Water Resources Research

RESEARCH ARTICLE
10.1029/2021WR031777

Key Points:

- Despite colder conditions, Arctic catchments may host microbes that reduce between 5% and 20% of the river-transported sulfate concentrations
- Favorable landscape characteristics include vegetated terrain with lakes and wetlands, enabling longer microbial contact times
- Catchment-scale microbial sulfate reduction can act as a nature-based solution for (acid) mine drainage

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

S. Fischer,
sandra.fischer@natgeo.su.se

Citation:

Fischer, S., Mörth, C.-M., Rosqvist, G., Chalov, S. R., Efimov, V., & Jarsjö, J. (2022). Microbial sulfate reduction (MSR) as a nature-based solution (NBS) to mine drainage: Contrasting spatiotemporal conditions in northern Europe. *Water Resources Research*, *58*, e2021WR031777. https://doi.org/10.1029/2021WR031777

Received 8 DEC 2021
Accepted 12 APR 2022

Author Contributions:

Data curation: Sandra Fischer
Formal analysis: Sandra Fischer, Carl-Magnus Mörth
Investigation: Sandra Fischer, Gunhild Rosqvist, Sergey R. Chalov, Vasiliy Efimov, Jerker Jarsjö
Supervision: Carl-Magnus Mörth, Gunhild Rosqvist, Jerker Jarsjö
Writing – original draft: Sandra Fischer
Writing – review & editing: Carl-Magnus Mörth, Gunhild Rosqvist, Sergey R. Chalov, Vasiliy Efimov, Jerker Jarsjö

Microbial Sulfate Reduction (MSR) as a Nature-Based Solution (NBS) to Mine Drainage: Contrasting Spatiotemporal Conditions in Northern Europe

Sandra Fischer[1], Carl-Magnus Mörth[2], Gunhild Rosqvist[1], Sergey R. Chalov[3], Vasiliy Efimov[3], and Jerker Jarsjö[1]

[1]Department of Physical Geography and the Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden, [2]Department of Geological Sciences, Stockholm University, Stockholm, Sweden, [3]Faculty of Geography, M.V. Lomonosov Moscow State University, Moscow, Russia

Abstract An emerging solution in mine waste remediation is the use of biological processes, such as microbial sulfate reduction (MSR), to immobilize metals, reducing their bioavailability and buffering the pH of acid mine drainage. Apart from laboratory tests and local observations of natural MSR in, for example, single wetlands, little is known about spatiotemporal characteristics of freshwater MSR from multiple locations within entire hydrological catchments. We here applied an isotopic fractionation (δ^{34}S values in SO_4^{2-}) and a Monte Carlo-based mixing analysis scheme to detect MSR and its variation across two major mining regions (Imetjoki, Sweden and Khibiny, Russia) in the Arctic part of Europe under different seasonal conditions. Results indicate a range of catchment-scale MSR values in the Arctic of ~5%–20% where the low end of the range was associated with the non-vegetated, mountainous terrain of the Khibiny catchment, having low levels of dissolved organic carbon (DOC). The high end of the range was related to vegetated conditions provided by the Imetjoki catchment that also contains wetlands, lakes, and local aquifers. These prolong hydrological residence times and support MSR hot spots reaching values of ~40%. The present results additionally show evidence of MSR persistence over different seasons, indicating large potential, even under relatively cold conditions, of using MSR as part of nature-based solutions to mitigate adverse impacts of (acid) mine drainage. The results call for more detailed investigations regarding potential field-scale correlations between MSR and individual landscape and hydroclimatic characteristics, which, for example, can be supported by the isotopic fractionation and mixing scheme utilized here.

1. Introduction

Microbial sulfate reduction (MSR) has increasingly been investigated for its potential to immobilize metals and reduce their bioavailability while also increasing the pH of acid mine drainage (AMD; e.g., Nielsen et al., 2018). The process involves microbes (bacteria and archaea) converting sulfate into sulfide that together with toxic dissolved metals precipitate into less mobile forms. Laboratory bioreactor experiments on MSR show a metal retention of 70% or more under favorable conditions (e.g., Sinharoy et al., 2020; Zhang & Wang, 2016). The activity depends on several factors, such as (bioavailable) carbon and sulfate supply, oxygen level, pH, and temperature (Xu & Chen, 2020). MSR has also been observed in the field at certain locations and time periods, for example, in individual wetlands or near tailing deposits at particular points of time (Mandernack et al., 2000; Praharaj & Fortin, 2004). Recently, Fischer, Jarsjö, et al. (2022) additionally showed evidence of ongoing and considerable MSR in multiple locations (so-called "hot spots") within an AMD-impacted catchment (Imetjoki, Northern Sweden), which is essential if MSR is to be used as an effective mitigation solution for spatially extensive mining sites and their downstream regions. However, large knowledge gaps remain regarding catchment-scale MSR in freshwater systems, where specific catchment and seasonal conditions could differ substantially from site to site. It is therefore not known to what extent MSR more generally could provide a basis for viable bioremediation, for instance, as part of nature-based solutions for sites impacted by (acid) mine drainage across the world. This includes the Arctic, which counts as one of the world's larger mining regions with numerous examples of large-scale mine drainage development, and where cold conditions and pronounced seasonality may hamper the activity of freshwater sulfur-reducing microbes (SRM).

Current evidence shows that point locations which are relatively favorable for MSR contain soil and sediments with sufficiently high organic matter content to support the metabolism of SRM, and that they are associated with wetlands, lakes, or groundwater systems that prolong hydrological residence times and the general contact time for SRM (Hampton et al., 2019; Lindström et al., 2005). Such characteristics are found in the Imetjoki catchment where relatively high catchment-scale MSR was detected through a summer (August) field campaign (Fischer, Jarsjö, et al., 2022). Here, we hypothesize that in contrast, low-MSR catchments should have relatively limited vegetation/forest cover and steep topography that limits the number of lakes and wetlands as well as reduces residence times and therefore also SRM contact times. A northern European example of this is the Khibiny region in northwestern Russia where an active apatite mining complex is located (Efimov et al., 2019). The Khibiny catchments have been increasingly industrialized and polluted as a result of more than 90 years of ore extraction (Malinovsky et al., 2002).

Apart from impacts on MSR by regional topography and land cover conditions, it is reasonable to assume that MSR is impacted by the seasonality of hydroclimatic conditions. For instance, laboratory experiments generally show increased microbial activity with higher temperatures (e.g., Pellerin et al., 2020) although steady-state batch tests have shown that cold-tolerant bacteria may successfully reduce metal concentrations (Nielsen et al., 2018; Virpiranta et al., 2019). Field studies in temperate climates show indications of locally increased MSR during warmer summer periods (e.g., Praharaj & Fortin, 2004) although there are also reports on potentially high MSR levels during the winter (e.g., Björkvald et al., 2009; Fortin et al., 2000). Colder regions furthermore have a strong seasonal effect in runoff generation (e.g., frozen conditions vs. spring flood), implying that the mixing of water from different landscape compartments differs greatly over the year. This, together with annual fluctuations of water temperature, fundamentally changes the ambient conditions for SRM, supporting our working hypothesis that large-scale MSR values should vary over a hydrological year. A better understanding of the magnitude of such potential large-scale seasonal variations would be desirable in assessments of the overall effectiveness of MSR as a suitable mitigation solution. For the Arctic, for example, the suitability would most likely be related to whether or not the measures would be efficient for only a few favorable months per year.

The degree of MSR detected in water samples from catchments can be calculated using the isotopic fractionation model developed by Fischer, Jarsjö, et al. (2022). The method is based on the fact that sulfur isotope composition (of $\delta^{34}S$ in SO_4^{2-}) in surface water shows a distinct signal from SRM preferentially taking up ^{32}S during sulfur reduction while leaving ^{34}S in the remaining sulfate. To quantify for the first time the large-scale MSR sensitivity to contrasting catchment and seasonal conditions, we apply the isotopic fractionation model by Fischer, Jarsjö, et al. (2022) onto two major cold-climate mining-impacted regions: the Imetjoki catchment in northern Sweden containing the abandoned Nautanen copper mines (where ambient conditions were shown to be favorable for MSR during summer) and the actively mined Khibiny catchments on the Kola Peninsula, Russia. Specifically, we aim to quantify the large-scale MSR under (a) contrasting catchment conditions (i.e., spatial characteristics) of Imetjoki and Khibiny, and (b) contrasting seasonal conditions (i.e., temporal characteristics) in Imetjoki, extending snapshot observations of high MSR in late summer (Fischer, Jarsjö, et al., 2022) with observations during less-favorable snowmelt conditions in spring.

