AN ECOLOGICAL RISK ASSESSMENT FOR ACID MINE DRAINAGE FROM COPPER-NICKEL MINING IN THE KAWISHIWI WATERSHED, MINNESOTA

by

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ABSTRACT

The mining of heavy metals such as copper and nickel has been identified as a potential source of acid mine drainage (AMD), which is a consequence of the oxidation of sulfide minerals that produces sulfuric acid due to mine wastes being exposed to air and water. Contamination of AMD to surface waters may pose detrimental effects on aquatic organisms. Accidental releases of process or seepage waters are likely to occur by mining ventures. The Kawishiwi watershed lies over a layered mafic intrusion known as the Duluth Complex, a mineral deposit rich in copper and nickel. Twin Metals Minnesota has renewed the mineral leases looking to develop an underground mine operation adjacently to Birch Lake and the South Kawishiwi River. Therefore, an aquatic ecological risk assessment is necessary to access and protect ecosystems that may be exposed to AMD. My study examined four potential contamination scenarios (A-D) in Birch Lake, Kawishiwi Watershed, Minnesota, based on hypothetical spills and metal concentrations. Concentrations reported in seepage waters from mines or from local sources that share the same mineral deposit or rock characteristics, were chosen to represent realistic scenarios. The concentrations varied for copper from 11 to 0.1 µg/L and for nickel from 1,580 to 9 µg/L. The scenarios also accounted for a determined size of spill, which varied from 10 to 0.3% of the total volume of the contact water pond 1. This pond is designated in the Twin Metal Minnesota operations plan to collect the waters from direct precipitation or stormwater that comes in contact with ore or tailings. The purpose of my assessment was to estimate the risks of this contamination to fish species living in the lakes. I used these final concentrations from the proposed scenarios to evaluate if exposure would exceed toxicity endpoints. The risk was assessed using the risk quotient (RQ) method, where the RQ is the ratio of exposure to effect. Risk quotient values < 0.5 are consider below regulatory levels of concern. My results suggest that the toxicity endpoint was exceeded for one of the four contamination scenarios by the most sensitive species: embryos of rainbow trout and bluegill. The contamination scenarios representing the two lowest concentrations for copper and nickel did not suggest levels of concern for either of the fish species. Based on my results, the water volume of Birch Lake would provide sufficient dilution in pollution events that are as much or less than ones represented by Scenarios C and D. Conversely, a spill representing Scenario A would pose risks to fish species exceeding levels of concern, especially to the most sensitive species. My assessment may be applicable when considering the risks that aquatic species could face in the event of a leak or spill of AMD of a sulfide mine in the Kawishiwi Watershed.

INTRODUCTION

The Maturi deposit located in northeastern Minnesota lies within the South Kawishiwi sub-intrusion basal portion as part of the layered mafic intrusion Duluth Complex. This intrusion is composed of low-grade copper-nickel disseminated sulfide ore averaging 0.66% copper and 0.2% nickel (Listerud & Meineke 1977). The growing demand for copper, nickel, and platinum group metals for various technologies and applications has made these minerals critical to human quality of life worldwide. Thus, mining nonferrous minerals within the Duluth Complex is of great interest because it contains one of the largest known undeveloped deposits in the United States, with more than seven billion tons of ore containing copper, nickel, and other precious metals (Miller et al., 2002).

In 2018, the US Bureau of Land Management (BLM) renewed mineral leases over an area of 4,865 acres in the Superior National Forest (NEPA 2018). The company Twin Metals Minnesota was allowed ten years to submit a mine plan of operations to the BLM for all necessary permits and milestones for mine construction. The waste generated during the operations can translate into a potential acid mine drainage (AMD) source. Thus, through the environmental requirements, the possible generation of AMD must be reviewed and assessed. Therefore, the environmental requirements are oriented to analyzing and predicting AMD before any mining project can begin.

Tailings and waste rock piles are considered potential acid-generating sources, because when they are exposed to oxygen and water, sulfide minerals containing copper, nickel, and other metals will oxidize, thus, causing acid rock drainage characterized by high concentrations of metal leachate and low pH levels (Kellogg & Chev 2014). The leaking of AMD into the environment can result in unacceptable risks to the ecosystem and human health, as the exposure and uptake of elevated concentrations of heavy metals can cause adverse effects to plants, invertebrates, and other wildlife (Frelich 2019). This mining project has raised concerns among local communities, scientists, for-profit, and non-profit organizations that fear the pollution of the valuable freshwater resources and a pristine and protected environment from the leaking of AMD (Pearson et al., 2020). Twin Metals Minnesota aims to process 18,000 tons of ore per day and other metals as by-products (TMM, 2020).

Consequently, my study evaluated the effect of possible AMD contributions of metal concentrations on the downstream aquatic ecosystem of the Kawishiwi Watershed by assessing the ecological risk of hypothetical contamination Scenarios in selected fish species representative of the aquatic ecosystem. My ecological risk assessment (ERA) was performed with the idea of connecting the observed adverse effects on fish species exposed to AMD pollution with selected fish species representative of the water bodies, likely to be affected by an eventual AMD contamination from the copper-nickel mining development. These species were chosen for risk assessment as they represent cold and warm aquatic environments of the subwatershed. They also represent the species present in the Boundary Waters Canoe Area, a protected area directly downstream from Birch Lake.

BACKGROUND

Soft water lakes with low alkalinity characterize the Kawishiwi Watershed. White Iron Lake and Birch Lake have background concentrations of 12-27 mg/L of $CaCO_3$, 5.1- 9.7 mg/L of calcium, and a specific conductance of 59 µS/cm (WICOLA 2020). These lakes also have high color, low dissolved solids and nutrients, and very low trace-metal concentrations (TMM 2020). The average copper and nickel concentrations are from 1 to 8 µg/L (TMM 2020). The pristine waters of this ecosystem support walleye populations. These lakes also support northern pikes, white suckers, yellow perch, ciscoes, and rock bass populations (Table 1) (Lind et al. 1978). White Iron and Birch Lakes lie within the Kawishiwi Watershed and are part of a chain of lakes. The South Kawishiwi River flows into the Birch Lake Reservoir, which then flows into White Iron Lake. These waters flow northwest and into the Boundary Waters Canoe Area Wilderness through the Garden Lake Reservoir, composed of Garden, Farm, South Farm (Figure 1) (WICOLA 2020). A dam at the outlet of Birch Lake controls lake levels on Birch Lake and influences water levels in the South Kawishiwi River and White Iron Lake (WICOLA 2020).

Table 1: Fish species representative of Birch Lake and White Iron Lakes.

