

regarding cyanide levels, but did not address the high nitrate concentrations left in the heap effluent from the degradation of cyanide.

1993 EA

According to the EA, iron sulfides including pyrite, pyrrhotite and marcasite were identified in the ore. Geochemical characterization tests performed include paste pH, total sulfur, ABA, leachate extraction tests and long-term field-based leachate extractions. Constituents of concern identified included cadmium, fluoride, sulfate, zinc, low pH, nitrate and arsenic. Major ores being mined contained both oxide and sulfide rock.

The EA identified mitigation including properly engineered caps over reclaimed dumps and heap leach pads. Pump-back systems were proposed to reduce impacts to groundwater by collecting acidified water below Sullivan Park dike and routing it into the pump-back system. A water treatment plant was required to be constructed at the Zortman Mine to treat mine drainage from both mines. The treatment plant was brought online in 1994. Slurry cutoff walls below the dike were proposed to reduce the volume of acidic water bypassing the contingency pond. Perforation of the leach pad liners would be delayed until leach pad seepage meets water quality standards. Diversion structures were designed to withstand 6-inch, 100-year, 24-hour storm events. Leach pad underdrains will capture water that is pumped to the contingency pond and not discharged to surface waters but directed to the processing circuit.

1996 EIS

Geochemical characterization tests performed include total sulfur, paste pH, ABA, kinetic testing (both long term and short term) and humidity cell tests for ore and waste rock, and cyanide speciation analysis. The HELP model was used to predict infiltration rates. Constituents of concern identified included cyanides, sulfate, TDS, nitrate and metals. Static tests performed on Zortman and Landusky ores showed a strong potential to generate acid. For both mine sites, waste samples having negative NNP's were considered potentially acid generating. At Landusky, short-term increases in TDS, sulfate and metals concentrations were predicted to occur at Sullivan Creek, Mill Gulch and Montana Gulch due to the lack of diluting water, but the loads were expected to be reduced rapidly.

Mitigation identified included segregating acid-generating waste from non-acid generating waste and using a combination of "water barrier" and "water balance" reclamation covers. Most of the historic mine workings would be removed by extended mining of Zortman pits. Old adits would be bulkheaded where exposed in the pits to minimize oxygen flow and discharge of transient water. A water quality improvement plan would be implemented. Capture systems, cutoff walls and recovery wells would be used to intercept poor quality surface water. Existing waste rock dumps would be removed and used as backfill material for pits. The Zortman pit complex was proposed to be backfilled with waste rock to an elevation necessary to drain freely into Ruby Gulch and Alder Spur, thereby reducing the potential for groundwater discharge to the north. Water treatment of collected groundwater and surface water for cyanide, nitrate, acid drainage, metals and other constituents would be implemented as required. The EIS predicted that the volume of acid drainage that would need water treatment over the next 20 years would be between 211 and 419 gpm. In 2005 the Zortman and Landusky water treatment plants treated at an annualized average of 490 gpm.

2001 EIS

According to the 2001 supplemental EIS, iron and iron/arsenic sulfides are present in the igneous intrusion responsible for the orebody. Carbonates exist in the area, but not in the ore deposit itself. Additional geochemical characterization tests were performed including paste pH, paste TDS, and ABA. Constituents of concern identified included sulfate, low pH, iron, aluminum, zinc, arsenic, copper, cadmium, cyanide and nitrate. It is expected that eventually most sources at the site (leach pads, waste rock, pits) have significant potential to generate acid drainage and to leach metals and other contaminants, although some units are not presently generating acid drainage. Water quality was generally expected to become acidic and have increased sulfate concentrations. The potential for infiltration of contaminated water to impact deeper groundwater was considered low due to surface water/groundwater interaction (groundwater losing to surface water in all cases) at higher elevations.

Mitigation included consolidation and backfilling of acid-generating waste, water barrier liners, water balance reclamation covers and revegetation to significantly reduce impacts to groundwater and surface water quality in the various drainages. Water treatment plants (lime precipitation with additional arsenic treatment) at the Zortman and Landusky mines would be used to treat water in perpetuity. Short-term biological treatment was also proposed to reduce cyanide, selenium and nitrate levels for leach pad waters being discharged.

According to the EIS, downgradient water quality predictions showed a wide range of possible concentrations. Therefore, continued monitoring and provisions for supplemental capture and treatment were proposed to prevent significant impacts to water quality. Spent ore on the L87/91 pad is expected to be a significant source of acid generation in the future. Water quality impacts in the northern drainages were predicted to increase if the acid generating material from the L87/91 pad was placed as pit backfill in the headwaters of these drainages. Concentrations of most contaminants from the Landusky Mine were predicted to increase over time. Pit backfilling was expected to increase loads of contaminants in the short term due to the disturbance of acid-generating material, the re-establishment of flowpaths and mobilization of soluble oxidation products (metal-sulfate salts).

6.3.17.2. ACTUAL WATER QUALITY CONDITIONS

1993 EA

Acid has developed from waste rock dumps and ore heap retaining dikes. The flow of acidic water from the toe of the dump and observed venting of sulfurous steam from portions of the dump are manifestations of the sulfide oxidation reactions occurring within the dump. Mill Gulch waste dump has generated acid drainage with pH periodically dropping as low as 3.9. Based on field inspections, BLM and DSL found that approved operating and reclamation plans were not preventing acid drainage. Mill Gulch and upper Sullivan Creek have become acidic as a result of pyrite oxidation in waste rock placed in Mill Gulch Waste Dump, the Sullivan Park dike, and possibly places within the excavated foundation of the 1991 leach pad. Surface water monitoring sites in Sullivan Creek were impacted by acid drainage from the 1991 leach pad, with pH between values between 2.6 and 2.8. Groundwater samples downstream of the Sullivan Park dike indicate that sulfate concentrations in the alluvial groundwater near the facility have increased.

1996 EIS

Acid drainage is currently being generated from pit walls and floors, leach pads and pad foundations, and waste rock piles.

2001 EIS

Acid drainage with metals, metalloids, nitrate and cyanide is common in groundwater at the site and is impacting surface water quality. Capture and treatment of discharges is effective at reducing discharges to below regulatory standards except for arsenic (treatment method is effective but was not always employed by Pegasus).

Recent Water Quality Monitoring Data

Recent (through 2005) surface water quality monitoring data from Montana DEQ indicates the 2001 EIS was correct in identifying mitigation and improving groundwater quality and protecting surface water quality. The notable exception has been in Swift Gulch where surface water quality has worsened, with higher sulfate and metals concentrations. Characterization of the source of Swift Gulch contamination has been difficult and has made identification of potential mitigation measures problematic.

6.3.17.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.22 provides a summary and comparison of potential, predicted and actual water quality information for the Zortman and Landusky mines. The accuracy of the predictions is discussed in this section.

Table 6.22. Zortman and Landusky, MT, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impacts	Mitigation	Predicted Impacts	Actual Impacts
Groundwater and Surface Water	Heap Leach Piles, Open Pit, and Waste Rock Dumps	• 1979 EIS: only oxide ore and no potential identified other than cyanide • 1993 EA: potential for impacts from acid drainage including pH, sulfate, Cd, F, Zn, As, and nitrate. • 1996 EIS: strong potential to generate acid drainage and high TDS, sulfate and metals values • 2001 EIS: high potential to generate acid drainage with pH, sulfate, metals, metalloids, cyanide and nitrate.	• 1979 EIS: only oxide ore to be mined; stormwater controls and liners to prevent cyanide seepage • 1993 EA: reclamation caps (water barrier); groundwater capture and treatment for acid drainage and cyanide, stormwater controls. • 1996 EIS: waste segregation; water balance and water barrier reclamation covers; groundwater and surface water capture and treatment for cyanide, nitrate, acid drainage, metals and other contaminants • 2001 EIS: waste consolidation; reclamation covers, water capture and perpetual treatment	• 1979 EIS: no water quality impacts predicted • 1993 EA: no additional water quality impacts predicted • 1996 EIS: reduced water quality impacts predicted • 2001 EIS: Contaminants to increase over time but surface water quality expected to meet standards. Concentrations of most contaminants from the Landusky Mine are going to increase over time. Pit backfill expected to increase loads of contaminants in the short term due to the disturbance of acid generating material, the re-establishment of flowpaths and mobilization of 'soluble oxidation products'	1993 EA: acid drainage from waste rock dumps and heap leach retaining dikes. Surface water impacted by acid drainage with pH 2.6-2.8. Increased sulfate in groundwater • 1996 EIS: multiple 100+-yr storm events; extensive groundwater and surface water contamination with acid drainage and metals/metalloids, nitrate, cyanides • 2001 EIS: acid drainage with metals, metalloids, nitrate, cyanide common throughout groundwater and in surface water

Low pH and elevated sulfate concentrations in surface water and groundwater: The 1979 EIS indicated no potential for contaminants other than cyanide, based only on oxide ore being mined. The potential for development of acid drainage and groundwater and surface water impacts from acid drainage was not acknowledged in the 1997 EIS. The 1993 EA identified the potential for impacts from acid drainage, sulfate, metals, arsenic and nitrate. Acid drainage from waste rock dumps and heap leach retaining dikes was already impacting groundwater and surface water, but no additional water quality impacts were predicted as a result of capture and treatment. The 1996 EIS indicated strong potential for acid drainage from waste rock and high TDS, sulfate and metals values. Multiple 100+-year storm events led to impacts to surface water and groundwater from acid drainage associated with both waste rock both in dumps and used as leach pad base material. Reduced impacts on water quality were predicted. The 2001 EIS

indicated a high potential to generate acid drainage from waste rock with pH, sulfate, metals and metalloids along with cyanide and nitrate. Metals and metalloids, nitrate and cyanide are common in groundwater and surface water, and contaminants were expected to increase over time; however, surface water quality was expected to be protected.

6.3.18. FLORIDA CANYON, NEVADA

The Florida Canyon Mine, owned by Florida Canyon Mining Company (parent company was formerly Pegasus Gold and now Apollo Gold), has been in operation since 1986. The primary commodities mined are gold and silver from open pit mining and heap leach processing operations. It disturbs 2,149 acres on BLM land. It has a current financial assurance amount of \$16.9 million.

6.3.18.1. WATER QUALITY PREDICTIONS SUMMARY

NEPA was required for the new project to be permitted, and an EA was completed in 1986 (not reviewed). In 1995 an EA was conducted for a mine expansion (not reviewed), in 1997 an EIS was conducted for a mine expansion and reclamation, and another expansion EIS was completed in 1999 (not reviewed). The following sections summarize the water quality predictions made in the NEPA documents reviewed.

1997 EIS

According to the 1997 EIS, old mineralization is associated with quartz-veining as auriferous pyrite and free gold. Static testing (ABA), whole rock analysis, short term leach testing (MWMP), kinetic testing (humidity cell and column leach testing) and petrographic analyses were performed. Constituents of concern identified in whole rock and MWMP tests included aluminum, arsenic, cadmium, iron, lead, mercury, antimony, thallium and total dissolved solids (TDS). Static tests showed that 41.5% of the rock had the potential to produce acid and an additional 36.2% of the whole rock had uncertain potential to produce acid. According to the EIS, the modified Sobek method was used to fine-tune the estimate. The result was that only 0.2% of mined rock was identified as having potential to generate acid drainage. Kinetic tests were inconclusive but tended to show a low acid generation potential. However, two of the 14 samples showed acid generating potential. MWMP tests also showed the potential for leaching aluminum, arsenic and iron. HELP, OPUS and UNSAT2 were used to model waste rock seepage.

The EIS characterized baseline groundwater quality; in some wells the EIS claims that concentrations already exceeded drinking water standards for arsenic, aluminum, chloride, manganese, sulfate, TDS, fluoride, and nickel. According to the EIS, even though these samples were taken just downgradient of the heap and pit eight years after the mine commenced construction, the results were attributed to different water quality in different aquifers rather than mining activities. However, the EIS also mentions that groundwater may be impacted by seepage from the heap leach facility, waste rock dumps and by the release of constituents from the pit backfill material. The potential was recognized for dissolution of constituents from the backfill to degrade groundwater quality. No information was presented on surface water quality impact potential or pit water impact potential.

According to the EIS, mitigation consisted of segregating and disposing of potentially acid generating materials within the waste rock dumps. The heap leach facility will be designed as a zero discharge facility and employ a leak detection system. Partial backfilling of the open pit above the water table will eliminate the formation of a pit lake. No impacts to ground water quality were expected as a result of backfilling of the pit with waste rock. Water quality impacts from waste rock dumps were not expected due to low seepage rate, low acid generation potential, natural attenuation properties of alluvium, depth to groundwater, and the waste rock management plan. Contamination of groundwater by leach solution was not expected.

6.3.18.2. ACTUAL WATER QUALITY CONDITIONS

Water quality monitoring data were obtained from the Nevada Department of Environmental Protection (NDEP) for the period 1999 to 2003. Twenty-four groundwater monitoring locations are noted, although not all are in use. No surface water monitoring locations were noted. Information was available on baseline water quality conditions and water quality violations.

Following the 1997 EIS, there were numerous water quality impacts. One monitoring well had elevated concentrations of cyanide (WAD CN = 0.225 mg/l) and other constituents (chloride, mercury, nitrate, and TDS) in groundwater beginning in 2000, suggesting contamination of groundwater with cyanide leach solutions. Following actions taken to address deficiencies in the heap leach pad leak detection pump back system, lower elevations of constituents were noted, although mercury concentrations still exceeds standards. A Notice of Violation was issued for using higher pumping rates than those for which the system had been designed.

Other groundwater monitoring wells on the site showed exceedences of drinking water standards for aluminum, arsenic, cadmium, chloride, iron, manganese, nickel and TDS.

6.3.18.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.23 provides a summary and comparison of potential, predicted and actual water quality information for the Florida Canyon Mine. The accuracy of the predictions is discussed in this section.

Table 6.23. Florida Canyon, NV, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impacts	Mitigation	Predicted Impacts	Actual Impacts
Groundwater	Leach Pads	1997 EIS: • Seepage from the heap leach facility. • Background water quality indicates natural exceedences.	1997 EIS: Facility design to prevent groundwater impacts (zero discharge with leak detection with pumpback of leaks if detected)	1997 EIS: No impacts to groundwater predicted	WQ Monitoring: Contamination of groundwater with cyanide and other constituents noted and partially mitigated with leak pumpback system
	Waste Rock, Open Pit, or baseline conditions	1997 EIS: Water quality would be same as pre-mining (background water quality indicates natural exceedences).	1997 EIS: • Backfill pit to prevent formation of pit lake. • Segregation/disposal of PAG rock in the waste rock dumps	1997 EIS: No impacts to groundwater predicted.	WQ Monitoring: Exceedences of drinking water standards noted in various monitoring wells, which could be attributed to waste rock and open pit leachate or baseline conditions.

Contamination of Groundwater by Seepage from the Leach Pad: Groundwater in at least one well has been impacted by cyanide, mercury, chloride, nitrate and TDS from heap pad leachate. Short-term leach tests results were elevated (above drinking water standards) for aluminum, arsenic, iron, lead, mercury, thallium, and TDS, so this test was predictive for mercury and TDS. The EIS noted that there was the potential for groundwater quality impacts by seepage from the heap leach facility, waste rock dumps, and by release of constituents from the pit backfill material.

The heap leach facility was designed as a zero-discharge operation with a leak-detection system, and contamination of groundwater by leach solution was not expected. Therefore, the potential groundwater quality forecast was correct, and the post-mitigation (predicted) groundwater quality impacts were incorrect. The assumption/prediction that leach pad mitigation (liner and leak detection system) would be effective in preventing groundwater contamination was inaccurate.

Elevated Concentrations of Metals and Sulfate in Groundwater: The possible causes of the observed exceedences are currently not known but include elevated background concentrations, seepage from the waste rock dumps, and infiltration from the open pit. The constituents that exceed concentrations in groundwater (aluminum, arsenic, cadmium, chloride, iron, manganese, nickel, TDS) are very similar to those exceeding standards in the MWMP (short-term leach) test (aluminum, arsenic, iron, lead, mercury, thallium, TDS). Therefore, the short-term leach tests were predictive in identifying constituents that would be elevated in groundwater, regardless of the cause.

6.3.19. JERRITT CANYON, NEVADA

The Jerritt Canyon Mine, owned currently by Queenstake Resources, has been in operation since 1980. The primary commodities mined are gold and silver from underground and open pit mining and heap and vat leach processing operations. It disturbs 3,411 acres on Humboldt-Toiyabe National Forest in U.S. Forest Service Region 4. It has a current financial assurance amount of \$7.1 million.

6.3.19.1. WATER QUALITY PREDICTIONS SUMMARY

NEPA was required for the new project to be permitted, and an EIS was completed in 1980. In 1991, an EA was completed in support of an increase in the height and an expansion of the seepage collection system of the tailings impoundment. In 1994 another EIS was conducted for a mine expansion. The following sections summarize the water quality predictions made in the NEPA documents reviewed.

1980 EIS

According to the 1980 EIS, results from short-term leach tests conducted on waste rock samples showed only minimal potential for leaching of heavy metals and other toxic substances to surface and groundwater. However, suspended solids from erosion were expected to increase. No other information was provided on tailings testing or potential for water quality impacts in the 1980 EIS.

According to the EIS, mitigation will consist of locating the mill and tailings impoundment in the headwaters of a small watershed, and this was expected to have negligible effects on water quality. The tailings impoundment will be lined to provide an impervious barrier to vertical movement. Horizontal seepage of liquids will be controlled by the dam embankment design. Diversion ditches will direct flow around the mine pit and back into natural drainages (run on controls). Groundwater flowing into the pits will be used for dust control, and at times, excess water may be discharged to Jerritt Canyon.

The EIS included information on background surface water sampling stations that showed elevated nitrate concentrations, anomalous values for zinc, and exceedences of the drinking water standard for mercury and chromium.

1991 EA

This EA was written to analyze a 50-foot height increase to the tailings impoundment and to install a seepage remediation system. There were no geochemical tests performed on tailings material.

Even though the EA analyzed the new seepage remediation system, it did not provide details of the ongoing contamination (see Section 6.3.19.2), other than to indicate that pre-mining background water quality was within

standards and that a plume of salt extended up to 1000 feet from the tailings impoundment. The EA indicated that concentrations of constituents seeping from the tails were relatively low. It indicated the six pumpback wells previously installed were not sufficient to prevent migration away from the impoundment.

1994 EIS

According to the EIS, geochemical testing on waste rock included static acid-base accounting, humidity cell, column leaching and short-term leach (MWMP) tests. Constituents of concern identified from waste rock leach tests included arsenic, selenium, nitrate and sulfate. Waste rock from the Roberts Mountain and Hanson Creek formations had low acid-generation potential. Waste rock from the Snow Canyon formation had moderate potential to generate acid. Waste rock from the unoxidized, strongly altered intrusive rock was acid-forming but would make up less than 2% of the waste rock in the proposed waste rock dumps. Groundwater quality would be potentially affected if waste rock and pits generate acid and mobilize metals and other compounds. Spring and seep water quality may be affected by contact with waste rock dumps, or by contact with pit walls. There is potential for acid drainage from waste rock, ore stockpiles or pits to affect waterways, and a potential increase in sedimentation resulting from roads, pits and waste rock dumps.

According to the EIS, mitigation would consist of the Saval, Steer, Burns Basin pits (proposed) lying above the regional groundwater table and not accumulating water. The New Deep deposit will be mined using underground techniques, so no pit lake will form. No existing pit has encountered the regional groundwater table. Acid mine drainage will be mitigated with selective handling and isolation of acid forming waste rock and capping, contouring, or drainage control to reduce infiltration. No impacts to surface or ground water were predicted due to the implementation of the waste rock characterization and handling program and plugging of the underground workings.

6.3.19.2. ACTUAL WATER QUALITY CONDITIONS

Water quality monitoring data was obtained from the Nevada Department of Environmental Protection (NDEP) for 1997-1998 and 2000- 2003. Twenty-one surface water monitoring locations and seven groundwater monitoring locations were identified. In addition, one Notice of Violation (NOV) was identified.

The records showed that following the 1980 EIS and 1994 EIS, water quality impacts occurred at the site including the following:

- A Finding of Alleged Violation (FOAV) was issued in 1991 due to a cyanide plume in the groundwater, caused by seepage from the tailings impoundment. A seepage collection system was installed to pump tailings seepage back to the tailings facility.
- Groundwater monitoring wells downgradient of the tailings impoundment showed exceedences for chloride (chloride and total dissolved solids (TDS), with values peaking at 30,000 mg/l (TDS) and 12,000 mg/l chloride in well GW-9. Exceedences of over times federal drinking water standards were common for these constituents, with exceedences of over 10 times standards occurring constantly between 1993 and 2004. Exceedences of federal arsenic and sulfate drinking water standards were also occasionally noted. The tailings impoundment is being gradually evaporated to eliminate seepage.
- Surface monitoring points in drainages below waste rock dumps on Burns Creek, Mill Creek, Jerritt Creek, Snow Creek and Sheep Creek showed exceedences of secondary federal drinking water standards for TDS and sulfate. One surface monitoring site showed a steady increase in TDS and sulfate concentrations from 2001-2004, with exceedences of over 10 times standards for both by early 2004. The exceedences were most likely related to the waste rock disposal pile.

6.3.19.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.24 provides a summary and comparison of potential, predicted and actual water quality information for the Jerritt Canyon mine. The accuracy of the predictions is discussed in this section.

Table 6.24. Jerritt Canyon, NV, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impacts	Mitigation	Predicted Impacts	Actual Impacts
Groundwater and Surface Water	Tailings	• 1980 EIS: No information provided for groundwater. Possibility of release of toxic materials to streams due to breakage of the tailings pipeline.	• 1980 EIS: Tailings located in headwaters of small water shed will protect water quality • 1980 EIS: Facility design to prevent groundwater impacts ○ Tailings disposal pond will be lined ○ Horizontal seepage controlled by embankment design.	• 1980 EIS: No impacts predicted • 1991 EA: Six pumpback wells are not effective at preventing migration of plume from impoundment	Water Quality Monitoring • 1991: Cyanide plume detected from tailings pond and seepage collection installed • 1993-2004: Groundwater monitoring wells downgradient of the tailing impoundment show exceedences for Cl and TDS consistently from 1993 –2004
	Waste Rock	• 1980 EIS: Minimum potential for some leaching of some heavy metals and other toxic substances in the waste rock into surface and ground water • 1994 EIS: Groundwater and surface water quality may be affected by acid drainage and other constituents in waste rock	• 1980 EIS: No information provided • 1994 EIS: Waste rock mitigation include: ○ Segregation and blending of PAG waste rock. ○ 1994 EIS: Capping, contouring and drainage controls ○ 1994 EIS: Waste rock characterization and handling (segregation, cap, contour, drainage) program	• 1980 EIS: Minimum impacts predicted • 1994 EIS: No impacts to groundwater or surface water predicted	Water Quality Monitoring • 2001-2004: Surface monitoring shows a steady increase in TDS and SO₄ concentrations downstream from waste rock piles from 2001-2004 with most recent data indicating exceedences of standards by 10 times
	Open Pit	• 1980 EIS: No information • 1994 EIS: Groundwater and surface water quality may be affected by acid drainage and other constituents in pit walls	1980 EIS: Divert surface water flow around pit and groundwater from pit used for dust control or discharged	• 1980 EIS: No impacts predicted • 1994 EIS: No pit lakes predicted to form	

Cyanide Plume and Exceedences of Chloride, TDS, Sulfate and Arsenic in Groundwater from Tailings Impoundment

Leakage: The tailings generated from the vat leach operation were responsible for creation of a cyanide plume in groundwater. Exceedences of chloride, TDS, arsenic and sulfate were also observed in wells downgradient of the tailings impoundment. Geochemical characterization in the 1994 EIS focused on the waste rock and noted the potential for leaching of arsenic, selenium, nitrate and sulfate. However, no geochemical testing was performed on tailings material. No information on potential (pre-mitigation) groundwater impacts from tailings was noted, but post-mitigation (related to waste rock and underground mine backfilling and sealing) groundwater quality was predicted to

be good. The only potential impact from tailings was the possibility of release of toxic materials to streams due to breakage of the tailings pipeline. The tailings impoundment was lined and had seepage control features, but these were not adequate to prevent groundwater contamination. Therefore, predictions about the impact of tailings on groundwater were non-existent, and the mitigation for the tailings system failed.

Impact of Waste Rock on Surface Water Quality: Exceedences of sulfate and TDS (by over 10 times the standard) were observed in surface water downstream/gradient of the waste rock piles. Acid-base accounting and short-term leach testing performed on waste rock showed moderate potential for acid drainage and minimal potential for leaching of arsenic, selenium, nitrate, and sulfate. Potential surface water impacts from waste rock were noted in the EISs. However, no impacts to surface water or groundwater were predicted post-mitigation due to the implementation of the waste rock characterization and handling program. Therefore, the potential (pre-mitigation) forecasts were more accurate than the post-mitigation predictions, and the mitigation and management approaches were not successful in preventing surface water impacts from waste rock. Geochemical characterization was able to predict the leaching of sulfate from waste rock, but the impact was larger (>10 times standards) than the “minimal” leaching predicted.

6.3.20. LONE TREE, NEVADA

The Lone Tree Mine, owned by Newmont Mining Company, has been in operation since 1991. The primary commodities mined are gold and silver from open pit mining and heap and vat leach processing operations. It disturbs 2,691 acres and is permitted to disturb 3,547 on both private land and BLM land. It has a current financial assurance amount of \$8.4 million.

6.3.20.1. WATER QUALITY PREDICTIONS SUMMARY

NEPA was not originally required for the new project in 1991 because it was located on private land. NEPA was required for mine expansion onto public land, and an EIS was completed in 1996. The following sections summarize the water quality predictions made in the NEPA documents reviewed.

1996 EIS

Geochemical characterization consisted of static (ABA), kinetic (humidity cell tests), and short-term leach (MWMP) tests and a mixing experiment using acid leachate from Lone Tree rocks and Wayne Zone groundwater. Modeling included water quantity and water quality using MINEDW to predict three-dimensional groundwater flow, and hydrogeochemical modeling of pit lake water by PTI (proprietary). Constituents of concern identified included arsenic, iron, sulfate and total dissolved solids (mine discharge water); antimony, arsenic, cadmium, nickel, fluoride, and sulfate (pit lake); and arsenic, copper, cyanide, iron and sulfate (tailings).

Although static testing indicated that tailings were potentially acid generating, kinetic testing indicated they were not. Sulfides were reported to be encapsulated in silica; humidity cells tests on overburden suggested that silicate buffering would be important. The contaminant leaching potential was predicted to be moderate to high.

Groundwater - Pit lake water was predicted to mix with groundwater after steady state groundwater levels are reached; due to natural attenuation, no groundwater exceedences were expected.

Surface Water - Water pumped from the ground and discharged into the Humboldt River is generally of good quality, except for recently increased concentrations of arsenic, iron and sulfate in mine discharge water (Draft EIS). The Final EIS stated that iron, copper and lead exceeded aquatic life criteria in mine discharge water.

Pit Lake - Pit lake water quality was predicted to be acidic and exceed the arsenic standard initially but become neutral after 10 years and not exceed standards for arsenic after that time; cadmium concentrations were predicted to exceed drinking water standards for one year; nickel, fluoride, and antimony for over 25 years; and sulfate until 10 years. Nickel and fluoride concentrations were predicted to exceed their respective limits by less than 10 times and

antimony by over 10 times. In the long term, the pit water was predicted to have exceedences of one to 10 times for aluminum, antimony, arsenic, fluoride, total dissolved solids and pH. The drinking water standard for thallium was predicted to be exceed by over 10 times in long term.

6.3.20.2. ACTUAL WATER QUALITY CONDITIONS

Water monitoring and compliance data for the period 1998-2002 were obtained from the Nevada Department of Environmental Protection (NDEP). There are 16 groundwater monitoring locations (11 monitoring wells and five production wells) at Lone Tree. No information on violations was found.

Possible mine water quality related impacts and exceedences were indicated including the following:

- Mine Water Supply Wells: Production well WW-13 exceeded the secondary standards for fluoride and manganese in 1998 and 2000. Concentrations of both constituents were less than twice the standard.
- Heap leach groundwater monitoring wells: Occasional exceedences of Secondary MCLs were recorded at wells MO15-1A, MO15-2A, MO15-3 3 from 1999-2000 for aluminum, iron, and TDS. Except for an aluminum concentration of 1.05 mg/l (standard is 0.05-0.2 mg/l), all concentrations were less than twice the drinking water standard.
- Tailings monitoring wells: Tailings monitoring wells recorded numerous exceedences of secondary drinking water MCLs from 1999-2002. Constituents of concern included fluoride, iron, manganese and TDS. Frequent fluoride SMCL exceedences were recorded from 1999-2001, but the primary MCL (4.0 mg/l) was not exceeded. Some tailings monitoring wells had arsenic concentrations at the level of the new standard (10 µg/l) in 2000 and 2002.
- The tailings impoundment experienced a major leak in November, 2000, but the leak was not detected below the vadose zone.
- Between 1998 and 2002, dewatering water discharged into the Humboldt River exceeded standards frequently for pH, total dissolved solids, fluoride, boron and un-ionized ammonia.

6.3.20.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.25 provides a summary and comparison of potential, predicted and actual water quality information for the Lone Tree mine. The accuracy of the predictions is discussed in this section.

Exceedence of Arsenic and Secondary Drinking Water Standards in Groundwater: Because information on background groundwater quality was not obtained, it is unknown if the observed exceedences in groundwater relate to seepage from facilities or background conditions. Heap leach monitoring wells had exceedences of arsenic, aluminum, iron and TDS. Tailings monitoring wells had exceedences of arsenic, fluoride, iron, manganese and TDS. Potential water quality impacts noted in the EIS included discharge of acid water from overburden, tailings, leach pads and ore stockpiles. Tailings MWMP extract for tailings exceeded drinking water standards for pH, TDS, sulfate, arsenic, copper, iron (all by <10x) and cyanide (>10x). These results did not predict noted exceedences of fluoride or manganese in tailings wells. No acid drainage has occurred to date.

Exceedence of Permit Limits for Dewatering Discharge: More information is needed on NPDES discharge water quality. The EIS predicted that no significant impacts would occur to the Humboldt River after mitigation were performed, which included cooling and treatment of discharge water to remove arsenic.

Table 6.25. Lone Tree, NV, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impacts	MITIGATION	Predicted Impacts	Actual Impact
Groundwater	Heap Leach	1996 EIS: No estimates of potential impacts to water quality	1996 EIS: No specific mitigation provided	1996 EIS: No estimates of predicted water quality	WQ Monitoring: possible exceedences of As, Al, Fe, and TDS
	Tailings	1996 EIS: No potential for acid drainage. Moderate to high potential for As, Cu, CN, Fe, and sulfate	1996 EIS: No specific mitigation provided	1996 EIS: No estimates of predicted water quality	WQ Monitoring: possible exceedences of secondary drinking water MCLs from 1999-2002 for fluoride, iron, manganese, and TDS
	Waste Rock	1996 EIS: No estimates of potential impacts to water quality	1996 EIS: Overburden mixing and segregation	1996 EIS: No estimates of predicted water quality	WQ Monitoring: No exceedences indicated
	Open Pit	1996 EIS: Pit lake water quality acidic initially, but after 10 yr neutral; would exceed standards for As, Cd, Ni, F, Sb (by >10x), TI (by >10x), and SO ₄ at different times	1996 EIS: Diversions to prevent runoff from entering pits	1996 EIS: Groundwater downgradient from mine pit would approach baseline quality of regional groundwater, not expected to exceed MCLs	
Surface Water	Pit Dewatering	1996 EIS: Fe, Cu, and Pb are the only parameters that exceeded aquatic life criteria in mine discharge water	1996 EIS: Affected springs mitigated by: piping in water, drilling into a deeper aquifer, improving existing springs to enhance yield, or developing/improving nearby springs to offset loss. Monitoring	1996 EIS: No significant impacts would occur, but discharge to Humboldt River would increase total dissolved solids and trace elements	Water pumped from the ground and discharged into the Humboldt River Discharge exceeds permit limits for TDS, B, F, pH and NH ₃ .

6.3.21. ROCHESTER, NEVADA

The Rochester Mine, owned by Coeur Rochester, Inc., has been in operation since 1986, although the site has been mined since the 1860s. The primary commodities mined are gold and silver from open pit mining and heap leach processing operations. It disturbs 1,447 acres on both private land and BLM land. It has a current financial assurance amount of \$8.4 million.

6.3.21.1. WATER QUALITY PREDICTIONS SUMMARY

NEPA was required for the new project to be permitted, and an EA was completed in 2001. In 2003 an EA was conducted for a mine expansion. There has never been an EIS completed for this facility, but beginning in 2004 the BLM began preparing a closure EIS. The following sections summarize the water quality predictions made in the NEPA documents.

2001 EA

The 2001 EA considered the Nevada Packard deposit, which was a satellite deposit from the primary Rochester project. Geochemical characterization consisted of acid-base accounting, short-term leach testing (MWMP) and whole rock analysis. Constituents of concern identified included antimony, arsenic, iron, lead, mercury and silver. No predictive modeling was performed. Acid drainage potential was estimated to be low. Rocks in the project area generally have low sulfur content and low neutralizing potential. Only two of 26 acid-base accounting results showed potential to generate acid. Whole rock (ICP) analyses of non-ore and unmineralized rock samples suggested that antimony, arsenic, lead, mercury and silver could produce leachate with elevated concentrations. Short-term leach test (MWMP) results showed that antimony, arsenic, iron and mercury could occur in elevated concentrations in discharge water from the non-ore material.

There was no information in the 2001 EA on potential impacts to groundwater. Due to historic mining in the area, the current site includes abandoned tailings material, waste dumps and leach pads that are likely to have an impact on surface water quality. The water table is 140 feet below the proposed pit bottom, so no pit lake is expected to form. No information on mitigation was provided.

The proposed action was considered unlikely to degrade groundwater resources or further degrade baseline surface water quality, since a part of the proposed action included reclamation of the abandoned pre-Coeur workings.

2003 EA

This was the most recent EA to consider continuing expansions of projects at the Rochester Mine. Reports of earlier testing showed that some of the lithologies above 6,600 feet were substantially acid generating, but no details were provided. Below 6,600, from 10 to 20 percent of the rock was classified as potentially acid generating (PAG), based on acid-base accounting and humidity cell analysis. MWMP tests showed limited metal mobility from non-PAG rock, but test pH values ranged from 4.0 to 6.4. For PAG rock, lead, cadmium, zinc, copper and aluminum concentrations were occasionally high.

The section on potential impacts claimed that the rock was mostly non-PAG, and the surrounding rock would neutralize any acid that may be generated.

Future developments at the Coeur operations could generate long-term impacts to groundwater. The potential for acid rock drainage from the present actions was identified.

6.3.21.2. ACTUAL WATER QUALITY CONDITIONS

Water quality monitoring and compliance data were collected from the Nevada Department of Environmental Quality (NDEP) for the period 2000- 2003. Three surface water monitoring locations and 17 groundwater monitoring locations were noted for the site. The following information on water quality was noted.

- Groundwater monitoring wells downgradient of the Stage I heap leach pad showed exceedences of arsenic, mercury, cadmium, nitrate and WAD cyanide during the period 2000 to 2003.
- Surface water monitoring sites in a spring downgradient of the Stage I heap leach pad showed exceedences of nitrate, lead, cyanide, arsenic, mercury.
- In 2003 NDEP issued Rochester a Finding of Alleged Violation (FOAV) for cyanide exceedences discovered during quarterly monitoring. The violation was issued in response to the discovery of cyanide exceedences in MW-16, a monitoring well screened in the shallow bedrock below the site. Contamination had been previously confined to the alluvium.
- In 1987 a release of process solution from the East Pregnant Pond occurred, causing pregnant solution to run into American Canyon for 12-18 hours at a rate of 5-10 gpm. The United States EPA issued a Notice of Violation to Coeur-Rochester on June 30th, 1988, for violating the Clean Water Act by discharging pregnant

solution to American Canyon. On July 20th, 1988, NDEP issued an FOAV to Coeur-Rochester for the December 27th, 1987, pregnant solution release. It does not appear that NDEP pursued a monetary settlement.

- In 1998 a broken pipeline resulted in the displacement of 200 tons of ore off the liner, causing 19,400 gallons of process solution containing 45.3 lbs. of cyanide to be released to the environment. Of this, 5,000 gallons of process solution containing 11.7 lbs. of cyanide were discharged off site to American Canyon, an intermittent drainage. A dike was installed in American Canyon to stop solution flows, and affected soil was treated with hydrogen peroxide to degrade cyanide. Displaced ore was moved back to containment.

6.3.21.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.26 provides a summary and comparison of potential, predicted and actual water quality information for the Rochester Mine. The accuracy of the predictions is discussed in this section.

Table 6.26. Rochester, NV, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impacts	Mitigation	Predicted Impacts	Actual Impact
Groundwater	Heap Leach, Open Pit, Waste Rock	2001 EA: None identified. 2003 EA: Future developments at the Coeur operations could generate long-term impacts to groundwater.	2001 EA: None identified 2003 EA: None identified	2001 EA: The proposed action is considered unlikely to degrade groundwater resources. 2003 EA: Water recharging the groundwater system from infiltration through Rock Disposal Sites not expected to differ from the current groundwater chemistry.	WQ Monitoring: Leaks from the Stage I heap leach pad and the N. Barren pond have resulted in numerous exceedences in groundwater monitoring wells. Exceeding constituents include WAD Cyanide, mercury, cadmium, nitrate and arsenic.
Surface Water and Springs	Heap Leach, Open Pit, Waste Rock	2001 EA: Due to historic mining, current site includes abandoned tailings, waste dumps, and leach pads that are likely to have an impact on t surface water quality. 2003 EA: There is a potential for increased sedimentation from surface disturbance associated with Proposed Action. There is potential for acid drainage from the present actions (2003)	2001 EA: Diversion ditches, as well as other sediment control measures. 2003 EA: Part of the proposed action includes reclamation of the Project, as well as some of the abandoned pre-Coeur mine workings.	2001 EA: Proposed action unlikely to further degrade surface water quality. 2003 EA: The proposed action is unlikely to further degrade baseline water quality, since part of the proposed action includes reclamation of project as well as some abandoned pre-Coeur mine workings.	Contamination of American Canyon (intermittent drainage) by process solution release of Nov. 29 th , 1998. Exceedences of nitrate and arsenic in American Canyon Springs from heap leach pad and process solution ponds.

Exceedences of Arsenic, Mercury, Cadmium, Nitrate and Cyanide in Heap Leach Monitoring Wells and Springs:

Short-term leach tests and whole rock analysis identified antimony, arsenic, iron, lead, mercury and silver as constituents of concern. Therefore, the potential for arsenic and mercury exceedences was identified, but the cadmium, nitrate and cyanide exceedences were anticipated. There was no information on potential or predicted

impacts to groundwater in the 2001 or 2003 EAs related to the heap leach pad. Therefore, the potential for some of the observed exceedences was noted in the 2001 EA, but the observed exceedences were not predicted to occur in groundwater.

Contamination of American Canyon by Cyanide from Process Solutions: Cyanide was not specifically identified as a constituent of concern, and no potential or predicted impacts from release of process solution to surface water were identified. Therefore, the observed impact to surface water was not predicted in the EAs.

6.3.22. ROUND MOUNTAIN, NEVADA

The Round Mountain Mine, owned by Round Mountain Gold Corporation, has been in operation since 1977. The primary commodities mined are gold and silver from open pit mining and heap leach and vat leach processing operations. It disturbs 4,431 acres on private, BLM and Forest Service lands. It has a current financial assurance amount of \$41.7 million.

6.3.22.1. WATER QUALITY PREDICTIONS SUMMARY

NEPA was required for the new project to be permitted, and an EA was completed in 1977. In 1987 and 1992, EAs were conducted for a mine expansions. In 1996 an EIS was conducted for further mine expansion. The following section summarizes the water quality predictions made in the only NEPA document obtained and reviewed, the 1996 EIS.

1996 EIS

The primary host rock for mineralization is the Tertiary Round Mountain tuff, in which gold occurs in quartz-carbonate and quartz-pyrite veins. Geochemical characterization consisted of short-term leach testing, static acid-base accounting, kinetic testing and soil attenuation tests. MWMP tests were performed on leach pad offload materials (spent ore), and TCLP and MWMP tests were performed on tailings materials. Net neutralization potential (NNP) and humidity cell tests were performed on pit wall materials. Soil attenuation tests were conducted on leachate from leach offload piles. The effects of mine dewatering and future inflow of water to the pit were predicted using MODFLOW. The pit lake was modeled with CE-THERM-R1 for thermal stratification and overturn, and MINTEQA2 for geochemistry of the pit lake. The Davis-Ritchie model was used to calculate the thickness of the oxidized zone in the wall rock. Groundwater quality was sampled for four different water types, including geothermal waters since 1986, which provides a baseline to compare this project against. The groundwater near the tailings impoundment was not monitored.

There are two facilities in which spent ore will be deposited: leach offload piles and tailings impoundments. Spent ore was identified as having the potential to generate elevated pH values and to leach antimony, arsenic, selenium, and cyanide, and possibly iron, mercury, nickel, nitrate, and fluoride, as well as generating elevated pH values. Geochemical test results suggested that degradation could occur if water were to seep through the leach offload piles and discharge directly into a protected surface water source or groundwater aquifer. The potential was identified for stormwater runoff to mobilize metals and cyanide from the spent ore materials. However, significant impacts to surface water or groundwater quality from leach offload piles was not anticipated due to attenuation in soils.

The potential was identified for carbon-in-leach tailings to leach iron, lead, manganese, TDS and sulfate in concentrations in excess of MCLs; carbon-in-leach tailings, however, would be only 5-10% of total tailings. MWMP test average concentrations on spent ore showed exceedences of over 10 times for arsenic and less than 10 times for antimony, selenium, and cyanide. The pH was also higher than standards. Based on TCLP tests, tailings did not exhibit hazardous properties. If tailings seepage reaches groundwater, there is potential for degradation.

The EIS proposed a zero-discharge tailings facility with a seepage underdrain system designed to alleviate head. If, after cessation of mine processing operations, seepage of tailings solution is still occurring through the underdrain

system, the seepage would create a potential impact to groundwater. Any metals and cyanide mobilized by snowmelt or rainfall that runs off the piles or seeps through the piles and later infiltrates the alluvial soils would be rapidly attenuated in the upper soil column, indicating that significant impacts to groundwater from the leach offload piles were not expected.

Excavation of the pit was predicted to expose sulfide minerals and form acid drainage. A 300-foot deep pit lake is expected to form in the pit after dewatering ceases. Forty percent of pit wall samples had potential to generate acid, but modeling indicated that the pit water will not be acidic. In the long run, pit water was predicted to exceed drinking water standards for aluminum, arsenic, fluoride, manganese, mercury, nickel, pH (high), TDS, sulfate and zinc. Modeling of final groundwater levels and flow rates, as well as predicted precipitation and evaporation rates suggested that the pit lake will have no net outflow to either groundwater or surface waters.

6.3.22.2. ACTUAL WATER QUALITY CONDITIONS

Water quality monitoring and compliance data were collected from the Nevada Department of Environmental Protection (NDEP) for the period 1999-2003. Ten groundwater monitoring locations were noted for the site. The following information on water quality was noted:

- Groundwater monitoring wells recorded a number of exceedences of secondary standards for aluminum, fluoride, iron, manganese and TDS. Aluminum exceedences occurred in the pit dewatering water. The other constituents all had exceedences in alluvial wells downgradient of the tailings, heap offload disposal sites and dewatering water. One of the wells had a substantial increase in fluoride concentration. Arsenic exceedences, of both the old and new standards, were very common and are mentioned as a background condition.
- Wells near the tailings also experienced frequent exceedences for antimony and lead. High pH values were also common.
- As noted, the trend in exceedences is for them to be clustered near the tailings and the heap offload sites. A second trend is for the highest concentrations to occur at the shallowest alluvial reaches, which could suggest a surface source. Most of the constituents, but not fluoride, also occur in dewatering water, which is another potential source.

6.3.22.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.27 provides a summary and comparison of potential, predicted and actual water quality information for the Round Mountain Mine. The accuracy of the predictions is discussed in this section.

Exceedences of Aluminum, Antimony, Fluoride, Iron, Lead, Manganese and TDS in Groundwater: The cause of the exceedences in groundwater is not known, but could be due to background groundwater quality and/or discharge from the tailings or heap leach facilities or dewatering water. Because the waste rock was shown to have a significant potential to leach contaminants, the fact that there is relatively little groundwater contamination indicates the mitigation may be working. However, there are trends that cannot be explained by assuming that all exceedences are background. Fluoride is the biggest issue especially since it is a constituent of concern for leaching from the waste rock. It suggests that the baseline water quality was not adequately determined.

Table 6.27. Round Mountain, NV, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impacts	Mitigation	Predicted Impacts	Actual Impacts
Groundwater	Tailings, heap leach offload, or baseline conditions.	Test results suggest some exceedences could occur if water were to seep through leach offload piles, discharge directly to a protected groundwater aquifer. MWMP tests show exceedences of over 10 times for arsenic, and less than 10 times for antimony, selenium and cyanide. pH is also higher than allowed. If, after cessation of mine operations, seepage of tailings is still occurring through underdrain, seepage would create potential impact to groundwater.	Tailings facility designed for zero discharge. Backfill and reclaim the tailings seepage collection pond after underdrain seepage has ceased.	No discharge from pit, so no impact to GW. Significant impacts to ground water quality from leach offload piles not anticipated due to attenuation in soils. Minimal impact to ground water quality from tailings facilities due to management, design. Any metals or cyanide mobilized by snowmelt or rainfall that runs off piles/seeps through piles and infiltrates alluvial soils would be attenuated in upper soil column.	Exceedences of secondary standards for aluminum, fluoride, iron, manganese, pH (high) and TDS and primary drinking water standards for arsenic, antimony, and lead all appear to be related to baseline conditions. No mining-related exceedences are evident.

6.3.23. RUBY HILL, NEVADA

The Ruby Hill Mine, owned by Barrick Goldstrike since its acquisition from Homestake, has been in operation since 1997. Mining ceased and reclamation commenced in 2002, although processing of gold and silver from its cyanide heap leaches continues to this day. It disturbs 696 acres on private lands. It has a current financial assurance amount of \$7.1 million. The mine issued a DEIS to reopen and expand its operations in 2005.

6.3.23.1. WATER QUALITY PREDICTIONS SUMMARY

NEPA was required for the new project to be permitted, and an EIS was completed in 1997. The following sections summarize the water quality predictions made in the NEPA documents reviewed.

1997 EIS

The ore is oxide and hosted in limestone, with some sulfides present. The following predictive tests were performed: whole rock analysis static ABA, MWMP, humidity cell and synthetic precipitation leach procedure (EPA method 1312). The average ANP:AGP was 813 for alluvial material and 955 for oxidized limestone samples; the potential for acid generation was considered low. Leach tests indicated there was a moderate potential for contaminant/metals leaching; meteoric water mobility procedure (MWMP) results from alluvial material and oxidized limestone showed occasional drinking water exceedences for aluminum, arsenic, antimony and TDS. EPA method 1312 leach tests showed exceedences for aluminum, arsenic and pH (high).

Modeling indicated low potential for groundwater degradation. Increased erosion was the only noted surface water quality concern. No impacts to surface or ground water were predicted, due to the nature of the rocks, as well as the distance to water. The pit bottom will be above the regional water table, so no pit lake was expected.

6.3.23.2. ACTUAL WATER QUALITY CONDITIONS

Water quality monitoring and compliance data were obtained from the Nevada Department of Environmental Protection (NDEP) for the period 1997-2003, and the 2005 DEIS also summarizes water quality at the site. Nine groundwater monitoring locations were noted for the site.

Only two constituents had substantially high concentrations: arsenic and nitrate. Two wells had high arsenic concentrations, often exceeding MCL values by two to four times; concentrations increased by about 20% between 1996 and 2003. However, the highest concentration occurred upgradient of the mine. Elevated pH values were also common in groundwater wells. Nitrate concentrations frequently approached the MCL in several wells. The 2005 EIS suggested these predated the mine and were due to septic systems.

There were lead exceedences (less than twice the drinking water standard) during the fourth quarter of 1997 and the first quarter of 1998 in monitoring well MW-4, although no problems were recorded after this point. Since the exceedences did not recur, it did not result in any action by NDEP.

6.3.23.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.28 provides a summary and comparison of potential, predicted and actual water quality information for the Ruby Hill Mine. The accuracy of the predictions is discussed in this section.

Table 6.28 Ruby Hill, NV, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impacts	Mitigation	Predicted Impacts	Actual Impact
Groundwater	Baseline conditions.	Low potential for degradation from leaching of Arsenic and Aluminum, according to the Horizontal Plane Source Model. Partial backfilling of pit (preferred alternative) would increase potential chemical impacts.	Zero discharge heap leach with a leakage detection/collection system; rinsing of heap leach during closure followed by a land application of rinse water.	Contamination of groundwater by leach solution not expected. Cumulative impacts from the waste rock and leach residue are not expected to occur.	None. Any exceedences appear to be related to baseline conditions.

Water quality impacts were not expected and did not occur. Therefore, assuming that the exceedences are related to baseline conditions, the water quality predictions were accurate.

6.3.24. TWIN CREEKS, NEVADA

The Twin Creeks Mine, owned by Newmont Mining Corporation since its acquisition from Santa Fe Mining, is the combination of the Rabbit Creek and Chimney Creek mines, which began operating in around 1988. The primary commodities mined are gold and silver from open pit mining and heap leach, vat leach, and oxide milling processing operations. It disturbs 4,549 acres on private land and 8,898 acres on BLM lands for a total disturbance of 13,447 acres. The current financial assurance amount is not known.

6.3.24.1. WATER QUALITY PREDICTIONS SUMMARY

Initially, the two mines, Chimney Creek and Rabbit Creek, were permitted with EAs. In 1996 an EIS was conducted for a mine expansion, which included combining the two existing mines. The following section summarizes the geochemical characterization, hydrologic analysis and predictions and water quality predictions made in the 1996 EIS.

1996 EIS

Arsenic-mercury mineralization occurs mostly in oxidized ore, but there is some sulfide ore in the South Pit deposit. Sulfide minerals associated with gold mineralization include pyrite, stibnite, realgar and orpiment. Sulfide ore from the Mule Canyon Mine will also be processed at the Twin Creeks Mine.

Waste rock and pit wall rock were analyzed with static (ABA), kinetic (20-wk humidity cell; 46 pit wall rock samples), mineralogy, and short-term leach tests (MWMP). Hydrologic modeling included MINEDW (proprietary) for groundwater dewatering. Mass balance modeling was used to predict the final pit lake elevation. CE-THERM-R1 was used to predict pit evaporation. DE-QUAL-W2 was used for modeling limnologic processes. Geochemical modeling included MINTEQA2 for predicting pit water chemistry and the Davis-Ritchie model for predicting the thickness of the oxidized zone in the pit walls over time.

Based on MWMP leachate results for waste rock, pit wall rock and tailings, and on humidity cell tests for pit wall rock, total dissolved solids, aluminum, antimony, arsenic, beryllium, cadmium, chloride, chromium, copper, iron, lead, manganese, mercury, nickel, nitrate, selenium, silver, sulfate, thallium and zinc were the constituents of concern. Waste rock (based on MWMP tests) leachate could exceed drinking water standards for total dissolved solids, beryllium, cadmium, selenium, zinc (all by 1 – 10 times), and for aluminum, antimony, arsenic, iron, manganese, mercury, nickel, sulfate and thallium (all by >10 times).

The acid generating potential of pit wall rock ranged from a net neutralizing potential (NNP) of -350 to +671t/kt, with an average of +162 t/kt (average is non acid generating). The majority (91%) of rocks in the proposed final pit surface were predicted to not be acid generating. Of the waste rock, approximately 9% was predicted to be potentially acid generating. Heap leach ore was apparently not tested, but sulfide ore had a NNP weighted average of -67 t/kt (acid generating). Juniper and Sage mill tailings were net acid neutralizing; Mule Canyon Mine ore, which is milled at Twin Creeks, was potentially acid generating. Tailings MWMP leachate concentrations exceeded drinking water standards for arsenic, antimony, cadmium, chromium, copper, iron, lead, mercury, silver, and selenium; tailings filtrate had elevated concentrations of zinc and chloride.

Infiltrating dewatering water was identified as having the potential to flush soluble salts, including chloride and nitrate, from the shallow alluvium to groundwater. The water also contained elevated concentrations of antimony, but observations prior to the DEIS indicate the alluvium could attenuate it. No significant impacts to groundwater quality were expected from the sulfide ore stockpiles or tailings due to low precipitation, groundwater depth and natural attenuation. The surface water in Rabbit Creek could be affected by the discharge of dewatering water, which has shown occasional exceedences of total dissolved solids (by 1-10 times) and arsenic (by >10 times). Testing showed that the pit lake could have water quality problems in both the short term and long term.

The DEIS proposed numerous mitigation; some were presented as design criteria and others were actual plans for monitoring and mitigation. Some waste rock would be placed over tailings, and thus seepage would be collected and discharged to process facilities, evaporated, or treated prior to discharge. Most waste rock dumps would be constructed on top of alluvium with net neutralizing potential and more than 100 feet to the groundwater after the dewatering drawdown recovers. A basal layer of acid neutralizing material would be placed underneath acid generating waste rock. Tailings facilities would be designed with liners, subdrains, collection ponds and pumpback systems to prevent migration of tailings waters into groundwater. Groundwater would be monitored to detect infiltration of mine water, with mitigation measures to follow if infiltration is detected. Heap leach pads would be designed with synthetic liner and leak detection system and operated as a zero-discharge facility; solution ponds were

planned to be double-lined with leak detection systems. A bioremediation facility was proposed to treat hydrocarbon-contaminated soil.

For surface water discharge and discharge to the infiltration basin, treatment was proposed for dewatering water to remove arsenic. The connection between Jake Creek and the regional groundwater system will be evaluated, followed by monitoring for water quantity and quality. Diversion structures will be inspected to ensure proper function and combat soil loss. Drainage structures will be stabilized after completion of mining. The pit lake water quality will be monitored, but there was no plan identified to mitigate problems.

Mine dewatering would lower the regional groundwater elevation, but re-infiltration would increase water levels in the re-infiltration pond area by up to 70 feet, even though stream flow increase was not expected. Drawdown would potentially reduce baseflow in perennial streams and springs, including Little Humboldt River and Jake Creek. Pit water was not expected to discharge to groundwater, so no impacts to downgradient groundwater were expected.

Tailings facilities would be designed to be zero discharge to prevent migration of tailings waters into groundwater systems. Potential for adverse effects to water quality from sludge disposal was considered minimal. Limited or no impact was expected to occur from bioremediation facilities. Modeling showed that drinking water standards were predicted to be exceeded for antimony and arsenic (>10 times) and thallium (1 – 10 times) for the life of the pit. Aluminum concentrations were predicted to exceed standards in the north lobe of the pit for the first 27 years, but after the pit lakes merged, no exceedences were predicted. Steady state pit water quality would exceed TDS standards by 1-10 times. No net outflow from the pit to groundwater or surface water was expected.

Dewatering water discharged to Rabbit Creek has shown occasional exceedences of total dissolved solids and arsenic. However, the receiving water, Rabbit Creek, is dry and the flow will rarely reach Jake Creek, so downstream surface water quality impacts were predicted to be minimal. Discharge to infiltration basins was also expected to leach some salts into the underlying groundwater from the alluvium.

6.3.24.2. ACTUAL WATER QUALITY CONDITIONS

Water quality monitoring and compliance data were collected from the Nevada Department of Environmental Protection (NDEP) for the period 2000-2003. Seven groundwater monitoring locations were noted for the site. The following information on water quality was noted:

- Monitoring reports submitted show high arsenic concentrations in many wells. These reports refer to arsenic levels as background. However, the concentrations fluctuated by as much as two-fold, and the wells are screened in shallow alluvium. Some wells are located near the tailings impoundments. Therefore, the claim that arsenic concentrations are baseline requires further analysis.
- Cyanide was detected in monitoring well MW-2 in October 1995, from seepage in the Pinon tailings impoundment. Seepage is believed to have occurred when the supernatant pool was filled too deeply, which may have resulted in seepage through the tailings embankment in excess of the collection pipe's capacity. Due to ongoing exceedences, there may be an ongoing leak. NDEP evaluated and characterized seepage fluids in the vadose zone below the facility and plugged well MW-2 because they believed it was acting as a conduit. The well was replaced with monitoring well MW-2R-1. Vadose zone wells (VW wells) were added to monitor seepage from the tailings impoundment. Vadose zone monitoring wells were added during 2003 to monitor seepage from the tailings impoundment (VW-1 through VW-26), and water quality in these wells is of poorer quality with multiple exceedences of TDS, sulfate, chloride, cyanide, aluminum, antimony, arsenic, manganese, iron and mercury. With possible exception of arsenic, it does not appear that tailings water regularly reaches the pre-existing alluvial groundwater.

6.3.24.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.29 provides a summary and comparison of potential, predicted and actual water quality information for the Twin Creeks Mine. The accuracy of the predictions is discussed in this section.

Table 6.29. Twin Creeks, NV, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impacts	Mitigation	Predicted Impacts	Actual Impacts
Groundwater	Tailings impoundment	Infiltrating dewatering water could flush soluble salts, including chloride and nitrate, from shallow alluvium to groundwater. Low potential for impacts from heap leach. No significant impacts from sulfide ore stockpiles or tailings.	Layer of acid-neutralizing material underneath overburden storage. Overburden placed over tailings, seepage collected and discharged to process facilities, evaporated, or treated prior to discharge. Tailings facilities have liners, subdrains, collection ponds, and pumpback systems. Heap leach pads have liner and leak detection, as well as double lined solution ponds with leak detection. Monitoring.	Dewatering would lower groundwater elevation, infiltration would increase levels in reinfiltration pond area up to 70 feet; stream flow increase not expected. Pit water not expected to discharge to GW, so no impacts. Tailings facilities have liners, subdrains, collection ponds, and pumpback systems.	The Pinon tailings impoundment formed a leak which caused a perched zone with poor water quality including high concentrations of WAD cyanide, arsenic, TDS and other constituents.
Surface Water	Dewatering water	Drawdown would potentially reduce baseflow in perennial streams and springs, including Little Humboldt River and Jake Creek.	Evaluation of connection between Jake Creek and groundwater system, followed by monitoring. Inspection of diversion structures to ensure function and combat soil loss. Stabilization of drainage structures after mining.	Potential for impacts from sludge disposal is considered minimal. Limited/no impact expected from bioremediation facilities.	Water discharged to Rabbit Creek has shown occasional exceedences (by 1-10 times) of total dissolved solids and arsenic (over 10 times).

Leakage of Cyanide from Tailings Impoundment to Groundwater: Geochemical testing showed that seepage from the tailings impoundment could degrade groundwater if the mitigation failed. The high concentrations of the vadose zone wells show that failure did occur. Therefore, the predictions that groundwater would not be degraded due to the zero discharge design were incorrect.

Elevated Arsenic Concentrations in Groundwater: There are questions about the baseline occurrence of arsenic in some of the wells. Because of their location and the variability of the concentrations, it cannot be determined whether the baseline condition, assumed by regulators, is correct. For this reason, it appears the characterization of the baseline water quality was insufficient.

6.3.25. FLAMBEAU, WISCONSIN

The Flambeau Mine, owned by Kennecott, was in operation from 1991 to 1995. The primary commodities mined were lead and zinc from open pit mining and flotation processing operations.

6.3.25.1. WATER QUALITY PREDICTIONS SUMMARY

NEPA was required for the new project to be permitted, and an EIS was completed in 1990. The following sections summarize the water quality predictions made in the NEPA document reviewed.

1990 EIS

Dominant rock types within the mineralized horizon are quartz-rich sediments and volcanic ash, massive sulfide, semi-massive sulfide, and chert. Economically valuable minerals are chalcocite, bornite and chalcopyrite, with trace amounts of gold and silver. The upper gossan cap is 30 feet thick. High-grade supergene copper (chalcocite, bornite in pyrite/chert) extends from below the gossan cap to a maximum depth of 225 feet. Lower grade copper sulfide minerals are present below the supergene-enriched zone.

Geochemical testing and modeling were conducted as part of the EIS. Wet/dry leach test (possibly humidity cell tests) and a second leach test of continued saturation of materials were conducted. Whole rock analysis and sulfur analysis were performed on waste rock (5 samples), topsoil, till, sandstone and saprolite samples. Acid production tests were performed on waste rock. Based on the results from leach tests and geochemical modeling, iron, manganese and sulfate were identified as constituents of concern. A geochemical model was used to predict the composition of leachate in the open pit backfill.

Acid drainage potential tests indicated that waste rock with a sulfur content of 2% or less would not be expected to produce acid. The matrix of the enriched horizon was made up of pyrite and chert. There was no indication of the amount of high sulfur material. Leach tests identified the potential for elevated concentrations of copper, iron, manganese and sulfate in interstitial waters in the backfilled pit. Waste rock from the mining operation would have the potential to leach contaminants to groundwater and surface water.

The EIS identified a number of proposed mitigation. High sulfur waste stockpiles and ore crushing/loading areas would be lined to prevent seepage. In the worst case scenario, leakage would leak into mine pit, where water would be treated before discharge. Settling ponds will collect runoff from low sulfur waste stockpiles for treatment prior to discharge to the Flambeau River. The ponds are proposed to be unlined, but seepage to groundwater would flow mostly to the open pit. Backfilling will eliminate the possibility of a pit lake, and the backfill will be limed. Water from the open pit, and the high sulfur waste rock pile would be routed through the wastewater treatment plant before being discharged to the Flambeau River.

The EIS identified a number of predicted impacts to groundwater, surface water and pit water. Slightly increased levels of TDS, hardness, sulfate, iron and manganese might be expected from leachate infiltration to groundwater. Contaminants would flow into the adjacent mine pit, where water would be treated prior to discharge to the Flambeau River. High sulfur waste stockpile, ore crushing and loading areas would be lined using a geomembrane; therefore, no impacts to groundwater quality were expected. Settling ponds would collect runoff from low sulfur waste stockpiles and seep into groundwater at a rate of at least 5,000-6,000 gallons/day; this could cause an increase in contaminant concentrations in the groundwater near the ponds. Most groundwater under the ponds would flow into the pit, limiting the potential zone of contamination. Surface water impacts could include increased soil erosion and discharge of sediment (increased turbidity) to the river. Discharge into the Flambeau River will not cause the concentration of any substances in the river to exceed the most stringent applicable water quality standards. The groundwater drawdown may affect additional acreage. A small amount of contaminants from the settling ponds may be transported in the groundwater to the Flambeau River but would not measurably affect the river water quality. After closure, discharge of contaminants would not likely be measurable in the Flambeau River due to dilution by the

large river flow. Pit backfilling will eliminate pit waters. Modeled leachate concentrations in pit backfill were predicted to be 0.014 mg/l copper, 0.32 mg/l iron, 0.725 mg/l manganese, and 1,360 mg/l sulfate.

6.3.25.2. ACTUAL WATER QUALITY CONDITIONS

Monitoring and compliance data for the period 2000-2003 were obtained from the 2003 Annual Report, Groundwater and Surface Water Trends (Flambeau Mining Company, January 1, 2004). One surface water monitoring location and four groundwater monitoring locations were noted. The following water quality data was noted.

Four monitoring wells in the backfilled pit showed exceedences of drinking water MCLs or secondary standards for iron (up to 12 mg/l), manganese (up to 37 mg/l), pH (as low as 6.1), sulfate (up to 1,700 mg/l) and total dissolved solids (up to 3,400 mg/l). One in-pit well showed continued increasing or elevated concentrations of iron, sulfate, TDS and manganese; other wells showed decreasing concentrations. Groundwater elevations were higher in the backfilled pit than they were between the pit and the river, so water potentially flows from the pit to the river. After groundwater elevations returned to pre-mining levels, concentrations of iron, manganese, sulfate and TDS increased and pH decreased. Values for pH before pumping began were quite variable (5.8 - ~8.3). Concentrations appeared to peak in 2000 and were slowly decreasing for manganese (from a high of over 5,000 µg/l), sulfate (from a high of almost 700 mg/l) and TDS (from a high of ~1,300 mg/l), but are continuing to increase for iron (up to ~6 mg/l). Zinc concentrations were variable and still (as of 2003) ~700 µg/l (Lehrke, 2004).

Although concentrations in surface water up and downgradient of the mine showed no temporal water quality trends, a report from the Great Lakes Indian Fish and Wildlife Commission stated that water parameters measured have changed from those measured during mine operation, and that the change makes it impossible to compare during- and post-mining water quality (Coleman, 2004). In addition, the report states that the downstream sample site SW-2 is above the discharge point for surface water coming from the southeast portion of the mine site and therefore may not capture all releases from the mine.

6.3.25.3. COMPARISON OF PREDICTED AND ACTUAL WATER QUALITY

Table 6.31 provides a summary and comparison of potential, predicted and actual water quality information for the Flambeau Mine. The accuracy of the predictions is discussed in this section.

Elevated Concentrations of Iron, Manganese, Sulfate, TDS and Acidity in Pit Backfill Leachate: The concentrations of copper, iron, manganese and sulfate in the backfilled pit were predicted using geochemical modeling in the 1900 EIS. The modeling apparently used concentrations from short-term leach tests, but the details of modeling were not provided in the EIS. Predictions were also made in 1996 and 1997 as part of the mine's backfill plan. Concentrations predicted in 1997 for copper, manganese, and iron were substantially higher than those predicted in the EIS. For example, copper concentrations predicted in 1997 were 0.18 to 0.56 mg/l, and concentrations in the EIS were 0.014 mg/l. Compared to EIS-predicted post-mining concentrations in the pit backfill, post-mining concentrations in the backfill were higher by up to 45 times for copper, 70 times for manganese, 30 times for iron, and 1.25 times for sulfate. Therefore, modeling underestimated actual concentrations of metals and other contaminants in the pit backfill leachate.

Table 6.31. Flambeau, WI, Potential, Predicted and Actual Impacts

Resource	Source	Potential Impact	Mitigation	Predicted Impact	Actual Impact
Pit Backfill Leachate	Pit backfill	Pit backfill will eliminate pit waters.	Backfilling to eliminate possibility of a pit lake. Liming of backfill.	Pit backfill will eliminate pit waters. Predicted leachate concentration in pit backfill was 0.014 mg/l copper, 0.32 mg/l iron, 0.725 mg/l manganese and 1,360 mg/l sulfate.	Four monitoring wells in the backfilled pit show exceedences of drinking water standards for iron, manganese, pH, sulfate and TDS. One in-pit well shows continued increasing or elevated concentrations of iron, sulfate, TDS and manganese; other wells show decreasing concentrations.
Groundwater	Pit backfill	Waste rock from the mining operation would have the potential to leach contaminants to ground water.	High sulfur waste stockpiles and ore crushing/ loading areas lined. Treatment of mine water before discharge; Liming of backfill. Settling ponds to collect runoff from low sulfur stockpiles.	Slightly increased TDS, hardness, sulfate, iron and manganese may be expected from leachate infiltration. No impacts from high sulfur stockpile, ore crushing areas. Worst-case leakage would leak into mine pit, where water would be treated before discharge. Groundwater under ponds flows to pit, limiting contamination.	Samples taken from a well between the river and the pit show exceedences of drinking water standards for iron (2.8-7.4 mg/l), manganese (3.1-4.2 mg/l), pH (5.9-6.2), sulfate (250-460 mg/l), and TDS (810-1,100 mg/l).
Surface Water and Springs	Pit backfill and mine operations	Waste rock from the mining operation would have the potential to leach contaminants to surface waters.	Settling ponds collect runoff from low sulfur stockpiles for treatment prior to discharge. Ponds unlined, but seepage to groundwater would flow mostly to pit. Contaminant flow to pit treated prior to discharge to river.	Increased erosion and discharge to river possible. Discharge will not cause concentration of any substance to exceed standards. Contaminants from ponds may be transported to river, wouldn't affect water quality. Post-closure discharge of contaminants not measurable in river due to dilution.	No observable changes in surface water quality, but sample locations may not capture all releases from mine.

7. SUMMARY OF CASE STUDY FINDINGS AND INHERENT FACTORS AFFECTING OPERATIONAL WATER QUALITY

Section 7 presents a general summary of predicted and actual water quality for the 25 case study mines. To determine the accuracy of water quality predictions, statements made in the NEPA documents about potential and predicted water quality impacts were compared with actual operational water quality data, using information from Section 6. Water quality impacts from acid drainage and other contaminants may be delayed, depending on the amount and availability of neutralizing and acid-generating material, the distance to water resources, and other factors (Maest et al., 2005). Because mines that have not had water quality impacts to date may have impacts in the future, a greater emphasis is placed in this report on comparing predictions for mines that have already had water quality impacts.

“Inherent” factors affecting operational water quality at the case study mines are also identified and discussed. The potential inherent factors identified in the EISs that can affect water quality at mine sites include geology and mineralization, acid drainage and contaminant leaching potential, climate and proximity to water resources. If a strong relationship exists between certain of these factors and operational water quality for the case study mines, it may be possible to estimate in advance – knowing only what can be gathered from EISs – which mines may have better and worse environmental performance.

Section 7.1 presents the general findings on the accuracy of water quality predictions in the EISs and EAs. Section 7.2 presents information on the relationship between inherent characteristics (or combinations of characteristics) and actual water quality at the case study mines. Although predictions from all EISs for a given mine were considered, the initial predictions (i.e., in the first EIS or EA) are often the most important, because, with the exception of separate expansions, the major mitigating measures are based on these initial predictions. Although sample sizes are not large enough for statically valid comparisons, general statistical measures (simple percentages for a population with a given characteristic) are presented to indicate the importance of the associations discussed.

7.1. ACCURACY OF WATER QUALITY PREDICTIONS: SUMMARY OF CASE STUDY FINDINGS

Findings for individual case study mines are presented in Section 6. In Section 7.1, predicted and actual water quality data are reviewed for all 25 case study mines to determine if there are patterns in the accuracy of EIS water quality predictions.

7.1.1. ACID DRAINAGE/CONTAMINANT LEACHING POTENTIAL AND DEVELOPMENT

The potential for acid drainage is usually determined using static acid-base accounting tests, while the potential for contaminant leaching is usually determined using the results from short-term leach tests and analysis of the leachate for metal concentrations. Kinetic test results can be used to determine both acid drainage and contaminant leaching potential. It is possible to have neutral or even basic drainage and elevated contaminant concentrations, especially for constituents such as arsenic and other oxyanions, cyanide, and anions such as nitrate and sulfate. Therefore, these two geochemical characteristics (acid drainage and contaminant leaching) are discussed separately.

The results for acid drainage and contaminant leaching potential and development are contained in Tables 7.1, 7.2 and 7.3. The majority of the case study mines (18/25 or 72%) predicted low potential for acid drainage in one or more EIS. Of the 25 case study mines, 36% have developed acid drainage on site to date. Of these nine mines, eight (89%) predicted low acid drainage potential initially or had no information on acid drainage potential. The Greens Creek Mine in Alaska initially predicted moderate acid drainage potential but later predicted low potential for acid drainage for an additional waste rock disposal facility. Therefore, nearly all the mines that developed acid drainage either underestimated or ignored the potential for acid drainage in their EISs.

Table 7.1. EIS and Operational Water Quality Information for Case Study Mines

Site	State	Highest (Lowest) Acid Drainage Potential	Acid Drainage Developed on Site?	Contaminant Leaching Potential	Standards Exceeded in SW?	Constituent Increasing or Exceeding in SW	Standards Exceeded in GW?	Constituents Increasing or Exceeding in GW or Seeps
Greens Creek	AK	Moderate (Low)	Yes	Low	Yes	low pH, Cd, Cu, Hg, Zn, SO ₄	No	GW: SO ₄ ; seeps: SO ₄ , Zn, pH, Cu, Pb, Se
Bagdad	AZ	Low	Yes	No info	Yes	As, Pb, Hg, Se	No info	NA
Ray	AZ	No info	Yes	No info	Yes	TDS, NH ₃ , As, Be, Cu, turbidity	No info	NA
American Girl	CA	Low (0 initial)	No	Low (No info initial)	No	None	No	None
Castle Mountain	CA	Low	No	Low	No	None	No	None
Jamestown	CA	Low	No	Low	No info	NA	Yes	SO ₄ , NO ₃ , As
McLaughlin	CA	Low	Yes	Moderate	Yes	SO ₄ , As, Cr, Cu, Pb, Mn, Ni, Hg, Fe, Zn	Yes	TDS, Cl, NO ₃ , SO ₄ , Cu, Fe, Mn, B, Zn
Mesquite	CA	Low	No	Low (No info initial)	No	None	No	None
Royal Mountain King	CA	Low	No	No info	Yes	NO ₃ , SO ₄ , TDS, As	Yes	Cl, NO ₃ , Ni, Se, SO ₄ , TDS, Mn, As, Sb, Cr, Cu, Ni, CN
Grouse Creek	ID	Moderate	No	Low	Yes	CN	Yes	GW: CN; Tail pore water: Al, Cu, As, Se, Ag, Zn, CN
Thompson Creek	ID	Moderate (Low initial)	Yes	Low	Yes	Cd, Cu, Pb, Zn, SO ₄	No info	Seeps: Fe, Zn, SO ₄ , Se; GW: NA
Beal Mountain	MT	Moderate (Low initial)	No	Low	Yes	NO ₃ , TDS, SO ₄ , CN	Yes	GW: NO ₃ , Fe, CN; TDS. Seeps: CN, Se, SO ₄ , NO ₃
Black Pine	MT	High (no info initial)	Yes	Moderate	Yes	SO ₄ , Cu, Zn, Fe, Cd, low pH	No info	Seeps: low pH, SO ₄ , Cu, Zn, Fe, Cd; GW: NA

Table 7.1. EIS and Operational Water Quality Information for Case Study Mines (continued)

Site	State	Highest (Lowest) Acid Drainage Potential	Acid Drainage Developed on Site?	Contaminant Leaching Potential	Standards Exceeded in SW?	Constituent Increasing or Exceeding in SW	Standards Exceeded in GW?	Constituents Increasing or Exceeding in GW or Seeps
Golden Sunlight	MT	High (Low initial)	Yes	High	No	NA	Yes	CN, Cu, low pH
Mineral Hill	MT	Low	No	Moderate	Yes	CN, NO ₃ , Mn, SO ₄ , As, TDS	Yes	CN, NO ₃ , Mn, SO ₄ , As, TDS
Stillwater	MT	Low	No	Moderate	No	NO ₃	No	Audit: Cd, Cu, Pb, Mn, Zn, NO ₃ . GW: Cr, Fe, SO ₄ , Cl, PO ₄ , Cd, Zn
Zortman and Landusky	MT	High (Low initial)	Yes	Moderate	Yes	metals, metalloids, NO ₃ , low pH, CN	Yes	low pH, As, metals, NO ₃ , CN
Florida Canyon	NV	Low	No	Moderate	No	NA	Yes	CN, Hg, NO ₃ , Cl, TDS
Jerritt Canyon	NV	Moderate	No	Moderate	Yes	TDS, SO ₄	Yes	CN, Cl, TDS, SO ₄
Lone Tree	NV	Moderate	No	High	Yes	pH, TDS, F, B, NH ₃	Yes (baseline?)	F, Fe, Mn, TDS, Al, B, NH ₄ , pH
Rochester	NV	Moderate (Low initial)	No	Moderate	Yes	NO ₃ , As	Yes	CN, Hg, Cd, NO ₃ , As
Round Mountain	NV	Low	No	High	No info	NA	Yes (baseline?)	Al F, Fe, Mn, TDS, Sb, Pb
Ruby Hill	NV	Low	No	Moderate	No info	NA	Yes (baseline?)	As, NO ₃ , Pb
Twin Creeks	NV	Moderate	No	High	Yes	TDS, As	Yes - perched GW	TDS, SO ₄ , Cl, CN, Al, Sb, As, Mg, Fe, Hg, Mn
Flambeau	WI	No info	Yes	Moderate	No	SO ₄ , Mn, low pH, Fe	Yes	Fe, Mn, pH, SO ₄ , TDS

No info = no information; NA = not applicable; Ag = silver; Al = aluminum; As = arsenic; B = boron; Be = beryllium; Cd = cadmium; Cl = chloride; CN = cyanide; Cr = chromium; Cu = copper; F = fluoride; Fe = iron; Hg = mercury; Mn = manganese; Ni = nickel; NO₃ = nitrate; NH₄ = ammonia; Pb = lead; Sb = antimony; Se = selenium; SO₄ = sulfate; TDS = total dissolved solids; Zn = zinc.

Table 7.2. Acid Drainage Potential Predictions and Results for Case Study Mines (Percentages)

Element	Number/Total	Percentage
Mines predicting low acid drainage potential	18/25	72%
Mines that have developed acid drainage	9/25	36%
Mines with acid drainage that predicted low acid drainage potential	8/9	89%

Table 7.3. Contaminant Leaching Potential Predictions and Results for Case Study Mines (Percentages)

Element	Number/Total	Percentage
Mines predicting low contaminant leaching potential	8/25	32%
Mines with mining-related exceedences in surface water or groundwater	19/25	76%
Mines with exceedences that predicted low contaminant leaching potential	8/19	42%
Mines with exceedences that predicted moderate contaminant leaching potential	8/19	42%
Mines with exceedences that predicted high contaminant leaching potential	3/19	16%

Eight case study mines predicted low contaminant leaching potential (Table 7.3). Of these eight mines, five (63%) had exceedences of standards in either surface water or groundwater or both after mining began. The three mines that predicted low contaminant leaching potential and had no exceedences of water quality standards were the three California desert mines: American Girl, Castle Mountain and Mesquite. Stated another way, 21 of the 25 case study mines (84%) had exceedences of water quality standards in either surface water or groundwater or both (Table 7.1). The exceedences at two of these mines may be related to baseline conditions. Of the remaining 19 mines, eight (42%) predicted low contaminant leaching potential (or had no information), eight (42%) predicted moderate contaminant leaching potential, and only three (16%) predicted high contaminant leaching potential. Therefore, nearly half of the mines that had exceedences of water quality standards underestimated or ignored the potential for contaminant leaching potential in EISs. The constituents that most often exceeded standards or that had increasing concentrations in groundwater or surface water included toxic heavy metals such as copper, cadmium, lead, mercury, nickel, or zinc (at 12/19 or 63% of case study mines), arsenic and sulfate (11/19, or 58% each), and cyanide (10/19, or 53%).

7.1.2. PREDICTED AND ACTUAL IMPACTS TO SURFACE WATER RESOURCES

Table 7.4 lists the case study mines, their potential and predicted surface water quality impacts from the EISs, and whether or not there were mining-related impacts or exceedences in surface water. The results in percentages are presented in Table 7.5. Sixty percent (15/25) of the case study mines had mining-related exceedences in surface water. One mine, (Stillwater Mine, MT) had mining-related increases of nitrate in surface water, but concentrations have not exceeded standards.

Table 7.4. Predicted and Actual Impacts and Proximity to Surface Water Resources at Case Study Mines

Site	State	Highest (Lowest) Potential Impact to SW	Highest Predicted Impact to SW	SW Impact?	Standards Exceeded in SW?	Perennial Streams or Discharge?
Greens Creek	AK	Low	Low	Yes	Yes	Both
Bagdad	AZ	Low	Low	Yes	Yes	Discharge
Ray	AZ	No info	No info	Yes	Yes	Discharge
American Girl	CA	Moderate (Low initial)	Low	No	No	No
Castle Mountain	CA	Low	Low	No	No	No
Jamestown	CA	Moderate	Low	No info	No info	Perennial
McLaughlin	CA	Moderate	Moderate	Yes	Yes	Discharge
Mesquite	CA	Moderate (Low)	Low	No	No	No
Royal Mountain King	CA	No info	No info	Yes	Yes	No info (Perennial); No discharge
Grouse Creek	ID	Moderate (Low initial)	Low (no info initial)	Yes	Yes	Perennial
Thompson Creek	ID	Moderate	Moderate (Low)	Yes	Yes	Both
Beal Mountain	MT	Moderate (no info initial)	Low	Yes	Yes	Both
Black Pine	MT	No info	Low	Yes	Yes	Perennial
Golden Sunlight	MT	Low	Low	No	No	No
Mineral Hill	MT	Low	Low	Yes	Yes	Both
Stillwater	MT	Low (no info initial)	Low	Yes	No	Discharge (unused)
Zortman and Landusky	MT	High (no info initial)	High (Low initial)	Yes	Yes	Both
Florida Canyon	NV	No info	Low	No	No	No
Jerritt Canyon	NV	Moderate	Low	Yes	Yes	Perennial
Lone Tree	NV	Moderate	Low	Yes	Yes	Discharge
Rochester	NV	Moderate	Low	Yes	Yes	No
Round Mountain	NV	Moderate	Low	No info	No info	No
Ruby Hill	NV	Low	Low	No info	No info	No
Twin Creeks	NV	High	Low	Yes	Yes	Both
Flambeau	WI	Moderate	Low	No	No	Discharge

Table 7.5. Predicted and Actual Impacts to Surface Water Resources at Case Study Mines (Percentages)

Element	Number/Total	Percentage
Mines with mining-related surface water exceedences	15/25	60
Mines with surface water exceedences predicting low impacts without mitigation	4/15	27%
Mines with surface water exceedences predicting low impacts with mitigation	11/15	73%

A little over one-third (nine or 36%) of the case study mines noted a low potential for surface water impacts. Ten (40%) of the case study mines noted a moderate potential, and one noted a high potential for surface water quality impacts in the absence of mitigating measures. Of the 15 mines with exceedences of standards in surface water, three (20%) noted a low potential (pre-mitigation), seven (47%) stated that there would be a moderate potential, two stated there would be a high potential, and three had no information in their EISs on surface water quality impact potential in the absence of mitigation (Table 7.4).

In terms of predicted (post-mitigation) surface water quality impacts, 73% (11/15) of the mines with surface water quality impacts predicted low water quality impacts in their initial EISs, two predicted moderate impacts, and two had no information on post-mitigation impacts to surface water resources (Table 7.5). Therefore, the predictions made about surface water quality impacts before the effects of mitigation were considered were more accurate than those made taking the effects of mitigation into account. Stated in another way, the ameliorating effect of mitigation on surface water quality was overestimated in the majority of the case study mines. No mine conducted field or laboratory studies to determine the effects of mitigation on water quality improvement; rather, the predictions for both surface water and groundwater quality appeared to be based on unstated assumptions or best professional judgment.

Of the mines with surface water quality exceedences, only one mine (McLaughlin, CA) was correct in predicting a moderate potential for surface water quality impacts with mitigation in place; the others predicted low potential (not exceeding standards) in at least one EIS. However, the McLaughlin Mine predicted low acid drainage potential, and acid drainage has developed on site. Of the mines without surface water quality exceedences (seven or 28%), all were correct thus far in predicting no impacts to surface water with mitigation in place. Three of the seven are desert mines in California, one (Stillwater, MT) has had increases in contaminant concentrations but no exceedences, and the other three have had no exceedences or increases in mining-related contaminant concentrations in surface water to date. Therefore, most case study mines predicted no impacts to surface water quality after mitigation are in place, but at the majority of these mines, impacts have already occurred.

7.1.3. PREDICTED AND ACTUAL IMPACTS TO GROUNDWATER RESOURCES

Table 7.6 lists the case study mines, their potential and predicted groundwater quality impacts from the EISs, and whether or not there were mining-related impacts or exceedences in groundwater or seeps. The results in percentages are presented in Table 7.7. The majority (64%, or 16/25) of the case study mines had exceedences of water quality standards in groundwater. However, exceedences at three of the mines, all in Nevada, may be related to baseline conditions; therefore, 52% of the case study mines clearly had mining-related exceedences of standards in surface water. Exceedences at one mine (Twin Creeks, NV) were said to be in “perched” groundwater. One mine (Greens Creek, AK) had mining-related increases of sulfate in groundwater, but concentrations have not exceeded standards. No information on groundwater quality impacts was available for four mines; however, two of these mines had mining-related exceedences in seeps. There were drinking water exceedences in adit water at the Stillwater Mine in Montana.

Table 7.6. Predicted and Actual Impacts and Proximity to Groundwater Resources at Case Study Mines

Site	State	Highest (Lowest) GW Impact Potential	Highest (Lowest) Predicted GW Impact	GW Impacts?	Standards Exceeded in GW?	Mining-related Exceedences in Seeps?	Shallow Groundwater or Discharge?
Greens Creek	AK	Moderate (Low)	Low	Yes	No	Yes	Shallow
Bagdad	AZ	Low	Low	NA	NA	NA	Shallow
Ray	AZ	No info	No info	NA	NA	NA	No
American Girl	CA	Moderate	Low	No	No	No	Shallow
Castle Mountain	CA	Low	Low	No	No	No	No
Jamestown	CA	Moderate	Low	Yes	Yes	NA	Shallow
McLaughlin	CA	High	High	Yes	Yes	NA	Shallow
Mesquite	CA	Moderate (Low initial)	Low	No	No	No	No
Royal Mountain King	CA	Moderate	No info	Yes	Yes	NA	No info
Grouse Creek	ID	Moderate (Low initial)	Low (no info initial)	Yes	Yes	NA	Shallow
Thompson Creek	ID	Moderate	Moderate (Low)	NA	NA	Yes	Shallow
Beal Mountain	MT	Moderate (no info initial)	Low	Yes	Yes	Yes	Shallow
Black Pine	MT	No info	Low	NA	NA	Yes	Shallow
Golden Sunlight	MT	High (Moderate)	High (Low initial)	Yes	Yes	Yes	Shallow
Mineral Hill	MT	Moderate	Low (no info initial)	Yes	Yes	NA	No
Stillwater	MT	Low (no info initial)	Low	No	No	Yes - adit	Both
Zortman and Landusky	MT	Moderate (Low)	High (Low)	Yes	Yes	Yes	Shallow
Florida Canyon	NV	Moderate	Low	Yes	Yes	NA	Shallow
Jerritt Canyon	NV	Moderate (Low initial)	Low (no info initial)	Yes	Yes	NA	Shallow
Lone Tree	NV	Low	Low	No? (baseline?)	Yes (baseline?)	NA	Shallow
Rochester	NV	Moderate (no info initial)	Low	Yes	Yes	NA	Shallow
Round Mountain	NV	High	Low	No? (baseline?)	Yes (baseline?)	NA	No
Ruby Hill	NV	Low	Low	No? (baseline?)	Yes (baseline?)	NA	No
Twin Creeks	NV	Moderate	Low	Yes	Yes - perched GW	NA	Discharge
Flambeau	WI	Moderate	Low	Yes	Yes	NA	Shallow

Table 7.7. Predicted and Actual Impacts to Groundwater Resources at Case Study Mines (Percentages)

Element	Number/Total	Percentage
Mines with mining-related groundwater exceedences	13/25	52%
Mines with groundwater exceedences predicting low impacts without mitigation	2/13	15%
Mines with groundwater exceedences predicting low impacts with mitigation	10/13	77%

About one-third of the case study mines (eight or 32%) noted a low potential for groundwater quality impacts in the absence of mitigating measures (Table 7.7). Of the 13 mines with mining-related exceedences in groundwater, only two noted a low potential for groundwater quality impacts in the original EIS, the majority (nine or 69%) stated that there would be a moderate potential, and two stated there was a high potential for groundwater impacts in the absence of mitigation (Table 7.7). In terms of predicted (post-mitigation) groundwater quality impacts, most of the case study mines (10 or 80%) predicted low groundwater quality impacts (not exceeding standards) after mitigation were in place. And an even higher percentage (10 or 77%) of the mines with exceedences in groundwater predicted low water quality impacts in their EISs (including mines predicting low impacts in the original EIS). Therefore, as with surface water, the predictions made about groundwater quality impacts without considering the effects of mitigation were somewhat more accurate than those made taking the effects of mitigation into account. Again, the ameliorating effect of mitigation on groundwater quality was overestimated in the majority of the case study mines.

Of the mines with mining-related groundwater quality exceedences (13), only one mine – the McLaughlin Mine in California – was correct in predicting a high potential for groundwater quality impacts with mitigation in place. This is the same mine that correctly predicted that there would be surface water exceedences. The others predicted low potential (not exceeding standards) for groundwater quality impacts in at least one EIS. Of the mines without groundwater quality exceedences (five or 25%), all were correct in predicting no impacts to surface water with mitigation in place. Again, three of the five are desert mines in California, one (Stillwater MT) has had increases in contaminant concentrations but no exceedences, and the other (Greens Creek, AK) has had mining-related exceedences in seeps. Therefore, most mines predicted no impacts to groundwater quality after mitigation were in place, but in the majority of case study mines, impacts have occurred.

7.2. INHERENT FACTORS AFFECTING WATER QUALITY AT CASE STUDY MINES

One of the goals of this study was to determine if there are certain factors that make a mine more or less likely to have water quality problems and more or less likely to accurately predict future water quality. Such factors could include: inherent characteristics of the mined materials; inherent characteristics of the mine; management approaches to handling mined materials and water; the type and number of geochemical tests that are performed on mined materials; and the interpretation of test results.

There are two types of water quality predictions in EISs: “potential” water quality (does not take mitigation into account) and “predicted” water quality (does take mitigation into account). As noted in Section 7.1, nearly all the EISs reviewed reported that they expected acceptable water quality (concentrations lower than relevant standards) after mitigation were taken into account. Indeed, if this prediction was not made in the EIS, the regulatory agency would not be able to approve the mine (with certain exceptions, such as pit water quality in states where pit water is not considered a water of the state).

Certain inherent characteristics of the mined materials or mining locations may make the mine more or less susceptible to water quality impacts and more or less likely to have accurate predictions about future water quality. Some of the inherent characteristics that may influence a mine’s environmental behavior include:

- ore type and association (e.g., commodity, sulfide vs. oxide ore, vein vs. disseminated)
- climate (e.g., amount and timing of precipitation, evaporation, temperature)
- proximity to water resources (distance to surface water resources, depth to groundwater resources, presence of springs)
- pre-existing water quality (baseline groundwater and surface water quality conditions)
- constituents of concern
- acid generation and neutralization potentials (and timing of their release), and
- contaminant generation potential.

In addition to the inherent characteristics of a mine and its location, the management of the mine and its wastes and waters, the processing chemicals used, and the type of operation (e.g., vat leach and tailings vs. heap leach facility; underground vs. surface mine) will have an important effect on a mine's environmental behavior. The management and mitigation measures used can be one of the root causes of water quality problems, and these issues are addressed in Section 8.

This section examines the inherent factors that can influence environmental behavior at mine sites. Information from the EISs presented in Section 5, was used to evaluate the inherent factors and the mitigation measured used, and information on operational water quality at the case study mines, presented in Section 6 was used to determine if the identified water quality potential was accurate.

For this evaluation, a water quality impact is defined as increases in concentration of water quality parameters as a result of mining operations, whether or not an exceedence of water quality standards or permit levels has occurred. Information on whether groundwater, seep or surface water concentrations exceeded standards as a result of mining activity is also included.

Information gathered from the EISs was used to categorize the inherent characteristics of the mine and its materials. All of the potential inherent factors listed above were listed in the database under NEPA information. The inherent factors evaluated include: geology and mineralization; proximity to water resources and climatic conditions; and geochemical characteristics of mined materials, such as acid drainage and contaminant leaching potential.

Mines with close proximity to water resources and moderate to high acid drainage or contaminant leaching potential are examined together to determine if this combination of inherent factors results in a higher risk of adverse water quality impacts. Results for case study mines with this combination of factors are included in Tables 7.1, 7.4 (surface water) and 7.6 (groundwater and seeps). The tables list: the acid drainage and contaminant leaching potential: the presence of surface water or groundwater impacts: the presence of acid drainage on site; exceedence of standards in surface water, groundwater or seeps; constituents that have increased in concentration over baseline conditions or exceeded standards; the presence of perennial streams or shallow groundwater on site; and the type of discharge to surface water or groundwater. The discharges to surface water are usually permitted National Pollution Discharge Elimination System (NPDES) discharges under the Clean Water Act. The tables also include information from the EISs on water quality predictions, including the potential (pre-mitigation) and predicted (post-mitigation) impact to water resources.

7.2.1. MINES WITH CLOSE PROXIMITY TO SURFACE WATER AND MODERATE TO HIGH ACID DRAINAGE OR CONTAMINANT LEACHING POTENTIAL

EIS and operational water quality information for mines with close proximity to surface water and elevated acid drainage or contaminant leaching potential is listed in Tables 7.1 and 7.4.

Mines with Moderate to High Acid Drainage Potential

The following case study mines have perennial streams on site or discharge directly to surface water and have a moderate to high acid drainage potential (see Table 7.1):

- Greens Creek, Alaska
- Grouse Creek, Idaho
- Thompson Creek, Idaho
- Beal Mountain, Montana
- Black Pine, Montana
- Zortman and Landusky, Montana
- Jerritt Canyon, Nevada
- Lone Tree, Nevada
- Twin Creeks, Nevada

Of these nine mines, all (100%) had mining-related exceedences of water quality standards in surface water. Of the nine mines with identified moderate to high acid drainage potential and close proximity to surface water resources, four (44%) have currently developed acid drainage on site. Impacts to surface water from the other five mines resulted from cyanide, nitrate, sulfate, metalloids, ammonia or other anions (Table 7.1).

At the Greens Creek Mine, elevated concentrations of sulfate and zinc and lower pH values were measured in smaller streams, most likely as a result of leaching of high sulfide material (tailings or waste rock) lying outside of the tailings pile capture area. At the Grouse Creek Mine, tailings impoundment leakage into groundwater resulted in cyanide in surface water. At the Thompson Creek Mine, creeks downgradient of the waste rock dumps had increasing concentrations of sulfate (to values in excess of water quality standards) over a six-year period. At the Beal Mountain Mine, nitrate, total dissolved solids, and sulfate concentrations in streams have increased relative to baseline conditions, and cyanide exceeded aquatic life standards. At the Black Pine Mine, springs impacted by waste rock flow into Smart Creek and have elevated concentrations of sulfate, copper, zinc, iron, and cadmium, and low pH values. At the Zortman and Landusky Mine, streams were impacted by acid drainage from waste rock and the heap leach pad. The Lone Tree Mine has been in general compliance with overall permit requirements for discharge of its dewatering water to the Humboldt River, but there were some exceedences of permit limits, and Newmont has been fined for these exceedences. Although no information was obtained on stream water quality at the Twin Creeks Mine, dewatering water discharged to Rabbit Creek has shown exceedences of total dissolved solids and arsenic standards by up to 10 times.

Each of these nine mines predicted low surface water impacts after mitigation were in place in at least one or all of the EISs (Table 7.4). For the Thompson Creek and Zortman and Landusky mines, later EISs predicted higher potential impact to surface water, but in both cases, the initial EIS predicted low impacts to surface water resources. In a number of cases, the mines expanded before the development of poor water quality conditions. These results suggest that even though mines may identify a moderate to high acid drainage potential, they predict that surface water resources will not be impacted after mitigation are implemented. In all cases where elevated acid drainage potential was identified, the predicted impact to surface water was identified as “low” in at least one EIS, yet impacts have occurred (see Tables 7.1 and 7.4).

Mines with Moderate to High Contaminant Leaching Potential

The following mines have perennial streams on site or discharge directly to surface water and identified a moderate to high potential for contaminant leaching in their EISs (see Table 7.1):

- McLaughlin, California
- Black Pine, Montana
- Mineral Hill, Montana
- Stillwater, Montana

- Zortman and Landusky, Montana
- Jerriitt Canyon, Nevada
- Lone Tree, Nevada
- Twin Creeks, Nevada
- Flambeau, Wisconsin

Of these nine mines, five also have moderate to high acid drainage potential and proximity to surface water resources and were discussed above. With the exception of the Flambeau Mine, which has developed acid drainage on site, all nine mines have had some impact to surface water quality from mining operations, as shown in Table 7.1. For nine mines with proximity to surface water resources and moderate to high contaminant leaching potential, eight (89%) have shown some impact to surface water quality, and seven (78%) of the nine mines have had exceedences of standards in surface water.

Of the remaining four mines, the McLaughlin Mine has had exceedences of sulfate (showing steady increases since mining began, and occasionally large exceedences of arsenic, chromium, copper, lead, manganese, mercury, iron and zinc. However, no surface water quality violations were recorded for the McLaughlin Mine because of the way baseline water quality is calculated. At the Mineral Hill Mine, tailings leachate containing cyanide, nitrate, manganese, sulfate, arsenic, and dissolved solids has escaped the liner system and caused exceedences in surface water. The Stillwater Mine does not have perennial streams on site, but it does have a NPDES permit for discharge of mine water to surface water. However, this permit has never been used. Nitrate concentrations in the Stillwater River have increased to as high as 0.7 mg/l (site-specific limit is 1.0 mg/l) as a result of mining activity, but no standards or limits were exceeded. At the Flambeau Mine, there were no observable changes in surface water quality, but there is some concern that surface water sample locations may not capture all releases from mine. The Flambeau Mine has had groundwater impacts from the backfilled pit. More monitoring of additional locations over a longer time period is required to determine if observed poor groundwater quality will adversely affect downgradient surface water.

In terms of EIS predictions, six of the nine mines identified moderate to high potential for surface water impacts without mitigation, but eight of the nine predicted low impacts to surface water after mitigation were in place (as noted above, the Zortman and Landusky Mine initially predicted a low impact to surface water resources). To date, predictions for surface water impacts at the McLaughlin, Stillwater and Flambeau mines were accurate, but the remaining six mines underestimated the actual impact to surface water in their EISs.

Comparison to All Case Study Mines

Surface water impacts for the mines with close proximity to surface water and high acid drainage or contaminant leaching potential are compared to surface water impacts for all the case study mines in Table 7.8. Overall, for the 13 mines with close proximity to surface water and high acid drainage or contaminant leaching potential (see Table 7.1), 12 (92%) have had some impact to surface water as a result of mining activity (see Table 7.5). For all case study mines, only 64% had some surface water quality impact. Eleven of the 13 (85%) have had exceedences of standards or permit limits in surface water as a result of mining activity. These results, although not comprehensive, suggest that the combination of proximity to surface water resources (including direct discharges to surface water) and moderate to high potential for acid drainage does increase the risk of water quality impacts. Although this finding makes intuitive sense from a risk perspective, a comprehensive study of cause and effect has never been conducted.

Of the 11 with exceedences, 10 (91%) predicted that surface water standards would not be exceeded. Considering the two mines that accurately predicted no surface water exceedences (Stillwater and Flambeau) and the one that accurately predicted exceedences (McLaughlin), 77% of mines with close proximity to surface water or direct discharges to surface water and moderate to high acid drainage or contaminant leaching potential underestimated actual impacts to surface water. For all case study mines, 73% of the mines with surface water quality exceedences predicted that there would be no exceedences. Compared to all case study mines, higher percentages of mines with

close proximity to surface water and elevated acid drainage or contaminant leaching potential had surface water quality impacts and exceedences. EIS water quality predictions made before the ameliorating effects of mitigation were considered (“potential” water quality impacts) were more accurate at predicting operational water quality than predictions based on assumed improvements from mitigation. Mines with these inherent factors are the most likely to require perpetual treatment to reduce or eliminate the long-term adverse impacts to surface water resources.

Table 7.8. Surface Water Quality Impacts for Mines with Close Proximity to Surface Water and Elevated Acid Drainage Potential Compared to Surface Water Impacts for All Case Study Mines

	# Mines	Percent (%) with Impact to Surface Water	Percent (%) with Exceedences of Standards in Surface Water	Percent (%) with Exceedences that Predicted no Exceedences
Mines with close proximity to surface water and elevated acid drainage and contaminant leaching potential	13	92 (12/13)	85 (11/13)	91 10/11)
All case study mines	25	64 (16/25)	60 (15/25)	73 (11/15)

7.2.2. MINES WITH SHALLOW DEPTH OR DISCHARGES TO GROUNDWATER AND WITH MODERATE TO HIGH ACID DRAINAGE OR CONTAMINANT LEACHING POTENTIAL

The operational water quality of mines with shallow groundwater or discharges to groundwater resources – and with moderate to high acid drainage or contaminant leaching potential – is evaluated in this section. Mines with close proximity to groundwater resources are often close to surface water as well. Therefore, a number of mines evaluated above will also appear in this section. Mines that discharge to groundwater usually do so through infiltration basins or some other kind of land application. Although this is not a direct discharge to groundwater, it does increase the likelihood that the discharge water and any associated contaminants will reach groundwater. EIS and operational water quality information for mines with close proximity to groundwater and elevated acid drainage or contaminant leaching potential is listed in Tables 7.1 and 7.6.

Mines with Moderate to High Acid Drainage Potential

The following mines have a relatively shallow depth to groundwater (0 to 50 feet), have springs on site, or discharge to groundwater – and have a moderate to high acid drainage potential (see Table 7.1):

- Greens Creek, Alaska
- Grouse Creek, Idaho
- Thompson Creek, Idaho
- Beal Mountain, Montana
- Black Pine, Montana
- Golden Sunlight, Montana
- Zortman and Landusky, Montana
- Jerriitt Canyon, Nevada
- Lone Tree, Nevada
- Rochester, Nevada
- Twin Creeks, Nevada

Of these 11 mines, some groundwater quality information was obtained for all but two (Thompson Creek, ID; Black Pine, MT). However, there is information about seepage water quality from both of these facilities. Of the 11 mines

with shallow depths to groundwater, springs on site or that discharge to groundwater and that have moderate to high acid drainage potential, 10 (91%) have had some impact to groundwater or seeps from mining operations (see Table 7.6). The one exception is the Lone Tree Mine, which has groundwater exceedences that may be related to baseline conditions.

The Greens Creek Mine in Alaska has a depth to groundwater that ranges from the ground surface up to 50 feet deep. Seepage/runoff from the waste rock piles has an average zinc concentration of 1.65 mg/l, and tailings seepage water (including underdrain water) has had pH values as low as 5.8, with elevated sulfate (up to 2,400 mg/l), zinc (up to 3.6 mg/l), copper, lead, and selenium concentrations. Anomalously high sulfate concentrations were observed in groundwater monitoring wells, but metal concentrations have not increased as of 2000.

The Grouse Creek Mine has springs and shallow groundwater (depths ranging from 0.5 ft in alluvial aquifers to 100 ft in upland areas). The tailings liner and French drains installed below the tailings impoundment were not successful in preventing contamination from tailings leachate, and cyanide has been detected in both surface water and groundwater monitoring stations. Some contamination of groundwater is still evident at the site.

No groundwater data were obtained for the Thompson Creek Mine, which has flowing artesian wells, alluvial groundwater that is connected to streams, and some groundwater in bedrock fractures. However, tailings seeps have shown increases in iron and zinc, and sulfate and selenium concentrations in waste rock seeps were increasing since 1991, with selenium concentrations in excess of water quality standards.

