How Do Long-Term Declines in Anthropogenic Sulfur Dioxide Emissions and Sulfate Wet Deposition Compare with Trends in Freshwater Chemistry in Scandinavian Rivers?

Hur kan långsiktiga minskningar av antropogena svaveldioxidutsläpp och sulfat i nederbörd jämföras med trender i sötvattenkemi i skandinaviska vattendrag?

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Sammanfattning

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Försurning av nederbörd är ett miljöproblem som uppstod under det senaste århundradet, särskilt efter andra världskriget. Försurningen orsakades främst av mänskliga utsläpp av SO_x (mestadels SO_2) och NO_x, vilka är oxiderade svavel- och kvävgaser. Huvudkällorna för dessa antropogena SO_x-utsläpp är malmförädling samt förbränning av fossila bränslen och biobränslen. SO_2 som släpps ut i atmosfären reagerar med vattenånga och bildar svavelsyra, vilket är en av huvudföreningarna ansvarig för sur nederbörd. På 1970- och 1980-talet fastställdes strängare bestämmelser beträffande utsläpp av luftföroreningar (som SO_x) i Västra Europa och i Nordamerika. Detta ledde till minskande nivåer av SO_2-utsläpp och genom denna sänkning även en minskning av försurning av ytvatten.

Det här arbetet utfördes genom att befintlig, offentligt tillgänglig data samlades in och analyserades. Antropogena SO_2-utsläpp för perioden 1970-2010 från tio olika regioner på norra halvklotet jämfördes med koncentrationer av SO_4^{2-} i nederbörd och i vattendrag i Sverige och Norge för samma period. Genom detta fastslogs att de regioner som har störst inflytande över koncentrationen i skandinaviska vattendrag är SO_2-utsläpp från nordvästra Europa, Storbritannien och Irland samt från USA. SO_4^{2-}-koncentrationen i vattendragen sjunker också snabbare än koncentrationen i nederbörden, med en snabbare nedgång i de södra delarna av Skandinavien.

Nyckelord: svaveldioxid, SO_2, SO_4^{2-}, vattendrag, Skandinavien, Sverige, Norge

Abstract

How Do Long-Term Declines in Anthropogenic Sulfur Dioxide Emissions and Sulfate Wet Deposition Compare with Trends in Freshwater Chemistry in Scandinavian Rivers?
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Acidification of precipitation is an important environmental problem that emerged during the past century, especially after the Second World War. Acidification was primarily caused by human-made emissions of SO_x (mostly SO_2) and NO_x, which are oxidized sulfur and nitrogen gases. The main sources of anthropogenic SO_x emissions are non-ferrous ore refining, and the burning of fossil fuels and biofuels. SO_2 emitted to the atmosphere combines with water vapor to produce sulfuric acid, which is one of the main compounds responsible for acid precipitation. In the 1970s and 1980s, more strict regulations regarding emissions of air pollutants such as SO_x were established in Western Europe and North America, which led to declining levels of SO_2 emissions and by this, declining levels of acidification in surface waters.

This project was preformed by assembling and analyzing existing, publicly-available datasets of anthropogenic SO_2 emissions for the period 1970 to 2010 from ten different regions in the Northern Hemisphere, and compare them with SO_4^{2-} concentrations in precipitation and river chemistry in Sweden and Norway for the same period. It was discovered that it is the SO_2 emissions from Northwestern Europe, the UK & Ireland and from the USA that have the greatest influence over the SO_4^{2-} concentration in Scandinavian rivers. The SO_4^{2-} concentration in stream water is also declining faster than the concentration in precipitation, with a faster decline in the southern parts of Scandinavia.

Key words: sulfur dioxide, SO_2, SO_4^{2-}, river chemistry, Scandinavia, Sweden, Norway

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1. Introduction

Acidification of precipitation is an important environmental problem that emerged during the past century. The acidification was primarily caused by human-made emissions of SO_x (mostly SO_2) and NO_x, which are oxidized sulfur and nitrogen gases. The main sources of anthropogenic SO_x emissions are non-ferrous ore refining, and the burning of fossil fuels and biofuels (Samyn et al., 2012; Grübler, 2002). Metals such as Cu, Zn, Ni and Pb are typically mined from the sulfide minerals $CuFeS_2$, ZnS, NiS and PbS. To separate the metals from the sulfur the ore is heated in a smelter, which produces SO_2 (g). Organic materials such as fossil fuels consist mostly of C, H, N, P and S. When burning these, oxidized sulfur is released into the air as SO_2 (g). The SO_2 combines with water vapor to produce sulfuric acid, which is one of the main compounds responsible for acid precipitation. After the Second World War the emissions accelerated, and reached its peak in the 1970s. In the 1970s and 1980s, more strict regulations regarding emissions of air pollutants such as SO_x were established in western Europe and North America, which led to declining levels of acidification in surface waters (Samyn et al., 2012).

   This project will investigate how long-term trends of sulfate levels (SO_4^{2-}) in rivers of Norway and Sweden compare with long-term trends in SO_4^{2-} wet deposition (i.e., precipitation chemistry) and anthropogenic sulfur dioxide emissions (SO_2). This will be accomplished by assembling and analyzing existing, publicly-available datasets. The goal of the project is to establish to what extent declines in acidification and SO_4^{2-} levels in streams of the Nordic countries during the late 20th and early 21st centuries reflected reduced SO_2 emissions, and whether there were any noticeable regional differences in stream chemistry response.

2. Background

Since the beginning of the 20th century human-made emissions of sulfur in the environment, mostly in the form of SO_2 gas, have surpassed natural flows (Grübler, 2002; Husar & Husar, 1990) causing environmental problems such as widespread acidification with the precipitation pH average dropping to as low as 4.2 in parts of both Europe and in the USA (Lajtha & Jones, 2013). There was an acceleration in SO_2 emissions after the Second World War due to the increasing use of the automobile and other industrial activities (Samyn et al., 2012; Grübler, 2002). The environmental problems caused by anthropogenic emissions of sulfur are not due to it intrinsic toxicity but rather from the magnitude of emissions and the acidification problems it causes (Husar & Husar, 1990).

   Sulfur is naturally occurring in all of the Earth's spheres. The bulk is in the lithosphere where it occurs in rocks in the forms of sulfides and sulfates. The other major part of Earth's sulfur is in the oceans, mostly in the form of inorganic sulfur (Husar & Husar, 1990). Some natural sources of sulfur emissions are volcanoes, biogenic emissions as well as weathering rocks and soils (Grübler, 2002), of which volcanoes are the largest. Although a volcano can pour out millions of tons of sulfur during one single eruption, on a yearly basis the total sulfur emissions from natural sources are still below the level of anthropogenic emissions produced yearly. According to the IPCC (Intergovernmental Panel on Climate Change) natural sources contribute 40 to 60 Tg of elemental sulfur yearly, compared to the 60 to 95 Tg of

elemental sulfur released through human-made emissions (Grübler, 2002; Husar & Husar, 1990; IPCC, 1996).

The most common forms of anthropogenic sulfur emissions are sulfur oxide gases, or SO_x. The main sources of human-made SO_x emissions are the burning of sulfur-rich fossil fuels and biofuels, and non-ferrous ore refining (Grübler, 2002). Metals such as Cu, Zn, Ni and Pb are typically mined from the sulfide minerals $CuFeS_2$, ZnS, NiS and PbS. To separate the metals from the sulfur the ore is heated in a smelter, which produces SO_2 (g) (Grübler, 2002).

Organic materials such as fossil fuels consist mostly of C, H, N, P and S. When burning these, oxidized sulfur is released into the air as SO_2 (g). The SO_2 emissions mainly come from burning sulfur-rich coal and some heavy oil products. Natural gas however is almost sulfur-free but sometimes a little hydrogen sulfide (H_2S) is added to the otherwise odorless natural gas to help identify gas leaks, since sulfur H_2S has a distinctive egg-like smell. This small contribution does not, however, have any significant impact on the total amount of sulfur emissions (Grübler, 2002).

2.1 Why is this issue important?

There are many problems associated with these large emissions of SO_2 both on a global and on a local scale. In the atmosphere, SO_2 (g) combines with water vapor to form sulfate aerosols (SO_4^{2-}). These sulfate particles can efficiently scatter and reflect solar radiation and also alter cloud amount and reflectivity, thereby acting as a cooling agent in the troposphere (IPCC, 1996; Hand et al., 2012; Klimont et al., 2013; Smith et al., 2011).

The dissolution of SO_2 (g) in water vapor also produces sulfuric acid (H_2SO_4), which is one of the main compounds responsible for acidic precipitation. The dissolved acid releases H^+, which causes the pH of precipitation to drop. The acidic precipitation has an impact on the health of humans and that of animals and vegetation. For example, a drop in the pH of streams can affect adversely fish populations, or cause changes in production or transport of DOC (dissolved organic carbon) that will modify the mobility, toxicity, speciation and bioavailability of toxic elements such as Hg, Cu, and Cs (heavy metals) as well as persistent organic pollutants, which are often bound to organic matter (Oni et al., 2013). The acidified precipitation also destroys materials, causing problems like corrosion of metals and damages to stone monuments and buildings (Grübler, 2002; Hand et al., 2012; Klimont et al., 2013; Smith et al., 2011).

Strong acids in soils mobilize base cations (Ca^{2+}, Na^+, Mg^{2+} and K^+), which can be displaced by hydrogen (H^+). The base cations are transported away by water, leaving the soils acidified (Lucas et al., 2013). Base cation depletion from soils has been associated with trends in atmospheric acid deposition.

2.2 Ways to study acidification

Acidification is characterized by a lowering in pH (higher concentration of H^+) in water, soils, etc. However, the pH can be affected by a number of factors such as the deposition of acids associated with SO_x and NO_x, and the amount of organic matter, or of base cations, making the study of what causes acidification difficult. According to Lajtha & Jones (2013), SO_4^{2-} levels in precipitation have declined more steeply than H^+ levels in response to 20th century pollution controls, indicating that

acidification is not caused by sulfuric acid alone. In addition to this, the rates and causes of acidification vary globally.

There are many ways of studying acidification of freshwaters. One of them is direct measurements of the SO_4^{2-} concentration. The SO_4^{2-}-ions released from sulfuric acid in acid precipitation are chemically stable in aqueous solution (Husar & Husar, 1990) and the concentration of SO_4^{2-} in precipitation is therefore directly related to the amount of SO_2 in the atmosphere at the time of deposition. The SO_4^{2-} trapped in snow that accumulates in glaciers captures variations in deposition rates through time. Ice cores therefore provide an indirect (proxy) record of emissions of SO_2 over a long period of time.

Another way to estimate acidification trends is by looking at the concentration of dissolved organic matter in stream water (shown by how "brown" the water is), which can provide information about pH or SO_4^{2-} levels, since high SO_4^{2-} levels or elevated pH tend to decrease the mobility of organic matter (Erlandsson et al., 2008). The concentration of organic matter have been increasing in many European and North American rivers in recent decades, a trend that some associate with a decrease in atmospheric sulfate deposition. But the increasing concentration of organic matter in streams can in turn reflect the acidification of water by soil organic solutions (Futter et al., 2014).

Another indirect method is to study base cation concentrations in stream water. Strong acids such as H_2SO_4, mobilize base cations in soils, which are displaced by hydrogen ions (H^+). The base cations are then transported by water together with SO_4^{2-} to maintain charge neutrality (Lucas et al., 2013).

Something to keep in mind is that SO_4^{2-} in stream water may not come from atmospheric deposition exclusively, but also from the weathering of sulfates and sulfides in rocks, soils and sediments (e.g. marine sediments) (Erlandsson al., 2008). Release of stored SO_4^{2-} by weathering leads to a delay of acidification recovery, and can, according to Prechtel et al. (2001), be caused by four major processes: Desorption of inorganic SO_4^{2-}, excess mineralization of organically-bound sulfur, oxidation of reduced sulfide minerals, and weathering of sulfur-containing minerals.

2.3 Why study SO_x and not NO_x?

Acidification in the 20th century has been primarily caused by human-made emissions of SO_x (mostly SO_2) and NO_x, which are oxidized sulfur and nitrogen gases. Monitoring NO_x in the environment is more difficult than monitoring SO_x due to its many different and highly reactive chemical forms, and as a result there are more sparse data on long-term records of NO_x in air and precipitation (Grübler, 2002; Lucas et al., 2013; Vuorenmaa et al., 2017).

Once emitted, SO_x can remain from days to weeks in the atmosphere. They therefore have relatively short lifespans compared to greenhouse gases, which have lifespans of decades to centuries. Consequently, the atmospheric concentration of SO_x responds more quickly to changes in emissions than that of greenhouse gases (IPCC, 1996). The dispersion of sulfur in the atmosphere typically occurs mostly over a region with a radius of 500-1000 km surrounding each point emission source (Husar & Husar, 1990), and this relatively short transport distance is an advantage when studying which sources contribute to the concentration of SO_4^{2-} and acidity in specific rivers.

2.4 Climate impacts on acidification

Climate change has an impact on freshwater chemistry and ecology and many SO_4^{2-}-releasing and retention processes are sensitive to climatic variables (Vuorenmaa et al., 2017). Both temperature and precipitation can affect the SO_4^{2-} concentration in streams and lakes.

Temperature has an impact on weathering and increasing temperatures leads to increased weathering, which in turn provides more base cations to buffer acidification (Lucas et al., 2013; Prechtel et al., 2001). During long, dry periods the water table is lowered. Soil horizons gets exposed to air and normally saturated soils get oxygenated. Reduced sulfides can get re-oxidized, and this can be a potential large source of SO_4^{2-} in the soil. The SO_4^{2-} can then be exported in surface waters during re-wetting of the soils. This phenomenon may help to explain short-term variations in the concentrations of SO_4^{2-} and acidity in surface waters (Lucas et al., 2013; Wright, 2008).

The amount of precipitation also affects SO_4^{2-} concentration, as years with high precipitation can result in dilution of base cation concentrations in soils and freshwaters. However, high levels of precipitation can also increase the wet deposition of $SO_{4,}^{2-}$. Extreme weather events may therefore influence the acidification rate of soil and waters. If extreme weather events become more frequent in the future as is predicted by many climate models, it may emerge as an increasingly important control on peak concentrations in SO_4^{2-} water chemistry in surface waters (Lucas et al., 2013).

2.5 SO₂ emission trends

According to Husar and Husar (1990) the Northern Hemisphere was during the late 1900s responsible for over 90% of the global sulfur emissions. In the 1970s and 1980s, strict regulations regarding emissions of air pollutants such as SO_x were established in Western Europe and North America (Samyn et al., 2012).

To regulate SO_2 emissions in the USA, the Clean Air Act was passed in 1963, with additional and significant amendments in 1970 and 1990, which resulted in declining concentrations of SO_4^{2-} in affected watersheds of the eastern USA. The Convention on Long-Range transboundary Air Pollution (LRTAP), established in 1979, entered into force in 1983 in Europe. The convention has since then been extended by eight specific protocols that have reduced emissions of SO_2 in Europe. In response to these actions SO_2 emissions have declined steeply since the 1970 in both the USA and in Europe (Lajtha & Jones, 2013).

To reduce their SO_2 emissions, many countries switched from sulfur rich coal to coal with less sulfur content (Smith et al., 2011). Measures were also taken to filter emissions from industrial activities (e.g. coal power plants) and 'scrubbers' were installed in many such facilities. However, these scrubbers also take away particles containing base cations that help neutralize acidification (Lajtha & Jones, 2013). Reductions in the use of petroleum and coal in some countries have also helped reduce SO_2 emissions, as well as moving towards renewable energy sources (Samyn et al., 2012). The reduction of SO_2 emissions have resulted in a long-term decline in atmospheric SO_4^{2-} deposition in much of the Northern Hemisphere (Oni et al., 2013), which in turn has led to a long-term decline in SO_4^{2-} concentrations in streamwaters of many, but not all, regions (Futter et al., 2014).

