A Comparison of Be and W in Mine Drainage Downstream Two Different Repositories Storing Tailings from a Skarn Ore

Re-mining as an alternative remediation method

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Abstract

The geochemical behaviour of beryllium (Be) and tungsten (W) in neutral mine drainage (NMD) downstream of two skarn tailings repositories (Smaltjärnen and Morkulltjärnen) was studied. Surface water was sampled monthly during 2018, with epilithic water diatoms used as bioindicators. Smaltjärnen (1918–1963) has been open to the atmosphere for over 30 years, while Morkulltjärnen (1969–1989) was covered and water-saturated directly after closure. NMD with high concentrations of dissolved Be from Smaltjärnen and dissolved W from Morkulltjärnen had negative environmental impacts as far as 5 km from the Yxsjöberg mine site. Re-mining could be a potential remediation method.

Keywords: Neutral Mine Drainage, Tungsten, Beryllium, Tailings, Re-mining, Remediation

Introduction

To ensure a sustainable mine waste and water management in the future, further geochemical knowledge regarding several high-tech critical elements is needed (Filella and Rodriquez-Murillo, 2017). Thus, the demand of beryllium (Be) and tungsten (W) in society are expected to increase due to their incorporation in green technology (European Comission, 2020). Consequently, there is a risk that the geochemical cycles of these elements in the environment will change as mining increases to meet industrial demand (Nuss and Blengini, 2018). At present, the speciation, mobility, transport and fate of Be and W from mine waste to the terrestrial environment is poorly studied although both are considered potentially harmful elements (Strigul *et al.*, 2009; Taylor *et al.*, 2003). Research regarding environmental problems related to mine drainage has mainly focused on acid mine drainage (AMD). As such, there is insufficient knowledge about the mobility and ecotoxicity of metals, including Be and W, in Neutral Mine Drainage (NMD). Understanding the geochemical behaviour of Be and W is important since a lack of knowledge can result in the implementation of inappropriate preventative measures for mineral weathering during the commissioning phase of mine closure, potentially increasing the extent to which these elements are released to the environment.

Skarn ores can be enriched in both Be and W, which may end up in the tailings due to inefficient extraction techniques. Furthermore, skarn tailings can contain high concentrations of carbonates and generate neutral mine drainage (NMD) (Kwak, 2012). This makes historical skarn tailings enriched in Be and W an ideal setting to study, to increase the knowledge regarding the geochemical behaviour and impact of mine drainage on the downstream water quality and ecosystems. In this study, mine drainage downstream of two tailings repositories (Smaltjärnen and Morkulltjärnen) from the same skarn ore were compared with respect to: 1) Be and W concentrations; 2) Be and W distribution between dissolved and particulate fractions; and 3) the mine drainage impact on epilithic water diatoms. Epilithic water diatoms can be used as a first bioindicator for discerning negative environmental impacts downstream of mine tailings (CEN, 2004b).

Furthermore, the feasibility of using re-mining as a potential remediation method was investigated for the Smaltjärnen tailings. Thus, re-mining historical and environmentally hazardous tailings enriched in Be and W could be used as a remediation method for decreasing adverse impacts to the surrounding environment, as well as supporting the domestic production of these critical metals (Hällström *et al.*, 2018).

Study site

The skarn tailings stored in the Smaltjärnen and Morkulltjärnen repositories originate from the former W, Cu and CaF_2 mine in Yxsjöberg, Sweden (Fig. 1). The Smaltjärnen repository was used between 1918–1963, and the tailings have been stored open to the atmosphere for more than 30 years. Previous studies have shown that the Smaltjärnen tailings are enriched in Be (284 mg/kg) and W (960 kg/mg), together with pyrrhotite (2 wt%), calcite (6 wt%), and fluorite (4%) (Hällström *et al.*, 2018). Beryllium is mainly hosted by the unusual mineral danalite ($Fe_4Be_3(SiO_4)_3S$) (Hällström *et al.*, 2020b), while W is found in scheelite ($CaWO_4$) (Hällström *et al.*, 2020a,b). Tailings generated between 1969–1989 were stored in Morkulltjärnens repository. The Morkulltjärnen impoundment was covered and water-saturated directly after closure. Mine water from Smaltjärnen drains into the Pumpbäcken stream, while the Morkulltjärnen tailings drain into the Nittälven River. The Pumpbäcken and Nittälven merge south of the Yxsjöberg mine site (Fig.1).

