Cumulative water quality impacts of iron mining, and their relation to mining environmental policies, in the Lake Superior Ojibwe Treaty-ceded Territories

By

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Abstract

Large-scale iron mining impacts include transformation of landscapes into mine waste and open pits and contamination of natural waters. Cumulative impacts assessment has the potential to provide a comprehensive appraisal of past and current impacts that can inform decision-making for new mining projects and contribute to planning that minimizes impacts. In this research, I evaluated cumulative impacts of large-scale iron mining in the Lake Superior Ojibwe Treaty-ceded Territories in Michigan, Minnesota, and Wisconsin. I determined the relationship between mine waste land cover and selenium and other contaminants in the Escanaba River watershed in Michigan. Mining there contaminated the surface waters with arsenic, boron, cadmium, molybdenum, phosphorus, and vanadium as well selenium. I identified the downstream extent of selenium, which contaminated at least 22% of the river-km in the watershed of the East Branch of the Escanaba River and probably negatively impacts fish in that system. Using specific conductance and major anion data that I collected and that I compiled, I compared two classification approaches to estimate the spatial extent of iron mine influence on surface waters in iron mining regions across the Territories. Mine influence on water quality was extensive, and contamination likely impacts wild rice, fish, and the availability of water for potential use as drinking water. Finally, I evaluated mining environmental policy in the three states around Lake Superior and in eight other mining states to understand how policies differed, to develop a preliminary index of precautionary mining environmental policy, and to relate policies to observed impacts. Results suggested that such an index may capture some of the measures assessed by industry to decide on initiating mining activity and the number of mines in a jurisdiction. Results overall indicate that mining contamination with selenium, sulfate, bromide, and other constituents of concern is widespread in the Lake Superior Ojibwe Treaty-ceded Territories and is likely affecting Ojibwe rights to fish and gather wild rice.

Chapter 1. A review of mining cumulative impacts and iron mining impacts in the Lake Superior Ojibwe Treaty-ceded Territories

Impacts of metals mining

Large-scale metals mining can greatly change the landscape and contaminate the environment. Surface mining turns pre-existing land cover into open pits, waste rock stockpiles, and tailings basins (Down & Stocks 1978, Lottermoser 2010, Schueler *et al*. 2011, Sonter *et al*. 2014). Those landscape changes can destroy, degrade, or fragment sensitive or other ecological areas of biodiversity importance (Akiwumi & Butler 2008). Such mining usually requires the lowering of the groundwater table in order to extract the rocks and may also require damming of rivers to provide a constant water supply for ore processing. The extraction and processing of ore can also contaminate the air with dust, emissions including greenhouse gases from use of fossil fuels, and metals such as mercury (Down & Stocks 1978). Waste rock piles and tailings can discharge toxic concentrations of metal(loid)s and processing reagents to surface and groundwater. The oxidation of sulfide minerals can lead to acid mine drainage that is difficult to remediate and may require treatment "in perpetuity" (Akcil & Koldas 2006, Kempton *et al*. 2010, Nordstrom 2011). Tailings facilities also pose a risk of catastrophic failure and associated downstream destruction and contamination. Those and other effects of metals mining have severe social consequences on Indigenous and other communities through disrespect for rights, displacement, and hazardous living and working conditions.

Iron mining water quality impacts

Large-scale iron mining creates obvious and often extensive land cover change, but can also contaminate the air and water at several points in the mining process. Mining for taconite pellet production involves the use of explosives and digging machines to excavate open pits to extract the iron ore. This can create dust emissions and contamination of waters with nitrogen compounds from the explosives (CCME 2012). Waste rock is piled in stockpiles, usually outside of the pit. Those piles can be a source of water contaminants in addition to the nitrogen, such as sulfate and selenium. Processing consists of grinding the ore and using magnetic or froth flotation chemical processes to remove the ore from the gangue (USEPA 1994). The waste from that process goes in a slurry to the tailings basins.

Generally after clarification, those tailings facilities then discharge effluent to surface waters and may also leak to groundwater. During the subsequent phases, the iron material is blended with limestone or dolomite and heated to high temperatures (USEPA 1994, Engesser 2006) This processing produces SOx, NOx, mercury, and other metals that the processor emits into the air or captures with scrubbers for subsequent disposal in the tailings (Jiang *et al*. 2000, Berndt 2003). Tailings basins and associated dams present risks of their own. The collapse of the iron mine tailings dam at Mariana in Brazil caused destruction and loss of life, and contamination with sediment apparently enriched in some heavy metals for 650 km downstream (Hatje *et al*. 2017). Iron mine tailings in China at Anshan have elevated lead and chromium concentrations (Zhang *et al*. 2017), and re-flooding underground iron mines in Poland contaminated groundwater with sulfate and high nickel concentrations (Razowska 2001). Iron mining in the Mesabi Iron Range and in the Upper Peninsula of Michigan have contaminated waters with heavy metals, asbestiform mineral fibers, fluoride, bromide, chloride, and sulfate, including in waters with wild rice (*manoomin*) that is vulnerable to sulfides from reduced sulfate (USEPA 1994, Berndt & Bavin 2012, Kelly *et al*. 2014, Von Korff & Bavin 2014, Cardiff & Coleman 2017). Iron mining in the Mesabi Range has also produced extensive landscape change (Baeten *et al*. 2016).

Cumulative impacts of mining

Assessing cumulative impacts of mining represents a means to understand the multiple impacts of several mining projects and their linear or non-linear interactions (Buschke & Vanschoenwinkel 2014). It is often intended to inform decision-making for individual projects, but also for assessing regional impacts and for strategic environmental assessments (Bravante & Holden 2009. Cavalcanti & La Rovere 2011, Banks 2013, USEPA 2014). A cumulative impact is an "impact on the environment which results from the incremental impact of the action when added to other past, present, and reasonably foreseeable future actions" (Council on Environmental Quality 1978). Cumulative impacts assessment is required for Environmental Assessments and Impact Statements and for coal mine reclamation in the US, but thorough assessments remain rare (Canter & Kamath 1995; Burris & Canter 1997; Senner 2011).

Studies have used a variety of approaches to assess cumulative impacts of large-scale mining (Johnson *et al*. 2005, Latifovic *et al*. 2005, Mouflis *et al*. 2008, USEPA 2014, Hogan *et al*. 2012, Weng *et al*. 2012, Moran & Brerton 2013). Most, however, have used a combination of land use patterns and water quality spatial analysis (Johnson *et al.* 2005, Latifovic *et al*. 2005, Lindberg *et al*. 2011, Merriam *et al*. 2011, Hogan *et al*. 2012, USEPA 2014). Understanding the relationship between land cover and water quality may allow for modeling of the water quality effects of expanded mine land cover.

Indigenous rights and mining

Mining can cause multiple negative social impacts, including on Indigenous peoples. Mining may affect Indigenous peoples in part through impacts on lands, water, air, and wildlife. For Indigenous peoples who are intricately connected to those lands and waters and rely on them for their lifeways, impacts can be severe (Kirsch 2014).

Large scale mining can also impact Indigenous rights that are recognized under international law. In 2007, the United Nations Declaration on the Rights of Indigenous Peoples (UNDRIP) recognized several rights that mining can affect (United Nations General Assembly 2007). Those rights include the right to secure enjoyment of means of subsistence (Art. 20), rights to conservation of the environment, land productive capacity, and medicinal plants and animals (Art. 24, 29), right to be free from hazardous waste (Art. 29), right to maintain spiritual land connections and cultural heritage (Art. 25, 31), right to conduct land use planning (Art. 32), right to withhold consent on mining projects (Art. 32), and rights to the observance and enforcement of treaties (Art. 37) "on their lands or territories" (United Nations General Assembly 2007). Though the U.S. government has yet to recognize those rights (US State Department 2010), many other countries have, at least in theory. Respecting the rights recognized under UNDRIP would probably help limit impacts of large-scale mining on Indigenous peoples.

In countries such as the US, Indigenous Peoples often also have treaty rights established under treaties with the national government. Extractive industry projects such as oil and gas projects and mining may impact on those treaty rights. The Lake Superior Ojibwe Treaty-ceded Territories on the

south and west shores of *Anishnaabeg Gichigami* (Lake Superior) represent zones in which internationally-recognized Indigenous rights and treaty rights ought to apply.

The Lake Superior Ojibwe, their treaty rights, and relation to mining

The history of Lake Superior Ojibwe (*Anishnaabe*) treaty rights and mining begins at least as early as the imposition of the treaties themselves. The U.S. officials advocating for and negotiating the treaties in the early and mid-1800's were seeking access to mining lands, as well as timber (Cleland 2000). An early treaty with Ojibwe bands in 1826 (Treaty of Fond du Lac of 1826) required in the treaty language that the "Chippewa tribe grant to the government of the United States the right to search for, and carry away, any metals or minerals from any part of their country" (7 Stat. 209; Case 2018). The Treaty of 1842 even required that the Ojibwe "residing on the Mineral district, ... be subject to removal therefrom at the pleasure of the President of the United States" (7 Stat. 591; Cleland 2000). Although not so obviously stated in the treaty language, access to mineral deposits also motivated US interests to conclude the Treaty of 1854 (Cleland 2000). Pressure from traders, implicit threat of military force, the threat of "removal" (forced displacement west of the Mississippi River), and translation errors or difficulties probably contributed to the Ojibwe not rejecting the treaties (Cleland 2000, Nichols 2000, Loew 2013). Although they apparently felt they had to accept, with assurances, some clauses such as the "removal" clause in the Treaty of 1842, the Ojibwe managed to include stipulations guaranteeing their right to hunt, fish, and gather in the Treaties of 1836, 1837, 1842, and 1854 (Cleland 2000, Loew 2013). They did so because of the great importance of those activities to their subsistence and lifeways (Loew 2013).

In spite of those rights reserved in the treaties, the Ojibwe faced restrictions on their treaty rights for more than 100 years after the treaties were concluded and after the formation of the states of Michigan, Minnesota, and Wisconsin (Cleland 2000, GLIFWC 2014). During that time, states claimed that Ojibwe had to follow state wildlife and fishing regulations, or were not allowed to hunt outside of reservation boundaries (Cleland 2000).

Native social movements for civil rights and treaty rights created impetus for greater respect of those rights in the 1960's and 1970's, and legal rulings eventually upheld treaty rights (Loew 2014). In 1974, following the "fish-in" protests, the *Boldt* decision (*U.S. v. Washington*) upheld treaty fishing rights and native fisheries management, and an equal share of harvest, in the Pacific Northwest region (Loew & Thannum 2011). After that precedent, the Lac Courte Oreilles Band filed suit against Wisconsin for imposing state law on off-reservation harvest by Band members in 1975 (GLIFWC 2014). A U.S. Court of Appeals eventually ruled in favor of the Lac Courte Oreilles Band and related cases were resolved affirming treaty right by 1991 (*LCO* or *Voigt* decision; GLIFWC 2014). A similar case by the Mille Lacs Band in 1990 eventually reached the U.S. Supreme Court, which ruled definitively in favor of the Ojibwe Bands in 1999 (*Minnesota v. Mille Lacs Band,* 526 US 172). The lengthy legal efforts that the Ojibwe bands took to have the courts affirm their treaty rights to hunt, fish, and gather is further evidence of the importance of those rights to the Ojibwe.

The legal cases were not the only struggles that the Ojibwe led to assert their treaty rights. After the first court rulings in favor of Ojibwe rights in Wisconsin, non-native people aggressively impeded Ojibwe spearfishing in racist and threatening ways (Whaley & Bresette 1999, Nesper 2002, Lipsitz 2008, Loew & Thannum 2011). The Ojibwe fishers continued to fish in spite of threats and acts of violence, and persevered through the racist protests to affirm their rights (Loew & Thannum 2011).

Similarly, Ojibwe have opposed a number of mine-related projects at least in part in order to safeguard the places where they can exercise their treaty rights. Although reservations formed largely by treaty in the mid-1800's may have been established in zones without known ore deposits at the time, more recent mining projects have been located not only on the Treated-ceded Territories, but also often close to reservations. When Exxon sought to build the Crandon sulfide mineral mine near the Sokaogon Band's reservation beginning in the 1970's, the community mobilized and joined with non-natives to stop the project (Gedicks & Grossman 2004, Lipsitz 2008, Willow 2013). Bad River Band members blocked trains carrying acid for copper solution mining in Michigan because of the risks to land and waters as well (Loew 2014). Multiple Ojibwe bands also protested the planned Gogebic Taconite mine in the

headwaters of the Bad River, just upstream from the Bad River Reservation in northern Wisconsin (Loew 2014). Those efforts illustrated not only Ojibwe determination to protect the places they hunt, fish, and gather, but also specifically to prevent impacts of mining on the waters in their Territories.

Treaty rights today remain of vital importance to the Lake Superior Ojibwe. Hunting and fishing are part of the seasonal round of Ojibwe lifeways, and every year Ojibwe harvest more than 1,000 deer (*waawaashkeshi*), more than 30,000 speared walleye (*ogaa*), hundreds of thousands of fish from Lake Superior, and thousands of pounds of *manoomin* (wild rice; David 2015, Hmielewski 2017, Mattes 2017, Falk 2018) off-reservation. *Manoomin* is of special importance. Traditional *manoomin* harvest involves a ceremony before harvest (Treuer 2001). *Manoomin* is part of the migration story of the Ojibwe to the Lake Superior region and essential to Ojibwe spirituality and well-being (Benton-Banai 1988, Treuer 2010, Loew 2013, 2014).

Guaranteeing Ojibwe fishing and wild rice harvest rights requires water quality that is at least adequate for ensuring abundant fish and wild rice. Waters and water quality may also relate to treaty rights more directly. During negotiations for the Treaty of 1837, the Ojibwe leader *Maghegabo* stated that the gathered Ojibwe wished to "reserve the streams where we drink the waters that give us life" (Cleland 2000, Nichols 2000, Loew 2014). Similarly, the leader *Aish-ke-bo-gi-ko-zhe* indicated that "without the lands, and the Rivers and Lakes, we could not live. We hunt, and make Sugar, and dig roots upon the former, while we fish, and obtain Rice, and drink from the latter" (Van Antwerp 1837 in Satz 1991). Although the importance of the waters was also related to the streams as a source of fish (Cleland 2000), those comments suggest that the waters themselves had value and that the Ojibwe intended that their use, including for drinking, be reserved or guaranteed under the treaty. As demonstrated by the Mother Earth Water Walk, clean water remains of importance to Ojibwe to this day (Loew 2013).

Iron mining water quality impacts in Lake Superior Ojibwe Treaty-ceded Territories and implications for Lake Superior Ojibwe treaty rights

Extensive mining over more than a century for iron, copper, and other metals (Fig. 1) has turned landscapes in the Lake Superior Ojibwe Treaty-ceded Territories into tailings, waste rock piles, and open pits (Kerfoot *et al*. 2012, Baeten *et al*. 2016, Langston 2017). The processing (beneficiation) of ores has emitted tons of mercury and other metals into the air (Jiang *et al*. 2000, Berndt 2003, Kerfoot *et al*. 2018). The mining has also contaminated waters with mercury, iron, cobalt, nickel, copper, zinc, cadmium, and uranium, as well as selenium and arsenic (USEPA 1994, MIDEQ 2009, Parsons *et al*. 2010, Cardiff & Coleman 2017, 2018a, b, c). Mines and their tailings facilities have also discharged asbestiform mineral fibers, fluoride, bromide, chloride, and sulfate to natural waters (USEPA 1994a, Berndt & Bavin 2012, Kelly *et al*. 2014; Von Korff & Bavin 2014, Cardiff & Coleman 2017, 2018a, b, c). Mining in the Mesabi Range is also associated with state-designated impaired waters (Baeten *et al*. 2017).

Water contamination from mining may be affecting Ojibwe treaty rights to fish. Fish may have suffered from the contamination, particularly from selenium and heavy metals. Mercury concentrations in some fish also exceed what people can safely consume, and some of that mercury came from the mining industry through water discharges in at least one region (Parsons *et al*. 2010) and probably from emissions to the air (Jiang *et al*. 2000, Berndt 2003, Lake Superior Binational Program 2012, Kerfoot *et al*. 2018). Sulfate from mining at certain intermediate concentrations also enhances methylation of mercury, which converts the element into a more toxic and biomagnifying form (Gilmour *et al*. 1992, Jeremiason *et al*. 2006). Iron mining also affects Ojibwe treaty rights by damaging *manoomin* beds. Sulfate from the mining, reduced to sulfide in sediments, is toxic to *manoomin* and also contributes to release of nutrients from sediment that can cause eutrophication (Myrbo *et al*. 2017a, b). *Manoomin* is an important part of Ojibwe culture and lifeways (Benton-Benai 1988, Loew 2013), and mining therefore is of great concern in part because of that effect on it.

The number of mines and apparent mining impacts seem to vary between the three states in the Lake Superior Ojibwe Treaty-ceded territories: Michigan, Minnesota, and Wisconsin. Although studies have assessed differences in mining policies between those states (NWF 2012), they have not sought to relate the policies to the number of mines or impacts. Placing those states in the context of other state

policies and corporate assessments of policy would help determine the influence of policy on mining impacts and could suggest policies that minimize impacts.

In spite of the impacts to treaty rights in Lake Superior Ojibwe Treaty-ceded Territories, studies have yet to thoroughly assess cumulative impacts of mining in this region, and permitting of new mines without thorough cumulative impact analysis has continued. The USEPA Region 5, with input from Lake Superior Ojibwe Bands and the Great Lakes Fish and Wildlife Commission (GLIFWC), produced a toolkit for cumulative impacts assessment on Indigenous Peoples in this region in August 2011 (USEPA 2011). No such thorough study, however, has proceeded. Although a full cumulative impacts assessment would include social, health, cultural, environmental, and economic impacts and might require extensive time and resources (Burris & Canter 1997; USEPA 2014), a study that examined water quality impacts and relations to mine land cover may contribute to development of a more comprehensive cumulative impacts study and help answer important questions about methods and impacts. This dissertation sought to achieve this with a detailed study of the Escanaba River watershed (Chapter 2), a broader analysis of water quality in iron mining regions across the Territories (Chapter 3), and an evaluation of the mining policies that may relate to cumulative impacts (Chapter 4).

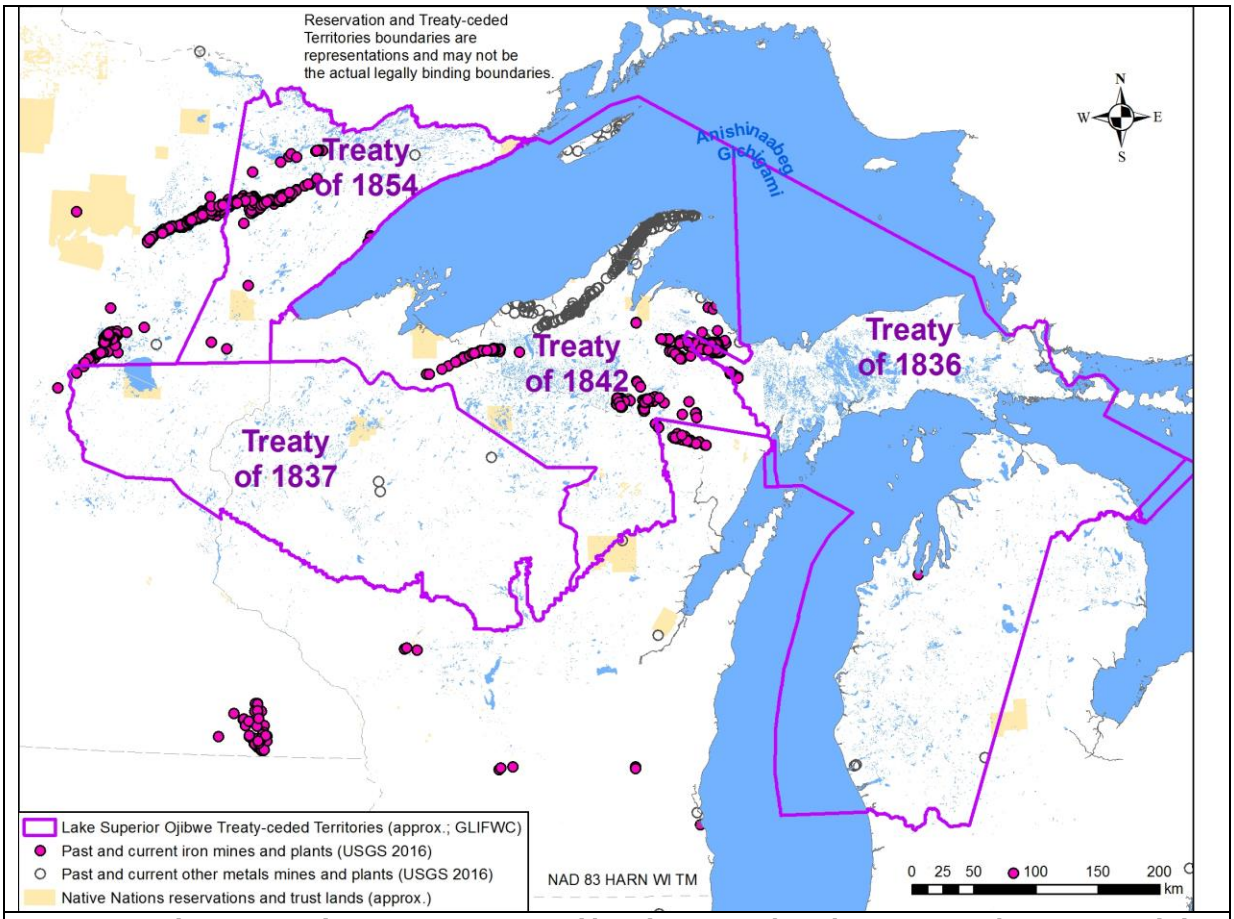

Fig. 1. Past and current metals mines occur in several broad ranges in the Lake Superior Ojibwe Treaty-ceded Territories. Territory boundaries are from the Great Lakes Indian Fish and Wildlife Commission (GLIFWC).

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Chapter 2. Selenium contamination and cumulative impacts of large-scale iron mining on surface water quality in the Escanaba River watershed

Abstract

Mining for metals at a large-scale can cause many impacts on land, air, and waters, but studies of the impacts of iron mining have been relatively limited. Examination of the cumulative impacts of iron mining has the potential to improve understanding of the past, current, and potential future effects. Large-scale iron mining for production of taconite pellets in the headwaters of the East Branch of the Escanaba River, part of the Lake Superior Ojibwe territories of the Treaties of 1836 and 1842, began in 1964. The mining has discharged selenium into the surface waters in concentrations exceeding state criteria in recent decades. I examined the cumulative water quality impacts of mining by sampling for metals and other trace elements along the main channels and tributary streams in this river system and evaluating relationships between mine waste land cover proportions and water quality characteristics. I classified land cover using Worldview-2 images, LiDAR data, and Landsat 8 image and related land cover to water quality data with several multiple regression analyses. Selenium and other water quality characteristics were significantly greater at sites downstream of mining relative to reference sites, and were related to distance downstream from mining waste, and the proportion of the watershed covered by mine waste. Those analyses and data from water samples acquired near tailings discharge indicated that the mining appears to be the source of contamination of the surface waters with Total Dissolved Solids, bromide, chloride, fluoride, sulfate, antimony, arsenic, boron, cadmium, molybdenum, phosphorus, selenium, vanadium, and other constituents. Selenium and TDS exceeded state criteria at many sites, and selenium exceeded or was within 10% of the EPA criterion in reaches representing an estimated 22% of the streams and flow paths of the East Branch of the Escanaba River watershed. That element remained at levels exceeding the state criterion at a site 23 river-km downstream of the nearest mine waste. Selenium is of particular concern because of its impact on fish, and selenium contamination may be impacting Lake Superior Ojibwe treaty rights in the region. Chloride, fluoride, arsenic, and cadmium exceeded Canadian criteria at some sites. Chloride, arsenic, phosphorus, sodium, and vanadium exceeded Michigan drinking water criteria in some samples. Total unfiltered mercury was associated with waste

rock, but watershed forest cover and Total Organic Carbon explained most variation in total and methylmercury concentrations. Results did not indicate that selenium affected mercury concentrations in the water. Sulfate may also have influenced mercury methylation, but the possible non-linear relationship was not significant. From limited historical data for some of the sites, I determined that current levels of specific conductance, pH, chloride, and sulfate were also greater than in pre-mining years. Through cluster analysis and tests of differences with reference sites, I determined that at a site at least 85 river-km downstream of the nearest mine, water remained influenced by mining, and that 15 % of the stream and river kilometers in the overall Escanaba River watershed were mine-influenced. Results also suggest that using Sector-Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS) is useful for identifying elements associated with mine waste at low concentrations. Conducting multiple statistical analyses also appears to be important for determining mine influence. The direct relation between watershed mine waste land cover and selenium is comparable to relationships established for selenium and coal mining in Appalachia. That relationship to land cover may allow for predictions of the water quality impacts of additional mine expansion, and improve our understanding of cumulative impacts of large-scale iron mining. This is particularly important as additional mining projects emerge in this region, and potentially relevant to other iron mining regions as well. In the Escanaba River watershed, the selenium contamination has proceeded for more than ten years and represents a significant concern for aquatic life and fisheries and the exercise of Lake Superior Ojibwe treaty rights.

1. Introduction

Impacts of metals mining

Large-scale metals mining transforms landscapes and can contaminate the air, soil, and surface and groundwater (Down & Stocks 1978, Lottermoser 2010). Mining of deposits with sulfide minerals often causes acid mine drainage and associated contamination with metals and trace elements (Akcil & Koldas 2006, Nordstrom 2011). Other water contaminants with potentially harmful impacts can include sulfate, fluoride, chloride, sediments, asbestiform mineral fibers, processing chemical such as xanthates, and petroleum products (USEPA 1994a, b; Appendix A). Sulfate contamination can harm wild rice and release nutrients to surface waters, and also enhance mercury methylation (Gilmour *et al*. 1992, Jeremiason *et al*. 2006, Myrbo *et al*. 2017a, b). Mercury concentrations and effects (Appendix A) can depend on concentrations of selenium, another potential mine contaminant, and multiple other biological and abiotic factors (Ullrich *et al*. 2001, Yu *et al*. 2011, Sonke *et al*. 2013).

Cumulative impacts

Assessing cumulative impacts of mining has the potential to improve understanding of those multiple mining impacts. A cumulative impact is an "impact on the environment which results from the incremental impact of the action when added to other past, present, and reasonably foreseeable future actions" (Council on Environmental Quality 1978). The analysis aggregates effects spatially or temporally and includes effects of interactions between impacts (Franks *et al*. 2013). Such efforts related to large-scale mining projects can help inform decisions about potential mining projects as part of project impact assessments (Banks 2013, USEPA 2014) or regional and strategic environmental assessments (Bravante & Holden 2009, Cavalcanti & La Rovere 2011).

Most partial estimates of cumulative impacts of mining have used a combination of land use patterns and water quality spatial analysis (Johnson *et al.* 2005, Latifovic *et al*. 2005, Petty *et al*. 2010, Lindberg *et al*. 2011, Merriam *et al*. 2011, Hogan *et al*. 2012, USEPA 2014). One version of this

approach to cumulative mining impacts consists of sampling water quality along the length of a river as it passes through an increasingly mined watershed. Lindberg *et al*. (2011) adopted such an approach in assessing cumulative water quality impacts of coal mining in Appalachia. By sampling contaminants such as selenium synoptically along a reach that received inputs from an increasing number of mined watersheds, they were able to evaluate the impact on the water quality of such increases (Lindberg *et al*. 2011).

Iron mining impacts

Although non-ferrous mines have received more research attention for their water quality and cumulative impacts, iron mining can also transform large extents of land and contaminate waters. Modern iron mines create large open pits, waste rock piles, and dammed tailings facilities. Even when not resulting from a massive tailings dam failure (Hatje *et al*. 2017), significant water contamination can occur. Contamination from iron mining in the Mesabi Iron Range in Minnesota and in Michigan has included heavy metals, asbestiform mineral fibers, fluoride, bromide, chloride, and sulfate (USEPA 1994a, Parsons *et al*. 2010, Berndt & Bavin 2012, Kelly *et al*. 2014; Von Korff & Bavin 2014, Cardiff & Coleman 2017). Those are of concern for aquatic life and human health (Appendix A). Contamination has occurred in waters with wild rice, which is sensitive to sulfides from reduced sulfate (Myrbo *et al*. 2017a, b, Vogt 2018). Watersheds near the iron range are also more likely to be rated impaired, and watersheds with greater historic mining intensity also had a greater proportion of impaired waters (Baeten *et al*. 2017).

The Escanaba River, and Ojibwe fishing rights

The Empire and Tilden mines occupy the headwaters of the East Branch of the Escanaba River, on Lake Superior Ojibwe Territories (Treaties of 1842 and 1836), on the Upper Peninsula of Michigan. The Escanaba River flows to Lake Michigan. Although several smaller mines operated in the area beginning before the 1890's (Van Hise & Bayley 1896, Gair & Han 1975), the Empire Mine became a

larger open pit operation in 1963, with an associated water reservoir dam on Schweitzer Creek (1962) and a tailings facility (1963; Wiitala *et al*. 1967; Sliter & Kulbieda 1975; Reynolds & Dawson 2011). The Tilden Mine began operation in 1974 after construction of the Greenwood Reservoir (1973) and the tailings facility subsequently expanded (Cannon *et al*. 1975). Waste rock piles have also expanded as mine pits went deeper.

In addition to land cover impacts, reports as early as 1972 indicated that the mines were degrading habitat for aquatic life in Warner Creek and Green Creek and that arsenic in sediment and sulfate in water were highest nearest mining in the headwaters of Warner Creek (Evans 1972; Jackson 1972; Willson 1972). Tilden Mine effluent was also chronically toxic to *Ceriodaphnia dubia* in a test in 1990 (Dimond 1990). Available data suggest that it was in the mid-1990's that selenium was first measured at high concentrations in groundwater. A well at the Empire mine reached concentrations exceeding drinking water limits in 1997, though it was greater than the current state surface water chronic criterion by 1990 (Thomas 2009). It was apparently not until 2000, however, that a study analyzed stream water samples for selenium and reported a high value for selenium in Warner Creek (Godby 2002). This was of concern because selenium causes deformities and reduced growth and survival in fish and birds, and in high concentrations is a human health concern as well (Appendix A). Tests also determined that selenium was high in discharge from the Empire north pit and waste rock piles by 2001 (Little 2004), in Empire tailings basin discharge by 2003 (MIDEQ 2009), and in Tilden tailings basin discharge by 2005 (Little 2005). A subsequent study in 2005 confirmed selenium exceeding the state criterion in Warner Creek and recommended further study (Kohlhepp 2007). This eventually lead to studies by the Michigan Department of Environmental Quality (MIDEQ 2009, Kohlhepp, 2010, Knauer *et al*. 2012) and subsequent reports by the mining company (e.g., Cliffs 2016) that established that water with selenium concentrations exceeding criteria was discharging from both tailings and waste rock seeps and that the contamination was widespread.

This mining and water contamination has all occurred on the territories of the Lake Superior Ojibwe (Anishnaabe). Ojibwe Bands on the southern and western sides of Lake Superior signed cession

treaties with the US government in the mid-1800's, but reserved their rights under those treaties to hunt, fish, and gather on those lands (Loew & Thannum 2011). Court rulings reaffirmed those rights in the 1980's and 1990's, and Lake Superior Ojibwe actively fish in many waters of this region (GLIFWC 2014). Mining activities may threaten those rights through, for instance, water quality impacts on fish populations that result in fish advisories or reduced fish abundance.