At the Beal Mountain Mine in Montana, there is limited information on groundwater depth, but there are springs on site, and groundwater depth below the pit is only 25 to 50 ft. Groundwater in the land application area exceeded standards for nitrate, iron and cyanide and had elevated total dissolved solids concentrations. Springs below the land application area also show appreciable increases in cyanide and selenium. Concentrations of selenium, sulfate, nitrate and total dissolved solids were elevated in springs sampled at the toe of the waste rock dump.

At the Black Pine Mine in Montana, groundwater depths are approximately 45 feet in the impoundment area, and there are 30 springs in the project area. Although no direct information on groundwater quality was available, seeps downgradient of waste rock and the soils barren areas are acidic (pH 2.6-4.7) and have elevated concentrations of sulfate, copper, zinc, iron and cadmium.

The Golden Sunlight Mine has alluvial groundwater at 50 to 60 feet deep and numerous springs on site. Tailings effluent has contaminated downgradient wells with cyanide and copper (up to 65 mg/l copper). Acid drainage is being produced from the waste rock dumps, ore stockpiles, tailings and adits.

The Zortman and Landusky Mine in Montana has perched groundwater at 140 to 150 feet, an overall depth to groundwater of <200 feet, and springs and seeps on site. Karst features control groundwater flow in some areas. Acid drainage has been generated from waste rock dumps (as low as pH 3.9), the ore heap retaining dikes, pit walls and floors, and leach pads and pad foundations. Sulfate concentrations have increased in alluvial groundwater downgradient of the heap retaining dikes.

The Jerritt Canyon Mine has perched groundwater at eight to 70 feet deep, and 23 springs and eight seeps on site. The regional groundwater depth is approximately 700 feet. Groundwater has been impacted by seepage from the tailings impoundment, and a cyanide plume exists on site. Groundwater in the vicinity of the tailings area also has exceedences of chloride (up to 12,000 mg/l), TDS (up to 30,000 mg/l) and sulfate.

Groundwater at the Lone Tree Mine ranges from 10 to >200 feet deep. Pre-mining groundwater levels have scored the mine as being close to groundwater resources, but the large dewatering rate for this mine has lowered groundwater levels considerably. The Lone Tree Mine in Nevada has had exceedences of primary and secondary drinking water standards in groundwater, but it is not clear if the cause is baseline conditions or seepage from mine facilities.

Depth to groundwater at the Rochester Mine ranges from <1 to 20 feet in the alluvial aquifer and from the ground surface to approximately 400 feet in the bedrock aquifer. There are springs on site. Leaks from the heap leach pad and the barren solution pond have caused numerous exceedences of WAD cyanide, mercury, cadmium, nitrate and arsenic in groundwater.

The Twin Creeks Mine, which operates a large dewatering system, has a groundwater depth of over 100 feet over most of the mine site; the pit floor is approximately 400 feet below pre-mining groundwater levels. However, the mine discharges to groundwater through infiltration basins. Degradation of groundwater (perched water) with cyanide and other constituents has occurred as a result of seepage from the tailings impoundment. The vadose zone monitoring wells that were added during 2003 to monitor seepage from the tailings impoundment have shown multiple exceedences of total dissolved solids, sulfate, chloride, cyanide, aluminum, antimony, arsenic, iron, mercury and manganese.

Therefore, for the 11 case study mines with close proximity to groundwater resources or that discharge to groundwater and that have moderate to high acid drainage potential, eight (73%) have shown some adverse impact to groundwater quality from mining activity. Of the remaining three mines in this category, two have contaminated seeps flowing from tailings and/or waste rock storage areas (Thompson Creek, ID; Black Pine, MT), but no groundwater quality data were obtained, for a total of 10 mines (91%) with mining-related impacts to groundwater or seeps. One mine in this category (Lone Tree, NV) has had no groundwater impacts. However, the groundwater table at the Lone Tree Mine has been lowered considerably from dewatering operations, and it is unlikely that groundwater impacts would be evident at this time.

For the 11 case study mines with close proximity to groundwater and elevated acid drainage potential, seven (64%) had mining-related exceedences in groundwater. Of the remaining four mines, three had mining-related exceedences in seeps, and one (Lone Tree) has baseline exceedences. All 11 mines (100%) predicted low groundwater impacts in one or more EIS after mitigation were in place (Table 7.6), but three mines (Thompson Creek, ID; Golden Sunlight and Zortman and Landusky, MT) also predicted higher impacts in at least one EIS. Only four mines predicted low groundwater impacts without mitigation. Therefore, the predictions that considered the effects of mitigation on groundwater quality were overly optimistic, and the predictions without mitigation were more accurate.

Mines with Moderate to High Contaminant Leaching Potential

The following mines have a relatively shallow depth to groundwater (0 to 50 feet), have springs on site, or discharge to groundwater – and have a moderate to high contaminant leaching potential (see Table 7.1):

- McLaughlin, California
- Black Pine, Montana
- Golden Sunlight, Montana
- Stillwater, Montana
- Zortman and Landusky, Montana
- Florida Canyon, Nevada
- Jerriitt Canyon, Nevada
- Lone Tree, Nevada
- Rochester, Nevada
- Twin Creeks, Nevada
- Flambeau, Wisconsin

Of these 11 mines, all but four (McLaughlin, CA; Stillwater, MT; Florida Canyon, NV; Flambeau, WI) also have moderate to high acid drainage potential and were discussed above. As noted earlier, all of these seven mines have had some impact to groundwater or springs/seeps as a result of mining activity with the possible exception of the Lone Tree Mine in Nevada, which has exceedences in groundwater that may be related to baseline conditions. In addition, the originally shallow groundwater table at the Lone Tree Mine has been lowered considerably from dewatering operations, and it is unlikely that groundwater impacts would be evident at this time.

The McLaughlin Mine in California has been touted by the mining industry as an example of a mine with laudable environmental behavior and has received numerous environmental awards. When the state of Wisconsin passed a requirement for new mines in sulfide ore bodies to demonstrate that other mines with net acid generation potential have operated and been closed for at least 10 years without polluting groundwater or surface water (Wisconsin Act 171 {Statute §293.50}, passed in 1997), the McLaughlin Mine was one of the three examples used by Nicolet Minerals in their application for a permit for the Crandon Mine (Nicolet Minerals, 1998). The McLaughlin Mine has a regulatory exclusion for groundwater at the site, so no groundwater enforcement actions can be brought by Regional Water Quality Control Board (RWQCB). At the McLaughlin Mine, wells downgradient of the tailings impoundment had exceedences of TDS (up to 12,000 mg/l), chloride, nitrate (up to ~37 mg/l), and sulfate, and increases of copper (up to 280 µg/l) and other metals from 1984 – 1992 (mine began operation in 1985). Wells downgradient of waste rock dumps had increasing concentrations of sulfate (up to 5,000 mg/l), boron, TDS, calcium, iron, manganese and other constituents from 1985 to 1998 and zinc (up to 1.7 mg/l) after this timeframe.

The Stillwater Mine in Montana has also received environmental awards, and acid drainage has not developed on the site to date, likely due in part to the unique ultramafic host rock and associated mineralogy. Depth to groundwater at the mine is 40 to 90 feet, and there are three springs on site; the mine discharges adit water to percolation ponds and a land disposal area on the site. Groundwater at the Stillwater mine in the area of the East land application disposal area has exceeded drinking water standards for chromium, but the cause is tailings from an historic government-operated World War II- era mine. The adit water that percolates to groundwater is unimpacted, except for nitrogen contamination, but contains cadmium, copper, lead, manganese, zinc and nitrogen concentrations in excess of baseline surface water values. Groundwater downgradient of the land application facility has slight elevations of sulfate, chloride, phosphorous, cadmium, iron and zinc, but these appear to be a baseline issue.

The pre-mining regional groundwater table at the Florida Canyon Mine was quite deep (~400 feet), but alluvial groundwater exists at 0 to 250 feet deep. A contaminant plume with elevated concentrations or exceedences of WAD cyanide, mercury, nitrate, chloride, and TDS exists in groundwater downgradient from the leach pad. Other groundwater monitoring wells on the site show exceedences of drinking water standards for aluminum, arsenic, cadmium, chloride, iron, manganese, nickel and TDS.

Depth to groundwater at the Flambeau Mine in Wisconsin before mining began was generally <20 feet and flowed toward the Flambeau River. Samples taken from a well between the river and the backfilled open pit showed elevated levels (compared to baseline values) or exceedences of drinking water standards for iron, manganese, pH, sulfate, and total dissolved solids. Concentrations appeared to peak in 2000 and have been slowly decreasing for manganese, sulfate and TDS, but are continuing to increase for iron. Zinc concentrations are variable and still (as of 2003) ~700 µg/l (Lehrke, 2004).

Of the mines that have close proximity to groundwater, springs on site, or that discharge to groundwater – and have a moderate to high contaminant leaching potential – eight of 11 mines (73%) had groundwater quality impacts, and two of the remaining three had seeps that were adversely impacted from mining activity (91% have mining-related impacts to groundwater, seeps, springs, or adit water). The remaining mine (Lone Tree, NV) has had exceedences of primary and secondary drinking water standards in groundwater, but it is not clear whether the cause is baseline conditions or seepage from mine facilities. All of the 11 mines had exceedences of standards in groundwater (8), or seeps, springs, or adits (4).

Of the 11 mines in this category, all but one (McLaughlin, CA) predicted low groundwater quality impacts after mitigation were installed. The Stillwater Mine in Montana predicted low impacts to groundwater, and no exceedences of standard have thus far resulted from current operations or operators. The Lone Tree Mine in Nevada also predicted low groundwater impacts, and current information suggests that this is true (assuming the exceedences are a baseline issue). However, the lowered water table likely prevents the observation of impacts to groundwater. EIS water quality predictions made before the ameliorating effects of mitigation were considered (“potential” water quality impacts) were more accurate at predicting operational water quality than predictions based on assumed improvements

from mitigation. Therefore, of the 11 mines in this category, eight (73%) underestimated actual impacts to groundwater resources from mining activity.

Comparison to All Case Study Mines

Groundwater impacts for the mines with close proximity to groundwater and high acid drainage or contaminant leaching potential are compared to groundwater quality impacts for all the case study mines in Table 7.9. Taken as a whole, there are 15 mines with close proximity to groundwater, springs on site, or discharges to groundwater – and with moderate to high acid drainage or contaminant leaching potential (see Table 7.1 and 7.6). Of these 15 mines, 11 have had mining-related impacts to groundwater, and three have had adverse impacts to seeps, springs, or adit water (with the one possible exception being the Lone Tree Mine in Nevada), for a total of 14 (93%) with impacts to groundwater, seeps, or adit water. For all case study mines, only 14 (56%) had mining-related impacts to groundwater and three had mining-related impacts to seeps, for a total of 17 (68%) with impacts to groundwater, seeps or adit water.

Table 7.9. Groundwater Quality Impacts for Mines with Close Proximity to Groundwater and Elevated Acid Drainage Potential Compared to Groundwater Impacts for All Case Study Mines

	# Mines	Percent (%) with Impact to Groundwater or Seeps	Percent (%) with Exceedences of Standards in Groundwater or Seeps	Percent (%) with Exceedences that Predicted no Exceedences
Mines with close proximity to groundwater and elevated acid drainage and contaminant leaching potential	15	93 (14/15)	93 (14/15)	86 (12/14)
All case study mines	25	68 (17/25)	68 (17/25)	52 (13/25)

For the 15 mines with close proximity to groundwater and elevated acid drainage or contaminant leaching potential, 10 had mining-related exceedences in groundwater and four had mining-related exceedences in seeps or adit water, for a total of 14 (93%) with impacts to groundwater, seeps, or adit water. For all case study mines, 13 had mining-related exceedences in groundwater, and four more had exceedences in seeps or adit water, for a total of 17 (68%) with exceedences in groundwater, seeps, or adit water. Of the mines with groundwater, seep or adit water exceedences, 12 (86%) of those with close proximity to groundwater and high acid drainage or contaminant leaching potential predicted that there would be no exceedences (including those that predicted low potential in their initial EIS). For all case study mines with exceedences, 13 (52%) predicted that there would be no exceedences, including those that predicted low potential in their initial EIS. These results, although not comprehensive, suggest that the combination of proximity to groundwater resources (including discharges to groundwater) and moderate to high acid drainage or contaminant leaching potential does increase the risk of water quality impacts and is a good indicator of future adverse groundwater quality impacts.

7.3. SUMMARY AND CONCLUSIONS

Overall Findings

Of the 25 case study mines, nine (36%) have developed acid drainage on site to date. Nearly all the mines (8/9) that developed acid drainage either underestimated or ignored the potential for acid drainage in their EISs. Of the 25 case study mines, 19 (76%) had mining-related exceedences in surface water or groundwater. However, nearly half of the mines with exceedences (8/19 or 42%) predicted low contaminant leaching potential in their EISs. The constituents that most often exceeded standards or that had increasing concentrations in groundwater or surface water included toxic heavy metals such as copper, cadmium, lead, mercury, nickel, or zinc (12/19 or 63%), arsenic and sulfate (11/19 or 58% each), and cyanide (10/19 or 53%).

Sixty percent of the case study mines (15/25) had mining-related exceedences in surface water. Of the mines with surface water quality exceedences, four (17%) noted a low potential, seven (47%) a moderate potential, two a high potential, and three had no information in their EISs for surface water quality impacts in the absence of mitigation measures. For the mines with surface water quality exceedences, only one mine, the McLaughlin Mine in California, was correct in predicting a moderate potential for surface water quality impacts with mitigation in place. However, this mine predicted low acid drainage potential, yet acid drainage has developed on site. The other mines with surface water exceedences predicted low potential (not exceeding standards) for impacts in at least one EIS. Therefore, most case study mines predicted no impacts to surface water quality after mitigation were in place, but at the majority of these mines, impacts have already occurred.

The majority (64% or 16/25) of the case study mines had exceedences of drinking water standards in groundwater. However, exceedences at three of the mines, all in Nevada, may be related to baseline conditions; therefore, 52% of the case study mines clearly had mining-related exceedences of standards in surface water. Of the 13 mines with mining-related exceedences in groundwater, only two noted a low potential for groundwater quality impacts in the original EIS, the majority (nine or 69%) stated that there would be a moderate potential, and two stated there was a high potential for groundwater impacts in the absence of mitigation. In terms of predicted (post-mitigation) groundwater quality impacts, 77% (10/13) of the mines with exceedences predicted low groundwater quality impacts in their EISs (including mines predicting low impacts in the original EIS). Therefore, as with surface water, the predictions made about groundwater quality impacts without considering the effects of mitigation were somewhat more accurate than those made taking the effects of mitigation into account. Again, the ameliorating effect of mitigation on groundwater quality was overestimated in the majority of the case study mines.

Findings on Relationship Between Inherent Factors and Water Quality

Overall, for the 13 mines with close proximity to surface water and high acid drainage or contaminant leaching potential, 12 (92%) have had some adverse impact to surface water as a result of mining activity. For all case study mines, only 64% had some surface water quality impact. Eleven of the 13 (85%) have had exceedences of standards or permit limits in surface water as a result of mining activity. Of the 15 mines with close proximity to groundwater and high acid drainage or contaminant leaching potential, all but one (93%) have had mining-related impacts to groundwater, seeps, springs, or adit water. For all case study mines, only 56% had mining-related impacts to groundwater.

For the 15 mines with close proximity to groundwater and elevated acid drainage or contaminant leaching potential, 13 (87%) had mining-related exceedences in groundwater. For all case study mines, only 52% had exceedences in groundwater. These results, although not comprehensive, suggest that the combination of proximity to water resources (including discharges) and moderate to high acid drainage or contaminant leaching potential does increase the risk of water quality impacts and is a good indicator of future adverse water quality impacts. Although this finding makes intuitive sense from a risk perspective, a comprehensive study of cause and effect has never been conducted. Mines with these inherent factors are the most likely to require perpetual treatment to reduce or eliminate the long-term adverse impacts to surface water resources.

8. FAILURE MODES AND ROOT CAUSES OF WATER QUALITY IMPACTS

This section identifies the underlying causes of water quality impacts at the case study mines. It uses information gathered from the case studies presented in Section 6 and conducts a “failure modes” and “root cause” analysis. A failure is an outcome that is different than intended or predicted. A failure mode is the general type of failure that occurred or is predicted to occur (e.g., prediction failure, mitigation failure), while a root cause is the underlying, more specific, reason for the failure. The objective of the analysis presented in this section is to identify the most common types and causes of failures in protecting water quality at existing mines so that the failures can be prevented in future. Results from this analysis can be used to make recommendations for improving both the policy and scientific/engineering underpinnings of EISs.

8.1. METHODOLOGY AND APPROACH

The approach presented in this section uses existing (“historical”) information from mines with EISs to identify the causes of water quality impacts that occurred during mining operations. In contrast, most failure modes effects analyses (FMEA) are conducted before operations begin and instead focus on generating predictions from engineering design information (e.g., likelihood of failure based on factor of safety calculations). Because our approach is retrospective rather than prospective, we know unequivocally whether a prediction has failed or a water quality failure has occurred. Therefore, the focus of this analysis is to determine what caused the failure to occur. The information used to determine how failure occurred is contained in Section 6, which summarizes and compares water quality predictions in EISs with actual water quality conditions during mining operation.

8.1.1. FAILURE MODES AND ROOT CAUSES

According to Robertson (2003), any approach or mitigation measure that does not achieve the intended result (e.g., to prevent water quality impacts) or that results in undesirable consequences is considered a “failure.” This study has identified two primary types, or modes, of failures: characterization and mitigation. Root cause refers to the specific reason or reasons for the failure. Table 8.1 summarizes the failure modes and root causes for all water quality or prediction failures that can be identified in the case studies.

There are two types of characterization failures identified in the case studies: hydrologic and geochemical. Inaccuracies in hydrologic and geochemical characterization can lead to failure to recognize or predict water quality impacts. The primary root causes of hydrologic characterization failures identified in this study are:

- dilution overestimated
- lack of hydrological characterization
- amount of discharge overestimated, and
- size of storms underestimated.

The primary root causes of geochemical characterization failures identified are:

- lack of adequate geochemical characterization, and
- sample size and/or representation.

The other failure mode identified in the case studies is mitigation failures. The primary root causes of mitigation failures identified are:

- mitigation not identified, inadequate or not installed
- waste rock mixing and segregation not effective
- liner leak, embankment failure or tailings spill, and
- land application discharge not effective.

Comparison of Predicted and Actual Water Quality at Hardrock Mines **FAILURE MODES AND ROOT CAUSES OF WATER QUALITY IMPACTS**

Table 8.1. Water Quality Predictions Failure Modes, Root Causes and Examples from Case Study Mines

Failure Mode	Root Cause	Examples
Hydrologic Characterization	Lack of hydrologic characterization	Royal Mountain King, CA; Black Pine, MT
	Dilution overestimated	Greens Creek, AK; Jerritt Canyon, NV
	Amount of discharge underestimated	Mineral Hill, MT
	Size of storms underestimated	Zortman and Landusky, MT
Geochemical Characterization	Lack of adequate geochemical characterization	Jamestown, CA; Royal Mountain King, CA; Grouse Creek, ID; Black Pine, MT
	Sample size and/or representation	Greens Creek, AK; McLaughlin, CA; Thompson Creek, ID; Golden Sunlight, MT; Mineral Hill, MT; Zortman and Landusky, MT; Jerritt Canyon, NV
Mitigation	Mitigation not identified, inadequate, or not installed	Bagdad, AZ; Royal Mountain King, CA; Grouse Creek, ID
	Waste rock mixing and segregation not effective	Greens Creek, AK; McLaughlin, CA; Thompson Creek, ID; Jerritt Canyon, NV
	Liner leak, embankment failure or tailings spill	Jamestown, CA; Golden Sunlight, MT; Mineral Hill, MT; Stillwater, MT; Florida Canyon, NV; Jerritt Canyon, NV; Lone Tree, NV; Rochester, NV; Twin Creeks, NV
	Land application discharge not effective	Beal Mountain, MT

8.2. EXAMPLES OF CHARACTERIZATION FAILURES FROM CASE STUDY MINES

The following sections provide examples of the various types of characterization failures that were identified from the case study mines in Section 6. The information provided is intended as a short summary identifying the failure modes, root causes and subsequent mitigation. More specific information describing the cause and effects in each case is available in Section 6.

8.2.1. HYDROLOGIC CHARACTERIZATION FAILURES

Incorrect or inadequate hydrological characterization was identified as a contributing factor to water quality impacts at six of the 25 mines evaluated. The failure modes and root causes and effects for each case study with hydrologic characterization failures identified in Table 8.1 are summarized in the following sections.

Greens Creek, Alaska

The original Greens Creek 1983 EIS predicted that dilution would prevent impacts to surface water; however, the 2003 EIS shows that surface water impacts were noticeable in the general mine area and in off-site streams. Stream tributaries were impacted by mine wastes, in part, due to smaller than predicted flows not providing sufficient dilution of contaminants coming from tailings and waste rock piles. The impacts to surface water were subsequently mitigated by relocating waste rock and capturing and treating tailings leachate.

Royal Mountain King, California

Current data for the Royal Mountain King site shows impacts to groundwater in the vicinity of the waste rock dumps due to near surface groundwater that is resulting in lateral flow and spread of contamination originating from waste rock dump seepage. A more adequate hydrological assessment would have indicated the presence of near surface groundwater and could have allowed for relocation of the waste rock dumps in locations that would not result in groundwater and surface water impacts.

Black Pine, Montana

The waste rock dump has impacted groundwater and springs on the site with acid drainage and is discharging to headwater streams. A lack of hydrologic characterization at the site has led to difficulties in identifying the association between the waste rock dump and springs and seeps at the site and in determining cost effective mitigation methods.

Mineral Hill, Montana

According to the original EIS, the initial low discharge rate (approximately 1gpm) from the underground workings would not result in an appreciable amount of leachate from the workings. At the higher discharge rates (approximately 10 gpm) that existed during operation the amount of discharges were significant and resulting arsenic concentrations exceeded non-degradation water quality standards. The hydrologic characterization conducted for the EIS did not predict significantly more groundwater being encountered by underground mining activities. A more accurate hydrologic evaluation could have allowed for planning of water treatment of mine discharge and may have encouraged a more accurate geochemical characterization.

Zortman and Landusky, Montana

Surface water impacts were associated with storm events exceeding the 100-year design criteria. During the past 25 years, at least four storm events have exceeded the predicted 100-year storm event. In addition to improper design criteria for the mine units and the lack of run-on ditches to prevent upgradient additions to storm events, this suggests that the extent of hydrologic characterization in terms of storm frequency and strength (i.e. amount of rainfall) prediction was inadequate to properly design mine units.

Jerritt Canyon, Nevada

The original 1980 EIS predicted that dilution would prevent impacts to surface water from contaminants. However, subsequent water monitoring data shows that surface water impacts have occurred in the headwaters of streams in the project area, most likely due to contamination from waste rock. Streams were impacted by waste rock in part due to smaller than predicted flows not providing sufficient dilution of contaminants. A more adequate hydrological assessment could have indicated that low flows in headwater streams would not provide adequate dilution.

8.2.2. GEOCHEMICAL CHARACTERIZATION FAILURES

Incorrect or inadequate geochemical characterization was identified as a contributing factor to water quality impacts at 11 of the 25 mines evaluated. The causes and effects for each case study with geochemical characterization failures are summarized below and in Table 8.2.

Greens Creek, Alaska

The Greens Creek 1988 EA predicted no potential for acid drainage in tailings. The 2003 EIS predicted that acid drainage from the tailings would occur but would not become evident for 10 to 33 years (based on static testing) or 500 years (based on modeling results). The 1983 EIS did not address water quality impacts from waste rock, whereas the 1992 EA recognized the potential for acid drainage from waste rock to impact water quality. However, acid drainage is already evident at the site in the general mine area in the form of metal-rich seepage from either the tailings, waste rock, or both sources, suggesting that the geochemical characterization for the predictions in the EISs were not accurate. The root cause of the failure to accurately predict acid drainage could be due to a single factor or a combination of factors such as sample representation, geochemical analysis, modeling and/or interpretation.

Comparison of Predicted and Actual Water Quality at Hardrock Mines FAILURE MODES AND ROOT CAUSES OF WATER QUALITY IMPACTS

Jamestown, California

The geochemical characterization testing (short-term leach tests only) performed for the 1983 and 1991 EIS/EIR did not accurately identify the potential for groundwater impacts that were evident by 1990. Test results indicated that the mine tailings would not contain contaminants that needed to be controlled, and that the overburden material was non-hazardous, non-toxic and non-acid generating. Arsenic and TDS drinking water standards were slightly exceeded in tailings leachate from short-term leach tests, but observed concentrations in groundwater were substantially higher. Therefore, the short-term leach tests were not effective at identifying the contaminants of concern (sulfate and nitrate were not identified as contaminants of concern but exceeded drinking water standards in groundwater) and also underestimated the actual concentrations of constituents in groundwater during operations. In addition, no short-term leach testing was performed on waste rock. The most likely reasons the geochemical characterization failed to identify the potential is due to either sample representation or inadequate geochemical analysis (e.g., failure to perform tests or to perform the appropriate tests, e.g., long-term kinetics tests).

McLaughlin, California

Geochemical characterization conducted in the original McLaughlin Mine EIS appears to have been inadequate, possibly due to inadequate sample representation, lack of kinetic testing, or modeling of results. Acid-base accounting results for waste rock removed from the pit showed that 92% of the waste rock was determined to be either neutral or neutralizing. These results were not accurate for longer-term weathering of waste rock as demonstrated by water quality impacts to groundwater, surface water and pit water at the site. Acid drainage has developed and water resources were impacted by multiple constituents (metals, arsenic, and sulfate).

Royal Mountain King, California

The Royal Mountain King 1987 EIS/EIR did not predict contamination associated with waste rock, however groundwater results show evidence of contamination indicating that geochemical characterization was inadequate. No contaminant leaching potential testing was conducted, but groundwater is contaminated with metals, anions and cyanide. The most likely cause of the failure of geochemical characterization to predict the potential for contamination was static testing results not being accurate for long-term weathering of waste rock. The TTLC levels (standards) used in the static tests also may not have been protective enough to prevent groundwater contamination, or the samples selected for testing may not have been representative.

Grouse Creek, Idaho

The Grouse Creek 1984 EIS did not predict that contaminant leaching from tailings would impact water quality. Initial geochemical characterization tests were apparently conducted on non-representative samples or the “weathering” tests performed were not adequate to infer contaminant potential. Although moderate acid drainage potential was identified in the 1992 EIS, only lead was predicted to exceed drinking water standards in tailings leachate. The 2002 EE/CA showed that prediction to be in error, with actual tailings pore water showing exceedences of standards for aluminum, copper, arsenic, selenium, silver, zinc and cyanide.

Thompson Creek, Idaho

Acid drainage potential tests were not performed on tailings material in the Thompson Creek 1980 EIS. Acid-base accounting tests conducted on waste rock for the 1980 EIS did not predict acid drainage potential, and the tailings were thought to be similar to waste rock in terms of acid drainage potential, although no support for this assumption was provided. The 1999 EIS geochemical characterization tests included kinetic testing and did indicate the potential for acid drainage from waste rock because the NP:AP ratio was 1.5 to 3.1. ABA and kinetic tests performed on tailings material for the 1999 EIS did note that tailings could become acid generating if exposed to air and water. However, the tailings were predicted to not generate acid as long as saturated, oxygen-free conditions were maintained in the impoundment. The characterization predictions failure for the tailings material was in part related to an incorrect assumption that such conditions would exist and be maintained in the impoundment and that they would prevent acid drainage from developing.

Comparison of Predicted and Actual Water Quality at Hardrock Mines FAILURE MODES AND ROOT CAUSES OF WATER QUALITY IMPACTS

Black Pine, Montana

The original Black Pine 1981 EA did not directly test for acid drainage potential but instead used the total sulfide in the ore (<0.2%) as indicative of low potential for acid drainage generation and impacts. The waste rock dump has since impacted groundwater and springs on the site with acid drainage and is discharging to headwater streams.

Golden Sunlight, Montana

The Golden Sunlight 1981 EIS specifically identified the potential for impacts to groundwater, and ABA testing did identify the potential for the ore to be acid producing. However, these results were dismissed because the ore used in the tests was finely ground (400 mesh) rather than being run-of-mine size, and was therefore considered to not be representative of field conditions. The results were also dismissed because previous historic mining activity and waste dump development on the project area did not result in acid drainage, and because there was no discharge from existing underground workings at the site. The ABA test results were qualified based on a statement from the testing laboratory (B.C. Research) that “Experience has shown that generally relatively more gangue than sulphides is exposed at the larger particle size although this may not always be the case.” According to the 1990 EA, the analysis was of a single “highwall composite,” and the exact location and means of obtaining the sample were unknown. After the 1981 EIS, all subsequent EISs or EAs acknowledged the high potential for acid drainage development.

Mineral Hill, Montana

The potential for elevated arsenic concentrations in groundwater from the mine workings was not specifically recognized in the geochemical characterization of the site conducted in the 1983 EIS or 1988 EA. No geochemical characterization tests were conducted on waste rock, ore or any material representative of the walls of the underground workings. Geochemical characterization on the tailings material did predict the observed increases in three of six constituents found in tailings leachate, and contaminated groundwater and surface water (cyanide, arsenic, and manganese), but not sulfate, nitrate, and TDS, which are not removed by commonly used mine water treatment techniques (e.g., lime precipitation).

Zortman and Landusky, Montana

The Zortman and Landusky 1979 new project EISs were conducted without any geochemical characterization. Acid drainage was not predicted to occur based on the assumption that only oxide ore would be mined. This resulted in heap leach dikes and foundations being constructed in surface water drainages using what later was determined to be a mixed oxide/sulfide waste rock with high acid drainage generating potential, and waste rock with high acid drainage potential to be similarly placed in surface water drainages. The consequences of mine expansion were not addressed until the 1996 EIS. By this time, many unpredicted impacts had occurred, resulting in significant contamination of groundwater and surface water resources.

Jerritt Canyon, Nevada

The initial geochemical characterization in the 1980 EIS did not include acid drainage potential tests and noted only minimal potential for leaching of contaminants from waste rock. The 1994 EIS, based on significant additional testing, did indicate potential for acid drainage and contaminant leaching from at least some materials. The geochemical characterization in the 1980 EIS most likely failed to predict a high enough potential for contamination due to either sample representativeness or the limited geochemical analysis methods employed. Although acid drainage has not developed, the waste rock contamination has since caused off-site impacts to surface water in the mine area for sulfate and TDS.

8.3. MITIGATION FAILURES

Failure of mitigation to perform was identified as a contributing factor to water quality impacts at 16 of the 25 mines evaluated. The cause and effects for each case study are summarized below.

Greens Creek, Alaska

The 1992 EA recognized the potential for acid drainage from waste rock and proposed mixing of acid generating and non-acid generating rock as a mitigation measure. The 2003 EIS water quality information shows that mixing was not

Comparison of Predicted and Actual Water Quality at Hardrock Mines FAILURE MODES AND ROOT CAUSES OF WATER QUALITY IMPACTS

effective to prevent water quality impacts in the general mine area. The 2003 EIS proposed backfilling of all waste rock to prevent acid drainage impacts.

Bagdad, Arizona

The Bagdad 1996 EIS did not predict any potential for impacts. Monitoring showed that impacts to off-site surface water occurred in 1998-2002, likely due to past tailings or pregnant leach solution spills or more recent events. The mitigation intended by the impoundment of tailings and pregnant leach solution failed in the form of a tailings spill or leak resulting in continued off-site impacts to surface water in the mine area.

Jamestown, California

The Jamestown project employed a sub-compacted liner and poorly designed embankment identified in the original EIS as mitigation for the tailings facility. The liner and embankment failed to protect groundwater quality.

McLaughlin, California

The McLaughlin 1983 EIS/EIR predicted that mitigation measures (underdrains, diversion ditches, segregation of PAG rock, lime addition to waste rock runoff) would avoid impacts to groundwater. However, groundwater wells downgradient of waste rock show water quality impacts indicating that the measures, such as mixing and segregation were not effective, resulting in widespread on-site impacts to groundwater and surface water.

Royal Mountain King, California

The Royal Mountain King 1987 EIS/EIR recognized the potential for impacts from tailings but assumed that low permeability material below the tailings would be sufficient as mitigation to protect groundwater. Similarly, the EIS/EIR recognized the potential for impacts from heap leach material, but assumed that a liner (material not specified) would prevent impacts to groundwater. Groundwater contamination downgradient of the tailings impoundment and heap leach area demonstrates that the low permeability material and liner have not prevented groundwater contamination.

Grouse Creek, Idaho

The contingency for groundwater capture and treatment during operations if necessary was mentioned in the Grouse Creek 1992 SEIS, however it was not installed at that time. The existing mitigation employed in the tailings impoundment (French drain designed to allow for capture of tailings leakage) proved to be ineffective at mitigating groundwater and subsequent surface water impacts to off-site water resources that occurred beginning in 1995. Additional mitigation in the form of groundwater capture and treatment has since been employed and has resulted in no detected impacts to surface water since 2001.

Thompson Creek, Idaho

According to the EIS, any acid-producing rock would be mitigated by special handling (segregation) and isolation techniques that are “demonstrated by their use throughout the mining industry.” The methods employed at the mine site did not result in mitigation of acid drainage producing rock and instead led to water quality impacts that have required additional mitigation.

Beal Mountain, Montana

The LAD of leach solution, proposed as mitigation in the Beal Mountain 1993 EIS, resulted in damage to vegetation and contamination of groundwater and surface water with cyanide. The LAD system has failed at Beal Mountain because pre-treatment did not adequately reduce contaminants of concern (in particular cyanide compounds, which proved to be toxic to vegetation) and because there was significant groundwater percolation of contaminated solution and relatively rapid (within the same year) transport to surface water.

Golden Sunlight, Montana

The mitigation for the tailings impoundments identified in the Golden Sunlight 1981 EIS and the later 1990 EA failed due to liner design and construction errors and did not prevent migration of leachate from tailings. Contaminated groundwater from the impoundments has sometimes escaped capture systems due to more extensive leakage than

Comparison of Predicted and Actual Water Quality at Hardrock Mines FAILURE MODES AND ROOT CAUSES OF WATER QUALITY IMPACTS

anticipated and operational deficiencies (periodic failure to maintain and operate pumpback system). The design approach for the tailings impoundment with respect to cyanide solution leakage was projected to achieve “from the practical engineering standpoint,” a zero discharge facility. The clay liner in the original tailings impoundment and the synthetic liner in the newer tailings impoundment both failed to meet expectations and have resulted in a discharging facility that requires extensive groundwater capture to prevent more extensive groundwater and surface water impacts.

Mineral Hill, Montana

According to the 2001 EIS, the tailings facility design resulted in unanticipated lateral flow that escaped the liner system, resulting in contamination of alluvial groundwater and surface water. The design error occurred due to a lack of consideration of leachate emanating from the tailings impoundment as well as failure to recognize the potential for lateral flow.

Stillwater, Montana

In 2003 it was determined that a tailings underdrain discharge pipe was improperly designed or constructed and was allowing a leak of approximately 10 gpm to groundwater in the vicinity of the dam toe. It was also determined that the LAD solution storage pond liner was not performing as specified (1×10^{-6} cm/sec) and that as much as 150 gpm of solution was seeping into groundwater. In both cases groundwater standards of 2.0 mg/l nitrate were not exceeded in compliance wells, although nitrogen concentrations increased in downgradient wells. The tailings underdrain pipe was repaired and the seepage is no longer detectable. The compacted clay liner in the LAD solution pond was replaced with a synthetic geomembrane liner.

Florida Canyon, Nevada

The exceedences of water quality standards at the Florida Canyon mine from the leach pads is primarily due to failure of mitigation (design, construction and/or operational errors) to adequately prevent leakage of leach solutions.

Jerritt Canyon, Nevada

The mitigation described in the 1980 EIS for the tailings impoundment, a compacted clay liner and embankment constructed to control seepage, failed as shown by the presence of a significant contaminant plume in the groundwater downgradient of the tailings facility. The failure of the liner and embankment seepage control system appears to be due to higher than design permeability most likely indicating either a problem with construction materials or construction practices.

The 1994 EIS proposed mixing and segregation as mitigation for potential acid drainage and contaminant leaching from waste rock. Subsequent monitoring data shows that waste rock continued to contaminate surface water despite implementation of the mitigation.

Lone Tree, Nevada

The tailings impoundment experienced a significant leak that resulted in leachate escaping into the vadose zone. An operational error (tailings were not placed against the embankment) was identified as the cause of the seepage. Newmont commenced remediation activities, which included trenching, and modified operations to promote drying of tails in the area of the embankments.

Rochester, Nevada

The mine has experienced exceedences of groundwater standards in the vicinity of the heap leach pile and ponds due to either spills or leaks in the liner system. Groundwater pump and treat is being used as a mitigation measure and is discussed in the 2003 EA.

Twin Creeks, Nevada

Leachate from the tailings impoundment has degraded groundwater in the vadose zone. An ongoing monitoring program is in place to determine the extent of vadose zone and potential groundwater contamination.

8.4. SUMMARY OF RESULTS

The Failure modes and effects identified in the study are summarized in Table 8.2. The results can be summarized as follows:

Six of 25 mines exhibited inadequacies in hydrologic characterization.

- At two of the mines, dilution was overestimated.
- At two of the mines, a lack of hydrologic characterization was noted.
- At one of the mines, the amount of discharge generated was underestimated.
- At one of the mines, the size of storms was underestimated.

Eleven of 25 mines exhibited inadequacies in geochemical characterization. Geochemical failures resulted from:

- assumptions made about geochemical nature of ore deposits and surrounding areas (e.g., mining will only be done in oxidized area)
- site analogs inappropriately applied to new proposal (e.g., historic underground mine workings do not produce water or did not indicate acid generation)
- inadequate sampling (e.g., geochemical characterization did not indicate potential due to composite samples or samples not being representative of actual mining)
- failure to conduct and have results for long-term contaminant leaching and acid drainage testing procedures before mining begins, and
- failure to conduct the proper tests, or to improperly interpret test results, or to apply the proper models.

Sixteen of 25 mines exhibited failures in mitigation measures.

- At three of the mines, mitigation was not identified, inadequate, or not installed.
- At four of the mines, waste rock mixing and segregation was not effective.
- At nine of the mines, liner leaks, embankment failures or tailings spills resulted in impacts to water resources.
- At one mine, land application disposal resulted in impacts to water resources.

Table 8.2. Summary of Failure Modes for Case Study Mines

Failure Mode	Number of Case Study Mines Showing Failure Mode	Percent of Case Study Mines Showing Failure Mode
Hydrologic Characterization	6	24%
Geochemical Characterization	11	44%
Mitigation	16	64%

8.5. CONCLUSIONS AND RECOMMENDATIONS

This study shows a variety of failure modes and root causes that have led to water quality impacts at hardrock mine sites in the U.S. As a general conclusion and recommendation, it is clear that regulatory review processes, such as EISs, should include an adequate analysis of baseline water quality, hydrological characterization and geochemical characterization and the full identification of appropriate mitigation and potential mitigation failures. The following sections provide conclusions and recommendations specific to the various failure modes identified in this study.

HYDROLOGIC CHARACTERIZATION

The case studies show the indirect cause and effect relationship between inadequacies in hydrologic characterization methods that were employed at mine sites and have resulted in impacts to water resources ranging from on-site contamination and contamination of headwater streams to more extensive off-site contamination of surface water with the potential need for long-term water treatment in some cases. Hydrological characterization failures are most often caused by over-estimation of dilution effects, failure to recognize hydrological features (e.g., springs and shallow or perched groundwater) and underestimation of water production and stormwater quantities. Requiring adequate hydrological investigations as well as making conservative assumptions about water quality and quantity can address hydrological failures.

GEOCHEMICAL CHARACTERIZATION

The case studies show the indirect cause and effect relationship between inadequacies in geochemical characterization methods that were employed at mine sites and impacts to water resources. The severity of impacts ranged from on-site contamination and contamination of headwater streams to the need for long-term water treatment in some cases. Failure to identify the potential for contaminant leaching and acid drainage development has been a reoccurring theme at mine sites throughout the U.S. The case studies demonstrate the range of impacts to water resources that have occurred as a result of proper or adequate testing. The case studies also demonstrate that inaccurate geochemical predictions often lead to lack of identification of adequate mitigation measures.

Geochemical characterization failures can be addressed by emphasizing fundamental scientific requirements in the regulatory process. Such requirements should include adequate sample representation and testing, and interpretations that recognize the fundamental uncertainties and limitations of characterization testing. Improved geochemical characterization will lead to improved identification and of mitigation measures. As the most common characterization failure mode, the elimination of geochemical characterization failures can provide a large contribution to ensuring accurate water quality predictions and outcomes at hardrock mine sites.

MITIGATION

Waste rock mixing and segregation

At many mines, waste rock containing acid generating materials is managed by mixing and segregation practices. In most cases no data is available to ascertain the effectiveness of those practices, particularly where there is a significant distance from the source to water resources. The cases cited all have nearby water resources that were impacted. The data suggests that distance to water resources is potentially the most significant factor as to the effectiveness of waste rock mixing and segregation. Mitigation may depend more on climate and factors such as distance and geology affecting travel time and attenuation of contaminants. Where acid drainage generating materials are present, particularly in areas of headwater streams, waste rock mixing and segregation may not prevent impacts to water resources. These types of failures can be addressed by requiring adequate geochemical and hydrologic characterization and ensuring that segregated wastes are placed away from potential water pathways.

Liner leak, embankment failure or tailings spill

The case studies show that mitigation intended to capture contaminants such as liners and tailing impoundments may fail and lead to groundwater and surface water quality impacts. While in most cases, impacts are limited to on-site groundwater and nearby surface water, in some cases the impacts can result in more extensive surface water impacts and potentially to long-term water treatment. In all cases, additional mitigation, most often in the form of groundwater capture and treatment (including perpetual treatment in those severe cases), has resulted in effective capture and treatment of contaminants.

Failure of liners and tailing impoundments to perform is typically caused by design, construction and operational mistakes. These features frequently fail to perform, so it is important to consider the likelihood and consequences of those failures and to identify and implement additional mitigation that can be employed in the event of such failures. In many cases where initial mitigation has failed, such as mines where liner leaks have occurred, additional mitigation in the form of groundwater capture and treatment are often necessary. Additional consideration needs to be given to including groundwater capture and treatment systems as original designed mitigation for high risk features such as tailings impoundments containing cyanide in high risk (near surface water or groundwater) areas.

Land application discharge

The case study shows that land application, instead of acting as a disposal mechanism to facilitate zero discharge, can result in impacts to groundwater and surface water. The impacts demonstrated in this case study were recognized at other land application sites. With the exception of land application for the disposal of low-levels of nutrients that can be applied at agronomic rates, land application disposal has demonstrated a high rate of failure and significant impact at hardrock mine sites in the United States.

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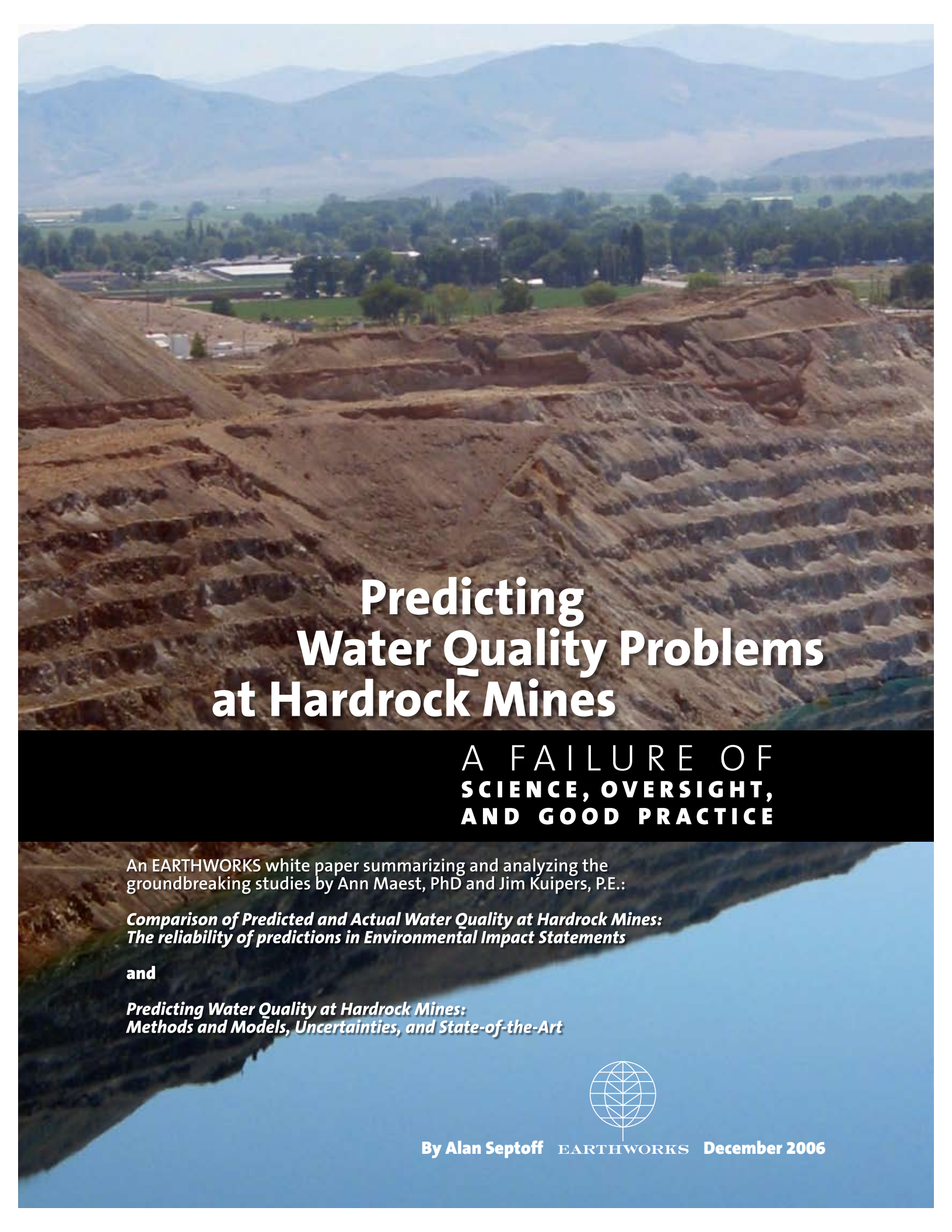
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Appendix A
Major Mine Statistical Information

(available at [www/kuipersassoc.com](http://www.kuipersassoc.com) or http://www.mineralpolicy.org/publications_welcome.cfm)

Appendix B
Case Study Detailed Information

(available at [www/kuipersassoc.com](http://www.kuipersassoc.com) or http://www.mineralpolicy.org/publications_welcome.cfm)



Predicting Water Quality Problems at Hardrock Mines

A FAILURE OF SCIENCE, OVERSIGHT, AND GOOD PRACTICE

An EARTHWORKS white paper summarizing and analyzing the groundbreaking studies by Ann Maest, PhD and Jim Kuipers, P.E.:

***Comparison of Predicted and Actual Water Quality at Hardrock Mines:
The reliability of predictions in Environmental Impact Statements***

and

***Predicting Water Quality at Hardrock Mines:
Methods and Models, Uncertainties, and State-of-the-Art***



By Alan Septoff EARTHWORKS December 2006

Introduction

A failure of science, oversight and good practice

This paper is a summary, written for the layperson, of the findings of a two-year research study on the accuracy of water quality predictions at hardrock mines. The study, conducted by Jim Kuipers and Ann Maest¹, brings to light a decades-long failure by government regulators, industry, and consultants to recognize and correct deficient procedures and methods for predicting contamination of water at hardrock mines.

Kuipers and Maest have discovered that, in practice, there is a failure to compare predictions made before the mines are permitted with the actual results. The predictive modeling results are not adjusted to account for real-life failures—this, despite the fact that at the vast majority of mines, problems were worse than predicted. Establishment of credibility in modeling requires that the predictions be tested, and then the models adjusted based on the results. This process appears broken when it comes to predicting the impact of mines on water quality for mine permits.

To permit mines, federal law² requires regulators to apply scientific approaches to predict the environmental impacts of the mine proposal – including surface water and groundwater quality impacts. The accuracy of these water quality predictions is of significant public concern. Mining's impacts on water quality may affect municipal, agricultural, and rural water supplies; important commercial, subsistence and sports fisheries; wildlife populations; tourism; and recreation. One of the reports from the study, *Comparison of Predicted and Actual Water Quality at Hardrock Mines (Comparison Report)*, asks a basic question that government regulators, industry officials and consultants should have asked long ago:

Do predicted water quality impacts match reality?

The answer, in short, is **no**. The *Comparison Report* reveals:

- 100 percent of mines predicted compliance with water quality standards before operations began (assuming pre-operations water quality was in compliance).
- 76 percent of mines studied in detail exceeded water quality standards due to mining activity.
- Mitigation³ measures predicted to prevent water quality exceedances⁴ failed at 64 percent of the mines studied in detail.

Along with more analysis of this question, the *Comparison Report* and the companion report on methods and models used to predict water quality (*Methods and Models Report*), also seek to answer the necessary follow-up questions:

- In cases where predicted water quality impacts fail to match reality, why do they fail?

- Do certain types of mines fail more often than others?
- What can be done to address current failures and prevent future failures?

The Kuipers-Maest reports were prepared for a professional audience. The purpose of this paper is to translate and summarize the main findings of their research (for the layperson and the interested public), and to offer common sense recommendations based on those findings with an eye toward protecting natural resources and public health.

The Context

Why this research was necessary

The Environmental and Public Costs of Faulty Predictions

The failure to accurately predict and manage water quality impacts can result in significant negative impacts on clean water and steep taxpayer liabilities for the costs of cleanup. Consider one often-cited example — the Summitville gold mine in Colorado. Water pollution at this mine has cost American taxpayers more than \$200 million in cleanup costs. The majority of that money has been spent mitigating acid drainage and cyanide releases that were not predicted during the permitting process. When pollution spilled from a containment pond, 18 miles of the Alamosa River were effectively killed – impacting not only the aquatic life in the river, but also the adjacent farms and ranches that relied upon the Alamosa for irrigation and livestock watering.

While it may be argued that Summitville is one of the worst-case examples, problems abound. According to the U.S. EPA's Abandoned Mine Land Team, the cost of mine cleanup at sites on the National Priorities List (i.e., Superfund sites, like Summitville) in the United States is \$20 billion – almost 3 times the EPA's FY 2007 budget request. Long term water treatment and management is often the single most significant cost associated with mine cleanup.

In fact, there is an increasing number of mine sites throughout the U.S. that will require water treatment in *perpetuity*. In the arid west, these types of long-term impacts place a tremendous burden on downstream communities who must deal with the consequences of failed predictions. For example, government regulators have determined that the Zortman Landusky mine, located near the Fort Belknap Reservation in Montana, will continue to generate acid mine drainage for thousands of years. As a result, the Fort Belknap Tribes are faced with a continual threat to important tribal water resources, and the state of Montana will be spending tens of millions in public funds for long-term water treatment.⁵

In order to ensure clean water and protect taxpayers from liability for cleanup costs it is important to understand the frequency and magnitude of failures in predicting water quality impacts. Consider that at most major mines, operators are required to post financial assurances prior to operating. This is the good news. These assurances are supposed to guarantee that, should the mine operator go bankrupt, the mine site will be reclaimed at no cost to the taxpayer. However, the bad news is that these financial assurances are based upon expected reclamation costs and expected reclamation costs are based in large part upon water quality predictions.

Previous research by Jim Kuipers demonstrates that taxpayers are potentially liable for up to \$20.4 billion⁶ in financial assurance shortfalls at existing mine sites (in addition to the \$20 billion for Superfund sites) – due in large part to inaccurate water quality predictions.

A Growing Problem

Without correction, the environmental and financial impacts of faulty predictions could grow. Recent increases in metals prices have triggered an increase in the number of new mines being proposed in the United States. According to the Bureau of Land Management, new mining claims filed in 2006 are on track to more than quadruple since metals prices began their precipitous rise in 2002.

In the United States alone there are approximately 180 large hardrock mines – in nearly all regions of the country – that are in various stages of permitting, development, operation or reclamation and closure. In order to better protect important water resources and reduce future economic liability, improvements must be made in the prediction and prevention of impacts to water quality at these sites. On the positive side, the increase in metals prices has resulted in fewer bankruptcies in the sector—and it is bankruptcies that trigger the use of reclamation bonds for mine site reclamation and water treatment. This may provide regulators and industry officials with a window of opportunity to solve the underlying problems with water quality prediction.

Unprecedented Research: the absence of previous studies and the data gap

When they began their research, the authors expected to incorporate data from some mines where government officials had already completed a comparison of predicted and actual water quality impacts. However, they were unable to find comparisons of water quality predictions and actual water quality impacts of mines.

The authors found that no single repository exists for the Environmental Impact Statements (EISs) currently mandated under federal law. EISs contain the water quality predictions analyzed in the study. In some cases, local

federal offices that processed the studies did not have copies of them. Furthermore, in many cases, the authors were forced to submit Freedom of Information Act requests and pay fees to obtain copies of these studies. Similarly, water quality from mines was inordinately difficult to obtain and in most cases required personal visits to agencies and long hours sorting through paper files.

Taken together, the absence of previously published research and the difficulty in gathering information is evidence of a data gap that surprised the authors and may help explain the previous lack of a comprehensive study of this nature.

It is important to note that the predictions data were available – no matter how difficult to obtain – only because the National Environmental Policy Act (NEPA) requires it. Without NEPA, this study would have been impossible to conduct.

A Tool for Many Audiences

While the research focuses on the underlying scientific and engineering processes that form the basis of water quality predictions, its recommendations are intended for use by many audiences to increase the effectiveness of future mine water quality predictions – directly and indirectly:

- This study should be useful to the scientific and engineering communities for suggesting ways to better characterize risks to water quality and to better apply mitigation methods to minimize or prevent potential impacts.
- The regulatory community can look to these reports, especially *Methods and Models*, for recommendations on how to fundamentally improve the permitting process to ensure a more accurate analysis of potential mining impacts. The inherent uncertainty in water quality predictions and mitigation failures should be conservatively viewed in order to ensure mine permitting decisions that are more protective of human health and the environment. The integrity of the mine permitting process is dependent on the use of accurate methods and models.
- This report can be utilized by the mining industry to improve current practices and more accurately predict consequences and ameliorate potential effects.
- It can be utilized by the insurance and investment industry as a tool to better understand the potential risks and costs associated with mining, and as a basis to reassess risks at current mines.
- And finally, it can be utilized by the interested public to more effectively advocate for water quality protections in the permitting process and to advocate in the public arena for legislative and regulatory changes that better protect water resources.



Do Predicted Water Quality Impacts Match Reality?

As indicated above, the answer is usually no — particularly when high risk mines, such as those with close proximity to water resources, are considered.

Sampled Mines

To arrive at this answer the authors initially reviewed 104 Environmental Impact Statements (EISs) and Environmental Assessments (EAs) for 71 major hardrock mines in the United States.⁷ The mines covered all important mineral sectors (gold, silver, copper, platinum group metals, molybdenum, lead, and zinc) and ten mining states (Alaska, Arizona, California, Idaho, Montana, New Mexico, Nevada, South Dakota, Utah, and Wisconsin).

A representative subset of 25 case study mines was then selected to evaluate the accuracy of the water quality predictions. Environmental impact reports for these mines were evaluated for predictions related to surface water, groundwater, and mine drainage quality during and after mining. These predictions were then compared with actual water quality conditions during and after mining.

Potential & Predicted Water Quality

The authors discovered a two-tiered system for water quality predictions, one-tier of which was based not on sound science, but on unsupported “good faith” projections.

The two tiers of “predictions” made about water quality in environmental assessments are referred to by the authors as “potential” and “predicted” water quality:

- **Potential** water quality is the expected water quality conditions in the absence of mitigation efforts by the operator.
- **Predicted** water quality takes the effect of mitigating measures into account. It is what mine operators forecast actual water quality will be during and after operations.

All the environmental reviews analyzed in the *Comparison Report* predict acceptable water quality after mitigation at mines where water quality standards were met before mining began. If this prediction were not made, the regulatory agency would not be able to approve the mine.

However, inadequate information was provided to demonstrate how the mitigation measures would actually prevent water quality impacts. Therefore, regulators were generally accepting the final water quality predictions on “faith.”

Major Findings: Chronic Underestimates of Water Quality Problems

Prediction vs. Reality: Overall Water Quality Impacts to Ground and Surface Water

Of the 25 mines sampled:

- 76% of mines polluted groundwater or surface water severely enough to exceed water quality standards.
- 60% of mines polluted surface water severely enough to exceed water quality standards.
- At least 13 mines (52%) polluted groundwater severely enough to exceed water quality standards.

Predictions vs. Reality: the Failure of Mitigation

In the cases where water quality standards were exceeded, in some cases the mine proponent anticipated the potential for pollution and prepared mitigation strategies (e.g. a mine waste dump lined with plastic to prevent acid drainage leaching into groundwater). Predictions of the efficacy of mitigation were no more reliable than overall predictions of water quality:

- 73% of mines exceeded surface water quality standards despite predicting that mitigation would result in compliance. The other 4 mines didn’t predict the need for mitigation.
- 77% of mines that exceeded groundwater quality standards predicted that mitigation would result in compliance. The other 3 mines didn’t predict the need for mitigation.

Predictions vs. Reality: Mines near Water with Elevated Acid Drainage or Contaminant Leaching Potential are High Risk

Some mine projects are so high risk that water quality exceedances are a near certainty: those mines that are both near groundwater or surface water resources, and possess an elevated potential for acid drainage or contaminant leaching.

- 85% of the mines near surface water with elevated potential for acid drainage or contaminant leaching exceeded water quality standards
- 93% of the mines near groundwater with elevated potential for acid drainage or contaminant leaching exceeded water quality standards.
- Of the sites that did develop acid drainage, 89% predicted that they would not.

Water Quality Pollutants

Of the 19 mines that exceeded water quality standards, the pollutants that exceeded standards were as follows

- Toxic heavy metals such as lead, mercury, cadmium, copper, nickel or zinc exceeded standards at 63% of mines.

- Arsenic and sulfate exceeded standards at 58% of mines.
- Cyanide exceeded standards at 53% of mines.

Why Do Predictions Fail?

In order to evaluate water quality impacts during the permitting process, government regulators rely on water quality predictions created by hydrologists and geochemists and mining engineers using computer models and other types of field or laboratory studies. Those predictions are only as good as the science upon which the models/tools are based, and the site characterization information supplied to those models. So when water quality predictions fail to predict water quality for mining operations, they fail for two general reasons:

1. the science of mine water quality prediction is imperfect
2. the science of mine water quality prediction is imperfectly applied at mine sites

The Imperfect Science of Mine Water Quality Prediction

The complexity of pollutants' interaction and movement in groundwater and surface water systems at mines is difficult to recreate in a model. This is addressed in detail in the companion report by Maest & Kuipers titled *Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties, and State-of-the-Art*.

According to *Methods and Models*, factors that complicate the prediction of water quality at mine sites range in scale from small to large. On a small scale, for example, it is not well known how minerals react in complex systems. On a large scale, geology, climate, methods of mining and mineral processing, and mine waste management approaches vary among and within mine operations. These large scale variations limit the degree to which information from one site can be applied to another.

Also, extrapolation from the laboratory to the mine must address complicating factors such as environmental conditions, water and gas transport, differences in particle size, and how these variables affect drainage quality over periods of decades or centuries. However, there is virtually no available field information describing the effect of these variables over extended periods of time. The lack of this field information introduces significant additional uncertainty into predictions.

Just as weather cannot be accurately predicted beyond a certain point because weather models and their inputs are not perfect, the transport of pollutants through complex geological and hydrological systems over the longer term, which can range from five years to tens of thousands of years is similarly difficult to predict.

One of the study's most significant findings, however, is where the practice of predicting weather and the practice of predicting water quality at mining operations part ways. Weather models are consistently reevaluated based on a comparison of predictions with actual weather conditions that occur subsequently.

Not so with the models used for predicting water quality at mining operations. The very fact that the study is unprecedented shows that *professionals who predict mine water quality do not revisit their predictions, and neither do the regulators responsible for ensuring the accuracy of those prediction*. The models used for the predictions cannot be improved if their failures and successes are not evaluated. Where predictions of water quality at mining sites are concerned, the scientific process is broken.

Imperfect Science, Imperfectly Applied

A mine water quality prediction model can only reach its potential at any individual mine site if that site is correctly characterized (in terms of its hydrology and geochemistry) to the extent possible. According to Maest and Kuipers, that potential is not being reached.

There are two types of characterization failures described in the *Comparison Report*: hydrologic (related to water flow at a mine site) and geochemical (the chemistry, geology and mineralogy of the materials/minerals that comprise the mine site).

The *Comparison Report* documents that six of the 25 case study mines were inadequately characterized hydrologically, and that eleven of the case study sites were inadequately characterized geochemically.

Another example of "imperfect science, imperfectly applied" is the bias of mine water quality predictions made by consultants hired by the prospective mine operator. This problem is implied by the number of site characterization failures, and by the failure to check the results of past mine water quality predictions.

Regulatory agencies, both federal and state, allow the mining company to select and directly pay consultants to predict mine water quality impacts, and to review and comment on (or even reject) those predictions, prior to release to the agency. It is an understatement to say that consultants heavily influence mine water quality predictions.

Unfortunately, given the client/customer relationship between prospective mine operators and their consultants, consultants are rewarded for having favorable predictions. On the other hand a prediction of poor water quality will usually delay a permit, which increases the permitting costs. While exceptions exist, consultants that predict poor water quality often are not rehired. This perverse incentive is contrary to the spirit of unbiased science, and contrary to the public interest.



Preventing Future Failures (and Addressing Current Failures)

Recommendations

Both the *Comparisons* and the *Methods and Models Reports* reveal that the prediction of future mine water quality is an uncertain business. And given the difficulty in modeling natural systems, even if all the recommendations included here and in the Kuipers-Maest research are implemented, mine water quality prediction will always be an uncertain business. However, there is considerable room for improvement.

Just as weather prediction has improved over time, so can mine water quality prediction — if regulators and professionals in the sector learn from past predictions and improve characterization efforts.

With that in mind, the following recommendations are intended to help improve mine water quality predictions today and in the future.

Addressing the Consequences of the Existing Prediction Process

Assess existing mines. If the results of the *Comparison Report* are extrapolated to all operating major mines, water quality standards would be exceeded at roughly 75% of all mines in the United States. Regulators should, in a public process, canvass all permitted mines to:

- determine which mines are exceeding water quality standards,
- evaluate how surrounding communities and the environment are being affected, and what cleanup steps are necessary,
- revisit the original predictions, and
- reassess the adequacy of the financial assurances provided by mine operators to guarantee mine cleanup and long-term water treatment.

Incorporate uncertainty into permitting process. Regulators should take a suitably precautionary approach to the mine permitting process, and require that mine design, mitigation and financial assurance calculations prepare for reasonable worst-case rather than best-case scenarios.

Better screen high-risk mines. Regulators must demonstrate concrete improvement in the accuracy of mine water quality predictions and mitigation efforts. For example, additional regulatory scrutiny should be given to the highest risk proposals such as those mines near water resources and with elevated acid drainage or contaminant leaching potential. In cases where the risks are too high, regulators should not permit mines. It should be noted

that this recommendation is supported by the *Comparison Report* which demonstrates that 93 % of such mines near groundwater, and 85% near surface water, exceeded water quality standards.

Some major mining companies are realizing that the life-cycle costs need to be clearly evaluated, including the costs of *perpetual maintenance and water treatment after mine closure*. While some leaders in the industry are using life-cycle cost estimates, this is still not a uniform industry standard, and regulators ultimately must make the determination for many mine proposals.

Inform the public about the uncertainty of water quality prediction. As part of the mine permitting process, regulators should inform the public of the history of the accuracy of mine water quality predictions so they can better determine the risk involved in a mine proposal.

Improving Future Mine Water Quality Predictions

Ease access to predictions and results. Information regarding pre-mining, mining and post-mining water quality should be publicly available online, along with the associated mine water quality predictions made during the permitting process. This will facilitate a more informed mine permit process for regulators and the public.

Review original predictions as water quality develops during mining. Mine operations should be regularly assessed to determine if they are departing from mine water quality predictions. This will allow regulators and mine operators to take early action when mine water quality begins to depart from the predicted.

Consult past predictions at other mines. When permitting a mine, regulators should be required to seek similar mines, or similar aspects of different mines, and determine what predictions were made and what water quality actually occurred. These mine analogs should be publicly disclosed.

Require improved characterization of mine sites. This recommendation is covered in much greater detail in the *Methods and Models Report*. In summary, regulators should require better information about the mine site — before, during and after operations.

Require more research on the effectiveness of mine water quality mitigation. The *Comparison Report* found that where predictions of good mine water quality were predicated upon the mine operator using mitigation strategies, mine water quality usually exceeded water quality standards. More research is needed to determine how and why these mitigation efforts fail, and how to improve them.

Change the procedure for selecting consultants to avoid the present conflict of interests. Agencies should independently select and pay the consultants to conduct the

studies. This will limit the ability of a mining proponent to influence the outcome of the predictions. The mine proponent can comment on the study, similar to public interest organizations, but they should not be able to exert sufficient influence to bias the outcome.

Increase government expertise. Many state and federal agencies are not sufficiently funded to employ staff with the technical expertise to provide appropriate analysis and oversight of the mine permitting process. Increased funding should be incorporated into agency budgets to ensure that technical expertise is available for permit review.



Endnotes

1. Jim Kuipers, PE, is a mining engineer with Kuipers & Associates in Butte, Montana, and Ann Maest, PhD, is an environmental geochemist with Buka Environmental in Boulder, Colorado.
2. The National Environmental Policy Act requires a science-based review of mine proposals when federally-owned land is affected, or when a federal permit is required (e.g. the Clean Water Act requires a permit when a mine discharges into waters of the United States). Many states have similar laws, based on NEPA, that apply to mine proposals even when federal land is not involved.
3. Mitigation is the effort by a mine operator to prevent or reduce pollution. For example, some mine waste (e.g., tailings impoundments) is underlain by thick plastic to prevent contaminants from moving into nearby water resources.
4. In this paper, an “exceedance” is the presence of a pollutant in concentrations higher than a water quality standard. This is different from a water quality “violation,” which is a breach in the terms of a water quality permit. A water quality permit, although based on standards, may allow exceedances under some conditions. A mine operator is legally liable for a water quality violation.
5. Mitchell, Larry D., a staff paper prepared for the Environmental Quality Council, “Zortman and Landusky Mines: HJ 43 Water Quality Impacts, October 2004.
6. Kuipers, J, 2003, Putting a Price on Pollution: Financial Assurance for Mine Reclamation and Closure. This report was funded by Mineral Policy Center.
7. Many mines have multiple EISs or EIAs for different eras of mining.



Wild Rice Sulfate Study

Summary and next steps

In 2010, the Minnesota Pollution Control Agency (MPCA) initiated a multi-year effort to clarify implementation of the state's wild rice sulfate standard. Based on a review of available information, the MPCA determined that additional studies were needed to evaluate the effects of sulfate on wild rice production. In 2011 the Minnesota Legislature provided direction, and funding from the Clean Water, Land and Legacy Amendment, to gather this additional information.

Study information

The goal of the Wild Rice Sulfate Standard Study is to enhance understanding of the effects of sulfate on wild rice and to inform a decision as to whether a revision of the wild rice sulfate standard is warranted. The Study consists of parallel research efforts (Study components) conducted by groups of scientists at the University of Minnesota Duluth and Twin Cities under contract with the MPCA.

The Study's main hypothesis is that wild rice is impacted by sulfate via the conversion of sulfate to sulfide in the rooting zone of the plants. Each of the Study components has a specific purpose and associated strengths and limitations, as noted in Table 1. The Study was designed so individual components together will provide a better understanding of the effects of sulfate on wild rice. The Study components are:

- **Field survey of wild rice habitats** to investigate physical and chemical conditions correlated with the presence or absence of wild rice, including sulfate in surface water and sulfide in the rooting zone
- **Controlled laboratory hydroponic experiments** to determine the effect of elevated sulfate and sulfide on early stages of wild rice growth and development
- **Outdoor container experiments using natural sediments** to determine the response of wild rice to a range of sulfate concentrations in the surface water, and associated sulfide in the rooting zone, across the growing season
- **Collection and analysis of rooting zone depth profiles** of dissolved chemicals at wild rice container experiments and field sites to characterize sulfate, sulfide, and iron
- **Sediment incubation laboratory experiments** to explore the difference ambient temperature has on the rate that elevated sulfate concentrations in water enter underlying sediment and convert to sulfide, and to what degree sulfate is later released back into the overlying water

Some of the reports include information about the sulfate or sulfide concentration(s) at which effects on wild rice were observed; however, it would be premature to conclude that those concentrations are directly comparable to the wild rice sulfate standard. Each Study component uses a different approach to examine how sulfate might affect wild rice. The results of each component must be analyzed and integrated with the other components before any recommendations can be made about the standard.

Data collection was completed in December 2013 and is documented in individual reports from the researchers. Some lab analysis will occur during January 2014 and be added to the report(s) when complete. During January and February 2014, MPCA staff will integrate the results; analyze the data as a whole; and review existing monitoring data, other relevant scientific studies/information, and the original basis for the wild rice sulfate standard to determine if a change to the standard is warranted and, if so, what it should be. The MPCA will release preliminary recommendations by the end of February 2014.

Table 1. Purpose, strengths, and limitations of Study components.

	Field Survey	Laboratory Hydroponic Experiments		Outdoor Container Experiments	Collection and Analysis of Rooting Zone Depth Profiles	Sediment Incubation Laboratory Experiments
		Sulfate (SO ₄)	Sulfide (H ₂ S)			
Main Purpose	Expand understanding of environmental conditions correlated with presence/absence of wild rice.	Evaluate effects of sulfate on wild rice seed germination and growth of sprouts.	Evaluate effects of sulfide on wild rice seed germination and growth of sprouts.	Evaluate effects of sulfate on wild rice plants over full life cycle, and multiple years.	Characterize sulfate, sulfide, and iron in the rooting zone of wild rice container experiments and field sites.	Evaluate effect of temperature on movement of sulfate into and out of underlying sediment.
Endpoints	Concentrations of chemicals in surface water & rooting zone (e.g. SO ₄ & H ₂ S vs. wild rice occurrence).	Growth of wild rice sprouts (biomass, root & shoot elongation). Germination rate of seeds.	Growth of wild rice sprouts (biomass, root & shoot elongation). Germination rate of seeds.	Growth of wild rice (biomass, plus number & weight of seeds). Sulfide concentrations in rooting zone.	Concentrations of sulfate, sulfide and iron in porewater.	Sulfate concentrations in overlying water over time; SO ₄ , iron, H ₂ S & anion tracers in sediment porewater. Simple model.
Key Strengths	Most reflective of actual environmental conditions. Multiple wild rice stands and breadth of characteristics sampled.	Controlled dose-response experiment. Controlled exposure to known concentrations of SO ₄ .	Controlled dose-response experiment. Controlled exposure to known concentrations of H ₂ S	Controlled dose-response experiment. Includes natural sediment matrix as rooting environment. Involves entire growth cycle, multiple years.	Provides additional data to understand and interpret container experiments and field sites.	Controlled experiment with natural sediment and water.
Key Limitations	Least controlled. Annual visit for most sites, 3x/year for a subset. Not definitive on cause and effect.	Only evaluates early growth stages. Leading hypothesis is that sulfate is converted to sulfide, which is directly toxic.	Only evaluates early growth stages. Unable to simultaneously keep roots anaerobic & shoots aerobic.	Full effect of sulfate may take longer than several years to realize. No groundwater movement.	Utility lies in the integration of this data with the other Study components, not in this data set alone.	Provides preliminary assessment of sediment from two sites that may inform but is not fully transferrable to other sites. No groundwater movement. No wild rice plants grown.

Summary of Study Components

The Study researchers provided reports and the associated data for each of the Study components. Appendix A lists the reports and data files associated with each of the Study components, all of which are available on the MPCA's FTP site at <http://files.pca.state.mn.us/pub/tmp/wildRice>. The reports include general conclusions from each component, but do not integrate the data and information across the Study components. The following paragraphs briefly summarize each Study component and highlight the MPCA's next steps and considerations in analyzing and integrating the Study components.

Field Survey of Wild Rice Habitats

The purpose of the field survey was to expand understanding of environmental conditions correlated with the presence and absence of wild rice. This included investigating both the water quality of the overlying water and the sediment characteristics of water bodies with and without the presence of wild rice. The data are valuable because the field survey collected and analyzed a wide range of environmental characteristics *in situ* (i.e. in the "natural" environment). However, they are limited because it is hard to determine the direct cause and effect mechanism of any observed correlations.

Minimal statistical analyses of the data are completed to date because laboratory analyses are still ongoing and the data have yet to be fully merged into a comprehensive database. Key activities to be completed by the MPCA in January and February include:

- Complete the merger of the field and laboratory data
- Develop summary statistics, and complete correlation and regression analysis of the variables
- Identify any patterns or differences in the data sets from the lake, stream and paddy rice sites
- Relate field water chemistry and sediment statistics to wild rice presence and absence

Controlled Laboratory Hydroponic Experiments

This involved evaluating the effects of sulfate and sulfide on wild rice seed germination and growth of sprouts in a laboratory setting. The data are valuable because the controlled laboratory setting allowed researchers to vary the concentration of a single parameter – in this case sulfate or sulfide – and measure any effect on the plants, thereby establishing a dose-response relationship. The laboratory experiments were limited as the wild rice proved very difficult to grow beyond the seedling stage in the laboratory. Consequently experiments were only conducted on early stages of wild rice germination and growth.

Over the next two months, MPCA research scientists will be further verifying and analyzing the experimental results, as follows:

- Review the data and statistical analyses for sulfate and sulfide; complete additional statistical analysis as needed to further evaluate the effects of sulfate and sulfide on seeds and sprouts

Outdoor Container Experiments

Container experiments were conducted to evaluate effects of sulfate on wild rice plants over the full growing cycle of the plants. Because of previous work done at the experimental research station where this Study component was conducted, the researchers observed wild rice over three years of sulfate additions. During the third year (2013) sulfide measurements were made in the sediments of these experiments.

The container experiments represent another type of dose-response experiment against which the laboratory results and field survey data can be compared. The container experiments are more representative of natural conditions in that the plants are growing in lake sediment. However, they have the limitation of being less controlled than the laboratory experiments and are still not a completely "natural" system as compared to data from the field survey. For example, the outdoor containers did not lose or gain any water to or from groundwater. This provided control to the experiment but did not fully mimic conditions in natural wild rice beds, where groundwater could be supplying chemicals that alter the effect of sulfate in the overlying surface water or sulfide in the sediments.

During January and February, MPCA analysis of the container experiment results will include:

- Review the data and statistical analysis; complete additional statistical analysis as needed to further analyze and describe the effect of elevated sulfate and sulfide on wild rice
- Compare the sulfate concentrations (calculated and measured) to the rooting-zone depth profile data, to examine the relationship between sulfate in the water column and sulfide in sediments
- Examine the cumulative effect of added sulfate over the three years, and the relationship between the sulfate doses and the accumulation of sulfide in the sediment

Collection and Analysis of Rooting Zone Depth Profiles

This Study component involved detailed analysis of the sediment at field survey sites and the container experiments to provide detailed information about the sediment and porewater chemistry (particularly sulfate, sulfide, and iron) of the wild rice rooting zone. The purpose of this effort was to provide data to help interpret the results of the field survey and container experiments. As noted in the summaries above, during January and February the data from this Study component will be evaluated with the water quality data from the field sites and container experiments to help understand what the wild rice roots are being exposed to, and also inform the understanding of how iron may mitigate the effects of sulfide production in the rooting zone of the sediment.

Sediment Incubation Laboratory Experiments

This Study component enhanced the understanding of the effect of temperature on movement of sulfate into and out of underlying sediment. The experiment was conducted in the laboratory with sediment and water collected from two sites in northeastern Minnesota, but did not include any wild rice or other rooted aquatic plant growth. While the experiment was not conducted using a flow-through design, water column mixing was part of the experimental method so this was not a completely static incubation. MPCA will review the data from this Study component to help inform the MPCA's recommendations about the current wild rice sulfate standard, particularly the "period during which the rice may be susceptible to damage by high sulfate levels."

Data integration and development of preliminary recommendations about the Wild Rice Sulfate Standard

During January and February 2014, MPCA staff will analyze the data and integrate the information gained from each Study component to inform recommendations regarding whether a revision of the wild rice sulfate standard is warranted and if so, what changes are needed. In addition to the further analysis identified above for each Study component, data integration efforts will include:

- Comparing the data from the hydroponic and outdoor container experiments to further describe:
 - The effect of sulfate on wild rice
 - The effect of sulfide on wild rice

Note: To inform the wild rice sulfate standard review, an important aspect of this analysis will be determining what concentrations of sulfate and sulfide are *protective* of wild rice, which may be different than the concentrations at which effects are observed in the study results.

- Integrating the laboratory experimental data with the field survey data to identify any patterns in wild rice impacts and water quality variables in the laboratory and field setting
- Comparing the data from the field survey, outdoor container experiments, and sediment incubation laboratory experiments to evaluate:
 - The relationship between sulfate in the overlying water and sulfide in the sediment
 - The role of iron in removing sulfide from solution and mitigating the production of sulfide
 - The time-course of net sulfide production after sulfate has been added to overlying water, given that there may be loss of sulfide through various mechanisms. For example, iron may remove sulfide from solution

MPCA staff will release their analysis in the form of preliminary recommendations regarding the wild rice sulfate standard, and accompanying reasoning, by the end of February 2014. Those recommendations will include:

- Does the scientific evidence indicate that the standard should go up or down and, if so, generally by how much?
- Should there be a different standard for lakes/wetlands, or streams, or paddy rice?
- What more can be said about the “period when the rice may be susceptible to high sulfate”?

Additional details, including a technical support document, will follow.

Opportunities for Public Input and Comment

The MPCA will share its preliminary recommendations with the Wild Rice Standards Study Advisory Committee for their input and feedback. Also, there may be an expert panel review of the study results and preliminary recommendations in spring 2014.

Any proposed change to the wild rice sulfate standard would be adopted into Minnesota’s water quality standards rule (Minnesota Rules Chapter 7050) in accordance with the requirements of the Minnesota Administrative Procedures Act and would require the approval of the U.S. Environmental Protection Agency.

Contact information

For more information visit www.pca.state.mn.us/ktqh1083.

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Appendix A

The following is a list of the folders (bold) and individual files that comprise the MPCA Wild Rice Standards Study on the MPCA's FTP site at <ftp://files.pca.state.mn.us/pub/tmp/wildRice>.

_Wild_Rice_Study_Summary

WildRice_summarydoc_Jan2014.docx

Literature_List

Wild_Rice_Literature_Holdings.pdf

Laboratory_Hydroponics_Experiments

Pastor_Hydroponics_Experiment_Report.pdf
Appendix1_Germination_Response_to_Sulfate_SOP.pdf
Appendix2_Juvenile_Seedling_Growth_Response_to_Sulfate_SOP.pdf
Appendix3_Germination_Response_to_Sulfide_SOP.pdf
Appendix4_Juvenile_Seedling_Growth_Response_to_Sulfide_SOP.pdf
Appendix5_Effects_of_Sulfate_on_Germination.xls
Appendix6_Effects_of_Sulfate_on_Juvenile_Growth.xls
Appendix7_Effects_of_Sulfide_on_Germination.xls
Appendix8_Rangefinder_Test_of_Effects_of_Sulfide_on_Juvenile_Growth.xls
Appendix9_Definitive_Tests_of_Effects_of_Sulfide_on_Juvenile_Growth_Trial 1.xls
Appendix10_Definitive_Tests_of_Effects_of_Sulfide_on_Juvenile_Growth_Trial 2.xls

Outdoor_Container_Experiments

Pastor_Mesocosm_report.pdf
Appendix1_Water_chemistry_of_mesocosms.xls
Appendix2_Mesocosm_Plant_Data.xls

2011_2012_2013_Field_Surveys

Myrbo_Final_Report_on_2011_2012_2013_Field_Surveys_20131231.pdf
LacCore_dataexport_finalreport.xls

Sediment_Incubation_Experiments

Temperature_Dependent_Diffusion_Rates_of_Sulfate_in_Aquatic_Sediments_final.pdf
UMDCE_Lab_Microcosm_MPCA_SulfateStudy_Summary_of_Surfacewater_samples.xlsx
UMDCE_Lab_Microcosm_SulfateStudy_PorewaterBromide.xlsx
UMDCE_Lab_Microcosm_SulfateStudy_PorewaterFluoride.xlsx
UMDCE_Lab_Microcosm_SulfateStudy_PorewaterSulfate.xlsx
Note: Data for pore water iron, sulfide, and pH will follow

Collection_and_Analysis_of_Rooting_Zone_Depth_Profiles

Sulfate_Manipulation_Rooting_Zone_Geochemistry_final.pdf
Porewater_Metals_Cu_Zn_Fe_at_Mesocosms_by_ICP-MSfinal_wParamID.xlsx
MPCA_Wild_Rice_Pore_Water_2013_12_31.accb



Wild Rice Sulfate Study

Summary and next steps

In 2010, the Minnesota Pollution Control Agency (MPCA) initiated a multi-year effort to clarify implementation of the state's wild rice sulfate standard. Based on a review of available information, the MPCA determined that additional studies were needed to evaluate the effects of sulfate on wild rice production. In 2011 the Minnesota Legislature provided direction, and funding from the Clean Water, Land and Legacy Amendment, to gather this additional information.

Study information

The goal of the Wild Rice Sulfate Standard Study is to enhance understanding of the effects of sulfate on wild rice and to inform a decision as to whether a revision of the wild rice sulfate standard is warranted. The Study consists of parallel research efforts (Study components) conducted by groups of scientists at the University of Minnesota Duluth and Twin Cities under contract with the MPCA.

The Study's main hypothesis is that wild rice is impacted by sulfate via the conversion of sulfate to sulfide in the rooting zone of the plants. Each of the Study components has a specific purpose and associated strengths and limitations, as noted in Table 1. The Study was designed so individual components together will provide a better understanding of the effects of sulfate on wild rice. The Study components are:

- **Field survey of wild rice habitats** to investigate physical and chemical conditions correlated with the presence or absence of wild rice, including sulfate in surface water and sulfide in the rooting zone
- **Controlled laboratory hydroponic experiments** to determine the effect of elevated sulfate and sulfide on early stages of wild rice growth and development
- **Outdoor container experiments using natural sediments** to determine the response of wild rice to a range of sulfate concentrations in the surface water, and associated sulfide in the rooting zone, across the growing season
- **Collection and analysis of rooting zone depth profiles** of dissolved chemicals at wild rice container experiments and field sites to characterize sulfate, sulfide, and iron
- **Sediment incubation laboratory experiments** to explore the difference ambient temperature has on the rate that elevated sulfate concentrations in water enter underlying sediment and convert to sulfide, and to what degree sulfate is later released back into the overlying water

Some of the reports include information about the sulfate or sulfide concentration(s) at which effects on wild rice were observed; however, it would be premature to conclude that those concentrations are directly comparable to the wild rice sulfate standard. Each Study component uses a different approach to examine how sulfate might affect wild rice. The results of each component must be analyzed and integrated with the other components before any recommendations can be made about the standard.

Data collection was completed in December 2013 and is documented in individual reports from the researchers. Some lab analysis will occur during January 2014 and be added to the report(s) when complete. During January and February 2014, MPCA staff will integrate the results; analyze the data as a whole; and review existing monitoring data, other relevant scientific studies/information, and the original basis for the wild rice sulfate standard to determine if a change to the standard is warranted and, if so, what it should be. The MPCA will release preliminary recommendations by the end of February 2014.

Table 1. Purpose, strengths, and limitations of Study components.

	Field Survey	Laboratory Hydroponic Experiments		Outdoor Container Experiments	Collection and Analysis of Rooting Zone Depth Profiles	Sediment Incubation Laboratory Experiments
		Sulfate (SO ₄)	Sulfide (H ₂ S)			
Main Purpose	Expand understanding of environmental conditions correlated with presence/absence of wild rice.	Evaluate effects of sulfate on wild rice seed germination and growth of sprouts.	Evaluate effects of sulfide on wild rice seed germination and growth of sprouts.	Evaluate effects of sulfate on wild rice plants over full life cycle, and multiple years.	Characterize sulfate, sulfide, and iron in the rooting zone of wild rice container experiments and field sites.	Evaluate effect of temperature on movement of sulfate into and out of underlying sediment.
Endpoints	Concentrations of chemicals in surface water & rooting zone (e.g. SO ₄ & H ₂ S vs. wild rice occurrence).	Growth of wild rice sprouts (biomass, root & shoot elongation). Germination rate of seeds.	Growth of wild rice sprouts (biomass, root & shoot elongation). Germination rate of seeds.	Growth of wild rice (biomass, plus number & weight of seeds). Sulfide concentrations in rooting zone.	Concentrations of sulfate, sulfide and iron in porewater.	Sulfate concentrations in overlying water over time; SO ₄ , iron, H ₂ S & anion tracers in sediment porewater. Simple model.
Key Strengths	Most reflective of actual environmental conditions. Multiple wild rice stands and breadth of characteristics sampled.	Controlled dose-response experiment. Controlled exposure to known concentrations of SO ₄ .	Controlled dose-response experiment. Controlled exposure to known concentrations of H ₂ S	Controlled dose-response experiment. Includes natural sediment matrix as rooting environment. Involves entire growth cycle, multiple years.	Provides additional data to understand and interpret container experiments and field sites.	Controlled experiment with natural sediment and water.
Key Limitations	Least controlled. Annual visit for most sites, 3x/year for a subset. Not definitive on cause and effect.	Only evaluates early growth stages. Leading hypothesis is that sulfate is converted to sulfide, which is directly toxic.	Only evaluates early growth stages. Unable to simultaneously keep roots anaerobic & shoots aerobic.	Full effect of sulfate may take longer than several years to realize. No groundwater movement.	Utility lies in the integration of this data with the other Study components, not in this data set alone.	Provides preliminary assessment of sediment from two sites that may inform but is not fully transferrable to other sites. No groundwater movement. No wild rice plants grown.

Summary of Study Components

The Study researchers provided reports and the associated data for each of the Study components. Appendix A lists the reports and data files associated with each of the Study components, all of which are available on the MPCA's FTP site at <http://files.pca.state.mn.us/pub/tmp/wildRice>. The reports include general conclusions from each component, but do not integrate the data and information across the Study components. The following paragraphs briefly summarize each Study component and highlight the MPCA's next steps and considerations in analyzing and integrating the Study components.

Field Survey of Wild Rice Habitats

The purpose of the field survey was to expand understanding of environmental conditions correlated with the presence and absence of wild rice. This included investigating both the water quality of the overlying water and the sediment characteristics of water bodies with and without the presence of wild rice. The data are valuable because the field survey collected and analyzed a wide range of environmental characteristics *in situ* (i.e. in the "natural" environment). However, they are limited because it is hard to determine the direct cause and effect mechanism of any observed correlations.

Minimal statistical analyses of the data are completed to date because laboratory analyses are still ongoing and the data have yet to be fully merged into a comprehensive database. Key activities to be completed by the MPCA in January and February include:

- Complete the merger of the field and laboratory data
- Develop summary statistics, and complete correlation and regression analysis of the variables
- Identify any patterns or differences in the data sets from the lake, stream and paddy rice sites
- Relate field water chemistry and sediment statistics to wild rice presence and absence

Controlled Laboratory Hydroponic Experiments

This involved evaluating the effects of sulfate and sulfide on wild rice seed germination and growth of sprouts in a laboratory setting. The data are valuable because the controlled laboratory setting allowed researchers to vary the concentration of a single parameter – in this case sulfate or sulfide – and measure any effect on the plants, thereby establishing a dose-response relationship. The laboratory experiments were limited as the wild rice proved very difficult to grow beyond the seedling stage in the laboratory. Consequently experiments were only conducted on early stages of wild rice germination and growth.

Over the next two months, MPCA research scientists will be further verifying and analyzing the experimental results, as follows:

- Review the data and statistical analyses for sulfate and sulfide; complete additional statistical analysis as needed to further evaluate the effects of sulfate and sulfide on seeds and sprouts

Outdoor Container Experiments

Container experiments were conducted to evaluate effects of sulfate on wild rice plants over the full growing cycle of the plants. Because of previous work done at the experimental research station where this Study component was conducted, the researchers observed wild rice over three years of sulfate additions. During the third year (2013) sulfide measurements were made in the sediments of these experiments.

The container experiments represent another type of dose-response experiment against which the laboratory results and field survey data can be compared. The container experiments are more representative of natural conditions in that the plants are growing in lake sediment. However, they have the limitation of being less controlled than the laboratory experiments and are still not a completely "natural" system as compared to data from the field survey. For example, the outdoor containers did not lose or gain any water to or from groundwater. This provided control to the experiment but did not fully mimic conditions in natural wild rice beds, where groundwater could be supplying chemicals that alter the effect of sulfate in the overlying surface water or sulfide in the sediments.

During January and February, MPCA analysis of the container experiment results will include:

- Review the data and statistical analysis; complete additional statistical analysis as needed to further analyze and describe the effect of elevated sulfate and sulfide on wild rice
- Compare the sulfate concentrations (calculated and measured) to the rooting-zone depth profile data, to examine the relationship between sulfate in the water column and sulfide in sediments
- Examine the cumulative effect of added sulfate over the three years, and the relationship between the sulfate doses and the accumulation of sulfide in the sediment

Collection and Analysis of Rooting Zone Depth Profiles

This Study component involved detailed analysis of the sediment at field survey sites and the container experiments to provide detailed information about the sediment and porewater chemistry (particularly sulfate, sulfide, and iron) of the wild rice rooting zone. The purpose of this effort was to provide data to help interpret the results of the field survey and container experiments. As noted in the summaries above, during January and February the data from this Study component will be evaluated with the water quality data from the field sites and container experiments to help understand what the wild rice roots are being exposed to, and also inform the understanding of how iron may mitigate the effects of sulfide production in the rooting zone of the sediment.

Sediment Incubation Laboratory Experiments

This Study component enhanced the understanding of the effect of temperature on movement of sulfate into and out of underlying sediment. The experiment was conducted in the laboratory with sediment and water collected from two sites in northeastern Minnesota, but did not include any wild rice or other rooted aquatic plant growth. While the experiment was not conducted using a flow-through design, water column mixing was part of the experimental method so this was not a completely static incubation. MPCA will review the data from this Study component to help inform the MPCA's recommendations about the current wild rice sulfate standard, particularly the "period during which the rice may be susceptible to damage by high sulfate levels."

Data integration and development of preliminary recommendations about the Wild Rice Sulfate Standard

During January and February 2014, MPCA staff will analyze the data and integrate the information gained from each Study component to inform recommendations regarding whether a revision of the wild rice sulfate standard is warranted and if so, what changes are needed. In addition to the further analysis identified above for each Study component, data integration efforts will include:

- Comparing the data from the hydroponic and outdoor container experiments to further describe:
 - The effect of sulfate on wild rice
 - The effect of sulfide on wild rice

Note: To inform the wild rice sulfate standard review, an important aspect of this analysis will be determining what concentrations of sulfate and sulfide are *protective* of wild rice, which may be different than the concentrations at which effects are observed in the study results.

- Integrating the laboratory experimental data with the field survey data to identify any patterns in wild rice impacts and water quality variables in the laboratory and field setting
- Comparing the data from the field survey, outdoor container experiments, and sediment incubation laboratory experiments to evaluate:
 - The relationship between sulfate in the overlying water and sulfide in the sediment
 - The role of iron in removing sulfide from solution and mitigating the production of sulfide
 - The time-course of net sulfide production after sulfate has been added to overlying water, given that there may be loss of sulfide through various mechanisms. For example, iron may remove sulfide from solution

MPCA staff will release their analysis in the form of preliminary recommendations regarding the wild rice sulfate standard, and accompanying reasoning, by the end of February 2014. Those recommendations will include:

- Does the scientific evidence indicate that the standard should go up or down and, if so, generally by how much?
- Should there be a different standard for lakes/wetlands, or streams, or paddy rice?
- What more can be said about the “period when the rice may be susceptible to high sulfate”?

Additional details, including a technical support document, will follow.

Opportunities for Public Input and Comment

The MPCA will share its preliminary recommendations with the Wild Rice Standards Study Advisory Committee for their input and feedback. Also, there may be an expert panel review of the study results and preliminary recommendations in spring 2014.

Any proposed change to the wild rice sulfate standard would be adopted into Minnesota’s water quality standards rule (Minnesota Rules Chapter 7050) in accordance with the requirements of the Minnesota Administrative Procedures Act and would require the approval of the U.S. Environmental Protection Agency.

Contact information

For more information visit www.pca.state.mn.us/ktqh1083.

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Appendix A

The following is a list of the folders (bold) and individual files that comprise the MPCA Wild Rice Standards Study on the MPCA's FTP site at <ftp://files.pca.state.mn.us/pub/tmp/wildRice>.

_Wild_Rice_Study_Summary

WildRice_summarydoc_Jan2014.docx

Literature_List

Wild_Rice_Literature_Holdings.pdf

Laboratory_Hydroponics_Experiments

Pastor_Hydroponics_Experiment_Report.pdf
Appendix1_Germination_Response_to_Sulfate_SOP.pdf
Appendix2_Juvenile_Seedling_Growth_Response_to_Sulfate_SOP.pdf
Appendix3_Germination_Response_to_Sulfide_SOP.pdf
Appendix4_Juvenile_Seedling_Growth_Response_to_Sulfide_SOP.pdf
Appendix5_Effects_of_Sulfate_on_Germination.xls
Appendix6_Effects_of_Sulfate_on_Juvenile_Growth.xls
Appendix7_Effects_of_Sulfide_on_Germination.xls
Appendix8_Rangefinder_Test_of_Effects_of_Sulfide_on_Juvenile_Growth.xls
Appendix9_Definitive_Tests_of_Effects_of_Sulfide_on_Juvenile_Growth_Trial 1.xls
Appendix10_Definitive_Tests_of_Effects_of_Sulfide_on_Juvenile_Growth_Trial 2.xls

Outdoor_Container_Experiments

Pastor_Mesocosm_report.pdf
Appendix1_Water_chemistry_of_mesocosms.xls
Appendix2_Mesocosm_Plant_Data.xls

2011_2012_2013_Field_Surveys

Myrbo_Final_Report_on_2011_2012_2013_Field_Surveys_20131231.pdf
LacCore_dataexport_finalreport.xls

Sediment_Incubation_Experiments

Temperature_Dependent_Diffusion_Rates_of_Sulfate_in_Aquatic_Sediments_final.pdf
UMDCE_Lab_Microcosm_MPCA_SulfateStudy_Summary_of_Surfacewater_samples.xlsx
UMDCE_Lab_Microcosm_SulfateStudy_PorewaterBromide.xlsx
UMDCE_Lab_Microcosm_SulfateStudy_PorewaterFluoride.xlsx
UMDCE_Lab_Microcosm_SulfateStudy_PorewaterSulfate.xlsx
Note: Data for pore water iron, sulfide, and pH will follow

Collection_and_Analysis_of_Rooting_Zone_Depth_Profiles

Sulfate_Manipulation_Rooting_Zone_Geochemistry_final.pdf
Porewater_Metals_Cu_Zn_Fe_at_Mesocosms_by_ICP-MSfinal_wParamID.xlsx
MPCA_Wild_Rice_Pore_Water_2013_12_31.accb



Acid mine drainage risks – A modeling approach to siting mine facilities in Northern Minnesota USA



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SUMMARY

Most watershed-scale planning for mine-caused contamination concerns remediation of past problems while future planning relies heavily on engineering controls. As an alternative, a watershed scale groundwater fate and transport model for the Rainy Headwaters, a northeastern Minnesota watershed, has been developed to examine the risks of leaks or spills to a pristine downstream watershed. The model shows that the risk depends on the location and whether the source of the leak is on the surface or from deeper underground facilities. Underground sources cause loads that last longer but arrive at rivers after a longer travel time and have lower concentrations due to dilution and attenuation. Surface contaminant sources could cause much more short-term damage to the resource. Because groundwater dominates baseflow, mine contaminant seepage would cause the most damage during low flow periods. Groundwater flow and transport modeling is a useful tool for decreasing the risk to downgradient sources by aiding in the placement of mine facilities. Although mines are located based on the minerals, advance planning and analysis could avoid siting mine facilities where failure or leaks would cause too much natural resource damage. Watershed scale transport modeling could help locate the facilities or decide in advance that the mine should not be constructed due to the risk to downstream resources.

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1. Introduction

Acid mine drainage (AMD) is a problem associated with mines throughout the world (Jacobs and Testa, 2014). In the United States, promoting mining on public lands has been a priority since the 1800s (Leschy, 1987), with little consideration for the waste other than getting it away from the mine site being the practice prior to about 1970 (Church, 1996; Ferderer, 1996). Mines were developed with little concern regarding AMD (Crews, 1973; Williams, 1975).

That is no longer the situation. Mining-caused contamination is a global problem and few sites are isolated or sufficiently under-used that potential contamination can be ignored. One example of global cooperation among the mining industry, conservation groups, and stakeholders to set a higher standard for mining, including the prevention of AMD and promotion of it remediation is the Initiative for Responsible Mining Assurance (IRMA) (<http://www.responsiblemining.net/>). The goal of IRMA is to promote responsibility by certifying the most responsible mines.

Watershed-scale planning is necessary to avoid the most serious problems. However, much watershed-scale research focuses

on remediation (Church et al., 2007; Crews, 1973; Kimball et al., 2006; Nimick and von Guerard, 1998; Skousen et al., 1999), often with the perspective of optimizing treatment (Crews, 1973; Kimball et al., 1999). Conceptual and numerical modeling at various scales can aid in prioritizing sites for remediation (Myers, 2013; Runkel et al., 2013). Herr et al. (2003) developed a watershed-scale model of AMD entering a river to show the contaminant sources and potentially demonstrate the effectiveness of remediation of specific sites. Runkel and Kimball (2002) simulated flow and equilibrium chemistry along a stream heavily impacted by AMD to demonstrate the effects of remediation. Related modeling showed that simulation results are most affected by model parameters affecting a nearby stream reach or watershed (Gooseff et al., 2005). Myers (2013) suggested priorities for remediating phosphate mines based on a groundwater model of a large western watershed contaminated with selenium. Statistical models also can show the mining features or geology that best explain the variability in salinity discharging from a mined watershed (Evans et al., 2014). These studies however do not suggest a means of avoiding AMD or other contamination issues as part of the planning process.

Preventing future mines from becoming AMD problems is often considered an engineering issue at the mine site (Jacobs et al., 2014; Buxton et al., 1997; EPA, 1994), although failures occur often

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(Caldwell and Charlebois, 2010; Kuipers et al., 2006; Rico et al., 2008). The level of damage caused by these failures can depend on their location in the watershed. Missing from the literature and generally from mine planning is research showing methods designed to site mines and mine facilities to avoid large-scale AMD problems when leaks occur.

The objective of this study was to use watershed-scale groundwater flow and transport modeling to predict which mine sites in a sulfide rich watershed would be more likely to cause downstream AMD problems if engineering controls fail. It demonstrates how watershed-scale modeling prior to the actual development of mines can improve mine planning to facilitate future remediation when engineering failures occur, a topic currently not substantially addressed in the literature. The setting is the Birch Lake watershed, located within the larger Rainy Headwaters watershed in northern Minnesota, USA (Fig. 1). The area has no current mining and one historic mine. Mining companies hold leases on at least six different copper/nickel deposits (MNDNR, 2014) within the watershed. The Boundary Waters Canoe Area Wilderness (BWCAW), a high value and one of the most-visited wilderness areas in the United States (Heinselman, 1996), lies directly downstream of the potential mining (Fig. 1).

The model could help to optimize mining and waste disposal locations or to decide whether the risks of mining are too high as well as providing information on where more information is needed for decision making. The model could be an example for countries and companies around the world contemplating entering relatively pristine watersheds currently valued for resources that could be damaged by mine pollution.

2. Method of analysis

2.1. Study area

The study area is in the Birch Lake watershed south of the South Kawishiwi River in northeastern Minnesota, USA (Fig. 1). The middle two thirds of the study area overlies the Duluth Complex while the north end abuts Granite Range granite (Fig. 2, Table 1). The Duluth Complex hosts nickel–copper–platinum sulfide deposits in the basal portion of the South Kawishiwi intrusion as much as 1200 m below ground surface (Miller et al., 2002; Parker and Eggleston, 2014). The deposits are potentially significant acid-producers (EPA, 1994; Lapakko, 1988; Lapakko and Olson, 2015; Polymet Mining, 2013b; Polymet Mining, 2012; Severson et al., 2002). The sulfide content of the Spruce Road deposit is 2–5% by volume and 3–4% by weight (Parker and Eggleston, 2014), which may on the high end of the range for the Duluth Complex (Seal et al., 2015). The host mineralized zone has previously produced AMD (EPA, 1994; Lapakko, 1988; Lapakko and Olson, 2015).

Most mining leases lie south of the South Kawishiwi River in the Birch Lake and Stone Creek watersheds (Fig. 2). Proposed mines are expected to initially be underground (Cox et al., 2009; Parker and Eggleston, 2014), including some underground waste rock and tailings disposal (Twin Metals, 2014). Waste rock is rock and overburden removed to reach the ore and tailings are the processed ore from which the valuable mineral has been removed. Waste rock and tailings are considered contaminant sources for this paper because mine planning as to the placement of either material is not sufficiently advanced to distinguish among the properties of either type.