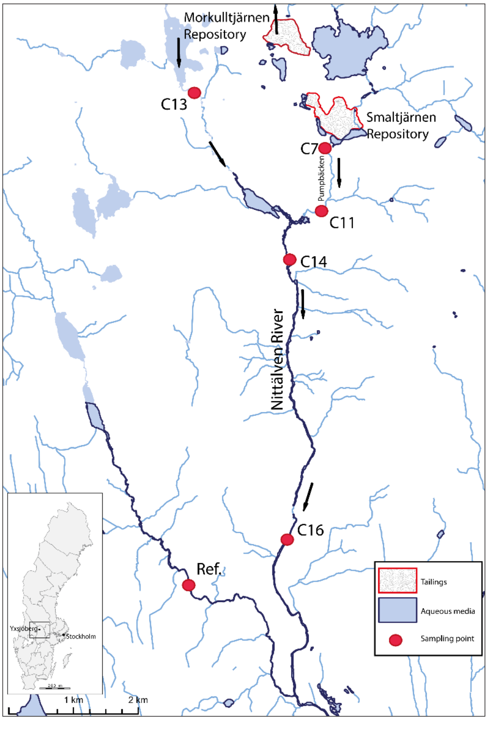

Figure 1 Catchment areas of the Morkulltjärnen (1) and Smaltjärnen (2) repositories, along with sampling locations downstream of the Yxsjöberg mining area.

Methods

Surface water was sampled at five sampling points downstream of the Smaltjärnen and Morkulltjärnen repositories, as well as at one reference point (Ref) (Fig. 1).

The pH, electrical conductivity (EC) and temperature were measured 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 surface water was pumped through Geotech polycarbonate and acrylic filter holders (Geotech Environmental Equipment Inc., Denver, CO) 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. Screening analyses (71 elements) 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 utilised method was validated with the certified reference materials SLEW-2, CASS- 2 and NASS-4 for all elements analysed by ALS Scandinavia (Rodushkin & Ruth, 1997). Total and dissolved F, SO_4 and Cl were analysed by ion chromatography (CSN ISO 10304-1, CSN EN 16192). 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 analysed 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.

Epilithic water diatoms were sampled from the Nittälven and Pumpbäcken at sampling points C7, C11, C13, C14 and Ref. in October 2018. The sampling procedure was carried out according to the European/ Swedish standard protocol (CEN, 2014a). The samples were sent to SLU Uppsala for analysis and were analysed 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 (Kahlert, 2012).

Results & Discussion

Total concentrations in surface water

The water quality at the outlet of Smaltjärnen lake (C7) was negatively affected by ongoing sulfide oxidation at the Smaltjärnen repository. The average pH in C7 was lower than in the Ref (pH: 5.7 and 6.2, respectively), and the average EC was higher (350 and 34 µS/cm, respectively), Tab 1. Furthermore, at the outlet of Smaltjärnen, the total concentrations of Be, Ca, F, and S (average values of 42 µg/L and 52, 1.7, and 51 mg/L, respectively) were strongly enriched compared to the Ref (Tab. 1). The release of Ca and S originates from secondary gypsum dissolution and F from fluorite weathering. Thus, the open storage of tailings in the Smaltjärnen repository has resulted in pyrrhotite oxidation, calcite depletion, fluorite weathering, and the secondary formation of hydrous ferric oxides (HFO) and gypsum in the upper-parts of the tailings (Hällström *et al.*, 2020a). The pH in the upper parts of the tailings has been lowered from 8 to 4, but calcite have had the potential to partly buffer the mine drainage, resulting in a release of NMD to the groundwater (Hällström *et al.*, 2020a) and the surface water in C7. The elevated concentrations of Be at C7 can be traced to ongoing oxidation at the Smaltjärnen repository. Thus, danalite ($Fe_4Be_3(SiO_4)_3S$) has oxidised down to a depth of 1.5 m, with Be mobilisation intensifying due to the acid produced from pyrrhotite oxidation (Hällström *et al.*, 2020b). Sampling site C7 also showed slightly enriched total concentrations of Fe and W (average values of 4.9 mg/L and 0.7 µg/L, respectively) relative to the reference site. Previous studies have provided evidence for W mobilisation at the Smaltjärnen repository, with the release of W as an indirect consequence of sulfide oxidation (Hällström *et al.*, 2020a). Thus, the acid produced has released CO_3^{2-}, which in turn has moved downwards and weathered scheelite (CaWO4) by anion exchange. Tungstate partly adsorbed to hydrous ferric oxides (HFOs) and remained immobilised within the Smaltjärnen repository (Hällström *et al.*, 2020a).