In spite of this evidence of selenium contamination from iron mining in the Escanaba River watershed and its potential implications for ecosystems and Indigenous rights, studies had yet to assess the downstream extent of mine contamination, thoroughly sample for other potential contaminants in recent years, compare current with historical measurements, or relate contamination to land cover. I sought to accomplish that and add to the understanding of cumulative impacts of mining and iron mining impacts.

2. Methods

a. Water quality data

Field methods—field measurements

At all sites, I used standard surface water monitoring protocols (USGS variously dated; USEPA 2012) and recorded temperature, specific conductance, and chloride concentration with a YSI Pro Plus multimeter in the field. In addition, at sites sampled for anions, I measured dissolved oxygen (DO), pH, and oxidation-reduction potential (ORP). I calibrated specific conductance, chloride, pH, and DO sensors daily, and verified ORP calibration daily (re-calibrating as necessary). At sites sampled for metals and trace elements, I also measured turbidity with a Hanna Instruments 93703 turbidimeter, calibrated once per sampling trip, and velocity and depth profiles for Equal Width Increment discharge calculations with a Swofford 3000 velocity meter (USGS, variously dated). Due to malfunction of my flow meter, I was

unable to measure flow for eight of the full sampling events. For those sites, I estimated flow from baseflow estimates for those sites (USGS 2005) and the ratio of flow on the sample date at a relevant stream gauge (USGS_04058200) to the estimated baseflow at that gauge. For calculating loadings for a site (SC016) without baseflow estimates and with flow noticeable but not registering on the meter, I used half of the lowest velocity measured (0.005 m/s) for the center flow interval.

Field methods – sample collection

I collected samples for major anions, alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), and metals and trace elements including total and methylmercury (Table S1). Where possible, I collected samples at well-mixed sites below a riffle zone. I used a hand dip sampling technique at the centroid of flow with the Clean Hands – Dirty Hands (CH-DH) technique (USGS variously dated, USEPA 1996). I rinsed bottles three times with sample water and kept bottles capped when submerging into or removing from the water. At some sites where I only sampled for major anions, I used a one-person modification of Clean Hands-Dirty Hands technique. This involved using one hand as CH and one as DH.

In 2015, I collected 37 anions samples, 20 trace element samples, 20 TDS/TSS/alkalinity samples, 20 Total Organic Carbon (TOC) samples, and 20 mercury/methylmercury samples in this study zone (Table S2). I also collected 3 field blanks (8%) and 1 field sequential replicate (3%) for anions, 2 field blanks (10%) and 1 field sequential replicate (5%) for trace elements, and 1 of each (5%) for TDS/TSS/alkalinity. In 2016, I collected 13 anion samples, and 1 field blank (8%) and 1 field sequential replicate (8%). I only collected 1 sample each for trace metals and TDS/TSS/alkalinity in 2016 in this zone and collected blank and sequential replicates elsewhere on the same trip. I filtered anion samples using syringes and 25 mm diameter, 0.45 µm polysulfone cartridge filters (Pall Acrodisc 4585). I did not filter the metal and trace element samples.

I recorded field measurements in the Escanaba River system and around the Empire and Tilden mines in May-August 2015 and June and August in 2016 (Table S2). I collected mercury samples only in

2015. Including sites sampled by rapid logging of measurements by kayak, I measured field characteristics at 187 sites, anion concentrations at 40 sites, and full trace element samples at 19 sites (Fig. 1).

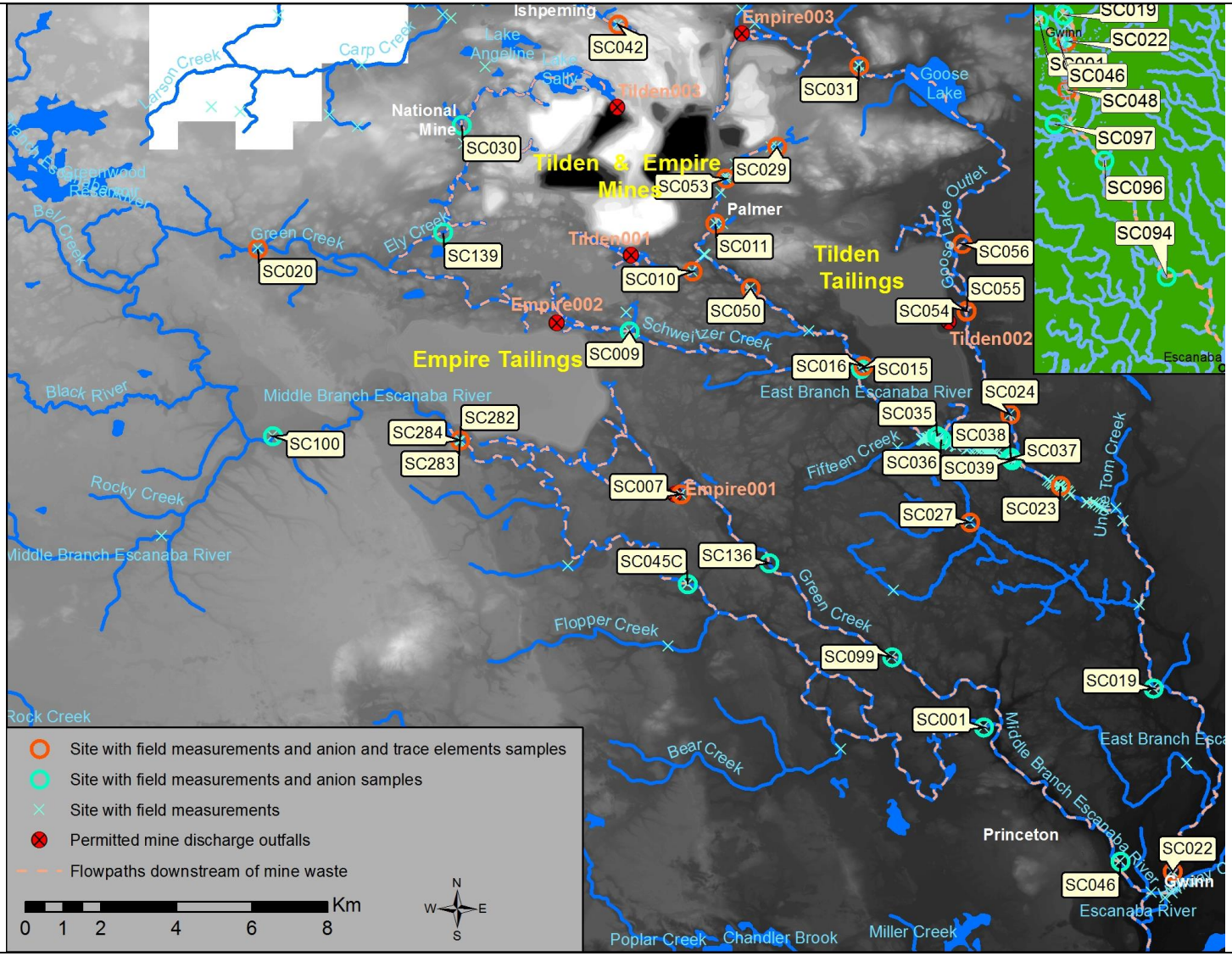

Fig. 1. Study sites from 2015-2016 in the Escanaba River system. Sites with anion or trace metals samples are labeled with site code. Image is 1-m Digital Elevation Model from LiDAR data. Inset is lower Escanaba River downstream of the confluence of the East and Middle Branches at Gwinn. Gap to the northwest of the mines represents zones outside of the study zone and LiDAR coverage.

Laboratory methods

I analyzed anion samples by ion chromatography within 28 (2015) or 8 (2016) days after sample collection. I conducted ion chromatography following EPA method 300.1, with a Dionex ICS-2100 and autosampler. I configured the instrument with a 4 mm x 250 mm Dionex IonPac AS11 column, AG-11 guard, and ASRS-4mm suppressor. I used a 100µL injection loop, flow rate of 0.6 ml/min (2016, 1.0 ml/min in 2015), suppressor current of 45 mA (2016, 65 mA in 2015), column temperature of 30° C, and 30 mM NaOH eluent. I measured Method Detection Limits (MDLs) by running seven standard-fortified samples through an analysis sequence in two different batches on two (2015) or three (2016) separate days (Table S3).

I delivered other samples to the USGS Mercury Research Laboratory in Middleton, Wisconsin, and to the Wisconsin State Laboratory of Hygiene (WSLH). The USGS laboratory analyzed samples for unfiltered total mercury (THg) and unfiltered methyl mercury (MeHg) and analyzed separate samples for Total Organic Carbon (Table S1). Detection limits for mercury were 0.04 ng/l. The Wisconsin State Laboratory of Hygiene analyzed metal and trace element samples for 51 elements using a Thermo-Finnigan Element 2 Sector-Field (Magnetic Sector) Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS). Nitric acid digestion at 85°C for 12 hrs preceded analysis. Laboratory Quality Control samples for each batch included sample duplicates and sample spikes for at least 14% of samples, and additional calibration blank and verification samples. Measurement uncertainty estimates included standard deviation of triplicate analyses of each sample and the standard deviation of 4-5 method blanks for each batch. The laboratory calculated limits of detection by multiplying the standard deviation of 18 laboratory check blanks by three for each element (Table S4). I used total concentrations of Ca and Mg to calculate total hardness in each sample.

To ensure adequate data quality control, I assessed blank and sequential replicate results and compared laboratory measurements with field measurements where applicable (Supplemental Information).

Historical water quality data

I obtained data on historical water quality in my study zone from the Water Quality Portal (National Water Quality Council 2018), other USGS data (Neal H. Craig, personal communication), and other reports (Evans 1972, Rozich 1972). I was able to sample at several sites with historical data collected before large-scale upstream mining: SC009, SC010, SC015, SC099, SC139 (Fig. 1). I also found historical data from the Goose Lake Inlet and Outlet, but discharges from the Tracy and related mines preceded discharges from the Empire and Tilden mines in that watershed. Consequently, I compared the following sites separately from that previous group: SC022, SC024, SC031, SC048, SC055, and SC056. Lastly, I sampled at several reference sites that also had pre-1974 data to compare to: SC020, SC043, and SC044. I discarded historical results of zero that lacked detection limits information.

b. Landscape analyses

I delineated watersheds for the principal sample points in the East Branch and Middle Branch of the Escanaba River using LiDAR data and Arc Hydrotools in ArcGIS (ESRI, Redlands, California). I first digitized streams missing in the NHD Plus (USEPA 2017) streams network at a scale of at least 1:5000 using heads-up digitizing with Google Earth imagery. To mosaic a DEM for the study region, I primarily used LiDAR DEM data from May and November 2015 and May 2016 at 2 ft original horizontal resolution from the Michigan Statewide Authoritative Imagery & LiDAR (MiSAIL) program. I supplemented that with LiDAR LAS data sampled at 1 m resolution from 2012 from the Natural Resources Conservation Service for one watershed in the southwest of the study region (West Branch of the Escanaba River).

I classified land cover in the study region using an analysis of Worldview-2 images (2 m spatial resolution) around the mines and supplemented that with an analysis of a Landsat 8 image (30 m spatial

resolution) for portions of watersheds extending beyond that zone (Table S5). Acquisition dates were 2015-08-21 for the Worldview-2 and 2015-08-28 for the Landsat 8. In addition, I used LiDAR Digital Elevation Model (DEM) data to calculate slope and roughness as the standard deviation of the DEM (filter of 5 pixels) in Geomatica 2017 (PCI Geomatics, Markham, Ontario). I also used the LiDAR data in ArcGIS to develop a Digital Surface Model and then calculated a Digital Height Model (DHM) by subtracting the DEM from the Digital Surface Model. Calculating the standard deviation of the DHM (filter of 5 pixels) also provided a measure of DHM roughness. I merged those LiDAR-derived bands with the original image bands and multiple band ratios from the images (Table S5) in the Support Vector Machine Object-Based Image Analysis tools in Geomatica 2017. I first segmented the image using the original image bands and some of the ratios (Table S5) and a scale factor of 10 (Worldview-2) and 15 (Landsat 8). Using feature extraction, I calculated means for each band and also segment circularity (all analyses), compactness (all analyses), elongation (WV-2 only), and rectangularity (WV-2 only; PCI Geomatics).

In selecting training and accuracy assessment segments, I adopted a stratified approach by selecting segments for each land cover class that were nearest a random point assigned to each cell of a fishnet grid in Arc GIS 10.3 and with the Geospatial Software Environment (Beyer 2014). I also ensured that I did not select segments that were closer than 50 m (WV-2) or 0.2 km (Landsat 8) from other selected segments. I determined the land cover class for training and accuracy assessment segments by comparison with visual interpretation of National Agriculture Imagery Program (NAIP; USDA 2016) 0.6 m imagery from August 2016, and Google Earth imagery from 2014. Land cover classes consisted of the following: tailings and process water; waste rock and pits; roads, bare earth, and urban; forest; other vegetation; and wetlands. In selecting segments, I did not select pit lakes or water near mine waste for the water class; I only selected other vegetation segments if outside of mapped wetlands (MIDNR 1999, USFWS 2017); and only selected wetlands if inside of those wetlands spatial layers. For the WV-2 images, I selected 200 training segments and 50 accuracy segments per class out of a total number of segments of 1094764 (image 1) and 1397436 (image 2). In the Landsat 8 analysis, I obtained 60 training

segments for each class, but only 30 segments for the Roads etc. class, and 20 accuracy assessment segments out of a total of 1048827. I checked the training sets for outliers and fixed apparent errors. I then classified the images, and ran an additional classification without LiDAR data to cover zones lacking that data on the margins of my study region for Landsat 8. I systematically checked the classification and corrected the following apparent classification errors: tailings in non-tailings zones; waste rock in non-rock zones; forest on processing plant; other vegetation on forest in zones without LiDAR data; roads etc. on water; shadows classified as water; wetlands on image margins, wetlands with DHM > 7m, and wetlands outside of mapped wetland zones.

c. Statistical and spatial analyses

To assess the relationship of mine waste to water quality characteristics, I tested the difference between measurements at reference sites with measurements at sites downstream of mining with Kruskal-Wallis tests. I also tested for the influence of mine waste with simple and multiple linear regression analyses of water quality characteristics relative to distance downstream from waste and proportion of a sample site's watershed in mine waste land cover. I assumed that a significant decreasing concentration with distance downstream of waste was an indication of an association of a given characteristic with mining waste. Relatedly, I evaluated the trend of water quality characteristics in successive downstream sites and analyzed the relationship between the proportion of a watershed with mining waste land cover and water quality at a set of successively downstream main-channel sites (no tributaries, Goose Lake Inlet and downstream of there) with regression analyses. In addition, I conducted the same statistical tests to determine differences between sites downstream of tailings relative to those downstream of waste rock, and separately tested for associations between water quality characteristics and those separate waste sources. For all analyses, I examined both all available data and a set of sites that were not downstream of each other (subwatershed data) that would be less sensitive to spatial autocorrelation.

I sought to identify measurements that were of concern based on their relation to water quality criteria and recommendations. I also calculated loadings for selenium to better understand prominent sources of that element, since selenium is a contaminant of concern in this zone.

To assist in identifying contamination from particular sources, I evaluated indicators, particularly previously published ratios of characteristics (weight ratios for ions and elements), that demonstrated affiliation with a given mine source. I also considered ratios to compensate for inclusion of data collected on multiple dates under different hydrologic conditions. I included ion ratios to specific conductance as characteristics that are relatively easily measured. I also included NASC-normalized Rare Earth Element (REE) ratios (Migaszewski *et al*. 2016) as Ce/Ce_{NASC}, Eu/Eu_{NASC}, and Ho/Ho_{NASC}. I sought indicators that were comparatively consistent between dates for sites that were repeatedly sampled, had their highest (or lowest) value at a site relatively close to tailings or waste rock, and were related to watershed waste proportion and distance downstream.

I conducted additional analyses to clarify relationships of mercury compounds to mine waste and other factors influencing their concentrations. I tested for those relationships with simple and multiple linear regressions, and also examined correlations of water quality characteristics.

To compare recent (2015-2016) data with pre-mining data, I used Kruskal-Wallis tests for available characteristics. I grouped the data, using one median measurement for each site, characteristic, and time period, into three groups: sites in the Goose Lake Inlet and downstream of there; other sites now downstream of mining in the Warner Creek, Schweitzer Creek, and Green Creek watersheds; and reference sites. I also analyzed pre- and post-mining data for individual sites where data were adequate.

Finally, I determined the extent of mine influence by first determining which sample sites were mine-influenced when this was not clear from concentrations of selenium and bromide. I used cluster analysis and Kruskal-Wallis tests to determine mine influence status for those uncertain sites. The cluster analysis, using Ward's hierarchical accumulative method with squared Euclidian distances and z-score standardization (Ward 1963), associated sites for which I was unsure of the mine influence on with either reference sites or mine-influenced sites. I also tested for differences between those uncertain sites and

reference sites with the Kruskal-Wallis test. Based on those and Kruskal-Wallis historical site results, I mapped the spatial extent of mine-influenced reaches in the Escanaba River watershed. For that mapping, I assumed that reaches between mine-influenced sampling sites were also mine-influenced, and that upstream mine sources were the most obvious sources closest to the related stream channel.

I conducted all statistical analyses using SAS 9.3 software (SAS Institute, Cary, NC). For parametric tests, I used an arcsine square root transformation on the watershed proportion data, a $\log_{10}(x + 1)$ or square root transformation on distance downstream of mine wastes, and a $\log_{10}$ or $\log_{10}(x + 1)$ transformation on all other data other than pH. I used un-transformed data for the non-parametric Kruskal-Wallis tests. For regressions, I used a stepwise selection method. In reporting and analyzing anion concentrations from ion chromatography and for one methylmercury measurement, I used ½ of the Minimum Reporting Limit (MRL) or detection limit for results that were below calibration MRLs or detection limits.

3. Results

Land cover analysis

The classification of the WV-2 and Landsat 8 images provided a land cover map with overall accuracy of 94% based on assessment segments from the WV-2 P1 (western) image and from the non-overlapped segments from the WV-2 P2 (eastern) image and the Landsat 8 image (Tables S6, S7). Accuracy for the individual maps ranged from 84 to 90 %, and classes with the lowest accuracies were the roads and bare ground, and the vegetation-other classes (Table S6, S7). Waste rock producer and user accuracies in the overall image were > 90%, as was tailings user accuracy (Table S6).

Contaminants of concern associated with mining

I determined that iron mining discharges and mine waste land cover explained patterns of several contaminants of concern in the East Branch of the Escanaba River. Kruskal-Wallis comparisons with reference sites, regressions analyses with distance downstream and mine waste land cover, and downstream trends indicated that mining waste was associated with contamination from characteristics including TDS, bromide, chloride, fluoride, sulfate, antimony, arsenic, boron, cadmium, molybdenum, phosphorus, selenium, sodium, and vanadium (Figs. 2-4, Tables 1, S8). Measurements from the Gribben (Tilden) tailings discharge as it entered the Goose Lake outlet and correlations with specific conductance, sulfate, and bromide provided additional evidence of association with mine waste for several of those contaminants (Tables 2, S9).

Other characteristics that also demonstrated association with mining, based on Kruskal-Wallis differences from reference sites and other statistical tests ($P < 0.05$), included characteristics (total alkalinity, K, W) decreasing with distance downstream of nearest mine waste (mine waste = tailings and waste rock), characteristics decreasing downstream of tailings (Li, Cs), and characteristics decreasing downstream of waste rock (Mg). Some were also directly related in the Goose Lake Inlet and downstream to watershed land cover proportion in mine waste (K, Rb), tailings (Cs, Si, W), or waste rock (Ca, Mg, Rh). Se loading was also related in subwatershed regressions to tailings land cover ($R^2 = 0.45$, $P < 0.05$) and tailings plus waste rock land cover ($R^2 = 0.47$, $P < 0.05$).

TDS and selenium downstream of mining exceeded Michigan chronic surface water criteria, and other characteristics exceeded drinking water or other criteria or recommendations at certain sites, including chloride, fluoride, arsenic, cadmium, phosphorus, and vanadium (Fig. 5, Table 2). Aluminum also exceeded USEPA aquatic life criteria (87 µg/l) downstream of the Tilden tailings effluent discharge (113 µg/l at SC055). This also occurred at my reference sites following a storm event that occurred a few days before sampling in May. Similarly, thallium reached its highest measurements in the Tilden tailings effluent discharge (0.0055 µg/l), but was only 10 % greater than my greatest measurements at reference sites, and was lower than the USEPA human health criterion (0.24 µg/l). Dissolved oxygen in the tailings

effluent and immediately downstream (both 5.2 mg/l) were lower than at most other sites, but that particular section of Goose Lake Outlet is not a designated trout stream with a more stringent DO criterion. Total alkalinity was > 200 mg/l as $CaCO_3$ near the tailings and waste rock, and hardness was > 250 mg/l as $CaCO_3$ at sites nearest waste rock in July. Lithium was also > 3 µg/l near waste rock in the Goose Lake Inlet and downstream of tailings discharges, though that remained below aquatic life effect concentrations (Kostich *et al*. 2017).

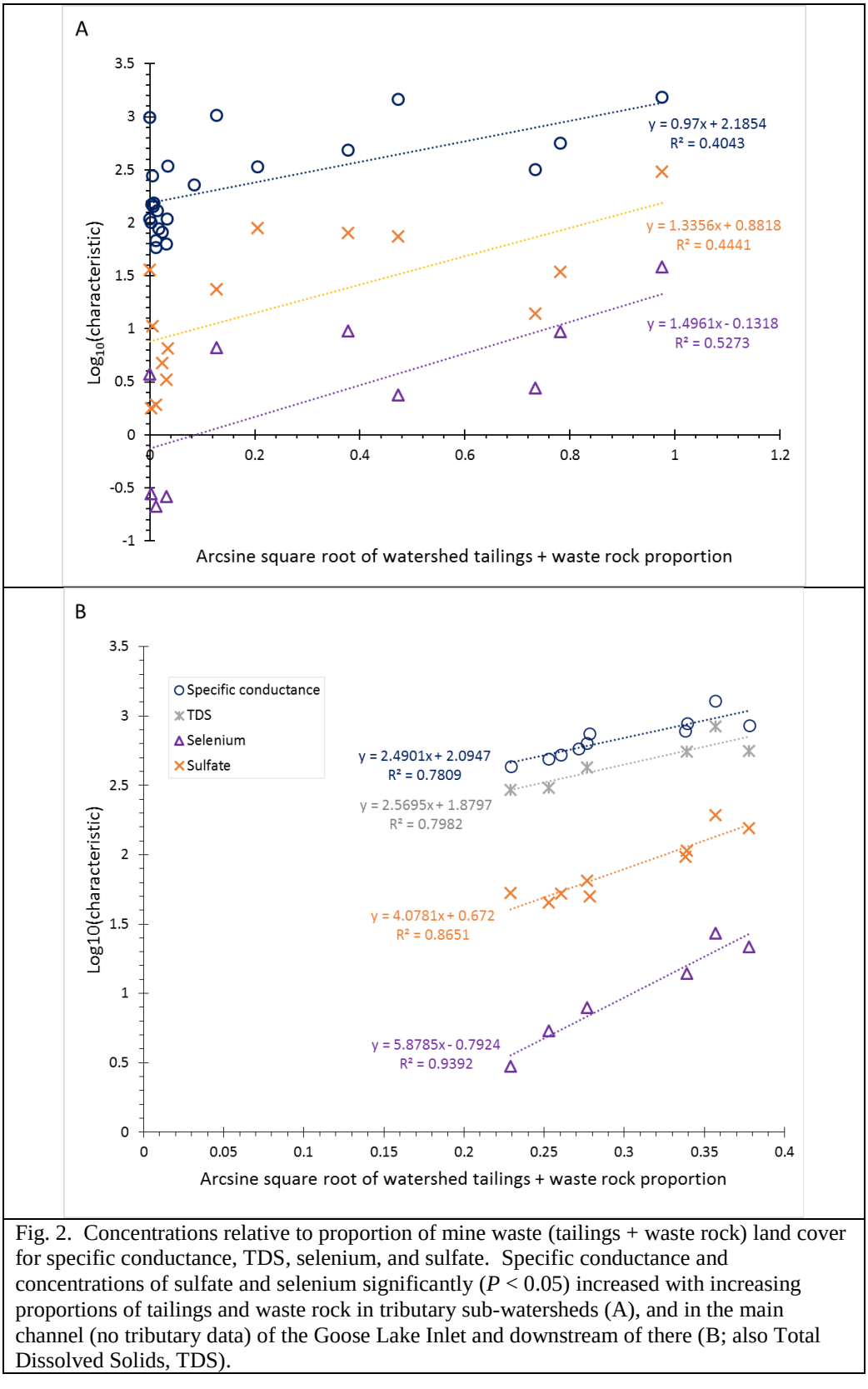

Fig. 2. Concentrations relative to proportion of mine waste (tailings + waste rock) land cover for specific conductance, TDS, selenium, and sulfate. Specific conductance and concentrations of sulfate and selenium significantly ($P < 0.05$) increased with increasing proportions of tailings and waste rock in tributary sub-watersheds (A), and in the main channel (no tributary data) of the Goose Lake Inlet and downstream of there (B; also Total Dissolved Solids, TDS).

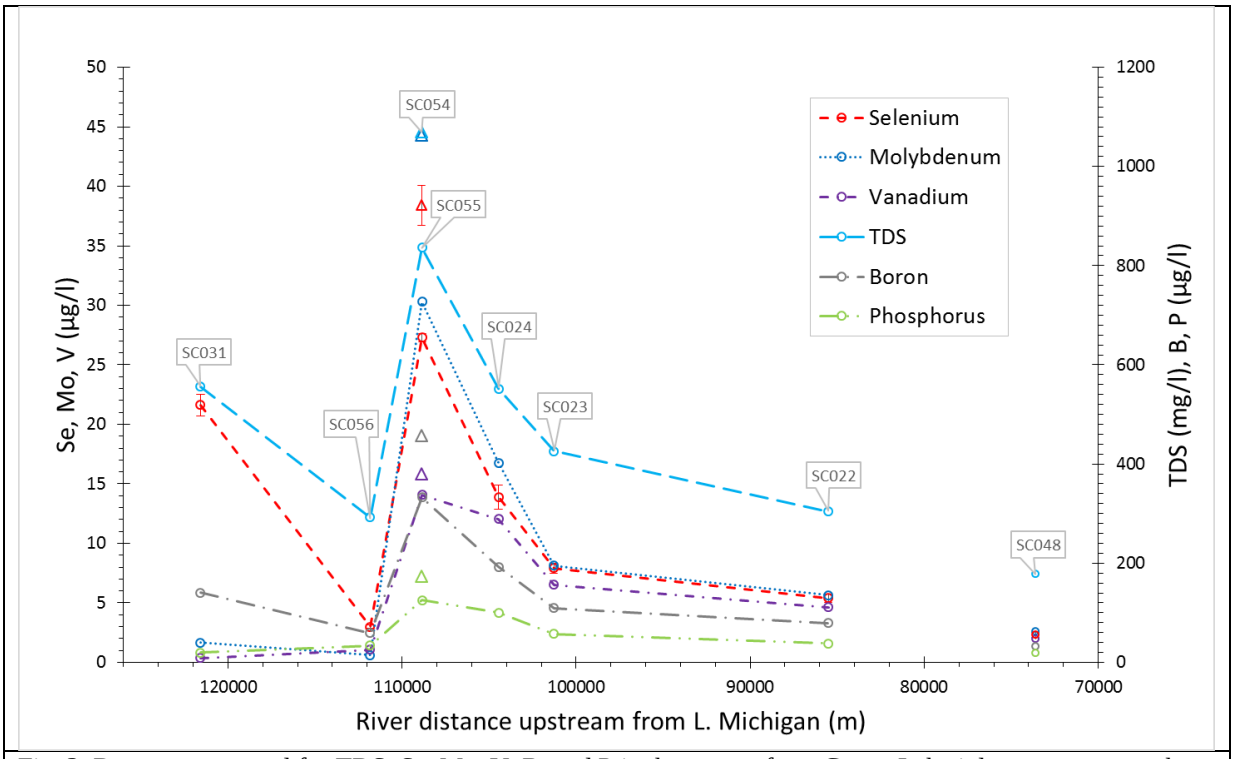

Fig. 3. Downstream trend for TDS, Se, Mo, V, B, and P in the stream from Goose Lake inlet near waste rock (SC031) to the Escanaba River (SC048). Tilden tailings effluent (SC054, △) joined the stream just upstream of site SC055. These data were from July 2015.

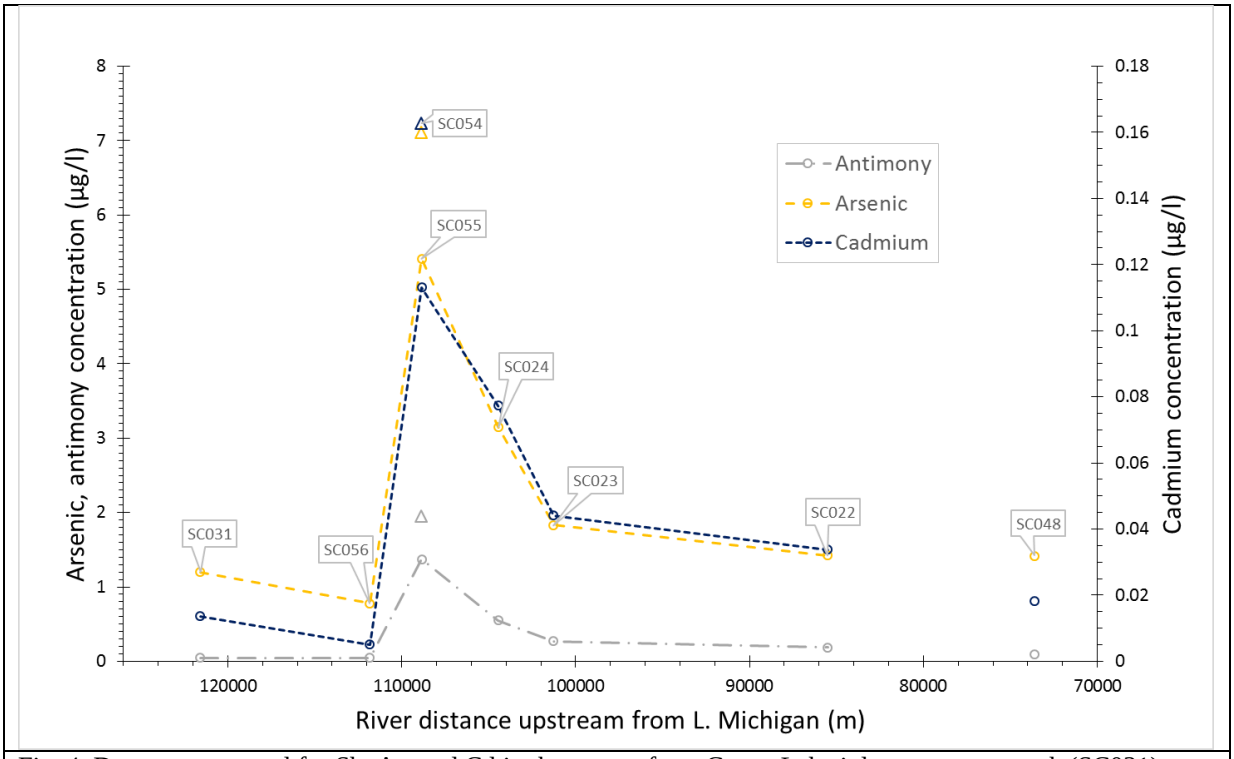

Fig. 4. Downstream trend for Sb, As, and Cd in the stream from Goose Lake inlet near waste rock (SC031) to the Escanaba River (SC048). Tilden tailings effluent (SC054, △) joined the stream just upstream of site SC055.