2. Materials and Methods

2.1. Site Descriptions

The Imetjoki catchment in northern Sweden covers 6.6 km^2 (Figure 1a–1c) and is underlain by igneous bedrock with sulfide deposits hosting iron oxide-copper-gold (IOCG) mineralization (Martinsson et al., 2016). Copper was mined mainly in five deposits distributed over the Imetjoki catchment. The mining operations were carried out between 1902 and 1908, resulting in about 20,000 ton of untreated mine waste still remaining on the site polluting the nearby environment (Fischer et al., 2020). The annual average temperature was −1.6°C (seasonal variation of 11 to −13°C) and the annual average precipitation was 560 mm/yr between the years 1993 and 2017 (Fischer et al., 2020). Annual average actual evaporation was 260 mm/yr (Fischer et al., 2020) and about 200 days per year were snow covered during the same time period (Berglöv et al., 2015). Forest and wetlands cover most of the Imetjoki catchment areas (SGU, 2020), except for the former so-called "Industrial area" where freely exposed tailings prevent revegetation (see also the detailed site characterization in Fischer et al., 2020).

The Khibiny alkaline massif on the Kola Peninsula (Figure 1d) consists of igneous rocks with titanite and apatite-nepheline deposits (Kogarko, 2018). The massif is surrounded by two larger lakes: the Umbozero Lake to the east and the Imandra Lake to the west with lake areas of 320 and 880 km^2, respectively (Figure 1; Dauvalter

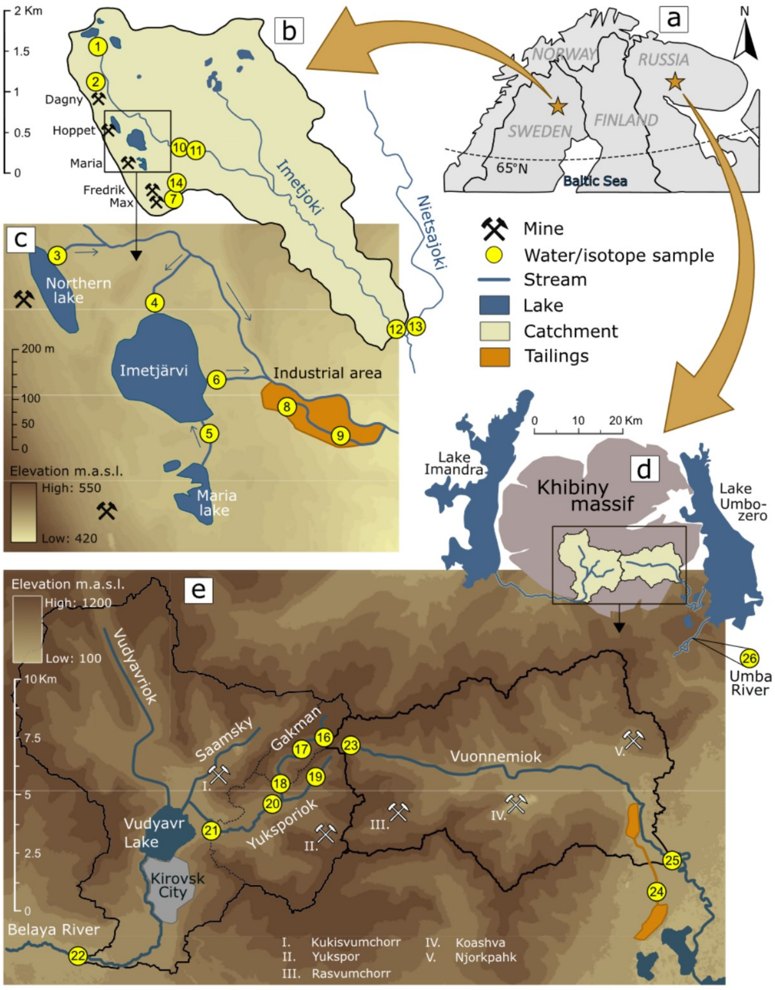


Figure 1. Map showing (a) the location of the two mining areas in northern Fennoscandia, namely (b) the Imetjoki catchment, including (c) the abandoned Nautanen copper mines and (d) the Khibiny massif with (e) the two investigated catchments Belaya and Vuonnemiok. ID 15 (reference Lina River) is not shown in the map and is located 5 km east of the Imetjoki catchment (see Fischer et al., 2020 for coordinates).

& Kashulin, 2010; Dinu et al., 2020). The Khibiny mountain valleys (Figure 1e) are characterized by sandy till deposits and a forest-tundra ecosystem, while the higher plateaus (with mountain peaks up to 1000 m above the Umbozero and Imandra Lakes) hold mostly weathered rocks and Arctic tundra (Pereverzev, 2010). The average annual temperature for the Khibiny massif was −0.59°C between 1993 and 2017 according to the data from the Climatic Research Unit (CRU) at the University of East Anglia described by Harris et al. (2014; see Supporting Information S1 on details). For the same time period, the annual average precipitation was 715 mm/yr and annual average actual evapotranspiration was 290 mm/yr (based on CRU data and same calculation procedure as for the Imetjoki catchment). About 210 days per year were snow covered between 1998 and 2007 (Callaghan et al., 2011). The southwestern part of the Khibiny massif is drained by the Belaya River that has a catchment area of 142 km^2 and an average annual discharge of 1900 l/s (ID 22 in Figure 1; derived from CRU data following the water balance calculation steps of Fischer et al., 2020) before reaching the Imandra Lake. Furthermore, the Belaya River (main branch) starts at the outlet of the Bolshoy Vudyavr Lake gathering tributary inflows from the Yuksporiok, Saamsky, and Vudyavriok sub-catchments (Figure 1e). The southeastern part of the massif is drained by the Vuonnemiok Stream with an annual average discharge of 1300 l/s (ID 25 in Figure 1; based on water balance calculations) that empties in the Umbozero Lake. Kirovsk City is the main settlement in the Khibiny massif where there are five apatite-nepheline ore deposits (Figure 1e) that have been actively mined since the 1930s. They are now owned by the company PhosAgro. The mining activity has led to elevated surface water concentrations of strontium (Sr) and aluminum (Al), as well as copper (Cu), zink (Zn), nickel (Ni), and chromium (Cr) in the Yuksporiok and Vuonnemiok basins (Efimov et al., 2019; Malinovsky et al., 2002). The Kola Peninsula also hosts several Cu-Ni ore smelters that have for decades emitted large volumes of sulfur dioxide into the air resulting in acid rain and high sulfur and metal atmospheric deposition (Moiseenko & Bazova, 2016).

2.2. Field Campaigns and Analyses

Surface water sampling and measurement campaigns were conducted in the Imetjoki catchment in the spring (end of May during snowmelt) and in the late summer (end of August) of 2017. Apart from element concentrations and general water quality parameters (e.g., pH, dissolved organic carbon, etc.; presented in Fischer et al., 2020), sulfur isotopes ($\delta^{34}S_{SO4}$ values in $SO_4{}^{2-}$) were measured. In total, 11 locations were sampled for sulfur isotopes and sulfur concentrations in the spring and 13 locations were sampled in the summer (the latter used here for comparison, being presented in Fischer, Jarsjö, et al., 2022). Nine sampling locations were common for both campaigns. The sampling locations were distributed over the upstream areas (undisturbed by mining; IDs 1–2 in Figure 1), the mining site itself (directly affected by AMD; IDs 3–9), and downstream of the mining site (IDs 10–12, 14). Two adjacent rivers were also sampled for reference (IDs 13, 15). The same sampling and analysis procedures were followed in both the spring and summer campaigns as described in Fischer, Jarsjö, et al. (2022), making the results directly comparable. The sulfur isotopic composition was determined from collecting 2L water samples that were dripped through ion exchange resin columns to collect the sulfate in water and for easier transportation to the laboratory. Instrumental analyses were carried out with an elemental analyzer (CarloErba NC2500) coupled to a stable isotope ratio mass spectrometer (Finnigan Thermo Delta plus; analytical accuracy was ±0.2‰) at the laboratories of the Department of Geological Sciences at Stockholm University. Sulfur isotopes are reported in parts per million (‰) through the δ-notation relative to the Vienna-Canyon Diablo Troilite (V-CDT) standard:

$$\delta_{sample}(‰) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) 1000 \tag{1}$$

where R represents the $^{34}S/^{32}S$ ratio.

