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TECHNICAL ARTICLE

Mobility of Be, Bi, F, Ga, Ge and W in Surface Water and the Water Quality Impact on Epilithic Diatoms Downstream of the Historical Yxsjöberg Mine Site, Sweden

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Abstract
There is a potential risk that the geochemical cycles of several critical metals will be affected when mining of these metals increases to meet the demand of green technology. The geochemistry of Be, Bi, Ga, Ge, and W, herewith called CM5, is lacking, yet is necessary to ensure responsible mine waste and water management. Beryllium, Bi, and W are all considered immobile, but in previous studies of skarn tailings in Yxsjöberg, Sweden, all three elements were mobilized. The tailings are enriched in CM5, together with pyrrhotite, calcite, and fluorite. The mobility and environmental impact of CM5 and F in surface waters downstream of the Yxsjöberg mine site, Sweden, were studied using monthly water samples from seven locations and analysis of diatoms at five of these locations. Bismuth, Ge, and W were present at low concentrations, transported in the particulate phase, and likely settled in the sediments hundreds of meters from the tailings. Beryllium and F were present at high concentrations and dominantly transported in the dissolved phase. At these pH conditions (5.6), Be should form insoluble hydroxides; however, elevated concentrations of dissolved Be were observed more than 5 km from the mine site. Diatoms downstream of the mine site were negatively affected by the mine drainage. The release of low quality neutral mine drainage will continue for hundreds of years if remediation actions are not undertaken since only a small portion of the tailings have weathered during 50–100 years of storage.

Keywords Neutral mine drainage · Be-fluorocomplexes · Bismuth mobilisation · Tungsten mobilisation · Epilithic water diatoms

Introduction

As the mining of several critical metals (CMs) increases to satisfy the growing demand of green technologies, there is a risk of affecting their geochemical cycles in the pristine environment (Filella and Rodriguez-Murillo 2017). However, basic research on the geochemical behavior of many of these elements (e.g. Be, Bi, Ga, Ge, and W, henceforth called CM5) is sparse, even though they are recognized by-products from mining in historical times (Filella and Rodríguez-Murillo 2017).

CMs are currently grouped based on their economic importance and supply risk rather than similarities in geochemical behavior (Filella and Rodríguez-Murillo 2017). However, the mobility of CM5 has gained little attention in the past since these elements are usually present at very low or undetectable concentrations in the environment (Filella and Rodríguez-Murillo 2017; Salminen et al. 2005). Beryllium, Ga, and Ge are mainly hosted by stable silicate minerals (Nordberg et al. 2015; Rosenberg 2008; Salminen et al. 2005). Bismuth is found in bismuthinite [Bi_2S_3], which is considered to have stability similar to galena [PbS] (Ball et al. 1982; Lottermoser 2003), while more than 50% of all W is primarily found in scheelite [$CaWO_4$] (Kwak 2012; Werner et al. 1998), which is considered a very stable mineral (Bokii and Anikin 1956). The transport and fate of CM5 in receiving waters largely depend on distribution in the dissolved and particulate fractions (Dahlqvist et al. 2007). In near-neutral aqueous solutions, Be, Bi, and Ge are expected to have low mobilities since they readily form insoluble hydroxides and/or salts (Neal 2003; Salminen et al. 2005) or adsorb to Fe and/or Mn oxyhydroxides (Åström et al. 2018;

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Boschi and Willenbring 2016b; Rosenberg 2008; Salminen et al. 2005). Adsorption to hydrous ferric oxides (HFO) is also believed to be a strong scavenging process for W in the environment (Cui and Johannesson 2017; Kashiwabara et al. 2013).

In recent decades, concerns have been raised about Be (Boschi and Willenbring 2016a; Mederos et al. 2001; Taylor et al. 2003; Veselý et al. 1989), Bi (Fahey and Tsuji 2006) and W leaching (Cui and Johannesson 2017; Datta et al. 2017; Koutsospyros et al. 2006; Lemus and Venezia 2015; Strigul et al. 2010; Strigul et al. 2009; Zoroddu et al. 2018). Beryllium is one of the most toxic elements in the periodic table (Boschi and Willenbring 2016a; Mederos et al. 2001; Taylor et al. 2003; Veselý et al. 1989). Inhalation of Be dust is recognized as the most hazardous exposure pathway (Deubner et al. 2001; Raymond et al. 2015; Taylor et al. 2003), but other pathways may also be relevant as research into Be exposure is limited. Both Bi and W have been used as non-toxic alternatives in different applications, e.g. ammunition (Fahey and Tsuji 2006; Koutsopyros et al. 2006). However, concerns have been raised that the current ecotoxicological knowledge base for both Bi (Fahey and Tsuji 2006; Fahey et al. 2008) and W (Cui and Johannesson 2017; Datta et al. 2017; Koutsospyros et al. 2006; Lemus and Venezia 2015; Strigul et al. 2010; Zoroddu et al. 2018) is too sparse. For example, there is contradictory evidence regarding Bi toxicity, with some reports classifying the element as harmless to ecosystems (National Research Council 2005) whereas others have shown that Bi can negatively affect the reproduction of earthworms (Ghaffari and Motlagh 2011; Omouri et al. 2018). In the USA and Russia, alarming reports of elevated W concentrations have led to this element being classified as an emerging and highly dangerous contaminant of concern (Strigul et al. 2009; US EPA 2014). In Sweden, no guideline values for Be, Bi, or W exist. Beryllium concentrations in aqueous media above 1 μg/L are believed to adversely affect ecosystems (Neal 2003). In Russia, a maximum allowed concentration of 0.8 μg/L dissolved W has been set for aquatic systems used for fishing (Strigul et al. 2009). Gallium and Ge are classified as relatively non-toxic to humans (Salminen et al. 2005), but their toxicity has also not been sufficiently discussed in the literature.

A high release of metals to the surrounding environment can severely impact aquatic life. Diatoms can be used as a first bioindicator to study adverse impact on ecosystems, but also to study improvement of water quality downstream of mining areas (Cattaneo et al. 2004). At a community level, adverse effects can be expressed as changes in species composition, along with structural changes such as decreased species diversity, evenness, and richness (Cunningham et al. 2005). Studying the effect of acidity, metals, and nutrients on epilithic diatoms is a well-established method for evaluations of freshwater streams and lakes (Hirst et al. 2002; Kahlert 2012; Kahlert et al. 2007; Swedish EPA 2007). Previous studies have also been conducted to monitor how trace elements affect diatoms in lakes and/or sediment cores downstream of mining areas with the overall goal of better understanding the environmental impacts of mine drainage (e.g. Cattaneo et al. 2004; Kauppila 2006; Kihlman and Kauppila 2010; Ruggiu et al. 1998).

Several studies by Hällström et al. (2018a, b, 2020a, b) and Salifu et al. (2018, 2019, 2020a, b) at the Yxsjöberg mine site have shown that the complex interplay between compounds (SO_4^{2-}, CO_3^{2-}, and F^-) released from the weathering of sulfides, carbonates, and fluorite has generated a geochemical environment in which Be, Bi, and W are mobilized from their primary minerals within the Smaltjärnen tailings. The Smaltjärnen tailings are enriched in F (1.9 wt%) and S (1.2 wt%), together with the trace elements Be, Bi, Ga, Ge, and W (284, 496, 24, 16, and 960 ppm, respectively), and have been stored open to the atmosphere for more than 50 years (Hällström et al. 2018a, b). These conditions make the surface water downstream of the Yxsjöberg mine site an interesting place to study the geochemical behavior of Be, Bi, and F. The source of W from the Smaltjärnen tailings, along with its mobilization, transport, and fate in sediments and the surface water, have recently been elucidated (Hällström et al. 2020a). The harsh geochemical environment in the tailings raises questions about whether Ga and Ge have also leached from the tailings and are now prevalent in the downstream surface waters.

Therefore, the mobility, transport, and fate of critical metals (Be, Bi, F, Ga, and Ge) in the tailings of the Yxsjöberg mine site were studied in the Nittälven River, and the release of these metals was backtracked to ongoing geochemical and mineralogical processes in the Smaltjärnen tailings. Epilithic water diatoms downstream of the mining area were also studied as a first step to evaluate the impact of the water quality on ecosystems.

