

Response of Sulfate Concentration and Isotope Composition in Icelandic Rivers to the Decline in Global Atmospheric SO₂ Emissions into the North Atlantic Region

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This study presents the changes in dissolved sulfate concentration and isotope composition of Icelandic river waters between the peak of SO₂ emissions in the United States and Europe and the present. Chloride concentration in Icelandic rivers has not changed much since 1972. The overall average change from 1972–1973 to 1996–2004 was –3%, indicating insignificant sea-salt contribution changes. More than 99% of the river-dissolved sulfur was in the form of sulfate. There are three main sources for dissolved sulfate in the rivers: rocks, sea-salts, and anthropogenic. Total dissolved sulfate, $_{td}SO_4^{2-}$, and non-sea-salt sulfate, $_{nss}SO_4^{2-}$, decreased in all of the rivers from the early 1970s to 1996–2004. The percentage decrease varies from 13% to 65%. The decrease is smallest in rivers where there is considerable rock-derived dissolved SO_4^{2-} . The overall average decrease was 39% for $_{td}SO_4^{2-}$ and 46% for $_{nss}SO_4^{2-}$. The anthropogenic sulfate fraction has declined making most of the river waters $\delta^{34}S$ values of sulfate higher through time. The overall decline in river sulfate and increase in $\delta^{34}S$, while SO₂ emissions from Iceland has been increasing, demonstrates the response of river chemistry in the remote North Atlantic to the decline in man-made emissions of SO₂ in North America and Europe.

Introduction

World man-made emissions of sulfur dioxide, SO₂, increased nearly continuously from the end of World War II until 1990; it was 56 million tons of SO₂ in 1945, and rose to 154 million tons of SO₂ in 1990, but declined to 142 million tons in 1995 (1–3). Man-made emissions of SO₂ have been declining for the last 30 years in North America. The emissions increased from 9 million tons in 1900, peaked in 1973 (4), and declined to about 15 million tons of emissions from the United States by the year 2000 (Figure 1). Man-made emissions of SO₂ have been declining for the last 30 years in Europe including the European part of Russia (Figure 1). As a result the concentration of SO₂ in the air in Europe has declined, and furthermore, the frequency and magnitude of high-concentration episodes for SO₂ in Europe, mainly in winter, has

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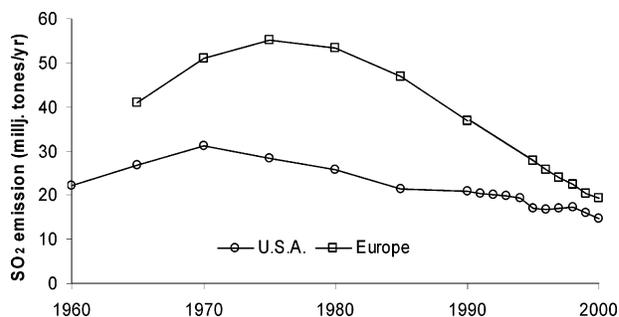


FIGURE 1. Man-made SO₂ emissions from the United States and Europe. The U.S. data from 1960 to 1980 are from ref 5, the 1985 data are SNAP National from ref 6, and the data for 1990 to 2002 are official U.S. numbers in the United Nations Greenhouse Gases Database (ref 7). The European data from 1965 to 1990 are from ref 8, the emission data for 1995 to 2000 are experts' estimates in the UNECE/EMEP database (ref 6) as described by ref 9 including Russia west of the Ural and excluding international shipping.

decreased (10). Thus, the winter concentrations of SO₂ in Europe have decreased relatively more than those of the summer, resulting in less pronounced seasonal variation toward the end of the last century (10).

Sulfate, SO_4^{2-} , particulate concentrations in air and dissolved in precipitation have decreased throughout Europe (10). This decrease has, however, not been as large as the reduction in sulfur emissions (Figure 1) or SO₂ concentrations (10). Oxidation of SO₂ was less oxidant-limited at the end of the last century than in the early 1980s (10). Sulfate concentration increased from the 1930s and 1950s in ice and snow in Greenland, depending on the locations. The concentration peaked in the early 1980s, shortly after maximum SO₂ emission occurred in Europe and the United States (Figure 1). There were no major changes in the 1980s, but decreases were detected at some stations at the end of these years (11). The sulfate concentration in air at Nye-Ålesund, Svalbard (Figure 2) decreased continuously from the mid-1980s to the end of the century (11).