Table 1. Results of statistical tests indicated that several constituents of potential concern were associated with mine waste in general (tailings + waste rock), tailings, and/or waste rock. Distance downstream was along path of main flow and characteristics were inversely related unless noted otherwise (+) and land cover directly related unless noted otherwise (-). Kruskal-Wallis tests results also indicate which group had a greater mean than the other (details in Table S8). * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

Characteristic	Comparisons by Kruskal-Wallis test by subwatershed / with all data		Distance downstream simple regression R^2 (all data)			Watershed land cover simple regression R^2 (by subwatershed)			Trend (-) in main flow downstream of tailings (T) or waste rock (WR)
	Reference (R) vs. downstream (D)	Tailings (T) vs. waste rock (WR)	From closest mine waste	From tailings	From waste rock	Tailings + waste rock	Tailings	Waste rock	
Specific. conductance	*** / *** (R<D)[1]	.	0.29***	0.10***	0.03*	0.40**[2,4]	0.24*[2]	0.20*[2]	T, WR
TDS	* / ** (R<D)[1]	.	0.42**	0.58**	.	.[4]	.	.	T, WR
DO as %	.	* / . (T<WR)	0.14* (+)	0.44**(+)	.	.	.	.	.
pH	. / * (R<D)[1]	.	.	0.35**(+)	0.22*(+)	.	.	.	.
Bromide	. / ** (R<D)[1]	* / ** (T>WR)	0.18*[3]	0.53***	.	.[2]	0.35*[2, 4]	.[4(-)]	T
Chloride	* / *** (R<D)[1]	.	0.09*	0.18***[3]	.	0.25*[2]	0.32**[2, 4]	.	T
Fluoride	* / * (R<D)[1]	* / ** (T>WR)	0.12*[3]	0.29**	.	0.34*[2]	0.46**[2, 4]	.	T
Sulfate	** / ** (R<D)[1]	.	0.17*	0.21*[3]	.	0.43*[2,4]	.[2]	.[2]	T, WR
Nitrate-N[5]	. / * (R<D)	* / ** (T<WR)	.	.	0.35*	.[2,4]	.	0.30*[2, 4]	WR
Antimony	.	.	0.26*[3]	.[3]	.	0.50*	0.57*[2, 4]	.	T
Arsenic	.	.	.	.[3]	.	.	.[4]	.	T, WR
Boron	* / ** (R<D)[1]	.	0.25*	0.51*[3]	.	.[4]	.	.	T
Cadmium	.	.	0.34*[3]	.	.	.	.[4]	.	T
Mercury, total	. / * (R>D)[1]	.	.	.	0.35*	0.76**[2](-)	0.97***[2](-)	.[4]	WR
Mercury, methyl	. / * (R>D)	.	.	.	.	0.70**[2,4](-)	0.81***[2](-)	.	.
Molybdenum	* / ** (R<D)[1]	.	.[3]	.	.	0.42*	.[2, 4]	.	T
Phosphorus	.	.	.	.	.	.	.[4]	.	T
Selenium	* / ** (R<D)[1]	.	0.30*[3]	0.52*[3]	.	0.53*[2,4]	0.42*[2]	.	T, WR
Sodium	* / ** (R<D)[1]	.	0.28*	.	.	.	.[4]	.	T, WR
Strontium	. / *(R<D)[1]	.	0.26*[3](+)	.	.	.	.[4(-)]	.	.
Vanadium	.	.	.	.	0.49*(+)	.	.[4]	.[4(-)]	T
Uranium	* / * (R<D)[1]	.	.	.	.	.	.	.	T, WR

[1.] Analysis also significant when using only data from May 2015
[2.] Analysis also significant when using all relevant data, not just subwatershed sites
[3.] Analysis also significant when using data from subwatershed sites only
[4.] Analysis also significant when using in-main channel only sites from Goose Lake Inlet and downstream from there
[5.] Sample analysis exceeded holding time

Table 2. Measurements of contaminants of potential concern in my study relative to state criteria or other recommended criteria or effect concentrations. My measurements exceeded criteria or recommendations that are underlined.

Characteristic	Measurements in this study			Criterion or recommended limit		
	At reference sites	Tailings effluent at SC054	At sites downstream of mining	MI streams chronic	MI drinking water	Other lower recommendation or standard limit
Spec. conduct. (µS/cm)	34-427	1523	157-1810			1000[1]; 300[2]
TDS (mg/l)	86-108	1070	194-986	500 / 750		500[3]
DO (%)	65-102	59	38-142			
DO (mg/l)	6.1-9.8	5.2	3.7-12.7	>4-6, 7		
pH	6.0-8.2	7.1	7.2-8.7	6.5-9.0	6.5-8.5	
Bromide (mg/l)	0.005-0.01	0.85	0.005-0.58			1.0[4]
Chloride (mg/l)	0.6-62	105	1-133		50	120[5]; 23[4]
Fluoride (mg/l)	0.06-0.11	0.6	0.07-0.54	2.1-2.7	2	0.12[5]
Sulfate (mg/l)	1.8-10.6	302	6.5-192		250	10[6]
Nitrate (mg/l)[3]	0.01-0.07	0.2	0.01-6.6		10	2[11]
Antimony (mg/l)	0.04-0.05	2.0	0.02-1.4	240	1.7 / 6	
Arsenic (mg/l)	0.54-0.66	7.1	0.28-10.8	150	10	2[7]; 5[5]
Boron (µg/l)	7.3-8.9	457	16-371	7200	500 / 4000	500[1]
Cadmium (µg/l)	0.013-0.021	0.16	0.005-0.11	1.6-5.3 (d)	2.5 / 5	0.11-0.42[5]
Copper (µg/l)	0.74-0.96	0.68	0.11-3.7	5.9-24 (d)	470 / 1000	2-4[5];0.55-42[4]
Mercury, total (ng/l)	6.39-9.45	0.58	0.63-9.34	1.3	1.8	
Molybdenum (µg/l)	0.03-0.13	44	0.27-30	3200	73 / 120	40[8]
Phosphorus (µg/l)	12-16	173	5.9-126	1000	63 / 240	12-90[9]
Selenium (µg/l)	0.21-0.28	38	2.4-55	5	50 / 120	3.1 or 1.5[10] ; 1[5]
Sodium (mg/l)	2.6-8.1	105	27-288		120 / 350	
Strontium (µg/l)	19-28	18	91-1237	21000	4600 / 13000	4000[8]; 32[4]
Vanadium (µg/l)	0.4-1.2	16	0.14-23	27	4.5 / 53	1.2[4]
Uranium (µg/l)	0.06-0.3	1.4	0.31-4.2			15[5]; 2.7[4]

[1] Minnesota 4A and C waters criterion
[2] USEPA recommended benchmark for Appalachia (USEPA 2011)
[3] USEPA drinking water standard
[4] Effect concentration used in Kostich *et al*. (2017)
[5] Canadian Council of Ministers of the Environment Environmental Quality Guidelines long-term criterion
[6] Minnesota wild rice waters criterion
[7] Minnesota 2A and 2Bd waters criteria
[8] USEPA health advisory lifetime level
[9] Minnesota trout and other lakes criteria
[10] USEPA (2016)
[11] Camargo *et al*. (2005)

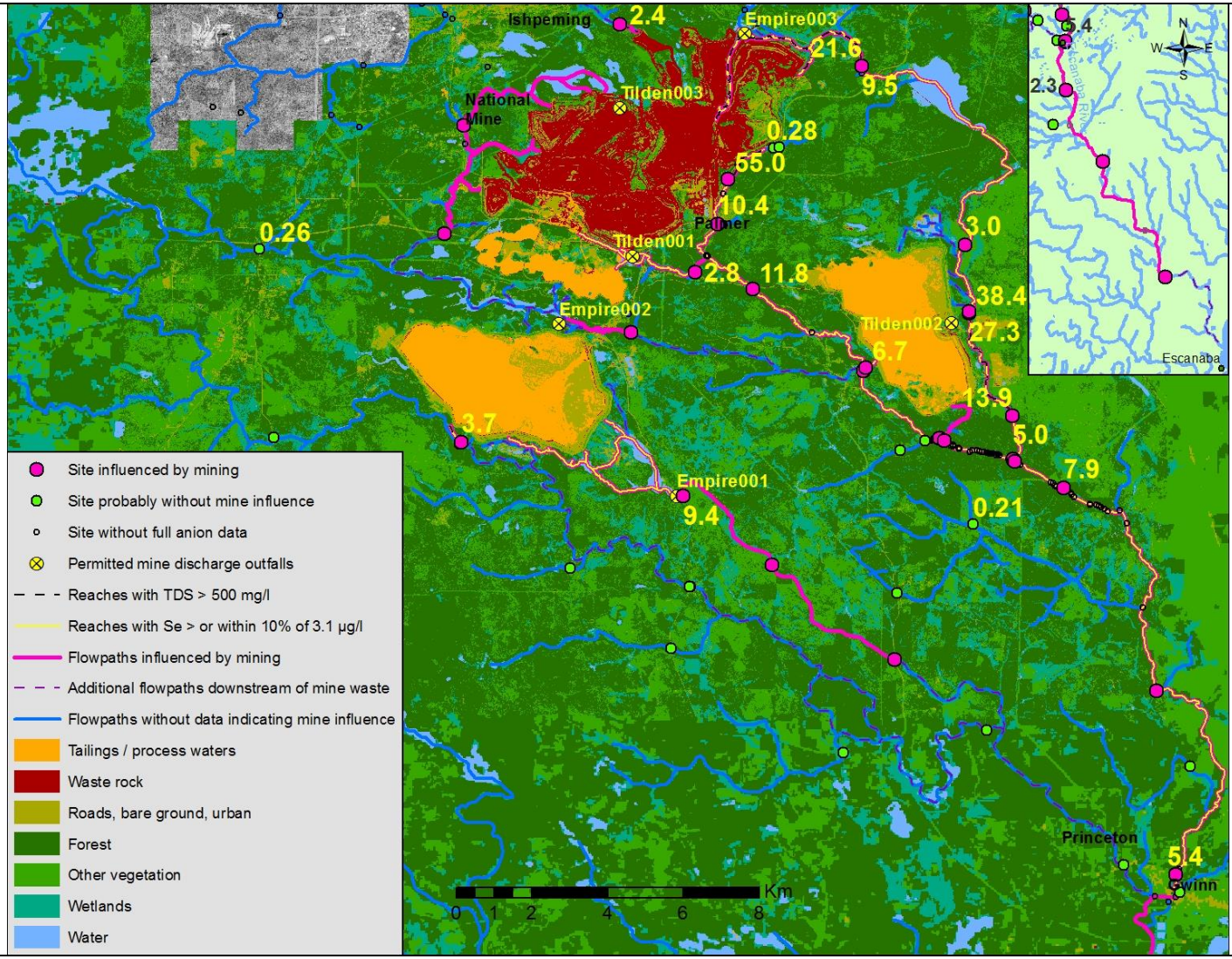

Fig. 5. Map of selenium concentrations (in yellow, in µg/l) in water downstream from mining and at three reference sites. Concentrations were greater than at reference sites and exceeded EPA recommended concentrations and the Michigan criterion at most sites downstream sites. Total Dissolved Solids (TDS) also exceeded state criterion in several reaches. Mine-influenced reaches represented 28% of the stream and lake flow path length in the watershed of the East Branch of the Escanaba River (Table 4). Image shows classification results from Worldview-2 and Landsat 8 images. Gap in classification to northwest of mines shows a portion of the Worldview-2 image. Inset is the lower Escanaba River.

Indicators of mine, tailings, and waste rock influence

Several of the contaminants of concern that were significantly associated with mine waste represented indicators of mine waste influence. In addition, a few ratios of characteristics were apparent indicators of mine waste influence. The following ratios differed between reference sites and sites downstream of mining by Kruskal-Wallis test, and/or were inversely related to distance downstream of waste source (Table S10): ratios of Se to Mn, Sc, and specific conductance; Si/K; sulfate to calcium and fluoride; Na / (Na+Ca); and Ce enrichment (Ce / Ce_{NASC}; Migaszewski *et al*. 2016). Most of those ratios were also related to the proportion of the watershed in tailings or waste rock, and also correlated with specific conductance and/or sulfate, which were related to mine waste (Tables S9, S10). The ratio of silicon to potassium and the ratio of Na to (Na+Ca) represented potential indicators of mine tailings and waste rock influence that were comparatively consistent between dates for sites repeatedly sampled, had their highest (or lowest) value at a site relatively close to tailings or waste rock, and were related to watershed waste proportion and distance downstream (Figs. S1-S2; Table S10). REE's, using all data, were correlated with each other and also with Al, Si, P, Ti, V, Cr, Fe, Cu, Ag, Sn, Th, and TOC, and most correlated with As. Phosphorus was correlated, using all data, with the REE's, Ti, Si, V, As, and others.

Certain characteristics or ratios of characteristics also demonstrated a difference between tailings or waste rock, or a more specific association with one of them. Nitrate was more related to waste rock than tailings (Table 1). Several other characteristics, including bromide, chloride, fluoride, antimony, boron, tungsten, and the ratios of bromide to specific conductance and sulfate to calcium were related to tailings influence (Table 1, S8, S10). Cerium enrichment also differed between sites downstream of tailings vs. waste rock, increased downstream of waste rock, and correlated with bromide, which is associated with tailings (Tables S8-10). Of the potential ratio indicators of tailings, bromide: specific conductance was comparatively consistent between dates where a sites was repeatedly sampled, had its highest value at a site relatively close to tailings or waste rock, and was positively related to watershed waste proportion and negatively related to distance downstream (tailings; Fig. S3-S4; Table S10). The ratio of silicon to potassium also exhibited those properties for both waste rock and tailings and

demonstrated different ranges of values for different tailings sources (Empire vs. Tilden; Fig. S1; Table S10).

Mercury interactions

Mercury concentrations were primarily related to factors unrelated to mining. Total and methylmercury were greater at reference sites than at sites downstream of mine waste (Table 1). Total mercury, however, was greater than 9 ng/l closest to waste rock and declined with distance downstream of waste rock (Table 1). It was also related, using in-main channel data, to watershed waster rock cover (Table 1). Separate multiple regressions of other factors likely to explain mercury distribution indicated that total and methyl mercury were positively related to watershed forest proportion and TOC (Table 3). TOC was in turn significantly related to low DO and high watershed forest and wetland cover proportions in multiple regressions (Table S11). Methylmercury was also related in multiple regression to THg concentration and to low DO (Table 3). In the multiple regressions for THg and for TOC, watershed water cover proportion was negatively related to those variables (Table 3). The ratio of methyl mercury to total mercury, an indicator for mercury methylation, was related in multiple and simple regressions only to low dissolved oxygen (Table 3).

Selenium demonstrated some relation to THg and MeHg in simple regressions, but was not a significant factor in multiple regressions and was also correlated to other factors that could explain those relations. In the simple regressions, selenium was inversely related to THg and MeHg, but explained less variation than did TOC and forest cover (Table 3). The regression parameter and R^2 of THg and Se were also within 10% of those of THg with sulfate, another product of the mine waste. In addition, selenium was significantly negatively correlated with watershed forest cover using the full and subwatershed data, and that correlation coefficient was within 20 % of the coefficient between Se and THg (Table S9). Selenium was also negatively correlated with TOC and wetland cover using the full data, and those also related positively to THg and MeHg in simple regressions (Table S9). Selenium was also strongly correlated with specific conductance, which was negatively correlated with forest cover and wetland

cover in the full and subwatershed (for forest) data (Table S9). Finally, the ratio of MeHg to THg was not significantly related to selenium in any regression (Table 3).

Table 3. Results of multiple regressions indicated that Total (unfiltered) mercury (THg) was directly related to Total Organic Carbon (TOC), proportion of watershed forest cover, and watershed waste rock cover, and inversely related to watershed water proportion. Unfiltered methylmercury (MeHg) was directly related to THg, TOC, and forest cover, and inversely related to Dissolved Oxygen (DO). The ratio of MeHg to THg was inversely related to DO. Three factors only significant in simple regression (Fe, Se, SO_4^{2-}) were negatively correlated with factors that were positively related to THg or MeHg. I included pH and ORP in regressions but neither was a significant factor in any of these regressions. Subw. = data from subwatershed sites only. All = data from all relevant sites. For simple regressions, the first number represents slope in the regression equation (then R^2). * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

Dependent variable	Data set, Simple (S) or Multiple (M) regression	THg	DO	TOC	Fe	Se	SO_4^{2-}	Forest cover	Water cover	wetland cover	Waste rock cover	Multiple Regression R^2 (n)
THg	Subw. (M)	--	.	.	.	.	.	1.86***	-0.95**	.	0.35**	0.995 (9)
	Subw. (S)	--	.	1.05** (0.68)	0.74* (0.55)	-0.43* (0.50)	.	1.87*** (0.94)	.	.	.	(9)
	All (M)	--	.	1.06***	.	.	.	.	.	.	.	0.54, (17)
	All (S)	--	.	1.06*** (0.54)	.	-0.31* (0.30)	-0.33* (0.27)	1.43** (0.44)	.	2.28* (0.26)	.	(18, 17)
MeHg	Subw. (M)	1.07***	-0.83**	.	.	.	.	.	.	.	.	0.97 (9)
	Subw. (S)	1.00*** (0.90)	.	1.23*** (0.85)	0.90** (0.75)	.	.	1.81** (0.81)	.	.	.	(9)
	All (M)	.	.	0.70*	.	.	.	0.95*	.	.	.	0.78 (17)
	All (S)	0.63** (0.41)	.	1.15*** (0.66)	0.81*** (0.59)	-0.33** (0.36)	.	1.67*** (0.64)	.	2.48* (0.32)	.	(18, 17)
MeHg: THg	Subw. (M)	.	-0.78**	.	.	.	.	.	.	.	.	0.67 (9)
	Subw. (S)	.	-0.78** (0.67)	.	.	.	.	.	.	.	.	(9)
	All (M)	.	.	.	.	.	.	.	.	.	.	(17)
	All (S)	.	.	.	.	.	.	.	.	.	.	(18, 17)

Iron and sulfate also demonstrated limited relationships to THg and MeHg in simple regressions. Iron was positively related to THg and MeHg, and sulfate was negatively related to THg in simple regressions (Table 3). Neither, however was related to the ratio of MeHg to THg, and both were also correlated with variables that influenced THg and MeHg in multiple regressions. Iron was strongly positively correlated with TOC and also positively correlated with forest cover (Table S9). Sulfate was negatively correlated with both forest cover and wetland cover (Table S9). Sulfate was also correlated with tailings and total waste land cover proportions, which were negatively correlated with MeHg (Table S9). Although it was not significant linearly related to MeHg/THg, the highest ratio values occurred at a moderate sulfate concentration of 45-55 mg/l (Fig. S5). THg was also strongly correlated with lead (Pb), which only occurred in concentrations less than 0.5 µg/l, in the full dataset and the subwatershed dataset (r=0.90, P<0.0002).

Additionality of constituents and Warner Creek/Goose L. downstream trends

Regression analysis of land cover of mine waste with constituents within the main channel of the Goose Lake Inlet/Outlet to East Branch of the Escanaba River at Gwinn indicated that the watersheds with a greater proportion of waste, with sampling sites often closer to waste, had higher specific conductance, sulfate, nitrate, and selenium (Fig. 2; Table 1). I found similar in-main channel log-linear relationships with other characteristics for proportion of a watershed in tailings or proportion in waste rock (Table 1).

Comparisons between analyses for detecting impacted water quality characteristics

Kruskal-Wallis tests identified 15 non-ratio characteristics of potential concern as lower at reference sites vs. sites downstream of mining, whereas the distance downstream regressions identified 15 characteristics, not all the same, as related to distance from mine waste (Table 1). Land cover proportion regressions identified 12 significant relations for the combined tailings + waste rock, but 15 with just

tailings (Table 1). Each analysis, however, identified at least one characteristic as related to mining that at least one of the others did not (e.g., arsenic, phosphorus, uranium; Table 2). Refining analyses to consider the different effects of tailings vs. waste rock also led to identification of bromide, nitrate, and total mercury as influenced by mining even though the broader version of those analyses had in some cases not identified those constituents (Table 1). For characteristics with significant relationships using both the distance downstream regression and the land cover regression, most R^2 values were greater using the land cover analysis except for bromide, nitrate, and selenium from tailings (Table 1).

Historical comparisons

Between the time of pre-mining data and data from 2015-2016, specific conductance, pH, chloride, and the ratio of chloride: specific conductance increased for a group of sites now downstream of mining in the Warner Creek, Schweitzer Creek, and Green Creek watersheds (Table S12). For sites in the Goose Lake Inlet and downstream of there, increases occurred for specific conductance, chloride, chloride: specific conductance, and alkalinity (Table S12). I found no significant difference for available pre-mining and recent data for a group of three reference sites (Table S12).

Tests of pre-mining and recent data for individual sites indicated differences in sites downstream of mining for the same characteristics as the group analyses, but also indicated increases in fluoride and sulfate at SC022, decreases in the ratio of sulfate to chloride at SC015 and SC022, and decreases in the ratio of sulfate to specific conductance at SC015 (Table S12).

Downstream extent of contamination

Cluster analyses of field data plus anion data, and those plus metals and trace elements data indicated that all sites downstream of mine waste in the East Branch of the Escanaba River watershed grouped together and were distinct from reference sites (Fig. S6). Waste rock sites downstream of the north waste rock piles clustered together in an analysis of specific conductance and anion data (SC030, 031, 042, 056, 139), but sites otherwise did not clearly cluster according to their status as downstream of

tailings, waste rock, or both (Fig. S7). In that same analysis, sites for which I was unsure of mine waste influence clustered most closely with mine-influenced sites in the case of sites in the East Branch watershed (SC009) and the Escanaba River (SC048, SC094, SC096), but clustered most closely with reference sites in the case of sites in the Middle Branch of the Escanaba (SC001, SC045C, SC046, SC100, SC283; Fig. S4). Without the additional anion data, field data results differed for some of the uncertain sites (Fig. S8).

Kruskal-Wallis comparisons of the uncertain sites with reference sites yielded similar results as the cluster analysis. Based on field characteristics and anion data, downstream Escanaba River sites differed from reference sites and Mid-Branch of the Escanaba River sites mostly did not differ from reference sites for most measured characteristics, though bromide differed in one analysis (Table S13).

The identified ratio indicators of mine waste also supported the determination that mine influence extended into the main Escanaba River. Silicon: potassium, Na/ (Na+Ca), and bromide: specific conductance in the Escanaba River (SC048) were within the range of values at other mine-influenced sites and distinct from the range for reference sites.

Based on the Kruskal-Wallis and cluster results, I mapped the estimated extent of mine influence and calculated that at least 165 river-km, including lake flow paths, of the Escanaba River system were influenced by iron mining during my periods of sampling (Fig. 5; Table 4). The influenced reaches represented 15.3 % of the length of streams and lake flow paths in the Escanaba River watershed (assessed at Lake Michigan confluence using USGS HU8 delineation) and 28 % of the length of streams and lake flow paths in the East Branch of the Escanaba River watershed as assessed at SC022 (Table 4). In the East Branch of the Escanaba River watershed, 22% of the stream and lake flow paths had selenium concentrations greater than or within 10% of the USEPA stream water criterion of 3.1 µg/l (Table 4). The mine influence extended to SC094, at least 85 km downstream of the nearest mine source (Fig. 5).

Table 4. Estimates of the extent of river-km in the East Branch of the Escanaba River watershed and the Escanaba River watershed that are downstream of mine waste and influenced by mining in different ways. I categorized sample sites as mine-influenced based on cluster analysis and Kruskal-Wallis tests of field and anion sample data.

Category	East Branch of the Escanaba River watershed		Escanaba River watershed	
	Km	%	Km	%
Estimate of reaches exceeding TDS of 500 mg/l	15.8	5.2	16.4	1.5
Estimate of reaches exceeding Se of 3.1 µg/l +- 10%	65.8	21.8	76.8	7.1
Estimate of reaches influenced by mining	84.2	28.0	165.0	15.3
Estimate of reaches downstream of mine waste	111.7	37.1	263.6	24.5

4. Discussion

My results from comparisons with reference sites and historical data and relations with distance downstream and watershed land cover indicated that mine waste was the source of several contaminants of concern in the waters of the East Branch of the Escanaba River system. The concentrations of several of those contaminants in the waters downstream of mining and the extent of contamination were previously unreported.

Selenium

Selenium was a contaminant of significant concern in this study. Concentrations exceeded state criteria at most sites measured downstream of mining, including 23 river-km downstream of the nearest mine waste. Selenium was above reference site levels at all sites downstream of mining, including 35 km downstream of the nearest mine waste. In the East Branch system, I estimated that 22% of the stream and lake flow paths had selenium concentrations greater than or within 10% of the USEPA stream water criterion of 3.1 µg/l, and that is probably an underestimate due to sampling gaps. The greatest concentration I recorded from a stream, 54 µg/l, was 10 times the state chronic criterion limit.

Selenium results largely agreed with results of the Michigan Department of Environmental Quality study of 2008 (MIDEQ 2009) for sites in comparable reaches downstream of mining. My results

also largely agreed with company reports where sites were comparable. In contrast with those previous studies, I sampled for contamination further downstream and found that selenium contamination continued into the Escanaba River and exceeded the Michigan chronic criterion all the way to Gwinn.

The extent and concentrations of selenium contamination in the Escanaba River system are likely to have important biological consequences. High concentrations of selenium cause deformities, reduced growth and reproduction, and mortality in fish and birds in particular, but also harm algae, invertebrates, amphibians, and mammals (Eisler 1985, Hamilton 2004, Santos *et al*. 2015, USEPA 2016). Selenium also bioaccumulates and can biomagnify (Santos *et al*. 2015). Selenium has the potential to impact human health if, for example, it contaminates drinking water wells or is consumed in fish. Selenium in humans at high levels can cause selenosis (brittle hair, nail deformities, other effects) and increase risk of diabetes, amyotrophic lateral sclerosis, endocrine disruption, and some cancers (ATSDR 2003, Sun *et al*. 2014, Vinceti *et al*. 2017), though it is an essential nutrient at low levels and may have an antagonistic relationship with mercury and arsenic under certain conditions (Koeman *et al*. 1973, Jin *et al* 1997, Belzile *et al*. 2006, Yang *et al* 2008).

Limited biological studies of selenium in the East Branch of the Escanaba River watershed support concern over the contamination. Selenium was at high concentrations near mining in macroinvertebrates, and in high concentrations exceeding effect thresholds in fish in 2008, 2009, and 2015 (MIDEQ 2009, Kohlhepp 2010, Cardno 2016). In 2010-2011, selenium was significantly greater in aquatic emergent insects (Diptera and Ephemeroptera) and Wood Ducks and Hooded Merganser eggs at mine-influenced than reference sites in this zone (Kaulfersch 2014). Insects of the order Ephemeroptera and Plecoptera were also relatively rare at most of the mine-influenced sites in that study (Kaulfersch 2014). Although the study only documented two avian teratological effects at that time, mean concentration in Wood Duck eggs near the Goose Lake Outlet exceeded toxicity thresholds (Kaulfersch 2014). Past and existing ecological monitoring work does not appear to include assessments of impacts on growth, reproduction, and diversity and abundance of aquatic life (Cardno 2017). New USEPA recommended standards to avoid impacts, when based on water rather than concentrations in fish, are 3.1

µg/l in lotic and 1.4 µg/l. in lentic systems rather than the state criterion of 5.0 µg/l that has been the goal for the mine discharges (USEPA 2016). Given that selenium can also biomagnify and that sediment contamination is widespread (MIDEQ 2009, Cardno 2016), selenium impacts are likely to continue even if the discharges meet the state criterion.

The effect on fisheries also represents a concern for respect for treaty rights in this region. Health authorities have recognized the risk of consuming fish with high selenium concentrations and placed advisories on the selenium-contaminated waters in the Escanaba River system (MIDHHS 2018). These advisories present appropriate warnings on fish consumption because concentrations are such that eating many fish could pose a health risk from selenium. Those advisories also help make clear that the contamination represents a restriction on fishing availability and, thus, Ojibwe fishing rights. Probable population effects of selenium on the fish would also represent such an infringement, but only anecdotal information on effects on fish populations appears available (MIDEQ 2009), even though most of the streams in the East Branch of the Escanaba River watershed are designated trout streams. Studies are apparently lacking in this zone on the effects on macroinvertebrate communities and on fish deformities and reduced growth, reproduction, diversity, and abundance even though the contamination problem has continued for already more than 10 years.

Management and regulatory efforts have apparently sought to reduce selenium contamination while allowing the mines to continue to operate, but those efforts may not adequately control the problem or restore ecological systems. Although problems with flow measurement may have influenced my loadings estimates, the Tilden tailings represented the single greatest selenium loading that I measured. Mine selenium mass balance studies indicate that the Tilden tailings discharge had represented one of the top three loadings of selenium to the river in several previous years (Cliffs 2016). Efforts to reduce contamination (Cliffs Natural Resources 2016) appear in company reporting to have reduced concentrations of selenium from that source (USEPA 2018) since my sampling. Efforts are also ongoing to pump waste rock seepage water to a mine pit (Cliffs 2016), but it remains unclear how those efforts will avoid groundwater contamination and exposure to waterfowl in pit lakes, or how long they will need

to continue upon mine closure. Limited data indicates that selenium in the Section 20 pit, where it is primarily in dissolved form, occurred at concentrations in the top meter of 17-29 µg/l in 2013 (CardnoENTRIX 2014), suggesting the potential for harm to waterfowl if consuming particulate matter or organisms in the pit lake. I also documented selenium contamination in seepage streams draining from the tailings basins that do not appear to be addressed in current management efforts (Cliffs 2016). The primary route for uptake of selenium by fish and birds in other systems is the consumption of prey and particles with absorbed selenium, and the accumulation in the food chain begins with primary producers absorbing dissolved selenium from the water column (Santos *et al*. 2015, USEPA 2016). The concentration in the sediment is important to assess for that reason and also because the sediment may store selenium and continue to contaminate the food chain even after point sources are controlled. The extent of water contamination that I documented both downstream and in streams adjacent to tailings, and information on sediment contamination occurring even where water concentrations were low (MIDEQ 2009), suggest a need for assessments of sediment contamination in wetlands, lakes, and streams that go beyond those previously tested (MIDEQ 2009, Cardno 2016).

Other contaminants

Previous work corroborates my findings of a mine influence on many of the other contaminants of concern I reported on. Reports documented high levels of nitrate (plus nitrite) closer to waste rock or high levels of specific conductance, alkalinity, chloride, or sulfate near mining zones (Evans 1972, Jackson 1972, Godby 2002, Villa 2003, Kohlhepp 2007). Regulatory permitting documents confirmed elevated concentrations in tailings and/or pit and waste rock discharges of those and most of the additional constituents of concern -- TDS, bromide, fluoride, aluminum, antimony, arsenic, boron, molybdenum, phosphorus, sodium, and vanadium (Little 2004, 2005, 2011, Schmitt 2011a, b, CardnoENTRIX 2014). Arsenopyrite (arsenic) and phosphorus were also previously documented as occurring in rocks in the mined zone (Gair & Han 1975). I have now confirmed the presence of those contaminants in the discharges at least during our period of study, and documented their concentrations in

the surface waters downstream of those discharges. I did not find prior data on additional contaminants in water that I reported on, particularly cadmium, though a report noted a composite sample result of 1.5µg/l of cadmium from the Empire tailings discharge in 2004 (Little 2004). It is possible that the facilities use wet scrubbers that discharge to tailings, and stack emissions from the processing facilities at Empire/Tilden have apparently included cadmium in addition to arsenic, beryllium, lead, mercury, nickel, particulate matter, selenium and other air contaminants (USEPA 2018).