Study Area

The Nittälven River receives water from the Yxsjöberg mine site, Sweden, which was in operation during three different periods between 1918 and 1989 for the mining of W, Cu, and CaF_2. Mine tailings were discharged into two repositories named Smaltjärnen (1918–1963) and Morkulltjärnen (1969–1989). The Smaltjärnen tailings contain approximately 2.8 million tons of tailings and the tailings have been stored open to the atmosphere for more than 50 years. The tailings were covered with sewage sludge in 1993, but barren areas exist, probably due to erosion. The tailings consist of 88 wt% of silicates together with considerable amounts of sulfides (pyrrhotite, pyrite, chalcopyrite, danalite, bismuthinite), calcite, fluorite, and oxides (magnetite, hematite,

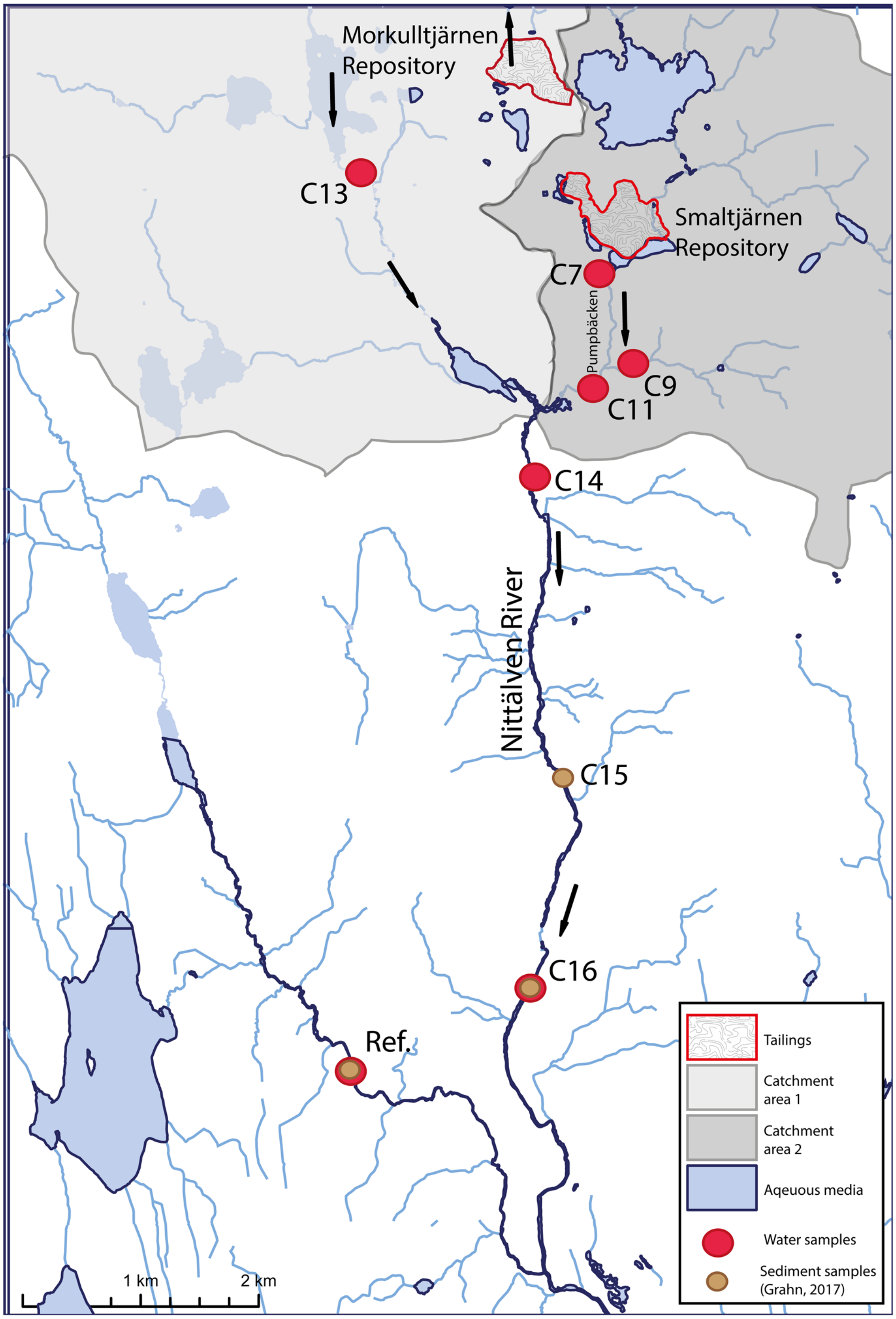

Fig. 1 HYPERLINK "sps:id::fig1||locator::gr1||mediaobject::0"Catchment areas of the Morkulltjärnen (1) and Smaltjärnen (2) repositories. Red dots (C7, C9, C11, C13, C14, C16 and ref) symbolize water sampling locations downstream of the Yxsjöberg mining area, and brown dots (C15, C16 and ref) symbolise sediment samples that were taken by Grahn (2017)

scheelite, cassiterite; Hällström et al. 2018a, b). The tailings were discharged to an area of bogs and swamps without any dams to control the mine waste (Rothelius 1957). Unlike Smaltjärnen, Morkulltjärnen is controlled by dams, covered by vegetation and partly saturated (Höglund et al. 2004). Detailed information about the Yxsjöberg mine site can be found in Hällström et al. (2018a, 2020a, b).

The Nittälven River starts ≈ 9 km northwest of the Yxsjöberg mine site. The first few kilometres of the Nittälven receive water from a 47 km^2 catchment area (labelled Catchment 1 in Fig. 1), which includes the Morkulltjärnen repository. Further south, the Nittälven co-mingles with the Pumpbäcken stream, which has a 19 km^2 catchment area (labelled Catchment 2) that includes the older Smaltjärnen repository (SMHI 2020). The two catchment areas are separated by a hydraulic barrier (Höglund et al. 2004). The region is characterized by winters with 4 months of snow and annual precipitation of 730 mm. The monthly average temperature

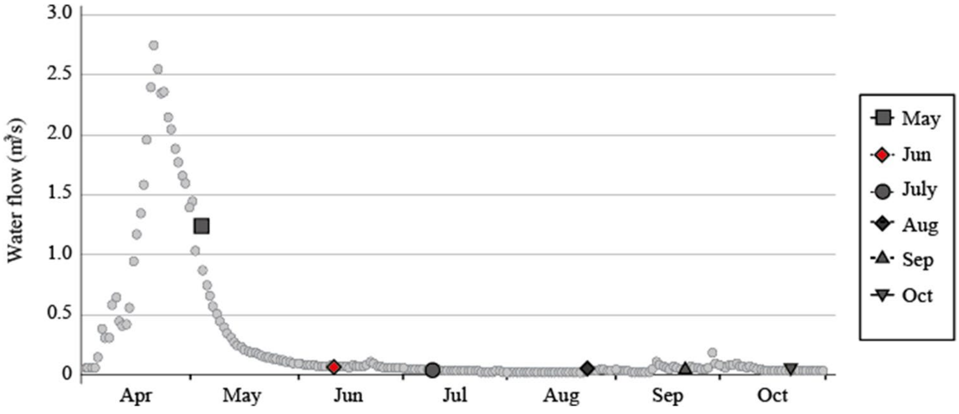

Fig. 2 Modelled water flow in the Nittälven River during the sampling campaign between May and October (SMHI 2020) with the sampling dates marked

ranges from – 5 °C in January to 15 °C in July[1] (SMHI 2018). Water flow in the Nittälven River during 2018 is shown in Fig. 2.

A study carried out by the county administrative board of Örebro found enriched concentrations of Be and W in the Nittälven sediments. The sediments at C15 and C16 (Fig. 1) contained elevated concentrations of Be (60 and 95 mg/kg, respectively) and W (800 and 500 mg/kg, respectively) compared to the reference sample with 3 mg/kg of Be and < 50 mg/kg of W (Grahn 2017). It was not interpreted if Be and W were enriched in the sediments due to chemical or physical weathering of the tailings in Smaltjärnen and/or Morkulltjärnens repositories.

Materials and Methods

Surface Water Sampling

Surface water was sampled at six sampling points downstream of the Smaltjärnen and Morkulltjärnen repositories as well as at one reference point (abbreviated: Ref) (Fig. 1). Sampling point C7 was located at the outlet of Smaltjärnen Lake. Sampling point C9 was in a first-order stream south of the Smaltjärnen repository, which flows into the Pumpbäcken stream south of C7. C11 was in the Pumpbäcken stream downstream of the outlet of C9. C13 was in the Nittälven River downstream of the Morkulltjärnen repository and C14 was located where the Nittälven and Pumpbäcken met. One sample was taken at Brattforsen (C16), 5 km downstream of C14 in the Nittälven River. The reference sample was taken from a location southwest of the mining area, which belonged to another catchment area.

The pH, electrical conductivity (EC), and temperature were measured directly in the surface water. A pHenomenal MU 6100H multi-parameter meter equipped with a pHenomenal 111 electrode (662-1157; VWR International, Radnor, PA) was used for the pH measurements. The electrode was calibrated prior to the measurements using standard pH 4 and 7 buffer solutions.

The surface water was pumped on-line through Geotech polycarbonate and acrylic filter holders (Geotech Environmental Equipment Inc., Denver, USA) with a diameter of 142 mm. The filters (0.22 µm cellulose acetate membrane filters) were pre-washed with 5% acetic acid for 72 h and rinsed with MilliQ water for 24 h (Ödman et al. 1999). Screening analyses (71 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, W, V, Y, Yb, Zn, and Zr) of the filtered surface water (dissolved phase) were carried out by ALS Scandinavia (ALS Scandinavia, Luleå, Sweden) using an inductively coupled plasma sector field mass spectrometer (ICP-SFMS). The utilized method was validated with the certified reference materials SLEW-2, CASS-2, and NASS-4 for all elements analyzed by ALS Scandinavia (Rodushkin and Ruth 1997). Total and dissolved F, SO_4, and Cl were analyzed by ion chromatography (CSN ISO 10304-1, CSN EN 16192) in May and June. There were no differences in the concentrations of: (1) total and dissolved F, (2) S and SO_4, and (3) no elevated concentrations of Cl compared to the reference sample in samples screened from May and June. Therefore, for samples taken in July, August, September, and October, only dissolved F, total S, and no Cl were analyzed. Duplicates of each sampling batch were carried out to control the reproducibility of the screening analysis. Blanks and standards were used for quality control. The filters used for surface water filtration were analyzed for the particulate phase according to the same procedure as the dissolved phase at ALS Scandinavia after lithium metaborate and HNO_3/HF/HCl digestion.