2.6 Trends in acidification and SO_4^{2-} deposition in Scandinavia

Numerous studies have shown a marked decrease in the SO_4^{2-} concentration in precipitation and in streams across Scandinavia over recent decades, with some regional variations (Borg and Sundbom, 2014; Prechtel et al. 2001; Futter et al., 2014; Lajtha & Jones, 2013; Vuorenmaa et al., 2017; Lucas et al., 2013; and others).

Overall, the pH in Swedish lakes has increased since 1987 (Futter et al., 2014), suggesting that they are recovering from earlier acidification. However, the pH is influenced by a number of factors and the rising pH cannot be considered caused by reduced SO_2 emissions alone. Lakes and rivers in the southwest of Sweden (Futter et al., 2014) and Norway (Vuorenmaa et al., 2017) have suffered the most from acidification but this can partly be explained by occasionally high sea salt deposition, which may lead to the mobilization of H^+ ions in soils (Wright, 2008).

The concentration of SO_4^{2-} in streams is larger than the input of SO_4^{2-} from precipitation in both Norway and Sweden compared to Finland where the input is about the same as the SO_4^{2-} concentration in streamwater (Vuorenmaa et al., 2017). Atmospheric deposition of SO_4^{2-} in Scandinavia has generally declined in the past three decades, with the greatest rate of decline in the south. The greater rate of decline there could be explained by the larger total annual atmospheric input of SO_4^{2-} in the southern and central parts of Scandinavia compared to the northern parts (Lucas et al., 2013; Vuorenmaa et al., 2017.)

Furthermore, there are many factors influencing the acid buffering capacity of soils and thereby the SO_4^{2-} concentration in streamwater. One factor is the regional geology. Most of Scandinavia consists of igneous bedrock. This makes it more sensitive to acid precipitation (Borg and Sundbom, 2014; Norwegian Environment Agency, 2017). Soils in Scandinavia are also thin compared to other parts of Europe, and this also makes Scandinavia more susceptible to acidification. Thinner soils have less capacity to store SO_4^{2-}, which reduces the delay in acidification recovery seen in locations with thicker soil horizons, like in Germany (Prechtel et al., 2001).

Changes in land use can alter the soil's ability to store SO_4^{2-}. Forest harvesting is one example of change in land use occurring in Scandinavia. In Sweden the harvesting of forests for biofuel production has increased, contributing to greater rates of base cation losses. Studies in Finland also suggest that intense forest harvesting can intensify the re-acidification of surface waters (Futter et al., 2014).

Concentrations of base cations have decreased in southern Sweden since 1990, in strong correlation with the decline in SO_4^{2-} deposition over the same period (Lucas et al., 2013).

3. Data and Methods

In order to estimate the effect of declining SO_2 emissions on SO_4^{2-} concentrations in rivers of Scandinavia, historical measurement series in publicly available datasets were gathered from international and national databases. First, SO_2 emission data were obtained from the Emissions Database for Global Atmospheric Research (EDGAR) maintained by the International Institute for Applied System Analysis (IIASA). Precipitation chemistry data were obtained from the portal EBAS, hosted by the Norwegian Institute for Air Research (NILU). Data for rivers in Finland exist but unfortunately have not yet been made available. Therefore Finland was excluded from this study. Stream water chemistry data for rivers in Sweden were obtained from the national database Miljödata MVM hosted by the Swedish Agricultural University (SLU) as well as from the research database for the Krycklan research catchment (SLU, 2017). Stream water chemistry data for rivers in Norway were obtained from the national database Vannmiljø hosted by The Norwegian Environment Agency (Miljødirektoratet).

3.1 Description of datasets

The SO_2 emission dataset from EDGAR is version 4.3.1 for the period 1970-2010. The dataset includes annual SO_2 emissions, divided by country and by source type (natural, anthropogenic). To limit the size of the dataset, only countries within the Northern Hemisphere, and which are either entirely located or have their largest part located north of 45°N were selected (see Appendix). The SO_2 emissions from these countries are the most likely contributors to SO_4^{2-} deposition in the Nordic countries. Small countries such as Iceland were excluded from the set since their SO_2 contribution are very small. Further description of the EDGAR SO_2 dataset can be found in Lamarque et al., (2010) and Smith et al., (2011).

For the concentration of SO_4^{2-} in precipitation, available time series were obtained from the EBAS portal (Tørseth et al., 2012). Unfortunately there were not very many long-term datasets available and therefore only three locations were chosen. These locations are Birkenes and Kårvatn (Norway), and Bredkälen (Sweden). The datasets were produced and complied by researchers at NILU (Anne Hjellbrekkel) and at the Swedish Environmental Research Institute (IVL; Karin Sjøberg).

The data for SO_4^{2-} concentration in Swedish rivers used in this project was obtained from the Swedish Agricultural University's environmental database for ground, water and environmental monitoring *Miljödata-MVM* (SLU, 2017). The data have been produced within environmental monitoring projects in Sweden by collaboration between the Swedish Environmental Protection Agency and the Swedish Agency for Marine and Water Management. The selected data are for the rivers Indalsälven, Dalälven, Upperudsälven and By- och Borgviksälven. The Stream water chemistry data from the Krycklan river are from sites 2, 4 and 7 in the research catchment network, and cover the time period 1992-2015 (Laudon et al., 2013).

The data on SO_4^{2-} concentrations in Norwegian rivers were selected for locations with the longest records, at Birkenes (1972-2015) and Kårvatn (1975-2009).
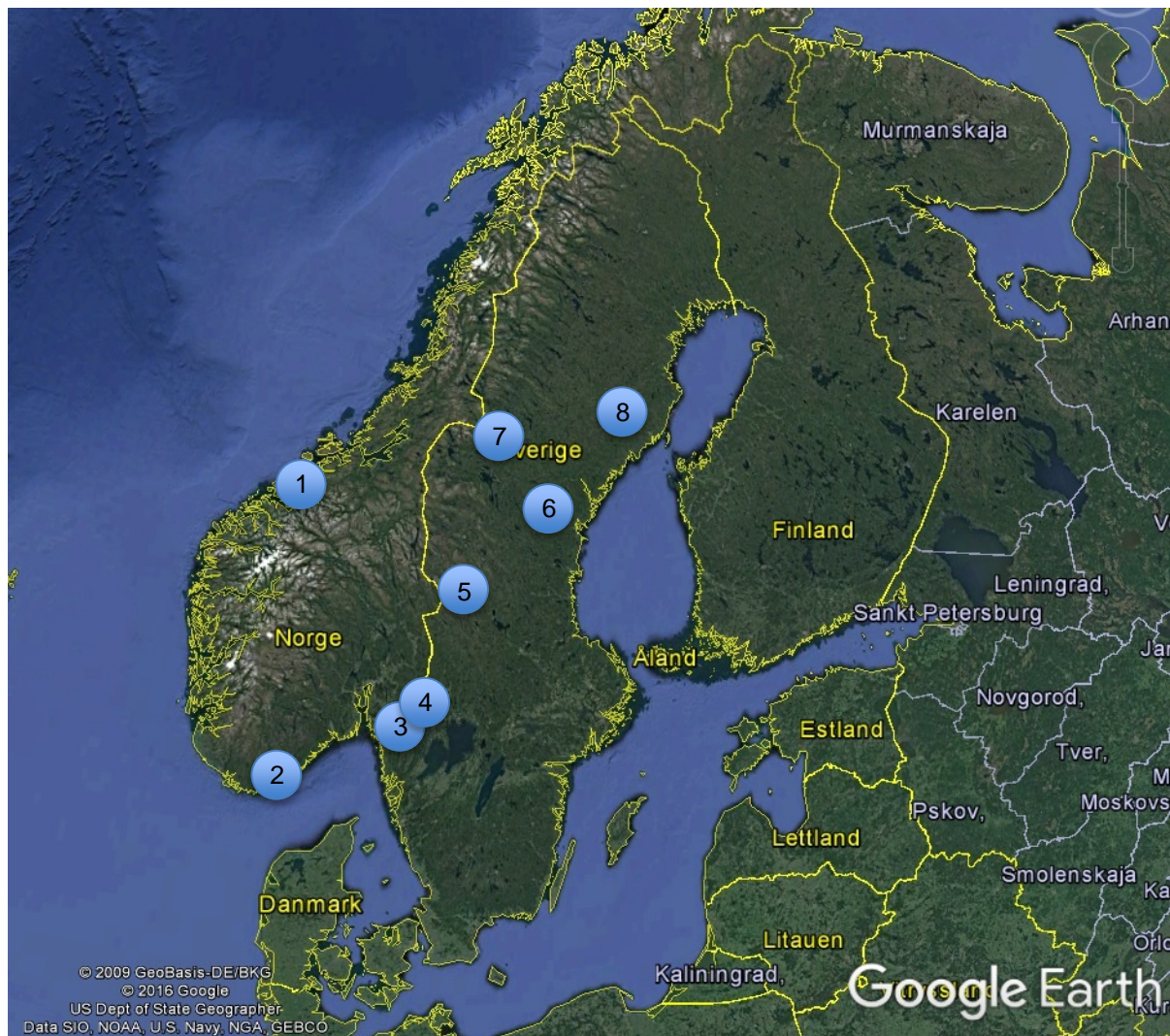
Figure 1. Map showing the locations of the stream and precipitation monitoring stations mentioned in the text: 1. Kårvatn, 2. Birkenes, 3. Upperudsälven (Foxens utlopp), 4. By- och Borgviksälven (Nysockensjöns utlopp Ottebol), 5. Dalälven (Fulan, Rotälven, Mora/Spjutmo), 6. Indalsälven (Liden, Höllefors), 7. Bredkälen, 8. Krycklan. (Map modified from Google Earth, 2017).

3.2 Processing the data

The SO$_2$ emission dataset from EDGAR were processed in Microsoft Excel to sum the emission values for each country into three main categories of emissions; emissions from burning fossil fuels, emissions from metallurgical production and emissions from burning biomass. The emission from burning fossil fuels is the largest category of the three since the use of fossil fuel is widespread and diverse. When calculating averages, different emission sources were merged into the three categories. For most countries this means that the category fossil fuels consists of many different sources while metallurgical production and biomass burning often had only one or two sources in the dataset from EDGAR. A list of the categories is presented in the Appendix.

The countries were then grouped into 10 larger regions; Canada, The United States of America, United Kingdom & Ireland, Northwestern Europe, Central Europe,

Southern Europe, Central Asia, Russia, China & Mongolia, and Japan & Korea. The list of countries for each of the larger regions is given in the Appendix. The total SO_2 emissions for each country and category were then summed into emissions by region. These data were assembled into graphs to help visualize temporal trends, and linear trends were calculated by ordinary least squares regression. Results were assembled in tables, together with the R^2 values of the (coefficient of determination) linear fits.

To help visualize the geographic distribution of SO_2 emission sources, maps were constructed in Matlab from the EDGAR dataset. The data used for these maps are average SO_2 emissions during the time period 1990-2000 showed using a polar stereographic projection on a 0.5° x 0.5° grid. The dataset has 10 categories showing emissions from agricultural waste burning (awb), domestic use (dom), energy production (ene), forest fires, grassland fires, industry (ind), transportation (tra) and commercial waste incineration (wst) (Smith et al., 2011).

The streamwater SO_4^{2-} datasets contained monthly concentration values that were recalculated into yearly averages to match the resolution of the SO_2 emission dataset from the EDGAR database. Some of the SO_4^{2-} data were also recalculated from units of milli- or micro equivalents per liter (meq/L, μeq/L) to mg/L, so as to make them more compatible with the mass units (Gg/year) used in the SO_2 emission dataset. The data were then assembled into graphs for comparison with the emission data and, as before, the linear trends and associated R^2 values were computed and assembled in tables.

For Kårvatn there were measurements missing for the years 1976 and 1977, which resulted in a data gap between 1975 and 1978. A high SO_4^{2-} value of 1975 compared to 1978 was suspect, and was therefore excluded when creating the graphs.

The precipitation chemistry data from EBAS, were downloaded as text files that first had to be converted into tabulated format in Excel. The data consisted of daily measurements of the SO_4^{2-} concentration for each year. The measurements were recalculated into yearly averages to be able to allow comparisons with the other datasets. The trends and R^2 values were then computed and tabulated in Excel and plotted into graphs.

In order to specifically compare trends (rates of change over time) between the different types of measurements (SO_2 emissions data, river and precipitation SO_4^{2-}) the data values were normalized (standardized) over their common period or record.

4. Results

4.1 Trends in SO_2 emissions

Figure 2 shows the geographic distribution of average SO_2 emissions from the transport sector within the decade 1990 to 2000. Similar emissions maps for other sectors of activity are presented in the Appendix. The largest SO_2 emissions for all sectors are from Europe, China and North America. The emissions from burning fossil fuels are more concentrated in populated areas and the distribution of SO_2 emissions from biomass burning are more concentrated in rural or remote areas.
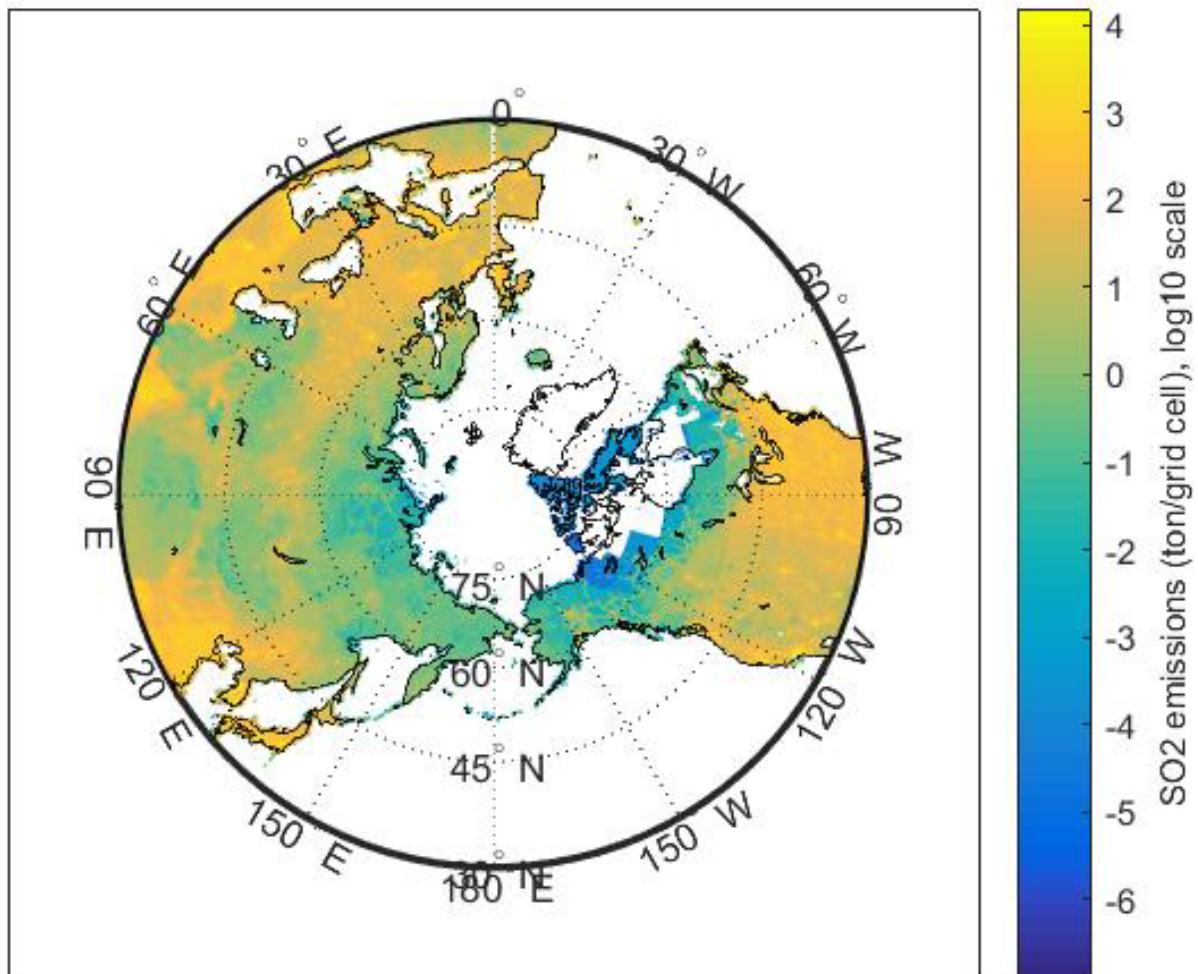
8

Figure 2. Map showing the distribution of mean annual Northern Hemisphere SO₂ emissions from the transport sector over the decade 1990-2000. The color bar is logarithmic an increasing yellow colors correspond to more intense SO₂ emissions. White areas on the map are areas with no data. Values are shown in ton per grid cell, per year. Polar stereographic projection with a grid of 0.5° x 0.5°. (Map created in Matlab with data from EDGAR, 2017).

