive to the air temperature, as NH_4NO_3, NH_3, and HNO_3 in the air are in equilibrium and temperature changes can affect the partitioning between gas and particle phases (Doyle et al., 1979; Harrison and Pio, 1982).

RNO$_3$ for 1989-1991 and 2014-2016, as well as the change of RNO$_3$ between the two periods are shown in Fig. S5. At the beginning of the period: (1) RNO$_3$ in the cold season was much higher than the warm season for all regions. RNO$_3$ of the cold season in regions 2 and 3 was more than double that for the warm season; (2) RNO$_3$ in region 2 was much higher than other regions, and was more than double that in regions 3 and 4. For the 25-year period of 1990-2015, RNO$_3$ significantly increased by more than 70% in regions 1, 3 and 4 during both seasons. In region 2, RNO$_3$ only increased by 12.8% and 8.0% during the cold and warm seasons respectively. The significant increase of RNO$_3$ in regions 1, 3, and 4 can be attributed to the significant reduction of SO_4^{2-} during the period, as it is explained in Section 4.4.

Fig. 7 shows that RNO_3 had an increasing trend with year for all regions and both seasons except for region 2 during the warm season. The trends can be described well by linear regressions in regions 1 and 2, and by quadratic regressions in regions 3 and 4. The linear regression shows that RNO_3 in region 2 had a decreasing trend for 1990-2010 during the warm season. The exact reason for this is unknown. One hypothesis is that due to the global warming trend in recent years, and the significant reductions of sulfate and nitrate aerosols (which cool the atmosphere by reflecting more solar radiation back to the space), the near surface temperature in the Midwest had an increasing trend during the period of 1990-2010 (National Climate Assessment, 2014). As region 2 is rich of NH_3, RNO_3 is more sensitive to the air temperature than to the availability of NH_3. An increasing trend of air temperature in the warm season can cause a decreasing trend of RNO_3.

4.4 Correlations of RNO_3 *vs.* SO_4^{2-}

Correlations between RNO_3 and the annual concentration of SO_4^{2-} for regions 2-4 and for the warm and cold seasons are presented in Fig. 10. For NH_3-rich region 2, RNO_3 increased slightly with the decrease of SO_4^{2-} during the cold season, and there was no obvious trend during the warm season. For regions 3 and 4, which were NH_3-limited, RNO_3 increased with the decrease of SO_4^{2-}. Especially RNO_3 increased steeply when the annual concentration of SO_4^{2-} was less than 4 $\mu g\ m^{-3}$ during the warm season, and less than 3 $\mu g\ m^{-3}$ during the cold season. The increase of RNO_3 with the decrease of SO_4^{2-} can be explained as follows: (1) in regions 3 and 4, the formation of NH_4NO_3 was limited by the availability of NH_3; (2) as SO_4^{2-} decreased, part of NH_3 previously forming $(NH_4)_2SO_4$ / NH_4HSO_4 was released, and was available to react with HNO_3 to form NH_4NO_3. In contrast, RNO_3 was much less sensitive to the SO_4^{2-} reduction in region 2 as the emissions of NH_3 there were much higher than that in regions 3 and 4, as seen in Fig. S6. Thus, in general there was always excess NH3 available to react with HNO_3 to form NH_4NO_3 in region 2, which resulted in a lack of trends in RNO3. This also explained while TNO_3 decreased by 40.1% and 46.4% respectively during the cold season in regions 3 and 4, the change of NO_3^- was negligible in these two regions.

4.5 Correlations of NH_4^+ *vs.* SO_4^{2-} and NO_3^-

Correlations of NH_4^+ *vs.* SO_4^{2-} and NH_4^+ *vs.* NO_3^- are shown in Fig. 11 for regions 2-4 and for the cold and warm seasons. During the warm season, NO_3^- in regions 3 and 4 changed little in value during 1990-2015, while NH_4^+ changed significantly and this change was mostly and linearly associated with the change of SO_4^{2-}. In region 2, the change of NH_4^+ was also mostly associated with the change of SO_4^{2-}, but the change of NO_3^- also made a contribution to it. During the cold season, NH_4^+ correlated with SO_4^{2-} linearly very well in regions 2-4. In region 2, NO_3^- also changed significantly during the period, and the variation of NO_3^- correlated with the variation of NH_4^+ well with R = 0.87, indicating part of the reduction of NH_4^+ in region 2 was associated with the reduction of NO_3^- during the period. The variations of NO_3^- in regions 3 and 4 were relatively small, and the correlations between NH_4^+ and NO_3^- , with R = 0.42 and 0.40 respectively, were much less significant than those for NH_4^+ *vs.* SO_4^{2-}. Fig. 11 shows that in the EUS and EC, the reduction of NH_4^+ during 1990-2015 was mainly due to the reduction of SO_4^{2-} in regions 2-4, but in region 2 the reduction of NO_3^- also made a substantial contribution to it.

4.6 Sulfate-nitrate-ammonium (SNA) aerosols

Sulfate, nitrate and ammonium are the major components of the secondary aerosols in the atmosphere in the EUS and EC (Bell et al., 2007; Dabek-Zlotorzynska et al., 2011). Time series of the annual total mass of sulfate-nitrate-ammonium aerosols during the warm and cold seasons are shown in Fig. 12. During the cold season, mainly due to the concentrations of NO_3^- and NH_4^+, SNA had the highest and second highest annual concentrations in regions 4 and region 3 respectively, and the lowest annual concentration in region 1. During the warm season, SNA in regions 2 and 3 was comparable, and a little higher than that in region 4. The trends in regions 2-4 are similar during the warm season and the SNA in regions 2-4 are much higher than that in region 1. Fig. 13 shows that SNA in region 1 during the warm season was higher than that during the cold season until 2007, and the trend was reversed after that. In region 2, SNA was generally higher during the warm season until 2005, and was opposite thereafter. SNA in region 3 was significantly higher during the warm season than cold season until 2007 and the trend was opposite after 2012. Similarly SNA in region 4 was much higher in the warm season until 2008 and was comparable between the warm and cold seasons after 2012. Two points can be derived from the above trends: (1) in the EUS and EC, SNA during the warm season was mainly due to $(NH_4)_2SO_4$ / NH_4HSO_4. When the emission of SO_2 over the region decreased significantly, SNA followed the decreasing trend of SO_4^{2-} even though the reduction in NO_3^- was not significant; (2) during the cold season, besides $(NH_4)_2SO_4$ / NH_4HSO_4, NH_4NO_3 also made considerable contribution to SNA. As SO_4^{2-} decreased significantly in both the warm and cold seasons, but NO_3^- changed little during the cold season except in region 2, the SNA during the cold season was getting comparable or even higher than the SNA during the warm season. Pollution of SNA in regions 2 and 3 was more of an issue during the cold season than during the warm season when the emissions of SO_2 were further reduced during 2006-2015.

5. Summary and conclusion

With the implementation of the Title V of the 1990 Amendments to the CAA in the US in the 1990s, the emissions of SO_2 and NO_x in the US reduced from 23.1 million tons/year to 3.7 million tons/year for SO_2 and from 25.2 million tons/year to 11.5 million tons/year for NO_x from 1990 to 2015. In

Canada, comparing to the emission level in 1990, SO_2 and NO_x emissions in 2015 were reduced by 65% and 25% respectively. In both the US and Canada, the reduction of the emissions was mainly in the eastern regions of the countries. With the significant reductions of SO_2 and NO_x emissions, the air concentrations of gases SO_2 and HNO_3, and particles SO_4^{2-}, NO_3^- and NH_4^+ had a very different nonlinear response to the emission reductions, both spatially and temporally.

In this study, we analyzed the air concentrations of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3 and SO_2 measured weekly by the CASTNET network in the US and daily by the CAPMoN network in Canada from 1990 to 2015 to reveal the temporal and spatial changes during the period. Four distinct regions, each with characteristic pattern of air quality in the EUS and EC, were identified: the northeastern US and Eastern Canada (region 1), the Midwest (region 2), the Mid-Atlantic (region 3), and the southeastern US (region 4). In the first 10-year period of 1990-2000, SO_2 and SO_4^{2-} decreased by more than 20% except for SO_4^{2-} in region 4 during the cold season and SO_2 in region 4 during the warm season. NH_4^+ declined by 12% to 29.8% during both seasons except that region 4 during the cold season had a negligible change. NO_3^- increased in regions 1-4 during the cold season, and changed little during the warm season. HNO_3 reduced in regions 1-3 by more than 9% during both seasons, and increased in region 4 by 5% and 5.7% during the cold and warm seasons respectively. In a 25-year period of 1990-2015, the reduction of SO_4^{2-} ranged from 60.1% in region 2 to 62.5% in region 3 during the cold season, and from 72.7% in region 1 to 78.7% in region 4 during the warm season. The reduction of SO_2 was the most significant among all species, ranging from 83.9% during the warm season in region 4 to 91.2% during the warm season for region 3. During the warm season, the reduction of NO_3^- was seen in all regions, ranging from 14.3% in region 1 to 57.5% in region 2. However, during the cold season, the reduction of NO_3^- was only seen in region 2 and it was reduced by 30.4%. The change of NO_3^- was negligible in regions 3 and 4 during the cold season. The reduction of HNO_3 during the warm season was relatively uniform in terms of percentage, ranging from 63.1% to 68.8%. During the cold season, region 2 had the lowest percentage of reduction at 56.0%, and region 1 had the highest at 63.5%. The reduction of NH_4^+ was the most significant during the warm season in terms of both percentage and absolute value. The reduction was ranging from 74.0% to 75.7% in regions 2-4 during the warm season, which was 20% more than the corresponding reduction during the cold season. The time series of the annual concentrations during the warm and cold seasons show that the reduction of each species was not even in time during the period. The reductions of SO_4^{2-} and SO_2 mainly occurred during 1990-1995 and 2007-2016 for the warm season, and during 1990-1995 and 2005-2016 for the cold season. The reduction of NO_3^- was mainly after year 2000.

RSO_4 is a metric indicating the gas-aerosol partition of sulfur in the air, and RNO_3 is indicator of the fraction of HNO_3 being aerosolized. RSO_4 increased by 48.6% to 166.3% during the cold season, and by 0.6% to 58.4% during the warm season. RSO_4 was found to increase quadratically with the decrease of SO_2 for regions 2-4 and the two seasons. The significant increase of RSO_4 during the cold season explains why the reduction rate of SO_2 was much higher than that of SO_4^{2-} during the period, as the reduction of SO_2 was due to not only the emission reduction, but also more SO_2 being converted to SO_4^{2-}. A faster reduction of SO_2 was observed for all 4 regions during the cold season, both before and after year 2000, and it was more significant after 2000. During the warm season, the difference in the reduction rate between SO_2 and SO_4^{2-} was much less. This is because the increase of RSO_4 during the warm season was much less significant than during the cold season. In regions 1 and 4, RSO_4 only increased by 0.6% and 12.4% percentage during the warm season. Differences in the reduction rate between SO_2 and SO_4^{2-} for these two regions during the warm season were only 1.7% and 5.2% respectively. For regions 1, 3 and 4, RNO_3 increased between 79.2% and 94.9% during the warm season, and between 73.9% and 92.3% during the cold season. For region 2, RNO_3 for the warm and cold seasons were only increased by 8.0% and 12.8% respectively as NH_3 in the region was excess to neutralize HNO_3. RNO_3 was found to increase with the decrease of SO_4^{2-} quadratically in regions 3 and 4.

In summary, with the significant reductions of SO_2 and NO_x emissions in the EUS and EC during 1990-2015, SO_4^{2-}, SO_2, NH_4^+, and HNO_3 were reduced significantly by 73.3%, 87.6%, 67.4% and 65.8% for the whole region. The reduction of NO_3^- was relatively less significant at 29.1%, and it mainly occurred: (1) after year 2000; (2) in regions 1-4 during the warm season; (3) in region 2 only during the cold season.

Author contributions

JF carried out the overall analysis and interpretation of the data as well as wrote the manuscript. EC did the initial data and trend analysis. RV provided the supervision of the study and discussed the results.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

We would like to thank Tom Butler and the anonymous reviewer. Their detailed, insightful and constructive suggestions and comments greatly improved the quality of the paper. We also thank Irene Cheng for the internal review. The CASTNET and CAPMoN data used in this study were provided by Environment and Climate Change Canada (ECCC) through the Canadian National Atmospheric Chemistry (NAtChem) Particulate Matter and Precipitation Databases.

References

Aas, W., Mortier, A., Bowersox, V., Cherian, R., Faluvegi, G., Fagerli, H., Hand, J., Klimont, Z., Galy-Lacaux, C., Lehmann, C. M. B., Myhre, C. L., Myhre, G., Olivié, D., Sato, K., Quaas, J., Rao, P. S. P., Schulz, M., Shindell, D., Skeie, R. B., Stein, A., Takemura, T., Tsyro, S., Vet, R., and Xu, X.: Global and regional trends of atmospheric sulfur, Nature, 9, 953, https://doi.org/10.1038/s41598-018-37304-0, 2019.