The decrease in SO₂ emissions in North America and Europe (Figure 1) has led to a widespread decrease in lake and stream SO_4^{2-} concentrations in the northeastern and midwestern United States, and central Europe, the U.K., and Scandinavia (15–18). The decrease varies considerably from one region to another. In Europe the decline in lake and stream SO_4^{2-} concentrations was largest in north central Europe, but smallest in northern Scandinavia, the U.K., and the Alpine part of Italy (15–17). Most of the regions in North America and Europe exhibited stronger downward trends in the 1990s than in the 1980s (15). In New England, the Adirondacks, and the northern Appalachian mountains of the United States, the percentage decline in sulfate concentrations occurring in precipitation was generally steeper than in surface waters. In the majority of aquatic systems, sulfate recovery lagged to some extent. However, the lakes and streams with the steepest decline in sulfate showed very similar rates to those in deposition, indicating that the most responsive catchments responded directly and rapidly to the sulfate decrease in deposition (18).

Iceland is thousands of kilometers away from the industrial centers of Europe and North America (Figure 2). It sits in the middle of the main route for atmospheric transport of pollution from Europe and North America to the Arctic, making it an ideal location for monitoring the response of aquatic systems to global SO₂ emission and transport. The

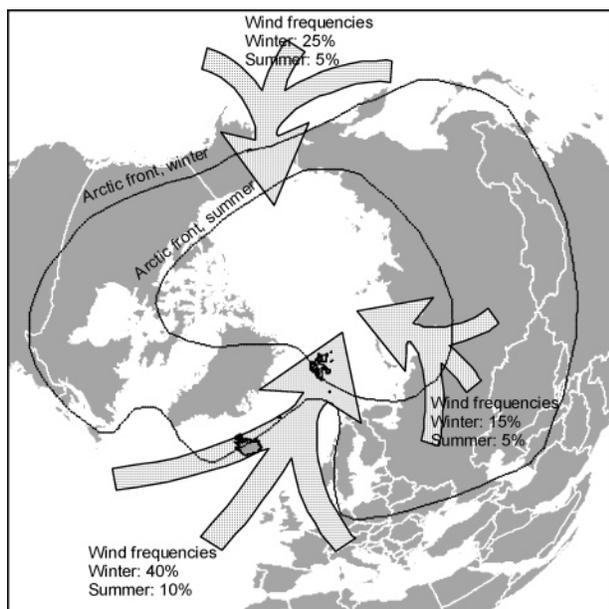


FIGURE 2. Mean position of the Arctic air mass in January and July and the winter and summer frequency of winds driving the major south-to-north transport (12–14). The North Atlantic transport route passes Iceland and Svalbard. Modified from ref 14.

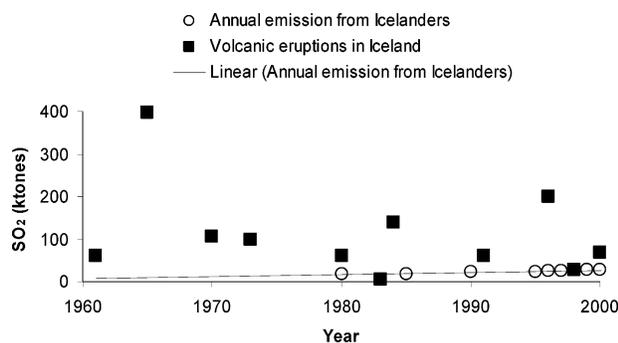


FIGURE 3. Emissions of SO₂ from Iceland. The man-made emissions from 1980 to 2000 are experts' estimates in ref 6 as described by ref 9 excluding international shipping. This data is regressional and extrapolated to the year 1960. Also shown is the estimated total SO₂ emissions from volcanic eruptions in Iceland. The estimate is based on the amount of erupted material (20) and the measured total SO₂ flux from the 1996 Gjalp eruption (21).

population in Iceland is less than 300 000, its aerial extent is 103 000 km², and more than 70% of its total energy use in 2003 was generated from hydroelectric or geothermal power plants (19). The man-made emissions of SO₂ in Iceland rose from 18 kilotons in 1980 to 27 kilotons in 2000 (Figure 3): a small flux increase but reverse to the decline in emissions from Europe and North America that occurred in the same period (Figure 1). The rock composition of Iceland is uniform, consisting mostly of basalt, and the island is sparsely vegetated and populated, making the catchments responsive to global SO₂ emission and transport. Volcanic eruptions are frequent in Iceland, resulting in periodic emission of SO₂ to the atmosphere. An estimate of the total SO₂ emissions of the eruptions between 1960 and 2000 is shown in Figure 3. The integrated 400 kilotons of emissions from the largest eruption in the period, the Surtsey eruption in 1963–1967, is 100 times smaller than the emissions from Europe in 1965.