Surface water was sampled from rivers draining the Khibiny massif in late August in 2017 using an equivalent sampling strategy as the one performed in the Imetjoki catchment (following Fischer et al., 2020; Fischer et al., 2022). More specifically, the Belaya catchment and Vuonnemiok catchments were sampled within three zones: the upstream areas unaffected by the mining sites (IDs 16–19, 23 in Figure 1), the mining areas comprising the mine effluents (IDs 20–21, 24), and the downstream areas (IDs 22 and 25). An additional sample was collected from the Umba River (ID 26; draining the Umbozero Lake catchment), which corresponds to about 30 km downstream of the Vuonnemiok catchment.

2.3. Isotopic Fractionation and Mixing Scheme

Both the Imetjoki and Khibiny catchments were assumed to have two major sulfur isotopic end-members: sulfur from atmospheric deposition (δ_{dep}; composed of sulfur from both sea spray and fossil fuel emissions) and geogenic sulfur from weathered bedrock (δ_{rock}). This allowed us to apply the sulfur isotopic fractionation and mixing scheme developed by Fischer, Jarsjö, et al. (2022) to quantify MSR and its variation within each site. The quantifications are made based on stream water samples from which net MSR values are estimated. These MSR values reflect net (downstream) impacts of local MSR along the sub-catchment's flow paths, some of which may support considerable MSR (e.g., flow paths through wetlands or deep groundwater), whereas other may not support MSR or have negligible MSR only (e.g., fast macropore flow through upper soil layers or water from melting snow). In summary, the method compares stream water field measurements (representing potential post-MSR conditions) with theoretical predictions derived from sulfur end-member mixing (representing initial or pre-MSR conditions). Deviations between these two are assumed to be due to MSR. Although other microbial processes apart from MSR could contribute to isotopic deviations, they either represent only smaller/negligible fractionation (e.g., assimilatory sulfate reduction; Sharp, 2017) or they can be registered only when sulfur concentrations are much higher (e.g., sulfur disproportionation in marine/laboratory environments; Böttcher et al., 2005) than in our study environments. A theoretical stream water sample (δ_{sample}) is then in the considered conservative case composed of proportional fractions of each end-member (f_{dep} and f_{rock}, respectively) according to the principle of mass balance:

$$\delta_{sample} = \delta_{dep} f_{dep} + \delta_{rock} f_{rock} \tag{2}$$

so that $f_{dep} + f_{rock} = 1$. This theoretical mixing was quantified by applying a Monte Carlo simulation (as similarly executed in, e.g., Samborska et al., 2013), where end-member parameter values were randomly sampled from their independently observed regional parameter distributions (obtained, e.g., from a literature review, see below) to create 10,000 different theoretical initial conditions (i.e., the assumed stream water isotopic composition before MSR). A Rayleigh fractionation model was then applied to calculate the residual fraction of sulfur concentration after reduction (f_{red}). The model is based on the initial isotopic composition of the stream water (δ_0; here represented by the 10,000 theoretical predictions of δ_{sample}) and the residual isotopic composition in the stream water (δ_R; represented by the observed isotopic value of stream water δ_{stream}), according to:

$$\delta_R = \left(\frac{0.001\delta_0 + 1}{0.001\varepsilon\,(1 - f_{red}) + 1} - 1 \right) 1000 \tag{3}$$

where ε represents the isotopic enrichment factor. This Rayleigh model (Equation 3) was developed from a standard Rayleigh model (Mariotti et al., 1981) by Druhan & Maher (2017) to better represent isotope fractionation processes in water mixtures subject to different travel times—such as the case for a stream water sample in a catchment, where travel times will differ between different flow pathways within the catchment. Further, MSR was assumed to be equally likely at both end-members as well as the point of mixing; this was in order to conserve pre-MSR end-member fractions to post-MSR conditions. MSR was finally quantified as the percentage of reduced sulfur concentration, that is, MSR = $100(1 - f_{red})$. Estimates of end-member parameter values (δ_{dep}, δ_{rock}, and the sulfur concentration of atmospheric deposition, c_{dep}) as well as the enrichment factor (ε) were derived from a synthesis of regional observations and previously reported literature values.

To better quantify the median and average Monte Carlo outputs when MSR values were close to 0%, we have modified the analysis methodology presented in Fischer, Jarsjö, et al. (2022) where a theoretical model output below 0% was truncated (since MSR cannot physically be lower than 0%). This truncation becomes problematic for the current study because we consider average values relatively close to 0% and get both positive and negative random errors of which only the negative random errors will be truncated following the rule. This leads to an overestimation of MSR values derived from the resulting ensemble statistics, and to keep the output unbiased, we omitted the truncation rule.

3. Results

3.1. Regional Data Synthesis

Regional sulfur isotopic end-member data (c_{dep}, δ_{dep}, and δ_{rock}) for the Kola Peninsula and northern Sweden are summarized in Table 1. The Kola Peninsula showed a higher average annual c_{dep} compared to northern Sweden. It is likely the result of nearby smelter emissions of sulfur dioxide (Forsius et al., 2010; Reimann et al., 1997), while also the higher δ_{dep} has been attributed to the processing of high sulfide ores, which were transported from the Norilsk mine in northcentral Russia to Kola smelters (de Caritat et al., 1997). No data were found on the specific δ_{rock} value of sulfide bedrock in Khibiny. We argue that since the Khibiny bedrock is of magmatic origin (Kogarko, 2018)—as is the bedrock in the Imetjoki catchment—sulfide minerals in Khibiny would most likely

Table 1
Regional Data Synthesis Over Sulfur (S_{SO4}) Concentration in Atmospheric Deposition (c_{dep}), Sulfur Isotopic Composition ($\delta^{34}S_{SO4}$) in Atmospheric Deposition (δ_{dep}), and Sulfur Isotopic Composition ($\delta^{34}S$) in Bedrock (δ_{rock}) in Northern Sweden and on the Kola Peninsula

Parameter		Median	Mean	Std Dev	Min	Max	Data source*
c_{dep}(mg/L)	N. Sweden	0.48	0.57	0.32	0.13	1.7	Observed annual c_{dep} between 1982 and 2017 from 11 locations in northern Sweden, also used in calculations presented in Fischer, Jarsjö, et al. (2022). c_{dep} is composed of 9% sea spray and 91% of fossil fuel combustion.
	Kola Peninsula	0.90	1.42	1.5	0.11	10.2	Observed annual c_{dep} between 1990 and 2017 from 13 locations on or in the vicinity of the Kola Peninsula (Arctic Monitoring and Assessment Programme, 2006; EBAS, 2021; Malinovsky et al., 2002; Reimann et al., 1997; Äyräs et al., 1995). c_{dep} is composed of 8% sea spray and 92% of fossil fuel combustion.
δ_{dep}(‰)	N. Sweden	+5.4	+5.3	0.69	+3.8	+7.0	Reported values of $\delta^{34}S_{SO4}$ in samples of snow and precipitation from the Kalix River Basin, which encompasses the Imetjoki stream, between 1990 and 1991 (Ingri et al., 1997), also used in Fischer, Jarsjö, et al. (2022).
	Kola Peninsula	+6.6	+6.9	1.07	+4.3	+8.7	Reported values of $\delta^{34}S_{SO4}$ in epiphytic moss samples (*Hylocomium splendens* and *Pleurozium schreberi*) from the Kola Peninsula during the summer 1994 (de Caritat et al., 1997). Since epiphytic mosses rely foremost on air for moisture and nutrients, they provide long-term average sulfur isotopic values close to the isotopic composition of atmospheric deposition with only minor (<1–2‰) isotopic fractionation (assimilation) during the uptake in the plant (Liu et al., 2009; Migaszewski et al., 2010; Xiao et al., 2015).
δ_{rock}(‰)	N. Sweden & Kola Peninsula	−0.60	−0.54	1.0	−3.4	+3.3	Reported $\delta^{34}S$ values for sulfide minerals of magmatic origin (pyrite-chalcopyrite deposits) at the copper mine Aitik in northern Sweden (Yngström et al., 1986) as also used in Fischer, Jarsjö, et al. (2022). Due to the magmatic origin of the Khibiny massif, sulfide minerals are likely to also have isotopic values close to 0‰, which justify using the values reported by Yngström et al. (1986) also for the Khibiny data set.