Bell, M. L., Dominici, F., Ebisu, K., Zeger, S. L., and Samet, J. M.: Spatial and temporal variation in PM2.5 chemical composition in the United States for health effects studies, Environ Health Perspect, 115, 989-995, doi:10.1289/ehp.9621, 2007.

Bloomer, B. J., Vinnikov, K. Y., Dickerson, R. R.: Changes in seasonal and diurnal cycles of ozone and temperature in the eastern U.S., Atmos. Environ., 44, 2543-2551, https://doi.org/10.1016/j.atmosenv.2010.04.031, 2010.

Butler, T. J., Likens, G. E., Vermeylen, F. M., and Stunder, B. J. B.: The relation between NO_x emissions and precipitation NO_3^- in the eastern USA, Atmos. Environ., 37, 2093-2104, https://doi.org/10.1016/S1352-2310(03)00103-1, 2003.

Butler, T. J., Vermeylen, F. M., Rury, M., Likens, G. E., Lee, B., Bowker, G. E., and McCluney, L.: Response of ozone and nitrate to stationary source NO_x emission reductions in the eastern USA, Atmos. Environ., 45, 1084-1094, https://doi.org/10.1016/j.atmosenv.2010.11.040, 2011.

CAA (Clean Air Act) 1990. The Clean Air Act – Highlights of the 1990 Amendments, https://www.epa.gov/clean-air-act-overview/clean-air-act-highlights-1990-amendments, accessed in November 2019.

Chan, E. and Vet, R. J.: Baseline levels and trends of ground level ozone in Canada and the United States, Atmos. Chem. Phys., 10, 8629-8647, https://doi.org/10.5194/acp-10-8629-2010, 2010.

Cheng, I., and Zhang, L.: Long-term air concentrations, wet deposition, and scavenging ratios of inorganic ions, HNO3, and SO2 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.

Clarke, J.-F., Edgerton, E. S., Martin, B. E.: Dry deposition calculations for the clear air status and trends network, Atmos. Environ., 31, 3667-3678, https://doi.org/10.1016/S1352-2310(97)00141-6, 1997.

Dabek-Zlotorzynska, E., Dann, T. F., Martinelango, P. K., Celo, V., Brook, J. R., Mathieu, D., Ding, L., and Austin, C. C.: Canadian National Air Pollution Surveillance (NAPS) PM2.5 speciation program: Metholodology and PM2.5 chemical composition for the years 2003-2008, Atmos. Environ., 45, 673-686, https://doi.org/10.1016/j.atmosenv.2010.10.024, 2011.

Doyle, G. J., Tuazon, E. C., Graham, R. A., Mischke, T. M, Winer, A. M, and Pitts Jr, J. N.: Simultaneous concentrations of ammonia and nitric acid in a polluted atmosphere and their equilibrium relationship to particulate ammonium nitrate, Environ. Sci. Technol., 13, 1416-1419, https://doi.org/10.1021/es60159a010, 1979.

Du E., de Vires, W., Galloway, J. N., Hu., X., and Fang, J. : Changes in wet nitrogen deposition in the United States between 1985 and 2012, Environ. Res. Lett., 9, 095004, https://doi:10.1088/1748-9326/9/9/095004, 2014.

Environment and Climate Change Canada (ECCC, 2019): Canadian Environmental Sustainability Indicators: Air pollutant emissions. Consulted on November 13, 2019. Available at: www.canada.ca/en/environment-climate-change/services/environmental-indicators/airpollutant-emissions.html.

EPA 2016: Our Nation's Air: Status and Trends through 2015. https://gispub.epa.gov/air/trendsreport/2016/.

Hand, J. L., Schichtel, B. A., Malm, W. C., and Pitchford, M. L.: Particulate sulfate ion concentration and SO_2 emission trends in the United States from the early 1990s through 2010, Atmos. Chem. Phys., 12, 10353-10365, https://doi.org/10.5194/acp-12-10353-2012, 2012.

EPA 2019: Air Emissions Inventories. Consulted on November 13, 2019. Available at: https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data.

Harrison, R. M., and Pio, C. A.: An investigation of the atmospheric HNO3-NH3-NH4NO3 equilibrium relationship in a cool, humid climate, Tellus, 35B, 155-159, https://doi.org/10.3402/tellusb.v35i2.14795, 1982.

Haywood, J. M. and Shine, K. P.: The effect of anthropogenic sulfate and soot aerosol on the clear sky planetary radiation budget, Geophys. Res. Lett., 22, 603-606, https://doi.org/10.1029/95GL00075, 1995.

Heroux M.-E., Anderson H. R., Atkinson, R., Brunekreef, B., Cohen, A., Forastiere, F., Hurley, F., Katsouyanni, K., Krewski, D., Krzyanowski, M., Kunzli, N., Mills, I., Querol, X., Ostro, B., and Walton, H.: Quantifying the health impacts of ambient air pollutants: recommendations of a WHO/Europe project, Int. J. Public Health, 60, 619-627, https://doi.org/10.1007/s00038-015-0690-y, 2015.

Jones, A. M. and Harrison, R. M.: Temporal trends in sulphate concentrations at European sites and relationships to sulphur dioxide, Atmos. Environ., 45, 873-882, https://doi.org/10.1016/j.atmosenv.2010.11.020, 2011.

Kajino, M., Ueda, H., Han, Z., Kudo, R., Inomata, Y., and Kaku, H.: Synergy between air pollution and urban meteorological changes through aerosol-radiation-diffusion feedback—A case study of Beijing in January 2013, Atmos. Environ., 171, 98-110, https://doi.org/10.1016/j.atmosenv.2017.10.018, 2017.

Kuklinska, K., Wolska, L., and Namiesnik, J.: Air quality policy in the U.S. and the EU – a review, Atmos. Pollution Res., 6, 129-137, doi:10.5094/APR.2015.015, 2015.

Kunzli, N., Kaiser, R., Medina, S., Studnicka, M., Chanel, O., Filiger, P., Herry, M., Horak Jr, F., Puybonnieux-Texier, V., Quenel, P., Schneider, J., Seethaler, R., Vergnaud, J-C., and Sommer, H.: Public-health imact of outdoor and traffic-related air pollution: A European assessment, The Lancet, 356, 795-801, https://doi.org/10.1016/S0140-6736(00)02653-2, 2000.

Lee, B.: Highlights of the Clean Air Act Amendments of 1990, J. of Air and Waste Management Asso., 41, 16-19, https://doi.org/10.1080/10473289.1991.10466820, 1991.

Lee C., Martin, R. V., van Donkellar, A., Lee, H., Dickerson, R. R., Hains, J. C., Krotkov, N., Richter, A., Vinnikov, K., and Schwab, J. J.: SO_2 emissions and lifetimes: Estimates from inverse modeling using in situ and global, space‐based (SCIAMACHY and OMI) observations, J. Geophys. Res., https://doi.org/10.1029/2010JD014758, 2011.

Lövblad, G., Tarrason, L., Tørseth, K., and Dutchak, S.: EMEP Assessment, Part I, European Perspective, Norwegian Meterological Institute, Oslo, Norway, available at: http://emep.int/publ/reports/2004/assessment_2004.html, 2004.

Mann, H. B.: Non-parametric tests against trend, Econometrica, 13, 245–59, https://doi.org/ 10.2307/1907187, 1945.

Makar, P. A., Moran, M. D., Zheng, Q., Cousineau, S., Sassi, M., Duhamel, A., Besner, M., Davignon, D., Crevier, L.-P., and Bouchet, V. S. : Modelling the impacts of ammonia emissions reductions on North America air quality, Atmos. Chem., Phys, 9, 7183-7212, https://doi.org/10.5194/acp-9-7183-2009, 2009.

Napolitano, S., Stevens, G., Schreifels, J., and Culigan, K.: The NOx Budget Trading Program: A collaborative, innovative approach to solving a regional air pollution problem, Elec. J., 20, 65-76, https://doi.org/10.1016/j.tej.2007.09.005, 2007.

National Climate Assessment, U.S. Global Change Research Program, 2014. Consulted on November 13, 2019. Available at: https://nca2014.globalchange.gov/report/regions/midwest/graphics/temperatures-are-rising-midwest.

Penner, J., Hegg, D., Andreae, M., Leaitch, D., Pitari, G., Annegarn, H., Murphy, D., Nganga, J., Barrie, L., Feichter, H: IPCC, Climate Change 2001: Aerosols and Indirect Cloud Effects, IPCC Third Assessment Report, Cambridge University Press, Cambridge, UK, pp. 289–348, 2001.

Pitari, G., Visioni, D., Mancini, E., Cionni, I., Di Genova, G., and Gandolfi, I. : Sulfate aerosols from non-explosive volcanoes: Chemical-radiative effects in the troposphere and lower stratosphere, Atmosphere, 7(7), 85, https://doi.org/10.3390/atmos7070085, 2016.

Reid, N., Misra, P. K., Bloxam, R., Yap, D., Rao, S. T., Civerolo, K., Brankov, E., and Vet, R. J.: Do We Understand Trends in Atmospheric Sulfur Species?, J. Air. Waste. Manage., 51, 1561-1567, https://doi.org/10.1080/10473289.2001.10464384, 2001.

Shah, V., Jaeglé, L., Thornton, J. A., Lopez-Hilfiker, F.D., Lee, B. H., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Guo, H., Sullivan, A. P., Weber, R. J., Green, J. R., Fiddler, M. N., Bililign, S., Campos, T. L., Stell, M., Weinheimer, A. J., Montzka, D. D., and Brown, S. S.: Chemical feedbacks weaken the wintertime response of particulate sulfate and nitrate to emissions reductions over the eastern United States, P. Natl. Acad. Sci. USA., 115, 8110-8115, https://doi.org/10.1073/pnas.1803295115, 2018.

Sickles II, J. E. and Shadwick, D. S.: Changes in air quality and atmospheric deposition in the eastern United States: 1990-2004, J. Geophys. Res., 112, D17301, https://doi.org/10.1029/2006JD007843, 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.

WHO (World Health Organization), 2006: WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide, Global update 2005, Summary of risk assessment, Geneva (2006), p. 22.

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.

Yoshizumi, K. and Hoshi, A.: Size distributions of ammonium nitrate and sodium nitrate in atmospheric aerosols, Environ. Sci. Technol., 19, 258-261, https://doi.org/10.1021/es00133a007, 1985.

Yu, H., Kaufman, Y. K., Chin, M., Feingold, G., Remer, L. A., Anderson, T. L., Balkanski, Y., Bellouin, N., Boucher, O., Christopher, S., DeCola, P., Kahn, R., Koch, D., Loeb, N., Reddy, M. S., Schulz, M., Takemura, T., and Zhou, M.: A review of measurement-based assessments of the aerosol direct radiative effect and forcing, Atmos. Chem. Phys., 6, 613-666, https://doi.org/10.5194/acp-6-613-2006, 2006.

Zhang, L., Vet, R., Wiebe, A., Mihele, C., Sukloff, B., Chan, E., Moran, M. D., and Iqbal, S.: 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.

Zhang, Y., West, J. J., Mathur, R., Xing, J., Hogrefe, C., Roselle, S. J., Bash, J. O., Pleim, J. E., Gan, C.-M., and Wong, D. C.: Long-term trends in the ambient $PM_{2.5}$- and O_3-related mortality burdens in the United States under emission reductions from 1990 to 2010, Atmos. Chem. Phys., 18, 15003-15016, https://doi.org/10.5194/acp-18-15003-2018, 2018.

Zhuang, H., Chan, C. K., Fang, M., and Wexler, A. S.: Size distributions of particulate sulfate, nitrate, and ammonium at a coastal site in Hong Kong, Atmos. Environ., 33, 843-853, https://doi.org/10.1016/S1352-2310(98)00305-7, 1999.