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[1] Data collected between 1901 and 2016 at Ställdalen, 16 km from Yxsjöberg, Sweden (SMHI 2018).

Epilithic Water Diatom Sampling

Epilithic water diatoms were sampled from the Nittälven and Pumpbäcken at C7, C11, C13, C14, and Ref in October 2018. The sampling procedure was carried out according to the European/Swedish standard protocol (CEN 2014a). Briefly, five rocks 10–15 cm in diameter were sampled along a distance of 10 m in the water column at each sampling location. The side of the rock facing the sun was brushed and rinsed. The eluates from all the rocks taken from the same sampling location were collected in two 250 mL plastic bottles and stored under cool and dark conditions during the field day. Later, the particles in each bottle were allowed to settle and 2/3 of the clear water was decanted and replaced with 96% pure alcohol for preservation. The samples were sent to SLU Uppsala for analysis and were analyzed according to the European/Swedish standard protocol, SS-EN 14407 (CEN 2014b).

A total of 400 diatom valves were counted under an optical microscope, and the species of each valve was identified to determine taxonomic richness and evenness. Deformed valves were counted, and deformations were identified by weak or abnormal valve shape and/or abnormal patterns on the valves (Kahlert 2012). The organic material was oxidized by hydrogen peroxide following the standard method of the Swedish environmental monitoring programs (Jarlman et al. 2017). The effects of acid stress on diatoms were determined by an acidity index for diatoms (ACID-index) according to the procedure described by Andrén and Jarlman (2008). The ACID-index indicates the pH in the water using the following intervals: alkaline (> 7.3), near-neutral (6.5–7.3), slightly acidic (5.9–6.5), acidic (5.5–5.9), and very acidic (< 5.5).

Results

In 2018, the spring flood resulting from snow melt was larger than normal in both catchment areas of Yxsjöberg due to heavy snowfall during the winter of 2017/2018 (SMHI 2020). The first samples were taken in May at the decline of the spring flood (Fig. 2). The water flow was modelled by SMHI (2020) and was shown to have decreased to very low levels during the summer, which was warmer and drier than normal. The water flow increased slightly in September and October but remained very low.

The pH of the surface water sampled at C7 ranged between 5.2 in July and 6.2 in October (Table 1). The pH values measured for Ref, C9, C11, C13, and C14 were 6.2, 5.9, 5.9, 6.6, and 6.4, respectively. EC was highest at C7 and C11 (average values of 346 and 271 µS/cm, respectively), and an order of magnitude lower at Ref, C9, C13, C14, and C16. Fluoride was detected in the dissolved phase at C7, C11, C14, and C16. The highest concentrations were measured at C7 with an average value of 1.7 mg/L in September. The lowest F concentrations were observed in May, and gradually increased with decreasing water flow until September. Moreover, F concentrations decreased as the distance from the Yxsjöberg mine site increased. At Ref, C9 and C13, the F concentrations were below the detection limit across all sampling occasions (< 0.2 mg/L).

Trace Elements

Beryllium was detected at elevated concentrations during all sampling occasions relative to reference samples both downstream of the Smaltjärnen repository (C7, C11) and the site that received water from both the Smaltjärnen and Morkulltjärnen repositories (C14) (Table 1). Beryllium concentrations were below the detection limit in the reference sample (Ref), at the tributary (C9) and downstream of Morkulltjärnen (C13). At C7, C11, and C14, Be was mostly transported in the dissolved phase (average value: 93 wt%). The dissolved concentrations increased as water flow decreased (June to September) at both C7 and C11 and decreased as the distance from the Smaltjärnen repository increased. Total Be concentrations at C7 ranged between 9 and 73 µg/L, with an average value of 41 µg/L. The Be concentrations at a sampling point 5 km from the repository (C16) were three times greater than what was measured from the reference sample.

Elevated concentrations of total Bi were found at C7 and C11 (average values of 0.7 and 0.4 µg/L, respectively) in comparison to the reference sample. Bismuth was mainly transported in the particulate phase (average value: 75 wt%) at these two locations. The highest total Bi concentration (max. 1.6 µg/L) occurred in June at C7. During June and July, low, yet steady, dissolved Bi concentrations between 0.1 and 0.2 µg/L were detected at C7, C9, C11, C14, and C15.Total Bi concentrations decreased as water flow decreased and the distance from the Smaltjärnen repository increased.

The total concentrations of Ga downstream of the Smaltjärnen (C7, C11) and Morkulltjärnen (C13) repositories, as well as at sites close to the junction between the two rivers (C14 and C16), did not differ noticeably from what was measured from the reference sample or at the tributary (C9). The highest concentrations, a maximum total concentration of 0.04 µg/L, were found at the tributary (C9). Gallium was transported equally in dissolved and particulate fractions at each sampling location.

Germanium was mainly found in the dissolved fraction (average value: 85 wt%) at all sampling locations and across all sampling occasions. The observed total concentrations of Ge were low (max. 0.09 µg/L), and of the same order of magnitude as concentrations in the reference sample (max: 0.07 µg/L).

Table 1 Sampled pH, EC (µS/cm), dissolved F (mg/L) and dissolved/particulate Be, Bi, Ga, and Ge (µg/L) values at Ref, C7, C9, C11, C13, C14 and C16 from May–Oct

	Date	pH	EC	F	Be		Bi		Ga		Ge	
				Dis	Dis	Par	Dis	Par	Dis	Par	Dis	Par
Ref.	May	5.0	18	< 0.20	0.04	0.01	0.01	0.01	0.01	0.01	0.01	< 0.01
	Jun	6.4	37	< 0.20	0.01	0.01	0.03	0.01	< 0.01	0.01	0.07	< 0.01
	Jul	6.6	38	< 0.20	0.09	0.06	0.04	0.38	< 0.01	0.01	0.02	< 0.01
	Aug	6.3	40	< 0.20	0.03	0.00	0.02	0.07	0.01	0.01	0.05	< 0.01
	Sep	6.5	35	< 0.20	0.04	1.50	0.01	0.13	0.01	< 0.01	0.02	0.01
	Oct	6.5	38	< 0.20	0.16	0.00	0.01	0.01	0.02	0.01	0.04	< 0.01
C7	May	5.7	100	0.45	8.72	0.30	0.14	0.23	0.01	0.01	0.01	< 0.01
	Jun	5.8	256	1.78	35.10	2.39	0.24	1.36	< 0.01	0.01	0.03	< 0.01
	Jul	5.2	306	1.35	35.30	2.37	0.25	0.57	0.01	0.01	0.03	< 0.01
	Aug	5.5	460	2.40	52.19	1.21	0.04	0.45	< 0.01	< 0.01	0.09	< 0.01
	Sep	5.9	555	2.46	72.12	1.60	0.02	0.59	< 0.01	0.01	0.01	0.02
	Oct	6.2	396	1.50	33.36	6.86	0.03	0.27	0.01	0.02	0.04	< 0.01
C9	May	5.2	18	< 0.20	0.09	0.00	0.10	0.00	0.02	< 0.01	0.01	< 0.01
	Jun	5.6	33	< 0.20	0.08	0.01	0.13	0.10	0.03	0.01	0.03	< 0.01
	Jul	6.4	41	< 0.20	0.11	< 0.01	0.13	0.00	0.03	< 0.01	0.04	< 0.01
	Aug	6.5	45	< 0.20	0.07	0.01	0.07	0.11	0.01	0.01	0.07	< 0.01
	Oct	6.0	37	< 0.20	0.18	0.00	0.12	0.04	0.02	0.01	0.04	< 0.01
C11	May	5.6	7	0.31	6.34	0.18	0.24	0.16	0.02	0.01	0.02	< 0.01
	Jun	5.7	163	0.83	14.90	1.14	0.14	0.59	0.01	0.02	0.06	< 0.01
	Jul	5.8	259	1.11	26.10	1.64	0.15	0.30	< 0.01	0.01	0.02	< 0.01
	Aug	5.8	402	2.00	42.42	0.85	0.02	0.26	0.01	< 0.01	0.02	< 0.01
	Sep	6.0	472	2.04	58.46	0.01	0.02	0.04	< 0.01	< 0.01	0.03	0.01
	Oct	6.4	322	1.18	26.08	5.57	0.10	0.19	0.01	0.01	0.02	0.01
C13	May	6.1	27	< 0.20	0.05	0.03	0.01	0.05	< 0.01	0.01	0.01	< 0.01
	Jun	6.5	27	< 0.20	0.03	0.01	0.11	0.02	0.02	0.01	0.03	< 0.01
	Jul	7.6	29	< 0.20	0.07	0.05	0.07	0.27	0.01	0.01	< 0.01	< 0.01
	Aug	6.7	29	< 0.20	0.05	0.01	0.07	0.05	0.01	< 0.01	0.09	< 0.01
	Sep	6.6	30	< 0.20	0.08	0.01	0.05	0.05	0.01	0.01	0.02	0.01
	Oct	6.6	30	< 0.20	0.10	0.06	0.07	0.57	0.02	0.02	0.02	< 0.01
C14	Jun	6.6	66	0.27	3.10	0.34	0.15	0.15	0.01	0.01	0.07	< 0.01
	Jul	6.4	63	0.26	2.11	0.23	0.14	0.17	0.01	< 0.01	0.01	< 0.01
	Aug	6.3	107	0.33	2.97	0.42	0.06	0.07	0.01	< 0.01	0.09	< 0.01
	Oct	6.2	8	0.30	5.92	0.55	0.08	0.05	0.01	< 0.01	0.03	< 0.01
C16	Jun	6.5	37	0.20	0.90	0.14	0.22	0.16	0.01	0.01	0.01	< 0.01

Epilithic Water Diatoms

Taxonomic Diversity, Richness, and Evenness

Taxonomic analyses revealed that the number of different diatom species varied between sampling sites. For example, only 27 species were found at C7, whereas 35 and 36 species were identified from C11 and Ref, respectively. A total of 48 species were present at C14, and the highest number of diatom species was found at C13 (56 different species). As shown in Fig. 3, site C7 was dominated by three species: *Brachysira neoexilis* (46%); *Frustulia crassinervia* (16%); and *Fallacia* sp. (11%). *Encyonema neogracile var. Neogracile* and *Frustulia saxonica* were also present, albeit at lower amounts (3%), and showed similar trends as *B. neoexilis* and *Fallacia* sp., that is, highest abundance at C7 and decreased presence at C11 and C14. Site C11 was dominated by *B. neoexilis* (38%), followed by *Tabellaria flocculosa* (12%), *Eunotia bilunaris* (10%), and *Fragilaria gracilis* (5%).