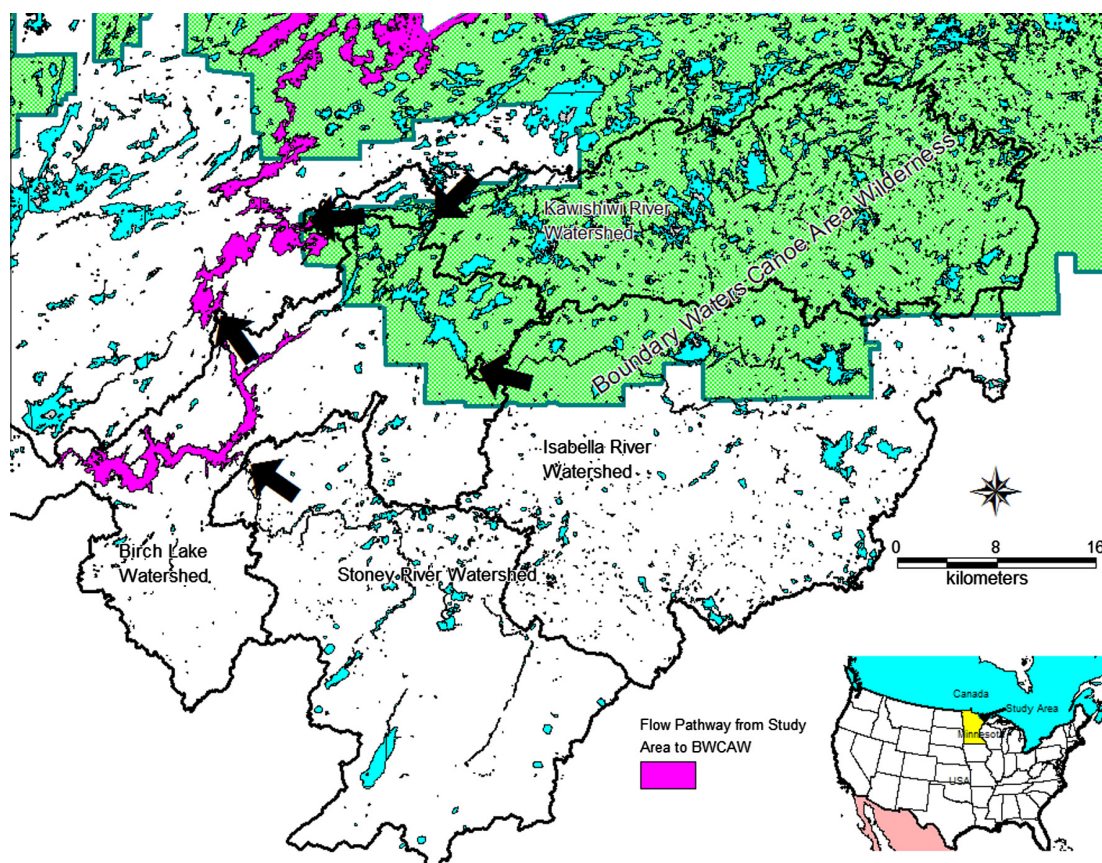


Fig. 1. Rainy Headwaters watershed and study area, showing subwatersheds, rivers, and lakes. Arrows are flow direction from watersheds. Watershed boundaries from Dnr100kwatersheds, www.mngeo.state.mn.us/chouse/metalong.html.

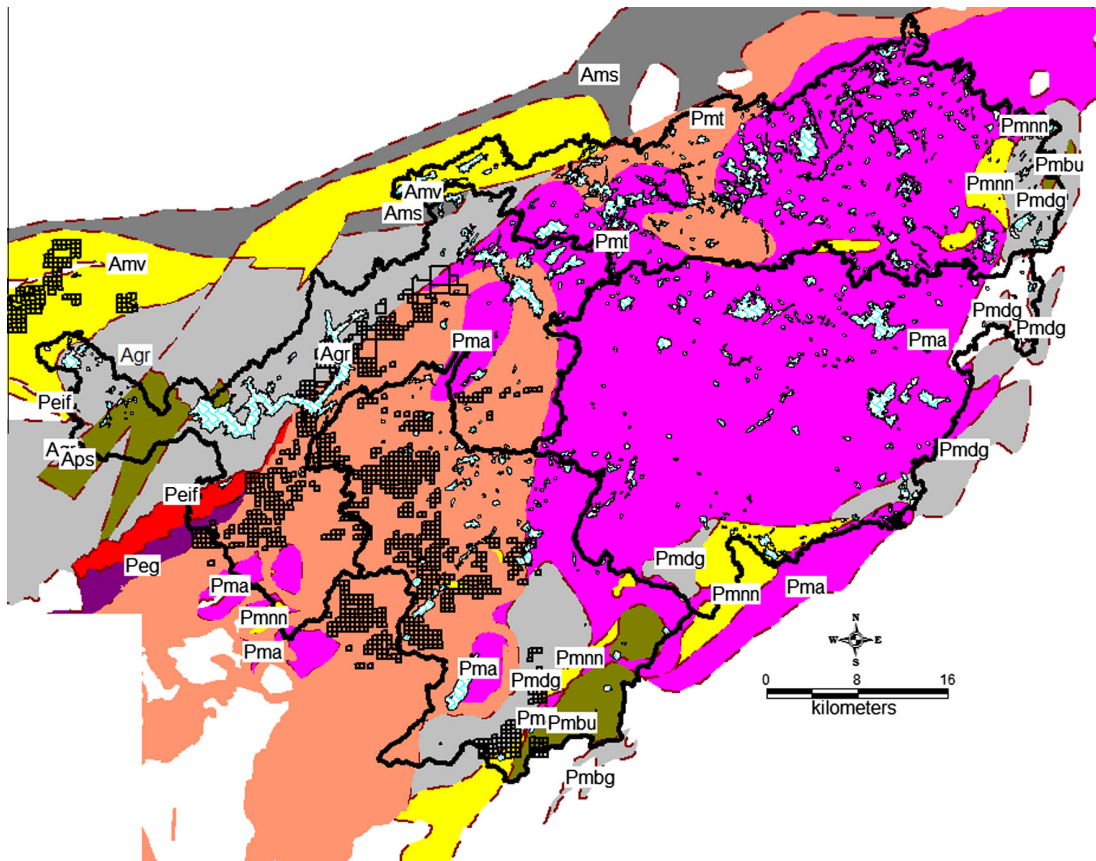


Fig. 2. Bedrock geology and watersheds of the study area. See Table 1 for a description of the formations. See Fig. 1 for the watershed names. The black rectangles are mining leases and approximate location of the mineral deposits.

Table 1

Geologic formations (Nicholson et al., 2007) along with model zone, layer and final calibrated horizontal and vertical conductivity (Kh and Kv, respectively) in meters/day. *n* is effective porosity, Sy is specific yield, and Ss is storage coefficient.

Formation/lithology		Zone	Kh	Kv	Sy	Ss	<i>n</i>	Layer
Duluth Complex, troctolite/gabbro	Pmt	2	0.307	0.01008	.07	.000001	.007	3
		12	0.342	0.137	.12	.00001	.012	2
		22	0.102	0.114	.12	.00001	.012	2
		32	0.00014	0.0182	.07	.000001	.007	3
		33	0.035	0.0145	.12	.00001	.012	2
Duluth Complex, anorthosite/gabbro	Pma	3	0.025	0.2	.07	.000001	.007	3
		13	2.9	0.4	.12	.00001	.012	2
Basalt/rhyolite	Pmnn	31	0.26	0.002	.12	.00001	.012	2
		4	0.05	0.025	.07	.000001	.012	3
Giants range Granite	Agr	14	0.1	0.06	.12	.00001	.012	2
		5	0.0015	0.0015	.02	.000001	.002	3
		15	0.214	0.2	.05	.00001	.005	2
Gabbro/troctolite	Pmbu	25	0.8	0.5	.05	.00001	.005	2
		6	0.27	0.01	.08	.000001	.008	3
Biwabik iron formation	Peif	16	2	0.09	.14	.00001	.014	2
		7	0.16	0.001	.3	.00001	.3	3
		17	0.36	0.0075	.4	.0001	.4	2
		27	0.3	0.001	.4	.001	.4	1
Shale/siltstone	Peg	37	26	0.02	.4	.001	.4	1
		8	0.1	0.01	.03	.000001	.003	3
Surficial aquifer		18	2	0.1	.05	.00001	.005	2
		38	7.4	0.16	.15	.01	.015	1
		39	1	0.05	.15	.01	.015	1
		40	5.2	0.1	.15	.01	.015	1

2.2. Conceptual flow model

Four HU10-scale (USGS et al., 2013) watersheds form the study area: Birch Lake, Stony River, Isabella River, and Kawishiwi River (Fig. 1). Surface water flows north and west from Birch Lake and the Kawishiwi River watershed through the Kawishiwi River and several lakes to the BWCAW. Rivers from the Stony River and Isabella River watersheds flow into the Birch Lake watershed (Figs. 1 and 3). Lakes and wetlands connected by low-gradient rivers cover much of the study area which generally has relief less than 10 m from a divide to nearby lakes and rivers.

A surficial aquifer consisting of glacial till or sand and gravel generally less than 3–6 m thick covers the area (Mast and Turk, 1999). Hydraulic conductivity (K) of the sand/gravel surficial aquifer ranges from 0.000003 to 1070 m/d, or over nine orders of magnitude, for the surficial aquifer (Siegel and Ericson, 1981; Stark, 1977; Winter, 1973). Well yields in the Kawishiwi watershed are less than 54 m³/d (Siegel and Ericson, 1981) reflecting the very thin to nonexistent surficial aquifers.

The Duluth Complex (Fig. 2) is a low-permeability intrusive formation with a very low K (Table 1) except possibly near some of the infrequent faulting, on which there is little available hydrogeologic data (Miller et al., 2002; Thorleifson, 2008), and in the upper 30 m which is relatively fractured with well yields from 27 to 82 m³/d. The plutonic rocks have primary porosity up to 3%, but the effective permeability is very low because the pores are isolated (Stark, 1977). The specific capacity of wells in the Duluth Complex ranges from 0.36 to 1.97 m³/d/m. In bedrock, fractures control permeability and secondary porosity, and also flow paths. Porosity in the fractured Biwabik formation is as high as 50%.

Total flow, or total runoff, from the watershed above the gage for US Geological Survey gaging stations in the area (Fig. 3), was divided into direct runoff and baseflow using methods of Lim et al. (2005, 2010) (Table 2). Yield is total stream flow per area and ranges from 21.6 to 31.2 cm per year (cm/y). Baseflow varies from 14.4 to 24.2 cm/y, although for watersheds with more than 160 square km, it varies from 17.0 to 20.8 cm/y. Assuming recharge is baseflow distributed over drainage area (Cherkauer, 2004; Scanlon et al., 2002), the average recharge is 19.2 cm/y, or 0.00052 m/d for the study area.

Based on gages 7, 5, 2, and 1 (Table 2), subwatersheds Birch Lake, Stony River, Isabella River, and Kawishiwi River (Fig. 3) yield recharge equal to 0.00052, 0.00047, 0.00049, and 0.00054 m/d, respectively. However, the low rates for the small watersheds, Dunka River near Babbitt and Filson Creek gages, 0.00044 and 0.00046 m/d, respectively, illustrate the heterogeneity of the recharge distribution.

Many factors control the recharge distribution, including wetlands, soil types, and soil landforms, including whether the soil is well drained, whether the soils contain substantial peat (Siegel et al., 1995), and whether the bedrock is shallow. Using several statewide GIS soils databases (Land Management Information Center, 1996), maps of wetland coverage, hydrologic soil classification (NRCS, 2007), soil type, surface and subsurface permeability were developed to illustrate the variability (Fig. 4a through e) (Cummins and Grigal, 1980).

A commonly-used method for estimating regional-scale recharge in Minnesota for areas less than 5000 km² based on precipitation, growing degree days, specific yield (based on Rawls et al. (1982)) and baseflow recession indices (Delin et al., 2007; Lorenz and Delin, 2007) yielded a recharge estimate for the

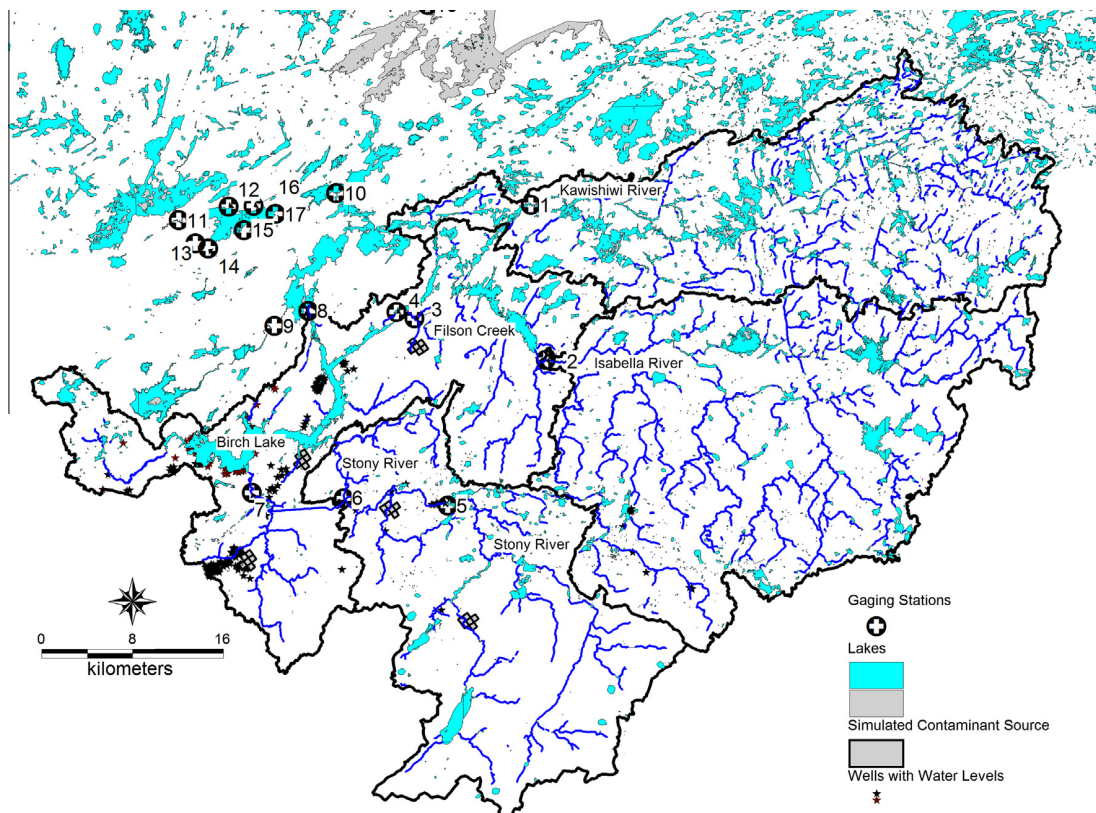


Fig. 3. Location of wells with water levels, gage stations, perennial streams, and lakes in the study area. See Table 2 for a list of gage stations. Source: http://mcc.mn.gov/gis.html#state_minerals_head.

Table 2

U.S. Geological Survey gaging stations and station parameters. See Fig. 3 for the location. BFI is baseflow index, the proportion of total flow that is baseflow.

No	USGS site no	USGS site name	Area (km ²)	Avg flow (m ³ /d)	Avg runoff (m ³ /d)	Base flow (m ³ /d)	BFI	Rech (m/d)
1	05124480	KAWISHIWI RIVER NEAR ELY, MN	657.9	461,164	108,226	352,938	0.77	0.00054
2	05124500	ISABELLA RIVER NEAR ISABELLA, MN	883.2	686,970	256,400	430,571	0.63	0.00049
3	05124990	FILSON CREEK IN SESW SEC. 24 NEAR WINTON, MN	25.0	18,642	7211	11,431	0.61	0.00046
4	05125000	SOUTH KAWISHIWI RIVER NEAR ELY, MN	0.05	991,271	248,969	742,301	0.75	0.00000
5	05125500	STONY RIVER NEAR ISABELLA, MN	466.2	307,811	89,744	218,067	0.71	0.00047
6	05126000	DUNKA RIVER NEAR BABBITT, MN	138.3	94,826	34,147	60,679	0.64	0.00044
7	05126210	SOUTH KAWISHIWI R ABV WHITE IRON LAKE NR ELY, MN	2167.8	1,573,205	443,911	1,129,295	0.72	0.00052
8	05126500	BEAR ISLAND RIVER NEAR ELY, MN	177.4	105,117	28,451	76,666	0.73	0.00043
9	05127000	KAWISHIWI RIVER NEAR WINTON, MN	3185.7	2,419,154	746,217	1,672,937	0.69	0.00053
10	05127205	BURNTSIDE RIVER NEAR ELY, MN	178.7	145,526	34,005	111,521	0.77	0.00062
11	05127207	BJORKMAN'S CREEK NEAR ELY, MN	3.5	2626	1239	1388	0.53	0.00039
12	05127210	ARMSTRONG CREEK NEAR ELY, MN	13.7	11,186	4516	6670	0.6	0.00049
13	05127215	LONGSTORFF CREEK NEAR ELY, MN	22.9	18,984	7403	11,581	0.61	0.00051
14	05127219	SHAGAWA RIVER Trib AT ELY, MN	1.8	259	155	103	0.4	0.00006
15	05127220	BURGO CREEK NEAR ELY, MN	7.9	7977	3477	4499	0.56	0.00057
16	05127230	SHAGAWA RIVER AT ELY, MN	256.4	219,331	49,307	170,025	0.78	0.00066
17	05127500	BASSWOOD RIVER NEAR WINTON, MN	4506.6	3,284,031	724,319	2,559,712	0.78	0.00057

Kawishiwi watershed of 20–30 cm/y. This estimate is similar to the total runoff yield and exceeds the recharge estimates made herein by approximately 20–30%. Surface storage in wetlands and small lakes and subsurface storage in the unsaturated zone and groundwater, which support long-term baseflow (Sophocleous, 2002), could explain the differences among estimates. Microscale topography embedded within larger flow systems connected by small surface drainages and interflow causes large variability in flowpath length (Winter, 1998). This may cause surface runoff hydrographs to have long receding legs which resemble groundwater discharge and are difficult to separate from the runoff hydrograph which may cause errors in estimates based on statistical analyses using baseflow recession (Delin et al., 2007; Lorenz and Delin, 2007).

Baseflow follows a seasonal pattern. Average monthly river flow at the Kawishiwi River near Ely gage peaks at more than 80 cm/y during May just two months after the low flow of less than 8 cm/y recorded in March. Much recharge would occur during this snow-melt freshet flood because water runs on the ground surface and river and stream levels are higher than the water levels in the streambanks. After reducing to less than 20 cm/y by September, the baseflow fluctuates between 10 and 20 cm/y until reaching its low in March.

2.3. Conceptual transport model

Waste rock and tailings developed from ore bodies in the study area would likely become sources of AMD-related contaminants because of accelerated oxidation of the ore's high sulfide contents (Bain et al., 2000; EPA, 1994; Jacobs et al., 2014; Johnson and Hallberg, 2005; Lapakko, 1988; Lefebvre et al., 2001; Nash and Fey, 2007; Polymet Mining, 2013b, 2012). Oxidation within a surface waste rock dump, the most common means of disposal (Lottermoser, 2010; Nash and Fey, 2007), is complex due to multiphase flow within the rock (Lefebvre et al., 2001). Pathways are either across the ground surface (Nordstrom, 2011) or through poorly-buffered groundwater (Bain et al., 2000; Jones et al., 2014; Mayes et al., 2007; Siegel, 1981; Siegel and Ericson, 1981) to streams. Often, the existence of groundwater seepage containing a contaminant load is found only through tracers or synoptic sampling that finds a load at a certain location not accounted for by surface samples (Kimball et al., 2002).

Waste may be backfilled underground to submerge the waste more quickly and decrease the discharge of contaminants (Johnson and Hallberg, 2005). This means of disposal can be a significant short-term source of contaminants (Kohfahl et al., 2004; Neal et al., 2005; Runkel et al., 2013) as the recovering groundwater

submerges backfilled waste and leaches oxidation products into the groundwater.

Sulfate transport in the Rainy Headwaters is conservative because of a lack of buffering in the watershed and in general is conservative at typical concentrations (>100 mg/l) (Nordstrom, 2011, 2008). Most transport through bedrock in this watershed is through fractures that have limited surface area limiting contact time with any carbonate rock. Sulfate transport in groundwater flow to streams has responded conservatively in other similar situations (Neal et al., 2005; Nordstrom, 2008; Runkel et al., 2013). A good example is Straight Creek in the Red River Valley of New Mexico; groundwater flowed through an unconfined debris-fan aquifer without attenuation of metals and with sulfate being diluted by fresher groundwater inflows (Nordstrom, 2008), as modeled herein.

2.4. Numerical flow and transport model

A reconnaissance-level numerical flow and transport model using MODFLOW-2000 (Harbaugh et al., 2000) and MT3DMS (Zheng and Wang, 1999) was developed to simulate the conceptual models described above. Model flowpaths and contaminant travel times were estimated using the MODPATH code (Pollock, 1994). The dominant model cell size is a 500-m square which approximates the 16.2-hectare mining leases, expanding to 1000-m squares away from the leases in the upper Kawishiwi and Isabella River watersheds (Fig. 5). Three model layers represent the general stratigraphy, with layer 1 being the surficial till and sand/gravel layer and layers 2 and 3 being bedrock, with layer 2 bedrock being more fractured with higher *K* (Table 1). The top elevation was based on 30-m and 10-m digital elevation models (DEMs) (Fig. 5). Layer 1 was 15-m thick, based on the median and mean depth to bedrock being 14 and 17.4 m. Layer 2 thickness was set so that the total thickness of layers 1 and 2 equaled 140 m. The bottom of layer 3 was set at elevation −1000 m.

MODFLOW DRAIN boundaries, head-controlled flux boundaries that only allow water to leave the model domain, were specified for larger lakes and rivers which cover most of the area due to close surface–groundwater connections (Fig. 6). The lake boundary head was set one m below the top elevation of the model cells so that lakes would receive inflow only when the groundwater level is close to the ground surface. The river head was set five m below the average top elevation of each model cell to simulate discharge to rivers with embedded channels. General head boundaries (GHB), with head and distance to head based on lake water levels just across the boundary, allow groundwater to cross the northern

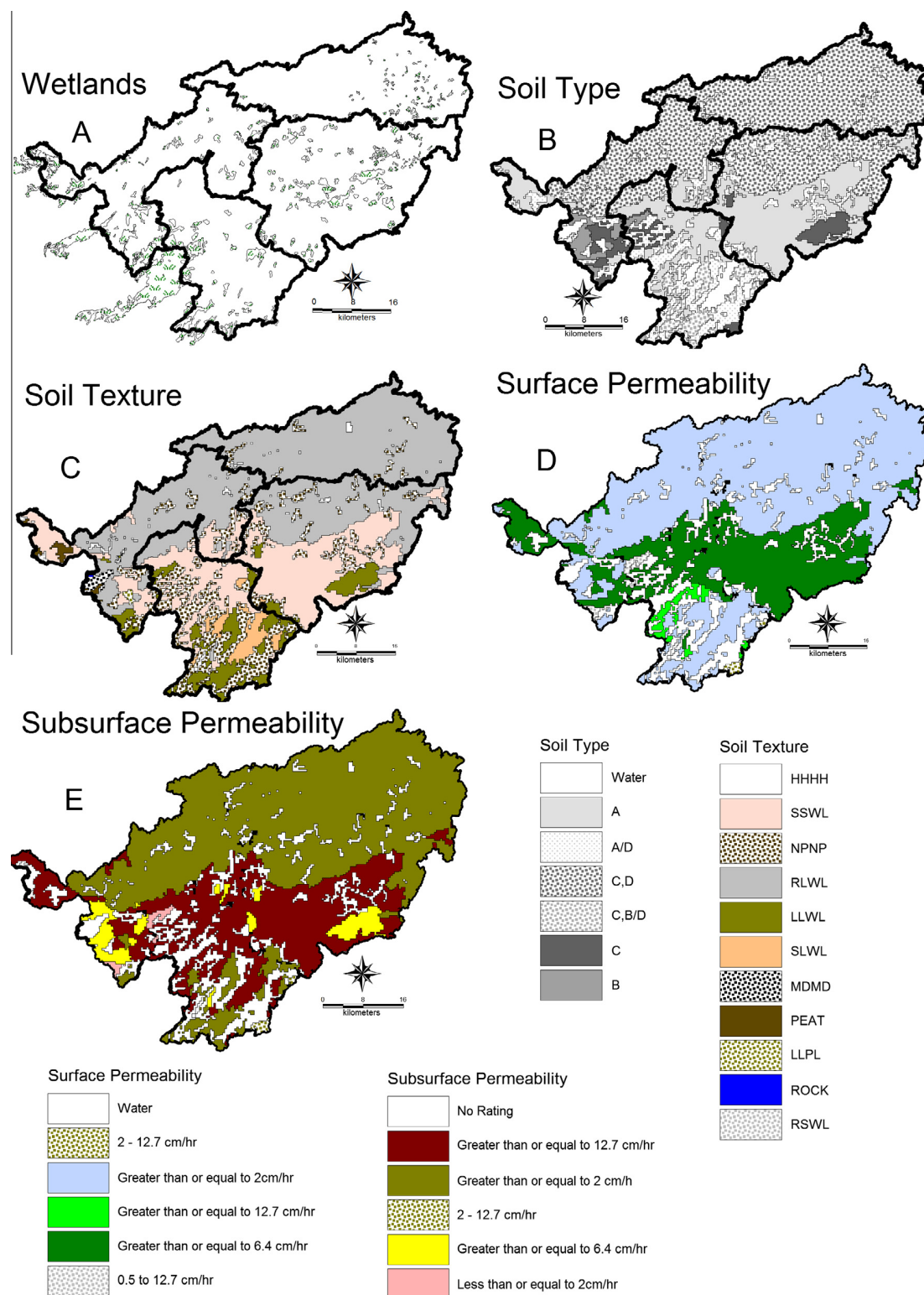


Fig. 4. Distribution of wetlands and soil types across the study area (Cummins and Grigal, 1980). Stream file Strm_baseIn3, lakes and wetlands from Dnr100hydrography, from www.mngeo.state.mn.us/chouse/metalong.html. Soil type: 1234; Factor 1: Texture of soil below 5 feet, S is sandy, L is loamy, C is clayey, X is mixed sand and loam, Y is mixed silt and clay, R is bedrock; Factor 2: Texture of soil in top 5 feet, as for factor 1; Factor 3: Drainage, W means well-drained, P means poorly drained; Factor 4: Color, D is dark, L is light.

Kawishiwi watershed boundary (Fig. 6) at topographic low points. Recharge zones were specified based on subwatershed (Fig. 6),

with rates set so that recharge equals the measured baseflow in the primary rivers.

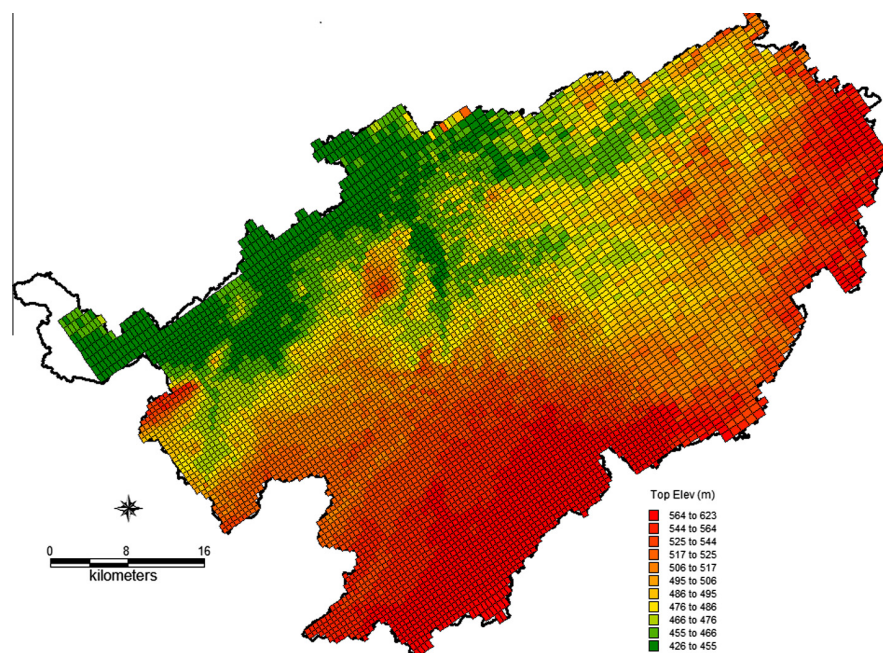


Fig. 5. Model grid and layer 1 top elevation by cell in meters.

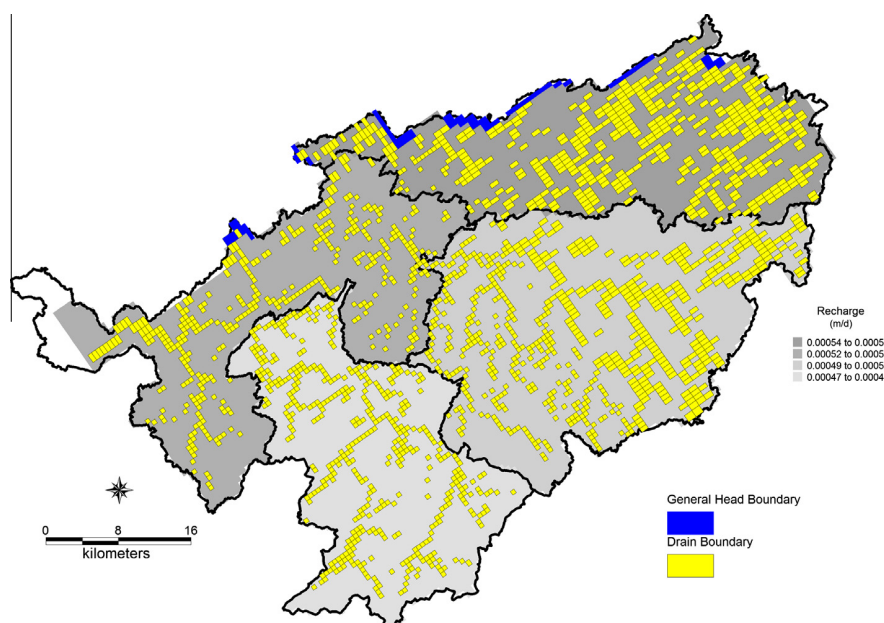


Fig. 6. Location of DRAIN and recharge boundaries in layer 1 and general head boundaries (GHBs) in layer 2. Final recharge rates equal 0.00054, 0.00049, 0.00047, and 0.00052 m/d for zones 2 through 5, respectively.

Transport modeling of sulfate was completed using MT3DMS (Zheng and Wang, 1999). In addition to advection controlled by the flow model and effective porosity (Table 1), the variation of which would simply proportionally increase or decrease contaminant arrival time, dispersion affects concentration by spreading the contaminants along and transverse to the flow path (Fetter, 1999). Dispersivity is a function of length of the flow path from source to sink (Fetter, 2002; Xu and Eckstein, 1995). The longest paths emanate from particle placement at mid-level in layer 3, and are approximately 33,000 m, which is much longer than the length

at which further increases in dispersivity with length became negligible, 1000 m (Xu and Eckstein, 1995). Because the flow paths in this model domain vary from less than 100 m to as much as 33,000 m, setting dispersivity for 1000 m is reasonable and avoids changing D for each source. The apparent longitudinal dispersivity therefore is 11.8 m. The transverse and vertical dispersivity equals 0.2 and 0.1 times the longitudinal dispersivity (Schulze-Makuch et al., 1999). This analysis treats sulfate as conservative to estimate the sources which could have the most significant impacts without relying on estimates of reactivity to attenuate the risk.

2.5. Flow model calibration

Steady state calibration is the process of adjusting K and boundary reach conductance so that simulated steady state groundwater levels match observed target groundwater levels and that simulated boundary fluxes equal measured fluxes (Anderson and Woessner, 1992). Within the four study area watersheds, the groundwater level database (MN Geological Survey and MN Department of Health, <http://www.mngeo.state.mn.us/chouse/metadata/wells.html>) contained 1238 wells with 362 having depth to water, water level elevation, well depth, and depth to bedrock (Fig. 3). There are few groundwater level measurements in the headwaters of the Isabella River and Kawishiwi River watershed, so nine artificial targets weighted 0.3 were set there in each model layer with head set equal to ground surface elevation minus 4 m, similar to methods of Halford and Plume (2011).

Calibration was deemed sufficiently reliable for comparative testing of the siting of contaminant sources (Nordstrom, 2012) when continued parameter estimation yielded composite scale sensitivity (CSS) within a few orders of magnitude for all parameters (Hill and Tiedeman, 2007), the parameter estimates ceased changing during automated calibration, and the sum of squared residuals (SSR) and actual mean residual was at a minimum.

2.6. Flow path simulation

Advective pathways from the mineral leases (Fig. 2) to respective discharge points, a DRAIN boundary, were determined and timed using MODPATH (Pollock, 1994). Contaminant particles were placed in approximately 630 model cells coincident with mineral leases (Fig. 2) at five different levels – the middle and top of layer 3 and the middle and top of layer 2 to represent contaminants leaching from underground, and the top of layer 1, or the water table, to represent surface leaks through the vadose zone.

2.7. Transient model scenarios

The modeling scenarios are generic but representative of mining which could occur in this area (Parker and Eggleston, 2014; Polymet Mining, 2013a) with relatively stringent and well-enforced regulations. The simulated contaminant loads are similar to values expected for waste at the nearby proposed Polymet mine (Polymet Mining 2013a, 2013b, 2013c, 2012) because the ore is of similar sulfide content and the hydrogeology is also similar. The two model scenarios include one for which waste is backfilled into underground workings and one for waste piled onto the ground surface where leaching can occur. Model simulations were transient, with a one-year period (20 time steps with 1.2 multiplier) of waste input, as described below, and a 1000-year period (60 time steps, 1.1 multiplier) of long-term transport. The one-year period of contaminant injection is conservative because if engineering plans go wrong or a leak goes undetected, the contaminant source could continue for much longer. Groundwater fluxes continue as simulated in steady state except for the small amount of injection used to simulate the underground waste. Simulations do not consider mine dewatering or other water management activities.

Waste in underground workings oxidizes, but the rate decreases manyfold after the water level recovers and saturates the waste (Demchak et al., 2004; Kohfahl et al., 2004). As the water level recovers, it flows through the waste leaching a contaminant load into the surrounding groundwater. To simulate this leaching as a sulfate load to groundwater, a low-flow ($60 \text{ m}^3/\text{d}$), high-concentration ($10,000,000 \text{ } \mu\text{g}/\text{l}$, based on concentrations expected at the nearby proposed Polymet mine (Polymet

Mining, 2013a, 2013c)), injection well was placed within each of five model cells in model layers 2 and 3 at five locations representative of the mineral leases (Fig. 2). The placement of a sulfate source at different levels and locations allows consideration of the sensitivity of the flow paths emanating from the different locations of backfilled waste. The one-year period accounts for the probable short-term cessation of oxidation as groundwater levels recover.

Above-ground sources, waste dumps, are simulated as a $10,000,000 \text{ } \mu\text{g}/\text{l}$ concentration added to the natural recharge over six cells located as for the underground sources. This concentration is an order of magnitude higher than observed in the field for similar ore (Lapakko and Olson, 2015), but justified because the samples in that paper were taken downstream of the source after some dilution. The one-year simulation period is the equivalent of the operator developing a waste rock storage area and covering it after discovering a leak, completing reclamation over a one-year time period, or moving the waste to a different location. Total load varies from 2,847,000 kg to 2,573,250 kg depending on cell size.

3. Results and discussion

3.1. Calibration

The final SSR was 4405 and 2173 for unweighted and weighted targets, respectively. The standard deviation is 4.2% and 3.0% of the 150-m range in observations, from the lowest to highest groundwater elevation. There is no detectable trend with observed groundwater elevation and simulations should yield no bias. Final K s for parameter zones (Fig. 7) are shown in Table 1.

Some of the wells cluster so closely (Fig. 3) they represent essentially the same information, so they were thinned, first by keeping just one well per layer within 200 m of each other, and second by keeping just one well per model cell with the head target equal to average head of the wells remaining after the first thinning (Wellman and Poeter, 2006).

Zones with few head observations were not sensitive so the final parameter values were selected on formation type and on values necessary to generate reasonable head values (ASTM, 1998). Horizontal conductivity (K_h) values in the surficial aquifer are high but within the observed values and vertical conductivity (K_v) values reflect highly stratified till. Each bedrock formation K varies over at least two orders of magnitude. Conductivity decreases with depth for most formations as expected due to compaction occurring due to overburden and less weathering with depth. In zones 32 and 3, K_h was much less than K_v (Table 1) which reflects a tendency for vertical flow in the upthrust Duluth Complex (Miller et al., 2002).

Simulated heads generally show groundwater movement from southeast to the north and northwest. The water table in the upper layer follows the irregular topography while in the deep layer contours reflect a consistent slope to the northwest with an upward gradient from layer 3 toward Birch Lake in the northwest portion of the study area near its primary surface water outlet (Figs. 3 and 8).

Recharge (Fig. 6) and simulated discharge were nearly equivalent in the Isabella and Stony River watersheds but varied by from 10% to 20% in the other watersheds due to interbasin groundwater flow. Percent differences among watersheds are small and indicate that the distribution of recharge and discharge through the model domain is accurate. All ten river reaches gain more flow in their lower reaches near their outlet due to converging flow. Ten simulated lakes received zero discharge because their bottom was above the water table which reflects their location in the upper recharge portions of the watersheds.

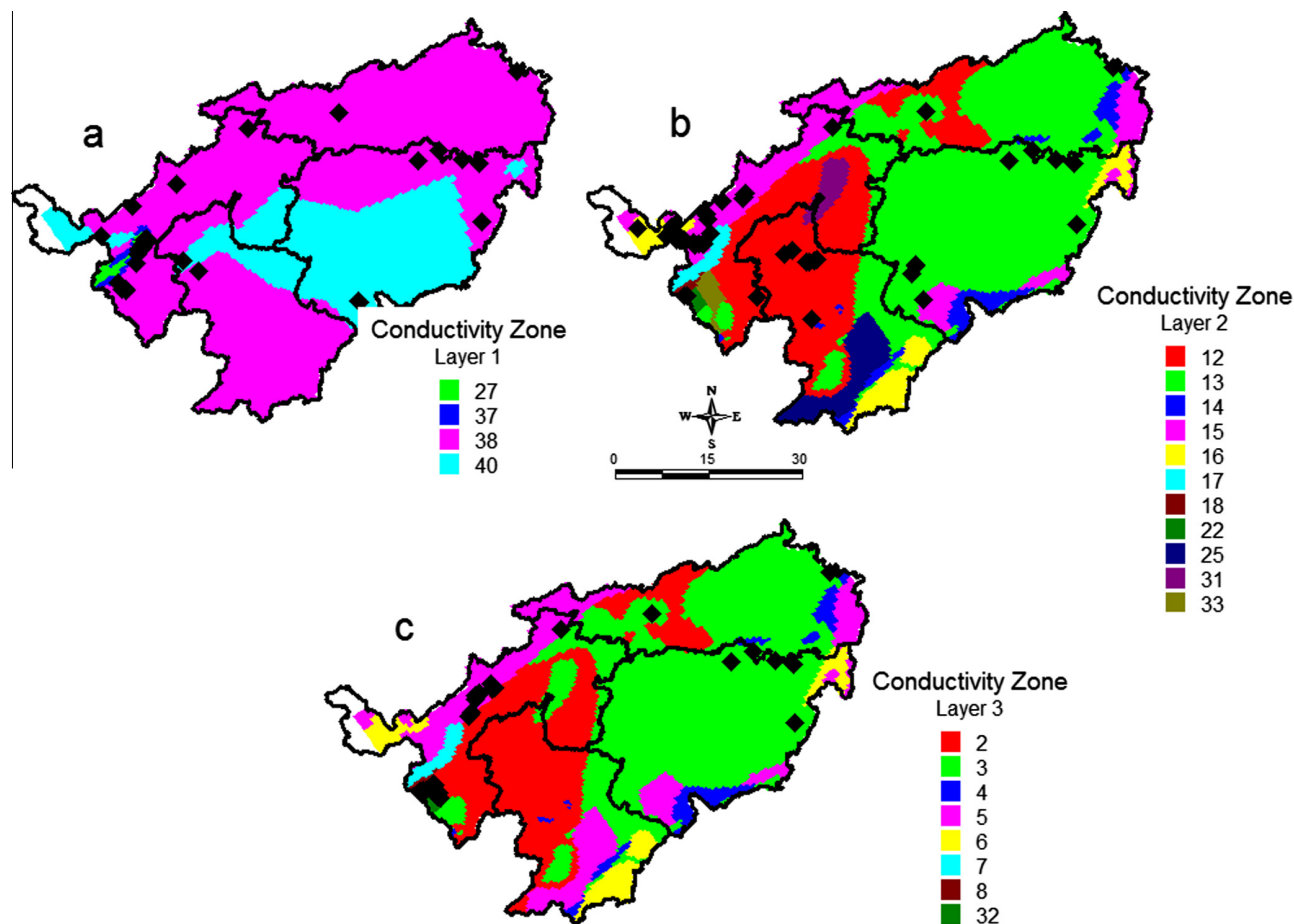


Fig. 7. Hydrogeology zones for three layers and steady state head target locations (black squares). Table 1 shows final conductivity values.

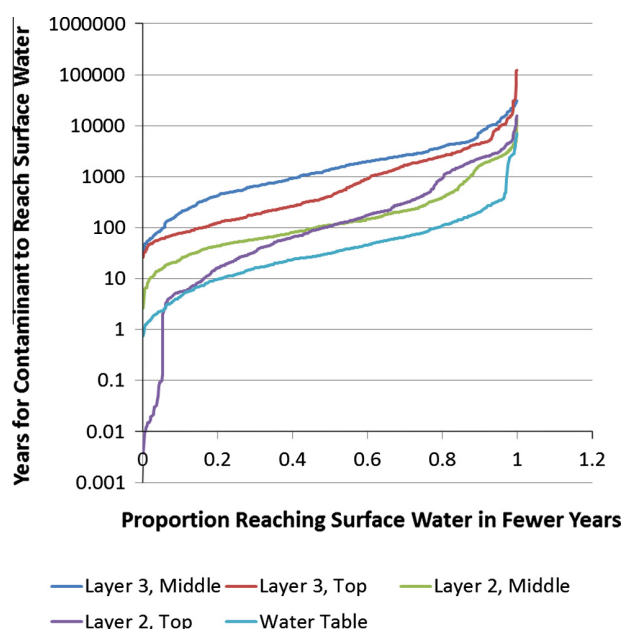


Fig. 8. Proportion of particles reaching surface water sources in a number of years for any location in the specified layer.

3.2. Particle tracking

Particles introduced at the middle level of layer 3, or about 750 m bgs, required the longest and those introduced at the water table required shortest time to reach surface water (Fig. 8), with minimum times varying from 26 years to less than a year, depending on layer. About 2.8% and 23.5% of the particles released at the top of layer 3 and middle of layer 2 reached surface water in less than 50 years, respectively (Figs. 8 and 9). Flow paths are longest through layer 3 because of the layer's thickness. The shortest pathways occur where a river boundary is close and there is an upward gradient, such as near Birch Lake (Figs. 3 and 9).

The shortest pathways, requiring less than two years, were from water table sources starting close to rivers (Fig. 9). Most particles reached surface water quickly, with 21% reaching surface water within 10 years and 62.9% in 50 years (Fig. 8). Longer transport times were for particles being transported deeply into layer 2 or 3 (Fig. 9).

The primary control on transport time, other than distance from the sink, is whether the particle sinks deeper into the bedrock (Gburek and Folmar, 1999), which would result from normal groundwater circulation. Contaminants released where they sink would present a less substantial risk to downstream resources. However, long pathways could result in contamination remaining a risk long after mining has ceased if it does not attenuate.

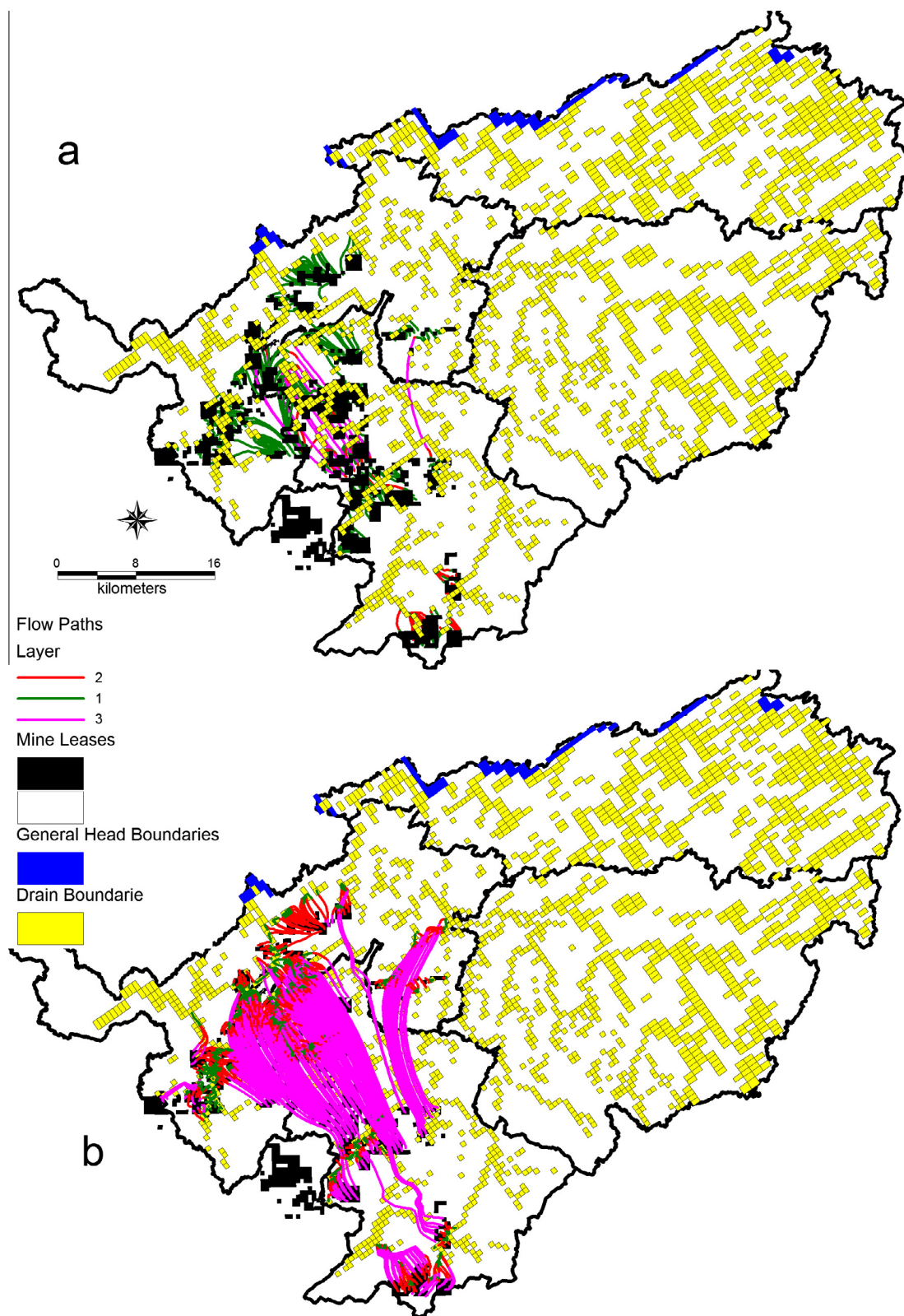


Fig. 9. Particle tracking for particles introduced at model cells near the mineral leases at the water table (a) or the top of layer 3 (b).

3.3. Contaminant transport modeling

Detectable sulfate, at $1 \mu\text{g/l}$, expanded through the groundwater domain variously depending on the location of the source (Fig. 10). Sulfate from deep sources flows to the northwest with various amounts of lateral and vertical dispersion (Fig. 10a and b). Detectable sulfate reached up to 2.5 km from the source with up to 1.5 km lateral dispersion (Fig. 10a). Near sources 1 and 2 (source numbers specified in Fig. 10a), vertical dispersion caused contours in the surface layer to almost mirror those in the source layer. Sulfate originating at depth transports further in a thousand years than does sulfate originating on the surface which is limited in extent by discharge to rivers (Fig. 10b).

Sulfate originating from surface sources disperses to the northwest from headwaters and radially from near-river sources (Fig. 10c). Sulfate from source 4 expanded to the northeast but was constrained from expanding to the south by a steep topographic slope (Fig. 10c). Between ten and a hundred years, the sulfate contours did not spread significantly (Fig. 10c) due to discharge to surface waters while concentrations near the source decreased by an order of magnitude.

The amount of groundwater affected depends on the source, flow paths and dispersion. Contaminants eventually reach surface water, but at widely varying travel times (Fig. 8). The load is most important with respect to discharge to the rivers, and peak loads reach the various river reaches at times depending on distance

and whether the source is surface or underground (Table 3). Peak loads from underground sources reached rivers in from ten to forty years and from surface sources in less than five years (Table 3 and Fig. 8).

The highest sulfate loads from surface sources were up to two orders of magnitude higher than those from underground sources and reach their peak at rivers in the Stony River watershed at the end of the first year, reflecting their close proximity of the source to the rivers. Filson Creek receives the highest load which translates to a concentration of near $120,000 \mu\text{g/l}$. Peak loads reach Birch Lake and Dunka River after two to five years but are lower than for Stony River and Filson Creek, due to dilution over the longer flow path. Surface leaks reach the streams quicker and have higher concentration due to there being much less attenuation due to the shorter flow paths.

Baseflow makes up as much as 70 percent of the flow in rivers in this area, so the simulated loads (Table 3) would not be significantly diluted during low flows. During critical low flow periods (Winterstein et al., 2007) the sulfate concentrations would equal that determined from the groundwater load and flux discharging to the rivers (Mayes et al., 2007; Runkel et al., 2013).

The sulfate loads reaching the rivers vary substantially based on the location and depth of the sources. Surface sources contribute load to rivers much sooner and with a higher peak than do underground sources. The load reaching the relatively close-by Birch Lake or Dunka River is much higher but also much shorter-lived

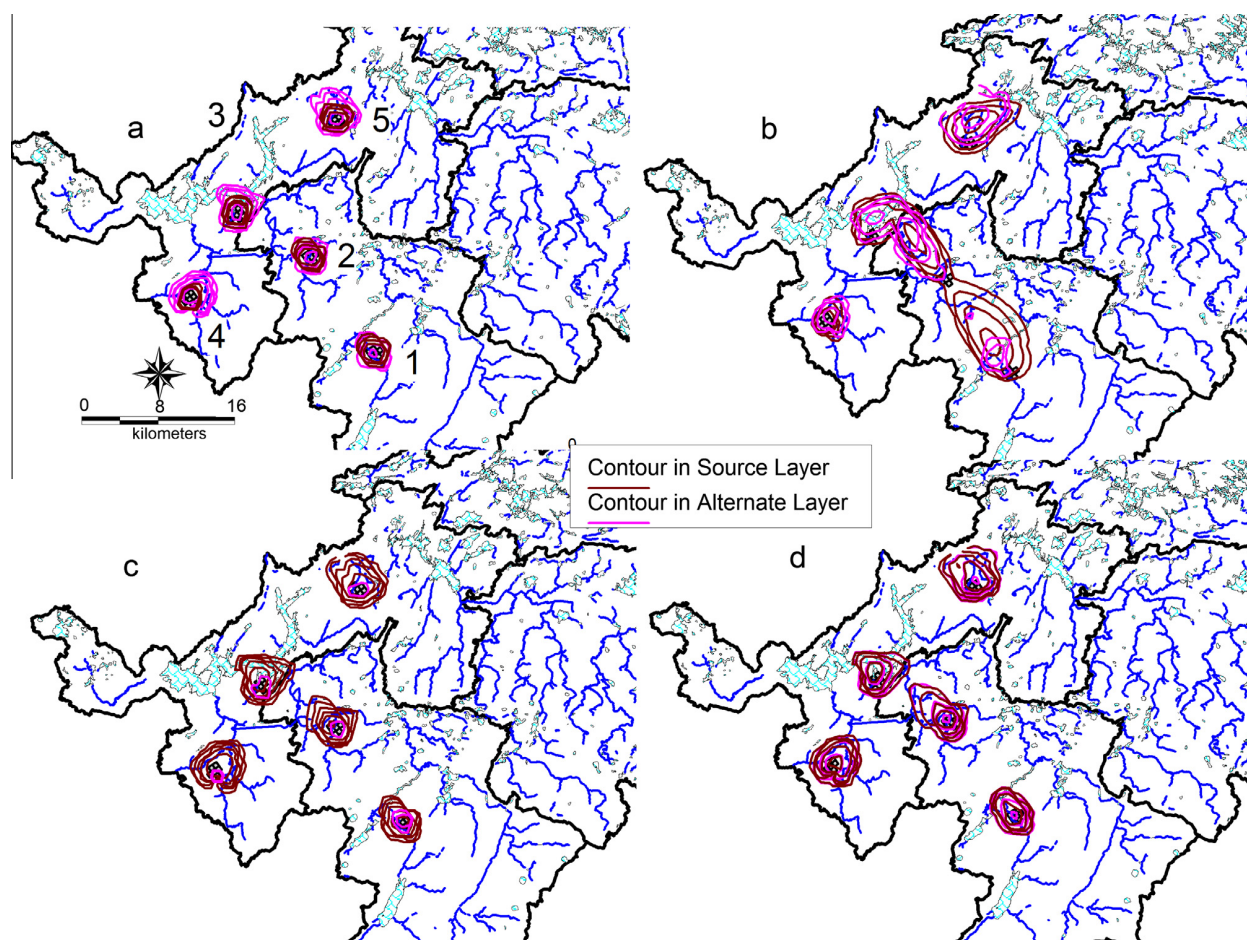


Fig. 10. Concentration contours for (a) underground source after 10 years, (b) underground source after 1000 years, (c) surface source after 10 years, and (d) surface source after 100 years. Underground source is layer 3, surface source is layer 1. Alternate layer is layer 1 in (a) and (b), layer 3 in (c), and layer 2 in (d). The contaminant source number is shown in (a). Contours range from 1 to 100,000 $\mu\text{g/l}$ from outer to inner.

Table 3

Sulfate load (kg/day) discharging to reaches 1, 71, 72, 73, and 75 at various times corresponding to stress periods (1 or 2) and time step (number in parentheses). Steady state discharge to reach 1, 71, 72, 73, and 75 is –74,916, –73,295, –31,383, –168,050, and –11,439 m³/d, respectively. The discharges are stated as a negative because they represent a loss from the groundwater domain. Reach 1 is Birch Lake, Reach 71 is Dunka River, Reach 72 is Stony River between Babbitt and Isabella, Reach 73 is Stony River above Isabella, Reach 75 is Filson Creek nr Ely, as shown in Fig. 3. Other reaches did not receive substantial load.

Period	Years	Reach				
		1	71	72	73	75
Deep sources						
1(20)	1	0.1	0.3	10.5	18.8	28.7
2(14)	10	12.4	14.9	38.7	43.0	45.6
2(21)	21.8	16.7	17.7	36.1	37.0	36.3
2(24)	30.2	17.5	18.1	32.7	32.9	31.3
2(27)	40.9	17.2	18.3	28.3	28.4	26.4
2(36)	99.4	9.9	15.3	12.2	12.4	11.9
2(60)	1000	1.3	0.3	0.0	0.2	2.2
Surface source						
1(20)	1	28.7	56.8	1033.5	1118.2	1378.2
2(1)	1.3	54.4	101.3	955.0	909.0	929.2
2(3)	2.1	115.2	184.2	782.6	589.4	524.5
2(5)	3	159.3	222.6	612.2	390.4	377.1
2(9)	5.5	161.7	192.8	313.1	187.7	211.1
2(11)	7.1	131.8	151.4	203.4	136.0	150.8
2(14)	10	86.9	94.3	105.0	90.2	93.9
2(21)	21.8	37.2	39.9	30.5	40.5	45.7
2(36)	99.4	8.2	25.4	10.1	15.0	15.2
2(60)	1000	0.0	0.0	0.0	0.0	0.0

than the load reaching the other rivers because distance slows the transport time assuring it will continue further into the future. Burying waste or placing it further from the resources to be protected will decrease the load reaching those rivers and substantially decrease the potential impacts of mining.

4. Conclusion

The reconnaissance-level fate and transport model presented herein simulates groundwater flows and estimates where, when, and at what concentration sulfate would discharge for various mine development scenarios in the Rainy Headwaters watershed. The model allows a comparison among sources to assess where mines and their associated waste facilities would cause less risk from spills and alternatively where mines could be riskier. Similar models should be developed for watersheds throughout the world that have substantial mineral deposits to prioritize development or alternatively to decide development is too risky. This type of model also shows where additional data should be collected, such as along the predicted pathways to reduce the uncertainty in advective flow rates and dispersion, a common need in most watersheds undergoing development (Caruso et al., 2008).

Groundwater with substantial contaminant concentrations discharges to streams whether sourced from deep underground or the ground surface. Even relatively short-term leaks on the surface could cause substantial loads to reach the rivers and valuable downstream resources. Longer-term leaks could cause peak concentrations reaching the rivers to be much higher than simulated herein. Underground sourced contaminant discharges last longer but have lower concentrations and are recommended for use in sensitive watersheds globally. In the Birch Lake watershed, leases trending southwest to northeast would discharge to surface water relatively quickly. Leases in the headwaters of the Stony River watershed would discharge to nearby surface water. These discharges would eventually coincide with critical low flow periods and cause potentially significant damage to rivers and the BWCAW.

Leaks into groundwater commence a long-term process in which contaminants travel to surface waters for a long time after the leaks have ceased discharging. Contamination may not be obvious until after a mine closes and impacts can continue for decades, with substantial concentrations still reaching rivers for hundreds of years even if the leaks cease. These factors should be considered when establishing bonds for long-term water quality remediation and modeling such as presented herein can be used to estimate the potential for future remediation.

Although mines are located based on the minerals, advance planning and analysis could avoid siting mine facilities where failure would cause too much natural resource damage. Reconnaissance-level modeling can provide the basis for more complete watershed-level studies as suggested to assess a watershed (von Guerard et al., 2007) and to determine where additional geochemical and hydrogeologic data should be collected (Caruso et al., 2008). Unless there is a clear geochemical sink for the contaminant, treating the transport as conservative will allow better decision making. Mine facilities should be located based on the potential for a leak or spill to damage downstream resources, as predicted with watershed-scale transport modeling. Such planning could lead to certification under responsible mining standards such as IRMA. Some areas should not be mined at all due to the risk to downstream resources.

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Technical Memorandum: Twin Metals Mining and the Boundary Waters Canoe Area Wilderness, Risk Assessment for Underground Metals Mining

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Summary, Conclusion and Recommendations

The study presented herein further develops an earlier conceptual flow and contaminant transport model for ground and surface water flow through the Rainy River Headwaters watershed, including the Kawishiwi River, Isabella River, Birch Lake, and Stony River watersheds, in Northeastern Minnesota. The purpose is to estimate pathways and rates for contaminant transport to reach the Boundary Waters Canoe Area Wilderness (BWCAW) due to the development of mining leases, which could occur within the Birch Lake and Stony River watersheds. The conceptual models are converted into reconnaissance level numerical models to estimate the risk of mine spills and leaks on the BWCAW, and lakes and rivers between the proposed mines and the wilderness.

There are two aquifers in the area- a surficial aquifer and a bedrock aquifer. The surficial aquifer, consisting of either glacial till or sand and gravel, is very thin, averaging about 15 m thick. The hydraulic conductivity is highly variable but generally higher than 1 ft/d. Underlying the surficial aquifer is bedrock generally of the Duluth Complex. Porosity depends on many factors but the summary is that shallow bedrock, except for shale and the Biwabik, should have porosity exceeding 10% and that below 2500 feet (750 m) porosity should be 5% or less. The Biwabik Iron Formation has porosity as high as 50%. The upper 125 m would have higher porosity due to a combination of fracture and matrix porosity. The primary bedrock conductivity is generally low but secondary conductivity is high. This means that groundwater may flow at relatively high rates through bedrock fractures but only in certain areas.

Baseflow, or recharge, varies from 5.66 to 9.52 inches/year (in/y), although for watersheds with more than 100 square miles, the range is from 6.7 to 8.2 in/y. This was based on baseflow recession analysis of the major stream gages within the watersheds. Baseflow is approximately 70% of total streamflow. Stream flow is about 39% of total precipitation across the watershed.

The numerical flow model accurately simulates groundwater flow around the model domain from recharge to discharge to rivers, streams and lakes. Calibration of model parameters was based on matching groundwater levels to observed levels in wells and mining boreholes and on matching discharges to measured baseflows. The wells used for calibration were clustered in a

few areas mostly near the mine leases (due to exploration activities). To improve the accuracy of the calibration, additional groundwater levels were added under the ridgelines where it was possible to assume a likely depth to water and by controlling the groundwater level with a connection with surface water.

Horizontal conductivity controlled flows in the numerical model more than vertical conductivity. Each bedrock formation had zones with conductivity varying over at least two and usually three or four orders of magnitude. There is substantial variability, especially in the bedrock as would be expected in a heterogeneous domain with fractures. Conductivity decreases with depth for most formations as expected due to compaction. In some areas, vertical conductivity is higher than horizontal, which establishes a tendency for vertical flow. Birch Lake and the South Kawishiwi River are convergence zones for flow with upward flow from deeper layers reaching these sinks.

The numerical transport model developed herein demonstrates that the time it takes for leaks to reach the BWCAW will depend on where they occur. Particle tracking along the flow paths show that deeper sources have a longer travel time to surface water, however deep sources near the rivers will transport through groundwater discharge to those rivers in times on the order of decades. Shallow leaks and leaks to groundwater from the surface will reach the streams more quickly, in some cases within less than a year but certainly within a few years. This does not account for leaks that travel on the surface to the rivers. These would not disperse through the groundwater and travel time would be immediate. Shallow leaks in the headwaters would reach tributaries and eventually flow into Birch Lake. Particle tracking showed that contaminants from deep sources in the Stony River watershed eventually reach the BWCAW to the northeast in the Kawishiwi watershed. This is an example of groundwater flowing across a topographic divide.

The choice of representative loads from the mines to be added to the systems was based on professional experience and the predicted loads expected at the nearby proposed Polymet Mine. At that mine, it was found that if the engineering design did not operate perfectly, aquatic conditions would be severely degraded¹. The assumption for developing the deposits in the Stony River or Birch Lake watershed is that strict engineering would apply, but that it would also fail and leaks would occur. Surface leaks were assumed to last for a year and underground sources were assumed to seep for a year, based on a typical scenario in which the deposit would be saturated and oxidation would cease.

¹ The conclusion regarding the reliance of the Polymet mine plan on engineering is the opinion of this author as detailed in Myers (2014). If any of the design functions less efficiently than modeled by Polymet (2013a), the resulting contamination would be much higher than predicted.

The transport analysis assumes conservative, meaning no geochemical transformations or sorption, transport of sulfate, but it could be any other conservative substance with the load added as described. The concentrations reported herein are entirely dependent on the assumptions made for the load and should not be considered predictions. Rather, they are an example of what could happen in the watershed if the leaks as assumed occur. The concentrations reported in Table 9 are those that could be seen in the streams during baseflow because the flow model simulates the entire baseflow discharge. Tracking them downstream, the entire baseflow can be considered a load. The table shows that the effect on the streams is highly dependent on the location of the source.

The modeling completed herein has shown that substantial contaminant loads can reach streams that drain to the BWCAW due to either deep underground or surface leaks. During much of the year, sufficient flow enters the system to dilute this load before it reaches the BWCAW. However, during baseflow conditions, the load could substantially affect the tributary streams, especially within the Stony River and Birch Lake watersheds. While the watershed is experiencing low flow conditions, the concentration at the Kawishiwi River at Winton, within the BWCAW, could be increased above that at baseflow by five orders of magnitude for the 7Q20² flow. This is due to the rivers losing flow in a downstream direction during very low flow periods. In other words, leaks that may have minimal effects much of the year could be devastating at low flow. Once started, leaks will continue to discharge to the rivers for decades due to dispersion during groundwater transport, and will likely coincide with 20-year or longer return period low flows. The potential that leaks will damage the Wilderness is high.

Major spills that could occur within the watersheds would affect the lakes and rivers much differently than the long-term discharge of leaks. Spills can devastate the local area but they mix through the lakes so that the concentration decreases before reaching the BWCAW. Birch Lake would attenuate loads entering it from any of the leases upstream of the lake. Effectively, the load mixes through the effective portion of the lake which in this analysis was assumed to be the eastern half due to freshwater entering the west end. The concentration leaving Birch Lake could be toxic, but will drop two orders of magnitude passing through White Iron Lake. Farm Lake and Garden Lake will further lower the concentration by two orders of magnitude. If the spill occurs downstream of Birch Lake (for instance, at the proposed processing site), White Iron Lake will attenuate the contaminants so that the concentration leaving the lake would be about a quarter that of the same load in Birch Lake. This much higher concentration flows north and continues to attenuate as described previously, but with a much larger chance of damaging the BWCAW. In summary, lakes will attenuate spills by mixing but the effects on the

² A low flow average flow rate Q over 7 days at a 20-year return interval.

lakes and wilderness can be devastating if the substance is highly toxic or if the load is sufficiently large.

These results show that leaks from mines in the watershed leading to the BWCAW could have substantial effects on the wilderness. Catastrophic spills were not considered but the impacts would be much more significant. Spills would not likely transport through the groundwater, so the potential concentrations would simply be the load divided by the flow rate.

This discussion focuses on the peak impact of a spill, but an important point is that leaks, even when stopped within a short time period, will continue discharging to the rivers for many years, sometimes as long as centuries due to dispersion during transport through the groundwater. A leak is not a simple thing to remediate, so it is critical to prevent leaks, which has historically been shown to be almost impossible. If mineral deposits in the Rainy Headwaters are developed, it is not a question of whether, but when a leak will occur that will have major impacts on the water quality of the Boundary Waters Canoe Area Wilderness.

Introduction

Myers (2013c) developed a conceptual flow and transport model for the Birch Lake watershed to assess the potential for contamination from developing mineral leases in the Rainy Headwaters reaching the Boundary Waters Canoe Area Wilderness (BWCAW). The BWCAW is downstream of flows and contaminants originating in the Rainy headwaters. Flow and contaminants pass through BWCAW to flow through Voyageurs National Park to Lake of the Woods. Myers (2013c) found there are seven primary risks to water resources in the BWCAW from the development of mines at the Twin Metals leases. They are risks to water quantity from mine dewatering and production water development; risks to water quality from the development and seepage of acid mine drainage (AMD), seepage of tailings water, tailings impoundment failures, and runoff of sediment from the site due to stormwater; and wetlands disturbance. Failure of pipelines used to slurry ore or tailings from the mines to sites outside of the watershed is an eighth threat.

This technical memorandum builds on the conceptual flow and transport model by expanding it to the entire Rainy Headwaters watershed and creating a reconnaissance level numerical model to assess potential transport of contaminants from the mineral deposits to the BWCAW. The conceptual flow model (CFM) includes groundwater and surface water, including runoff processes, recharge (and seepage of waste), groundwater flow, and discharge to surface water. This technical memorandum develops the quantitative water balance for the area by estimating recharge and actual baseflow by watershed.

The numerical model simulates the pathways and flow times for contaminants discharging from the different deposits at different depths to the streams which transport them to the BWCAW. The modeling utilized the USGS flow and transport codes MODFLOW2000 (Harbaugh et al. 2000) and MT3DMS (Zheng and Wang 1999). Reconnaissance level means the model is designed to detect general trends and order of magnitude time estimates rather than make exact predictions. The model developed herein does provide a base for more detailed modeling as more data becomes available or if more detailed assumptions become justified. The model also provides a base for more detailed simulation of various mining scenarios including contaminant sources emanating from any location or depth within the domain. The model, with estimates of transient parameters for the modeled formations, could also be used to estimate the effects of mine dewatering due to underground or open pit mining.

Conceptual Flow and Transport Model

General Area

The Twin Metals leases lie south of the South Kawishiwi River. The South Kawishiwi River flows west from the BWCAW after splitting from the Kawishiwi River and then rejoins the Kawishiwi and flows back into the BWCA. The Kawishiwi watershed is in the Rainy River Headwaters watershed (<http://www.dnr.state.mn.us/watersheds/map.html>) (Fig. 1). The river system connects many lakes, some of which are manmade, with more than 40% of the channel length within lakes (Siegel and Ericson 1981). The area lies in two Minnesota groundwater provinces, the Arrowhead and Central Region, and in the fractured igneous or metamorphic bedrock province (<http://www.dnr.state.mn.us/groundwater/provinces/index.html>). In this area both surficial and bedrock groundwater is considered limited.

Hydrogeology

The mineral leases are hosted in the Duluth Complex, which is “composed of multiple discrete intrusions of mafic to felsic tholeiitic magmas that were episodically emplaced into the base of a comagmatic volcanic edifice between 1108 and 1098 Ma” (Miller et al. 2002, p 109). The complex dips southeastward with basement rock of Archaean age, which means it becomes deeper in that direction. The Duluth Complex has not been significantly deformed, but displacements due to reactivated basement faults and some cross faults have affected it (Miller et al. 2002). Faults trend north-northeasterly with the maximum offset being 400 feet. Many of the streams may coincide with fault/fracture zones (Stark 1977).

There are two aquifers in the area- a surficial aquifer and a bedrock aquifer. The surficial aquifer, consisting of either glacial till or sand and gravel, is very thin, generally less than 10 feet thick but with some areas especially in the west being 20 feet or slightly more thick (Mast and

Turk 1999). One study found the hydraulic conductivity (K) of the sand gravel ranged from 0.4 to 362 ft/d and for Rainy lobe till from 0.04 to 6.7 ft/d (Stark 1977). Another study found that K for sand gravel ranged from 0.004 to 15.5 ft/d and for Rainy lobe till from 0.000021 to 0.13 ft/d (Siegel and Ericson 1981). These authors (Id.) concluded based on additional data sources that K ranged from 10 to 3500 ft/d for sand and gravel, 0.01 to 30 ft/d for Rainy lobe till, and from 0.00001 to 0.1 ft/ for peat and Des Moines lobe till (Id.). Overall, K ranges from 0.00001 ft/d to 3500 ft/d (0.00000305 to 1067 m/d), or nine orders of magnitude, for the surficial aquifer.

South of the South Kawishiwi River, the bedrock underlying the surficial aquifer is generally of the Duluth Complex (Miller et al. 2002) (Fig. 2, Table 1). Much of the bedrock data is from a study of CO₂ sequestration potential (Thorleifson 2008). Hydrogeologically, the Duluth Complex is a low-permeability intrusive formation with a very low K except possibly near some of the infrequent faulting, on which there is available little hydrogeologic data. Porosity depends on many factors but the summary is that shallow bedrock, except for shale and the Biwabik, should have porosity exceeding 10% and below 2500 feet (750 m) porosity should be 5% or less. The Biwabik has porosity as high as 50% and shale is probably less than 5%. Fractures increase the porosity indicating the upper 125 m would have higher porosity due to a combination of fracture and matrix porosity.

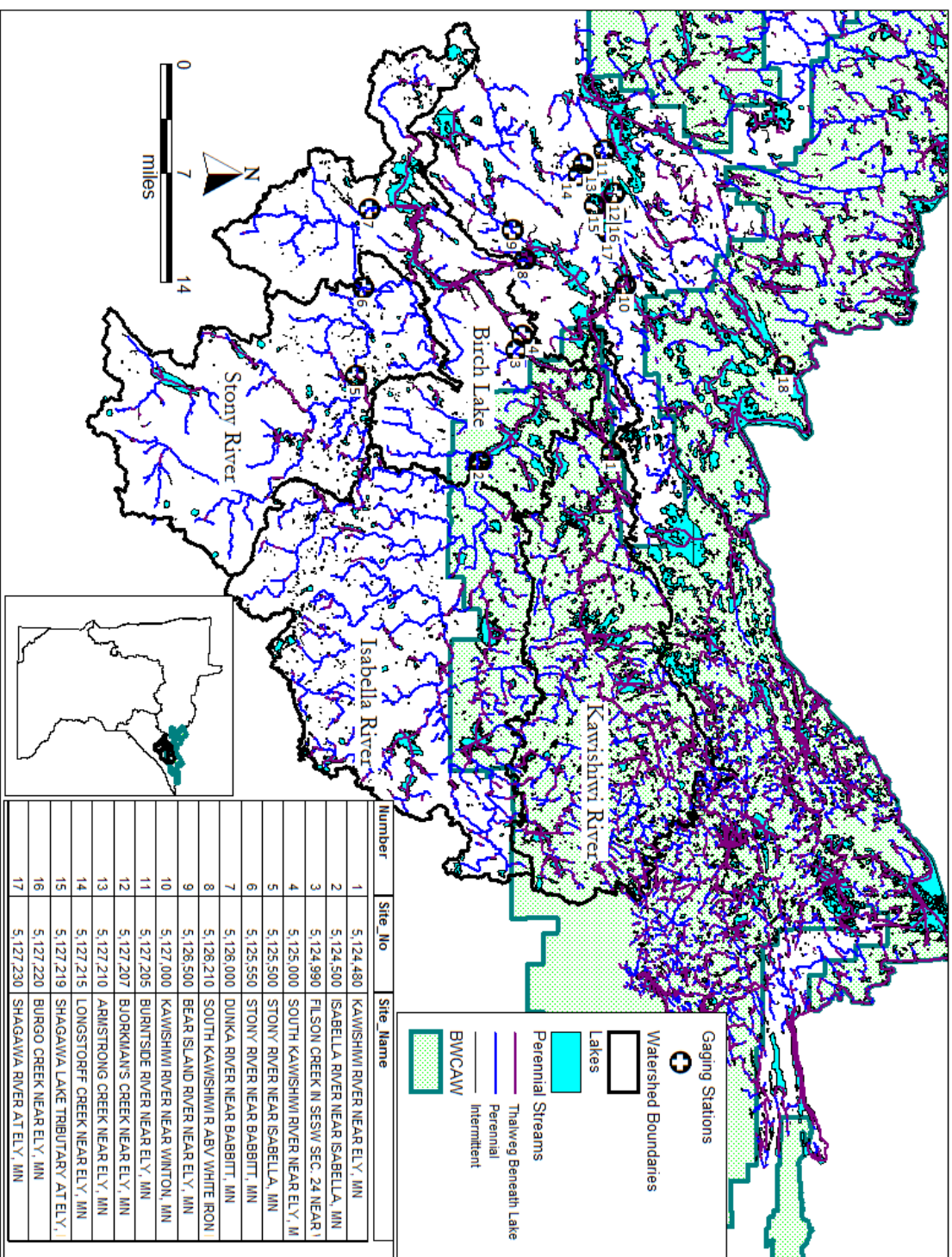


Fig. 1: Rainy headwaters watershed and study area, showing subwatersheds, gaging stations (Table 2), and flow arrow for general flow direction through the watershed. Watershed boundaries from Dnr100kwatersheds, www.mngeo.state.mn.us/chouse/metalong.html

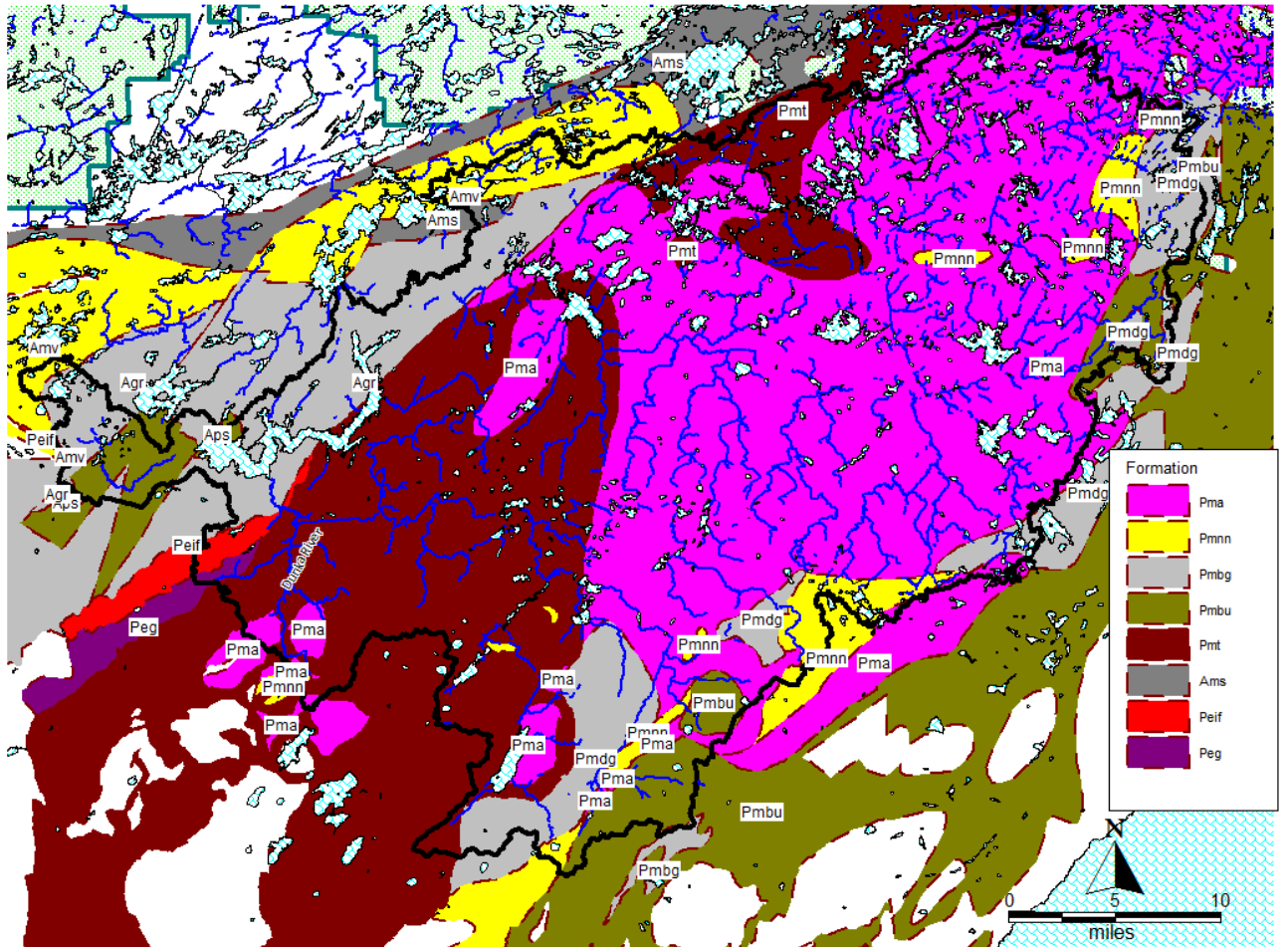


Fig. 2: Bedrock geology of the study area. See Table 1 for a description of the formations.

Table 1: Geologic formations and basic properties.

Label	Primary Rock Type	Secondary Rock types	
Pmt	troctolite	gabbro,	Duluth Complex
Pma	anorthosite	gabbro	Duluth Complex
Pmnn, Amv	basalt	rhyolite, sedimentary rocks	
Agr	granite	granodiorite	Giants Range Granite
Pmbu	gabbro	troctolite	
Peif	iron formation	arenite	Biwabik
Peg	shale	siltstone	

Groundwater in near-surface bedrock is unconfined and hydraulically connected with that in the surficial aquifers, except where the overlying K is extremely low (Siegel and Ericson 1981). Where the surficial aquifer has low K, the bedrock aquifer may be confined. The bedrock tends to be relatively fractured in its upper several hundred feet (Id.). The plutonic rocks have primary porosity up to 3%, but this is not effective and the permeability is very low in the Duluth complex because the pores are isolated (Stark 1977). Weathering and faulting can increase the permeability along fracture zones. The specific capacity of wells in the Duluth Complex ranges from 0.02 to 0.11 gpm/ft, in the Giants Range granite around 0.03 gpm/ft, and in the Biwabik formation from 0.24 to 6.55 gpm/ft.

Well yields throughout the Kawishiwi watershed are less than 10 gpm (Siegel and Ericson 1981) which reflects the very thin to nonexistent surficial aquifers and the low permeability bedrock, which transmits very little groundwater except in fractures. The aquifer along the river is not a target for production water pumping because it is too thin (Siegel and Ericson 1981). The Duluth Formation is relatively fractured for the upper two to three hundred feet, but the well yields range from 5 to 15 gpm, especially in the South Kawishiwi intrusion which hosts the nickel/copper ore body (Cox et al. 2009; Siegel and Ericson 1981). The best bedrock aquifer of the province is the Biwabik formation, in which most of the area iron mines were developed.

Surface Flow Pathways

The primary inflow to the watershed is meteoric water, or precipitation falling as either rain or snow. Precipitation, or snowmelt, becomes evapotranspiration (ET), runoff or infiltration into the soil. Infiltration becomes ET, interflow or shallow groundwater flow, or recharge to the groundwater aquifers. ET includes direct evaporation and transpiration of soil water through the vegetation. River flow includes direct runoff from the surface, interflow, and groundwater discharge of recharge. Interflow is flow through the soils and unsaturated zone above the

water table to rivers. Wintertime precipitation is frozen along with the soils so little direct runoff or recharge occurs during that time period. Baseflow consists of groundwater discharge to the rivers (Cherkauer 2004).

Four HU10 watersheds form the study area (Fig. 1). The general conceptual flow model through the study area, shown with arrows in Fig. 1, includes as outlets the Kawishiwi River and the South Kawishiwi River which are gaged at stations shown in Fig. 1 and tabulated in Table 1. Upstream from the mineral deposits, the Kawishiwi River flows from east to west and splits into two branches. The South Kawishiwi was dammed to form Birch Lake, the center of one of the four watersheds. Downstream from the mineral deposits, the main branch of the Kawishiwi River enters the east side of Farm Lake and rejoins the South Kawishiwi waters flowing north from Birch Lake (Fig. 3).

The Stony River and Isabella River watersheds are tributaries to the Birch Lake watershed (Fig. 1 and 3). Much of the Isabella River watershed heads south of and flows north into the BWCAW. The main river, the Isabella, flows from east to west on the northern portion of the watershed from the BWCAW to the west. There are no apparent mining leases in this watershed (Fig. 3). West of the Isabella River watershed is the Stony River watershed which flows into the Birch Lake watershed near the center of Birch Lake (Fig. 3). The Stony River and Birch Lake watersheds are the host watersheds for the contaminant sources considered in this analysis because they contain substantial mining leases (Fig. 3). None of the Stony River watershed lies within or flows directly into the BWCAW, rather flow from that watershed reaches BWCAW by way of the Birch Lake watershed.

The Kawishiwi River downstream of both the Birch Lake and Kawishiwi River watersheds flows into the BWCAW, after flowing through several lakes (Fig. 3 and Table 10). This would be the primary surface pathway for contaminants reaching the Wilderness.

Lakes and wetlands connected by low-gradient rivers cover much of the study area. The boundaries between the watersheds within the study area are topographic divides but have very low relief, with just a couple tens of feet from the top of the divide to lakes and rivers within each watershed. Lakes lie within a few hundred feet of the divides, therefore it cannot be assumed that the groundwater divides between watersheds coincide directly with the topographic divides. The east and northern bounds of the study area generally coincide with topographic divides, but along the southern portion of the study area, the watershed boundary connects high points across wetlands where surface and groundwater could flow in either direction. However, the flux would likely be very low due to the almost flat gradient.

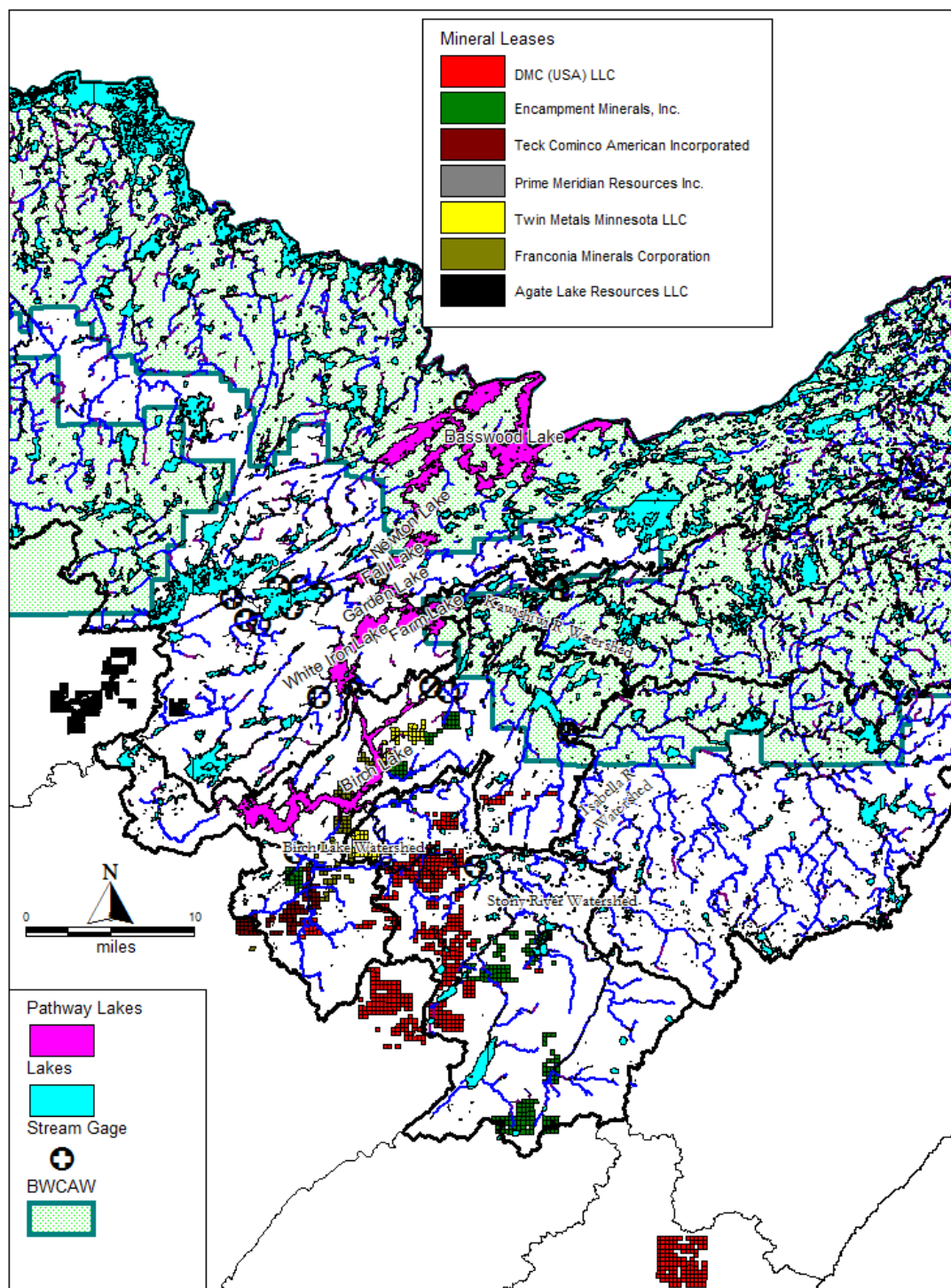


Fig. 3: Surface water pathway to the Boundary Waters Canoe Area Wilderness and the location of mining leases in the Stony River and Birch Lake watersheds.

Runoff, Baseflow and Recharge

Flow data for all US Geological Survey gaging stations in the area were obtained. Total flow, or total runoff from the watershed above that point, was divided into direct runoff and baseflow using methods of Lim et al. (2005) found at <https://engineering.purdue.edu/~what/main.html> (accessed 4/29/14) (Table 2). The calculation yields total flow in cfs-days (cubic feet per second x days). This was converted into average flow in cfs and m^3/d (the units used in the numerical groundwater model) (Table 2). The same units apply to direct runoff and base flow. Flow values are totals and averages for the dates and total days shown on Table 2. The baseflow index is the proportion of total flow that is baseflow. Yield is total streamflow per area, so the difference between total precipitation and yield is the average ET from the watershed. Recharge is the baseflow per area, assuming that all recharge becomes baseflow (Cherkauer 2004). However, the area recharge rate is an average of distributed recharge (through the ground surface over the watershed) and recharge of runoff through the bottom of the streams. Also, Table 2 does not account for flow management in the watersheds. Reservoir releases are partially controlled and at least attenuated. The Dunka River receives mine pit dewatering discharges from the Embarrass River watershed (Polymet 2013a) which would affect total flow and could affect baseflow estimates.

Table 2: US Geological Survey gaging stations and station parameters. Flow statistics described in text.

Site No	Site Name	Altitude	Area (sq miles)	Begin Date	End Date	Days	Total Flow (cfs-days)	Avg Flow (cfs)	Flow (m3/d)	
5124480	KAWISHWI RIVER NEAR ELY, MN		254	24259	41758	17470	3290459	188.35	461164	
5124500	ISABELLA RIVER NEAR ISABELLA, MN	1453.1	341	27607	41758	3835	1075997	280.57	686970	
5124990	FILSON CREEK IN SESW SEC. 24 NEAR WINTON, MN		9.66	27303	31336	4034	30714	7.61	18642	
5125000	SOUTH KAWISHWI RIVER NEAR ELY, MN	1430		18902	41758	8585	3475685	404.86	991271	
5125500	STONY RIVER NEAR ISABELLA, MN	1632.45	180	19268	23742	4475	562582	125.72	307811	
5126000	DUNKA RIVER NEAR BABBITT, MN	1488.98	53.4	18902	29530	6123	237136	38.73	94826	
5126210	SOUTH KAWISHWI R ABV WHITE IRON LAKE NR ELY, MN		837	27607	41758	5165	3318666	642.53	1573205	
5126500	BEAR ISLAND RIVER NEAR ELY, MN	1388.86	68.5	19268	28410	4609	197873	42.93	105117	
5127000	KAWISHWI RIVER NEAR WINTON, MN		1230	2009	41547	35702	35274735	988.03	2419154	
5127205	BURNTSIDE RIVER NEAR ELY, MN		69	24601	28763	4163	247431	59.44	145526	
5127207	BJORKMAN'S CREEK NEAR ELY, MN		1.36	26481	28763	2283	2449	1.07	2626	
5127210	ARMSTRONG CREEK NEAR ELY, MN		5.29	24601	28763	4163	19018	4.57	11186	
5127215	LONGSTORFF CREEK NEAR ELY, MN	1360.67	8.84	24601	28763	4163	32278	7.75	18984	
5127219	SHAGAWA RIVER Trlb AT ELY, MN		0.71	26024	28763	2740	290	0.11	259	
5127220	BURGO CREEK NEAR ELY, MN		3.04	24601	28763	4163	13563	3.26	7977	
5127230	SHAGAWA RIVER AT ELY, MN		99	24602	28789	4188	375159	89.58	219331	
5127500	BASSWOOD RIVER NEAR WINTON, MN	1296.8	1740	11324	41758	30254	40578673	1341.27	3284031	
Continued, Site No	Direct Runoff (cfs-days)	Direct Runoff (cfs)	RO (m3/d)	Base Flow (cfs-days)	Base flow (cfs)	Base flow (m3/d)	Base Flow Index (BFI)	Yield (in/y)	Baseflow yield (in/y)	Recharge (m/d)
5124480	772206	44.2	108226	2518252	144.1	352938	0.77	10.1	7.70	0.000536
5124500	401597	104.7	256400	674400	175.9	430571	0.63	11.2	7.00	0.000487
5124990	11881	2.9	7211	18833	4.7	11431	0.61	10.7	6.56	0.000457
5125000	872960	101.7	248969	2602725	303.2	742301	0.75			
5125500	164024	36.7	89744	398558	89.1	218067	0.71	9.5	6.72	0.000468
5126000	85393	13.9	34147	151744	24.8	60679	0.64	9.8	6.30	0.000439
5126210	936426	181.3	443911	2382240	461.2	1129295	0.72	10.4	7.48	0.000521
5126500	53557	11.6	28451	144317	31.3	76666	0.73	8.5	6.20	0.000432
5127000	10880914	304.8	746217	24393822	683.3	1672937	0.69	10.9	7.54	0.000525
5127205	57817	13.9	34005	189613	45.5	111521	0.77	11.7	8.96	0.000624
5127207	1155	0.5	1239	1294	0.6	1388	0.53	10.7	5.66	0.000394
5127210	7678	1.8	4516	11340	2.7	6670	0.60	11.7	6.99	0.000487
5127215	12586	3.0	7403	19691	4.7	11581	0.61	11.9	7.26	0.000506
5127219	174	0.1	155	116	0.0	103	0.40	2.0	0.81	0.000056
5127220	5912	1.4	3477	7650	1.8	4499	0.56	14.5	8.21	0.000571
5127230	84337	20.1	49307	290821	69.4	170025	0.78	12.3	9.52	0.000663
5127500	8949944	295.8	724319	31628729	1045.4	2559712	0.78	10.5	8.16	0.000568

Yield is relatively unvarying near and around the study area; if the high and low outliers are removed, the yield ranges from 8.5 to 12.3 inches/year (in/y). The outliers are small tributaries with small watersheds (Table 2), so small scale geologic factors could control the yield (and also the recharge).

Baseflow, or recharge, varies from 5.66 to 9.52 in/y, although for watersheds with more than 100 square miles, the range is from 6.7 to 8.2 in/y. Assuming the Kawishiwi River near Winton gage is representative, the average recharge is 7.54 in/y, or 0.00052 m/d for the study area. For the subwatersheds, Birch Lake, Stony River, Isabella River, and Kawishiwi River, the S Kawishiwi River above White Iron Lake near Ely, the Stony River near Isabella, the Isabella River near Isabella, and the Kawishiwi River near Ely gages provide the most representative data and yield recharge equal to 0.00052, 0.00047, 0.00049, and 0.00054 m/d, respectively. The low rates for the Dunka River near Babbitt and Filson Creek gages, 0.00044 and 0.00046 m/d, respectively, suggest the overall rates for the Birch Lake watershed could be high because these small watersheds are embedded within the Birch Lake watershed. Filson Creek is a 25.2 km² tributary to the S Kawishiwi River described by Siegel (1981) as having two substantial lakes and being 60% covered by upland forest, 30% covered by wetlands and lakes, and the remainder by stands of pine. The watershed has less than one meter of drift covering the bedrock which outcrops over about 10% of the watershed (Id.). Under the wetlands, there is a layer of peat with thickness up to 15 meters (Id.). Peat generally has very low permeability (Siegel et al. 1995) and wetlands underlain by peat are usually perched, so that little recharge through the wetlands occurs.

The several gages for small watersheds near Ely (Table 2), but outside the study area, show more variability which probably reflects small scale heterogeneity. The rates also represent different time periods (Table 2) but there is little reason to expect substantial changes due to land use due to the relatively undeveloped nature of the watershed. Climate change may eventually affect (or may have already affected) the recharge rates (IPCC 2007). Spatial heterogeneity is discussed below.

Climate, geomorphology and land cover are the primary factors to consider when estimating recharge (Scanlon et al. 2002). Lorenz and Delin (2007) derived a regression equation to estimate regional scale recharge for all areas of Minnesota based on precipitation, growing degree days, specific yield based on Rawls et al. (1982) and baseflow recession indices, similar to the method used to estimate recharge herein. Specific yield is a landscape characteristic estimated as the moisture difference between field capacity and the wilting point over the basin. Growing degree days, a surrogate for ET, was used because estimates are widely available. They estimated recharge as baseflow from a set of basins with an upper size limit of 5000 km². They did not consider recharge variability with drainage area. Their method yielded

a recharge estimate for the Kawishiwi watershed equaling 20 to 30 cm (8 to 11 in/y). This estimated recharge is similar to the yield for study area watersheds estimated herein and exceeds the recharge estimates by approximately 20 to 30 %. This suggests the equation (Delin et al 2007) is not accurate for northeast Minnesota, although gaging stations from that area were part of the data base used to develop it.

Long-term drainage from surface storage in areas with numerous lakes supports long-term baseflow which complicates the estimate of recharge (Sophocleous 2002) and could have caused the overestimates for this area discussed above. The watershed is a system of connected local flow systems defined by microscale topography embedded within a larger flow system (Winter 1998). Water storage in the Kawishiwi River basin includes surface storage in wetlands and small lakes and subsurface storage in the unsaturated zone and groundwater.

Interflow is both unsaturated and saturated flow just below ground surface to streams that occurs during and just after a storm, with saturation causing temporary perched zones (Sophocleous 2002). Because of the shallowness and flatness of the groundwater table in this watershed, especially in wetland areas, interflow should be limited and should soon discharge to the ground surface and become overland flow among the wetlands. Short-term shallow groundwater discharge to the rivers may be caused by groundwater ridging, which would rapidly increase the groundwater head and substantially increase the gradient for flow to surface drainages (Sophocleous 2002). Interflow may therefore resemble groundwater recharge and be difficult to separate from the runoff hydrograph which may cause recharge estimates to be erroneous.

Spatial Heterogeneity

Many factors control the heterogeneity of the surficial aquifer including recharge and K. Wetlands, soil types, and soil landforms control recharge. That includes whether the soil is well drained, whether the soils contain substantial peat, and whether the bedrock is shallow. Minnesota has several well-developed GIS databases describing soils at a statewide level with accuracy to a 40 acre scale. All are described in Land Management Information Center (1996) and associated GIS databases and briefly in the following paragraphs with maps for the study area (Fig. 4 through 8).

Wetlands cover just 7.6% of the 1103 square mile study area, with most of the wetlands being in the southern portion (Fig. 4). If the wetlands are perched, these could be areas with little recharge. If they are connected to the groundwater, they could be alternately recharge and discharge areas. Based on the small area included and their overlap with lower permeability soils (discussed below), the area of wetlands is of less importance in the spatial distribution of

recharge. Perennial streams draining perched wetland areas however could convey runoff and focus recharge along the streams.

The hydrologic soil classification shows that almost half of the study area (mostly over the northern portion (Fig. 5)), is mostly slow draining, being rated C, D (Table 4). The A group is the second largest area (Table 3) and covers the central portion just south of the C, D area (Fig. 5); these soils have high infiltration (Table 3). The remaining areas along the southern boundary of the study area have infiltration rates intermediate to the C, D and A groups.

Soil type is a soil landscape unit based on four characteristics, each with a letter description (Table 5), although some soils, such as PEAT, are self explanatory and not represented in Table 5 because their characteristics do not break down easily into the categories. Most of the soils are relatively free-draining based on soil type, although a substantial amount has bedrock for a sublayer (Fig. 6 and Table 5). Type RLWL covers the largest area and mostly coincides with the C, D hydrologic soil classification (Fig. 5). This type is free draining but underlain with bedrock (Table 5). Loamy is similar to the fine-grained description for hydrologic soil classification C. SSWL, the second largest landscape unit area, has sand throughout and is free draining, so its correspondence with hydrologic soil classification A, fast infiltration, is expected. Groups south of SSWL are LLWL and SLWL, which have slower infiltration than those discussed above.

Maps of surface permeability (Fig. 7) and subsurface permeability (Fig. 8) show that the central region of the study area has the highest infiltration rates through the soil profile. The northern region has much lower infiltration rates, less than 0.8 inches/hour. Much of the southern portion of the study area is unclassified or a mixture of the rates from the northern and central region.

The descriptions of soils resulting from Figs 4 through 8 indicate the study area has three different basic classifications which can be used to understand surficial layer conductivity. The northern portion, encompassing much of the Kawishiwi and Birch Lake watershed, has free-draining surface soil underlain by bedrock. Meteoric water would enter the soil but the bedrock would restrict its downward movement. The majority of the higher recharge in this area may quickly reach the stream discharge points without circulating deeply. The K zone for this area should have a high vertical anisotropy, near 100. In contrast, a larger proportion of recharge in the central portion should reach deeply into the groundwater. The vertical anisotropy for layer one through this zone should be lower, no higher than 10. The southern portion of the area is mixed and should have K intermediate to the other zones.

Table 3: Area (square miles) of soils groupings by category. Hydrologic soil group is the NRCS soil classification (see Table 4). Sub perm is permeability (in/h) of the layer 5 feet below ground surface. Surface perm is permeability (in/h) of the top 5 feet of soil. The total study area is 1103 sq miles. Categories do not add to 1103 sq miles because the area of unclassified and water ratings do not have areas listed for Sub or Surface Perm.

Hydrologic Soil Group	Area	Sub perm	Area	Surface perm	Area
C,D	548.9	Greater than or equal to .8	587.3	.8 - 5	3.2
A	245.1	Greater than or equal to 5	288.4	.2 - 5	5.7
A/D	155.1	Greater than or equal to 2.5	45.1	Greater than or equal to 5	16.0
C	47.2	Less than or equal to .8	5.7	Greater than or equal to 2.5	278.9
C,B/D	44.5	.8 - 5	3.2	Greater than or equal to .8	630.0
No Rating	31.2				
B	21.4				
Water	7.9				
Total	1101.3		929.8		933.9

Table 4: Description of soil properties with respect to infiltration by hydrologic soil group (NRCS 2007).

Hydrologic soil group	Description
A	Soils having high infiltration rates even when thoroughly wetted, consisting chiefly of deep, well to excessively drained sands and or gravel. These soils have a high rate of water transmission and would result in a low runoff potential.
B	Soils having moderate infiltration rates when thoroughly wetted, consisting chiefly of moderately deep to deep, moderately well to well drained soils with moderately fine to moderately coarse textures. These soils have a moderate rate of water transmission.
C	Soils having slow infiltration rates when thoroughly wetted, consisting chiefly of (1) soils with a layer that impedes the downward movement of water, or (2) soils with moderately fine to fine texture and slow infiltration rate. These soils have a slow rate of water transmission.
D	Soils having very slow infiltration rates when thoroughly wetted, consisting chiefly of (1) clay soils with a high swelling potential, (2) soils with a high permanent water table, (3) soils with claypan or clay layer at or near the surface, and (4) shallow soils over nearly impervious materials. These soils have a very slow rate of water transmission.

Table 5: Description of soil type.

Factor number	Description
1	Texture of the soil material below 5 feet of the surface, with "S" designating sandy; "L" for loamy or silty; "C" for clayey "X" for mixed sandy and loamy; "Y" for mixed silty and clayey; and "R" for bedrock.
2	Texture of the material in the first 5 feet below the surface, or a significant part of it, with "S" for sandy; "L" for loamy, and "C" for clayey.
3	Drainage of the unit, where "W" means well-drained (water table commonly below the rooting zone), and "P" means poorly-drained (water table within the rooting zone).
4	Color of the surface horizon with "D" for dark-colored and "L" for light colored (Darker colors associated with higher organic matter content).
For example, RLWL means bedrock below 5 feet below the surface, loamy for the top 5 feet, well-drained below the root zone, and light colored.	