*Note.** See details in Text S2 in Supporting Information S1.

also have δ_{rock} values close to 0‰ justifying the use of the isotopic data set for Imetjoki also for the Khibiny catchments (Table 1). A reasonable range for the enrichment factor (ε) in shallow groundwater and surface waters was assumed to be −33 to −1‰, considering that most studies report values between −20‰ and −10‰ (Knöller et al., 2004; Robertson & Schiff, 1994; Wu et al., 2011), while some estimates reach as low as −33‰ (Massmann et al., 2003) and as high as −1‰ (Xia et al., 2017).

3.2. Surface Water Measurements

The measurement campaigns in the Imetjoki catchment in the spring (May) and summer (August) of 2017 revealed high surface water concentrations (15–5,000 μg/L) of Cu, Zn, and Cd at and downstream of the mining site, where the dissolved organic carbon (DOC) ranged between 1.3 and 11.6 mg/L and pH-levels were between 3.3 and 7.1 (Fischer et al., 2020). No systematic differences in concentrations could be seen between the seasons except for DOC, which were higher in all samples (on average 30%) from the summer compared to the spring. The measured sulfur isotope composition (δ_{stream}) and total sulfur (S) concentrations (c_{stream}) are plotted in Figure 2a together with a so-called "theoretical mixing line," which shows a hypothetic proportional mixing between the two end-members without the influence of MSR. The mixing line is defined through corresponding average regional values for each end-member (Table 1) where the gray area conveys the ±1 standard deviation range. Overall, δ_{stream} values measured in the spring (May) in Imetjoki (hollow circles; Figure 2a) lie closer to the theoretical mixing line than δ_{stream} measured in the summer (August). This is further illustrated in Figure 2b where the highest difference in δ_{stream} between spring and summer was seen in the Imetjärvi Lake inlet (ID 4; +2.8‰) and the Northern Lake outlet (ID 3; +2.5‰). The samples from the Northern Lake, Downstream 1, and Maria Lake sites (IDs 3, 5, and 10) all show an increase in c_{stream} by 60%–70% over the summer, while the values for the stream in the lower Industrial area (ID 9) only increased by 11% (i.e., from 20.5 mg/L in the spring to 22.8 mg/L in the summer; Table S2 in Supporting Information S1). The only decrease in c_{stream} was detected in samples from the small brook in the upper Industrial area (ID 8) where the concentration decreased from 48 to 17 mg/L over the summer.

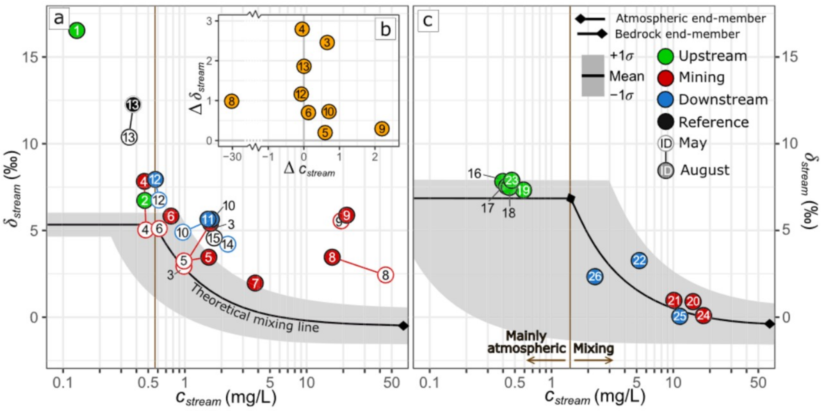


Figure 2. Measured stream water $\delta^{34}S_{SO4}$ values (δ_{stream}) and total sulfur (S) concentration (c_{stream}) for (a) the Imetjoki catchment and (b) corresponding seasonal difference between August and May and (c) Khibiny catchments. The theoretical mixing line represents proportional mixing of two average end-members based on the regional data synthesis in Table 1, where the gray area covers the respective ±1 standard deviation (σ) for each end-member. The regional mean sulfur (S_{SO4}) concentration in atmospheric deposition (c_{dep}) for each site is illustrated with a vertical line at 0.57 mg/L for the Imetjoki catchment and at 1.42 mg/L for the Khibiny catchments.

The surface waters within the Khibiny catchments showed clearly higher metal concentrations (3–24 μg/L for Cu, Zn, and Cr) close to the mining areas compared to the concentrations in the upstream areas unaffected by mining (with average concentrations of 0.2–0.7 μg/L for Cu, Zn, and Cr; see Table S6–S7 in Supporting Information S1 and Fischer, Mörth et al. (2022) for full analysis results). DOC levels were generally low in upstream areas (~1 mg/L) and increased only slightly (1.7–3.2 mg/L) in the mining-impacted and downstream areas. The pH ranged between 6.8 and 10.6 for all Khibiny samples and all measured (total) sulfur concentrations occurred in the form of sulfate. All of the measured δ_{stream} values in Khibiny are falling either on or within 1 standard deviation from the theoretical mixing line (Figure 2c), which indicates that end-member mixing alone (with no/little isotopic fractionation) explains most of the spread in the values. Compared to the wide spread in sulfur isotopic data within the Imetjoki catchment, the Khibiny values formed two clear clusters; all upstream sampling points (IDs 16–19, 23) grouped toward the top-left corner with a small range in both δ_{stream} and c_{stream}, displaying a clear signal from the atmospheric deposition end-member, while results from the mining impacted sampling points (IDs 20, 21, and 24) grouped in the lower right corner in a similarly narrow range, likely portraying the bedrock end-member (see detailed results in Table S6–S7 in Supporting Information S1). The Yuksporiok 3 data (ID 21) represent a 3-day average value from which the corresponding coefficients of variation (CVs) were 0.22 and 0.14 for δ_{stream} and c_{stream}, respectively. A clear mining-impacted signal was derived from the downstream Vuonnemiok 3 sampling point (ID 25), while samples from the Umba River (ID 26) and Belaya River (ID 22) show a mix of the two end-members, however still within 1 standard deviation from the mixing line.

3.3. Calculated MSR in the Imetjoki and Khibiny Catchments

The Monte Carlo simulations for sampling points within the Imetjoki catchment resulted in an overall interquartile range between 10% and 37% MSR for both the spring and summer with the catchment-scale median MSR being 19% (mean: 27%; see full output details in Table S3–S4 in Supporting Information S1). A clear difference can be seen between the seasons (Figure 3), where the Monte Carlo MSR outputs in the spring (yellow probability density distributions) lie closer to the 0% line compared to the MSR distributions in the summer (purple density distributions). For locations sampled in both seasons, the difference in catchment-scale MSR was 9% units over the summer (i.e., 14% median MSR in the spring and 23% in the summer; Figure 3). The highest increase in MSR was detected at the Northern Lake outlet (from a median of 5% in spring to 24% in summer) and the Imetjärvi inlet (from 4% to 20%, respectively), which is also shown in Figure 2b where these two sampling points (IDs 3 and 4) had the highest increase in measured isotopic value from spring to summer. The smallest seasonal change was found in samples representing the Industrial area (ID 9), where high median MSR was found both in the spring (32%) and in the summer (34%).

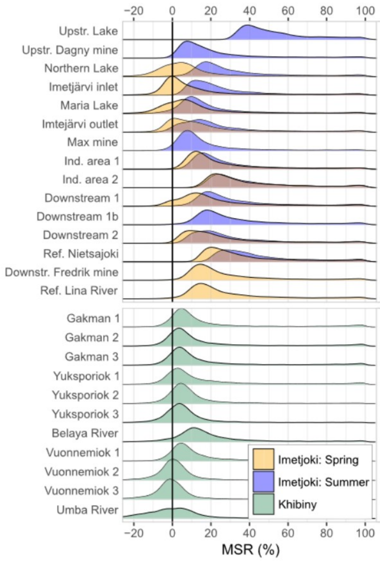
The samples from the Khibiny catchments show an interquartile range of MSR values between 0% and 15% with a catchment-scale median MSR value of 7% for Yuksporiok (mean: 16%) and as low as 2% for Vuonnemiok (mean: 7%; see full output details in Table S5 in Supporting Information S1). The highest MSR (14%) in Khibiny was found in the Belaya River (ID 22), which may be impacted by potential MSR in the Vudyavr Lake and the other two (unmonitored) tributaries (Vudyavriok and Saamsky; Figure 1). However, the estimation for this location is uncertain as it may be biased from a potential release of additional sulfur from Kirovsk City, for example, as municipal wastewater having another and here unaccounted for isotopic signal.

