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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

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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 $PM_{2.5}$ mass in the eastern US (Bell et al., 2007) and are dominant components of $PM_{2.5}$ during many smog events (Dabek-Zlotorzynska et al., 2011). H_2SO_4 and HNO_3, formed from the 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 $t\,yr^{-1}$ in 1990 to 3.7 and 11.5 million $t\,yr^{-1}$ 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 in 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 a major environmental risk to human health by the World Health Organization (WHO). Air pollution is also linked to stroke and heart disease, and the improvement of air quality can significantly reduce the $PM_{2.5}$- 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 in 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 six 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 ($PM_{2.5}$) 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 participates in the formation of tropospheric O_3, which is another criteria pollutant and an important atmospheric oxidant. Title IV of the Clean Air Act 1990 specifically targets SO_2 and NO_x emissions from stationary fuel combustion facilities. The first phase of Title IV of the 1990 CAA amendment, which was implemented on 1 January 1995, requires 110 power plants to reduce SO_2 emissions to a level calculated as the product of an emissions rate of 2.5 lbs (1 lb is equal to 0.4636 kg) of SO_2 per million British thermal units (Btu; 1 Btu is equal to 1055.056 J) multiplied by an average of their 1985–1987 fuel use (Lee, 1991). The second phase, which took effect on 1 January 2000, requires approximately 2000 utilities to reduce SO_2 emissions to a level of 1.2 lbs of SO_2 per million British thermal units multiplied by the aver-

age of their 1985–1997 fuel use (Lee, 1991). Since 1990, the national emissions of SO_2 in the US have 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, 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 in the emissions was accelerated with an annual reduction rate of 1.34 million $t\,yr^{-1}$ during the period. The emissions of SO_2 leveled off during 2012–2015. In 1990, 87.9 % of SO_2 emissions was from stationary fuel combustion facilities, 2 % from on-road vehicles, and 2 % from off-road mobile sources. By 2007, SO_2 emissions from on-road vehicles were 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 emissions during the 1990s were relatively small (Butler et al., 2003). Total NO_x emissions remained generally constant from 1990 to 1998. From 1999 there was a decrease in NO_x emissions from stationary fuel combustion due to the implementation of Title IV of the 1990 CAA amendment as well as the implementation of the NO_x Budget Trading Program (NBP). Title IV of the 1990 CAA amendment not only required the reduction of SO_2, but also stipulated the reduction of NO_x emissions from power plants, and it took effect in 1996. The NBP 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, last access: 13 November 2019). 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. After 2002, on-road emissions of NO_x decreased continuously and steadily. The trend of NO_x emissions from off-road mobile operations generally increased during the period 1990–2002, up from 3.8 to 4.9 t, but after that it was reduced gradually to 2.7 t in 2014. Combining the emissions from stationary fuel combustion, on-road vehicles, and off-road mobile operations, the nationwide emissions of NO_x in the US changed little during 1990–1998 and decreased during 1998–2001. After 2002, they decreased steeply up to recent years.

Note that there was a change in NO_x measurement methodology from 2001 to 2002, and it caused a sharp increase in the reported NO_x emissions in the US from 2001 to 2002 (EPA, 2019)

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, the 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 NO_x 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 interest for both scientific communities and the general public. For the eastern part of the 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 II and Shadwick, 2007; Sickles II and Shadwick, 2015; Cheng and Zhang, 2017). Sickles II 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 the 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 that 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 to 2015. These trends are not only important for the assessment of the improvement of air quality due to emissions reductions, but are also essential for the evaluation 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, as well as 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 the reaction of these oxidants with NH_3.

2 Data and methods

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 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 concentrations 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 1978. The network measures 24 h integrated air concentrations of pollutants (from 08:00 to 08:00 LT, local time) through filter pack sampling and 24 h wet deposition by the 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 concentrations 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 methods

As we focus on the long-term trends of air pollutants over the region, annual means for all seasons and seasonal means for the warm and cold seasons were derived for each site from the weekly measurements of CASTNET and daily measurements of CAPMoN. To be precise, the seasonal mean concentrations in this study refer to the mean concentrations calculated for the warm (May–October) and cold (November–April) seasons for each year. In order to avoid the fluctuations of annual or seasonal mean 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 nonparametric test to detect the trend of a time series and it does not require the variable of the time series to follow 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 in air pollutants in response to emission reductions of SO_2 and NO_x, we looked at the following 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 yearly regional means during the warm and cold seasons; and

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 concentrations 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 four different regions. The reasons for selecting the cold season are the following: (1) NO_3^- is mainly in the form of NH_4NO_3 (Zhang et al., 2008), and it is 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, and 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, and therefore RNO_3 during the cold season is an indicator of the abundance of NH_3 to form NH_4NO_3. The mean concentrations at the beginning

of the period were used to cluster the sites as the emission rate of SO_2 was the highest.

Based on the spatial patterns of the mean air concentration of NO_3^-, SO_2, and RNO_3 during the cold season of 1989–1991, which are shown in Table S1b and Fig. S1b in the Supplement, four regions in the EUS and EC were clustered.

- Region 1: sites located north of latitude 40° and with a concentration of SO_2 less than 6.4 µg m^{-3} in the cold season.

- Region 2: sites with a 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 and seasonal mean 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 seasonal mean concentrations of each site vs. the averaged values of the cluster during the warm 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

The 3-year averages of the air concentrations of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3, SO_2, and TNO_3, as well as RSO_4 and RNO_3 for 1989–1991 are used to describe the air quality at the beginning of the study period and are shown in Table S1a and b for the warm and cold seasons. Mapping of 3-year average for each species is also provided as Fig. S1. Among
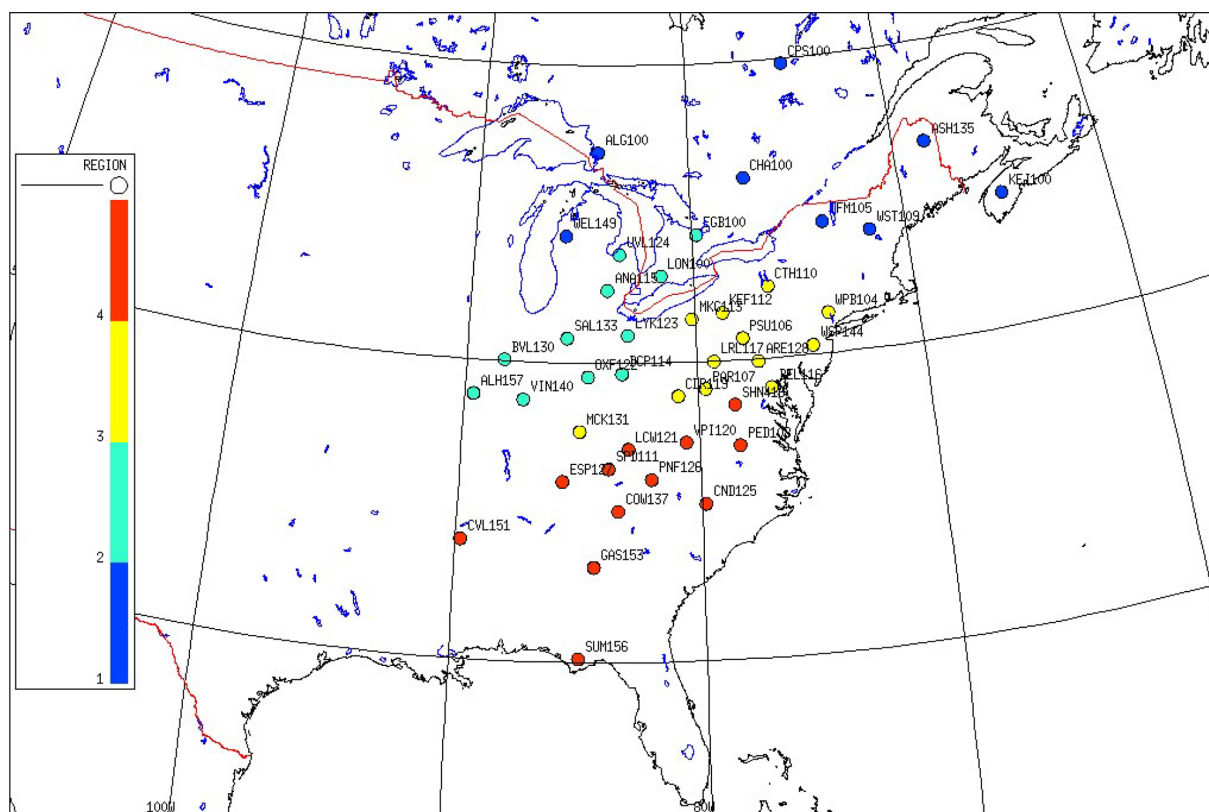
Figure 1. Clustered sites of CASTNET and CAPMoN in regions 1–4.