By comparing Figure 2 with Figures A3-A10 (Appendix) showing the distribution of SO₂ emissions from other sectors, it is clear that the emissions from other sources than the burning of fossil fuels are much smaller. The map showing agricultural waste burning (awb) has a logarithmic scale reaching from -5 to 2, which is significantly lower than the rest of the scales reaching as high as 4. The grassland fires and forest fires contribute lower SO₂ emissions compared to the other categories.

The EDGAR data show that total anthropogenic SO₂ emissions have been decreasing in all regions in the Northern Hemisphere during the late 20th century and the beginning of the 21th century, except for China and Mongolia.

By comparing the different categories of SO₂ emissions (Fig. 3 and Fig. A11-A13 in the Appendix) it is clear that the burning of fossil fuels contribute with the majority of the anthropogenic SO₂ emissions, followed by metallurgical production. Even within Scandinavian countries, this predominance of SO₂ emissions from burning fossil fuels is undeniable (Fig. A14-A17 in the Appendix).
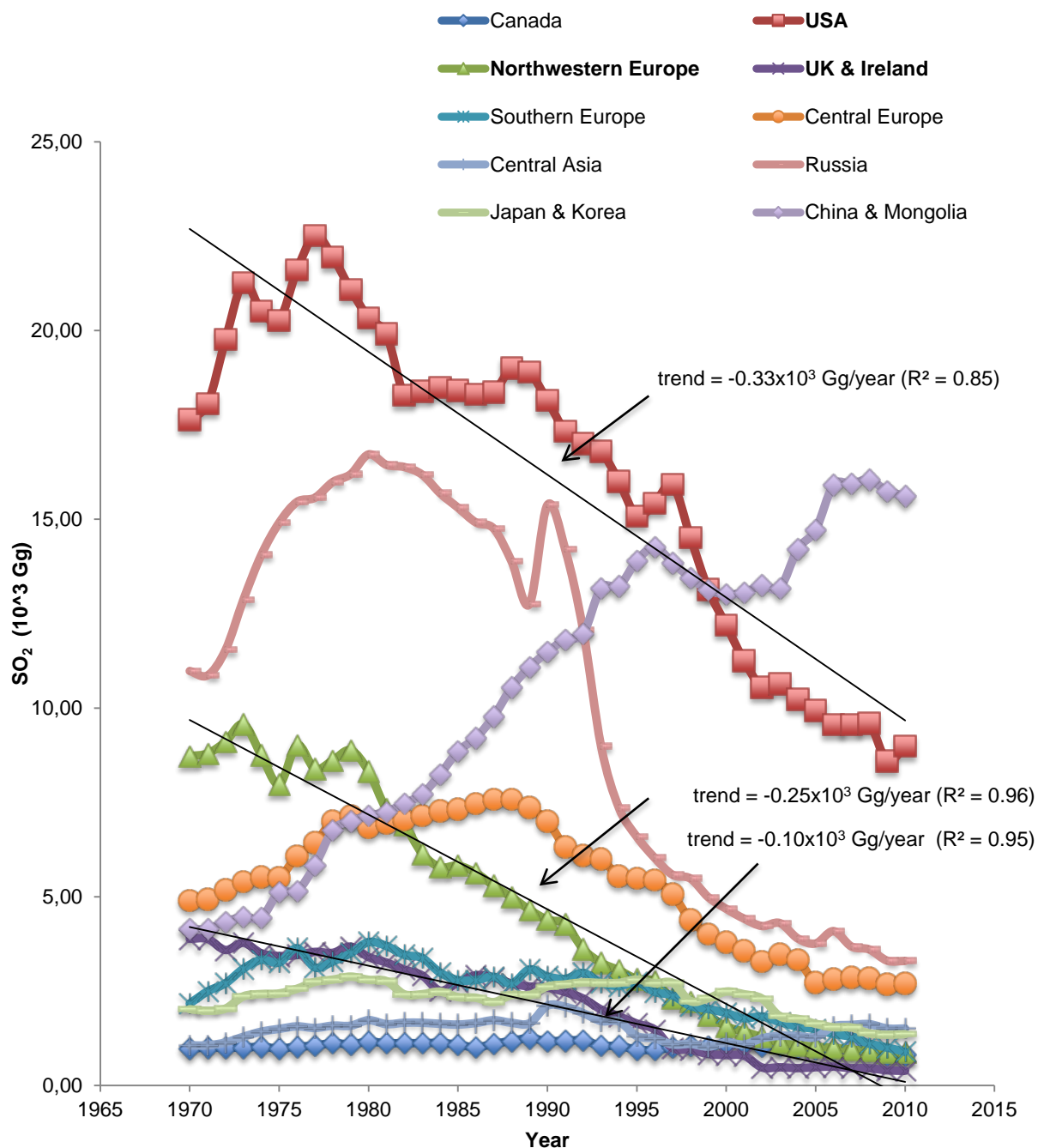
Figure 3. Total annual SO$_2$ emissions from burning fossil fuels, biomass burning and metallurgical production for ten regions of the Northern Hemisphere between 1970-2010. Linear trends added to the regions (bold) that have the largest impact on the concentration of SO$_4^{2-}$ in Scandinavian rivers. (Data source: EDGAR, 2017).

The regions Northwestern Europe, USA, UK & Ireland and Russia are the regions with the highest rate of decline in their trend. The R^2 values are high compared to those of other regions, implying sturdy linear negative trends without large variations (Table 1).

The R^2 values describe how close the relationship between different measurements corresponds to the general linear trends. An R^2 value close to 1 indicates that almost all of the measurements are on, or close to the trend line. A low R^2 value means that the measurements are scattered and have a low correspondence to the general trend.

Table 1. SO_2 emission linear trends from burning fossil fuels, metallurgical production and the burning of biomass from ten regions within the Northern Hemisphere for the time period 1970-2010.

Region	Total	R^2	Fossil fuel	R^2	Metal	R^2	Biomass	R^2
	10^3 Gg/yr		10^3 Gg/yr		Gg/yr		Gg/yr	
Canada	0.00	0.11	0.00	0.07	-4.90	0.85	0.02	0.52
USA	-0.33	0.84	-0.32	0.84	-0.60	0.81	-0.02	0.07
Northwestern Europe	-0.25	0.96	-0.25	0.96	0.02	0.02	0.00	0.00
UK and Ireland	-0.10	0.95	-0.10	0.95	-0.01	0.09	0.00	0.19
Southern Europe	-0.05	0.67	-0.05	0.67	-0.01	0.03	-0.06	0.89
Central Europe	-0.10	0.47	-0.10	0.47	-0.20	0.55	-0.02	0.12
Central Asia	0.00	0.00	0.00	0.01	1.10	0.29	-0.01	0.04
Russia	-0.36	0.70	-0.36	0.70	1.80	0.41	-0.09	0.34
Japan and Korea	-0.02	0.27	-0.02	0.27	-0.20	0.45	0.00	0.17
China and Mongolia	0.32	0.95	0.32	0.95	2.90	0.54	0.04	0.86

Data Source: EDGAR database, 2017

4.2 Trends in SO_4^{2-} concentration in precipitation

It is to generalize interpretations about trends in SO_4^{2-} concentration in precipitation in Scandinavia from only a few locations. However, the trends seen in Figures 4 and 5 as well as in Table 2 seem to be quite closely related to the trends in Northern Hemisphere SO_2 emissions.
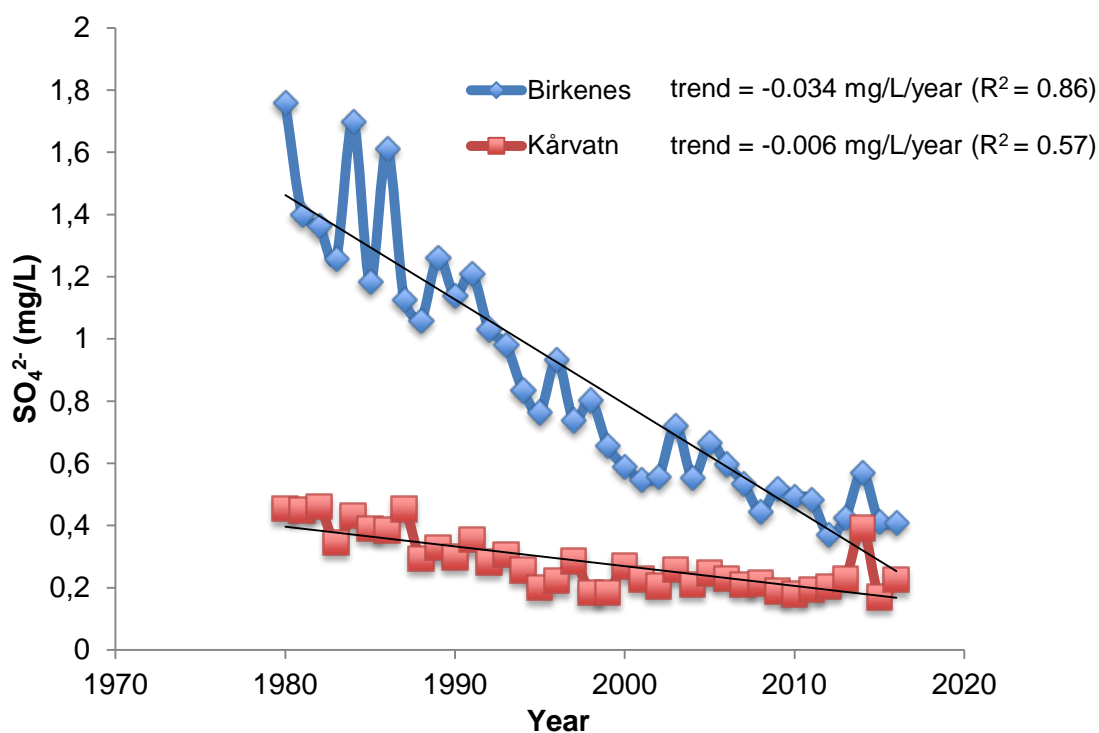

Figure 4. Mean annual concentration of SO_4^{2-} in precipitation for two locations in Norway between1980 to 2015. (Data source: EBAS, 2017).
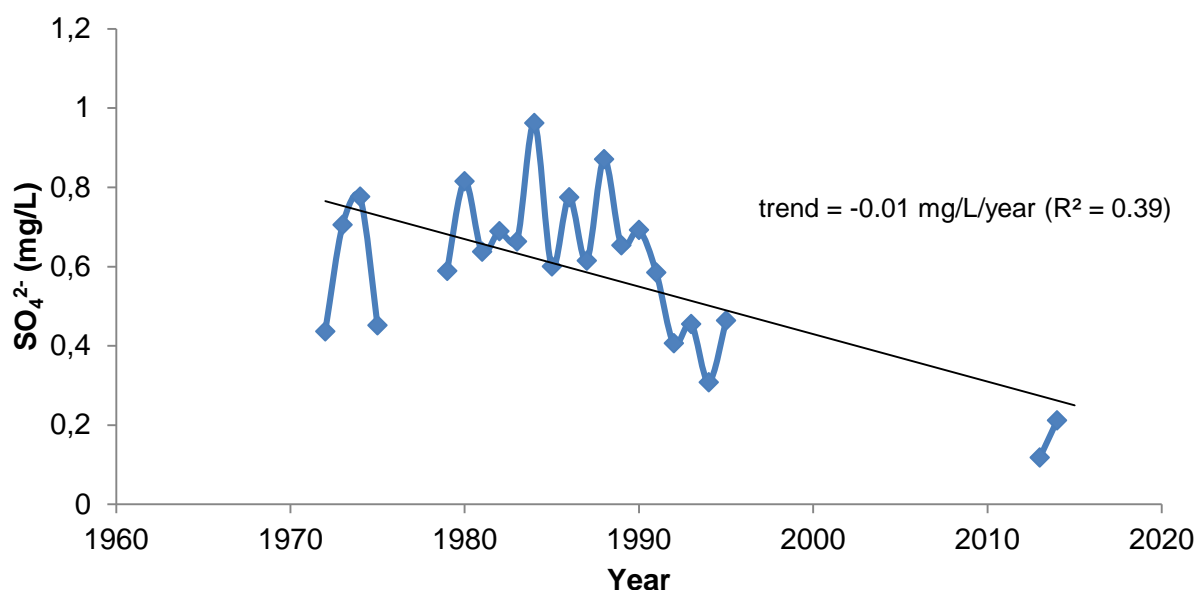
Figure 5. Mean annual concentration of SO_4^{2-} in precipitation measured at Bredkälen in Sweden between 1972 and 2014. Gaps are due to interruptions in the measurements series. (Data source: EBAS, 2017).

The rate of decline in SO_4^{2-} concentrations in precipitation is faster in Birkenes than in Kårvatn and Bredkälen (Table 2). The southern location Birkenes is likely also receiving more SO_4^{2-} deposition since the concentration is higher compared to Kårvatn further north (Fig. 4).

Table 2. Linear trends for SO_4^{2-} concentration in precipitation measured at three locations in Sweden and Norway between 1972-2014 (Sweden) and 1980-2016 (Norway).

Country	Location	Time period	Trend	R^2
			mg/L/yr	
Sweden	Bredskälen	1972 - 2014	-0.01	0.39
Norway	Kårvatn	1980 - 2016	-0.01	0.57
	Birkenes	1980 - 2016	-0.03	0.86

Data source: EBAS portal, 2017

The average concentration of SO_4^{2-} in precipitation for Bredkälen in Sweden were the longest time-series of precipitation measurements available from the EBAS portal. , although it suffers from large temporal gaps. But since only the general long-term trend in SO_4^{2-} concentration is of interest for this project, it was considered adequate. The trend from the existing measurements is declining in the same way as the other precipitation measurements from Norway (Fig. 4). The general trend is more similar to that of Kårvatn, and the two locations are more closely related geographically than Bredkälen and Birkenes. The concentration of SO_4^{2-} in precipitation at Bredkälen is slightly higher than Kårvatn.