The object of this study was to determine the sulfate concentration and isotope composition of Icelandic river waters since the peak occurrence of SO₂ emissions in the United States and Europe to the present and thereby define

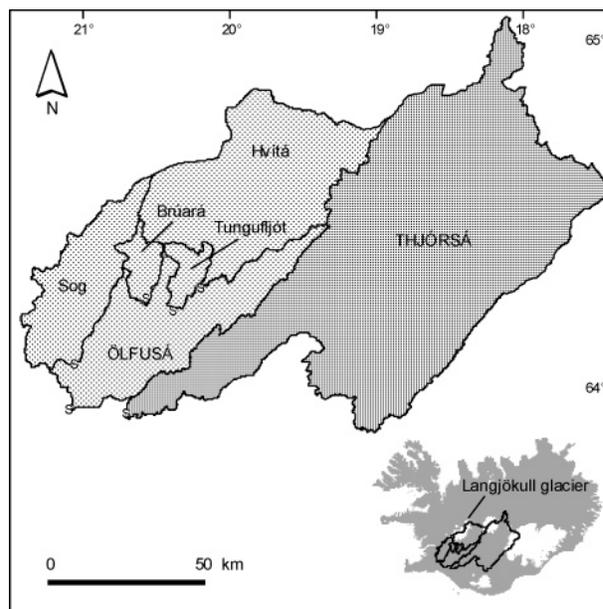


FIGURE 4. River catchments of the present study and the Langjökull glacier.

the source of the dissolved sulfate and river catchment response to decreased global atmospheric SO₂ emissions into the North Atlantic region.

Materials and Methods

The 421 samples for this study were collected in 93 expeditions from the main channel of the 6 rivers in Figure 4. They were sampled all year around from February 1972 until December 1973 and then again in November 1996 until December 2004 (Figure 4; 22–25). Four to twelve samples were collected from each river per year. Integrated samples of the winter precipitation in 1997–2003 were collected on the Langjökull glacier in six expeditions (Figure 4), one mass-weighted average sample for each winter. For each river sample, discharge, suspended particle concentration, air and water temperature, pH, conductivity, alkalinity, and the dissolved organic and inorganic concentration of from 12 to 33 constituents were measured. Sulfur isotope ratios were measured in samples taken after November 1998. More detailed chemical analyses of dissolved constituents were carried out on selected samples.

Two duplicate cores of the winter precipitation on the Langjökull glacier were taken each winter from 1997 to 2003 prior to the onset of the spring thaw in late March as described in detail in ref 26. The average of the two samples was assumed to represent the composition of the winter precipitation on the Langjökull glacier (Figure 4).

The waters sampled from 1972 to 1973 (22, 23) were immediately filtered in the laboratory after each expedition, through a 0.2 μm membrane filter. Dissolved chloride was measured by AgNO₃ titration; the precision of the titration was 3–6%, and the detection limit was at 30 μmol/kg (27). Dissolved SO₄²⁻ was measured gravimetrically, after precipitation of barium sulfate in HCl solution after removal of silica (27). The detection limit was at 10 μmol/kg.

The water samples collected after October 1996 (24, 25) were filtered immediately after sampling through 0.2 μm Millipore membranes (cellulose acetate). Samples were stabilized by various acidifications and treatments as described in detail in Gislason et al. (21). The dissolved major and trace elements were measured in three laboratories: Institute of Earth Sciences, University of Iceland (IES); Analytica AB Luleå, Sweden, and Stockholm University,