Common Name	Order	Family	Species
Northern Pike	Esociformes	Esocidae	*Esox lucius*
Black Crappie	Perciformes	Centrarchidae	*Pomoxis nigromaculatus*
Bluegill	Perciformes	Centrarchidae	*Lepomis macrochirus*
Smallmouth Bass	Perciformes	Centrarchidae	*Micropterus dolomieu*
Rock Bass	Perciformes	Centrarchidae	*Ambloplites rupestris*
Walleye	Perciformes	Percidae	*Sander vitreus*
Yellow Perch	Perciformes	Percidae	*Perca flavescens*
Cisco, Lake Herring	Salmoniformes	Salmonidae	*Coregonus artedi*

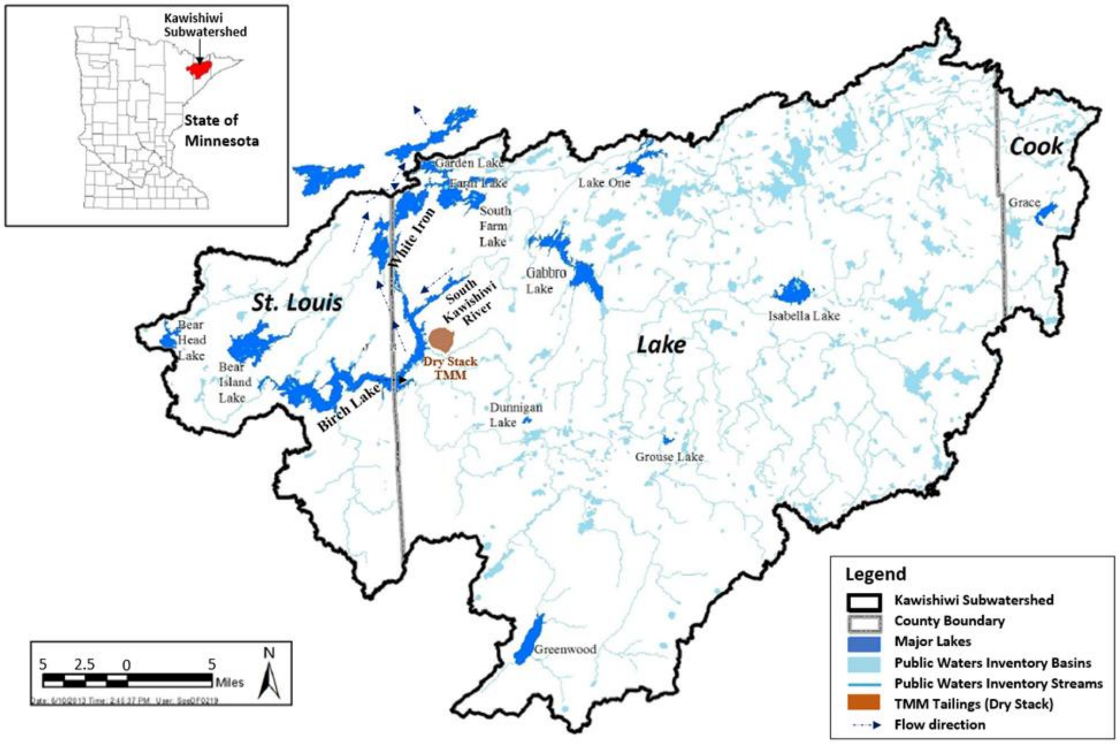

Figure 1: Kawishiwi Watershed. Birch Lake, South Kawishiwi River, and White Iron Lake (Adapted from WICOLA (2020)).

The preliminary analysis performed by Twin Metals Minnesota with respect to the potential for AMD from waste rock stockpiles and tailings suggests that it would be non-existent. This is because Twin Metals Minnesota argued that (1) the project would not be placing waste rock stockpiles on the surface, and (2) the project would recover most sulfides from the ore, producing tailings with sulfur less than 0.2% sulfur. This percentage of sulfur in tailings is important because according to reported tests on Duluth Complex tailings, concentrations at this level would be non-acid generating (Lappako 1988, TMM 2020). Sulfur-containing more than 0.9% has been shown to have an acidic-generating response (Lappako 1988). The metal leaching potential of the tailings is currently being analyzed through kinetic testing, and the data have not been publicly published (TMM 2020).

As mentioned briefly above, AMD is metal-laden and sulfate-rich in liquid form and occurs during land disturbance when sulfur or metal sulfides are exposed to atmospheric conditions (Kellog et al. 2014). It forms from the oxidation of sulfide minerals when the acidity exceeds the alkalinity, with subsequent release of sulfides and metal leaching that can reach high concentrations, becoming detrimental to the environment (Simate & Ndlovu 2014). The primary sulfide minerals responsible for AMD generation are pyrite (FeS_2) and pyrrhotite (FeS) (Lapakko 1988; Kellog et al. 2014). Other minerals are also susceptible to oxidation and subsequent metal release, such as chalcopyrite ($CuFeS_2$) (Heikkinen et al. 2009). Mine drainage of approximately neutral pH may occur when sulfide oxidation is sufficiently weak and/or when sufficient neutralization is available in the mine tailings (Kellog et al. 2014; Heikkinen et al. 2009). Under these conditions, neutral effluents are generated, but some toxic metals and metalloids (such as Ni, Zn, Co, As, and Sb) may be solubilized (Heikkinen et al. 2009).

The natural presence of acid rock generation and metal leaching is a process that has occurred throughout geological time in sulfide ores (Downing & Gravel 2014). Anthropogenic activities such as mining can exacerbate this process by breaking up acid-generating material, solubilizing significant amounts of heavy metal, and increasing metal leaching rates (Jacobs et al. 2014, Downing & Gravel 2014). Responsible care in removing and disposing of acid-generating material is an essential task in these types of ventures (Simate & Ndlovu 2014), due to its potential negative impacts on the environment.

The toxicity of metals in the water does not depend only on the exposure dose but also on their chemical and physical speciation (Newman et al. 2014), along with other factors such as the ionic strength of the medium, hardness of the water, organic matter, pH, redox potential, and valence state. The term speciation refers to the occurrence of an element in different forms in a system, which is essential in determining its potential toxicity and mobility in the environment (Templeton et al. 2000, Paiva Magahlnaes et al. 2014). The combined action of all these factors is involved and could favor the formation of different metal species, resulting in a toxic metal with a higher or lower bioavailability (Bjerregaard and Anderson 2007, Paiva Magahlnaes et al. 2014). The toxicological effects from metals have shown that metal complexes and precipitates are nontoxic or much less toxic to aquatic life than are metal ions.

The concept of the aquatic life water quality criterion, for most metals, recognizes and accounts for the influence that water hardness has on metal toxicity. This relationship shows that with increasing hardness there is less metal toxicity (Stephan et al. 1985). Most current metals criteria are not single numbers but instead are hardness-dependent equations designed to be protective across a range of water hardness. I acknowledge the requirements from the state of Minnesota, ruled by the Pollution Water Agency (Minn. R 7050.0220).

Heavy metal exposure and potential environmental effects can affect fish species living in the receiving waters. Thus, ecological risk for these species could be assessed using a process that entails problem formulation, exposure analysis, effects assessment, and risk characterization (EPA 1998). When evaluating ecological risk involving heavy metals, it is necessary to understand that the metal characteristics (i.e., chemical species) play a fundamental role in their bioaccessibility, bioavailability, fate, and effects (EPA 2007). Therefore, some ecosystems represent a more fragile scenario than others when perceiving metal toxicity according to their physicochemical characteristics.