Certain contaminants in addition to selenium and TDS, which exceeded state criteria, were also of potential concern. Chloride, fluoride, arsenic, and cadmium all exceeded Canadian criteria, and chloride, arsenic, phosphorus, sodium, and vanadium exceeded Michigan drinking water criteria. In addition, few toxicity tests with accessible results appear to have occurred on the tailings discharges and waste rock runoff (USEPA 2018), and interactions between constituents in the water influenced by the mining could lead to otherwise unexpected toxicity. The concentrations that I measured also probably do not represent the highest that occurred in those years. Indeed, specific conductance and anion concentrations in the river were higher at sites downstream in August 2015 than they were during my earlier trace element sampling, and so trace element concentrations were probably greater in August, and potentially other times of the year, than what I recorded. I also did not sample for metals and trace elements in certain reaches such as Ely Creek, and so contamination is probably more widespread than I have estimated. Waterfowl landing directly in the tailings basins or pit lakes would also be exposed to higher concentrations of all tailings- or pit-associated constituents.

Studies have documented the potential impacts of most of the contaminants of concern on aquatic life and human health (Appendix A), but the impacts of bromide and sulfate have gained additional attention relatively recently. Bromide is of concern when waters with organic carbon are disinfected by chlorination because it can result in the production of disinfection by-products that are human carcinogens (Flury & Papritz 1993, Regli *et al*. 2015, Winid 2015). In addition to being at risk from selenium contamination (Thomas 2009), drinking-water wells that use groundwater contaminated by tailings could therefore be at risk if chlorinated, as could any chlorinating drinking water systems using tailings-

influenced river water far downstream (Good & VanBriesen 2017). Indeed, concentrations in streams nearest the tailings reached > 400 µg/l and even the furthest downstream site in the Escanaba River in August 2015 still had 23µg/l of bromide. Studies suggest that a 50 µg/l increase in bromide to a public drinking water facility can significantly raise the risk of bladder cancer from disinfection byproducts (Regli *et al*. 2015).

As for sulfate, data have long demonstrated its role in limiting wild rice and methylating mercury when in reduced form as sulfide in the sediment (Moyle 1944, Ullrich *et al*. 2001, Sonke *et al*. 2013, Pastor *et al*. 2017). Recent studies in Minnesota have also confirmed that sulfate and sulfide in sediment can cause the release of nutrients and inorganic mercury from sediment (Myrbo *et al*. 2017a, b). Those released nutrients could enhance eutrophication. Given those dynamics, it seems that the sulfate from the mine may be contributing to eutrophication dynamics in Goose Lake (Premo *et al*. 2003, Villa 2003).

The extra concentrator or other activities at the Tilden tailings discharge appear to have reduced concentrations of arsenic and vanadium in addition to selenium since my sampling, according to Discharge Monitoring Report data (USEPA 2018). Other constituents such as dissolved iron and fluoride, however, may have increased and elevated copper concentrations have occurred intermittently (USEPA 2018). Monitoring data for certain characteristics of concern or potential concern in my measurements, including dissolved oxygen, bromide, chloride, sulfate, aluminum, antimony, boron, cadmium, molybdenum, and thallium, are apparently not available for the tailings discharges (USEPA 2018).

Uncertainties

Although my results represent a clear assessment of contamination associated with iron mining in this watershed during my sampling and many results match previous assessments of water quality in this zone, the study is a snapshot in time that is not necessarily representative of conditions occurring in other seasons or other years. Concentrations in surface waters in this system probably vary over time depending on meteorological and seasonal conditions as well as mining activities and discharges. I did

not fully characterize variation within the season during which I sampled and in some cases combined data from multiple days into one analysis. Determining temporal patterns of contamination, including during winter and periods of greater biological sensitivity, would provide important additional information.

I also did not sample water for other possible contaminants such as PCB's (Thierry 2006), beryllium, cyanide (Schmitt 2011b), or asbestiform mineral fibers from grunerite or other potentially hazardous amphiboles known to occur in the zone (Gair & Han 1975). I did not assess other locations that may also be contaminated. Selenium contamination and its risks are likely more widespread than I have reported because I did not sample for metals and trace elements in Ely Creek, in Schweitzer Creek downstream of the Empire tailings discharge, or further downstream in Green Creek. I did not obtain samples from tailings facilities or mine pit waters where waterfowl may land either. I also did not examine groundwater contamination or drawdown impacts, or effects on aquatic biota. Finally, I did not study fractionation and speciation of selenium, or develop a hydrological model to understand transport and fate of selenium and other contaminants. Further research should examine these questions as well.

Additional work is also necessary to better understand the source of nutrient contaminants near the mining. Nitrate was associated with waste rock in multiple analyses, but it is unclear if that nitrate is from explosives residue on the waste rock, runoff from fertilizer and revegetation attempts on the waste rock piles, or another source (Griffiths *et al*. 2012). Possible use of the same material used for explosives as a fertilizer (Koski 2007) might complicate source identification. Nitrate + nitrite was at similar concentrations in 2002 in the Goose Lake Inlet, when the dominant source was from the mine discharge, as the nitrate I measured in 2015 (Premo *et al*. 2003, Villa 2003). It is possible that the nitrate from the waste rock, along with sulfate, has contributed to eutrophication of Goose Lake. Nitrate is also of concern in this zone because of its potential role in limiting reduction of selenate (Dockrey *et al*. 2015). Phosphorus patterns also require further clarification. The Tilden tailings discharged large concentrations of phosphorus to the river system, but it is unclear how much of that was from the phosphorus known to

be in some of the ore rocks (Gair & Han 1975) or if another waste source is adding to that discharge. Correlations of P with REE, Ti, and Si suggests an aluminosilicate mineral association (Crissman 1988).

Mercury

Patterns of mercury concentration also require additional study in this zone. Watershed forest cover and TOC explained the greatest amount of variation in total mercury. I expected those factors to be significant based on forest scavenging of atmospheric mercury, disturbed status of forests, and the capacity of organic carbon to transport mercury (Hurley *et al*. 1995, Ward *et al*., 2010). TOC was also related to watershed forest cover and wetland cover as expected, and to low DO, which I would expect in wetlands. Low DO also explained patterns of MeHg and MeHg/THg, probably because methylation is greatest in sediments and near the redox boundary (Ullrich *et al*. 2001). In addition, THg was related to distance downstream of waste rock, was related to watershed proportion in waste rock for the in-channel analysis, and was high near waste rock. This indicates that waste rock was also associated with increased total mercury. Results of some other studies also suggest that the waste rock could be a source of mercury to the water. Mercury in Goose Lake was >2 ng/l in water and amongst the highest of eight lakes sampled in sediment in 2008 (Knauer *et al*. 2012). Lake Sally, however, on the north side of waste rock, did not have high mercury concentrations in water or sediment in 2008 (Knauer *et al*. 2012).

It remains uncertain what the source of mercury near waste rock may be. For mercury in the Goose Lake watershed, possibilities include old blasting caps or other mercury from the Tracy mine, Marcy Charlotte Pit, or other old mines in the Goose Lake Inlet watershed, and mining assay laboratory effluent (Knauer *et al*. 2012). For that watershed as well as the Partridge Creek (to Carp River), and Warner Creek watersheds, possibilities include the waste rock itself, dispersed regional (Kerfoot *et al*. 2018) or broader atmospheric deposition somehow concentrated in the elevated waste rock zone, and deposition from possible surface-air fluxes from tailings (Granke *et al*. 2006, Eckley *et al*. 2013). Tailings in other sampling from the mines, including from a spill from a tailings pipeline, have demonstrated higher mercury than in this study (Schmitt 2011a, Kochevar 2013, USEPA 2018). A final

possibility is local deposition from taconite induration. Taconite processing plants in Minnesota have emitted an estimated 200-400 kg/yr. of mercury into the air in past decades, representing 20% of state emissions in 2000 (Jiang *et al*. 2000, Berndt 2003). Limited data on the taconite plants in Michigan indicated that they emitted at least 32 kg in 2002 (Tilden only), an estimated 27 kg in 2005, 33 kg in 2008, and less than 1 kg in 2011 and 2014 (McGeen 2011, Kerfoot *et al*. 2018, USEPA 2018). Estimates in Kerfoot *et al*. (2018) also suggest comparable and greater emissions for years prior to that. The Pioneer Pellet Plant just 3 km north of Goose Lake also produced taconite pellets for many years (Reynolds & Dawson 2011), but I lack data on its mercury emissions. The correlation of total mercury with lead may be compatible with a local atmospheric source, since the Empire and Tilden plants also emit hundreds of kilograms of lead into the air yearly (USEPA 2018), but many other sources of lead are possible. Additional localized sampling and tracing of mercury in water and sediments in this region could assist in a better understanding of provenance.

The interaction between mercury and other water quality constituents also requires further assessment. Given correlations with other factors, iron and sulfate did not appear to significantly affect MeHg concentrations or MeHg/THg as expected (Ullrich *et al*. 2001, Yu *et al*. 2011, Sonke *et al*. 2013). The influence of sulfate on methylation actually depends on formation of sulfide and so sulfate will not necessarily be significantly related to mercury methylation in mine-influenced waters (Jeremiason *et al*. 2016). Periodic or short-term sulfate additions may also not relate to long-term mercury methylation patterns (Johnson *et al*. 2016). For sulfate, however, the greatest MeHg/THg that I detected occurred at sulfate concentrations that were intermediate in the range I measured, so my results are actually consistent with the expectation that the greatest effect of sulfate on mercury methylation occurs at moderate sulfate concentrations (Gilmour *et al*. 1992, Weber 1993, Myrbo *et al*. 2017a). This suggests that sulfate may have been enhancing methylation as predicted in my study zone and additional sampling of sites with such sulfate concentrations could have demonstrated a bell-shaped relationship. Chloride and other mine-related constituents could also affect mercury speciation and bioavailability (Bjørkland *et al*. 2017).

I also did not detect a clear relationship between selenium and methylmercury. Selenium is an antagonist of mercury that has the potential to reduce MeHg concentrations in biota and possibly in water and sediment, probably through formation of HgSe complexes and other mechanisms (Koeman *et al*. 1973, Jin *et al* 1997, Belzile *et al*. 2006, Yang *et al* 2008). MeHg in fish was unexpectedly low in Goose Lake in fish given sediment concentrations (Knauer *et al*. 2012), and selenium was negatively related to THg and MeHg in some of my simple regressions. Detailed examination, however, suggested that I did not find evidence of an influence of selenium on MeHg in my study. The apparent negative relationship of Se with THg and MeHg in simple regressions was most likely the result of the negative correlations of selenium with the factors that strongly influenced THg and MeHg in multiple regressions: watershed forest cover and TOC. I also did not find a relationship between MeHg/THg and selenium. Further, Goose Lake was high in selenium but also high in sediment MeHg in 2008 (Knauer *et al*. 2012). This suggests that any selenium influence on reducing concentrations and/or toxicity of MeHg may not be detectable in water in this system during my sampling, though it could be in fish. This was the case for lakes in the mining region of Sudbury, Ontario (Belzile *et al*. 2006). The lack of a relation between selenium and mercury in water could be because the possible abiotic effect depends on factors such as selenium concentration and pH (Jin *et al*. 1997, Yang *et al*. 2008). It remains unclear if the moderating effect of selenium is occurring in this zone biotically. A study in the same zone in 2010-2011 found that both selenium and mercury were lower at reference sites than at mine-influenced sites for certain orders of aquatic insects, and no apparent correlation occurred in bird eggs between selenium and mercury (Kaulfersch 2014). Even if the moderating effect of selenium on mercury toxicity does occur in this area for fish, it may not prevent harm to fish populations. Dietary organic selenium in one study reduced mercury impacts on fish growth and survival but had a synergistic negative effect with mercury on fish reproduction (Penglase *et al*. 2014).

Spatial extent of contamination

The extent of contamination during my study was also greater than previously documented. The distance downstream at which I detected high selenium and high bromide concentrations suggests an extensive contamination problem. My cluster results did not group any of my Middle Branch of the Escanaba sites with mine-influenced sites, but bromide concentration and the ratio of bromide to specific conductance (Fig. S4) increased relative to the upstream sample past the Empire Tailings (site SC045C relative to SC100; Fig. 1). It is possible, therefore, that the Middle Branch of the Escanaba is also mine-influenced past the stream originating near tailings seeps.

Indicators

Certain water quality characteristic ratios were also associated with mine waste and may have potential to serve as indicators of waste. Silicon/potassium (Wee 1989) and Na/(Na+Ca) (after Gibbs 1970 in Wanty *et al*. 2009) represented potential indicators of mine waste influence, and bromide/specific conductance exhibited that potential for tailings. Silicon/potassium appeared to distinguish igneous rock types elsewhere in this region (Wee 1989). That ratio in my study may even allow differentiation between reference sites, waste rock, and the Tilden vs. Empire tailings in this zone. The REE ratios that I assessed, on the other hand, did not present a clear signal of mine influence. They did, however, reflect some patterns observed in Empire mine rocks (Crissman 1988). Just as in that study, REE correlated with each other, Al, and Ti, suggesting they were affiliated with aluminosilicate minerals. The other REE correlations in my study suggest that As, P, V contaminants may occur in association with aluminosilicate minerals. Nonetheless, Crissman (1988) found that the no single mineral phase determined REE patterns, and the lack of distinction in REE enrichment measures that I used suggest that aluminosilicates do not exhibit a distinct pattern between the reference sites and mine waste sites in this study. Attempts at determining various indicators of wastes may also be confounded by the routing of some waste rock waters to process waters (Casey 2016) and the addition at different times of compounds including lime,

sodium hydroxide, aluminum sulfate, sulfuric acid, carbon dioxide, and ferric chloride in the past treatment of tailings prior to discharges (Tilden Mining Company 2012, MIDEQ 2017).

Cumulative impacts assessment

The results of this study also add to our understanding of cumulative impacts of mining and methods of studying them. Similarly to this study's findings, previous work found that increasing proportion of mine waste (and pits) in a watershed was related to increases in constituent concentrations. In the Mud River system of Appalachia, specific conductance, sulfate, and selenium exhibited relationships to proportion of the watershed in coal mining land cover that resembled my findings, though at lower selenium concentrations (Lindberg *et al*. 2011). The log-linear relationships in this study between watershed mine waste and specific water quality characteristics varied by characteristic, but could provide a prediction of the water quality consequences of further mine waste expansion. In addition, they may be useful in comparing with other studies and in further cumulative impacts assessment. Additional methods such as estimating the watershed yields of key constituents (Hurley *et al*. 1995), volume of waste (Ross *et al*. 2015), or using additional landscape metrics (Xiao & Ji 2007) could also better predict the water quality impacts of mining based on landscape characteristics.

My work improves our understanding of appropriate analyses for identifying water quality characteristics related to mining as well. Using SF-ICP-MS allowed for the detection of ultra-low concentrations that helped reveal downstream trends and differences between reference sites in statistical analyses. Using SF-ICP-MS would be an appropriate tool for others assessing trace elements that may occur at such concentrations in other studies. Even with SF-ICP-MS, however, it appears that a single type of statistical analysis to identify characteristics influenced by mining can be inadequate. As in this study, multiple statistical analyses may be necessary to adequately determine which characteristics are mine-influenced, including comparisons with reference sites, downstream trend regressions, and land cover regressions.

Iron mining elsewhere and selenium

This work also expands available information about the potential water quality impacts of iron mining. Peer-reviewed studies of iron mining impacts have apparently yet to document water quality impacts with selenium, which I found at concentration comparable or greater than at some sites in Appalachian coal-mined zones (Lindberg *et al*. 2011). Elsewhere in Michigan, the Michigan Department of Environmental Quality sampled the closed Republic and the Groveland mines and found sediment selenium contamination of concern in a Republic Mine pond (Kohlhepp 2010), suggesting that such problems may not be confined to the Empire/Tilden mine zone. In addition, studies have recently found elevated selenium concentrations in rocks of the Pilbara iron mining zone in Australia (Tabesh 2014). Given that, it appears that iron mining may need to be added to the list of sources of selenium contamination (Lemly 2004).

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7. Supplemental Material

Methods details

Table S1. Types of water quality samples and associated sampling, preservation, and analysis methods.

Analysis category	Analytes	Analysis type	Laboratory method	Field sampling bottle type	Field filtration and/or preservation	Analysis location
General	Alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS)	Titration (alkalinity), gravimetry (TDS and TSS)	SM2320B (alkalinity), SM2540C (TDS), SM2540D (TSS)	High Density Polyethylene (HDPE) 950 ml	< 4 C	WI Lab of Hygiene
Major anions	Bromide, chloride, fluoride, nitrate, sulfate	Anion ion chromatography	EPA 300.1	HDPE 60 ml or 125 ml	Syringe filtration (0.45µm Pall polysulfone Acrodisc), < 4 C	UW-Madison WSEL
Metals & trace elements	51 metal(loid)s (unfiltered)	Inductively-coupled plasma mass spectrometry	Magnetic Sector ICP-MS	Polytetra-fluoroethylene (PTFE) 250 ml	< 4 C	WI State Lab of Hygiene
Mercury	Unfiltered total mercury & methylmercury		EPA 1631 Rev. e, USGS Open-File Report 01-445	PTFE	< 4 C	USGS Middleton
Total Organic Carbon	TOC	TOC analyzer		Borosilicate amber 40ml	< 4 C	USGS Middleton

Table S2. Sampling dates and characteristics in the Escanaba River region in 2015 and 2016.

Year	Dates	Field characteristics	Anion samples	Metals and trace elements
2015	14-16 May	x		
	28-31 May	x	x	x
	19-21 June	x	x	
	02-05 July	x	x	x
	27-28 August	x	x	
2016	20-21 June	x	x	
	23 August	x		
	27 August	x	x	x

Table S3. Ion chromatography Method Detection Limits (MDL) for major anions analyzed. Nitrate is nitrate as N.

	Year	F^-	Cl^-	SO_4^{2-}	Br^-	NO_3^-
MDL concentration (mg/l)	2016	0.00835[1]	0.00919	0.0268[2]	0.00528[1]	0.00548
	2015	0.01676[2]	0.01127[3]	0.0302[3]	0.00162	0.00449

[1] MDL from 6 samples only (other failed QAQC)
[2] MDL from 5 samples (2 others failed QAQC)
[3] MDL was lower than Minimum Reporting Limit.

Table S4. Limits of detection (LOD) for SF-ICP-MS analysis at Wisconsin State Laboratory of Hygiene

Element and isotope (Low Resolution, Medium Resolution, or High Resolution)	LOD (ng/l)		Element and isotope (Low Resolution, Medium Resolution, or High Resolution)	LOD (ng/l)
Li7(LR)	3.3		Mo95(LR)	2.2
B11(LR)	45		Rh103(LR)	0.73
Na23(MR)	780		Pd108(LR)	0.15
Mg25(MR)	460		Ag109(LR)	0.18
Al27(MR)	35		Cd111(LR)	0.14
Si28(HR)	12,500		Sn118(MR)	2.2
P31(MR)	50		Sb121(MR)	0.45
S32(MR)	970		Cs133(LR)	0.55
K39(HR)	220		Ba137(MR)	3.5
Ca44(MR)	740		La139(LR)	0.012
Sc45(MR)	2.2		Ce140(LR)	0.18
Ti49(MR)	3.5		Pr141(LR)	0.025
V51(MR)	0.45		Nd146(LR)	0.11
Cr52(MR)	2.1		Sm149(LR)	0.085
Mn55(MR)	12		Eu151(LR)	0.22
Fe56(MR)	22		Dy163(LR)	0.14
Co59(MR)	0.25		Ho165(LR)	0.011
Ni60(MR)	1.9		Yb173(LR)	0.35
Cu63(MR)	1.4		Lu175(LR)	0.012
Zn66(MR)	17		W184(LR)	0.32
As75(HR)	4.5		Pt195(LR)	0.12
Se82(LR)	30		Tl205(LR)	0.095
Rb85(LR)	2.5		Pb(sum)	0.35
Sr88(MR)	85		Th232(LR)	0.081
Y89(LR)	0.35		U238(LR)	1.1
Nb93(LR)	0.28			

QAQC

I verified that anion blank samples with any detections (chloride, sulfate, and nitrate) were < 10% of the lowest actual measure. Only a blank sample for nitrate, which also exceeded holding times, did not meet this criterion. For metals and other trace elements, I first verified that blank measurements minus standard deviations were ≤ 0. For samples that did not meet that condition, I checked that measurements were < 10% of the lowest actual measure. Cr, Co, Ni, Cu, Se, Nb, Mo, Rh, Ag, Sn, Sb, and W each had one or two blank samples that exceeded that 10%, but in all cases blank measurements were < 0.2 µg/l.

I also confirmed that field sequential replicate samples were not more than 20% different than concentrations in the original sample. This was the case for all analytes in 2015 except Sn and W, and all in 2016 except Sc, Co, Ni, Nb, Pd, Ag, Cd, Sn, La, Ce, Pr, Nd, Sm, Ho, Yb, Lu, W, and Th. Measurements for those samples were < 0.4 µg/l for W, Ni, Sn, and Ce; < 0.05µg/l for Co, La, and Nd; < 0.03µg/l for Sc, and Cd; and < 0.01 µg/l for all others.

In addition to collecting and assessing field and laboratory blanks and replicates, I verified that field and laboratory measurements of samples for pH and specific conductance differed by less than 10% for sampling events with both field and laboratory measurements. I also verified that a minimum estimate of TDS, as the sum of element concentrations from ICP-MS (which did not include all constituents) and anion concentrations minus TSS, was less than the TDS measured in the laboratory.

Table S5. Identification and properties of bands used in land cover analysis

	Worldview-2 images (Catalog 103001004857BE00 and 10300100470CD800 of 2015-08-21)		Landsat 8 image (LC08_L1TP_024028_20150528_20170226_01_T1 of 2015-05-28)	
Band category	Analysis bands, original horizontal spatial resolution if different from 2m	WV-2 bands used in segmentation	Analysis bands, original horizontal resolution if different from 30m	Landsat 8 bands used in segmentation
Principal image bands	WV-2 Coastal (0.40-0.45µm)	x	1 Coastal Aerosol (0.435-0.451µm)	x
	WV-2 Blue (0.45-0.51µm)	x	2 Blue (0.452-0.512µm)	x
	WV-2 Green (0.51-0.58µm)	x	3 Green (0.533-0.590µm)	x
	WV-2 Yellow (0.585-0.625µm)	x		
	WV-2 Red (0.63-0.69µm)	x	4 Red (0.636-0.673µm)	x
	WV-2 Red edge (0.705-0.745µm)	x		
	WV-2 Near IR1 (0.760-0.895µm)	x	5 NIR (0.851-0.879µm)	x
	WV-2 Near IR2 (0.86-1.04µm)	x		
			6 SWIR 1 (1.566-1.651 µm)	x
			7 SWIR 2 (2.107-2.294 µm)	x
			10 TIR 1 (10.60-11.19µm), 100m	x
			11 TIR 2, (11.50-12.51µm), 100m	x
Vegetation and other indices	NDVI (Rouse *et al*. 1973)	x	NDVI (Rouse *et al*. 1973)	x
	MSAVI2 (Qi *et al*. 1994)	x	MSAVI2(Qi *et al*. 1994)	
	Red/Blue)	x	Red/Blue (Sabins 1999)	x
	WVSI (WV-2 Soil Index, Wolf 2012)	x		
	NHFD (Non-Homogeneous Feature Difference, Wolf 2012)	x		
	NDWI (Normalized Difference Wetness Index, Wolf 2012)	x	NDWI (Xu 2006)	
	Green/Red (Wang *et al*. 2014)	x	Green/Red (Mwaniki *et al*. 2015)	
	NIR1/Red (Cundill *et al*. 2015)	x	NIR/Red (Sultan *et al*. 1987)	
	NDBSI (Normalized	x		

	Difference Bare Soil Index, Zhou *et al*. 2012)			
	NDRE (Normalized Difference Red Edge, Zhou *et al*. 2012)	x		
	Yellow/Coastal (Wang *et al*. 2014)	x		
			NDMI (Wilson & Sader. 2002)	
			SWIR1/SWIR2 (Sultan *et al*. 1987)	
			SWIR1/NIR (Sultan *et al*. 1987)	x
			SWIR2/NIR (Laake 2011)	
			Green/SWIR1 (Ducart *et al*. 2016)	x
			(Red + SWIR1)/NIR (Rockwell 2013, Ducart *et al*. 2016)	
			(SWIR1/SWIR2)/(NIR/red) (Ducart *et al*. 2016)	
			(SWIR1/NIR) * (Red/NIR) (Sultan *et al*. 1987)	
			SWIR1/Blue (Sultan *et al*. 1987)	
			Red/SWIR1 (Sabins 1999)	
LiDAR derived	varDEM (filter of 5), 1m	x	varDEM (filter of 5), 1m	
	Slope, 1m	x	Slope, 1m	
	DHM, 1m	x	DHM, 1m	x
	varDHM (filter of 5), 1m	x	varDHM (filter of 5), 1m	

Results details

Table S6. Accuracy assessment of land cover classifications.

Analysis	Class Name	Tailings	Waste rock	Roads, bare, urban	Forest	Veget., other	Wetlands	Water	Overall
Combined image	Producer Accuracy(%)	87.2	96.7	92.5	100.0	98.1	84.1	96.3	93.7
	User Accuracy(%)	98.7	96.7	87.6	100.0	84.4	92.8	99.0	
	Kappa Statistic	0.99	0.96	0.85	1.00	0.82	0.92	0.99	0.93
WV-2 Image 1	Producer Accuracy(%)	90.0	78.0	92.0	100.0	88.0	86.0	98.0	90.3
	User Accuracy(%)	80.4	90.7	90.2	100.0	86.3	87.8	98.0	
	Kappa Statistic	0.77	0.89	0.89	1.00	0.84	0.86	0.98	0.89
WV-2 Image 2	Producer Accuracy(%)	72.0	86.0	86.0	100.0	76.0	82.0	94.0	85.1
	User Accuracy(%)	92.3	87.8	82.7	100.0	80.9	75.9	79.7	
	Kappa Statistic	0.91	0.86	0.80	1.00	0.78	0.72	0.76	0.83
Landsat 8	Producer Accuracy(%)	60.0	100.0	45.0	100.0	95.0	95.0	95.0	84.3
	User Accuracy(%)	100.0	71.4	90.0	100.0	95.0	61.3	100.0	
	Kappa Statistic	1.00	0.67	0.88	1.00	0.94	0.55	1.00	0.82

Table S7. Confusion matrices for land cover analyses

Analysis	Classified Class	Tailings	Waste rock	Roads, bare, urban	Forest	Veget., other	wetlands	Water	Total (User)
Combined image	Tailings	75	0	1	0	0	0	0	76
	Waste rock	1	89	0	0	0	0	2	92
	Roads etc.	10	3	99	0	0	0	1	113
	Forest	0	0	0	107	0	0	0	107
	Veget., other	0	0	2	0	103	17	0	122
	wetlands	0	0	4	0	2	90	1	97
	Water	0	0	1	0	0	0	104	105
	Unknown	0	0	0	0	0	0	0	0
	Total (Producers)	86	92	107	107	105	107	108	712
WV-2 Image 1 (W)	Tailings	45	9	2	0	0	0	0	56
	Waste rock	1	39	2	0	0	0	1	43
	Roads etc.	3	2	46	0	0	0	0	51
	Forest	0	0	0	50	0	0	0	50
	Veget., other	0	0	0	0	44	7	0	51
	wetlands	0	0	0	0	6	43	0	49
	Water	1	0	0	0	0	0	49	50
	Unknown	0	0	0	0	0	0	0	0
	Total (Producers)	50	50	50	50	50	50	50	350
WV-2 Image 2 (E)	Tailings	36	1	1	0	0	0	1	39
	Waste rock	2	43	3	0	0	0	1	49
	Roads etc.	7	1	43	0	0	0	1	52
	Forest	0	0	0	50	0	0	0	50
	Veget., other	0	0	0	0	38	9	0	47
	wetlands	0	0	1	0	12	41	0	54
	Water	5	5	2	0	0	0	47	59
	Unknown	0	0	0	0	0	0	0	0
	Total (Producers)	50	50	50	50	50	50	50	350
Landsat 8	Tailings	12	0	0	0	0	0	0	12
	Waste rock	7	20	1	0	0	0	0	28
	Roads etc.	1	0	9	0	0	0	0	10
	Forest	0	0	0	20	0	0	0	20
	Veget., other	0	0	0	0	19	1	0	20
	wetlands	0	0	10	0	1	19	1	31
	Water	0	0	0	0	0	0	19	19
	Unknown	0	0	0	0	0	0	0	0
	Total (Producers)	20	20	20	20	20	20	20	140

Table S8. Kruskal-Wallis statistics for tests comparing sites downstream of mining with reference sites and sites downstream of tailings vs. sites downstream of waste rock (and which group was greater than the other). * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

Characteristic	Reference vs. downstream of mining, all data	Reference vs. downstream of mining, subwatershed data	Reference vs. downstream of mining, May 2015 data	Tailings vs. waste rock, all data	Tailings vs. waste rock, subwatershed data
Specific conductance	44.8***(R<D)	15.9*** (R<D)	5.4* (R<D)	0.0	0.3
TDS	7.2** (R<D)	5.7* (R<D)	5.4* (R<D)	1.5	0.1
DO as %	0.5	0.1	0.0	0.7.	4.1* (T<W)
pH	5.4 * (R<D)	2.9	5.4* (R<D)	0.5	0.8
Bromide	8** (R<D)	3.3	4.1	10.5** (T>W)	6.1* (T>W)
Chloride	26.9*** (R<D)	5 * (R<D)	4.3* (R<D)	1.5	1.3
Fluoride	4.6* (R<D)	6.1* (R<D)	4.3* (R<D)	8.4** (T>W)	6.0 * (T>W)
Sulfate	9** (R<D)	6.9 ** (R<D)	5.4* (R<D)	3.4	2.2
Nitrate[3]	5.2* (R<D)	0.9	0.7	7.1** (T<W)	6.2* (T<W)
Antimony	0.6	0.0	0.1	0.5	0.1
Arsenic	2.1	0.3	0.1	0.0	0.5
Boron	7.2** (R<D)	5.7 * (R<D)	5.4* (R<D)	1.0	0.1
Cadmium	0.2	0.3	0.3	2.9	1.1
Copper	2.5	1.1	2.4	1.5	2
Mercury, total	5.3* (R>D)	3.3	5.4* (R>D)	1.8	2.3
Mercury, methyl	3.8* (R>D)	1.7	3.3	0.6	0.4
Molybdenum	7.2** (R<D)	5.7 * (R<D)	5.4* (R<D)	2.9	1.1
Phosphorus	1.5	0.6	0.3	0.2	0.1
Selenium	7.2** (R<D)	5.7 * (R<D)	5.4* (R<D)	0.0	0.1
Sodium	7.2** (R<D)	5.7 * (R<D)	5.4* (R<D)	2.2	0.5
Strontium	5.5* (R<D)	2.9	5.4* (R<D)	0.5	0.1

Table S8 (cont.)