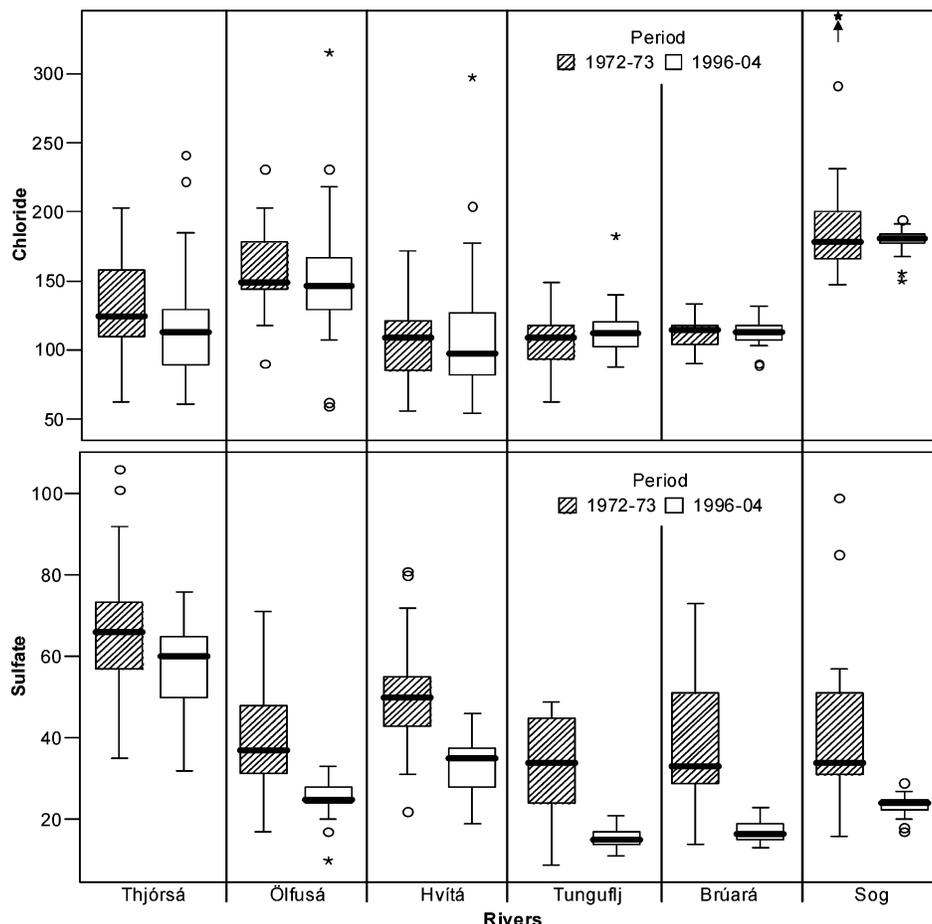


FIGURE 5. Comparison of total river-dissolved sulfate, ${}_{td}\text{SO}_4^{2-}$ ($\mu\text{mol/kg}$), and chloride concentrations ($\mu\text{mol/kg}$) from the two periods, 1972–1973 and 1996–2004. The box-plots show median (bold horizontal line), interquartile range, and extreme measurements (dots and stars).

Sweden. The average relative error in the charge balances of major elements was less than 3%. The Cl^- , F^- , and SO_4^{2-} measurements were performed using a Dionex high-pressure ion chromatograph. Total dissolved sulfur was measured on acidified samples by inductively coupled plasma atomic emission spectrometry (ICP-AES). The average difference between total dissolved sulfur measured by ICP and SO_4^{2-} by the ion chromatograph was 0.85%, ranging from 0.1% to 1.8% for individual rivers. Thus the total dissolved sulfur is essentially all in the form of sulfate (SO_4^{2-}).

The total dissolved sulfate, ${}_{td}\text{SO}_4^{2-}$, was differentiated according to its origin into non-sea-salt sulfate, ${}_{nss}\text{SO}_4^{2-}$, and sea-salt-derived sulfate, ${}_{ss}\text{SO}_4^{2-}$. The sea-salt-derived sulfate was calculated from the river-dissolved Cl^- , assuming all the Cl^- to be derived from seawater, using the $\text{SO}_4^{2-}/\text{Cl}^-$ molar ratio of 0.05222 (28). This has been proved to be a good assumption (e.g., 29) for the rivers of southwest Iceland, because of the overall low average concentration of Cl^- in basaltic rocks, 180 ppm (30), high runoff and relief, and sparse vegetation and population (less than 3 inhabitants per km^2). The ${}_{nss}\text{SO}_4^{2-}$ is probably mostly due to global anthropogenic emission and oxidation of SO_2 , ocean surface emission and oxidation of dimethyl sulfide (DMS), and dissolution of basaltic rock as will be discussed later.

Information on the distribution of the data is given by box-plots which show the median, interquartile range, and extreme measurements (Figure 5). The nonparametric Mann–Whitney test was used to compare the sample values from 1996 to 2004 with the sample values from 1972 to 1973. The main difference in the distributions of the two sample values is appropriately given by the difference in the medians.

Linear regression models were used, where the slopes with 95% confidence intervals demonstrate linear time evolutions of the data from 1996 to 2004. The p -values used are two-tailed, and the level of significance was set at 0.05 (31).

Dissolved sulfate was converted to BaSO_4 for sulfur isotopic analyses (e.g., 32). The BaSO_4 was mixed with an equal amount of V_2O_5 and reacted in an online elemental analyzer converting the BaSO_4 to $\text{SO}_2(\text{g})$, which was then analyzed in a continuous flow isotope ratio mass spectrometer (CF-IRMS; Finnigan Delta+). The sulfur isotope composition was defined as a deviation in ‰ of the ratio ${}^{34}\text{S}/{}^{32}\text{S}$ between a sample and a standard, expressed in the conventional $\delta^{34}\text{S}$ notation relative to V-CDT. The accuracy of the measurements based on standard measurements was better than $\pm 0.2\text{‰}$ for all samples.