4. Discussion

4.1. Catchment Conditions Affecting Natural MSR

The Imetjoki and Khibiny catchments share similar climatic features (e.g., temperature and number of days with snow coverage), and the sulfur concentrations of their water systems show overlapping ranges. However, we found that catchment-scale median MSR values in Imetjoki (summer season) were about 18% units higher than the catchment-scale median MSR values in Khibiny during the same summer season (23% MSR vs. 5%). This supports our working hypothesis that some fundamental conditions are more favorable for MSR in the Imetjoki catchment compared to the Khibiny catchments. For instance, organic material was more abundant in the Imetjoki stream water most likely due to its forest cover, yielding higher DOC concentrations from decomposing vegetation. Direct effects of an increase in organic matter concentration on natural MSR have previously been observed in southern Finland (Bomberg et al., 2015), where organic material was added to acidic water in flooded

10.1029/2021WR031777



ID	MSR (%) Median Spring	MSR (%) Median Summer	MSR (%) Average Spring	MSR (%) Average Summer
1	-	47.9	-	53.4
2	-	14.5	-	23.4
3	5.3	24.1	10.9	32.8
4	4.4	20.2	13.7	28.8
5	7.1	13.5	13.1	21.2
6	10.0	17.6	17.9	25.5
7	-	11.0	-	18.4
8	17.4	22.0	26.2	30.8
9	31.7	33.6	40.3	41.5
10	16.0	25.4	23.8	34.1
11	-	24.8	-	33.5
12	18.8	23.8	27.3	32.2
13	29.0	38.3	36.9	45.4
14	20.4	-	29.3	-
15	20.5	-	29.2	-
16		8.6		19.6
17		7.0		18.1
18		7.5		18.4
19		7.5		18.6
20		5.9		10.6
21		4.5		8.3
22		14.2		20.7
23		8.8		19.9
24		0.6		1.7
25		−1.2		−1.0
26		−1.2		1.3

Figure 3. Probability density distributions from the Monte Carlo simulations for calculated microbial sulfate reduction (MSR) for the Imetjoki (upper panel) and Khibiny (lower panel) catchments. MSR distributions in the Imetjoki catchment also reflect the two seasonal conditions from the spring (yellow density distributions) and the summer (blue density distributions).

mine shafts to induce MSR, which over the course of 15 years successfully increased the pH and decreased the metal concentrations. Although stream water DOC concentrations reflect the general supply of organic matter in the catchment, the available fraction of DOC for SRM is usually much smaller than the stream water concentrations since SRMs require already degraded organic matter (e.g., low molecular weight substrates; Muyzer & Stams, 2008), which means that the type of organic matter is also important to MSR (Berggren et al., 2007; van Hees et al., 2005). Furthermore, the anoxic environments required for MSR (Pester et al., 2012) as well as relatively slow residence times allowing for longer exposure to SRM (Nelson et al., 2009) are likely present at multiple "hot spot" locations within the Imetjoki catchment, which contains 11 small lakes and has about 16% of its total area covered by peatlands (SGU, 2020). High $\delta^{34}S$ values in wetland-dominated sub-catchments (relative to other sub-catchments) have previously also been attributed to MSR (Björkvald et al., 2009). Notably, although most surface waters were only slightly acidic (pH 5.7–7.1), a few locations within the Imetjoki catchment displayed high metal concentrations and/or strongly acidic water (pH 3.3–4.8), which are potentially harmful to SRM (Xu & Chen, 2020). These strongly acidic waters were nonetheless associated with nonnegligible MSR levels. For example, the Industrial area (ID 8) had in the spring a pH of 3.3 and a Cu concentration of 5,000 μg/L and still showed a median MSR of 17%. An explanation could be that the local stream network has developed acid-tolerant SRM, considering that mine drainage from the Nautanen mines has been developed during a long time over the past 110 years, reaching a condition that can be described as nearly a steady state with regard to the considerable downstream pollution transport (Fischer et al., 2020).

The water from Belaya and Vuonnemiok catchments of Khibiny on the other hand showed low median MSR values (5%), which is consistent with the prevailing high alpine environments characterized by bare rocks and snow fields remaining over the summer, and the fact that they have been increasingly industrialized over the last century (Moiseenko et al., 2009). Both these factors contribute to the sparse forest cover of the Khibiny catchments, occurring only in the lower valleys outside of built areas, yielding generally low DOC concentrations (1–3 mg/L), as measured within the catchments in 2017. Furthermore, the high alpine environment spanning elevations between 100 and 1,200 m above sea level is characterized by steep slopes and a thin soil layer, which contributes to relatively fast throughflow of precipitation (i.e., shorter hydrological residence times). For instance, the Gakman sub-catchment (6.2 km^2; IDs 16–18) has a slope of 0.07 m/m, while the Imetjoki catchment (6.6 km^2) has a slope of 0.03 m/m. Whereas the Gakman sub-catchment in Khibiny on average had relatively similar pH (6.8–7.4) as Imetjoki, the Yuksporiok mining area in Khibiny (IDs 20–21) had highly basic pH (10.2–10.6), which potentially is another factor that can limit the MSR values. Conclusive evidence regarding how much (high) pH may limit natural MSR seem however still to be lacking, since some studies have shown the presence of considerable SRM in alkaline waters, for example, up to pH 9.8 in mine shafts in southern Finland (Bomberg et al., 2015) and in mine tailings with pH up to 9.3 in New Zealand (Chappell & Craw, 2003).

4.2. Seasonal Conditions Affecting Natural MSR

The presented results regarding impacts of seasonality show that the catchment-scale MSR values under spring conditions with ongoing snowmelt were lower (14%) compared to MSR values under summer conditions (23%). This difference suggests that there is a summer "boost" in the activity of SRM. For instance, between early spring (May) and summer (August), the average catchment-wide water temperatures rose from 3.8 to 11.5°C, which is more favorable even for cold-tolerating bacteria (Virpiranta et al., 2019). However, the isolated effect of temperature (and the seasonal changes of it) on field-scale MSR is difficult to determine since multiple factors are likely interacting (Khan et al., 2019; Praharaj & Fortin, 2004). Two such factors that showed pronounced seasonality in Imetjoki are DOC, which increased on average with 30% over the summer (Fischer et al., 2020), and sulfur concentrations, which increased with 26% (Figure 2b; excluding ID 8 that decreased by almost 3 times). This also means that sites in warmer climates with usually increasing summer bioproductivity and DOC turnover would likely enable even higher such "boosting."

Another potentially influential factor is that the sampled spring stream water represents a mixture of groundwater-dominated baseflow and more surficial flows including meltwater. The latter may remain on top of or near the soil surface since the ground would still be frozen during spring, hindering infiltration and groundwater recharge. MSR along meltwater flow paths may therefore be negligible, implying that the associated flows would be isotopically characterized by sulfur from atmospheric deposition in contrast to the groundwater-dominated baseflow, which potentially can be affected by MSR. Hence, a key issue for understanding the mechanisms behind seasonal changes in net MSR is then to assess the dilution caused by meltwater as given by the relative fractions of meltwater and baseflow in the sampled stream water. Thorough investigations by Laudon et al. (2007) showed that meltwater percentages during the spring flood ranged between 10% and 30% of the total water volume in stream water in forested catchments of northern Sweden. This implies that even during the here considered spring campaign at Imetjoki, most (70%–90%) of the sampled stream water volumes are likely to have originated from flow paths with potentially active MSR. Considering a hypothetical case in which the meltwater presence is at the high end of the range (30%), recognizing that the meltwater should have an isotopic composition relatively similar to the composition of the atmospheric deposition (because of the essentially lacking MSR in meltwater), mass balance considerations then allow the estimation of the isotopic composition of the remaining 70% of the sample originating from baseflow as well as the associated MSR value. Results for instance showed that compared to downstream net MSR values (including snowmelt impacts) of 16–19% (at IDs 10 and 12; Figure 3), the MSR in the baseflow component would be somewhat higher, namely 18–23%. This is however not as high as the downstream MSR values observed during the summer campaign (24–25; at IDs 10 and 12; Figure 3), implying that snowmelt impacts only partially can explain the differences in MSR values between spring and summer. Snowmelt impacts will however likely vary from location to location as well as from region to region and may therefore need further attention in future studies.