Achnanthidium minutissimum group II accounted for 58% of all valves identified from C13, while *B. neoexilis* (7%) was present at lower levels. At C14, *B. neoexilis* (31%) and *A. minutissimum group II* (22%) were highly abundant, while *Aulacoseria* (6%), *Tabellaria flocculosa* (5%), *Eunotia implicate* (5%) were less prevalent. The reference sample demonstrated higher taxonomic evenness than other samples, with several species accounting for between 4 and 20% of the total diatoms, in the following order: *Tabellaria*

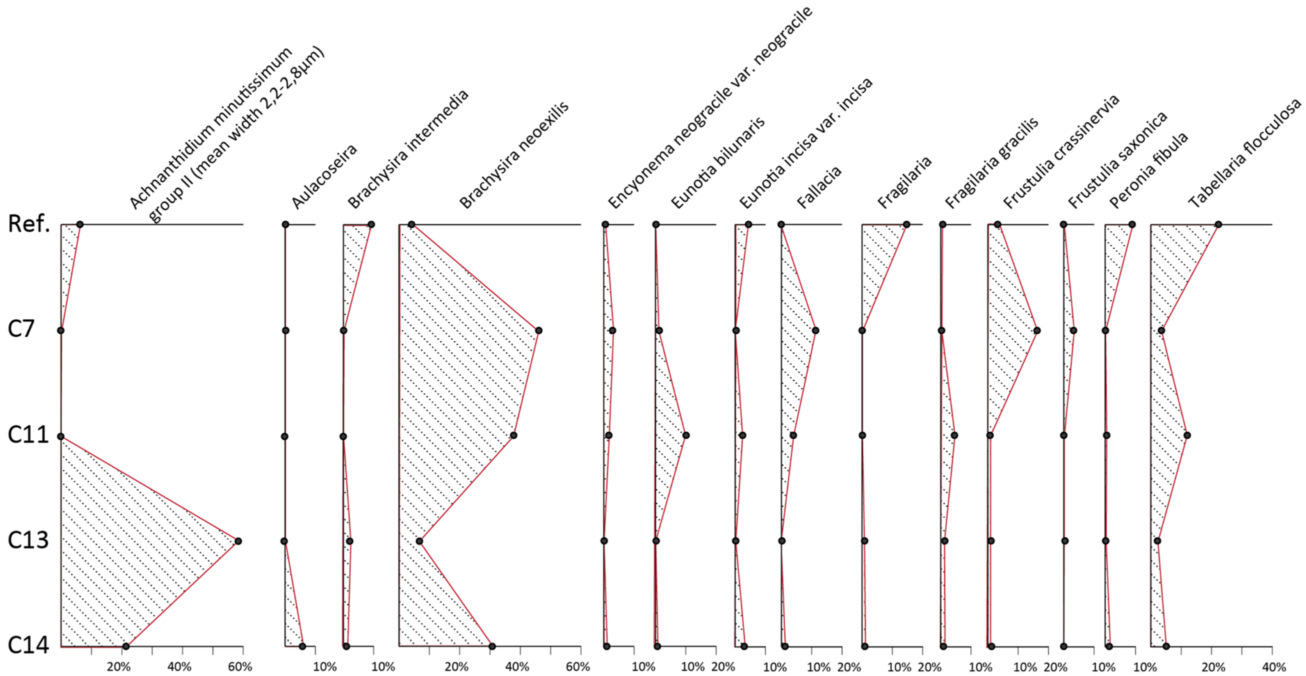


Fig. 3 Distribution of epilithic water diatoms in Ref, C7, C11, C13 and C14 samples from October 2018 (selected taxa shown)

flocculosa > *Fragilaria* > *Brachysira intermedia* > *Peronia fibula* > *A. minutissimum group II* > *Eunotia incisa var. incisa* > *Eunotia faba* > *B. neoexilis*.

ACID-Index and Diatom Deformities

In surface waters downstream of the Yxsjöberg mine site, the ACID index ranged between 1.98 at C7 and 6.8 at C13 (Table 2). Based on the ACID-index, the environments at C7, C11, and Ref, C14, and C13 (downstream of Morkulltjärnen) were classified as "very acidic", "acidic", "slightly acidic", and "near-neutral", respectively (Kahlert 2012). The ACID-index and the average measured pH were similar at sampling sites C11, C13, and C14. The pH measured at the Ref and C7 sites was slightly higher than the reconstructed pH provided by the ACID-index.

In the samples from Ref, C7, and C11, more than 1% of the 400 studied diatom valves were deformed. The C11 samples showed the highest degree of deformation, i.e. 1.75% deformed shells. No shells were deformed in the C13 sample, while very few shells were deformed in the C14 sample.

Discussion

Water quality in the Pumpbäcken stream was highly affected by the major geochemical processes in the tailings of the Smaltjärnen repository, i.e. pyrrhotite oxidation, calcite neutralization, fluorite weathering, and formation of secondary minerals (Hällström et al. 2020a). Previous studies have shown that neutral mine drainage from Smaltjärnen released high concentrations of Ca and SO_4 to the Pumpbäcken stream, with this release attributed to the dissolution of secondary gypsum. The gypsum has formed from SO_4 released during pyrrhotite weathering and Ca from calcite neutralization in the upper parts of the tailings. Iron from pyrrhotite oxidation has formed HFO in the tailings and co-precipitation of W has likely scavenged W released from scheelite weathering (Hällström et al. 2020a).

The large variations in water flow—from the strong spring flood during May to the dry summer during July

Table 2 The indices used to evaluate adverse effects on silica algae: ACID (indicated pH), shell deformation and taxonomy were studied at the reference point, C7, C11, C13 and C14

Sampling site	ACID	Indicated pH based on ACID	Average measured pH	Shell deformation (%)
Ref	3.94	5.5–5.9	6.2	1.25
C7	1.98	< 5.5	5.7	1.5
C11	2.49	5.5–5.9	5.9	1.75
C13	6.8	6.5–7.3	6.7	0
C14	5.04	5.9–6.5	6.4	1

The ACID index includes the following categories: (1) very acidic (ACID < 2.2); (2) acidic (ACID 2.2–4.2); slightly acidic (ACID 4.2–5.8); near-neutral (ACID 5.8–7.5); and alkaline (ACID > 7.5). The average measured pH shows the average pH at 6 sampling occasions and each sampling point and August—significantly affected the concentrations of various elements in the surface waters of the Pumpbäcken and Nittälven (C7, C11, C14, and C16). The dissolved concentrations of several major elements (Ca, K, Mg, Na, S; Hällström et al. 2020a) demonstrated R^2-correlation values higher than 0.9 with F, indicating that water flow is a controlling parameter of the surface water system. Normalizing data using a Me/Mg ratio is a common procedure for eliminating any effects of dilution, as Mg does not easily form secondary minerals and is not easily taken up in biota (Ingri et al. 2005). However, this ratio may be problematic when considering mine drainage from Yxsjöberg mine site, since Mg and F can form strong complexes (Ozsvath 2009), and the Me/Mg ratios for mine drainage from the Smaltjärnen and Morkulltjärnen repositories differ. Modelling with PHREEQC (database: wateq4) and the F/Mg ratio measured downstream of the Smaltjärnen repository did not support any substantial formation of F-Mg complexes. According to the Mg ratios, dissolved Ca, F, and S were transported by the Pumpbäcken stream, and the small decrease in Ca, F, and S concentrations between C7 and C11 was due to dilution of water from C9 rather than precipitation (Fig. 4). The decrease in Ca/Mg, F/Mg, and S/Mg ratios between C11 and C14 is most likely explained by dilution from the Nittälven River, since the Ca/Mg, F/Mg, and S/Mg ratios were much lower at C13 than at C11.

Mixing calculations based on K, Mg, and Na concentrations from C13 and C11 to C14 revealed that 70–90% of the water at C14 originated from C13 across all sampling occasions. Therefore, the decrease in concentrations between C11 and C14 was due to dilution rather than the precipitation of Ca, F, and S. The mixing calculations and mass balance suggested that Al and Mn partly precipitated between C11 and C14. Potassium continued to be transported in the dissolved phase along both the Pumpbäcken and Nittälven. The Na/Mg ratio increased between C11 and C14, with the input of Na from road salts from a nearby road one possible explanation for this increase. Aluminium had a different pattern than the other major elements. The R^2-correlation between Al and F was 0.55, and the highest concentrations of dissolved Al were found at C11 during August. In Pumbäcken, the Al/Mg-ratio increased between C7 and C11. The source of Al at C11 needs to be studied further.