Results and Discussion

The total dissolved sulfate and chloride concentrations in rivers in Southwest Iceland for the two periods, 1972–1973 and 1996–2004, are compared by the box-plots in Figure 5. The total river-dissolved sulfate concentration for the period 1996–2004 is shown as a function of time for the same rivers in Figure 6. The diagrams show regression lines of all the data, reflecting overall changes. The slopes are negative for all the time series, although not statistically significant for the rivers Tungufljót (p -value, 0.059), Thjórsá (p -value, 0.09) and Hvítá (p -value, 0.99). The mean of dissolved Cl^- , total dissolved SO_4^{2-} (${}_{td}\text{SO}_4^{2-}$), and non-sea-salt dissolved (${}_{nss}\text{SO}_4^{2-}$) in the rivers for 1972–1973 and 1996–2004 are shown in Table 1. Also shown is the percentage change in the mean between the two periods and the statistical significance of

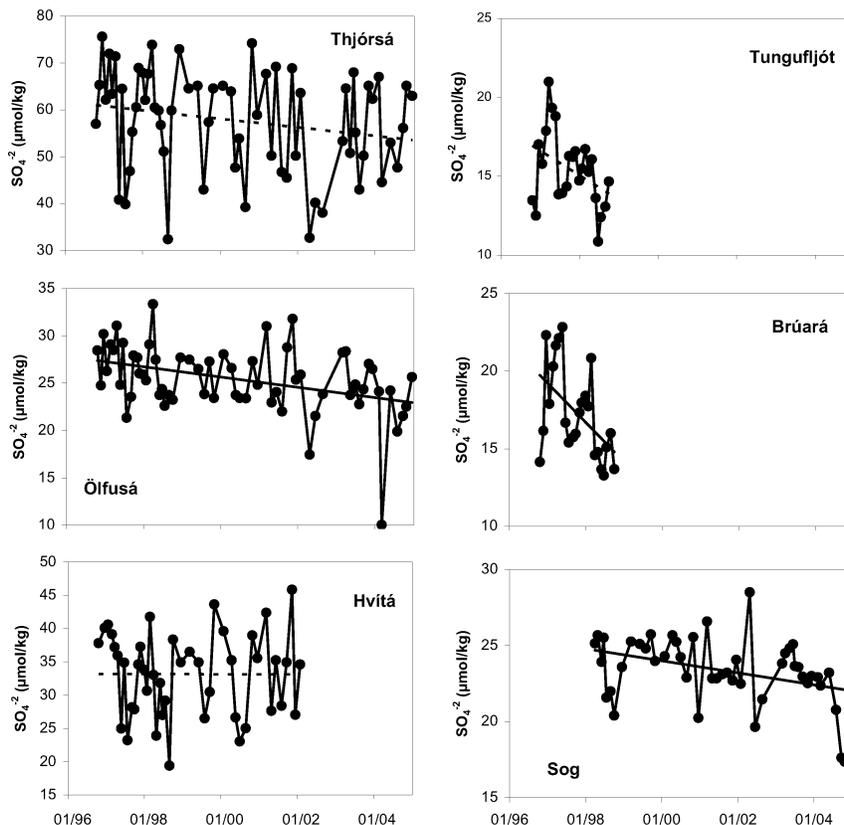


FIGURE 6. Total dissolved sulfate (tdSO_4^{2-}) concentrations of the Icelandic rivers from 1996 to 2004. The diagrams show regression lines of all the data. Solid lines have statistically significant slopes.

TABLE 1. Mean of Dissolved Cl^- , Total Dissolved Sulfate (tdSO_4^{2-}), and Non-Sea-Salt Dissolved Sulfate (nssSO_4^{2-}) in the Rivers for 1972–1973 and 1996–2004^a

periods	1972–1973 ($\mu\text{mol/kg}$)			1996–2004 ($\mu\text{mol/kg}$)			Cl^-		tdSO_4^{2-}		nssSO_4^{2-}			
	species	Cl^- mean	tdSO_4^{2-} mean	nssSO_4^{2-} mean	Cl^- mean	tdSO_4^{2-} mean	nssSO_4^{2-} mean	change % ^c	p -value ^d	change % ^c	p -value ^d	change % ^c	p -value ^d	
rivers														
Thjórsá	23	129	66	60	64	115	58	52	-12	0.077	-13	0.041	-13	0.054
Ölfusá	23	158	39	31	64	150	25	18	-5	0.231	-34	<0.001	-41	<0.001
Hvítá	22	105	51	46	44	109	33	27	4	0.833	-35	<0.001	-40	<0.001
Tungufljót	22	107	33	27	24	114	15	10	6	0.397	-53	<0.001	-65	<0.001
Brúará	22	113	39	33	24	113	17	11	0	0.982	-55	<0.001	-65	<0.001
Sog	22	198	41	31	47	179	23	14	-10	0.417	-43	<0.001	-54	<0.001

^a Also shown is the percentage change in the mean between the two periods and the statistical significance of the change (p -value). ^b n is the number of the samples. ^c Change in means between two comparable samples. ^d A two-tailed Mann–Whitney p -value. Significant change is considered to have a p -value of less than 0.05.

the change (p -value). The percent changes in the median values are similar or slightly lower than the percent change in the mean.