4.3 Trends in SO$_4^{2-}$ concentration in stream water

The average concentration of SO$_4^{2-}$ in stream water compared to precipitation show a significantly lower concentration of SO$_4^{2-}$ in precipitation. The average concentration of SO$_4^{2-}$ in precipitation is below 2 mg/L (Fig. 4 and 5) in reference to the freshwater chemistry where the average is above 2 mg/L in all rivers studied (Fig. 6-11).
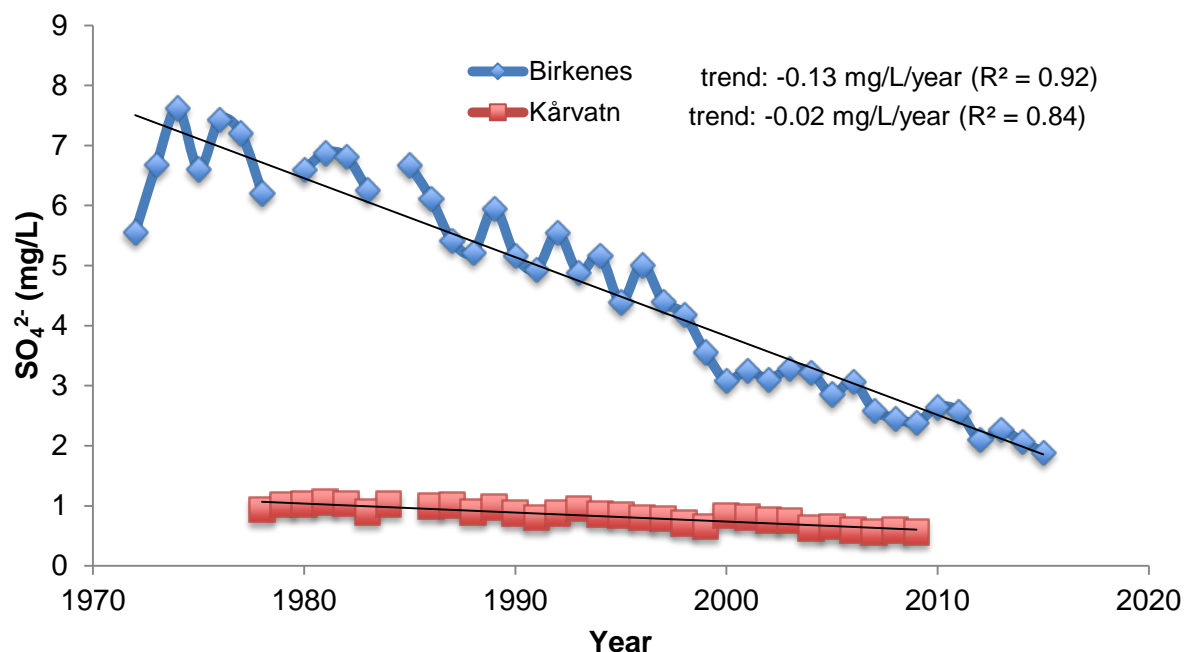

Figure 6. Mean annual SO$_4^{2-}$ concentrations in stream water measured at Birkenes (1972-2015) and at Kårvatn (1978-2009) in Norway. Gaps for 1979, 1984 and 1985 are due to interruptions in the measurements series. (Data source: Vannmiljø, 2017).
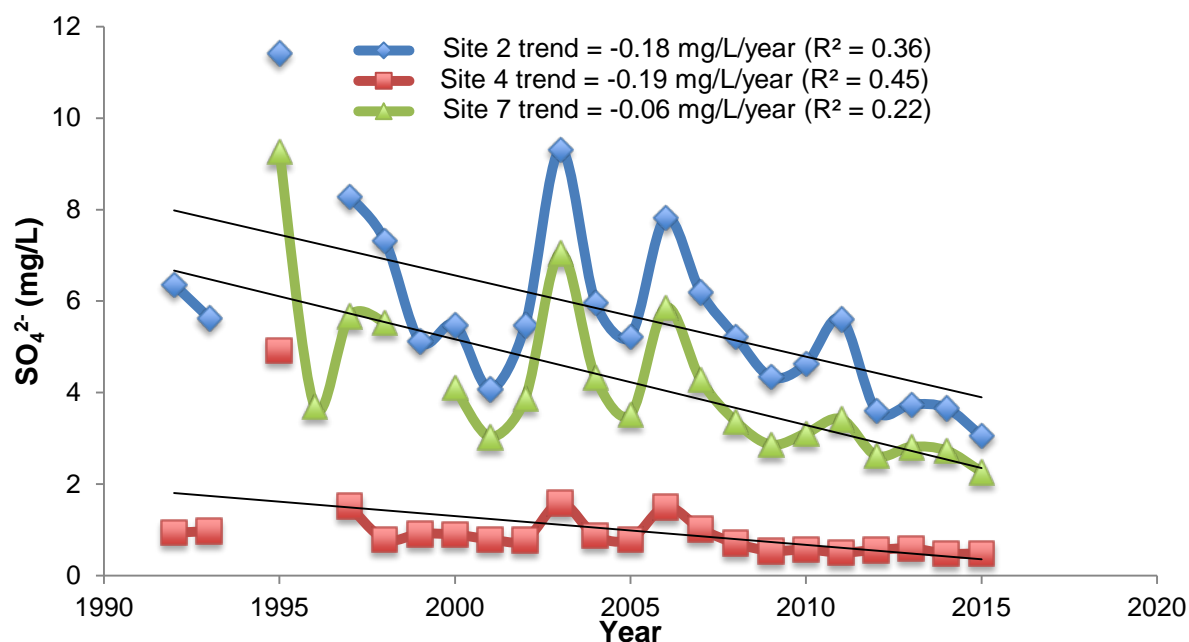
Figure 7. Mean annual SO$_4^{2-}$ concentration in stream water measured at three sites (2,4 and 7) in the Krycklan catchment in northern Sweden between 1992 and 2015. Gaps are due to interruptions in the measurement series. (Data source: Krycklan, 2017).
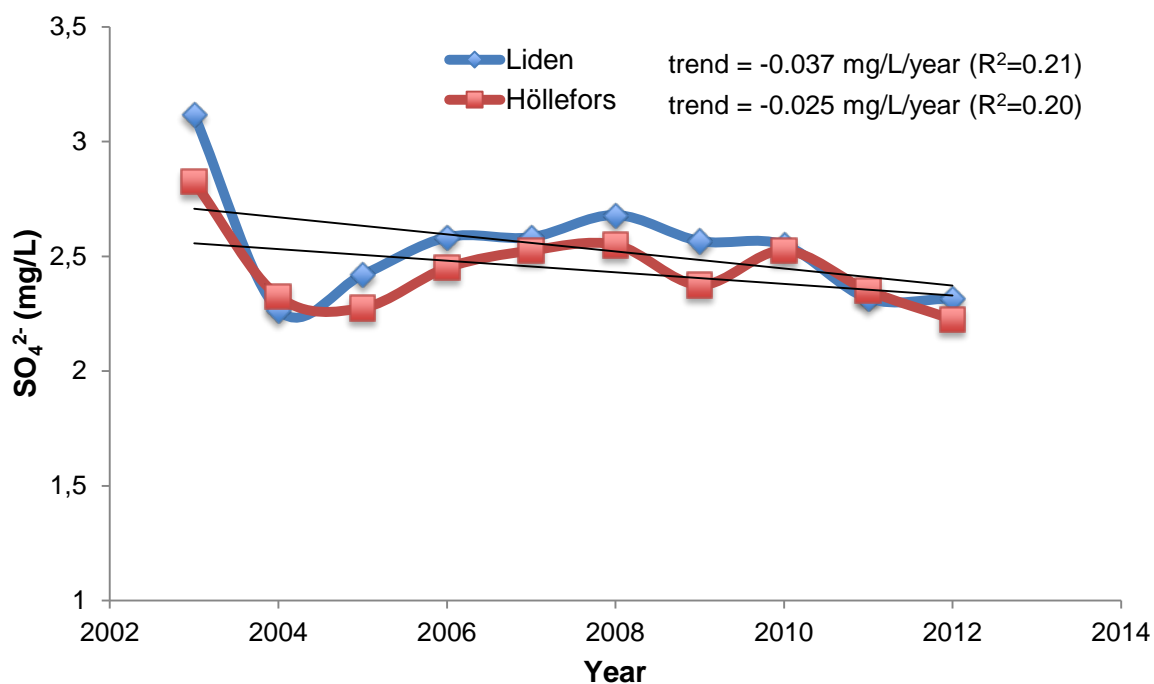
Figure 8. Mean annual SO_4^{2-} concentration in Indalsälven measured at two stations between 2003-2012. (Data source: Miljödata, 2017).
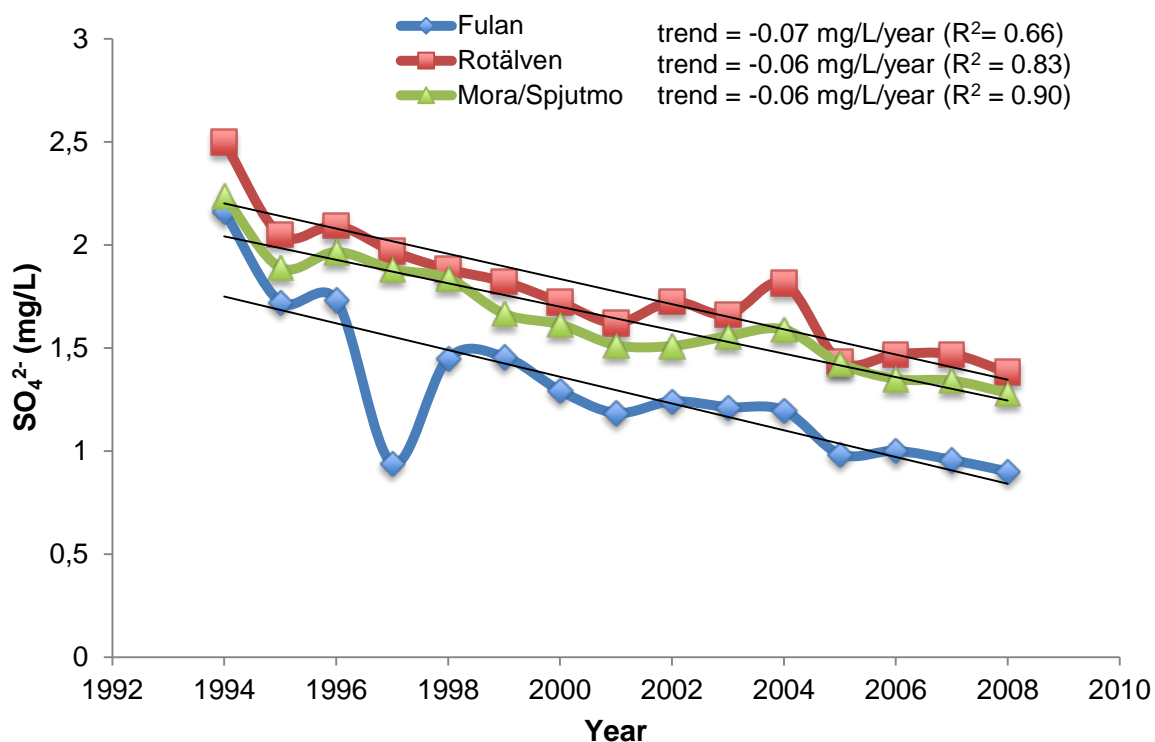

Figure 9. Mean annual SO_4^{2-} concentration in the river Dalälven measured at three sites between 1994 and 2008. (Data source: Miljödata, 2017).
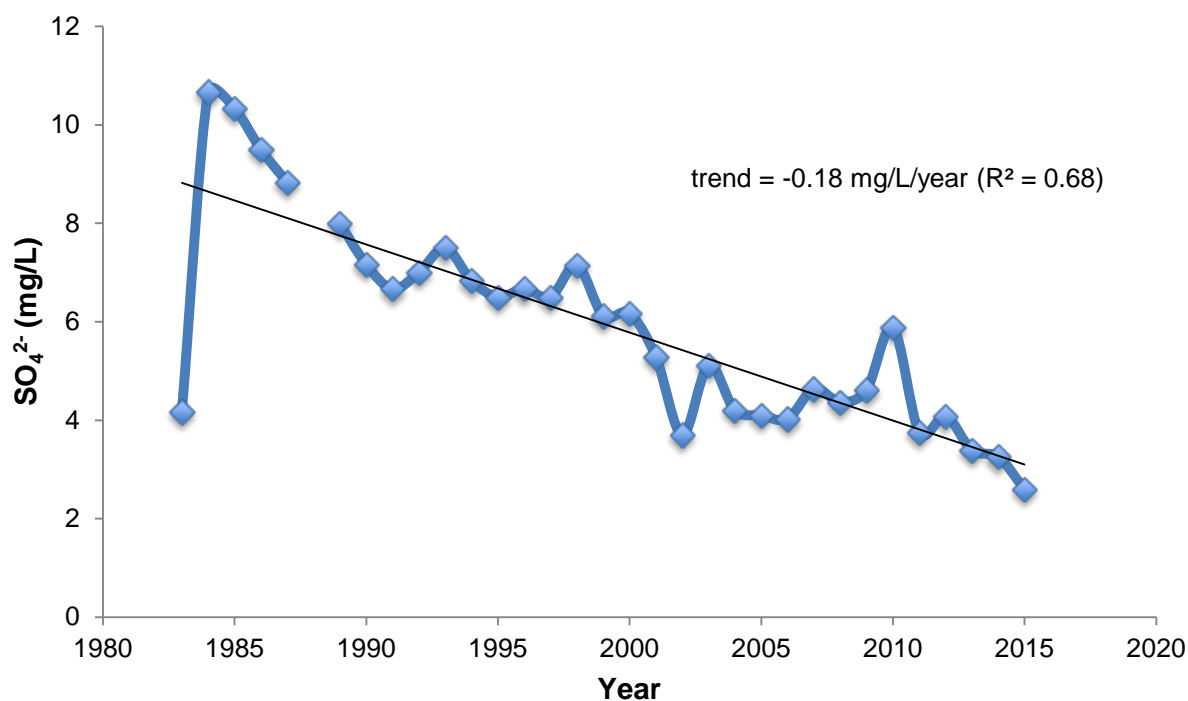
Figure 10. Mean annual SO_4^{2-} concentration in Uppereudälven at the Foxens utlopp measuring station between 1983-2015. (Data source: Miljödata, 2017).
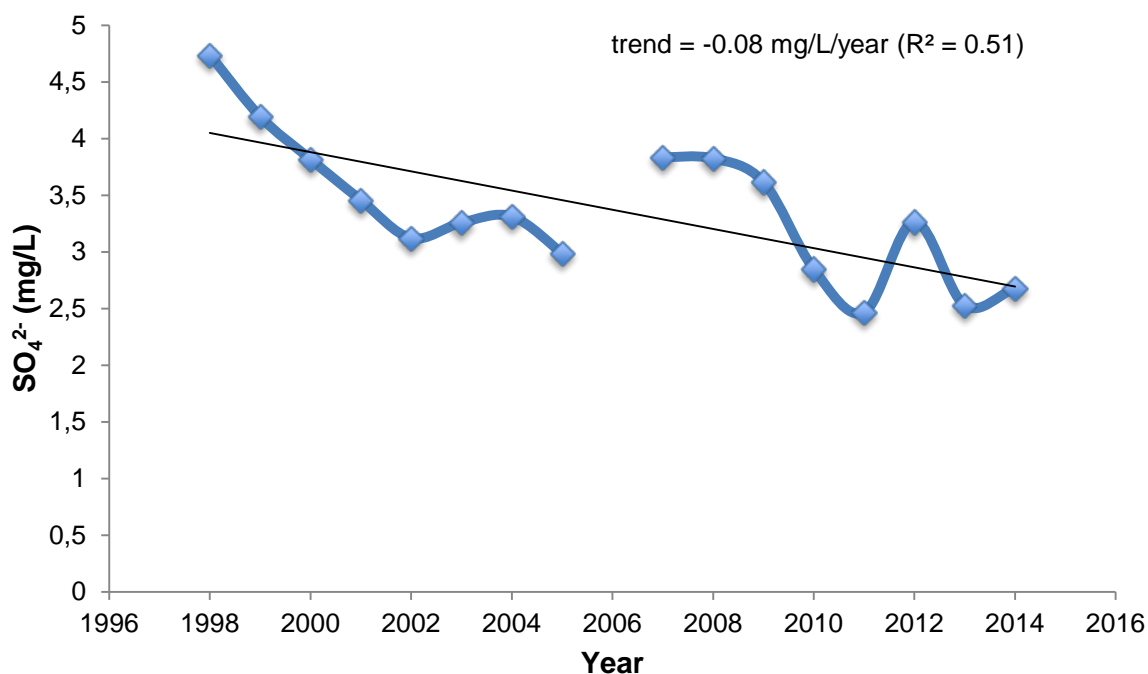

Figure 11. Mean annual SO_4^{2-} concentrations in the By- och Borgviksälven river, measured at the Nysockensjöns utlopp Ottebol station between 1998 and 2014. Gaps are due to interruptions in the measurement series. (Data source: Miljödata, 2017).