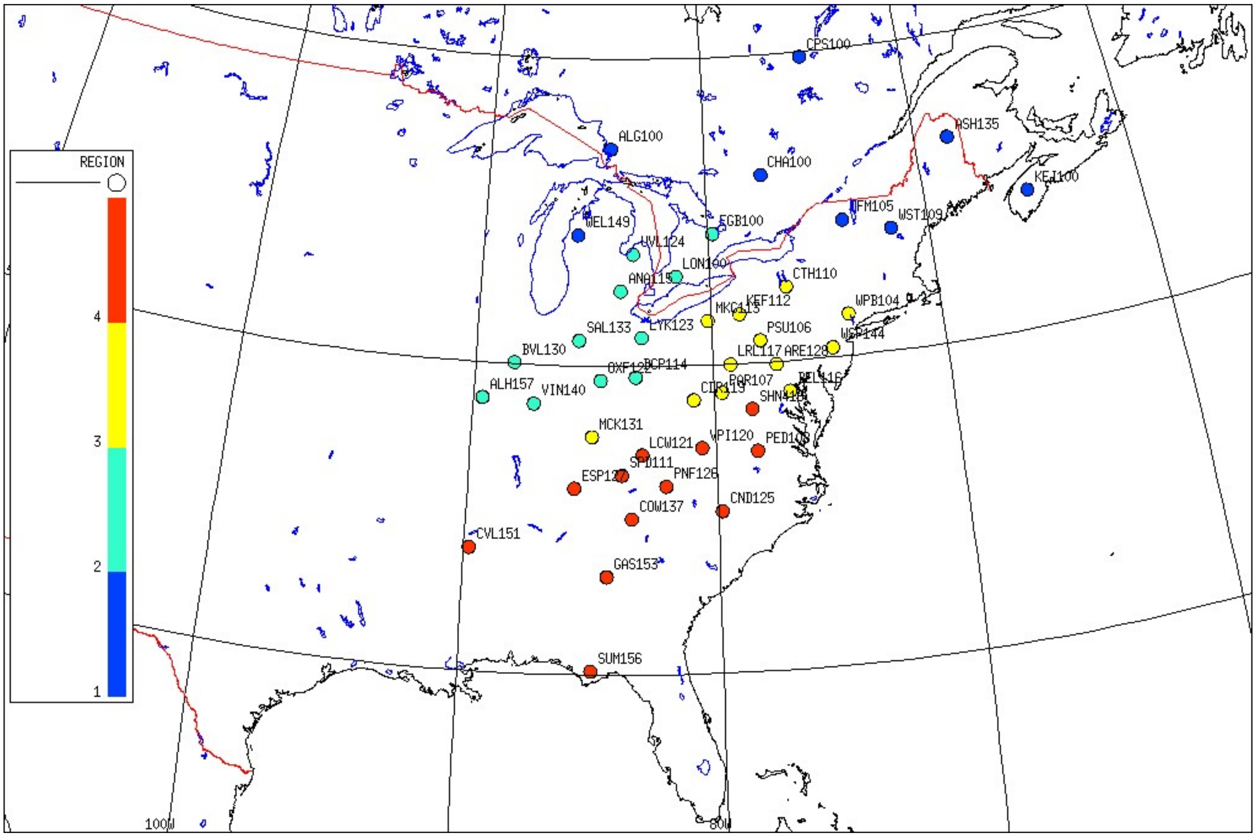
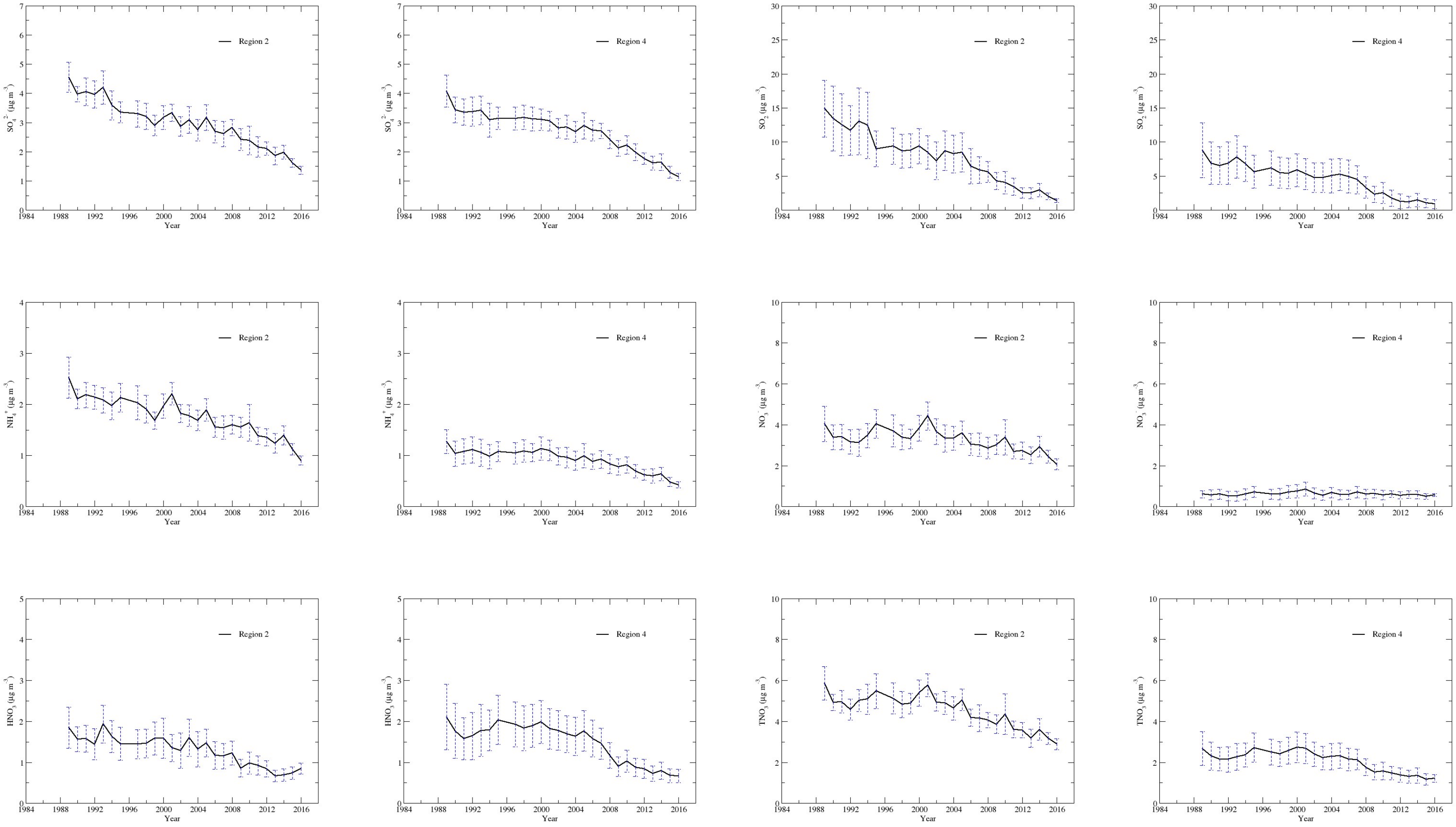
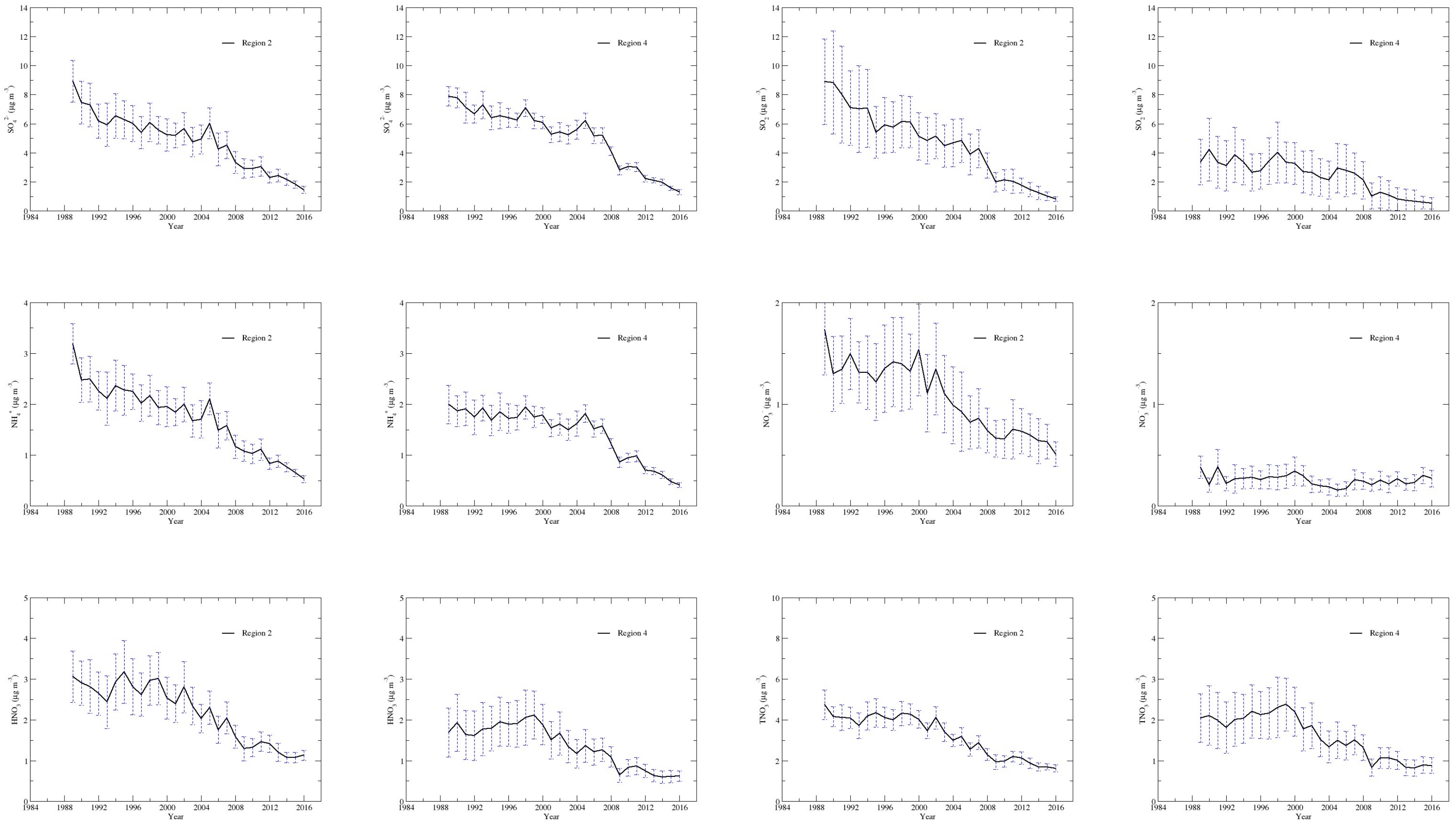


Fig. 1. Clustered sites of CASTNET and CAPMoN in regions 1-4.



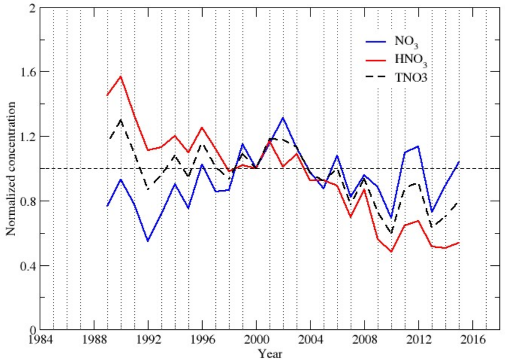
(a) Cold season

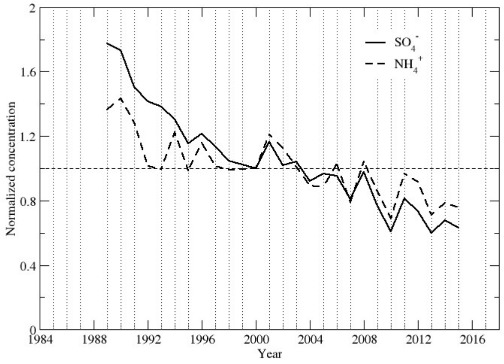


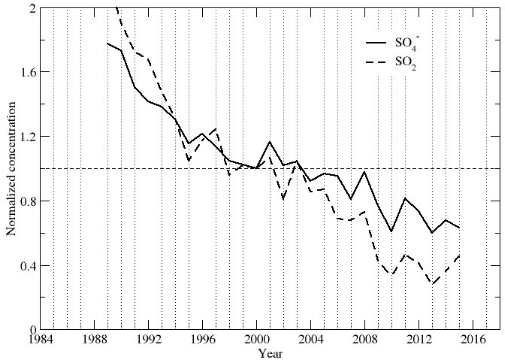
(b) Warm season

Fig. 2 Time series of the regionally averaged annual concentrations during the cold (a) and warm (b) seasons for each species in region 2 (Midwest) and region 4 (Southeast). The vertical dash line represents the standard deviation of the regionally averaged annual concentration. The regionally averaged annual concentrations in regions 2 and 4 during the cold season were not generated for year 1996 because of insufficient number of measurements.