Apart from above-discussed systematic differences between the MSR values in spring and in summer, we note that locally high MSR values can occur (also) during the spring season. For instance, the MSR value was 30%

during spring at ID 9. Observations of relatively high MSR (before onset of dilution of meltwater) were similarly observed at the Krycklan catchment in northern Sweden (e.g., Björkvald et al., 2009) and at Lake Mjösjön in central Sweden where winter ice-coverage gave a gradual decrease in lake water oxygen levels and by that favored MSR (e.g., Andersson et al., 1992).

4.3. Implications—MSR as a Nature-Based Solution to Mine Drainage Under Ambient Changes

The present study supports previous cold region studies (e.g., Fischer, Jarsjö, et al., 2022) in detecting high MSR values locally (30%–40% under natural conditions). We additionally found novel evidence of a more general presence of MSR over different seasons even under the considered cold (Arctic) conditions, which indicates that there is large potential for using MSR as part of nature-based solutions to mitigate adverse impacts of (acid) mine drainage in the Arctic and elsewhere. For instance, this can be obtained through managing and taking advantage of favorable MSR conditions in (constructed) wetland and lake systems. Enhancement measures could be carried out by adding organic material in sedimentation ponds or mining shafts (e.g., Bomberg et al., 2015) utilizing already existing structures to provide prolonged residence times and possible anaerobic bottom layers.

The Arctic is currently subject to considerable climate-driven shifts in the carbon cycle that are projected to continue in the foreseeable future. There is notably an observed trend of increasing DOC values in streams (Guo et al., 2007), which is favorable for MSR (Bomberg et al., 2015), and will therefore probably act to enhance MSR over vast regions. Conversely, the increasing number of snow- and ice-free days (e.g., Box et al., 2019) will increase vertical fluxes of water and oxygen in upper soil layers, which in turn may decrease MSR in some locations by removing associated pockets of anaerobic conditions (e.g., see similar discussion in Palomo et al., 2013). Unless such MSR-driven changes and their impact on the retention of metals and other substances along their transport pathways are recognized and understood, they may—if detected through downstream monitoring—be misinterpreted as changes in metal mobilization. For instance, increased retention by (neglected) MSR may be at risk of being misinterpreted as decreased source zone mobilization of metals. The metal mobilization (e.g., at mining waste heaps) is notably also expected to be impacted by ongoing hydroclimatic changes although through quite different processes (e.g., Hotton et al., 2020; Jarsjö et al., 2020; Shrestha et al., 2020). A key challenge in understanding the role of MSR in mitigation solutions to (acid) mine drainage is therefore to consider how it may impact the balance between mobilization and retention under conditions of future ambient changes.

5. Conclusions

We here interpret and compare the results from multiple stream water measurements in two major Arctic mining regions, allowing us for the first time to quantify net impacts of catchment conditions and seasonality on large-scale MSR. This reflects a combination of multiple drivers and large-scale processes that, for example, are difficult to reproduce in laboratory experiments. Specifically, we conclude that:

1. A likely range of catchment-scale MSR values in the Arctic is ∼5%–20% during the summer season with catchments located in vegetated terrain containing wetlands, lakes, or voluminous groundwater systems that allow longer reaction times for SRM being more likely to show median MSR values of around ∼20%.
2. Local values of MSR can be as high as ∼40% at hot spot conditions, for example, near lakes, indicating large potential for using MSR as part of nature-based solutions to mitigate adverse impacts of (acid) mine drainage.
3. Evidence of persistent field-scale MSR over different seasons in the Arctic indicate that microbial processes and their interactions with the environment may be more persistent than previously anticipated.

The present results showing widespread and persistent MSR even under cold conditions call for more detailed investigations regarding potential field-scale correlations between MSR and individual landscape and hydroclimatic characteristics (e.g., DOC, water temperature, ice cover, vegetation, and slope), which, for example, can be supported by the here utilized isotopic fractionation and mixing scheme.

Data Availability Statement

The resulting data sets from the field measurement campaign in Khibiny 2017 are available through Zenodo at https://doi.org/10.5281/zenodo.6448039.

Acknowledgments
This research was funded by Nordforsk Centre of Excellence for Resource Extraction and Sustainable Arctic Communities (REXSAC, project no. 76938). Fieldwork was funded by Göran Gustafsson Foundation and EU INTERACT (International Network for Terrestrial Research and Monitoring in the Arctic) Transnational Access project "Baseline Conditions and Arctic Mining Impacts under Hydro-Climatic Change (BCAM)." Additionally, this paper has been supported by the Kazan Federal University Strategic Academic Leadership Program. We further acknowledge Heike Siegmund (Department of Geological Sciences) at the laboratory at Stockholm University for her helpful assistance during the sulfur isotope analysis. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Andersson, P., Torssander, P., & Ingri, J. (1992). Sulphur isotope ratios in sulphate and oxygen isotopes in water from a small watershed in Central Sweden. *Hydrobiologia*, *235*(1), 205–217. https://doi.org/10.1007/BF00026213

Arctic Monitoring and Assessment Programme. (2006). *AMAP assessment report: Acidifying pollutants, Arctic haze, and acidification in the Arctic*. Arctic Monitoring and Assessment Programme.

Äyräs, M., de Caritat, P., Chekushin, V. A., Niskavaara, H., & Reimann, C. (1995). Ecogeochemical investigation, Kola peninsula: Sulphur and trace element content in snow. *Water, Air, and Soil Pollution*, *85*(2), 749–754. https://doi.org/10.1007/BF00476919

Berggren, M., Laudon, H., & Jansson, M. (2007). Landscape regulation of bacterial growth efficiency in boreal freshwaters. *Global Biogeochemical Cycles*, *21*(4). https://doi.org/10.1029/2006GB002844

Berglöv, G., Asp, M., Berggreen-Clausen, S., Björck, E., Axén Mårtensson, J., Nylén, L., et al. (2015). *Framtidsklimat i Norrbottens län - enligt RCP-Scenarier [English: Future Climate in Norrbotten County - Based on RCP Scenarios]* (Vol. 32, p. 91). Swedish Meteorological and Hydrological Institute, Klimatologi Nr. (in Swedish).

Björkvald, L., Giesler, R., Laudon, H., Humborg, C., & Mörth, C.-M. (2009). Landscape variations in stream water SO_4^{2-} and δ34SSO4 in a boreal stream network. *Geochimica et Cosmochimica Acta*, *73*(16), 4648–4660. https://doi.org/10.1016/j.gca.2009.05.052

Bomberg, M., Arnold, M., & Kinnunen, P. (2015). Characterization of the bacterial and sulphate reducing community in the alkaline and constantly cold water of the closed Kotalahti Mine. *Minerals*, *5*(3), 452–472. https://doi.org/10.3390/min5030452

Böttcher, M. E., Thamdrup, B., Gehre, M., & Theune, A. (2005). $^{34}S/^{32}S$ and $^{18}O/^{16}O$ fractionation during sulfur disproportionation by desulfobulbus propionicus. *Geomicrobiology Journal*, *22*(5), 219–226. https://doi.org/10.1080/01490450590947751

Box, J. E., Colgan, W. T., Christensen, T. R., Schmidt, N. M., Lund, M., Parmentier, F.-J. W., et al. (2019). Key indicators of Arctic climate change: 1971–2017. *Environmental Research Letters*, *14*(4), 045010. https://doi.org/10.1088/1748-9326/aafc1b

Callaghan, T. V., Johansson, M., Brown, R. D., Groisman, P. Y., Labba, N., Radionov, V., et al. (2011). The changing face of Arctic snow cover: A synthesis of observed and projected changes. *Ambio*, *40*(1), 17–31. https://doi.org/10.1007/s13280-011-0212-y