Table 3. Linear trends for SO_4^{2-} concentration in rivers of Sweden and Norway.

Country	River	Monitoring station	Time period	Trend	R^2
				mg/L/yr	
Sweden	Krycklan	Site 2	1992 - 2015	-0.18	0.36
		Site 4	1992 - 2015	-0.06	0.22
		Site 7	1992 - 2015	-0.19	0.45
	Indalsälven	Liden	2003 - 2012	-0.04	0.21
		Höllefors	2003 - 2012	-0.03	0.19
	Dalälven	Fulan	1994 - 2008	-0.07	0.66
		Rotälven	1994 - 2008	-0.06	0.83
		Mora/Spjutmo	1994 - 2008	-0.06	0.90
	By- och Borgviksälven	Nysockensjöns utlopp. Ottebol	1998 - 2014	-0.08	0.51
	Upperudälven	Foxens utlopp	1983 - 2015	-0.18	0.68
Norway	Kårvatn		1978 - 2009	-0.02	0.84
	Birkenes		1972 - 2015	-0.13	0.92

Data source: Miljödata and Vannmiljø, 2017

In general the SO_4^{2-} concentration is declining faster in the southern parts compared to the northern parts of both Norway and Sweden (Table 3).

Table 4. Normalized trend values for SO_2 emissions from ten regions within the Northern Hemisphere between 1970 and 2010, together with trends in SO_4^{2-} concentration in rivers and precipitation of Sweden and Norway for time periods between 1970 and 2015.

SO₂ emissions		SO₄²⁻ concentration			
Total emissions		River chemistry		Precipitation chemistry	
Region	Trend	River	Trend	Location	Trend
Canada	-0.03	Krycklan	-0.09	Bredskälen	-0.06
USA	-0.08	Indalsälven	-0.15		
Northwestern Europe	-0.08	Dalälven	-0.20		
UK and Ireland	-0.08	By- och Borgviksälven	-0.14		
Southern Europe	-0.07	Upperudälven	-0.09		
Central Europe	-0.06				
Central Asia	-0.01	Kårvatn	-0.10	Kårvatn	-0.07
Russia	-0.07	Birkenes	-0.07	Birkenes	-0.09
Japan and Korea	-0.04				
China and Mongolia	0.08				

Data source: EDGAR, Miljödata, Krycklan (SLU) and Vannmiljø, 2017

5. Discussion

In this study SO_2 emissions from countries south of 45°N have not been taken into account. With industrialization of developing countries the total amount of global anthropogenic SO_2 emissions is likely to increase. Together, China and Mongolia form the only region in the study that has an increasing trend in emissions of SO_2 (Fig. 3 and Table 1). By studying Figure 2 and A3-A10 (in the Appendix), the largest part of the region's emissions are in the categories domestic use, industry, energy production, and transportation, which all are within the fossil fuel sector. With a growing population the emissions from these categories will most likely continue to increase. Other developing countries with fast growing populations such as India also contribute with large amounts of SO_2 emissions globally. However, due to the relatively short lifespan of SO_2 in the atmosphere the concentration of SO_4^{2-} in streams of Scandinavia should not be affected by emissions from countries located as far away as India (Klimont, 2013).

By comparing the rate of decline of SO_2 emissions from different regions (Table 1) and the rate of decline of SO_4^{2-} concentration in precipitation (Table 2) it is clear that the most likely source for atmospheric deposition SO_4^{2-} in Scandinavia are SO_2 emissions from Northwestern Europe, the UK & Ireland as well as the USA (Table 4). These regions are also relatively close to Scandinavia geographically (Fig. 2). Due to the rather short residual time of SO_2 in the atmosphere combined with dominant wind patterns, which moves from Northwestern Europe and the Atlantic up towards Scandinavia, these regions are likely the largest sources for the SO_4^{2-} deposited in Scandinavia. The major part of the emissions gets deposited in the southwestern part of Sweden and Norway since it is closer to these source regions.

The trend in precipitation chemistry is more closely related to the emission trends than to the trends in river chemistry (Table 4). In general all rivers have a faster decline in SO_4^{2-} concentration than the decline of SO_4^{2-} in precipitation (Table 2 and 3). The average concentration of SO_4^{2-} in precipitation is below 2 mg/L for all three locations (Figure 4 and 5) compared to the freshwater chemistry where the general concentration is above 2 mg/L in all rivers studied. This show that a large portion of the SO_4^{2-} found in streams in Scandinavia must either come from dry atmospheric deposition (rather than from wet deposition) or from weathering (e.g., re-oxidation of sulfides stored in soils), or from sea salt deposition (Wright, 2008).

When comparing SO_4^{2-} concentrations in precipitation and freshwater for the Norwegian locations Kårvatn and Birkenes (Fig. 4 and 6) the two graphs look similar. The concentration of SO_4^{2-} is higher in Birkenes for both categories (precipitation and freshwater) relative to Kårvatn. But when comparing the linear trends in SO_4^{2-} concentration for these two locations and categories (Table 2 and 3) the decline in SO_4^{2-} concentration in stream water is proceeding much faster in Birkenes relative to precipitation, than at Kårvatn. This could be due to the greater importance of dry SO_4^{2-} deposition at locations further south. Most likely Birkenes receives more dry deposition due to its location further south, which contributes to the higher concentration of SO_4^{2-}, and thereby also the faster response to SO_2 emission decline. Kårvatn is located further north and show a much slower decline in SO_4^{2-} concentration in river chemistry compared to Birkenes. The small difference in the rate of decline of SO_4^{2-} between precipitation and river chemistry in Kårvatn and Birkenes could be explained by the lower amount of SO_4^{2-} in deposition, both wet and dry, received at this latitude, compared to Birkenes.

Wright (2008) made a study of the acidification in the Birkenes catchments for the time period 1972 to 2004. In this study it was discovered that drought periods play an important role for the SO_4^{2-} concentration in the catchment were reduced sulfur is stored in the soil during the dry period, only to be re-oxidized and released when re-wetting occur. Dry periods in 1974-1977, 1981-1984 and 1989-1997 (Wright, 2008) can be detected in Figure 6, with more variation in the SO_4^{2-} concentration during these periods. According to Wright (2008) there were no droughts between 1998 and 2004 (the year when the study was ended), and the SO_4^{2-} concentration for this period can also be seen to be more stable (Fig 6). There is, however, a risk that reduced sulfur may be accumulating in the catchment, which could cause a severe acidification episode in the event of a new major drought. However, the declining rate of SO_4^{2-} deposition from anthropogenic SO_2 emission sources presumably means that there is probably less anthropogenic sulfur stored in the soils compared to earlier years (Wright, 2008).

In all of the rivers studied in Sweden, the rate of decline in SO_4^{2-} concentration exceeds that of decline in both SO_4^{2-} concentration in precipitation chemistry and the decline in anthropogenic SO_2 emissions from countries in the Northern Hemisphere (Table 4). The Krycklan catchment is the northernmost site considered in this study. The SO_4^{2-} concentration in the catchments streams has varied between 0 and 10 mg/L during the measurement period (Fig. 7). The closest river chemistry measurements are from Indalsälven with SO_4^{2-} concentrations varying between 1 and 3.5 mg/L (Fig. 8). Bredkälen, further east and inland, close to the Norwegian border, receives wet SO_4^{2-} deposition with concentrations of 0-1 mg/L (Fig 5), and an average concentration of SO_4^{2-} in wet deposition close to the one in Bredkälen. This may be assumed to apply for the Krycklan catchments as well since the two locations are relatively close geographically. The large difference in SO_4^{2-} concentrations in streams between Krycklan and Indalsälven suggests that the major part of the SO_4^{2-} in the Krycklan catchment comes from other sources than atmospheric deposition, (whether it is wet or dry deposition), such as oxidation of sulfides in soils (Lucas et al., 2013). The linear trends in the stream SO_4^{2-} measurement series for the Krycklan catchment also have low R^2 values (0.36, 0.22 and 0.45), as expected given the scatter of the measurements, and this makes the interpretation of linear trends more uncertain.

Variations in SO_4^{2-} concentration occur within the Dalälven River as well (Fig. 9) but not as significant as for the Krycklan catchment. The Upperudälven and By- och Borgviksälven (Fig 10 and 11) are located on the southwestern part of Sweden, near the border to Norway. The two locations are relatively close to Birkenes and all these rivers have a similar concentration of SO_4^{2-} (when focusing on the common time period, since By- och Borgviksälven has a much shorter measurement series). The variations in the concentration also seem to be following the same pattern, although the gaps in the measurement series for By- och Borgviksälven should be kept in mind as well as the fact that the measurements have been carried out for different time periods for the three sites.

5.1 Sources of uncertainties

Several limitations must be kept in mind with respect to the findings from this study. First, since there are much fewer precipitation or stream monitoring locations with long data series in the far northern parts of Sweden and Norway than further south, it is difficult to properly evaluate the impact of reduced SO_2 emissions on the concentration of SO_4^{2-} in streams for these regions.

The measurement series of SO_4^{2-} concentration in river chemistry are shorter and not covering the same time series as the precipitation chemistry. Longer time series of measurements would therefore be preferable.

Further studies are needed in order to confirm general trends in the relationship between declining SO_2 emissions and the concentration of SO_4^{2-} in precipitation and stream waters. Such studies can include comparing variations in SO_4^{2-} concentration with precipitation data for each catchment, climate data, base cation concentration, sulfate concentration in soils etc.

Changing climate with more frequent dry periods could lead to re-oxidation of sulfides in soils and thereby be a potential large source of SO_4^{2-} in the future, even with decreasing concentrations from SO_2 emissions (Wright, 2008; Lucas et al., 2013). A climate change with more precipitation can also influence the concentration of SO_4^{2-} by diluting the concentration.

6. Conclusions

- The regions contributing to SO_4^{2-} concentration in precipitation and river chemistry in Scandinavia by emissions of SO_2 the most are Northwestern Europe, USA and UK & Ireland.
- The rate of SO_4^{2-} decline in Norway and Sweden is occurring faster in regions receiving more SO_4^{2-} deposition, which are concentrated in the southern parts of Scandinavia.
- The concentration of SO_4^{2-} is generally decreasing much faster in stream water, compared to precipitation in both Sweden and Norway.

This study is consistent with other studies of surface water chemistry that show clear decreasing concentrations of SO_4^{2-} in surface waters as a result to decreasing anthropogenic SO_2 emissions. Acidification as a problem however cannot be considered solved by reducing anthropogenic SO_2 emissions alone. Acidification caused by other elements than sulfur is becoming a more prominent factor and further studies and measures for handling the situation have to be considered.

Acknowledgments

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Appendix

A1. List of fields for SO_2 emission sources in the SO_2 emission dataset from EDGAR used to summarize the dataset into the three main categories; Fossil fuel, Metallurgical production and Biomass burning.

1. Fossil fuel: sum of yellow fields below
2. Biomass burning: sum of blue fields below
3. Metallurgical production: green field below

1A1a   Public electricity and heat production
1A1bc Other Energy Industries
1A2   Manufacturing Industries and Construction
1A3a   Domestic aviation
1A3b   Road transportation
1A3c   Rail transportation
1A3d   Inland navigation
1A3e   Other transportation
1A4   Residential and other sectors
1B2   Fugitive emissions from oil and gas
2B   Production of chemicals
2C   Production of metals
2D   Production of pulp/paper/food/drink
4E   Savanna burning
4F   Agricultural waste burning
5A   Forest fires
5C   Grassland fires
6C   Waste incineration
7A   Fossil fuel fires

A2. Countries within the Northern Hemisphere summed into ten larger regions used to illustrate SO$_2$ emissions for the Northern Hemisphere between 1970 and 2010.

Table A2. Countries within the Northern Hemisphere summarized into 10 larger regions.

Canada	USA	Northwestern Europe	UK & Ireland	Southern Europe	Central Europe	Central Asia	Russia	Japan & Korea	China & Mongolia
Canada	USA	Norway	UK	Spain	Albania	Kazakhstan	Russian Federation	Japan	China
		Sweden	Ireland	Greece	Bulgaria	Kyrgyzstan	Armenia	South Korea	Mongolia
		Denmark		Italy	Bosnia and Herzegovina	Tajikistan	Azerbaijan	North Korea	
		Finland		Portugal	Cyprus	Turkmenistan	Georgia		
		Austria			Czech Republic	Uzbekistan	Belarus		
		Belgium			Estonia		Moldova		
		Switzerland			Croatia		Ukraine		
		Germany			Hungary				
		Luxembourg			Lithuania				
		Netherlands			Latvia				
		France			Macedonia, the former Yugoslav Republic of				
					Malta				
					Poland				
					Romania				
					Serbia and Montenegro				
					Slovakia				
					Slovenia				

A3-10. Figures show the distribution of mean annual Northern Hemisphere SO$_2$ emissions from different sectors over the decade 1990-2000. The different sectors are: agricultural waste burning (awb), domestic use (dom), energy production (ene), forest fires, grassland fires, industry (ind), and commercial waste incineration (wst) (Smith et al., 2011). The color bar is logarithmic and increasing yellow colors correspond to more intense SO$_2$ emissions. White areas on the maps are areas with no data. Values are shown in ton per grid cell, per year, as a polar stereographic projection with a grid of 0,5° x 0,5°. The maps were created in Matlab with data from EDGAR (2017).