METHODS

Problem Formulation

The oxidation of sulfide minerals promotes the creation of sulfuric acid and metal leaching that can reach water bodies and persist in a natural ecosystem for an extended period and bioaccumulate in the biological chain's successive levels, with consequently acute and chronic effects to the living organisms (Neuman et al. 2014). Copper-nickel mining from sulfide ores has an extensive history of surface and groundwater pollution from AMD (Pearson et al. 2019). The main reason is that despite effectively adopting best practice guidelines for managing waste-rock and tailings to reduce risk, uncertainties in long-term climate, hydrology, and performance of mitigation strategies, residual risks always exist, including the potential for catastrophic impacts (Ossa-Moreno et al. 2018).

Kuipers et al. (2006) studied 25 operating hard rock mines across the US and their respective Environmental Impact Statements, finding that near-mine groundwater and surface water exceeded water quality standards in most operations. Another study that surveyed fourteen sulfide copper mines found that the totality had experienced pipeline spills or other accidental releases (Pearson et al. 2019, Gestring 2012). Most of these contaminants released to surface waters or groundwater from mine failures included toxic heavy metals such as copper and nickel (Kuipers et al. 2006). If Twin Metals Minnesota plans a sulfide-ore copper-nickel mine on public lands along the Kawishiwi River and Birch Lake adjacent to the Boundary Waters Canoe Area, a potential exposure to toxic copper and nickel concentrations is in existence. My study, therefore, aims to assess the risks to selected fish species to these heavy metals on Birch Lake's receiving waters as a result of hypothetical spill scenarios.

Hazard Identification and Dose-Response Relationships

For fish species, metal exposure can occur through the food chain across their gut from their diet or across their gills (Newman et al. 2014). Several biological factors influence metals bioavailability, such as the route of exposure, the mechanism of sequestration and the transport of metals by organic ligands, and the exposed organism (Newman et al. 2014, Paiva Magalhaes et al. 2001, Wood 2012). The mode of uptake plays a role in survival. Its dose-response relationship ranges from biological deficiencies when intakes are low and overdose when intakes are high (Wood 2012).

The effects of metal toxicity on various aquatic organisms have been studied to describe routes and times of exposure and toxic effects. These metal toxicity effects can also range from the determination of small concentrations to no observed effect concentrations using ecotoxicological tests (Paiva Magalhaes et al. 2001). Because the fish organs can be reached within hours of exposure, their toxic effects can be measured, for example, as changes in physiology (metallothionein), sublethal effects (reduced growth and reproduction), and survival (direct toxicity) (Newman et al. 2014). The presence and abundance of fish can be affected by sublethal effects such as slower growth rates, lower fecundity, and metal-contaminated water avoidance (Maret and MacCoy 2002). These sublethal effects can eventually depress or extirpate populations (Woodward et al. 1997, Farag et al. 1999). Here, I estimate the risk of mortality using the LC_{50} of different fish species for copper and nickel, based on the water hardness model of Minn. R 7050.0220. The LC_{50} is the dose that is required to kill 50% of the test-animal population.

For copper and nickel, the primary mode of action is most likely oxidative stress and respiratory disruption (Pane et al. 2003a, Pane et al. 2004b). For copper, accumulation is higher in the liver and for nickel it is higher in the gill (Pane et al. 2004b). In Minnesota, white sucker, walleye, and lake whitefish populations declined and spawning of white suckers was impaired in a lake containing 9-15 µg /L Cu (Lind et al. 1978). Chronic effects on several species have been observed at copper concentrations less than 50 µg/L. For most fish species, the LC_{50} for acute nickel exposure in adults is 4-14 mg/L (96 h) for soft water and 24-44 mg/L (96 h) for hard water (Eisler 1998). The chronic nickel effects on fathead minnows are recorded at 730 µg/L Ni, while acute effects on this species and others are greater than 4,500 µg/L Ni (Table 2, 3) (Lind et al. 1978). The lowest LC_{50} values for embryos of the rainbow trout species was 12.7 µg/L for copper and 1280 µg/L for nickel.

Waters classified as “2B surface” are intended to permit the propagation and maintenance of a healthy community of cool or warm water aquatic biota and their habitats. Water quality criteria values for copper and nickel are calculated dependent on the hardness according to the Minn R. 7050.0218. For FAV “Final acute value” which is an estimate of the concentration of a pollutant corresponding to the cumulative probability of 0.05 in the distribution of all the acute toxicity values for the genera or species from the acceptable acute toxicity tests conducted on a pollutant. The equations are as follows:

Copper. FAV: Exp (0.9422[ln total hardness] – 0.7703) (eq 1)

Nickel. FAV: Exp (0.846[ln total hardness] + 4.0543) (eq 2)

Table 2: The calculated concentrations to comply with the quality of class 2Bd. The standards used for toxic pollutant are “chronic standard” CS, “maximum standard” MS and “final acute value” FAV. TH “total hardness”.

	TH mg/L	CS µg/L	MS µg/L	FAV µg/L
Copper	CaCO3	Cu µg/L	Cu µg/L	Cu µg/L
Hardness (100 mg/L)	100	10	18	35
Birch Lake	27	4	5	10
White Iron	15	3	3	6
Nickel	CaCO3	Ni µg/L	Ni µg/L	Ni µg/L
Hardness (100 mg/L)	100	158	1418	2836
Birch Lake	27	51	463	925
White Iron	14	32	285	570

Table 3: Toxicity values LC_{50}, for copper exposure on fish species of the orders Perciformes and Salmoniformers.

Common Name	Species	CuSO4 µg/L	Life stage	Days	CaCO3 mg/L	Reference	Reference Type
Bluegill	*Lepomis macrochirus*	3545	-	4		Bailey et al. 1985	Ecotox Database ECOREF #7398
Bluegill	*Lepomis macrochirus*	2970	-	1	45	Caims et al. 1978	EPA (2007)
Bluegill	*Lepomis macrochirus*	1800	-	4	-	Mayer et al. 1986	Ecotox Database ECOREF #6797
Rainbow trout	*Oncorhynchus mykiss*	1100	Juvenile	3	320	Lloyd 1961	EPA (2007)
Bluegill	*Lepomis macrochirus*	770	-	1	-	Inglis et al. 1972	Ecotox Database ECOREF #2135
Rainbow trout	*Oncorhynchus mykiss*	580	Juvenile	3	250	Brown et al., 1974	EPA (2007)
Bluegill	*Lepomis macrochirus*	468	-	4	365	Inglis et al., 1972	Ecotox Database ECOREF #2135
Bluegill	*Lepomis macrochirus*	410	Juvenile	4	-	Lemke 1968	Ecotox Database ECOREF # 118102
Bluegill	*Lepomis macrochirus*	390	Juvenile	1	-	Soucek et al. 1998	Ecotox Database ECOREF#9058
Bluegill	*Lepomis macrochirus*	340	-	4	-	Academy of Natural Science Academy 960	Ecotox Database ECOREF#5683
Bluegill	*Lepomis macrochirus*	254	-	4	52	Inglis et al., 1972	Ecotox Database ECOREF #2135
Bluegill	*Oncorhynchus mykiss*	169	-	4	Hard	Taylor et al., 2003	Ecotox Database ECOREF #71719
Rainbow trout	*Oncorhynchus mykiss*	150	Juvenile	1	45	Cairns et al., 1978	EPA (2007)
Rainbow trout	*Oncorhynchus mykiss*	100	Embryos	2	87	Shazili and Pascoe 1986	EPA (2007)
Flathead Minnow	*Pimephales promelas*	84	-	4	31	Mount and Stephan 1969	EPA (2007)
Bluegill	*Lepomis macrochirus*	71	-	4	Soft	Taylor et al., 2003	Ecotox Database ECOREF #71719
Rainbow trout	*Oncorhynchus mykiss*	13.8	Juvenile	4	41.3	Buhl and Hamilton 1990	EPA (2007)
Rainbow trout	*Oncorhynchus mykiss*	12.7	Embryos	4	24.2	Marr et al. Manuscript	EPA (2007)

Table 4: Toxicity values LC_{50}, for nickel exposure on fish species of the orders Perciformes and Salmoniformers.