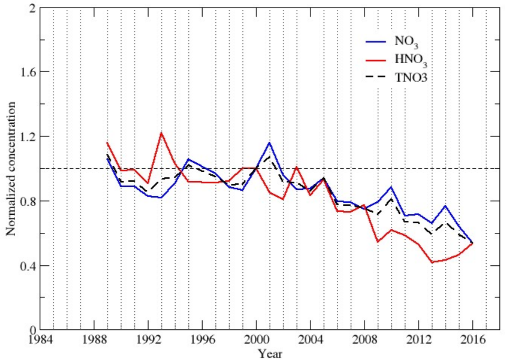
Region 1

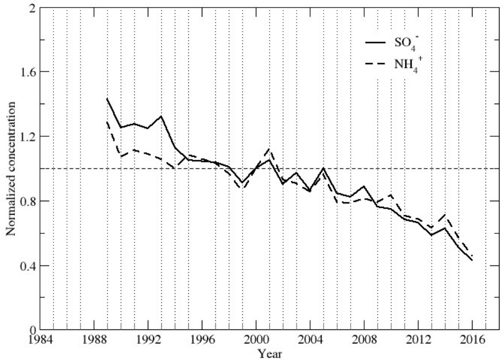


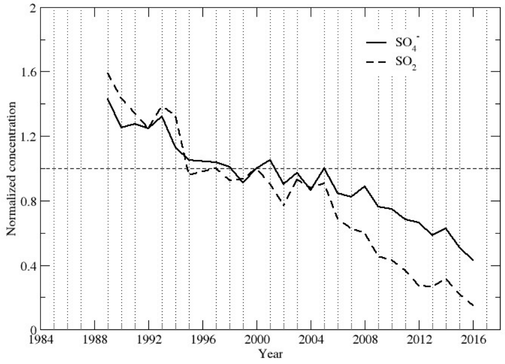




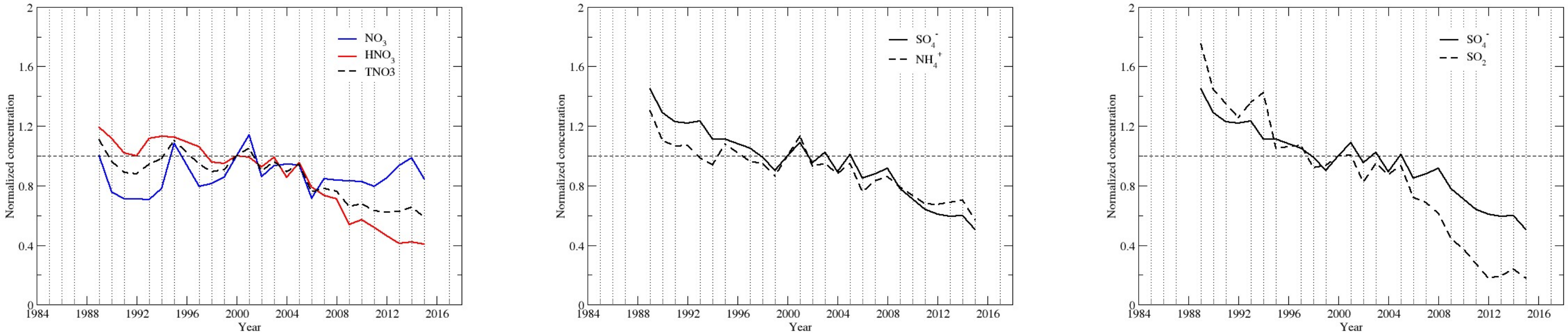
Region 2



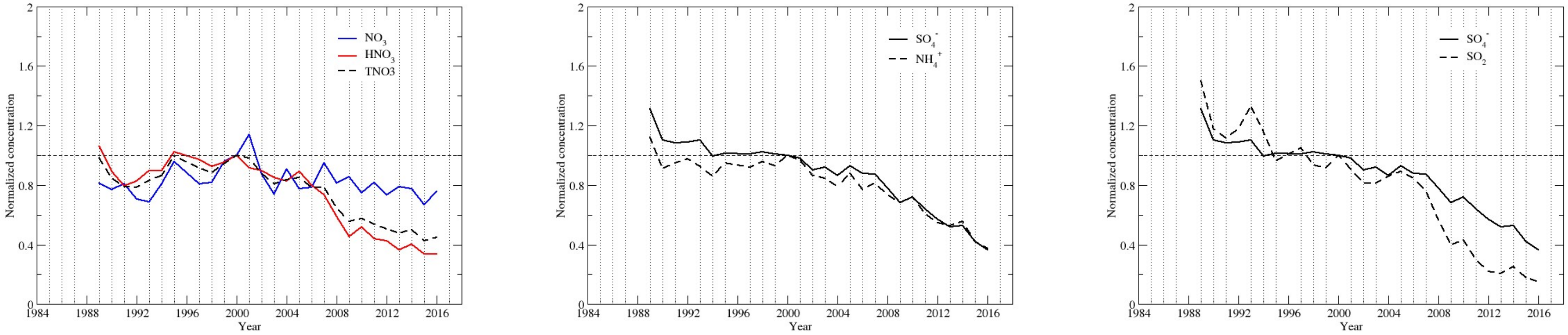




Region 3

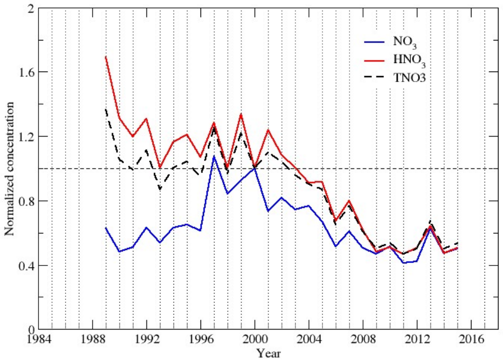


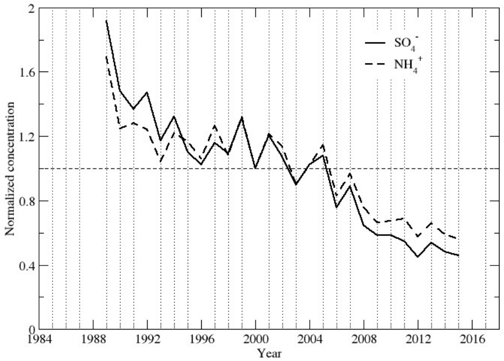
Region 4

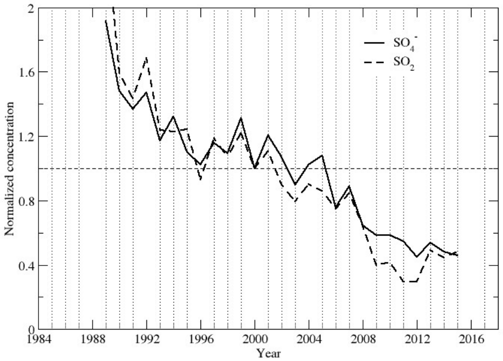


(a) Cold Season

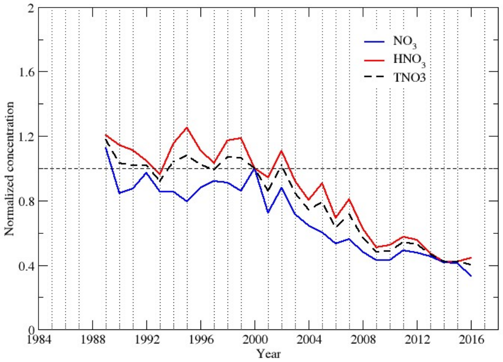
Region 1

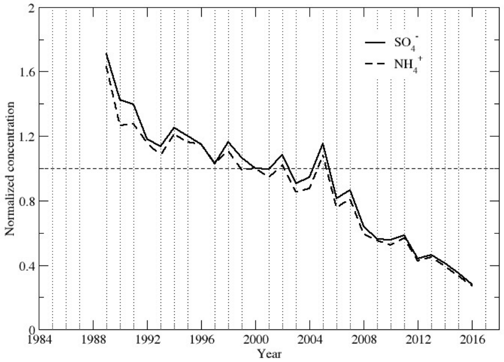


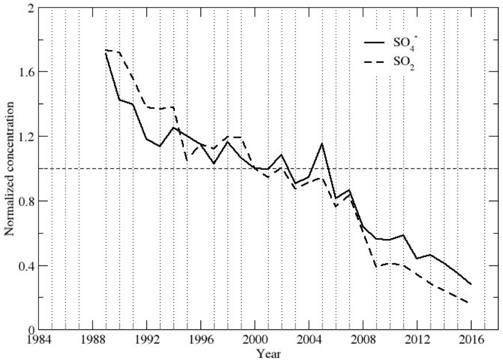




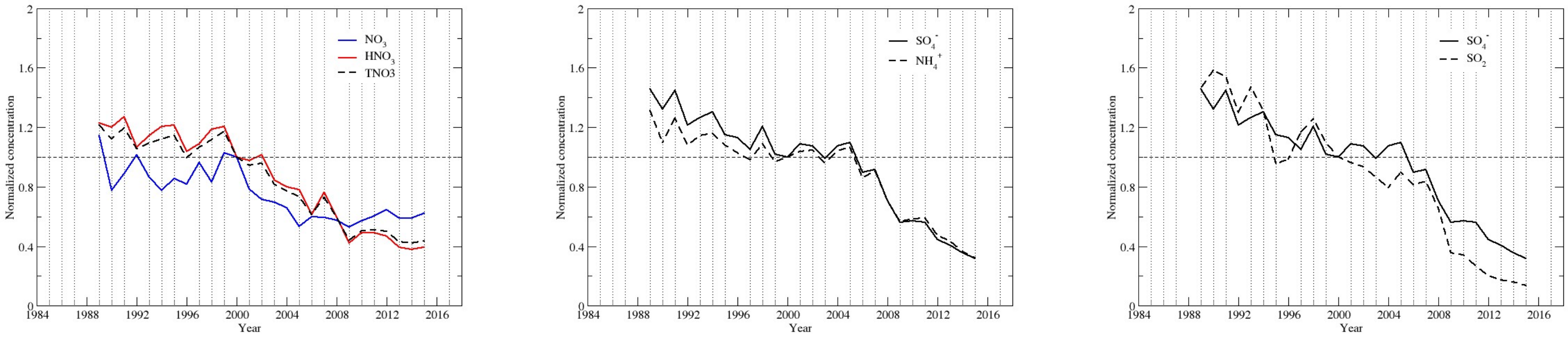
Region 2



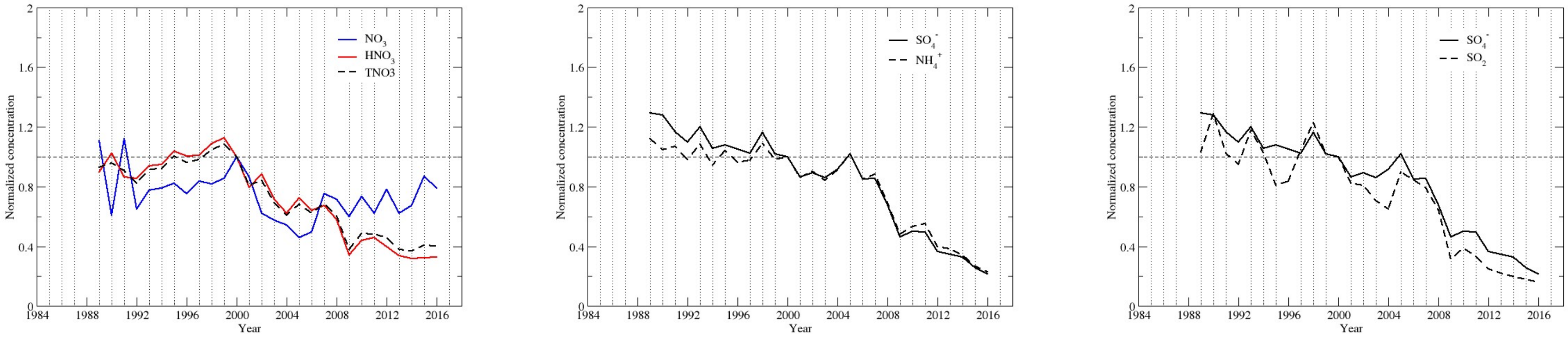




Region 3

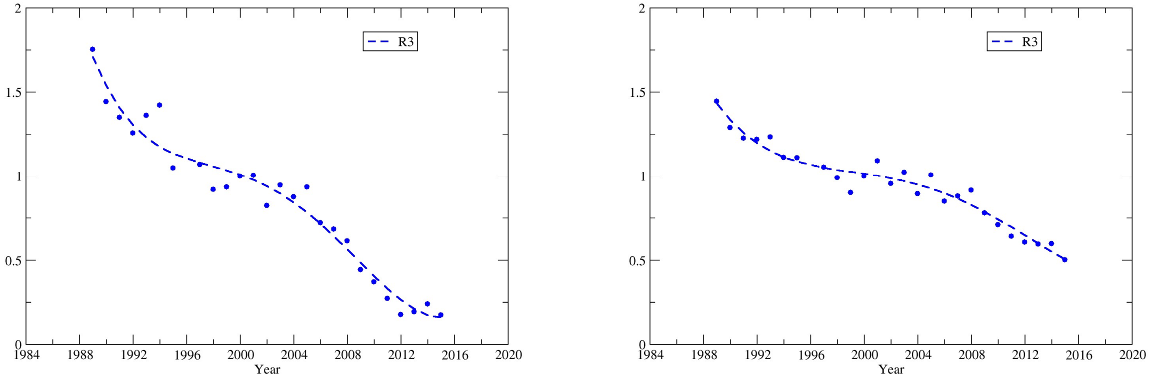


Region 4



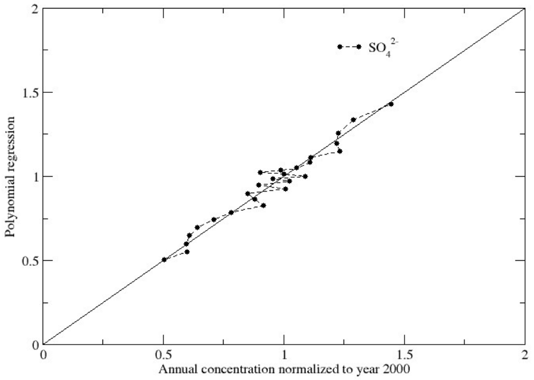
(b) Warm season

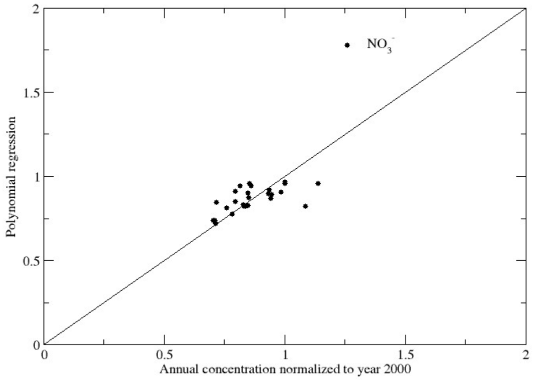
Fig. 3 Time series of the regional annual concentrations normalized to year 2000 for each species during the cold (a) and warm (b) seasons.