Iron released from pyrrhotite and danalite oxidation was partly scavenged within the Smaltjärnen tailings due to the formation of HFO in the oxidized tailings (Hällström et al. 2020a). Iron released from the tailings to the Pumpbäcken partly oxidized and formed HFO in the surface water and was transported at close to equivalent rates in the particulate and dissolved phases. Particulate Fe likely settled in the sediments of the Pumpbäcken between C7 and C11, and between C11 and C14 (Fig. 5). When compared to the reference sample, water discharged into the Nittälven did not contain elevated concentrations of Fe (average values of 920 and 740 µg/L for particulate and dissolved Fe, respectively).

Mobility of Be, Bi, Ga, Ge, and W

The trace elements found at concentrations of concern downstream of the Yxsjöberg mining area were Be and W. Based on the presented results, elevated concentrations of Be were found in the Pumpbäcken stream (Fig. 6), while Hällström et al. (2020a) reported high concentrations of W in the Nittälven River downstream of Morkulltjärnen (C13). In the surface waters downstream of the Smaltjärnen repository, Be and Ge were mainly transported in the dissolved phase, whereas Bi, Ga, and W were transported in the particulate phase, demonstrating a pattern like that noted for particulate Fe.

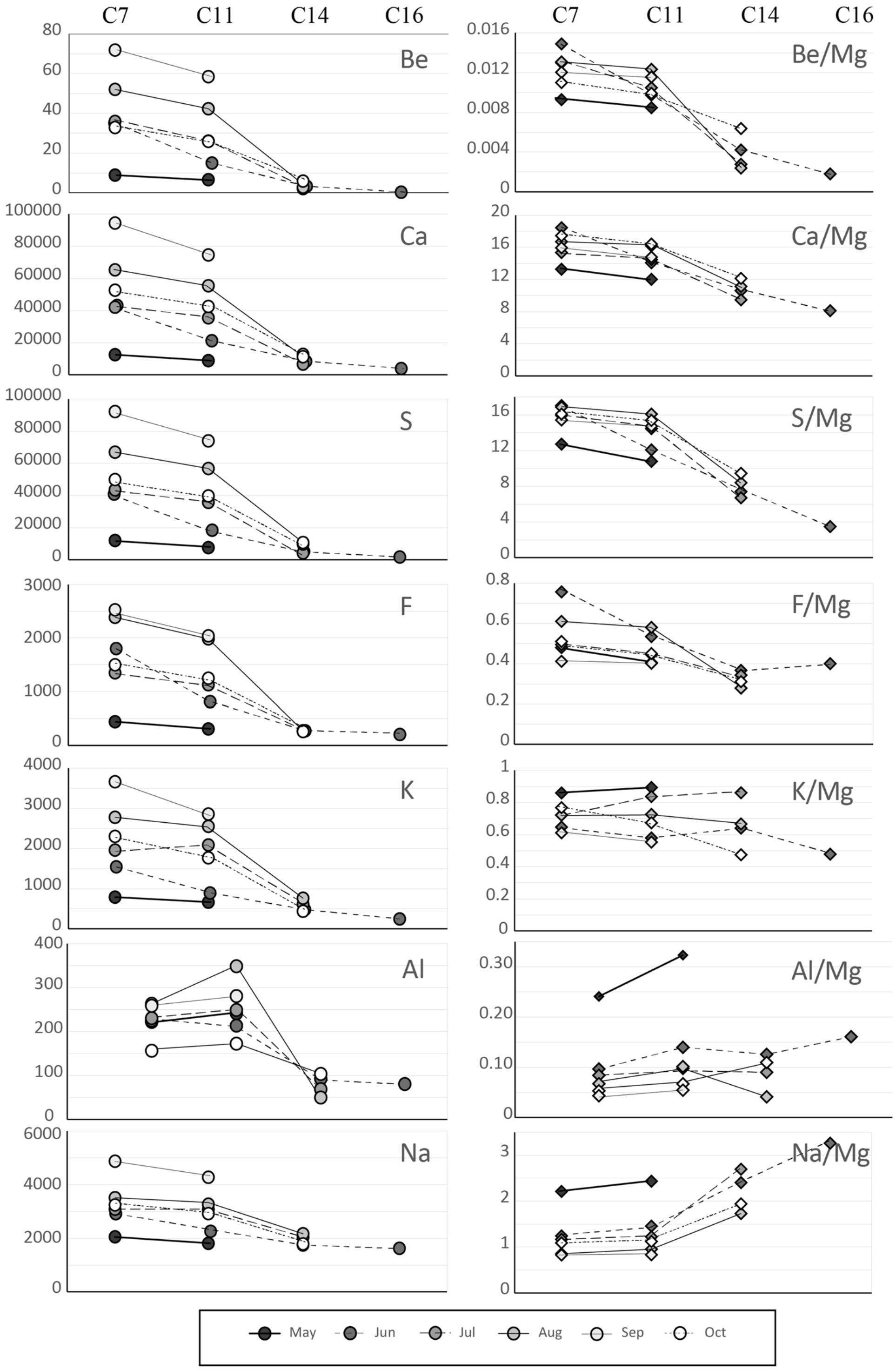
Bismuth, Ga, and W are known to readily adsorb to HFO (Salminen et al. 2005). The concentrations of Ga and Ge at the various sampling sites were similar, or even lower, than what was measured in the reference sample; this indicates that these elements have not leached from the tailings. However, the whole study area is a mineralized area, and the reference sample may have been affected by mineralization at another nearby site. At all locations, including the Ref site, the Ga and Ge concentrations were high compared to what has been measured in pristine waters in Sweden (0.0015 µg/L for Ga and 0.015 µg/L for Ge) (Salminen et al. 2005) and elsewhere (Rosenberg 2008 and references therein).

Mobility and Transport of Be

Dissolved Be was detected at high concentrations in all of the surface water samples downstream of the Smaltjärnen tailings (Fig. 6). The concentrations of Be were very high (average value: 41 µg/L at C7) relative to the reference sample (average value: 0.06 µg/L) and Be concentrations detected in other surface water studies (e.g. Neal 2003; Nordstrom 2008; Salminen et al. 2005; Taylor et al. 2003).

The Be detected at the study area originated from the unusual mineral danalite [$Be_3(Fe_{4.4}Mn_{0.95}Zn_{0.4})(SiO_4)_{3.2}S_{1.4}$], which is unstable in oxic and/or acidic conditions (Burt 1980) and had weathered in the upper parts of the Smaltjärnen tailings (Hällström et al. 2020b). Previous studies had hypothesized that the released Be has entered secondary Al-minerals and gypsum in the tailings and was later released to the groundwater by gypsum dissolution (Hällström et al. 2020b; Salifu et al. 2019). A strong correlation between Be, Ca, and S was detected in the surface waters downstream of Smaltjärnen (Fig. 4). Other studies have yielded similar results (Navrátil 2000; Nordstrom 2008); nevertheless, the relationship between these three elements is not fully known.

Fig. 4 Dissolved concentrations of Be, together with dissolved Ca, S, F, K, Al, and Na (in µg/L) from Hällström et al. 2020a, along with the normalized data based on the Mg ratio at C7, C11, C14 and C16 from May to October



In the surface water, Be was transported between C7 and C11 without precipitation to the sediments, yet partially precipitated between C11 and C14, with concentrations in the water column decreasing threefold in this stretch of river. According to the mixing calculations, the decrease in Be concentrations was partly due to precipitation, possibly together with Mn, which decreased in similar molar proportions. Sediments at C15 and C16 contained enriched concentrations of Be. Elevated concentrations of Be in the sediments at C15 and C16 (60 and 96 mg/kg TS, respectively) compared to the reference sample (3 mg/kg) indicating that the Be partly settled to the sediments in the Nittälven river (Grahn 2017). Precipitation of Be with secondary Mn mineral formations was

Fig. 5 Dissolved and particulate Fe (µg/L) at C7, C11, C14 and C16, along with the corresponding average reference values, during sampling from May to October (from Hällström et al. (2020a))