Common Name	Species	Ni^{2+} µg/L	Life stage	Days	$CaCO_3$ mg/L	Reference	Reference Type
Banded killifish	*Fundulus diaphanus*	46,100	-	4	53	Rehwoldt et al. 1971	USEPA (1980)
Bluegill	*Lepomis macrochirus*	39,600	-	4	360	Pickering & Henderson 1966	USEPA (1980)
Rainbow trout	*Oncorhynchus mykiss*	35,700	Adult	2	42	Wilford 1966	USEPA (1980)
Rainbow trout	*Oncorhynchus mykiss*	31,700	Adult	4	100	Segner et al. 1994	
Rainbow trout	*Oncorhynchus mykiss*	25,100	Alevins	4	-	Buhl and Hamilton 1991	
Bluegill	*Lepomis macrochirus*	5,400	-	4	20	Pickering & Henderson 1966	USEPA (1980)
Pumpkinseed	*Lepomis gibbosus*	5,200	-	4	20	Pickering & Henderson 1966	USEPA (1980)
Flathead Minnow	*Pimephales promelas*	4,600	-	4	20	Pickering & Henderson 1966	USEPA (1980)
Flathead Minnow	*Pimephales promelas*	3,100	-	4	-	Schubauer-Berigan et al. 1993	
Rock Bass	*Ambloplites rupestris*	2,480	-	4	26	Lind et al. 1978	USEPA (1980)
Rainbow trout,	*Oncorhynchus mykiss*	1,280	Embryos	4	-	Kazlauskieneet al. 1999	ECOREF #17573

Exposure Assessment

My assumption is that the water column would be contaminated from the waters of the underground mine. A direct intake by the gill from the water column is considered the route of exposure. Because the components of AMD spills are dependent on the kind of rock, I assume copper and nickel exposure, taking into consideration historical records and similar rock composition ventures because, to date, this mining project is in the beginning stages. Spill or leak events have occurred in mining operations, from processing water pipeline ruptures to tailing impoundment failures, ranging from millions of liters to just a few thousand liters (Gestring 2012). Therefore, my hypothetical scenarios consider a leak or spill from the "Contact Water Pond 1" into Birch Lake (Figure 2). This pond is designed to collect the contact waters of the tailing facility and excess from the dewatering plant.

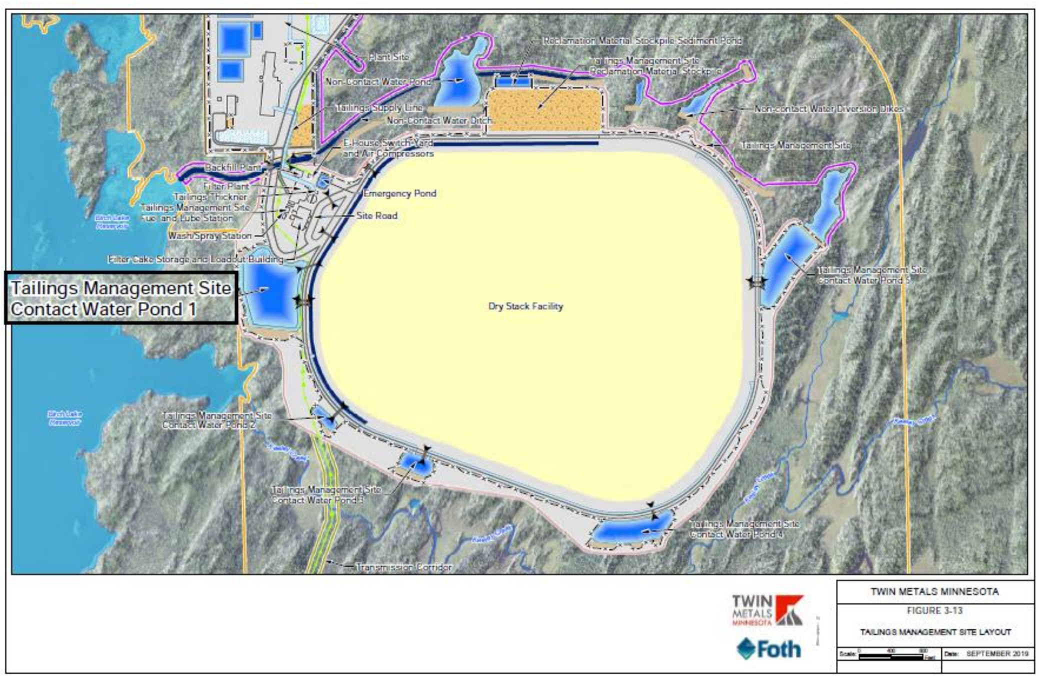

Figure 2: Tailing Management Site. Dry stack facility and Contact Water Pond 1 and Birch Lake waters (Adapted from TMM (2020)).

In the spill estimation, I consider the percentages of the total volume of the Contact Water Pond 1 of 249,917 m^3. The percentages will range from 10 to 0.3% of the total volume, therefore from 737,280 to a maximum of 25 million liters (Table 5). The receiving waters are a portion of Birch Lake, with a total of 1.45 billion liters. The pollution would disperse in the flow direction, carried out to White Iron Lake. This lake is 10 times greater than the receiving waters volume of Birch Lake, suggesting that the dilution would be greater in this water body (Figure 3).

Figure 3: The marked grey area in the lake waters, represents the estimated water volume of the receiving waters from the tailing area (Source: USGS. https://maps.waterdata.usgs.gov).

For this assessment, I present four scenarios labeled from A-D ranging from high to lower concentrations of copper and nickel. The final concentrations found in the water column would be dependent on the spill size and its concentration. For a worst-case scenario (Scenario A), the water column's highest concentration would represent the larger size of a spill with most metals. Conversely, the lowest concentration scenario (Scenario D) would represent the smaller size of a spill with the least metal concentration.

Scenario A represents the concentrations found in seepage water from sulfide tailings impoundment of an active mine in Finland (Heikkinen et al. 2009). This mine produced neutral drainage, but the concentrations were high in nickel at 1,580 µg/L. The copper concentrations in Scenario A represent a sulfide-ore copper mine in Whistle, in the Sudbury Basin in Ontario (Vos et al. 1975). This mine has similar geological settings of layered mafic intrusions. The tailing seepage is acidic at pH 4.5, and copper was 11 mg/L.

Scenario B represents historical concentration found near Birch Lake, MN 1988 Seep 3 from the Dunka Pit reached nickel concentrations of 80 mg/L (Lapakko & Antonson 2012) while copper was at concentrations of 1 mg/L near Filson Creek at the “foot of a bulk sample site” (old mine rock from an exploration site of the same rock intrusion) (Thingvold et al. 1979). Both of these locations are within the Kawishiwi Watershed and part of the Duluth Complex rock intrusion.