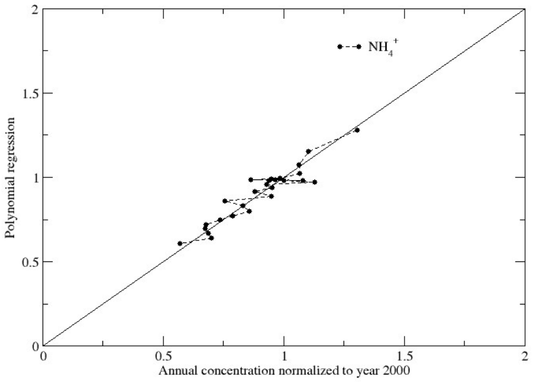


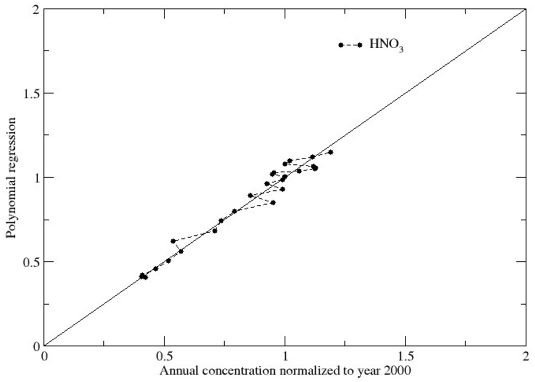
(a) SO_2 (b) SO_4^{2-}

Fig. 4 Examples of 4th Polynomial regressions of SO_2 (a) and SO_4^{2-} (b) for region 3 during the cold season.


SO_4^{2-}
Polynomial regression
Annual concentration normalized to year 2000
0
0.5
1
1.5
2


NO_3^-
Polynomial regression
Annual concentration normalized to year 2000
0
0.5
1
1.5
2


NH_4^+
Polynomial regression
Annual concentration normalized to year 2000
0
0.5
1
1.5
2


HNO_3
Polynomial regression
Annual concentration normalized to year 2000
0
0.5
1
1.5
2

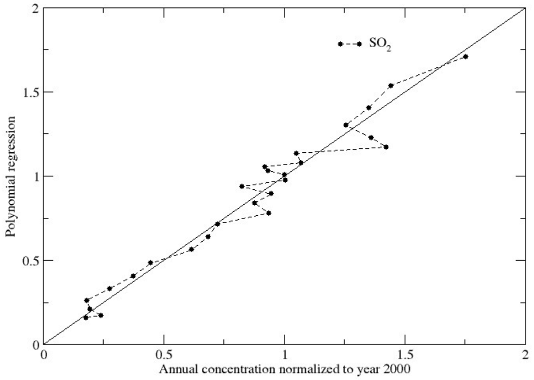
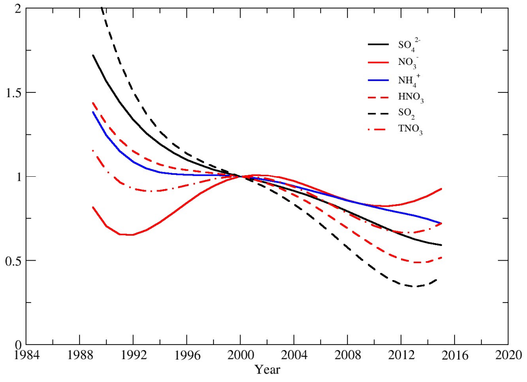


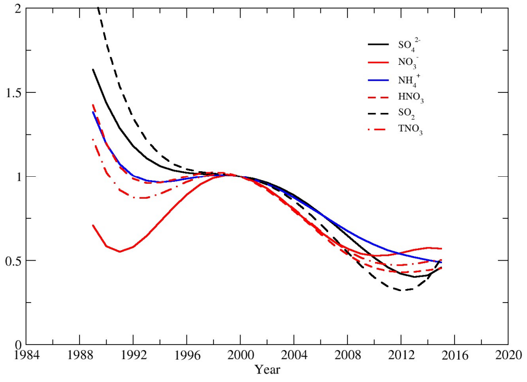
Fig. 5 Comparisons of the normalized annual concentrations with the ones regressed with polynomial regressions for SO_4^{2-}, SO_2, NH_4^+, NO_3^- and HNO_3 for region 3 during the cold season. The dot lines link the annual concentrations from 1990 to 2016 for species except for NO_3^- to show the temporal trends.

Cold season

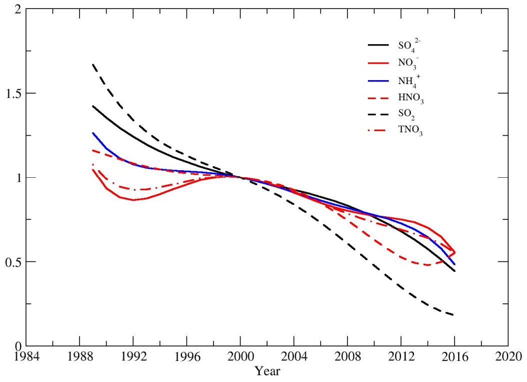
Warm Season

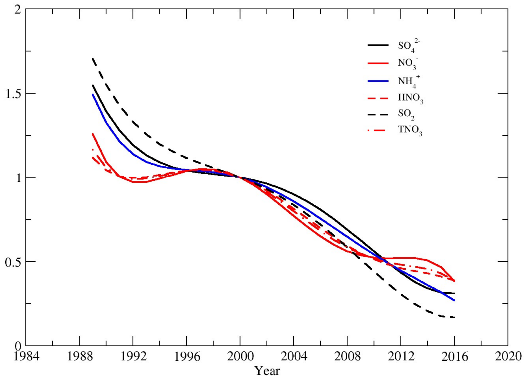
Region 1

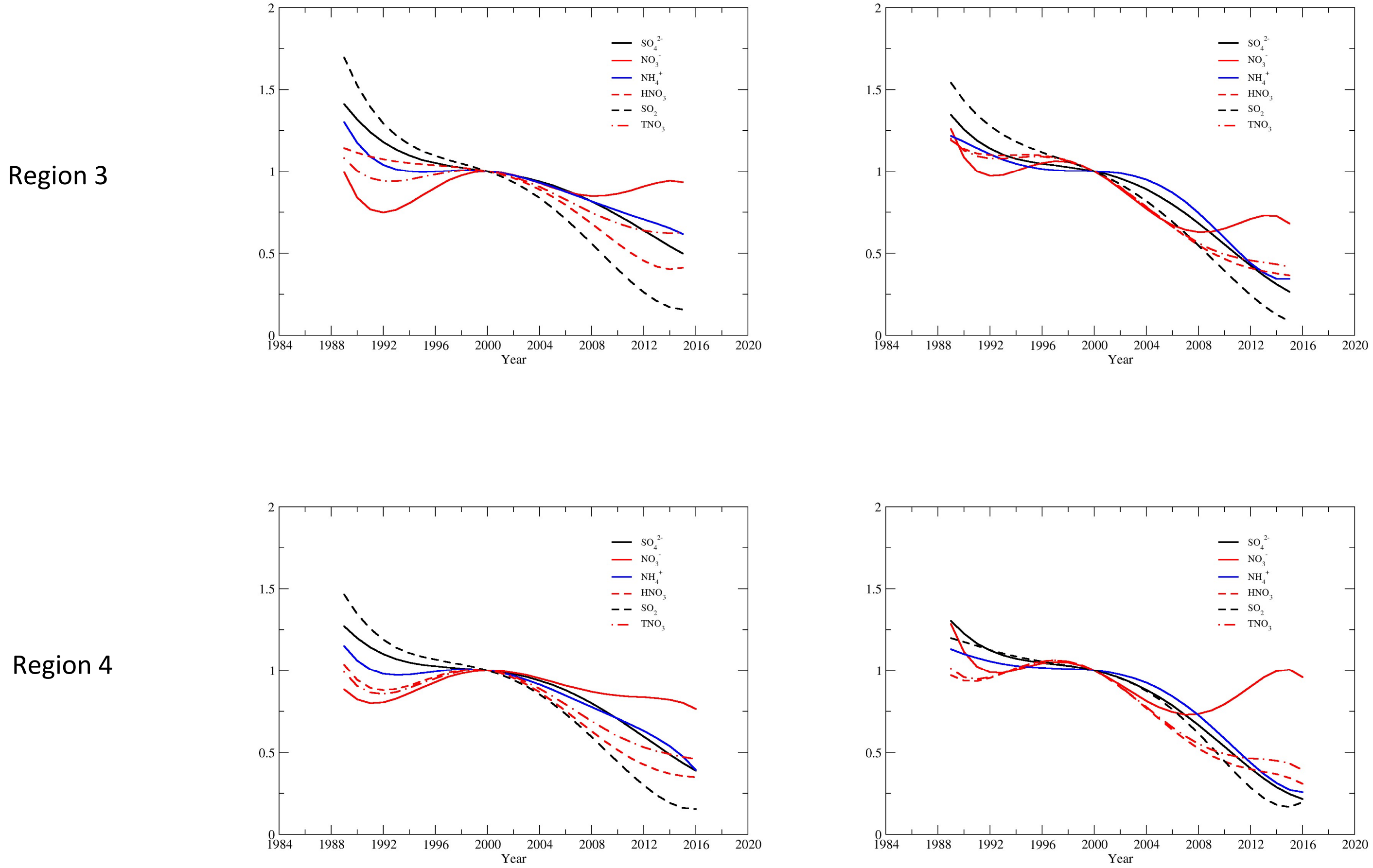




Region 2





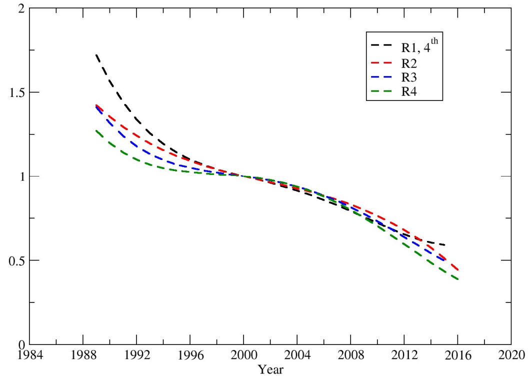


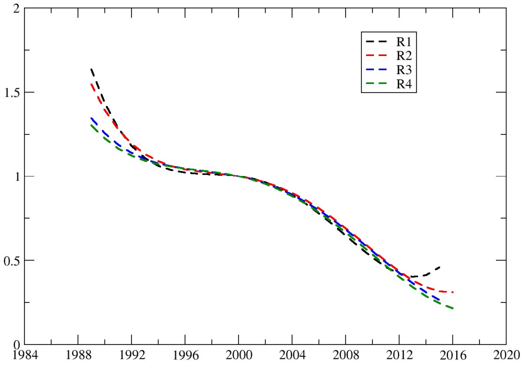
(a) Long-term trends for different species in each region