Characteristic	Reference vs. downstream of mining, all data	Reference vs. downstream of mining, subwatershed data	Reference vs. downstream of mining, May 2015 data	Tailings vs. waste rock, all data	Tailings vs. waste rock, subwatershed data
Tungsten	3.6	3.8	5.4* (R<D)	0.5	0.1
Vanadium	0.1	0.1	0.6	0.5	0.1
Uranium	6.6* (R<D)	5.7* (R<D)	4.3* (R<D)	1.5	0.1
Br^- / spec. cond.	2.2	1.5	0.6	10.5** (T>W)	6.0* (T>W)
Cl^- / spec. cond.	0.1	0.1	1.7	1.1	0.9
Ce/Ce_{NASC}	2.5	5.7 * (R<D)	2.4	4.9* (T>W)	4.5* (T>W)
Eu/Eu_{NASC}	0.6	0.6	0.3	0.1	0.1
Ho/Ho_{NASC}	0.3	0.1	0.3	1.0	1.1
MeHg / THg	0.3	0.0	0.0	0.2	1.2
Mo / spec. cond.	2.1	2.2	0.6	2.9	2.0
Na / (Na+Ca)	7.2** (R<D)	4.7 * (R<D)	4.3* (R<D)	2.9	1.1
Se / Mn	6.1* (R<D)	3.8	4.3* (R<D)	0.1	0.0
Se / Sc	6.6* (R<D)	4.7 * (R<D)	4.3* (R<D)	0.5	0.1
Se / Spec. cond.	5* (R<D)	2.2 (R<D)	5.4* (R<D)	0.5	0.5
Silicon / potassium	7.1** (R>D)	5.4 * (R>D)	5.4* (R<D)	0.6	0.4
Sulfate / Ca	6.6* (R<D)	4.7 * (R<D)	4.3* (R<D)	0.5	1.1
Sulfate / chloride	1.5	1.2	2.4	4.8* (T<W)	4.9* (T<W)
Sulfate / fluoride	6.4* (R<D)	4.7 * (R<D)	5.4* (R<D)	9.8** (T<W)	6.0* (T<W)
Sulfate / spec. cond.	5* (R<D)	1.5	1.7	3.4	2.2
Tungsten / spec. conduct.	0.2	1.1	0.6	1.0	0.5

Table S9. Correlations of water quality and land cover characteristics in subwatershed dataset. Pearson's correlation coefficient (R^2). * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$. [1] also significant using full dataset.

	Specific conductance	DO, %	ORP	SO_4^{2-}	Br^-	TOC	Fe
Specific conductance	--			0.86*** (14)[1]	0.62* (14)1		
DO, %		--	0.55* (14)[1]		-0.63* (13)[1]		
pH	0.64* (14)[1]	[1]	[1]	[1]			
ORP		0.55* (14)[1]	--				
Fluoride	0.66** (14)[1]			0.58* (14)[1]	0.81*** (14)[1]	-0.82** (9)[1]	-0.76* (10)[1]
Chloride	0.42* (26)[1]	-0.66* (14)[1]		[1]	0.79*** (14)[1]		
Sulfate	0.85*** (14)[1]			--	[1]	[1(-)]	
Bromide	0.62* (14)[1]	-0.63* (13)[1]		[1]	--		
Nitrate	[1]	[1]	[1]	0.63* (14)[1]			
TDS	0.97*** (10)[1]			0.87*** (10)[1]	[1]		
TOC				[1(-)]		--	0.96*** (9)1
THg				[1(-)]	-0.80** (9)[1]	0.82** (9)[1]	0.74* (9)
MeHg						0.92*** (9)[1]	0.86** (9)[1]
Boron	0.94*** (10)[1]			0.96*** (10)[1]	[1]	[1(-)]	
Sodium	0.97*** (10)[1]			0.81** (10)[1]	[1]		
Phosphorus	[1]			[1]			
Vanadium					[1]		
Iron						0.96*** (9)1	--
Arsenic	[1]			[1]			
Selenium	0.86** (10)[1]			0.93*** (10)[1]	0.69* (10)[1]	[1(-)]	
Strontium	[1]			[1]			
Molybdenum	0.88*** (10)[1]			0.90*** (10)[1]	[1]	-0.68* (9)[1]	
Cadmium	[1]			[1]	[1]		

Table S9 (cont.)

	Specific conductance	DO, %	ORP	SO_4^{2-}	Br^-	TOC	Fe
Antimony				[1]	[1]		
Tungsten	0.66* (10)[1]			0.77** (10)[1]	[1]		
Uranium	0.83** (10)[1]			0.71* (10)[1]	0.66* (10)[1]		
MeHg / THg		-0.82** (9)					
Sulfate / calcium	0.68* (10)[1]			0.88*** (10)[1]		-0.73* (9)[1]	
Sulfate / chloride	[1]	[1]		0.65* (14)[1]			
Sulfate / fluoride	0.66** (14)[1]			0.88*** (14)[1]			
Silicon / potassium	[1(-)]			[1(-)]		[1]	[1]
Selenium / spec. conduct.				[1]		-0.77* (9)[1]	
Selenium / scandium	[1]			0.79** (10)[1]		-0.96*** (9)[1]	-0.87** (10)[1]
Selenium / manganese	[1]			0.75* (10)[1]		-0.84** (9)[1]	-0.72* (10)
Sodium / (sodium + calcium)	0.91*** (10)[1]			0.76* (10)[1]	[1]		
Bromide / spec. conduct.		-0.69** (13)[1]	-0.56* (13)		0.87*** (14)[1]		
Molybdenum / spec. conduct.	[1]			0.74* (10)[1]	[1]	-0.79* (9)[1]	-0.77** (10)
Tungsten / spec. conduct.					[1]	-0.69* (9)	
Distance downstream	[1(-)]	[1]		[1(-)]	[1(-)]		
Forest cover %	-0.57** (23)[1]			-0.60* (14)[1]	[1(-)]	0.80** (9)[1]	0.65* (10)[1]
Tailings cover, %	0.48* (23)[1]			[1]	0.59* (14)[1]	-0.76* (9)[1]	[1(-)]
Waste rock cover, %	0.45* (23)[1]			[1]			
Water cover, %							
Wetlands cover, %	[1(-)]			-0.60* (14)[1]		0.69* (9)[1]	
Tailings + waste rock, %	0.63** (23)[1]			0.66** (14)[1]	[1]	-0.82** (9)[1]	[1(-)]

Table S9 (cont.).

	Se	Ce / Ce_{NASC}	Eu / Eu_{NASC}	Ho / Ho_{NASC}	Forest cover %	Tailings cover, %	Waste rock cover, %	Wetlands cover, %	Tailings + waste rock, %
Specific conductance	0.86** (10)[1]	0.65* (10)			-0.57** (23)[1]	0.48* (23)[1]	0.45* (23)[1]	[1(-)]	0.63** (23)[1]
DO, %									
pH	[1]		[1]						
ORP									
Fluoride	0.72* (10)	[1]			-0.70** (14)[1]	0.67** (14)[1]			0.58* (14)[1]
Chloride	[1]				-0.70*** (23)[1]	0.57** (23)[1]	[1]		0.49* (23)[1]
Sulfate	0.93*** (10)[1]	0.77** (10)		[1]	-0.60* (14)[1]	[1]	[1]	-0.60* (14)[1]	0.66** (14)[1]
Bromide	0.69* (10)[1]	[1]			[1(-)]	0.59* (14)[1]			[1]
Nitrate	[1]						0.55* (14)[1]	[1(-)]	[1]
TDS	0.80** (10)1								
TOC	[1(-)]		[1(-)]		0.80** (9)[1]	-0.76* (9)[1]		0.69* (9)[1]	-0.82** (9)[1]
THg	-0.71* (9)[1]	[1(-)]			0.96*** (9)[1]	-0.98*** (9)[1]		[1]	-0.87** (9)[1]
MeHg	[1(-)]				0.89** (9)[1]	-0.90*** (9)[1]		[1]	-0.84** (9)[1]
Boron	0.85** (10)[1]	[1]							
Sodium	0.78** (10)[1]	[1]							
Phosphorus		[1]		0.84** (10)[1]				-0.64* (10)[1]	
Vanadium		[1]	[1(-)]	0.69* (10)[1]					
Iron					0.65* (10)[1]	[1(-)]			[1(-)]
Arsenic		[1]		0.74* (10)[1]				-0.67* (10)1	
Selenium	--	0.82** (10)			-0.79** (10)[1]	0.64* (10)		[1(-)]	0.72* (10)[1]
Strontium	[1]		[1]						
Molybdenum	0.83** (10)[1]	[1]			-0.69* (10)[1]	[1]			0.64* (10)
Cadmium		[1]							

Table S9 (cont.).

	Se	Ce / Ce_{NASC}	Eu / Eu_{NASC}	Ho / Ho_{NASC}	Forest cover %	Tailings cover, %	Waste rock cover, %	Wetlands cover, %	Tailings + waste rock, %
Antimony		[1]		0.83** (10)[1]	-0.70* (10)	0.75* (10)[1]		-0.76* (10)[1]	0.70* (10)
Tungsten	0.77** (10)[1]	[1]		0.71* (10)[1]	-0.83** (10)[1]	0.80** (10)[1]		-0.91*** (10)[1]	0.90*** (10)1
Uranium	0.73* (10)[1]	0.67* (10)[1]							
MeHg / THg		[1]	-0.81** (9)[1]						
Sulfate / calcium	0.78** (10)[1]	[1]		0.69* (10)[1]	-0.73* (10)[1]	0.66* (10)[1]		-0.78** (10)[1]	0.78** (10)1
Sulfate / chloride									
Sulfate / fluoride	0.79** (10)[1]	0.76* (10)					0.58* (14)[1]	-0.57* (14)[1]	
Silicon / potassium			-0.81* (9)1						
Selenium / spec. conduct.	0.74* (10)[1]	0.71* (10)			-0.78** (10)	0.73* (10)		[1(-)]	0.67* (10)
Selenium / scandium	0.82** (10)[1]	0.64* (10)	[1]		-0.82** (10)[1]	0.68* (10)[1]		[1(-)]	0.73* (10)[1]
Selenium / manganese	0.82** (10)[1]	0.68* (10)		[1]	-0.87** (10)[1]	0.77** (10)[1]		[1(-)]	0.78** (10)[1]
Sodium / (sodium + calcium)	0.76** (10)[1]	[1]							
Bromide / spec. conduct.		[1]			[1(-)]	[1]			
Molybdenum / spec. conduct.	0.65* (10)	[1]			-0.68* (10)	[1]			
Tungsten / spec. conduct.		[1]	[1(-)]	0.74* (10)	-0.72* (10)	0.80** (10)[1]		-0.90*** (10)	0.82** (10)
Distance downstream	-0.76* (7)[1]			-0.79* (7)				[1]	
Forest cover %	-0.79** (10)[1]				--	-0.81*** (23)[1]	[1(-)]		-0.83*** (23)[1]
Tailings cover, %	0.64* (10)				-0.81*** (23)[1]	--		[1(-)]	0.90*** (23)[1]
Waste rock cover, %					[1(-)]		--	[1(-)]	0.59** (23)[1]
Water cover, %									
Wetlands cover, %	[1(-)]			-0.67* (10)[1]		[1(-)]	[1(-)]	--	-0.42* (23)[1]
Tailings + waste rock, %	0.72* (10)[1]				-0.83*** (23)[1]	0.90*** (23)[1]	0.59** (23)[1]	-0.42* (23)[1]	--

Table S10. Results of statistical tests indicated that several ratios of water quality characteristics were associated with mine waste in general, tailings, and/or waste rock. Distance downstream was along path of main flow and characteristics were inversely related unless noted otherwise (+) and land cover directly related unless noted otherwise (-). Kruskal-Wallis tests results also indicate which group had a greater mean than the other. * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

Characteristic	Comparisons by Kruskal-Wallis test by subwatershed / with all data		Distance downstream simple regression R^2 (all data)			Watershed land cover simple regression R^2 (by subwatershed)			Trend (-) in main flow downstream of tailings (T) or waste rock (WR)
	Reference (R) vs. downstream (D)	Tailings (T) vs. waste rock (WR)	From closest mine waste	From tailings	From waste rock	Tailings + waste rock	Tailings	Waste rock	
Br^- / spec. cond.	.	* / ** (T>WR)	.	0.40***	.	.	. [2, 4]	. [4(-)]	T
Cl^- / spec. cond.	.	.	.	0.04*	.	.	. [4]	. [4(-)]	.
Ce / Ce_{NASC}	* / . (R<D)	* / * (T>WR)	.	.	0.55**(+)	.	.	. [4(-)]	.
Eu / Eu_{NASC}	.	.	.	.	.	.	. [4(-)]	. [4]	.
Ho / Ho_{NASC}	.	.	. [3]	0.41*[3]	.	.	.	. [4]	.
MeHg / THg	.	.	.	.	0.51**(+)	.	.	. [4(-)]	.
Mo / spec. cond.	.	.	.	.	0.51**(+)	0.40*	. [2, 4]	.	T
Na / (Na+Ca)	* / ** (R<D)[1]	.	0.30*[3]	.	.	.	. [4]	.	T, WR
Se / Mn	. / * (R<D)[1]	.	0.31*	0.48*	.	0.61**[2,4]	0.60**[2]	.	T, WR
Se / Sc	* / * (R<D)[1]	.	.	.	.	0.54*[2]	0.47*[2]	. [4]	T, WR
Se / spec. cond.	. / * (R<D)[1]	.	.	.	.	0.46*[4]	0.54*	.	T, WR
Si / K	* / ** (R>D)[1]	.	.	.	0.37*(+)	. [2]	. [4]	.[2, 4(-)]	T(-), WR(+)
Sulfate / Ca	* / * (R<D)[1]	.	0.37*[3]	0.42*[3]	.	0.62**[2]	0.44*[2]	.	T
Sulfate / chloride	.	* / * (T<WR)	.	. [3]	.	.	. [4(-)]	. [4]	
Sulfate / fluoride	* / * (R<D)[1]	* / ** (T<WR)	.	. [3]	0.20*	.	. [4(-)]	0.34*[2, 4]	WR
Sulfate / spec. cond.	. / * (R<D)	.	.	. [3]	.	.	. [2, 4]	.	T
W / spec. conduct.	.	.	.	.	0.40*(+)	.	. [4]	.	T

[1] Analysis also significant when using only data from May 2015
[2] Analysis also significant when using all relevant data, not just subwatershed sites
[3] Analysis also significant when using data from subwatershed sites only
[4] Analysis also significant when using in-channel only sites from Goose Lake Inlet downstream from there

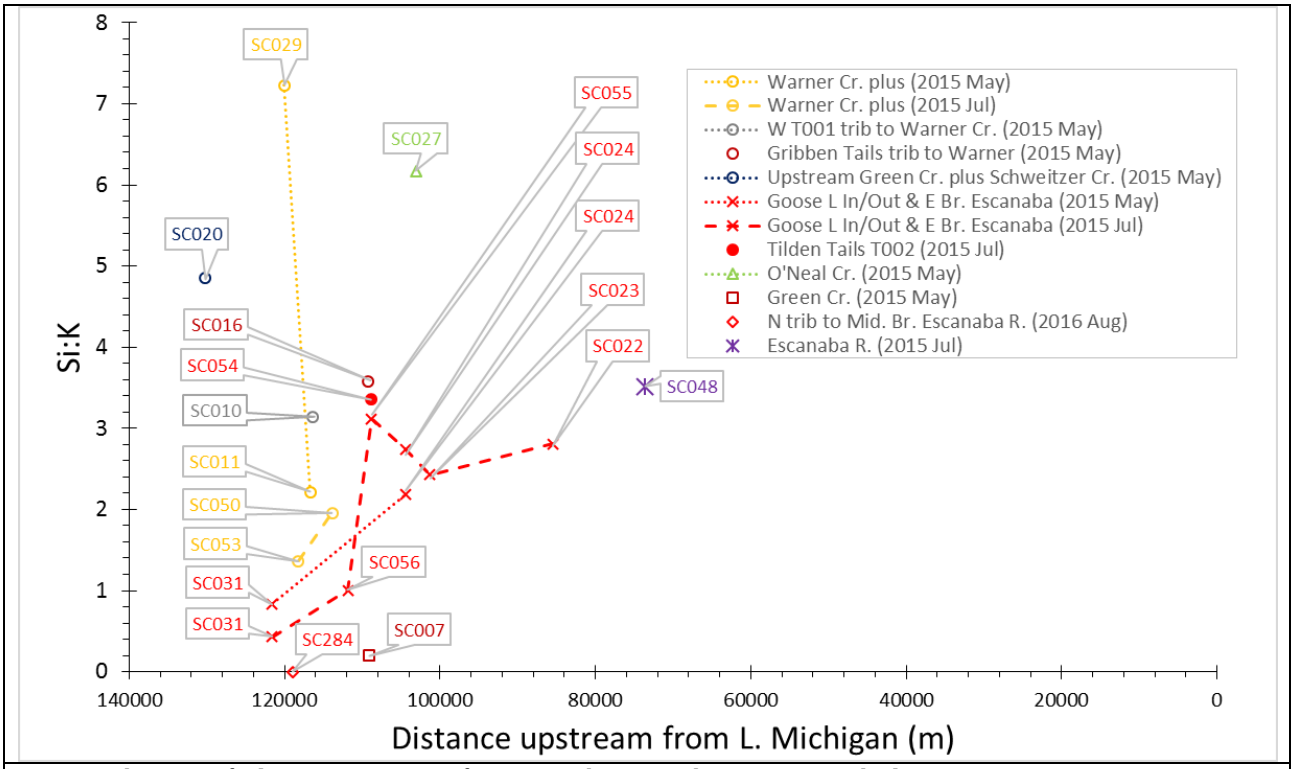

Fig. S1. The ratio of silicon to potassium for sites in the Escanaba River watershed.

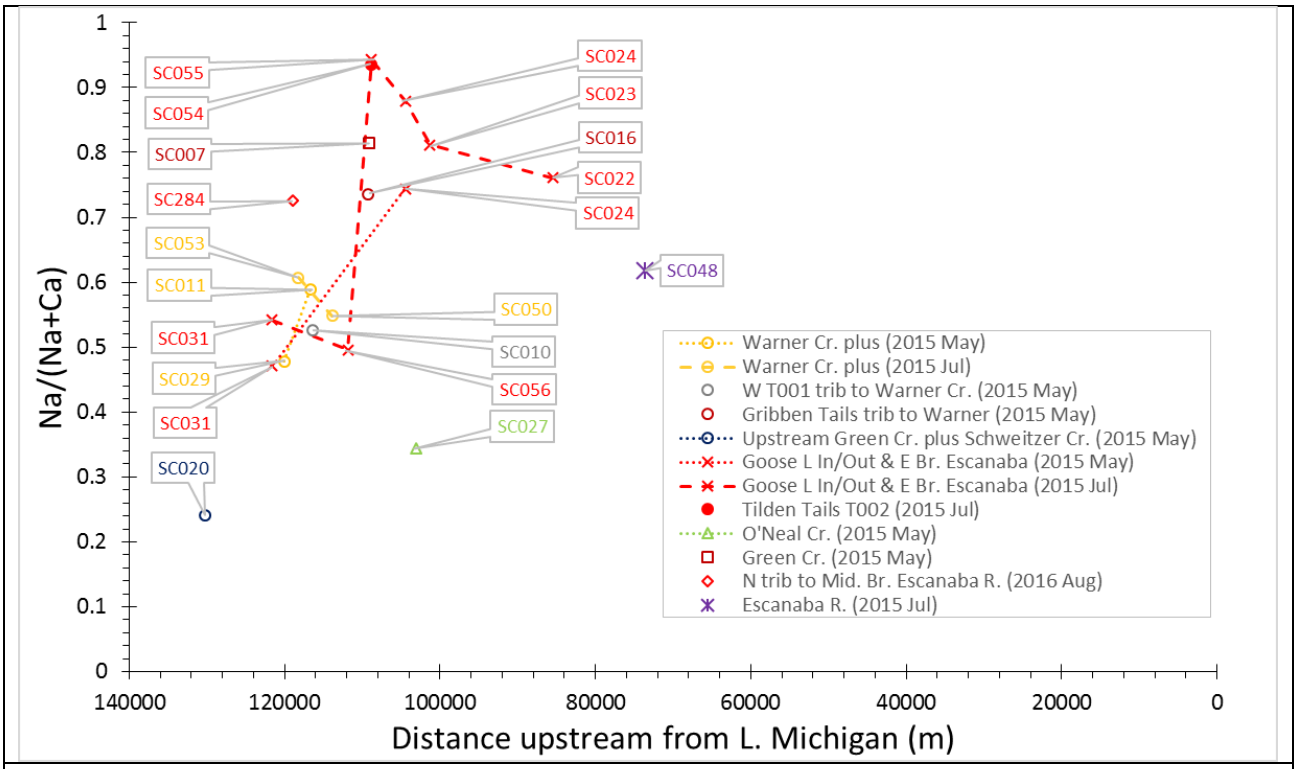

Fig. S2. The ratio of sodium to the sum of sodium and calcium in the Escanaba River watershed.

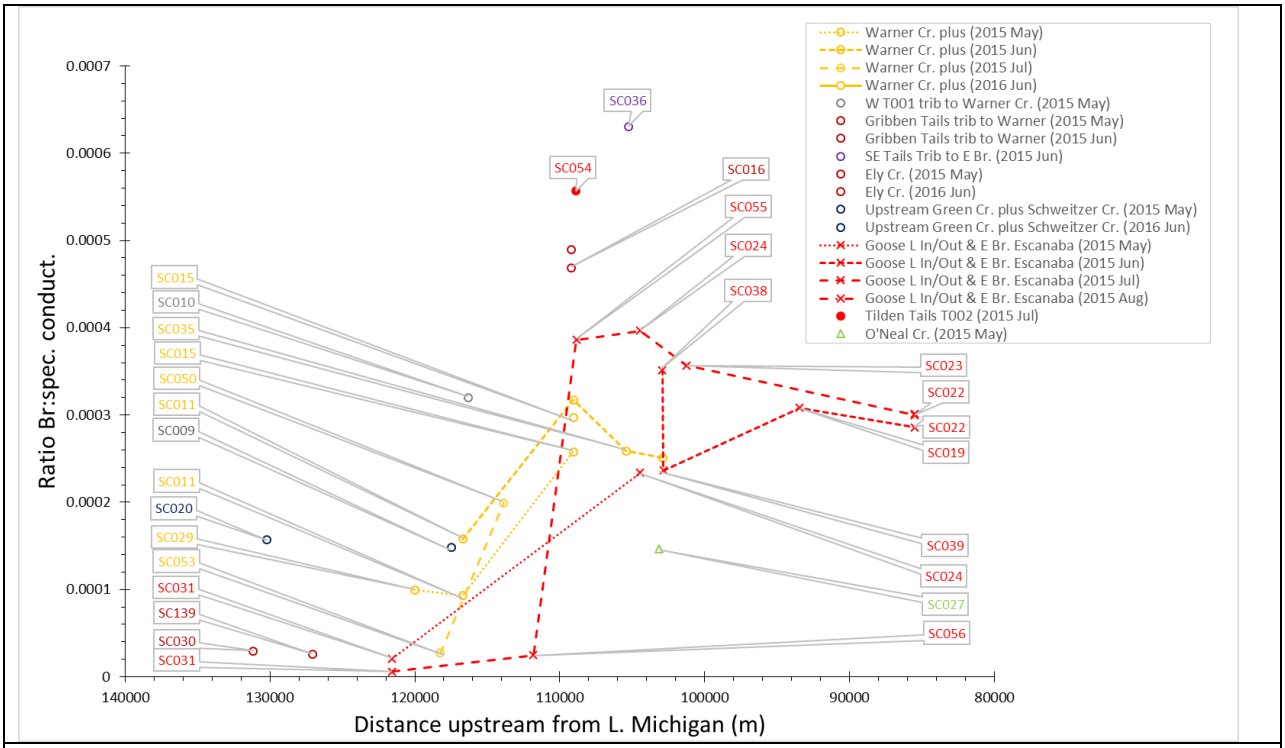

Fig. S3. The ratio of bromide to specific conductance in the East Branch of the Escanaba River watershed.

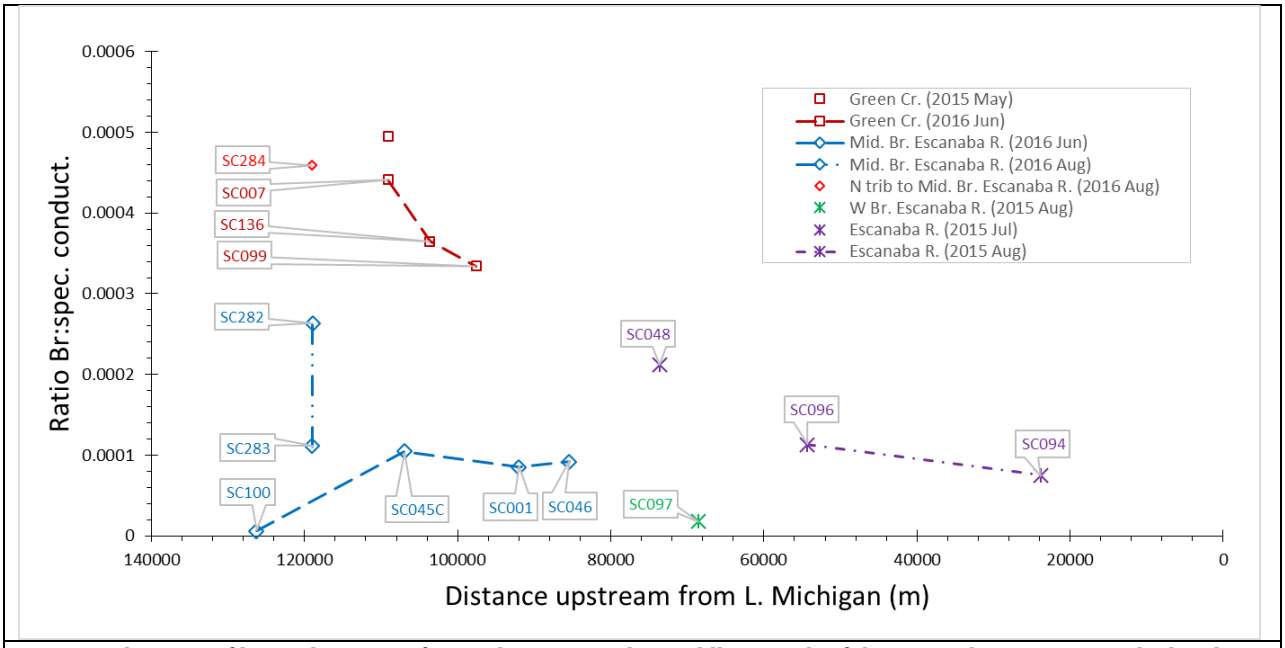

Fig. S4. The ratio of bromide to specific conductance in the Middle Branch of the Escanaba River watershed and in the Escanaba River downstream.

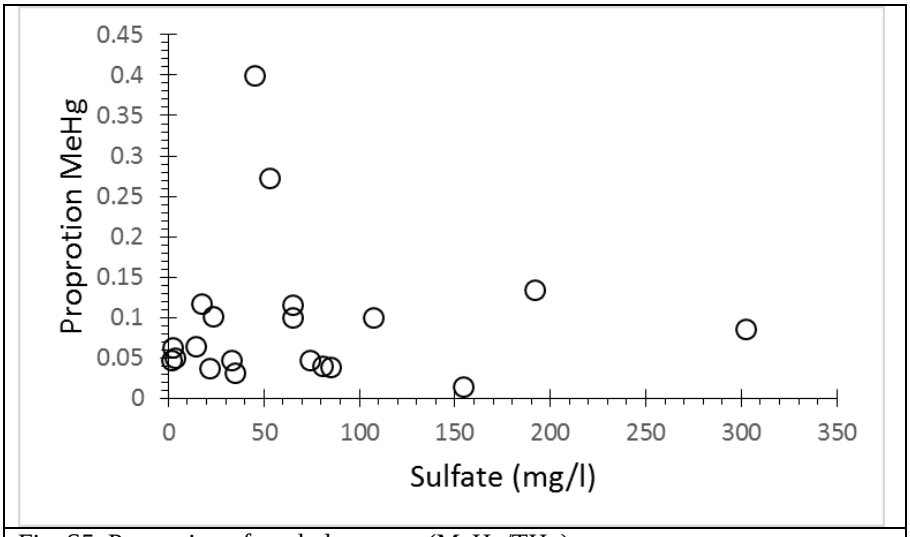

Fig. S5. Proportion of methylmercury (MeHg/THg) was greatest at an intermediate sulfate concentration.

Table S11. Results of simple and multiple regressions indicated that Total Organic Carbon was inversely related to Dissolved Oxygen (DO), and directly related to forest cover and wetland cover. Subw.= subwatershed sites only. All = all relevant sites. * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

Data set, Simple (S) or Multiple (M) regression	DO	Forest cover	Water cover	Wetland cover	Waste rock cover	Multiple Regression R^2 (n)
Subw. (M)	-1.13*	1.42***	.	.	--	0.88 (9)
Subw. (S)	.	1.22** (0.66)	.	2.26* (0.49)	.	(9)
All (M)	.	0.54*	-1.89***	1.48*	--	0.83 (17)
All (S)	.	1.01** (0.47)	.	2.08** (0.45)	.	(18)

Table S12. Kruskal-Wallis statistics for tests comparing data from before mining began with data from 2015-2016. * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

Sampled sites with pre-mining data (*n* max pre-mining, *n* max recent measurements used for median for that site)	Main group	Goose Lake Inlet and downstream	Reference sites
	SC009 (6, 2)[1,2] SC010 (17, 2)[1] SC015 (3, 5)[1,2,5,6,7] SC099 (4, 2) SC139 (4, 1)	SC022 (4, 9)[1,2,3,4,5,6] SC024 (19, 3)[1,2,5] SC031 (4, 3) SC048 (1, 1) SC055 (1, 1) SC056 (15, 1)	SC020 (2, 3) SC043 (1, 1) SC044 (2, 1)
Specific cond. (*n* pre-mining, *n* recent)	6.8** (5, 5), pre<new	4.0* (5, 6), pre<new	0.0
pH (*n* pre-mining, *n* recent)	4.8* (5, 5), pre<new	3.7 (6, 6)	0.2
DO (mg/l; *n* pre-mining, *n* recent)	0.4 (1, 5)	0.1 (3, 6)	0.0
Chloride (*n* pre-mining, *n* recent)	6.9** (5, 5), pre<new	5.8* (6, 6), pre<new	0.0
Fluoride (*n* pre-mining, *n* recent)	--	0.3 (1, 6)	0.0
Sulfate (*n* pre-mining, *n* recent)	3.8 (4, 5)	2.6 (6, 6)	1.5
Nitrate (n pre-mining, *n* recent)	2.5 (5, 5)	1.7 (3, 6)	0.0
TDS (n pre-mining, *n* recent)	2.0 (4, 1)	2.4 (3, 6)	1.5
Alkalinity (n pre-mining, *n* recent)	--	6.5* (4, 6), pre<new	0.0
Chloride: spec. cond. (*n* pre-mining, *n* recent)	4.9* (4, 5), pre<new	4.8* (5, 6), pre<new	--
Sulfate: chloride (n pre-mining, *n* recent)	2.9 (4, 5)	2.6 (6, 6)	--
Sulfate: spec. cond. (*n* pre-mining, *n* recent)	1.5 (4, 5)	0.3 (5, 6)	--

[1] site differed between pre-mining and recent data for specific conductance
[2] site differed between pre-mining and recent data for chloride
[3] site differed between pre-mining and recent data for fluoride
[4] site differed between pre-mining and recent data for sulfate
[5] site differed between pre-mining and recent data for chloride: specific conductance
[6] site differed between pre-mining and recent data for sulfate:chloride
[7] site differed between pre-mining and recent data for sulfate: specific conductance

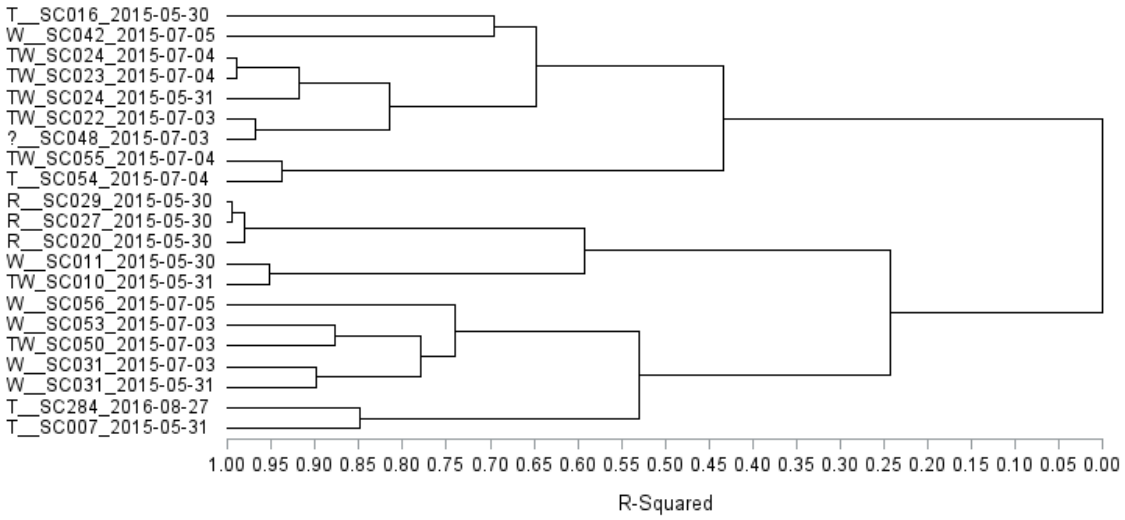

Fig. S6. Cluster analysis of field measurements, anions except nitrate, and all other laboratory measurements (except Hg and individual REEs, which I included as Ce, Eu, and Ho enrichment ratios) indicated that references sites (R) were distinct from sites influenced by mine waste. A site in the Escanaba River (SC048) was more closely related to other influenced sites than to reference sites. Pseudo T-squared analysis indicated the optimal number of clusters was six (R^2 of 0.65). T=downstream of tailings; W=downstream of waste rock; R=reference site; ? = previously uncertain if influenced by mining.