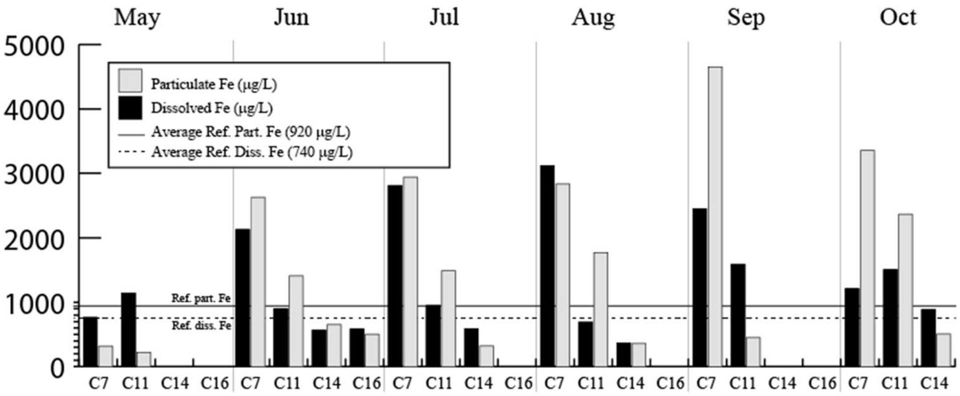
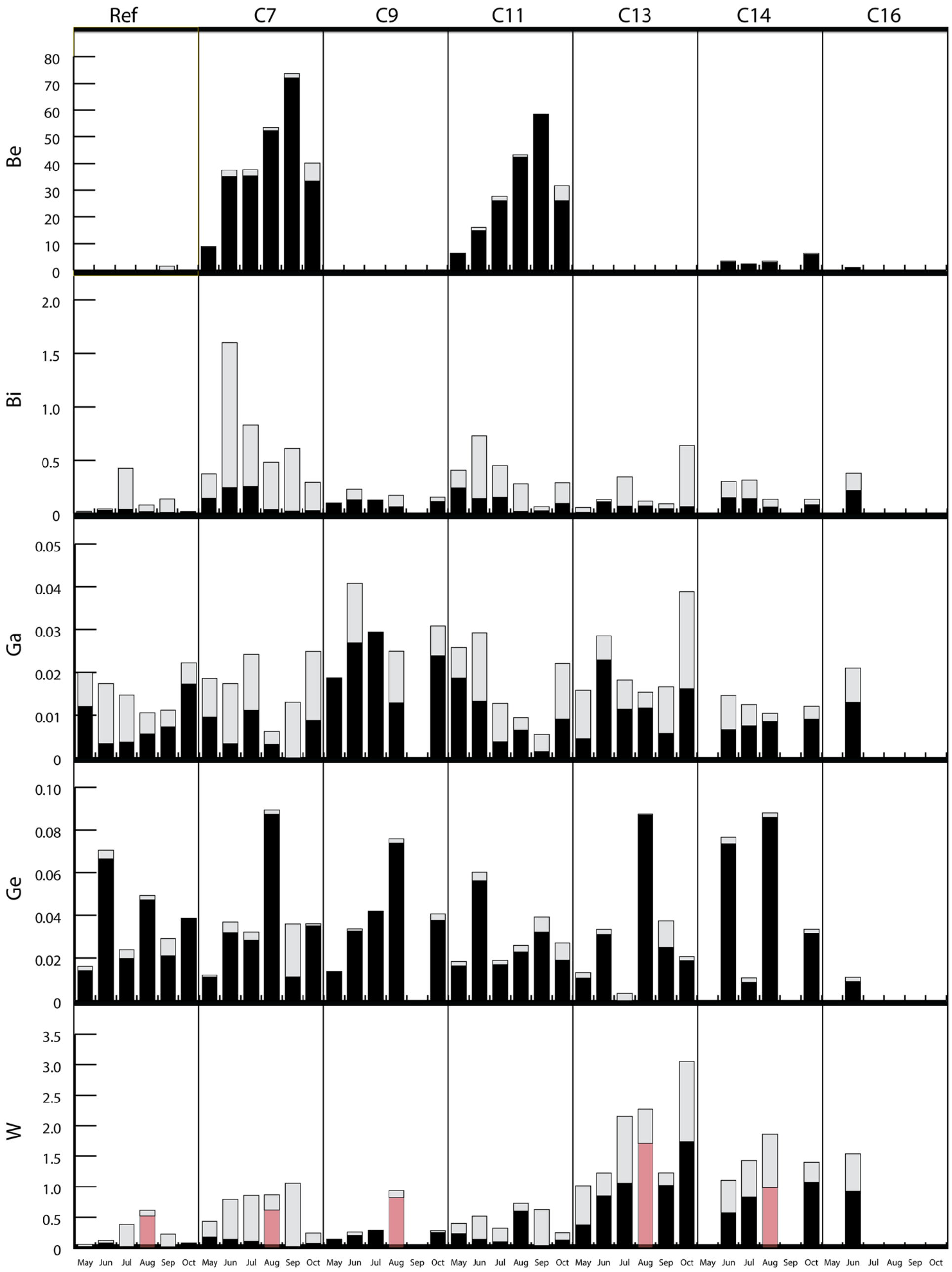


Fig. 6 Dissolved (black) and particulate (gray) fractions of Be, Bi, Ga, Ge and W (µg/L) at the seven sampling locations (Ref, C7, C9, C11, C13, C14 and C16) during May-Oct. Tungsten concentrations were published by Hällström et al. (2020a) and the red bars for W show potential contamination based on the high W concentrations measured in the reference sample



not confirmed mineralogically in the Nittälven sediments and needs to be studied further.

Although Be was partly removed from the water column based on settlement to the sediment, elevated concentrations of dissolved Be were still observed in the surface waters of both the Pumpbäcken and Nittälven. The surface water at C7 had an average pH of 5.6 and was highly oxygenated ($O_2 = 11$ mg/L) (Hällström et al. 2020a). Under these geochemical conditions, dissolved Be should precipitate as insoluble $Be(OH)_2$ in the absence of complexing ligands (Alderighi et al. 2000). Beryllium tends to form strong complexes with both organic and inorganic species due to its small atomic size and relatively high charge (Alderighi et al. 2000; Nordberg et al. 2015). However, the speciation of Be in water is complex even with simple ligands (Alderighi et al. 2000; Taylor et al. 2003) and studies of Be thermodynamics in aqueous solutions are limited due to Be toxicity (Alderighi et al. 2000; Mederos et al. 2001; Schmidbaur et al. 2001). A very strong correlation between Be and F concentrations was observed in the surface waters downstream of the Smaltjärnen repository. The high affinity at which Be complexes with F in aqueous solutions at $pH < 8$ has also been reported in other studies (e.g. Navrátil 2000; Nordstrom 2008; Veselý et al. 1989). Furthermore, Be-fluorocomplexes can transport Be long distances and are small enough to pass through 0.2 µm filters (Veselý et al. 1989). Thus, according to Alderighi et al. (2000) and Veselý et al. (1989), BeF^+ should be the dominant species downstream of Smaltjärnen based on the measured pH values (5.2–6.6). Aluminium and Be are known to compete for the same fluorocomplexes in water. The two have a similar atomic structure and are believed to show similar geochemical behavior (Nordberg et al. 2015). However, in the surface waters downstream of Yxsjöberg, Al had a different pattern than Be and F (Hällström et al. 2020a); both Be and F were transported more than 5 km from the Yxsjöberg mine site.

Mobility and Transport of Bi and W

Elevated concentrations of Bi were found in the particulate phase of C7 and C11 at all sampling occasions compared to the reference samples. In contrast to the major elements (Ca, S, Fe) and trace elements (Be, W), Bi concentrations peaked in June, with lower concentrations observed between July–October. The high release of Bi during June indicates that the element was flushed out by the spring flood. This could be due to either the physical movement of Bi particles directly to Smaltjärnen Lake and C7, or the chemical weathering of Bi minerals under the snow-covered tailings during winter, which would then be flushed out by water percolating through the tailings. Very little information about the mobility of Bi in mine waste and drainage is currently available (Hällström et al. 2018a, b; Jung et al. 2002). Bismuth is known to behave similarly to As, Sb, and Pb; as such, this element readily adsorbs to HFO (Salminen et al. 2005). For example, in Korea, Bi was found at high concentrations in sediments but at low concentrations in surface waters downstream of the Dalsung Cu-W mine (Jung et al. 2002). The authors suggested that the high sediment concentrations could be because particulate Bi is transported by erosion due to wind and water, as dissolved Bi has low mobility under acidic and oxidizing conditions (Jung et al. 2002).

The results from Yxsjöberg are more indicative of the chemical weathering of primary minerals from the tailings and subsequent adsorption to HFO in downstream surface waters. In the Smaltjärnen tailings, Bi was predominantly present in bismuthinite, with a few grains of pure Bi also present. Both bismuthinite and pure Bi were found as inclusions in silicate minerals (Hällström et al. 2018a). None of the major elements in silicates (Ca, Al, Mg, K, Si) showed peak concentrations in June, which suggests that erosion was not the dominant transport mechanism for Bi. Furthermore, the upper parts of the tailings, which have $pH < 5$, showed lower Bi concentrations than deeper sections with $pH \approx 6$ (Hällström et al. 2018a; Fig. 7). Furthermore, water soluble phases of Bi leached out in the deeper tailings where HFO were absent (Hällström et al. 2018b). This is similar to what was observed for W in the tailings (Hällström et al. 2020a), suggesting that Bi geochemically weathers in the upper parts of the Yxsjöberg tailings, partly adsorbing to HFO (Fig. 6).

Bismuth released from the deeper tailings, which have a higher pH, leached to Pumpbäcken, where Bi most probably adsorbed to HFO. As was the case for Fe and W, the particulate concentrations of Bi decreased substantially between C7 and C11, indicating sedimentation between the two sampling locations (Fig. 7). The sediments in C15 and C16 contained enriched concentrations of W (800 and 500 mg/kg, respectively) compared to the reference sample (< 50 mg/kg; Grahn 2017), indicating that W coprecipitated with Fe. Bismuth in the sediments has not been analysed.

The dissolved Bi concentrations in surface water decreased with increasing water flow from May to September, which was a similar trend to what was observed for the major elements. In June and July, the dissolved Bi concentrations were relatively stable (0.25–0.15 µg/L) between C7, C11, C14, and C16, indicating that dissolved Bi had been transported more than 5 km from the site. The release of dissolved Bi strengthens the hypothesis that Bi was released by geochemical weathering rather than physical movement. A detailed study of Bi with environmental mineralogy in the tailings profile is needed to fully understand its geochemical behavior.