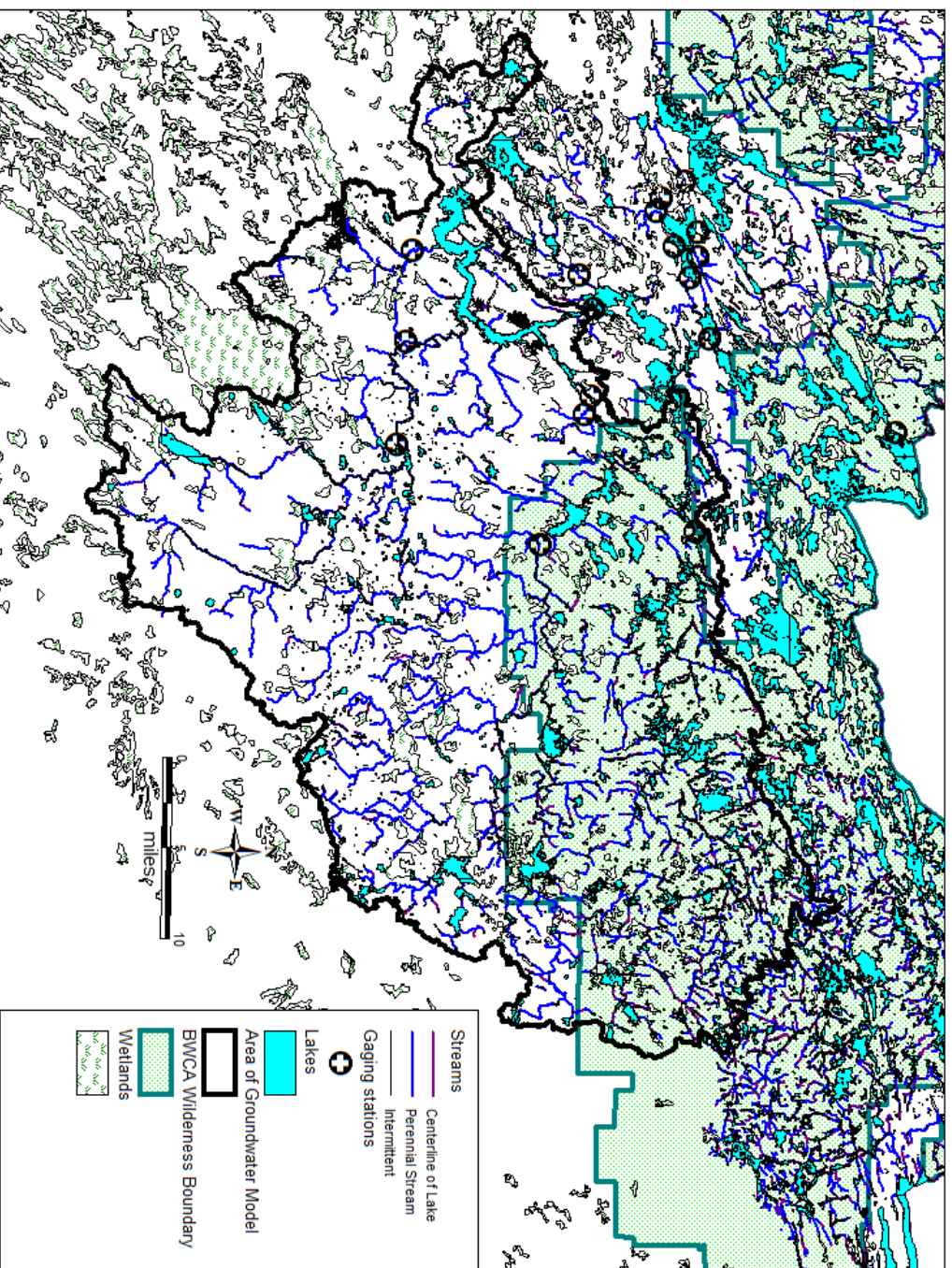


Fig. 4: Distribution of wetlands and lakes across the study area. Stream file Strm_baseIn3, lakes and wetlands from Dnr100khydrography, from www.mngeo.state.mn.us/chouse/metalong.html

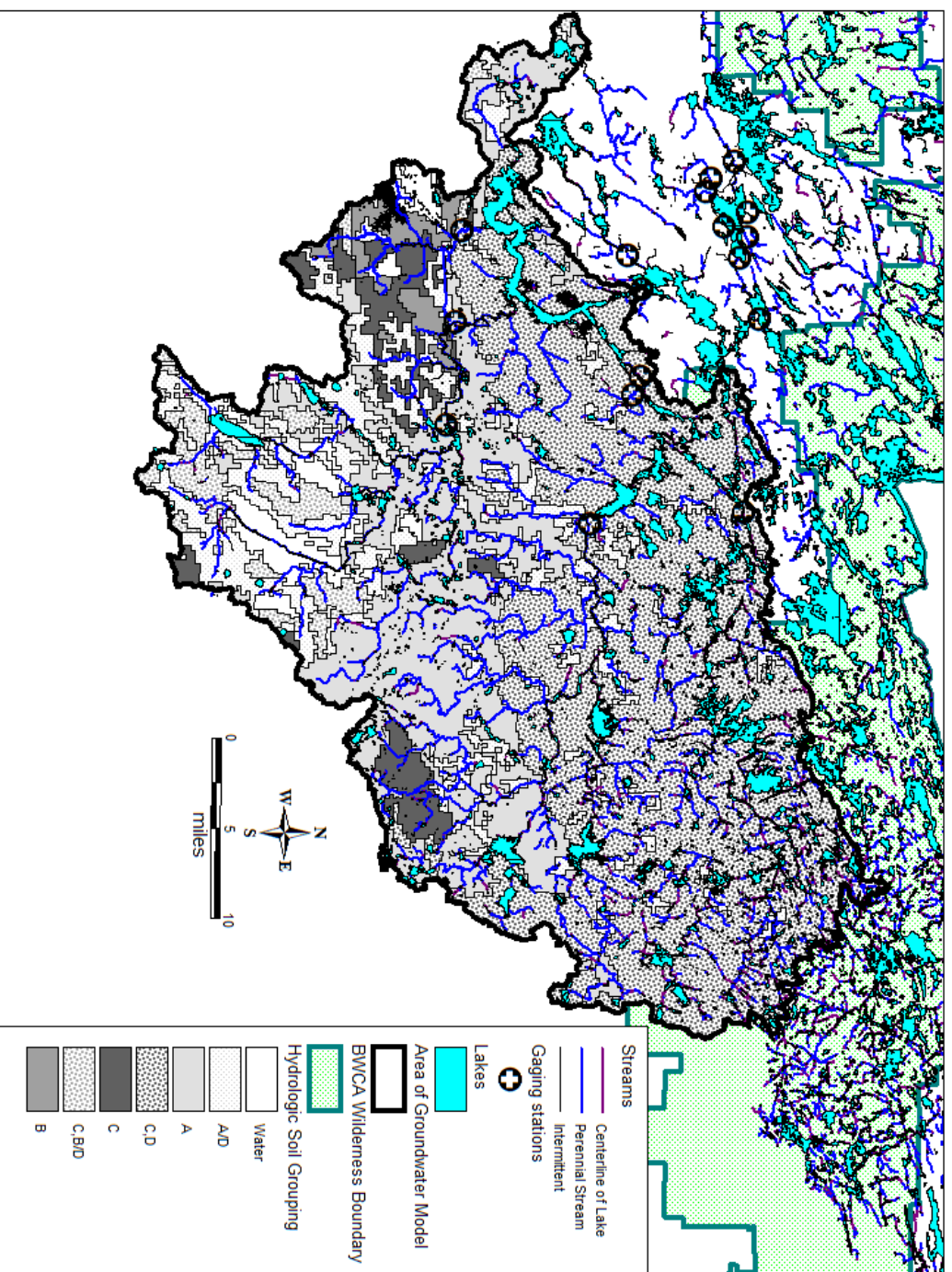


Fig. 5: Distribution of hydrologic soil grouping (NRCS 2007) across the study area. See Table 3 for a description of soil grouping. From Minnesota soil atlas: http://www.mngeo.state.mn.us/chouse/metadata/soil_atlas.html

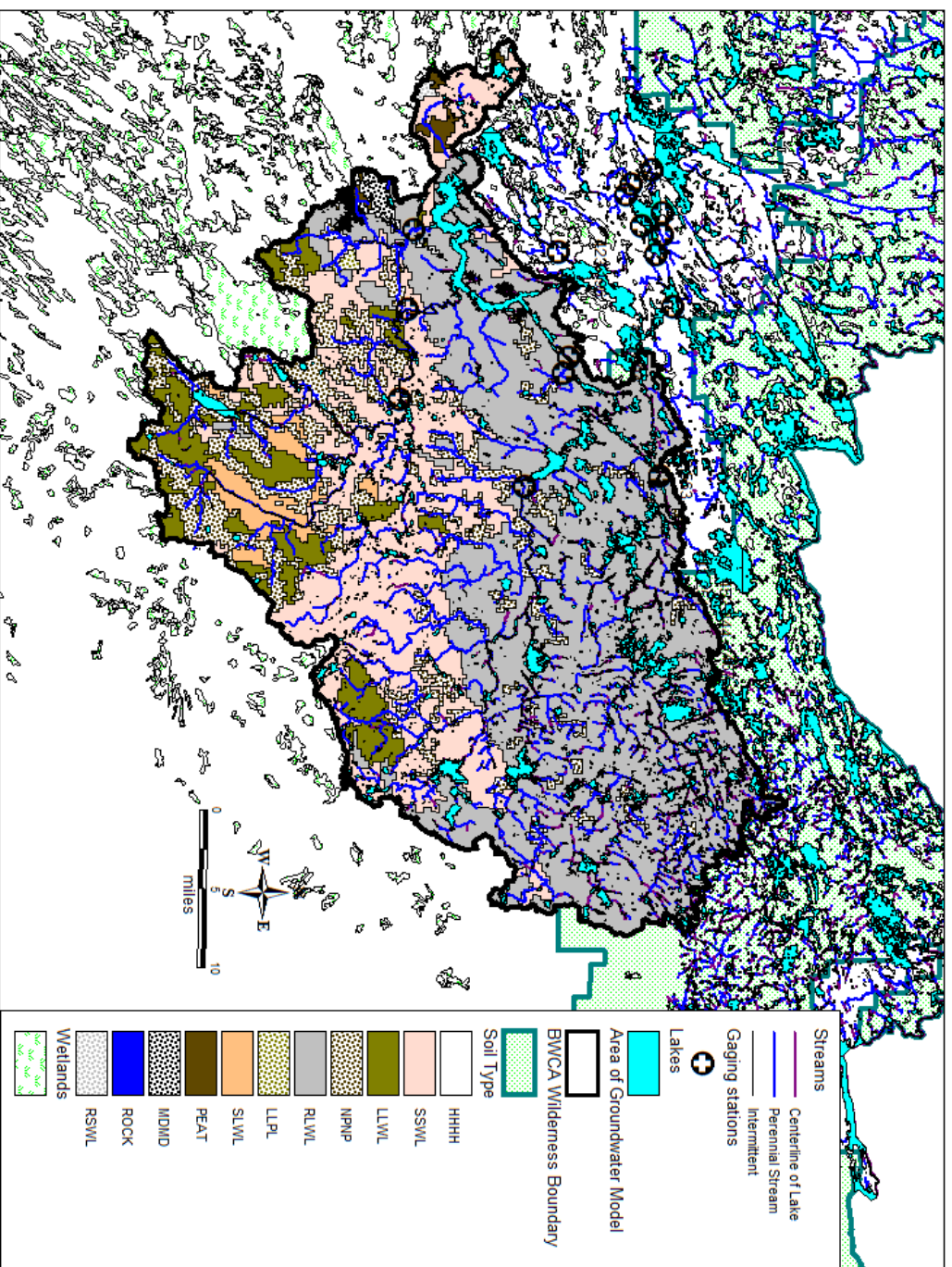


Fig. 6: Distribution of soil landscape units over the study area. See Table 5 for a description of the units. From Minnesota soil atlas: http://www.mngeo.state.mn.us/chouse/metadata/soil_atlas.html

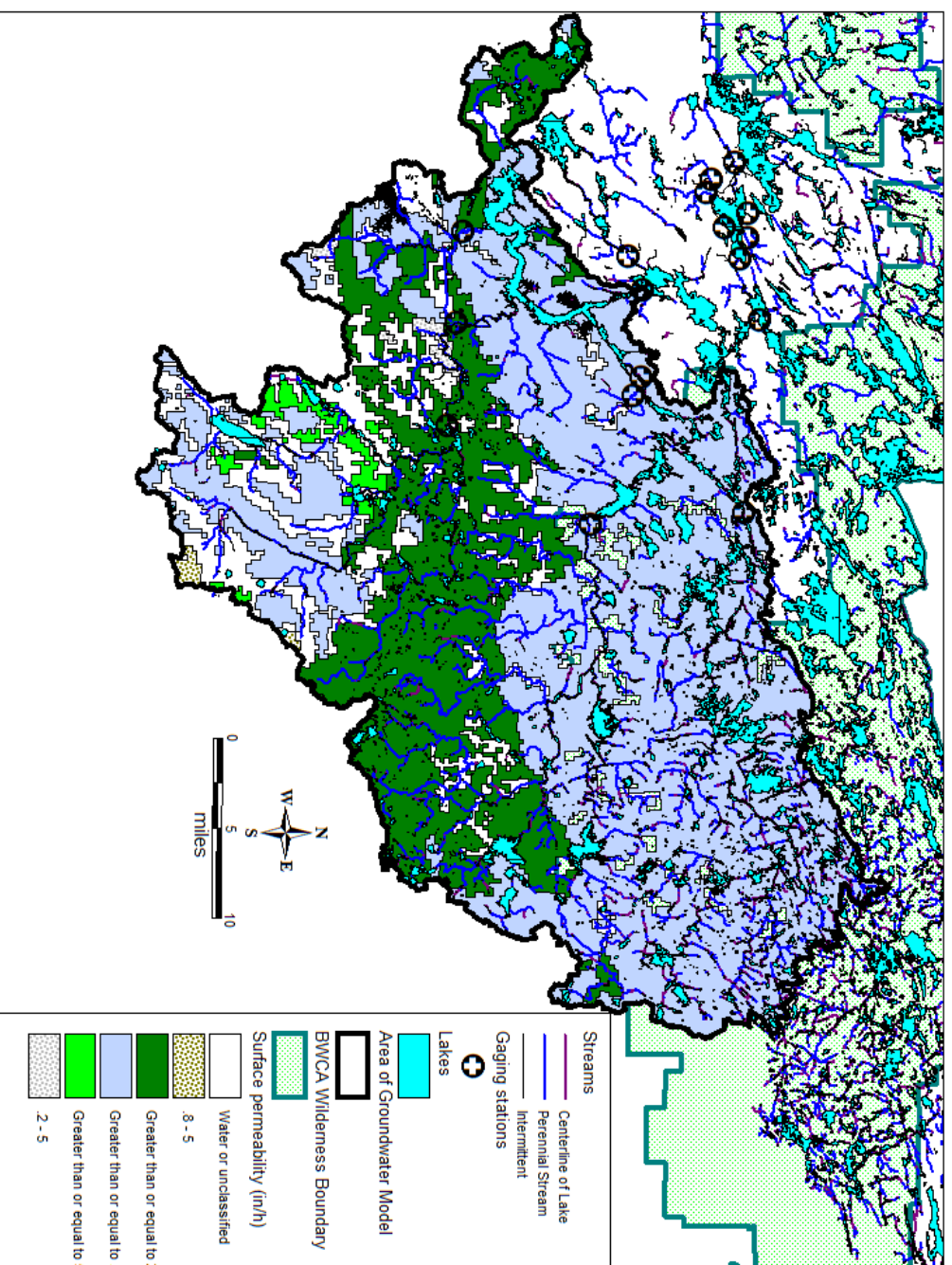


Fig. 7: Distribution of surface soil permeability across the study area. From Minnesota soil atlas:
http://www.mngeo.state.mn.us/chouse/metadata/soil_atlas.html

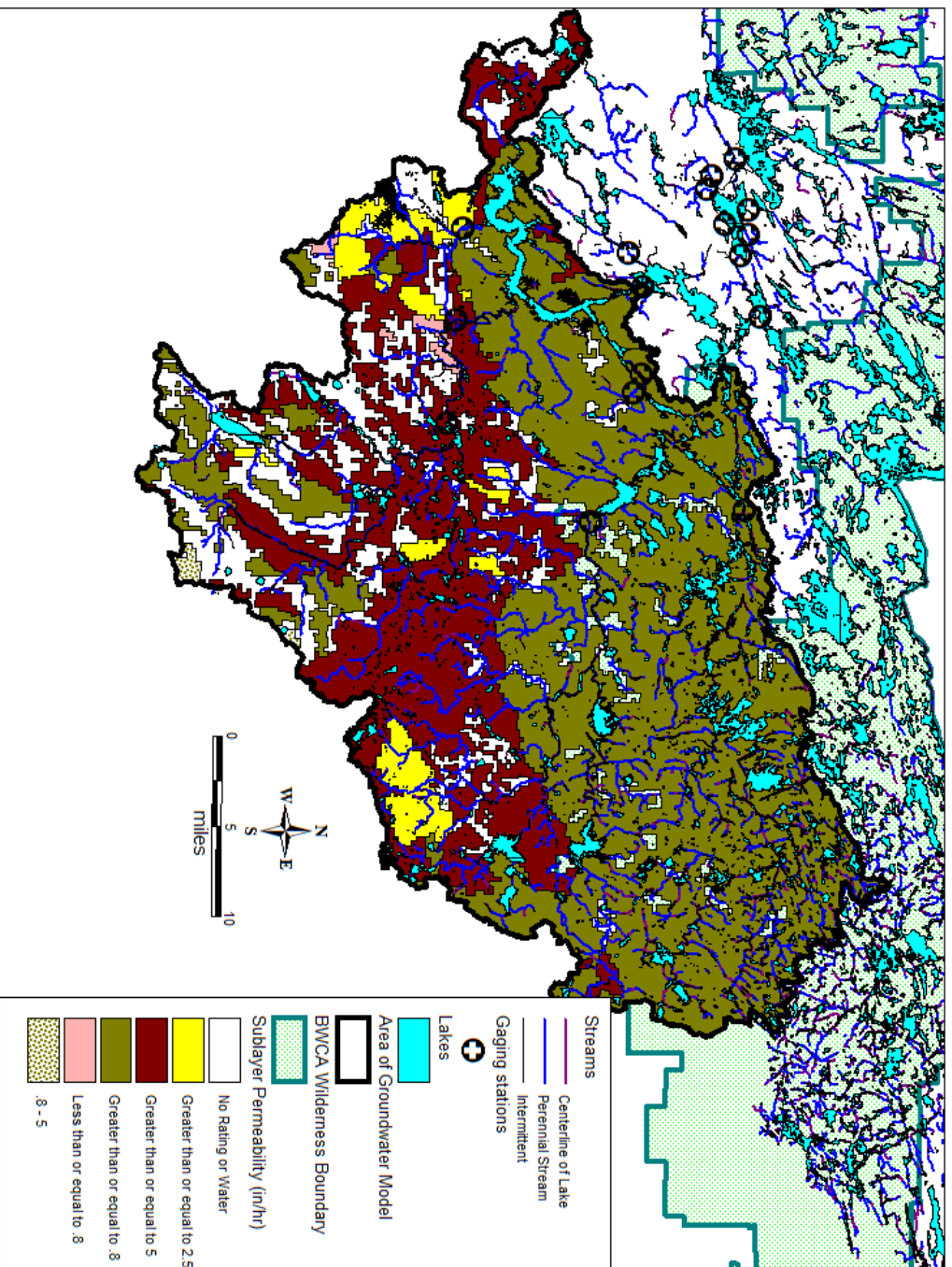


Fig. 8: Distribution of subsurface soil permeability across the study area. From Minnesota soil atlas:
http://www.mngeo.state.mn.us/chouse/metadata/soil_atlas.html

Seasonal Variability

During the spring snowmelt, flow from the watershed reaches a peak and there is a substantial wetting of the aquifers due to recharge. Average monthly river flow at the Kawishiwi River near Ely gage peaks at more than 30 in/y during May just two months after the low flow of less than 3 in/y recorded in March (Fig. 9). Much recharge would likely occur during this snowmelt freshet flood because there is water running on the ground surface and river and stream levels are higher than the water levels in the streambanks. Siegel and Ericson (1981) noted that 60 percent of runoff occurs during snowmelt from April through June and less than 11 percent occurs from December through March. Climate change could affect this distribution, but trends for northern Minnesota are unclear; higher precipitation could be offset by higher evapotranspiration so that the net change in recharge could be negligible (IPCC 2007). No groundwater level data is published by the US Geological Survey for this area, but studies in support of mining in the Partridge River watershed just west of the Kawishiwi River include data showing that groundwater levels fluctuate up to six feet during the spring (Polymet 2013b).

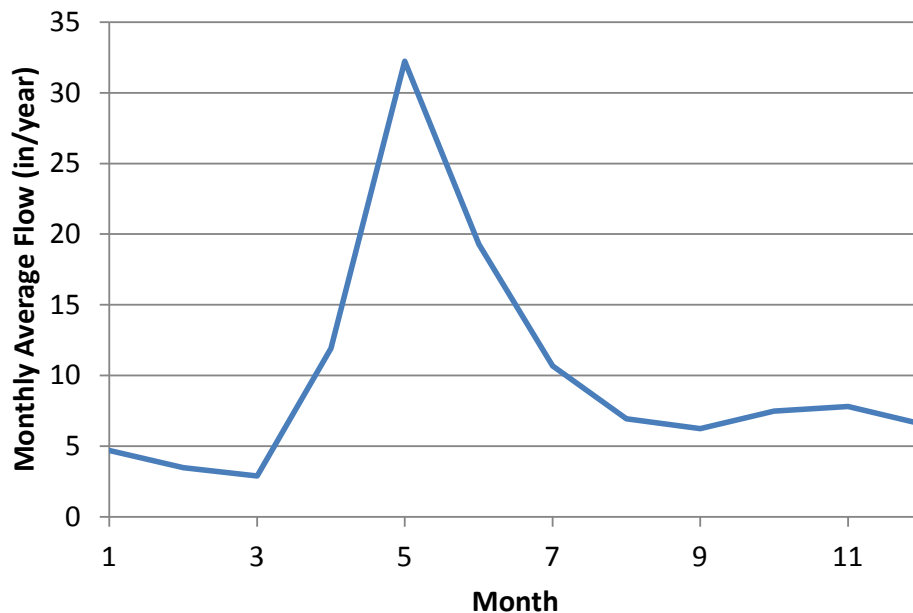


Fig. 9: Average flow by month (1=January, 12=December) in inches per year for the Kawishiwi River near Ely, MN.

It is common to assume that the 30-day low flow rate equals groundwater recharge over the basin (Cherkauer 2004; Scanlon et al. 2002), but in the Partridge River basin, just west of the Laurentian Divide, Myers (2013a) found that this is not possible because the long time period since recharge would have occurred (recharge cannot occur while precipitation is frozen and the

watershed is ice-in) is much longer than the travel time through the aquifers due to the high K and thin surficial aquifers. In other words, during the winter when the watershed is frozen, groundwater is draining to the streams but not being replenished by recharge so the baseflow rates are much lower than they are when the watershed groundwater is fully recharged. Spring baseflow represents recharge that occurs more than a 5-month travel time from the stream because recharge cannot occur when the precipitation and soils are frozen.

Transport

Contaminant transport is the process whereby a contaminant moves from a source (here, a spill or leak at a potential mine) to a sink, or receptor (here, the water resources of the BWCAW). Three processes control contaminant movement - advection, dispersion, and sorption (Fetter 1999). Advection, the movement of the contaminant along with the flow of the water, is controlled by the properties of the formation rather than the contaminant. Dispersion occurs because the particles in a plume move at different rates due to the different sizes and connectivity of pores in the formations; contaminants move slower following a tortuous route or when flowing through larger pores, and faster when being squeezed through small pores (Fetter 1999; Anderson and Woessner 1992). Sorption, the process of a constituent becoming bound on soil particles, is a function of the particular constituent and the geochemistry of the formation. Myers (2013c) reviewed the groundwater and surface water chemistry of the area and found basically that the water quality is very good but has poor buffering capacity, so that little attenuation of contaminants would occur.

If there is no sorption, the constituent discharged from a source will eventually reach a sink. Such transport is considered conservative, meaning the contaminant is not transformed chemically or sorbed to aquifer materials during transport. The seepage rate affects how quickly a certain concentration reaches a point, such as a well or the river. At a sink, the concentration will eventually approach a steady state concentration lower than the source concentration if the source rate and concentration remain constant. The steady state concentration depends on advection and dispersivity. Higher vertical and lateral dispersivity will cause the contaminant to spread more so that the concentration along the primary flow path is lessened. Sorption, if it occurs, slows the transport because the constituent adsorbs to sites along the pathway and decreases the total load eventually reaching the sink.

In surface water, transport follows the river and river turbulence causes dispersion. As the flow in the river increases in a downstream direction, dispersion will cause the contaminants to spread through the increased flow and be diluted. Sorption may also attenuate the concentration. For example, mercury often binds to river sediments and only moves through the river system during high flows (Wershaw 1970; Jenne 1970).

Contaminants emanating from underground mines in the Birch Lake or Stony River watersheds will move laterally and vertically through the groundwater until they reach a river, if there is an upward vertical gradient. If no vertical gradient exists, the contaminants may never reach the surface within the watershed; the present numerical analysis estimates whether and where vertical gradients exist that would cause groundwater to flow from depth to the surface. Discharge to the surface could occur to any of the tributaries, wetlands, or lakes being modeled in the study area. Contaminants in that discharge would flow through downstream lakes and rivers to the BWCAW.

Contaminant transport through groundwater and discharge to surface waters would occur at a relatively constant rate, although short-term recharge events could prevent discharge to surface water at certain times. During high flow periods, dispersion and dilution are substantial. The critical period for surface transport occurs during dry periods, when the streams are limited to baseflow. As seen in Table 2, the baseflow does not increase substantially in a downstream direction. Low frequency low flows such as the 7Q10 flow (the seven-day annual low flow with ten-year return interval), actually decrease in a downstream direction, meaning that the river loses flow rather than receiving sufficient tributary or groundwater discharge to maintain its normally gaining river flow character. During low flows, it is unlikely that the river discharges into groundwater (Sophocleous 2002), so flow reductions would be due to evaporation which would concentrate the contaminant in the downstream direction. At low flows, the load remains the same in the downstream direction, but the flow decreases and concentration increases.

Most of the aquifer and streamside soils are poorly buffered which means that acid leaving a mine or reaching a stream would not be neutralized (Siegel 1981). Acid precipitation has depleted the soils of neutralizing capability in some areas (DeSallas et al. 2014), although portions of the Duluth Complex have neutralizing capability due to silicate mineralization (Lapakko 1988). Acid-dependent transport would not be attenuated under these conditions. It is even possible some elements, such as cadmium, iron, or selenium, could be dissolved along the flow path downgradient from the mine source. Consideration of this potential dissolution is beyond the scope of this project.

Waste stored on the ground surface is subject to seepage by meteoric waters and leaching of contaminants. This water can either infiltrate to shallow groundwater through which it can move to streams through the interflow, or, it can flow across the ground surface to the streams. In either case the flow path is much shorter than for waste deposited underground. Because such seepage may depend on there being wet antecedent conditions, the seepage may reach the stream at a time when river flows are not critically low. This would be most likely for seeps

that flow on the surface. Seeps that enter the surficial aquifer may lag several months before discharging to streams, possibly at their most critical flow periods.

Development of Numerical Model

The conceptual model of groundwater flow developed above is the basis for a numerical groundwater and transport model using MODFLOW-2000 (Harbaugh et al. 2000) and MT3DMS (Zheng and Wang 1999). Additionally, flowpaths were determined from MODFLOW-2000 using the MODPATH code (Pollock 1994). The purpose of this modeling is to simulate the potential for contaminants released due to mining the various deposits in the Birch Lake and Stony River watershed to reach surface water and the BWCAW. The strategy is to develop a numerical model that accurately represents the flow and transport through the system at a reconnaissance level of accuracy. The first section below describes the development and calibration of the flow model, the second section briefly describes how the mineral deposits would be developed based on descriptions in mining company documents and web pages, the third section describes particle tracking through the domain, and the fourth section describes contaminant transport modeling and how the seepage or leaks from the potential mining were simulated. Following the modeling, a simple discussion of transport through the surface waters to the BWCAW provides relative sulfate concentrations for the simulated loads.

Model Domain and Discretization

The study area described above is the model domain (Fig. 1). The general cell size is 500 m square which approximates the 40 acre lease size and would be appropriate for adding loads to the transport model. The cells expand to 1000 m square on the fringes in the upper Kawishiwi and Isabella River watersheds (Fig. 10). The model domain has three layers, with layer 1 being the surficial till and sand/gravel layer and layers 2 and 3 being bedrock. The top of layer 1 was set based on 30 m and 10 m digital elevation models (DEMs) (Fig. 11). Layer 1 was set to be 15 m thick, based on the median and mean depth to bedrock for the well database being 14 and 17.4 m. However, thickness can be variable, with the maximum depth being 75 m and in a few locations the bedrock outcrops, which means the calibrated K may vary to reflect the differences in transmissivity due to thickness. Layer 2 thickness was set so that the total thickness of layers 1 and 2 equaled 140 m. The bottom of layer 3 was set at elevation -1000 m, so layer 3 was near 1200 m thick.

Head-controlled flux boundaries: MODFLOW DRAIN boundaries, were specified for larger lakes (reach numbers less than 50) and rivers (reach number greater than 70) (Table 7 in the water balance identifies reach numbers) because they should be discharge points or sinks for the groundwater (Fig. 12). Lakes have a lower conductance due to fine sediments on their bottom. The conductance of larger rivers would be higher than lakes due to the sorting of

sediments and higher than that of smaller streams because the area in contact with the groundwater is larger. The head of the lakes was set to less than a meter below the top elevation of the cells represented by the boundary. Therefore, lakes received groundwater inflow only when the groundwater level is close to the ground surface. In areas with lower groundwater levels, the model does not simulate a connection. The head of rivers was set 5 m below the average top elevation of each model cell containing a stream. This allowed for more consistent discharge to rivers which tend to have eroded channels of several meters below the surrounding ground surface. The conductance for lakes was set according to a 400x400 m cell area, $K=0.001$ m/d, and thickness equal to 0.3 m. The conductance for rivers was set as for lakes, but with area being 400x10 m and $K=1.0$ m/d. DRAIN reaches which flow to a gaging station for which the baseflow is known were given separate reach numbers for calibration, as follows.

- Reach 71 – Dunka R
- Reach 72 – Stony R between Babbitt and Isabella (upstream)
- Reach 73 – Stony R above Isabella
- Reach 74 – Isabella R above Isabella
- Reach 75 – Filson Creek nr Ely
- Reach 76 – S Kawishiwi R between Iron Lake gage (DS end of reach) and S Kawishiwi R nr Ely, Dunka R, and Stony R nr Babbitt gages, this section includes Reach 1, Birch Lake. The reach gains the difference in flow between the DS gage and the three upstream gages. Reach 75, Filson Creek, enters above the S Kawishiwi R nr Ely gage
- Reach 77 – river and tributaries above the Kawishiwi R nr Ely gage
- Reach 78 – S Kawishiwi R between split and S Kawishiwi R nr Ely
- Reach 79 – Kawishiwi R between split and flow from watershed – not gaged.

Recharge: Four recharge zones were specified based on subwatershed (Fig. 13), with rates set so that recharge equals the measured baseflow in the primary rivers. The total distributed recharge equals approximately $1,425,000 \text{ m}^3/\text{d}$. This rate was based on the average baseflow for the four subwatersheds and equals about 0.000504 m/d over the study area. The Kawishiwi River at Winton gage drains all of the study area plus about 130 square miles and has an average recharge rate of 0.00052 m/d . Recharge rates were not adjusted during calibration.

Hydrogeologic Parameter Zones: The initial parameter zones were based on the bedrock geology (Fig. 2) for layers 2 and 3, and on the soils maps (Figs. 5 through 8) for layer 1. Zones with few or no targets were not sensitive to parameter changes so the final values were selected on formation type and on values necessary to generate reasonable head and flux values. Zones with many targets would be sensitive to changes, and the final values for these zones were chosen based on automated calibration. Sensitive zones were also split once or

twice to improve the fit for various areas. The final parameter zones are shown in Figs. 14 through 16.

Calibration Targets: Minnesota does not maintain any groundwater level data in the study area (http://www.dnr.state.mn.us/waters/groundwater_section/obwell/locations.html, accessed 4/30/14). The USGS database contains just ten wells. The county wells index prepared by the MN Geological Survey and MN Department of Health includes data from drill holes completed for mining industry exploration; some of them include groundwater levels (<http://www.mngeo.state.mn.us/chouse/metadata/wells.html>, accessed 4/30/14). Within the four watersheds that define this study area, there were 1238 wells in the database. The wells from this database with depth to water and water level elevation were selected as targets. They were segregated by model layer based on depth and digitized into the groundwater model. The target wells cluster near the deposits because much of the well level data is from exploration wells. Other information in the database includes well depth and depth to bedrock, which was used to select the model layer to match the measured groundwater level and to calculate the thickness of the surficial aquifer. (Fig. 17). Some of the exploration wells were clustered within tens of meters and were impossible to distinguish at the model scale, hence Fig. 17 does not show their names.

The problem with the observed water levels is that the wells are so close together they represent essentially the same information. There was variability in the heads for clustered wells at depth but there was no trend with well depth. Head would differ as much as 10 m for wells within a 100 m square, but there was no consistent trend with depth. This finding suggests the different wells tap different fracture zones at a scale much finer than the detail used for the modeling. The head targets were thinned, first by keeping just one well per layer within 200 m of each other, and second by keeping just one well per model cell. This was done because the MODFLOW-2000 parameter estimation routine would not converge due to the correlation among residuals. Additionally, as noted, there were few measurements in parts of the domain, particularly in the Isabella River and Kawishiwi River watershed. For these areas, artificial targets were created based on the ground surface. At nine locations, a target was set in the three model layers at ground surface elevation minus 4 m, but with a weight of 0.3 to limit the effect of these artificial targets on the calibration. This was similar to the strategy used by Halford and Plume (2011), who set points 1 m below ground surface in wetland areas.

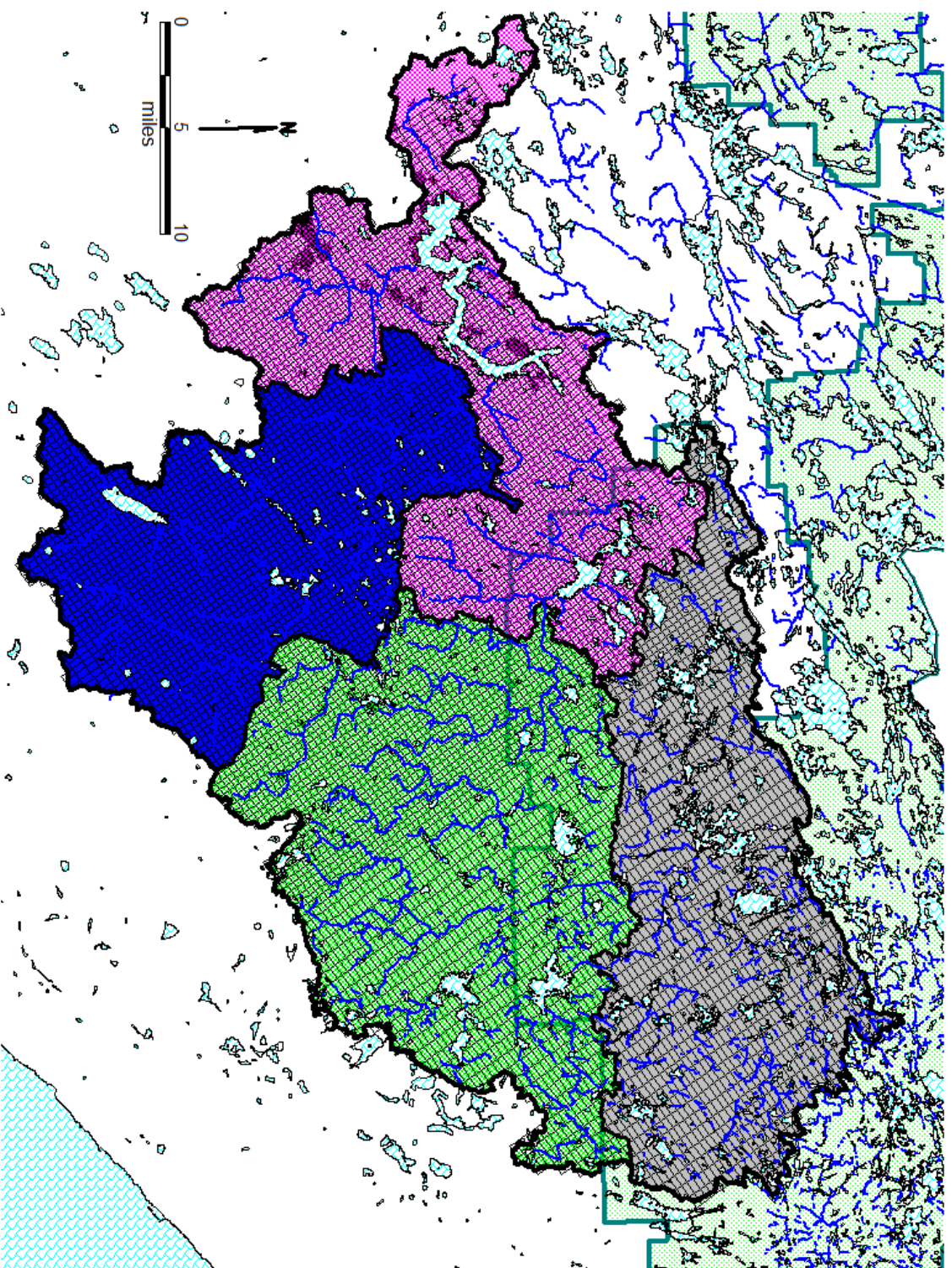


Fig. 10: Model grid over the domain, showing watersheds and recharge zones. See Fig. 1 for watershed labels.

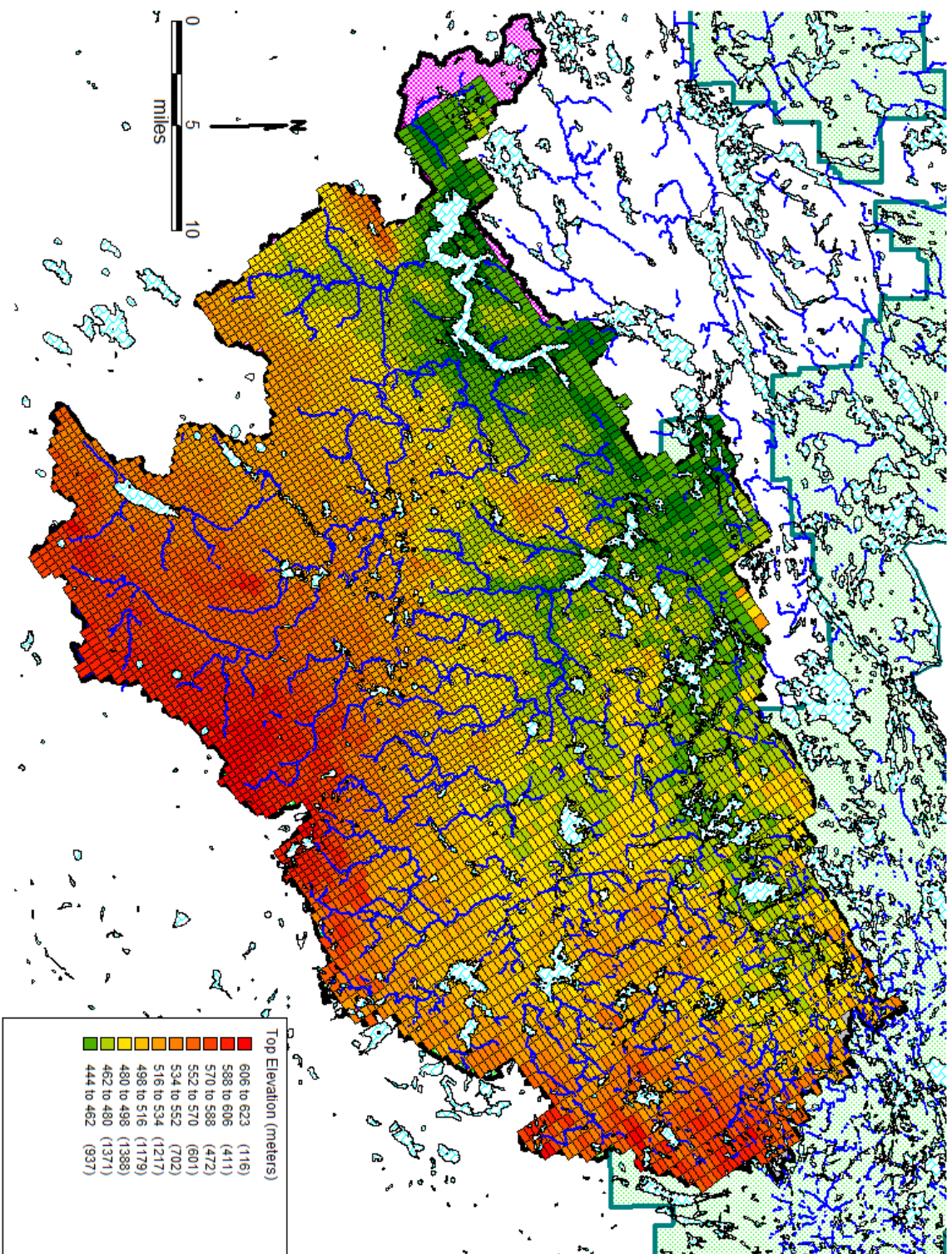


Fig. 11: Layer 1 top elevation by cell in meters.

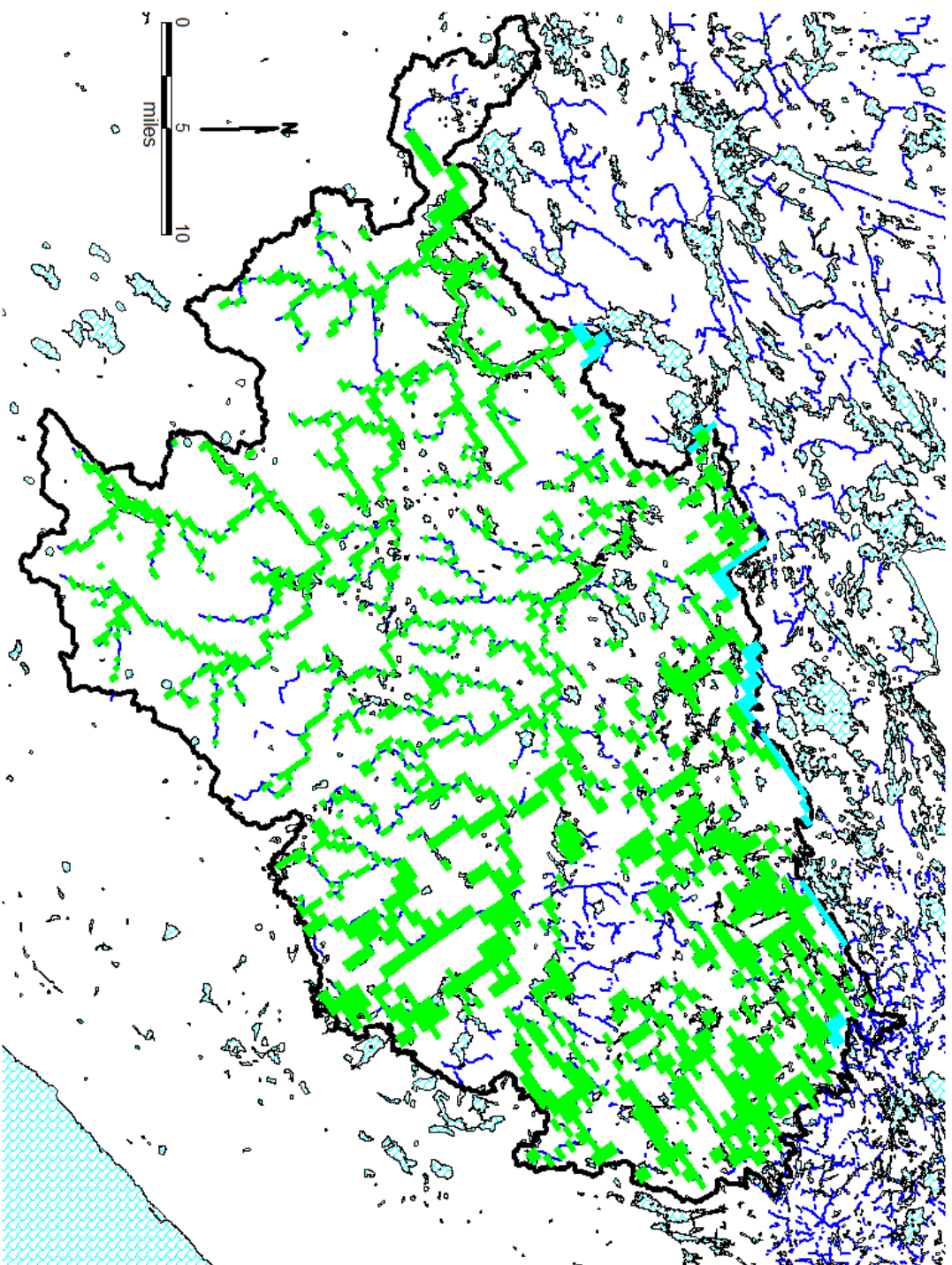


Fig. 12: Location of DRAIN boundaries in green, layer 1, and general head boundaries (GHBs) in blue, layer 2. Lakes with blue thatching were used to set distance and head values in the GHBs.

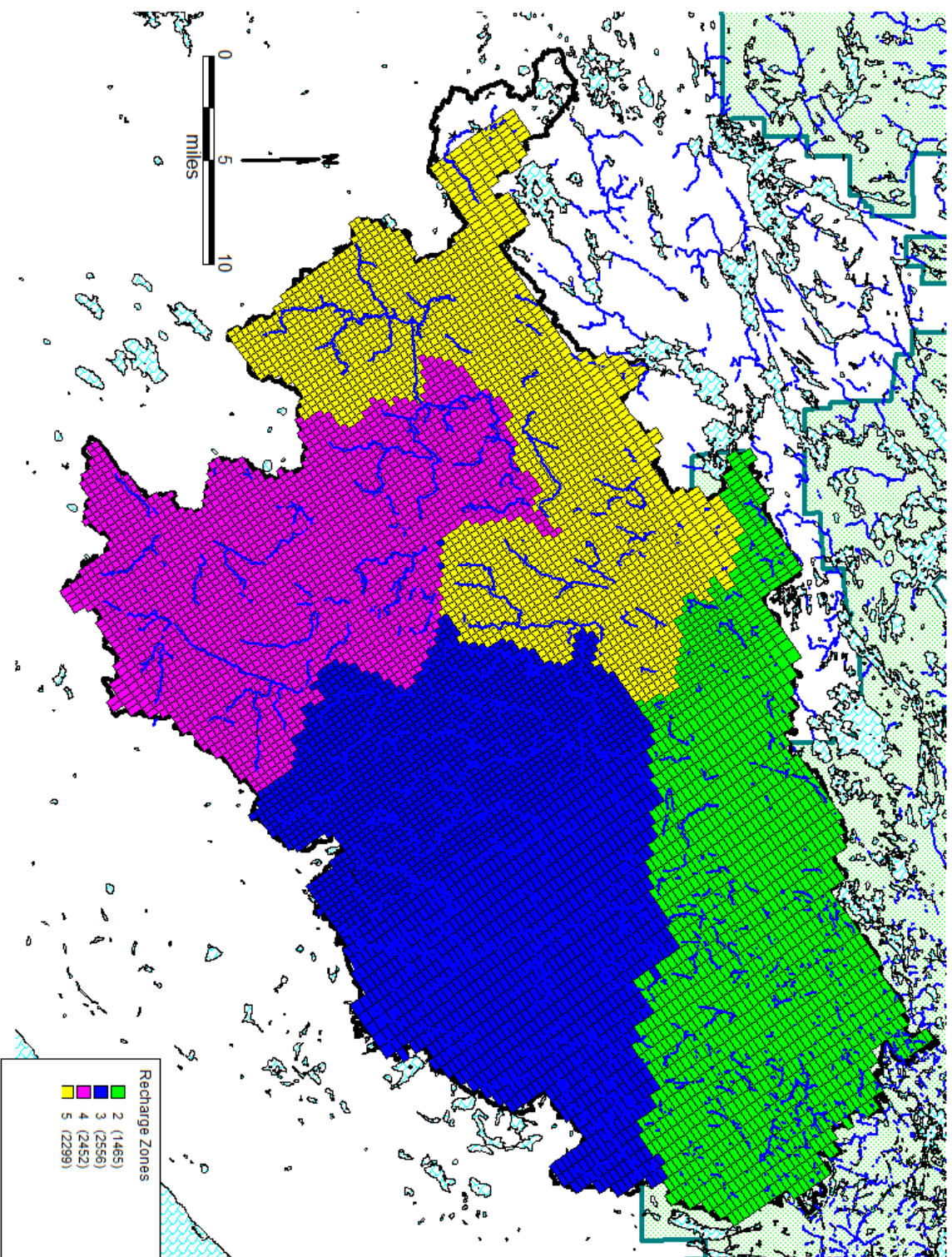


Fig. 13: Model recharge zones. Final recharge rates equal 0.00054, 0.00049, 0.00047, and 0.00052 m/d for zones 2 through 5, respectively.

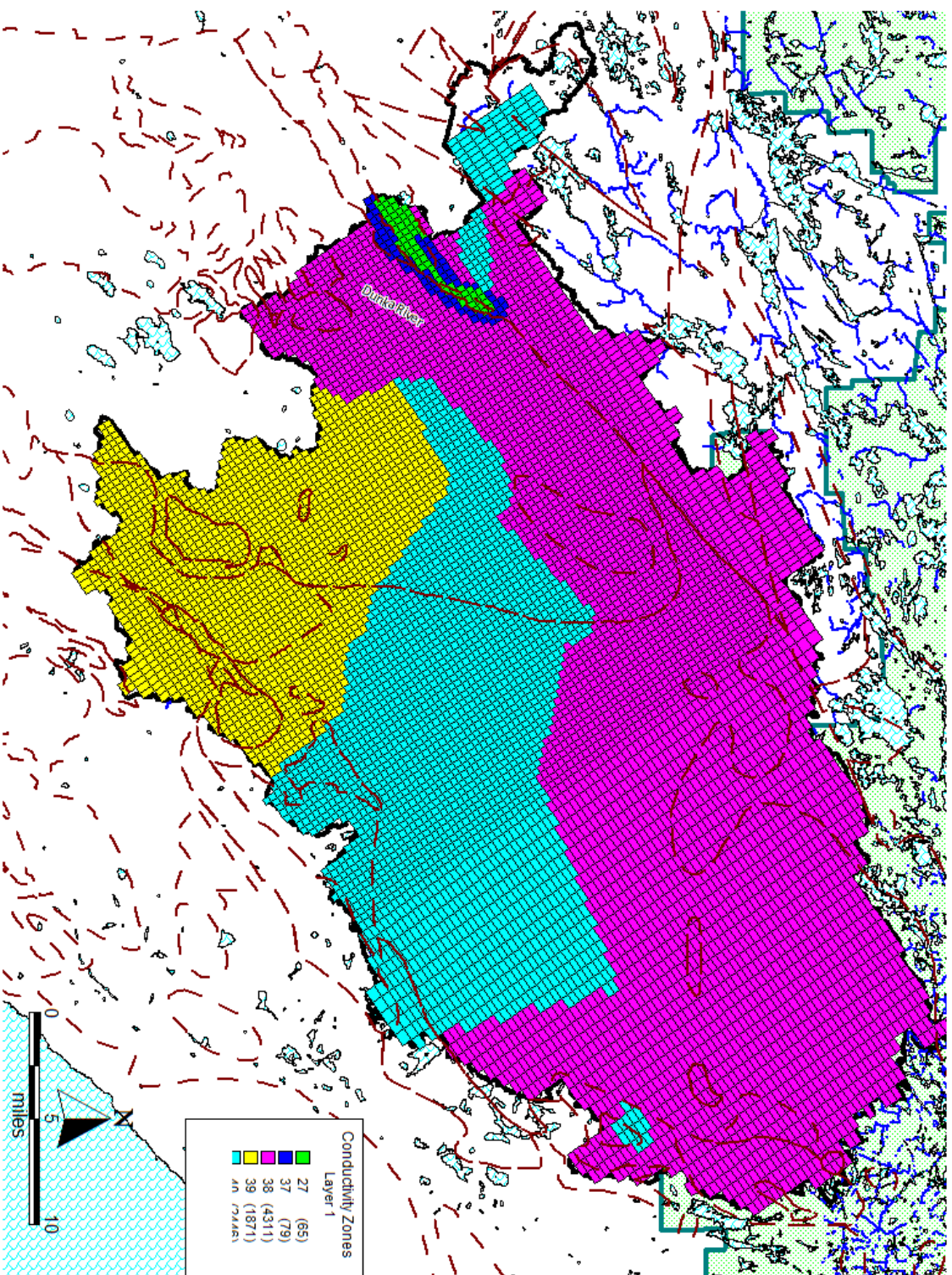


Fig. 14: Layer 1 hydrogeology zones. See Table 7 for final values. The outlines of geologic formations, which are mapped in Fig. 2, are included on this map.

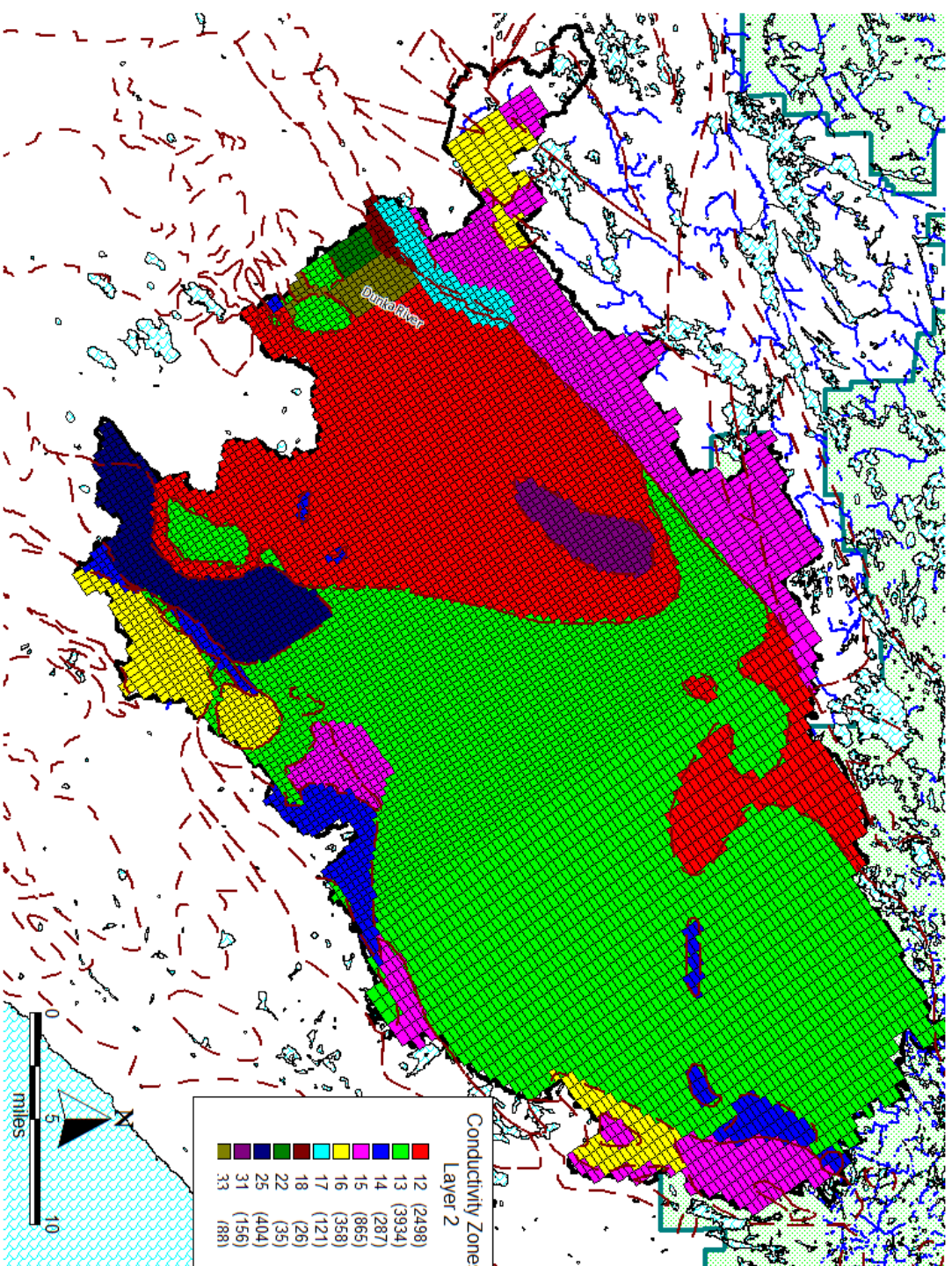


Fig. 15: Layer 2 hydrogeology zones. See Table 7 for final values. Geologic formation outlines, which are mapped in Fig. 2, are included on this map.

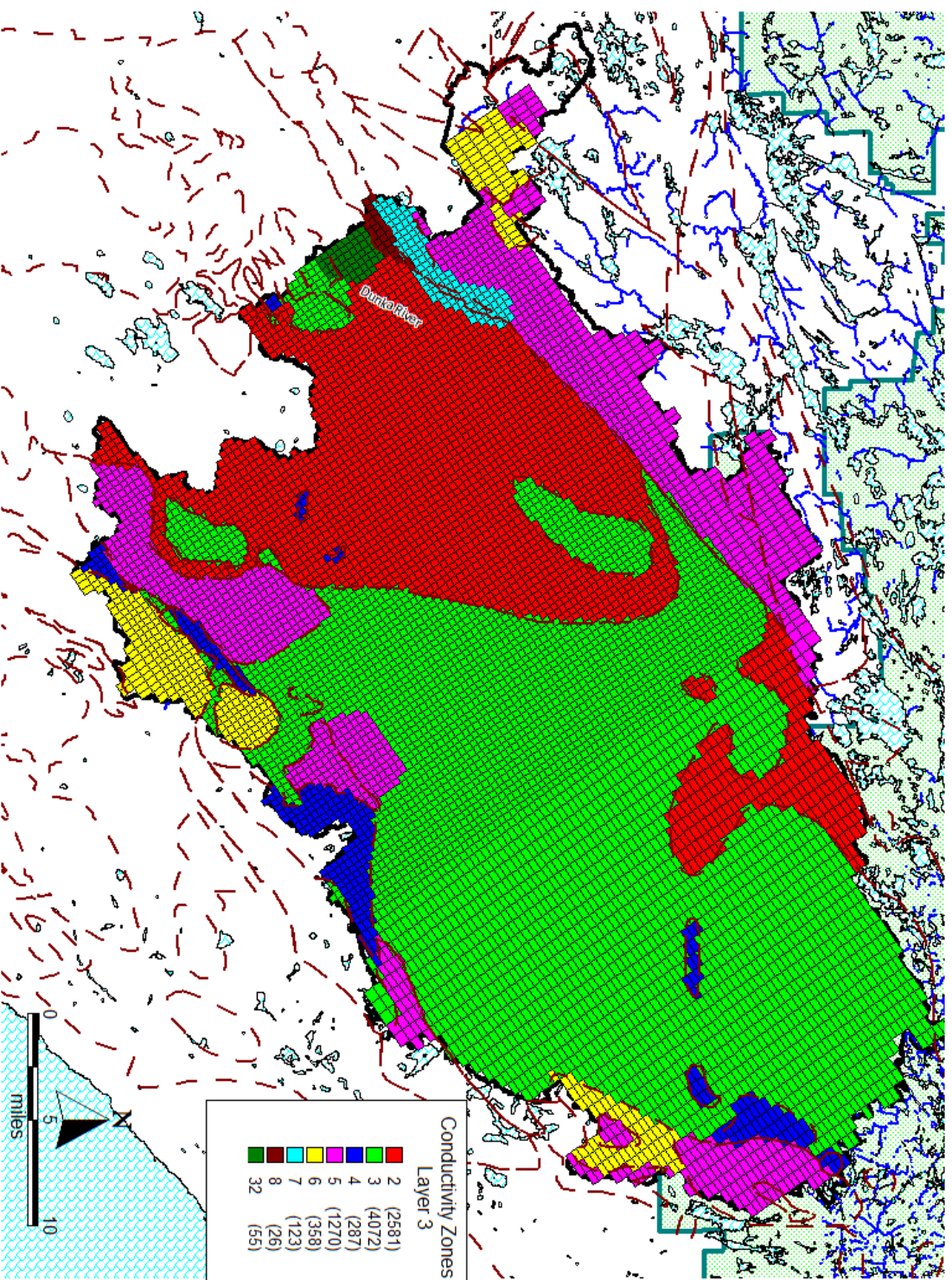


Fig. 16: Layer 3 hydrogeology zones. See Table 7 for final values. Geologic formation outlines, which are mapped in Fig. 2, are included on this map.

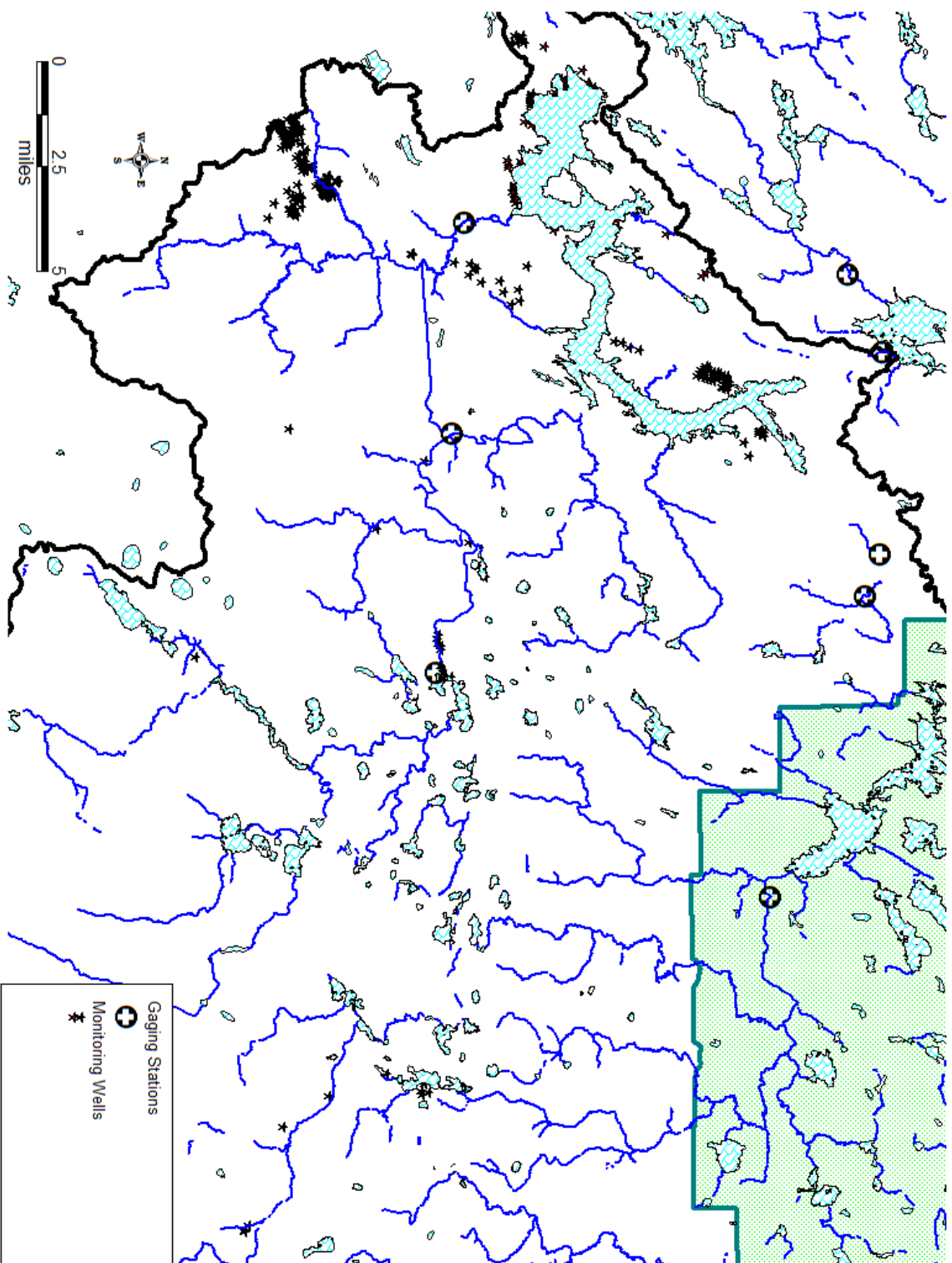


Fig. 17: Location of target wells in the study area.

Calibration

Calibration was completed in steady state mode because of the lack of transient data and because pumping stress is not simulated. Calibration is the process of adjusting K and boundary reach conductance to minimize certain test statistics, most specifically sum of squared residuals (SSR) and the actual mean (which should approach 0.0). A residual is the difference between the simulated and observed value so squaring the residuals and summing them provided an objective function which when minimized provides the best fit of the model to the observed data. Initial K values were 1 and 0.1 for bedrock layers 2 and 3, respectively. The high value for layer 2 was based on fractures and scale effects.

Initial calibration was completed using trial and error. Then, sensitivity analyses were conducted wherein the K value was multiplied by multipliers ranging from 0.5 to 2.0 times, to find the value which minimized SSR. Sometimes the analysis would yield local minimums, wherein the SSR is lower than for parameters values both higher and lower, but the calibration would continue until a global minimum SSR was found (if possible). Also analyzed in this way were various boundary conductance values. Finally, the automated MODFLOW-2000 parameter estimation routine was used to estimate composite sensitivities and to fine-tune the final parameter values.

Initial head for the steady state analysis for all layers was the ground surface, so simulated drawdown equals depth to water.

During calibration there was a tendency for groundwater to flow to and be prevented from crossing the no flow boundary on the north. The topographic divide along this border is less than 10 m above the surrounding areas in some locations and may not be a groundwater divide, at least not in all model layers. Because the simulated water level in all three layers was close to the observed values and they suggest a potential for cross-divide flow at depth, a general head boundary (GHB) was established in layers 2 and 3 to allow groundwater to cross the boundary in controlled locations. The GHB head and distance to the head was based on the water level in the lakes nearest the boundary (Fig. 12). Reaches were chosen based on low points in the topography and the location of lakes on both sides of the divide. The location of the GHBs influence flow paths through the domain, mostly through the Kawishiwi watershed. Adding the GHBs increased the SSR by just 400 (from 7900), so they did not have a huge effect on the simulated head values.

Calibration was deemed complete at a point where continued parameter estimation yielded composite scaled sensitivity (CSS) values within a few orders of magnitude for all parameters, the parameter estimates ceased changing, and the SSR was at a minimum. CSS is a dimensionless number that allows a comparative assessment of how sensitive a parameter is to

the observations available (Hill et al. 2000). If changing a parameter's value has little effect on the test statistics, the parameter is not sensitive. Correlation among parameters is also important. The relative size of the CSS can be used to consider whether to create additional parameter zones by splitting existing zones or, alternatively, whether to combine zones (which would occur if the CSS for a value is substantially lower than for other parameters).

Table 6 shows the unweighted and weighted test statistics. The SSR was 4405 and 2173 for unweighted and weighted targets, respectively. The standard deviation is 4.2 and 3.0% of the range in observations, from the lowest to highest groundwater elevation, which was 150 meters. The most interesting difference between the weighted and unweighted statistics was that the unweighted mean was slightly negative and the weighted skew was 0.82 which reflects that many of the ground surface targets had positive residuals because the simulated head was lower than the assumed observed depth below ground surface, which were near watershed divides in recharge zones.

Table 6: Steady state calibration test statistics for weighted and unweighted residuals. RMS is sum of root mean squared error.

	Residual	Weighted residual
Residual mean	-0.70	0.22
Median	-0.12	-0.08
Abs Res Mean	4.95	3.51
Res Std Dev	6.35	4.48
SSR	4404.94	2173.06
RMS error	6.39	4.49
Standard Deviation	6.38	4.50
Sample Variance	40.67	20.26
Kurtosis	0.27	1.23
Skewness	-0.09	0.82
Min Residual	-17.18	-8.96
Max Residual	14.97	14.97
Minimum	-17.18	-8.96
Maximum	14.97	14.97
Number	108	108
Range	150	150
Scaled Std Dev	0.0423	0.0299
Scaled Abs Mean	0.0330	0.0234
Scaled RMS	0.0426	0.0299

The relation of simulated to observed groundwater elevations scatters around a 1:1 line as it should (Fig. 18). There is no detectable trend with observed groundwater elevation and simulations should yield no bias. The trend of residuals with observed groundwater elevation also shows a nice scatter around the zero value. However, there is a slight tendency for residuals to slope up and to the right in a couple clusters on the graph. Each cluster corresponds to the clusters of observation wells (Fig. 19). The apparent trend could reflect a slope in the water table that is not simulated exactly in this model, or could indicate horizontal anisotropy (K_x differs from K_y) which would cause groundwater to flow preferentially in one direction. The slope of observed heads is steepest to the northeast, which suggests that K is highest in southeast to northwest direction. However, this is not conclusive because the wells are laid out in that general direction (along the string of mineral deposits) which also intersects at right angles with lakes. Birch Lake provides a sink which could draw the flow from higher points near the divides. This is more obvious in layer 2 in which the groundwater is more obviously connected to rivers and lakes. If the observations regarding K and the slope of observed heads just discussed are accurate, there would be a tendency for more flow and transport from the Stony River watershed toward Birch Lake and the BWCAW.

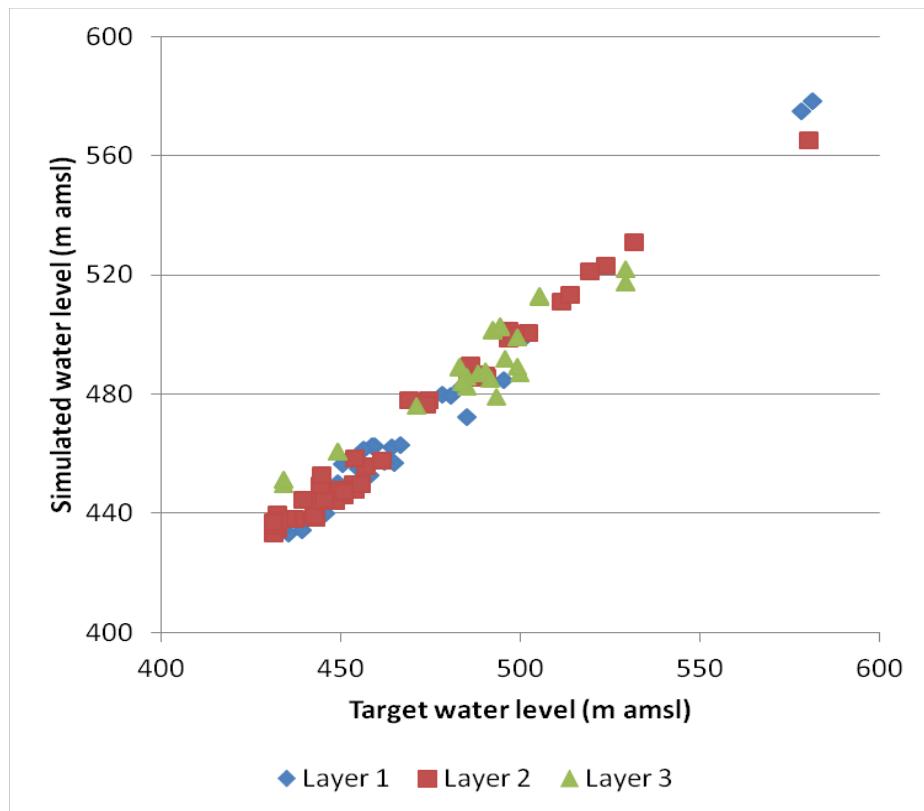


Fig. 18: Relation of simulated to observed water level, by model layer.

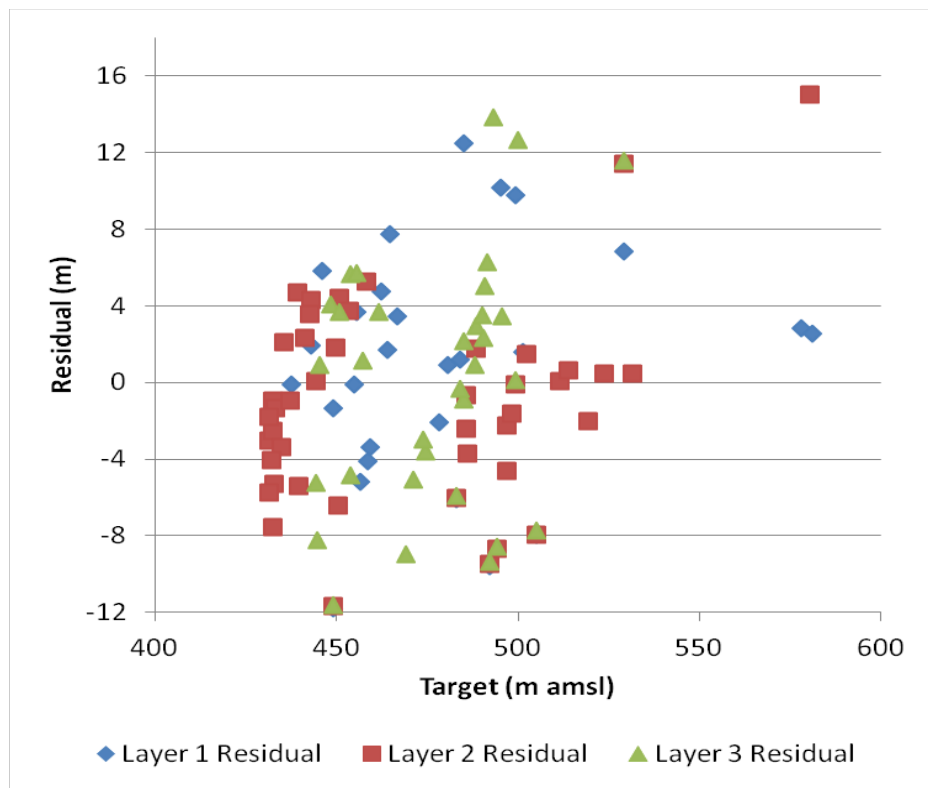


Fig. 19: Relation of residual to target groundwater elevation, by layer.

Final K zone values are shown in Table 7. The values for K_h in the surficial aquifer in layer 1 are high but well within the observed values discussed above while the K_v values reflect highly stratified till. Zone 37 has a high K_h but is an outcrop of Biwabik iron formation which has high measured values (Siegel and Ericson 1981).

Each bedrock formation has zones with K varying over at least two and usually three or four orders of magnitude. The parameter values show substantial variability, especially in the bedrock as would be expected in a heterogeneous domain with fractures. The simulated values may show additional variability because calibration was based on clusters of observations.

K decreases with depth for most formations, meaning that values in layer 3 are less than in layer 2, as expected due to the compaction occurring due to more weight and less weathering with depth. In zones 32 and 3, K_h was much less than K_v (Table 7). This demonstrates a tendency for vertical flow, and should be expected considering the zones are near the domain boundaries. The zones were adjacent and both are Duluth Complex, thus it is reasonable that the layers have upthrust so that the bedding has become vertical (Miller et al. 2002), which causes the observed high vertical anisotropy.

Table 7: Final calibrated conductivity values. Kh is horizontal K; Kv is vertical K.

Formation/lithology	Zone	Kh	Kv	Layer
Duluth Complex, troctolite/gabbro	2	0.307	0.01008	3
	12	0.342	0.137	2
	22	0.102	0.114	2
	32	0.00014	0.0182	3
	33	0.035	0.0145	2
Duluth Complex, anotrholite/gabbro	3	0.025	0.2	3
	13	2.9	0.4	2
	31	0.26	0.002	2
basalt/rhyolite	4	0.05	0.025	3
	14	0.1	0.06	2
Giants Range granite	5	0.0015	0.0015	3
	15	0.214	0.2	2
	25	0.8	0.5	2
gabbrow/ troctolite	6	0.27	0.01	3
	16	2	0.09	2
Biwabik iron formation	7	0.16	0.001	3
	17	0.36	0.0075	2
	27	0.3	0.001	1
	37	26	0.02	1
shale/siltstone	8	0.1	0.01	3
	18	2	0.1	2
Surficial aquifer	38	7.4	0.16	1
	39	1	0.05	1
	40	5.2	0.1	1

Layer 1 started out as just one zone, not the five shown in Fig. 14, but simulations were unstable, which caused SSR to vary both higher and lower with the parameter value multiplier. Varying K lowered residuals in one area while increasing them in other areas. Therefore, layer 1 was split into zones 38, 39, and 40 according to the soil maps as described above and zones 27 and 37 were added to reflect an outcrop. At one point during calibration it appeared that zones 27 and 37 were not sensitive, but combining them caused a several percent increase in SSR so the split was retained. Zones 39 and 40 were not sensitive while zone 38, which extends across much of the Kawishiwi and Birch Lake watershed, was sensitive, especially in the horizontal direction (Fig. 20, Layer 1). This zone affects the water table slope over much of the area that

has observation wells. The outcrops, zones 27 and 37, also influenced the water table slope near Birch Lake.

Zones 12 and 13 are sensitive in layer 2 (Fig. 20, Layer 2). Zone 13 is especially sensitive because it controls the water levels near the watershed divide where the artificial targets based on ground surface were added. Even with adjusting K_{x13} , these observations added the most to the SSR because they were among the highest residuals. Presumably this was because the zone was near topographic highs as described above. The weights are 0.3 which lessens their influence on K , but Fig. 20 does not account for weight. These areas are east of the mineral leases so the high residuals have little effect on the simulated transport. The only effect could be in the flux rate to the west across the study area.

Zones which cover larger areas also are more sensitive in layer 3 (Fig. 20, Layer 3). Varying the parameter multiplier from 0.5 to 2.0 added up to 300 to the SSR. Lowering or raising the value of a couple parameters, most notably K_{v32} , actually decreased the SSR by up to 100. However, doing so renders other parameters less than optimal.

CSS varied from 0.011 to 10.1, three orders of magnitude, although only five parameters had values greater than 1.0 (Fig. 21). Eleven of the lowest fourteen, and the lowest four, CSS were for vertical K . Fourteen of the highest seventeen CSS values were for horizontal K . This result indicates that K_h controls head values much more than K_v . The highest CSS is for zone 13, which controls the head values near the ground surface level observations, which were shown above to affect the model SSR more than other observations. In general, the CSS range is acceptable for final model calibrations.

The higher values for zones 38 and 40 indicate that the model accuracy could be improved substantially with more shallow wells throughout the domain. The DRAIN heads helped to control the head in these areas, which indicates that at least the water table elevation should be accurate. Without observations it does not affect SSR.

None of the eight lowest CSS values are in layer 3, which suggests that deep parameter zones have substantial influence over the head in upper layers. This indicates that additional deep wells spread throughout the domain would be useful to improve modeling and predictions should hydrology studies ever be undertaken to develop these deposits.

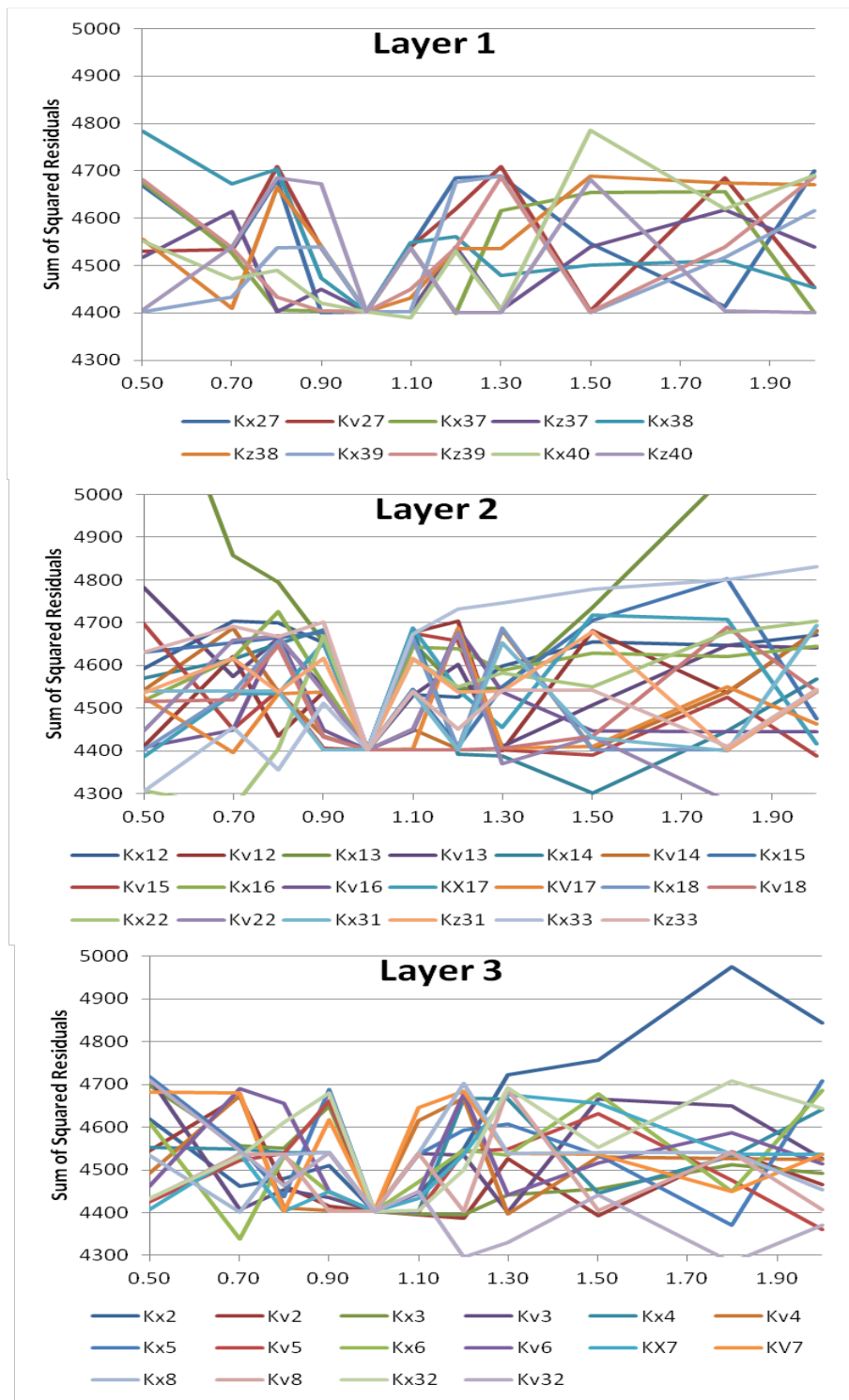


Fig. 20: Sensitivity of individual conductivity parameters, by layer. Note the different vertical axis scales.

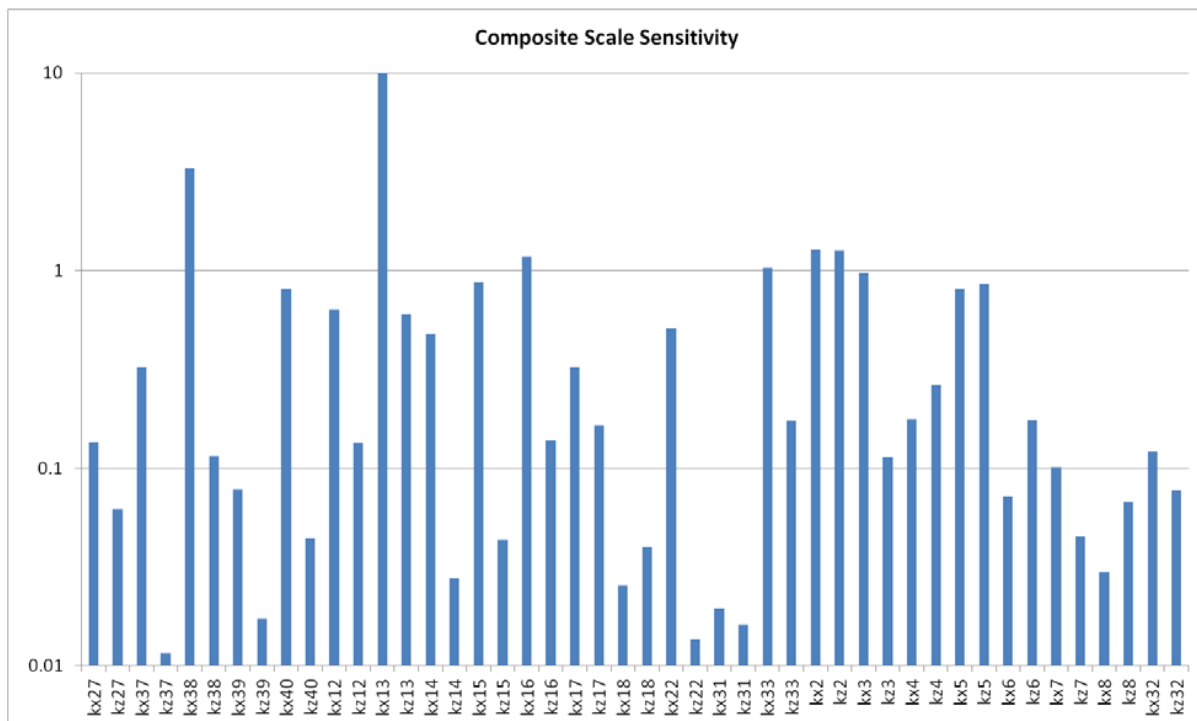


Fig. 21: Composite sensitivity for most hydraulic conductivity parameters. Note the logarithmic vertical scale.

Simulated head values generally show groundwater movement from southeast to the north and northwest, as discussed above with respect to the GHBs (Figs. 22 through 24). The water table in layer 1 follows the irregular topography (Fig. 22) with higher points being dry. The contours in deeper layers reflect a more consistent slope to the northwest (Fig. 23 and 24).

Nuances in the head contours reflect heterogeneities in and variations in the values of the calibrated K zones. The most obvious area is above zone 31 (most obviously in layer 2) about five to seven miles east of Birch Lake (Fig. 23).

The depth to water in layer 1 primarily ranges from zero to about 10 m, although a few areas in the west and south have head levels above ground surface, reflected as a negative depth to water (Fig. 25). These areas reflect an upward gradient with the very low Kv. Areas in all layers that have substantial positive depth to water occur under the small ridges where the water table slope is less than ground surface slope (Figs. 25 through 27). Negative values in layer 3 demonstrate an upward gradient to Birch Lake (Fig. 27).

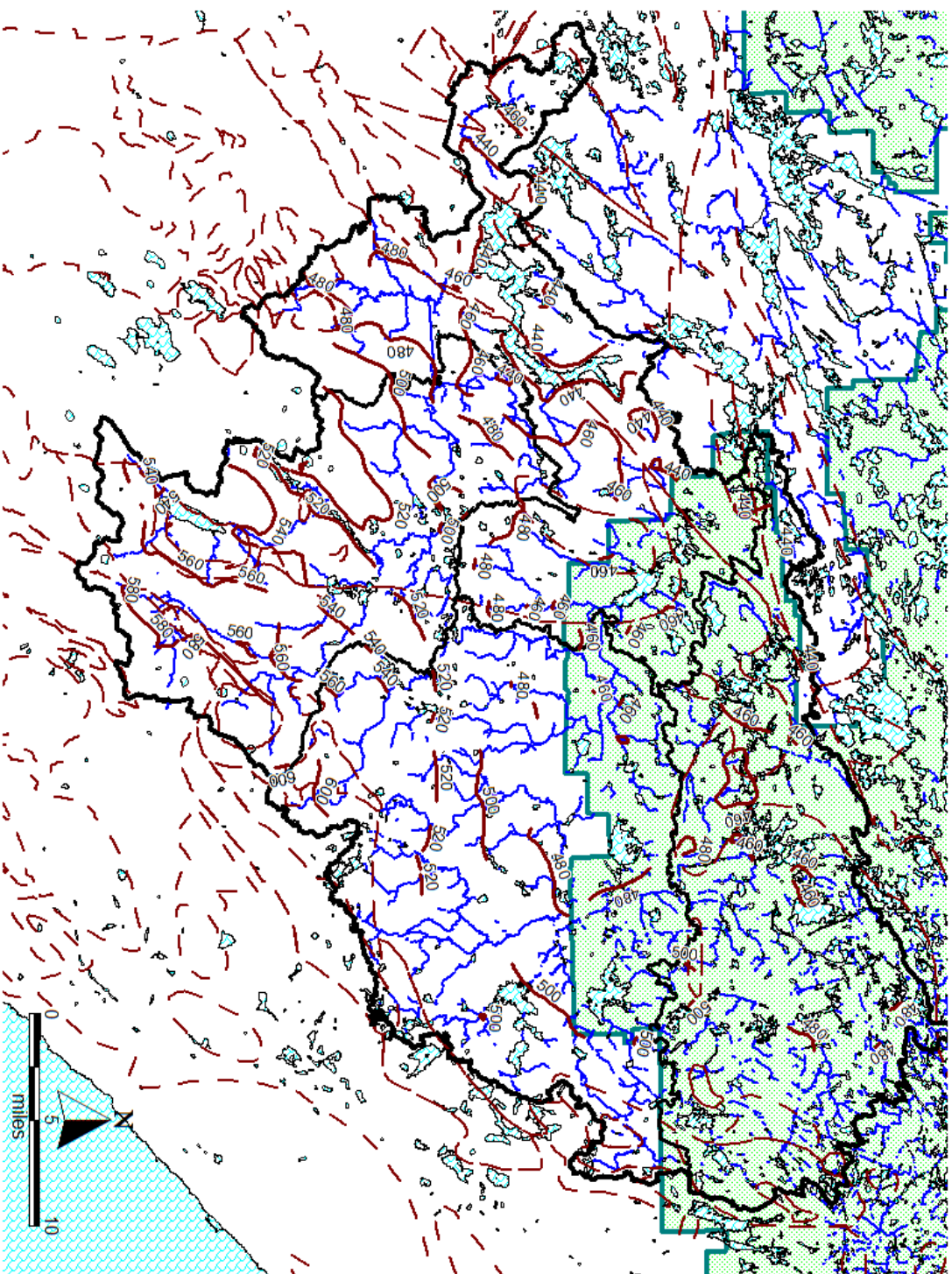


Fig. 22: Steady state head contours, layer 1. Areas without contours are dry.

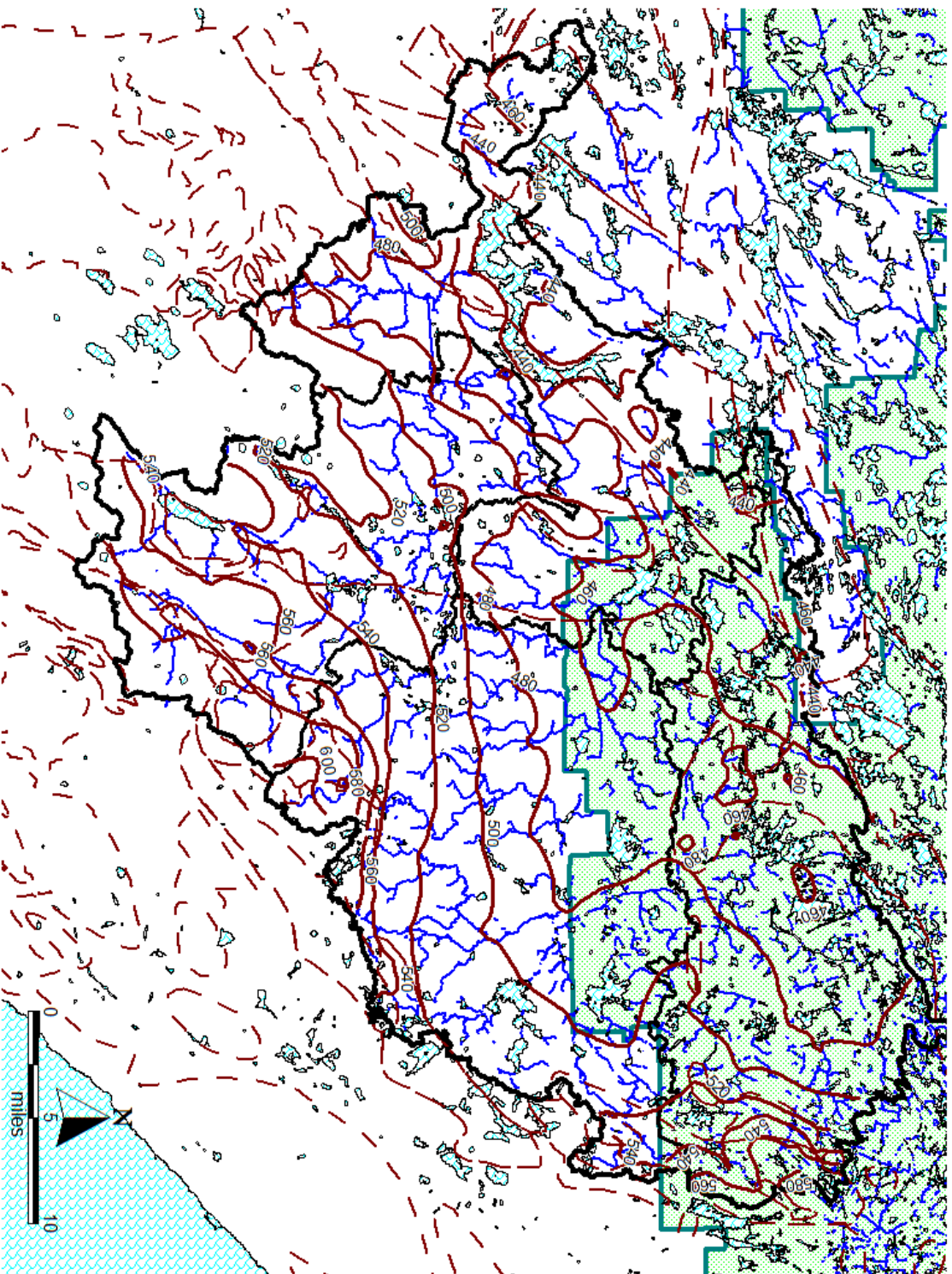


Fig. 23: Steady state head contours, layer 2.

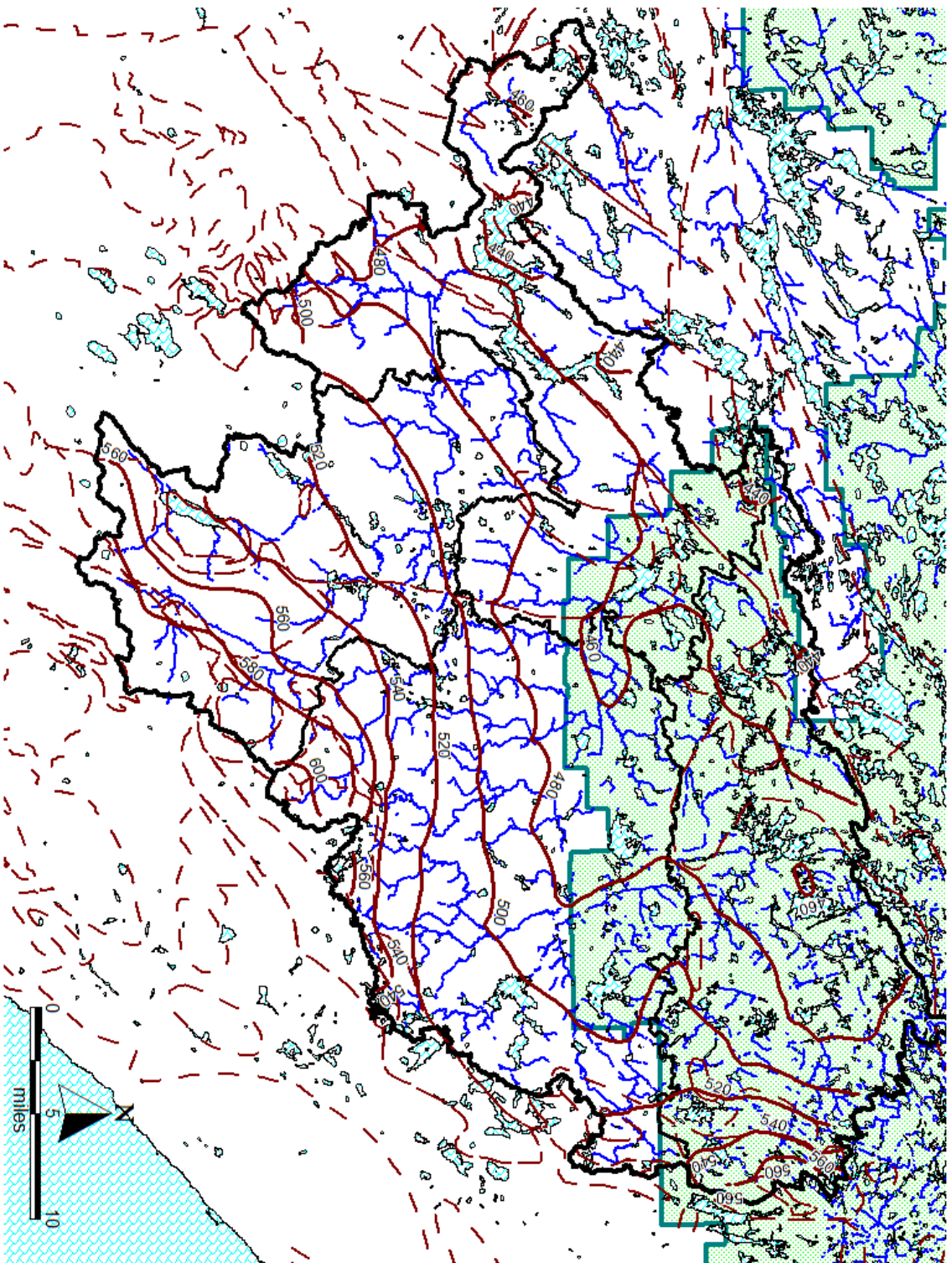


Fig. 24: Steady state head contours, layer 3.

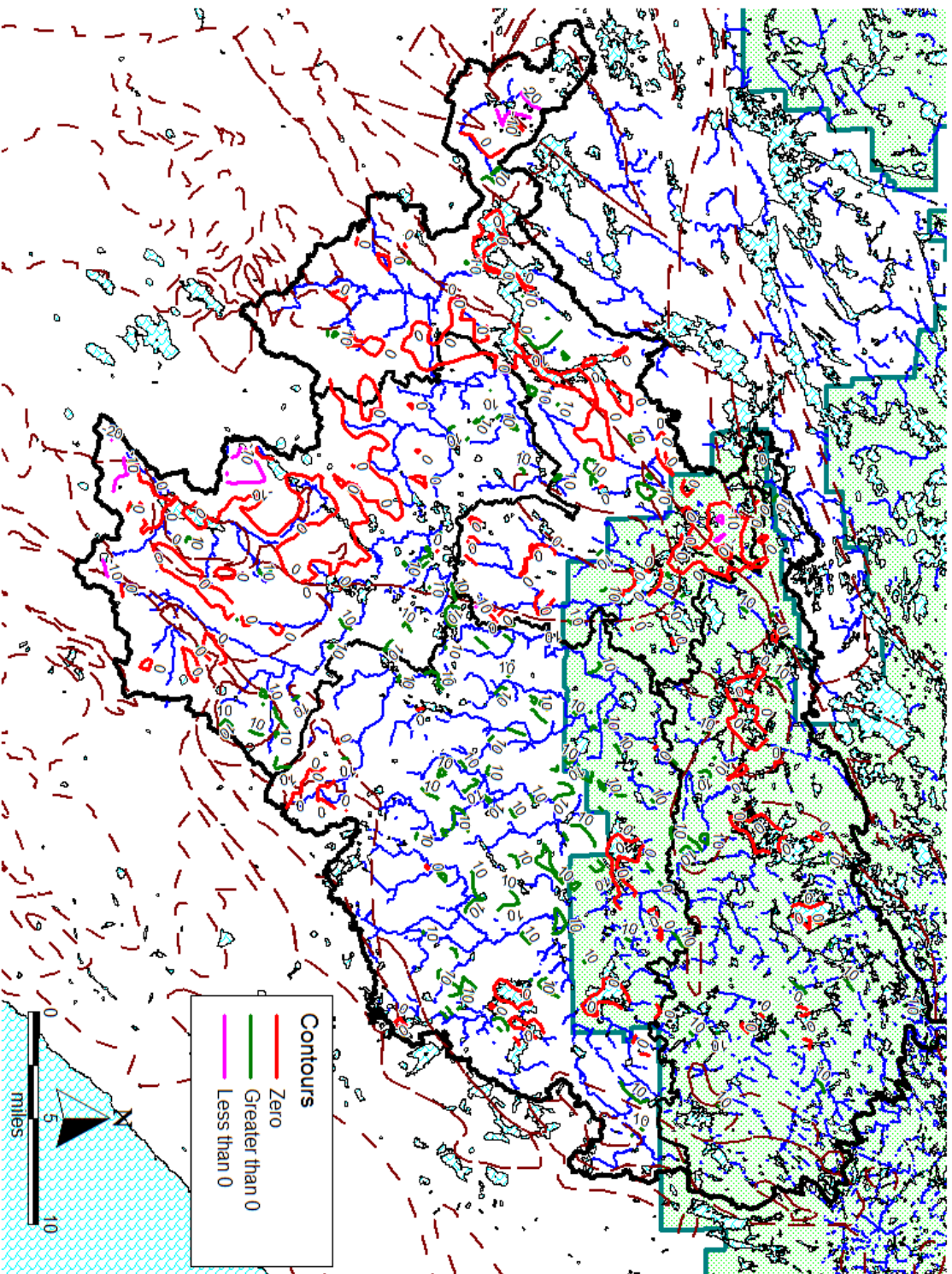


Fig. 25: Steady state difference from ground surface contours, layer 1.