Downstream Morkulltjärnen repository (C13), neutral pH (average 6.7), low EC (29 µS/cm) and low concentrations of Be, Ca, F, and S were present (Tab. 1). These results indicate that the preventative measures of physical cover and water saturation have decreased sulfide and danalite oxidation at the Morkulltjärnen repository, as well as indirectly affected calcite depletion, fluorite weathering and the secondary

Table 1 *Average total concentrations of the major elements (Al, Ca, F, Fe, Mn, S; mg/L) and trace elements (Be and W; µg/L) in surface water collected from Ref, C7, C11, C13, C14 and C16. N represents the number of samples taken.*

		pH	EC	Al	Ca	F	Fe	Mn	S	Be	W
	N		µS/cm			mg/L				µg/L	
Ref	6	6.2	34	0.1	3.8	<0.2	1.7	0.1	0.9	0.3	0.2
C7	6	5.7	350	0.3	52	1.7	4.9	1.4	51	42	0.7
C11	6	5.9	270	0.3	40	1.2	2.4	0.9	39	31	0.5
C13	6	6.7	29	0.1	3.0	<0.2	1.1	0.3	1.2	0.1	1.8
C14	4	6.4	61	0.1	9.9	0.3	1.1	0.5	7.5	3.9	1.4
C16	1	6.5	37	0.1	4.1	0.2	1.1	0.2	2.1	1.1	1.5

formation of HFO. C13 samples showed high concentrations of total W (average 1.8 µg/L), with concentrations up to seven times higher than what was measured in Ref. In C14, water from Smaltjärnen and Morkulltjärnen has co-mingled. There, total concentrations of Be, W and S (average 3.9 and 1.4 µg/L, and 7.5 mg/L, respectively) relative to Ref, while F concentrations were also above the detection limit (0.2 mg/L). At C16, 5 km downstream of the Yxsjöberg mine site, Be, Bi, S and W concentrations were still 2-6 times higher than what was measured in the reference sample. This shows that Be released from Smaltjärnen, along with W released from Morkulltjärnen, were transported more than 5 km from the Yxsjöberg mine site and contradicts previous claims that Be and W are immobile elements.

Element distribution between dissolved and particulate fractions

At C7 and C11, more than 90% of Be and F was transported in the dissolved phase (Fig. 3). As mentioned in the introduction, Be should precipitate as insoluble hydroxides in the absence of complexing ligands. A strong correlation between dissolved Be and F 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., Nordstrom, 2008). Furthermore, Be-fluorocomplexes can transport Be long distances and are small enough to pass through 0.2 µm filters (Veselý *et al.*, 1989). Based on the measured pH values (5.2-6.6), BeF^+ should be the dominant species downstream of Smaltjärnen.

Iron was present in similar proportions (40-50%) in the dissolved and particulate fractions at all sampling locations. The Fe concentrations decreased between C7 and C11, ultimately reaching values similar to what was measured in Ref. Iron is known to form HFO under oxidising conditions, and – in this way – has most likely settled into the sediments of the Pumpbäcken. In the surface water downstream of Smaltjärnen, W showed a similar pattern as Fe, i.e., it was mainly transported in the particulate fraction (70%). Furthermore, W concentrations also decreased between C7 and C11, with adsorption or co-precipitation with HFO the most likely mechanism underlying this observation. Tungsten is known to have a high affinity for HFO when the pH is below 8 (Gustafsson, 2003), and subjecting the

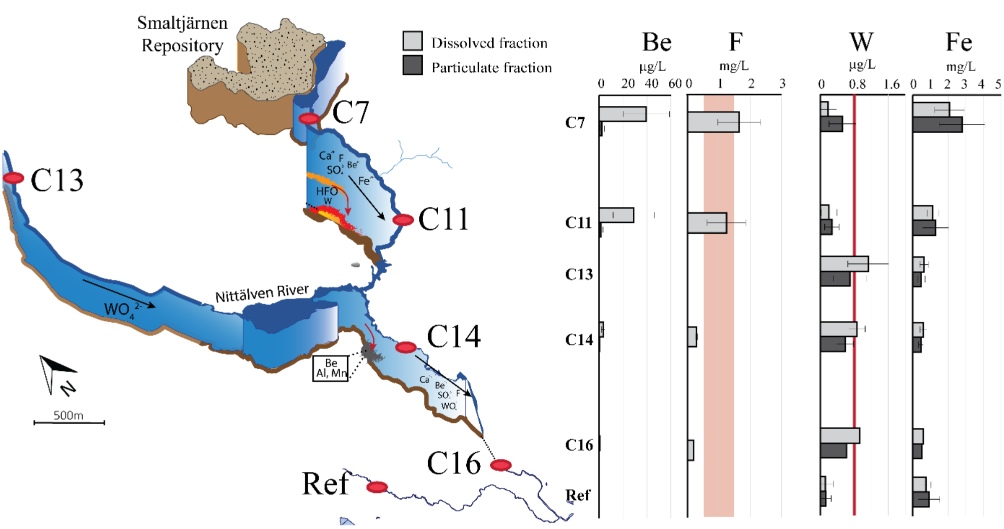

Figure 3 Dissolved and particulate concentrations of Be, F, W and Fe in surface waters downstream of the Smaltjärnen (C9, C11) and Morkulltjärnen repositories (C13), as well as the Nittälven River (C14, C16). The red lines in the concentration illustrations represents the guideline values for W (0.8 µg/L) and F (0.5-1.5 mg/L).