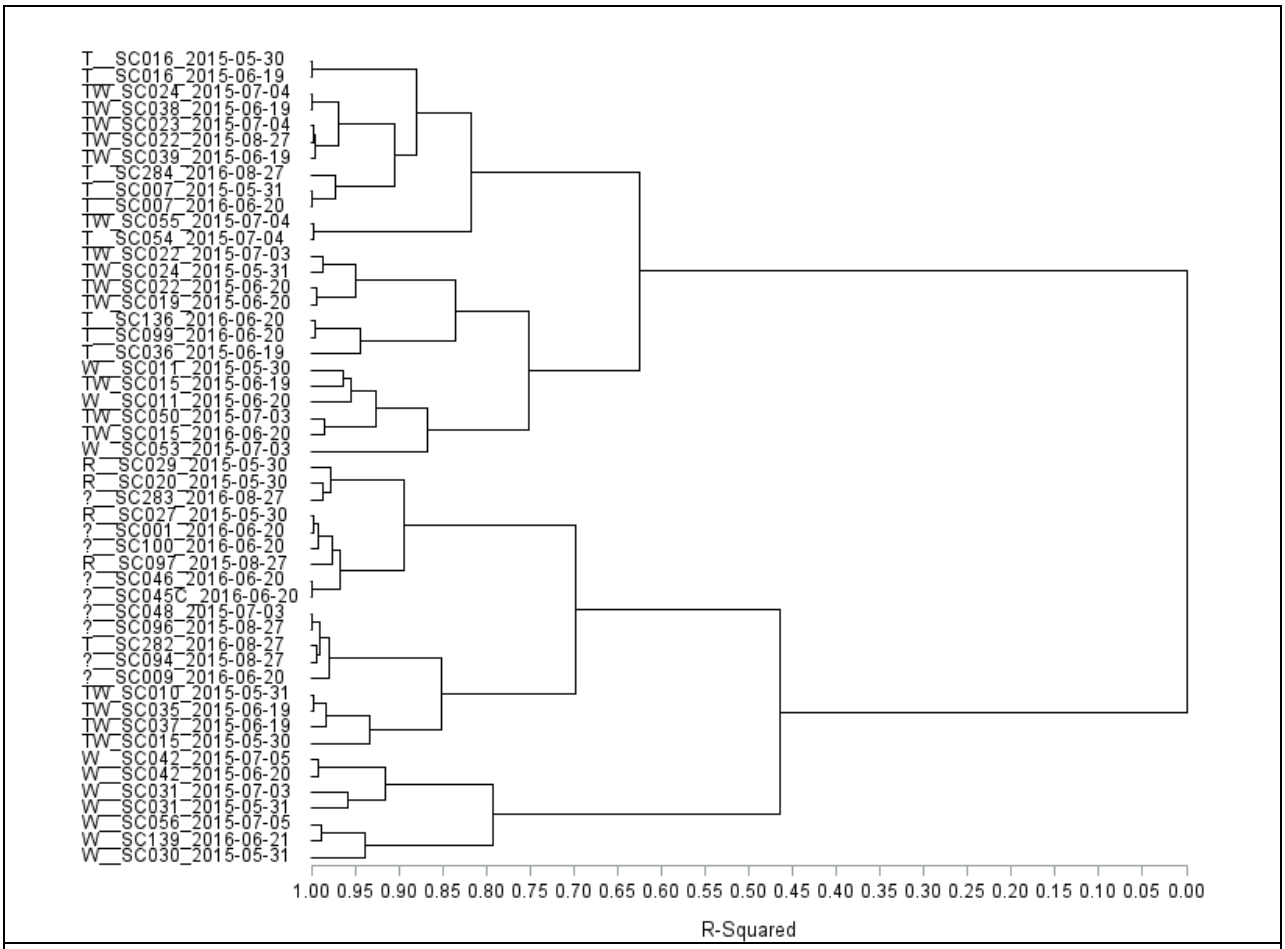

Fig. S7. Cluster analysis of specific conductance, bromide, chloride, fluoride, and sulfate indicated that references sites (R) were distinct from sites influenced by mine waste. The analysis demonstrated that some sites for which the influence of mining was unclear (SC009, SC048, SC094, SC096) clustered most closely with mine-influenced sites, whereas other sites (SC001, SC045C, SC046, SC100, SC283) clustered most closely with reference sites. Pseudo T-squared analysis indicated the optimal number of clusters was 5 (R^2 of 0.75). T=downstream of tailings; W=downstream of waste rock; R=reference site; ? = previously uncertain if influenced by mining.

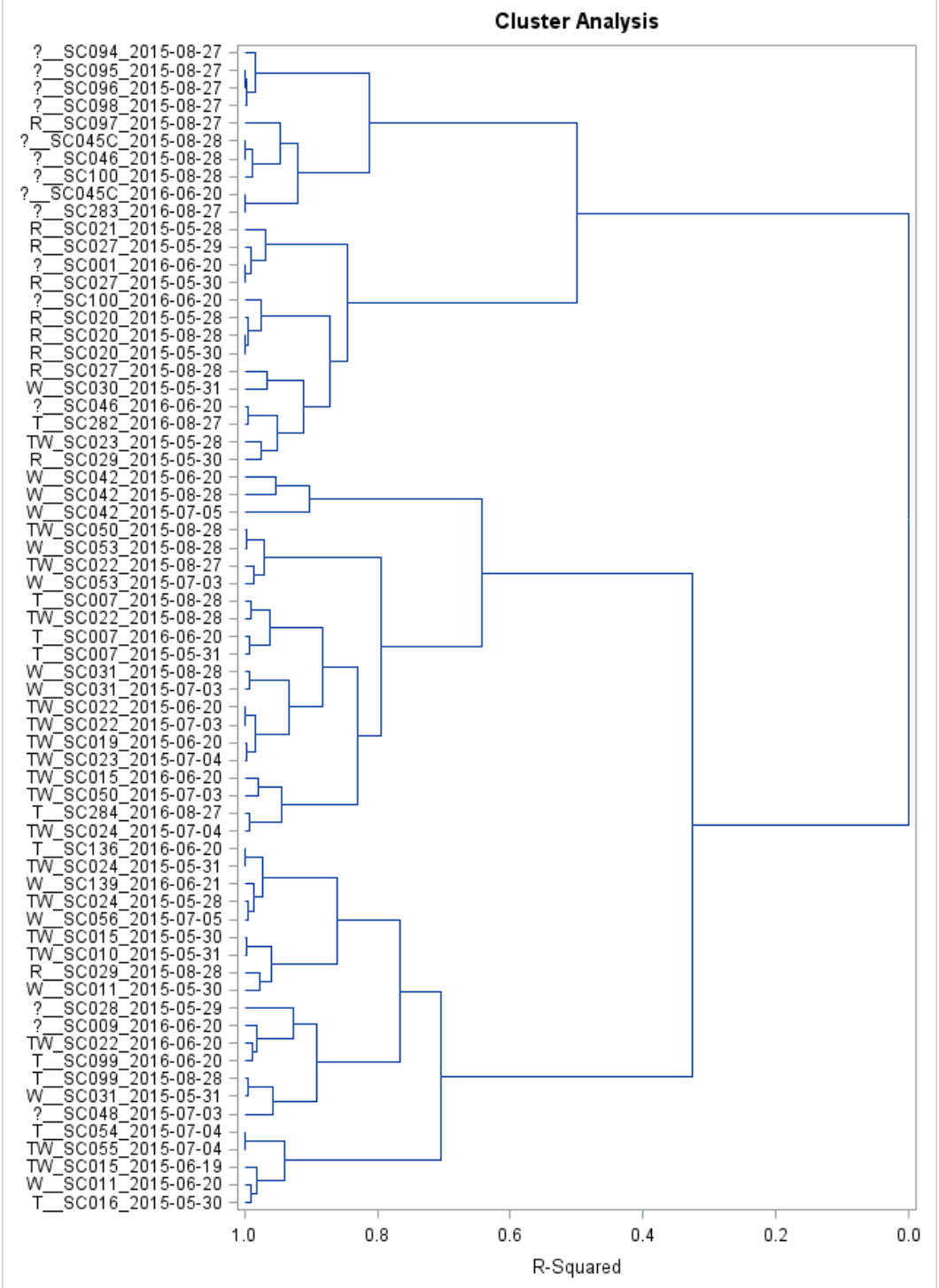

Fig. S8. Cluster analysis of specific conductance, DO, pH, and chloride data. The analysis indicated that most references sites (R) clustered most closely with each other rather than with sites influenced by mine waste, but one reference site (SC029) in August 2015, when streams had higher specific conductance, clustered with mine-influenced sites measured earlier in the year. Certain sites that were mine-influenced or classified as such in the anion cluster analysis (SC023 in May, SC030, SC094, SC095, SC096, SC098, SC282) clustered most closely with reference sites in this analysis that only included field data. Pseudo T-squared analysis indicated the optimal number of clusters was 9 (R^2 of 0.83). T=downstream of tailings; W=downstream of waste rock; R=reference site; ? = previously uncertain if influenced by mining.

Table S13. Kruskal-Wallis statistics for tests comparing sites for which the influence from mining was uncertain and sites that were not downstream of mining. R = reference sites. Only underlined site codes included anion data in addition to chloride. * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

	Group 1		Group 2		
	Aug 2015	May-Aug 2015-2016	Aug 2015	Jun-Jul 2015	May-Aug 2015-2016
Uncertain group sites	SC094, 95, 96, 98	SC009, 94, 95, 96, 98	SC045C, 46	SC001, 45C, 46	SC001, 45C, 46, 283
Reference sites	SC020, 27, 97	SC002, 4, 5, 20, 21, 26, 27, 29, 34, 43, 43B, 44, 97, 138, 279	SC020, 27, 97, 100	SC034, 43, 43B, 44, 100, 138	SC002, 4, 5, 20, 21, 26, 27, 29, 34, 43, 43B, 44, 97, 100, 138, 279
Specific conductance	5.3*	10.9*** (Group1>R)	0.9	0.1	0.2
pH	4.7*	6.1* (Group1>R)	0.9	0.2	1.6
DO (%)	1.3	4.8* (Group1>R)	1.9	0.2	0.4
Chloride	5.3*	1.5	3.4	0.6	0.4
Fluoride	1.5	2.7	--	1.8	0.5
Sulfate	1.5	5.0* (Group1>R)	--	1.8	2.2
Bromide	1.5	5.2* (Group1>R)	--	1.8	6.3* (Group2 > R)
Nitrate	1.5	1.1	--	1.8	1.5
Chloride : spec. cond.	0.3	0.4	0.0	0	0.1
Sulfate: chloride	1.5	1.8	--	1.8	1.0
Sulfate: spec. cond.	1.5	1.8	--	1.8	0.5
Sulfate: fluoride	1.5	2.7	--	0.2	0.5
Bromide: spec. cond.	1.5	0.2	--	1.8	0.0

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Chapter 3. Assessing the spatial extent of iron mining influence on surface water quality in the Lake Superior Ojibwe Treaty-ceded Territories

Abstract

Iron mining can contaminate surface waters with heavy metals, other trace elements, asbestiform mineral fibers, and major anions such as bromide, chloride, fluoride, and sulfate. Such contamination can affect fish and plants that are of importance for Indigenous lifeways and treaty rights. Evaluating the extent of such contamination can contribute to assessment of cumulative impacts of mining. Classifying water quality data as mine-influenced or not represents a means of determining the downstream extent of mining influence where contamination may occur. Studies have yet to determine appropriate statistical classifiers for such determination of mine influence. I evaluated different classifiers and the extent of iron mining contamination in the iron mining regions of the Lake Superior Ojibwe Treaty-ceded Territories. I based those evaluations on specific conductance and major anion data that I collected in 2015-2016 along with compiled data available in the Water Quality Portal and from other reports for 2000-2018. I used training data to classify sites for which I was uncertain of the mine influence using both a Support Vector Machine (SVM) classification and a Discriminant Function Analysis (DFA). Overall accuracy was greater for most combinations of characteristics using the DFA. I therefore used DFA results to map the extent of mine influence based on records thus classified, and determined that at least 900 river-km in the iron mining zones of the Lake Superior Ojibwe Treaty-ceded Territories were mine-influenced during at least a portion of the period of study. The extent of mine-influence fit within the bounds of my cumulative impacts study region, which included USGS HUC8 watershed overlapping the boundaries of the Treaty-ceded Territories. Concentrations of chloride and fluoride were sufficient to cause concern for aquatic life. Sulfate concentrations that I mapped represented a source of enhanced methylation of mercury, a potential source of nutrient release from sediments, and a threat to wild rice (*manoomin*), which is of vital cultural importance to Lake Superior Ojibwe. The tailings discharges also likely render the waters downstream and connected groundwater unsuitable as a source of drinking water because chlorination of the bromide-enriched waters could produce carcinogenic trihalomethanes.

1. Introduction

Iron mining water quality impacts

Large-scale iron mining environmental impacts include the potential for multiple effects on surface water quality. Iron mining can lead to oxidation of sulfide minerals in waste rock or ore that release trace elements of concern to natural waters. Such trace elements can include selenium and arsenic and heavy metals such as chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, lead, and uranium (USEPA 1994, Razowska 2001, Cardiff & Coleman 2017, Zhang *et al*. 2017, Chapter 2 in this work). Iron mining has also caused contamination with asbestiform mineral fibers to surface waters from tailings (USEPA 1994).

Discharges from waste rock and tailings also exhibit high concentrations of total dissolved solids and major anions from waste rock and tailings (USEPA 1994, Kelly *et al*. 2014, Cardiff & Coleman 2017). Those discharges have the potential to harm aquatic life and even human health (Appendix A). High chloride concentrations can harm invertebrate and fish reproduction and survival (USEPA 1988, CCME 2011). Fluoride can disrupt fish migration and reduce survival of fish and aquatic invertebrates (CCME 2001). Sulfate, reduced to sulfide, harms wild rice, increases mercury methylation at certain concentrations, and contributes to eutrophication (Gilmour *et al*. 1992, Jeremiason *et al*. 2006, Myrbo *et al*. 2017a, b). Bromide along with dissolved organic carbon, if chlorinated in a drinking water treatment facility, can form trihalomethanes that are human carcinogens (Flury & Papritz 1993, Regli *et al*. 2015).

Specific conductance and major anions have the potential to serve as indicators of mining influence that are relatively feasible to sample for. For a given level of monitoring resources, a monitoring program can sample for TDS, or its surrogate specific conductance, and for major anions more extensively and inexpensively than if sampling for many trace elements. Specific conductance, chloride, and sulfate are already common components of monitoring programs. Laboratory analyses such as ion chromatography can measure concentrations of not only chloride and sulfate, but also bromide,

fluoride, and nitrate. Nitrate can indicate mine influence on waters, though many other sources can also contribute to nitrate levels (CCME 2012). Monitoring programs also use a variety of measurements for nitrogen compounds that are not all comparable and some methods have limited holding times (e.g., EPA 300.1). The combination of specific conductance, bromide, chloride, fluoride, and sulfate, therefore, have the potential to act as relatively practical and representative indicators of mine influence on surface waters.

Cumulative impacts and mine-influenced waters

Assessing the extent of mine-influenced waters using such indicators may represent an important aspect of cumulative impacts assessment. A cumulative impact is an "impact on the environment which results from the incremental impact of the action when added to other past, present, and reasonably foreseeable future actions" (Council on Environmental Quality 1978). The analysis can use spatial or temporal approaches to pool effects (Franks *et al*. 2013). Assessing cumulative impacts can improve understanding of the consequences of new projects or assist in strategic environmental assessments (Bravante & Holden 2009). Mining influence and impacts can extend downstream beyond the zones of highest contamination that are often the focus of remediation (Garvin *et al*. 2017). This also affects the determination of appropriate study extents for cumulative impacts assessment (MacDonald 2000). Other studies of cumulative effects of mining on aquatic systems have used sub-basins (USGS HUC8; Strager *et al*. 2009, Petty *et al*. 2010) or broader reaches of rivers (Squires *et al*. 2009). The extent of mine-influenced waters, therefore, represents an important component of cumulative impacts and a means of determining appropriate assessment scale.

Several analytical techniques could provide an estimate of the extent of mining influence on surface waters. One approach is to use tracers to determine the distribution of mine influence based on the distribution of that tracer. Such tracers can include individual elements or ions, element or ion ratios, and stable isotopes (Fey *et al*. 2008, Miller *et al*. 2015, Wiederhold 2015). Alternatively, or in conjunction with this technique, multivariate statistical analyses can indicate sources and extent of

contamination. Marqués *et al*. (2018) used a measure of a graphical representation of Principal Components Analysis to identify sites with mine influence. Other approaches involve classifying sites based on training data. Classifiers include multivariate linear Discriminant Function Analysis (DFA), which can accurately classify water quality data into groupings such as pollution sources and identify characteristics that most influence classification (Alberto *et al*. 2001, Shrestha & Kazama 2007). More complex techniques include machine learning methods such as the Support Vector Machine (SVM) and neural networks that do not have the data distribution assumptions required by DFA (Bourel & Segura 2018). In at least some cases, SVM can model water quality data with less uncertainty than other complex techniques (Modaresi & Araghinejad 2014; Isazadeh *et al*. 2017) and has demonstrated higher accuracy than DFA for classification of some ecological data (Bourel & Segura 2018). It appears uncertain, however, which of these classifiers may be most accurate for classification of water quality data by mine influence.

Lake Superior Ojibwe Treaty-ceded Territories

The Lake Superior Ojibwe Treaty-ceded Territories represent an appropriate region for the study of cumulative impacts of iron mining and the extent of iron mine influence on surface waters. US negotiators of the Lake Superior Ojibwe treaties of the mid-1800s sought access to iron deposits and timber and mining companies built hundreds of small to large iron mines across the Lake Superior Ojibwe Territories over the next century (Cleland 2000, Baeten *et al*. 2016, Thistle & Langston 2016; Fig. 1). The region eventually became the biggest iron producing region in the US. It also transformed parts of the landscape into tailings, waste rock piles, and open pits (Baeten *et al*. 2016). The mining has contaminated surface waters in certain zones with toxic concentrations of heavy metals and other trace elements, asbestiform mineral fibers, fluoride, bromide, chloride, and sulfate, including in wild rice waters (USEPA 1994, Berndt & Bavin 2012, Kelly *et al*. 2014; Von Korff & Bavin 2014, Vogt 2015, 2018, Cardiff & Coleman 2017, Chapter 2 in this work). The mining has contaminated wild rice beds,

which are of great importance to Ojibwe lifeways (Benton-Banai 1988, Loew 2013), with concentrations of sulfate that, as sulfide in the sediment, are toxic to wild rice (Myrbo *et al*.2017a, b).

Studies had yet to assess the downstream extent of mine influence and contamination with sulfate and bromide in the iron mining regions of the Lake Superior Ojibwe Treaty-ceded Territories. I sought to accomplish that and also add to understanding of appropriate techniques for assessing extent of mine influence on surface waters and cumulative impacts of iron mining.

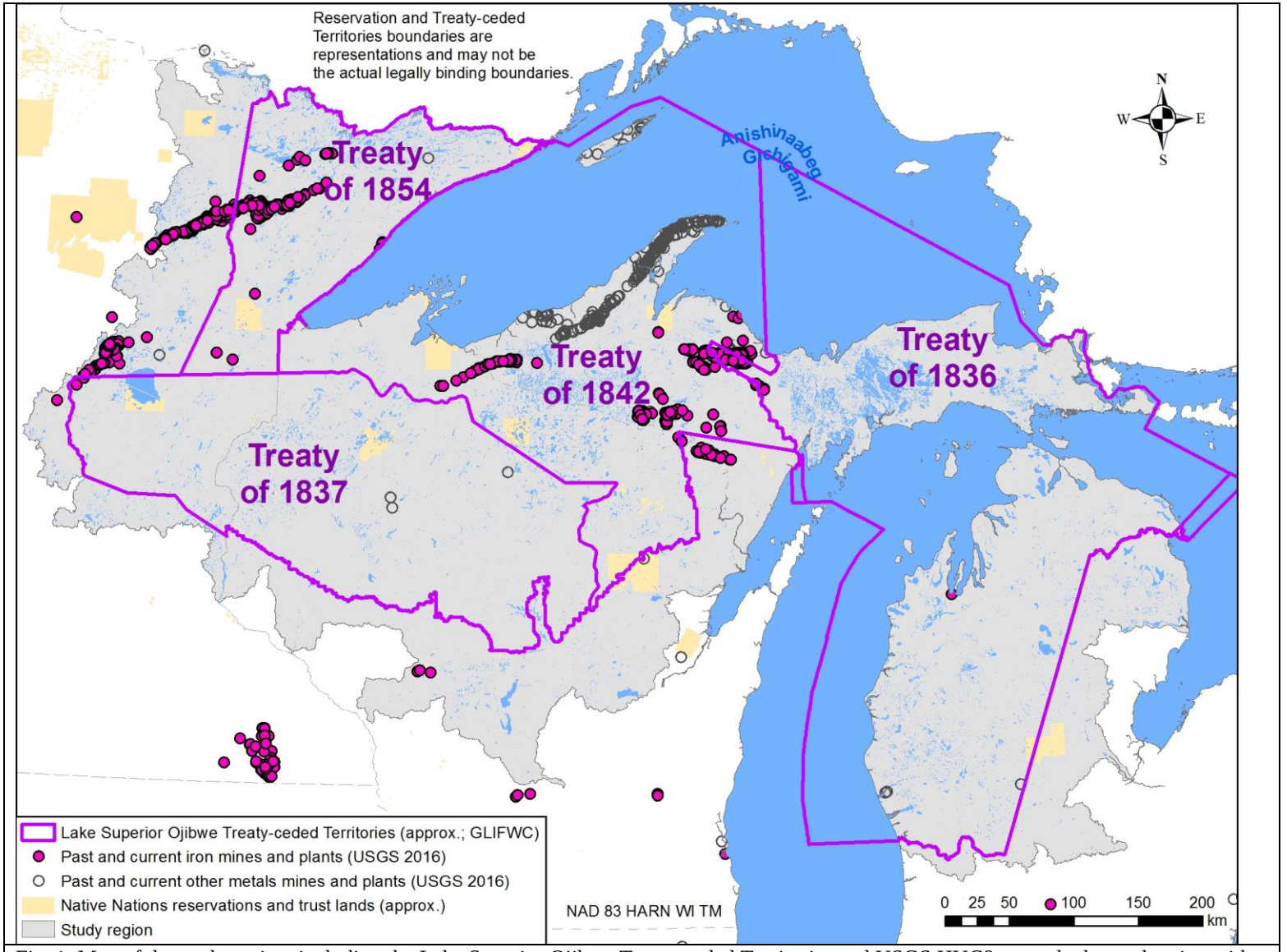

Fig. 1. Map of the study region, including the Lake Superior Ojibwe Treaty-ceded Territories and USGS HUC8 watersheds overlapping with their borders. Past and present metals mining occurs in several zones of the Territories.

2. Methods

Water quality data compilation

I selected a study region that would include the iron mining regions of the Lake Superior Ojibwe Treaty-ceded Territories but that would be likely to also include water quality impacts extending beyond those boundaries (Fig. 1). For this I selected the USGS HUC8 sub-basins that were within or intersected the boundaries of the Territories (Fig. 1).

I compiled existing water quality data from 2000 to April 2018 from the Water Quality Portal (National Water Quality Council 2018), which includes data from the USEPA, the USGS, and other agencies. I selected surface water data measurements for specific conductance, bromide, chloride, fluoride, and sulfate from the study zone. I corrected obvious errors in station geographic coordinates and verified that sites were in the counties they indicated they were and were not groundwater sampling sites. I also converted to a single unit for each characteristic and removed duplicate records that were from the same site, date, and time. I then joined the data for different characteristics based on a common location ID, date, and time combination. I retained only data that had specific conductance measurements as well as at least one of the major anions other than chloride. To that Water Quality Portal data, I added data from several other reports by agencies in the region (Table S1).

Water quality sampling

After identifying gaps in water quality data relative to past and current iron mining in the Treaty-ceded Territories from my compiled database, I conducted supplemental water sampling. I assessed water quality in the Escanaba (Chapter 2) and Carp River watersheds and near the Iron River, Republic and Groveland mines and other sites in Michigan (Cardiff & Coleman 2017, 2018c). I also sampled water quality in the Dark and Dunka River watersheds in Minnesota (Cardiff & Coleman 2018a, b).

At all sites, I used standard surface water monitoring protocols (USGS variously dated; USEPA 2012) and recorded specific conductance and chloride concentration with a YSI Pro Plus multimeter in the field (calibrated daily). Where possible, I collected samples at well-mixed sites below a riffle zone. I used a hand dip sampling technique at the centroid of flow with the Clean Hands – Dirty Hands technique or a one-person modification thereof (USGS variously dated). I rinsed bottles three times with sample water and kept bottles capped when submerging into or removing from the water. In 2015, I collected 54 anions samples, 3 field blanks, and 1 field sequential replicate. In 2016, I collected 102 anion samples, 8 field blanks, and 8 field sequential replicates. I filtered anion samples using syringes and 25 mm diameter, 0.45 µm polysulfone cartridge filters (Pall Acrodisc 4585).

Laboratory methods

I conducted ion chromatography following EPA method 300.1, with a Dionex ICS-2100 and autosampler. I configured the instrument with a 4 mm x 250 mm Dionex IonPac AS11 column, AG-11 guard, and ASRS-4mm suppressor. I used a 100µL injection loop, flow rate of 0.6 ml/min (2016, 1.0 ml/min in 2015), suppressor current of 45 mA (2016, 65 mA in 2015), column temperature of 30° C, and 30 mM NaOH eluent. I measured Method Detection Limits (MDLs) by running seven standard-fortified samples through an analysis sequence in two different batches on two (2015) or three (2016) separate days (Table S2).

I verified that anion blank samples with any detections (chloride and sulfate) were < 10% of the lowest actual measure (1 chloride blank exceeded that). I also confirmed that field sequential replicate samples were not more than 20% different than concentrations in the original sample, or were near the detection limit if they did (1 fluoride replicate exceeded that).

Spatial and statistical analyses

I combined the data from other sources with the data that I collected into one database. I mapped records from the compiled database and then identified training and accuracy assessment reference sites and sites downstream of mining. For training and accuracy reference sites, I selected records that were not downstream of mining, but in the same or adjacent HUC8 watershed as mining. In Minnesota, I also ensured that those reference sites were zones overlapping bedrock geological formations matching the formation underlying mine pits and mine waste (Cannon *et al*. 1999). In identifying mine-influenced training and accuracy records, I used sites from the following:

- sites in the Escanaba River watershed (Kohlhepp 2007; Chapter 2 of this work);
- sites near the Republic Mine in Michigan (Cardiff & Coleman 2018c);
- sites around Iron River in Michigan (Cardiff & Coleman 2017);
- sites in the Dark River in Minnesota (Cardiff & Coleman 2018b);
- Twin Lakes sites east of Minntac tailings (Vogt 2015; GLIFWC unpublished);
- sites downstream of mines in Minnesota (SC069 downstream of Dunka Pit in Cardiff & Coleman 2018a; MNPCA-69-0729-00-201, MNPCA-S001-085, MNPCA-S007-212, MNPCA-S007-471, MNPCA-S007-691; National Water Quality Council 2018); and
- data from Minntac water discharge monitoring (MNPCA 2016).

For the mine-influenced sites from data that I collected, I had previously determined which sites were mine-influenced using cluster analyses and Kruskal-Wallis tests comparing downstream sites with reference sites (Chapter 2, Cardiff & Coleman 2017, Cardiff & Coleman 2018b, c). The other mine-influenced sites were sites directly downstream of known mine discharges, including site SC069 in Cardiff & Coleman (2018a).

I used the ArcGIS 10.3 (ESRI, Redlands, California) Subset tool to randomly select 80% of the training and accuracy records and assign them to be training data. I assigned the other 20% to be accuracy assessment data. Because I conducted analyses on multiple different combinations of specific

conductance and anions, the actual number of training and accuracy sites depended on data availability for those characteristics. The remainder of water quality records were available for classification as mine-influenced or lacking evidence of mine influence.

I conducted two analyses on the specific conductance and major anion data: discriminant function analysis (DFA), and Support Vector Machine (SVM) classification. Using each method, I conducted the analyses separately for all the different possible combinations of measurements.

I conducted the DFA statistical analyses using SAS 9.3 software (SAS Institute, Cary, NC) I used a $\log_{10}$ or $\log_{10}(x + 1)$ transformation on water quality data. I did not include ratio variables in the DFA analysis because of pooled covariance matrix singularity.

For the SVM classification, I used the SVM option in object-based image analysis in the remote sensing software PCI Geomatica 2017 (PCI Geomatics, Markham, Ontario). I first assigned each water quality record to a rectangular fishnet polygon grid in ArcGIS 10.3, then classified those polygons by SVM based on the training data. Finally, I tested accuracy based on the training data separately retained for accuracy assessment. I also classified training records as influenced by tailings, by waste rock, by both, or not influenced. I determined those classes for training data based on what type of waste was upstream of those associated sites. I conducted two SVM classification analyses: one for type of mine waste vs. reference sites, and one for overall mine waste (tailings or waste rock) vs. reference sites. In these analyses, I included anion to specific conductance ratios and relevant anion/anion weight ratios (Cl^-:Br^-, SO_4^{2-}:Cl^-, SO_4^{2-}:F^-, Cl^-:F^-; Chapter 2).