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

Region	Characteristics of region
1	$SO_2 < 6.4\,\mathrm{g}\,^{-3}$ for all sites; on average the region had the lowest seasonal mean concentrations of SO_4^{2-}, NO_3^-, NH_4^+, HNO_3, and SO_2.
2	$NO_3^- > 2.5\,\mathrm{g}\,\mathrm{m}^{-3}$ and $RNO_3 > 54.0\,\%$ for all sites; $AVE\_NO_3^- = 4.2\,\mathrm{g}\,\mathrm{m}^{-3}$; $AVE\_SO_2 = 13.6\,\mathrm{g}\,\mathrm{m}^{-3}$; $AVE\_RNO_3 = 68.5\,\%$.
3	$NO_3^- < 2.2\,\mathrm{g}\,\mathrm{m}^{-3}$, $RNO_3 < 47\,\%$, and $SO_2 > 15.2\,\mathrm{g}\,\mathrm{m}^{-3}$ for all sites; $AVE\_NO_3^- = 1.2\,\mathrm{g}\,\mathrm{m}^{-3}$; $AVE\_SO_2 = 19.2\,\mathrm{g}\,\mathrm{m}^{-3}$; $AVE\_RNO_3 = 32.3\,\%$.
4	$SO_2 < 11.7\,\mathrm{g}\,\mathrm{m}^{-3}$ and $NO_3^- < 0.7\,\mathrm{g}\,\mathrm{m}^{-3}$ for all sites; $AVE\_NO_3^- = 0.6\,\mathrm{g}\,\mathrm{m}^{-3}$; $AVE\_SO_2 = 7.2\,\mathrm{g}\,\mathrm{m}^{-3}$; $AVE\_RNO_3 = 28.3\,\%$.

the four 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 $1.0\,\mu\mathrm{g}\,\mathrm{m}^{-3}$. The mean air concentration of NO_3^- during the warm season was only $0.14\,\mu\mathrm{g}\,\mathrm{m}^{-3}$. Mean SO_4^{2-} concentrations were 2.9 and $2.3\,\mu\mathrm{g}\,\mathrm{m}^{-3}$ during the warm and cold seasons, respectively, and SO_2 was 1.6 and $3.6\,\mu\mathrm{g}\,\mathrm{m}^{-3}$ 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 $8.2\,\mu\mathrm{g}\,\mathrm{m}^{-3}$ during the warm season and 3.6 to $4.2\,\mu\mathrm{g}\,\mathrm{m}^{-3}$ during the

cold season. The difference in the regional mean of SO_4^{2-} between region 2 and 3 was less than $0.1\,\mu\mathrm{g}\,\mathrm{m}^{-3}$ 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. The 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 $13.7\,\mu\mathrm{g}\,\mathrm{m}^{-3}$, respectively, showed the two highest concentrations and the only two concentrations greater than $10.0\,\mu\mathrm{g}\,\mathrm{m}^{-3}$ among all

species in four regions and during the warm and cold seasons. The difference in SO_2 between region 3 and 2 was less than $1.0\,\mu g\,m^{-3}$ during the warm season but was more than $5.0\,\mu g\,m^{-3}$ 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 seasonal mean concentration of SO_2 in region 3 was higher than that in region 4 by $10.0\,\mu g\,m^{-3}$, but the corresponding difference in SO_4^{2-} was only $0.7\,\mu g\,m^{-3}$. This can be attributed to the fact that the lifetime of SO_4^{2-} ($\sim$ 5–7 d) in the air is much longer than that of SO_2 ($\sim$ 2 d) (Penner et al., 2001; Pitari et al., 2016). Lee et al. (2011) estimated the mean SO_2 lifetime in the eastern US to be $19 \pm 7\,h$ in summer and $58 \pm 20\,h$ in winter. Comparing SO_2 in the cold season to that in the warm season, it was about 2 times higher in regions 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 $1.5\,\mu g\,m^{-3}$ during the warm season and $3.6\,\mu g\,m^{-3}$ during the cold season; these values 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 $0.6\,\mu g\,m^{-3}$ for the warm and cold seasons, respectively. The lowest value for stations in region 2 during the cold season was $2.5\,\mu g\,m^{-3}$ at ALH157, higher than the highest value of $2.1\,\mu g\,m^{-3}$ at BEL116 in region 3. During the warm season, HNO_3 ranged from $1.7\,\mu g\,m^{-3}$ in region 4 to 2.8 and $2.9\,\mu g\,m^{-3}$ 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 $1.8\,\mu g\,m^{-3}$, 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 $5.3\,\mu g\,m^{-3}$ 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 $3.5\,\mu g\,m^{-3}$ for region 3 and 2.0 and $2.3\,\mu g\,m^{-3}$ for region 4 during the warm and cold seasons. NH_4^+ in regions 2–4 varied from 1.9 to $2.7\,\mu g\,m^{-3}$ during the warm season and 1.1 to $2.3\,\mu g\,m^{-3}$ 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 four 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 regions 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.
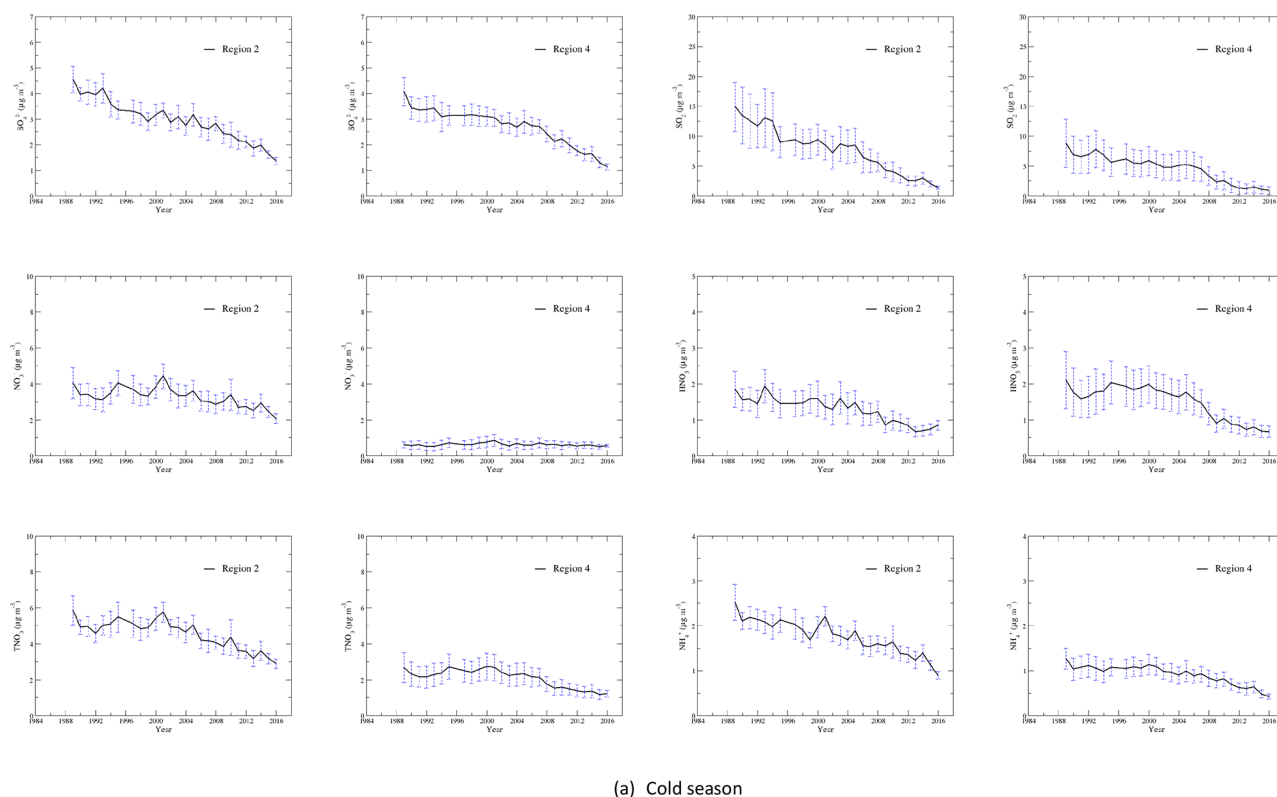
3.2 Time series of seasonal mean concentrations of SO_4^{2-}, SO_2, NO_3^-, HNO_3, TNO_3, and NH_4^+ during 1990–2015

Time series of seasonal mean 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. S3a for the cold season and Fig. S3b for the warm season. As an example, time series of regional averaged seasonal mean concentrations in regions 2 and 4 are shown in Fig. 2a and b for the cold and warm seasons. Time series of regional averages for regions 1–4 normalized to the year 2000 are presented in Fig. 3a and b for the warm and cold seasons. The year 2000 was chosen for normalization because (1) emissions of NO_x changed little during the first 10 years, and (2) 10 and 25 years of change in annual and seasonal mean concentrations of each species will be discussed in Sect. 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 four regions. The discussion in this section is based on the time series of seasonal mean concentrations presented in Fig. S3 as well as Fig. 3.