Forest fires

Grassland fires

SO2 emissions (ton/grid cell), log10 scale
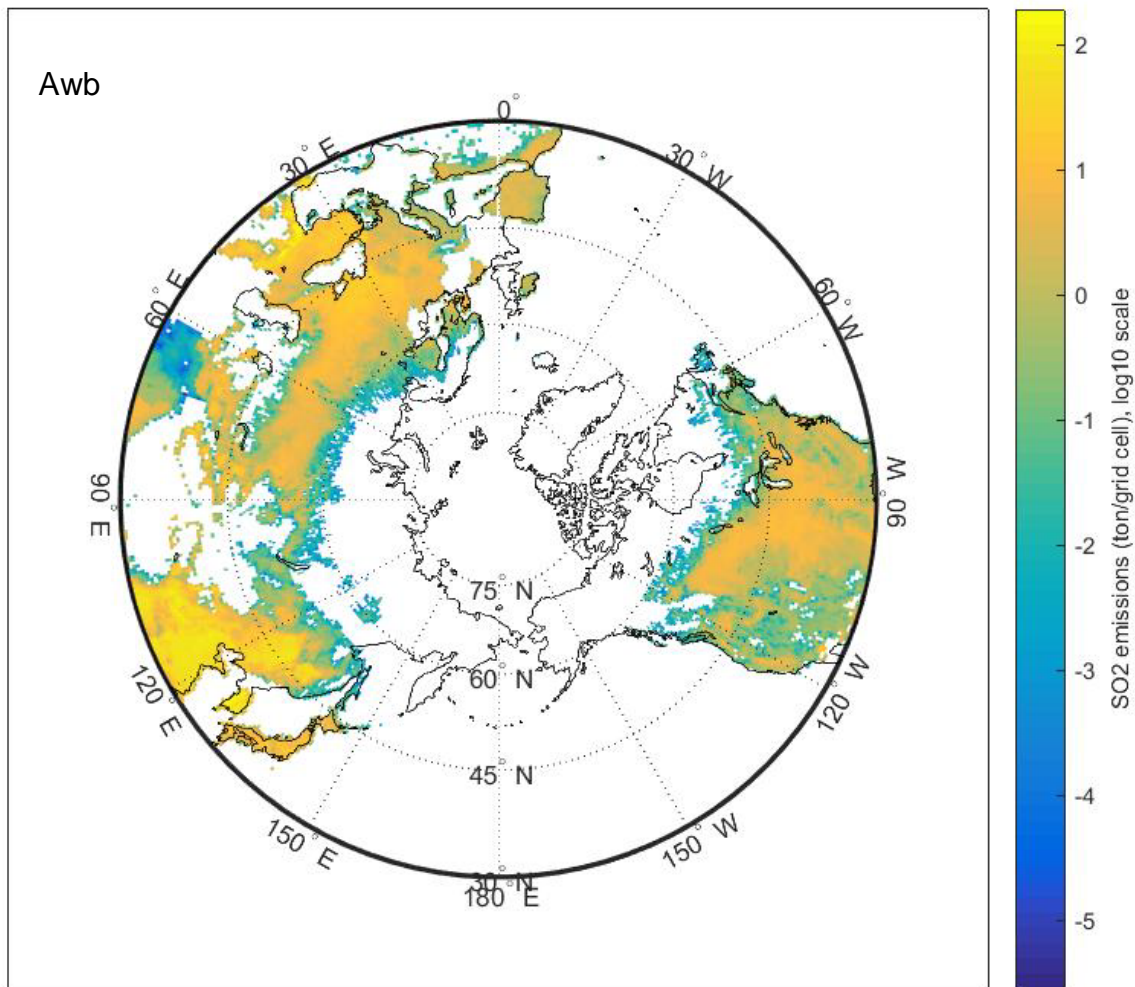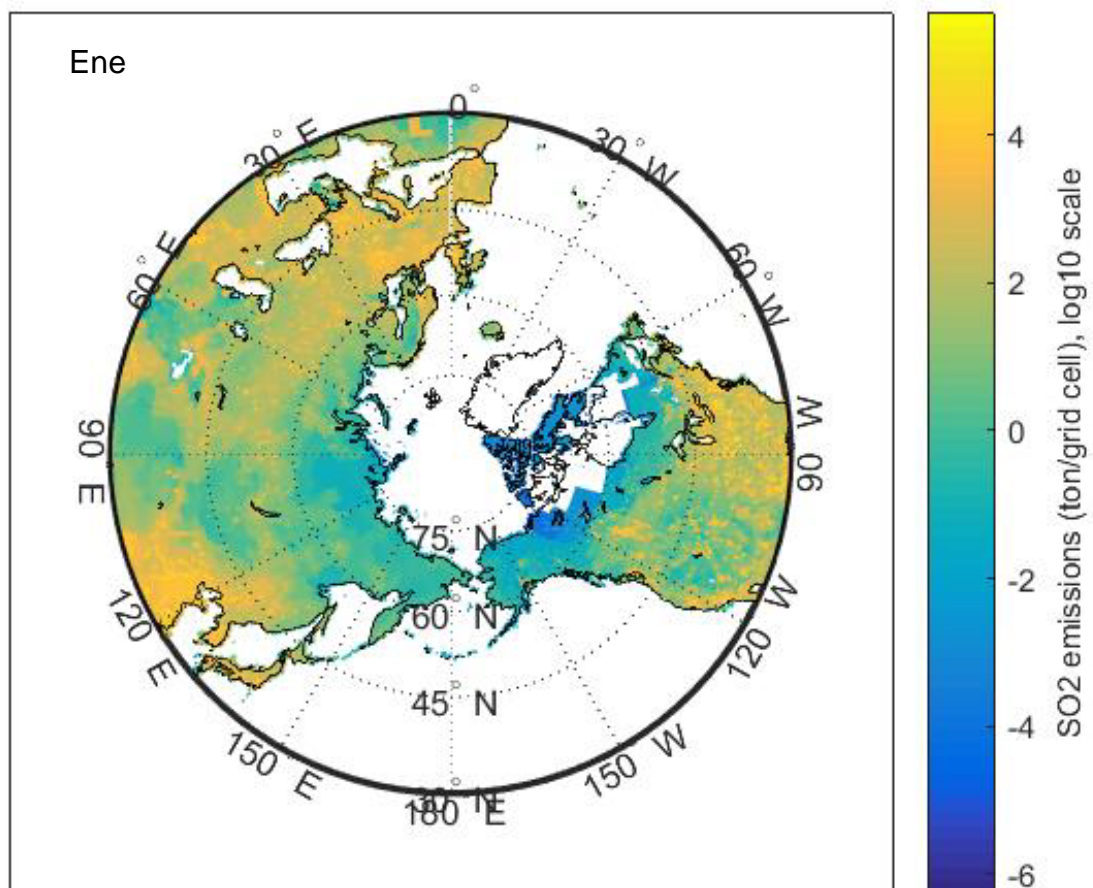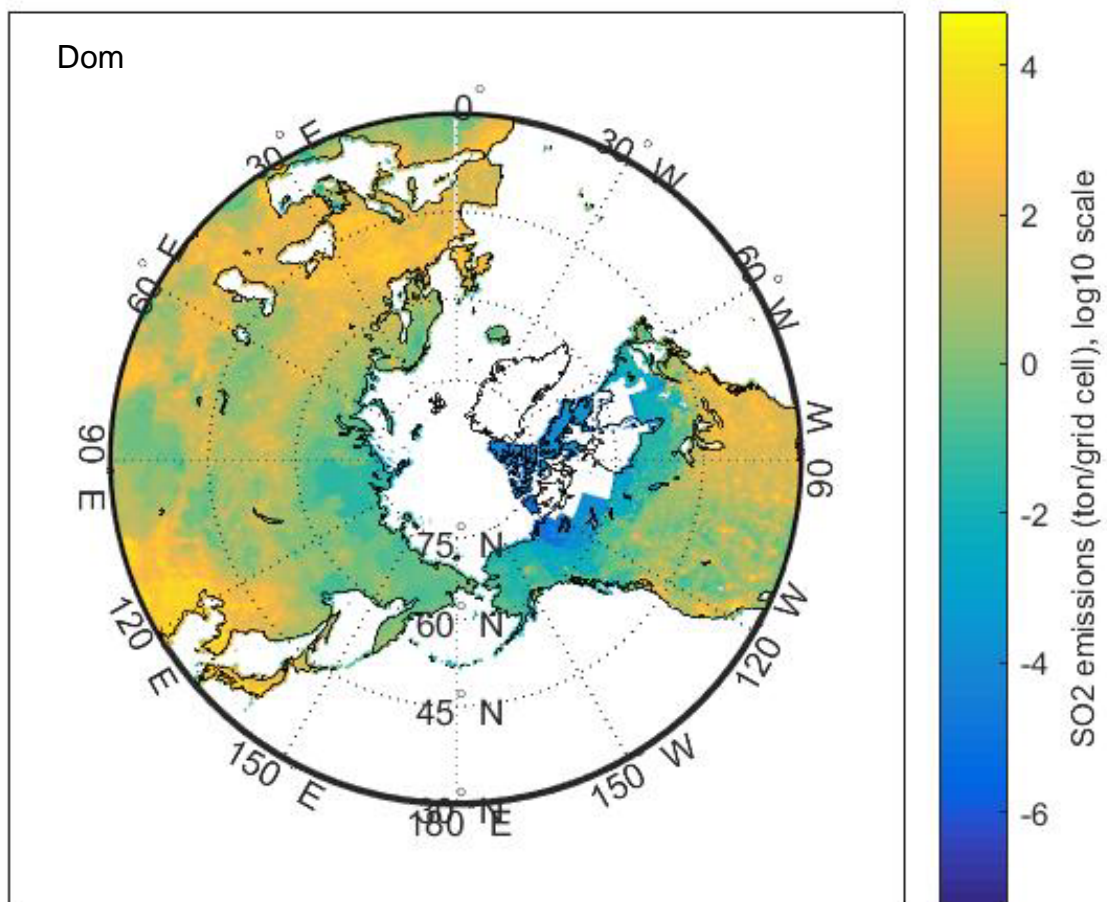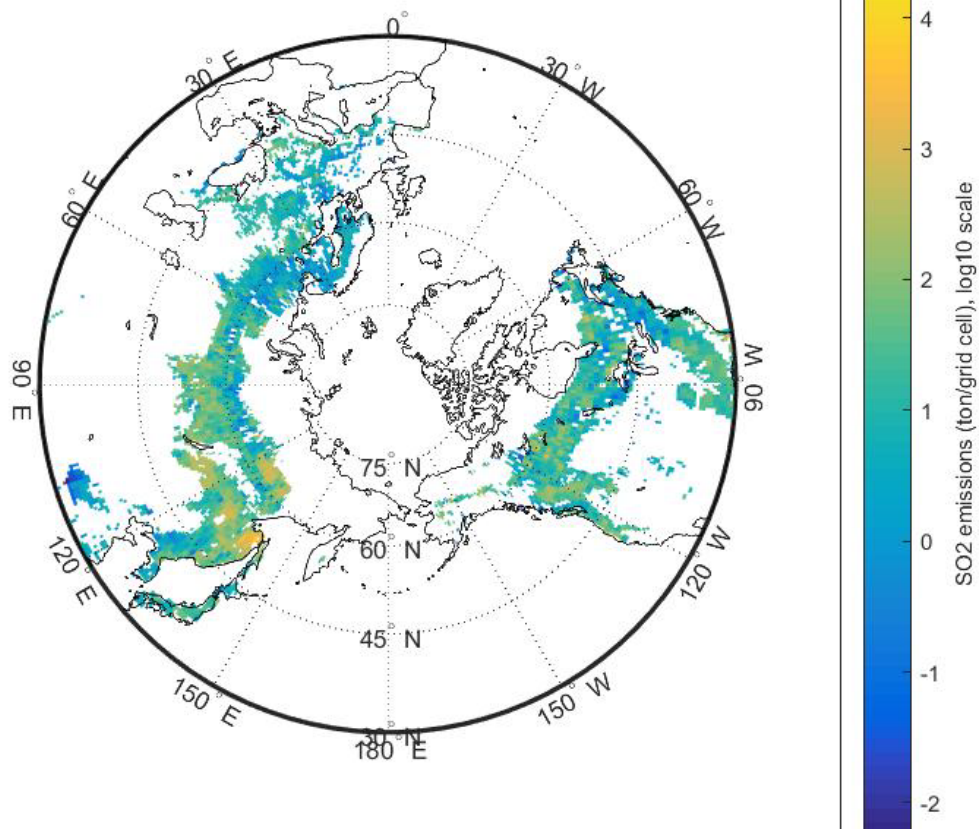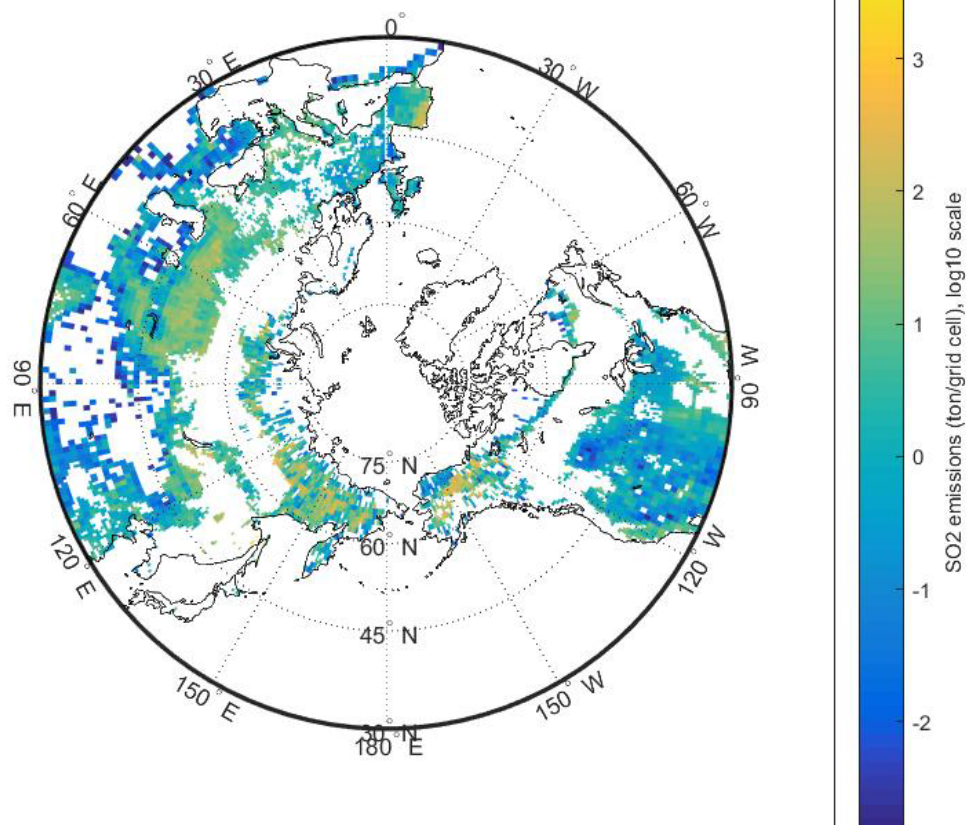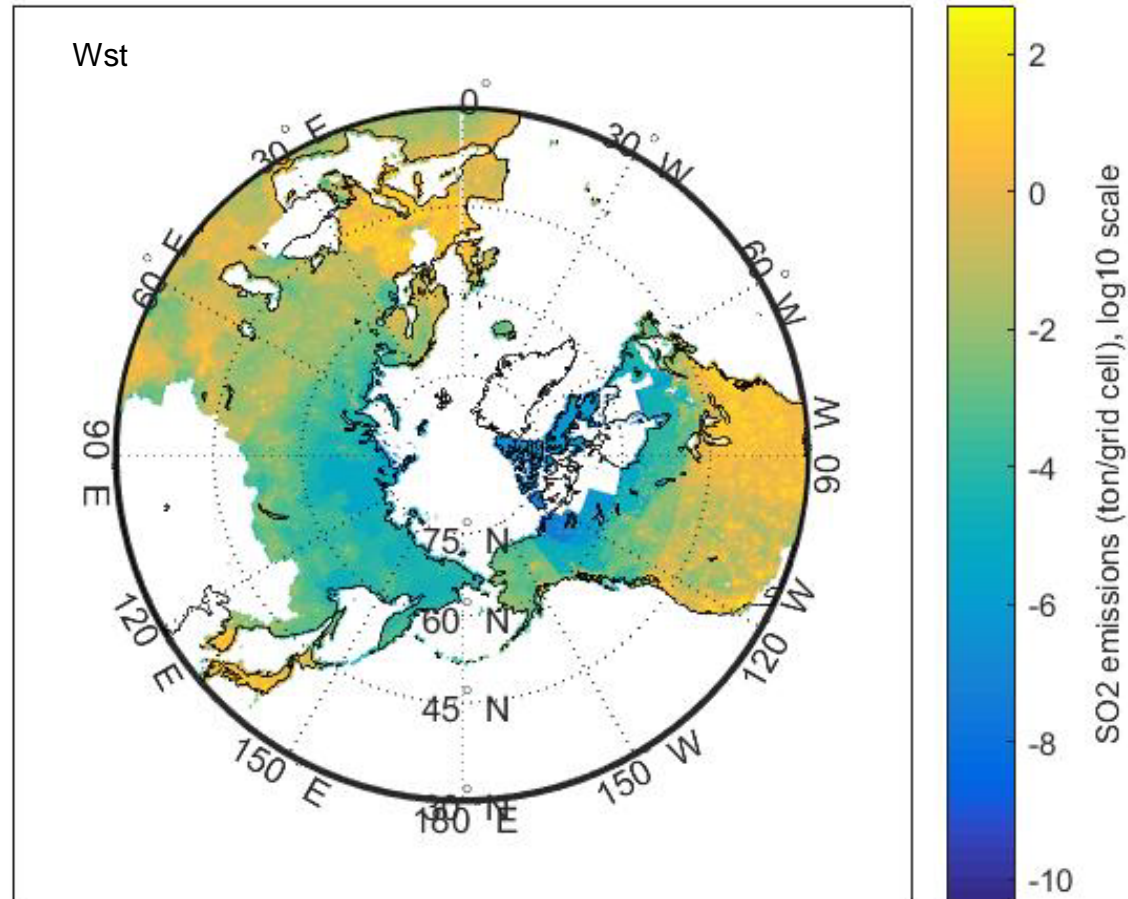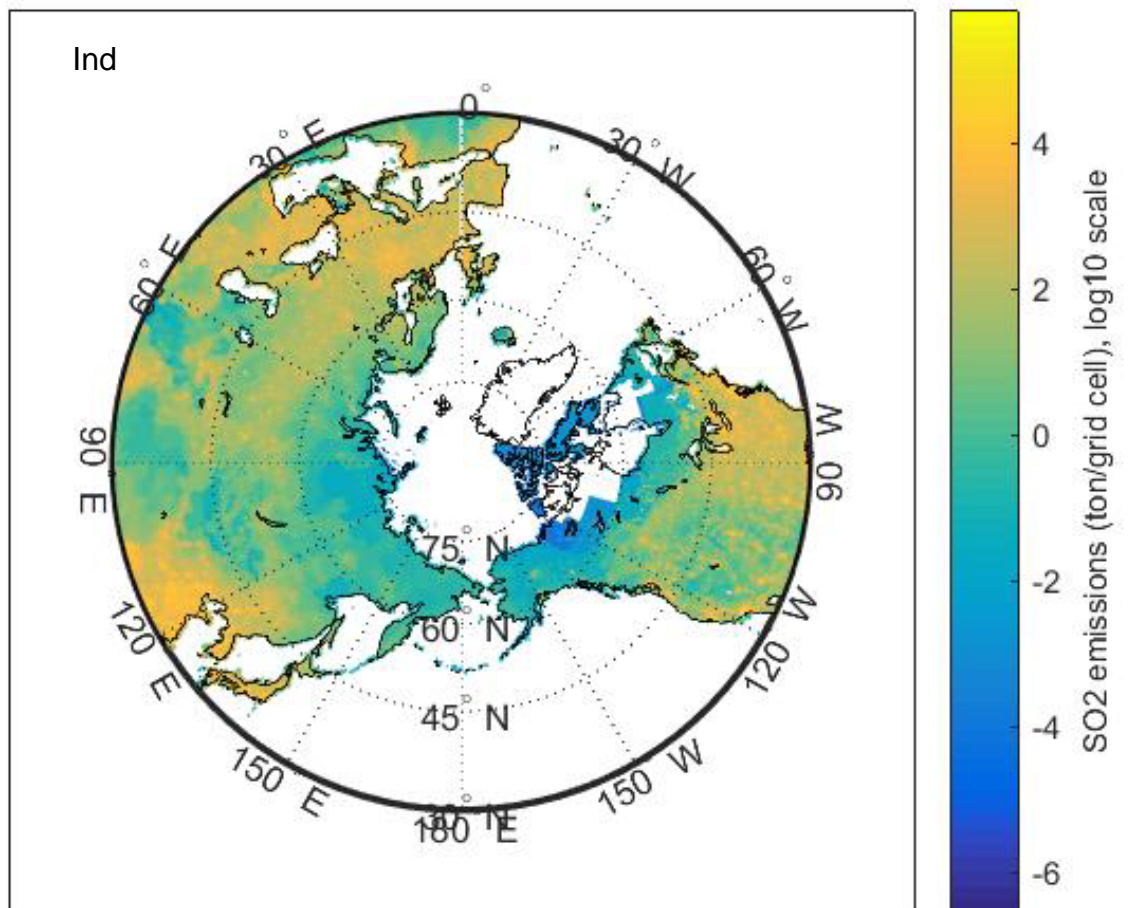
A11-13. Graphs for annual SO$_2$ emissions from ten regions within the Northern Hemisphere for the time period 1970-2010. The graphs show three separate emission sources.