Scenario C represents concentrations reported by Thingvold et al. (1979) from Filson Creek, Lake county, MN with 13 mg/L for nickel and 0.36 mg/L for copper. Filson Creek historically has reported the highest trace metal levels in this watershed due to its natural seepage.

Scenario D represents the nickel concentrations on the Vangorda mine site, in Yukon, Canada, used to predict AMD in a neighboring copper-nickel project (PolyMet Mining 2015). The concentrations found in this mine site were 9 mg/L for nickel and 0.1 mg/L for copper. This scenario represents the minor concentrations in the contact waters.

Once the spill has reached the receiving waters of Birch Lake, the time that the pollution will reside would be dependent on the surface water flows. This study would assume that if the average is 98 cfs for Birch Lake, the spill will take approximately six days to dissipate. Thus, these hypothetical pollutions represent scenarios of acute exposure. According to Minnesota environmental regulations, the concentrations calculated exceeded standards of Final Acute Values for Scenarios A and B (Table 2).

These worst-case scenarios do not consider a contaminant dispersion model and do not account for the lake's physicochemical properties. These worst-case scenarios are intended to represent pollution with nominal concentrations for copper and nickel to illustrate possible exposure to fish to these pollutants and to assess the resulting acute risk.

As previously described, water hardness plays an important role in determining the toxicity of the metals in the water column. Softer waters pose a greater toxicity, making the species less tolerable to its concentrations. Thus, it is necessary to select the most sensitive endpoint according to the alkalinity. The risk quotient was determined only on endpoints observed at low alkalinities.

Table 5: Concentrations for copper and nickel in the water column. These were calculated on hypothetical spills ranging from 1,580 to 9 (mg/L) for nickel and 11 to 0.1 (mg/L) for copper, dependent on contact water pond 1(CWP1) spill volume and concentration. The values in bold font show the concentrations that exceeded standards of Final Acute Value.

Volume of receiving waters on Birch Lake water: 1.45 billion L		Hypothetical Nickel concentrations (mg/L) in Contact Water Pond 1				Hypothetical Copper concentrations (mg/L) in Contact Water Pond 1			
		Scenario A	Scenario B	Scenario C	Scenario D	Scenario A	Scenario B	Scenario C	Scenario D
		1,580	80	13	9	11	1	0.36	0.1
%	Spill Volume (L)	Approx. nickel concentrations in the water column (µg/L)				Approx. copper concentrations in the water column (µg/L)			
10	25,000,000	**26779**	**1,355**	220.34	152.54	**186**	**16.95**	6.1	1.69
9	22,500,000	**24143**	**1,222**	198.64	137.52	**168**	**15.28**	5.5	1.53
8	20,000,000	**21497**	**1,088**	176.87	122.45	**149**	**13.61**	4.9	1.36
7	17,500,000	**18842**	**954**	155.03	107.33	**131**	**11.93**	4.29	1.19
6	15,000,000	**16177**	819	133.11	92.15	**112**	**10.24**	3.69	1.02
5	12,500,000	**13504**	683	111.11	76.92	**94.02**	8.55	3.08	0.85
4	10,000,000	**10822**	547	89.04	61.64	**75.34**	6.85	2.47	0.68
3	7,500,000	**8130**	411	66.9	46.31	**56.60**	5.15	1.85	0.51
2	5,000,000	**5430**	274	44.67	30.93	**37.80**	3.44	1.24	0.34
1	2,500,000	**2719**	137	22.38	15.49	**18.93**	1.72	0.62	0.17
0.9	2,250,000	**2448**	123	20.14	13.94	**17.04**	1.55	0.56	0.15
0.72	1,800,000	**1959**	99.19	16.12	11.16	**13.64**	1.24	0.45	0.12
0.58	1,440,000	**1568**	79.37	12.9	8.93	**10.91**	0.99	0.36	0.1
0.46	1,152,000	**1254**	63.51	10.32	7.14	**8.73**	0.79	0.29	0.08
0.37	921,600	**1004**	50.81	8.26	5.72	**6.99**	0.64	0.23	0.06
0.3	737,280	**803**	40.66	6.61	4.57	**5.59**	0.51	0.18	0.05

RISK CHARACTERIZATION

The risk was assessed using the risk quotient (RQ) method, where RQ is the ratio of exposure to effect (RQ = Exposure ÷ Effect). The risk quotient was calculated using the estimated concentrations in the water columns divided by the toxic endpoints. Risk quotients < 0.5 are considered below regulatory levels of concern (EPA 2007).

I calculated the RQ for different species and exposure times. As expected, the results show that the risk increases with the spill's size and the metal concentration (i.e., risk increases with increasing exposure). The species show sensitivity to the various concentrations, and all of them show levels of concern greater than 0.5 in the worst-case scenario of pollution. The RQ for fish species indicates exceeding levels of concern in at least two of the four scenarios for copper exposures. Therefore, levels of concern would be reached for embryos of rainbow trout in spills with concentrations ranging from 11 to 1 µg/L, while for bluegill embryos and rainbow trout juvenile, levels would only be reached at 11 µg/L of copper (Table 6, 7). This is because the species can tolerate different levels of copper that vary with the order, life stage and exposure period (Tables 3, 6). As opposed to the estimated exposures at 24 h, at endpoints of 2,970 µg/L, levels of concern were not reached in any scenario (Table 7).

The RQs obtained for each scenario at different spill sizes show that RQ is likely to be greater than 0.5 when considering the worst-case scenario, Scenario A. In contrast, Scenario B shows a considerable decrease, indicating levels of concern only when the size of the spill was significant. This scenario represents concentrations of copper of 1 µg/L found in natural seeps near the mine. No levels of concern were reached for Scenarios C and D, which represent moderate and low copper concentrations. Scenario C represents concentrations found in a natural seepage near the mine, while Scenario D was low in concentrations from a sulfide ore mine. All these results indicate that if a spill were to happen with concentrations representing Scenarios C and D, the dilution would be greater, allowing lower concentrations in the water column.

The RQs indicates risk exceeding levels of concern in at least two of the four scenarios for nickel exposures. Levels of concern were reached for embryos of rainbow trout and rock bass in spills with nickel concentrations ranging from 1,580 to 80 µg/L (Table 8). The levels would only be reached in spills with nickel concentrations at 1,580 µg/L of nickel for bluegill and rainbow trout. This is due to the different species and their life stages that can tolerate higher levels of copper (Tables 4, 9). Similarly, there were no levels of concern exceeded for Scenarios C and D, representing moderate and low copper concentrations. Scenarios C represent concentrations found in a natural seepage near the mine, while Scenario D was low in concentrations from a sulfide ore mine.

Table 6: Risk quotients for LC_{50} values on rainbow trout, and bluegill embryos for 96 h of acute exposure to different copper concentrations in the water column. The values in bold font show the concentrations levels of concern >50 µg /L.