3.2.1 SO_4^{2-} and SO_2

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

As seen from the time series of the seasonal mean 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 to 2008. There was a smooth decreasing trend from 2008 to 2016, and the drop in the seasonal mean 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 seasonal mean concentrations of SO_4^{2-} during the periods being 3.4, 3.1, and $2.8\,\mu g\,m^{-3}$, respectively. There were only two major drops between the periods, in 1994 and 2002. 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 decreas-

(a) Cold season

Figure 2.

ing 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 would be 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, and 1.13 $\mu g\,m^{-3}\,yr^{-1}$ in region 3; and 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 2005–2016. For regions 1–4 combined, the corresponding reduction rates were 0.72, 0.16, and 0.48 $\mu g\,m^{-3}\,yr^{-1}$. For the third period, if we only consider 2005–2012, the annual reduction rate was 0.61 $\mu g\,m^{-3}\,yr^{-1}$. Although the trend of SO$_2$ during 2012–

2016 was generally flat, the decrease in SO$_4^{2-}$ during the period was still significant, especially in terms of percentage.
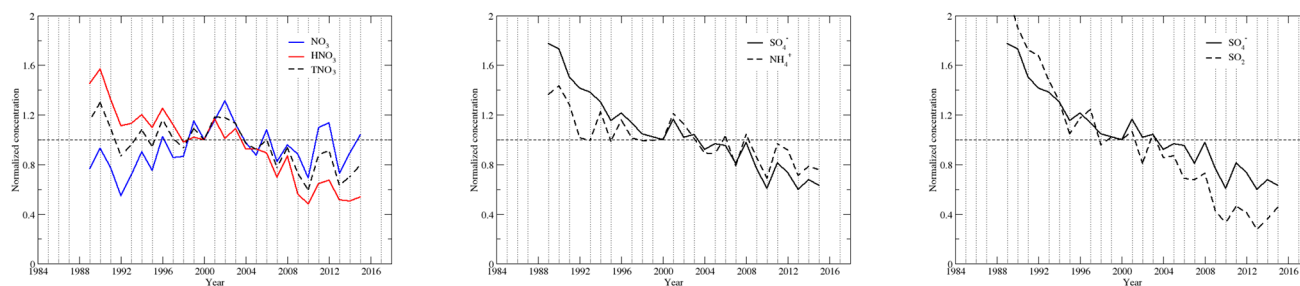
SO$_4^{2-}$ and SO$_2$ during the warm season

SO$_4^{2-}$ in region 1 had a significant decrease from 1989 to 1996, followed by a leveling-off until 2005 and a decreasing trend from 2005 to 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 leveling-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 leveling-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$_4^{2-}$ at 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

(b) Warm season

Figure 2. Time series of the regionally averaged seasonal mean concentrations during the cold **(a)** and warm **(b)** seasons for each species in region 2 (Midwest) and region 4 (Southeast). The vertical dashed line represents the standard deviation of the regionally averaged seasonal mean concentration. The regionally averaged seasonal mean concentrations in regions 2 and 4 during the cold season were not generated for 1996 because of an insufficient number of measurements.
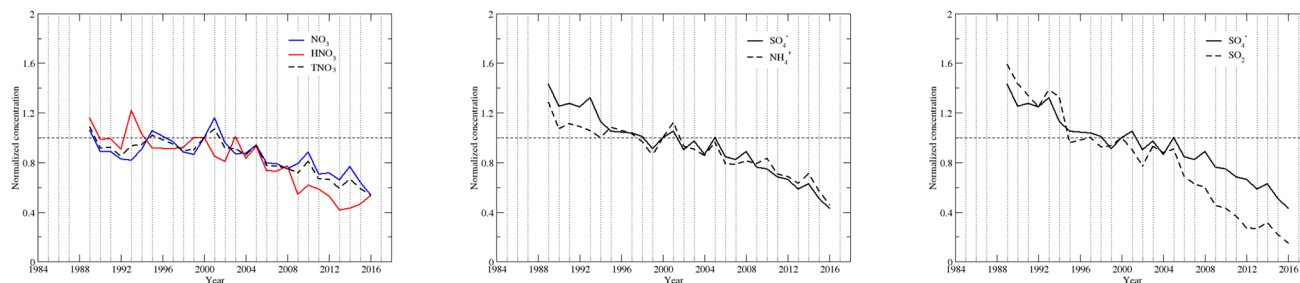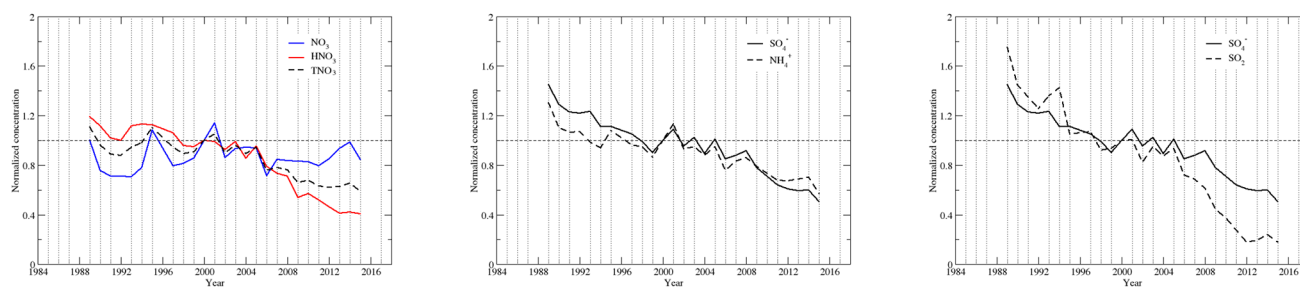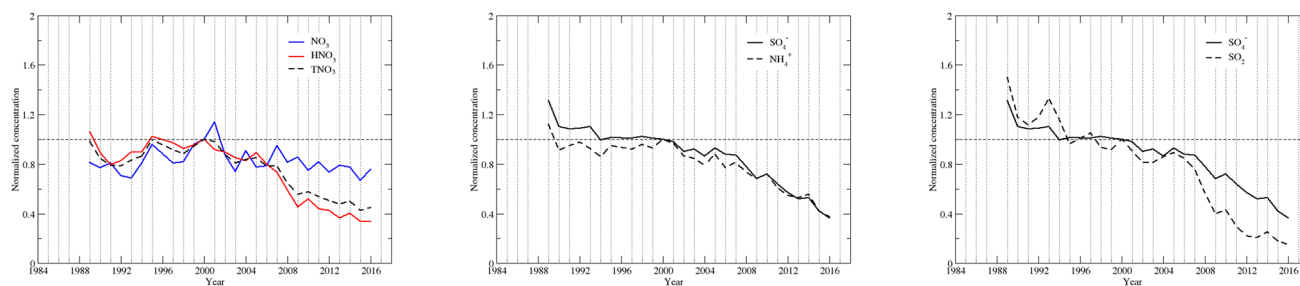
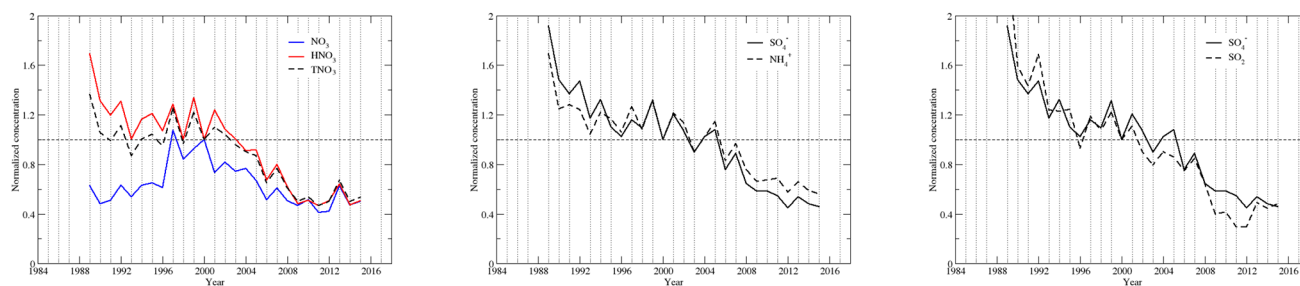Region 1

Region 2

Figure 3.

Region 3

Region 4

(a) Cold season

Figure 3.
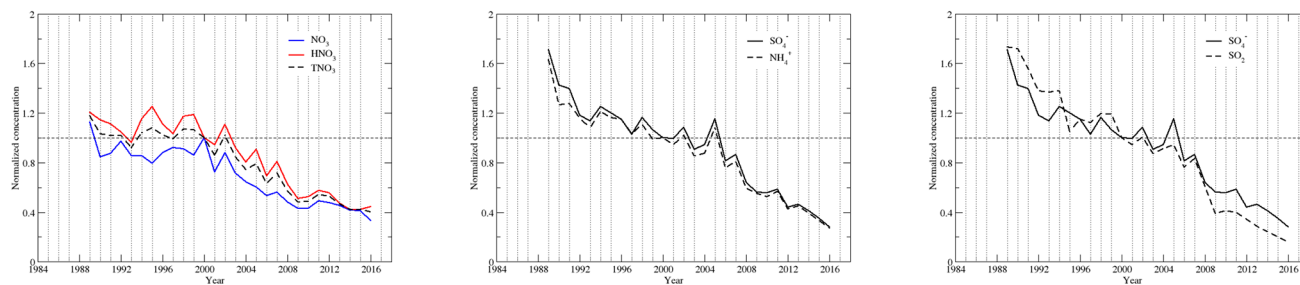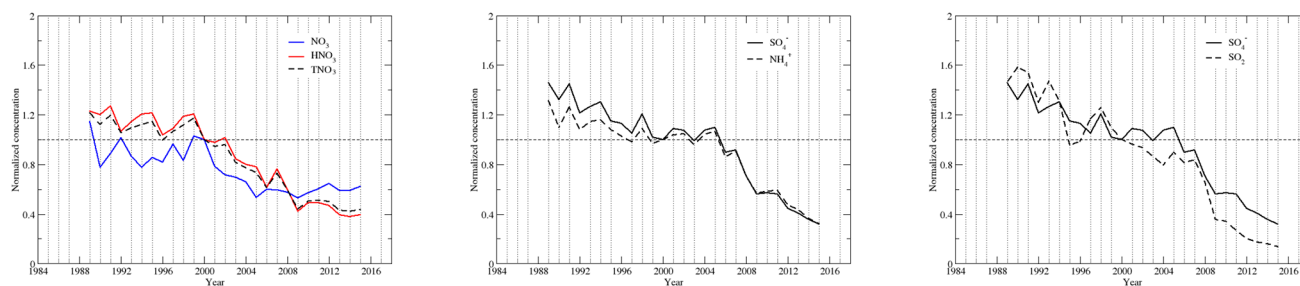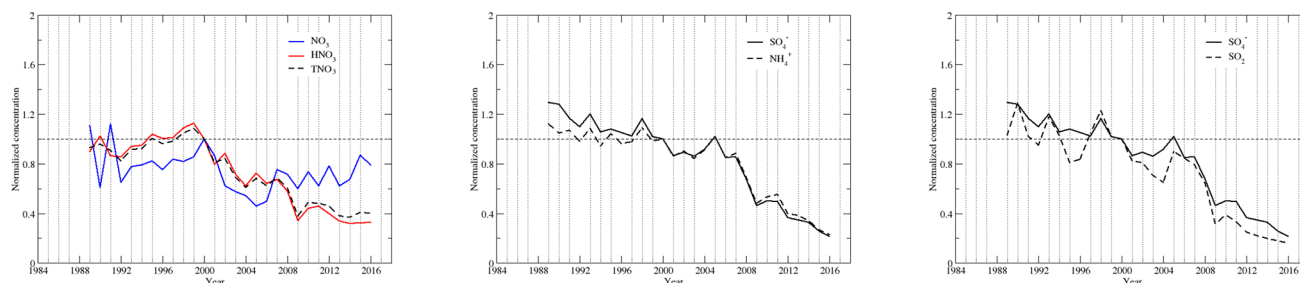
Region 1