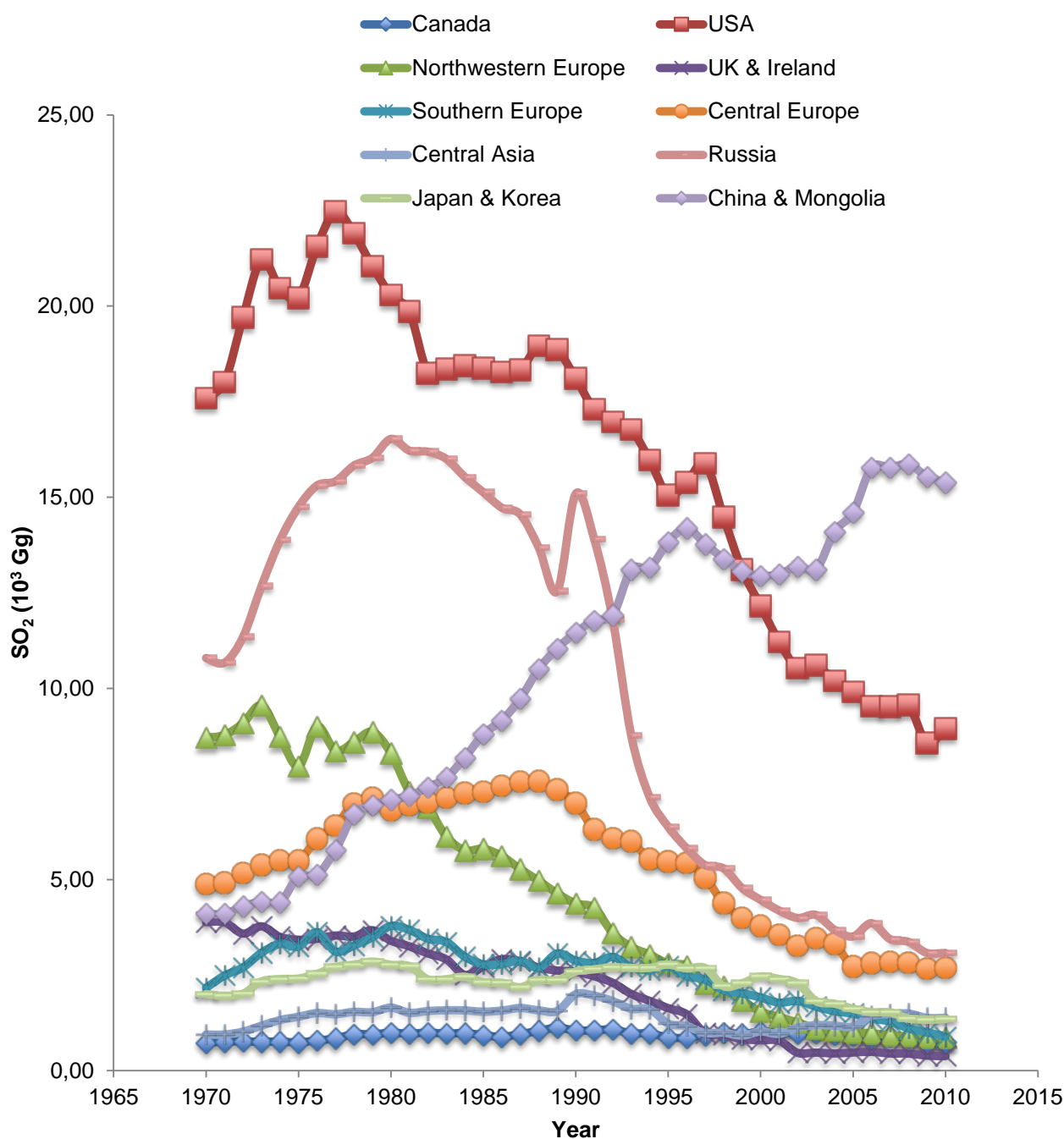
Figure A11. Total annual SO$_2$ emissions from burning fossil fuel for ten regions of the Northern Hemisphere between 1970-2010 (Data source: EDGAR, 2017).
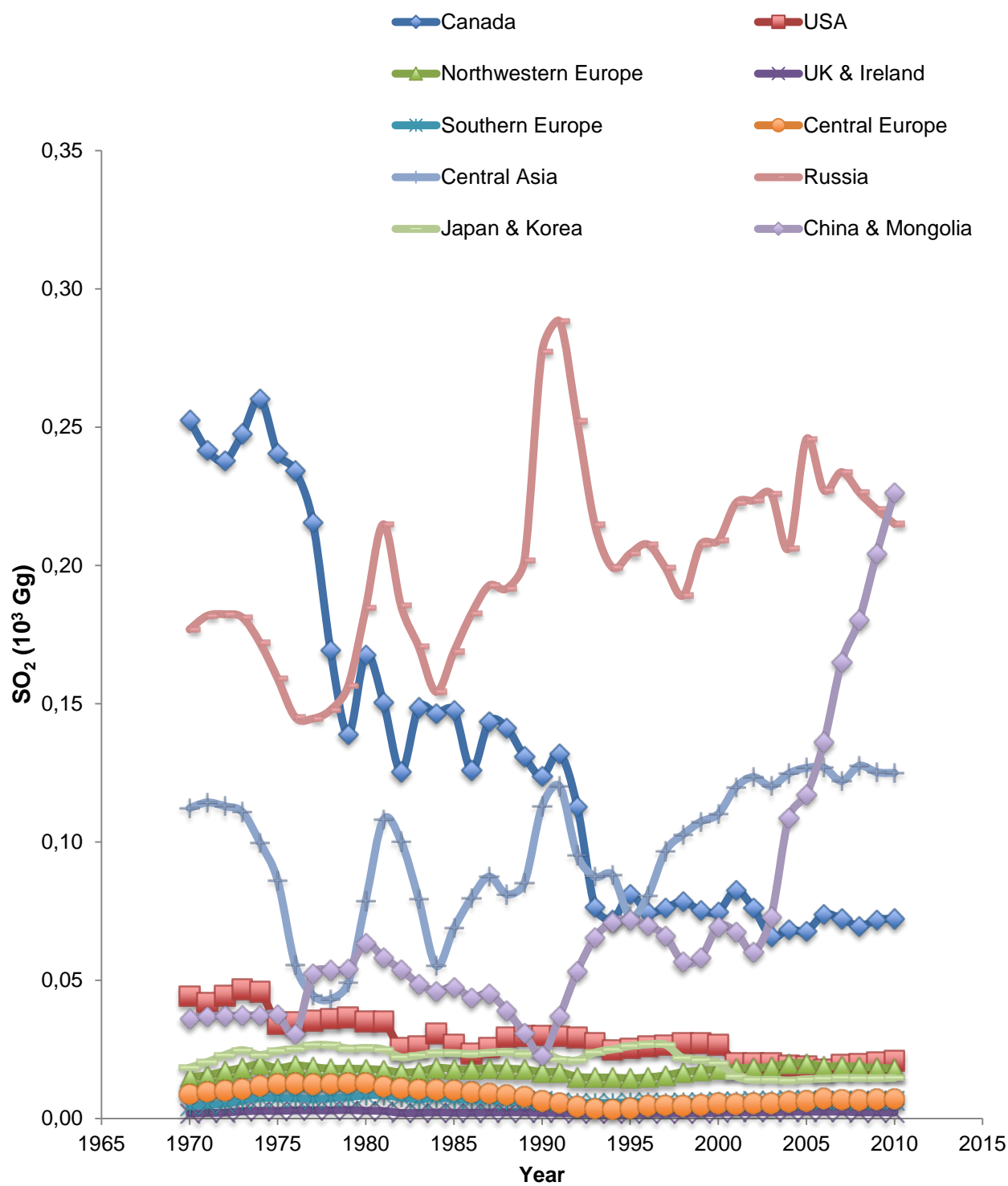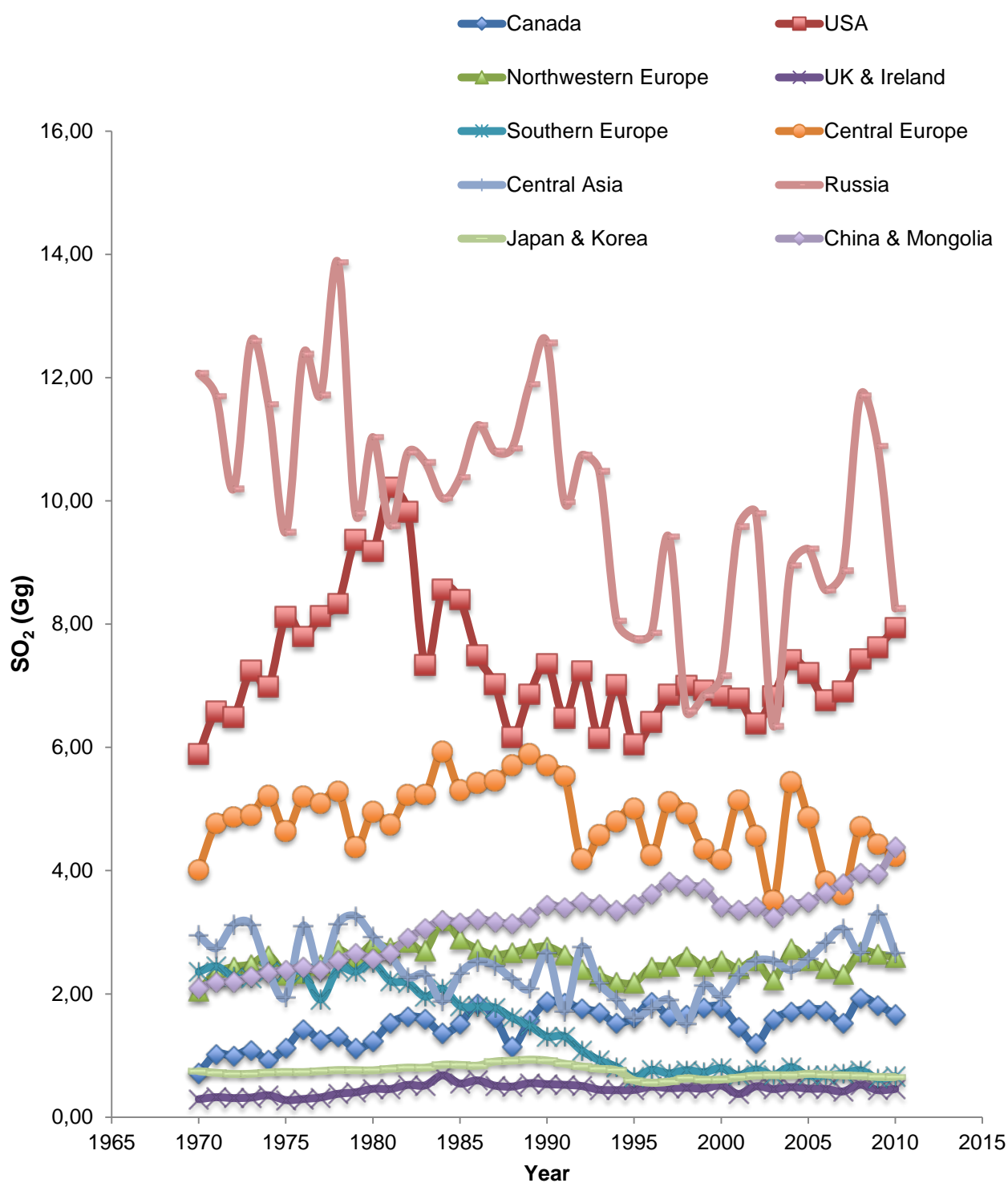
Figure A12. Total annual SO₂ emissions from metallurgical production for ten regions of the Northern Hemisphere between 1970-2010 (Data source: EDGAR, 2017).