Cold season

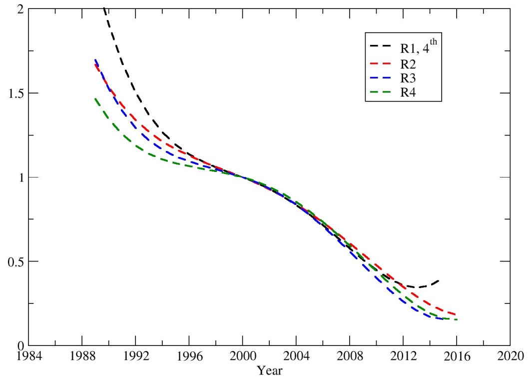
Warm Season

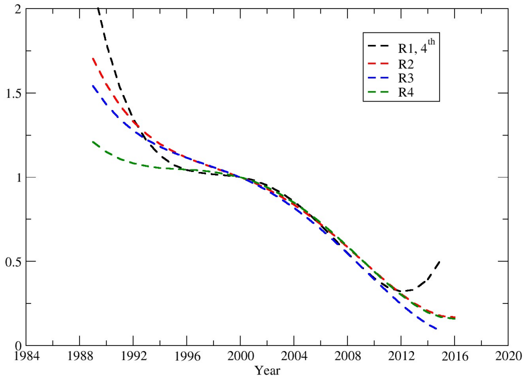
SO_4^{2-}



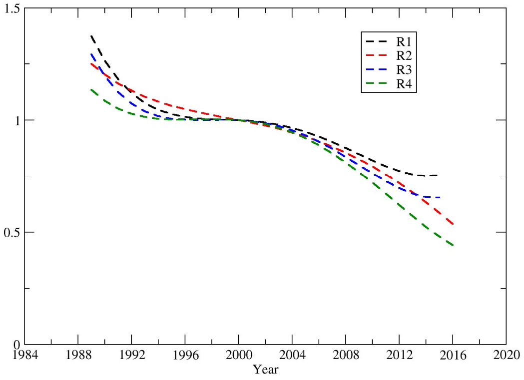


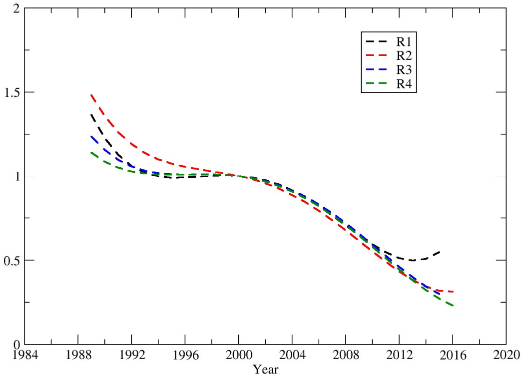
SO_2



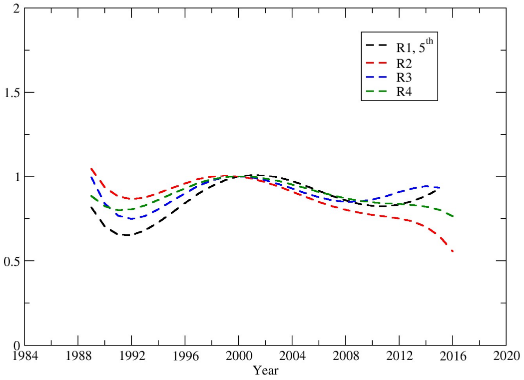


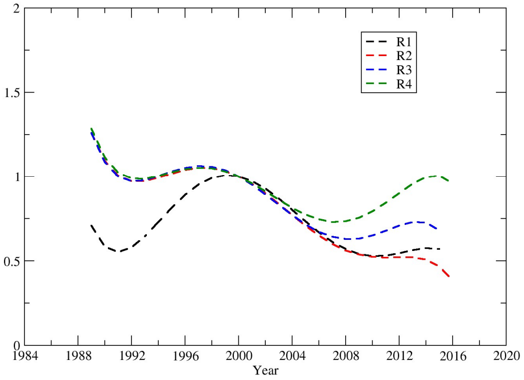
NH_4^+

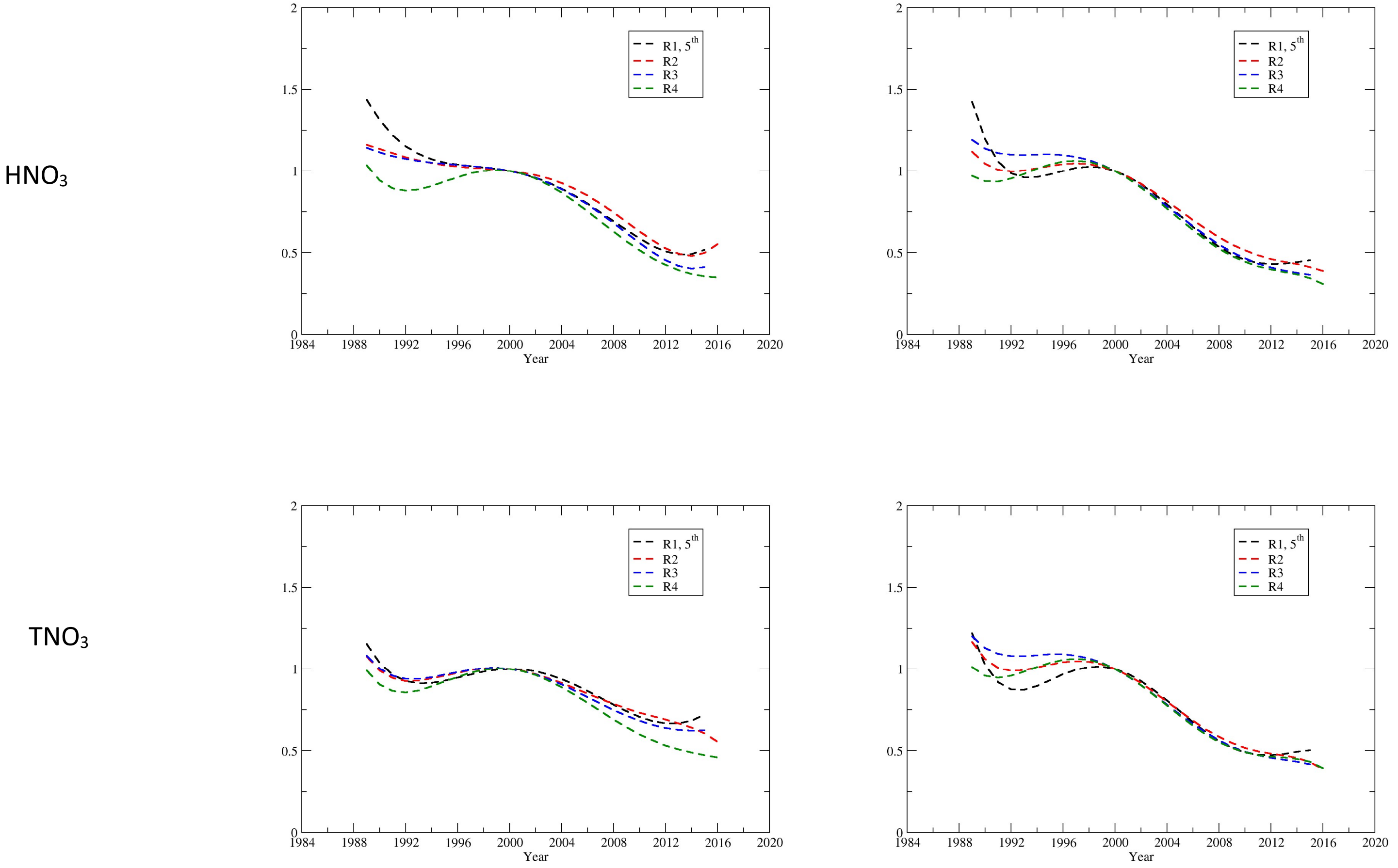

R1
R2
R3
R4
0
0.5
1
1.5
1984
1988
1992
1996
2000
2004
2008
2012
2016
2020
Year


R1
R2
R3
R4
0
0.5
1
1.5
2
1984
1988
1992
1996
2000
2004
2008
2012
2016
2020
Year

NO_3^-

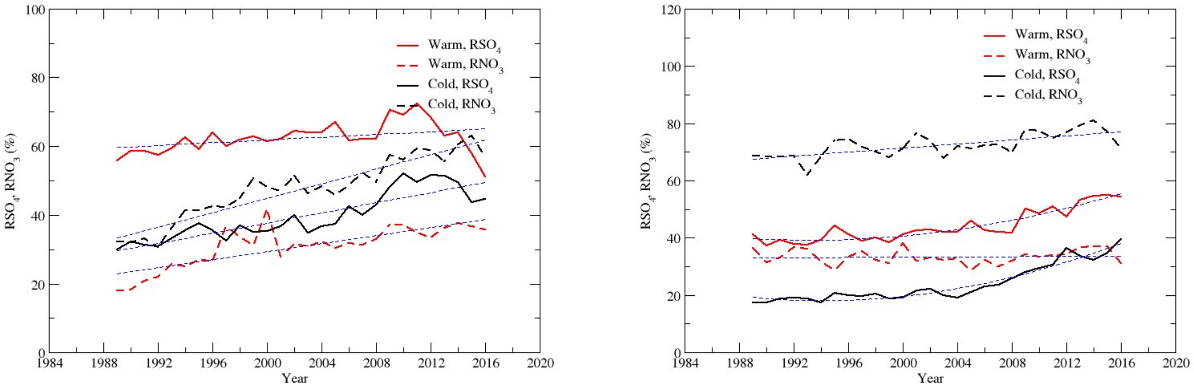

R1, 5th
R2
R3
R4
0
0.5
1
1.5
2
1984
1988
1992
1996
2000
2004
2008
2012
2016
2020
Year


R1
R2
R3
R4
0
0.5
1
1.5
2
1984
1988
1992
1996
2000
2004
2008
2012
2016
2020
Year



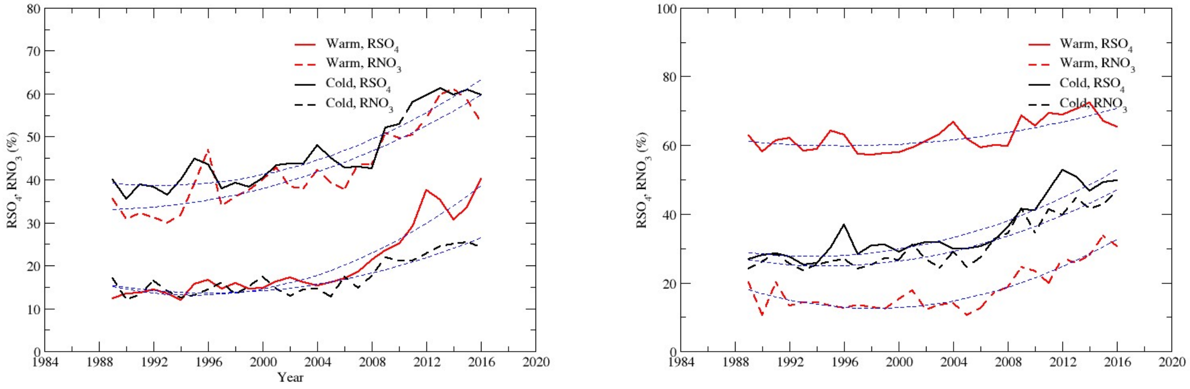
(b) Long-term trends for different region and each species

Fig. 6 Long-term trends derived with 4th polynomial regressions for SO_4^{2-},SO_2 and NH_4^+, and 5th polynomial regressions for NO_3^-, HNO_3 and TNO3 during the warm and cold seasons.



Region 1

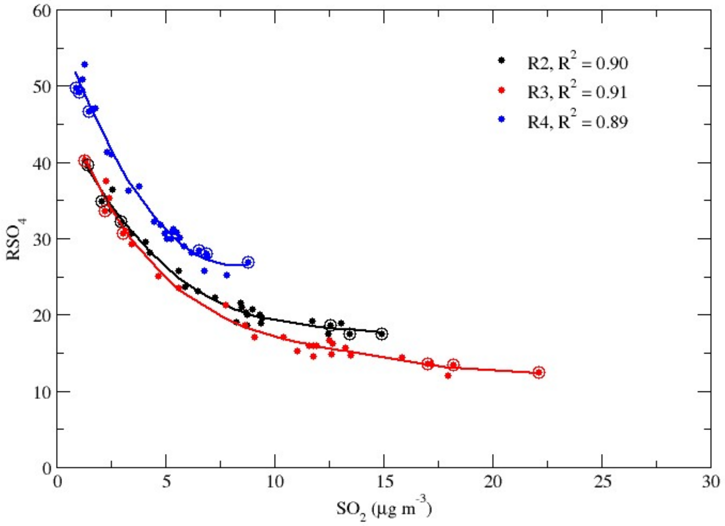
Region 2



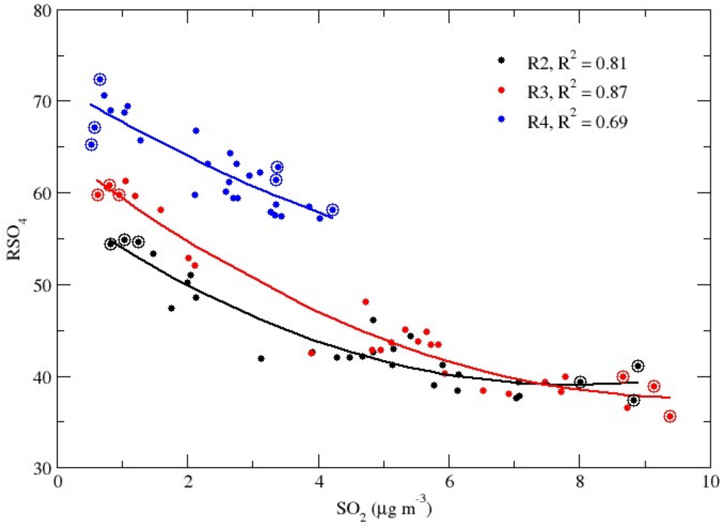
Region 3

Region 4

Fig. 7 Time series of RSO$_4$ and RNO$_3$ for regions 1-4 during the cold and warm seasons.