Region 2

Figure 3.

Region 3

Region 4

(b) Warm season

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

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 $\mu g\,m^{-3}\,yr^{-1}$ for region 1; 0.39, 0.03, and 0.43 $\mu g\,m^{-3}\,yr^{-1}$ for region 2; 0.28, 0.01, and 0.52 $\mu g\,m^{-3}\,yr^{-1}$ for region 3; and 0.24, 0.04, and 0.50 $\mu g\,m^{-3}\,yr^{-1}$ for region 4. For regions 3 and 4, the most significant decrease occurred in 2007–2009.

SO_2 concentrations during the warm season were 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 a very low concentration ($< 1.0\,\mu g\,m^{-3}$) 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 leveling-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. For the three periods, SO_2 had annual reduction rates of 0.12, 0.03, and 0.04 $\mu g\,m^{-3}\,yr^{-1}$ for region 1; 0.55, 0.08, and 0.43 $\mu g\,m^{-3}\,yr^{-1}$ for region 2; 0.46, 0.11, and 0.48 $\mu g\,m^{-3}\,yr^{-1}$ for region 3; and 0.13, 0.05, and 0.22 $\mu g\,m^{-3}\,yr^{-1}$ for region 4. For the whole region, the annual reduction rates during the warm season were 0.31,

0.04, and 0.38 $\mu g\,m^{-3}\,yr^{-1}$ for SO_4^{2-} and 0.34, 0.08, and 0.30 $\mu g\,m^{-3}\,yr^{-1}$ for SO_2 for the periods of 1989–1995, 1995–2007, and 2007–2016.

3.2.2 NO_3^-, HNO_3, and TNO_3

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 the following: (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 $\mu g\,m^{-3}$ 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 regions 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 in TNO_3 over the three regions. For region 3, it occurred mainly during the period 2001–2009.

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 the NO_3^- seasonal mean 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 the NO_3^- concentration until 2009 and a steady decreasing from 2011 to 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. The seasonal 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 ($< 1.0\,\mu g\,m^{-3}$) 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 weak 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, 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 de-

creasing trends. For 2009–2016, the trends in the three regions were generally flat.

3.2.3 NH_4^+

NH_4^+ during the cold season

NH_4^+ during the cold season in region 1 had a flat trend in 1990–1999 and 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.

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. Figure 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 to 2005, the trend of NH_4^+ in region 3 was almost flat. There was a major decrease in 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 to 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 in 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 Sect. 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 did not decrease or even increased, as shown in Sect. 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 in 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 sum-

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

Region		SO_4^{2-}	NO_3^-	NH_4^+	HNO_3	SO_2	TNO_3	RSO_4	RNO_3
(a) Cold season									
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									
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 %

marized in Sect. 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 as 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 in NO$_3^-$ during

Table 3. Changes in the regionally averaged air concentrations of air pollutants ($\mu g\,m^{-3}$), RSO$_4$ (%), and RNO$_3$ (%) between 1989–1991 and 2014–2016 for the eastern US and Eastern Canada. Bold in **(a)** indicates the 3-year average concentrations still exceeding $1.0\,\mu g\,m^{-3}$ in 2014–2016. Bold in **(b)** and **(c)** indicates reduction and increase rates exceeding 50 %.

		SO_4^{2-}	NO_3^-	NH_4^+	HNO_3	SO_2	TNO_3	RSO_4	RNO_3
(a) All regions in the eastern US and Eastern Canada									
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									
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									
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 %**

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 µg 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. Except for a negligible change in region 4, NH_4^+ decreased by 13.5 % to 22.8 % for regions 1–3 during the cold season; during warm season, it decreased by 12.0 % to 29.8 % for regions 1–4.

6. In summary, over the first 10-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 was reduced in regions 1–3. NO_3^- increased in regions 1–4 during the cold season and changed very little (< 0.15 µg 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 in 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 1990–2015, air quality in the EUS and EC changed significantly and is summarized as follows.

1. Among all species, the most significant reduction during the period was for 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 seasonal mean concentration was reduced from 19.2 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 four 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 experience 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. The 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 Sect. 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 less 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 greater 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 II 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. RSO4 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, RSO4 increased by 54.9 % and 58.4 % in regions 2 and 3, respectively. The increase in RSO4 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. RNO3 increased significantly in regions 1, 3, and 4 in both seasons, ranging from 73.9 % to 94.9 %, but RNO3 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, the following points apply for the whole region: (1) among the five 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 mean 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) RSO4 increased by 97.7 % in the cold season, much higher than 26.2 % in the warm season. RSO4 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

The 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 season.

As at the beginning of the period, region 1 had the cleanest air among all regions, with the lowest air concentrations of less than $1.0\,\mu g\,m^{-3}$ for all species and for both the warm and cold seasons. Unlike at the beginning of the period when 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 $2.0\,\mu g\,m^{-3}$ in all regions and both seasons. For regions 2–4 the regional averages ranged from 1.6 to $1.8\,\mu g\,m^{-3}$ during the warm season and from 1.4 to $1.7\,\mu g\,m^{-3}$ during the cold season. SO_2 during the warm season was only from 0.6 to $1.0\,\mu g\,m^{-3}$ for regions 2–4. In the cold season, SO_2 in regions 2 and 3 was the same at $2.2\,\mu g\,m^{-3}$ and was only $1.1\,\mu g\,m^{-3}$ in region 4. NH_4^+ during the warm season varied from 0.5 to $0.7\,\mu g\,m^{-3}$ for regions 2–4. During the cold season, it was 0.5 and $0.8\,\mu g\,m^{-3}$ in regions 4 and 3, respectively, and it was much higher in region 2 with the value of $1.2\,\mu g\,m^{-3}$. The air concentration of NO_3^- during the warm season was very low in regions 3 and 4, with values of $0.3\,\mu g\,m^{-3}$, and it was doubled in region 2, being $0.6\,\mu g\,m^{-3}$. During the cold season, NO_3^- was much higher than during the warm season, being 2.5, 1.3, and $0.5\,\mu g\,m^{-3}$ for regions 2, 3, and 4, respectively. HNO_3 in regions 2–4 varied from $0.6\,\mu g\,m^{-3}$ in region 4 to $1.1\,\mu g\,m^{-3}$ in region 2 during the warm season and from $0.7\,\mu g\,m^{-3}$ in region 4 to $0.9\,\mu g\,m^{-3}$ in region 3 during the cold season. There was little difference between the warm and cold seasons in regions 3 and 4. TNO3 was the highest in region 2 in both seasons, being 1.7 and $3.2\,\mu g\,m^{-3}$ for the warm and cold seasons, respectively. Region 3 had the second-highest TNO3 with values of 1.2 and $2.1\,\mu g\,m^{-3}$ for the warm and cold seasons, and the corresponding values for region 4 were 0.9 and $1.3\,\mu g\,m^{-3}$.