In reporting and analyzing anion concentrations, I used ½ of the Minimum Reporting Limit (MRL) or detection limit for results that were below calibration MRLs or detection limits.

For estimating the extent of mine-influenced waters, I examined the results of the analysis with the highest overall accuracies. I designated a site as mine-influenced if it had one record that the analysis classified as mine-influenced for at least one of the combinations of specific conductance and anion(s). For mapping the influenced reaches, I also assumed that the reach upstream between a mine-influenced point and the probable mine waste source was also influenced.

3. Results

Accuracy of classification methods

For the SVM analysis, using specific conductance, chloride, and sulfate in classification resulted in the greatest overall accuracy for both the analysis of type of waste influence and the analysis of mine-influenced vs. reference records (Table 1). The only combinations for tailings influence that resulted in user accuracy of 100% were those including bromide measurements (Table 1).

In the DFA classifications, overall and user accuracies were greatest with combinations of anions including sulfate. Most DFA classifications for determination of mine waste influence were more accurate than comparable analyses with SVM (Tables 1, 2).

Table 1. Support Vector Machine classification of water quality data demonstrated that a combination of specific conductance, Cl^-, and SO_4^{2-} resulted in the highest overall accuracy. User accuracy of classification of tailings-influenced sites was greatest in analyses that included bromide.

Characteristics	total *n*	Classification of sites as influenced from tailings, or waste rock, or as non-influenced			Overall accuracy, Mine waste, Reference		
		Overall accuracy	Tailings producer accuracy	Tailings user accuracy	Overall accuracy	Mine waste Producer Accuracy	Mine waste User Accuracy
Sp. cond., Br^-	367	84.6	60.0	100	94.9	90.5	100
Sp. cond., Cl^-	3102	90.4	87.3	86.1	97.7	94.4	98.8
Sp. cond., F^-	651	68.9	20.0	50.0	97.8	95.2	100
Sp. cond., SO_4^{2-}	3536	93.5	100.0	89.9	97.6	92.2	100
Sp. cond., Br^-, Cl^-	367	82.0	80.0	100	89.7	85.7	94.7
Sp. cond., Br^-, F^-	273	67.7	20.0	100	77.4	95.2	76.9
Sp. cond, Br^-, SO_4^{2-}	365	87.2	60.0	100	94.9	90.5	100
Sp. cond., Cl^-, F^-	648	70.4	20.0	100	95.4	95.2	95.2
Sp. cond., Cl^-, SO_4^{2-}	3100	94.2	100	91.0	98.1	95.5	98.8
Sp. cond., F^-, SO_4^{2-}	649	44.1	50.0	50.0	48.4	88.4	35.0
Sp. cond., Br^-, Cl^-, F^-	273	67.7	20.0	100	77.4	95.2	76.9
Sp. cond., Br^-,Cl^-, SO_4^{2-}	365	84.6	60.0	100	89.7	85.7	94.7
Sp. cond., Br^-, F^-, SO_4^{2-}	271	80.6	20.0	50.0	96.8	100	95.4
Sp. cond., Cl^-, F^-, SO_4^{2-}	646	68.2	20.0	50.0	95.4	90.5	100
Sp. cond., all 4	271	80.6	40	66.7	96.8	100	95.4

Table 2. Discriminant Function Analysis (DFA) classification of water quality data indicated that including sulfate yielded the highest overall and user accuracy.

Characteristics	Total *n*	Overall accuracy, Mine waste, Reference	Mine waste Producer Accuracy	Mine waste User Accuracy
Sp. cond., Br^-	367	92.3	100	87.5
Sp. cond., Cl^-	3102	98.4	97.8	97.8
Sp. cond., F^-	651	91.1	100	84.0
Sp. cond., SO_4^{2-}	3536	99.0	96.7	100
Sp. cond., Br^-, Cl^-	367	92.3	100	87.5
Sp. cond., Br^-, F^-	273	90.3	100	87.5
Sp. cond., Br^-, SO_4^{2-}	365	100	100	100
Sp. cond., Cl^-, F^-	648	90.9	100	84.0
Sp. cond., Cl^-, SO_4^{2-}	3100	99.6	98.9	100
Sp. cond., F^-, SO_4^{2-}	649	100	100	100
Sp. cond., Br^-, Cl^-, F^-	273	87.1	100	84.0
Sp. cond., Br^-,Cl^-, SO_4^{2-}	365	100	100	100
Sp. cond., Br^-, F^-, SO_4^{2-}	271	100	100	100
Sp. cond., Cl^-, F^-, SO_4^{2-}	646	100	100	100
Sp. cond., all 4	271	93.6	100	91.3

Specific conductance and anion measurements

Specific conductance and anion measurements in the analyzed data had greater averages at mine-influenced sites than in records that the DFA did not classify as mine-influenced. Specific conductance at mine-influenced sites reached concentrations more than double the Minnesota water quality criterion (Table 3). Bromide reached concentrations greater than 600 µg/l (Table 3). Chloride at its greatest concentration in the mine-influenced waters was greater than 250 mg/l, exceeding the USEPA chronic criterion (Table 3). Fluoride measurements ranged up to 5.9 mg/l, 50 times the Canadian chronic criterion (Table 3). Finally, sulfate reached concentrations more than 100 times the wild rice water criterion in Minnesota of 10 mg/l, and five times the drinking water criterion (Table 3).

Table 3. Summary statistics for water quality records that I classified as mine-influenced or not mine-influenced in classification results and training and accuracy assessment data. Averages were greater in mine-influenced records than in records that were not mine-influenced for all characteristics. Results are mean ± standard deviation (range).

Characteristic	Classified results		Training and accuracy assessment data	
	Mine-influenced	Not mine-influenced	Mine-influenced	Not mine-influenced
Specific conductance (µS/cm)	459 ± 263 (44-2421)	183 ± 102 (1-993)	794 ± 502 (150-2689)	125 ± 91 (1-637)
Bromide (mg/l)	0.033 ± 0.078 (0.001-0.612)	0.007 ± 0.006 (0.001-0.025)	0.109 ± 0.186 (0.001-0.91)	0.006 ± 0.005 (0-0.025)
Chloride (mg/l)	24 ± 27 (0-251)	6 ± 5 (0-38)	34 ± 25 (1-139)	3 ± 5 (0-58)
Fluoride (mg/l)	0.23 ± 0.64 (0.05-5.9)	0.09 ± 0.08 (0.03-0.68)	0.19 ± 0.22 (0.03-1.4)	0.07 ± 0.04 (0.02-0.31)
Sulfate (mg/l)	66 ± 91 (5-1100)	7 ± 5 (0-33)	200 ± 214 (1-1343)	3 ± 3 (0-28)

The DFA classifications weighted several of these characteristics more than others (Table 4). Chloride discriminant function coefficients were smaller than the coefficients of other anions when analyzed together except in the case of chloride with just specific conductance and sulfate. Specific conductance had the largest coefficients in the analysis that included all four anions.

Table 4. The magnitude of coefficients of discriminant functions for water quality characteristics for different analyses indicated that chloride was less important for classification than other characteristics for most analyses.

Anions in analysis	Reference (R) or Mine waste (M) class	Constant	Coefficients				
			Specific conductance	Bromide	Chloride	Fluoride	Sulfate
Br^-	M	-66.6	49.4	-106.7			
	R	-38.9	37.7	-95.2			
Cl^-	M	-43.7	33.4		-6.7		
	R	-25.7	27.2		-8.7		
F^-	M	-133.0	76.8			-59.3	
	R	-87.9	59.7			-54.5	
SO_4^{2-}	M	-41.5	26.0				3.5
	R	-21.9	23.0				-5.8
Br^-, Cl^-	M	-69.7	53.7	-89.5	-5.3		
	R	-43.9	43.1	-73.5	-6.7		
Br^-, F^-	M	-93.3	55.8	-35.7		32.8	
	R	-63.9	43.3	-35.1		45.2	
Br^-, SO_4^{2-}	M	-69.4	55.7	-96.1			-6.5
	R	-49.1	49.5	-105.4			-11.7
Cl^-, F^-	M	-146.0	91.2		-11.6	-59.5	
	R	-101.4	74.3		-11.8	-54.7	
Cl^-, SO_4^{2-}	M	-45.0	31.3		-6.9		4.6
	R	-27.3	29.4		-8.3		-4.8
F^-, SO_4^{2-}	M	-132.7	75.5			-60.3	1.1
	R	-91.9	64.4			-55.2	-8.2
Br^-, Cl^-, F^-	M	-94.3	57.8	42.7	-3.1	-35.4	
	R	-66.5	46.6	61.1	-5.0	-34.6	
Br^-, Cl^-, SO_4^{2-}	M	-71.7	58.4	-73.3	-4.7		-5.4
	R	-51.8	52.4	-80.8	-5.1		-10.5
Br^-, F^-, SO_4^{2-}	M	-102.9	71.2	29.0		-35.1	-12.3
	R	-82.0	64.7	20.0		-34.3	-16.8
Cl^-, F^-, SO_4^{2-}	M	-145.8	89.8		-11.6	-60.6	1.2
	R	-105.4	78.8		-11.7	-55.6	-8.0
All four anions	M	-103.2	72.0	38.1	-1.9	-34.9	-12.0
	R	-83.0	65.9	34.7	-3.1	-34.0	-16.2

Extent of mine influence

I found that mining had influenced at least 1435 km of flow paths in the broader study region, and 997 km in the Lake Superior Ojibwe Treaty-ceded Territories. Most of the mine-influenced reaches were within the 1854 Treaty-Ceded Territory, where they represented at least 4 % of all the flow paths in the Territory (Figs. 2, 3). Within the St. Louis River watershed, at least 10% of flow paths were mine-

influenced, including 81% of the length of the river itself (252 km of 311 km; Fig. 2). Most of the length of the main channels of the Escanaba River and the Carp River in Michigan also demonstrated an influence of mining (Fig. 3).

Wild rice and trout waters

Mine influenced waters flowed through several lakes and river sections with recorded wild rice (*manoomin*). These included sites downstream of the Minntac tailings (Sandy Lakes and Sand and Pike Rivers, Lake Vermilion, and Dark Lake); the Embarrass River; Birch Lake and the South Kawishiwi River; Hay Creek and Swan Lake; and the lower St. Louis River (Fig. 2; Vogt 2018). Mine-influenced waters also overlapped with four Minnesota state-designated trout water reaches and multiple designated trout streams in Michigan (Figs. 3)

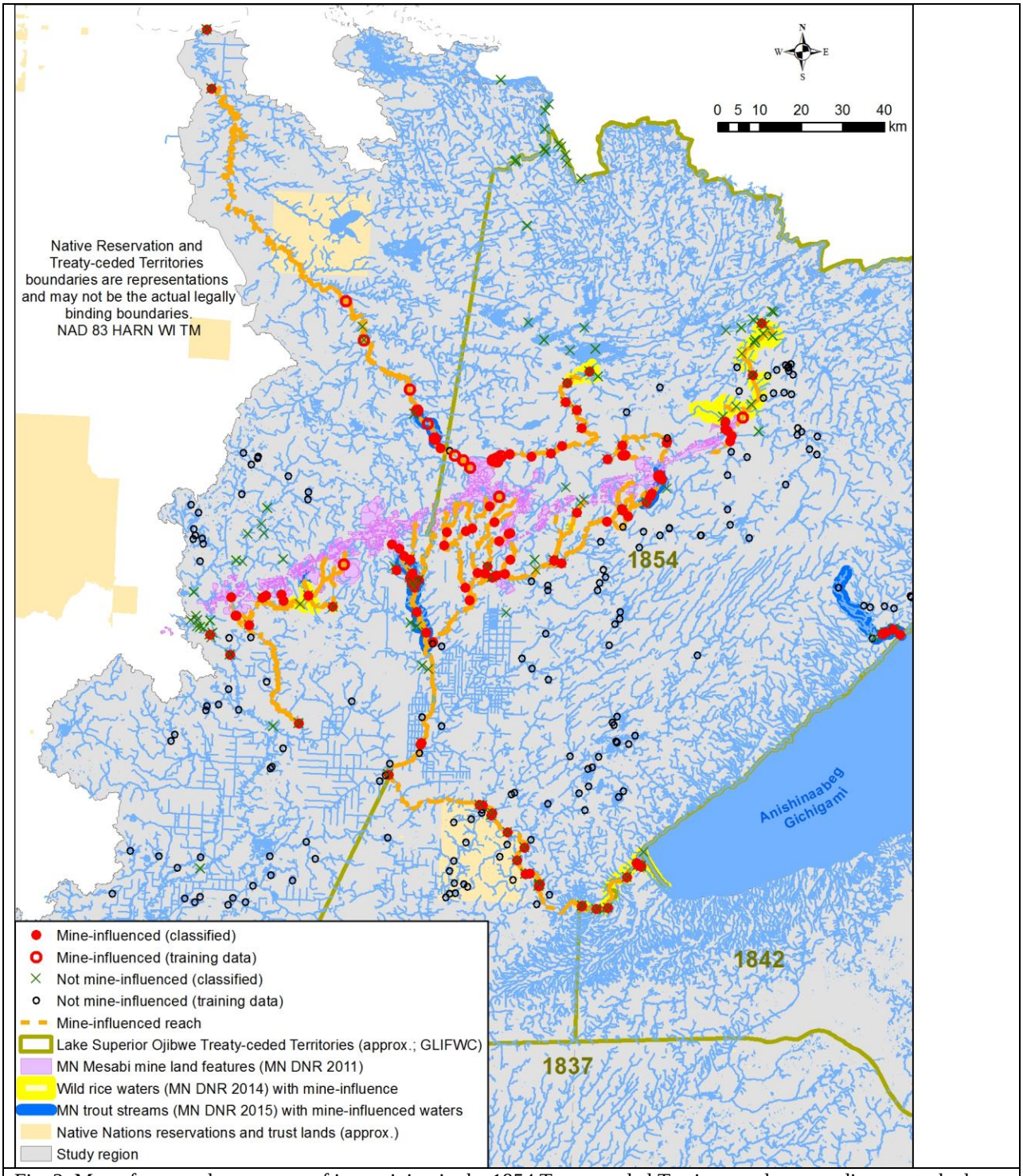

Fig. 2. Map of waters downstream of iron mining in the 1854 Treaty-ceded Territory and surrounding watersheds. Analyses demonstrated mine influence from several sources in the Mesabi Iron Range. Influence extended to the Little Fork River in the north and the St. Louis River Estuary in the south. Mine-influenced waters coincided with several wild rice waters and trout streams.

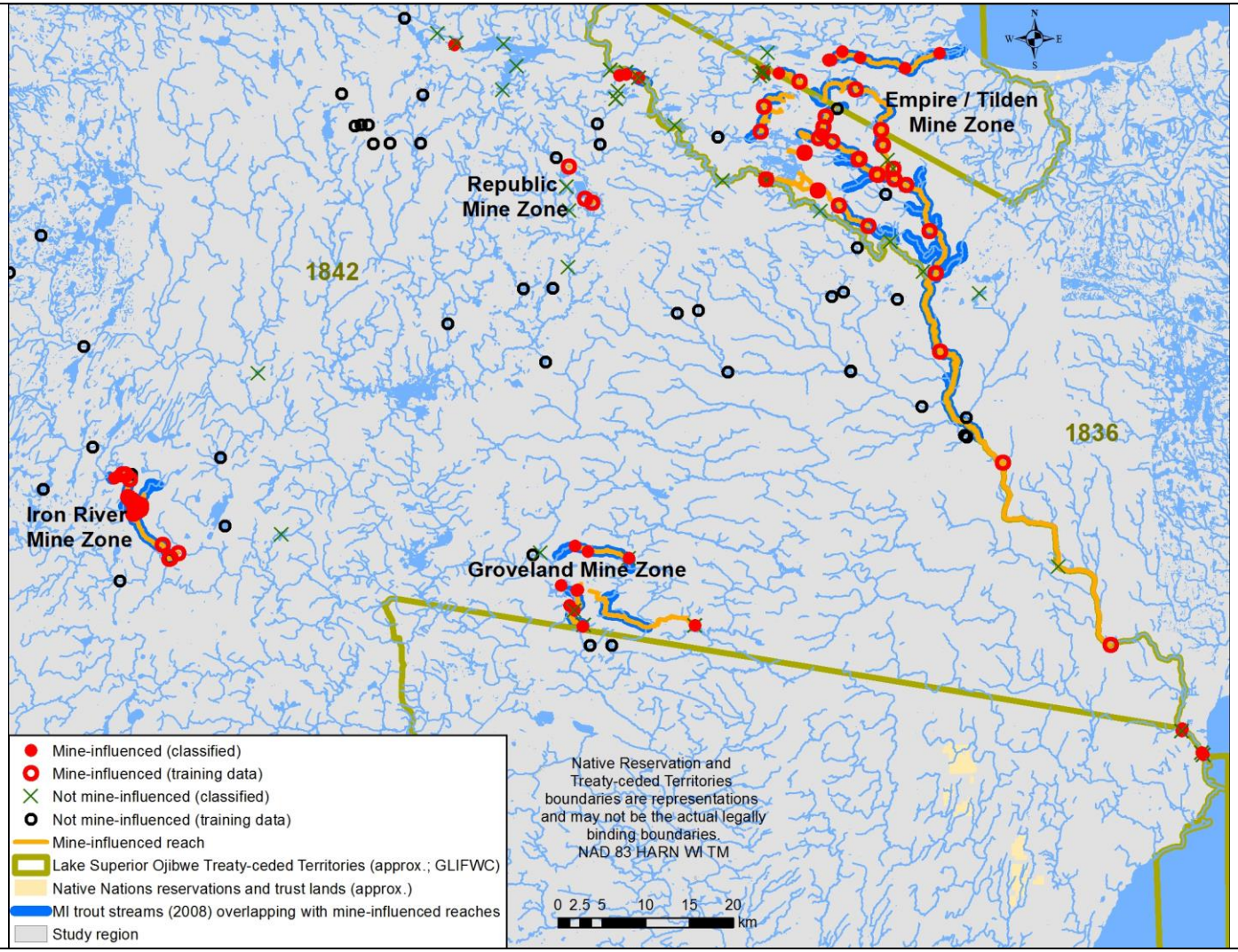

Fig. 3. Map of the waters downstream of iron mining in the 1842 and 1836 Treaty-ceded Territories. Results demonstrated mine influence from around the Empire Tilden Mines in the Escanaba River watershed, old mines in the Carp River watershed, old mines around Iron River, and around the former Republic and Groveland mines. Mine-influenced water coincided with 14 trout streams.

4. Discussion

My mapping of water quality data classified into mine-influenced records and records without mine influence indicated that mine influence on the surface waters was extensive around iron mining ranges in the Lake Superior Ojibwe Treaty-Ceded Territories. I determined that approximately 1000 km of stream and river flow paths were mine-influenced based on data from 2000-2018.

This is most likely an underestimate even though I made several assumptions in modeling the extent of mine influence. I mapped a site as mine-influenced even if the analysis classified only one of multiple records for that site as mine influenced. I also assumed that the upstream reaches from a mine-influenced site were mine-influenced from that point upstream to probable mine sources. Although I included reference sites from throughout the region assessed, it is possible that in some cases un-mined geological deposits influenced the characteristics analyzed but not the reference sites. The analysis may also have conflated influence of other industries with similar discharge characteristics with the influence of mining. Coal-fired power plants discharges, municipal waste water treatment plant discharges, and runoff from chemically-intensive agriculture can include many of the same anions as contamination from taconite mines (Hao *et al*. 2014, Winid 2015). I excluded, however, sites downstream from other known major industries from the mapping of influenced reaches. In spite of such estimation uncertainties, my results are probably an underestimate because of data gaps in many streams and rivers downstream of mining throughout the region. For example, the Shannon, Swan, and upper Partridge Rivers in Minnesota and many smaller streams lacked adequate data, as did the former iron mine zones of the Gogebic Range and zones around Crystal Falls in Michigan.

Some of the reaches that I mapped as mine-influenced may not experience significant impact on aquatic life, but the range of mine-influenced characteristic measurements suggest that in other cases the mine influence represents a concern for aquatic life and human health. High measurements of chloride and fluoride can represent a threat to fish survival and reproduction (USEPA 1988, CCME 2001, CCME

2011). Sulfate, through its reduction to sulfide, is harmful to wild rice and can enhance mercury methylation at moderately high concentrations (Gilmour *et al*. 1992, Jeremiason *et al*. 2006). It can also increase nutrient release from sediment and contribute to eutrophication (Myrbo *et al*. 2017a, b). Bromide is primarily a concern where tailings-influenced water is chlorinated for treatment as drinking water. Such chlorination can cause the formation of carcinogenic trihalomethanes (Flury & Papritz 1993, Regli *et al*. 2015). Iron mines in this region also discharge several other constituents of concern that I address elsewhere (see Chapters 1-2).

Those high concentrations and the extent of mine influence appear to have important implications for Lake Superior Ojibwe treaty rights in the Treaty-ceded Territories. The mine-influenced waters flow into several wild rice waters and the sulfate from the mining may have eliminated some historical wild rice beds. Wild rice is a fundamental part of Ojibwe culture and lifeways (Benton-Benai 1988, Loew 2013), and mining that reduces wild rice availability therefore constitutes a significant concern. Fishing rights may also be impacted by mining and enhanced mercury methylation from sulfate contamination.

Availability of safe drinking water represents a potential impact on Ojibwe rights and human health in the Treaty-ceded Territories. Although availability of drinking water is not explicitly discussed in the Lake Superior Ojibwe Treaties, statements by Ojibwe leaders during negotiations indicated that it was recognized as important to them as a retained right (Van Antwerp 1837 in Satz 1991, Cleland 2000, Loew 2014). The influence of taconite tailings on potential drinking water sources downstream, however, renders them unsuitable as public drinking water sources that would be chlorinated. It is unclear if bromide from tailings in the Mesabi Range, and downstream to Lake Superior, or in the Escanaba River watershed in Michigan, has contaminated existing groundwater or other drinking water sources that may be chlorinated as part of the drinking water treatment.

This work has implications for assessment of cumulative impacts of mining in this and other regions. First, the extent of mining influence approached but did not exceed my study region bounds. This suggests that the selection of a study region for cumulative impacts based on watersheds and that extends far downstream is appropriate for mining of this type (MacDonald 2000). I also found that SVM

and DFA methods resulted in accurate classification of mine-influenced water quality data. The linear DFA without the use of ratios of water quality characteristics provided a more accurate classification for most combinations of anions than did the more complex SVM with the ratios. It also provided an indication of the relative importance of different water quality characteristics in the classification. SVM has performed well in other classifications of water quality data and it has in some cases demonstrated greater accuracy than DFA in ecological studies (Modaresi & Araghinejad 2014, Isazadeh *et al*. 2017, Bourel & Segura 2018). It was, therefore, unexpected that the DFA would be more accurate than the SVM in my study for most characteristic combinations. I included characteristic ratios in the SVM but not the DFA, and it is possible that an SVM without those ratios would have exhibited greater accuracy. At a minimum, this study suggests that the DFA, which is more commonly available in statistical packages, can be adequate for classifying water quality data to determine mine influence.

For cumulative impacts assessment and other assessments, several aspects of my study require further work to refine estimates of mine influence and understand the consequences of iron mine contamination in the Lake Superior Ojibwe Treaty-ceded Territories. Collection of specific conductance and anion water quality data in reaches lacking data would allow for confirmation of mine-influence where I mapped it, and for assessment of mine influence where I lacked necessary data for mapping. That includes numerous old iron mines in the Gogebic Range and near Crystal Falls, Michigan. Future work should also sample for other potential constituents of concern in mining zones (e.g., cadmium, selenium, asbestiform mineral fibers), evaluate groundwater contamination, assess the distribution of drinking water treatment by chlorination relative to bromide-contaminated waters in the region, assess additional classification methods and inputs, and further assess cumulative impacts of mining.

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7. Supplemental Material

Table S1. Additional water quality data sources

Reference	Region	Characteristics
Berndt & Bavin 2012	St. Louis River watershed	Sp. cond., Br^-, Cl^-, F^-, SO_4^{2-}
GLIFWC (Great Lakes Indian Fish and Wildlife Commission) unpublished	Various	Sp. cond., Cl^-, SO_4^{2-}
Kohlhepp 2007	Escanaba River	Sp. cond., Cl^-, SO_4^{2-}
Vogt 2015, 2018	Sand River	Sp. cond., Cl^-, SO_4^{2-}

Table S2. Ion chromatography Method Detection Limits (MDL) for major anions analyzed.

	Year	**F^-**	**Cl^-**	**SO_4^{2-}**	**Br^-**
MDL concentration (mg/l)	2016	0.00835[1]	0.00919	0.0268[2]	0.00528[1]
	2015	0.01676[2]	0.01127[3]	0.0302[3]	0.00162

[1] MDL from 6 samples only (other failed QAQC)
[2] MDL from 5 samples (2 others failed QAQC)
[3] MDL was lower than Minimum Reporting Limit.

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Chapter 4. Developing an index of metallic mining environmental policies for comparison with mine outcomes in Lake Superior states relative to other states in the U.S.

Abstract

Comparisons of mining environmental policy have the potential to help identify policy characteristics that can reduce environmental impacts of large-scale metals mining. A policy index might reflect such characteristics and allow for relative assessment of the potential for environmental impacts across multiple jurisdictions. Previous mining environmental policy comparisons, however, have yet to identify key characteristics, develop such an index, or compare policies with actual impacts in different regions. I analyzed the mining environmental policies in 11 different U.S. states and developed a preliminary Precautionary Environmental Policy Index for Mining (PEPIM) to reflect relative differences in policies between those states. Index results were inversely related to a published measure of mining industry perceptions of the attractiveness to investment in mineral exploration and mining in those states and to the number of active mines, suggesting that the index may reflect processes that may limit mine development or impacts. A separate measure of industry perception of environmental policy for mining was related to published data on regulatory agency budgets and staffing. The relationship between the PEPIM and the number of mines in the states assessed suggested that some of the policies may exhibit properties of regulatory chill or pollution havens dynamics. I also considered alternative explanations and related the policy index to the measured extent of mine influence on surface waters on states around Lake Superior. Further work could refine this index and assess more jurisdictions in order to better contribute to efforts to determine the influence of policy characteristics on mining environmental impacts and identify policies that minimize negative impacts.

1. Introduction

The permitting, construction, and operation of a large-scale mine and the environmental impacts of that mine depend on biophysical and social conditions. Social determinants of impacts include mining corporation practices, community resistance and acquiescence, and government and international financial institution policy (Bridge 2002, 2004, Cooke & Johnson 2002, Sarrasin 2006, O'Faircheallaigh 2009, Kharitonovo *et al.* 2013, Prno & Slocombe 2014). Although not always the dominant factor, government mining regulations and environmental policies also can influence industrial environmental outcomes (Press 2007).

Several studies have investigated differences in government policy on mining with the aim of understanding conditions that encourage or discourage mining or certain mining practices. Many such comparisons have focused on mining law generally (e.g., Naito *et al.* 1999, Bastida *et al*. 2005). Others have analyzed environmental aspects of individual mining laws (Wälde 1992, Campbell 2004, Hámor 2004, Elvan 2013). Additional studies have compared mining environmental law characteristics between jurisdictions (Congressional Research Service 1977, Smith & Naito 1998, Omalu & Zamora 1999, Farrington 2005, Hamilton 2005, McElfish *et al.* 2006, Beeby 2007, Otto 2009, Kempton *et al.* 2010, NWF 2012, IMCC 2013). Previous work, however, has not associated mining environmental policies to particular environmental outcomes.

An index of mining environmental policies could facilitate comparisons between jurisdictions and comparisons with impacts. The Fraser Institute uses an index of mining policy based on a survey of mining industry manager perceptions of mining policy in 91 countries or sub-national jurisdictions around the world (Stedman & Green 2018). Although that index is focused on determining which zones are most attractive for mining exploration investment, it includes generalized aspects of mining environmental policies. A more detailed review and indexing of policies could contribute to understanding of key aspects of policies that may influence mine executive decision-making as reflected in the Fraser index, and also influence mine construction and environmental impacts. Such an index could also focus on

policies that are more precautionary, or that limit the risk of environmental and social impacts (COMEST 2005).

Comparing state laws is potentially revealing because much of mining environmental regulation in the US depends on state policies. Though the Clean Water Act and Clean Air Act require permits and discharge standards for mines, the US Federal Mining Law for federal lands includes few environmental aspects. The Federal government essentially does not regulate mine waste because it was excluded, under the 1980 Bevill Amendment (Solid Waste Disposal Act Amendments of 1980, Public Law 96-482), from the Resource Conservation and Recovery Act (RCRA). Local government policies may also institute zoning and other conditions for mining, but are generally limited and only affect their local area. Variation and innovation in the regulation of mine permitting, monitoring, and reclamation are, thus, primarily the responsibility of individual states.

Studies had yet to formulate a precautionary index of mining environmental policies and relate environmental policy to mine permitting and construction in the US. I sought to provide a preliminary assessment of such an index across the US and relate policy to extent of water quality impacts from mining in the Lake Superior states, where I have assessed the extent of water quality influence from mining.

2. Methods

Precautionary mining environmental policy index

To compare policies and develop a mining environmental policy index, I evaluated mining policy in 11 states in the US with current or recent metallic mines. I reviewed statutes and rules for mining and reclamation and environmental assessment (Table 1). Policies were in transition during evaluation in 2017 for Maine and Wisconsin, and I included the updated policy for Maine but not for Wisconsin. For assessing the state policies, I determined 11 different policy criteria (Table 2) based on previous research

on important policies related to mining impacts (McElfish *et al*. 1996, ELI 1999, Miranda *et al*. 2003, Kempton *et al*. 2010, Elvan 2013). I then scored each state's policies relative to those criteria.

After scoring the policies, I calculated the relative rank of each state for each policy characteristic (value for that state) / (maximum – minimum for that characteristic)). I then calculated the Precautionary Environmental Policy Index for Mining (PEPIM) as the mean relative rank for each state across the multiple policy characteristics (equal weighting of each policy criterion).

Table 1. State statutes and rules reviewed

State	Principal mining statutes	Other statutes	Mining regulations	Other regulations
California	Public resources Div. 2 Chap. 9; Water code Div. 7 Chap 5.7		title 14 div. 2 chap. 8	
Idaho	Title 39-118A, 47		IDAPA 20.03, 51.01.13	
Maine	Titles 5, 12, 36, 38 (MRSA)		DEP chapter 200	
Michigan	324 § 631, 632		R 324, 425	
Minnesota	Chapters 93, 103G.297, 103I.601, 116D.04, 273.1651, 298		6125, 6130, 6132	4410
Montana	Title 82 chap. 4; Title 90 chap. 6	Title 75 chap. 1 (EIS)		Rule 36.2.4 (streambed protection)
Nevada	Chapters 445A.300-445A.730, 519A.010-519A.280 (NRS)		NAC445A, NAC 519A	
Utah	Title 40		R647-4	
Virginia	Title 45.1		4VAC25-31, 35, 40, 130	4VAC25-11, 130 (public participation)
Washington	Chapters 78.44, 78.56 (RCW)	43.21 RCW (SEPA)	WAC 332-18	WAC 197-11 (SEPA)
Wisconsin	Chapters 293, 295		NR 130, 131, 132, 182, 185	

I compared the PEPIM with Fraser Institute measures of mining and exploration company perception of environmental regulations and protected areas policies as not being deterrents to investment (Stedman & Green 2018). Greater numbers for those Fraser Institute measures that I used indicated that the industry sees that policy as favorable, or at least not a deterrent to them (Stedman & Green 2018). I also compared the PEPIM and the Fraser Institute index of mineral potential (Stedman & Green 2018),

which represented the industry's perception of the potentially available geological resources, with the total number of active metal mines in a state (MSHA 2018). To assess the role of enforcement capacity, I tested the relationship of agency staff numbers and most recent available budget (IMCC 2013) with total number of active metal mines and the Fraser Institute ratings for environmental regulations and protected areas policy perception (Stedman & Green 2018). I transformed index proportions (arcsine square root) and the total number of mines ($\log_{10} + 1$) and tested relationships using simple linear regression in SAS 9.3.