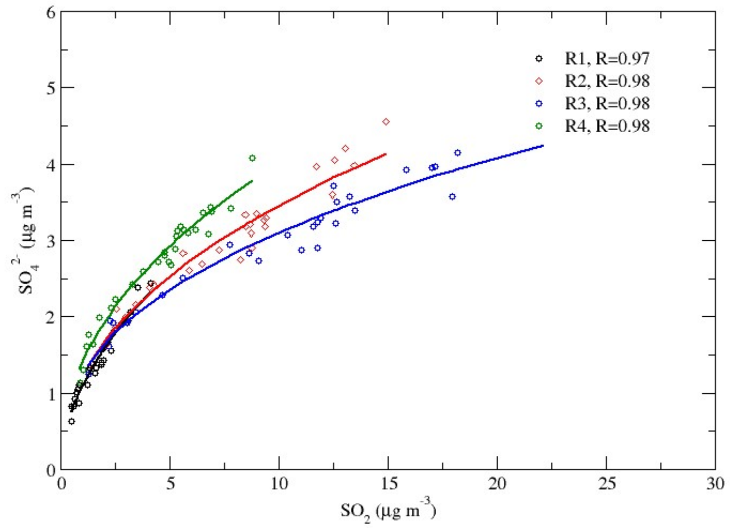


(a) Cold season

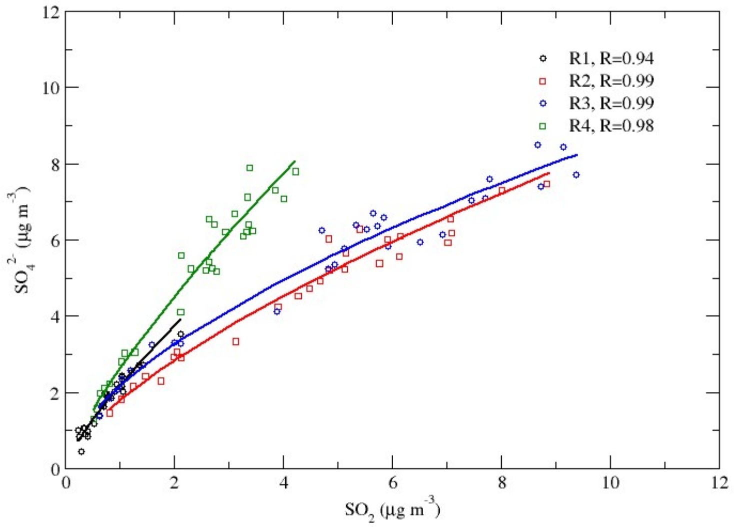


(b) Warm season

Fig. 8 Correlations of the annual means during the cold and warm seasons: RSO$_4$ *vs.* SO$_2$ for regions 2-4. 4th polynomial and quadratic regressions were applied for the cold and warm seasons respectively. R2, 3 and 4 refer to regions 2, 3 and 4. The dots with circles represent the annual means in the first and last 3 years.

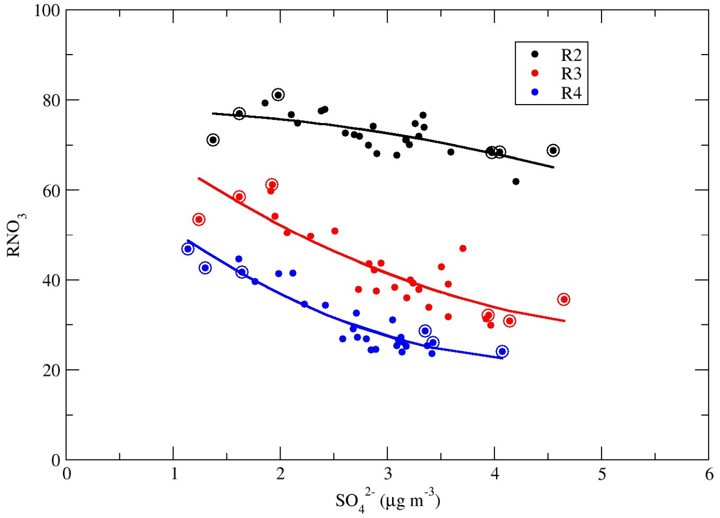


(a) Cold season

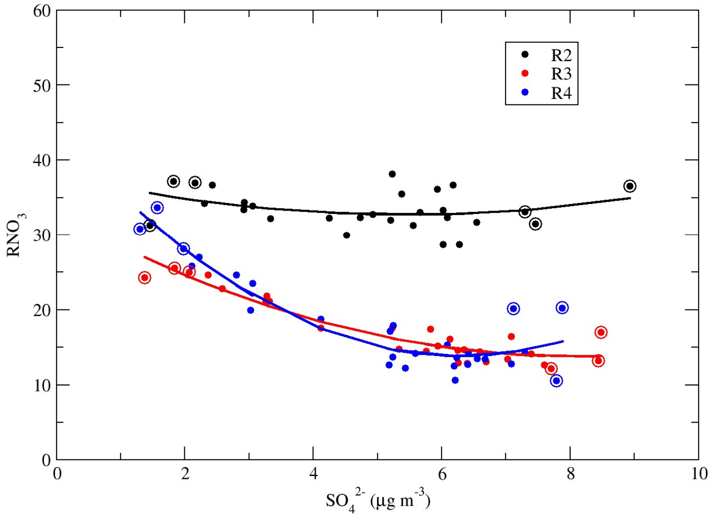


(b) Warm season

Fig. 9 Correlations of the annual means during the cold and warm seasons: SO_4^{2-} *vs.* SO_2 for regions 1-4. R1, 2, 3 and 4 refer to regions 1-4.

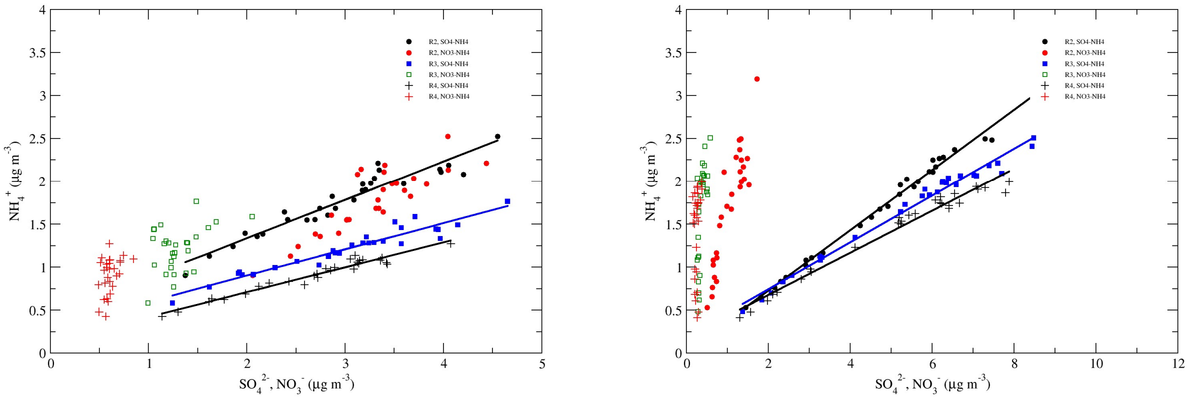


(a) Cold season



(b) Warm season

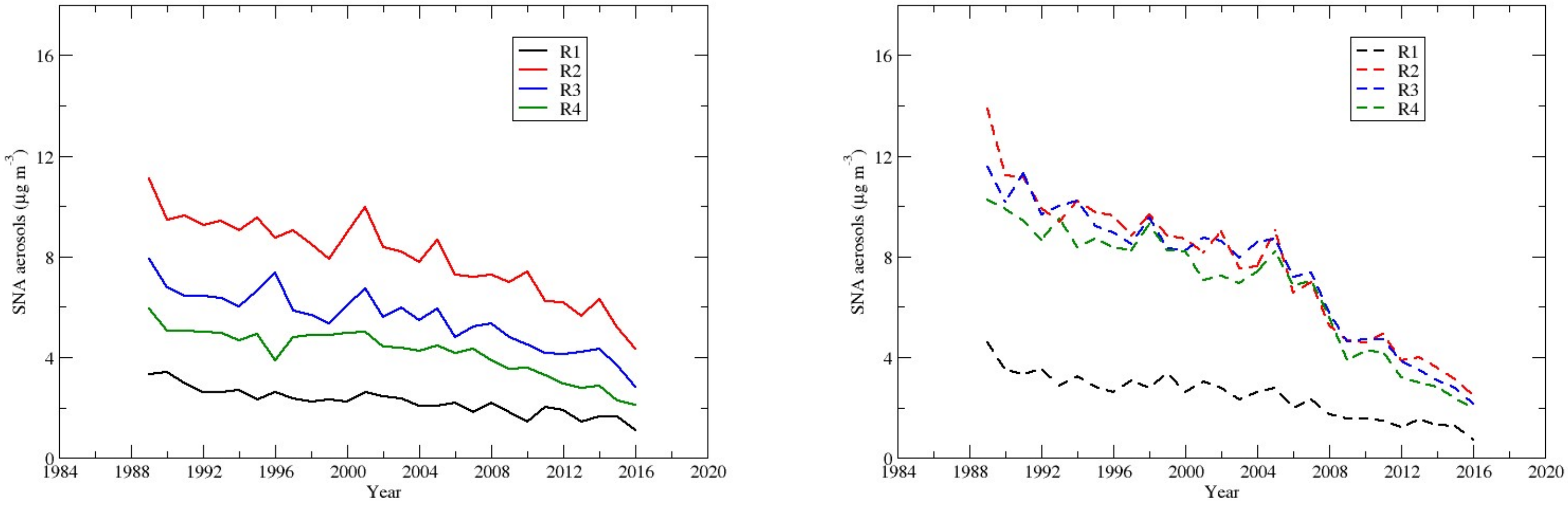
Fig. 10 Correlations of the annual means during the cold and warm seasons: RNO_3 *vs*. SO_4^{2-} for regions 2-4. The dots with circles represent the annual means in the first and last 3 years. R2, 3 and 4 refer to regions 2, 3 and 4.



(a) Cold season

(b) Warm season

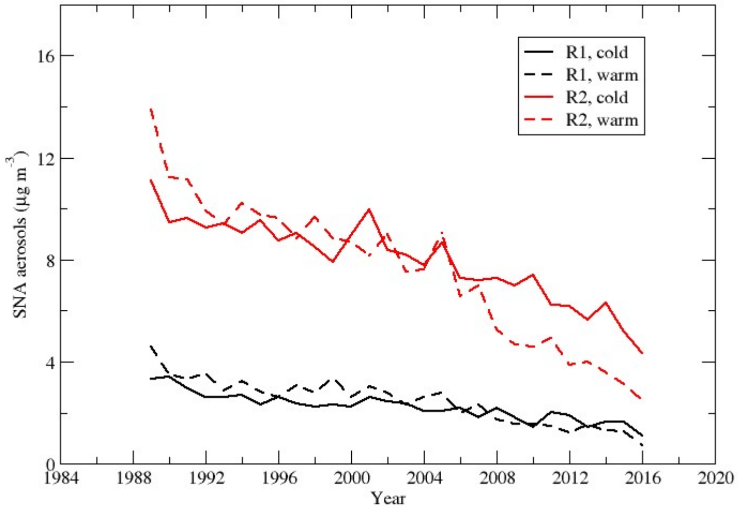
Fig. 11 Correlations of NH_4^+ *vs*. SO_4^{2-} and NH_4^+ *vs*. NO_3^- during the cold and warm seasons. R2, 3 and 4 refer to regions 2, 3 and 4.

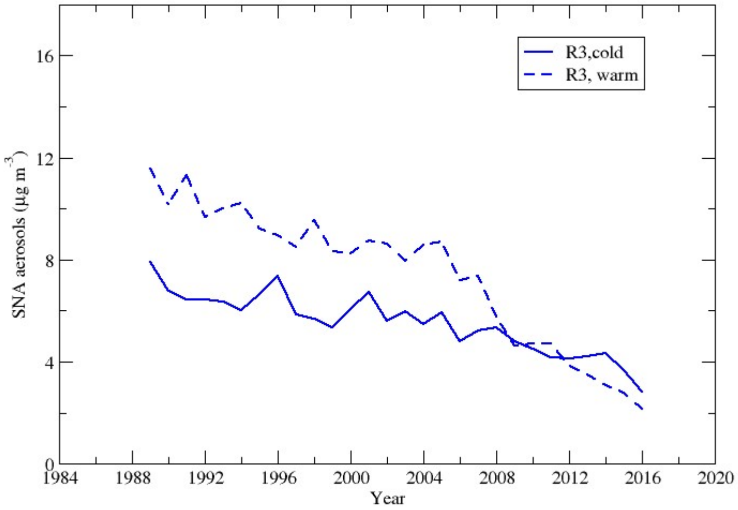


(a) Cold season

(b) Warm season

Fig. 12 Time series of the annual means of sulfate-nitrate-ammonium aerosols during the cold and warm seasons.