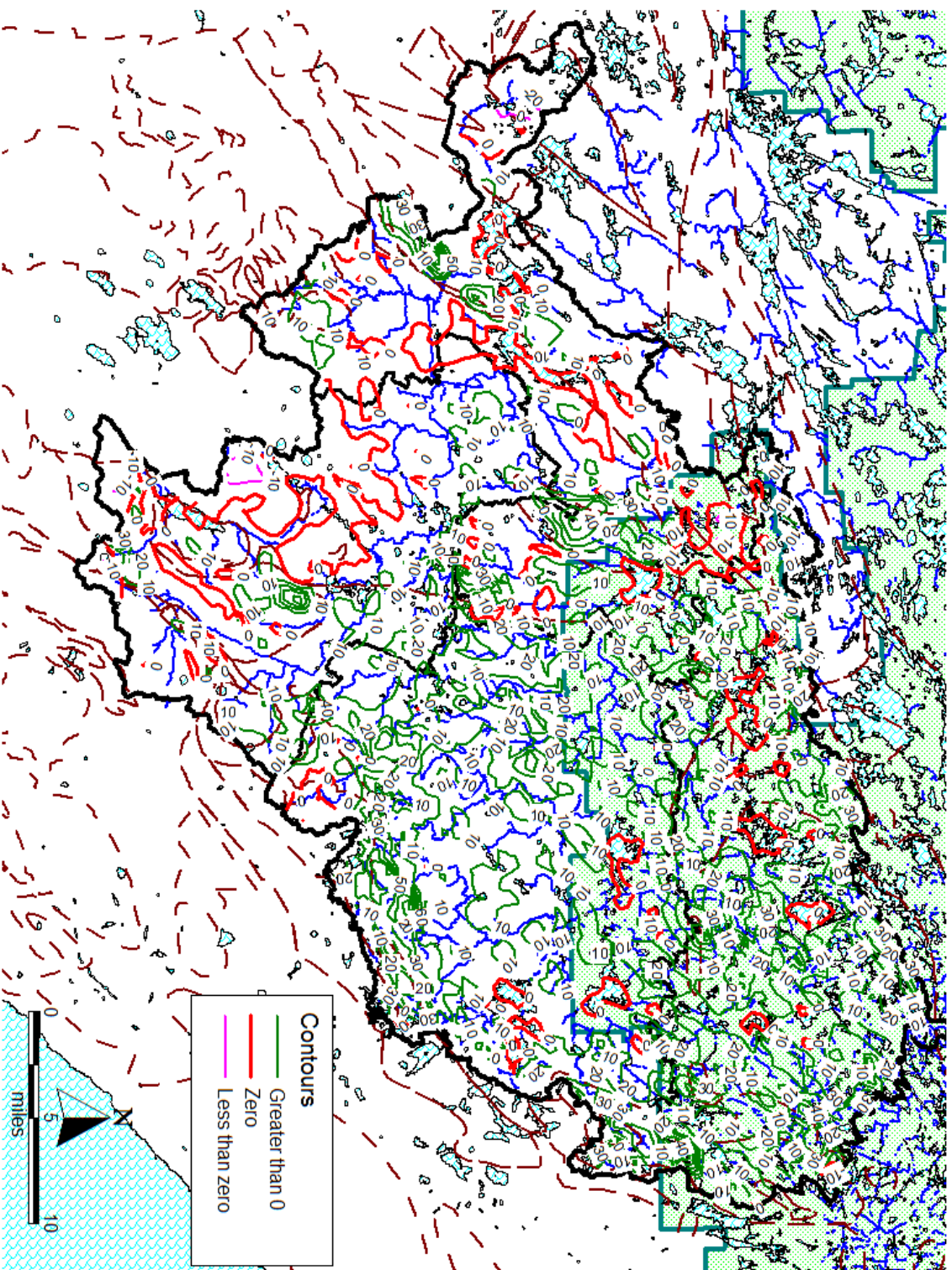


Fig. 26: Steady state difference from ground surface contours, layer 2.

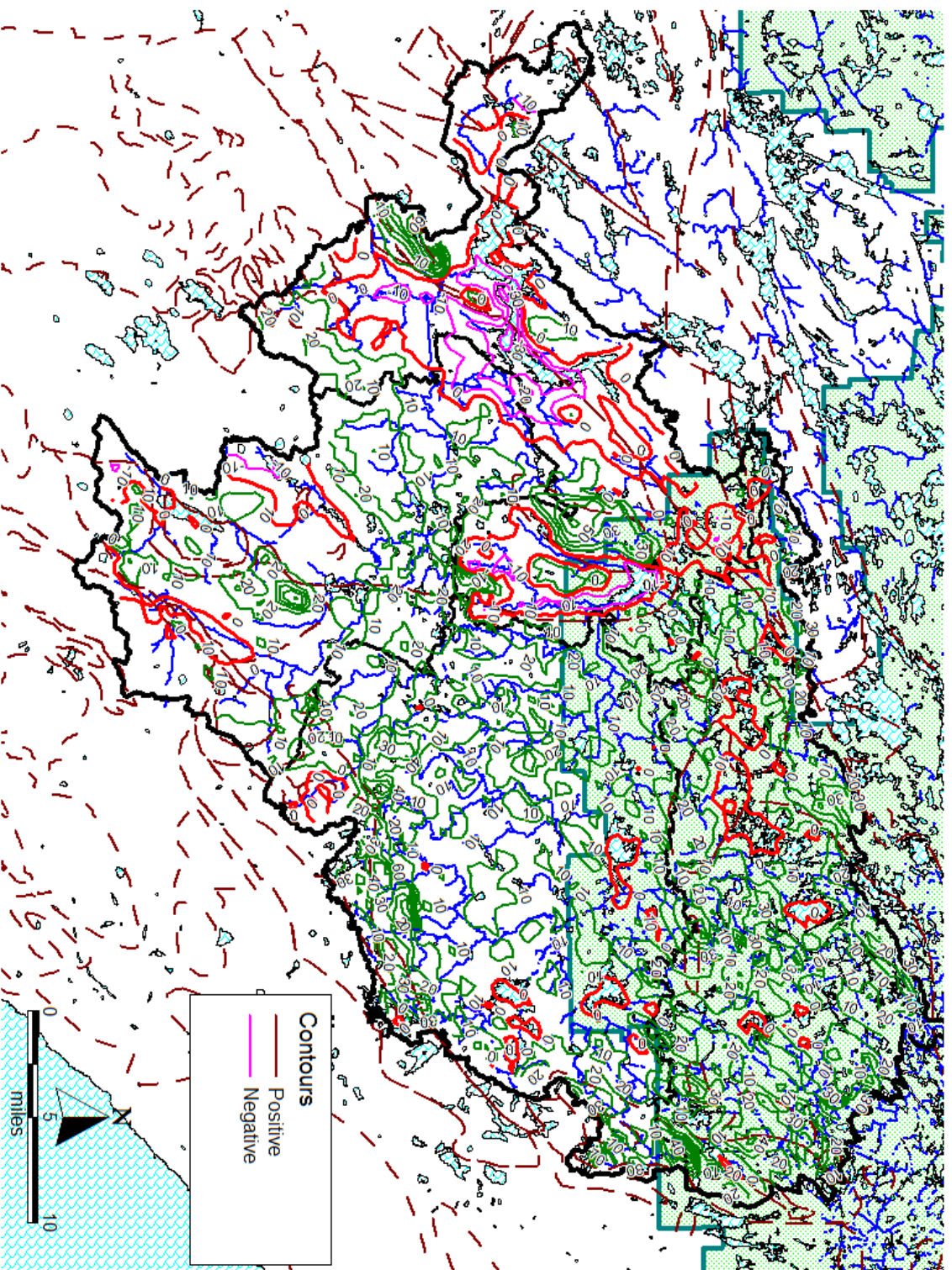


Fig. 27: Steady state difference from ground surface contours, layer 3.

Water Balance and Flux to the Rivers

The water balance table (Table 8) shows that total flux from the model is within about $12 \text{ m}^3/\text{d}$ of the total recharge, as it must be if the model converges. Total recharge in zones 2 through 5 was set equal to the estimated baseflow from the watershed that ultimately discharges to the rivers and lakes (which are assumed to be hydraulically connected to the rivers)³. Recharge was close to discharge in the Isabella and Stony River watersheds but varied by from 10 to 20% in the other watersheds (Table 8). The Kawishiwi River watershed is somewhat lower and the general groundwater flow direction was toward that watershed (Figs. 22 through 24). Groundwater was allowed to flow northeast through GHBs, which account for much of the additional discharge from that watershed. Net discharge from the model through GHBs was about $28,000 \text{ m}^3/\text{d}$. The Birch Lake watershed has less discharge than recharge. However, the percent differences between watersheds are small and show that the distribution of recharge and discharge through the model domain is accurate.

All ten river reaches gain flow more slowly in their headwaters (more horizontal cumulative flux line) and gain more rapidly toward the outlet from the watershed (Fig. 28). Ten of the simulated lakes received zero discharge because they were in the upper portions of the watersheds. Both reflect that the headwaters are primarily recharge rather than discharge zones in the watersheds, as may also be seen on the depth-to-water maps showing areas near higher points having a much deeper water table (and dry areas in model layer 1) (Figs. 25 through 27).

The GHBs prevented the head contours from extending above the ground surface near the model boundary. The GHB discharge is a very small proportion of the recharge so little transport across the boundary would occur.

Birch Lake is a large lake near the outlet from the study area. The model simulated discharge into the lake (reach 1) is almost $75,000 \text{ m}^3/\text{d}$. Head contours and velocity vectors (not shown) demonstrate converging flow at the lake, so it would be a natural sink for contaminants. Especially in layer 3, the difference from ground surface contours are negative, demonstrating an upward gradient from that layer toward the lake. The boundaries for the S Kawishiwi and the Kawishiwi River also show converging flow due to the discharge to the river.

³ These boundaries were originally set to be RIVER boundaries to allow water to flow in and out of the surficial aquifer. It became difficult during calibration to balance distributed recharge with river recharge and the RIVER boundaries kept the groundwater level too high. Using DRAIN boundaries may lose some of the surface/groundwater interaction, but this primarily would be in areas that are perched, or above the actual water table.

Table 8: Water balance (m³/d) from groundwater model, including DRAIN, general head boundary (GHB), and recharge fluxes, by watershed (BL-Birch Lake, IR- Isabella R, SR- Stoney R, KR - Kawishiwi R.) See Fig. 12 for GHBs.

Name		Reach or Zone	Watershed	Flux	Sum GHB and DRAIN by Watershed	
	Recharge	2	KR	373302	-409668	
	Recharge	3	IR	432989	-439274	
	Recharge	4	SR	291247	-288608	
	Recharge	5	BL	327444	-287444	
Total				1424982	-1424994	
	GHB	1	BL	-1549		
Birch Lake	DRAIN (lake)	1	BL	-74868		
Argo	DRAIN (lake)	2	BL	0		
Bruin	DRAIN (lake)	3	BL	-7064		
Clear	DRAIN (lake)	4	BL	-646		
Bald Eagle	DRAIN (lake)	36	BL	-21722		
August	DRAIN (lake)	37	BL	-1687		
Filson Cr	DRAIN	75	BL	-11230		
S Kawishiwi R, Keeley Cr	DRAIN	76	BL	-60906		
Snake R, Robin Cr, Bald Eagle Cr, August Cr	DRAIN	78	BL	-107772		
Hog	DRAIN (lake)	22	IR	0		
Clear	DRAIN (lake)	23	IR	0		
Perent	DRAIN (lake)	25	IR	-8821		
Silver Island	DRAIN (lake)	26	IR	-4425		
Harriet	DRAIN (lake)	27	IR	-1979		
Dumbbell	DRAIN (lake)	28	IR	0		
Isabella Lake	DRAIN (lake)	41	IR	-3657		
Isabella River, tributaries	DRAIN	74	IR	-420392		
	GHB	2	KR	-904		
	GHB	3	KR	261		
	GHB	4	KR	-13427		
	GHB	5	KR	-8866		
Pickeral	DRAIN (lake)	5	KR	-4415		
	GHB	6	KR	-1905		
Greenstone	DRAIN (lake)	6	KR	-285		
	GHB	7	KR	-1787		
	DRAIN (lake)	7	KR	-4496		
	GHB	8	KR	3781		
One Lake	DRAIN (lake)	8	KR	-2143		

Table 8: Continued						
Three, Four Lake	DRAIN (lake)	9	KR	-13081		
Hudson	DRAIN (lake)	10	KR	-510		
Insula	DRAIN (lake)	11	KR	-12912		
Alice Lake	DRAIN (lake)	12	KR	-8851		
Bow Lake	DRAIN (lake)	13	KR	0		
Boulder Lake	DRAIN (lake)	14	KR	0		
	DRAIN (lake)	15	KR	-1182		
	DRAIN (lake)	16	KR	0		
Koma	DRAIN (lake)	17	KR	-802		
Polly	DRAIN (lake)	18	KR	-3157		
Phoebe	DRAIN (lake)	19	KR	0		
Grace	DRAIN (lake)	20	KR	0		
Beth	DRAIN (lake)	21	KR	-647		
Kawishiwi Lake	DRAIN (lake)	24	KR	-1214		
Headwaters, Kawishiwi R	DRAIN	77	KR	-280643		
Kawishiwi R nr outlet	DRAIN	79	KR	-11417		
Denley, Nira, & Harris Cr	DRAIN	80	KR	-41067		
Greenwood	DRAIN (lake)	29	SR	-3036		
Sand	DRAIN (lake)	30	SR	-3684		
McDougal	DRAIN (lake)	31	SR	-1004		
Bongaa	DRAIN (lake)	32	SR	-1364		
Wampus	DRAIN (lake)	33	SR	-1411		
West Chub	DRAIN (lake)	38	SR	0		
Slate	DRAIN (lake)	39	SR	-342		
Stony Lake	DRAIN (lake)	40	SR	-5758		
Dunka R and tribs	DRAIN	71	SR	-73129		
Nip Creek	DRAIN	72	SR	-31066		
Stony R, Greenwood R, Stockade Cr, Homestead Cr, Mary Ann Cr, Spur End Cr, Wilbur Cr	DRAIN	73	SR	-167814		

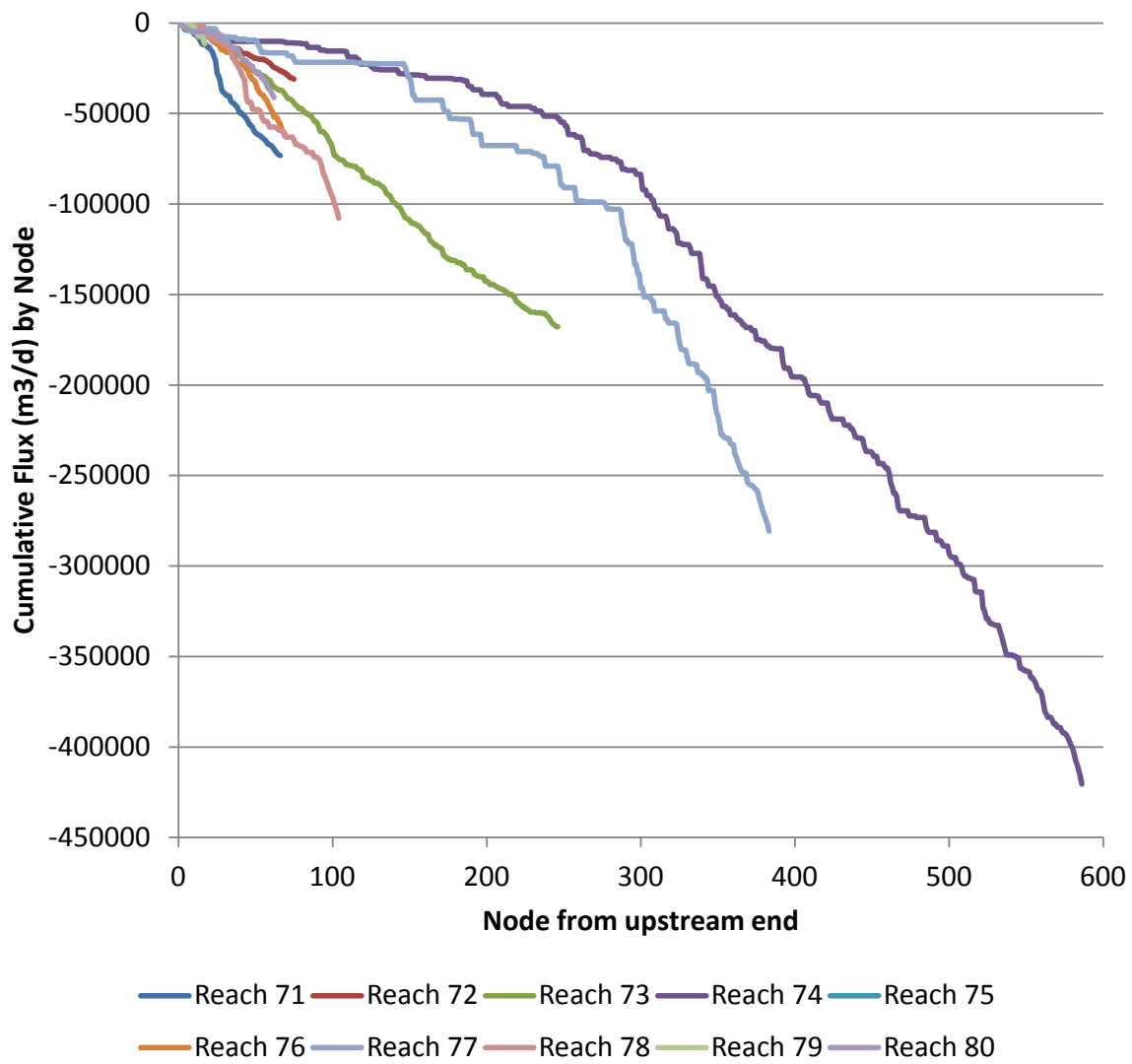


Fig. 28: Cumulative flux from upstream to downstream, by model node.

Potential Twin Metals Copper Mining

There are mineral leases throughout the Stony River and Birch Lake Watersheds (Fig. 29), which are the contaminant sources simulated below. Myers (2013c) reported on the leases held by Twin Metals, although they are just a portion of the potential mineral leases in the area. Twin Metals is a joint venture between Duluth Metals Corporation and Antofagasto Minerals (http://www.miningminnesota.com/who_companies.php, accessed 6/16/14). Duluth Metals has acquired Franconia Minerals (Id.).

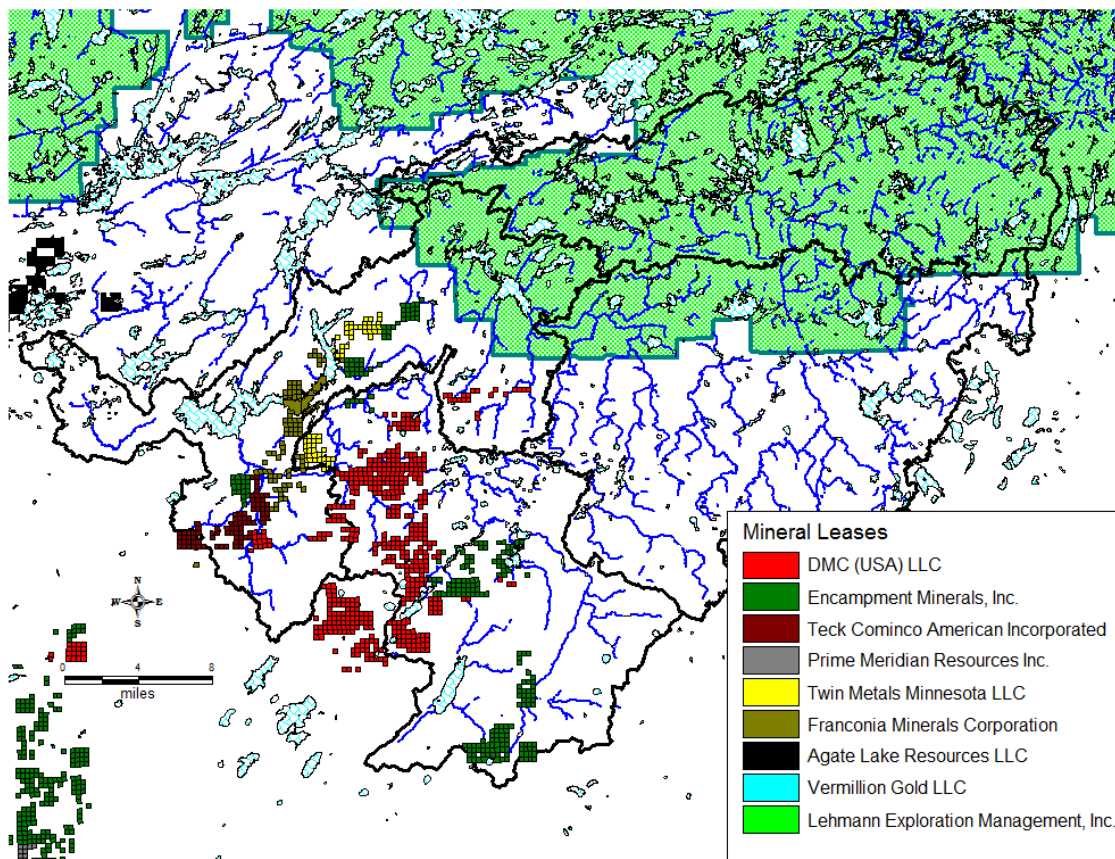


Fig. 29: Location of mineral leases in the study area. See Fig. 1 to identify the watersheds. Many leases in the Birch Lake watershed lie next to the lake.

Twin Metals proposes mining at four mineral deposits – Maturi, Maturi Southwest, Spruce Road, and Birch Lake - located 10 miles east of Babbitt, MN and 15 miles southeast of Ely MN. All four deposits are in the Birch Lake watershed and lie south of the South Kawishiwi River or adjacent to the west end of Birch Lake (Fig. 30). Each deposit would likely be accessed with underground methods (Parker and Eggleston 2014; Cox et al 2009). The reserve calculations

were based on underground mining methods but some deposits, including Maturi Southwest, reach close to the surface which could lead to some surface mining. Twin Metals (2014) suggests that 55% of the tailings could be deposited underground. A tailings impoundment may be constructed at the Dunka Mine site, with some tailings backfilled into the abandoned open pit (Cox et al 2009); this is not simulated herein.

The deposits are all hosted in the Duluth Complex, a composite intrusion, in the basal portion of the South Kawishiwi intrusion. The mineralized zone is as much as 1000 feet thick in locations. All deposits are magmatic nickel-copper-platinum group element deposits which are mostly considered sulfide deposits (Parker and Eggleston 2014). They occur in localized areas along the basal zone of the South Kawishiwi at the contact (Miller et al. 2002, p 167). The sulfide content of the Spruce Road deposit is 2 to 5% by volume and 3 to 4% by weight, with chalcopyrite being the primary copper sulfide; it is the only deposit with sulfide content specified. This exceeds the sulfide concentration at the proposed Polymet mine (Polymet 2013a).

The Maturi deposit extends from near ground surface to as much as 4500 feet below the ground surface. The depth of the Spruce Road deposit ranges from the ground surface to about 1500 feet bgs. The Birch Lake deposit ranges 700 to 2200 feet below ground surface. The Birch Lake deposit contains up to eight possible significant faults (Parker and Eggleston 2014), which are identified as substantial issues which will potentially affect the underground mining operations and the location of high grades of mineralization. Faults can also affect groundwater flows, but there is little evidence available to determine whether they are conduits or blockages to flow.

Based on the head contours, showing a southeast to northwest trend, developed in the numerical modeling above (Figs. 22 through 24), contaminants released from these leases will move toward rivers that flow into the BWCAW. Most will flow through the Birch Lake watershed. Surface waters from both Stony River and Birch Lake watersheds drain through Birch Lake and the S Kawishiwi River to the Kawishiwi River and into the BWCAW.

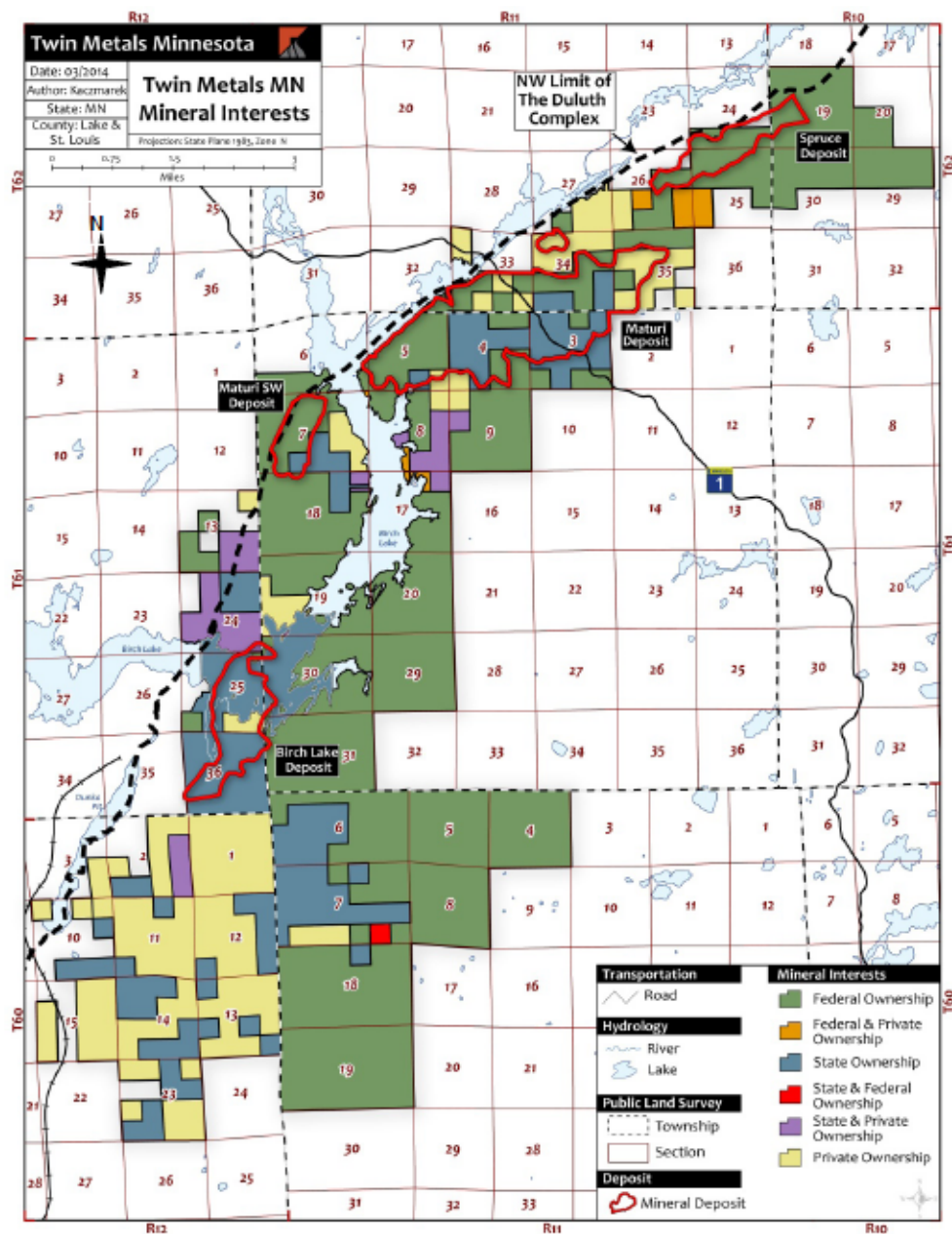


Fig. 30: Snapshot from Figure 4-3 in Parker and Eggleston (2014) showing the location of the Birch Lake, Maturi, Maturi Southwest, and Spruce Road deposits. Scale is provided by the squares which are approximate townships.

Particle Tracking

A particle tracking analysis of the flow model developed above determines the advective pathway for contaminants introduced at any given point to their final sink, or discharge point. Advective pathway means simply the path that a particle will follow if not subject to dispersion or attenuation. Particle tracking was completed using the final steady state flow model using the program MODPATH (Pollock 1994).

Contaminants were placed in approximately 630 model cells coincident with mineral leases (Fig. 29) at five different levels - the middle and top of layer 3, the middle and top of layer 2, and the top of layer 1, or the water table. The first four placements would represent a contaminant leaching from an underground mine facility. The middle of layer 3 is approximately 750 m (c 2460 ft) below ground surface (bgs), although it is variable. The top of layer 3 and middle and top of layer 2 are 140, 77.5, and 15 m bgs, respectively (460, 254, and 49 ft). The water table entry point would represent the point of a surface leak or spill seeping through the vadose zone to the water table. This analysis tracks the path a particle would take and the time for it to travel from source to sink. Neither the load nor concentration is important in this analysis.

All analyses were completed in the forward mode, meaning that particles were released at time zero and tracked forward in time until they reach a sink, which in all cases was a DRAIN boundary. MODPATH utilizes the head and cell-by-cell flow solution from MODFLOW. It does not directly use aquifer properties beyond the solution other than porosity, which controls the rate that a particle advects along with the groundwater flow.

In bedrock, fractures control permeability and secondary porosity, and also flow paths. In the Biwabik formation, porosity is as high as 50% due to leaching. This is zone 17 and 7, for which porosity was set to 0.4 and 0.3, reflecting the compaction with depth. Zones 18 and 8 are shale in layers 2 and 3 with porosity set at 0.05 and 0.03, reflecting little-fractured shale and compaction. Zones 15 and 5 are Giants Range granite, which typically has very low porosity; here zone 15 is set at 0.05 and zone 5 at 0.03, for layers 2 and 3 respectively. These values are slightly elevated because the calibrated K suggests some fracturing. The remaining formations are Duluth complex including some intrusions (Fig. 2). They are a combination of sedimentary and volcanic rock. The upper portions would have porosity exceeding 0.1; porosity in deep portions, below 750 m, would be less than 0.05. Zones 12 and 13 would have porosity equal to 0.12, and zones 2 and 3, layer 3, were set to 0.07 (they are not as deep as Thorfeison 2008, Fig. 38). Zones 16 and 6 are mafic intrusive rock, which likely has slightly higher porosity, so are set to 0.14 and 0.08, respectively. Zone 4 and 32 were combined with zones 2, 3, 12, and 13, based on being adjacent. See Figs. 14 through 16 for maps of parameter zones.

Results of Particle Tracking

Each contaminant introduction into a cell starts a transport pathway to a sink, so the useful results are a determination of which areas would drain contaminants to a river through which they can reach the BWCAW, and how long it takes for a particle to reach a river. The longer the transport time, the more dilution and attenuation that could occur to a contaminant plume. The analysis tends to overestimate the shorter times, however, because actual bedrock fractures could be much tighter in certain areas which would concentrate more flow in a smaller area than considered in individual model cells.

Particles introduced at the middle level of layer 3, or about 750 m bgs, required the longest time of any of the particle introductions to reach surface water (Fig. 31). The minimum time was 26 years, and approximately 5.7% of the locations reached sinks in less than 100 years, with travel times extending to greater than 10,000 years for many pathways. About 2.8 and 23.5% of the particles released at the top of layer 3 and middle of layer 2 reached the surface in less than 50 years, respectively (Fig. 31). The risk clearly increases as the source becomes closer to the surface.

The primary factor controlling transport time, other than distance from the sink, is whether the particle sinks deeper into the bedrock. As seen above and in Figs. 32 and 33, groundwater travels downward in certain areas. Contaminants released in such an area would not present substantial risk to the BWCAW at least for a short-term period after mine construction. However, the transport through fractures could speed the travel time more than indicated herein. Also, longer pathways could result in contamination reaching the BWCAW after mining has ceased.

Most particles released at the water table reach surface water quickly, with 21% of particles reaching surface water within 10 years and 62.9 % in 50 years. Transport of some particles was only a year or two. The short layer 1 pathways demonstrate this (Fig. 32). Short pathways from the water table source were generally those located closer to larger rivers. Interestingly, some of the longer transport times occurred because particles were transported deeply into layer 2 or even layer 3 (Fig. 33). These pathways originate in the west-central portion of the Stony River watershed and flow northwest toward tributaries to Birch Lake. These sites are distant from sinks, in locations where recharge dominates the vertical flow in layer 1.

Certain particles released at the top of layer 2 exhibited different behavior than those at other release levels (Fig. 31). Particles simulated to be released into a cell with upward flow into a DRAIN cell in layer 1 reached surface water in less than a year, and in some cases in just a few days. In some instances the bottom of a DRAIN cell intersected the top of layer 2. These extremely short times did not occur for releases in layer 1 because the water table in those cells

was several meters above the river level. These very short transport time estimates are likely unreliable.

Between less than 0.2 and 0.5 proportion (Fig. 31), particles released at the top of layer 2 appeared to transition from resembling layer 1 to middle of layer 2 releases (Fig. 31). This indicates that some of the particles that were not quickly captured by the DRAINS were transported deeper into the layer.

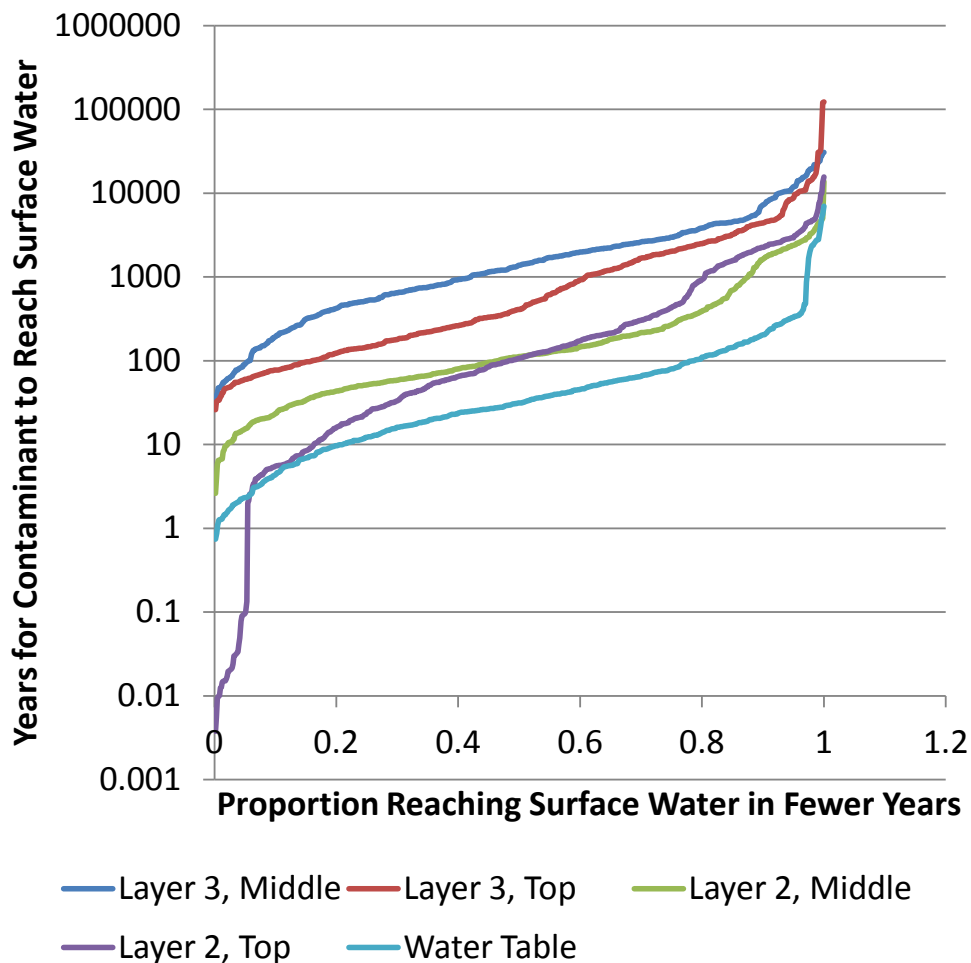


Fig. 31: Proportion of particles reaching surface water sources in a number of years. Note that years are on a logarithmic scale.

Adding the particles at the top of layer 3 resulted in generally much longer pathways, primarily through layer 3 (Fig. 33). Some of the pathways originate in the Stony River watershed and flow into the BWCAW. Pathways through layer 2 are much shorter in each direction (Figs. 32

and 33). This reflects the higher vertical anisotropy through that layer and generally higher vertical K. The longer flow paths through layer 3 reflect the layer's thickness and the variable vertical flow direction. Short pathways result from particle introduction in layer 3 where a river boundary is close; in these areas the flow is upward toward the sink and the particles advect along with the flow. The flow pathways for particle introduction in the middle of layers 2 and 3 are similar to that for the particles introduced at the top of layer 3 (Fig. 33).

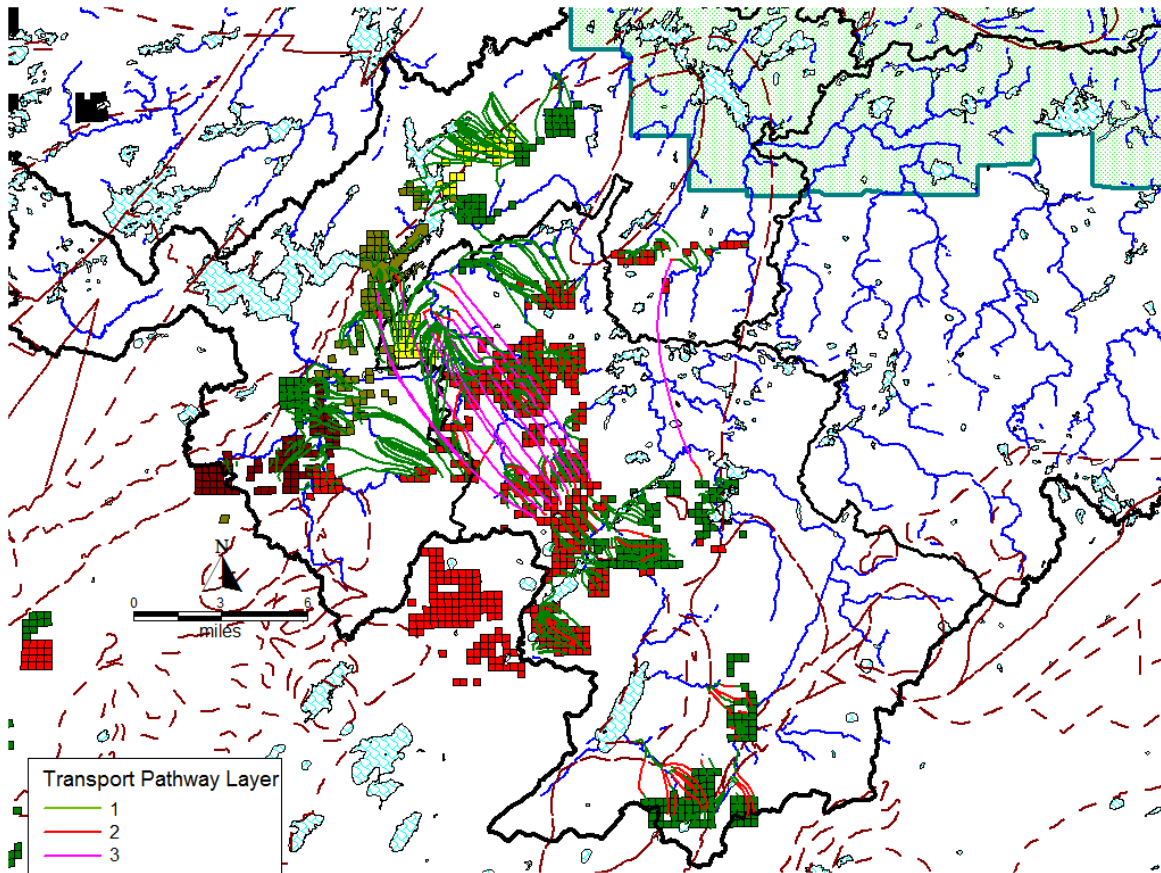


Fig. 32: Particle tracking for particles introduced at the water table at model cells near all of the mineral leases.

The particle pathways generally indicate that leases trending southwest to northeast within the Birch Lake watershed will discharge to surface water relatively quickly, after which they transport north toward the BWCAW as described below. These include leases held by Franconia, Twin Metals, and Teck Cominco (Fig. 29). Leases held by Encampment in the headwaters of the Stony River watershed would discharge to surface water relatively nearby. The large cluster of leases primarily held by DMC in the west-central portion of the Stony River watershed generally followed a longer pathway into the Birch Lake watershed and discharge

directly to the South Kawishiwi River or Birch Lake. However, for placement of the contaminant at the water table some pathways end at the Stony River. As noted, particles originating at depth in the middle of the Stony River watershed flow northeast into the BWCAW, below a surface water divide.

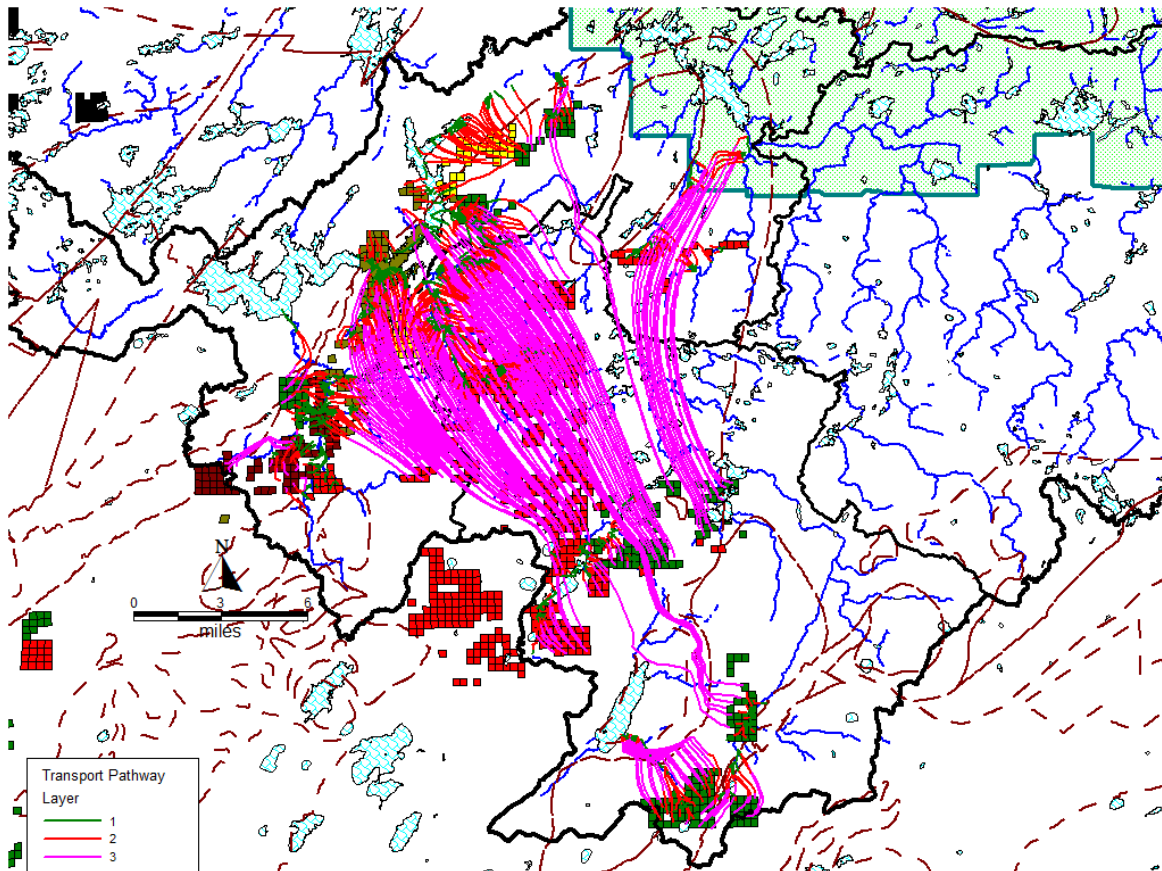


Fig. 33: Particle tracking for particles introduced at the top of layer 3 at model cells near all of the mineral leases.

Contaminant Transport Analysis

The second step of risk analysis is to consider the potential concentration of contaminants entering rivers moving to the BWCAW. Transport analysis translates the concentration at the source to a monitoring point or a sink according to the processes of advection, dispersion, and sorption (Fetter 1999). Contaminant transport analysis was completed with the MT3DMS model (Zheng and Wang 1999)

Dispersion coefficient, the new parameter required for transport analysis, depends on the flowpath length through the aquifer (Fetter 1999; Xu and Eckstein 1995). Sorption, the process of a constituent becoming bound on soil particles, is a function of the particular constituent and the geochemistry of the formation. Sorption is not considered herein.

Dispersivity is a function of length of the flow path from source to sink (Fetter 2002, Xu and Eckstein 1995). In this model, the longest paths are those that emanate from particle placement at mid level in layer 3, and are approximately 33,000 m. This length is much longer than the length at which Xu and Eckstein (1995) found that further increases in dispersivity with length became negligible, 1000 m. Because the flow paths from different sources in this model domain vary from less than 100 m to as much as 33,000 m, using dispersivity for 1000 m is reasonable and avoids changing D for each source. The apparent longitudinal dispersivity therefore is 11.8 m. As noted by Fetter (1999), transverse dispersion is usually given as a fraction of the longitudinal dispersion. For this analysis, the transverse and vertical dispersivity equals 0.2 and 0.1 times the longitudinal dispersivity (Schulz-Makuch et al. 1999, as used by Myers 2013b). The initial longitudinal, transverse, and vertical dispersivity for the analysis is thus 11.8, 2.4, and 1.2 m respectively.

Two contaminant sources are considered for the transport model – underground and surface. This discussion uses sulfate as a contaminant, but the contaminant could be of any conservative substance. There are an infinite number of potential waste simulations, but those chosen are representative of mining in a sensitive area with substantial oversight. The sources analyzed, both in location and load, are representative of average leaks that will occur from mining in any relatively well-regulated area. The regulatory environment would at least require mines to attempt to contain their wastes, therefore the scenarios chosen herein are not the worst imaginable. However, simple scaling or summing the results for additional years could give representative results for higher annual loads or longer durations of a leak.

An underground source would result from waste being backfilled into underground workings and from oxidation of the rock walls. The waste oxidizes while the rock is being backfilled, but oxidation decreases manyfold after the water level recovers. A waste load was simulated as discharge from three different points within layers 2 and 3, coincident with the mineral leases discussed above. Five representative locations centered in the mineral leases were chosen as underground sources (Fig. 34). The waste load is added to the flow stream with a high concentration but low discharge injection well boundary over six cells in the middle of lease clusters for a period of one year, the first transient model stress period. Six cells cover 1.5 million square meters which is representative of the likely extent of a mine. The simulation is of the natural flow leaching through the waste, so there is no new flow added to the system. For that reason, injection into each of the cells is done at the rate of $60 \text{ m}^3/\text{d}$. Concentration is

10,000,000 ug/l, a reasonable estimate and of the same order of magnitude as expected concentrations from sources at the proposed Polymet mine (Myers 2013a, 2014; Polymet 2013a). Total load from each source is 2,628,000 kg/y. This load is about half of the total load projected to be discharged into the West Pit at the Polymet Mine in 13 years or about 5% of the load to be dumped as backfill into the East Pit in three years at the proposed Polymet Mine (Myers 2013a; Polymet 2013a). Thus, the contaminant load introduced into the simulation is on the higher side of discharges expected at Polymet, except for the huge load they would introduce as high sulfide backfill into the pit. The short time frame for seepage, one year, represents the fact that rising groundwater levels would submerge the waste and decrease oxidation.

Above-ground sources result from meteoric water leaching contaminants from waste stored on the ground surface. For comparison with the underground source, these are simulated as a 10,000,000 ug/l concentration added to the natural recharge in layer 1 of the same cells analyzed for the underground sources. The contaminated recharge occurs for just one year to compare with the deep sources described in the previous paragraph (Fig. 34). This would be the equivalent of the operator developing a waste rock storage area and covering it after discovering a leak, completing reclamation over a one-year time period, or moving the waste to a different location that removes the contaminant source. Total load considered for a source in the Birch Lake watershed is 2,847,000 kg and for the Stony River watershed 2,573,250 kg. It is possible that the seepage could continue for much longer than this, but this analysis assumes that mines would be required to cover, monitor, and ultimately remediate waste piles.

The model was run in transient mode for two time periods, or stress periods – for a one-year period as explained for contaminant injection to the model and then for a 1000-year period to simulate long term movement of the contaminant. The waste injection during the first period was the only flow change implemented to the model. The first, one-year stress period had 20 time steps with a 1.2 time step multiplier and the second 1000-year stress period had 60 time steps with a 1.1 time step multiplier. The time steps increase in length through the time period based on the following time step being longer than the previous time step by a multiple of the time step multiplier.

Ten simulated wells monitoring concentrations in all three layers were added to the model (Fig.34). Five (MW-1 through MW-5) were added near the center of the waste sources and five (MW-1d through MW-5d) were added downgradient of the sources, near the middle of the thousand year concentration contours. Loads to various simulated DRAIN reaches were monitored to determine peak loading, which would correlate with highest load to the BWCAW.

Dispersion from the five sources was not so great as to cause substantial overlap in the contaminant plumes from two sources, at least until far into the simulation well beyond the

peaks. For this reason, the model simulated all five sources in one run. The concentration contours show the dispersion and concentration contours emanating from each source.

Results of Contaminant Transport Modeling

After ten years, the plume shapes extend lengthwise in the direction expected from the particle tracking (Fig. 35). Sources 1 and 2 in the Stony River watershed disperse along a lengthwise line toward the northeast. The 1 ug/l contour is about 4000 m from those sources. The contours also expand southeast due to lateral dispersion. Concentration contours do not expand as far around sources 3 through 5 in the Birch Lake watershed because there is a greater vertical flow component in those areas. The contours expand a bit more in layer 3 than 2 (not shown because it mirrors layer 3) due to lower porosity and specific storage. After 1000 years, the contours have expanded much more and there is overlap among sources for the 1 and 10 ug/l contour (Fig. 36). It clearly affects a much larger area over time, although with a smaller concentration.

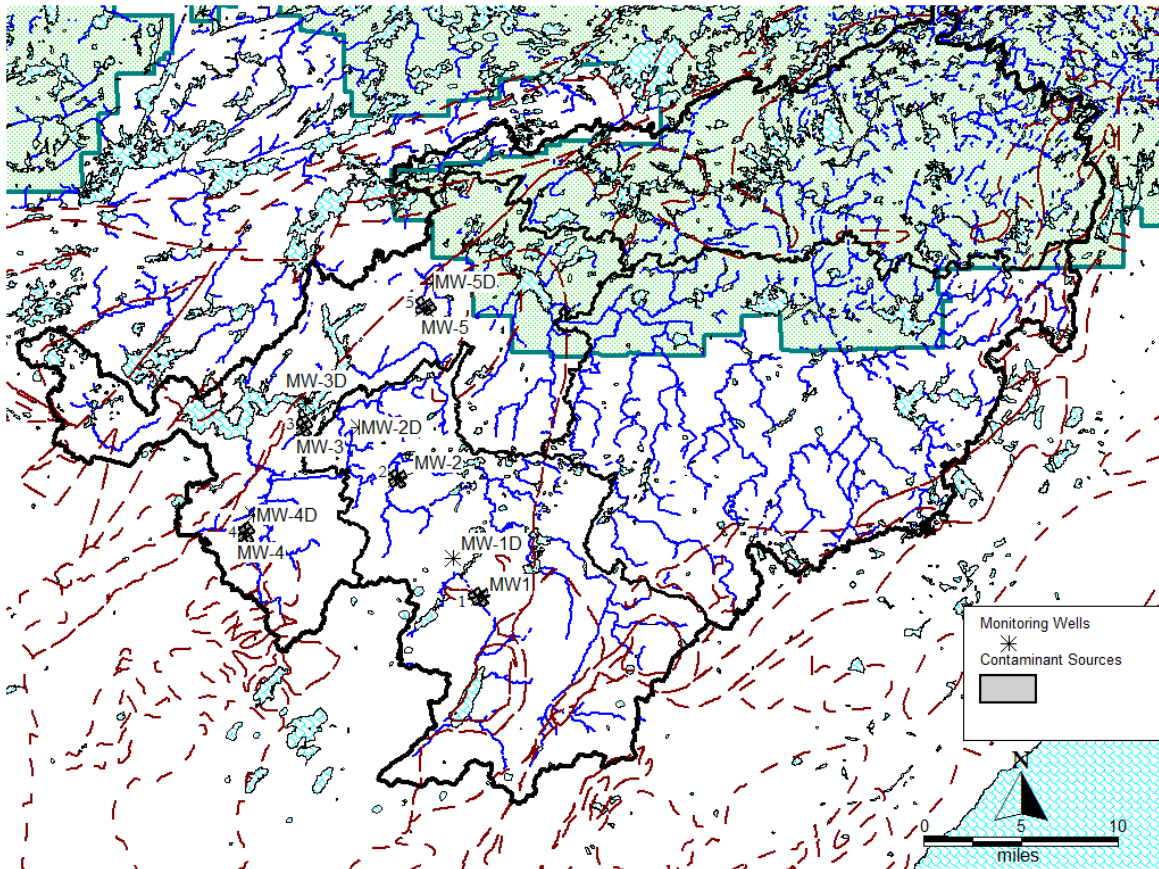


Fig. 34: Location of simulated contaminant sources and monitoring wells. Underground contaminant sources are in layers 2 and 3. Sources in Layer 1 leach to recharge zones. Monitoring wells measure contaminant concentrations in all three layers, and are located at the center of the contaminant sources and downgradient of those sources near the center of the 1000-year concentration contours.

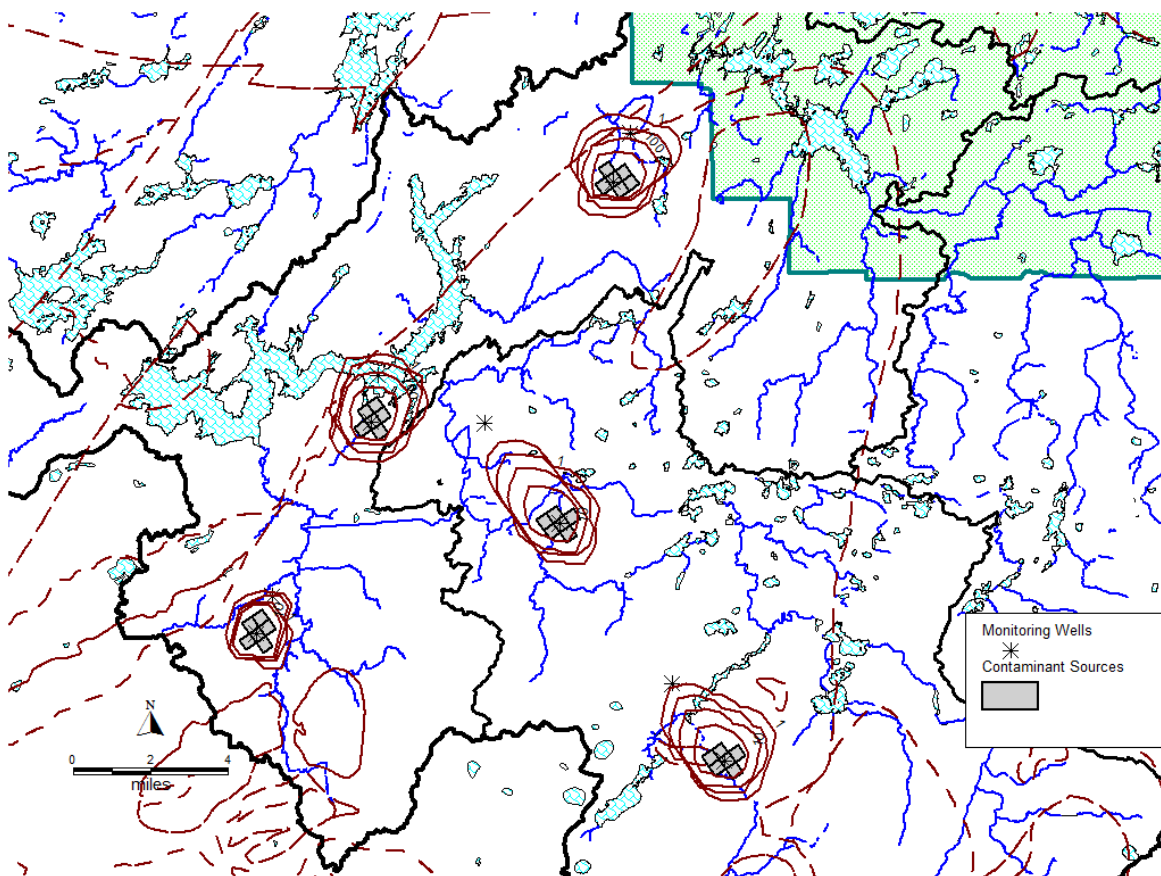


Fig. 35: Concentration contours, layer 3 after 10 years, for underground sources. The contours range from 1 to 10,000 ug/l from outer to inner.

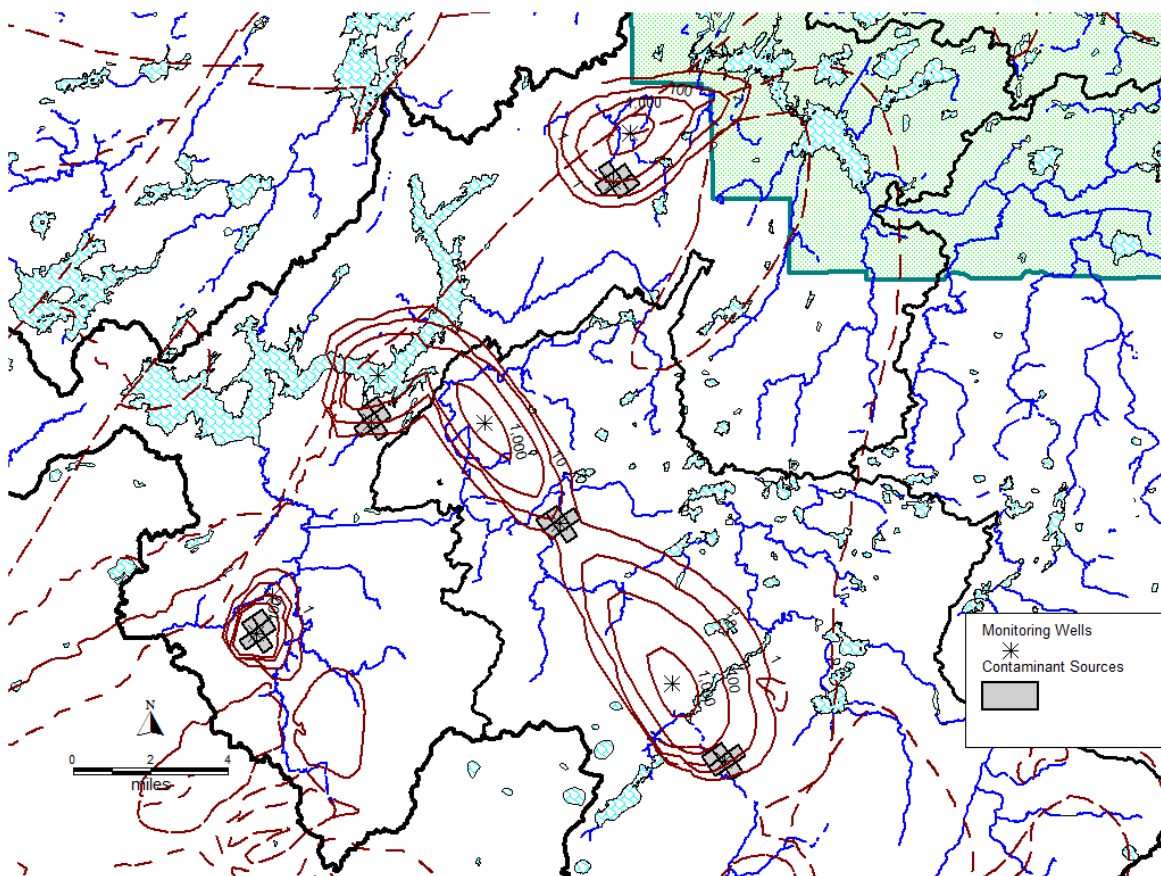


Fig. 36: Concentration contours, layer 3 after 1000 years, for underground sources. The contours range from 1 to 10,000 ug/l from outer to inner.

The surface sources primarily affect the surface layer, although vertical dispersion and advection causes some to move into layers 2 and 3. After just one year, at the end of the contaminant seepage, concentrations are highest around the sources (Fig. 37). Layer 1 concentrations exceed 100,000 ug/l and contours extend up to 2000 m from the source. After 100 years, concentrations at the source still are near 10,000 ug/l and the 1 ug/l contours extend up to 10,000 m from the Stony River sources. The trend due to flow direction is less obvious for surface sources in layer 1, in part because of dry cells and irregular topography. Concentrations in deeper layers are substantially lower than in layer 1, although contaminants plunge deeply into layer 3 from the surface for the Stony River sources; this reflects some of the longer particle transport times discussed above.

The contaminant contours in summary show that mining sources could affect substantial areas of groundwater. All groundwater eventually reaches surface water, but the travel time can vary

greatly, as seen above. Surface sources will clearly reach the rivers more quickly, as discussed in the following paragraphs.

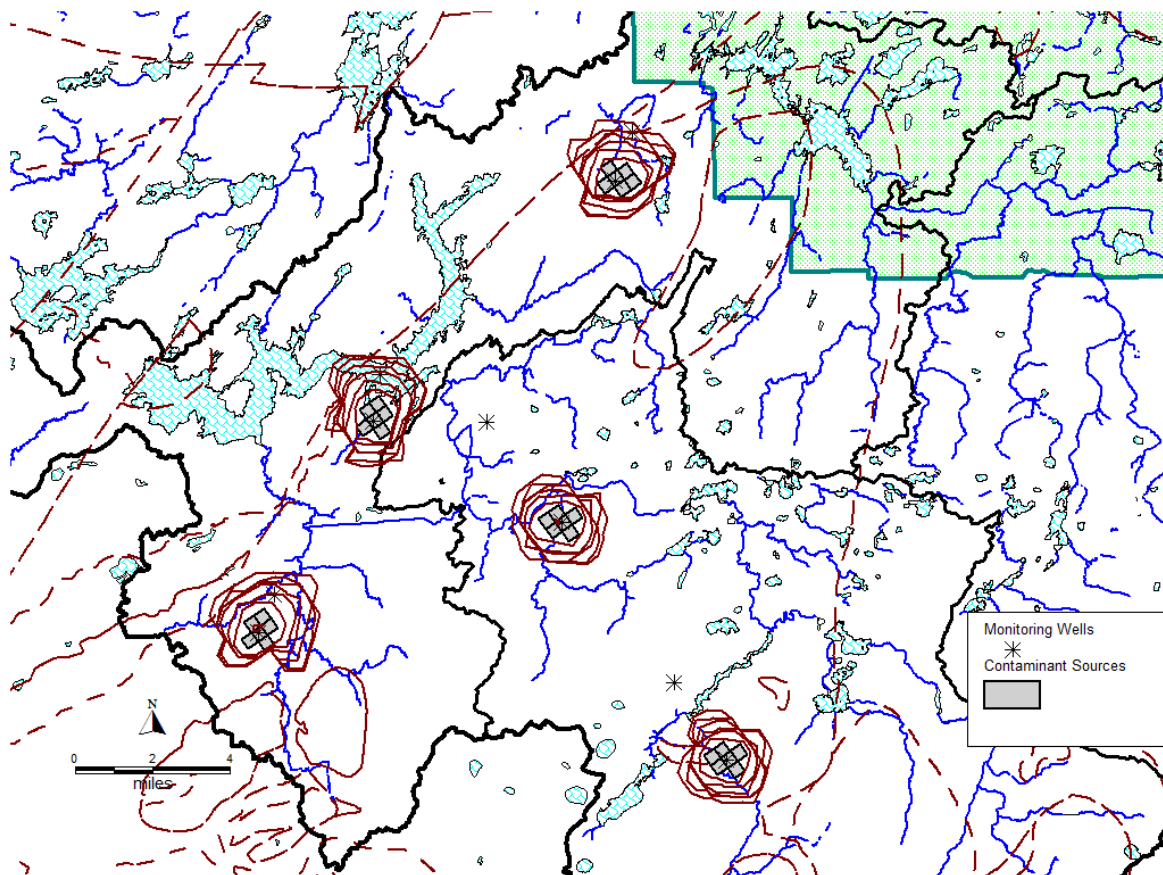


Fig. 37: Concentration contours, layer 1 after 1 year, for surface sources. The contours range from 1 to 100,000 ug/l from outer to inner.

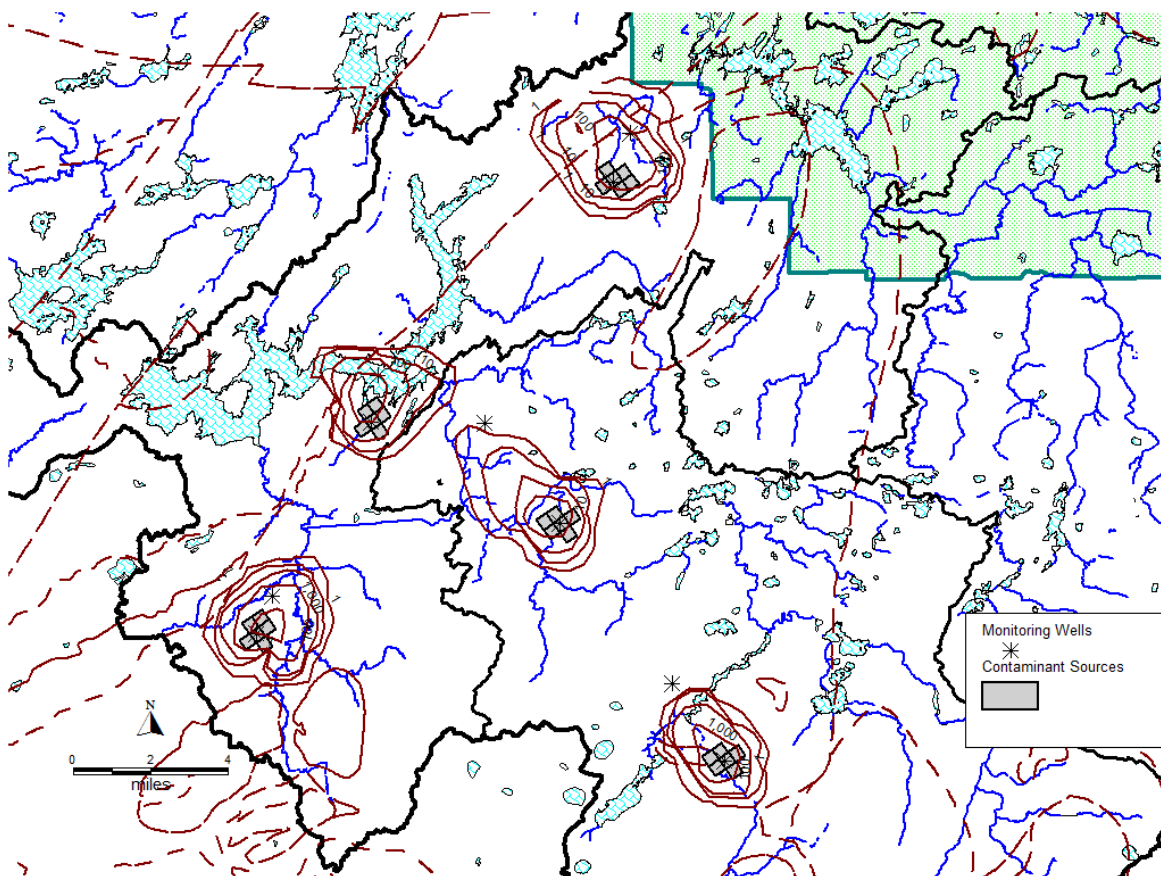


Fig. 38: Concentration contours, layer 1 after 100 years, for surface sources. The contours range from 1 to 10,000 ug/l from outer to inner.

Peak concentrations reach various river reaches at times depending on whether the source is underground or on the surface and on the distance the source is from the river (Table 9). Except for Filson Creek, the peak concentration reaching a river from an underground source is 1232 ug/l, reaching the Stony River after ten years. Filson Creek received almost 4000 ug/l at a point about ten years after the contaminant release. The peaks from underground sources all require from ten to forty years to reach a river, although fracture flow could decrease that time. The times reflect the particle travel times above.

The peak concentrations for the surface sources in the Stony River watershed reach the river at the end of the first year. This reflects the close proximity of the sources to the sinks. Contaminants reaching the Stony River peak at almost 33,000 ug/l. Also, the source near Filson Creek reaches that creek at the end of the first year, and ranges as high as 120,000 ug/l. These routings do not account for surface flows to the rivers which could either add load or dilute it, depending on the source. Contaminants reach Birch Lake and Dunka River after two to five

years, but the peak concentrations are lower than those to Stony River and Filson Creek, due to longer distance from the sources allowing more dilution. It is apparent that the magnitude, duration and time until effects begin depend on the exact location and depth of the leak and the geology between the leak and the streams. Leaks from the surface reach the streams quicker and with less attenuation due to shorter flow paths.

Leaks through groundwater commence a long-term process in which contaminants travel to surface waters for a long time after the leaks have been discovered and plugged. Impacts from such leaks can continue for decades, with substantial concentrations still reaching the rivers up to 100 years after the leaks cease.

Table 9: Concentrations (ug/l) discharging to reaches 1, 71, 72, 73, and 75 at various times corresponding to stress periods (1 or 2) and time step (number in parentheses). Steady state discharge to reach 1, 71, 72, 73, and 75 is -74,916, -73,295, -31,383, -168,050, and -11,439 m³/d, respectively. The discharges are stated as a negative because they represent a loss from the groundwater domain. Reach 1 is Birch Lake, Reach 71 is Dunka River, Reach 72 is Stony River between Babbitt and Isabella, Reach 73 is Stony River above Isabella, Reach 75 is Filson Creek nr Ely. Other reaches did not receive substantial load.

Deep Sources		Reach				
Stress period	Years	1	71	72	73	75
1(20)	1.0	1.64	3.71	334.04	112.22	2512.98
2(14)	10.0	166.56	203.85	1232.08	256.04	3989.01
2(21)	21.8	223.47	242.32	1149.71	220.85	3172.49
2(24)	30.2	233.54	247.74	1043.41	196.92	2738.44
2(27)	40.9	230.76	249.63	903.37	169.44	2308.54
2(36)	99.4	132.55	209.85	389.83	74.32	1037.91
2(60)	1000.0	18.05	4.51	0.32	0.95	190.01
Surface Source						
1(20)	1.0	383.2	775.1	32931.9	6654.5	120482.6
2(1)	1.3	726.7	1382.4	30431.2	5409.8	81234.8
2(3)	2.1	1538.2	2513.6	24938.2	3507.8	45849.5
2(5)	3.0	2127.6	3037.2	19507.2	2323.1	32963.3
2(9)	5.5	2158.2	2630.2	9977.2	1117.3	18451.0
2(11)	7.1	1759.4	2066.7	6482.5	809.8	13179.9
2(14)	10.0	1160.8	1287.9	3346.0	537.5	8207.6
2(21)	21.8	496.0	544.5	971.2	241.2	3998.0
2(36)	99.4	110.0	347.9	322.4	89.0	1327.0
2(60)	1000.0	0.2	0.1	0.1	0.0	1.2

The analysis herein shows that even relatively small leaks could cause substantial loads to reach the rivers and drain to the BWCAW. These could be long-term sources of contamination. Underground sources maintain higher concentrations longer, but surface sources could be much more damaging to the resource.

Surface Water Transport Analysis

Contaminant transport through rivers and lakes is substantially different than through groundwater. In rivers, advection controls the average rate of movement downstream and dispersion caused by turbulence spreads the contaminants throughout the river cross-section. Turbulence causes some of the contaminant to flow faster downstream than the river and some to flow more slowly. A slug of contaminant causes a high concentration peak after mixing below the point of entry to the river, which decreases with distance downstream as the contaminant disperses. The contaminant is observed at downstream locations for a longer timeframe than the length of the actual discharge, but the peak concentration decreases. Longitudinal dispersion is much less important for steady state discharges into the river, and the stream concentration will equal the discharge concentration adjusted for dilution by streamflow. As streamflow decreases, the concentration will increase if the discharge load remains constant. The following sections detail the surface water routing of groundwater contaminant discharges estimated herein.

Surface Water Transport of Groundwater Discharges

The primary sources of contaminants would be located in the Stony River and Birch Lake watersheds. Depending on the location within the source watersheds, contaminants will reach one of the streams that drain to Birch Lake or discharge directly to the lake (Figs. 32 & 33). This applies to underground sources and to spills on the surface, as simulated herein. Contaminants would reach the BWCAW by way of Birch Lake and then transport through a series of lakes into the Wilderness and eventually into the border-spanning Basswood Lake (Fig. 3). The lakes include White Iron, Farm, Garden, Fall, Newton, and then Basswood Lake (Fig. 3 and Table 10).

Table 10: Morphometric characteristics for lakes along the flow path. Volume is calculated by assuming the average depth of the littoral area is 7.5 feet and the average depth of remainder is the average of 15 and the max depth.

Lake	Area (ac)	Littoral area (ac)	Max Depth (ft)	Volume (af)	Flushing time per lake	source: http://www.dnr.state.mn.us/lakefind/showreport.html?downum=11041200
Birch	1267	754.9	45	28715	0.06	showreport.html?downum=11041200
White Iron	3238	1603	47	87251	0.19	showreport.html?downum=69000400
Farm	1292	459	56	45505	0.10	showreport.html?downum=38077900
Garden	653	239	55	22509	0.03	showreport.html?downum=38078200
Fall	2258	1178	32	50433	0.07	showreport.html?downum=38081100
Newton	516	358	47	9964	0.01	showreport.html?downum=38078400
Basswood Lake	22722	7034	111	1276419		showreport.html?downum=38064500

The Kawishiwi River and Isabella River watersheds discharge into the river system and would dilute contaminant concentrations, as discussed above. Because of decreasing low flows in a downstream direction (Table 2 and associated text), dilution was shown to be effective only during normal base flows, not during low flows. Groundwater contaminant discharges reach close to steady state so the contaminants will mix through the lakes and eventually reach a concentration at the downstream end that depends on the discharge concentration adjusted by dilution. During dry periods, dilution is minimal and the stream concentration becomes close to that at the point of discharge. During the driest periods, the dilution is based on the flow at the point of interest.

The Kawishiwi River at Winton gage is representative of the flows leaving the study area and reaching the wilderness. It monitors flow leaving the Rainy Headwaters watershed, including the Kawishiwi River watershed and some area north of the Rainy Headwaters (Fig. 1), so the flow is higher than observed discharging from the Birch Lake or Stony River watershed (Tables 2 and 9), except during low flows at which time the river is a losing system. Baseflow at the Winton gage is 1,672,937 m³/d, or 683 cfs. This is substantially higher than the cumulative flows simulated for the tributary reaches by the model (Table 9). However, this gage occasionally has much lower flows. The critical 7-day low flow statistics for a 2-, 5-, 10-, 20-, 50- and 100-year return interval are 182, 84.1, 42.9, 4.6, 0.0, and 0.0 cfs, respectively at this gage (Winterstein et al. 2007).

Leaks that coincide with these low flows could have substantial impacts on the river system and BWCAW. As shown above, once a leak commences it will flow through groundwater and discharge to surface water for years, so the chance that it will coincide with low flow conditions is high. Table 11 shows the concentrations that will reach the BWCAW based on groundwater

load discharges to specific reaches and the assumption that the simulated groundwater discharges continue during low flows.

Table 11: Concentration in ug/L at the Kawishiwi River at Winton gage for various loads generated by leaks from potential mines reaching various tributaries. The load would be diluted according to the flows at this gage. The values are for loads from individual reaches, assuming no overlap among discharges. This table shows the potential concentration reaching the wilderness for conditions simulated herein. Low flows from Winterstein et al. (2007).

	Reach	Load (m3/d x ug/l)	Baseflow	7Q2	7Q5	7Q10	7Q20
Underground	1	-17495785	7	39	85	167	1555
	71	-18296353	8	41	89	174	1626
	72	-38666385	16	87	188	368	3436
	73	-43027269	18	97	209	410	3823
	75	-45630324	19	102	222	435	4054
Surface Sources							
	1	-161683995	67	363	786	1540	14366
	71	-222608665	92	500	1082	2121	19780
	72	-1033502013	427	2321	5023	9847	91832
	73	-1118290617	462	2511	5435	10655	99366
	75	-1378200404	570	3095	6698	13131	122460

The modeling completed herein has shown that substantial contaminant loads can reach streams that drain to the BWCAW due to either deep underground or surface leaks. During much of the year, sufficient flow enters the system to dilute this load before it reaches the BWCAW. However, during baseflow conditions, the load could substantially affect the tributary streams, especially within the Stony River and Birch Lake watersheds, although dilution occurs before the load reaches the wilderness. When the watershed is experiencing low flow conditions (Winterstein et al. 2007), the concentration at the Kawishiwi River at Winton (immediately upstream of entry to the BWCAW) would be increased above that at baseflow by five orders of magnitude for the 7Q20 flow. In other words, leaks that may have minimal effects much of the year could be devastating at low flow. Because once started, leaks will continue for decades and likely coincide with 20-year or longer return period low flows, the potential that leaks will impact the Wilderness is high.

Surface Water Transport of Spills

A large spill that causes a rapid flow of contaminants into the surface water system could be very damaging. Many of the potential mines are on or near Birch Lake, so a spill quickly reaching that lake is possible. Treating a spill as a single impulse to the lake that quickly mixes

through the applicable volume, the concentration within and exiting the lake decreases with time according to the following equation (Thomann and Mueller 1987):

$$s(t) = \frac{M}{V} e^{\left(\frac{K't}{V}\right)}$$

Here, s is concentration at time t , M is the total impulse load, and V is the lake volume (Table 10). K' is $Q+KV$ where Q is flow through the lake (assumed to be the flow at the S Kawishiwi River above the White Iron Lake gage) and K is the reaction coefficient, which is 1 for a conservative substance. A standard assumption for transport analysis is that the load fully mixes into the lake, but that clearly would not occur in Birch Lake due to its large area and large littoral zone (Table 9) and significant flows entering the lake from different directions. Based on the location of the leases (Figs. 29 & 30), the load would enter the lake somewhere in its east half. River flow entering the west end would prevent the load from dispersing in that direction. For this simplified analysis, Birch Lake's volume was assumed to be half its actual volume.

Continuing downstream to subsequent lakes, the outflow from one lake becomes the inflow to the next. The response in subsequent lakes can be analyzed using a response equation due to a step load (Thomann and Mueller 1987):

$$s = \frac{W}{Q + KV} \left\{ 1 - e^{-\left(\frac{Q}{V} + K\right)t} \right\} + s_0 e^{-\left(\frac{Q}{V} + K\right)t}$$

All variables are described above except that s_0 is the initial concentration, or that occurring at the end of the previous calculation period. If the analysis time step is 0.01 years, the concentration at year = 0.01 is the initial concentration for the calculation for time step year 0.01 to 0.02.

Spills were simulated with an instantaneous input of 3,000,000 kg of a conservative substance. The mass was chosen for comparison with the loads simulated as leaking into groundwater. It is 10% of the amount of sulfate proposed to be added to the East Pit at the proposed Polymet Mine during the eleventh year, when the category 4 temporary waste rock is dumped into the pit. Total category 4 rock mass at Polymet is 6.2 mil tons. For input directly into Birch Lake, the concentration in Birch Lake initially exceeded 120 mg/l and dropped to less than 1 mg/l within 0.16 years (Fig. 39). Flow from Birch Lake with the simulated concentration becomes inflow to White Iron Lake which sees concentrations exceed 3 mg/l in about 0.02 years. Continuing downstream the concentration peaks at 0.16 mg/l in 0.03 years at Farm Lake. Although not shown in Fig. 39, the concentration continues to decrease with distance downstream from Birch Lake.

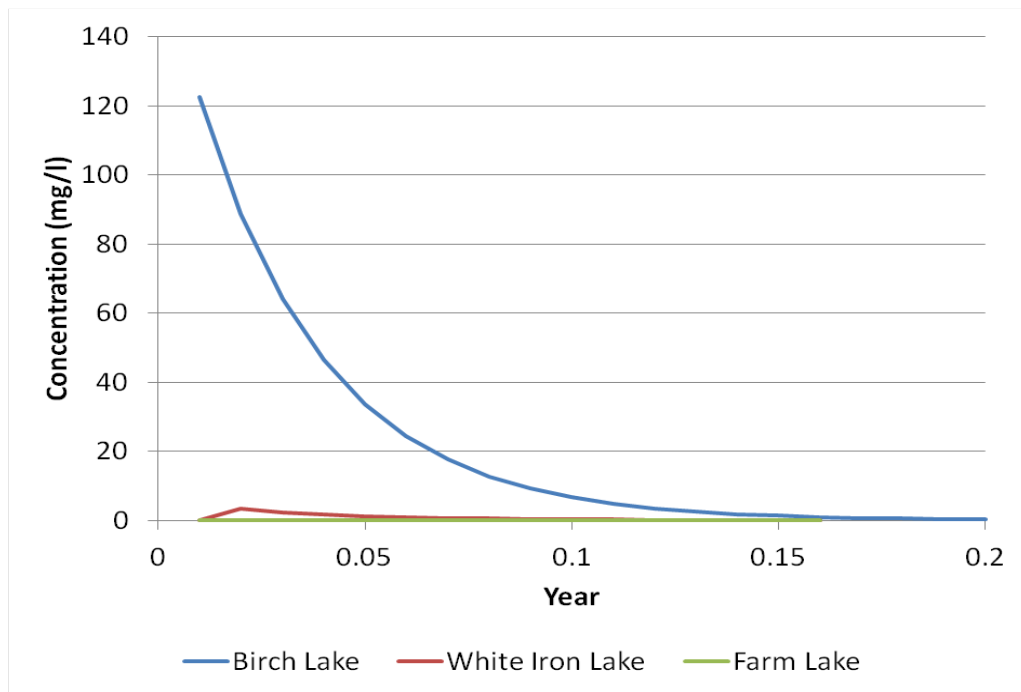


Fig. 39: Concentration hydrographs for three lakes with an initial load of 3,000,000 kg input to Birch Lake.

A second scenario is a spill occurring downstream of Birch Lake in the potential vicinity of an ore processing plant. In this scenario, the spilled contaminant would initially mix through White Iron Lake. Concentrations would peak at 26 mg/l in that lake and at 1.3 and 0.13 mg/l in Farm Lake and Garden Lake, respectively. The Garden Lake concentration would be the concentration effectively reaching the BWCAW. Depending on the substance, this concentration could have substantial effects on the wilderness, although lakes just upstream of the wilderness would experience the most extreme effects.

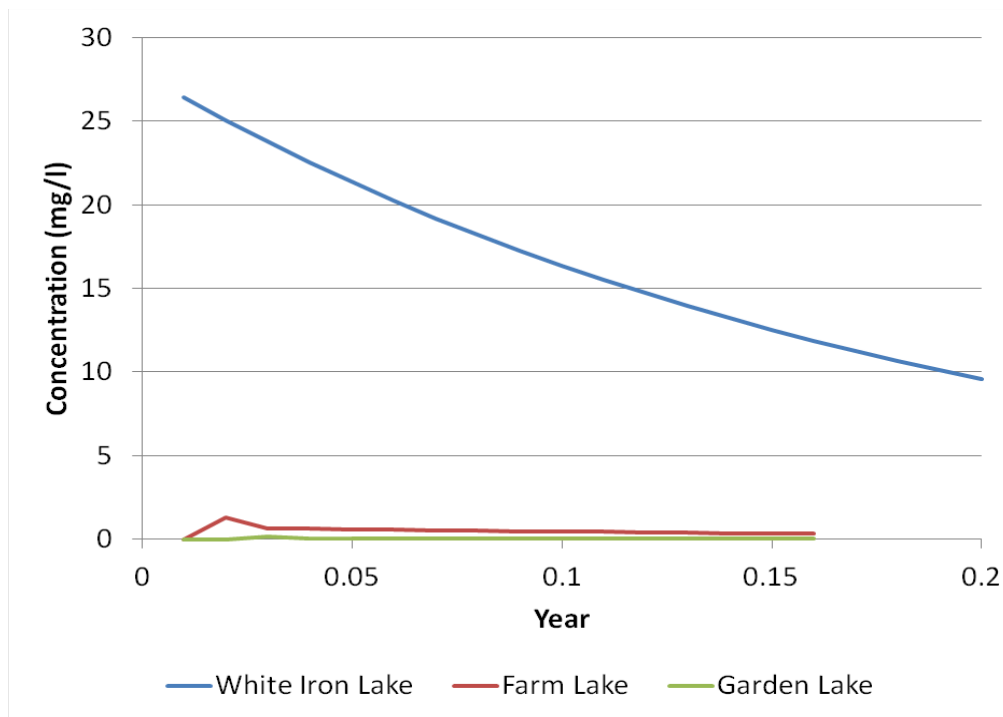


Fig. 40: Concentration hydrographs for three lakes with an initial load of 3,000,000 kg input to White Iron Lake.

The times to peak concentrations within the lakes are less than the retention times (Table 10). This could result in the concentrations being overestimated because it ignores a small amount of dilution. However, the assumption of complete mixing in the lakes inherent in the equations used for analysis causes the method to underestimate the concentration.

An upper end analysis was tested using the same amount of conservative waste as input into a hypothetical stream with dimensions, flows, and dispersivity based on the water volume within the lakes (Thormann and Mueller 1987). The estimated stream dispersivity is very low because the effective stream is very wide (to account for lake volume). Because the analysis treated transport almost as a plug flow, due to limited dispersivity, concentrations were unrealistic. For this reason, this upper end analysis is not shown in this paper.

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RESEARCH ARTICLE

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This article is a companion to Myrbo et al. (2017), <https://doi.org/10.1002/2017JG003787> and Pollman et al. (2017), <https://doi.org/10.1002/2017JG003785>.

Key Points:

- Sulfate addition increased organic matter mineralization in wetland sediment, releasing C, N, P, and Hg to the water column
- Sulfate reduction caused not only higher methylmercury concentrations but higher total mercury concentrations in the surface water
- Increased sulfate loading to freshwaters can cause deleterious effects separate from direct sulfide toxicity to organisms

Supporting Information:

- Supporting Information S1
- Figure S1
- Data Set S1

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Increase in Nutrients, Mercury, and Methylmercury as a Consequence of Elevated Sulfate Reduction to Sulfide in Experimental Wetland Mesocosms

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Abstract Microbial sulfate reduction (MSR) in both freshwater and marine ecosystems is a pathway for the decomposition of sedimentary organic matter (OM) after oxygen has been consumed. In experimental freshwater wetland mesocosms, sulfate additions allowed MSR to mineralize OM that would not otherwise have been decomposed. The mineralization of OM by MSR increased surface water concentrations of ecologically important constituents of OM: dissolved inorganic carbon, dissolved organic carbon, phosphorus, nitrogen, total mercury, and methylmercury. Increases in surface water concentrations, except for methylmercury, were in proportion to cumulative sulfate reduction, which was estimated by sulfate loss from the surface water into the sediments. Stoichiometric analysis shows that the increases were less than would be predicted from ratios with carbon in sediment, indicating that there are processes that limit P, N, and Hg mobilization to, or retention in, surface water. The highest sulfate treatment produced high levels of sulfide that retarded the methylation of mercury but simultaneously mobilized sedimentary inorganic mercury into surface water. As a result, the proportion of mercury in the surface water as methylmercury peaked at intermediate pore water sulfide concentrations. The mesocosms have a relatively high ratio of wall and sediment surfaces to the volume of overlying water, perhaps enhancing the removal of nutrients and mercury to periphyton. The presence of wild rice decreased sediment sulfide concentrations by 30%, which was most likely a result of oxygen release from the wild rice roots. An additional consequence of the enhanced MSR was that sulfate additions produced phytotoxic levels of sulfide in sediment pore water.

Plain Language Summary In the water-saturated soils of wetlands, which are usually anoxic, decomposition of dead plants and other organic matter is greatly retarded by the absence of oxygen. However, the addition of sulfate can allow bacteria that respire sulfate, instead of oxygen, to decompose organic matter that would not otherwise decay. The accelerated decay has multiple consequences that are concerning. The bacteria that respire sulfate “breathe out” hydrogen sulfide (also called sulfide), analogous to the conversion or respiration of oxygen to CO₂. Sulfide is very reactive with metals, which makes it toxic at higher concentrations. In addition to the release of sulfide, the sulfate-accelerated decomposition of plants releases phosphorus and nitrogen, fertilizing the waterbody. Decomposition also mobilizes mercury (which is everywhere, thanks to atmospheric transport) into the surface water. The microbes that convert sulfate to sulfide also methylate mercury, producing methylmercury, the only form of mercury that contaminates fish. This study demonstrates that adding sulfate to a wetland can not only produce toxic levels of sulfide but also increase the surface water concentrations of nitrogen, phosphorus, mercury, and methylmercury.

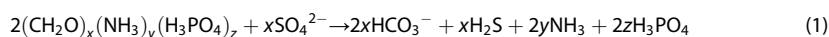
1. Introduction

Organic matter (OM) accumulates in the sediments of aquatic systems when sediment concentrations of terminal electron acceptors (TEAs) are too low for microbes to completely decompose OM, especially when the supply of the most energy-efficient TEA, oxygen, is low. In water-saturated, organic-rich sediment, microbial sulfate reduction (MSR) can be a dominant pathway for the respiration of OM because oxygen is depleted in the uppermost sediment (Boye et al., 2017). Dissolved sulfate (SO₄) concentrations in continental surface

waters are often low (less than 50 mg L^{-1} or 0.5 mmol L^{-1}) (e.g., Gorham et al., 1983) compared to ocean concentrations ($2,800 \text{ mg L}^{-1}$ or 29 mmol L^{-1}). Because of lower SO_4 concentrations, and because MSR rates can be limited by SO_4 concentrations (Holmer & Storkholm, 2001), the biogeochemical significance of MSR is often considered minimal in freshwater and low-salinity systems (e.g., Capone & Kiene, 1988; Nielsen et al., 2003; Stagg et al., 2017). However, absolute rates of MSR are not clearly lower in freshwater systems than in marine systems (Pallud & Van Cappellen, 2006), and in some cases, rapid cycling between oxidized and reduced forms of S can occur (Hansel et al., 2015).

In this study, we investigated the cascade of biogeochemical effects associated with increased MSR that result from increased surface water SO_4 . We simultaneously quantified three different categories of biogeochemical responses related to MSR: (1) mineralization of organic matter and associated release of dissolved C, N, P, and Hg; (2) methylation of Hg; and (3) production of sulfide.

The stoichiometric release of the constituents of OM during MSR, notably C, N, and P, is a phenomenon long recognized by marine scientists. For instance, Boudreau and Westrich (1984) constructed a model of the MSR-mediated decomposition of marine sediment. They showed that SO_4 is reduced to sulfide (H_2S) in stoichiometric proportion to the mineralization of C, N, and P according to the reaction



C is released as both dissolved inorganic carbon (DIC, from complete oxidation, produced as bicarbonate alkalinity in stoichiometric proportion to sulfide (reaction (1); Boudreau & Westrich, 1984)) and dissolved organic carbon (DOC, from partial oxidation). The nutrients N and P are released in forms that are readily taken up by plants; N is released as ammonia, and P as phosphate. The mineralization of sediment organic matter associated with MSR releases sulfide (S^{2-}) into sediment pore water, which speciates, depending on the pH, into hydrogen sulfide (H_2S) and bisulfide (HS^-), henceforth collectively termed sulfide. If reduced S compounds accumulate in the sediment, there may be additional consequences to an aquatic system, such as toxic concentrations of sulfide in pore water (Lamers et al., 2013; Pastor et al., 2017; Myrbo et al., 2017) or conversion of sediment Fe(III) to FeS compounds, which enhances the mobilization of P (Curtis, 1989; Maynard et al., 2011).

The multiple biogeochemical consequences of MSR in freshwater systems have been investigated and documented in more than two dozen publications (Table S1 in the supporting information), which typically address a single issue, such as the production of alkalinity that neutralizes atmospherically deposited H_2SO_4 (Baker et al., 1986; Cook et al., 1986; and others) or the methylation of Hg (Gilmour et al., 1992; Branfireun et al., 1999, 2001; and others). Experimental studies addressing SO_4 reduction, sulfide production, associated OM mineralization, and release of nutrients have been broader (Lamers et al., 2001, 2002; Weston et al., 2006, 2011; and others), but aside from the results reported in this paper, only the experiments of Gilmour, Krabbenhoft, et al. (2007) and Gilmour, Orem, et al. (2007) have investigated all three categories of biogeochemical consequences of SO_4 reduction: OM mineralization, Hg methylation, and sulfide accumulation (Table S1). We also investigated the potential for Hg to be released by mineralization, a phenomenon proposed by Regnell and Hammar (2004).

Sulfate-driven enhanced mineralization of sediment OM and release of dissolved sulfide, N, P, DOC, DIC, and associated increases in alkalinity and pH have the potential to change the nature of an aquatic ecosystem. The immediate release is to the sediment pore water, but these dissolved materials can diffuse into the surface water. Increased internal loading of N and P can drive a system toward eutrophy, which can increase carbon fixation and amplify the cascade of biogeochemical effects associated with increased MSR. Increases in DOC also have the potential to fundamentally change the nature of a waterbody. DOC influences many processes in freshwater ecosystems, including light availability for macrophyte growth, thermal stratification, and bioavailability of metals, P, and C. In addition, DOC interferes with drinking water purification (Williamson et al., 1999). Increases in DIC, alkalinity, and pH can also change the nature of a system. Aquatic macrophyte and algal species often have different optimal alkalinity concentrations (e.g., Moyle, 1945; Vestergaard & Sand-Jensen, 2000), so increases in alkalinity may change aquatic community composition. Because pH is a master variable in aquatic systems (Stumm & Morgan, 2012), increases in pH can cause changes in both aquatic chemistry and the biota that dominate a system, as best documented by changes in diatom assemblages (Patrick et al., 1968).

The release of sulfide into sediment pore water has multiple biological and geochemical consequences, several of which are related to the reactivity of sulfide with metals. If dissolved sulfide accumulates in pore water, it can negatively affect multicellular organisms inhabiting the sediment because sulfide can denature a range of metal-containing biomolecules, including cytochrome C oxidase, which is essential for respiration by both animals and plants (Bagarinao, 1992). Because aquatic sediment is a primary site of sulfide production, plants that root in sediment are vulnerable to toxic sulfide concentrations (Lamers et al., 2013; Pastor et al., 2017). However, if the watershed supplies sufficiently high loading of reactive Fe or other metals to the sediment, pore water sulfide concentrations may stay below toxic levels even while MSR proceeds as an important mineralization process (Pollman et al., 2017). The formation of FeS compounds effectively detoxifies sulfide (e.g., Marbà et al., 2007; Van der Welle et al., 2007). When Fe availability exceeds the production of sulfide, the accumulation of FeS is a measure of cumulative SO_4 reduction, which can be quantified as acid-volatile sulfide (AVS) (Heijs & van Gemerden, 2000). In addition, phosphorus is mobilized when oxidized Fe compounds with significant capacity to bind phosphate are converted to FeS compounds, which are incapable of binding phosphate (Lamers et al., 1998; Maynard et al., 2011). Thus, MSR mobilizes P both by mineralization of P-containing OM and by changing the form of Fe in sediment.

In addition to releasing C, N, and P, producing potentially toxic concentrations of sulfide, and reducing the solubility of metals, MSR is a primary process leading to the formation of MeHg, the bioaccumulative form of Hg (Gilmour et al., 1992; Hsu-Kim et al., 2013), although other microbial groups can also methylate Hg (Podar et al., 2015). In some cases, MSR can lead to toxic levels of MeHg higher in the food chain. The relationship between SO_4 concentrations and MeHg production is complex, however, and both field and laboratory studies in freshwater and saline ecosystems suggest that there is a dual effect of S on Hg methylation. At low SO_4 concentrations, the addition of SO_4 can stimulate MSR and Hg methylation (Jeremiason et al., 2006). At higher SO_4 concentrations, a greater abundance of inorganic sulfide appears to decrease the availability of inorganic Hg for Hg methylation (Hsu-Kim et al., 2013; Johnson et al., 2016). Because it has been observed that low SO_4 additions often increase Hg methylation and higher SO_4 concentrations decrease methylation, it has been proposed that there is a range of SO_4 and sulfide concentrations are optimal for Hg methylation, above which methylation is inhibited (Hsu-Kim et al., 2013). There is some debate regarding the underlying mechanism, but there is substantial evidence suggesting that dissolved inorganic sulfide above concentrations of 300–3,000 $\mu\text{g L}^{-1}$ has an inhibitory effect on Hg methylation (Bailey et al., 2017).

This study presents results from 30 wetland mesocosms in which the surface waters were treated to maintain a wide range of SO_4 concentrations over the course of 5 years (2011–2015) to assess the impact on wild rice, *Zizania palustris* (Pastor et al., 2017). We took advantage of this experiment to analyze the geochemical conditions in surface and pore water in the mesocosms during late summer 2013, 3 years into the experiment. Pastor et al. (2017) specifically examined the effect of increased SO_4 loading on wild rice, whereas this paper examines the broader biogeochemical impact of augmenting SO_4 to a low- SO_4 system.

2. Materials and Methods

2.1. Experimental Design

The experimental setup (Figure S1 in the supporting information), described in detail by Pastor et al. (2017), consisted of thirty 375 L polyethylene stock tanks containing sediment from a wild rice lake (Rice Portage Lake; +46.6987°, −92.6886°) in which wild rice was grown in self-perpetuating populations at five SO_4 treatment levels (control, 50, 100, 150, and 300 mg L^{-1}). SO_4 concentrations in six replicate mesocosms were routinely monitored, and amendments of SO_4 were added as Na_2SO_4 during the growing season as SO_4 was removed by MSR (Figure 1). Due to MSR, the mesocosm surface waters actually had time-weighted average concentrations of 7, 27, 59, 93, and 207 mg L^{-1} , respectively. Local well water containing an average of 10.6 mg L^{-1} SO_4 was added as needed to compensate for evapotranspiration. Precipitation in the region contains an average of 2.1 mg L^{-1} SO_4 , and Rice Portage Lake has an average SO_4 concentration of 2.2 mg L^{-1} (Fond du Lac Band, 2016), so the control was slightly elevated above the ambient SO_4 concentration of the sediment source for the experiment. During the ice-free period (generally May through October), the surface water temperature (T) measured in the morning was correlated with the previous day's mean air temperature (mesocosm $T = 0.72$ air $T + 4.4$ °C; $R^2 = 0.65$). Peak air temperature is reached in July, when the average

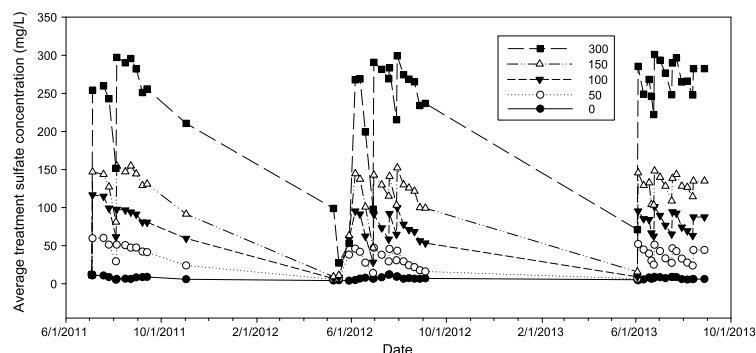


Figure 1. SO_4 concentrations in surface waters of each treatment, showing repetitive depletion and periodic amendment with Na_2SO_4 (average of six mesocosms per treatment on each sampling date).

temperature is 18.8°C (based on 1981–2010 air temperatures measured at the Duluth, Minnesota, airport, 10 km from the experimental site).

The experiments had been in progress for three growing seasons at the time of the sampling for this study, 27 and 28 August 2013, and for five growing seasons at the time of the second, less intensive, sampling (August 2015). The sediment of each mesocosm was divided into two parts for the 2013 growing season by a clear acrylic plate and all wild rice plants removed from one side in order to evaluate the effects of plant root presence on the geochemistry of the sediments. The plate was situated near one end of each mesocosm, such that about 10% of the surface area of 0.6 m^2 was plant-free (Figure S1). The plate was positioned to segregate the sediment without impeding the circulation of the surface water above all of the sediment. Sediment chemistry results presented here are from the side with wild rice plants present, except when analyzing the difference in AVS between the two sides.

2.2. Methods

2.2.1. Sample Collection

Rhizon[™] samplers with a 10 cm long, 2.5 mm diameter, cylindrical porous tip (hydrophilic membrane pore size $0.12\text{--}0.18\text{ }\mu\text{m}$ (Rhizosphere.com, Netherlands; Shotbolt, 2010)), were connected by Teflon-taped Luer-Lok connectors and silicone tubing to a syringe needle. The sampler was inserted into the sediment, and the needle was then inserted through the 20 mm thick butyl rubber septum of an evacuated serum bottle (Bellco Glass) to initiate pore water draw through the tubing and displace air. After water was observed entering the serum bottle, the needle was removed from the first sacrificial bottle and inserted through the septum of a second evacuated serum bottle to collect the sample. One Rhizon and bottle were used to collect a sample for dissolved iron, preserved with 20% nitric acid. A second Rhizon and evacuated, N_2 gas-flushed sealed bottle, preloaded with 0.2 mL 2 N zinc acetate, 0.5 mL 15 M NaOH, and a stir bar, was used to collect a sample for dissolved sulfide analysis. Each Rhizon was positioned to sample pore water from the top 10 cm of sediment and to avoid collecting water from above the sediment surface. However, it is conceivable that some surface water was able to follow the path of the Rhizon into the sediment and dilute or partially oxidize the pore water sample.

Surface water in each mesocosm was collected for analysis of nitrate + nitrite, TP, TN, DOC, pH, temperature, and alkalinity from 5 cm below the surface of the water. Surface water samples for analysis of total Hg (THg) and MeHg were collected using clean hands/dirty hands protocols in September 2013, filtered through $0.45\text{ }\mu\text{m}$ glass fiber filters, and immediately acidified with 0.5% (by volume) trace metal hydrochloric acid. Samples were stored on ice during transport and at 4°C until analysis.

Pore water P availability was measured with three mixed bed ion exchange bags (Fisher Rexyn 300 resin) placed in the sediment of each tank in spring and harvested at the end of the growing season in 2013. A 3.8 cm diameter piston corer was used to obtain 10 cm long sediment samples for various analyses. Sediment samples for the analysis of AVS were taken monthly from June to October 2013 from replicate mesocosms of four SO_4 treatments (control, 50 150, and 300 mg L^{-1} ; no mesocosm was sampled more

than once). Sediment samples were also taken on 8 October 2013 for the analysis of THg in bulk sediment and on 6 October 2015 for the analysis of total organic carbon (TOC).