3. Results

The state policies examined exhibited a range of properties for most characteristics evaluated (Table 2). The Precautionary Environmental Policy Index for Mining (PEPIM) measures for those states ranged from 0.05 (Nevada and Utah) to 0.66 (Maine). Certain policies were unique in the dataset, such as a ban on open pit gold and silver mining with cyanide (Montana), a backfilling requirement for open pits (California), a requirement for dry-stacking of tailings (Maine), and a ban on open pit mining (Maine). Several states also had a ban on uranium or radioactive ore mining (Maine, Minnesota, and Virginia) and a ban on some form of leach mining (*in situ* leaching in Minnesota, heap/percolation leaching in Maine and Michigan).

Table 2. Measures for each mining environmental policy characteristic and Precautionary Environmental Policy Index for Mining (PEPIM) for 11 states.

Policy characteristic	CA	ID	ME	MI	MN	MT	NV	UT	VA	WA	WI
Number of No-go zones [1]	0	0	15	0	8	1	0	0	0	0	11
Number of natural feature buffers [2]	1	0	3	0	4	0	0	0	1	0	3
Number of ore restrictions [3]	0	0	2	0	1	0	0	0	1	0	0
Number of major mining/processing technique restrictions [4]	0	0	2	1	1	1	0	0	0	0	0
Post-closure monitoring > 20yrs.	0	0	1	1	0	0	0	0	0	0	1
No perpetual treatment	0	0	0	1	0	0	0	0	0	0	0
Backfilling waste or dry-stacking tailings	1	0	1	0	0	0	0	0	0	0	0
Prove-it-first reclamation rule [5]	0	0	0	0	0	0	0	0	0	0	1
Bad actor provision [6]	0	1	0	0	0	1	0	0	1	0	1
EIS requires cumulative impacts assessment, no action alternative, biodiversity inventory	2	0	0	2	2	1	0	0	0	2	1
Bonding is strict (not self-bonding); covers at least 100% of reclamation costs; bond release after 30+ yrs.	2	2	3	1	2	2	1	1	1	2	2
PEPIM	0.30	0.18	0.66	0.36	0.41	0.28	0.05	0.05	0.20	0.18	0.54

[1] No-go zones were zones in which some form of mining is not allowed
[2] Buffers were setbacks that prevented some form of mining within a distance of features such as streams
[3] Ore restrictions included bans on uranium mining
[4] Major mining/processing technique restrictions included a ban on open pit cyanide gold and silver mining
[5] Wisconsin's Prove-it-first provision required companies to show that a sulfide mine had been successfully reclaimed for 10 years. This part of the law was removed in late 2017 but is still included here
[6] Bad actor provisions included policies that prevented companies or individuals that failed to reclaim a mine site elsewhere to obtain permits

The PEPIM was inversely related to the Fraser Institute measure of perception of protected area uncertainty ($P = 0.039$; Fig. 1, Table 3), but was not significantly related to the perception of environmental regulatory uncertainty ($P > 0.05$; Table 3; Stedman & Green 2018). The PEPIM, on the other hand, was significantly inversely related to the total number of metals mines in a state ($P = 0.027$; Fig. 1, Table 3). The Fraser Institute perceived Mineral Potential Index, however, explained more of the variation in the number of mines ($R^2 = 0.51$; Fig. 2) than did the PEPIM ($R^2 = 0.44$; Fig. 1).

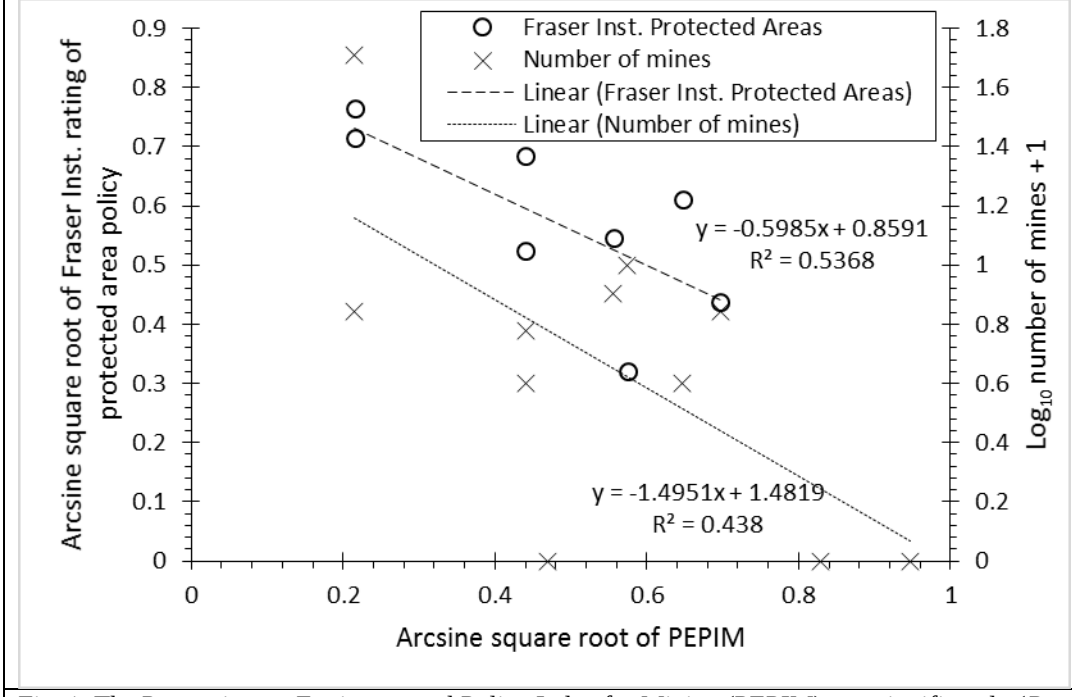

Fig. 1. The Precautionary Environmental Policy Index for Mining (PEPIM) was significantly (P = 0.039) inversely related to the Fraser Institute rating for mining management perception of protected area policy uncertainty as not being deterrents to exploration investment (Stedman & Green 2018). The PEPIM was also significantly (P = 0.027) inversely related to the total number of active metal mines (MSHA 2018).

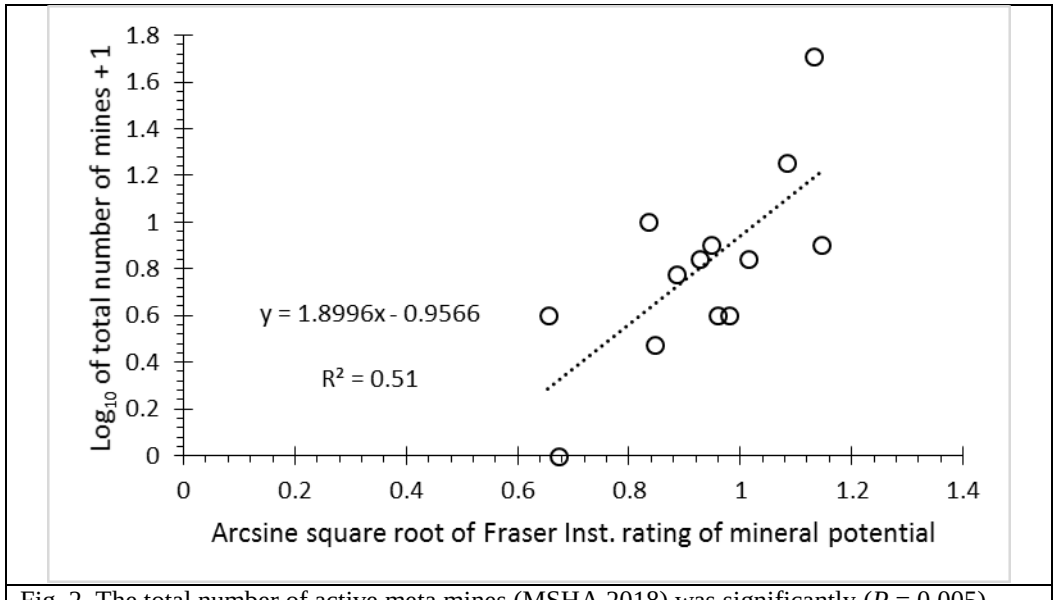

Fig. 2. The total number of active meta mines (MSHA 2018) was significantly (P = 0.005) related to the Fraser Institute rating of state mineral potential (Stedman & Green 2018).

Table 3. Number of mines in states assessed in the Fraser Institute survey, Fraser Institute measurements, and the Precautionary Environmental Policy Index for Mining (PEPIM) for 11 of those states.

State	Number of active mines (MSHA 2018)			Fraser Institute mine investment perception measures (Stedman & Green 2018)			Precautionary Environmental Policy Index for Mining
	Iron	Non-ferrous metallic	Total metallic	Envtl. regulatory uncertainty as not a deterrent	Protected areas uncertainty as not a deterrent	Mineral Potential Index 2017	
Alaska	0	7	7	34	28	83	
Arizona	0	17	17	47	45	78	
California	2	7	9	10	10	55	0.21
Colorado	0	3	3	27	29	69	
Idaho	0	5	5	43	40	60	0.18
Maine	0	0	0				0.52
Michigan	2	1	3	44	33	67	0.27
Minnesota	6	0	6	27	18	64	0.39
Montana	0	7	7	19	27	66	0.20
Nevada	0	50	50	46	48	82	0.00
New Mexico	0	2	2	47	47	56	
Utah	0	6	6	32	43	72	0.00
Virginia	0	0	0				0.10
Washington	0	3	3	31	25	37	0.19
Wisconsin	0	0	0				0.42
Wyoming	0	0	0	22	44	39	

Unlike the PEPIM, enforcement capacity as estimated with agency staff numbers and budget (IMCC 2013) was significantly ($P < 0.05$; Figs. 3-4) inversely related to the Fraser Institute ranking for environmental regulations not deterring investment (Stedman & Green 2018). Enforcement capacity, however, was not significantly related for protected area policy ($P > 0.05$).

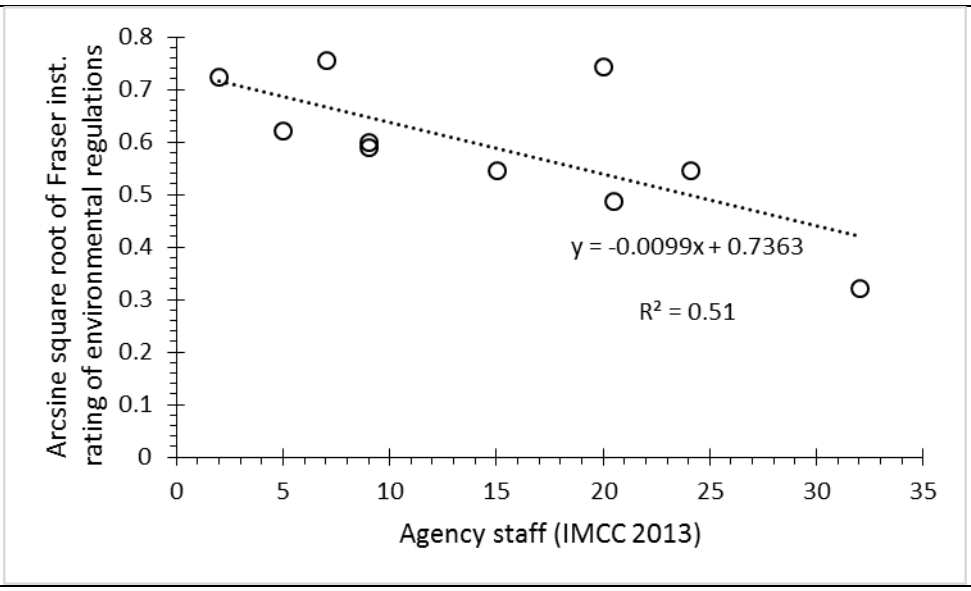

Fig. 3. The Fraser Institute rating of the perception of environmental regulations as not deterring investment (Stedman & Green 2018) was significantly (P = 0.019) inversely related to an estimate of agency staffing (IMCC 2013).

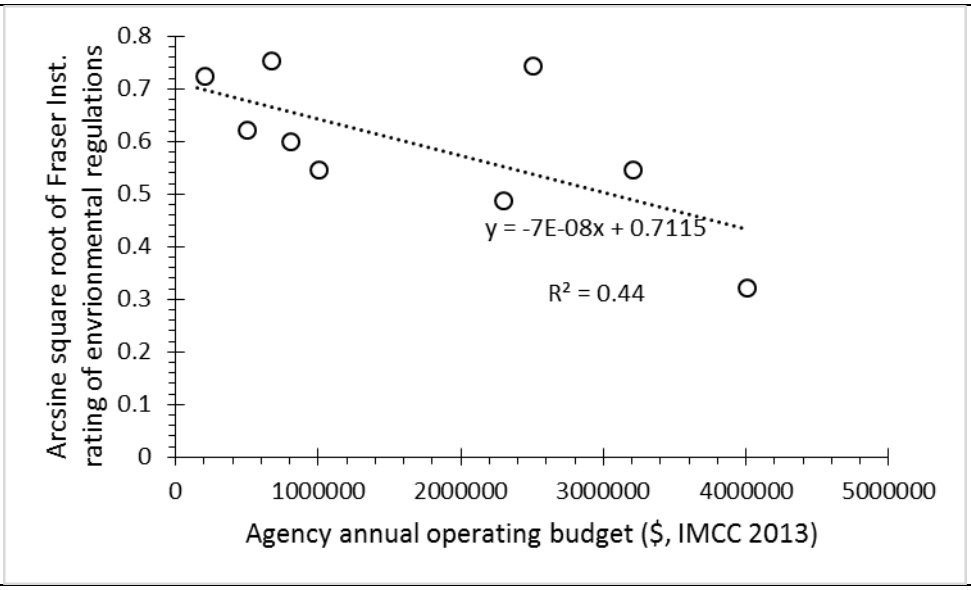

Fig. 4. The Fraser Institute rating of the perception of environmental regulations as not deterring investment (Stedman & Green 2018) was significantly (P = 0.049) inversely related to estimates of regulating agency annual budget (IMCC 2013).

4. Discussion

My analysis of state mining environmental policies indicated that the PEPIM of key policy characteristics was inversely related to a mining company management perception of state policies as

non-deterrent to investment and inversely related to number of metallic mines in those jurisdictions. This suggests that the sets of precautionary policies I assessed are also the policies that mining companies consider, or are correlated to other polices that they consider. The inverse relationship of my index with the number of mines suggests that regulatory chill (Neumayer 2001, Clapp 2005, Shoaf 2013) or pollution haven effects (Clapp 2002, Kearsley & Riddel 2010) may be influencing the number of mines in some of those states. This could be the case for Michigan, which had a moderately low PEPIM and several metals mines. Conversely, the precautionary policies may either deter potential companies from conducting mineral exploration in those regions, or may reduce the likelihood of compliance with regulations and likelihood of successfully building a mine in those regions. This could have been the case for Wisconsin, which had no active metal mines and a relatively precautionary policy at least until 2017. Wisconsin policy has changed since my assessment of the early 2017 policy to be less precautionary, and mining industry may be developing renewed interest in Wisconsin ore bodies as well. Exceptions to that pattern of fewer mines with more precautionary policy, and vice versa, may include Minnesota and might be indicative of jurisdictions developing more precautionary policies after experiencing development and impacts of many mines.

Several alternative processes could, however, also explain those relationships. States with less geological potential for development of many mines may be more likely to enact policies with more regulation of mining if a project arises. Many other factors also affect the development of a mine at a given site (Bridge 2002, 2004, Cooke & Johnson 2002, Sarrasin 2006, O'Faircheallaigh 2009, Kharitonovo *et al.* 2013, Prno & Slocombe 2014). Geology is an important driver (Stedman & Green 2018) and the mining industry perceptions of mineral potential explained the total number of mines in this study better than the PEPIM did. Policy in statutes may also differ from implemented policies because of judicial rulings. Enforcement also influences mines and impacts, as the inverse relationship between number of agency staff and their budget with perceived deterrent effect of environmental regulations suggests. Finally, civil society organizations and social concern are important factors that relate to individual mine development, policy, and enforcement (Kirsch 2014). Social movements that may

oppose a particular mining project might also successfully advocate for additional policies regulating mining, but the public opposition to individual projects may represent a stronger dissuasion than the policies.

Additional work related to these policies could help clarify the influence of policies on mine construction and impacts. Such work could assess additional state policies, policy characteristics such as options for public opposition to projects in hearings and civil suits, cumulative mining impacts, and rates of application approval. Additional policies to assess should include the role that states accord to Native Nations with territories or reservations in those states. Analysis that accounted carefully for what policies were in place when mines received permits would also assist with that effort. Indeed, mine permitting and construction may take many years and may occur after under a different policy than when mineral exploration began (Kharitonova *et al*. 2013). Local policies and the policies of Native Nations may also have a strong influence on mine development and impacts, could include innovative approaches, and should receive research attention as well.

In the Lake Superior zone, the PEPIM index does not appear to relate directly to an assessment of the extent of mine-influenced surface waters (Chapter 2). Those impacts increased in the order WI < MI < MN, and yet the PEPIM increased in the order MI < MN < WI. Although Wisconsin thus had the smallest extent of impacts and the more precautionary policy based on that index, Minnesota had ranked higher for its policy than I might have expected based on the extent of mine-influenced water (Chapter 2). Michigan, however, also has active or recent and many historical non-ferrous metallic mines (Kerfoot *et al*. 2018) and I did not assess the influence on water of those sites. Including the extent of those mine-influenced waters and looking at the percent of waters that are mine-influenced could provide additional insight into those relationships. The Wisconsin policy assessment should also be updated after changes that occurred in December 2017.

The Fraser Institute presents its survey as a “report card” on the attractiveness of policies to mineral exploration and mining (Stedman & Green 2018). My preliminary development of a

precautionary environmental policy index suggests that such an index could also serve as a "report card" for those who would like jurisdictions to adopt more environmentally and socially precautionary policies.

5. Acknowledgements

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Conclusion

This work has contributed to the understanding of methods to evaluate cumulative impacts of mining, of how water quality impacts relate to mining land cover, and of the constituents and extent of water contamination from large-scale iron mining in the Lake Superior Ojibwe Treaty-ceded Territories. My water quality analyses validated the study zone extent selected for cumulative impacts assessment for such large-scale mining. The Escanaba River study also demonstrated a relationship between mine land cover and selenium and other contamination from mining that may assist in modeling the consequences of expansion of mine land cover. Using trace elements laboratory methods that can detect ultra low concentrations, as well as the use of multiple statistical analyses, helped identify contaminants associated with mining. In addition, the broader study of the extent of mine-influenced waters suggested some promising water quality classification approaches for cumulative impacts assessment. My water quality assessments also revealed extensive contamination downstream from mining with selenium, bromide, sulfate, and other contaminants. Such contamination threatens fisheries and wild rice waters that are of critical importance to Lake Superior Ojibwe culture and lifeways. Because of that as well the influence of mining on the availability of clean drinking water, iron mining represents a concern for Lake Superior Ojibwe Treaty rights.

My analysis of state mining policies found relationships of a precautionary index with number of mines and an industry assessment of mining policy. Such policy assessments have the potential to indicate how mining policies influence mine construction and impacts. Additional work could refine the precautionary policy index and render it more useful for indicating which particular policies can help minimize mining impacts.

Other future work should add to and synthesize the growing data set on cumulative mining impacts in this region. As regulators continue to permit or consider permitting new mines in the region, thorough evaluations of mining impacts on water quality, land cover, air, and Ojibwe rights are urgently required to inform decision-making.

Appendix A. Summary of potential effects of water quality constituents referred to in this work on human health and other organisms.

Toxic effects are based on data from exposure in water or ingestion unless noted otherwise (e.g., air). Aquatic plants, invertebrates, and fish are primarily freshwater species unless otherwise noted. Actual toxicity in a given system depends on factors that include the dose, biological characteristics (e.g., species, development stage), physical conditions (e.g., temperature), and chemical conditions (e.g., pH, DOC, alkalinity, hardness, other synergistic or antagonist compounds). Adverse effects in addition to those listed here may also occur.

Constituent	Potential effects on human health	Potential effects on other organisms
Aluminum	Possible links to Alzheimer's disease and bone or brain disease if kidney already damaged; nervous system effects (lab animals); lung effects (air) [1].	Fish weight loss, olfaction impairment, and mortality; invertebrate reduced reproduction and survival; amphibian embryo malformation, reduced hatching, and mortality; algae/plant reduced growth, and mortality. Bioaccumulates.[2] [3] [4]
Antimony	Increased cholesterol and decreased sugar in blood.[5] Vomiting, anemia, cardiovascular problems; eye, lung, skin, heart, stomach effects (air); liver damage and fewer red blood cells (lab animals).[6] Possible carcinogen as Sb_2O_3.[7]	Reduced growth of aquatic plants/algae; mortality of fish and invertebrates. [8]
Arsenic	Carcinogen (skin, lung, liver, bladder lymph…). [9] [10] [11] Vomiting, diarrhea, decreased blood cell production (and related fatigue, abnormal heart rhythm, blood vessel damage, impaired nerve function), diabetes, skin dark/wart patches, death; possibly lower child IQ. [12]	Fish reduced growth and survival; amphibian embryo malformation and mortality; invertebrate reduced growth, reproduction, mobility, and survival; plant reduced growth; mammal behavior changes, development defects and embryo mortality, and adult mortality; bird behavior changes, seizures, and mortality. Bioaccumulates. [13] [14]
Asbestos	Carcinogenic. [15] [16]	
Boron	Gastrointestinal, liver, kidney, and brain adverse effects, and death (large dose); male reproductive impairment (lab animals); nose, throat, eye irritation (air).[17]	Fish development impairment and mortality; amphibian development and reproduction impairment, and mortality; invertebrate growth and reproduction impairment and mortality; mammal reduced growth, reproduction, and survival; bird development and growth impairment, and mortality; and plant/algae growth inhibition. Bioaccumulates.[18] [19]
Bromide	Water with high bromide concentrations, if chlorinated and reacting with organic carbon, can form carcinogenic brominated disinfection byproducts; ozone-treated wastewaters may form carcinogenic bromate.[20]	

Cadmium	Carcinogen.[21] [22] Vomiting, diarrhea, lung damage, kidney damage, fragile bones, death.[23]	Fish deformities and altered behavior, and decreased weight, growth, reproduction, and survival; amphibian embryo deformities and reduced weight; invertebrate decreased feeding, growth, biomass, reproduction, mobility, and survival; mammal blood changes, embryo deformities, and mortality; bird reduced growth, impaired reproductive and cardiovascular function, and hyper-responsiveness; algae/plant decreased growth, and chlorosis. Bioaccumulates. [24] [25] [26] [27]
Chromium	Carcinogen (VI, air).[28] [29] Allergic dermatitis. [30] Breathing problems (air); gastrointestinal irritation & ulcer, anemia, male reproductive system damage (Cr (VI)).[31]	Plant/algal reduced growth; invertebrate altered movement, and reduced growth, fecundity, and survival; fish altered movement and metabolism, and reduced growth and survival; mammal kidney damage, embryo deformities, and mortality; bird embryo deformities and mortality; (most effects from Cr (VI)). Bioaccumulates. [32] [33]
Chloride		Fish reduced embryo viability and mortality; amphibian mortality; invertebrate reduced growth, weight, reproduction, and increased immobilization and mortality; algae mortality; plant decreased growth. Bioaccumulates.[34]
Cobalt	Possible/reasonably anticipated to be a carcinogen. [35] [36] Lung damage (air); thyroid effects; heart, liver, kidney, blood, testes effects (lab animals); (radiation damage radioactive Co).[37]	Reduced growth and survival of invertebrates in particular, and also algae and fish.[38]
Copper	Vomiting, diarrhea; liver and kidney damage, death (high dose); mucous membrane irritation, headaches, nausea, diarrhea (air). [39] [40]	Fish liver and skin problems, gill damage, olfactory organ/receptors damage, disrupted migration pattern and behavior, embryo deformities, impaired reproduction, reduced feeding and survival; amphibian reduced hatching and embryo survival; invertebrate impaired movement and reproduction, and reduced feeding, growth, and survival; plant/algae reduced growth and survival; mammal liver, kidney, and brain damage, impaired male reproduction, and reduced growth and survival (high doses); bird reduced growth, weight, and survival (high doses). Bioaccumulates (and may biomagnify in marine systems). [41] [42] [43] [44]
Fluoride	Skeletal fluorosis (denser, fragile bones, & joint problems); vomiting, diarrhea, heart effects, death (large dose).[45]	Fish migration pattern disruption, reduced survival; invertebrate reduced reproduction and survival; algae reduced growth.[46]
Iron		Fish reduced hatching; invertebrate reduced growth and survival. [47]

Lead	Possible/probable carcinogen. [48] [49] Neurological damage, weakness in extremities, high blood pressure, anemia; brain and kidney damage, miscarriage, premature birth, low birth weight, male reproductive damage, death (high doses); child developmental impairment, blood & behavior effects.[50]	Fish anemia, altered pigmentation, spinal deformities, inhibited reproduction, reduced stamina and survival; amphibian skin sloughing, sluggishness, anemia, reduced survival; invertebrate reduced reproduction, mobility, and survival; mammal impaired learning, altered behavior, visual impairment, motor nerve problems, reduced growth, impaired nervous, gastrointestinal, muscular, and blood production systems, mortality; bird impaired mobility and balance, lethargy, reduced feeding, damage to nervous system, kidneys, and liver, muscular paralysis, mortality; (organoleads more toxic). Bioaccumulates. [51] [52]
Manganese	Child brain development impairment; slow, schizophrenia-like disorder, muscle control problems (manganism), male reproductive system damage, pneumonia (air, large dose); behavior changes, kidney, urinary tract, & sperm damage, impaired female fertility (lab animals).[53]	Decreased invertebrate and fish growth and survival. Decreased mammal motor performance.[54]
Mercury and methylmercury	Possible carcinogen (methyl-Hg). [55] Vomiting, diarrhea, ulcers, increased blood pressure & heart rate, brain & kidney damage, child development impairment; irritated lungs & eyes, mouth & lung lining damage (air); immune, nervous, & reproductive system adverse effects (mostly lab animals).[56]	Fish behavior change, deformities, reduced feeding, growth, and reproduction, brain lesions, weight loss, cataracts, sluggishness, loss of equilibrium, and mortality; amphibian delayed development, mortality; invertebrate reduced reproduction and survival; mammal loss of appetite, neurological impairment, embryo defects, stillbirths and mortality; plant/algae reduced growth, diversity, and survival; bird reduced activity and coordination, impaired growth, development, and reproduction, and mortality. Organomercury more toxic. Bioaccumulates and biomagnifies. [57] [58] [59]
Molybdenum	Gout-like disease, weakness, head, gastric, and joint pain, renal calculi (kidney stones; high doses). [60]	Fish egg mortality (trout), mortality (high concentrations); invertebrate immobilization and mortality (high concentrations); mammal copper deficiency, reduced growth and reproduction, bone abnormalities, joint lesions, loosening and loss of teeth (particularly cattle, for high doses); bird inhibited growth and reproduction, anemia, and mortality (high doses). Bioaccumulates (algae, invertebrates). [61] [62]
Nickel	Possible/probable carcinogen (air). [63] [64] Allergic skin rash, stomach ache, kidney & blood changes; bronchitis, reduced lung function (air).[65]	Fish gill damage, impaired reproduction, equilibrium loss, convulsions, mortality; amphibian malformations; invertebrate reduced growth, reproduction, and survival; algae reduced growth; mammal chromosomal aberrations, malformations, pancreatic damage, reduced growth and reproduction, testicular damage, mortality; bird malformations, reduced growth and survival.[66]

Nitrate	Methemoglobinemia from reduced oxygen-transporting hemoglobin; possible thyroid dysfunction; possible link to childhood diabetes; possible birth defects. Probable carcinogen as nitrite in combination with amines/amides (conditions that result in endogenous nitrosation).[67]	Fish methemoglobin formation (and consequent liver problems, inhibited "cough response," blood and kidney damage, reduced swimming speeds, anoxic death); invertebrate and amphibian methemocyanin and methemoglobin formation. Fish, amphibian, and invertebrate deformities, reduced embryonic/larval growth, or survival. Can also cause eutrophication of freshwater bodies with low N:P.[68]
Phosphorus		Eutrophication of freshwater bodies.[69]
Selenium	Selenosis (brittle hair, deformed nails, loss of feeling in arms and legs, etc.); at high levels risk of amyotrophic lateral sclerosis/neurodegenerative effect, diabetes, endocrine disruption, possibly some cancers; reproductive effects (lab animals); mucous membrane irritation, fatigue, dizziness, pulmonary edema, bronchitis (air).[70] (possible carcinogen as SeS_2) [71]	Fish avoidance, chromosomal aberrations, deformities, edema, reduced growth, and death; bird deformities, reduced growth and reproduction, and death; algae reduced growth and species shifts; invertebrate reduced swimming and death; amphibian death; mammal selenosis, behavior change, skin lesions, malformations, impaired reproduction, death; bioaccumulates and probably biomagnifies.[72]
Sodium	Hypertension. Additional harmful effects at high doses.[73]	May reduce salmonid growth (as NaCl, relative to $MgCl_2$ and $CaCl_2$). Can cause invertebrate mortality at high concentrations, depending on calcium and anions. May contribute to changes in seasonal mixing of lakes and resulting changes in plankton communities.[74]
Sulfate	Enhanced methylation of mercury may results in increased methylmercury exposure for humans.[75]	Sulfate as sulfide in sediment enhances methylation of mercury, releases nutrients to sediment and may contribute to eutrophication, and is harmful to wild rice.[76]
Strontium	Bone growth problems & possible breast cancer risk; weak bones (lab animals); (decreased blood cells, leukemia & other cancer risk for radioactive ^{90}Sr, a carcinogen).[77] [78] [79]	Fish and amphibian mortality.[80] [81]
Thallium	Hair loss, skin effects, gastroenteritis, pains, blindness, probable reproductive system adverse effects, cardiac and nervous system damage, death; reproductive system damage (lab animals).[82]	Plant reduced growth & mortality; fish amphibian and invert mortality; mammal hair loss, reproductive effects & mortality; bird develop. effects. Bioaccumulates.[83]
Tungsten	Possible effect on immune system (lab animals). Possible link to pulmonary fibrosis (air).[84]	At high concentrations, fish and invertebrate mortality and reduced algal growth, particularly for polytungstates.[85]
Uranium	Kidney damage; neurobehavioral effects (lab animals); respiratory tract damage (air). [86] (decay products include carcinogens).	Mammal kidney damage. Fish kidney and liver damage, decreased growth and reproduction, and increased mortality. Invertebrate digestive organ damage, inhibited growth and reproduction, and

		increased mortality. Algae inhibited growth. Bioaccumulates. (potential radiological damage, particularly from decay products).[87]
Vanadium	Stomach cramps, diarrhea, possible cause of Parkinson's Disease; decreased red blood cells, increased blood pressure, birth defects, neurological and development effects (lab animals).[88] [89](possible carcinogen as V_2O_5) [90]	Fish mortality.[91] Plant reduced growth and chlorosis.[92]

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