Figure A13. Total annual SO_2 emissions from burning biomass for ten regions of the Northern Hemisphere between 1970-2010 (Data source: EDGAR, 2017).

A14-17. Graphs for annual SO$_2$ emissions from Scandinavian countries from 1970 to 2010 divided into four categories; total emissions, emissions from burning fossil fuels, emissions from metallurgical production and emissions from burning biomass.
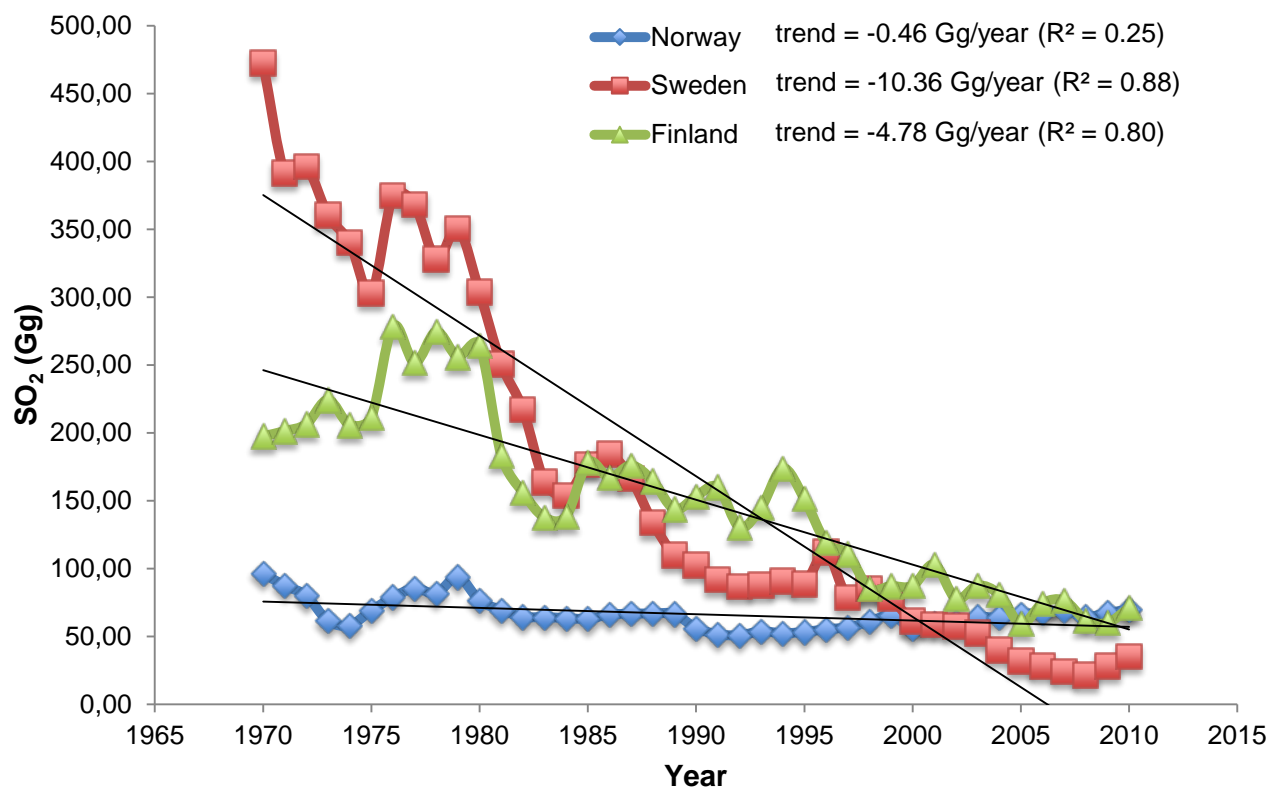

Figure A14. Total annual SO$_2$ emissions from the Scandinavian countries including burning fossil fuels, metallurgical production and burning biomass. (Data source: EDGAR, 2017).
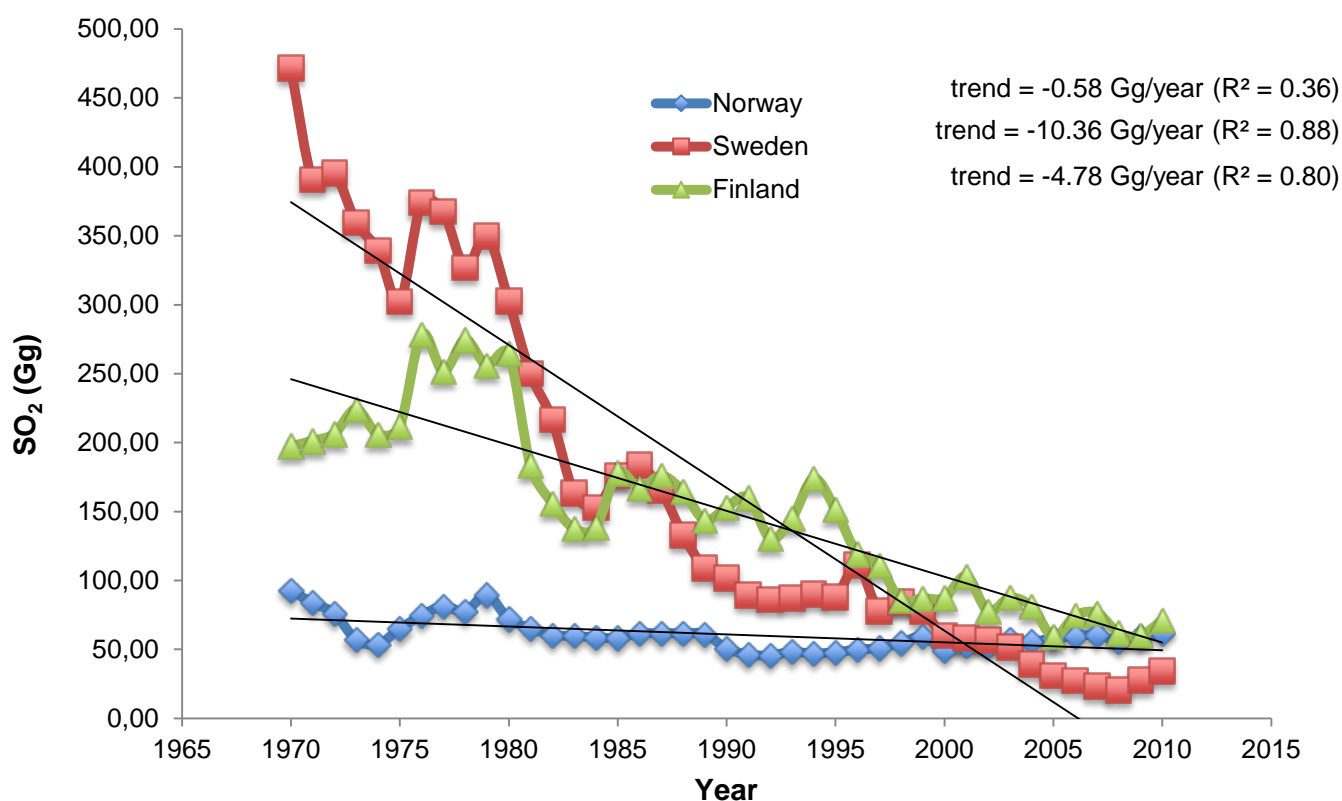

Figure A15. Total annual SO$_2$ emissions from burning fossil fuels in the Scandinavian countries. (Data source: EDGAR, 2017).
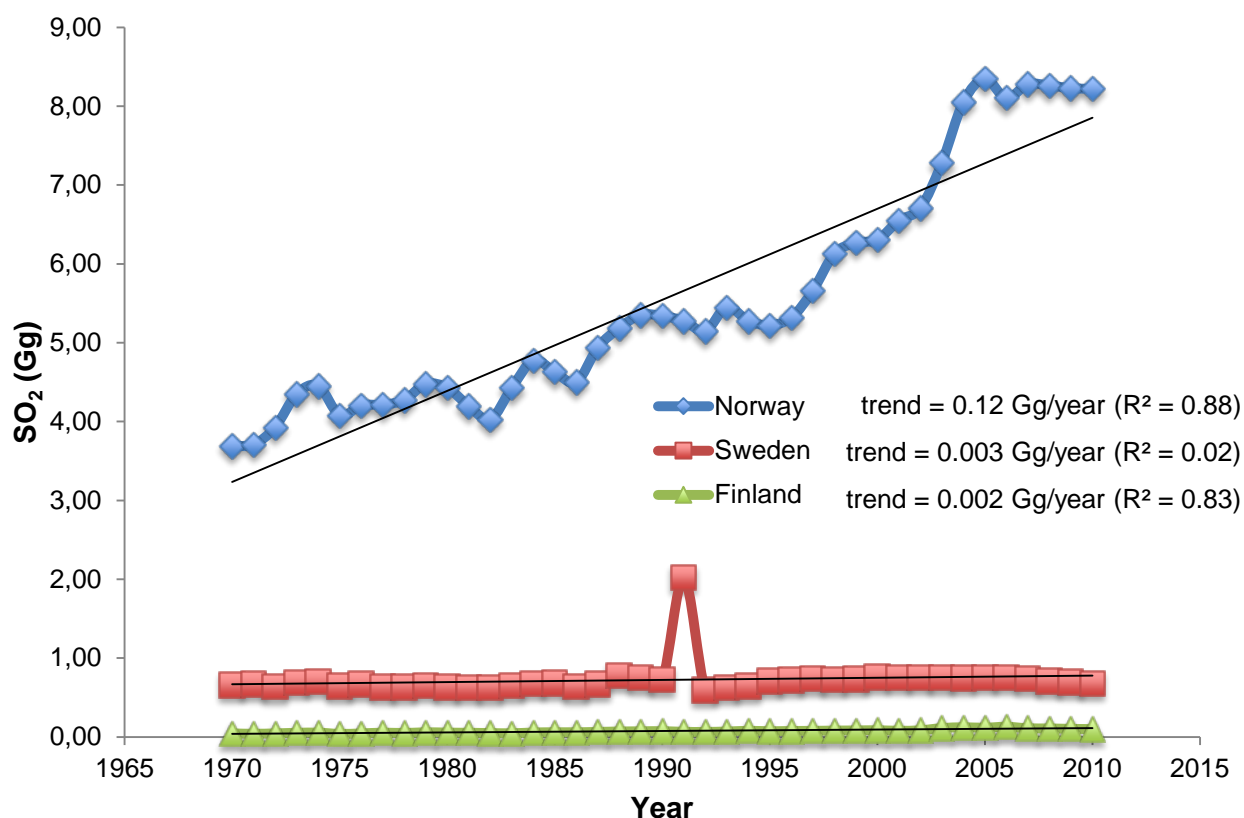
Figure A16. Total annual SO_2 emissions from metallurgical production in the Scandinavian countries. (Data source: EDGAR, 2017).
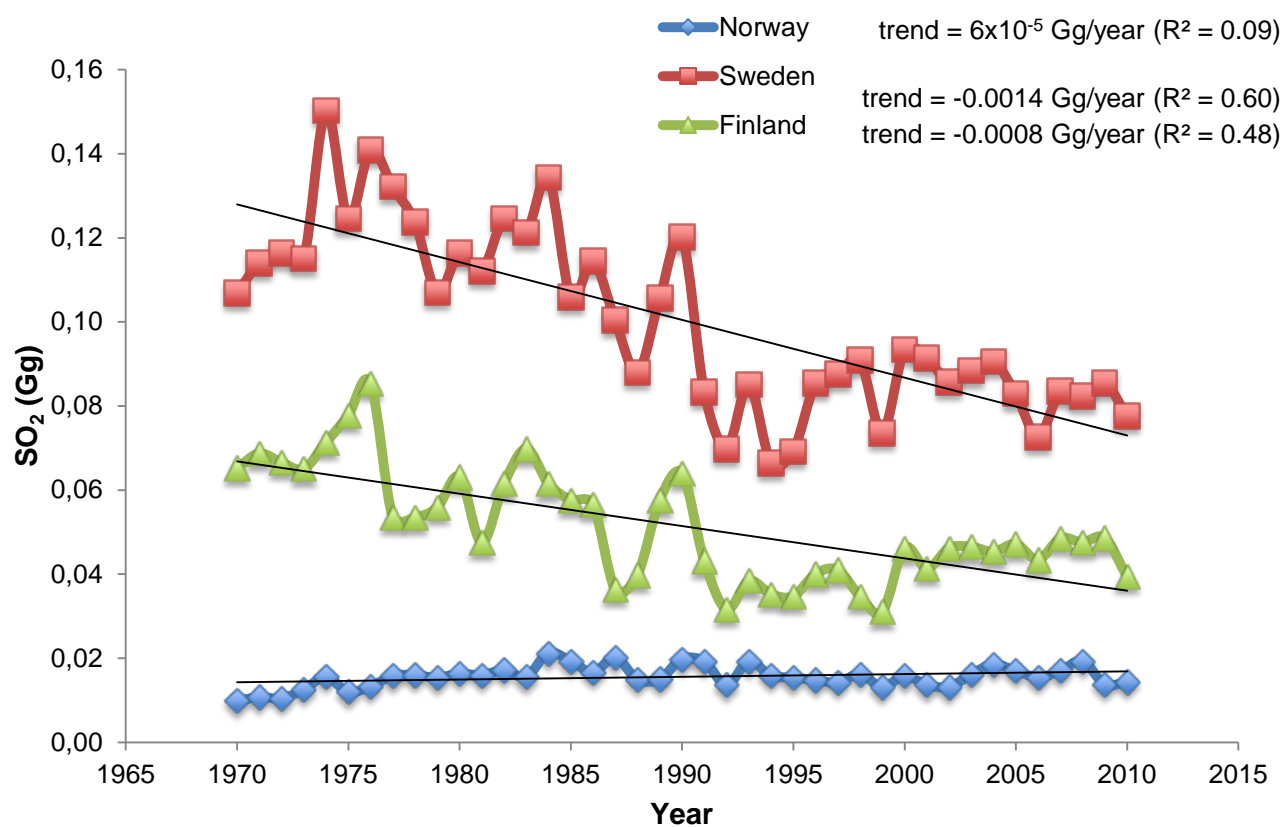

Figure A17. Total annual SO_2 emissions from burning biomass in the Scandinavian countries. (Data source: EDGAR, 2017).