2.2.2. Laboratory Analyses

Surface water and pore water analyses were conducted by the Minnesota Department of Health Environmental Laboratory (MDHEL). Total P was measured by in-line ultraviolet/persulfate digestion and flow injection (APHA, 2005, 4500 P-I), DOC by persulfate-ultraviolet oxidation and IR CO₂ detection (APHA, 2005, 5310-C), and alkalinity by automated titration (APHA, 2005, 2320-B). Pore water sulfide samples were prepared for inline distillation and flow injection colorimetric analysis using procedures that avoided exposure to oxygen. The sulfide serum bottle was weighed to determine the amount of sample collected and to adjust for the slight dilution factor of an alkaline antioxidant that was added by injection through the stoppers. The sealed samples were then placed on a stir plate for at least 1 h and subsamples withdrawn for analysis through a needle. Reanalysis of sealed, processed samples 12 months later shows no significant difference in sulfide concentrations, indicating that the sulfide samples were stable prior to analysis (data not shown). SO₄ concentration was measured using a Lachat QuikChem 8000 Autoanalyzer (Lachat Method 10-116-10-1-A). The resin was eluted using a KCl solution and analyzed for PO₄ using a Lachat Autoanalyzer, following the methods of Walker et al. (2006).

An aliquot of the nitrate + nitrite/TP/TN/DOC serum bottle was filtered in the lab within 10 days of sampling using a 0.45 μm filter, preserved to a pH < 2 with 10% sulfuric acid, and transferred to a 250 mL polyethylene bottle for DOC analysis. The remaining sample was preserved to a pH < 2, with 10% sulfuric acid and transferred to 250 mL polyethylene bottle for nitrate + nitrite/TP/TN analysis. The contents of the metal serum bottle were transferred to a 250 mL polyethylene bottle and preserved to a pH < 2 with 10% nitric acid. Analyses were conducted within 30 days of sampling.

THg in surface water and bulk sediment were analyzed with EPA method 1631 by MDHEL, and surface water MeHg was analyzed with EPA method 1630 by Frontier Global Sciences (Bothell, Washington). Inorganic Hg (iHg) was calculated as the difference between THg and MeHg. Sediment AVS was analyzed colorimetrically, as above for pore water sulfide, following acid distillation and in-line alkaline trapping (APHA, 2005; SM 4500-S2). Sediment TOC was analyzed following SM5310C (APHA, 2005), using an OI Analytical Aurora 1030 at Pace Analytical Services, Virginia, Minnesota.

3. Data Analysis

3.1. Sulfate Depletion as the Independent Variable

Because SO₄ is relatively unreactive under oxidized conditions, its loss is attributable to diffusion or transpiration-driven advection (Bachand et al., 2014) into sediment and conversion to sulfide by bacteria. Surface water SO₄ concentrations decreased partly due to dilution by precipitation but largely from loss after movement into the sediment and reduction to sulfide. Sulfide would largely be retained in the sediment as FeS compounds, although some could be lost to the atmosphere as H₂S gas (Bagarinao, 1992) or as volatile organic sulfur compounds (Lomans et al., 2002). The cumulative SO₄ lost from surface water was calculated from a mass balance for each mesocosm from the inception of the experiment in spring 2011 through fall 2013; this quantity, termed here SO₄ depletion, (SO₄)_{Depl}, is used as a proxy for net MSR, following Weston et al. (2006). The surface water remained frozen from approximately 1 December to 1 April each winter, and the mesocosms were covered with plastic from November to late April each year and not amended with SO₄. SO₄ reduction was the major biogeochemical process altered by the experimental treatments, and therefore, (SO₄)_{Depl} is the independent variable used in subsequent data analyses. It was only possible to perform a complete mass balance for SO₄, the only parameter consistently quantified in source water, precipitation, and overflow water.

3.2. Calculation of DIC From Measured Alkalinity

Dissolved inorganic carbon (DIC ≡ [CO₃²⁻] + [HCO₃⁻] + [CO₂*], where [CO₂*] = [CO_{2(g)}] + [H₂CO₃]) was calculated from measured alkalinity and speciated using pH, temperature, and specific conductance of the surface water. At the pH range of the mesocosms (7.60–8.84), 95–98% of DIC is in the form of HCO₃⁻, so DIC concentration on a molar basis is nearly the same as alkalinity (ALK) on an equivalent basis (DIC = 0.988 ALK + 0.077, R² = 0.995). In studies of freshwater, most inorganic carbon data are presented in terms of alkalinity because

alkalinity is a familiar metric; however, in comparisons with DOC, inorganic carbon data are presented as DIC so that the units are directly comparable. PHREEQC version 3 geochemical modeling software (Parkhurst & Appelo, 2013) was used to calculate saturation indices for carbonate minerals.

3.3. Statistical Analysis

Statistical analysis was conducted with R version 3.2.3 and STATA (StataCorp, 2015). The effect of increased sulfate availability was assessed through both categorical analysis of the sulfate treatments (Kruskal-Wallis ANOVA test, followed by Dunn's test for multiple comparisons with Holm-Sidak corrections) and through linear regression and nonparametric Spearman rank correlations. We rely primarily on regressions against SO_4 depletion to detect the effects of enhanced sulfate-reduction driven mineralization, rather than categorical analysis of the sulfate treatment results, because (a) biogeochemical changes are not driven directly by SO_4 concentration, but rather by MSR, quantified as SO_4 depletion; (b) although SO_4 depletion may be highly correlated to SO_4 concentration, deviations between experimental mesocosms develop over time, so cumulative SO_4 depletion values eventually no longer align exactly with treatment categories, but rather become continuous variables; and (c) regression provides more statistical power than ANOVA and builds models that allowed us to describe the relationships between SO_4 depletion and response variables (Cottingham et al., 2005). However, when the relationship is not linear, ANOVA and comparison of treatments through Dunn's analysis can help describe the nature of a relationship.

4. Results and Discussion

4.1. The Impact of SO_4 Reduction on Mineralization of Sediment Organic Matter

Increased concentrations of surface water SO_4 resulted in increased sulfate reduction, which necessarily increased the mineralization of organic carbon, as described by reaction (1). Concentrations of surface water DOC and DIC increased in proportion to sulfate reduction, as measured by $(\text{SO}_4)_{\text{Depl}}$ (Table 1 and Figure 2). The marine literature generally assumes complete mineralization of particulate organic carbon (POC) to DIC in the water column (e.g., Boudreau & Westrich, 1984) (reaction 1), but in freshwater systems and especially wetlands, not all carbon is completely oxidized during decomposition, and a portion of POC may be mobilized as DOC (Howes et al., 1985; Selvendiran et al., 2008). In principle, the constituents of organic matter, such as the nutrients N and P, are mobilized in proportion to the mass of carbon mineralized as a result of MSR-driven decomposition. Surface water DOC and DIC, and the sum $\text{DOC} + \text{DIC}$, are therefore used as indicators of OM mineralization in interpreting the mobilization of N, P, and Hg to surface waters (Figure 2 and Tables 2 and 3).

In contrast to many marine systems, it is likely that SO_4 reduction in these sediments was limited more by SO_4 than by organic carbon, given that $(\text{SO}_4)_{\text{Depl}}$ was linearly proportional to the average SO_4 concentration (Figure S2a; $R^2 = 0.87$), without any obvious curvature to the relationship that would indicate saturation of MSR.

Regressions of surface water DOC and DIC against SO_4 depletion demonstrate that, on a net basis, about 60% more DIC than DOC was mobilized to the surface water as a result of MSR-driven mineralization (slope of 0.235 mM C per unit SO_4 depletion compared to 0.148; Table 2). The significantly positive slope of the DIC:DOC ratio against SO_4 depletion (Table 2) indicates that increasingly more DIC than DOC was observed in the surface water as sulfate depletion increased. Some mineralization of DOC to DIC likely occurs in the surface water as a result of exposure to oxygen, aerobic bacteria, and sunlight, processes that could have a larger effect as DOC increases.

Not only did surface water DIC and DOC increase in concert with sulfate reduction, but parallel increases occurred in surface water concentrations of constituents of organic matter: N, P, and Hg (Table 1 and Figure 2). DIC, DOC, total P, total N, ammonia, and total Hg in surface water all had increases from the control to the highest SO_4 addition of about twofold, (2.3, 1.7, 1.9, 1.8, 1.7, and 2.6-fold, respectively, Table 1). However, available phosphate in the sediment, an estimate of P availability in pore water, had a larger increase (7.5-fold). MSR consumes acidity as the DIC-based alkalinity is produced (Baker et al., 1986), which increased the average pH from 7.57 to 7.81, a 44% decrease in hydrogen ion concentration (Table 1). If the sulfide subsequently oxidizes (which could happen in a natural system during drought (Laudon et al., 2004) or intentional dewatering), a proportional quantity of alkalinity is consumed as acid is produced

Table 1

Summary of Effects of Experimentally Increased SO_4 Concentrations on SO_4 Reduction (Quantified as SO_4 Depletion), Organic Matter Mineralization, and Mercury Methylation

		Average of each sulfate treatment (n = 6 for each treatment)						Correlation with SO ₄ depletion (Spearman)	
Variable	Matrix	Control	50	100	150	300	Max/Min	Rho	p value
Variables mainly associated with SO ₄ reduction									
SO ₄ (T-W mean mg SO ₄ L ⁻¹)	sw	6.7 ^a	26.9 ^{ab}	58.5 ^{abc}	93.2 ^{BC}	206.5 ^C	31.0	0.93	<0.0001
SO ₄ depletion (mg S cm ⁻²)	sw	0.14 ^a	2.52 ^{ab}	3.63 ^{abc}	4.28 ^{BC}	6.90 ^C	48.5	1	
Pore water sulfide (μg S L ⁻¹)	pw	69 ^a	184 ^a	224 ^a	393 ^b	728 ^b	10.5	0.81	<0.0001
Pore water iron (μg L ⁻¹)	pw	12,883 ^a	11,122 ^{ab}	6,808 ^{abc}	4,483 ^{BC}	3,032 ^C	4.25	-0.82	<0.0001
AVS (mg S kg ⁻¹)	sed	102 ^a	483 ^{ab}	NA	826 ^{ab}	1,413 ^b	13.8	0.77	<0.0001
pH	pw	7.57 ^a	7.52 ^a	7.55 ^a	7.75 ^a	7.81 ^a	1.03	0.39	=0.03
H ⁺ ion (μmol L ⁻¹)	pw	0.027	0.030	0.028	0.018	0.015	1.72	0.39	=0.03
Variables mainly associated with mineralization of organic matter									
TOC (% dry mass)	sed	9.26 ^a	7.90 ^a	8.18 ^a	7.17 ^a	8.22 ^a	1.29	-0.34	=0.065
DIC (mg C L ⁻¹)	sw	28.9 ^a	47.2 ^{ab}	56.3 ^{BC}	56.7 ^{BC}	66.3 ^C	2.30	0.94	<0.0001
DOC (mg C L ⁻¹)	sw	16.3 ^a	21.4 ^a	26.8 ^{BC}	24.0 ^{abc}	28.3 ^{bc}	1.74	0.79	<0.0001
Total N (mg N L ⁻¹)	sw	1.42 ^a	1.75 ^a	2.35 ^{BC}	2.03 ^{abc}	2.57 ^{BC}	1.81	0.77	<0.0001
Ammonia (mg N L ⁻¹)	sw	0.09 ^a	0.09 ^a	0.10 ^a	0.10 ^a	0.16 ^a	1.70	0.38	=0.04
Total P (μg P L ⁻¹)	sw	13 ^a	16 ^{ab}	22 ^{ab}	21 ^{ab}	25 ^b	1.92	0.73	<0.0001
Available P (μg P g ⁻¹ resin)	Resin in sed	0.34 ^a	0.40 ^a	0.59 ^{ab}	0.92 ^{ab}	2.56 ^b	7.45	0.86	<0.0001
Total Hg (ng L ⁻¹)	sw	1.83 ^a	2.09 ^a	3.61 ^{ab}	3.25 ^{ab}	4.80 ^b	2.63	0.82	<0.0001
Variables mainly associated with Hg methylation									
Methylmercury (ng Hg L ⁻¹)	sw	0.20 ^a	0.49 ^{ab}	1.21 ^b	1.08 ^b	1.18 ^b	5.91	0.66	<0.0001
Inorganic Hg (ng L ⁻¹)	sw	1.63 ^a	1.60 ^{ab}	2.40 ^{abc}	2.17 ^{BC}	3.62 ^C	2.22	0.80	<0.0001
Percent methylmercury	sw	11% ^a	23% ^{ab}	30% ^b	32% ^b	23% ^{ab}	2.90	0.45	=0.02

Note. Matrix abbreviations: sw = surface water, pw = pore water, sed = bulk sediment. Averages with superscript letters in common are not significantly different at the 0.05 level.

(Hall et al., 2006). However, the sulfide reoxidation does not reverse the mobilization of the constituents of organic matter (C, N, P, and Hg) or the production of methylmercury (MeHg; see below). Rather, any production of SO_4 from sulfide oxidation creates the potential for additional MSR-driven OM mineralization and Hg methylation (Coleman Wasik et al., 2015; Hansel et al., 2015).

The slope of linear regressions of the C, N, and P in surface water against $(\text{SO}_4)_{\text{Depl}}$ is an estimate of the increase of that variable in mesocosm surface waters per unit SO_4 reduction (Table 2). The regression slopes provide a basis for estimates of stoichiometric ratios of the constituents mobilized from the sediment solid phase, similar to the calculation that Weston et al. (2006) performed for pore water. The calculation of stoichiometric ratios from the slopes of regressions with $(\text{SO}_4)_{\text{Depl}}$ is more accurate than calculating ratios from surface water concentrations alone, as the use of slopes accounts for the concentrations of the control (the intercept of the linear regression).

The regression slopes of surface water C versus surface water N, P, and Hg in mesocosms are estimates of the net release of each element relative to that of C (Table 3). These estimates can then be compared to the ratio of these constituents in the primary source material—the sediment—to determine the efficiency of mobilization of sediment N, P, and Hg to surface water, compared to C (Table 3). Although we present efficiency relative to only DOC and only DIC, calculating efficiency relative to the sum of mineralized OM (DOC + DIC) represents the overall net efficiency of mineralization, which ranges from 8% to 38% for the three constituents (Table 3). Although the increases in surface water N, P, and Hg are consistent with the hypothesis that those elements were released to the surface water through sulfate-enhanced mineralization of sediment OM, their lower mobilization efficiencies relative to carbon suggest that other processes were operating to either increase carbon, decrease N, P, and Hg mobilization relative to carbon, and/or increase N, P, and Hg losses. It is likely that some carbon was introduced to the surface waters from sources other than the sediment (e.g., photosynthetic fixation of atmospheric carbon) and that there were losses for N, P, and Hg from the surface water (though adsorption, settling, biological uptake, or atmospheric evasion of N and Hg).

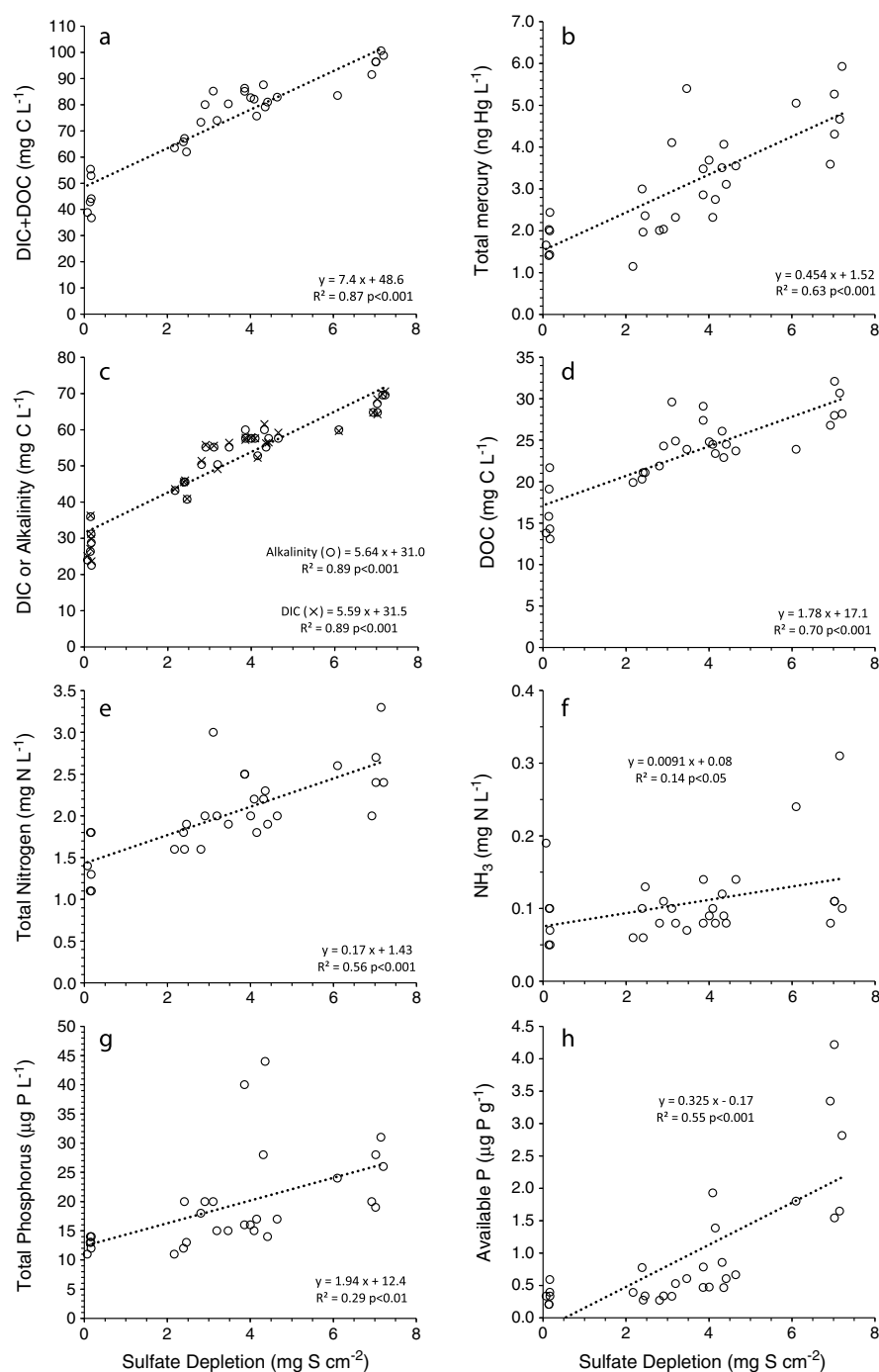


Figure 2. The release of constituents of sedimentary organic matter as a function of SO_4 depletion, showing linear regressions (dotted lines). (a) Sum of surface water DIC and DOC; (b) surface water total mercury; (c) surface water alkalinity and DIC (symbols $\circ$ and $\times$, respectively; the two regressions are superimposed); (d) surface water DOC; (e) surface water total nitrogen; (f) surface water ammonia; (g) surface water total phosphorus; (h) available phosphate in the sediment, as quantified on ion-exchange resin.

Table 2
Slopes of Regressions of Surface Water Parameters (mM) Against SO_4 Depletion ($\text{mg } 5 \text{ cm}^{-2}$)

Surface water variable (molar basis)	Regression against $(\text{SO}_4)_{\text{Depl}}$ ($\text{mg } 5 \text{ cm}^{-2}$)		
	Slope	R^2	p
DIC	0.235	0.89	<0.0001
DOC	0.148	0.70	<0.0001
DIC + DOC	0.383	0.84	<0.0001
DIC: DOC	0.044	0.56	<0.0001
TN	0.0121	0.56	<0.0001
TN: DIC	−0.0028	0.25	<0.01
TN: DOC	0.0004	0.01	NS
TN: DIC + DOC	−0.0006	0.08	NS
TP	6.26E−05	0.29	<0.002
TP: DIC	−7.00E−06	0.03	NS
TP: DOC	7.00E−06	0.02	NS
TP: DIC + DOC	−1.00E−07	0.00	NS
THg	2.26E−09	0.63	<0.0001
THg: DIC	9.00E−06	0.46	<0.0001
THg: DOC	6.00E−06	0.23	<0.01
THg: DIC + DOC	2.00E−05	0.42	<0.0001

Note. When a sediment constituent's ratio to DIC or DOC has a significant slope against sulfate depletion, it indicates that the constituent was mobilized to the surface water at a significantly different rate than the DIC or DOC.

In addition to increases of TP in the surface water, the sediment pore water in the highest SO_4 treatment contained 7.5-fold greater available phosphate than the controls, as quantified with ion-exchange resin (Table 1 and Figure 2h). In comparison, the increase in surface water TP was only 1.9-fold (Table 1 and Figure 2g). The difference between phosphorus response in the resin and the surface water may be partly due to (a) loss of TP from the surface water after mobilization or (b) irreversible trapping of mobilized P on the resin. If phosphorus is released from sediment en masse in response to an S-induced shift from iron oxides to iron sulfides, the sediment pore water would experience this release first, while release to surface waters would take longer due to diffusion-limited transport and potentially an iron-oxide barrier at the sediment-water (anoxic-oxic) interface.

DIC in surface water is not conservative, being subject to exchange across the air-water interface, carbonate mineral precipitation, and photosynthetic uptake. Surface water pCO_2 in all mesocosms was above saturation with respect to atmospheric equilibrium by a factor of 1.4–15.5 (based on the DIC speciation calculations discussed earlier; data not shown), so the mesocosms were losing, not gaining, C through gas exchange with the atmosphere. The pCO_2 values in the mesocosms are similar to those reported from epilimnia of small, organic-rich, temperate lakes of low to moderate salinity (Cole et al., 1994; Myrbo & Shapley, 2006). With respect to mineral precipitation, based on geochemical equilibrium calculations, surface waters were undersaturated with respect to all carbonate minerals. Thus, although DIC in surface water is subject to several transport and transformation processes, the sustained presence of CO_2 at quantities

significantly above saturation with respect to the atmosphere and the observation of increasing DIC and DOC with increasing $(\text{SO}_4)_{\text{Depl}}$ (Table 1) provide strong evidence of sulfate-induced increases in net carbon mineralization in the mesocosms.

In addition to the carbon originally present in the sediment, organic carbon was also photosynthetically fixed by wild rice and algae in the mesocosms and subsequently subjected to respiration and some decomposition, adding to the DIC and DOC in surface waters. DOC may also have been released into sediment pore water as an exudate from the wild rice roots (Rothenberg et al., 2014; Windham-Myers et al., 2009). Exudate DOC, however, does not account for the observed increase in DOC, since a negative relationship between the number of wild rice plants and DOC was observed (Spearman's $\rho = -0.63$, $p < 0.001$, Table S2).

4.2. Effects of SO_4 Reduction on Mercury and Methylmercury in Surface Water

We interpret Hg mobilization to the surface water in an analogous manner to C, N, and P, as Hg tends to associate strongly with organic matter in sediment (Feyte et al., 2010). In the mesocosm surface waters,

Table 3
Elemental Ratios in Sediment and Surface Water Across the Range of SO_4 Depletion

Molar ratio in sediment ^a	Molar ratio in surface water ^b			Efficiency of mobilization of sediment N, P, or Hg to surface water, relative to carbon		
	DIC	DOC	DOC + DIC	DIC	DOC	DOC + DIC
C: N	12 ^a	19	32	63%	100%	38%
C: P	463 ^a	3,752	6,118	12%	20%	8%
C: Hg	1.90E + 07	1.04E + 08	1.69E + 08	18%	29%	11%

Note. Together, the ratios are used to calculate the efficiency of mobilization of the constituents of particulate organic matter into the surface water.
^aSediment data from Hildebrandt, Pastor, and Dewey (2012), a mesocosm study that obtained sediment from the same natural wild rice stand. ^bRegression slopes of C versus N, P, and Hg in mesocosm surface waters; calculations are made based on surface water DIC alone, surface water DOC alone, and the sum of surface water DOC + DIC.

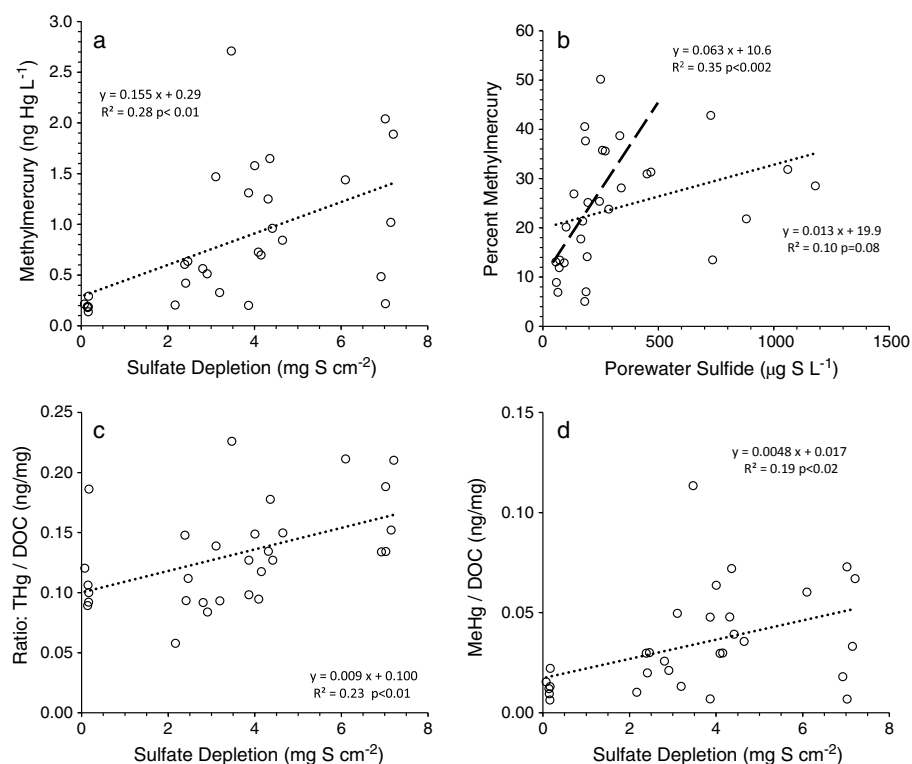


Figure 3. The response of surface water Hg variables to SO_4 depletion and the production of pore water sulfide, showing linear regressions. (a) MeHg as a function of SO_4 depletion; (b) percent MeHg as a function of pore water sulfide, showing regressions for all data (dotted line) and for the subset of data extending only to a pore water sulfide concentration of $468 \mu\text{g S L}^{-1}$ (dashed line); (c) ratio of THg to DOC as a function of SO_4 depletion; (d) ratio of MeHg to DOC as a function of SO_4 depletion.

THg, inorganic Hg (iHg), and MeHg all increased significantly with increased $(\text{SO}_4)_{\text{Depl}}$ (Table 1 and Figures 2b and 3a, $p < 0.0001$) and were greater in the highest sulfate amendment by factors of 2.6, 2.2, and 5.9, respectively (Table 1). The relative increase in THg (2.6-fold) is greater than that for DIC, DOC, TN, and TP, which range from 1.7 to 2.3-fold (Table 1). DOC enhances the solubility of both iHg and MeHg and can facilitate the movement of Hg from sediment into surface water (Ravichandran, 2004). The 5.9-fold increase in MeHg indicates that MeHg flux to surface waters was enhanced by sulfate loading disproportionately more than sedimentary release of THg (2.6-fold) and the increase in surface water DOC (1.7-fold).

The genes required to methylate Hg have been found in a wide variety of anaerobic bacteria, including SO_4 -reducing bacteria, iron-reducing bacteria, and methanogens (Podar et al., 2015). Though some pure culture and experimental evidence exist for mercury methylation by other bacteria, extensive pure culture, experimental, and landscape-scale observations suggest SO_4 -reducing bacteria dominate Hg methylation in many freshwater and marine environments. The relatively large increase in surface water MeHg in response to increased $(\text{SO}_4)_{\text{Depl}}$ in this experiment supports the assumption that MSR was responsible for most of the observed production of MeHg. It is likely that increased SO_4 loading to low- SO_4 aquatic systems with organic sediment will result in increased Hg methylation even though the relative importance of Hg methylation in the environment by different groups of bacteria is still a subject of debate (Paranjape & Hall, 2017).

If movement of DOC from sediment to surface water were the sole mechanism for the Hg increase in surface water, a constant Hg:DOC ratio would be expected on the $(\text{SO}_4)_{\text{Depl}}$ gradient. However, THg:DOC, iHg:DOC, and MeHg:DOC ratios in surface water are all significantly correlated with SO_4 depletion (Table S2 and Figures 3c and 3d). Therefore, all forms of Hg (THg, iHg, and MeHg) increase in surface waters more than

does DOC, indicating that a sulfate-induced enhancement of carbon mineralization may act in combination with either enhanced methylation or an enhanced capacity of DOC to carry Hg. Changes to the binding strength of the DOC in heavily S-impacted mesocosm sediment are possible, as thiol groups on DOC are dominant binding sites for Hg (Skylberg, 2008). The dual role of organic carbon and sulfur in driving both the production of MeHg and the transport of MeHg could be responsible for the substantially larger maximum increase in MeHg:DOC ratio relative to the increase in the THg:DOC ratio (an average 206% increase relative to a 63% increase, Figures 3c and 3d), as postulated by Bailey et al. (2017).

Regnell and Hammar (2004) identified three MSR-driven processes that might cause mobilization of Hg from sediment in a wetland, (1) mineralization of organic matter; (2) extraction of iHg by reduced S compounds, which could be associated with mobilized DOC; and (3) enhanced production of MeHg, which is more mobile than iHg. They argued that enhanced production of MeHg explained THg mobilization in the minerotrophic peat bog that they studied. However, in this study, increases in surface water MeHg concentrations (Figure 3a) are not sufficient to explain the linear increase in THg observed in this experiment (Figure 2b) because most (67%) of the increase is iHg (Table 1). Some of the increase in surface water iHg could be the result of increased production of MeHg that moved to surface water and was subsequently demethylated. Regardless of the underlying mechanism, our observations clearly show increases in surface water Hg that were greater than the increases in C, N, and P (Table 3); this corroborates other studies (Bouchet et al., 2013; Merritt & Amirbahman, 2007; Regnell & Hammar, 2004) that suggest sediment Hg may be synergistically mobilized to surface waters through mineralization, methylation, and enhanced mobility with DOC.

Recent research has shown that in many ecosystems, higher concentrations of pore water sulfide may inhibit MeHg production through either thermodynamically or kinetically controlled reactions with inorganic Hg (Benoit et al., 2003; Hsu-Kim et al., 2013). We plotted %MeHg, rather than the MeHg concentration, against pore water sulfide because we are interested in identifying the pore water sulfide zone of greatest efficiency for the methylation and mobilization of mercury. In this experiment the MSR-driven mineralization of OM released THg to surface water in addition to producing pore water sulfide. Accordingly, because THg is not constant, plotting %MeHg is the most accurate way to identify peak methylation efficiency. In principle, the restricted bioavailability of Hg to methylating bacteria results in a maximum in MeHg production at intermediate concentrations of pore water sulfide. Consistent with previous research in sulfate-impacted freshwater ecosystems (Gilmour et al., 1998; Gilmour, Krabbenhoft, et al., 2007; Gilmour, Orem, et al., 2007; Bailey et al., 2017), MeHg production was most efficient at intermediate sulfide concentrations. In the control, where average sulfide was $69 \mu\text{g S L}^{-1}$, MeHg averaged only 11% of THg in surface waters. In the intermediate SO_4 treatments, which had average sulfide concentrations of 224 and $393 \mu\text{g S L}^{-1}$, MeHg production efficiency peaked significantly higher, at averages of 30% and 32%, respectively (Table 1). %MeHg declined to an average of 23% in the highest SO_4 treatment, which had an average sulfide concentration of $728 \mu\text{g S L}^{-1}$. Given the relatively great scatter in the relationship between %MeHg and sulfide (Figure 3b), it would be most defensible to conclude that the decrease in %MeHg began to occur somewhere between 300 and $700 \mu\text{g S L}^{-1}$. There is a strong positive relationship ($p < 0.001$) between sulfide and %MeHg if the five sulfide concentrations greater than $727 \mu\text{g S L}^{-1}$ are excluded from the regression (which leaves only sulfide concentrations less than $468 \mu\text{g S L}^{-1}$, since there is a gap in sulfide concentrations; Figure 3b). Other studies have identified sulfide zones of peak methylation roughly comparable to that found here. In South Florida, Orem et al. (2011) found that sulfide ranging from 5 to $150 \mu\text{g S L}^{-1}$ did not inhibit methylation but that sulfide concentrations greater than $1,000 \mu\text{g S L}^{-1}$ did. In a subboreal Minnesota wetland enriched in SO_4 from mining discharge, Bailey et al. (2017) found that sulfide concentrations above $\sim 650 \mu\text{g S L}^{-1}$ inhibited methylation.

The relationship between surface water SO_4 and Hg methylation can be strongly affected by site-specific conditions. Because of the variable conversion of SO_4 in surface water to sulfide in pore water—primarily due to differences in OM and Fe availability (Pollman et al., 2017)—researchers have found a broad range in the SO_4 concentration associated with maximum efficiency of Hg methylation. For example, Orem et al. (2014) observed that two different areas in the Everglades Protection Area had peak surface water MeHg concentrations at SO_4 concentrations of 2 and 10–15 mg L^{-1} . In the mesocosms presented here peak surface water %MeHg was observed in the two sulfate treatments that averaged 59 and 93 mg L^{-1} (Table 1).

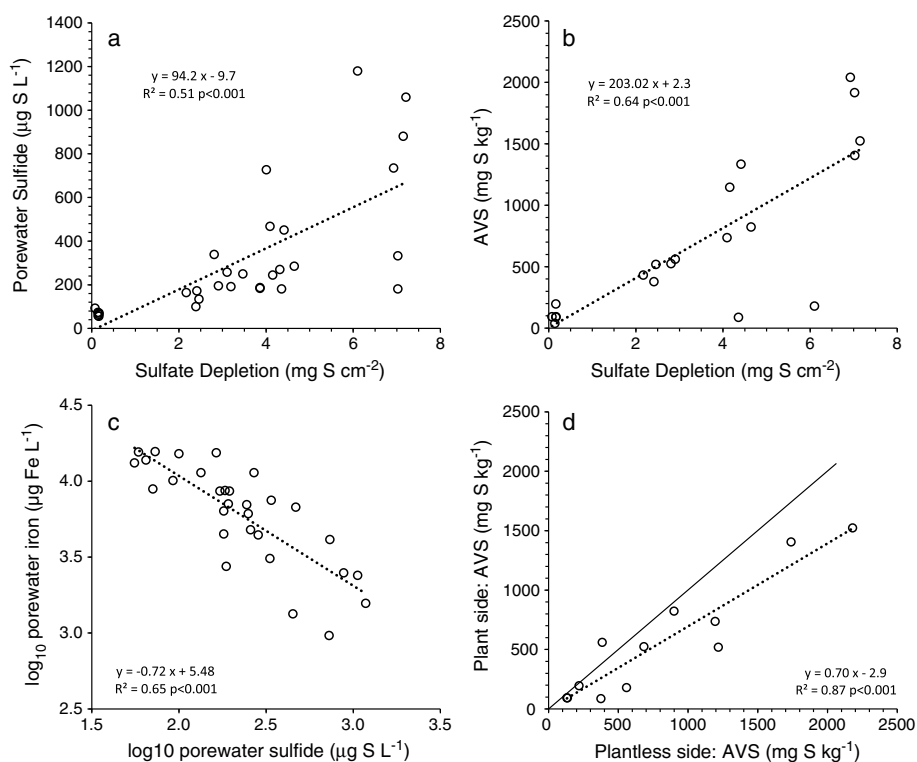


Figure 4. AVS and pore water sulfide, as related to SO_4 depletion, pore water iron, and presence of rooted plants. (a) Pore water sulfide as a function of SO_4 depletion; (b) AVS from the vegetated side of the mesocosms as a function of SO_4 depletion; (c) pore water iron as a function of pore water sulfide; (d) AVS compared between the vegetated side and nonvegetated side. The solid 1:1 line shows that in almost all mesocosms more AVS is found in the side without plants.

4.3. Effects of SO_4 Reduction on Pore Water and Sediment Sulfide

Pore water sulfide increased at higher $(\text{SO}_4)_{\text{Depl}}$, although with greater variance at higher $(\text{SO}_4)_{\text{Depl}}$ (Figure 4a), possibly as a result of variable oxidation of sulfide that may depend on the proximity of the Rhizon sampler to plant roots (Schmidt et al., 2011) or of variable bioturbation by invertebrates (Lawrence et al., 1982). When SO_4 is reduced through MSR, the sulfide produced has a number of nonexclusive potential fates: the sulfide could (1) be oxidized within the sediment; (2) remain in the sediment pore water as free sulfide; (3) diffuse into oxygenated surface water, to be oxidized; (4) react with metals in the sediment, forming insoluble precipitates (dominated by iron-sulfide compounds); or (5) be lost to the atmosphere as H_2S gas or as volatile organic sulfur compounds. Because precipitation reactions are fast relative to redox reactions and diffusion, most of the sulfide probably forms metal precipitates if metals are available. When precipitation dominates the fate of sulfide produced from MSR, the continuous reduction of SO_4 and precipitation of iron sulfides form quasi-steady states between surface water SO_4 and pore water sulfide (Figure S2b) and between pore water sulfide and pore water iron (Figures 3 and 4c). The overall mass of sulfide in the mesocosm sediment, quantified through analysis of AVS (from sediment in the vegetated area), is closely correlated with SO_4 depletion (Figure 4b) even though AVS may not include all the reduced sulfide in sediments. It is likely that most of the AVS in these sediments is present as an FeS precipitate because other metals are at low concentrations in these sediments, which came from a relatively pristine (unpolluted) lake (Fond du Lac Band, 2016; Pastor et al., 2017). Note that there are two mesocosms with especially low AVS concentrations (Figure 4b). It is possible that the AVS in the specific location in these mesocosms where sediment core samples were collected was influenced by

a spatially heterogeneous oxidization process (e.g., root oxygen or benthic invertebrates) that limited the accumulation of sulfide.

AVS was 30% lower in the vegetated side of the mesocosms, suggesting that wild rice released oxygen into the sediment, inhibiting the production of sulfide and/or decreasing sulfide concentrations through oxidation (Figure 4d; Wilcoxon paired test, $p = 0.007$). It is notable that this 30% difference developed in just one growing season, despite the previous 2 years of sulfate treatment. Pore water sulfide showed no statistically significant difference between the two sides owing to high variability within treatments. Numerous investigations have found that rooted aquatic plants release oxygen from their roots, a phenomenon that is usually interpreted as an adaptation to limit the toxicity of reduced chemical species in the pore water, especially sulfide (Lamers et al., 2013). Although oxygen release has been observed in white rice, *Oryza sativa* (Colmer, 2002), it has never been documented in wild rice, which is in the same tribe (Oryzaceae) of grasses as white rice, and also develops aerenchyma (Jorgenson et al., 2013), plant structures that provide a low-resistance internal pathway for movement of oxygen to the roots. Since the growth and reproduction of rooted plants can be inhibited by sulfide (Pastor et al., 2017), there may be a tipping point of exposure to sulfide above which oxygen release is insufficient to mitigate phytotoxic effects, and the plant population declines over time, possibly to extirpation. In this experiment, in the third treatment year, the increase in pore water sulfide was the apparent cause of a decrease in the average number of wild rice stems from 17 in the control mesocosms to 3 in the highest-sulfate treatment mesocosms (Pastor et al., 2017).

4.4. Mesocosms as Models for Ecosystem-Scale Effects of SO_4 Reduction

Although mesocosms, as contained ecosystems, are useful because they mimic ecological and biogeochemical processes that occur in the field, extrapolating findings to nature is challenging when plastic walls have prevented exchange of water and materials (Petersen et al., 2009). These wall-based challenges are manifest in three phenomena in this experiment, (1) relatively long surface water residence times due to the lack of a constant throughflow; (2) the presence of the wall itself, which provides a surface for periphyton; and (3) lack of either overland or groundwater loading of external materials:

1. Relatively long surface water residence times: the increased loading of N, P, C, Hg, and MeHg to the surface water of the mesocosms was readily detected because the lack of hydraulic loading from a watershed minimized dilution and loss through the outflow. The impact of an increase in SO_4 loading on surface water concentrations of N, P, C, Hg, DIC, and DOC would be lower in waters with shorter residence times. For instance, Baker and Brezonik (1988), in modeling increases in alkalinity from atmospheric SO_4 loading, noted that net increases in alkalinity would be most important in waters with long residence times (>5 years) and that there would be little increase in alkalinity in waters with much shorter residence times (<1 year). However, the measured concentrations may not represent the maximum impact of MSR-driven mineralization because the mesocosm wall may enhance removal from the surface water (point number 2, below).
2. Presence of the mesocosm wall: the mesocosms have a relatively high ratio of wall and sediment surfaces to the volume of overlying water, enhancing the removal of surface water nutrients and Hg to periphyton or inorganic sinks such as iron oxyhydroxides. Natural aquatic systems have less proportional loss to surfaces. The quantitative estimates of internal loading of N, P, and Hg in response to MSR-induced carbon mineralization may have been underestimated by the measured surface water concentrations, given that significant loss of these constituents to periphyton may have occurred. In addition, THg was filtered prior to analysis, which would have removed any Hg associated with phytoplankton or other suspended particles.
3. Lack of either overland or groundwater loading of particulate and dissolved material, specifically iron: the availability of iron in sediment is a primary controller of the fate of MSR-produced sulfide (Pollman et al., 2017). In natural aquatic systems, iron would be supplied at a relatively constant rate from the system's watershed over the long term, although varying in magnitude from watershed to watershed (Maranger et al., 2006; Winter, 2001). This experiment was not an accurate long-term mimic of pore water sulfide concentrations because the external supply of iron was cut off at the inception of the experiment. With no loading of iron, but continued loading of SO_4 , the continued production of sulfide would be expected to eventually consume all available Fe, allowing pore water sulfide levels to exceed those expected in a natural system at equivalent surface water SO_4 concentrations. This mesocosm experiment provides

evidence for just such a result. The experiment continued for 2 years after the 2013 sampling presented here. In the fifth year (August 2015) pore water sulfide was much greater than had been observed in 2013, and disproportionately so in the highest SO_4 treatment, which was most likely to consume available Fe. Between the 2013 and 2015, pore water sulfide increased in the control SO_4 treatment (about $7 \text{ mg SO}_4 \text{ L}^{-1}$) from an average value of $69 \mu\text{g L}^{-1}$ in 2013 to $116 \mu\text{g L}^{-1}$ in 2015, a 68% increase. Pore water sulfide in the highest treatment (nominally $300 \text{ mg SO}_4 \text{ L}^{-1}$, Table 1) increased from an average value of $728 \mu\text{g L}^{-1}$ in 2013 to $9,350 \mu\text{g L}^{-1}$ in 2015, a 1,184% increase (Pastor et al., 2017). In a survey of 108 Minnesota waterbodies with a wide range of surface water sulfate, only two exceeded a pore water sulfide level of $3,200 \mu\text{g L}^{-1}$ (Myrbo et al., 2017).

5. Conclusions

This study demonstrates that increased SO_4 loading to inland waters with organic-rich sediments can significantly increase the decomposition of sedimentary organic matter, which increases internal loading to surface water of the chemical constituents of organic matter, including DIC, DOC, P, N, and Hg. Associated changes include increased production of sulfide and methylmercury and increased alkalinity and pH. Any one of these changes could alone cause significant secondary changes in the structure of an aquatic ecosystem but, taken together, could cause a cascade of primary and secondary environmental changes: increased availability of nutrients (N and P), which can alter dominant plant species, organic carbon production, oxygen consumption, and redox; increased pore water sulfide, which can be toxic to benthic animals and plants; increased MeHg production, which can affect fish and other consumers in the aquatic food web; increased DOC, which can alter light transmission, thermal stratification, and aquatic chemistry; and increased DIC production, which increases alkalinity and pH, affecting aquatic chemistry and biota. Each of these changes resulting from higher surface water SO_4 and consequent increases in MSR has been documented in the literature, but the entire suite of associated changes in aquatic chemistry has not heretofore been demonstrated in an integrated fashion. The degree to which an increase in SO_4 loading affects the ecological structure of the receiving water will depend on the relative increases in N, P, DIC, DOC, Hg, MeHg, pH, and sulfide, which will be a function of background geochemistry and hydrology of the specific system. In this experiment, the changes in these parameters were linearly proportional to SO_4 reduction, which, in turn, was linearly proportional to the time-weighted average SO_4 concentration. The linear responses of the parameters to SO_4 additions suggest that ecologically significant changes may occur even when SO_4 concentrations are elevated only modestly and that dramatic changes may occur with higher sulfate loading.

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RESEARCH ARTICLE

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Key Points:

- Sulfate loading to freshwater ecosystems may alter aquatic plant communities when sulfate is reduced to sulfide in the anoxic rooting zone
- The occurrence of self-sustaining wild rice populations is mainly controlled by pore water sulfide concentrations
- Even if pore water sulfide is low, wild rice is less likely to be found if the surface water is turbid or warm

Supporting Information:

- Table S1
- Table S2
- Table S3
- Data Set S1
- Figure S1

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Sulfide Generated by Sulfate Reduction Is a Primary Controller of the Occurrence of Wild Rice (*Zizania palustris*) in Shallow Aquatic Ecosystems

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Abstract Field observations suggest that surface water sulfate concentrations control the distribution of wild rice, an aquatic grass (*Zizania palustris*). However, hydroponic studies show that sulfate is not toxic to wild rice at even unrealistically high concentrations. To determine how sulfate might directly or indirectly affect wild rice, potential wild rice habitat was characterized for 64 chemical and physical variables in over 100 sites spanning a relatively steep climatic and geological gradient in Minnesota. Habitat suitability was assessed by comparing the occurrence of wild rice with the field variables, through binary logistic regression. This analysis demonstrated that sulfide in sediment pore water, generated by the microbial reduction of sulfate that diffuses or advects into the sediment, is the primary control of wild rice occurrence. Water temperature and water transparency independently control the suitability of habitat for wild rice. In addition to generating phytotoxic sulfide, sulfate reduction also supports anaerobic decomposition of organic matter, releasing nutrients that can compound the harm of direct sulfide toxicity. These results are important because they show that increases in sulfate loading to surface water can have multiple negative consequences for ecosystems, even though sulfate itself is relatively benign.

Plain Language Summary Research in the 1940s and 1950s found that wild rice grew best in low-sulfate Minnesota lakes, but it was not known why. The correlation was a puzzle, since sulfate is not very toxic to plants or animals. This study found that the problem is sulfide, not sulfate. Sulfate can be converted into toxic levels of sulfide in the soil in which wild rice germinates and roots. Wild rice is an annual plant that must sprout each spring from seed that was dropped the previous fall into wet soil. Anaerobic microbes in the soil make sulfide from sulfate in the overlying water. Lakes, streams, and wetlands that have high concentrations of dissolved sulfide in the sediment therefore have a low probability of hosting wild rice. The study also found that wild rice prefers high-transparency water and cold winters.

1. Introduction

Minnesota is unique among U.S. states and Canadian provinces in having a water quality standard that regulates sulfate (SO_4) to protect wild rice, *Zizania palustris* and *Zizania aquatica*. The more common wild rice species in Minnesota, *Z. palustris* (northern wild rice), is an annual emergent aquatic grass that forms monocultures in shallow freshwaters (wetlands, lakes, and rivers) in the area of the Laurentian Great Lakes (Minnesota, Wisconsin, Michigan, Ontario, and Manitoba). Wild rice is culturally important to multiple groups in Minnesota, especially Ojibwe, Dakota, and other Native Americans, and also provides habitat and food for waterfowl and other wildlife (Vennum, 1988). In 1977, the Minnesota legislature voted to make wild rice the Minnesota state grain. Minnesota Rule 7050.0224, promulgated in 1973, seeks to limit the exposure of wild rice to SO_4 concentrations exceeding 10 mg L^{-1} (0.1 mmol L^{-1}). This value was based on empirical research that correlated water chemistry to aquatic plant assemblages and included the observations that no large populations of *Z. palustris* occur in waters exceeding $10 \text{ mg L}^{-1} \text{ SO}_4$ and that stands are uncommon where SO_4 concentrations exceed 50 mg L^{-1} (Moyle, 1944, 1945). In addition, Moyle (1956) noted that plantings of wild rice seed in high- SO_4 regions generally failed. A larger unpublished Minnesota Department of Natural Resources data set also shows that sites with reported wild rice

presence (DNR, 2008) are generally correlated with surface water SO_4 below 10 mg L^{-1} (Figure S1 in the supporting information).

We report here on a multiyear field survey that was part of a larger study (Myrbo et al., 2017; Pastor et al., 2017; Pollman et al., 2017) designed to reevaluate the 10 mg L^{-1} SO_4 standard by testing potential mechanisms by which SO_4 might be harmful to wild rice. SO_4 is a relatively nontoxic and unreactive compound under aerobic conditions. Pastor et al. (2017) and Fort et al. (2014) have shown that SO_4 is not directly toxic to wild rice at concentrations up to $1,600 \text{ mg L}^{-1}$, which exceeds concentrations in virtually all natural surface waters of the upper Midwest (Gorham, Dean, & Sanger, 1983). The U.S. Environmental Protection Agency's nonmandatory drinking water standard of 250 mg L^{-1} SO_4 (2.6 mmol L^{-1}) is based on taste rather than toxicity (EPA, 2010).

1.1. Potential Effects of Elevated Sulfate and Sulfide in Freshwater Systems

SO_4 concentrations in most freshwaters are less than a few percent of the mean concentration in seawater ($2,800 \text{ mg L}^{-1}$ (29.1 mmol L^{-1})). We surveyed 108 different lakes, streams, and wetlands across Minnesota, where the median SO_4 concentration in lakes is 10 mg L^{-1} (10th and 90th percentiles of 0.2 and 285 mg L^{-1} (MPCA, 2016)). In the much higher SO_4 concentrations of marine waters, it is well established that SO_4 can diffuse into sediment and be converted by microbial sulfate reduction (MSR) to potentially toxic sulfide that influences the presence and absence of rooted macrophytes, such as seagrasses (Borum et al., 2005; Ingold & Havill, 1984; Koch & Erskine, 2001; Lamers et al., 2013).

Despite a long-standing assumption that SO_4 is benign (Pester et al., 2012; Schindler, 1986; Urban et al., 1994) and plays a negligible role in freshwater biogeochemistry (e.g., Capone & Kiene, 1988), there is evidence that SO_4 availability in freshwaters can control the concentration and therefore the toxicity of hydrogen sulfide (H_2S) in sediment pore water to plants and animals (Bagarinao, 1992; Kinsman-Costello, O'Brien, & Hamilton, 2015; Lamers et al., 2013; Wang & Chapman, 1999). The chemical species of H_2S varies with pH; below pH 7, H_2S dominates, and above pH 7, the bisulfide ion (HS^-) dominates. For simplicity in this discussion we refer to the sum of the two species as sulfide.

1.1.1. Sulfide Toxicity to Freshwater Plants

Remarkably little attention has been given to the potential toxicity of sulfide in sediment pore water, even after Bagarinao (1992) concluded in a major review that sulfide had been "largely overlooked as an environmental factor for aquatic organisms." In a discussion of sediment toxicity testing, Wang and Chapman (1999) also observed that the biological implications of sulfide in sediments are poorly understood and "all too often ignored." They suggested that sulfide may be more important than ammonia in determining sediment toxicity to organisms and made a suite of recommendations to fill the knowledge gap, including the measurement of sulfide in undisturbed sediments. Kinsman-Costello et al. (2015) measured sulfide in undisturbed sediments and concluded that the potential toxicity of pore water sulfide is likely shaping the plant and animal communities of freshwater ecosystems. Lamers et al. (2013), in a review of sulfide toxicity to aquatic plants, pointed out that traditional toxicity testing generally neglects the chemistry of the rooting zone. Simkin, Bedford, and Weathers (2013) showed that pore water sulfide in a wetland controlled the distribution of plants more than did nutrients.

The toxicity of elevated sulfide to freshwater plants was first recognized in paddy-grown white rice (*Oryza sativa*) in the 1950s (Lamers et al., 2013; Pearsall, 1950). Rice paddies and other water-saturated soils present a profound challenge for rooted plants because of the chemical changes caused by the absence of oxygen and resulting potential toxicity of the pore water (Ponnamperuma, 1972). Anaerobic decomposition of organic matter results in elevated pore water concentrations of ammonia, organic acids, and variable concentrations of sulfide and ferrous Fe, depending on the availability of SO_4 and Fe. The interaction of Fe and the S cycle is complicated (Hansel et al., 2015), but because under anoxic conditions sulfide forms an insoluble precipitate with Fe, elevated pore water sulfide concentrations occur when Fe availability is relatively low (Ponnamperuma, 1972; van der Welle et al., 2006). It is thought that the iron sulfide precipitates are relatively inert and that only sulfide dissolved in pore water is potentially toxic. The concentration of sulfide in pore water is the balance between production and competing fates of sulfide, including precipitation with metals such as Fe, oxidation by oxygen introduced by bioturbation or by release from the roots of macrophytes (Armstrong & Armstrong, 2005), and by downward advection of surface water due to groundwater movement or transpiration by dense macrophyte stands (Bachand et al., 2014).

1.1.2. Geochemical Consequences of Enhanced Microbial Sulfate Reduction

Increased SO_4 availability can allow increased anaerobic decomposition of organic matter, releasing the inorganic nutrients that generally limit growth of higher plants (N, P, and K) (Lamers, Tomassen, & Roelofs, 1998; Myrbo et al., 2017; Weston et al., 2006, 2011). Enhanced decomposition breaks down particulate and dissolved organic carbon (DOC) in the sediment, which can increase DOC and dissolved inorganic carbon (DIC) in the overlying water (Myrbo et al., 2017).

In addition to supporting organic matter mineralization, MSR production of sulfide causes a cascade of reactions that can alter ecosystem functioning independent of any toxicity to plants and animals. First, sulfide can participate in redox reactions, chemically reducing Fe, which converts Fe from solid phase Fe(III) oxyhydroxides to water-soluble Fe(II) (Hansel et al., 2015). The dissolution of the Fe oxyhydroxides releases sorbed ions into solution, including phosphate and trace metals (Caraco, Cole, & Likens, 1993; Davranche & Bollinger, 2000; Søndergaard, Jensen, & Jeppesen, 2003). Second, sulfide can precipitate dissolved metals, including essential plant nutrients Fe, Cu, and Zn, decreasing their bioavailability and leading to nutrient deficiency (Kirk, 2004; Lamers et al., 1998; Neue & Bloom, 1989; Neue & Lantin, 1994). In systems unpolluted with heavy metals, the sulfide precipitate is overwhelmingly dominated by iron sulfide compounds, consisting of a range of stoichiometries and minerals (Schoonen, 2004), which we here term "FeS compounds." Third, the conversion of SO_4 to sulfide entails the production of DIC, or alkalinity, an effect not fully appreciated in freshwater systems until the mechanistic consequences of acid rain were investigated in the 1980s (Baker, Brezonik, & Pollman, 1986; Cook et al., 1986; Schindler, 1986). Alkalinity is thought to be a major factor influencing the distribution of aquatic species, including macrophyte species (Moyle, 1945; Vestergaard & Sand-Jensen, 2000). In addition, elevated alkalinity may further enhance decomposition, producing a positive feedback to the effects of SO_4 -driven mineralization (Geurts et al., 2009; Roelofs, 1991).

1.2. Multiple Plausible Negative Effects of Elevated Sulfate and Sulfide Production on Wild Rice

The purpose of this study was to examine the multiple ways that increases in SO_4 concentration and sulfide production can change the biogeochemical functioning of freshwater ecosystems and potentially negatively affect the growth and reproduction of wild rice populations. Before any field data were collected for this study, alternative hypotheses regarding the most likely negative effects were identified (MPCA, 2011), so that appropriate data would be available to test them. The primary hypotheses of how increases in surface water concentrations of SO_4 could harm wild rice populations include direct toxicity by elevated pore water sulfide; reduced bioavailability of Fe, Cu, or Zn; and increased P bioavailability promoting the growth of phytoplankton and macrophytes that compete for light and space. Additional variables were quantified so that exploratory data analysis could be pursued in addition to evaluation of the primary hypotheses. Surface water, pore water, and sediment physical and chemical properties were collected from 108 different sites, both with and without wild rice present, to inform evaluation of these multiple interrelated hypotheses.

2. Methods

2.1. Study Area

2.1.1. Physical Environment

SO_4 concentrations in surface water vary with geology and climate (Gorham et al., 1983) in a northeast-southwest gradient across Minnesota. Bedrock and bedrock-derived glacial deposits of northeastern Minnesota (the "arrowhead") comprise slowly weathered crystalline materials, generally low in S, and surface waters are dilute (specific conductance of <140 and often $<30 \mu\text{mho cm}^{-1}$; Gorham et al., 1983). Within this area of naturally low SO_4 , iron-mining activities in the "Iron Range" district of northeastern Minnesota have created an "island" of lakes and streams elevated in SO_4 (Figure 1), a result of the weathering of sulfide minerals in waste rock piles and tailing basins. The surficial geology of southwestern Minnesota, in contrast, is derived from marine shales and carbonates that are relatively S-rich and readily weathered: surface waters often exceed $500 \mu\text{mho cm}^{-1}$ and may exceed $7,000 \mu\text{mho cm}^{-1}$ (Gorham et al., 1983). SO_4 concentration is positively correlated with conductivity above about $200 \mu\text{mho cm}^{-1}$ and 10 mg L^{-1} or 0.1 mmol L^{-1} SO_4 (Figure 7B in Gorham et al., 1983). Overprinting this geological pattern is a strong climatic gradient with warmer, drier conditions toward the southwest (toward the northern Great Plains) and colder, more humid conditions to the northeast (toward the Laurentian Great Lakes), which enhances the conductivity gradient: more evaporative conditions in the southwest serve to concentrate surface waters and further increase ionic

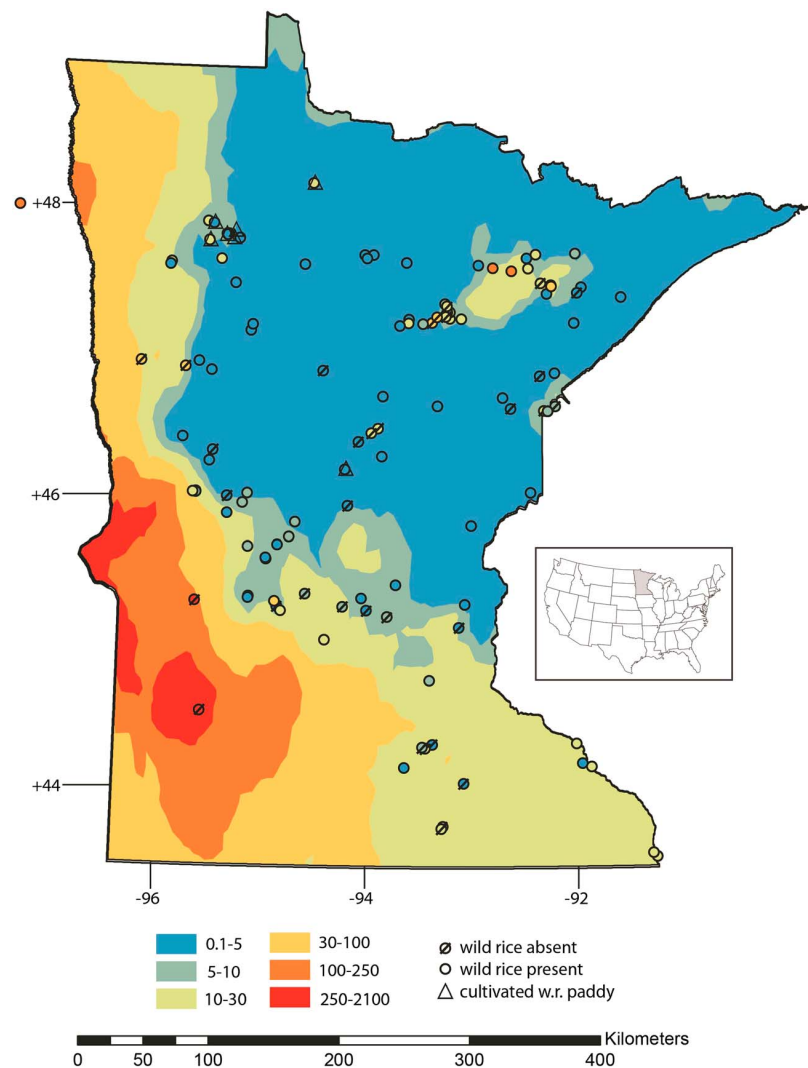


Figure 1. Map of Minnesota showing field sites overlain on kriged contours of average surface water SO_4 concentrations from 4,998 waterbodies (data from MPCA and DNR databases). The symbols are filled with the color corresponding to the site's surface water sulfate concentration. Site to the northwest of the Minnesota map is within the state of North Dakota, 40 km west of the border with Minnesota (see text). Sites where wild rice was not found have a diagonal line through the symbol.

strength, while moister conditions in the northeast maintain low ionic strength in surface waters (Gorham et al., 1983).

2.1.2. Habitat Preferences of Wild Rice

Although the scientific literature contains many assertions concerning the environmental preferences of wild rice regarding water and sediment quality (e.g., DNR, 2008, 2016; Lee, 2002; Moyle, 1944; Moyle & Krueger, 1964; Pillsbury & McGuire, 2009), sometimes little evidence was presented to support the putative preferences. The shallow freshwaters in which wild rice is found are usually relatively transparent because wild rice and other rooted macrophytes do best if they can photosynthesize as they grow each spring from the sediment to the water surface (Scheffer, 1998). Otherwise, any particular habitat preference of wild rice, such as specific chemical ranges of the sediment or surface water, is challenging to identify. Since wild rice is an opportunistic annual plant, a primary habitat requirement is periodic environmental disturbance (Grime, 1977) that keeps perennial plants such as water lilies from controlling the space and light of the shallow waters in which these species cooccur (Pillsbury & McGuire, 2009). Wild rice does not seem to have specific sediment requirements, as it has been observed growing in a variety of substrates (Aiken et al., 1988; Lee,

1986) within its range. Annual plants are adapted to exploit environments intermittently favorable for rapid plant growth and to maximize seed production (Grime, 1977). Wild rice produces between 25 and 150 relatively large seeds per stem (Eule-Nashoba, Biesboer, & Newman, 2012). Seeds buried in the sediment can survive for up to several decades until conditions are again favorable for germination and growth (DNR, 2008). *Zizania palustris* seeds germinate at low rates unless they have been exposed to near-freezing temperatures for at least 3 months (Kovach & Bradford, 1992), although the environmental cues for subsequent germination are poorly understood, aside from elevated temperature.

Because *Z. palustris* does not normally self-pollinate and is wind-pollinated (which implies that the pollen source must be relatively nearby; Friedman & Barrett, 2009), does not reproduce asexually, and has an annual life cycle (Aiken et al., 1988), in this analysis the presence of wild rice plants is taken to mean that the waterbody hosts a successfully reproducing and self-sustaining population. A few of the sites in this study may have experienced recent watershed changes such that steady state has not yet been reached among environmental variables and wild rice reproduction, but the balance of the 108 sites should have been in steady state at the time of sampling. The population of wild rice in a given lake can exhibit large fluctuations from year to year, which has been attributed to disturbances such as abrupt increases in water level (DNR, 2008) and to cyclical changes in N availability (Walker et al., 2010). Wild rice fills a unique ecological niche, in that there are virtually no other annual aquatic macrophytes across the Great Lakes region (Eggers & Reed, 2011).

2.1.3. Site Selection

The goal of the field survey was to identify and sample potential wild rice habitat across a gradient of SO_4 concentrations. Potential wild rice habitat was defined simply as shallow water (30–120 cm deep, though some sampled sites had water as shallow as 5 cm) that was sufficiently transparent to support rooted aquatic macrophytes. Turbidity from dense phytoplankton blooms or suspended solids may effectively exclude rooted macrophytes due to light limitation (Scheffer, 1998).

Most Minnesota lakes that host wild rice populations have low SO_4 concentrations; the median concentration of wild rice lakes is 1.8 mg L^{-1} , and the 75th percentile is 3.6 mg L^{-1} (MPCA, 2014). If only those waters hosting abundant wild rice were sampled, most of those would be low in SO_4 , and little would be learned about how elevated SO_4 concentrations (or other important variables) might affect wild rice. Conservation biologists commonly identify important habitat variables through binary (i.e., is the species present or absent at a given site?) logistic regression, which requires the sampling of sites that do not support the species of interest (e.g., Carroll, Zielinski, & Noss, 1999; Peeters & Gardeniers, 1998; van der Heide et al., 2009). Consequently, potential wild rice habitats with a range in SO_4 concentrations were sampled without regard to whether the waterbody hosted or was known to host wild rice. An effort was made to sample waterbodies that covered the range of SO_4 concentrations across Minnesota and especially to sample sites in high- SO_4 regions that had reports of recent or historical presence of wild rice. This strategy also resulted in the sampling of a high- SO_4 wild rice site in the North Branch of the Turtle River ($198 \text{ mg SO}_4 \text{ L}^{-1}$), 40 km into North Dakota from northwestern Minnesota (Figure 1). A gradient of SO_4 concentrations was sampled by identifying potential wild rice habitat in two areas of elevated SO_4 , the “island” of elevated SO_4 in the Iron Range region of northeastern Minnesota and waters naturally elevated in SO_4 to the west and south of the known range of wild rice (Figures 1 and S1). Nutrient (N and P) availability (reflecting natural soil fertility as well as agricultural runoff) also increases to the west and south, potentially supporting phytoplankton growth sufficient to exclude macrophytes, including wild rice. Consequently, in western and southern Minnesota, DNR lake databases were screened for the presence of water lilies (*Nuphar variegata* or *Nymphaea odorata*), the occurrence of which indicates transparency sufficient to support rooted macrophytes that also often cooccur with wild rice. In an analysis of DNR aquatic plant surveys from 1,753 shallow lakes, we found that the odds of finding wild rice where there are water lilies are 26 times the odds of finding wild rice where there are no water lilies, with a 95% confidence interval of 20–36 times (neither wild rice nor water lilies = 968; wild rice but not water lilies = 60; no wild rice but water lilies = 272; both wild rice and water lilies = 453).

With these considerations, water bodies were selected for sampling based on preliminary data including average water depth, presence of water lilies, conductivity or SO_4 concentration, and geographic distribution (i.e., to sample widely across the state). Both rivers and lakes were sampled, as were seven different cultivated wild rice paddies. Within a given water body, the field team chose a location for sampling based on a decision tree (Table S1 in the supporting information).

2.2. Field Methods

Sampling occurred in August–September 2011 and June–September 2012 and 2013. Sampling efforts were focused in late summer to capture physical and chemical conditions when wild rice plants were maturing and when identification of wild rice is most certain; voucher specimens of wild rice were always taken. Samples were collected from an anchored canoe or small boat, except in the cultivated wild rice paddies when the water was too shallow to float a canoe, and samples were collected on foot. A Hach model HQ40d or Hydrolab Quanta sonde, calibrated daily, was used to measure temperature, specific conductance, dissolved oxygen, and pH in the surface water. Water transparency was determined with a 1 m long Secchi-tube (Water Monitoring Equipment & Supply, USA), and apparent color was measured using a Hach model CO-1 color test kit. Surface water samples (later split into separate subsamples; see below) were collected by a technician wearing long nitrile gloves in two 2 L amber Nalgene bottles that had been previously triple rinsed with deionized water and rinsed 3 times with water from the site before filling. Water samples were stored on ice.

Short (~50 cm) sediment cores with ~10–20 cm of overlying water were collected at eight undisturbed locations at least 1 m apart around the boat using an HTH corer (Pylonex, Sweden) with a 7 cm diameter polycarbonate barrel. A piston was inserted in the bottom end of each core as it was retrieved. Cores were kept upright and shaded prior to sample processing.

Aquatic macrophytes were identified and percent cover estimated within a plastic hoop 1 m in diameter placed at 4 locations around the boat. In 2012 and 2013, the number of stems of wild rice inside each hoop was also quantified.

Pore water samples were obtained from cores processed on shore using 10 cm Rhizon™ filters (pore size 0.12–0.18 μm) (Rhizosphere.com, Netherlands; Shotbolt, 2010) inserted vertically into the core tops, following extrusion of overlying water, and connected to evacuated serum bottles with PVC/polyethylene tubing and a stainless steel needle. Three separate cores were sampled, one for nutrients (nitrate + nitrite, TP, and TN) and DOC (70 mL), a second for metals (50 mL), and a third for dissolved silica, Cl, and SO_4 (30 mL). A fourth core was sampled for pore water sulfide, but in this case, the serum bottle was preloaded with 0.2 mL of 2.0 N zinc acetate, 0.5 mL of 15 M sodium hydroxide, and a stir bar, flushed with a nitrogen atmosphere, evacuated, and preweighed. Air was flushed from the Rhizon-tubing assembly with sample pore water using a second evacuated bottle before the needle was inserted into the sulfide sample bottle. In 2011 only pore water samples for sulfide and metals were collected. Pore water pH was measured on a fifth core by inserting the probe of a Hach model HQ40d pH meter into the sediment to a depth of 5 cm and allowing the reading to stabilize.

A composite sediment sample was collected from the uppermost 10 cm of the sixth, seventh, and eighth cores, placed into a stainless steel bowl, and stirred under nitrogen atmosphere to homogenize. A 50-mL subsample was placed in a polypropylene sample bottle along with 1.0 mL of 1.0 N zinc acetate for analysis of acid-volatile sulfide (AVS). The headspace of the AVS sample bottle was flushed with N_2 and the bottle capped; that bottle was placed in a larger glass jar and that jar flushed with N_2 and tightly sealed. The sample was immediately placed in a cooler with dry ice to freeze. The remaining composited sediment was placed into a polycarbonate container and stored on ice for later analysis.

Water subsamples were taken from the large amber Nalgene bottles by a technician wearing nitrile gloves. Sulfuric acid (5 mL of 10%) was immediately added to subsamples for the analysis of P, TKN (total Kjeldahl nitrogen), ammonia, and nitrate + nitrite in 250 mL polyethylene bottles. Nitric acid (2.5 mL of 20%, to acidify to $\text{pH} < 2$) was immediately added to subsamples for the analysis of total metals in 250 mL polyethylene bottles. Samples for dissolved metals were subsampled in 250 polyethylene bottles and subsequently filtered using a 0.45 μm filter and preserved with nitric acid in the laboratory. Samples were stored on ice.

2.3. Laboratory Methods

Surface water, pore water, and most sediment analyses were conducted by the Minnesota Department of Health Environmental Laboratory (MDHEL) in 2012 and 2013, following standard methods. In 2011 other laboratories conducted the analyses (University of Minnesota Soils Laboratory (UMNSL), St. Croix Watershed Research Station (SCWRS), and Gustavus Adolphus College (GAC)); methodological differences are noted, and the laboratory is identified where relevant.

Surface and pore water samples were analyzed for anions (Cl and SO₄) by ion chromatography on a Dionex ICS-3000 (MDHEL), Fe, Ca, Na, Mg, and K by inductively coupled optical emission spectrometry on a Varian 715-ES (MDHEL), Mn, Cu, Zn, Co, Ni, Al, As, and Se by inductively coupled mass spectrometry on a Perkin Elmer Elan DRCE (MDHEL), and DOC by UV-persulfate oxidation on a Tekmar-Dohrmann Phoenix 8000 (SCWRS and MDHEL). N and P were measured by colorimetric methods (on a Lachat Quikchem Flow-Injection Autoanalyzer) at SCWRS and MDHEL following cadmium-reduction (nitrate and ammonia) or dual alkaline-persulfate digestions (TP and TN). Silica was measured colorimetrically at SCWRS on the Lachat Autoanalyzer and at MDHEL on a Beckman Coulter DU 800 UV/VIS spectrophotometer. Pore water sulfide was analyzed colorimetrically on each lab's Lachat Autoanalyzer following in-line acid distillation and NaOH trapping (SM 4500-S2). Alkalinity was measured by potentiometric acid titration (MDHEL) or as DIC by acid digestion and IR detection (SCWRS). DIC was converted to alkalinity using pH, temperature, and specific conductance of the surface water.

Sediment samples from 2011 were analyzed by combustion for total carbon (TC), total nitrogen (TN), and total sulfur (TS) using, respectively, a Tekmar Phoenix 8000 CO₂ analyzer, an Elementar Vario Max N analyzer, and a LECO sulfur analyzer (UMNSL). Samples from 2012 and 2013 were analyzed for CHN on a Costech 4010 Elemental Analyzer (UMN Stable Isotope Laboratory). Total inorganic carbon (carbonate) was analyzed by coulometric titration on a UIC CM5015 CO₂ coulometer, while water and organic matter content were determined by loss-on-ignition methods (Heiri, Lotter, & Lemcke, 2001) in the UMN LacCore facilities. Sediment AVS was analyzed colorimetrically, as above for pore water sulfide, following acid-distillation and in-line alkaline trapping (SM 4500-S2; Hsieh & Shieh, 1997).

Sediment phosphorus was extracted from freeze-dried sediments following methods of Engstrom and Wright (1984) for total-P and Hietjes and Lijklema (1980) for P fractions (NH₄Cl-extractable, NaOH-extractable, HCl-extractable, and residual (organic)-P). The P extracts were measured colorimetrically by flow-injection autoanalyzer (SCWRS). Extractable iron and trace metals were quantified from a 0.25 g homogenized freeze-dried sediment subsample incubated in 0.5 M HCl for 30 min at 80°C. The samples were centrifuged, decanted, and analyzed by ICP-MS at GAC. This extraction releases metal oxyhydroxides, sulfides, and loosely bound phases from the sediment without appreciably attacking the silicate matrix (Balogh et al., 2009).

2.4. Data Subsets and Statistical Analysis

From 2011 to 2013, 260 site visits were conducted in 108 different natural waterbodies, including lakes, small streams, backwaters of the Mississippi River, and wetlands, plus 7 different cultivated wild rice paddies. For a variety of logistical reasons, the full suite of samples could not be collected on some site visits. Three subsets of the field data were identified for the analyses reported here. A subset that consists of all of the samples from natural waterbodies (excluding the cultivated paddies) with virtually complete analyses (surface water, pore water, and bulk sediment; $n = 194$) was termed for internal purposes Class D. Pollman et al. (2017) used Class D to develop a structural equation model to elucidate key variables that govern the concentration of sulfide in sediment pore water. A second subset, Class S, of 51 samples from 7 stream and 8 lake sites was each sampled 3 to 5 times from 27 May to 19 September 2013, to provide a data set to assess seasonality in variables. A third subset, Class B, was used for conducting probabilistic analyses to identify the most likely parameters controlling the presence and absence of wild rice and to examine Spearman nonparametric correlations among field variables. Class B consists of one sample from each site ($n = 108$) and excludes samples collected in 2011, which were analyzed with slightly different lab methods. Although Class B was not created as a random sample of Minnesota waterbodies, the frequency distribution of SO₄ concentrations is intermediate between a probability-based survey conducted by USEPA (MPCA, 2016) and a list of known wild rice water bodies, which are overwhelmingly low-SO₄ lakes (MPCA, 2014). Therefore, the Class B data set is reasonably representative of potential wild rice habitat, and binary logistic regressions can be used to approximate the probability of wild rice occurrence as a function of field variables such as pore water sulfide. The Class B data set is used in all analyses presented here, with two exceptions: (1) Figures 3a–3c present the full Class D data set, plus for comparison, data from the cultivated wild rice paddies; (2) Statistical analysis was performed with the software package R version 3.2.3.

To identify variables associated with the presence and absence of wild rice, we relied on binary logistic regressions (BLR), using the glm function in R. BLR does not require normally distributed data, but

Table 1Field Variable Correlation With the Presence-Absence of Wild Rice, Assessed Through Binary Logistic Regression (BLR), Plus Spearman Correlations Between Variables^a

Field variable	Binary logistic regression (BLR) correlation with field variable			Spearman correlation with field variable (rho)				
	Log transformed?	p value	Correlation direction	Wild rice density (only wild rice sites) n = 67	Pore water sulfide	Sediment AVS	Water transparency	Water temperature
pw K	Y	0.0008***	Negative	−0.27*	0.46***	0.11	−0.10	0.33***
pw sulfide	Y	0.0012***	Negative	−0.31**	1.00	0.29**	−0.07	0.17
Water depth (m)	N	0.0028***	Negative	0.07	0.11	0.08	0.22*	0.19*
Transparency (cm)	N	0.0031***	Positive	0.11	−0.07	−0.13	1.00	−0.08
sw TN	Y	0.0054**	Negative	−0.12	0.22*	0.08	−0.61***	0.23*
sed Se % dry	N	0.0059**	Negative	0.12	0.08	0.27**	−0.21*	0.13
sw Temp	N	0.0077**	Negative	0.08	0.17	0.11	−0.08	1.00
pw Fe	Y	0.0109*	Positive	0.20	−0.58***	0.00	0.04	0.09
sw pH	N	0.0200*	Negative	−0.14	0.28**	0.08	−0.05	0.35***
sw TP	Y	0.0353*	Negative	0.15	0.05	0.29**	−0.58***	0.27**
Latitude	N	0.0376*	Positive	−0.04	−0.06	−0.09	0.13	−0.51***
sed TS % dry	Y	0.0483*	Negative	0.20	0.40***	0.42***	0.03	−0.08
sw K	Y	0.0922		−0.03	0.29**	0.21*	−0.18	−0.08
sed AVS % dry	Y	0.1317		0.02	0.29**	1.00	−0.13	0.11
sw sulfate	Y	0.1475		−0.10	0.44***	0.45***	−0.07	0.04
sed TP % dry	N	0.2697		−0.10	0.07	0.30**	−0.14	0.14
sw alkalinity	Y	0.2786		0.25*	0.22*	0.26**	0.11	0.17
pw TN	Y	0.2963		−0.30	0.31***	0.14	−0.20*	0.34***
pw NH4	Y	0.4505		−0.33**	0.33***	0.22*	−0.17	0.26**
sed Fe % dry	Y	0.4795		0.16	−0.35***	0.38***	−0.10	−0.06
pw DOC	Y	0.4865		0.08	−0.05	−0.1	−0.21*	0.09
pw Si	N	0.5548		0.03	0.33***	0.18	0.07	0.29**
pw TP	Y	0.6341		0.02	0.12	0.30**	−0.26**	0.26**
sed TN % dry	N	0.6807		−0.06	0.14	0.04	0.06	−0.06
sed water content	N	0.7274		−0.07	0.15	0.10	0.10	0.02
sed TOC % dry	N	0.7854		−0.10	0.10	0.02	0.10	−0.06

^aNote. The variables are ordered by the significance of the BLR. The first 12 variables have BLR significance of $p < 0.05$. The additional 14 variables are listed because of their correlation with pore water sulfide, sediment AVS, or surface water transparency or temperature—or their notable lack of correlation with wild rice presence-absence (pw = pore water; sw = surface water; sed = sediment).

* $p < 0.05$. ** $p < 0.01$. *** $p < 0.001$.

nevertheless, we transformed some variables (Table 1) to achieve approximately normal distributions. BLR also yields the probability of occurrence at a given value of the variable. Spearman nonparametric correlations (rho) between field variables in Class B were examined as part of the effort to identify the major biogeochemical interactions in these shallow-water systems. Seasonality in a variable was assessed using linear mixed effects models, with time (fraction of a year) as a fixed variable and site as a random factor (to account for multiple samples per site). In the model developed for each field variable, we accounted for the seasonal cycle using the following equation (Crawley, 2007), where A , B , and C are fitted model coefficients:

$$y = A + B \sin(2\pi \text{ time}) + C \cos(2\pi \text{ time}) \quad (1)$$

3. Results and Discussion

3.1. Field Variables Associated With Wild Rice Presence and Absence

Of the 64 field quantified variables, BLR identified 12 that are associated with the presence/absence of wild rice at the 0.05 probability level or better (Table 1): pore water sulfide, K, and Fe (Figures 2a, 2b, and 2f); surface water temperature, TP, TN, and pH (Figures 2d, 2m, 2n, and 2o); sediment Se and TS (Figures 2c and 2p); water depth and transparency (not shown; Figure 2e); and latitude of the site (Figure 2g). These variables may be important in controlling the presence or absence of wild rice or may merely be correlated with one or more actual causative factors. Because we are primarily interested in factors that control presence or absence of wild rice, in contrast to the density of wild rice, we place primacy on the BLR results and use the Spearman

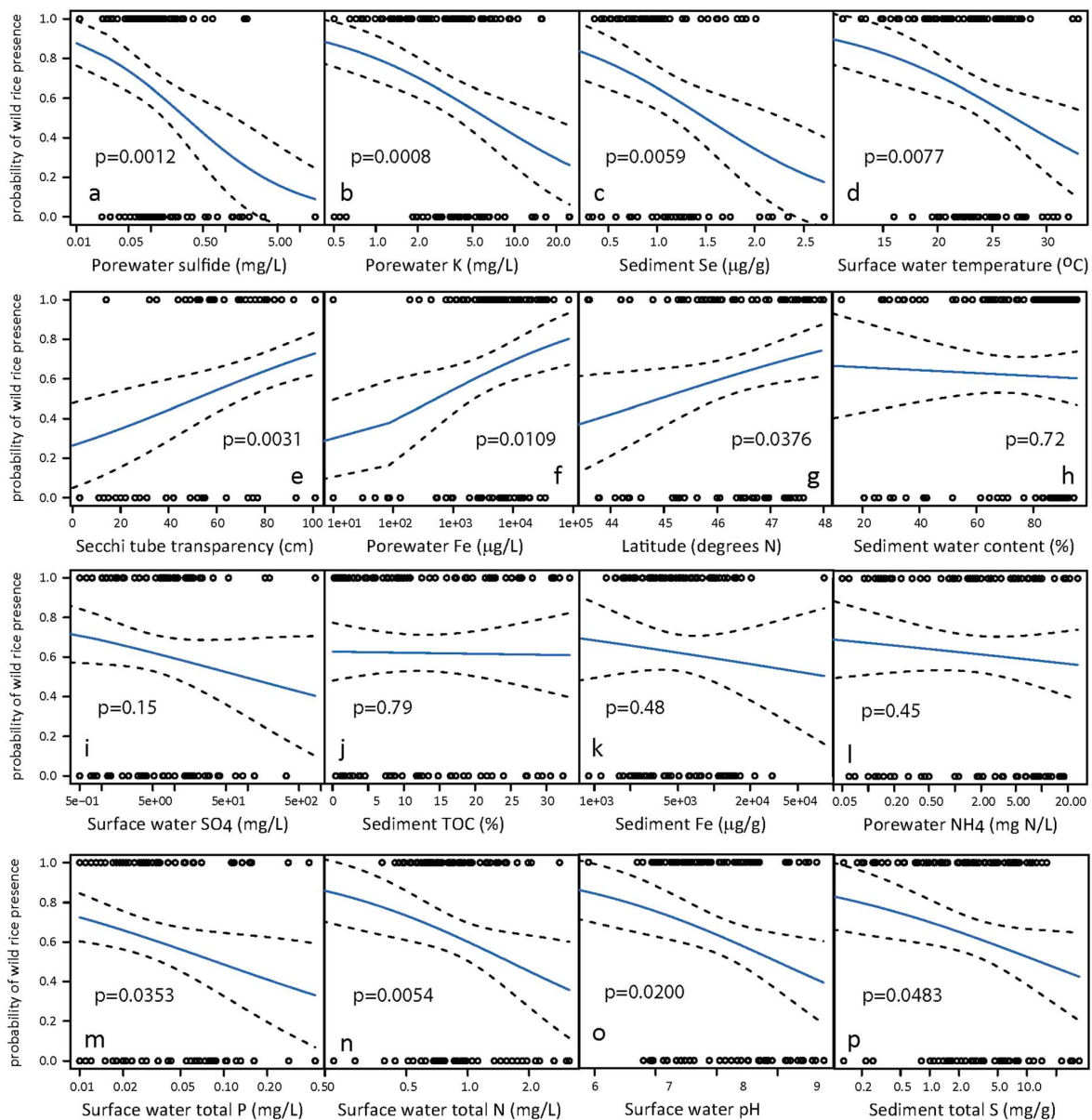


Figure 2. Binary logistic regressions for 16 variables found to be statistically significant in this study or indicated in the literature as important for wild rice habitat. The open circles indicate the value for a given parameter of each site used in the analysis; the circles at the top of a plot indicate sites with wild rice present; the circles at the bottom of a plot indicate sites with wild rice absent. The span of the dashed lines around the solid line indicates the 95% confidence interval.

correlations to help understand the relationships between environmental factors of interest. Wild rice density is negatively correlated with pore water sulfide, potassium (K), and NH_4 and positively correlated with surface water alkalinity (Table 1). There are likely factors controlling the density of wild rice at any particular location in addition to the variables measured, such as herbivory and hydrological disturbances.

One should be cautious in the interpretation of statistically significant associations between wild rice and field variables, in that true cause and effect are not necessarily obvious. For instance, is the toxic quality of pore water sulfide sufficient explanation for its negative associations with both the presence and density of wild rice? Do sites with greater density of wild rice have lower pore water sulfide because low sulfide allows wild rice to grow, or because plants release oxygen from their roots, oxidizing sulfide? The true explanation is likely a combination of the two mechanisms: elevated pore water sulfide can eventually extirpate a wild rice

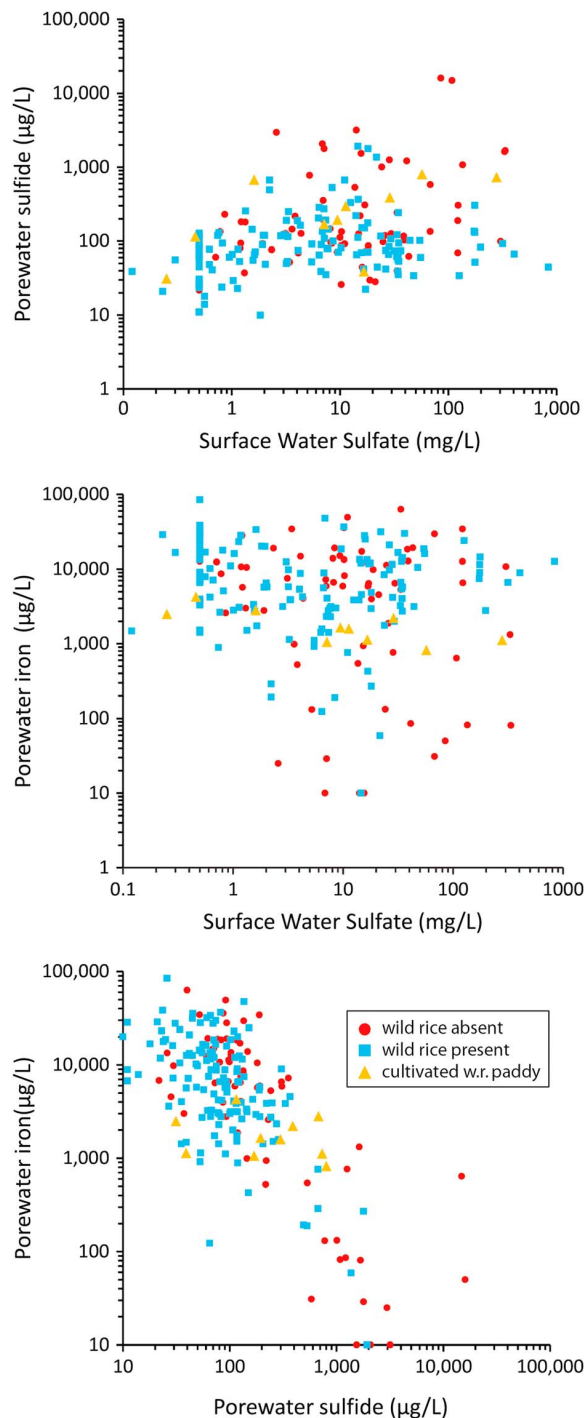


Figure 3. Class D data plus cultivated wild rice paddies (yellow triangles) showing sites with wild rice present (blue squares) and absent (red circles). Note that (a) pore water sulfide is not linearly related to surface water SO_4 , indicating that additional factors besides SO_4 concentration contribute to the sulfide concentration in pore water; (b) wild rice can occur in sites over a wide range of surface water SO_4 values as long as pore water Fe is relatively high; and (c) pore water Fe and sulfide have a strong negative relationship, due to the energetically favorable formation of FeS compounds, and that wild rice mainly occurs where pore water sulfide is $<1,000 \mu\text{g L}^{-1}$.

population by reducing seedling survival and seed production, weight, and viability (Pastor et al., 2017), but oxygen release from roots when sulfide concentrations are low enough to allow wild rice to successfully reproduce drives sulfide to even lower concentrations than would have occurred without the plants (Myrbo et al., 2017). Although the negative correlation between pore water sulfide and wild rice density ($\rho = -0.31, p < 0.01$, Table 1) could be interpreted to mean that lower sulfide allows a larger population to grow, it is also possible the correlation is partly caused by oxygen release from the wild rice roots, decreasing sulfide concentrations. This hypothesis is supported by the observation from a controlled experiment that acid-volatile sulfide (AVS) sediment concentrations were 30% lower when wild rice was present (Myrbo et al., 2017).

Of the 12 variables significantly associated with the occurrence of wild rice, we propose that nine are noncausal and merely related to one or more of three truly causative factors: (1) pore water sulfide, (2) water transparency, and (3) water temperature. These three variables are not significantly correlated with one another (Table 1), and there are plausible mechanisms for each to independently exclude wild rice from otherwise suitable habitat: (1) elevated sulfide reduces the growth of wild rice (Pastor et al., 2017); (2) low water transparency plausibly constrains the ability of a germinated wild rice seed to reach sufficient light before it runs out of endosperm energy (Aiken et al., 1988; DNR, 2008); and (3) warmer winter water temperature at lower latitudes may limit seed germination, as the seeds of *Z. palustris* must experience at least 3 months in cold water to break seed dormancy (Kovach & Bradford, 1992) (although summer temperatures were measured in this study, winter and summer temperatures would be correlated).

3.2. Pore Water Sulfide as a Causal Variable and Associated Correlated Variables

Our primary a priori hypothesis was that elevated surface water SO_4 can produce elevated pore water sulfide concentrations which, in turn, negatively affect potential wild rice habitat. A plot of pore water sulfide against SO_4 , with wild rice presence noted (Figure 3a), suggests that wild rice is generally not found at sites with elevated sulfide. Of the sites with pore water sulfide greater than $1,000 \mu\text{g L}^{-1}$, wild rice was present in 23% (3 of 13, with only a few plants found at 2 of those 3 sites). In contrast, wild rice was present at 74% of the sites where sulfide was less than $1,000 \mu\text{g L}^{-1}$. Despite historical reports of *Zizania aquatica* in Minnesota, inspection of voucher specimens, following the taxonomy of Terrell et al. (1997), found only *Z. palustris* at all sites sampled. *Zizania aquatica* (Southern wild rice) is rare in Minnesota, but its range extends east through Wisconsin and the southern part of the Great Lakes region to New England and occurs in freshwater tidal marshes south to Florida and west to Louisiana (Terrell et al., 1997). The findings of this study, especially those related to temperature, may not apply to *Z. aquatica*.

Despite a strong relationship between sulfide and wild rice, the relationship between SO_4 and pore water sulfide among the 108 field sites was not a simple linear function. High surface water SO_4 did not always result in high pore water sulfide (above $1,000 \mu\text{g L}^{-1}$), and some samples with surface water SO_4 less than 10 mg L^{-1} had pore water sulfide greater

than $1,000 \mu\text{g L}^{-1}$ (Figure 3a). The 33 samples with surface water SO_4 below 1.0 mg L^{-1} all had pore water sulfide less than $200 \mu\text{g L}^{-1}$, suggesting that surface water SO_4 might limit maximum sulfide production.

Wild rice was present at high and low SO_4 concentrations as long as pore water Fe was high and sulfide was low (Figures 3b and 3c): pore water Fe and sulfide each exert antipathetic control over the concentration of the other (Figure 3c; Pollman et al., 2017), and wild rice mainly persists in sites where pore waters are low in sulfide and high in Fe. Pollman et al. (2017) developed a structural equation model showing that variations in three variables (SO_4 , sediment TOC, and sediment extractable Fe) contribute nearly equally to the observed variations in pore water sulfide among the sites in this study. Sulfate-reducing bacteria are simultaneously limited in their production of pore water sulfide by surface water SO_4 and sediment TOC (which are roughly proportional to available SO_4 and labile organic matter, respectively). Concentrations of sulfide in pore water are then constrained by the availability of pore water Fe, which is in turn controlled by the overall supply of Fe in the sediment (Pollman et al., 2017).

If pore water sulfide concentration is a causative factor controlling the presence of wild rice, as hypothesized, then other variables may be statistically significant because they either vary with the process of SO_4 reduction or with the sulfide itself. Pastor et al. (2017) showed that wild rice growth declines in proportion to sulfide concentrations in both hydroponic and outdoor mesocosm experiments. In a study of the Pastor et al. mesocosms, Myrbo et al. (2017) showed that the enhanced mineralization of plant litter associated with SO_4 reduction produced increases in surface water P and N, and increases in pore water sulfide caused decreases in pore water Fe. These effects from the controlled mesocosm experiment are consistent with correlations observed among sites in the field data between pore water sulfide and surface water N and pore water Fe (Table 1). Surface water P is not significantly correlated with pore water sulfide in the field data, despite dual mechanisms of P mobilization from sediment, (1) the interaction between sulfide and Fe (Caraco et al., 1993; Maynard, Dahlgren, & O'Geen, 2011; Smolders & Roelofs, 1993) and (2) mineralization of organic matter. The lack of correlation of surface water P with pore water sulfide in this field study is not surprising because given the wide variety of landscapes sampled, there is no reason that pore water sulfide would be proportional to the mass of Fe that has reacted with sulfide and released sorbed P. In SO_4 addition experiments where the P and Fe content of the sediment is held constant, there is often a significant correlation between pore water sulfide and mobilized P (Myrbo et al., 2017). In contrast to the lack of correlation of pore water sulfide with surface water P in this field study, AVS is significantly correlated with surface water P ($\rho = 0.30$, $p < 0.01$, Table 1), presumably because AVS is proportional to the iron that has reacted with sulfide.

Elevated pore water sulfide is a product of SO_4 reduction-driven mineralization of sediment organic matter, which also releases the constituents of the decaying plant material, N, P, K, silica, and C (either as DIC, which increases alkalinity, or DOC) into sediment pore water and the overlying surface water (Myrbo et al., 2017). Consequently, the occurrence of wild rice is negatively associated not only with pore water sulfide ($p = 0.001$) but also with elevated pore water K ($p = 0.0008$) and surface water TN ($p = 0.005$, Table 1). Median concentrations of these variables are lower in wild rice waters compared to waters with no observed wild rice (88 versus $126 \mu\text{g L}^{-1}$ sulfide, 2.4 versus 4.3 mg L^{-1} pore water K, and 0.74 versus 0.95 mg L^{-1} TN, Table S3). Pore water sulfide is itself positively correlated with pore water K, TN, NH_4 , and silica, surface water K, alkalinity, and pH, and sediment TS and AVS (Tables 1 and S4).

The strong evidence for the association of elevated pore water K with the absence of wild rice (Table 1) is interesting, as K is an essential plant nutrient, and therefore, it is unlikely that the association is based on toxicity to wild rice. Rather, it is likely that the association is a result of the simultaneous mobilization of K with the production of sulfide as plant matter is mineralized. Potassium does not bond covalently with organic compounds and is readily leached out of dead organic matter (Troeh & Thompson, 2005). Silica phytoliths dissolve as plant matter is mineralized, allowing additional K that had been trapped within the phytoliths to be released into sediment pore water (Nguyen et al., 2015). Wild rice and other wetland macrophytes develop abundant phytoliths that release dissolved silica upon decomposition (Struyf & Conley, 2009). Additional dissolved silica is likely released to pore water as epiphytic diatoms are mineralized. Pore water silica, K, and sulfide are all significantly correlated with each other (Tables 1 and S5). The negative correlation of pore water K with wild rice may be magnified by its additional positive correlation with elevated water temperature (Table 1), which plausibly accelerates dissolution of silica in organic matter (Gudasz et al., 2010; Kamatani, 1982).

AVS largely consists of solid-phase sulfide, which is not available to plants and therefore is not significantly associated with wild rice presence/absence ($p > 0.10$, Table 1). AVS is a measure of cumulative sulfide production, which is proportional to past mineralization of organic matter, consistent with significant positive correlations between AVS and pore water TP and NH_4 , and surface water TP and alkalinity ($p < 0.01$, 0.05, 0.01, and 0.01, respectively, Table 1).

The negative association of sediment total-S (TS) with wild rice presence (BLR $p = 0.048$, Table 1) is likely the result of both TS and wild rice being controlled by sulfide production; the median TS concentration at sites with wild rice is 2.6 mg g^{-1} , compared to 4.1 mg g^{-1} at sites without wild rice (Table S3). Sediment TS is correlated with both pore water sulfide and AVS. The negative association of sediment Se with wild rice (BLR $p = 0.006$) is surprising, given that median Se concentrations are very low (0.9 and $1.2 \text{ } \mu\text{g g}^{-1}$ in sites with and without wild rice, respectively). The slightly higher Se at sites without wild rice may be caused by the coprecipitation of Se and S by SRB, as shown by Hockin and Gadd (2003). Selenium is correlated with sediment total S ($\rho = 0.35$; $p < 0.001$).

3.3. Water Transparency as a Causal Variable and Associated Correlated Variables

Lower water transparency is associated with a lower probability of wild rice occurrence (BLR $p = 0.003$). Transparency is not related to wild rice density ($\rho = 0.11$, $p > 0.20$, Table 1); however, low transparency can apparently exclude wild rice (11 of the 12 sites with transparency $< 30 \text{ cm}$ had no wild rice), but above that threshold, other variables control wild rice density. Low water transparency decreases photosynthesis of wild rice seedlings while growing to the water surface, which (a) decreases oxygen production that could otherwise be used to detoxify sulfide internally (Krüssel et al., 2014), or externally if released into pore water from the roots (Colmer, 2003); and (b) decreases the energy available for root development, enhancing vulnerability to a sudden increase in water depth, which can uproot an entire year's cohort (DNR, 2008). Wild rice is unusual among grasses in that the stem develops before the root, probably because the seedling may have to grow over 50 cm before reaching the water surface, at which time floating leaves are developed that can supply energy for root development (Aiken, 1986). If transparency is too low, or the water too deep, the energy stored in the seed can be insufficient for the seedling to reach the water surface.

Water transparency can be controlled by the density of phytoplankton, which was not measured in this study. However, transparency is highly correlated with the nutrient concentrations that control phytoplankton growth, total phosphorus ($\rho = -0.58$, $p < 0.001$), and total nitrogen ($\rho = -0.61$, $p < 0.001$). Transparency can also be controlled by colored dissolved organic matter, consistent with the observed significant correlation between transparency and water color ($\rho = -0.68$, $p < 0.001$, Table S4).

3.4. Temperature as a Causal Variable and Associated Correlated Variables

Wild rice germinates at higher rates following longer exposure at temperatures closer to freezing (Kovach & Bradford, 1992), consistent with the significant association of wild rice absence with lower latitudes (BLR $p = 0.04$) and warmer summer water temperature (BLR $p = 0.008$; medians of 21.9° and 23.7°C with and without wild rice, respectively). Sites with warmer summer water temperatures generally also have warmer winter temperatures. Warmer and shorter winters would cause lower germination rates, ultimately reducing the probability that a population could persist over the long term. For this reason, the Minnesota Department of Natural Resources hypothesizes that climate change may push the range of wild rice farther north (DNR, 2008, 2016). However, the temperature control of wild rice germination has not been adequately investigated to rigorously assess this hypothesis. The observed association of wild rice with lower pH surface waters (BLR $p = 0.04$; median pH values of 7.8 and 8.5 at sites with and without wild rice, respectively) may be due simply to the correlation of wild rice with cooler surface waters: the solubility of CO_2 is higher in colder water, leading to lower pH (Spearman correlation between temperature and pH = 0.35 , $p < 0.0001$).

Lower latitude sites are negatively associated with wild rice presence and density (Table 1). Lower latitude sites are correlated with higher water temperature ($\rho = -0.51$, $p < 0.001$). Geological and land use gradients also correlate with latitude, producing correlations with surface water N and P ($\rho = -0.25$ and -0.31 , $p < 0.01$). Despite these correlations with nutrients, latitude is not significantly correlated with water transparency ($\rho = 0.13$), so the general unsuitability of lower latitudes for wild rice may be a combination of warmer winters and some reduced transparency as a result of nutrient enrichment. Latitude is not significantly correlated with pore water sulfide ($\rho = -0.06$).

3.5. Synergy Among the Three Causal Variables of Sulfide, Temperature, and Transparency

While temperature may control wild rice presence/absence through winter temperatures too warm to achieve high rates of seed germination in the spring, higher summer temperatures may act synergistically on variables correlated with pore water sulfide. Elevated summer temperatures likely enhance microbial activity, no matter which electron acceptor is respired by the dominant microbes (Gudas et al., 2010). Water temperature is indeed correlated with pore water concentrations of the plant nutrients N, P, and K released by decomposition, which are also significantly correlated with either pore water sulfide or AVS (Table 1). Although sulfide production may be enhanced by elevated temperature, the correlation between sulfide and temperature is weak ($\rho = 0.17$; $p > 0.05$).

The production of sulfide plausibly contributes to the significant correlation of six of the nine variables with wild rice occurrence: P and N in surface water, Fe and K in pore water, and S and Se in sediment. Water temperature is significantly correlated with three of these variables (P, N, and K), and therefore, synergistically reinforces their associations with the absence of wild rice. Elevated surface water P and N are further synergistically associated with the absence of wild rice because their release via MSR-driven mineralization also enhances phytoplankton growth, reducing light available to wild rice seedlings; P and N are highly correlated with reduced transparency ($p < 0.001$, Table 1).

In this data set greater water depth is negatively associated with the occurrence of wild rice, not because wild rice grows better in shallower water, which it may, but because of where field crews took samples when wild rice was not present. Following a decision tree (Table S1), when wild rice was not present, field crews usually sampled among water lilies, which, on average, were observed in slightly deeper water than wild rice (67 cm compared to 52 cm).

Finally, *multiple* BLR was employed to investigate the question of whether any of the correlated variables provided additional explanatory power for the occurrence of wild rice beyond the models with sulfide, transparency, or temperature as base predictors. Surface water temperature is predictive of wild rice presence independent of sulfide ($p = 0.03$). Pore water K improves models based on sulfide ($p = 0.02$) or temperature ($p = 0.004$) alone but provides no significant additional explanatory power beyond a model built on both sulfide and temperature ($p = 0.07$). Overall, multiple BLR analysis confirms that other variables provide no additional explanatory power and that the three base predictors are independent of each other.