Chappell, D. A., & Craw, D. (2003). Environmental controls on iron-oxidising, sulfur-oxidising and sulfate-reducing bacteria in mine wastes, New Zealand. *New Zealand Journal of Marine & Freshwater Research*, *37*(4), 767–775. https://doi.org/10.1080/00288330.2003.9517207

Dauvalter, V. A., & Kashulin, N. A. (2010). Chalcophile elements (Hg, Cd, Pb, As) in lake Umbozero, Murmansk province. *Water Resources*, *37*(4), 497–512. https://doi.org/10.1134/S0097807810040093

de Caritat, P., Krouse, H. R., & Hutcheon, I. (1997). Sulphur isotope composition of stream water, moss and humus from eight arctic catchments in the Kola Peninsula region (NW Russia, N Finland, NE Norway). *Water, Air, & Soil Pollution*, *94*(1/2), 191–208. https://doi.org/10.1023/A:1026498824698

Dinu, M. I., Shkinev, V. M., Moiseenko, T. I., Dzhenloda, R. K., & Danilova, T. V. (2020). Quantification and speciation of trace metals under pollution impact: Case study of a subarctic lake. *Water*, *12*(6), 1641. https://doi.org/10.3390/w12061641

Druhan, J. L., & Maher, K. (2017). The influence of mixing on stable isotope ratios in porous media: A revised Rayleigh model. *Water Resources Research*, *53*, 1101–1124. https://doi.org/10.1002/2016WR019666

EBAS. (2021). *EBAS database*. Norwegian Institute for Air Research. (NILU) [WWW Document]. URL Retrieved from http://ebas.nilu.no/

Efimov, V. A., Chalov, S. R., Efimova, L. E., Ivanov, V. A., Jarsjö, J., & Fischer, S. (2019). Impact of mining activities on the surface water quality (case study of Khibiny mountains, Russia). *IOP Conference Series: Earth and Environmental Science*, *263*, 012008. https://doi.org/10.1088/1755-1315/263/1/012008

Fischer, S., Jarsjö, J., Rosqvist, G., & Mörth, C.-M. (2022). Catchment-scale microbial sulfate reduction (MSR) of acid mine drainage (AMD) revealed by sulfur isotopes. *Environmental Pollution*, *292*, 118478. https://doi.org/10.1016/j.envpol.2021.118478

Fischer, S., Mörth, C.-M., Rosqvist, G., Chalov, S.R., Efimov, V., & Jarsjö, J. (2022). *Water quality dataset from stream water in the Khibiny massif, Kola Peninsula (Russia) in August 2017* [Dataset]. Zenodo. https://doi.org/10.5281/zenodo.6448039

Fischer, S., Rosqvist, G., Chalov, S. R., & Jarsjö, J. (2020). Disproportionate water quality impacts from the century-old nautanen copper mines, northern Sweden. *Sustainability*, *12*(4), 1394. https://doi.org/10.3390/su12041394

Forsius, M., Posch, M., Aherne, J., Reinds, G. J., Christensen, J., & Hole, L. (2010). Assessing the impacts of long-range sulfur and nitrogen deposition on Arctic and sub-Arctic ecosystems. *Ambio*, *39*(2), 136–147. https://doi.org/10.1007/s13280-010-0022-7

Fortin, D., Goulet, R., & Roy, M. (2000). Seasonal cycling of Fe and S in a constructed wetland: The role of sulfate-reducing bacteria. *Geomicrobiology Journal*, *17*(3), 221–235. https://doi.org/10.1080/01490450050121189

Guo, L., Ping, C.-L., & Macdonald, R. W. (2007). Mobilization pathways of organic carbon from permafrost to arctic rivers in a changing climate. *Geophysical Research Letters*, *34*(13). https://doi.org/10.1029/2007GL030689

Hampton, T. B., Zarnetske, J. P., Briggs, M. A., Singha, K., Harvey, J. W., Day-Lewis, F. D., et al. (2019). Residence time controls on the fate of nitrogen in flow-through lakebed sediments. *Journal of Geophysical Research: Biogeosciences*, *124*(3), 689–707. https://doi.org/10.1029/2018JG004741

Harris, I., Jones, P. D., Osborn, T. J., & Lister, D. H. (2014). Updated high-resolution grids of monthly climatic observations – The CRU TS3.10 Dataset. *International Journal of Climatology*, *34*(3), 623–642. https://doi.org/10.1002/joc.3711

Hotton, G., Bussière, B., Pabst, T., Bresson, É., & Roy, P. (2020). Influence of climate change on the ability of a cover with capillary barrier effects to control acid generation. *Hydrogeology Journal*, *28*(2), 763–779. https://doi.org/10.1007/s10040-019-02084-y

Ingri, J., Torssander, P., Andersson, P. S., Mörth, C. M., & Kusakabe, M. (1997). Hydrogeochemistry of sulfur isotopes in the Kalix River catchment, northern Sweden. *Applied Geochemistry*, *12*(4), 483–496. https://doi.org/10.1016/S0883-2927(97)00026-7

Jarsjö, J., Andersson-Sköld, Y., Fröberg, M., Pietroń, J., Borgström, R., Löv, Å., & Kleja, D. B. (2020). Projecting impacts of climate change on metal mobilization at contaminated sites: Controls by the groundwater level. *The Science of the Total Environment*, *712*, 135560. https://doi.org/10.1016/j.scitotenv.2019.135560

Khan, U. A., Kujala, K., Nieminen, S. P., Räisänen, M. L., & Ronkanen, A.-K. (2019). Arsenic, antimony, and nickel leaching from northern peatlands treating mining influenced water in cold climate. *The Science of the Total Environment*, *657*, 1161–1172. https://doi.org/10.1016/j.scitotenv.2018.11.455

Knöller, K., Fauville, A., Mayer, B., Strauch, G., Friese, K., & Veizer, J. (2004). Sulfur cycling in an acid mining lake and its vicinity in Lusatia, Germany. *Chem. Geol., Applications of Stable Isotope Techniques to Geological and Environmental Problems*, *204*(3–4), 303–323. https://doi.org/10.1016/j.chemgeo.2003.11.009

Kogarko, L. (2018). Chemical composition and petrogenetic implications of apatite in the Khibiny apatite-nepheline deposits (Kola peninsula). *Minerals*, *8*(11), 532. https://doi.org/10.3390/min8110532

Laudon, H., Sjöblom, V., Buffam, I., Seibert, J., & Mörth, M. (2007). The role of catchment scale and landscape characteristics for runoff generation of boreal streams. *Journal of Hydrology*, *344*(3–4), 198–209. https://doi.org/10.1016/j.jhydrol.2007.07.010

Lindström, E. S., Kamst-Van Agterveld, M. P., & Zwart, G. (2005). Distribution of typical freshwater bacterial groups is associated with pH, temperature, and lake water retention time. *Applied and Environmental Microbiology*, *71*(12), 8201–8206. https://doi.org/10.1128/AEM.71.12.8201-8206.2005

Liu, X.-Y., Xiao, H.-Y., Liu, C.-Q., Xiao, H.-W., & Wang, Y.-L. (2009). Assessment of atmospheric sulfur with the epilithic moss Haplocladium microphyllum: Evidences from tissue sulfur and $\delta^{34}S$ analysis. *Environmental Pollution*, *157*(7), 2066–2071. https://doi.org/10.1016/j.envpol.2009.02.020

Malinovsky, D., Rodushkin, I., Moiseenko, T., & Öhlander, B. (2002). Aqueous transport and fate of pollutants in mining area: A case study of Khibiny apatite-nepheline mines, the Kola peninsula, Russia. *Environmental Geology*, *43*(1–2), 172–187. https://doi.org/10.1007/s00254-002-0641-9

Mandernack, K. W., Lynch, L., Krouse, H. R., & Morgan, M. D. (2000). Sulfur cycling in wetland peat of the New Jersey Pinelands and its effect on stream water chemistry. *Geochimica et Cosmochimica Acta*, *64*(23), 3949–3964. https://doi.org/10.1016/S0016-7037(00)00491-9

Mariotti, A., Germon, J. C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, A., & Tardieux, P. (1981). Experimental determination of nitrogen kinetic isotope fractionation: Some principles; illustration for the denitrification and nitrification processes. *Plant and Soil*, *62*(3), 413–430. https://doi.org/10.1007/BF02374138