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 $1.0\,\mu g\,m^{-3}$ for all species in both seasons. For regions 2–4, NO_3^- was less than $1.0\,\mu g\,m^{-3}$ 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 $1.3\,\mu g\,m^{-3}$, respectively; HNO_3 was less than $1.0\,\mu g\,m^{-3}$ except region 2 during the warm season with a value of $1.1\,\mu g\,m^{-3}$; NH_4^+ was less than $1.0\,\mu g\,m^{-3}$ for all regions except region 2 during the cold season at $1.2\,\mu g\,m^{-3}$; SO_4^{2-} was greater than 1.0 but less than $2.0\,\mu g\,m^{-3}$ for regions 2–4 and both seasons; SO_2 was greater than 1.0 but less than $2.5\,\mu g\,m^{-3}$ for regions 2–4 and both seasons, except regions 3 and 4 during the warm season, being 0.8 and $0.6\,\mu g\,m^{-3}$. Among the four regions, region 2 had the highest air concentration for all species except HNO_3 during the cold season. NO_3^- in region 2 was especially high, double the second-highest value in region 3 in both seasons. Also, NO_3^- in region 2 had the highest value (at $2.5\,\mu g\,m^{-3}$) among all species in four regions and both seasons, although it significantly decreased from $3.6\,\mu g\,m^{-3}$ 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
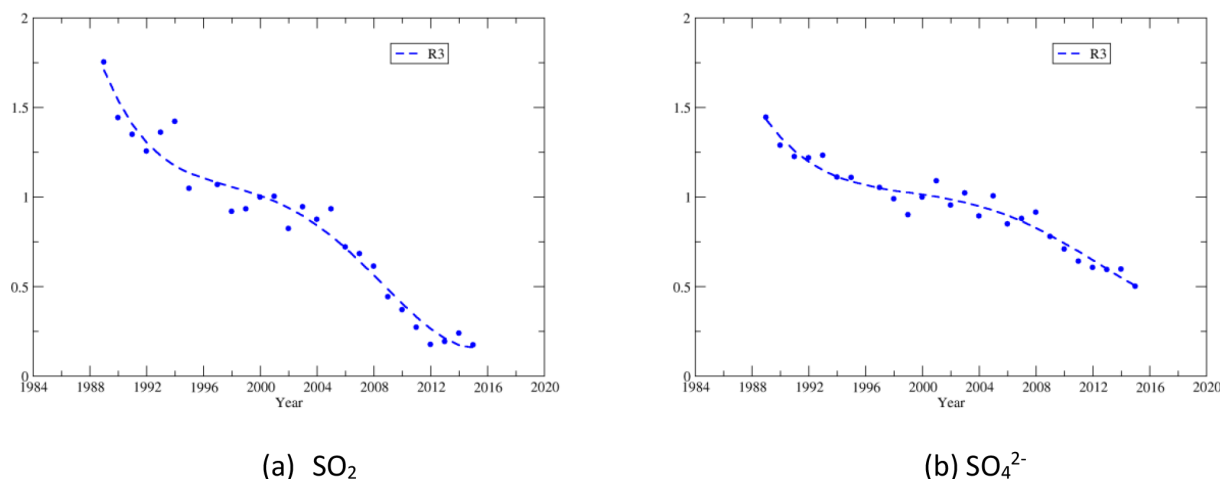
(a) SO_2 (b) SO_4^{2-}

Figure 4. Examples of fourth-order polynomial regressions of SO_2 **(a)** and SO_4^{2-} **(b)** for region 3 during the cold season.

for the period. Through these regressions, we can elimi-
nate the relatively short-term variations due to meteorology.
Fourth-order polynomial regressions were applied to the nor-
malized seasonal 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 ap-
plied fifth-order polynomial regressions to better capture the
trends. The regressed trends are normalized to the regressed
values of the 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.
Figure 5 shows comparisons between the normalized sea-
sonal means during the cold season in region 3 and the cor-
responding regressed values.

The regressed trends for SO_4^{2-}, SO_2, NH_4^+, NO_3^-, HNO_3,
and TNO_3 for the four regions during the cold and warm
seasons are shown in Fig. 6a. The regressed trends for re-
gions 1–4 clearly show that (1) the most significant reduction
of all species was SO_2, and (2) there were significant dispar-
ities in 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 they were much less significant
than the cold season; (3) among all species, the least signif-
icant reduction was for NO_3^- during the period. Figure 6b
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 in the trends during 1990–2000
between regions 1 and 4. The trends of NH_4^+ were different
for the four 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   Discussion

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 oxi-
dized from gas SO_2 to particulate SO_4^{2-}. A 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 II and Shadwick (2015). RSO$_4$ is also
an indicator of the gas–particle partition ratio for sulfur in
the air as SO_2 and SO_4^{2-} exist in the air as a gas and particle,
respectively. This metric 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 lo-
cal site. Generally, the longer it takes to transport an upwind
air parcel, the higher the percentage of SO_2 oxidized into
SO_4^{2-}, and more SO_2 is dry-deposited than SO_4^{2-}, so RSO$_4$
is higher. Also, the lower the percentage of SO_2 emitted lo-
cally and the higher the atmospheric oxidation capacity, the
higher RSO$_4$. RSO$_4$ for 1989–1991 and 2014–2016, and the
changes in 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 the 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. Figure S4 shows that during the cold season, RSO$_4$ in-
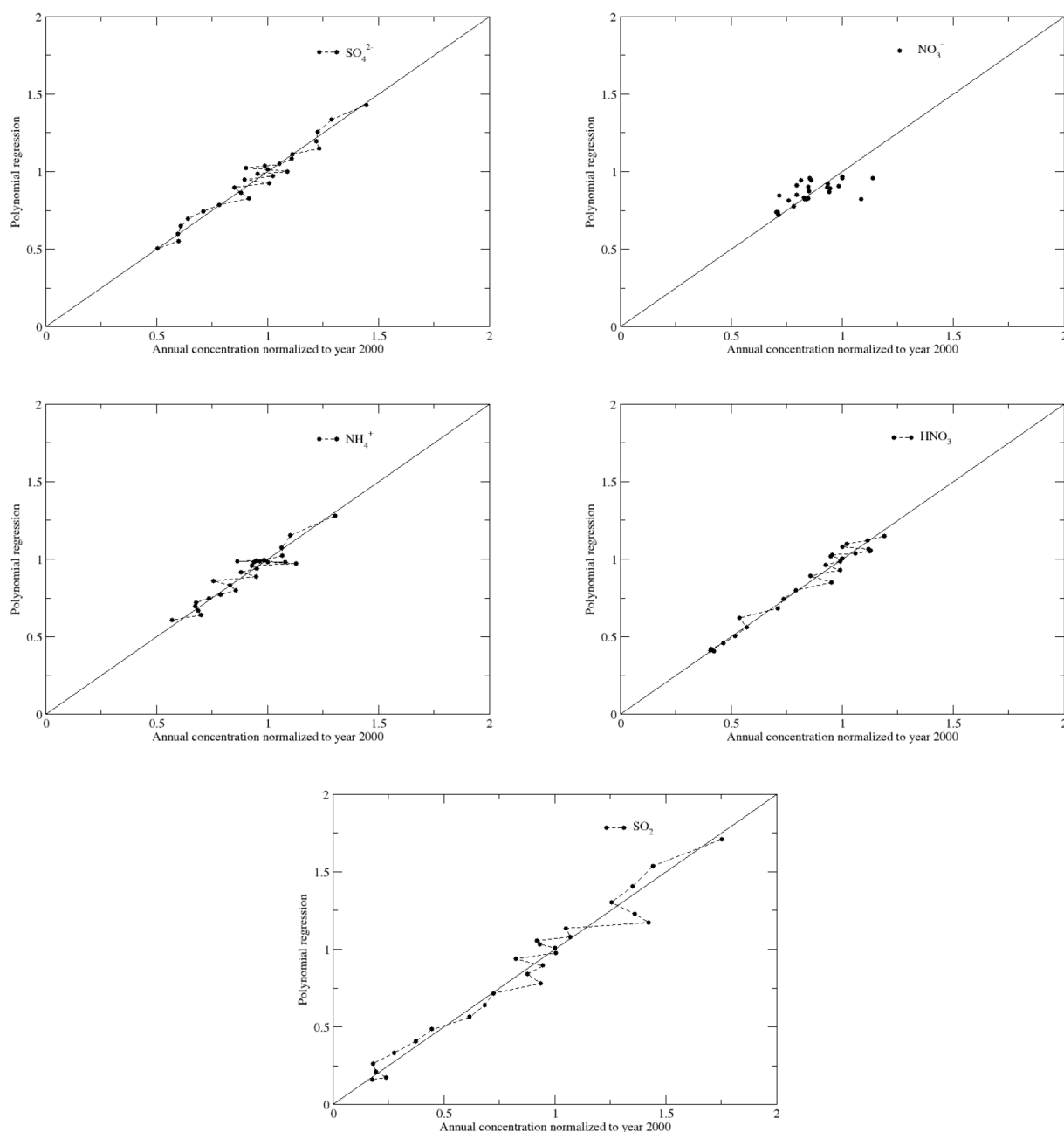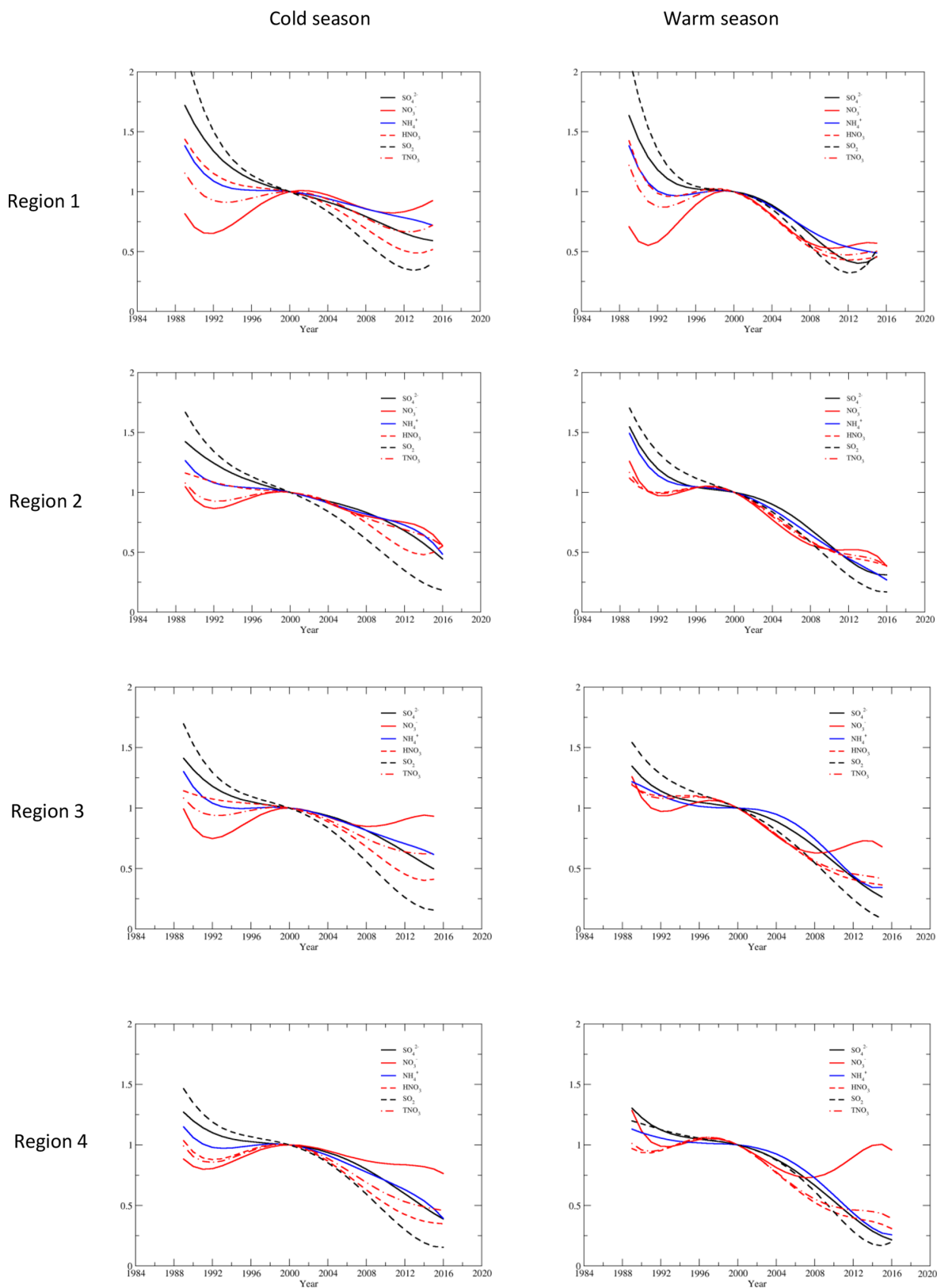creased by more than 40 % at all sites except for VPI120,