R1, cold
R1, warm
R2, cold
R2, warm
SNA aerosols (μg m^{-3})
0
4
8
12
16
1984
1988
1992
1996
2000
2004
2008
2012
2016
2020
Year


R3,cold
R3, warm
SNA aerosols (μg m^{-3})
0
4
8
12
16
1984
1988
1992
1996
2000
2004
2008
2012
2016
2020
Year

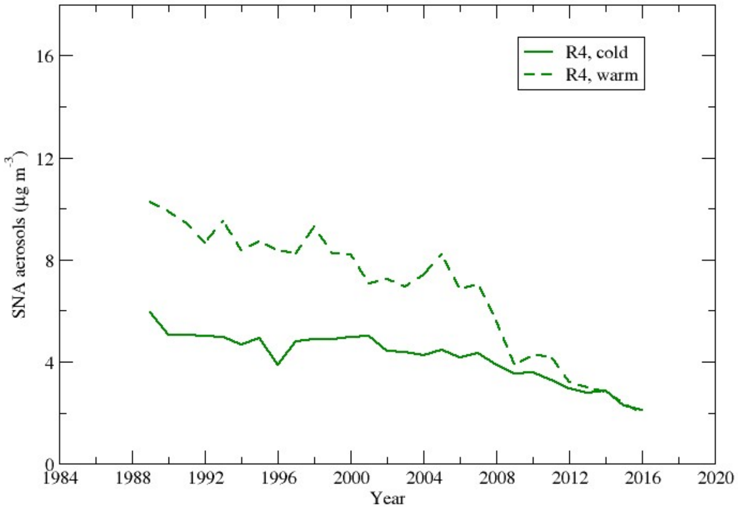


Fig. 13 Time series of the annual means of sulfate-nitrate-ammonium aerosols in regions 1-4.

Table 1. Characteristics of 4 regions based on 3-year averages of 1989-1991 during the cold season.

Region	Characteristics of region
1	SO_2 < 6.4 μg μ^{-3} for all sites; in average the region had the lowest annual concentrations of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3, and SO_2.
2	NO_3^- > 2.5 μg m^{-3} and RNO_3 > 54.0% for all sites; AVE_NO_3^- = 4.2 μg m^{-3}; AVE_SO_2 = 13.6 μg m^{-3}; AVE_RNO_3 = 68.5%.
3	NO_3^- < 2.2 μg m^{-3}, RNO_3 < 47% and SO_2 > 15.2 μg m^{-3} for all sites; AVE_NO_3^- = 1.2 μg m^{-3}; AVE_SO_2 = 19.2 μg m^{-3}; AVE_RNO_3 = 32.3%.
4	SO_2 < 11.7 μg m^{-3} and NO_3^- < 0.7 μg m^{-3} for all sites; AVE_NO_3^- = 0.6 μg m^{-3}; AVE_SO_2 = 7.2 μg m^{-3}; AVE_RNO_3^- = 28.3%.

Table 2. Changes of the regionally averaged air concentrations of pollutants (μg m^{-3}), RSO$_4$ (%) and RNO$_3$ (%) between 1989-1991 and 1999-2001 for regions 1-4.

(a) Cold season

Region		SO$_4^{2-}$	NO$_3^-$	NH$_4^+$	HNO$_3$	SO$_2$	TNO$_3$	RSO$_4$	RNO$_3$
1	1989 - 1991	2.29	0.37	0.57	0.74	3.62	1.1	31.13	32.53
	1999 - 2001	1.46	0.49	0.44	0.54	1.91	1.01	35.7	48.58
	Δ	-0.83	0.12	-0.13	-0.2	-1.71	-0.09	4.57	16.05
	Δ %	**-36.2%**	**32.4%**	**-22.8%**	**-27.0%**	**-47.2%**	**-8.2%**	**14.7%**	**49.3%**
2	1989 - 1991	4.19	3.62	2.27	1.66	13.65	5.25	17.92	68.49
	1999 - 2001	3.14	3.86	1.95	1.51	8.87	5.35	19.77	71.93
	Δ	-1.05	0.24	-0.32	-0.15	-4.78	0.1	1.85	3.44
	Δ %	**-25.1%**	**6.6%**	**-14.1%**	**-9.0%**	**-35.0%**	**1.9%**	**10.3%**	**5.0%**
3	1989 - 1991	4.24	1.21	1.56	2.31	19.2	3.49	13.11	32.76
	1999 - 2001	3.21	1.48	1.35	2.05	12.35	3.5	15.27	40.13
	Δ	-1.03	0.27	-0.21	-0.26	-6.85	0.01	2.16	7.37
	Δ %	**-24.3%**	**22.3%**	**-13.5%**	**-11.3%**	**-35.7%**	**0.3%**	**16.5%**	**22.5%**
4	1989 - 1991	3.57	0.55	1.09	1.81	7.24	2.33	28.29	25.14
	1999 - 2001	3.09	0.77	1.1	1.9	5.52	2.66	30.36	28.31
	Δ	-0.48	0.22	0.01	0.09	-1.72	0.33	2.07	3.17
	Δ %	**-13.4%**	**40.0%**	**0.9%**	**5.0%**	**-23.8%**	**14.2%**	**7.3%**	**12.6%**

(b) Warm season

Region		SO_4^{2-}	NO_3^-	NH_4^+	HNO_3	SO_2	TNO_3	RSO_4	RNO_3
1	1989 - 1991	2.93	0.14	0.73	0.62	1.56	0.75	57.71	19
	1999 - 2001	2.16	0.23	0.62	0.53	0.94	0.73	62.18	33.52
	Δ	-0.77	0.09	-0.11	-0.09	-0.62	-0.02	4.47	14.52
	Δ %	**-26.3%**	**64.3%**	**-15.1%**	**-14.5%**	**-39.7%**	**-2.7%**	**7.7%**	**76.4%**
2	1989 - 1991	7.9	1.46	2.72	2.93	8.58	4.34	39.3	33.68
	1999 - 2001	5.33	1.32	1.91	2.65	5.37	3.93	40.73	33.76
	Δ	-2.57	-0.14	-0.81	-0.28	-3.21	-0.41	1.43	0.08
	Δ %	**-32.5%**	**-9.6%**	**-29.8%**	**-9.6%**	**-37.4%**	**-9.4%**	**3.6%**	**0.2%**
3	1989 - 1991	8.2	0.47	2.33	2.79	9.11	3.22	37.98	13.91
	1999 - 2001	6.04	0.48	1.91	2.4	6.06	2.84	40.7	15.74
	Δ	-2.16	0.01	-0.42	-0.39	-3.05	-0.38	2.72	1.83
	Δ %	**-26.3%**	**2.1%**	**-18.0%**	**-14.0%**	**-33.5%**	**-11.8%**	**7.2%**	**13.2%**
4	1989 - 1991	7.61	0.32	1.92	1.74	3.67	2.04	60.76	16.99
	1999 - 2001	5.85	0.31	1.69	1.84	3.1	2.12	58.29	15.22
	Δ	-1.76	-0.01	-0.23	0.1	-0.57	0.08	-2.47	-1.77
	Δ %	**-23.1%**	**-3.1%**	**-12.0%**	**5.7%**	**-15.5%**	**3.9%**	**-4.1%**	**-10.4%**

Table 3. Changes of the regionally averaged air concentrations of air pollutants (μg m^{-3}), RSO_4 (%) and RNO_3 (%) between 1989-1991 and 2014-2016 for the eastern US and Eastern Canada. Red color in (a) indicates the 3-year average concentrations still exceeding 1.0 μg m^{-3} in 2014-2016. Red color in (b) and (c) indicates reduction/increase rates exceeding 50%.

(a) All regions in the eastern US and Eastern Canada

		SO_4^{2-}	NO_3^-	NH_4^+	HNO_3	SO_2	TNO_3	RSO_4	RNO_3
All seasons	1989 - 1991	5.44	1.1	1.78	1.96	8.73	3.02	33.6	31.72
	2014 - 2016	1.45	0.78	0.58	0.67	1.08	1.43	50.6	51.91
	Δ	-3.99	-0.32	-1.2	-1.29	-7.65	-1.59	17	20.19
	Δ %	**-73.3%**	**-29.1%**	**-67.4%**	**-65.8%**	**-87.6%**	**-52.6%**	**50.6%**	**63.7%**
Cold season	1989 - 1991	3.73	1.58	1.49	1.76	11.71	3.31	21.41	40.98
	2014 - 2016	1.4	1.21	0.68	0.66	1.5	1.86	42.33	61.04
	Δ	-2.33	-0.37	-0.81	-1.1	-10.21	-1.45	20.92	20.06
	Δ %	**-62.5%**	**-23.4%**	**-54.4%**	**-62.5%**	**-87.2%**	**-43.8%**	**97.7%**	**49.0%**
Warm season	1989 - 1991	7.02	0.66	2.06	2.18	6.15	2.81	47.86	21.29
	2014 - 2016	1.6	0.41	0.53	0.75	0.75	1.15	60.4	34.32
	Δ	-5.42	-0.25	-1.53	-1.43	-5.4	-1.66	12.54	13.03
	Δ %	**-77.2%**	**-37.9%**	**-74.3%**	**-65.6%**	**-87.8%**	**-59.1%**	**26.2%**	**61.2%**

(b) Regions 1-4 during the warm season

Region		SO_4^{2-}	NO_3^-	NH_4^+	HNO_3	SO_2	TNO_3	RSO_4	RNO_3
1	1989 - 1991	2.93	0.14	0.73	0.62	1.56	0.75	57.71	19.0
	2014 - 2016	0.8	0.12	0.28	0.21	0.4	0.33	58.03	37.04
	Δ	-2.13	-0.02	-0.45	-0.41	-1.16	-0.42	0.32	18.04
	Δ %	**-72.7%**	-14.3%	**-61.6%**	**-66.1%**	**-74.4%**	**-56.0%**	0.6%	**94.9%**
2	1989 - 1991	7.9	1.46	2.72	2.93	8.58	4.34	39.3	33.68
	2014 - 2016	1.83	0.62	0.66	1.08	1.03	1.68	54.85	36.38
	Δ	-6.07	-0.84	-2.06	-1.85	-7.55	-2.66	15.55	2.7
	Δ %	**-76.8%**	**-57.5%**	**-75.7%**	**-63.1%**	**-88.0%**	**-61.3%**	39.6%	8.0%
3	1989 - 1991	8.2	0.47	2.33	2.79	9.11	3.22	37.98	13.91
	2014 - 2016	1.77	0.3	0.6	0.87	0.8	1.16	60.15	24.92
	Δ	-6.43	-0.17	-1.73	-1.92	-8.31	-2.06	22.17	11.01
	Δ %	**-78.4%**	-36.2%	**-74.2%**	**-68.8%**	**-91.2%**	**-64.0%**	**58.4%**	**79.2%**
4	1989 - 1991	7.61	0.32	1.92	1.74	3.67	2.04	60.76	16.99
	2014 - 2016	1.62	0.27	0.5	0.61	0.59	0.86	68.29	30.8
	Δ	-5.99	-0.05	-1.42	-1.13	-3.08	-1.18	7.53	13.81
	Δ %	**-78.7%**	-15.6%	**-74.0%**	**-64.9%**	**-83.9%**	**-57.8%**	12.4%	**81.3%**

(c) Regions 1-4 during the cold season

Region		SO_4^{2-}	NO_3^-	NH_4^+	HNO_3	SO_2	TNO_3	RSO_4	RNO_3
1	1989 - 1991	2.29	0.37	0.57	0.74	3.62	1.1	31.13	32.53
	2014 - 2016	0.87	0.44	0.32	0.27	0.75	0.71	46.25	62.54
	Δ	-1.42	0.07	-0.25	-0.47	-2.87	-0.39	15.12	30.01
	Δ %	**-62.0%**	18.9%	-43.9%	**-63.5%**	**-79.3%**	-35.5%	**48.6%**	**92.3%**
2	1989 - 1991	4.19	3.62	2.27	1.66	13.65	5.25	17.92	68.49
	2014 - 2016	1.67	2.52	1.16	0.73	2.19	3.24	35.18	77.29
	Δ	-2.52	-1.1	-1.11	-0.93	-11.46	-2.01	17.26	8.8
	Δ %	**-60.1%**	-30.4%	-48.9%	**-56.0%**	**-84.0%**	-38.3%	**96.3%**	12.8%
3	1989 - 1991	4.24	1.21	1.56	2.31	19.2	3.49	13.11	32.76
	2014 - 2016	1.59	1.25	0.77	0.86	2.17	2.09	34.91	57.95
	Δ	-2.65	0.04	-0.79	-1.45	-17.03	-1.4	21.8	25.19
	Δ %	**-62.5%**	3.3%	**-50.6%**	**-62.8%**	**-88.7%**	-40.1%	**166.3%**	**76.9%**
4	1989 - 1991	3.57	0.55	1.09	1.81	7.24	2.33	28.29	25.14
	2014 - 2016	1.36	0.55	0.51	0.71	1.13	1.25	48.53	43.71
	Δ	-2.21	0	-0.58	-1.1	-6.11	-1.08	20.24	18.57
	Δ %	**-61.9%**	0.0%	**-53.2%**	**-60.8%**	**-84.4%**	-46.4%	**71.5%**	**73.9%**