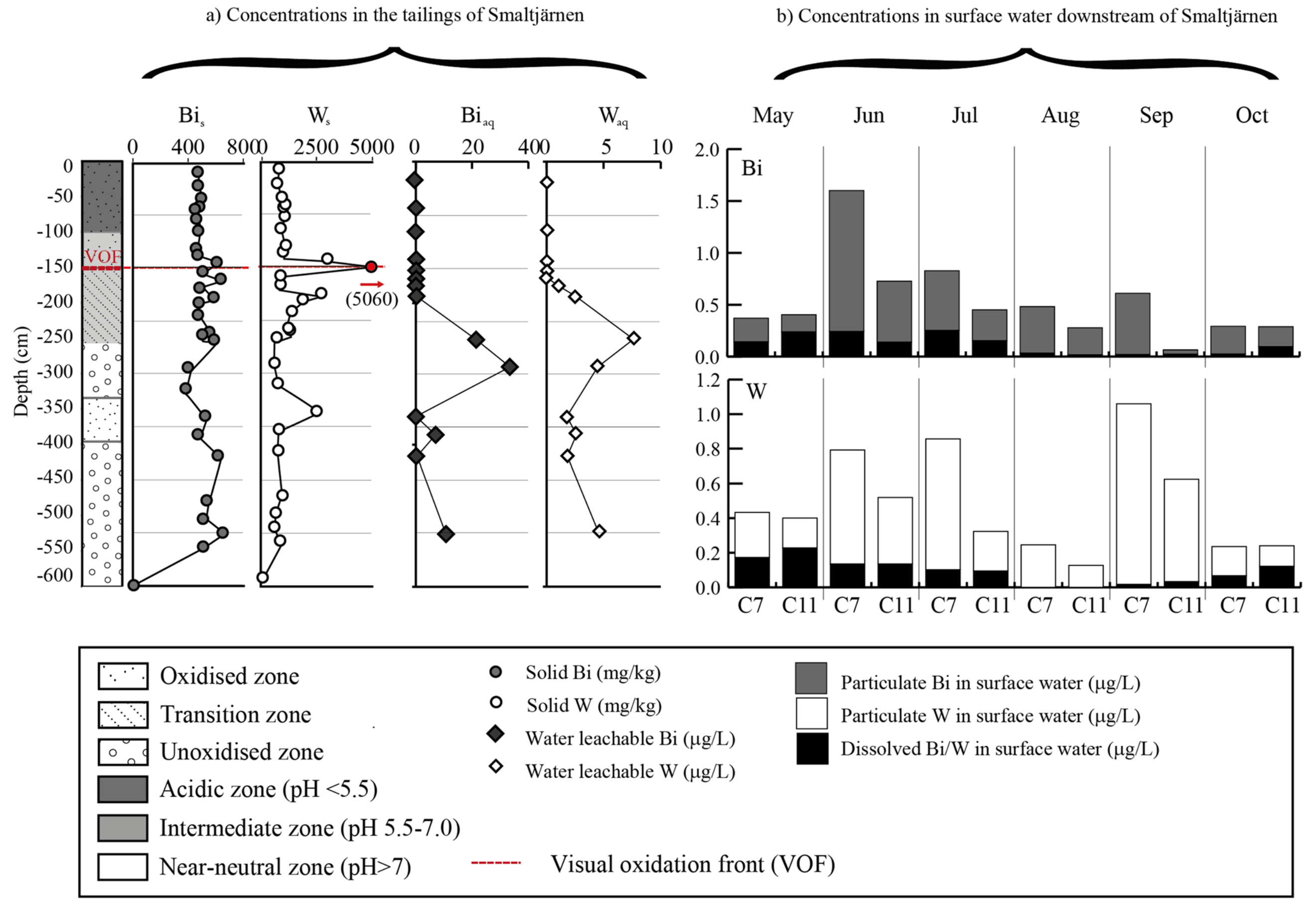


Fig. 7 (**a**) Changes in Bi and W concentrations in Smaltjärnen tailings along a depth gradient in both solid (Hällström et al. 2018a) and water soluble (Hällström et al. 2018b) phases, and (**b**) particulate and dissolved Bi and W concentrations in the surface waters at C7 and C11 from May to October

Diatom Response to the Water Quality Downstream of the Yxsjöberg Mine Site

A high abundance of *Brachysira neoexilis* at C7, C11, and C14, high levels of *Achnanthidium minutissimum group II* at C13 and C14, and a decrease in the amount of *Tabellaria flocculosa* at C7, C13, and C14 indicate that water discharged from both the Morkulltjärnen and Smaltjärnen repositories degraded water quality in the Nittälven at least 2 km from the Yxsjöberg mine site.

Adaptive Diatoms Downstream of the Smaltjärnen Repository

Surface water quality changes downstream of Smaltjärnen generated an increased abundance of *B. neoexilis, Frustulia crassinervia,* and *Fallacia* sp. at the outlet of Smaltjärnen Lake (C7), Fig. 8. *B. neoexilis* was also abundant in C11 and C14, and *Fallacia* was present in C11. *B. neoexilis* is an adaptive species that tolerates high metal concentrations and acidic environments (Kahlert 2012). In Pumpbäcken, dissolved Be, Ca, F, Fe, and S were found at high concentrations (average values of 0.04, 52, 2, 1.7, 33 mg/L, respectively) relative to the reference sample (Fig. 9). Based on the presented results, it is not possible to determine which of the elements had the most adverse impact on the diatoms. However, it should be noted that the Be and F concentrations were above the threshold limits for aquatic organisms, while Ca and S concentrations did not exceed drinking water standards (WHO 2004) and the pH was near-neutral.

Concentrations of Be above 1 µg/L are believed to have adverse effects on ecosystems in aqueous media (Neal 2003). Downstream of the Smaltjärnen repository, Be concentrations were well above 1 µg/L at C7, C11, and C14. Fluorine is known to be toxic to algae, aquatic plants, invertebrates, and fish in aqueous media, especially soft water (Camargo 2003). The bioavailability of F decreases as the ionic strength of the water increases due to F-complexation with Ca. Therefore, toxic values of F range from anything exceeding 0.5 mg/L in soft water to values above 1.5 mg/L in marine water (Camargo 2003). At C7, the average F concentration was above 1.7 mg/L, while the average F

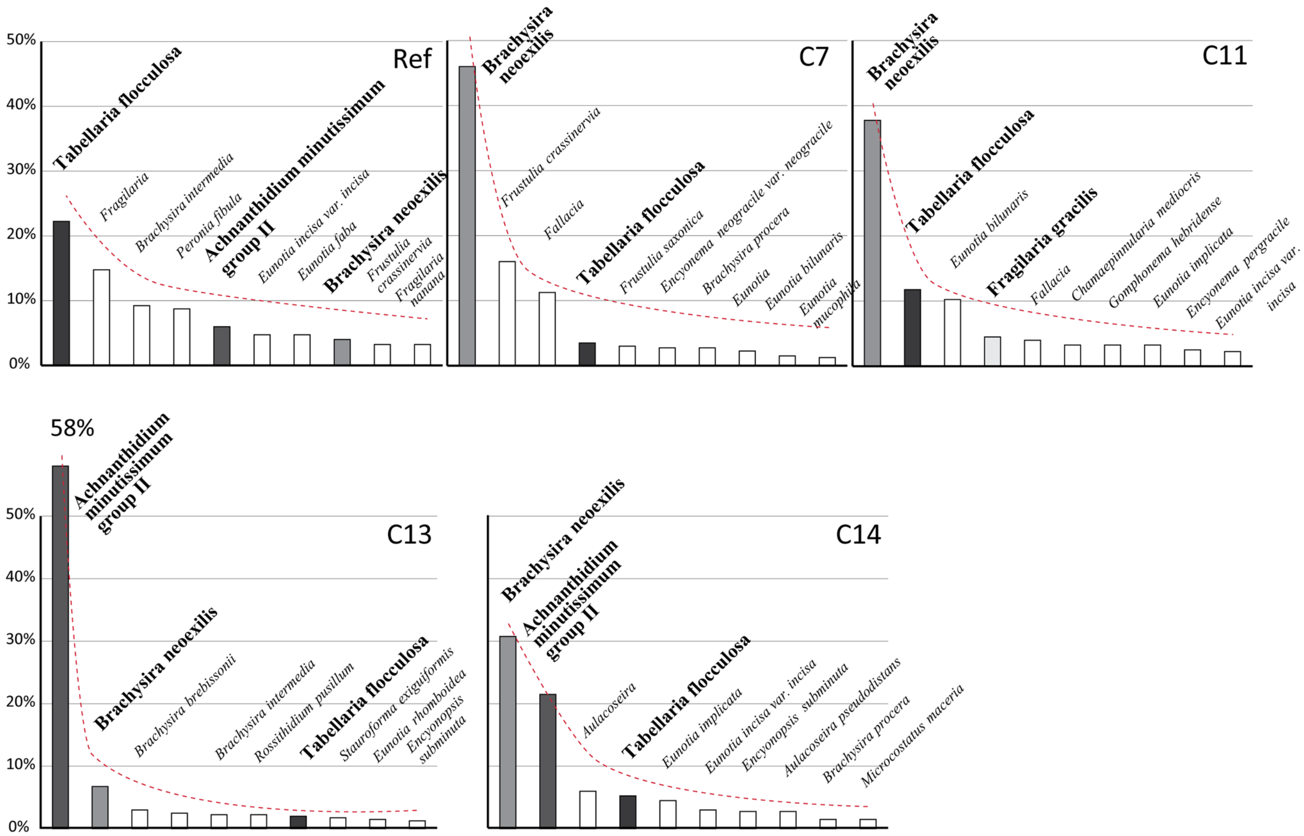


Fig. 8 The taxonomy of the 10 most abundant species at Ref, C7, C11, C13 and C14, with gray bars for the metal tolerant (*Achnanthidium minutissimum group II, Brachysira neoexilis and Fragilaria gracilis*) and metal intolerant (*Tabellaria flocculosa*) species

concentration was 1.2 mg/L at C11. High concentrations of Be and F could explain the decreased species diversity, increased prevalence of *Brachysira neoexilis,* and > 1% deformed valves at these sites. The F concentration had decreased considerably (0.3 mg/L) at C14, which could explain the more significant changes to diatom diversity at C7 relative to C14.