Figure 5. Comparisons of the normalized seasonal mean 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 dotted lines link the seasonal mean concentrations from 1990 to 2016 for species except for NO_3^- to show the temporal trends.

at which it increased by 18.7 %. During the warm season, RSO4 increased at all sites except for VPI120, ASH135, and WST109, at which it decreased by 25.0 %, 12.5 %, and 3.9 %, respectively. The most significant increase in RSO4 was in region 3 during the cold season, with a regional average of 166.3 %.

Figure 7 shows that RSO4 increased linearly with the year for region 1 and quadratically for regions 2–4 for both sea-

sons. RSO4 increased significantly after 2005 in regions 2–4. Figure 8 shows the correlations of RSO4 vs. SO2 for regions 2–4, and it is clear that RSO4 increased with the decrease in SO2. The increase in RSO4 was relatively slow when the concentration of SO2 was greater than $5\,\mu g\,m^{-3}$ in the cold season and $7.5\,\mu g\,m^{-3}$ in the warm season. RSO4 soared when SO2 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

Cold season　　　　　　　　　　　　　　　Warm season

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

Figure 6.

Figure 6.

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

Figure 6. Long-term trends derived with fourth-order polynomial regressions for SO_4^{2-}, SO_2, and NH_4^+ and fifth-order polynomial regressions for NO_3^-, HNO_3, and TNO_3 during the warm and cold seasons.

in regions 2 and 3. The increase in RSO_4 with the decrease in SO_2 can be explained as follows: (1) the atmospheric oxidants did not decrease as much as SO_2 emissions did. For example, the daily maximum 8 h 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 it decreased by 4 %–15 % during 1997–2006 for regions 2, 3, and 4 (Chan, 2009). No decreasing trend was found for the EUS during the cold season for 1997–2006 (Chan, 2009). Sickles II 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 in SO_2 caused the decrease in H_2SO_4 formation. Together this made cloud or rain droplets or snow particles less acidic, which was beneficial for the ox-

idation of SO_2 by H_2O_2 in the aqueous phase (Makar et al., 2009; Jones and Harrison, 2011).

The disparity in the reduction of SO_2 and SO_4^{2-} in response to emission reductions of SO_2, namely the fact that 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 clearly show the disparity during the period of 1990–2015. The significant increase in 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 not only due to the emission reductions, but also to the fact that a higher fraction of SO_2 was converted to SO_4^{2-}. A faster reduction of SO_2 was observed for all four regions during the cold season, both before and after the year 2000, and it was more significant after 2000. This can be explained by the fact that the increase in RSO_4 with time was nonlinear. As shown in Table 2, in the first 10 years of the study period, the increase in RSO_4 was relatively limited. During
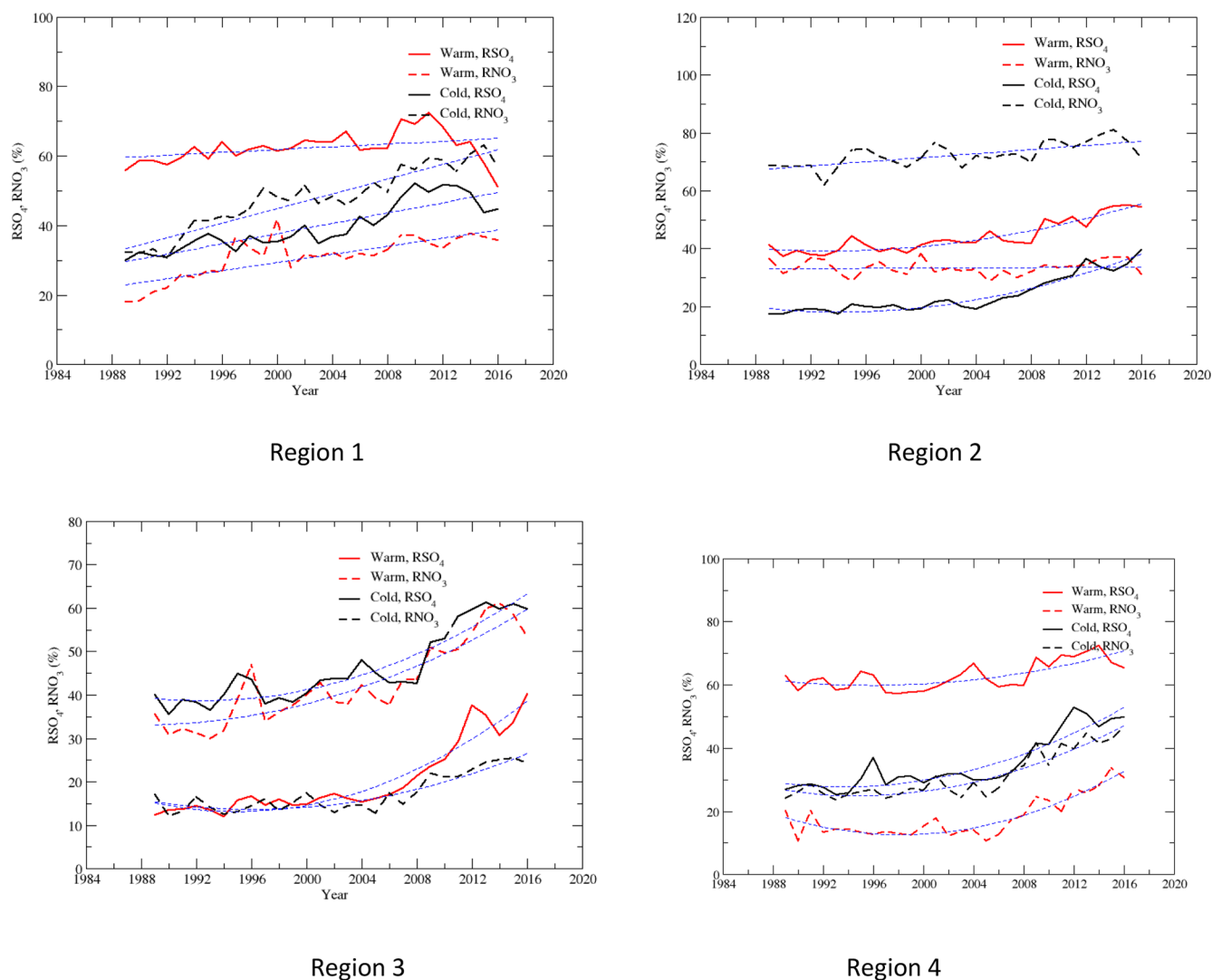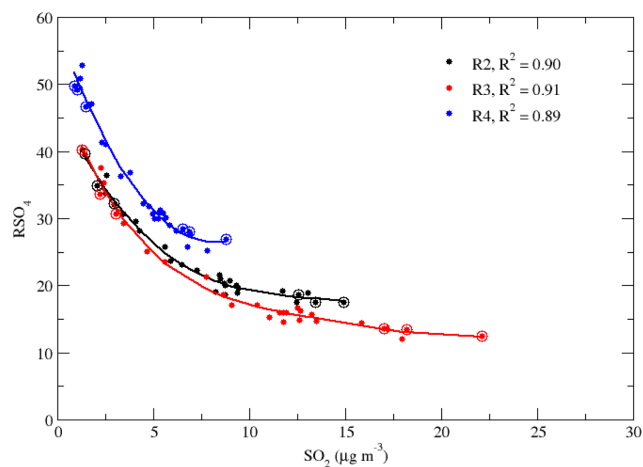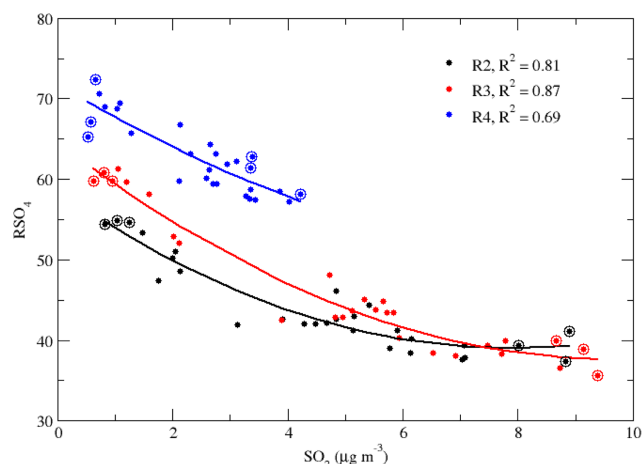
Region 1