Multiple BLR was used to model the probability of wild rice occurrence (WR presence) as a function of pore water sulfide (pw sulfide, in mg L^{-1}), water transparency as measured by the Secchi tube (trans, in cm), and water temperature (Temp, in $^{\circ}\text{C}$):

$$\text{Logit (WR presence)} = 0.532 + 0.0183 (\text{trans}) - 1.169 (\log_{10} \text{pw sulfide}) - 0.107 (\text{Temp}) \quad (2)$$

where odds = $\exp(\text{logit})$ and probability = $(\text{odds}/(1 + \text{odds}))$.

Pore water sulfide and water transparency are significant variables in the multiple BLR ($p = 0.012$ and $p = 0.016$, respectively), whereas water temperature is only marginally significant ($p = 0.056$). To visualize the interaction of the variables, a 3-D plot was constructed that predicts the probability of wild rice occurrence as a function of sulfide and transparency, while holding constant the marginally significant variable, temperature, at the median value of the Class B data set (23.2 $^{\circ}\text{C}$; Figure 4). Within the range of variables in Class B, modeled probabilities of wild rice occurrence range from a high of 89.8% (trans = 100 cm, which was the maximum of the measurement device, and pw sulfide = 11 $\mu\text{g L}^{-1}$, which was the reporting limit) to a low of 9.6% (trans = 3 cm, which was the minimum observed, and pw sulfide = 2,000 $\mu\text{g L}^{-1}$). Modeling was cut off at a sulfide concentration of 2,000 $\mu\text{g L}^{-1}$ because only three Class B sites had pore water sulfide greater than 2,000 $\mu\text{g L}^{-1}$ and none of the three hosted wild rice.

3.6. Field Variables not Evidently Associated With Wild Rice Presence and Absence

Some variables included among the initial hypotheses, or in the past cited as important attributes of wild rice habitat, were not found to be significantly associated with wild rice presence and absence. These include sediment TOC ($p = 0.79$, Figure 2j; DNR, 2008; Lee, 1986; Moyle & Krueger, 1964), flocculent sediment (quantified here as the sediment water content; $p = 0.72$, Figure 2h; DNR, 2008; Lee, 1986; Moyle & Krueger, 1964), sediment N ($p = 0.68$, Table 1; Carson, 2002; Walker et al., 2010), sediment P ($p = 0.27$, Table 1; Carson, 2002; DNR, 2008), and surface water alkalinity ($p = 0.28$, Table 1; Moyle, 1944).

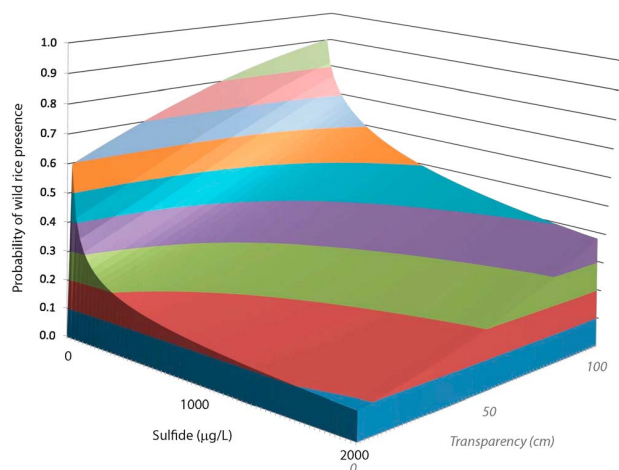


Figure 4. Visualization of the relationship, determined by multiple binary logistic regression, between water transparency and pore water sulfide in controlling the probability of wild rice occurrence at 23.2°C, the median temperature for all sites in the class B data set.

Reduced sediments are generally regarded as producing pore water constituents that are potentially toxic to rooted plants; potentially toxic agents, in addition to sulfide, include ammonia and Fe (Pezeshki & DeLaune, 2012). Analysis of the binary logistic regressions showed no evidence for ammonia toxicity (BLR $p = 0.45$, Figure 2l) or Fe toxicity (wild rice presence is positively correlated with pore water Fe, BLR $p = 0.01$, Figure 2f). As a product of decomposition, ammonia is correlated with pore water sulfide, K, and silica (Spearman correlations $p < 0.001$, Table S4).

The field data provide little evidence that elevated sulfide production excludes wild rice by producing Fe, Cu, or Zn deficiency (Table S3). The possibility that *low* pore water Fe limits wild rice growth is difficult to distinguish from sulfide toxicity because of the strong negative correlation between pore water Fe and pore water sulfide ($\rho = -0.58$, $p < 0.0001$, Table 1). Hydroponic studies using chelated Fe in combination with elevated sulfide (Pastor et al., 2017) show reduced growth, implying that the mechanism is sulfide toxicity, rather than Fe limitation, assuming that the chelated Fe remains bioavailable in the presence of sulfide (Li et al., 2009). The median pore water Fe levels at sites with and without wild rice are similar, 5.7 and 5.9 mg L⁻¹, respectively;

average levels are 11.0 and 7.0 mg L⁻¹, respectively, which produced the significant BLR positive correlation between pore water Fe and wild rice presence. On balance, there is little evidence to support the hypothesis that elevated sulfide reduces wild rice growth through Fe deficiency rather than by direct sulfide toxicity. Pore water Cu concentrations were often below the detection limit in the field sites sampled, precluding analysis of their correlation with wild rice presence and absence. The BLR for pore water Zn concentrations with wild rice presence and absence was not statistically significant (data not shown). Neither Cu nor Zn had a significant Spearman correlation with pore water sulfide (data not shown), unlike Fe.

3.7. Seasonality in Field Variables

Fifteen natural wild rice sites were sampled 3 to 5 times in 2013 to determine which field variables exhibit statistically significant seasonal trends that might be important to consider in the overall analysis, given that different sites were sampled in different months. Some variables conformed to expected seasonal trends, such as water temperature ($p = 0.001$), which increased in early summer, peaked about 1 August, and then declined. Some of the surface water variables exhibited monotonic increased concentrations over the summer (alkalinity, Na, Mg, and SO₄; $p = 0.0009$, 0.008, 0.021, and 0.05, respectively). One hypothesis that explains this observation is that waterbodies in Minnesota, after being diluted by spring snowmelt, in general become more concentrated as the summer progresses due to evaporation and, for waterbodies with shorter residence times, greater influence of groundwater flux. Cl and Ca had nonsignificant positive slopes ($p = 0.29$ and 0.37, respectively), whereas K exhibited no trend ($p = 0.48$). As expected, none of the solid-phase variables of the homogenized 10 cm long sediment cores showed any significant seasonal trends (e.g., sediment extractable Fe $p = 0.93$, sediment TOC $p = 0.96$). Among the pore water variables, only K and pH exhibited significant trends. Pore water K values decreased over the summer ($p = 0.006$), likely as a result of diffusion into surface water or uptake by growing rooted macrophytes. Pore water pH generally increased over the summer ($p = 0.003$), which may reflect loss of CO₂ as the sediment warmed over the summer, reducing the solubility of gases. The lack of seasonality in pore water sulfide ($p = 0.62$) indicates that sulfide concentrations were in steady state with the variables that exert primary control over its concentration, surface water SO₄, extractable Fe, and sediment TOC (Pollman et al., 2017). Of the variables controlling pore water sulfide, only SO₄ exhibited even marginally significant seasonal trends ($p = 0.05$, 0.93, and 0.97, for SO₄, extractable Fe, and sediment TOC, respectively). Despite the finding of seasonal variation in SO₄, Pollman et al. (2017) found that SO₄ is one of the primary variables that control pore water sulfide concentrations. Seasonal variation in SO₄ concentrations undoubtedly contributes to noise in the statistical relationship documented by Pollman et al. (2017). Myrbo et al. (2017) found that the microbial production of pore water sulfide in a wild rice sediment is proportional to the long-term average SO₄ surface water concentration.

3.8. Cultivated Wild Rice Paddies

Commercial wild rice paddies have been reported with healthy stands of wild rice growing under surface water SO_4 levels as high as 170 mg L^{-1} (Aiken et al., 1988). Our limited measurements in seven different paddies ranged from 0.3 mg L^{-1} to $279 \text{ mg L}^{-1} \text{ SO}_4$, with a median of 8.3 mg L^{-1} ($n = 7$, Table S3). Natural wild rice waters in our study had a median SO_4 concentration of 4.1 mg L^{-1} . Surprisingly, median pore water sulfide in paddies was $182 \mu\text{g L}^{-1}$, greater than the medians of natural wild rice waters ($88 \mu\text{g L}^{-1}$; $n = 67$) and waters without wild rice ($126 \mu\text{g L}^{-1}$; $n = 41$). The median sediment extractable Fe concentration of paddies (4.5 mg g^{-1}) is similar to that of natural wild rice waters (4.8 mg g^{-1}). In contrast, median sediment TOC is much higher in paddies (25.2%) than natural wild rice waters (9.1%). It thus appears that the greater TOC driving enhanced SO_4 reduction (Pollman et al., 2017) and driving median pore water Fe lower than in natural wild rice sediments (1.6 and 5.7 mg L^{-1} , respectively), despite the similar reservoirs of Fe in the sediment. Elevated production of sulfide coupled with the consumption of the available Fe may put some paddies on the brink of sulfide toxicity to wild rice.

However, the physical setting of cultivated wild rice paddies differs from that of natural lakes and streams in a number of important ways. Often paddies and their surface sediments are dewatered during the growing season through use of buried drainage tiles, allowing tillage after harvesting and enhanced aerobic decomposition of rice straw and roots, and possibly reoxidation of sulfide and reduced Fe. Prior to drainage tile installation in the 1980s, failure of wild rice crops was sometimes attributed to elevated sulfide (Grava & Rose, 1975; Gunvalson, personal communication, 2016). Water depth in paddies is also typically shallower (median of 30 cm) than wild rice habitat in natural lakes and rivers (median of 52 cm), allowing seedlings to emerge above water with less energy expended, photosynthesize sooner, and release oxygen from roots to oxidize sulfide. The use of nitrogen fertilizers may further enable seedlings to elongate more quickly through the water and into the air. Fertilized plants have been shown to be more resistant to sulfide toxicity than are control plants (Geurts et al., 2009). The production of sulfide would be inhibited if N fertilizers were applied as nitrate—but N fertilizers are applied as ammonia or urea (Oelke et al., 1997).

3.9. Conclusions and Implications

Analysis of an extensive suite of physical and chemical parameters from 108 different sites with potential wild rice habitat shows that pore water sulfide toxicity is a primary biogeochemical factor controlling the occurrence of wild rice populations in otherwise favorable habitat. High concentrations of pore water sulfide greatly decrease the probability that a wild rice population will be found in a waterbody. When pore water sulfide is low enough to support reproducing wild rice populations, however, it is likely that the relationship between sulfide and wild rice becomes more complicated and analysis of cause and effect more ambiguous. The variation in sulfide concentration is correlated to the density of wild rice, at least partially as a result of oxygen release from roots, and thus, not only does sulfide affect wild rice but wild rice affects sulfide.

Aside from low pore water sulfide, favorable wild rice habitat has long, cold winters and transparent surface water in the ice-free season. *Zizania palustris* seeds germinate at low rates if the winter is too warm or too short. The probability that wild rice seedlings successfully grow to maturity is reduced if photosynthesis is inhibited by low water clarity. Thus, pore water sulfide (itself a function of surface water SO_4 , sediment Fe, and sediment organic matter (Pollman et al., 2017)), water temperature, and water transparency together largely determine wild rice presence and absence. These three factors are independent of one another but may act synergistically on other related processes.

In addition to generating sulfide, SO_4 reduction supports organic matter mineralization that releases nutrients and alkalinity to the surface water, which has the potential to change plant community structure even if Fe is high enough to keep pore water sulfide from reaching phytotoxic levels (Myrbo et al., 2017). Natural and anthropogenic SO_4 loading to freshwaters may thus strongly affect ecosystem composition and function, despite the low direct toxicity of SO_4 under oxic conditions.

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Effects of sulfate and sulfide on the life cycle of *Zizania palustris* in hydroponic and mesocosm experiments

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Abstract. Under oxygenated conditions, sulfate is relatively non-toxic to aquatic plants. However, in water-saturated soils, which are usually anoxic, sulfate can be reduced to toxic sulfide. Although the direct effects of sulfate and sulfide on the physiology of a few plant species have been studied in some detail, their cumulative effects on a plant's life cycle through inhibition of seed germination, seedling survival, growth, and seed production have been less well studied. We investigated the effect of sulfate and sulfide on the life cycle of wild rice (*Zizania palustris* L.) in hydroponic solutions and in outdoor mesocosms with sediment from a wild rice lake. In hydroponic solutions, sulfate had no effect on seed germination or juvenile seedling growth and development, but sulfide greatly reduced juvenile seedling growth and development at concentrations greater than 320 µg/L. In outdoor mesocosms, sulfate additions to overlying water increased sulfide production in sediments. Wild rice seedling emergence, seedling survival, biomass growth, viable seed production, and seed mass all declined with sulfate additions and hence sulfide concentrations in sediment. These declines grew steeper during the course of the 5 yr of the mesocosm experiment and wild rice populations became extinct in most tanks with concentrations of 250 mg SO₄/L or greater in the overlying water. Iron sulfide precipitated on the roots of wild rice plants, especially at high sulfate application rates. These precipitates, or the encroachment of reducing conditions that they indicate, may impede nutrient uptake and be partly responsible for the reduced seed production and viability.

Key words: hydroponics; life cycles; sulfate; sulfide; toxicity; wetlands; wild rice; *Zizania palustris*.

INTRODUCTION

Under oxygenated conditions, sulfate, the most abundant form of dissolved sulfur in aquatic systems, is relatively non-reactive, and is therefore relatively non-toxic. However, where oxygen is absent and organic matter is present, sulfate can serve as an electron acceptor for heterotrophic microbial metabolism, producing reactive reduced sulfur species. When sulfate concentrations limit the activity of sulfur-reducing microbes, an increase in sulfate can enhance the decomposition of organic matter and initiate a cascade of interrelated biogeochemical reactions (Garrels and Christ 1965) that alter the bioavailability of phosphorus and other nutrients (Lamers et al. 2002), and generate alkalinity (Giblin et al. 1990). One of the most reactive products of sulfate reduction is hydrogen sulfide, which we here term “sulfide.” If dissolved sulfide

persists in the rooting zone of aquatic plants, it can inhibit root growth and metabolism (Mendelssohn and McKee 1988, Koch and Mendelssohn 1989, Koch et al. 1990, Lamers et al. 2002, 2013, Gao et al. 2003, Armstrong and Armstrong 2005, Geurts et al. 2009, Martin and Maricle 2015) and photosynthesis (Pezeshki 2001). If root biomass and metabolism are reduced by elevated sulfide concentrations, then the plant's ability to take up limiting nutrients may be impaired (DeLaune et al. 1983, Koch et al. 1990, Gao et al. 2002, 2003, Armstrong and Armstrong 2005, Lamers et al. 2013).

Although the direct effects of sulfide on the physiology of individual plants of a few species have been studied in some detail, the cumulative effects of sulfide on a plant's life cycle through possible inhibition of seed germination, seedling survival, and seed production have been less well studied. Sulfide could affect any or all of these stages of a plant's life cycle, either directly by toxicity to seeds and seedlings or indirectly by decreasing nutrient uptake through roots during seed formation. If so, then populations may become sparser and less viable over several life cycles. Population effects could be realized rapidly in non-clonal annual aquatic emergent plant species that

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rely exclusively on seed production, germination, and seedling survival to produce the next generation of emergent shoots. A seed bank in the sediment would facilitate recovery of a population after one or two catastrophic growing seasons, but would become depleted if chronic sulfide toxicity does not allow occasional successful growth and reproduction to restock the seed bank.

Northern wild rice (*Zizania palustris* L., hereafter wild rice) is an annual graminoid (Family Poaceae, Tribe Oryzeae), which is most abundant in the rivers and lakes in the Lake Superior region. Because of its widespread distribution and tendency to form large monotypic stands, wild rice is an important component of the food supply for the aquatic and avian herbivores and seed consumers, such as muskrats and waterfowl. Reduction of these wild rice populations could, therefore, have cascading effects on diverse aquatic food webs. In addition, the native Ojibwe people of the Lake Superior and Lake Michigan region teach that they were led to this region to find “the food that grows upon the water,” which is wild rice. The Ojibwe identify their origins with wild rice and consider themselves “people of the rice” (Vennum 1998). The resource is also important to Menominee and Dakota peoples of the region. Efforts to enhance the productivity, perpetuation, and restoration of natural wild rice populations are of great importance to state and tribal natural resource agencies for both ecological and cultural reasons.

The wild rice life cycle begins when seeds from the previous year or years germinate in mid to late May. Juvenile seedlings grow through the water column in early to mid-June. Upon reaching the surface, the seedling generates a floating leaf that fixes carbon into carbohydrates for root production and nutrient uptake. By the end of June, nitrogen and other nutrients are translocated out of the floating leaf into an aerial shoot emerging from the leaf axil, and the floating leaf dies. The early stages of the vegetative growth of the aerial shoot happen during the next two weeks and vegetative growth continues until the emergence of flowering heads in late July. Seed production and ripening begins in early to mid-August with seed production completed by early- to mid-September. The productivity of wild rice is primarily limited by nitrogen and secondarily by phosphorus; increased nitrogen supply accelerates development of the life cycle and reduces allocation to roots (Sims et al. 2012a) and increases the number of inflorescences, seeds per inflorescence, and mean seed mass, resulting in more seedlings produced the following year, and hence greater fitness (Sims et al. 2012b).

Historic observations suggested that wild rice usually occurs in waters where sulfate concentrations were near or below 10 mg/L and populations are uncommon where sulfate concentrations exceeded 50 mg/L (Moyle 1944, 1945). Based on Moyle's (1944, 1945) research, the State of Minnesota sulfate standard for waterbodies supporting wild rice is 10 mg/L; Wisconsin, Michigan, and Ontario currently do not have sulfate standards for wild rice waters. For comparison, the EPA non-enforceable,

aesthetic (taste) secondary water quality sulfate standard for human consumption is 250 mg/L (*available online*).⁷

This research is part of a larger study coordinated by the Minnesota Pollution Control Agency on the effect of sulfate on wild rice, which included an extensive survey of potential wild rice waters across Minnesota containing surface water sulfate ranging from <2 mg/L to >600 mg/L. This study was carried out because of recent interest in the nature of the relationship between sulfate and wild rice, especially with respect to potential anthropogenic sulfate enhancements to wild rice ecosystems such as sewage treatment plants, agricultural runoff, and mining of ores containing metallic sulfides. The mechanisms responsible for the decreased wild rice density with increased sulfate concentrations observed by Moyle (1944, 1945) have not been investigated until this study.

Although we have a fairly extensive understanding of the general aspects of the life cycle of wild rice in natural stands in relation to nutrient availability and sediment chemistry (Keenan and Lee 1988, Day and Lee 1990, Meeker 1996, Lee 2002, Pastor and Walker 2006, Walker et al. 2010, Hildebrandt et al. 2012, Sims et al. 2012a, b), the way in which sulfate in surface water can affect the life cycle of wild rice, and hence its population dynamics, is much less well understood. The objectives of our research are to (1) determine the relative effects of sulfate and sulfide on seed germination, seedling viability, vegetative growth, and seed production; (2) determine the response of wild rice populations and population viability to sulfate in the overlying water and the production of sulfide in sediment porewaters.

METHODS

The effects of sulfate and sulfide on wild rice were tested in two different ways: (1) a laboratory hydroponic culture system and (2) an outdoor mesocosm system that better mimicked natural wild rice waters, but does not control the chemical exposures as precisely as the hydroponic experiments did. Short-term (10 or 11 days) hydroponic exposures of seeds and seedlings to sulfate and sulfide were conducted to examine effects on seed germination, seedling growth, and survival. Full life cycle tests were conducted in mesocosms where wild rice grew in sediment taken from a natural wild rice lake. These multi-year outdoor tests examined the effects of elevated surface water sulfate and the associated increased sedimentary sulfide concentrations on germination, survival, growth, and reproduction.

Hydroponic experiments

Li et al. (2009) published one of the few dose-response studies of aquatic macrophytes (*Typha* and *Cladium*) to sulfide, which requires the maintenance of anaerobic

⁷ <http://water.epa.gov/drink/contaminants/secondarystandards.cfm>

conditions. Malvick and Percich (1993) developed a simple hydroponic system to investigate effects of nutrients on germination and early growth of wild rice, but their system could only be implemented under aerobic conditions. We used these two studies as starting points for the development of our methods.

Wild rice seeds used for all hydroponic experiments were collected on 30 August 2012 from Little Round Lake (Minnesota Lake ID 03-0302, 46.97° N, 95.74° W; average surface water sulfate <0.5 mg/L and porewater sulfide = 77 µg/L, $n = 5$). The seeds were stored at 4°C in polyethylene bottles in a darkened room until needed for experiments. Immediately before each experiment, a subsample of these seeds was selected that were intact, filled, not green (unripe), and not moldy. To obtain seedlings for juvenile seedling response to sulfate or sulfide, the selected seeds were allowed to germinate in aerobic deionized water until a 1–2 cm long mesocotyl shoot appeared, which usually occurred 5–7 days after germination. The mesocotyl is the embryonic stem that will develop into the mature stem.

Once the seeds or seedlings were selected, they were picked up with forceps and transferred to the appropriate test in appropriate containers. The hydroponic solution was one-fifth strength Hoagland's solution in 5 mmol/L PIPES buffer to maintain a pH of 6.8 ± 0.03 (mean $\pm$ SD) in the solution, similar to that observed in the porewater of mesocosm experiments. Nitrogen was supplied only as ammonium (0.16 mmol/L NH_4Cl) to mimic natural concentrations of inorganic nitrogen in wild rice waters (Walker et al. 2010). The Hoagland's solution contained sulfate only in trace amounts as ZnSO_4 (0.5 µmol/L) and CuSO_4 (0.15 µmol/L). This nutrient solution was then augmented with appropriate amounts of anhydrous Na_2SO_4 or $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ to achieve desired sulfate or sulfide treatment concentrations. The one-fifth Hoagland's solution and PIPES buffer were chosen based on previous trials to determine proper strengths and buffers that would support seedling growth without adverse effects (see Appendix S1 for composition of our modification of Hoagland's Solution).

Germination of wild rice seeds under aerobic conditions subject to various concentrations of sulfate.—The selected seeds were placed into each of six numbered plastic cups to total 50 seeds each, then randomly assigned and transferred to each of six 1-pint Mason jars (1 pint = 473 mL) containing six sulfate treatment concentrations of 0 (trace), 10, 50, 100, 400, or 1600 mg SO_4/L . These sulfate treatments (trace to 1600 mg/L) bracket the large range encountered across Minnesota's geologically diverse landscape (10th and 90th percentiles of 0.2 and 285 mg/L, respectively; MPCA 2016), plus some mine pits over 1000 mg/L that may overflow into wild rice waters. This seed counting and random transfer was repeated twice more to result in six treatment levels with three replicate jars per treatment. The jars were covered with plastic covers fitted with rubber stoppers to facilitate solution

exchanges. Two holes in the plastic lids were left open to facilitate air exchange and to prevent the solutions from becoming anaerobic. The experiment proceeded in a growth chamber at 20°C in the dark to simulate conditions measured in sediments during the growing season, which we have measured in our mesocosms (see *Results*). The solutions were exchanged with fresh solution of the appropriate treatment concentration every three days. Dissolved oxygen in the solutions across all treatments was initially 8.280 ± 0.218 mg/L (mean $\pm$ SD) and dropped to 2.85 ± 0.60 mg/L by the end of three days, still well above anoxic levels required for production of sulfide. Solution pH and sulfate were measured on each initial batch of sulfate treatment and on the exchanged solution from each jar. The germinated seedlings were harvested after 11 days. The number of successfully germinated seeds, determined as those that produced a mesocotyl at least 1 cm in length, were counted. The length of the mesocotyl was measured for each seed. The germinated seeds were then dried at 65°C for 3 d. The mesocotyl was then carefully separated from the seed hull and weighed.

Germination of wild rice seeds under anoxic conditions subject to various concentrations of sulfide.—The techniques used here were the same as for the germination trials under various sulfate concentrations, except that extra care was necessary to ensure anaerobic conditions. Fifty seeds were chosen as above and then placed in 700 mL borosilicate glass bottles capped using phenolic screw caps with chlorobutyl septa 5 mm thick. The one-fifth Hoagland's nutrient solution was deoxygenated with oxygen-scrubbed nitrogen before being added to the bottles. PIPES buffer was added to the test solution to maintain consistent pH levels of 6.8 ± 0.03 throughout an experiment. Bottles were filled completely with the deoxygenated nutrient solution and without introducing any air bubbles and then capped with the septa. Stock sulfide solutions (20–30 mmol/L) were prepared as needed by adding $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (sodium sulfide nonahydrate) to deionized and deoxygenated water. The concentration of the stock sulfide solution was checked periodically against a stock solution that had been standardized using an iodimetric titration. An appropriate amount of the stock solutions was added to each bottle with a Hamilton gas-tight glass syringe through the septa while simultaneously withdrawing an equivalent volume of the Hoagland's solution by means of a second syringe through the septum. All of the syringes used in this and other experiments were purged three times with oxygen-scrubbed ultra-pure nitrogen from a tilled PVDF gas sampling bag (Saint-Gobain No. D1075016-10), which had also been purged three times before filling. Added stock sulfide solution volumes range between 0.2 and 3.0 mL depending on target exposure concentrations and the nominal concentration of stock sulfide solution. The target sulfide concentrations were 0 (trace), 96, 320, 960, and 2880 µg/L. These sulfide treatments (trace to 2880 µg/L) bracket the range encountered across shallow

aquatic systems in Minnesota that potentially could host wild rice (5th and 95th percentiles of 26 and 1631 $\mu\text{g/L}$, $n = 108$; A. Myrbo, *unpublished data*).

The bottles were placed in a growth chamber in continuous darkness at $20^\circ \pm 1^\circ\text{C}$. Solutions were exchanged every two days if during the week or three days if over a weekend. The solution in each jar was sampled for sulfide analysis at the beginning and end of each two- or three-day cycle. The pH of the solution in each jar was measured at the end of each two- or three-day cycle. To obtain the initial pH of the solution, one additional replicate jar for each treatment but without seeds was filled with one-fifth Hoagland's solution, then the sulfide treatment was added using syringes as above and the jar was opened and pH was measured immediately. Total dissolved sulfide ($\text{H}_2\text{S} + \text{HS}^-$) was measured on a Hach DR5000 spectrophotometer using a colorimetric methylene blue method (4500 S2-D; Eaton et al. 2005) as implemented with Hach method 8131. The method was adapted for a lower detection limit ($\sim 15 \mu\text{g/L}$) using a photo cell with a 5 cm path length. All measurements of dissolved sulfide in both hydroponics and mesocosm experiments refer to the sum of all dissolved inorganic reduced sulfur ($\text{H}_2\text{S} + \text{HS}^-$). The samples of hydroponic water were added directly from the gas tight syringe to the sulfuric acid reagent, followed immediately by the potassium dichromate reagent. After 11 days, the germinated seeds were harvested and measured as described for the experiments on effects of sulfate on germination.

Growth of juvenile wild rice seedlings under aerobic conditions subject to various concentrations of sulfate.—We examined growth of juvenile seedlings at concentrations of 0, 10, 50, 100, 400, and 1600 $\text{mg SO}_4/\text{L}$. Twenty replicated 70-mL unsealed glass Kimax tubes (Cole-Parmer, Vernon Hills, IL, USA) were used for each test concentration. One seedling germinated and selected as described was placed with forceps into each Kimax tube, which was then filled with one-fifth Hoagland's solution and an appropriate amount of sulfate. The filled tubes (solution and seed) were placed into every other opening in Nalgene Resmer (ThermoFisher Scientific, Waltham, MA, USA) test tube holding racks so that light could penetrate to all sides of each tube. A total of six 40-tube racks, each containing 20 tubes, were used to hold the test tubes. Screw caps were placed loosely on the tubes to allow for oxygen exchange across the solution surface and thereby prevent the development of anaerobic conditions. The tubes were placed in a Percival environmental growth chamber where we measured $288 \pm 22 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ of photosynthetically active radiation immediately above the plants using a Decagon PAR – 80 Ceptometer (Decagon Devices, Pullman, WA, USA). Tests were performed under a 16 h:8 h light:dark schedule. All racks were placed in the growth chamber so that the spaces between the racks were the same as the spaces within the racks and the tops of the tubes are within 30 cm of the bottom of the lights. The location of each rack in the growth chamber

remained the same for the test duration. Test solutions in the tubes were renewed every two days. Temperature was maintained at 21°C during lighted periods and 19°C during dark periods and the humidity was maintained at 85%. Plants were harvested after 10 days and the seed hull was carefully removed. Stem and leaf length was measured to the nearest millimeter by placing the stem with leaf stretched out on a flat surface next to ruler with the zero mark aligned with the point of stem-root transition. Total root lengths were measured in duplicate scans of the entire root system using the program WinRhizo (Regent Instruments, Quebec, Canada). Seedlings were weighed after drying at 100°C for 48 h. Control juvenile seedlings did not have any visible phytotoxic or developmental symptoms at any time and the controls had additional stem growth of at least 5.0 cm during the 10-d test.

Growth of juvenile wild rice seedlings under anaerobic conditions subject to various concentrations of sulfide.—Germinated seedlings were chosen using the same techniques described for aerobic conditions. Seven seedlings 1–2 cm in length that fit the criteria as described, were placed with a forceps in 125-mL borosilicate glass jars capped using phenolic screw caps with 5 mm thick chlorobutyl septa. Each sulfide concentration was replicated in this way in three separate jars. Deoxygenated Hoagland's nutrient solution was added as described above. Seedlings were grown in the same environmental growth chamber under the same temperature and light conditions as for the sulfate experiments but with solution sulfide concentrations of 0, 96, 320, 960, and 2880 $\mu\text{g/L}$. Solutions were exchanged every two days if during the week or three days if over a weekend. Sulfide concentrations were measured at the beginning and end of each two–three day solution exchange period. Because the plants were photosynthesizing and producing oxygen, the sulfide concentration declined during these two–three day periods. This was especially so for the lowest sulfide concentrations (less than $\sim 300 \mu\text{g/L}$) in which less than 10% remained after two days, but 70–90% of sulfide remained after two days for sulfide concentrations greater than 650 $\mu\text{g/L}$. We therefore used the time-weighted average sulfide concentration over the 10 days period to characterize the sulfide concentrations the plants were exposed to. Seedlings were harvested after 10 days, the seed hull was carefully removed, and the stem and leaf lengths and total plant mass were determined. Because many of the plants, especially at high sulfide concentrations, did not grow at all (see Results below) the roots and shoots were very fragile and no attempt was made to dissect the plants into subcomponents as with the experiment on the effects of sulfate on seedling growth.

Statistical analyses of hydroponic experiments.—The general procedure for each set of sulfate and sulfide exposure experiments was first to examine seed germination or seedling growth response across a wide range of concentrations spanning three orders of magnitude of either sulfate or sulfide as noted. The main effect of

sulfate or sulfide concentrations on the variable of interest was then tested with an analysis of variance using SigmaPlot (SYSTAT Software, San Jose, CA), USA. When the residuals were not normally distributed or the data did not have equal variance between treatments, then the data were transformed by taking the natural logarithms, which then passed normality and equal variance tests. If there were no effects across this wide range of concentrations in this experiment, then it was repeated to test whether the results were a false negative. If there were significant main effects, then Tukey's pairwise comparisons were performed to determine in which part of the range of concentrations significant effects occurred. Further experiments were then conducted twice using this narrower range of concentrations centered on the region of significant change to more precisely refine the range of response of seedling germination or growth to sulfate or sulfide concentrations.

If there was a significant effect of sulfide on seedling growth, then the biomass growth of seedlings (mg) over the 10-d period was regressed against the time-weighted total dissolved sulfide concentrations ($\mu\text{g/L}$) with a four-parameter sigmoidal function using SigmaPlot nonlinear regression

$$\text{Plant growth} = y_{\min} + \frac{y_{\max}}{1 + \exp\{ -[(S^{2-} - x_0)/b] \}} \quad (1)$$

where $y_{\min}$ is the right-side (minimum) horizontal asymptote (minimum growth response) $y_{\max}$ is the height of the left-side horizontal asymptote (maximum growth response) above $y_{\min}$, S^{2-} is total dissolved inorganic sulfide ($\text{H}_2\text{S} + \text{HS}^-$), x_0 is the sulfide concentration at the inflection point of the curve, and b is a parameter that scales $\mu\text{g/L}$ of sulfide concentration to mg of biomass growth. The 50% effects concentration (EC50, the concentration of sulfide that caused a 50% reduction in change in plant mass compared to controls) was calculated from this regression.

The sulfate experiment had to be conducted under aerobic conditions while the sulfide experiment had to be conducted under anaerobic conditions. Therefore, redox statuses of the solutions were necessarily confounded with sulfur speciation. To test the effect of redox status on seedling growth, we compared the growth of plants from both the lowest concentrations of the sulfate (aerobic) and sulfide (anaerobic) experiment using a single-factor analysis of variance.

Mesocosm experiments

Experimental design.—We constructed mesocosms using the same procedures and designs previously reported by Walker et al. (2010) for a 5-yr experiment on the interaction of the nitrogen cycle and wild rice population dynamics.

In late spring of 2011, polyethylene stock tanks (400 L, $132 \times 78 \times 61$ cm; High Country Plastics, Caldwell, ID, USA) were fitted with overflow drain pipes and buried to ground level. The drain pipes are connected to 20-L polyethylene overflow buckets buried adjacent to each tank. Water tables were set by the inflow to the drain pipe at 23 cm above the sediment surface. The tanks were leveled

and then partly filled with 10 cm of clean sand washed with the same well water later added to the tanks (see next paragraph). The sand layer was then covered with 12 cm of surface sediment collected from a natural wild rice bed in Rice Portage Lake (Minnesota Lake ID 09-0037, 46.70° N, 92.70° W) on the Fond du Lac Band of Lake Superior Chippewa Reservation, Minnesota. Rice Portage Lake is approximately 337 ha, of which approximately 50 ha are wild rice beds (Minnesota Department of Natural Resources 2008). Ten to 20 cm of sediment over sand is sufficient to support the rooting depths we have observed in natural wild rice lakes. The sediments were kept saturated and then thoroughly homogenized in a large stock tank prior to distribution into the tanks. Analyses of five volumetric samples of the mixed sediment indicate a homogenous material ($\text{C} = 14.8\% \pm 1.7\%$, $\text{N} = 1.12\% \pm 0.13\%$, $\text{S}[\text{acid volatile sulfur}] = 0.005\% \pm 0.003\%$). Sediment bulk density was $0.27 \pm 0.01 \text{ g/cm}^3$ (Walker et al. 2010). These nutrient and bulk density values are similar to those of other wild rice beds (Keenan and Lee 1988, Day and Lee 1990). No new sediment has been added to the stock tanks since the mesocosms were established in 2011.

The tanks were immediately filled with water obtained from a nearby well after sediment additions to prevent the sediment from drying. Water was added cautiously from a garden hose to prevent redistribution and suspension of sediment. During the growing season, water levels were maintained at 23 cm above the sediment surface by weekly additions of water to the drain pipe heights or by allowing water to drain through the pipe into the overflow buckets. Rainfall N concentrations as $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ ranged from 0.2 to 1.99 mg/L while the $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations in the well water are always $<0.2 \text{ mg/L}$ (Walker et al. 2010). Sulfate concentrations in well water averaged $10.73 \pm 0.75 \text{ mg/L}$ ($n = 36$) and in rainwater averaged $2.13 \pm 1.02 \text{ mg/L}$ ($n = 16$). The sediments comprise a natural inoculation source for microbes and a background supply of nutrients for plant growth source. The sediments and plant litter remain submerged in the mesocosms year round with water levels set at approximately 20 cm in late fall.

Wild rice was planted once in late spring 2011 from seeds obtained from Swamp Lake (Minnesota Lake ID 16-0256, 47.85° N, 90.58° W), a 37-ha lake on the Grand Portage Band of Lake Superior Chippewa Reservation, Minnesota. Seeds from each year's crop were allowed to fall unimpeded into the tanks to provide the seed source for the next year's population; no further seeding from external seed sources occurred.

End-of-season plant density in Minnesota wild rice lakes monitored by the 1854 Treaty Authority averages 40 plants/ m^2 (Vogt 2010). Accordingly, the seedlings were thinned to this density (30 plants per tank) in late spring or early summer each year before the floating leaf stage was achieved. The seedlings removed from each tank during thinning in 2012–2015 were counted to estimate seed germination and early seedling success.

Immediately after installation and seeding, beginning in late June 2011, the tanks were treated with different amounts

of sulfate to achieve several target sulfate concentrations in the overlying water. There were five overlying water sulfate concentrations and six replicate tanks per sulfate concentration, for a total of 30 tanks. Nominal water column sulfate concentrations of 50, 100, 150, and 300 mg SO_4/L were maintained in sulfate-amended tanks. Aside from incidental sulfate in the make-up water from a well and rainwater, control tanks did not receive any sulfate amendments and overlying water concentrations ranged from 2 to 10 mg/L (average of 7 mg/L) depending on rainfall, evapotranspiration, and loss via sulfate reduction in the sediment. The overlying water sulfate concentrations in the mesocosm experiments bracket both the existing 10 mg/L Minnesota statutory standard for wild rice waters and the EPA drinking water standard of 250 mg/L. Samples of the water column were taken weekly and analyzed for sulfate concentration using a Lachat QuikChem 8000 Autoanalyzer (Method 10-116-10-1-A, Hach Co., Loveland, CO, USA). When necessary (approximately every two weeks), the sulfate concentration was adjusted to near the desired nominal concentrations with appropriate amounts of 10 g/L sodium sulfate (Na_2SO_4 ; Fisher Chemical S421, Thermo Fisher Scientific, Waltham, MA, USA) stock solution and well water. The sodium sulfate stock solution was first mixed in 1–2 L of water from the tank, then added back to the tank's overlying water with mild mixing.

Plant, sediment, and water sampling and analyses.—In each year from 2011 to 2015, five plants in each tank were randomly chosen in early summer for detailed measurements throughout the growing season and to be destructively sampled at the end of the growing season. In late August to September, ripe seeds from these plants were collected every two or three days by gently removing them, leaving unripe seeds behind for the next collection date. The seeds from each individual plant were placed in a paper envelope and marked with the tank identification number. The plants were then harvested for determination of biomass, root:shoot mass ratios and total seed production by counting seed peduncles along the flowering stem.

Seeds from each of the five sampled plants were separated into filled (viable) seeds and empty (nonviable) seeds, counted, and weighed. A subsample of seeds collected in all years except 2013 were dried at 60°C for determination of moisture content to convert wet mass to dry mass. The five sample plants were separated into root and shoot (stem + leaves), and then weighed. Root:shoot ratios and seed masses and numbers from the five sampled plants were applied to total aboveground population masses and total plant numbers to determine total root and seed biomass and number and total biomass in each tank.

While harvesting the plants for growth and biomass measurements, we noticed that plants in the tanks amended with sulfate had blackened roots while plants grown in the control tanks had white or light tan or orange roots. To investigate this further, a sample of roots from a plant from one control tank and a plant from one 300 mg/L amended tank were collected and placed immediately in water in

which dissolved oxygen had been purged by bubbling with oxygen-free N_2 . These samples were analyzed for Fe and S concentrations by energy-dispersive X-ray spectroscopy (EDS) using a Hitachi TM-1000 scanning electron microscope (Hitachi High Technologies, Schaumburg, IL, USA) fitted with a Quantax EDS unit (Bruker Corporation, Billerica, MA, USA). The nominal spot size was 0.2 μm and the analysis volume was $\sim 5 \mu\text{m}^3$. The sample of blackened roots was analyzed at seven points and the sample of tan/orange control roots was analyzed at five points.

All aboveground plant material was collected from each tank at the end of the growing season and weighed to determine total aboveground biomass. A subsample was taken to determine wet:dry ratios for moisture correction after drying at 60°C. All aboveground plant material except for the five sample plants were returned to each tank. All stems in each tank were counted at the time of harvesting the aboveground plant biomass to determine end of growing season plant density.

In 2013, significant seedling mortality occurred in all tanks after thinning but before the floating leaf stage. We believe this early season mortality was due to a record cold and late spring in northern Minnesota in April and May of 2013; ice stayed on lakes an average of 3 weeks later than the median ice-out date (data available online).⁸ The reduced overall emergence of plants in the spring of 2013 precluded the destructive sampling of five sample plants in each tank at the end of the 2013 growing season because this harvesting would have greatly decreased the number of viable seeds returned to the sediment for the following growing season. Instead, during 2013 all seeds were harvested from each and every plant in the tanks, sorted as described above on each collection day, and returned to the tanks within 24 h of collection without drying in order to maintain their viability for future populations. To determine wet-dry conversion ratios for these seeds, additional seeds were collected at the same collection times from an adjacent experiment on wild rice (Walker et al. 2010) for moisture determination after drying them at 60°C.

Polycarbonate porewater equilibrators (peepers) with sampling ports spaced 1.5 cm intervals were used to make in situ measurements of geochemical profiles of sulfur and iron species at discrete depths in the sediment porewater of a subset of tanks in August of 2013. Care was taken that the installation and extraction of the peepers did not disturb any plants. The method for collecting samples for sulfate, sulfide, and ferrous iron with peepers was modified from Koretsky et al. (2007). Sulfide and iron were quantified in samples immediately with minimal oxygen exposure using a colorimetric methylene blue method (4500 S2-D; Eaton et al. 2005) as implemented with Hach method 8131 for sulfide and a colorimetric phenanthroline method for iron (3500-Fe-B; Eaton et al. 2005). Sulfate was quantified with ion chromatography on a Dionex ICS 1100 system (Thermo Fisher Scientific, Waltham, MA, USA) after acidifying samples to pH < 3

⁸ http://climate.umn.edu/doc/journal/ice_out_recap_2013.htm

using hydrochloric acid and purging gently with oxygen-free nitrogen gas.

In August 2013 and 2015, we also used 10-cm long Rhizon samplers (Rhizosphere Research Products B.V., Wageningen, The Netherlands) to obtain porewater for sulfide analysis. The sampler was inserted vertically into the sediment and connected to an evacuated 125-mL serum bottle. Sulfide samples were prepared without removing the butyl rubber stopper for inline distillation by automated flow injection colorimetric analysis (4500 S2-E; Eaton et al. 2005).

On 6 October 2015, a 10-cm long sediment core was taken from each mesocosm and homogenized. Extractable iron was quantified following a 30-min exposure to 0.5 mol/L HCl, following Balogh et al. (2009), at the Minnesota Department of Health Environmental Laboratory. Total organic carbon was determined using the method of oxidative combustion-infrared analysis (U.S. EPA 2004), after pre-treatment with acid to remove inorganic carbon, at Pace Analytical Services in Virginia, Minnesota, USA.

Statistical analyses of mesocosm experiments.—The effects of sulfate concentrations on plant attributes were tested by repeated measures analysis of variance followed by pairwise comparisons between attributes of plants in the control tanks and each higher sulfate concentration. We also regressed each plant attribute against average annual sulfate concentration for each year. Correlations were assessed using Pearson's correlation test. This combination of both analysis of variance and regression was used as recommended by Cottingham et al. (2005). We used target sulfate concentrations as categorical variables in analyses of variance and growing season actual sulfate concentrations in regression analyses.

RESULTS

Hydroponic experiments

Effect of sulfate on seed germination.—Between 71% and 76% of the seeds pre-selected as filled and mold-free germinated at each sulfate concentration. Sulfate exposure concentrations of 0, 10, 50, 100, 400, and 1600 mg SO_4/L did not affect germination success, mesocotyl lengths, or the masses of the stem plus leaf (if any) and roots ($P > 0.10$ for each test). The experiment was repeated with the same results.

Effect of sulfide on seed germination.—Sulfide concentrations of 0, 96, 320, 960, and 2880 $\mu\text{g}/\text{L}$ did not affect germination success of seeds, mesocotyl masses, or mesocotyl lengths ($P > 0.10$ for each test). The experiment was repeated with the same results.

Effect of aerobic and anaerobic conditions on seed germination.—There were no differences in germination rates under anaerobic compared with aerobic conditions when concentrations of sulfur were at trace ($<1 \mu\text{mol}/\text{L}$) amounts of CuSO_4 and ZnSO_4 in the Hoagland's solution. Mean

mesocotyl lengths in the anaerobic solutions (7.8 cm) were significantly reduced ($P < 0.05$) by 38% compared with mean mesocotyl lengths in the aerobic solutions (12.5 cm).

Effect of sulfate on seedling growth.—Sulfate concentrations of 0, 10, 50, 100, 400, and 1600 mg SO_4/L did not affect the growth of juvenile seedling stem length, juvenile stem mass, juvenile root mass, or total juvenile seedling mass ($P > 0.10$ for each test). Sulfate decreased juvenile root length slightly ($P < 0.02$) but only at 1600 mg SO_4/L compared with 50 mg SO_4/L . The experiment was repeated with the same results.

Effect of sulfide on seedling growth.—To examine the effects of sulfide on early seedling growth, we began by growing juvenile seedlings under a wide range of nominal sulfide exposure concentrations of 0, 96, 320, 960, and 2880 $\mu\text{g}/\text{L}$ in anoxic solutions in a first trial. Both roots and stems of control plants (no added sulfide) increased significantly ($P < 0.05$) over the exposure, approximately doubling in size compared with initial lengths and masses. In seedlings exposed to sulfide concentrations 320 $\mu\text{g}/\text{L}$ or more, stem and leaf masses ($P < 0.01$) and total plant masses ($P < 0.001$) were significantly depressed by an average of 60% and 75%, respectively, relative to controls. Root lengths were only weakly depressed with increasing sulfide concentration ($P < 0.10$).

To narrow the range of toxicity, we then conducted two additional trials focusing on the effects of sulfide on juvenile seedling growth at concentrations less than 1600 $\mu\text{g}/\text{L}$ sulfide. The second trial examined growth at exposure concentrations of 0, 200, 400, 800, 1600 $\mu\text{g}/\text{L}$ sulfide and the third trial examined growth at exposure concentrations of 0, 160, 320, 640, and 1280 $\mu\text{g}/\text{L}$ sulfide. Consistent with the first trial, the biomass of all control plants increased significantly ($P < 0.05$) during the 10 d of

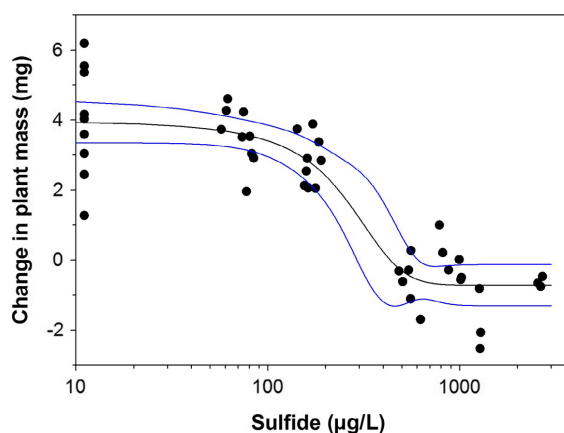


FIG. 1. Growth of wild rice seedlings declines with increasing sulfide concentrations in hydroponic solutions. Individual data points are from three separate experimental runs (see *Methods* and *Results* sections). Fitted sigmoidal response curve (Eq. 1) is shown in black, 95% confidence intervals in blue; $r^2 = 0.80$, $y_{\min} = -0.7172$, $y_{\max} = 5.1353$, $x_0 = 245.9051$, $b = -103.8853 \mu$ (Color figure can be viewed at wileyonlinelibrary.com.)

exposure, approximately doubling in size compared with initial lengths and masses, and exposure to sulfide across these narrower ranges of concentration again significantly depressed stem plus leaf lengths and total masses of juvenile seedlings.

Because all three trials produced similar effects, we performed a pooled analysis of variance using data from all three. Exposures of seedlings to sulfide concentrations of 320 $\mu\text{g/L}$ or greater significantly reduced growth rates ($P < 0.01$) of wild rice seedlings compared to the control by 88% or greater (Fig. 1). Seedlings exposed to sulfide concentrations at 320 $\mu\text{g/L}$ or greater hardly grew at all and in some cases their mass decreased during the 10-d course of the exposure (Fig. 1). But exposures at sulfide concentrations less than 320 $\mu\text{g/L}$ did not significantly reduce growth rates ($P > 0.10$) compared with the controls (Fig. 1). There was a sigmoidal response of seedling growth to elevated sulfide concentrations, with an inflection point at approximately 245 $\mu\text{g/L}$ (Fig. 1; see figure caption for parameter values and r^2 for Eq. 1). The EC50 calculated from this regression was 227 $\mu\text{g/L}$.

Effect of aerobic and anaerobic conditions on seedling growth.—Under micromolar concentrations of sulfur

from trace amounts of CuSO_4 and ZnSO_4 in the Hoaglands solution, stem lengths were 10% longer ($P < 0.02$), root lengths were 73% shorter ($P < 0.001$), and total plant masses were 16% less ($P < 0.01$) under anaerobic conditions compared to aerobic conditions.

Mesocosm experiment

Sulfate concentrations in overlying water.—The average monthly measured sulfate concentrations in amended tanks were consistently within 80–100% of nominal target concentrations of 50, 100, 150, and 300 mg/L (Table 1). The sulfate concentrations sometimes decreased after large rainfall events.

Porewater sulfide concentrations with sulfate additions.—Profiles of sulfate, sulfide, and iron in the mesocosm porewaters showed patterns consistent with sulfate diffusion from the overlying water into the surficial 5 cm of sediment with subsequent reduction to sulfide (Fig. 2). Concentrations of sulfide were typically highest in upper 3–5 cm, which is the rooting zone of seedlings. Sediment in tanks contained on average $8.3 \pm 0.8 \text{ mg/g}$ extractable iron; extractable iron did not vary with average surface

TABLE 1. Target and measured sulfate concentrations in overlying water in the mesocosm experiment.

Target sulfate concentration	Measured growing season mean sulfate concentrations (mg/L)					
	12 Jul–30 Aug 2011	6 Jun–28 Aug 2012	5 Jun–27 Aug 2013	27 May–26 Aug 2014	5 May–4 Sep 2015	Average over all years
0	8.05 (0.34)	8.0 (0.31)	7.05 (0.18)	5.8 (0.16)	6.16 (0.25)	7.01 (0.45)
50	50.0 (1.58)	34.0 (1.26)	37.2 (1.02)	43.3 (0.8)	41.7 (1.26)	41.2 (2.73)
100	97.7 (4.33)	77.1 (1.76)	79.7 (1.41)	87.2 (1.29)	85.3 (2.03)	85.4 (3.58)
150	135.0 (3.73)	126.0 (2.08)	127.0 (1.55)	131.0 (1.68)	132.0 (2.56)	130.0 (1.57)
300	254.0 (7.35)	263.0 (3.32)	268.0 (2.37)	273.0 (2.52)	272.0 (4.08)	266.0 (3.50)

Note: Values in parentheses are SE.

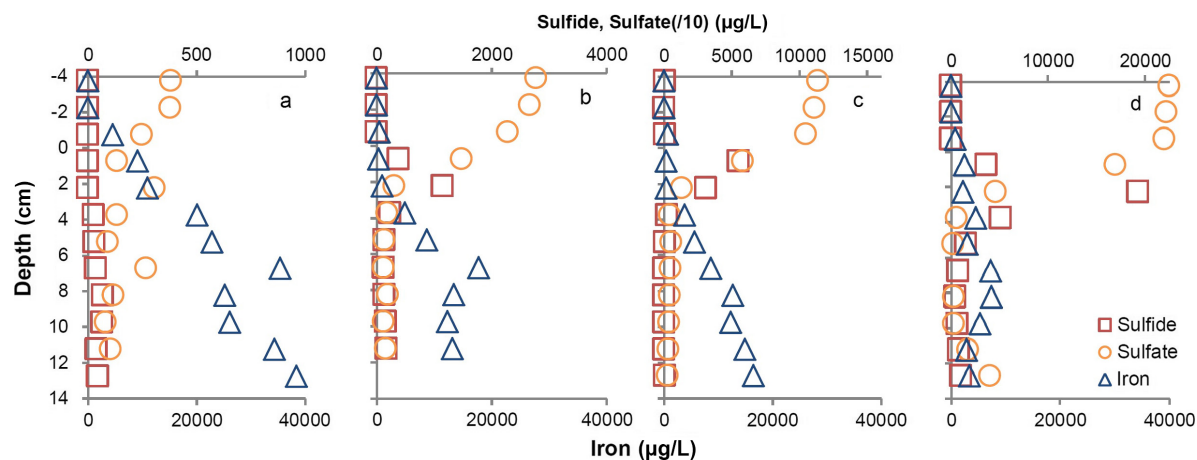


FIG. 2. Vertical profiles of sulfate, sulfide, and iron in mesocosms with different measured sulfate concentrations in the overlying water measured during August 2013. Average annual overlying water sulfate concentrations were (a) 7.05 mg/L , (b) 37.2 mg/L , (c) 127 mg/L , and (d) 268 mg/L . Note different scales for sulfate and sulfide in panels b, c, and d. (Color figure can be viewed at wileyonlinelibrary.com.)

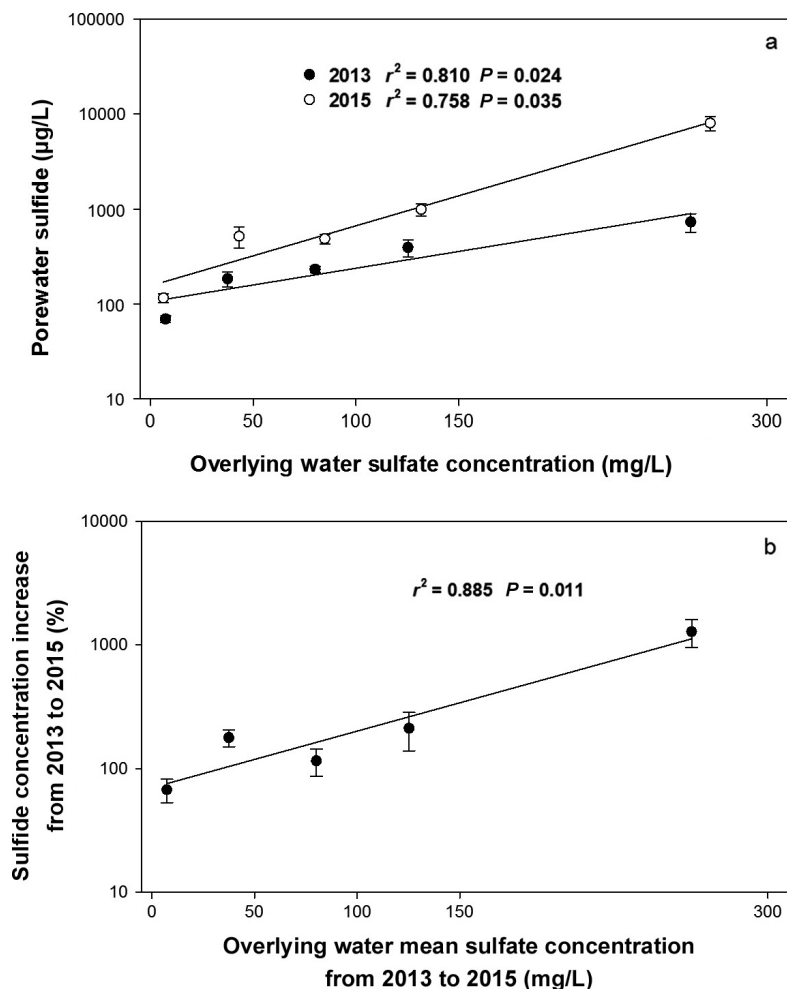


FIG. 3. (a) Porewater sulfide concentrations are strongly correlated with measured concentrations of sulfate in overlying water in the mesocosms and (b) the sulfide concentrations increased from 2013 to 2015 in proportion to sulfate concentrations. Symbols are means and standard errors.

water sulfate concentration (linear regression $r^2 = 0.02$). Sediment in control tanks contained less than 0.15 mg/g acid volatile sulfides (1 mol/L hydrochloric acid, Allen et al. 1991) while sediment in 300 mg/L sulfate tanks contained over 1.75 mg/g in 2013.

Porewater sulfide concentrations obtained from the upper 10 cm of sediment with Rhizon samplers were highly correlated with sulfate concentrations in the overlying water in both 2013 and 2015 (Fig. 3a). Concentrations were higher in 2015, and disproportionately higher in the higher sulfate treatments (Fig. 3b), which could be a consequence of progressively less precipitation with iron, which was a limited quantity.

Effects of sulfate and sulfide on seedling emergence rate and seedling survival.—In each spring after the initial planting in 2011, the number of seedlings that emerged from the sediment (Fig. 4a) declined significantly with increased sulfate concentrations ($P < 0.001$). Emergence rates differed from year to year ($P < 0.001$) but the rate

of decline in seedling emergence with amended sulfate concentrations (slopes of regressions in Fig. 4a) did not change significantly from year to year (sulfate $\times$ year interaction $P = 0.598$).

The subsequent survival of those seedlings remaining after thinning (Fig. 4b) also declined significantly with increased sulfate concentrations ($P < 0.001$) and year ($P < 0.001$). The rate of decline in seedling survival with amended sulfate was twice as high in 2014 and 2015 than in 2012 and 2013. The number of surviving seedlings was not correlated with the number of seedlings that had been removed by thinning in any given year ($P > 0.10$), so the magnitude of thinning itself had no effect on seedling survival in the same year. The number of surviving seedlings was also not correlated ($P > 0.10$) with the production of straw litter from the previous year, so the decline in seedling survival was not an artifact of inhibition by thatch accumulation or nitrogen immobilization into fresh litter (Walker et al. 2010).

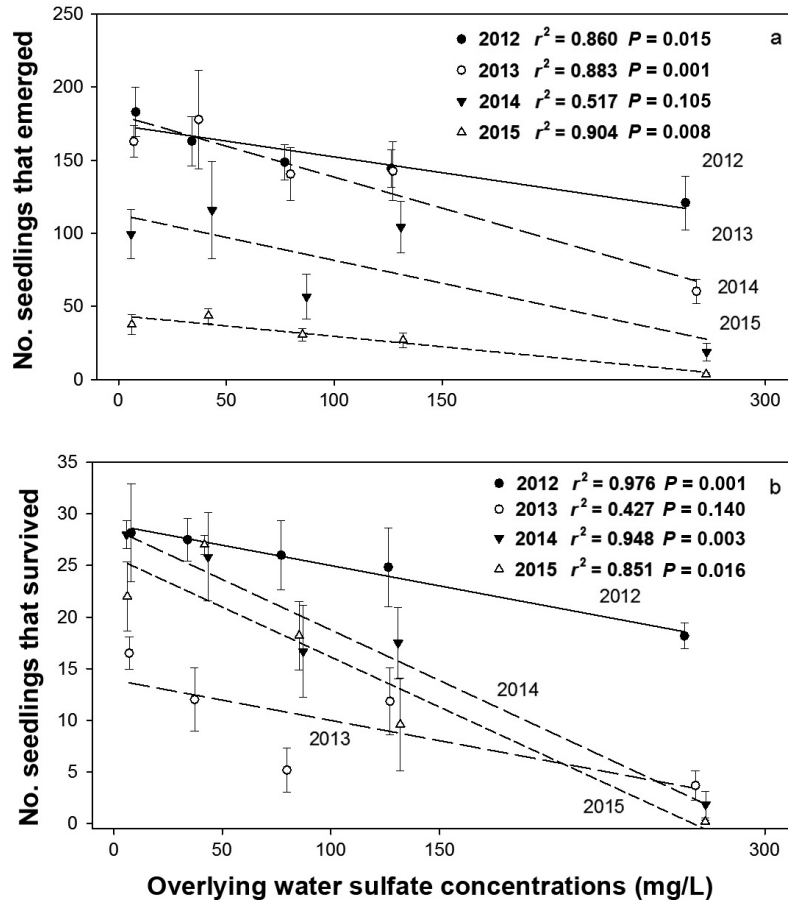


FIG. 4. Emergence (a) and survival (b) of seedlings in mesocosms declines with increasing measured sulfate concentrations in the overlying water. Symbols are means and standard errors.

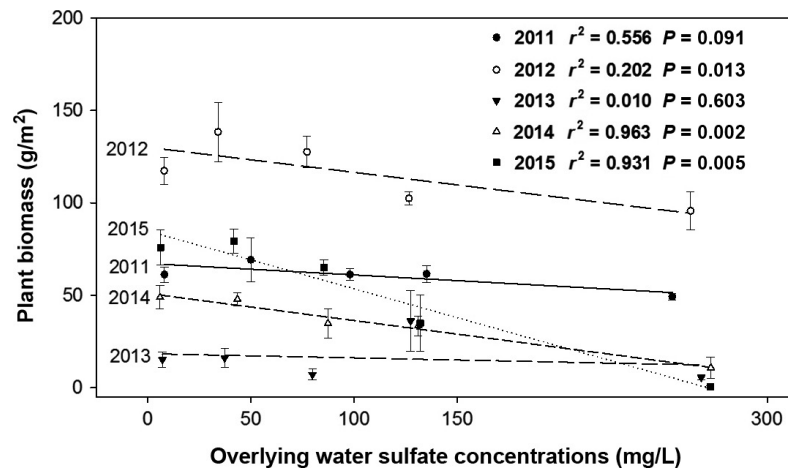


FIG. 5. Vegetative biomass in mesocosms declines with increasing measured sulfate concentrations in the overlying water. Symbols are means and standard errors.

In each year, there were no differences between control tanks and tanks amended to 50 mg/L SO_4 , but seedling emergence and survival were significantly lower ($P < 0.05$) in tanks amended to 100 mg/L SO_4 or greater compared to control tanks.

Effects of sulfate and sulfide on vegetative growth.—Elevated sulfate and presumably sulfide concentrations decreased plant biomass ($P < 0.001$) and the rate of decline increased significantly during the course of the experiment, but most especially in 2015 (sulfate $\times$ year

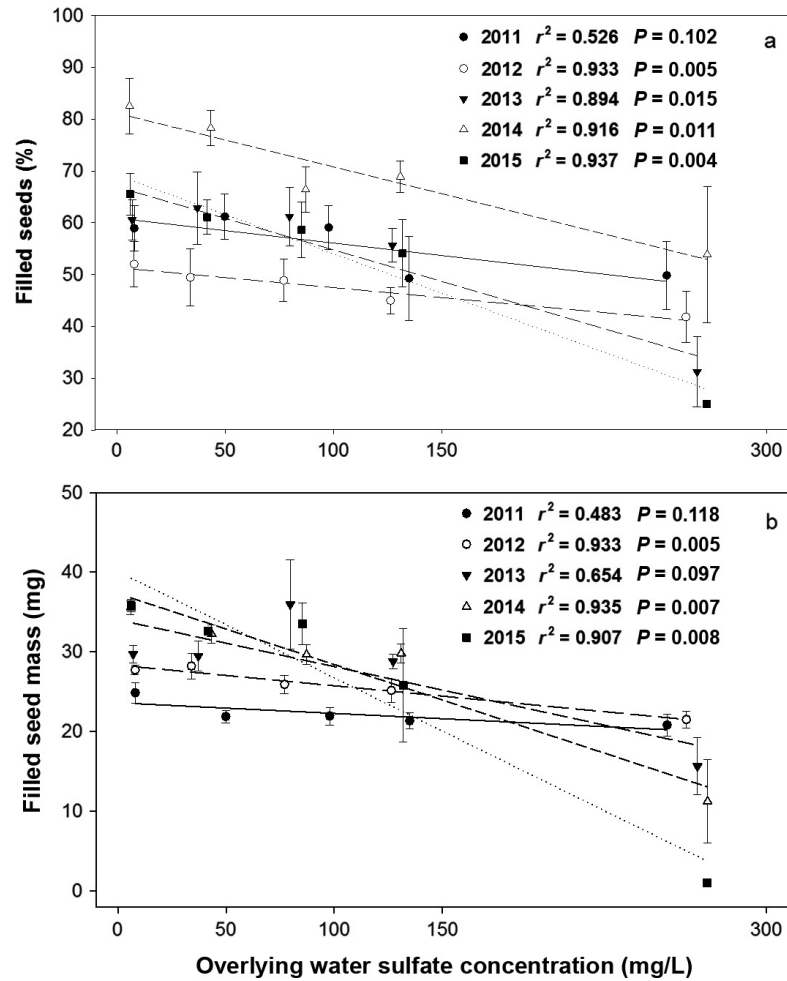


FIG. 6. (a) The proportion of seeds that were filled and (b) the mean seed mass in mesocosms both declined with increasing measured sulfate concentrations in the overlying water. Symbols are means and standard errors.

interaction statistically significant at $P < 0.001$; see Fig. 5 and the figure legend for r^2 and P levels). By 2015, wild rice was extinct in all but one replicate in the 300 mg/L treatment, which supported only two plants. Root and shoot masses of individual plants were highly correlated ($r = 0.998$, $P < 0.001$) and root:shoot ratios were nearly constant between 0.210 and 0.224. Therefore, while the amounts of root and shoot productions were significantly affected by elevated sulfate concentrations, the proportional allocation of production between roots and shoots was not.

Effects of sulfate and sulfide on seed production.—The number of seeds produced per plant (both filled and empty, as determined from peduncle counts) did not change significantly across all sulfate concentrations (not displayed), but the proportion of seeds produced that were filled declined significantly with increasing sulfate concentrations (Fig. 6a, $P < 0.001$). Although 55–80% of seeds from control plants were filled during all four years, the slopes of the regressions of the proportions of filled

seeds against sulfate concentration declined more steeply with each successive year (sulfate $\times$ year interaction significant at $P < 0.001$). By 2015, the proportions of filled seeds were as low as 25% in the tanks with the highest sulfate concentrations.

Individual seed masses declined with increased sulfate concentrations (Fig. 6b, $P < 0.001$). The seed masses declined more steeply with increasing sulfate concentrations with each successive year (sulfate $\times$ year interaction significant at $P < 0.001$).

In each year, seed production did not differ between control tanks and tanks amended to 50 mg/L SO_4 , but seed mass and the proportion of viable seeds were significantly lower ($P < 0.05$) in tanks amended to 100 mg/L SO_4 or greater compared to control tanks.

Blackened roots associated with elevated sulfate.—Beginning in 2012 and continuing for each subsequent year, plants in the tanks amended with sulfate had blackened roots while plants grown in the control tanks had white or light tan or orange roots when we

TABLE 2. Summary of the effects of sulfate and sulfide on the stages in the life cycle of wild rice.

Wild rice life cycle stage	Effects of increased sulfate and/or sulfide	
	Hydroponic experiments	Mesocosm experiments
Germination rate	no effect of sulfate or sulfide	not assessed
Juvenile seedling growth	significant negative effect of sulfide, no effect of sulfate	not assessed
Seedling emergence from sediment	not assessed	significant negative effect of sulfate addition, probably a result of reduced seed viability rather than direct effects of sulfide
Seedling survival	not assessed	significant negative effect of sulfate addition, most likely through sulfide production
Mature plant growth	not assessed	significant negative effect of sulfate addition, most likely through sulfide production
Seed production (number of seeds per plant)	not assessed	no effect of sulfate or sulfide
Seed viability, both individual seed mass and proportion of filled seeds	not assessed	significant negative effect of sulfate addition, most likely through sulfide production

harvested them at senescence. Visual estimates of the proportion of blackened roots increased progressively from approximately 50% in the tanks with sulfate concentrations approximately 50 mg/L to 100% in tanks with sulfate concentrations approximately 300 mg/L. These roots were pliable and white in cross sections cut with a knife, so they appeared to be still alive. In these cross sections, the blackening appeared to be crusted plaques on the root surfaces. The blackened roots from the 300 mg/L amended tank averaged $28.3\% \pm 9.8\%$ Fe and $13.4\% \pm 4.6\%$ S by mass, both much greater than tan/orange roots from the control tanks, which averaged $5.0\% \pm 3.9\%$ Fe and $0.34\% \pm 0.29\%$ S. We are investigating the chemistry of these plaques further, but our analyses thus far suggest that the blackening was caused by precipitation of some form of iron sulfide.

DISCUSSION

Table 2 summarizes the major effects of sulfate and sulfide in these experiments. In the mesocosms, the correlation between sulfate concentrations in overlying water and sulfide concentrations in porewater (Fig. 3a) is so strong within a given year that we can reasonably use sulfate concentrations in overlying water as a surrogate for increased sulfide concentrations in sediment porewater. Porewater sulfide increased substantially between 2013 and 2015 (Fig. 3a, b). The sulfide production in these sulfate-amended mesocosms will eventually overwhelm the available iron and accumulate free sulfide in the porewater, which may be responsible for the disproportionately higher sulfide in the highest treatment in 2015 (Fig. 3b). The mesocosms did not mimic the steady state that occurs in the natural environment because sulfate in overlying water was resupplied but iron was not. Mechanistic models that include the interaction between sulfide and iron (e.g., Wang and Van Cappellen 1996, Eldridge and Morse 2000) include the continuous addition of iron from the overlying to the sediment, successfully modeling the steady-state relationship between sulfate, sulfide, and iron observed in the environment.

The sedimentation of new iron to the sediment occurs in the natural environment, but was not included in this mesocosm experiment. Nevertheless, the experiment successfully exposed wild rice to progressively higher concentrations of porewater sulfide and documented the biological effects.

The porewater sulfide concentrations observed in natural waterbodies will vary depending on each site's surface water sulfate and sedimentary concentrations of organic matter and iron (Eldridge and Morse 2000). The sediment organic matter and extractable iron in this experiment (8.1% and 8.3 mg/g) are within the range of 67 Minnesota wild rice waterbodies; organic matter is lower than the median of 9.1%, and the iron is higher than the median of 4.8 mg/g (5th to 95th percentiles of 0.9–31.0% and 1.6–15.3 mg/g, respectively; A. Myrbo, unpublished data).

Upwelling groundwater through sediment would cause a waterbody to deviate from the conceptual model presented here; upward groundwater flow would not only counter downward diffusion of sulfate, but could also supply water with chemistry completely different than the overlying water. In a survey of 46 Wisconsin lakes, Nichols and Shaw (2002) found that the occurrence of wild rice is associated with areas of inflowing groundwater. In some cases, upwelling groundwater may supply sulfate to the reduction zone in littoral sediments (Krabbenhoft et al. 1998), so the effect of groundwater is unpredictable. Wild rice waters most likely to exhibit elevated porewater sulfide are those with relatively high organic matter, which allows enhanced microbial activity, and relatively low iron, which minimizes removal of porewater sulfide as a FeS precipitate (Heijs et al. 1999, Eldridge and Morse 2000).

Elevated sulfate concentrations were not directly toxic to wild rice seedlings in hydroponic solutions, in agreement with results reported by Fort et al. (2014). But adding sulfate to overlying waters in the mesocosms with wild rice sediment increased porewater sulfide concentrations most strongly in the upper 5 cm of sediment in 2013, after three field seasons of sulfate amendments (Fig. 2).

Sulfide was clearly toxic to early seedling growth in hydroponic experiments at concentrations above 320 $\mu\text{g/L}$, as indicated by slower growth or even zero or negative growth in a few cases (Fig. 1). Sulfide concentrations in excess of 320 $\mu\text{g/L}$ were observed in the upper 5 cm of sediment when sulfate concentrations in the overlying water exceeded 20–50 mg/L (depending on season, Fig. 2).

The upper 2–5 cm of sediment is where seed germination and very early seedling growth most likely takes place. Wild rice seeds are shaped like torpedoes and penetrate the sediment aided by their long awns, which act as rudders and keep the seed vertical as it falls through the water column (Ferren and Good 1977). It is likely that the seeds are buried in the upper 2–5 cm of this sediment where oxygen is low and sulfide concentrations are greatest (Fig. 2). To survive, the seedling must germinate in and grow through this zone of high sulfide concentrations. In nature, the mesocotyl may elongate up to 6 cm (Aiken 1986), allowing a buried seed to emerge through up to “3 inches of flooded soil” (Oelke et al. 1982). After emergence into the overlying oxygenated water, the mesocotyl differentiates into the mature stem. Wild rice is unusual among grasses in that the stem develops before the root, probably because the seedling may have to grow between 50 and 100 cm before reaching the water surface, at which time floating leaves supply energy for root development (Aiken 1986). This is consistent with the enhanced stem plus leaf growth of seedlings we observed under anaerobic conditions without elevated sulfide concentrations. Root growth, in contrast, was reduced by anaerobic conditions in our hydroponic experiments, as it has been previously observed for wild rice (Campiranon and Koukkari 1977) and white rice (Kordan 1972, 1974a, b).

Elevated sulfide concentrations greatly reduced shoot and leaf elongation in our hydroponic experiments, particularly at concentrations greater than 320 $\mu\text{g/L}$. The toxic effect of sulfide on shoot and leaf elongation and seedling growth (Fig. 1) overrides the enhanced growth that normally happens under anaerobic conditions. Seedlings in the mesocosms with elevated sulfate (and hence sulfide) concentrations likely were inhibited from emerging successfully from the sediment and reaching aerobic conditions higher in the water column, resulting in reduced survival in the mesocosms.

It is possible that high ionic strength or salinity in the mesocosms with the higher concentrations of elevated sulfate could be the cause of reduced seedling emergence and survival. However, the hydroponic experiments demonstrated that seeds and seedlings could withstand sulfate concentrations of up to 1600 $\text{mg SO}_4/\text{L}$ without adverse effects. This sulfate concentration is half the salinity of seawater (Schlesinger 1991). Electrical conductivity in the mesocosms was correlated with sulfate concentrations but, in 2012, we saw only small effects of sulfate on seedling emergence and survival even though electrical conductivity was high then as it was in 2015. High ionic strength alone is therefore probably not the

cause of the progressively greater declines in seedling emergence and survival in the mesocosms.

It is likely that the observed negative effects on wild rice seedling growth and survival can be directly attributed to the toxic effects of sulfide because of the coherence between the mesocosm experiments and the hydroponic experiments, which isolated the toxic effect of sulfide on seedling growth from any direct effect of sulfate. The progressive decline in seedling emergence and survival during the 5-yr course of the experiment could have resulted from increasingly greater sulfide concentrations (Fig. 3) and progressive titration of reactive forms of ferrous iron out of the system as insoluble iron sulfide. The cumulative effects of this progressive loss of reactive ferrous iron could have allowed more sulfide to remain in solution (Fig. 3) and thereby have increasingly toxic effects on seedling emergence and survival. The possible loss of reactive ferrous iron during the 5-yr course of the experiment may have been partly responsible for the declines in population densities, even to extinction at the highest sulfate concentrations.

Elevated sulfate concentrations in the mesocosm water progressively reduced vegetative production over the five years, but to much less extent than seed production was reduced. The proportion of seeds that were filled, as well as their mean masses, decreased by over 30% and as much as 50% in the 300 mg/L mesocosm treatment by year five of the experiment. Reduced seed production and seed masses followed by reduced seedling emergence and survival the following year depressed population growth in successive years eventually driving wild rice populations to extinction at high sulfate concentrations. It is likely that this extinction was driven by reduced seed production, seedling emergence, and seedling survival that depleted the seed bank over the five years of the experiment, and cumulative impacts on sediment chemistry from repeated sulfate additions could have exacerbated the decline.

The strong decline in measures of seed viability with increased sulfate concentrations at the end of the growing season (Fig. 6) compared with the weaker decline in vegetative growth in early to mid-growing season (Fig. 5) could not have been due to decreased N or P availability late in the growing season. Litter from the previous year has begun mineralizing N and P at this point in the growing season (Walker et al. 2010, Hildebrandt et al. 2012). The production of sulfide is correlated with many other chemical changes associated with the sulfate-enhanced anaerobic decay of organic matter (Lamers et al. 2002), including increased phosphate solubility. Phosphorus availability could not be controlled independent of sulfide in sediment, and sediment porewater and overlying water phosphate concentrations were elevated in sulfate amended tanks (A. Myrbo, *unpublished data*) most likely because precipitation of sulfide with reduced iron liberates phosphate (Caraco et al. 1989, Lamers et al. 2002). Since N and P availability were likely not limiting late in the growing season, it is unlikely that

reduced N or P availability were responsible for the decline in seed production with increased sulfate concentrations. Therefore, by deduction, it must have been uptake that was limiting.

Sixty percent of annual N uptake in wild rice plants occurs early in the growing season but there is a second burst of nitrogen and phosphorus uptake in August during seed filling and ripening (Grava and Raisanen 1978, Sims et al. 2012a). Even though N and P were most bioavailable in August when wild rice seeds were being developed and filled, there was coincident peak accumulation of sulfide in the sediment porewater (Fig. 2). When exposed to high sulfide concentrations, roots of white rice (*Oryza sativa*) often become suberized (Armstrong and Armstrong 2005) with subsequent possible reduction in nutrient uptake across the thicker root membranes (DeLaune et al. 1983, Koch et al. 1990, Armstrong and Armstrong 2005, Lamers et al. 2013). Suberization of roots in response to high sulfide concentrations at this stage in wild rice's life cycle might inhibit nutrient uptake, resulting in fewer and smaller filled seeds.

Another possible mechanism for impaired nutrient uptake might be the precipitation of black iron sulfide plaques on the roots of plants that grew in mesocosms with elevated sulfate and sulfide concentrations. Our EDS analyses suggest that the tan or orange coatings on roots of plants grown under low sulfate concentrations may be iron hydroxide plaques, which are often found on healthy wild rice roots (Jorgenson et al. 2012). The existence of tan or orange coatings, consistent with iron hydroxide plaques, strongly suggests that the immediate vicinity of the roots is oxidized when sulfate concentrations are low, most likely due to radial oxygen loss through the aerenchyma tissues within the roots (Stover 1928, Colmer 2003, Yang et al. 2014). Blackened roots, however, are often observed in white rice (*Oryza sativa*) populations subjected to elevated sulfate concentrations or organic carbon (Jacq et al. 1991, Gao et al. 2003, Sun et al. 2015) and our EDS observations suggest that the blackened plaques on our roots are some form of iron sulfide. Sun et al. (2015) also found that these black plaques contain substantial amounts of iron sulfides. Precipitation of iron sulfide plaques on roots, whether a direct inhibitor of nutrient uptake or a harbinger of the encroachment of reducing conditions to nearer the root tissue, may be partly responsible for the reduced proportion of filled seeds as sulfate concentrations increased (Fig. 6). Further experiments using labeled ^{15}N would be useful to determine whether reduced nutrient uptake during seed filling is the cause of reduced seed production.

Suberization of roots and precipitation of iron sulfide plaques may not be independent. Enhanced suberization when the root tissue is exposed to sulfide (Armstrong and Armstrong 2005) might cause decreased radial oxygen loss from roots of wetland plants (Joshi et al. 1975, Gao et al. 2002, Armstrong and Armstrong 2005). If radial oxygen loss from roots is essential to maintaining low concentrations of hydrogen sulfide in the immediate vicinity of roots

(Eldridge and Morse 2000), then sulfide concentrations in the rhizosphere could encroach nearer to the root surface when radial oxygen loss from roots is impaired. Iron (hydr)oxide present on or near the roots under these conditions could be reduced to iron sulfide and precipitated on the roots. Nutrient uptake during the stage of seed filling therefore might be impaired directly by suberization of roots followed by precipitation of iron sulfides on the roots if suberization reduces radial oxygen loss.

CONCLUSIONS

In our hydroponic experiments, elevated sulfide concentrations are directly toxic to seedlings. In our mesocosm experiments, sulfate amendments increased sulfide concentrations in the rooting zone, which then apparently decreased seedling emergence and survival. The reductions in seedling emergence and survival in the mesocosms are consistent with the toxic effects of sulfide on seedling growth in the hydroponic experiments.

The vegetative growth phase of wild rice's life cycle did not appear to be as strongly affected by sulfide as the production of viable seeds. The mechanisms behind reduced seed production and viability with increased sulfate and hence sulfide production in sediments are more difficult to discern, but may involve reduction of nutrient uptake during seed set by iron sulfide plaques on roots of mature plants (Jacq et al. 1991) or by increased suberization with elevated sulfide concentrations later in the summer (Armstrong and Armstrong 2005).

In natural wild rice ecosystems, the extent to which sulfate is reduced to sulfide, and to which sulfide persists in porewaters, are controlled by factors such as the sedimentary concentrations of iron and organic matter, and groundwater flow, among others, all of which may differ from the conditions in our mesocosms. But our experiments strongly suggest that the reduction of sulfate to sulfide in sediments, to the extent that it occurs in natural systems, may cause populations to decline by adversely affecting the reproductive phases of wild rice's life cycle.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online at: <http://onlinelibrary.wiley.com/doi/10.1002/eap.1452/full>

RESEARCH ARTICLE

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This article is a companion to Myrbo, Swain, Engstrom, et al. [2017], <https://doi.org/10.1002/2017JG003787> and Myrbo, Swain, Johnson, et al. [2017], <https://doi.org/10.1002/2017JG003788>.

Key Points:

- Factors controlling pore water sulfide, which can be toxic to wild rice, were identified with structural equation modeling
- Structural equation modeling was used to quantify the relative effects of sulfate, iron, and TOC on pore water sulfide concentrations
- The concentration of pore water sulfide is controlled nearly equally by sulfate in surface water and sediment organic carbon and iron

Supporting Information:

- Supporting Information S1
- Data Set S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Figure S6
- Figure S7
- Figure S8

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The Evolution of Sulfide in Shallow Aquatic Ecosystem Sediments: An Analysis of the Roles of Sulfate, Organic Carbon, and Iron and Feedback Constraints Using Structural Equation Modeling

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Abstract The generation of elevated concentrations of sulfide in sediment pore waters that are toxic to rooted macrophytes is problematic in both marine and freshwaters. In marine waters, biogeochemical conditions that lead to toxic levels of sulfide generally relate to factors that affect oxygen dynamics or the sediment iron concentration. In freshwaters, increases in surface water sulfate have been implicated in decline of *Zizania palustris* (wild rice), which is important in wetlands across the Great Lakes region of North America. We developed a structural equation (SE) model to elucidate key variables that govern the evolution of sulfide in pore waters in shallow aquatic habitats that are potentially capable of supporting wild rice. The conceptual basis for the model is the hypothesis that dissimilatory sulfate reduction is limited by the availability of both sulfate and total organic carbon (TOC) in the sediment. The conceptual model also assumes that pore water sulfide concentrations are constrained by the availability of pore water iron and that sediment iron supports the supply of dissolved iron to the pore water. A key result from the SE model is that variations in three external variables (sulfate, sediment TOC, and sediment iron) contribute nearly equally to the observed variations in pore water sulfide. As a result, management efforts to mitigate against the toxic effects of pore water sulfide on macrophytes such as wild rice should approach defining a protective sulfate threshold as an exercise tailored to the geochemistry of each site that quantitatively considers the effects of ambient concentrations of sediment Fe and TOC.

Plain Language Summary Aquatic plants, such as wild rice, white rice, and waterlilies that have roots in the saturated soils of wetlands are vulnerable to the buildup of toxic levels of hydrogen sulfide (also called sulfide). Anaerobic bacteria in the soil make the sulfide from sulfate that penetrates the soil from the overlying water. When sulfate in the waterbody is low, sulfide in the soil is low. But when sulfate is high, sulfide has been hard to predict—sometimes low, sometimes high. The analysis of hundreds of wetland samples finds that sulfide can be predicted if two variables in addition to sulfate are considered: organic carbon in the soil, which is the food for the bacteria, and iron in the soil, which removes sulfide from solution. A model of the chemical reactions finds that the three variables, sulfate, organic carbon, and iron, are equally important in determining sulfide. The sensitivity of individual waterbodies to sulfate pollution effects on wild rice toxicity can thus be predicted from the analysis of the carbon and iron concentrations in the soil of a wetland.

1. Introduction

The evolution of sulfide concentrations in sediment pore waters can be toxic to rooted macrophytes in both marine and freshwater environments. Pore water sulfide is the product of anaerobic microbial respiration of sulfate in sediments. Despite the much different sulfate concentrations between the two environments—sulfate concentrations are generally orders of magnitude higher in marine systems than most continental waters—the biogeochemical principles governing the reduction of sulfate to sulfide are the same, and there should be recognition of the commonality of sulfide toxicity concerns and biogeochemical relationships. Here we describe a model of the roles of sulfate, sediment total organic carbon (TOC), and sediment iron (Fe) in determining potentially phytotoxic concentrations of sulfide in relatively sulfate-poor waters. Essentially the same question, the potential toxicity of sulfide to coastal seagrasses as a function of sulfate,

TOC, and Fe has been pursued since at least 2000 (e.g., Eldridge & Morse, 2000). The biggest difference in the approaches between the two environments is that the primary option to reduce sulfide toxicity in freshwater systems has been to control sulfate, whereas other controlling variables (e.g., TOC or water clarity) are not only more practical for control in coastal systems but are more likely to have been altered by human activity.

For example, sulfide has been implicated as the causative agent in a global decline of coastal seagrasses. In this case, the perturbations to sulfur cycling that lead to increased sulfide toxicity relate to anthropogenic activities that reduce light availability. Seagrasses are dependent on high light levels to produce sufficient oxygen to detoxify pore water sulfide and so are particularly vulnerable to any actions that reduce light availability, such as eutrophication or dredging (Orth et al., 2006). In addition, other factors that enhance pore water sulfide concentrations have been implicated in the decline of seagrasses, such as increased temperature (Koch & Erskine, 2001), increased sediment organic matter (Govers et al., 2014), iron-poor sediments (Marbà et al., 2008), and low water column oxygen (Borum et al., 2005).

Similar concerns about sulfide toxicity extend to freshwater systems (Lamers et al., 2013). For example, based on laboratory experiments demonstrating that *Cladium* is less tolerant of sulfide than *Typha*, sulfate enrichment has been implicated in the expansion of *Typha domingensis* (cattail) into areas once dominated by *Cladium jamaicense* (sawgrass) in the Florida Everglades (Li et al., 2009). One plant species of particular concern with respect to sulfide toxicity is *Zizania palustris* (wild rice), which is important in wetland environments across the Great Lakes region of North America, where it can occur in dense monocultures. This importance includes both its role as a food resource for waterfowl and humans and its economic significance to those who harvest and market it. Wild rice is also a very important cultural resource to many Minnesotans, including indigenous peoples such as the Ojibwe peoples who consider wild rice as sacred (Vennum, 1988).

Wild rice is an annual grass that grows best at water depths of 0.3 to 1.0 m in lakes, rivers, and wetlands with soft organic sediment, although it can be found rooting in a wide variety of sediment types, ranging from muck to sand (Aiken et al., 1988). Wild rice seeds are dropped into the water in the fall, lie in the sediment throughout the winter, and germinate in spring. Its occurrence and distribution are influenced by a variety of physical, hydrologic, and biogeochemical factors (Myrbo, Swain, Engstrom, et al., 2017). For example, the rate of seed germination declines greatly if the seeds dry; as a result, wild rice is usually found in permanent waterbodies. Reduced light availability, from turbidity or water color, limits the ability of wild rice to maintain a population in a waterbody (Myrbo, Swain, Engstrom, et al., 2017), because seedlings need photosynthesis to augment the seed's energy reserves in order to successfully reach the water surface (Aiken, 1986).

Sulfate has long been implicated as a variable that influences the occurrence and distribution of wild rice in Minnesota. The first such implication was by Moyle (1944) who, in an analysis of spatial variations in water chemistry in Minnesota surface waters, observed "No large stands of rice occur in waters having a SO_4 content greater than 10 ppm, and rice generally is absent from water with more than 50 ppm." This cognition that wild rice occurrence was associated with waters containing lower levels of sulfate, coupled with the importance of wild rice in Minnesota, led to the adoption of a sulfate standard to protect wild rice of 10 mg/L in 1973 by the state of Minnesota. However, the role of sulfate in limiting wild rice habitat has long been confusing, given that wild rice has been observed to grow well in elevated sulfate waters overlying silica sand substrate and in commercial paddies with sulfate concentrations of 170 mg/L (Aiken et al., 1988).

More recently, a series of studies commissioned by the Minnesota Pollution Control Agency (MPCA) indicate that sulfide in sediment pore water is a causative agent for adverse effects to wild rice and that any effect of sulfate is rather more likely indirect through any controls it exerts on the development of sulfide concentrations in pore waters. These studies include a field survey comprising one or more sampling trips to 93 lakes, 32 stream sites, and 7 wild rice paddies (Myrbo, Swain, Engstrom, et al., 2017), 10 day hydroponic experiments, and multiyear mesocosm studies (Myrbo, Swain, Johnson, et al., 2017; Pastor et al., 2017).

The goal of the MPCA-sponsored research is to determine if it is appropriate to regulate sulfate in order to protect wild rice from sulfide toxicity. The relationship between surface water sulfate and pore water sulfide concentrations, however, is complex, and a standard that seeks to mitigate against the occurrence of sulfide concentrations harmful to the occurrence of wild rice by limiting sulfate concentrations should consider these complexities. These complexities are illustrated by considering the effects of both substrate limitation and geochemical thermodynamics. More specifically, sulfate reduction to sulfide is a microbially mediated process that involves sulfate-reducing bacteria using sulfate as a terminal electron acceptor to metabolize

organic matter in the absence of oxygen. Thus, the availability of both sulfate (Capone & Kiene, 1988; Cook et al., 1986; Perry et al., 1986; Sinke et al., 1992; Myrbo, Swain, Johnson, et al., 2017) and of organic carbon (Al-Raei et al., 2009; Glombitza et al., 2013) can limit sulfate reduction. Conditions favorable to sulfate reduction also can result in iron reduction from insoluble Fe(III) to soluble Fe(II). Fe(II) in turn can react with sulfide to form insoluble FeS and other iron-sulfide minerals (Hansel et al., 2015; Hines & Jones, 1985; van Cappellen & Wang, 1996).

Any model that relates surface water sulfate to pore water sulfide concentrations thus has to consider issues related to model specification—that is, whether the model includes the appropriate variables and whether the intervariable relationships posed in the model are truly representative of the underlying processes and satisfy the inherent assumptions of the model framework. Model specification errors thus can lead to erroneous coefficient estimates for a governing variable, including errors in both magnitude and direction. *Statistical* models that might be developed for the sulfate-sulfide problem also have to accommodate intervariable relationships that include both indirect (mediated) and nonrecursive (i.e., feedback) relationships. Traditional multivariate regression models only control for direct or apparent direct (net) effects and thus are ill suited for quantifying relationships that are either mediated or nonrecursive. As a result, similar to model estimation problems imposed by specificity errors, the misapplication of multivariate regression models can lead to misleading parameter coefficient estimates and a failure to properly quantify the components contributing to the *total* effect of a variable such as sulfate on a response variable such as sulfide, particularly if the model includes mediating variables (Grace et al., 2009; Pollman, 2014).

One approach that allows for and more properly accounts for the effects of mediating variables is structural equation modeling (SEM). Based on the hypothesized relationships that constitute the model, SEM seeks to reproduce the covariance structure of the observed data (Ullman, 2007). SEM can include models comprising measured or observed variables only (path analysis), models that include latent variables representing unmeasured processes (confirmatory factor analysis), or models that link both path and confirmatory analysis together. SEM is often referred to as *causal analysis* (Ullman, 2007) because the approach often is used to test or confirm an a priori, hypothesized model (Austin, 2007). While SEM does not actually prove causality (Bollen & Pearl, 2013; Weston & Gore, 2006), it does provide a framework for selecting or rejecting hypotheses based on the empirical data (Iriondo et al., 2003). Examples include using SEM to model macroinvertebrate distribution in riverine ecosystems (Bizzi et al., 2013) and estuaries (Malaeb et al., 2000), aquatic and estuarine macrophytes (Gustaffson & Boström, 2013; Hung et al., 2007), lacustrine phytoplankton dynamics (Arhonditsis et al., 2006; Korhonen et al., 2011; Liu et al., 2010), and methyl Hg cycling and bioaccumulation in the Florida Everglades, including mediated effects of surface water sulfate (Pollman, 2014). In addition, SEM has been used to construct models with a clear environmental management focus (La Peyre et al., 2001; Reckhow et al., 2005; Stober et al., 2001). For example, La Peyre et al. (2001) used SEM to model national wetland protection efforts as a function of five latent variables (defined as economic capital, social capital, government characteristics, environmental characteristics, and land use pressure). Their model suggested that variations in social capital had the greatest influence on wetland protection efforts and concluded that continued focus on social development was necessary to further wetland protection.

2. Objectives and Conceptual Model

The objective of this paper is to use SEM to define the functional role of surface water concentrations of sulfate vis à vis the development of pore water concentrations of sulfide, recognizing that the relationship is complex and likely involves direct, mediated, and feedback pathways. Based on the functional relationships we believe a priori to be important, we can construct a conceptual model that reflects those relationships and use SEM to test both the overall reasonableness of the model and the significance and importance of the individual components or pathways. Conceptually, our model has four components. The first component considers that the magnitude of sulfide production in the sediment pore water expectedly is related to sulfate concentrations in the water column (e.g., Cook & Schindler, 1983; Geurts et al., 2009; Siver et al., 2003; Myrbo, Swain, Johnson, et al., 2017). The second component is that the availability of sedimentary organic carbon can limit sulfate reduction (Al-Raei et al., 2009; Glombitza et al., 2013). The third component is that amorphous FeS or mackinawite formation governs the dynamics of pore water sulfide and Fe(II) concentrations:

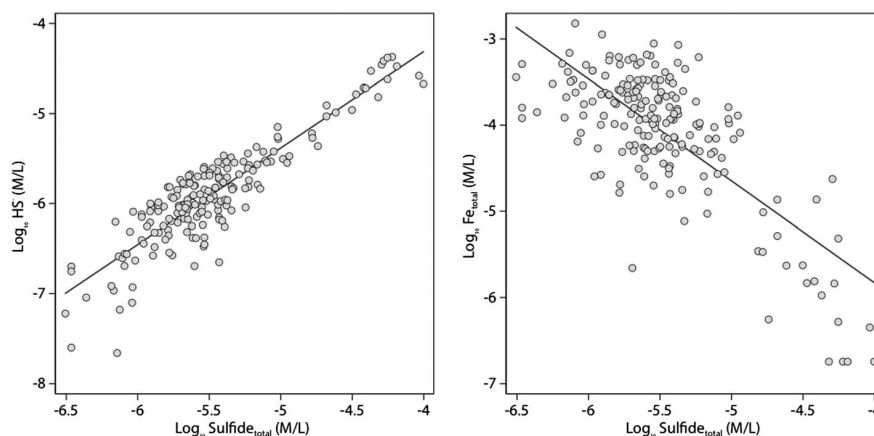


Figure 1. Key bivariate relationships for pore water sulfide relevant to assumptions in conceptual sulfide model. Left-hand panel: HS^- concentrations as a function of measured total pore water sulfide. HS^- concentrations based on acidity constants for H_2S and measured pore water pH. Right-hand panel: total dissolved pore water Fe concentrations as a function of measured total pore water sulfide. All variables are $\log_{10}$ molar concentrations. Solid lines denote line of best fit obtained from linear regression. The 70.4% of the variance in the calculated values of the ($\log_{10}$ -transformed) concentration of HS^- is due to the variance in ($\log_{10}$ -transformed) concentrations of total sulfide; shared variance between total sulfide and the pH-dependent speciation fraction for HS^- accounts for another 5.0%. The coefficient of determination for the pore water Fe and total sulfide relationship (both variables $\log_{10}$ transformed) is 0.547 ($p < 0.0001$).



Inherent in our implementation of the model is the notion that pore water concentrations of total sulfide are a reasonable proxy for HS^- . Given that assumption, pore water Fe(II) and total sulfide concentrations should be inversely related (cf. Maynard et al., 2011); both assumptions are borne out by bivariate plots of the variables of interest (Figure 1; see also Myrbo, Swain, Engstrom, et al., 2017) constructed from our field data (see

section 3.1 below). The last component of the conceptual model is that sediment Fe concentrations influence the pore water Fe concentrations that can develop under reducing conditions. This is an extension of the fact that sediment Fe must be present for dissolved Fe(II) concentrations to develop in the pore water, unless an alternative source of dissolved Fe(II) such as via shallow groundwater discharge is important.

The resultant conceptual model is shown schematically in Figure 2 and includes pore water sulfide, pore water Fe, and sediment total sulfur (S) as dependent or endogenous variables and sulfate, sediment Fe, and sediment total organic carbon (TOC) as independent or exogenous variables. The model also includes a mediated pathway for the effect of sulfate on pore water sulfide through links between sulfate and sediment total S and between sediment total S and pore water sulfide. This mediated pathway considers that a second route for sediment sulfur accretion is by biogenic uptake of sulfate in the water column (Pérez-Castiñeira et al., 1998) followed by deposition to and incorporation within the bottom sediments. An important feature of the conceptual model is that, consistent with the thermodynamic or equilibrium chemistry defined by equation (1), the link between pore water sulfide and Fe is nonrecursive rather than recursive. Recursive models allow for causation to flow in a single direction only, while nonrecursive models allow for feedback relationships such as the thermodynamic relationship between pore water Fe(II) and HS^- . While the use of nonrecursive models to model aquatic ecosystems has precedent—for example, evaluating the reciprocal relationships between sediment substrate

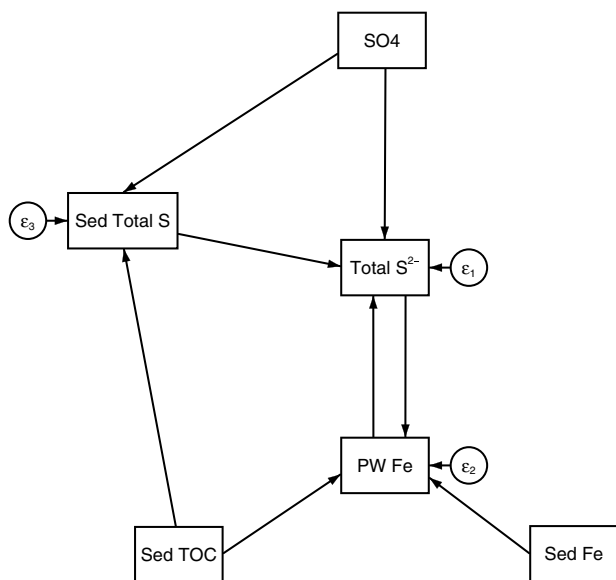


Figure 2. Conceptual model for biogeochemical controls on pore water sulfide in wetland sediments. Sed refers to sediment solid phase concentrations (mass parameter per dry mass sediment). PW Fe is pore water Fe; total S_2^- is total pore water sulfide, and SO_4 is surface water SO_4 .

characteristics and seagrass density (Folmer et al., 2012; van der Heide et al., 2011)—we believe that our use of a nonrecursive SEM to model pore water chemistry is the first such application.

3. Materials and Methods

3.1. Data

The data used to construct and evaluate the structural equation (SE) model were collected by the MPCA as part of a field survey designed to investigate the relationship between physical and chemical conditions in shallow waterbodies and the presence and absence of wild rice (Myrbo, Swain, Engstrom, et al., 2017). The field survey included pilot sampling conducted in 2011 comprising 58 samples collected from 48 different lake and stream sites, followed in 2012 and 2013 by a field survey that was broadened to include more sites with elevated sulfate concentrations and 7 different cultivated wild rice paddies. The broader survey included 121 different waterbodies, of which 40 were sampled on multiple occasions across time (2 to 6 times, except for one site sampled 10 times). The broader survey also included some sites that were also sampled during the pilot survey; thus, the total number of unique sites sampled during the entirety of the 3 year field survey included 131 different sites, with a total of 260 site visits. Field sampling included surface water, sediment, and pore water samples for a variety of physical, chemical, and habitat related variables, although some site visits were not able to collect the full suite of samples. Sampling protocols and methods for more than 65 parameters potentially measured at each site are detailed in Myrbo, Swain, Engstrom, et al., (2017).

Several considerations guided the selection of observations from the field survey data set for developing the SE model. SEM is generally regarded as data intensive, although perhaps not more so than multivariate regression (McCune & Grace, 2002). Estimates of minimum sample sizes to adequately conduct SEM vary but generally are related to the complexity of the model. Simulation studies by Jackson (2003), for example, suggest that improved model performance is achieved as the ratio of the number of observations to fitted model parameters increases. Model performance, however, appears to be more sensitive to the absolute number of samples (Jackson, 2003), with a typical sample size for SE models published in the literature approximating 200 (Kline, 2011). As a result, our overarching principle in data selection was to maximize the number of samples available to fit the model without compromising the integrity of the analysis. For example, we excluded paddy sites from the wild rice model data set because modeling natural systems is our ultimate goal, and paddies are manipulated in ways that likely cause the biogeochemistry to differ from natural sites. For instance, N and P fertilizers are used and, in a fundamental departure from natural sites, paddies are dewatered each summer, which may alter the oxidation state of the sediment. After eliminating paddies, we further screened the data set to exclude those sites that did not have a complete set of measurements for surface water sulfate, pore water sulfide, pore water Fe, sediment Fe, sediment TOC, and sediment total S. This latter set of criteria also resulted in the exclusion of a relatively small number of samples. In an effort to assess potentially redox-active Fe, sediment Fe in this data set was quantified using a 0.5 N HCl extraction (Myrbo, Swain, Engstrom, et al., 2017), rather than a stronger acid digestion, which would have included relatively inert Fe.

We conducted preliminary multiple linear regression (MLR) analyses, using pore water sulfide as the dependent variable and surface water sulfate, sediment TOC, and sediment Fe as the independent variables, to identify possible outliers and influential observations. Based on the MLR analyses, we identified two clear outliers (Hoffs Slough and one sample from Sandy Lake) based on both inspecting model residuals and plotting values for hat leverage versus Cook's D distance (Hamilton, 2013). Hoffs Slough is a ditch in an agricultural area, while the Sandy Lake observation is one of a total of 10 samples collected from Sandy Lake; as a result, both outliers were excluded from further analysis. In addition, we excluded two observations with unusually high pore water sulfide (Bean and Lady Slipper; pore water sulfide 16.0 and 14.8 mg/L, respectively; the next highest sulfide concentration was 3.19 mg/L).