The dissolved Cl^- concentration has not changed much from 1972, and variations are both an increase and a decrease (Figure 5 and Table 1). The change in the Cl^- concentrations from the two periods has no statistical significance as reflected by the p -values in Table 1 (p -values > 0.05). The observed change is closest to being significant in the Thjórsá river. The overall mean concentration of Cl^- for the period of 1972–1973 was $135 \mu\text{mol/kg}$, compared to $130 \mu\text{mol/kg}$ for 1996–2004, which translates to an insignificant 3% decrease. The dissolved sulfate concentration, both tdSO_4^{2-} and nssSO_4^{2-} , has decreased in all of the rivers, from the early 1970s to 1996–2003, as reflected by the median tdSO_4^{2-} values in Figure 5 and the mean percent decrease in Table 1. The percentage decrease in the mean varies from 13% for the river Thjórsá to 65% for the rivers Tungufljót and Brúará. The change in

tdSO_4^{2-} and nssSO_4^{2-} concentrations from the two periods is statistically significant as reflected by the p -values in Table 1 (p -values < 0.05) for all the rivers except the Thjórsá river, the reason being that most of the sulfur in this river is of rock origin as will be described later. The overall decrease in the mean was 39% for tdSO_4^{2-} and 47% for nssSO_4^{2-} and is much larger than the insignificant overall 3% decrease in Cl^- . Thus the SO_4^{2-} river-dissolved concentration changes during the past decades in Icelandic rivers are mostly SO_2 emission controlled like SO_4^{2-} river-dissolved concentration changes in Europe and the United States (15–18). Furthermore, as can be seen in Figure 5 the variations in tdSO_4^{2-} were much greater in the early 1970s than in 1996–2004. This is in concert with the observed decline in the frequency and magnitude of episodically high concentrations of SO_2 in Europe as described in the Introduction (10).

The decline in both tdSO_4^{2-} and nssSO_4^{2-} varies from one river to another. This is mainly because the rock-derived

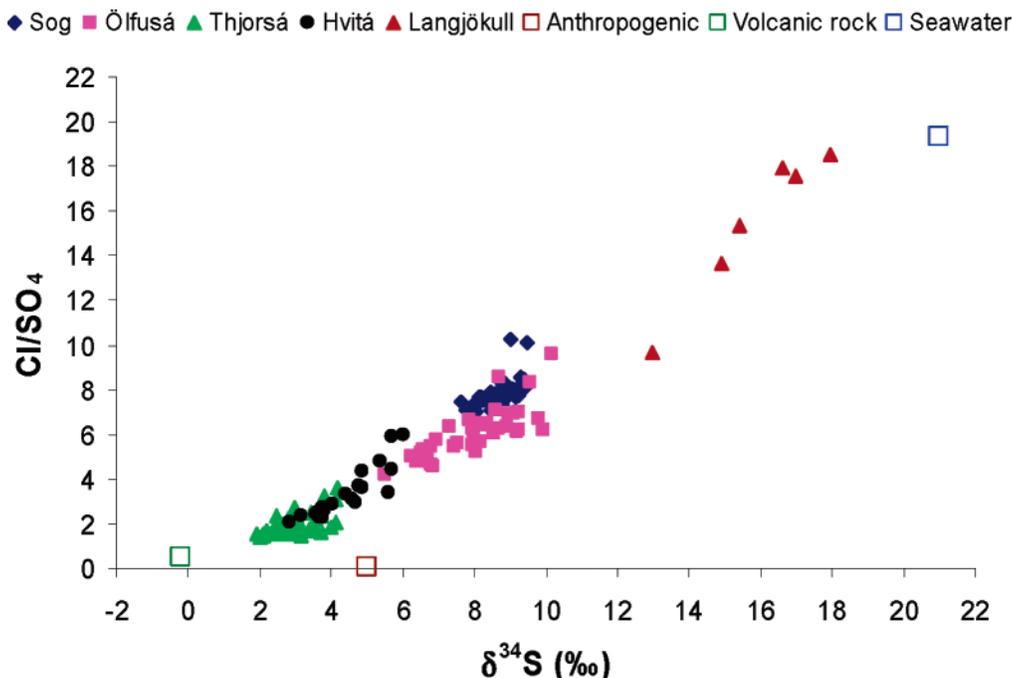


FIGURE 7. Concentration ratio of $\text{Cl}^-/\text{SO}_4^{2-}$ vs the sulfur isotope ratio, $\delta^{34}\text{S}$, of the rivers Thjorsá, Hvítá, Sog, and Ölfusá (Figure 4). Also shown on the diagram are the winter precipitation values on the Langjökull glacier (Figure 4) and average seawater, volcanic rock, and anthropogenic ratios as referred to in the text.