Region 2

Region 3

Region 4

Figure 7. Time series of RSO_4 and RNO_3 for regions 1–4 during the cold and warm seasons.

the cold season, it only increased by 7.3 % in region 4 to 16.5 % in region 3. It was in the last 10 years from 2005 to 2015 when SO_2 was further reduced so that RSO_4 increased dramatically. As shown in Tables 2 and 3, during the cold season in region 3, RSO_4 only increased by 16.5 % in the first 10 years, 1990–2000, but it increased by 149.8 % for the last 15 years of 2000–2015. During the warm season, the disparity in the reduction between SO_2 and SO_4^{2-} was much lower, as clearly shown in Fig. 3. This is because the increase in 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 % in regions 1 and 4. The disparity in 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 being available than in the cold season, so the 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 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 in RSO_4; (3) furthermore, in the EUS, the seasonal mean O_3 concentration decreased in the warm season and increased in the cold season for the study period (Sickles II 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.
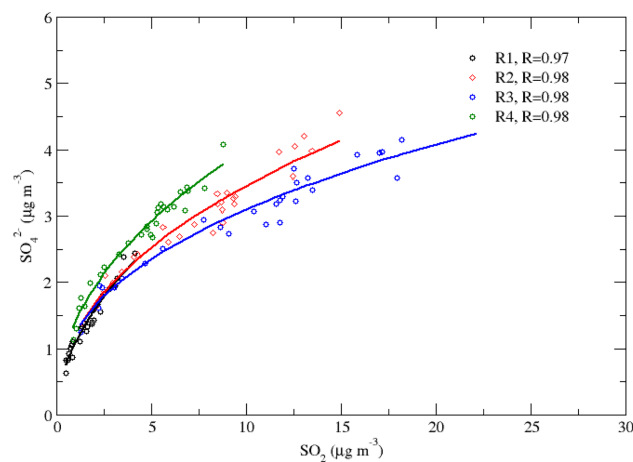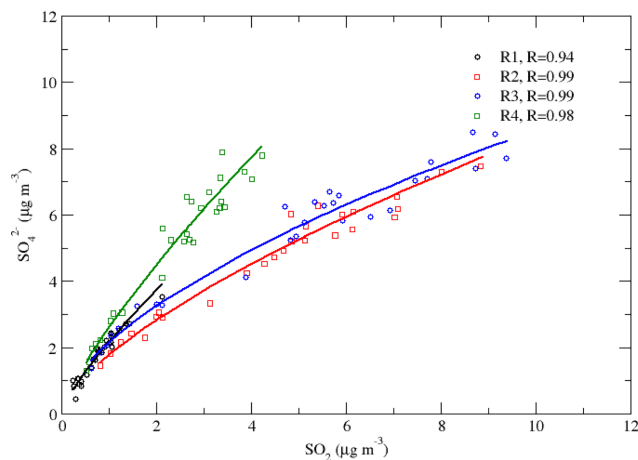
(a) Cold season

(a) Cold season

(b) Warm season

(b) Warm season

Figure 8. Correlations of the seasonal means during the cold and warm seasons: RSO_4 vs. SO_2 for regions 2–4. Fourth-order polynomial and quadratic regressions were applied for the cold and warm seasons, respectively. R2, 3, and 4 refer to regions 2–4. The dots with circles represent the seasonal means in the first and last 3 years.

Figure 9. Correlations of the seasonal 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.

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 for the period of 1990–2010 can be described by linear regressions (not shown in the graph), 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 the slopes for regions 2 and 3. A linear relationship between the seasonal mean concentrations of SO_4^{2-} and SO_2 indicates that there is 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. 9. In some previous studies (e.g., Jones and Harrison, 2011), nonlinear power-law relationships have been found for observations at different sites for different seasons and periods. Our results indicate that a linear relationship between SO_4^{2-} and SO_2 ex-

ists for a subperiod of a long-term 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 that is aerosolized (Sickles II 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 and (2) reaction with existing aerosols such as sea salts and crustal materials to form $NaNO_3$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$. 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 in 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 in 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 in RNO_3 in regions 1, 3, and 4 can be attributed to the significant reduction of SO_4^{2-} during the period, as is explained in Sect. 4.4.

Figure 7 shows that RNO_3 had an increasing trend with the 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 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 in 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 the seasonal mean RNO_3 and the seasonal mean concentration of SO_4^{2-} for regions 2–4 and for the warm and cold seasons are presented in Fig. 10. For
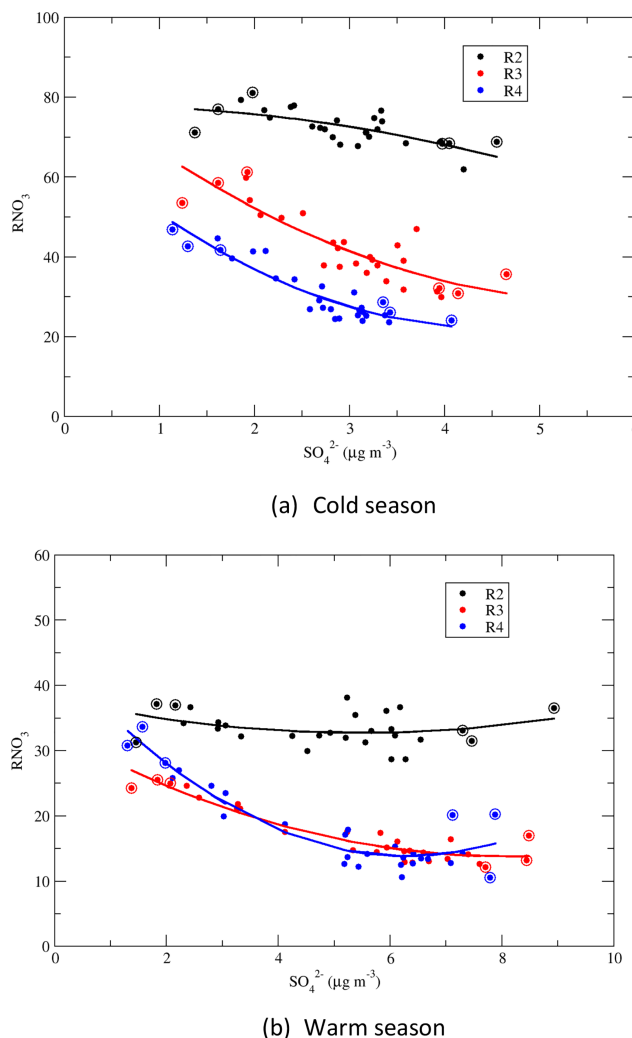

(a) Cold season

(b) Warm season

Figure 10. Correlations of the seasonal means during the cold and warm seasons: RNO_3 vs. SO_4^{2-} for regions 2–4. The dots with circles represent the seasonal means in the first and last 3 years.