Martinsson, O., Billström, K., Broman, C., Weihed, P., & Wanhainen, C. (2016). Metallogeny of the northern norrbotten ore province, northern fennoscandian shield with emphasis on IOCG and apatite-iron ore deposits. *Ore Geology Reviews*, *78*, 447–492. https://doi.org/10.1016/j.oregeorev.2016.02.011

Massmann, G., Tichomirowa, M., Merz, C., & Pekdeger, A. (2003). Sulfide oxidation and sulfate reduction in a shallow groundwater system (Oderbruch Aquifer, Germany). *Journal of Hydrology*, *278*(1–4), 231–243. https://doi.org/10.1016/S0022-1694(03)00153-7

Migaszewski, Z. M., Dołęgowska, S., Hałas, S., & Trembaczowski, A. (2010). Stable sulphur isotope ratios in the moss species Hylocomium splendens (Hedw.) B.S.G. and Pleurozium schreberi (Brid.) Mitt. from the Kielce area (south-central Poland). *Isotopes in Environmental and Health Studies*, *46*(2), 219–224. https://doi.org/10.1080/10256016.2010.488725

Moiseenko, T. I., & Bazova, M. M. (2016). Effects of water acidification on element concentrations in natural waters of the Kola North. *Geochemistry International*, *54*(1), 112–125. https://doi.org/10.1134/S0016702916010092

Moiseenko, T. I., Gashkina, N. A., Sharov, A. N., Vandysh, O. I., & Kudryavtseva, L. P. (2009). Anthropogenic transformations of the Arctic ecosystem of Lake Imandra: Tendencies for recovery after long period of pollution. *Water Resources*, *36*(3), 296–309. https://doi.org/10.1134/S0097807809030051

Muyzer, G., & Stams, A. J. M. (2008). The ecology and biotechnology of sulphate-reducing bacteria. *Nature Reviews Microbiology*, *6*, 441–454. https://doi.org/10.1038/nrmicro1892

Nelson, C. E., Sadro, S., & Melack, J. M. (2009). Contrasting the influences of stream inputs and landscape position on bacterioplankton community structure and dissolved organic matter composition in high-elevation lake chains. *Limnology & Oceanography*, *54*(4), 1292–1305. https://doi.org/10.4319/lo.2009.54.4.1292

Nielsen, G., Janin, A., Coudert, L., Blais, J. F., & Mercier, G. (2018). Performance of sulfate-reducing passive bioreactors for the removal of Cd and Zn from mine drainage in a cold climate. *Mine Water and the Environment*, *37*(1), 42–55. https://doi.org/10.1007/s10230-017-0465-1

Palomo, L., Meile, C., & Joye, S. B. (2013). Drought impacts on biogeochemistry and microbial processes in salt marsh sediments: A flow-through reactor approach. *Biogeochemistry*, *112*(1–3), 389–407. https://doi.org/10.1007/s10533-012-9734-z

Pellerin, A., Antler, G., Marietou, A., Turchyn, A. V., & Jørgensen, B. B. (2020). The effect of temperature on sulfur and oxygen isotope fractionation by sulfate reducing bacteria (Desulfococcus multivorans). *FEMS Microbiology Letters*, *367*(9). https://doi.org/10.1093/femsle/fnaa061

Pereverzev, V. N. (2010). Genetic features of soils in altitudinal natural zones of the Khibiny Mountains. *Eurasian Soil Science*, *43*(5), 509–518. https://doi.org/10.1134/S1064229310050042

Pester, M., Knorr, K.-H., Friedrich, M., Wagner, M., & Loy, A. (2012). Sulfate-reducing microorganisms in wetlands – Fameless actors in carbon cycling and climate change. *Frontiers in Microbiology*, *3*, 72. https://doi.org/10.3389/fmicb.2012.00072

Praharaj, T., & Fortin, D. (2004). Indicators of microbial sulfate reduction in acidic sulfide-rich mine tailings. *Geomicrobiology Journal*, *21*(7), 457–467. https://doi.org/10.1080/01490450490505428

Reimann, C., De Caritat, P., Halleraker, J. H., Volden, T., Äyräs, M., Niskavaara, H., et al. (1997). Rainwater composition in eight arctic catchments in northern Europe (Finland, Norway and Russia). *Atmospheric Environment*, *31*(2), 159–170. https://doi.org/10.1016/1352-2310(96)00197-5

Robertson, W. D., & Schiff, S. L. (1994). Fractionation of sulphur isotopes during biogenic sulphate reduction below a sandy forested recharge area in south-central Canada. *Journal of Hydrology*, *158*(1–2), 123–134. https://doi.org/10.1016/0022-1694(94)90049-3

Samborska, K., Halas, S., & Bottrell, S. H. (2013). Sources and impact of sulphate on groundwaters of Triassic carbonate aquifers, Upper Silesia, Poland. *Journal of Hydrology*, *486*, 136–150. https://doi.org/10.1016/j.jhydrol.2013.01.017

SGU. (2020). Geological survey of Sweden. *Map Viewer Website*. Soil type 1:25000 - 1:100000. [WWW Document]. URL Retrieved from https://apps.sgu.se/kartvisare/. accessed 12 20 20.

Sharp, Z. D. (2017). Chapter 10: Sulfur. In *Principles of stable isotope geochemistry* (2nd ed.). The University of New Mexico.

Shrestha, S., Gunawardana, S. K., Piman, T., & Babel, M. S. (2020). Assessment of the impact of climate change and mining activities on streamflow and selected metal's loading in the Chindwin River, Myanmar. *Environmental Research*, *181*, 108942. https://doi.org/10.1016/j.envres.2019.108942

Sinharoy, A., Pakshirajan, K., & Lens, P. N. L. (2020). Biological sulfate reduction using gaseous substrates to treat acid mine drainage. *Curr Pollution Rep*, *6*(4), 328–344. https://doi.org/10.1007/s40726-020-00160-6

van Hees, P. A. W., Jones, D. L., Finlay, R., Godbold, D. L., & Lundström, U. S. (2005). The carbon we do not see—The impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: A review. *Soil Biology and Biochemistry*, *37*, 1–13. https://doi.org/10.1016/j.soilbio.2004.06.010

Virpiranta, H., Taskila, S., Leiviskä, T., Rämö, J., & Tanskanen, J. (2019). Development of a process for microbial sulfate reduction in cold mining waters – cold acclimation of bacterial consortia from an Arctic mining district. *Environmental Pollution*, *252*, 281–288. https://doi.org/10.1016/j.envpol.2019.05.087

Wu, S., Jeschke, C., Dong, R., Paschke, H., Kuschk, P., & Knöller, K. (2011). Sulfur transformations in pilot-scale constructed wetland treating high sulfate-containing contaminated groundwater: A stable isotope assessment. *Water Research*, *45*(20), 6688–6698. https://doi.org/10.1016/j.watres.2011.10.008

Xia, D., Ye, H., Xie, Y., Yang, C., Chen, M., Dang, Z., et al. (2017). Isotope geochemistry, hydrochemistry, and mineralogy of a river affected by acid mine drainage in a mining area, South China. *RSC Advances*, *7*(68), 43310–43318. https://doi.org/10.1039/C7RA07809A

Xiao, H.-Y., Li, N., & Liu, C.-Q. (2015). Source identification of sulfur in uncultivated surface soils from four Chinese provinces. *Pedosphere*, *25*(1), 140–149. https://doi.org/10.1016/S1002-0160(14)60084-9

Xu, Y.-N., & Chen, Y. (2020). Advances in heavy metal removal by sulfate-reducing bacteria. *Water Science and Technology*, *81*(9), 1797–1827. https://doi.org/10.2166/wst.2020.227

Yngström, S., Nord, A. G., & Åberg, G. (1986). A sulphur and strontium isotope study of the Aitik copper ore, northern Sweden. *Geologiska Foreningen i Stockholm Forhandlingar*, *108*(4), 367–372. https://doi.org/10.1080/11035898609454727

Zhang, M., & Wang, H. (2016). Preparation of immobilized sulfate reducing bacteria (SRB) granules for effective bioremediation of acid mine drainage and bacterial community analysis. *Minerals Engineering*, *92*, 63–71. https://doi.org/10.1016/j.mineng.2016.02.008