Volume of receiving waters on Birch Lake Water: 1.45 billion L		Hypothetical Copper concentrations (mg/L) in contact water pond 1				Hypothetical Copper concentrations (mg/L) in contact water pond 1			
		Scenario A	Scenario B	Scenario C	Scenario D	Scenario A	Scenario B	Scenario C	Scenario D
		11	1	0.36	0.1	11	1	0.36	0.1
%	Spill Volume (L)	96 h copper exposure: rainbow trout - embryos. LC50: 12.7 µg /L. TH: 24.2 mg/L RQ= concentration in the water column/LC_{50}				96 h copper exposure: bluegill - embryos. LC50: 71 µg /L. TH: <50 mg/L RQ= concentration in the water column/LC_{50}			
10	25,000,000	**16.01**	**1.33**	< 0.5	< 0.5	2.86	< 0.5	< 0.5	< 0.5
9	22,500,000	**14.44**	**1.2**	< 0.5	< 0.5	2.58	< 0.5	< 0.5	< 0.5
8	20,000,000	**12.86**	**1.07**	< 0.5	< 0.5	2.3	< 0.5	< 0.5	< 0.5
7	17,500,000	**11.27**	**0.94**	< 0.5	< 0.5	2.02	< 0.5	< 0.5	< 0.5
6	15,000,000	**9.67**	**0.81**	< 0.5	< 0.5	1.73	< 0.5	< 0.5	< 0.5
5	12,500,000	**8.08**	**0.67**	< 0.5	< 0.5	1.44	< 0.5	< 0.5	< 0.5
4	10,000,000	**6.47**	**0.54**	< 0.5	< 0.5	1.16	< 0.5	< 0.5	< 0.5
3	7,500,000	**4.86**	< 0.5	< 0.5	< 0.5	0.87	< 0.5	< 0.5	< 0.5
2	5,000,000	**3.25**	< 0.5	< 0.5	< 0.5	0.58	< 0.5	< 0.5	< 0.5
1	2,500,000	**1.63**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.9	2,250,000	**1.46**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.72	1,800,000	**1.17**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.58	1,440,000	**0.94**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.46	1,152,000	**0.75**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.37	921,600	**0.6**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5

Table 7: Risk quotients for LC_{50} values on rainbow trout juvenile for 72 h of acute exposure and bluegill embryos for 24 h of acute exposure to different copper concentrations in the water column. The values in bold font show the concentrations levels of concern >50 µg /L.

Volume of receiving waters on Birch Lake Water: 1.45 billion L		Hypothetical Copper concentrations (mg/L) in Contact Water Pond 1				Hypothetical Copper concentrations (mg/L) in Contact Water Pond 1			
		Scenario A	Scenario B	Scenario C	Scenario D	Scenario A	Scenario B	Scenario C	Scenario D
		11	1	0.36	0.1	11	1	0.36	0.1
%	Spill Volume (L)	72 h copper exposure: rainbow trout - embryos. LC_{50}: 150 (µg/L). RQ= concentration in the water column/ LC_{50}				24 h copper exposure bluegill - embryos. LC_{50}: 2,970 µg/L. TH: 45 mg/L. RQ= concentration in the water column/LC50			
10	25,000,000	**1.24**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
9	22,500,000	**1.12**	< 0.5	< 0.5	< 0.5	0.5	< 0.5	< 0.5	< 0.5
8	20,000,000	**1.00**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
7	17,500,000	**0.87**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
6	15,000,000	**0.75**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
5	12,500,000	**0.63**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
4	10,000,000	**0.50**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
3	7,500,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
2	5,000,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
1	2,500,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.9	2,250,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.72	1,800,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.58	1,440,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.46	1,152,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.37	921,600	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5

Table 8: Risk quotients for LC_{50} values on rainbow trout embryos and rock bass for 96 h of acute exposure to different nickel concentrations in the water column. The values in bold font show the concentrations levels of concern >50 µg /L.

Volume of receiving waters on Birch Lake Water: 1.45 billion L		Hypothetical Nickel concentrations (mg/L) in Contact Water Pond 1				Hypothetical Nickel concentrations (mg/L) in Contact Water Pond 1			
		Scenario A	Scenario B	Scenario C	Scenario D	Scenario A	Scenario B	Scenario C	Scenario D
		1,580	80	13	9	1,580	80	13	9
%	Spill Volume (L)	96h nickel exposure: rainbow trout-embryos LC_{50}: 1,280 µg /L. TH: 52 mg/L. RQ= concentration in the water column/LC_{50}				96h nickel exposure: rock bass LC_{50}: 2480 µg /L. TH: 40 mg/L RQ= concentration in the water column/LC_{50}			
10	25,000,000	**20.92**	**1.06**	< 0.5	< 0.5	**10.80**	**0.55**	< 0.5	< 0.5
9	22,500,000	**18.86**	**0.96**	< 0.5	< 0.5	**9.73**	< 0.5	< 0.5	< 0.5
8	20,000,000	**16.79**	**0.85**	< 0.5	< 0.5	**8.67**	< 0.5	< 0.5	< 0.5
7	17,500,000	**14.72**	**0.75**	< 0.5	< 0.5	**7.60**	< 0.5	< 0.5	< 0.5
6	15,000,000	**12.64**	**0.64**	< 0.5	< 0.5	**6.52**	< 0.5	< 0.5	< 0.5
5	12,500,000	**10.55**	**0.53**	< 0.5	< 0.5	**5.45**	< 0.5	< 0.5	< 0.5
4	10,000,000	**8.45**	< 0.5	< 0.5	< 0.5	**4.36**	< 0.5	< 0.5	< 0.5
3	7,500,000	**6.35**	< 0.5	< 0.5	< 0.5	**3.28**	< 0.5	< 0.5	< 0.5
2	5,000,000	**4.24**	< 0.5	< 0.5	< 0.5	**2.19**	< 0.5	< 0.5	< 0.5
1	2,500,000	**2.12**	< 0.5	< 0.5	< 0.5	**1.10**	< 0.5	< 0.5	< 0.5
0.9	2,250,000	**1.91**	< 0.5	< 0.5	< 0.5	**0.99**	< 0.5	< 0.5	< 0.5
0.72	1,800,000	**1.53**	< 0.5	< 0.5	< 0.5	**0.79**	< 0.5	< 0.5	< 0.5
0.58	1,440,000	**1.22**	< 0.5	< 0.5	< 0.5	**0.63**	< 0.5	< 0.5	< 0.5
0.46	1,152,000	**0.98**	< 0.5	< 0.5	< 0.5	**0.51**	< 0.5	< 0.5	< 0.5
0.37	921,600	**0.78**	< 0.5	< 0.5	< 0.5	**0.40**	< 0.5	< 0.5	< 0.5

Table 9: Risk quotients for LC_{50} values on bluegill and rainbow trout for 96 h of acute exposure to different nickel concentrations in the water column. The values in bold font show the concentrations levels of concern >50 µg /L.