sulfate (SO_4^{2-}) concentration varies from one catchment to another as illustrated in Figure 7. The sulfur isotope composition ($\delta^{34}\text{S}$) versus the $\text{Cl}^-/\text{SO}_4^{2-}$ concentration ratio for the rivers Thjorsá, Hvítá, Sog, and Ölfusá is plotted in Figure 7. The rivers were sampled from November 1998 to December 2004. Also shown in Figure 7 is the average winter precipitation on the Langjökull glacier for the same period based on one mass-weighted average sample for each winter.

Seawater sulfate has a remarkably homogeneous $\delta^{34}\text{S}$ value of 21‰ (33) and a $\text{Cl}^-/\text{SO}_4^{2-}$ ratio of 19.15 (28) that plot in the upper right corner of Figure 5, while Icelandic volcanic rocks plot in the lower left corner with an average $\delta^{34}\text{S}$ value of -0.2 ‰. This is based on sulfur isotope measurements of 54 unaltered Icelandic rocks, (34, 35) and a Cl and S average concentration of 180 and 366 ppm, respectively, for Quaternary rocks in Iceland (30, 34, 36). Another important S source shown in Figure 7 is man-made, mostly generated by burning of fossil fuels. It has a very low $\text{Cl}^-/\text{SO}_4^{2-}$ ratio and an estimated $\delta^{34}\text{S}$ value of 5‰ from anthropogenic deposition. This value is based on the following $\delta^{34}\text{S}$ values from Europe and the United States: between 2.5 and 6.6‰ in the Czech Republic (37), 4.5‰ in Scandinavia (38, 39), and around 5‰ on the United States east coast (40, 41). A triangle, with the end-members seawater, volcanic rock, and anthropogenic ratios, covers almost all the Icelandic river samples in Figure 7.

The dissolved SO_4^{2-} in the winter precipitation on Langjökull Glacier is dominated by S from anthropogenic and marine sources; bedrock S is considered to be a minor source (Figures 4 and 7), and there is a considerable variation from one winter to another. They also plot at relatively high $\text{Cl}^-/\text{SO}_4^{2-}$ ratios, because of the low concentrations, elemental fractionation during freeze and thaw cycles in snow accumulation processes (42), and the relatively large presence of biogenic DMS as a S source ($\delta^{34}\text{S}$ values between 15 and 18‰ (e.g., 43).

Decreases in anthropogenic S deposition would cause individual river water samples to move on trajectories radiating away from the corner representing the anthropogenic atmospheric S component in Figure 7, assuming that

contribution from weathering and sea-salt remain unchanged. Increases in $\delta^{34}\text{S}$ toward the seawater end-member occur when the mole fraction of sea-salt compared to that of weathering (bedrock) is >0.25 or $\delta^{34}\text{S} > 5$ ‰. Hence, for the Thjorsá river waters, dominated by a rock weathering component, the trajectories for most samples would be in the rock direction. The trajectory for the River Hvítá waters would be in direction to both end-members, while all the waters from the Ölfusá and Sog rivers would become heavier as a consequence of reducing the anthropogenic atmospheric sulfur contribution. However, it is most likely that the rock-weathering contribution would not remain constant, but decrease, following a decrease in anthropogenic atmospheric sulfur and thereby projecting all the proposed sample paths a little away from the rock end-member toward the seawater end-member. To summarize, the $\delta^{34}\text{S}$ values of rock-dominated water does not have to increase with a decrease in anthropogenic sulfur, but the $\delta^{34}\text{S}$ values of waters with a considerable seawater fraction will increase with a decrease in anthropogenic sulfur. This is in accord with the whole catchment experimental manipulation at Lake Gårdsjön in SW Sweden, where decreased anthropogenic deposition responded in runoff with decreased sulfate concentrations and increase in $\delta^{34}\text{S}$ (32, 38).