The highest proportion of deformed valves (1.75%) was found at C11, a site at which *Fragilaria gracilis* was far more abundant than at the Ref site and C7. C11 demonstrated higher dissolved Al concentrations, along with lower dissolved F and Fe concentrations, than C7. *F. gracilis* is a metal-tolerant species (Kahlert 2012); the high abundance in C11 could indicate a higher tolerance to Al than other diatom species.

Adaptive Diatoms Downstream of the Morkulltjärnen Repository

In the surface water downstream of Morkulltjärnen (C13), *A. minutissimum* group II were very abundant (58%; Fig. 8). There, the water had a near-neutral pH (6.6) and high concentrations of dissolved W (average value: 1.2 µg/L; Fig. 9). No other elements were detected at high dissolved concentrations in the surface water. A high abundance of *A. minutissimum* group II were also found in C14, where the Nittälven River had co-mingled with Pumpbäcken. *A. minutissimum* is classified as a circumneutral, metal-tolerant diatom (Dixit et al. 1991; Witkowski et al. 2011) that is often found at high levels in streams and lakes under oligotroph conditions and that contain elevated concentrations of trace metals (Cattaneo et al. 2004; Ruggiu et al. 1998). Previous studies have found that *A. minutissimum* abundance increases during active mining periods, more specifically, increased concentrations of Cu and Ni (Kihlman and Kauppila 2009) or Zn, Cd, and Fe with neutral pH conditions (Cattaneo et al. 2004).

Metal-Intolerant Species Affected by Mine Drainage from the Yxsjöberg Mine Site

The understanding of the metal tolerance of *Tabellaria flocculosa* differs between different researchers. In Sweden, it is classified as a metal-tolerant species (Kahlert 2012), whereas others have reported that it disappears from sediments polluted by mining activities related to Cu, Zn, Fe,

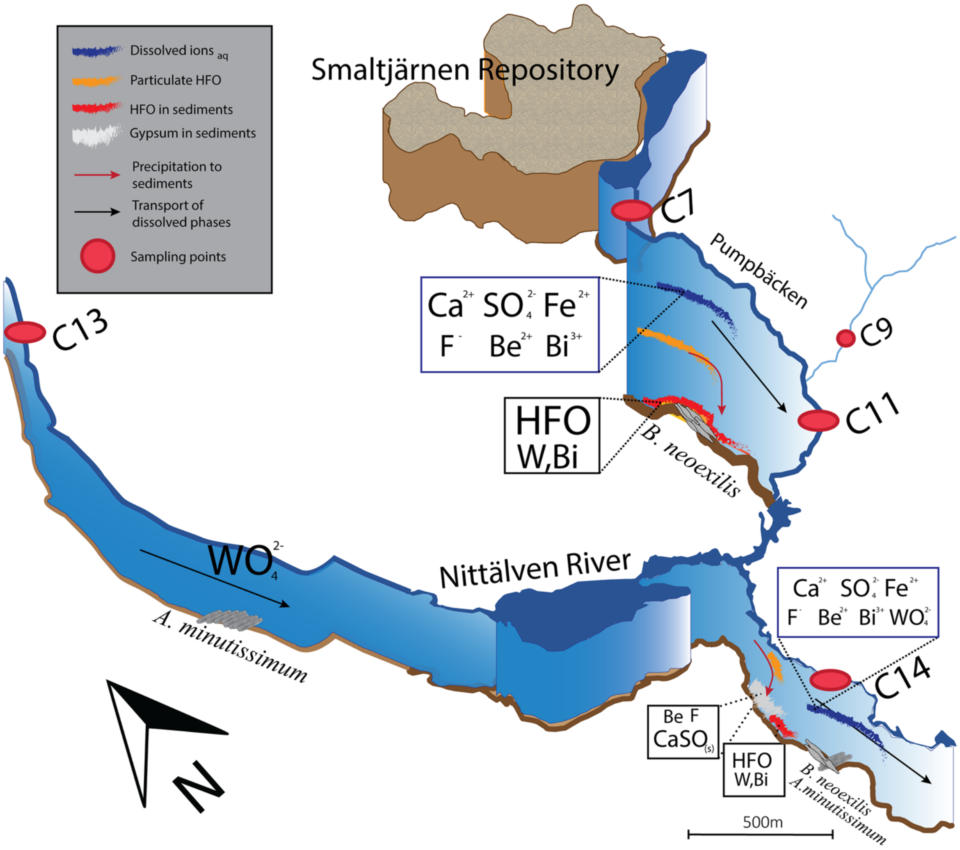


Fig. 9 Schematic illustration of the transport and precipitation of Be, Bi, Ca, F, HFO, SO_4 and WO_4 along Pumpbäcken stream (C7 and C11) and the Nittälven River (C13, C14) downstream of the Yxsjöberg mine site. The dominant adaptive diatom species (*Brachysira neoexilis* and *Achnanthidium minutissimum*) at these sites are also shown. Note: the depths of the Pumpbäcken stream and Nittälven River are not representative of the actual depth

and Cd (Austin and Munteanu 1984; Cattaneo et al. 2004; Hirst et al. 2002). In Yxsjöberg, the highest content of *T. flocculosa* relative to all other identified diatoms (22%) was found in the reference sample, while very low levels were found at C7, C13, and C14 (Fig. 8). It should be noted that *T. flocculosa* accounted for 12% of total diatoms at C11. These results indicate that *T. flocculosa* is sensitive to pH values between 5.6 and 6.6 and elevated concentrations of dissolved Be, F, Fe, and/or W.

Conclusion

Mine drainage from the Smaltjärnen repository has degraded water quality in the Pumpbäcken stream, which now has a slightly acidic pH (5.6–5.9) and elevated dissolved Be, Ca, F, Fe, and SO_4 concentrations relative to the reference sample. Elevated, but low, concentrations of Al and Bi were also detected in the Pumpbäcken stream. Under these pH conditions (< 6), Be is expected to form insoluble hydroxides and precipitate from the water; however, elevated concentrations of Be were transported more than 5 km from the repository. Moreover, Be and F concentrations in the surface water were strongly correlated and is most likely explained by the formation of Be-fluorocomplexes.

Secondary formations of hydrous ferric oxides (HFO) has likely controlled the mobility of Bi and W by co-precipitation and likely settled into the sediment before the water from the Pumpbäcken reaches the Nittälven River. Both Bi and W has previously been considered as immobile elements but have leached from the Smaltjärnen tailings by geochemical weathering and entered the Pumpbäcken stream. After the Pumpbäcken and Nittälven co-mingled, the concentrations of Be, Ca, F, and S decreased, likely due to dilution rather than precipitation. Water quality in the Nittälven River was affected by near-neutral mine drainage from the Morkulltjärnen repository, which had elevated concentrations of dissolved W.

The water quality accompanying elevated concentrations of dissolved Al, Be, F, Fe, and W downstream of the Yxsjöberg mine site had a negative impact on epilithic water diatoms, with decreased taxonomy diversity, richness, and evenness. The taxonomic analyses of diatoms revealed that metal-tolerant species dominated downstream of Smaltjärnen (*B. neoexilis)* and Morkulltjärnen *(A. minutissimum)*of metal-intolerant species (e.g. *T. flocculosa)* decreased downstream of both repositories. More than 1% of the diatoms in surface water downstream Smaltjärnen were deformed, and the ACID-index indicated a very acidic environment, while water downstream of the Morkulltjärnen repository had a low abundance of deformed valves and near-neutral ACID-index. These results of epilithic water diatoms show that the water quality downstream of the Smaltjärnen repository has a more negative impact on ecosystem functioning than the water quality downstream of the Morkulltjärnen repository. The water quality, along with the negative impact on diatom biodiversity, stress the need for remediation. The release of Be, Bi, F, Fe, and W from the Smaltjärnen tailings will continue for hundreds of years if remediation measures are not taken because only a small portion of the tailings have been weathered during > 50 years of storage (Hällström et al. 2020a, b).

The low Be, Bi, Ca, F, Fe, and S concentrations, along with a near-neutral pH (average pH 6.6), downstream of the Morkulltjärnen repository suggest that a cover and water saturation could inhibit sulfide and danalite oxidation, and indirectly prevent fluorite weathering. However, the high dissolved W concentrations downstream of the Morkulltjärnen repository demonstrate that such measures can increase W mobility.

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