Smaltjärnen tailing to a seven-step sequential extraction indicated that W co-precipitates with Fe (Hällström *et al*., 2020a). However, W demonstrated different geochemical behaviour downstream of Morkulltjärnen. There, W was mainly transported in the dissolved phase, and at concentrations that exceeded the suggested guideline value for fish in aqueous media (0.8 mg/L) (Strigul *et al*., 2009). High concentrations of dissolved W were also observed from C14 and C16 samples. It is likely that the high concentrations of dissolved W are due to the lack of HFO, which means that the lack of sulfide oxidation in the tailings of the Morkulltjärnen repository has indirectly increased the mobility of W. The higher release of W from Morkulltjärnen compared to Smaltjärnen needs to be studied further.

Mine drainage impacts epilithic water diatom community structure

The diatoms *Achnanthidium minutssiumum*, *Aulacoseira*, *Brachysira neoexilis*, *Fragilaria gracilis* and *Tabellaria flocculosa* are all considered to be metal-tolerant species that can adapt to surface waters with high concentrations of metals (Kahlert, 2012). Cases in which these species have a joint relative abundance over 50% indicate that metal pollution has negatively impacted the surrounding ecosystem. Downstream of both Smaltjärnen and Morkulltjärnen, the metal-tolerant species of diatoms showed a relative abundance more than 50%. At C7 and C11, *Braschysira neoexilis* was the dominant species. The strong growth of *Braschysira neoexilis* at these sites can most likely be explained by low pH values and enriched concentrations of dissolved Be, Ca, F, Fe, and S. Based on the presented results, it is impossible to determine which of the elements had the strongest impact on the diatom community. 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).

At C13, *Achnanthidium minutssiumum* showed a relative abundance of 58%. *Achnanthidium minutissimum* is classified as a circumneutral, metal-tolerant diatom (Dixit *et al*., 1991) that is often found at high levels in streams and lakes under oligotrophic conditions and that contain elevated concentrations of trace metals (Cattaneo *et al*., 2004;). At C13, only dissolved W was present at elevated concentrations and is likely the cause of the *Achnanthidium minutssiumum* dominance.

Conclusion

This study shows the importance of studying the mobility of critical metals in neutral mine drainage (NMD). Beryllium and W have previously been considered immobile elements. However, analyses of the NMD from the Smaltjärnen and Morkulltjärnen repositories showed that both dissolved Be and W can be transported more than 5 km under favourable conditions, as well as exert negative impacts on the surrounding ecosystem. Furthermore, the results have revealed that neither open storage nor storage with cover and water-saturation is an optimal mine waste strategy for the skarn tailings of Yxsjöberg.

***Table 2** The relative abudances of metal-tolerant diatom species (Achnanthidium minutssiumum, Aulacoseira, Brachysira neoexilis, Fragilaria gracilis and Tabellaria flocculosa) in Ref, C7, C13 and C14.*

Taxonomy	Ref	C7	C13	C14
Achnanthidium minutissimum group II	6%	0%	58%	22%
Aulacoseira	0%	0%	0%	6%
Brachysira neoexilis	4%	46%	7%	31%
Fragilaria gracilis	1%	0%	1%	1%
Tabellaria flocculosa	22%	4%	2%	5%
Sum:	33%	50%	68%	64%

The water quality downstream of the Smaltjärnen repository was strongly affected by a decrease in pH and high concentrations of Be, Ca, F and S in the mine drainage. Consequently, the metal-tolerant species *Brachysira neoexilis* has become dominant in the downstream ecosystem, and serves as a bioindicator of the negative impact of mine drainage on the surrounding environment. The noticeable decrease in water quality can be explained by pyrrhotite and danalite oxidation, calcite depletion and fluorite weathering in the exposed tailings. The Smaltjärnen tailings can be expected to weather for hundreds of years since only a small part has weathered during 50-100 years of storage.

The near-neutral pH and low concentrations of Be, Ca, F and S measured downstream of the Morkulltjärnen repository showed that cover and water saturation have limited the geochemical weathering in those tailings. However, high dissolved W concentrations and a strong abundance of the metal tolerant diatom *Achnanthidium minutssiumum* in the surface waters downstream of this repository are indicative of the negative environmental impacts of Morkulltjärnen.

Both the noticeable decrease in water quality and substantial changes in diatom community structure emphasise the need to find a more effective remediation approach. Re-mining could be a beneficial remediation method for the Smaltjärnen tailings since most W was found in intact scheelite grains. If re-mining were to be implemented as a remediation method, the residues produced by the process must be environmentally safe. This means that both primary and secondary minerals hosting Be, F and W need to be extracted. More research regarding mineral processing and metallurgy is needed to ensure that a sustainable extraction process is applied at this site.

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