There is a clear distinction between each river in Figure 7: Thjorsá has the highest concentration of rock-derived sulfate (SO_4^{2-}), then in decreasing order Hvítá, Ölfusá, and Sog. This explains why the percent decline in total dissolved sulfate from 1972–1973 to 1996–2003 is small in Thjorsá compared to most other rivers (Table 1, and Figures 5–7). Close to 90% of the total dissolved sulfate, SO_4^{2-} , in Thjorsá was non-sea-salt sulfate, SO_4^{2-} , in 1972–1973 and in 1997–2003 using the $\text{Cl}^-/\text{SO}_4^{2-}$ ratio of seawater and assuming all Cl⁻ to stem from seawater (Table 1). As can be seen in Figure 7, most of the SO_4^{2-} stems from rocks in Thjorsá, explaining the relatively small decrease in SO_4^{2-} and SO_4^{2-} in Thjorsá (13%) compared to that of the other rivers (33–65%; Table 1).

The sulfur isotope variation from November 1998 to December 2004 for the rivers Thjorsá, Ölfusá, Hvítá, and Sog

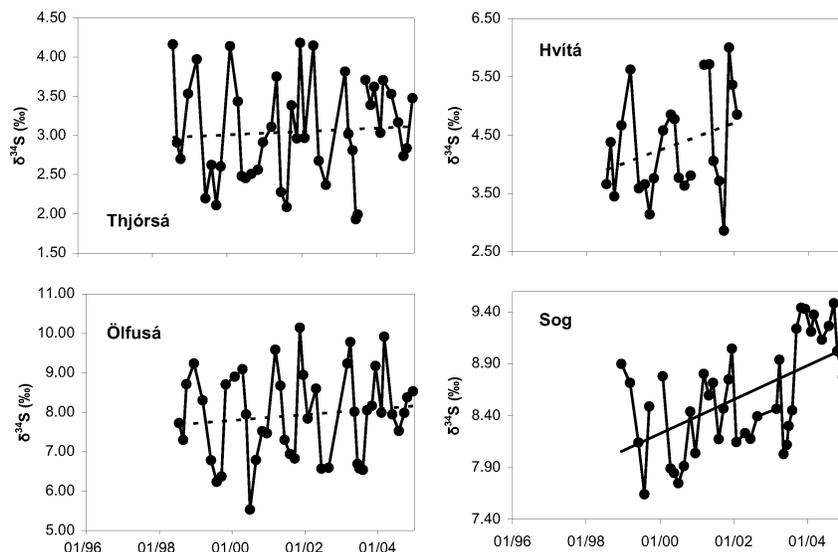


FIGURE 8. $\delta^{34}\text{S}$ values for rivers Thjórsá, Ölfusá, Hvítá, and Sog (Figure 4) as a function of time. The diagrams show regression lines of all the data. The solid line has a statistically significant slope.

is shown in Figure 8. Linear regression models of all the data reflect overall changes. The slopes are positive for all the time series, although only statistically significant for the river Sog. The $\delta^{34}\text{S}$ values increase with time for the rivers Sog, Hvítá, Ölfusá, and to a lesser extent for the river Thjórsá, in concert with the general decline in SO_2 emissions from Europe and the United States (Figure 1), the overall decline in dissolved SO_4^{2-} concentration of the Icelandic rivers (Figure 5; Table 1), the source of the dissolved sulfate (Figure 7; Table 1), and the projected relative change in $\delta^{34}\text{S}$ values of individual river waters following a decline in anthropogenic SO_2 emissions. The seawater, DMS, and rock source for the dissolved sulfate in the river waters has stayed relatively constant, while the man-made sulfate has declined from 1998 to 2004, increasing the $\delta^{34}\text{S}$ value of most of the rivers, keeping in mind the $\delta^{34}\text{S}$ values of all the endmembers. The least response is from the river Thjórsá since most of its sulfate is rock derived (Table 1 and Figures 7 and 8).

The overall decline in Icelandic river-dissolved sulfate, and increase in $\delta^{34}\text{S}$, demonstrates, without doubt, the response of river chemistry in the remote North Atlantic to the decline in man-made emission of SO_2 during the last 3 decades in North America and Europe. This underscores the importance of a global man-made source of SO_4^{2-} rather than a local Icelandic anthropogenic source and short-lived volcanic eruptions (Figures 1 and 3). These findings show that international agreements aimed at decreasing SO_2 emissions in North America and Europe have affected the sulfate concentration of Icelandic rivers, thousands of kilometers away from its source. Furthermore, this decline will extend into the Arctic, since Iceland sits in the main atmospheric transport route from Europe and North America to the Arctic (Figure 2).

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Authority, Iceland, Institute of Earth Sciences, University of Iceland, and the University of Stockholm.

Supporting Information Available

Excel tables with river names, sample number, date and time of sampling, Cl^- , SO_4^{2-} , and $\delta^{34}\text{S}$ values for the period from 1996 to 2004. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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