Volume of receiving waters on Birch Lake Water: 1.45 billion L		Hypothetical Nickel concentrations (mg/L) in Contact Water Pond 1				Hypothetical Nickel concentrations (mg/L) in Contact Water Pond 1			
		Scenario A	Scenario B	Scenario C	Scenario D	Scenario A	Scenario B	Scenario C	Scenario D
		1,580	80	13	9	1,580	80	13	9
%	Spill Volume (L)	96h nickel exposure: bluegill. LC_{50}: 5,400 µg /L. TH: 20 mg/L. RQ= concentration in the water column/LC_{50}				96h nickel exposure: Rainbow Trout. LC_{50}: 35700 µg /L. TH: 42 mg/L. RQ= concentration in the water column/LC_{50}			
10	25,000,000	**4.96**	< 0.5	< 0.5	< 0.5	0.75	< 0.5	< 0.5	< 0.5
9	22,500,000	**4.47**	< 0.5	< 0.5	< 0.5	0.68	< 0.5	< 0.5	< 0.5
8	20,000,000	**3.98**	< 0.5	< 0.5	< 0.5	0.60	< 0.5	< 0.5	< 0.5
7	17,500,000	**3.49**	< 0.5	< 0.5	< 0.5	0.53	< 0.5	< 0.5	< 0.5
6	15,000,000	**3.00**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
5	12,500,000	**2.50**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
4	10,000,000	**2.00**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
3	7,500,000	**1.51**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
2	5,000,000	**1.01**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
1	2,500,000	**0.50**	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.9	2,250,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.72	1,800,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.58	1,440,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.46	1,152,000	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
0.37	921,600	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5

DISCUSSION

My results indicated that the risk increased for the fish species with the concentrations and spill-size of the hypothetical scenarios of contamination compared to specific toxic endpoints for acute exposure. These scenarios represented realistic concentrations and contamination release magnitudes. The RQ calculated for each scenario expressed order of magnitude variations as is evident with the substantial decrease from Scenario A to Scenario B for a given spill size. In Scenario A, the RQ is greater than in B, with an RQ of 20.9 versus an RQ of 1.1, observed for rainbow trout embryos exposed to nickel. For the same species but for copper exposure, the decrease was from an RQ of 10.8 in Scenario A to an RQ of 0.6 in Scenario B.

Scenarios A and B represented the higher levels of concentrations in the contact water ponds. These scenarios were represented by a mine in Canada and in Finland, and local collections of seepage waters that showed similar rock composition characteristics and elevated concentrations of metals. Thus, my results suggest that these reasonable worst-case scenarios may pose an unacceptable risk if a spill with these characteristics ever reaches the Birch Lake waters. Conversely, Scenarios C and D represented the lower-end metal concentrations and did not represent a risk exceeding the level of concern for any species. Consequently, the difference in RQs shows how the receiving waters have the capability to dilute concentrations of metals.

Rainbow trout embryos were identified as the most sensitive species and life stage for copper and nickel exposures. For a 96-h copper exposure, the LC_{50} was 12.7 μg/L, considering a spill that represents 4% of the contact water pond and with concentrations represented by Scenario B (1 mg/L). For nickel, it was 1,280 μg/L considering a spill representing 5% of the contact water pond and with concentrations given by Scenario B (80 mg/L). In contrast, bluegill can tolerate copper concentrations of 3,545 μg/L and nickel concentrations of 39,600 μg/L. Rainbow trout and bluegill represent the orders, Salmoniforme and Perciforme, respectively. The risk calculated for these species can be extrapolated for the fish species living in the water bodies, suggesting that there can be a risk of lethality for 50% of the species if a spill from at least the worst-case scenarios were to happen.

The importance of hardness and alkalinity in influencing metal toxicity has been demonstrated in many studies. Elevated concentrations of metals become less toxic to fish when the water's hardness and alkalinity are both increased. Thus, in my study, it was possible to observe this relationship. The variation between toxicological responses of species to nickel and copper concentrations in different water hardness shows that softer waters pose more significant toxicity, making the species less tolerable to metals concentrations (Table 4).

Metal-solubility reactions are also alkaline- and pH-dependent. Birch and White Iron Lakes have low alkalinity, meaning that the potential acidity would not have a neutralizing potential in case of AMD contamination, thus increasing the risk of metal toxicity and losing pristine water quality. Moreover, the Final Acute Value determined for both lakes according to their water hardness showed more sensitivity for White Iron Lake (Table 2), suggesting that White Iron Lake is more vulnerable to lose its water quality in the event of AMD contamination.

Twin Metals Minnesota indicates that no-acid drainage will be generated due to the rock's nature and processing technologies. However, this does not exempt the generation of metal leaching, since in non-acidic drainage, nickel can still be mobile and present at high concentrations, such as in a sulfide nickel mine in Finland (Heikkinen et al. 2009). As seen in the exposure scenarios, the nickel concentration represented levels of concern for all the species evaluated, for at least the worst-case scenario. In addition, levels of concern were also reached in

Scenario B. This scenario represents concentrations of 80 mg/L found on Seep 3 from the former Taconite mine, near Babbitt, MN. Since nickel concentrations historically have been found in higher concentrations in seepage either naturally or from closed mining operations, it could be expected that the potential and more persistent contamination from the proposed mine could originate from nickel contributions due to the nature of the rock composition.

The uncertainties in my study are mostly related to the fact the variety of exposure scenarios could be infinite, when considering that the spill size and concentration come from hypothetical scenarios. Other scenarios can include the seepage, estimated at millions of gallons/year, of continuous discharges to a stream which flows into Birch Lake that could increases the concentrations of metals and other AMD components, in the lake or waters downstream, to levels higher than the regional average. Since the mining project has not begun operation, there are no actual values for the characterization of the contact waters.

In this study, I considered direct uptake from the gills as the route of exposure. However, fish species that feed on contaminated detritus can experience detrimental health effects from metal toxicity. Also, feeding has been found to be the primary route of exposure and accumulation of metals (Newman et al. 2014). Therefore, this suggests that fish could experience toxicity from those two routes in the event of pollution of these waters.

Another limiting factor is that AMD is not only a mixture of copper and nickel, but it is also a mixture of metals and sulfides. Thus, it is necessary to consider that in mixtures some metals could inhibit or favor the assimilation of other metals. Changes in the biota have been found to be an effective method to evaluate the impact of environmental pollution because it reflects integrated effects of mixtures of chemicals among the major groups of organisms used as bioindicators (Paiva Malghanes et al. 2014).

I propose that the possible effects from a potential contamination from the mining project should be assessed though the use of biomonitoring programs. These have served as an early warning of pollution when concentrations are low and in a short-exposure period, and as an assessment tool for metals toxicological impact (Paiva Malghanes et al. 2014). Contrarily, if the water of the Kawishiwi watershed becomes contaminated, phytoremediation could be presented as a potential alternative to remove trace metals from polluted sites.

In conclusion, the risk associated with metal toxicity to fish would be determined by the magnitude and the temporal variability of the pollution event and the rock composition that would determine the AMD characteristic. The mineral deposit associated with Twin Metal Minnesota is likely to produce AMD despite laboratory predictions. In the event of a large spill (with elevated concentrations of metals) or a small spill (with lower concentrations for a prolonged period), levels of concern on fish species living in the receiving water bodies could be reached, indicating loss of habitat quality that could adversely affect the ecosystem.

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APENDIX A

Minnesota water quality classification

Surface waters in Minnesota are classified according to their best use and the need for water quality by Minnesota Pollution Control Agency protection (Minn. R 7050.0140). If the standards are exceeded, it is considered indicative of a polluted condition that is actually or potentially deleterious, harmful, detrimental, or injurious with respect to designated uses or established classes of the state's waters. All surface waters are protected for multiple beneficial uses, for which are four categories that are given a numeric water quality standard tabulated for all applicable use categories. Birch Lake and White Iron supports classes 2Bg, 3C, 4A, 4B, 5, 6.