NH_3-rich region 2, RNO_3 increased slightly with the decrease in 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 in SO_4^{2-}. RNO_3 increased steeply when the seasonal mean 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 in RNO_3 with the decrease in 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, some of the 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 in regions 3 and 4, as seen in Fig. S6. Thus, in general there was always

excess NH_3 available to react with HNO_3 to form NH_4NO_3 in region 2, which resulted in a lack of trends in RNO_3. This also explains why TNO_3 decreased by 40.1 % and 46.4 %, respectively, during the cold season in regions 3 and 4, while the change in 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 linearly associated with the change in SO_4^{2-}. In region 2, the change in NH_4^+ was also mostly associated with the change in SO_4^{2-}, but the change in 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 well with the variation of NH_4^+ with $R = 0.87$, indicating that some 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-}. Figure 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 seasonal means of the 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 seasonal mean concentrations in region 4 and region 3, respectively, and the lowest seasonal mean 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 is much higher than that in region 1. Figure 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 it was opposite thereafter. SNA in region 3 was significantly higher during the warm season than the 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
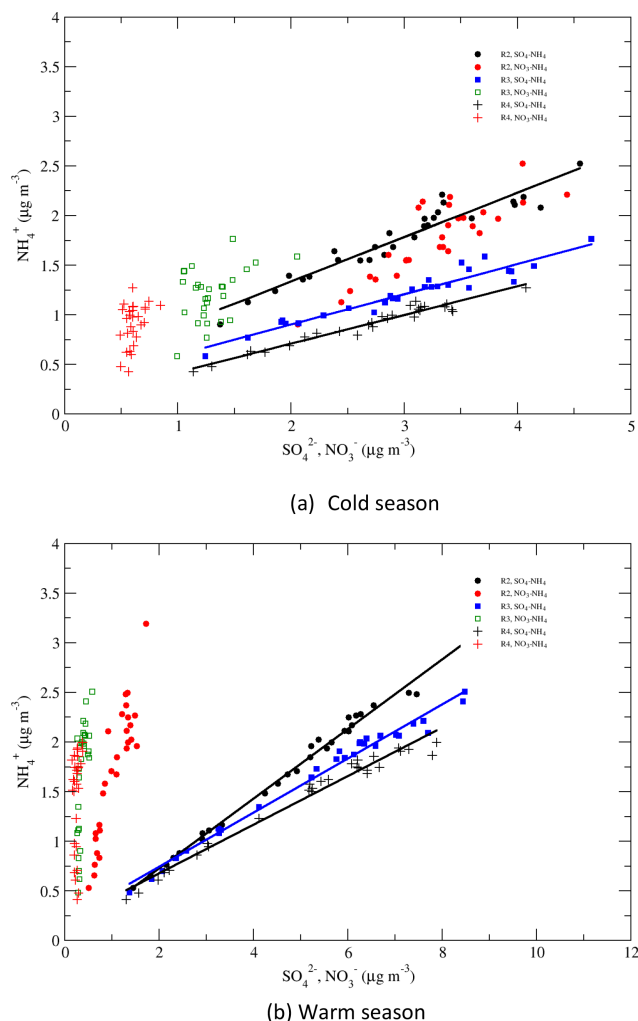

(a) Cold season

(b) Warm season

Figure 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 2–4.

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 a 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 became comparable or even higher than the SNA during the warm season. SNA pollution 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.
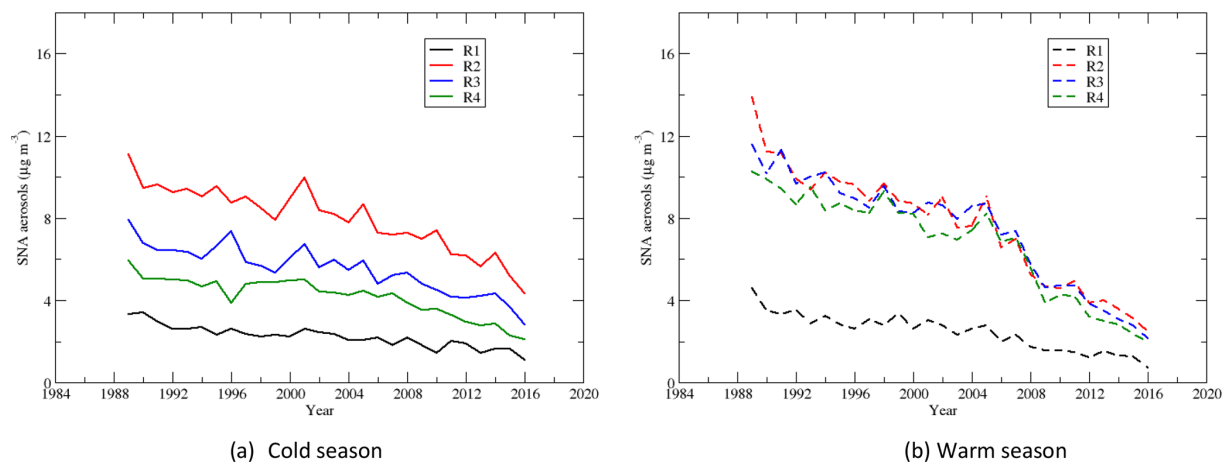
Figure 12. Time series of the seasonal means of sulfate–nitrate–ammonium aerosols during the cold and warm seasons.
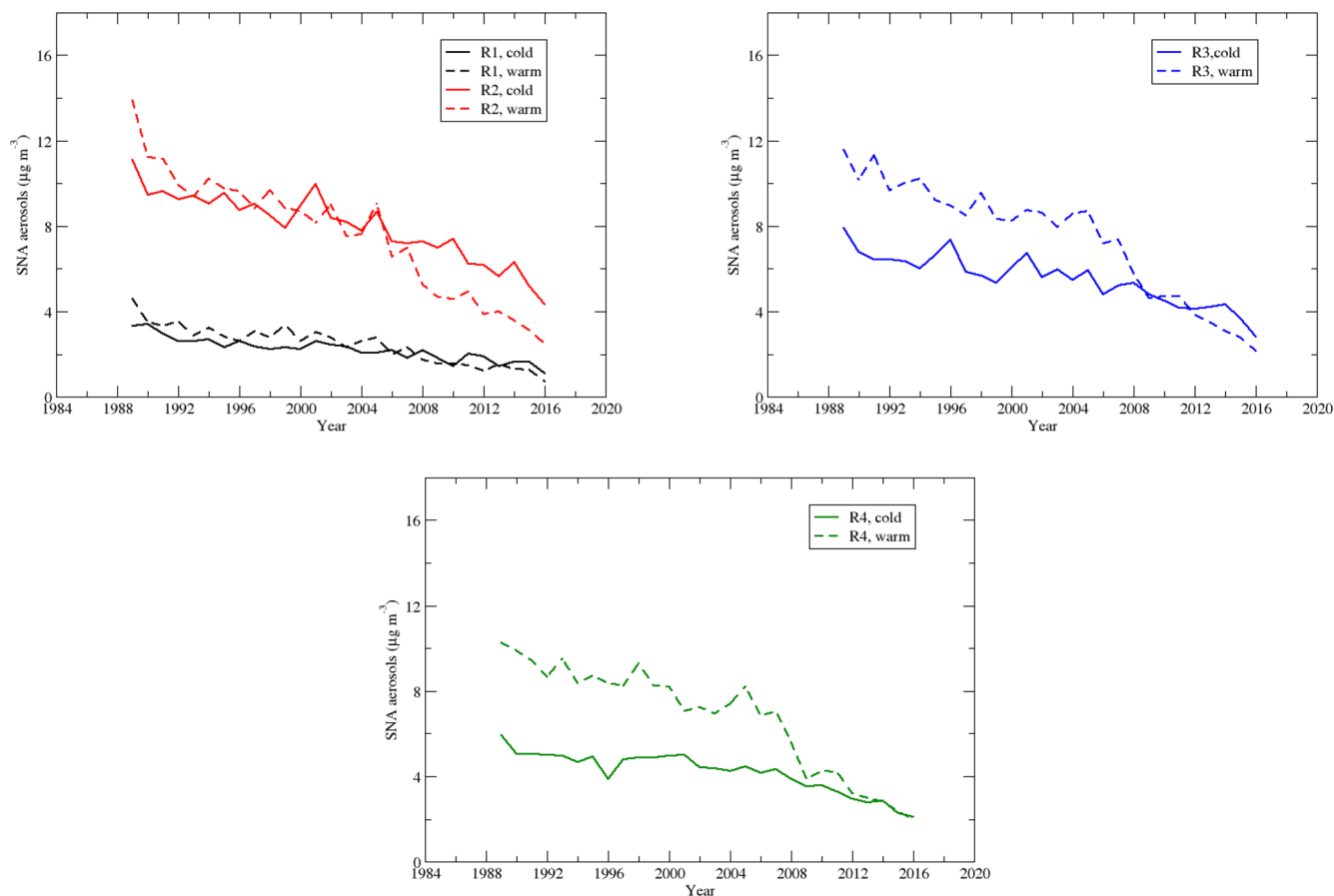

Figure 13. Time series of the seasonal means of sulfate–nitrate–ammonium aerosols in regions 1–4.

5   Summary and conclusion

With the implementation of the Title IV of the 1990 amendments to the CAA in the US in the 1990s, the emissions of SO_2 and NO_x in the US were reduced from 23.1 million to 3.7 million $t\,yr^{-1}$ for SO_2 and from 25.2 million to 11.5 mil-

lion $t\,yr^{-1}$ for NO_x from 1990 to 2015. In Canada, compared 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 emissions was mainly in the eastern regions of the countries. The air concentrations of gases SO_2 and HNO_3, as well as particles SO_4^{2-}, NO_3^-, and

NH_4^+, had a very different nonlinear response, both spatially and temporally, to the significant reductions of SO_2 and NO_x emissions.

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 CAST-NET 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 a 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 was 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 in 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 ranged 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 seasonal mean 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 the year 2000.

RSO_4 is a metric indicating the gas–aerosol partitioning of sulfur in the air, and RNO_3 is an 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 quadrat-

ically with the decrease in SO_2 for regions 2–4 and the two seasons. The significant increase in 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 not only due to the emission reduction, but also more SO_2 being converted to SO_4^{2-}. A faster reduction of SO_2 was observed for all four regions during the cold season, both before and after the 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 lower. This is because the increase in 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 % 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 only increased by 8.0 % and 12.8 %, respectively, as NH_3 in the region was in excess to neutralize HNO_3. RNO_3 was found to increase quadratically with the decrease in SO_4^{2-} 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 the year 2000, (2) in regions 1–4 during the warm season, and (3) in region 2 only during the cold season.

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