Values for copper and nickel are calculated dependent on the hardness. The equations are as follows: Standards used for toxic pollutant includes the "chronic standard" CS "Maximum standard" MS, and "Final acute value" FAV. CS means the highest water concentration or fish tissue concentration of a toxicant or effluent to which aquatic life, people, or wildlife can be exposed indefinitely without causing chronic toxicity. MS means the highest concentration of a toxicant in water to which aquatic organisms can be exposed for a brief time with zero to slight mortality. FAV means an estimate of the concentration of a pollutant corresponding to the cumulative probability of 0.05 in the distribution of all the acute toxicity values for the genera or species from the acceptable acute toxicity tests conducted on a pollutant (MPCA 7050.0218, subpart 3).

Class 2B surface waters' quality is intended to permit the propagation and maintenance of a healthy community of cool or warm water aquatic biota and their habitats. These waters shall be suitable for aquatic recreation of all kinds, including bathing, for which the waters may be usable. All requirements for class 2B warm or cool water stream and river habitats in parts continue to apply in addition to requirements for 2Bg; These subclass designators are applied to lotic waters only (Minn. R 7050.0222 and 7052.0100). This class of surface water is not protected as a source of drinking water. The equations are as follows:

Copper:

CS: Exp (0.620[ln total hardness] – 0.570) (eq1)

MS: Exp (0.9422[ln total hardness] – 1.464) (eq2)

FAV: Exp (0.9422[ln total hardness] – 0.7703) (eq3)

Nickel:

CS: Exp (0.846[ln total hardness] +1.1645) (eq4)

MS: Exp (0.846[ln total hardness] – 3.3612) (eq5)

FAV: Exp (0.846[ln total hardness] +4.0543)(eq6)

Table 10: Beneficial Use Designations for Stream Reaches: Rainy River - Headwaters Watershed (09030001).

1A	Domestic Consumption (does not require treatment)	2D	Aquatic Life and Recreation - Wetlands
1B	Domestic Consumption (requires moderate treatment)	3A	Industrial Consumption (no treatment)
1C	Domestic Consumption (requires heavy treatment)	3B	Industrial Consumption (moderate treatment)
2Ae	Aquatic Life and Recreation - Exceptional Cold Water Habitat (streams)	3C	Industrial Consumption (heavy treatment)
2Ag	Aquatic Life and Recreation - General Cold Water Habitat (lakes and streams)	3D	Industrial Consumption (wetlands - moderate treatment)
2Bde	Aquatic Life and Recreation also protected as a source of drinking water - Exceptional Warm Water Habitat (streams)	4A	Agriculture and wildlife (irrigation)
2Bdg	Aquatic Life and Recreation also protected as a source of drinking water - General Warm Water Habitat (lakes and streams)	4B	Agriculture and Wildlife (livestock and wildlife)
2Bdm	Aquatic Life and Recreation also protected as a source of drinking water - Modified Warm Water Habitat (streams)	4C	Agriculture and Wildlife (wetlands - livestock and wildlife)
2Be	Aquatic Life and Recreation - Exceptional Warm Water Habitat (streams)	5	Aesthetic Enjoyment and Navigation
2Bg	Aquatic Life and Recreation - General Warm Water Habitat (lakes and streams)	6	Other Uses
2Bm	Aquatic Life and Recreation - Modified Warm Water Habitat (streams)	7	Limited Resource Value Water

Table 11: 4 common categories

Categories	A	B	C	D
	Cold water aquatic life and habitat, also protected for drinking water	Cool and warm water aquatic life and habitat, also protected for drinking water	Cool and warm water aquatic life and habitat and wetlands	Limited resource value waters
Classes	1B; 2A, 2Ae, or 2Ag; 3A or 3B; 4A and 4B; and 5 (subpart 3a)	1B or 1C; 2Bd, 2Bde, 2Bdg, or 2Bdm; 3A or 3B; 4A and 4B; and 5 (subpart 4a)	2B, 2Be, 2Bg, 2Bm, or 2D; 3A, 3B, 3C, or 3D; 4A and 4B or 4C; and 5 (subpart 5a)	3C; 4A and 4B; 5; and 7 (subpart 6a).

Physicochemical characteristics of the lakes

This is a region is composed of forests, marshes, and wetlands. The surface water quality is generally considered good, with dilute cation/anion concentrations and broadly characterized as a calcium-bicarbonate type water, with the exception of some locations where is magnesium-bicarbonate (Oswald 2020; TMM 2020). These water generally present low turbidity, low TSS, and neutral pH (7.2-8.3) (MPCA 2017). The levels of nutrient concentrations are low with insufficient nitrogen levels for nitrogen-induced algae blooms (Oswald 2020). These are soft water with low alkalinity, low total dissolved solids (TDS), low nutrients, high color, very low trace metals concentrations, and low fecal coliform counts (TMM 2020).

Because of low alkalinity, the data demonstrate stream water quality at these waters is weakly buffered, with dilute cations/anions, exhibiting fairly low specific conductance (TMM 2020). These lakes, alkalinity ranges from 12.0 mg/L to 27 mg/L and calcium from 9.7 mg/L to 5.1. In freshwater, calcium is found from 0 to 100 mg/L, where 50 mg/L is the recommended upper limit for drinking water (Oswald 2020). When the calcium ion concentration in freshwater drops below 5 mg/L, it can only support sparse plant and animal life. Specific conductance for both lakes is approximately 59 uS/cm. Total organic carbon (TOC) averaged 13.5 mg/L in White Iron Lake (Oswald 2020). Much of the TOC in water is due to incompletely dissolved organic material. Lakes with high amounts of forest and wetlands in their watershed often have correspondingly higher color and TOC values (MPCA 2009).

White Iron Lake presents a mixed Scenario respecting dissolved oxygen and temperature profiles. The lake is likely to be stratified during the summer, with a thermocline between 5 and 10 m. Birch Lake also follows similar trends for dissolved oxygen as well as the temperature, tending to be consistent throughout the water column. Surface concentrations exceeded 7 mg/L. Sulfate as SO4 has fluctuated over the years for White Iron Lake but has remained stable at 3.14 mg/L since 2011. The SO4 level for Birch Lake is the highest within the chain of lakes, with an average of 8.48 mg/L that has ranged from 5.94 to 12.43 mg/L (Oswald 2020). Because lakes generally have a large surface area of bottom sediments and longer residence times, the chemistry of outflow water can differ from the inflow water with respect to trace metals concentrations. Large lakes, such as Birch Lake, also exhibit variability in the concentration of metals. Average copper, nickel, and zinc concentrations range from approximately 1 to 8 μg/L (TMM 2020).

Birch Lake sampled in the center shows that average concentrations of many parameters were similar between the two locations at the surface, including alkalinity, chloride, dissolved oxygen, and nutrients such as phosphorus and nitrogen. At this point, pH decreases with depth from 7.4 to 7.0 at lower lake depths, while measured redox potential increases. These redox and pH changes exert some control on metal concentrations, and average nickel, copper, and lead concentrations decreased slightly from the surface to the lake's bottom.