The resultant screened data set, which was named for internal purposes "Class D," includes a total of 194 observations from 111 different waterbodies. This number of observations was considered sufficient to engage in SEM given the relatively simple nature of the conceptual model and is consistent with the number of observations used by many published studies (Kline, 2011). The data include 20 observations collected in 2011, 107 in 2012, and 67 in 2013. Because 43 of the Class D sites were sampled more than once, we created a subset called "Class B" with which to compare results. Class B consists of one sample from each site and excludes samples collected in 2011, which were analyzed with slightly different lab methods (see Myrbo,

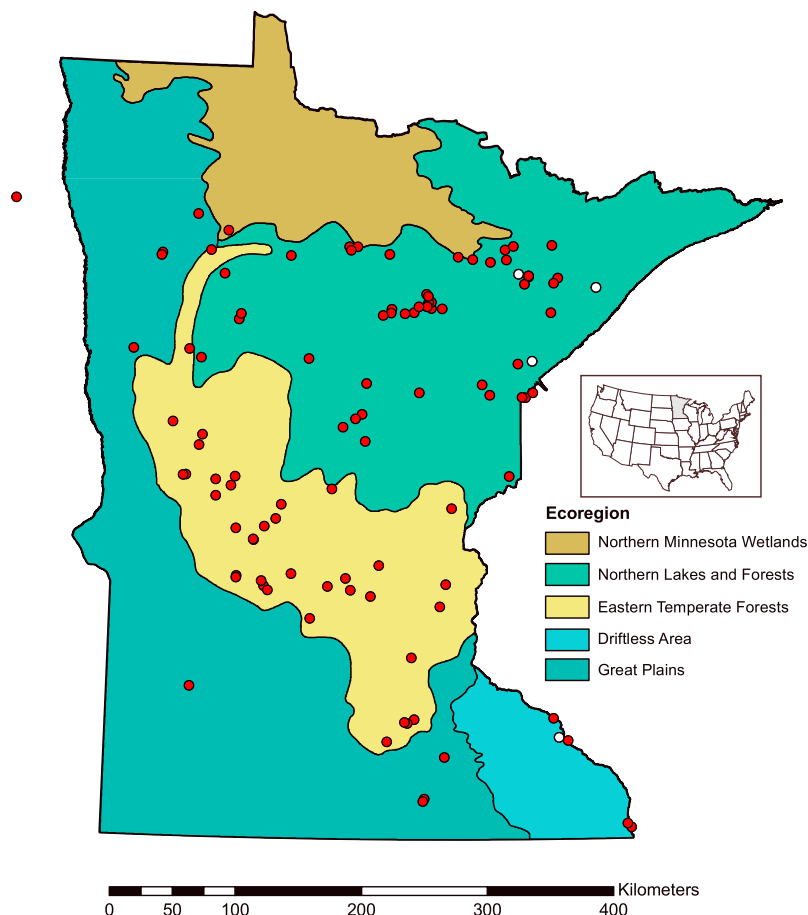


Figure 3. Locations for lakes and stream sites (Class D and Class B) sampled by Myrbo, Swain, Engstrom, et al. (2017) used to construct the SE model. Red-filled circles show sites that belong to both Class D and Class B data sets, while the open circles show sites that belong solely to Class D. The single site in North Dakota (westernmost site) lies in the Great Plains ecoregion.

Swain, Engstrom, et al., 2017). The Class B data thus include a set of 105 unique observations with a full complement of measured model parameters, including 78 lake and 27 stream sites (Figure 3).

3.2. Statistical Analysis and Modeling

3.2.1. Model Estimation

We conducted all statistical analyses, including SEM, using Stata 14 (StataCorp, 2015). Two key underlying assumptions with SEM are multivariate normality of the endogenous variables and linear relationships between the endogenous and exogenous variables (Kline, 2011; Ullman, 2007). We $\log_{10}$ -transformed all variables both to improve linearity and to yield variable distributions that more closely approximated normality, although multivariate normality was not achieved.

When multivariate normality is uncertain, estimation methods that assume multivariate normality can produce misleading or incorrect estimates of the standard error of the individual model coefficients. Several approaches are potentially useful when estimating SEM models with nonnormal multivariate data distributions. These methods include *asymptotic distribution-free* (*adf*) estimation (Acock, 2013; Kline, 2011), bootstrapping (Acock, 2013; McIntosh, 2007; Tomarken & Waller, 2005), and estimation using the Satorra-Bentler scaled χ^2 test (StataCorp, 2015; Tomarken & Waller, 2005). The *adf* method makes no assumptions regarding data normality but may require in excess of 200 to 500 observations for even relatively simple models (Kline, 2011). Bootstrapping, which uses resampling with replacement of the individual observations to produce estimates of the standard errors and resulting significance of the model coefficients, also makes

no assumptions regarding underlying multivariate normality and thus produces more robust estimates of coefficient confidence. The Satorra-Bentler test seeks to correct the χ^2 statistic by scaling the estimate based on the kurtosis of the data (Kline, 2011). Initial analyses implemented all three methods. Bootstrapping was conducted using 1,000 replications. We used comparative evaluations of the fitted model coefficients (the *adf* method can yield model coefficients that differ compared to the maximum likelihood estimation used by the bootstrapping and Satorra-Bentler methods) and their significance, which indicated that estimation of the final model was relatively insensitive to the choice of estimation method coefficients. However, because *adf* methods can be misleading with sample sizes of fewer than 200, final model estimation was conducted using the Satorra-Bentler test and bootstrapping.

3.2.2. Model Robustness

A critical assumption that SEM shares with linear regression is that the underlying relationships between a given endogenous variable and the variables that influence it are indeed linear. Unlike SEM, MLR has a rich set of tools available for a variety of post hoc analyses to evaluate adherence to underlying model assumptions. Given the similarities between path analysis (of which our modeling herein is a form) and MLR (Li, 1975), we verified linearity by initially conducting MLR on pore water sulfide concentrations using the same variables used to directly model pore water sulfide in the SE model. We then evaluated the presence of nonlinearities and apparent outliers by constructing augmented component plus residual (ACPR) plots for each direct independent variable (Hamilton, 2013; Mallows, 1986; see supporting information Figure S1).

3.2.3. Assessment of Goodness of Fit

We assessed model goodness of fit using several different metrics. Because SEM seeks to reproduce the observed covariance matrix for the variables in the model, a primary metric for model performance is a chi-square (χ^2) test that assesses the magnitude and significance of the discrepancy between the fitted covariance matrix for the model in question and the observed covariance matrix. Restated, the χ^2 statistic compares the covariance matrix for the model we seek to evaluate with that of a model that has no degrees of freedom and thus fits the observed data perfectly. The null hypothesis is that the two models are not different. χ^2 *p* values <0.05 appear to be a commonly used threshold for rejecting the null hypothesis and thus rejecting the model (e.g., Bizzi et al., 2013; Hayduk & Glaser, 2000; Hu & Bentler, 1999), although this threshold is controversial (cf. Barrett, 2007; Lance et al., 2006; McIntosh, 2007).

The χ^2 test is the approach most used to evaluate the fit of SEM models (Grace, 2008) and was used in this study as the initial criterion for retaining a given model. Other fit indices used as alternatives or adjuncts to the χ^2 test include both absolute and incremental or approximate fit indices (Hu & Bentler, 1999; Kline, 2011). Stata provides several alternative fit indices of both types, including the root-mean-square error of approximation (RMSEA), the standardized root-mean-square residual (SRMR), the comparative fit index (CFI), and the Tucker-Lewis index (TLI). Recommended target values for the RMSEA and SRMR are 0.05 and 0.08, respectively, while values greater than 0.95 are recommended targets for both the CFI and TLI (Acocck, 2013; Hu & Bentler, 1999).

3.2.4. Model Validation

We validated the SE model by conducting a “leave one out cross validation” or jackknife analysis where we refit the SEM model by withholding a single observation from model estimation and then used the refit model to predict the log₁₀-transformed value for pore water sulfide of the withheld observation. This process was repeated for each of the observations comprising the Class D and Class B data sets. A major advantage of this process is that it uses all of the available observations to both fit and validate the model.

3.2.5. Alternative Model Specifications

As mentioned previously, the issue of model specification is an important consideration. As a result, we also expanded our conceptual model to consider several other model specifications. These models included

1. expanding the model to include sediment acid volatile sulfide (AVS). AVS is an operationally defined, reactive sulfide fraction that is believed to comprise dissolved hydrogen sulfides and mackinawite (Morse & Rickard, 2004) and thus arguably better represents the pool of reduced sedimentary sulfur actively exchanging with pore water sulfide. A primary feature of this model thus was to include a second reciprocal relationship involving pore water sulfide—viz., a path between pore water sulfide and sediment AVS;
2. identifying pore water dissolved organic carbon (DOC) as an exogenous variable. The rationale behind evaluating pore water DOC was twofold. First, DOC forms strong complexes with dissolved Fe²⁺ (Jansen et al., 2002) that can then reduce the concentration of free Fe²⁺ available to bind with sulfide and form amorphous FeS or mackinawite. The SE model does not consider dissolved Fe or sulfide speciation, and

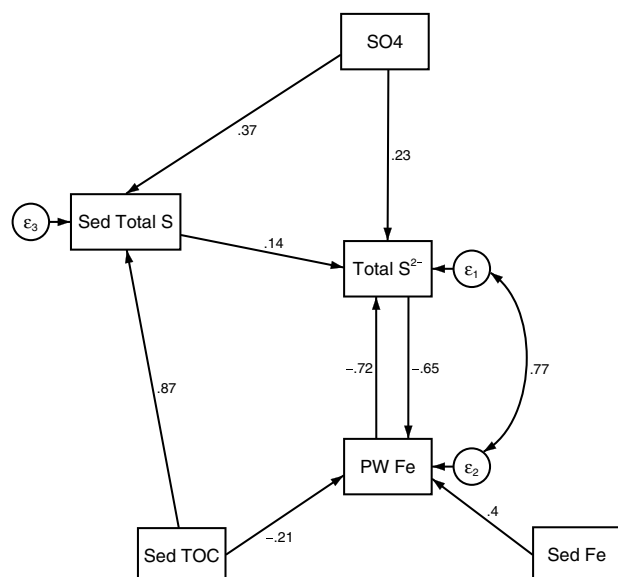


Figure 4. Final SE model for biogeochemical controls on pore water sulfide in wetland sediments. Final model extends conceptual model (Figure 1) by allowing for the correlation of errors between pore water Fe and sulfide. The diagram also shows the standardized path coefficient for each interaction pathway.

thus, inclusion of pore water DOC was considered as a first-order approximation for evaluating the potential efficacy of modeling with speciated values; and

- including surface water total phosphorus (TP) as an exogenous variable in the model. Increasing eutrophication is expected to increase sulfide production and sedimentary AVS through both the stimulatory effects of additional phosphorus on bacterial activity and rates of organic matter decomposition and through the increased delivery of autochthonous organic matter to the sediments, which in turn serves as a substrate to drive the development of anaerobic conditions and promote dissimilatory sulfate reduction. Anaerobic conditions are a necessary prerequisite for the solubilization of solid phase Fe(III) through its reduction to Fe(II). This alternative model thus considered direct pathways between TP and both pore water Fe and sediment AVS.

4. Results and Discussion

4.1. Model Fit and Evaluation With Class D data

The initial fit of the conceptual model was conducted using maximum likelihood estimation. This resulted in a model that performed reasonably well with respect to predicting the variations in the three endogenous variables (corrected r^2 values ranging from 0.582 to 0.650) but also resulted in a χ^2 value reflecting overall model fit that was unacceptably large ($\chi^2 = 35.54$, degrees of freedom [df] = 4, and $p < 0.0001$).

Evaluation of the effect of different structural changes to the model that would result in statistically significant reductions in the χ^2 value (modification indices) indicated several choices: (1) linking sediment Fe (negatively) to pore water sulfide, (2) linking either or both sulfate and sediment total sulfur directly (and negatively) to pore water Fe, and (3) allowing the error terms for pore water Fe and sulfide to be correlated. Correlating the error terms recognizes the possibility of either other variables missing from the model or sampling error (or both) affecting both pore water Fe and sulfide. For example, both dissolved Fe and sulfide are highly sensitive to oxidizing shifts in the redox environment of the pore water that potentially can occur during sampling or sample handling and transportation. The effect of such shifts in redox on both constituents is a reduction in concentration. Given its current framework, the other possible choices for improving the overall fit of the model are more reasonably considered only as indirect pathways and do not necessarily add to the conceptual understanding of the model or otherwise lead to an improvement in the utility of the model. For example, the conceptual model includes an indirect pathway defining the effect of sediment Fe on pore water sulfide. Allowing sediment Fe to directly interact with pore water sulfide negates the statistical significance of this pathway; removing the pathway in turn considerably weakens our ability to predict pore water sulfide.

As a result, we modified the conceptual model to allow error correlation between pore water Fe and sulfide (Figure 4). The resultant χ^2 value for the modified model was reduced to an acceptable level ($\chi^2 = 1.110$, $df = 3$, and $p = 0.775$). In addition, the values for the incremental fit indices reported by Stata were all below recommended target levels (Table 1). We further evaluated model fit by examining the matrix of fitted covariance residuals (Table 2). Kline (2011) suggests that values >0.10 indicate that the model does not fit the covariance matrix particularly well, and large residuals can provide guidance regarding possible modifications to improve model fit (StataCorp, 2015). The maximum absolute value for the covariance residuals was 0.007, which is well below this suggested threshold and provides further confidence that the fitted model is well supported by the data.

Model estimation of the modified conceptual model conducted by bootstrapping and the Satorra-Bentler method both verify that the model overall fit is good ($\chi^2 = 0.998$, $p = 0.874$, and Table 1) and that the estimates of the model coefficients are highly significant when accounting for multivariate nonnormality. With the exception of the path coefficient for the effect of sediment total sulfur on pore water sulfide ($p = 0.011$), all path coefficients had $p < 0.001$. We estimated the fit between each observed and predicted

Table 1

Comparison of Goodness of Fit Statistics Resulting From Fitting the Pore Water Sulfide SEM Model to the Class D and Class B Data Sets

Metric	Threshold or target value	Class D	Class B	Class B (no sediment TS)
χ^2 —degrees of freedom		3	3	1
χ^2 (maximum likelihood)		1.110	3.019	2.268
$p > \chi^2$ (maximum likelihood)	>0.05	0.775	0.389	0.132
χ^2 (Satorra-Bentler)		0.998	3.000	2.098
$p > \chi^2$ (Satorra-Bentler)	>0.05	0.802	0.392	0.148
RMSEA ^a (maximum likelihood)	0.05	<0.001	0.008	0.110
RMSEA (Satorra-Bentler)	0.05	<0.001	<0.001	0.102
90% CI ^b , lower bound	0	<0.001	<0.001	<0.001
90% CI, upper bound	0.1	0.080	0.165	0.308
p RMSEA $\leq$ 0.05		0.874	0.501	0.182
Comparative fit index (maximum likelihood)	0.95	1.000	1.000	0.993
Tucker-Lewis index (maximum likelihood)	0.95	1.014	1.001	0.954
Comparative fit index (Satorra-Bentler)	0.95	1.000	1.000	0.994
Tucker-Lewis index (Satorra-Bentler)	0.95	1.016	1.001	0.959
SRMR ^c	0.08	0.007	0.017	0.020
Residuals coefficient of determination		0.959	0.974	0.947
Stability index		0.687	0.733	0.786
Pore water total sulfide (log ₁₀ -transformed) coefficient of determination ^d		0.622	0.633	0.623
Pore water Fe (log ₁₀ -transformed) coefficient of determination		0.685	0.687	0.676
Sediment total S (log ₁₀ -transformed) coefficient of determination		0.650	0.697	
<i>N</i>		194	105	105

Note. Pore water sulfide coefficient of determination is the Bentler-Raykov squared multiple correlation coefficient.

^aRMSEA—root-mean-square error of approximation. ^bCI—confidence interval. ^cSRMR—standardized root-mean-square residual. ^dBentler-Raykov squared multiple correlation coefficient.

endogenous variable using the Bentler-Raykov squared multiple correlation coefficient (StataCorp, 2015). This coefficient is a corrected version of the coefficient of determination (r^2) that should be implemented when evaluating the explained variance of variables in nonrecursive models that have reciprocal causations such as pore water Fe and sulfide. Corrected r^2 values ranged from 0.622 to 0.685 for pore water sulfide and Fe, respectively (Table 1). Figure 5 plots the actual fit between observed and predicted values for log₁₀-transformed pore water sulfide. Included in the plot is a locally weighted scatterplot smoothing (LOWESS) curve that is useful for elucidating any undesired curvilinearity in the predicted relationship. The LOWESS curve shows no such evidence.

One concern with nonrecursive models relates to possible inherent instabilities owing to the fact that variables involved in feedback relationships are dependent upon themselves. The potential for such instability is evaluated through a *stability index* that estimates whether direct effects influencing variables in the model can become infinitely larger (Kline, 2011). Stata uses the method of Bentler and Freeman (1983) to calculate this index. Stability requires that the index value be less than 1; the stability index for the modified model was 0.687 (Table 1).

Results from jackknife cross-validation simulations showing the agreement between the full model predictions and the out-of-sample predictions are shown in Figure 6. Those results illustrate that the out-of-sample predictions closely match the predictions obtained from the fully calibrated model. As a result, the root-mean-square error (RMSE) for the out-of-sample predictions (0.300) agrees well with, and is only slightly

Table 2

Matrix of Fitted Covariance Residuals for the Final SE Model Fitted With Class D Data (See Figure 4 for Model Structure)

Variable	Pore water sulfide	Pore water Fe	Sediment total S	Sulfate	Sediment Fe	Sediment TOC
Pore water sulfide	0.001					
Pore water Fe	−0.001	0.002				
Sediment Total S	0.003	0.004	0.000			
Sulfate	−0.001	−0.007	0.000	0.000		
Sediment Fe	0.002	0.001	−0.003	0.000	0.000	
Sediment TOC	0.007	0.001	0.000	0.000	0.000	0.000

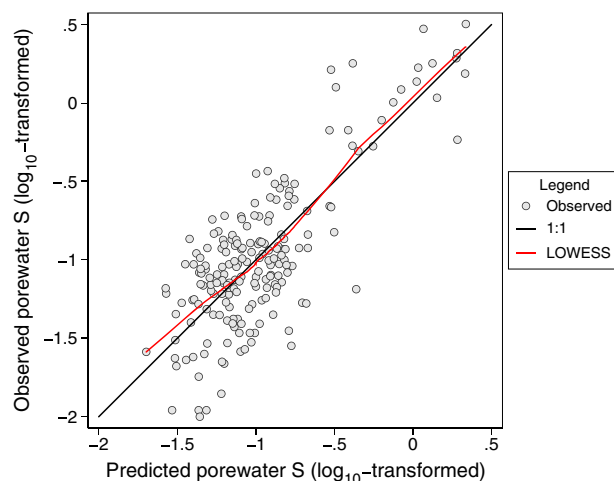


Figure 5. Comparison of observed with predicted pore water sulfide (both $\log_{10}$ transformed) for the SE model fit with Class D data. Plot includes lines showing expected 1:1 fit and the fit obtained from LOWESS smoothing (bandwidth = 0.8).

4.2. Model Results With Class B Data

The conceptual model with linked covariance between the pore water Fe and sulfide error terms was fit with the Class B data to further evaluate whether excluding sites with multiple observations would result in a substantively different set of results. Initial results indicated that the path between sediment total S and pore water sulfide was no longer significant, although the overall fit was acceptable with the exception of the upper limit for the RMSEA (Table 1). Thus, we refit the model without this pathway. In addition, eliminating this pathway also rendered modeling sediment total S irrelevant; as a result, and in order to avoid biasing the overall significance of the fit statistics, we dropped sediment total S from the model.

While the overall fit of the subsequent reduced form model is still significant ($\chi^2 = 2.268$ and $p = 0.132$), the RMSEA values were further degraded, such that the RMSEA value itself, and not just the upper limit, was unacceptably high.

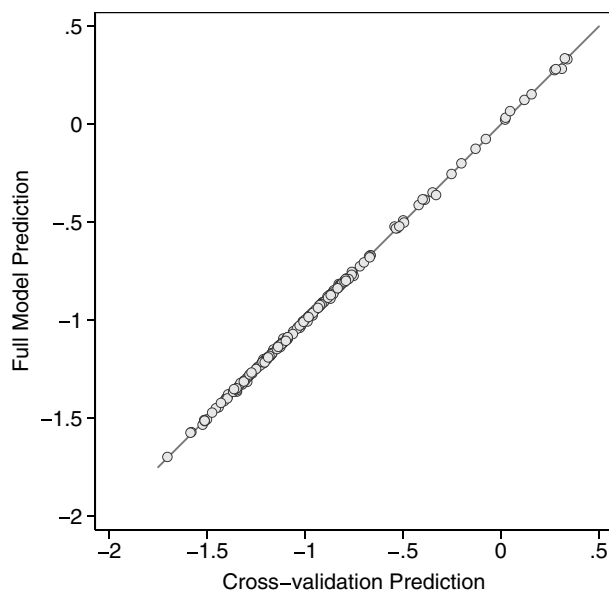


Figure 6. Comparison of predictions of pore water sulfide ($\log_{10}$ transformed) obtained for the SE model fit with Class D data and “out-of-sample” predictions obtained from jackknife cross validation.

larger than, the calibration RMSE 0.294. The jackknife analysis also demonstrates no problems with unusually influential observations in the Class D data set.

As mentioned previously, the Class D data set includes a number of sites with multiple observations over time. The inclusion of sites with multiple observations raises the possibility that the resultant model errors are not truly independent from a spatial perspective, unless each observation can be regarded as an independent characterization of the biogeochemical quasi steady state existing among pore water, sediment, and surface water parameters. We tested the possibility of such spatial autocorrelation of errors post hoc using analysis of variance (ANOVA). The analysis focused on Class D sites with four or more observations (10 sites with 48 observations). Figure 7 is a box plot that shows the distribution of model residuals for each of the sites with four or more observations; the plot also includes the residuals distribution for the remaining sites with only a single observation. The ANOVA indicates no overall significant clustering of residual values related to inclusion within a given site group ($p = 0.541$) and thus supports the use of multiple observations from the same site.

This degradation in model performance for both forms of the model is likely more a reflection of using an inadequate number of observations to fit the model, rather than a fundamental weakness in the model structure. This evidenced by (1) the significance of all the model path coefficients (all values of $p \leq 0.002$, with exception of the sediment total S—pore water sulfide path coefficient) and (2) a comparison of the fitted model coefficients that express the total effect (direct plus indirect) of all three exogenous variables influencing pore water sulfide for the two Class B models and the Class D model (Figure 8). This comparison shows that the differences in the coefficient estimates are small and lie well within the coefficient standard errors. Model integrity was further demonstrated by MLR conducted with the Class B data using pore water sulfide as the dependent variable and each of the SE model variables with direct paths to pore water sulfide. We constructed ACPR plots post hoc to evaluate linearity for each connection. Those results, which are included in the supporting information (Figures S2 and S3) confirm the underlying linearity of these pathways.

4.3. Alternative Models

We compared the set of postulated alternative models with the original model by evaluating both the suite of exact and approximate fit statistics described previously as well as the Akaike and Bayesian

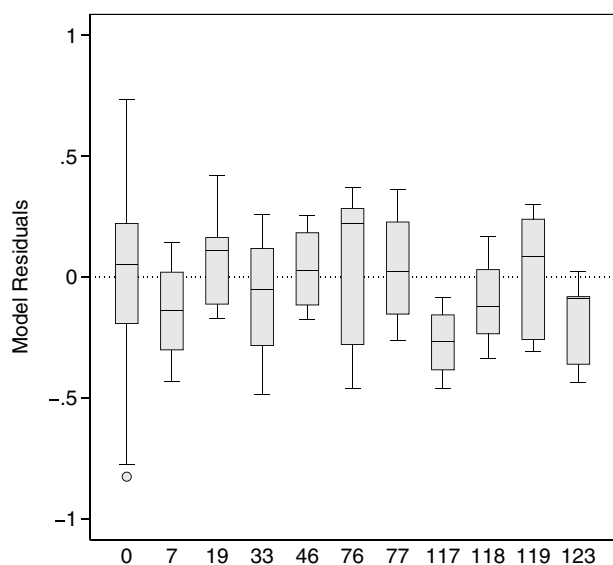


Figure 7. Box and whisker plot of the distribution of model residuals for individual sites with four or more observations. Each number on the abscissa denotes a unique site except for “0,” which includes values for all sites ($N = 68$) without multiple observations.

more parsimonious model is superior. Moreover, the ability to predict pore water sulfide, pore water Fe, or sediment total sulfur is not markedly improved by inclusion of sediment AVS (Table S1). Lastly, including sediment AVS as an endogenous variable does not change the overall relationship between the exogenous variables and the endogenous variables of interest. This is illustrated in Table S2, which compares the total effects of a given variable on a specific endogenous variable. Using pore water sulfide as an example, the coefficient

information criteria (AIC and BIC) values for each model. Comparing AIC/BIC values are meaningful only if the same number of observations is used to fit each model. Because several of the alternative models included variables with a missing observation, all the models thus were fit with the same set of reduced observations ($N = 193$).

The path diagrams for the original conceptual model along with each of the alternative models are included in the supporting information (Figures S4–S7). The diagrams depict the models in “final form” with the fitted standardized coefficients; final form is intended to convey that no further changes in the model structure are suggested by either modification indices that are conceptually supportable or by eliminating nonsignificant ($p > 0.05$) pathways.

Based on χ^2 values, the strongest models are the original model and the conceptual model modified to include sediment AVS (AVS model, Figure S6). This latter model includes a reciprocal relationship between pore water sulfide and AVS, as well as direct pathways between sulfate and sediment AVS and pore water Fe and AVS. This structure is consistent with the hypothesis that increased sulfate leads to increased dissimilatory sulfate reduction, and thus increases in AVS (Ramamoorthy et al., 2009). While this model is conceptually more satisfying, it is not necessarily superior to the original model for several reasons. First, the value for the SRMR was somewhat higher for the AVS model (0.013 versus 0.007). Second, AIC and BIC values indicate the original, more parsimonious model is superior. Moreover, the ability to predict pore water sulfide, pore water Fe, or sediment total sulfur is not markedly improved by inclusion of sediment AVS (Table S1). Lastly, including sediment AVS as an endogenous variable does not change the overall relationship between the exogenous variables and the endogenous variables of interest. This is illustrated in Table S2, which compares the total effects of a given variable on a specific endogenous variable. Using pore water sulfide as an example, the coefficient for the total effect of sulfate for the original and AVS models is 0.539 and 0.529, respectively; for sediment Fe and TOC, the coefficients are -0.551 versus -0.557 and 0.515 versus 0.532 , respectively.

The other two alternative models—inclusion of pore water DOC effects on pore water sulfide and pore water Fe (Figure S5) and inclusion of sediment AVS, pore water DOC, and surface water TP effects (Figure S7)—were somewhat inferior models, although both models were well supported based on χ^2 significance. In particular, weaker model fits were suggested based on an unacceptably high RMSEA value for the DOC model (0.058 compared to a guideline threshold of 0.05) and elevated RMSEA value for the AVS-DOC-TP model (0.028); this accordingly resulted in lower probabilities that the $\text{RMSEA} \leq 0.05$. CFI and TLI values were somewhat lower as well. While increasing TP concentrations can directly promote higher rates of microbial activity, the lack of importance of TP in the models may indicate that the effects of TP on pore water sulfide are predominantly indirect and exerted through its effect on the accretion of sediment organic matter (which in turn stimulates sulfate reduction). Because sediment organic matter content is only weakly related to trophic state variables such as TP (cf. Brenner & Binford, 1988) and more strongly reflects the physical depositional environment, the statistical relationship between TP and sulfide dynamics expectedly would be weak as well. Nonetheless, in freshwater wetlands such as portions of the Florida Everglades where high sulfate loadings are coupled with high phosphorus loadings, extremely high sulfide concentrations can occur, although the primary

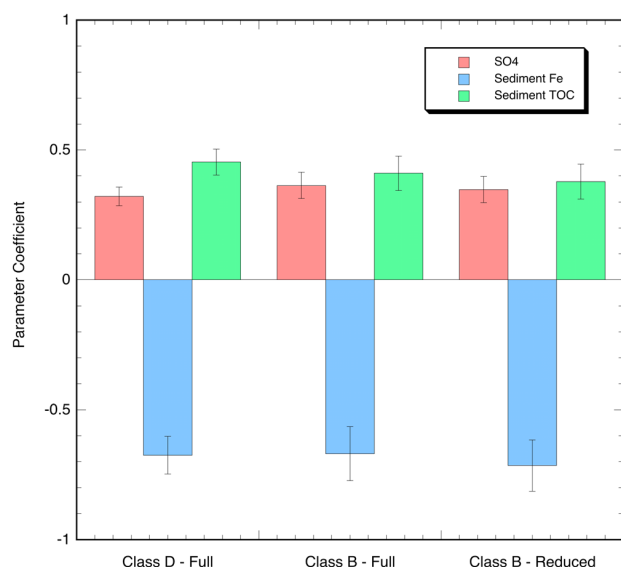


Figure 8. Comparison of the estimated coefficients depicting variable total effect on pore water sulfide for the three exogenous variables included in the SE model. The comparison includes fitting the SE model to the Class D and Class B data to the full conceptual model and fitting the Class B data to the conceptual model without including sediment total sulfur as a variable. Error bars are standard errors for the individual coefficient estimates.

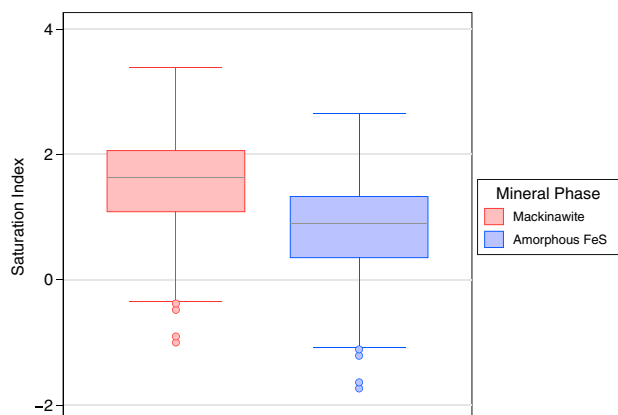


Figure 9. Distribution of amorphous FeS and mackinawite saturation index (SI) values calculated for the Class D data set. Values greater than 0 indicate supersaturation, while values less than 0 indicated undersaturation.

determinant appears to be high concentrations of sulfate more than phosphorus (Figure S8 and data from Scheidt & Kalla, 2007).

4.4. Geochemical Implications

The core of the conceptual model is the reciprocal relationship between pore water concentrations of Fe and sulfide, and which is embodied in the equilibrium dynamics of amorphous FeS or mackinawite precipitation and dissolution (equation (1)). We can test this hypothesis by calculating the ratio of the ion activity products (IAP) for equation (1) to the equilibrium solubility product constant (K_{sp}) for both solid phases ($10^{-3.915}$ and $10^{-4.648}$ for amorphous FeS and mackinawite, respectively) (Parkhurst & Appelo, 2013). Log ratios or saturation index (SI) values in excess of 0 suggest supersaturation, while values less than 0 are indicative of under or subsaturation (Appelo & Postma, 2010). Free concentrations of Fe^{2+} and HS^- were calculated based on measured pore water pH, and the hydrolysis constant for Fe^{2+} and dissociation constants for H_2S (Parkhurst & Appelo, 2013). Because they do not include corrections for ionic strength nor

the possible effects of other ions such as DOC effects on Fe^{2+} speciation, the resultant IAP values are biased somewhat high. Thus, these SI calculations can provide evidence only of conditions not sufficiently adequate for amorphous FeS or mackinawite precipitation to occur, rather than confirm that either phase is controlling.

The distribution of SI values calculated for both mineral phases are shown in the box plot contained within Figure 9. Only a small fraction of Class D sites had $\text{SI}_{\text{mackinawite}} < 0$ (6.7%), with over 75% of the sites suggesting supersaturation by an order of magnitude. SI_{FeS} values were, by definition, lower but still largely supportive of supersaturation (84% of the sites with values $\text{SI} \geq 0$). Holdren and Armstrong (1986) conducted similar IAP calculations for Lake Mendota sediments and, based on those calculations, concluded that FeS precipitation may control Fe solubility in sediment pore waters as well.

Our SE modeling coupled with the SI calculations thus suggest a solid aqueous phase dynamic between Fe supply and sulfide sequestration that buffers the evolution of pore water sulfide concentrations resulting from dissimilatory sulfate reduction. This buffering system is well recognized—for example, Heijs et al. (1999) developed a quantitative measure for the ability of sediments to buffer free S^{2-} concentrations dependent on the availability of both Fe(II) and Fe(III). In part, this buffer system includes the reduction of Fe(III) minerals such as ferrihydrite by H_2S , leading to the formation of metastable FeS (Poulton et al., 2002).

It should be noted that sediment organic matter also can react with sulfides to form organic sulfur, including thiols, organic monosulfides, and organic disulfides (Zeng et al., 2013), and that this pathway can be an important removal mechanism for pore water sulfide in many lakes (e.g., Holmer & Storkholm, 2001; Rudd et al., 1986; Urban et al., 1999). Moreover, this mechanism may be particularly important as a constraint on pore water sulfide concentrations in aquatic ecosystems where low iron availability is coupled with high sediment organic content. Because the SE model does not include a sediment organic S-sulfide relationship, modifying the SE model to account for organic sulfur formation likely will be important if it is extended to such ecosystems.

A key advantage of the SE model is that it provides a framework for quantifying the relative effects of different variables on pore water sulfide concentrations. Such an analysis can include direct effects, indirect effects, and total effects. Placing the effects of different variables in context with each other is perhaps most easily understood through the use of standardized coefficients. Standardized coefficients give the corresponding response relative to a single standard deviation for a dependent variable when a given independent variable has been increased by a single standard deviation. As such, standardized coefficients provide a convenient means for directly comparing the relative importance or strength of association of different independent variables, while the unstandardized coefficients reflect the form of the relationship (Acock, 2013).

Figure 10 compares the standardized coefficients for model variable effects on pore water sulfide. These results indicate that internal dynamics between pore water Fe and sulfide exert the greatest degree of control on pore water sulfide (standardized coefficients for total effects equal to -1.37 and 0.90 , respectively).

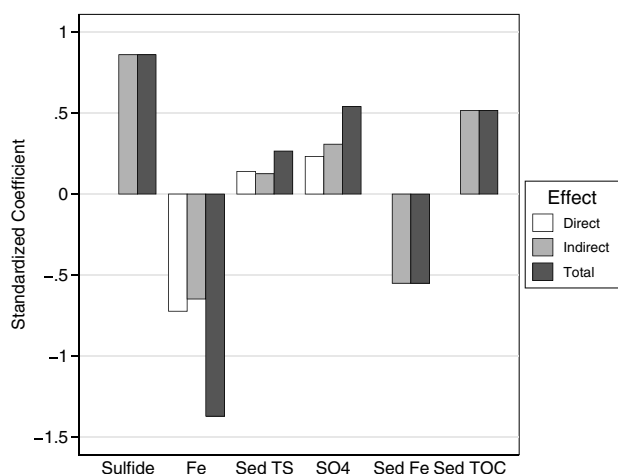


Figure 10. Standardized coefficients for direct, indirect, and total effects of each of the variables influencing pore water sulfide in the SE model. The use of standardized coefficients allows direct comparison of the relative importance of each variable relationship on variations in pore water sulfide, while the estimated coefficients (cf. Figure 8) allow one to estimate the marginal or instantaneous effects of changing a given exogenous variable on pore water sulfide while holding all other exogenous variables constant. Note that categories labeled as “sulfide” and “Fe” refer to pore water.

The effect of pore water sulfide on itself is of course indirect and exerted through its direct relationship with pore water Fe. The effect of pore water Fe in turn is largely direct, although it also exerts a substantial indirect effect through the pore water Fe-pore water sulfide feedback loop.

From a management perspective, the effects of the exogenous variables are of particular interest. Our comparison indicates the magnitudes of relative total effects for the exogenous variables are nearly identical: sulfate (0.54), sediment Fe (−0.55), and sediment TOC (0.52). These results thus suggest that given their distributional characteristics in our model data set, the ambient variations in each of the exogenous variables contribute in nearly an equivalent manner to the observed variations in pore water sulfide. In other words, while the importance of the role of sulfate as a controlling variable for pore water sulfide concentrations is validated both conceptually and statistically with respect to significance, the SE model also underscores the importance of the sediment Fe buffering system and the effect of the availability of sediment organic matter. The practical consequence of this buffering system is that the sensitivity of macrophytes such as wild rice that are adversely impacted by the occurrence of sulfide is likely exacerbated in sediments relatively low in iron. In such sediments, increases in organic carbon and sulfate will, *ceteris paribus*, result in higher concentrations of sulfide (cf. Calleja et al. 2007).

5. Practical Application of the SE Model

The ultimate goal of the MPCA-sponsored field survey upon which this modeling effort is based (Myrbo, Swain, Engstrom, et al., 2017) is to determine if it is appropriate to regulate sulfate and, if so, how to structure the regulation in order to protect wild rice from exposure to pore water sulfide concentrations above a protective threshold—the identification of which is a separate task from the modeling exercise described here. This modeling effort demonstrates that pore water sulfide concentrations can be successfully modeled with three exogenous variables—sulfate, sediment TOC, and sediment Fe. The latter two measurements are the average concentrations in the top 10 cm of sediment in a wild rice waterbody and likely reflect the natural ambient condition of the wild rice habitat. Although our modeling shows that both sediment TOC and sediment Fe are important contributors to the toxic impacts of sulfide, regulating sulfate is the only viable mechanism to protect wild rice against sulfide toxicity.

However, because each wild rice waterbody has different sediment TOC and Fe concentrations, any given fixed sulfate standard applied to multiple wild rice waters would produce a wide range of sulfide concentrations, some of which would likely be above the protective threshold. Because of the varying efficiency in converting sulfate to sulfide, if the goal is to keep wild rice waters below a particular sulfide threshold, then sulfate limits should be different for each waterbody.

To identify a protective sulfate concentration for a particular waterbody, it would be logical to employ the relationships revealed by the SE model and to work backward from an identified protective sulfide threshold to calculate a surface water sulfate standard tailored to the geochemistry of that particular waterbody. A direct way to accomplish this task would be to first arrange the SE model into a single equation that expresses pore water sulfide as a function of the exogenous variables in the model (sulfate, sediment Fe, and sediment TOC). By substituting the protective sulfide concentration in for that variable and rearranging the equation, a revised equation for the protective sulfate concentration as a function of Fe and TOC concentrations can be derived. Such an equation could be applied to any wild rice waterbody for which sediment Fe and TOC are known.

An important concern with the above approach, however, relates to both confidence intervals associated with predicted sulfide concentrations and biases in predicted values resulting from back-transforming a predicted log-transformed concentration to its original arithmetic form (Duan, 1983). Stata does not

provide confidence intervals for predicted endogenous variables obtained from SEM. With respect to the latter problem, solutions have been proposed (Duan, 1983; Manning & Mullahy, 2001), but they are complicated.

There are at least two approaches toward resolving the difficulty of practicably using the SEM results to predict sulfate concentrations that reflect a target or threshold pore water sulfide concentration. Both approaches rely on the SE model to define the driving variables of interest—viz., sediment Fe and TOC and surface water sulfate. The first approach uses generalized linear modeling with an appropriate link function (in this case a log link for the dependent variable) and specification of the residual error distribution. This approach capitalizes on the fact that path analysis and MLR are very similar (Li, 1975) and yield very similar estimated model coefficients for predicting pore water sulfide; with proper error distribution specification, it also avoids the issue of back-transformation bias. The second approach is multiple binary logistic regression (MBLR). MBLR simulates the likelihood that the response variable of interest exceeds a defined threshold given a set of independent variables. This type of binary response modeling is particularly well suited for the management question of whether, *ceteris paribus*, a given sulfate concentration is likely to result in pore water sulfide concentrations above or below a specified toxicity threshold. This approach also avoids the problem of back-transformation bias.

A MBLR model can be developed using the same field data that were used to construct, calibrate, and validate the SE model. MBLR would directly predict the probability of exceeding the protective sulfide concentration threshold as a function of sulfate, Fe, and TOC. An acceptable probability threshold can then be defined (for example, 0.5 or some other value; the choice would be a policy decision), and the model used to “inverse” predict the sulfate concentration that will produce the threshold as a function of Fe and TOC. Operationally, this equation to determine the protective sulfate threshold for any particular waterbody could then be applied in the same manner as the equation derived from the SEM, as described above.

In summary, it is desirable to use SEM to better understand and characterize the relationships between the important parameters in the system that relates sulfate and sulfide but then to use MBLR to translate the understanding gleaned from SEM into a water quality standard for sulfate. A standard that is an equation, rather than a uniform concentration that is applied to all waterbodies, would be a reflection of the biogeochemical diversity of the environment. New approaches are needed as environmental regulation progresses from protecting organisms from pollutants that are directly toxic, to pollutants whose negative effects are indirect and a function of environmental conditions that vary from site to site.

6. Conclusions

We used SEM to help elucidate and quantify the underlying structure of water quality and sediment chemistry variables governing the evolution of pore water sulfide concentrations in lakes and streams in the Upper Midwest/Great Lakes region. Three key “external” variables were initially hypothesized to be important—surface water sulfate, sediment Fe, and sediment TOC. Intermediate, mediating variables included pore water Fe and sediment total sulfur. Inherent in the model structure is a reciprocal relationship between pore water Fe and sulfide. This structure defines a sediment iron-based buffering system that is supported both empirically by other observational studies in wetlands and conceptually by the thermodynamics of amorphous FeS or mackinawite dissolution. The conceptual structure of the SE model is well supported both by model fit statistics and a suite of model diagnostic and post hoc analyses and by SI analyses that suggest that amorphous FeS or mackinawite precipitation-dissolution dynamics help control or impose constraints on the reciprocal relationship between pore water Fe and sulfide. Our use of SEM to model pore water chemistry dynamics, including the nonrecursive nature of those dynamics in particular, is believed to be the first such application in the open literature.

An important consequence of the sediment buffering system is that it serves to help limit the effects of increases in either surface water sulfate or sediment organic carbon on pore water sulfide. Based on total effects estimated from the SE model, all three external variables all essentially equivalent in importance with respect to influencing pore water sulfide. When considering the policy implications of trying to protect wild rice against the toxic effects of sulfide by limiting sulfate inputs to the ecosystem, our results thus demonstrate that the problem is multidimensional and that any such standard must consider the effects of

ambient concentrations of sediment Fe and sediment TOC to ensure the imposed sulfate standard is neither unduly or insufficiently protective. Multiple binary logistic regression would be a practical way to tailor sulfate standards to the specific geochemistry of sites so that a uniform level of protection for organisms sensitive to sulfide would be achieved.

Acknowledgments

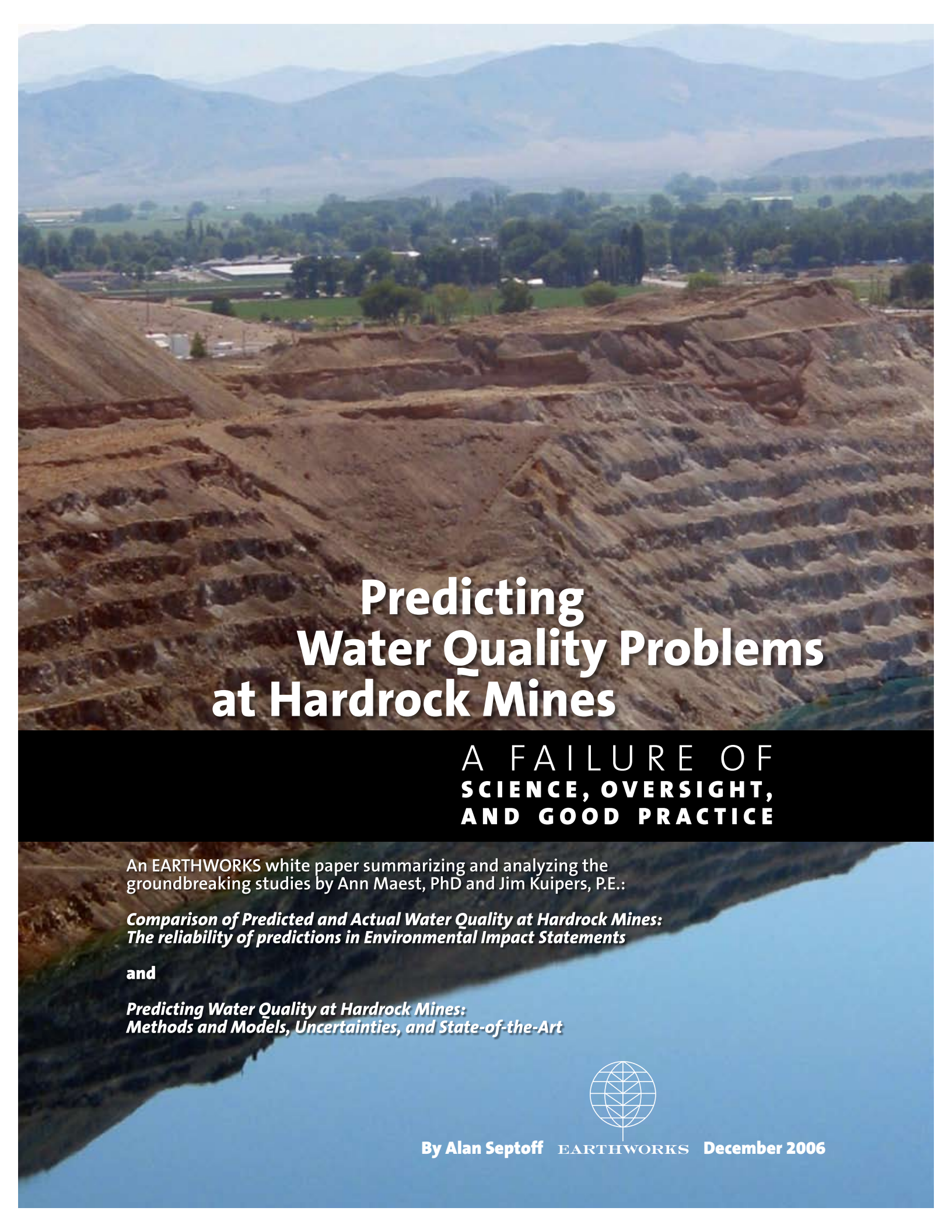
This study was supported by the Clean Water Fund, created by the Clean Water, Land and Legacy Amendment to Minnesota's constitution. We thank the many members of the field crew who collected the field data upon which this analysis is based. LacCore was supported by the National Science Foundation (EAR-0949962). The field data modeled in this study are included as a supporting information. A partial data set is available in the EarthChem database: DOI: 10.1594/IEDA/100681. The full data set is available in the Data Repository for U of M (DRUM): DOI: 10.13020/D6130R; <http://conservancy.umn.edu/handle/11299/185506>.

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Predicting Water Quality Problems at Hardrock Mines

A FAILURE OF SCIENCE, OVERSIGHT, AND GOOD PRACTICE

An EARTHWORKS white paper summarizing and analyzing the groundbreaking studies by Ann Maest, PhD and Jim Kuipers, P.E.:

***Comparison of Predicted and Actual Water Quality at Hardrock Mines:
The reliability of predictions in Environmental Impact Statements***

and

***Predicting Water Quality at Hardrock Mines:
Methods and Models, Uncertainties, and State-of-the-Art***



By Alan Septoff EARTHWORKS December 2006

Introduction

A failure of science, oversight and good practice

This paper is a summary, written for the layperson, of the findings of a two-year research study on the accuracy of water quality predictions at hardrock mines. The study, conducted by Jim Kuipers and Ann Maest¹, brings to light a decades-long failure by government regulators, industry, and consultants to recognize and correct deficient procedures and methods for predicting contamination of water at hardrock mines.

Kuipers and Maest have discovered that, in practice, there is a failure to compare predictions made before the mines are permitted with the actual results. The predictive modeling results are not adjusted to account for real-life failures—this, despite the fact that at the vast majority of mines, problems were worse than predicted. Establishment of credibility in modeling requires that the predictions be tested, and then the models adjusted based on the results. This process appears broken when it comes to predicting the impact of mines on water quality for mine permits.

To permit mines, federal law² requires regulators to apply scientific approaches to predict the environmental impacts of the mine proposal – including surface water and groundwater quality impacts. The accuracy of these water quality predictions is of significant public concern. Mining's impacts on water quality may affect municipal, agricultural, and rural water supplies; important commercial, subsistence and sports fisheries; wildlife populations; tourism; and recreation. One of the reports from the study, *Comparison of Predicted and Actual Water Quality at Hardrock Mines (Comparison Report)*, asks a basic question that government regulators, industry officials and consultants should have asked long ago:

Do predicted water quality impacts match reality?

The answer, in short, is **no**. The *Comparison Report* reveals:

- 100 percent of mines predicted compliance with water quality standards before operations began (assuming pre-operations water quality was in compliance).
- 76 percent of mines studied in detail exceeded water quality standards due to mining activity.
- Mitigation³ measures predicted to prevent water quality exceedances⁴ failed at 64 percent of the mines studied in detail.

Along with more analysis of this question, the *Comparison Report* and the companion report on methods and models used to predict water quality (*Methods and Models Report*), also seek to answer the necessary follow-up questions:

- In cases where predicted water quality impacts fail to match reality, why do they fail?

- Do certain types of mines fail more often than others?
- What can be done to address current failures and prevent future failures?

The Kuipers-Maest reports were prepared for a professional audience. The purpose of this paper is to translate and summarize the main findings of their research (for the layperson and the interested public), and to offer common sense recommendations based on those findings with an eye toward protecting natural resources and public health.

The Context

Why this research was necessary

The Environmental and Public Costs of Faulty Predictions

The failure to accurately predict and manage water quality impacts can result in significant negative impacts on clean water and steep taxpayer liabilities for the costs of cleanup. Consider one often-cited example — the Summitville gold mine in Colorado. Water pollution at this mine has cost American taxpayers more than \$200 million in cleanup costs. The majority of that money has been spent mitigating acid drainage and cyanide releases that were not predicted during the permitting process. When pollution spilled from a containment pond, 18 miles of the Alamosa River were effectively killed – impacting not only the aquatic life in the river, but also the adjacent farms and ranches that relied upon the Alamosa for irrigation and livestock watering.

While it may be argued that Summitville is one of the worst-case examples, problems abound. According to the U.S. EPA's Abandoned Mine Land Team, the cost of mine cleanup at sites on the National Priorities List (i.e., Superfund sites, like Summitville) in the United States is \$20 billion – almost 3 times the EPA's FY 2007 budget request. Long term water treatment and management is often the single most significant cost associated with mine cleanup.

In fact, there is an increasing number of mine sites throughout the U.S. that will require water treatment in *perpetuity*. In the arid west, these types of long-term impacts place a tremendous burden on downstream communities who must deal with the consequences of failed predictions. For example, government regulators have determined that the Zortman Landusky mine, located near the Fort Belknap Reservation in Montana, will continue to generate acid mine drainage for thousands of years. As a result, the Fort Belknap Tribes are faced with a continual threat to important tribal water resources, and the state of Montana will be spending tens of millions in public funds for long-term water treatment.⁵

In order to ensure clean water and protect taxpayers from liability for cleanup costs it is important to understand the frequency and magnitude of failures in predicting water quality impacts. Consider that at most major mines, operators are required to post financial assurances prior to operating. This is the good news. These assurances are supposed to guarantee that, should the mine operator go bankrupt, the mine site will be reclaimed at no cost to the taxpayer. However, the bad news is that these financial assurances are based upon expected reclamation costs and expected reclamation costs are based in large part upon water quality predictions.

Previous research by Jim Kuipers demonstrates that taxpayers are potentially liable for up to \$20.4 billion⁶ in financial assurance shortfalls at existing mine sites (in addition to the \$20 billion for Superfund sites) – due in large part to inaccurate water quality predictions.

A Growing Problem

Without correction, the environmental and financial impacts of faulty predictions could grow. Recent increases in metals prices have triggered an increase in the number of new mines being proposed in the United States. According to the Bureau of Land Management, new mining claims filed in 2006 are on track to more than quadruple since metals prices began their precipitous rise in 2002.

In the United States alone there are approximately 180 large hardrock mines – in nearly all regions of the country – that are in various stages of permitting, development, operation or reclamation and closure. In order to better protect important water resources and reduce future economic liability, improvements must be made in the prediction and prevention of impacts to water quality at these sites. On the positive side, the increase in metals prices has resulted in fewer bankruptcies in the sector—and it is bankruptcies that trigger the use of reclamation bonds for mine site reclamation and water treatment. This may provide regulators and industry officials with a window of opportunity to solve the underlying problems with water quality prediction.

Unprecedented Research: the absence of previous studies and the data gap

When they began their research, the authors expected to incorporate data from some mines where government officials had already completed a comparison of predicted and actual water quality impacts. However, they were unable to find comparisons of water quality predictions and actual water quality impacts of mines.

The authors found that no single repository exists for the Environmental Impact Statements (EISs) currently mandated under federal law. EISs contain the water quality predictions analyzed in the study. In some cases, local

federal offices that processed the studies did not have copies of them. Furthermore, in many cases, the authors were forced to submit Freedom of Information Act requests and pay fees to obtain copies of these studies. Similarly, water quality from mines was inordinately difficult to obtain and in most cases required personal visits to agencies and long hours sorting through paper files.

Taken together, the absence of previously published research and the difficulty in gathering information is evidence of a data gap that surprised the authors and may help explain the previous lack of a comprehensive study of this nature.

It is important to note that the predictions data were available – no matter how difficult to obtain – only because the National Environmental Policy Act (NEPA) requires it. Without NEPA, this study would have been impossible to conduct.

A Tool for Many Audiences

While the research focuses on the underlying scientific and engineering processes that form the basis of water quality predictions, its recommendations are intended for use by many audiences to increase the effectiveness of future mine water quality predictions – directly and indirectly:

- This study should be useful to the scientific and engineering communities for suggesting ways to better characterize risks to water quality and to better apply mitigation methods to minimize or prevent potential impacts.
- The regulatory community can look to these reports, especially *Methods and Models*, for recommendations on how to fundamentally improve the permitting process to ensure a more accurate analysis of potential mining impacts. The inherent uncertainty in water quality predictions and mitigation failures should be conservatively viewed in order to ensure mine permitting decisions that are more protective of human health and the environment. The integrity of the mine permitting process is dependent on the use of accurate methods and models.
- This report can be utilized by the mining industry to improve current practices and more accurately predict consequences and ameliorate potential effects.
- It can be utilized by the insurance and investment industry as a tool to better understand the potential risks and costs associated with mining, and as a basis to reassess risks at current mines.
- And finally, it can be utilized by the interested public to more effectively advocate for water quality protections in the permitting process and to advocate in the public arena for legislative and regulatory changes that better protect water resources.



Do Predicted Water Quality Impacts Match Reality?

As indicated above, the answer is usually no — particularly when high risk mines, such as those with close proximity to water resources, are considered.

Sampled Mines

To arrive at this answer the authors initially reviewed 104 Environmental Impact Statements (EISs) and Environmental Assessments (EAs) for 71 major hardrock mines in the United States.⁷ The mines covered all important mineral sectors (gold, silver, copper, platinum group metals, molybdenum, lead, and zinc) and ten mining states (Alaska, Arizona, California, Idaho, Montana, New Mexico, Nevada, South Dakota, Utah, and Wisconsin).

A representative subset of 25 case study mines was then selected to evaluate the accuracy of the water quality predictions. Environmental impact reports for these mines were evaluated for predictions related to surface water, groundwater, and mine drainage quality during and after mining. These predictions were then compared with actual water quality conditions during and after mining.

Potential & Predicted Water Quality

The authors discovered a two-tiered system for water quality predictions, one-tier of which was based not on sound science, but on unsupported “good faith” projections.

The two tiers of “predictions” made about water quality in environmental assessments are referred to by the authors as “potential” and “predicted” water quality:

- **Potential** water quality is the expected water quality conditions in the absence of mitigation efforts by the operator.
- **Predicted** water quality takes the effect of mitigating measures into account. It is what mine operators forecast actual water quality will be during and after operations.

All the environmental reviews analyzed in the *Comparison Report* predict acceptable water quality after mitigation at mines where water quality standards were met before mining began. If this prediction were not made, the regulatory agency would not be able to approve the mine.

However, inadequate information was provided to demonstrate how the mitigation measures would actually prevent water quality impacts. Therefore, regulators were generally accepting the final water quality predictions on “faith.”

Major Findings: Chronic Underestimates of Water Quality Problems

Prediction vs. Reality: Overall Water Quality Impacts to Ground and Surface Water

Of the 25 mines sampled:

- 76% of mines polluted groundwater or surface water severely enough to exceed water quality standards.
- 60% of mines polluted surface water severely enough to exceed water quality standards.
- At least 13 mines (52%) polluted groundwater severely enough to exceed water quality standards.

Predictions vs. Reality: the Failure of Mitigation

In the cases where water quality standards were exceeded, in some cases the mine proponent anticipated the potential for pollution and prepared mitigation strategies (e.g. a mine waste dump lined with plastic to prevent acid drainage leaching into groundwater). Predictions of the efficacy of mitigation were no more reliable than overall predictions of water quality:

- 73% of mines exceeded surface water quality standards despite predicting that mitigation would result in compliance. The other 4 mines didn’t predict the need for mitigation.
- 77% of mines that exceeded groundwater quality standards predicted that mitigation would result in compliance. The other 3 mines didn’t predict the need for mitigation.

Predictions vs. Reality: Mines near Water with Elevated Acid Drainage or Contaminant Leaching Potential are High Risk

Some mine projects are so high risk that water quality exceedances are a near certainty: those mines that are both near groundwater or surface water resources, and possess an elevated potential for acid drainage or contaminant leaching.

- 85% of the mines near surface water with elevated potential for acid drainage or contaminant leaching exceeded water quality standards
- 93% of the mines near groundwater with elevated potential for acid drainage or contaminant leaching exceeded water quality standards.
- Of the sites that did develop acid drainage, 89% predicted that they would not.

Water Quality Pollutants

Of the 19 mines that exceeded water quality standards, the pollutants that exceeded standards were as follows

- Toxic heavy metals such as lead, mercury, cadmium, copper, nickel or zinc exceeded standards at 63% of mines.

- Arsenic and sulfate exceeded standards at 58% of mines.
- Cyanide exceeded standards at 53% of mines.

Why Do Predictions Fail?

In order to evaluate water quality impacts during the permitting process, government regulators rely on water quality predictions created by hydrologists and geochemists and mining engineers using computer models and other types of field or laboratory studies. Those predictions are only as good as the science upon which the models/tools are based, and the site characterization information supplied to those models. So when water quality predictions fail to predict water quality for mining operations, they fail for two general reasons:

1. the science of mine water quality prediction is imperfect
2. the science of mine water quality prediction is imperfectly applied at mine sites

The Imperfect Science of Mine Water Quality Prediction

The complexity of pollutants' interaction and movement in groundwater and surface water systems at mines is difficult to recreate in a model. This is addressed in detail in the companion report by Maest & Kuipers titled *Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties, and State-of-the-Art*.

According to *Methods and Models*, factors that complicate the prediction of water quality at mine sites range in scale from small to large. On a small scale, for example, it is not well known how minerals react in complex systems. On a large scale, geology, climate, methods of mining and mineral processing, and mine waste management approaches vary among and within mine operations. These large scale variations limit the degree to which information from one site can be applied to another.

Also, extrapolation from the laboratory to the mine must address complicating factors such as environmental conditions, water and gas transport, differences in particle size, and how these variables affect drainage quality over periods of decades or centuries. However, there is virtually no available field information describing the effect of these variables over extended periods of time. The lack of this field information introduces significant additional uncertainty into predictions.

Just as weather cannot be accurately predicted beyond a certain point because weather models and their inputs are not perfect, the transport of pollutants through complex geological and hydrological systems over the longer term, which can range from five years to tens of thousands of years is similarly difficult to predict.

One of the study's most significant findings, however, is where the practice of predicting weather and the practice of predicting water quality at mining operations part ways. Weather models are consistently reevaluated based on a comparison of predictions with actual weather conditions that occur subsequently.

Not so with the models used for predicting water quality at mining operations. The very fact that the study is unprecedented shows that *professionals who predict mine water quality do not revisit their predictions, and neither do the regulators responsible for ensuring the accuracy of those prediction*. The models used for the predictions cannot be improved if their failures and successes are not evaluated. Where predictions of water quality at mining sites are concerned, the scientific process is broken.

Imperfect Science, Imperfectly Applied

A mine water quality prediction model can only reach its potential at any individual mine site if that site is correctly characterized (in terms of its hydrology and geochemistry) to the extent possible. According to Maest and Kuipers, that potential is not being reached.

There are two types of characterization failures described in the *Comparison Report*: hydrologic (related to water flow at a mine site) and geochemical (the chemistry, geology and mineralogy of the materials/minerals that comprise the mine site).

The *Comparison Report* documents that six of the 25 case study mines were inadequately characterized hydrologically, and that eleven of the case study sites were inadequately characterized geochemically.

Another example of "imperfect science, imperfectly applied" is the bias of mine water quality predictions made by consultants hired by the prospective mine operator. This problem is implied by the number of site characterization failures, and by the failure to check the results of past mine water quality predictions.

Regulatory agencies, both federal and state, allow the mining company to select and directly pay consultants to predict mine water quality impacts, and to review and comment on (or even reject) those predictions, prior to release to the agency. It is an understatement to say that consultants heavily influence mine water quality predictions.

Unfortunately, given the client/customer relationship between prospective mine operators and their consultants, consultants are rewarded for having favorable predictions. On the other hand a prediction of poor water quality will usually delay a permit, which increases the permitting costs. While exceptions exist, consultants that predict poor water quality often are not rehired. This perverse incentive is contrary to the spirit of unbiased science, and contrary to the public interest.



Preventing Future Failures (and Addressing Current Failures)

Recommendations

Both the *Comparisons* and the *Methods and Models Reports* reveal that the prediction of future mine water quality is an uncertain business. And given the difficulty in modeling natural systems, even if all the recommendations included here and in the Kuipers-Maest research are implemented, mine water quality prediction will always be an uncertain business. However, there is considerable room for improvement.

Just as weather prediction has improved over time, so can mine water quality prediction — if regulators and professionals in the sector learn from past predictions and improve characterization efforts.

With that in mind, the following recommendations are intended to help improve mine water quality predictions today and in the future.

Addressing the Consequences of the Existing Prediction Process

Assess existing mines. If the results of the *Comparison Report* are extrapolated to all operating major mines, water quality standards would be exceeded at roughly 75% of all mines in the United States. Regulators should, in a public process, canvass all permitted mines to:

- determine which mines are exceeding water quality standards,
- evaluate how surrounding communities and the environment are being affected, and what cleanup steps are necessary,
- revisit the original predictions, and
- reassess the adequacy of the financial assurances provided by mine operators to guarantee mine cleanup and long-term water treatment.

Incorporate uncertainty into permitting process. Regulators should take a suitably precautionary approach to the mine permitting process, and require that mine design, mitigation and financial assurance calculations prepare for reasonable worst-case rather than best-case scenarios.

Better screen high-risk mines. Regulators must demonstrate concrete improvement in the accuracy of mine water quality predictions and mitigation efforts. For example, additional regulatory scrutiny should be given to the highest risk proposals such as those mines near water resources and with elevated acid drainage or contaminant leaching potential. In cases where the risks are too high, regulators should not permit mines. It should be noted

that this recommendation is supported by the *Comparison Report* which demonstrates that 93 % of such mines near groundwater, and 85% near surface water, exceeded water quality standards.

Some major mining companies are realizing that the life-cycle costs need to be clearly evaluated, including the costs of *perpetual maintenance and water treatment after mine closure*. While some leaders in the industry are using life-cycle cost estimates, this is still not a uniform industry standard, and regulators ultimately must make the determination for many mine proposals.

Inform the public about the uncertainty of water quality prediction. As part of the mine permitting process, regulators should inform the public of the history of the accuracy of mine water quality predictions so they can better determine the risk involved in a mine proposal.

Improving Future Mine Water Quality Predictions

Ease access to predictions and results. Information regarding pre-mining, mining and post-mining water quality should be publicly available online, along with the associated mine water quality predictions made during the permitting process. This will facilitate a more informed mine permit process for regulators and the public.

Review original predictions as water quality develops during mining. Mine operations should be regularly assessed to determine if they are departing from mine water quality predictions. This will allow regulators and mine operators to take early action when mine water quality begins to depart from the predicted.

Consult past predictions at other mines. When permitting a mine, regulators should be required to seek similar mines, or similar aspects of different mines, and determine what predictions were made and what water quality actually occurred. These mine analogs should be publicly disclosed.

Require improved characterization of mine sites. This recommendation is covered in much greater detail in the *Methods and Models Report*. In summary, regulators should require better information about the mine site — before, during and after operations.

Require more research on the effectiveness of mine water quality mitigation. The *Comparison Report* found that where predictions of good mine water quality were predicated upon the mine operator using mitigation strategies, mine water quality usually exceeded water quality standards. More research is needed to determine how and why these mitigation efforts fail, and how to improve them.

Change the procedure for selecting consultants to avoid the present conflict of interests. Agencies should independently select and pay the consultants to conduct the

studies. This will limit the ability of a mining proponent to influence the outcome of the predictions. The mine proponent can comment on the study, similar to public interest organizations, but they should not be able to exert sufficient influence to bias the outcome.

Increase government expertise. Many state and federal agencies are not sufficiently funded to employ staff with the technical expertise to provide appropriate analysis and oversight of the mine permitting process. Increased funding should be incorporated into agency budgets to ensure that technical expertise is available for permit review.



Endnotes

1. Jim Kuipers, PE, is a mining engineer with Kuipers & Associates in Butte, Montana, and Ann Maest, PhD, is an environmental geochemist with Buka Environmental in Boulder, Colorado.
2. The National Environmental Policy Act requires a science-based review of mine proposals when federally-owned land is affected, or when a federal permit is required (e.g. the Clean Water Act requires a permit when a mine discharges into waters of the United States). Many states have similar laws, based on NEPA, that apply to mine proposals even when federal land is not involved.
3. Mitigation is the effort by a mine operator to prevent or reduce pollution. For example, some mine waste (e.g., tailings impoundments) is underlain by thick plastic to prevent contaminants from moving into nearby water resources.
4. In this paper, an “exceedance” is the presence of a pollutant in concentrations higher than a water quality standard. This is different from a water quality “violation,” which is a breach in the terms of a water quality permit. A water quality permit, although based on standards, may allow exceedances under some conditions. A mine operator is legally liable for a water quality violation.
5. Mitchell, Larry D., a staff paper prepared for the Environmental Quality Council, “Zortman and Landusky Mines: HJ 43 Water Quality Impacts, October 2004.
6. Kuipers, J, 2003, Putting a Price on Pollution: Financial Assurance for Mine Reclamation and Closure. This report was funded by Mineral Policy Center.
7. Many mines have multiple EISs or EIAs for different eras of mining.

“Mining by its nature and scale causes significant changes in the landscape and ecosystem” (Mining Minnesota/Global Minerals Engineering PP)



Example of a slurry pipeline



Example of a paste plant



Example of a processing facility

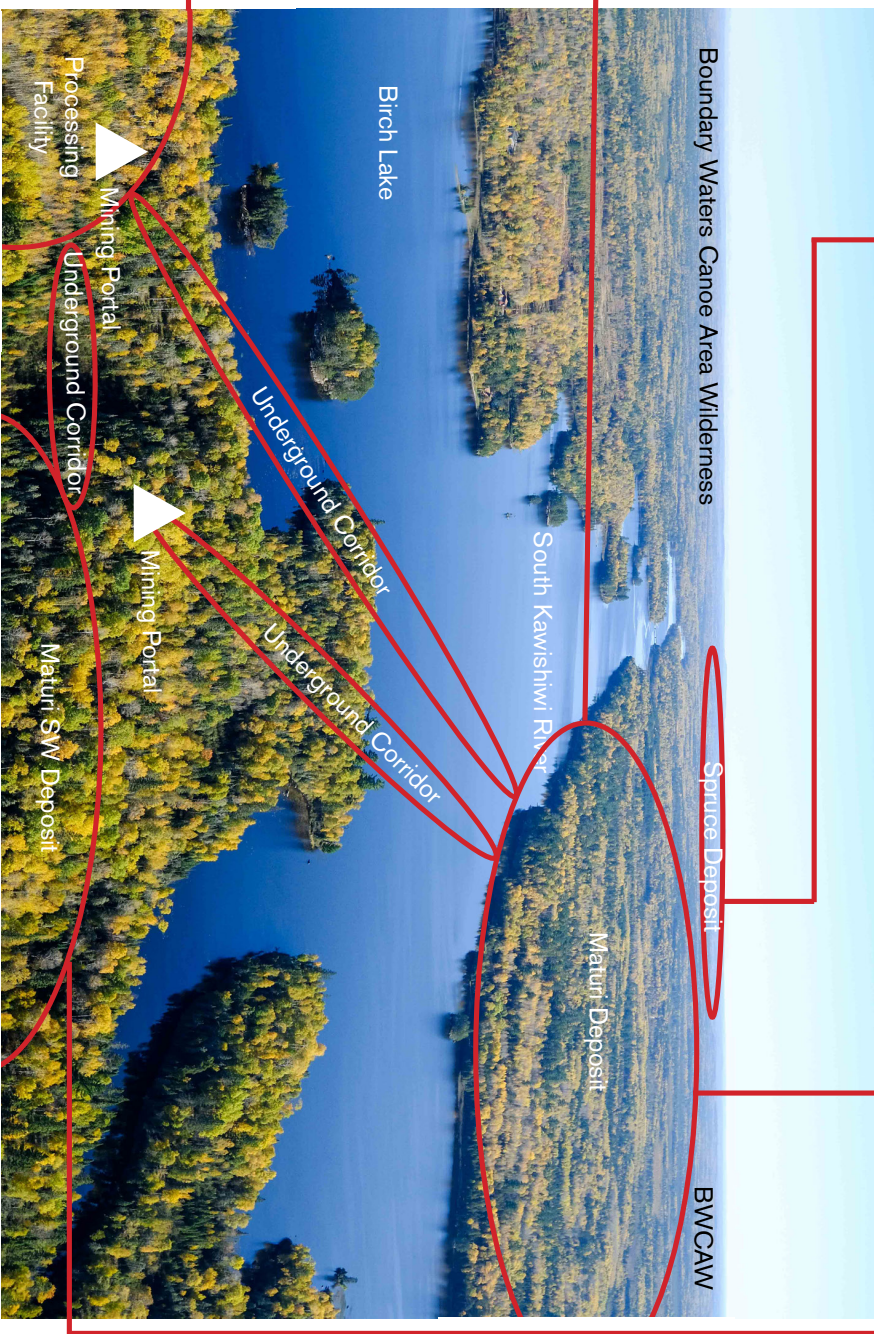
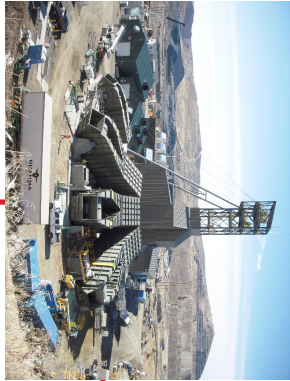


Example of a tailings pile

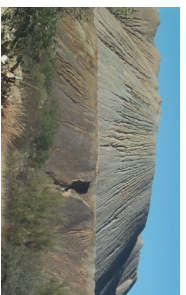


<< Example of an open pit mine

>> Example of a mine ventilation facility for underground mines. There will be 4 intake and 4 exhaust raises at the Maturi Deposit.



Example of a sulfur pile



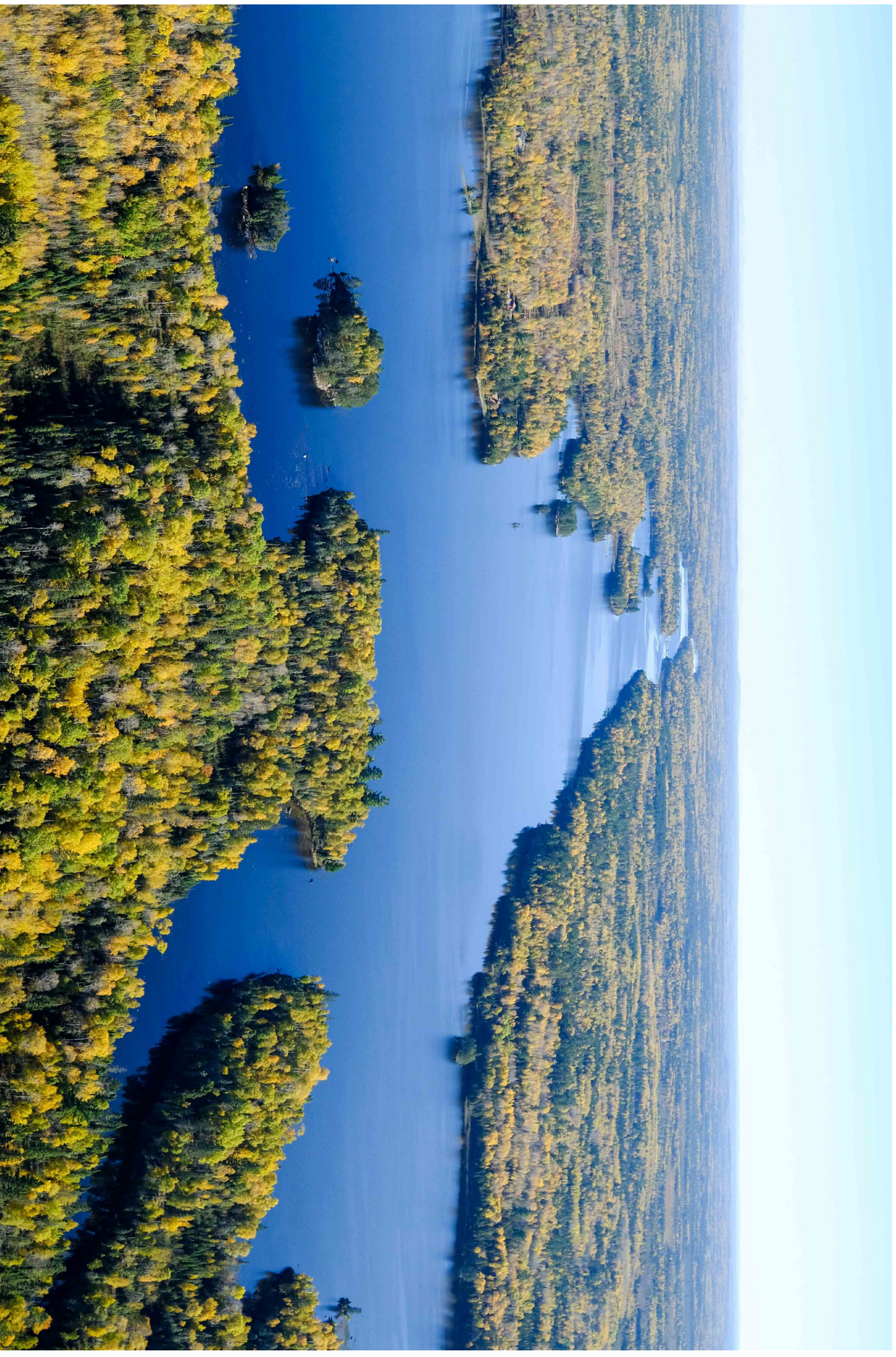
Example of a waste pile



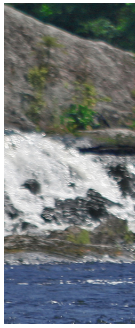
Example of a mining portal

Lands in the Superior National Forest next to the Boundary Waters Canoe Area Wilderness

Massive sulfide-ore copper mines are proposed in the area pictured below, along the South Kawishiwi River where it flows out of the Wilderness, joins Birch Lake, and flows back into the Wilderness.



This area contains two popular Wilderness entry points to the Boundary Waters Canoe Area Wilderness (BWCAW). The area also has two popular National Forest campgrounds, hundreds of homes, 28 businesses, a major snowmobile trail, a popular hunting area, and one of the most popular recreational lakes in the Superior National Forest.



THE SCIENCE: Sulfide-Ore Copper Mining Threatens Aquatic and Terrestrial Ecosystems of the South Kawishiwi River area, Mining Protection Area, Boundary Waters Canoe Area Wilderness, and other parts of the Superior National Forest including the Withdrawal Study area; Voyageurs National Park; and Quetico Provincial Park (the Boundary Waters Region)

October 2017

Predicted Ecological Impacts to the Boundary Waters Region of Sulfide-Ore Copper Mining

Tom Myers, Ph.D. 2013. In his report entitled “Technical Memorandum: Twin Metals Mining and the Boundary Waters Canoe Area Wilderness, Risk Assessment for Underground Metals Mining,” Dr. Myers focused on essential facts demonstrating why sulfide-ore copper mining threatens irreparable harm to priceless northern forest ecosystems (Parentheticals explain why facts identified by Dr. Myers are significant):

- Waters that would receive acid mine drainage (AMD) are currently of extremely high quality (therefore, pollution caused by mining would degrade an increasingly rare resource).
- The waters that would receive AMD contain few base compounds (therefore, natural buffering of AMD will be extremely low).
- The many streams, wetlands, lakes and aquifers downstream of the mine sites are massively interconnected (therefore, damage from AMD will be widespread and uncontrollable).
- Mine sites lie in close proximity to these water resources (therefore, preventing AMD from entering the waters would be impossible).
- The high probability of AMD coming from the mine sites, waste rock piles, and tailings pond failures (no practical possibility exists of preventing air, rainwater and snowmelt from reaching sulfide-bearing rock).
- The difficulty of predicting when and where AMD may occur because of the nature of cracks and faults in the bedrock (therefore, no practical possibility exists of effectively blocking AMD movement through the ground).
- The potential that AMD could impact waters far downstream from the mine sites (therefore, major waterways of the Boundary Waters Canoe Area Wilderness, Quetico Provincial Park and Voyageurs National Park would be threatened).
- The high cost and low probability of remediating AMD when it occurs.
- River discharge and aquifer recharge are highly seasonal, with the bulk of it occurring between mid-April and mid-June (therefore, drawdowns of surface water and groundwater by mining activity outside that period of higher flows will deplete water available in the affected ecosystems at times when the flows are already at annual or decadal low points).

Dr. Myers later developed a model for the Rainy Headwaters that shows the flow of ground and surface water and the transport of contaminants. 2014. “Technical Memorandum: Twin Metals Mining and the Boundary Waters Canoe Area Wilderness, Risk Assessment for Underground Metals Mining.” The Rainy Headwaters includes the South Kawishiwi, Birch Lake, and Stony River watersheds. The purpose of the model is to estimate pathways and rates for contaminants to reach the Boundary Waters Canoe Area Wilderness if sulfide-ore copper mining occurs within these watersheds. The model can be used to estimate the risk of mine spills and leaks affecting the Boundary Waters Canoe Area Wilderness

and the lakes and rivers between the proposed mines and the Wilderness. Dr. Myers modeled three scenarios for underground mines and a proposed concentration facility in the South Kawishiwi and Birch Lake watersheds based on the Twin Metals Minnesota Pre-Feasibility Study.

- First scenario: a release of a conservative pollutant (sulfate) from five locations in underground mines using a realistic concentration of sulfate for closed and flooded underground mines in the Duluth Complex and a low discharge rate.
- Second scenario: a one-year release to groundwater from mine waste stored on the surface in the watershed, representing a range of releases that can occur.
- Third scenario: a mid-level spill at the Maturi mine site and at the proposed concentration facility site.
- Scenarios one and two (releases) show that substantial contaminant loads from leaks typical of sulfide-ore mining could impact waters that drain into the Boundary Waters Canoe Area Wilderness.
 - Once started, leaks would continue for decades (even a short-term spill would take years or decades to travel through groundwater) and would thus likely coincide with low flow periods and could create devastating impacts.
 - Contaminants entering the rivers and lakes during low flow conditions have a high potential to impact water in the Boundary Waters Canoe Area Wilderness.
 - Historically, it has been almost impossible to stop leaks at similar mines.
 - Leaks would have a significant impact on streams, rivers, wetlands, rivers and other waters adjacent to the sulfide-ore copper mine sites and in the Superior National Forest.
 - Pollution from sulfide-ore copper mines in these areas would extend into the Boundary Waters Canoe Area Wilderness.
- Scenario three (a spill at the proposed concentration plant) could devastate adjoining lakes, rivers and streams in the Superior National Forest.
- A spill could have a devastating impact on the Boundary Waters Canoe Area Wilderness, depending on level of toxicity, load and location.
- “If the sulfide mines are developed in the Rainy Headwaters, it is not a question of whether, but when, a leak will occur that will have major impacts on the water quality of the Boundary Waters Canoe Area Wilderness.”

Dr. Myers extended his analysis to consider the risks posed to Voyageurs National Park from the development of metallic mineral leases in the watersheds draining to and through it, including the Rainy Headwaters, Vermillion Lake, and Rainy River-Rainy Lake Watersheds. In his 2015 “Technical Memorandum: Potential Metals Mining and the Voyageurs National Park Risk Assessment for Upstream Metals Mining” prepared for the Voyageurs National Park Association and National Parks Conservation Association,” Dr. Myers reported:

- Streams draining toward Voyageurs National Park have high water quality and would be affected by small amounts of contamination for a long time.
- The low buffering capacity of the rivers in the Rainy Headwaters watershed could allow contamination from mining waste to be transported a long distance downstream, including to Voyageurs National Park.
- Contaminant seepage into groundwater could last for decades, and there would be little chance of preventing the pollution from reaching Voyageurs National Park.
- Mercury contamination is already present in Voyageurs National Park, and AMD seepage over a long time period would likely exacerbate the existing mercury problem.
- A spill in the Vermilion watershed could pose critical threats to Voyageurs National Park, especially if the waste flowed through Vermilion Lake instead of mixing.
- Discharge or leaking of high salinity water resulting from mine dewatering could ruin nearby streams and increase total dissolved solids from the Kawishiwi River to Voyageurs National Park.

- Development of tailings impoundments presents a large risk to Voyageurs National Park, especially considering their proximity to the river system, the need for a tailings impoundment to not fail forever, the connectivity of the surface waters in the watershed and increases in extreme weather events due to climate change.

Dr. Myers condensed and submitted for publication his numerical hydrological model in the peer-reviewed Journal of Hydrology. In the paper, published in February, 2016 and titled, “Acid mine drainage risks – A modeling approach to siting mine facilities in Northern Minnesota USA,” (*J. Hydrology* 533: 277-290.), Dr. Myers demonstrated that:

- Groundwater with substantial contaminant concentrations would discharge to streams whether sourced from deep underground or on the ground surface.
- Even relatively short-term leaks on the surface could cause substantial loads of pollutants to reach the rivers and valuable downstream resources. Underground leaks have lower discharge concentrations but continue for long time periods, such that contamination may not be obvious until after a mine closes and impacts can continue for hundreds of years.
- Longer-term leaks could cause peak concentrations reaching the rivers to be much higher than simulated.
- Releases trending southwest to northeast in the Birch Lake area would discharge to surface water relatively quickly.
- Releases in the headwaters of the Stony River would discharge to nearby surface water.
- Under the course of normal operations, proposed mines near the Boundary Waters Wilderness could cause significant damage to rivers and the Boundary Waters due to leaks to surface waters or substantial groundwater contamination.

Dr. Myers developed and applied a numerical groundwater model to assess the relationship between the proposed Twin Metals Minnesota tailings storage facility and the management and closure of the Peter Mitchell Pit, which is a series of taconite mine pits that have substantial effect on the local groundwater system. The Laurentian Divide, the boundary separating the Boundary Waters Canoe Area Wilderness and Lake Superior watersheds, naturally and originally ran across what is now the location of the Peter Mitchell Pit. Dr. Myers summarized the findings of the model in his 2016 technical memo titled “Twin Metals Mine and the Peter Mitchell Pit, Simulation of the Development of the Peter Mitchell Pit and Its Effects on the Proposed Twin Metals Tailings Impoundment:”

- Removal of bedrock pillars separating the Lake Superior and Boundary Waters watersheds during mining prior to closure of the Peter Mitchell Pit, will essentially move the watershed boundary for a period of time.
- Heavily contaminated seepage from the proposed Twin Metals tailings storage facility would flow from the tailings facility through the bedrock and into the Peter Mitchell Pit for a period of 25-50 years, and thus into the Boundary Waters Wilderness watershed.

Lawrence A. Baker, Ph.D. 2013. In his report entitled “Potential Ecological Impacts of the Twin Metals Mine,” Dr. Baker stated the following conclusions, among others:

- “The potential impacts of the mine are high because this is a very large mine located in an ecologically sensitive area.”
- Fish in these waters are sensitive to acidification; even small changes in pH caused by acid mine drainage (AMD) would result in losses of species. If pH were to decline below 5.0 most species would be lost.
- Leaching of heavy metals associated with AMD impairs fish and other aquatic life.
- Because wild rice is harmed or destroyed by sulfate levels greater than 10 mg/L, and because background sulfate levels in these waters are around 6 mg/L, elevated sulfate levels associated with sulfide-ore copper mining would likely impair wild rice production. It may also harm other rooted aquatic plants.
- Sulfates are a factor in the creation of methyl mercury, which is the form of mercury taken up in the food chain. The increased methylation would increase the concentrations of mercury in fish and thus expose human and other consumers of fish to the risks associated with elevated levels of mercury in their bodies.

- AMD input and elevated sulfate levels would affect the natural cycling of phosphorus between sediments and waters. The release of phosphorus to waters would cause increased algal growth, loss of water clarity and eutrophication.
- AMD and associated contamination may affect a large number of shallow, easily contaminated domestic drinking wells in the area.
- Tailings dam failures, because of an extreme weather event, human error or other reason, pose a serious risk to downstream ecosystems; the downstream distribution of acidic water and sediments contaminated with heavy metals would pollute many kilometers of waters. Damage from metal-laden sediments would persist for years.

Dr. Baker extended his analysis to model the chemical impacts of a possible spill at the Twin Metals mine site, the impacts of water usage by the mine, and the confounding influence of climate change on mine impacts. He reported:

- A mixing model based on observations and studies of realistic AMD generation potential would result in elevated sulfate levels “well above” Minnesota’s 10 mg/liter wild rice standard and likely accelerate mercury methylation in sediments.
- Water withdrawal for copper production is projected by company documents to be 0.8 million gallons per day; water usage in Ely is estimated to be about 0.94 million gallons per day for comparison. Water usage for sulfide-ore copper mining could reduce the decadal low flow of the South Kawishiwi River by 7-13%.
- Water usage, energy usage and tailings productions per unit copper produced increase over the life of a mine.
- Climate change will make it even more difficult to predict impacts, especially those triggered by more extreme precipitation events that threaten mine infrastructure like tailings dams, process ponds and tailings pipelines.

Daniel Engstrom, Ph.D. 2017. Dr. Engstrom is one of the lead scientists studying the effects of sulfate on mercury cycling, wild rice, and sulfur biogeochemistry in Minnesota. In his comment letter to the Forest Service, Dr. Engstrom describes the risk of sulfide-ore copper mining to the Boundary Waters Canoe Area Wilderness and concludes:

“The BWCAW is classified as ‘outstanding resource value water’ under the Minnesota statutes (MAR 7050.0180), whereby: ‘The agency [MPCA] recognizes that the maintenance of existing high quality in some waters of outstanding resource value to the state is essential to their function as exceptional recreational, cultural, aesthetic, or scientific resources. To preserve the value of these special waters, the agency will prohibit or stringently control new or expanded discharges from either point or nonpoint sources to outstanding resource value waters.’ (MAR 7050.0180 Subpart 1). Given the abundance evidence...that sulfate releases from mining operations through the Kawishiwi watershed and into the BWCAW pose substantial environmental risk to these outstanding resource value waters, it is scientifically prudent that mining leases held by Twin Metals and other mining interests be withdrawn by the Secretary of the Interior for a 20-year term as requested by the Forest Service.”

Paul Venturelli, Ph.D., and Bruce Vondracek, Ph.D. 2017. Drs. Venturelli and Vondracek describe in their report “The Fish and Fisheries of the Boundary Waters Canoe Area Wilderness and Voyageurs National Park, and Their Vulnerability to Copper Sulfide Mining” the fish and fisheries of the Boundary Waters Canoe Area Wilderness and Voyageurs National Park, and their vulnerability to copper sulfide mining. Important points include:

- The Boundary Waters Canoe Area Wilderness and Voyageurs National Park support important, healthy recreational and subsistence fisheries with high species and genetic strain richness, which are a direct result of past efforts to maintain the pristine nature and ecological integrity of the region;
- A comparison of fish catches inside and outside of the Boundary Waters Canoe Area Wilderness and Voyageurs National Park suggests that anglers target the Boundary Waters Canoe Area Wilderness and Voyageurs National Park when fishing for lake trout (and other prized cold-water species) and smallmouth bass. State survey data suggest that some game fish species are larger in the Boundary Waters Canoe Area Wilderness and Voyageurs National Park, probably due to relatively large lakes and pristine habitat, and low fishing pressure;

- The scientific literature indicates that acid mine drainage causes long-term declines in fish abundance, species number, and genetic diversity, and may facilitate the establishment of invasive species;
- Acid mine drainage lowers pH and exposes fish and other aquatic organisms to toxic metals (e.g., copper, cadmium, lead, mercury, nickel, and zinc), which accumulate in all major organs, impair system function, cause deformities, behavioral changes, reproductive failure, and mortality, and may render fish unfit for human consumption; and
- Evidence from previous hard rock mines demonstrates overwhelmingly that a copper-sulfide mine in the Rainy River watershed will impact fish, and that such damage is likely to extend far from the mine site and persist for centuries causing damage to a relatively pristine region of the state, and the diversity of popular and rare fishes that it supports

Lee Frelich, Ph.D. 2014. Dr. Frelich, in his report “Forest and Terrestrial Ecosystem Impacts of Mining” has determined that significant negative impacts of sulfide-ore mining would likely occur on terrestrial ecosystems of the Boundary Waters Canoe Area Wilderness and adjacent areas of the Superior National Forest. Those impacts include, among others:

- Forest fragmentation within the mining area, the effects of which would extend into the Boundary Waters Canoe Area Wilderness.
 - Forest fragmentation results in changes to both plant and wildlife communities.
 - Of particular concern are species such as fisher, pine marten and interior forest songbirds that need large tracts of unfragmented forest.
- Disruption of the intricate web of water that flows through the soil, forest roots and other organisms lying on top of bedrock throughout the Quetico-Superior ecosystem. Construction of roads, waste storage and water drawdown would repeatedly disrupt water flow and cause significant additive and cumulative impacts:
 - Interference with the interaction between forests, streams and groundwater.
 - Interference with the flow and chemistry of the water in the ecosystem, resulting in changes in decomposition and nutrient cycling, changes in balance of vegetation types and tree mortality.
 - Because of the interconnectedness of the systems, activities outside the Boundary Waters Canoe Area Wilderness would have impacts within the Wilderness.
- Dispersal of invasive plant species, which would extend beyond the actual surface disturbance from mines and transportation infrastructure.
- Dispersal of nonnative earthworms, which are present but not yet well-established in the area.
 - The movement of soils associated with mining would very likely spread nonnative earthworms to areas not currently infested.
 - Fragmentation would speed nonnative earthworms’ movement across the landscape.
 - Earthworms can trigger a variety of impacts with a wide range of ecological repercussions.
- Loss of native biodiversity.
 - Soil dwelling species that have not yet been discovered, including insects, worms, bacteria and fungi, probably exist in the mining area and could be lost both within the mining footprint and beyond.
- Effects of a vast increase in traffic, including heavy truck traffic, close to the Boundary Waters Canoe Area Wilderness that mining would entail. For example, road salt is likely to cause root damage and tree death for species such as white pine, basswood, red oak, bur oak and red maple. Other impacts of roads on ecosystems and wildlife are well known.
- Changes in wildlife migration and habitat use patterns.
- Effects of windblown dust and other forms of air pollution.
- Additive and synergistic effects of mining with the effects of climate change.
 - Mining would add a significant stressor to a system that will already be stressed, perhaps beyond the point of resiliency.

- Loss to science: the Boundary Waters Canoe Area Wilderness provides a baseline for a landscape otherwise affected by logging, mining, roads, housing and other human activities.
 - “This role of wilderness and other natural areas as a scientific baseline has become critical in the last few decades, to assess the overall impacts of human activity at local, regional and global scales. Without these baselines, we are essentially ‘flying blind’ in our ability to manage ecosystems to provide the many types of services needed by humanity.”

Roger A Powell, Ph.D. 2017. In his report, “Mammals and Mining for Minerals in Sulfur-Bearing Rock Formations in Northeastern Minnesota”, Dr. Powell describes the life histories and vulnerabilities of the mammals of the Boundary Waters Region to effects of sulfide-ore copper mining. Effects of sulfide-ore copper mining on mammals of the Boundary Waters Region would result via numerous pathways, such as:

- pollution of water (all mammals drink);
- pollution, diminishment, or eradication of aquatic vegetation on which many mammals rely as habitat, for forage, or for nutrients like sodium;
- contamination and bioaccumulation of toxic metals such as methyl-mercury in fish and in mammals that consume fish;
- the direct, indirect, and cumulative effects caused by fragmentation of terrestrial habitat required for foraging, mating, rearing, denning, and dispersal; and
- destruction of important habitats, such as mature forested habitats and mature forest-wetland complexes.

John W. Fitzpatrick, Ph.D., Executive Director, Cornell Lab of Ornithology. 2017. In his report, “Birds of Minnesota’s Boundary Waters Canoe Area and Adjacent Upstream Regions, with Comments on Conservation Implications of New Copper Mining Under Consideration,” Dr. Fitzpatrick summarizes the outstanding bird resources of the Boundary Waters Canoe Area Wilderness and adjacent mosaic of habitats located in the Superior National Forest, immediately outside of the Boundary Waters Canoe Area Wilderness, with specific attention to those areas subject to potential copper mining. The Boundary Waters Region is very well known and popularly visited by birders worldwide, who are drawn to the area because the extremely high water quality and mosaic of habitat types in the Laurentian Mixed Forest hosts extraordinary bird species diversity. Key points raised include:

- 225 bird species regularly occur in the Superior National Forest;
- 163 of those species are documented as breeding within the Boundary Waters Canoe Area Wilderness and surrounding areas, *representing 74% of the list of bird species that regularly breed in Minnesota*;
- 60 additional bird species regularly depend on the Boundary Waters Canoe Area Wilderness and surrounding areas as stop-over sites on spring and fall migration;
- 13 of the 86 bird species identified as of significant “continental concern” by North America’s two premier bird conservation consortia (Partners In Flight or PIF, and the North American Bird Conservation Initiative (NABCI)), are hosted in the Boundary Waters Region. “Every possible effort to conserve or restore their highest-quality habitats is essential for conservation of the species,” and “therefore, maintaining the pristine condition of all BWCAW regional habitats” is vital to their long-term conservation.
- The coniferous forests and forest wetlands of the Boundary Waters Region support from 25% to 100% of the habitat of Minnesota’s boreal-zone species, most of which are designated by PIF as “species of stewardship priority for Minnesota.”
- The Boundary Waters Region supports the highest diversity of breeding wood warbler species anywhere in the world – 24 species of wood warblers, which represent 2/3 of all species breeding east of the Great Plains.
- 99 bird species depend on the Boundary Waters Region’s superb aquatic habitats, 31 species for breeding, and 68 for pass-through feeding and resting during migrations.
- The common loon – the iconic state bird and bio-indicator of freshwater ecosystem health – is a top trophic-level consumer and thus highly susceptible to bioaccumulation of methylmercury and other potent heavy metal

toxins. Numerous studies have shown these cause negative effects on loon physiology, feather symmetry, behavior, chick survival, and reproductive success.

- The common loon population on the Superior National Forest experienced an annual decline of 4.2% from 1995 to 2016.
- Even marginal increases in mercury methylation from mining operations could substantially impair common loon populations, and the larger community of fish-eating bird species that rely on the pristine resources of the Boundary Waters Region.

Dave Chambers, Ph.D. 2014. Dr. Chambers reviewed sulfide-ore copper mining in the Duluth Complex and currently available copper mining technologies in his November 2014 report, “The Potential for Acid Mine Drainage and Other Water Quality Problems at Modern Copper Mines Using State-of-the-Art Prevention, Treatment, and Mitigation Methods.” Dr. Chambers found:

- Most of the waste rock and pit wall rock so far studied in the Duluth Complex would contain some sulfur, mainly as the mineral pyrrhotite, a primary cause of AMD. There are essentially no acid-neutralizing carbonate minerals in the waste rock.
- Copper is particularly toxic to aquatic organisms, but current National Ambient Water Quality Criteria for Protection of Aquatic Life for copper are not totally protective of all aquatic species.
- Uncertainties based in the inherent complexity of natural materials and their environments prevent predictive ability, which prevents the conclusion that a mine will have only insignificant impacts.
- Difficulties of adjusting water treatment and seepage collection technologies to meet real-world chemical composition, geomorphology and water cycle variation are much greater than suggested by assumptions within the environmental assessment process.
- No significantly new water treatment technologies have been developed in recent decades. The most complete systems, including reverse osmosis, are highly expensive and require their own follow-up treatment systems.
- No tailings storage facility seepage collection system is perfect (“all liners leak”), and disposing of tailings or waste rock in an old facility would likely use an unlined system.
- The U.S. Environmental Protection Administration has observed that mines continue to operate even if they know their treatment does not meet established water quality standards.
- Records of analogous mines indicate a high likelihood that any mine would release water exceeding its environmental permit within its lifetime.
- “It is not feasible, given today’s or tomorrow’s technology, to reduce the risk of impacting waters downstream from a copper/nickel mine in a sulfide ore body to zero.”

Emmons and Olivier Resources, Inc. 2006. “Cumulative Effects Analysis on Wildlife Habitat Loss/Fragmentation and Wildlife Travel Corridor Obstruction/Landscape Barriers in the Mesabi Iron Range and Arrowhead Regions of Minnesota.” Prepared for the Minnesota Department of Natural Resources, May 15, 2006

This report presents a cumulative effects analysis performed in 2006 for past, present, and what were at the time reasonably foreseeable actions examined the total land loss and impacts on known wildlife corridors for sensitive species in northeastern Minnesota. It found that six of the 12 known wildlife corridors in the 100-mile Mesabi Iron Range will likely become isolated, fragmented, or lost completely, and almost 9,000 acres of habitat will likely be destroyed by mining, economic development, and forestry practices.

Minnesota Environmental Quality Board. 1979. “Minnesota Regional Copper-Nickel Study 1976-1979.” Available < <http://www.leg.state.mn.us/edocs/edocs.aspx?oclnumber=05579755>>, accessed 22 April 2017.

When Minnesota faced the first wave of interest in copper-nickel sulfide-ore mining in the 1970s, it undertook a regional-wide study of the impacts that such mining would have on northeastern Minnesota. The study was

“commissioned because it was believed that conventional site-specific environmental impact statements (EIS’s) and the corresponding regulatory process were inadequate to deal with the broader issues involving this unexploited resource” (Executive Summary, p. i). The resulting 5-volume, 36-chapter study details the study area and the environmental, economic, and social impacts of copper-nickel sulfide-ore mining in the region, and is based on over 180 original technical reports conducted by Environmental Quality Board staff and other experts. Minnesota enacted statewide moratorium on copper-nickel sulfide-ore mining while the study was completed.

Predicted Human Health Impacts to the Boundary Waters Region of Sulfide-Ore Copper Mining

E. Onello, M.D., et al. 2016. “Sulfide Mining and Human Health in Minnesota.” *Minnesota Medicine* 2016 (6) 51-55. This review in *Minnesota Medicine*, the magazine of the Minnesota Medical Association, addresses from a public health perspective the ways in which sulfide-ore copper-nickel mining in the Duluth Complex is distinct from and potentially more hazardous than Minnesota’s traditional iron (taconite) mining. Key points addressed include:

- Sulfide-ore copper mining may affect public health through the release into the environment of amphibole fibers, fugitive dust, and heavy metals;
- Some of the heavy metals expected to be released from Duluth Complex rock include arsenic, asbestos, cadmium, lead, and mercury, which are identified by the World Health Organization as being of major public health concern;
- Mercury is already a public health threat, as the results of a Minnesota Department of Health study found (one in ten infants in Minnesota’s Lake Superior region were born with unsafe amounts of mercury in their blood);
- Sulfide-ore copper mining would exacerbate mercury contamination and bioaccumulation due to the release of additional sulfate – which plays a key role in mercury methylation – into groundwater and groundwater inflows to water bodies; and
- A Health Risk Assessment and Health Impact Assessment should be part of any environmental review on the question of future sulfide-ore copper-nickel mining.

Patricia McCann. “Mercury Levels in Blood from Newborns in the Lake Superior Basin” (Nov. 30, 2011) Final Report. Minnesota Department of Health Division of Environmental Health. GLNPO ID 2007-492. This Minnesota Department of Health study documents that ten percent of newborns in the Minnesota portion of the Lake Superior basin have blood methyl-mercury levels greater than 5.8 ug/L (the U.S. EPA Reference Dose for methyl-mercury), a level associated with loss of IQ. Fetal blood appears to concentrate methyl-mercury at levels 1.7 times higher than maternal blood. Fetuses, infants, and children are four to five times more vulnerable to the harmful effects of mercury.

Minnesota Department of Health, Minnesota Climate & Health Program, Environmental Impacts Analysis Unit. 2014. “Minnesota Climate Change Vulnerability Assessment 2014: Executive Summary.” At <<http://www.health.state.mn.us/divs/climatechange/docs/mnclimvulnreport.pdf>>, accessed 22 April 2017.

Minnesota Department of Health conducted the Minnesota Climate Change Vulnerability Assessment from 2013-2014, and this executive summary and full report presents the findings. The five climate hazards listed as primary threats to Minnesota at large include extreme heat, vector-borne diseases, flooding and flash flooding, and drought.

Minnesota Department of Health, Minnesota Climate & Health Program, Environmental Impacts Analysis Unit. 2015. “Minnesota Climate and Health Profile Report 2015.” Available <<http://www.health.state.mn.us/divs/climatechange/docs/mnprofile2015.pdf>>, accessed 22 April 2017.

Minnesota Department of Health presents a comprehensive assessment of climate change effects, trends, and projections; describes how the changes are linked to potential health impacts; and the resulting burden for the

state. Health hazard pathways described include air pollution, extreme heat, floods and drought, and ecosystem change-related threats to human health.

Predicted Economic Impacts to the Boundary Waters Region of Sulfide-Ore Copper Mining

Spencer Phillips, Ph.D. and Carolyn Alkire, Ph.D. 2017. In their report, “Sulfide-Ore Copper Mining and/or A Sustainable Boundary Waters Economy: The Need to Consider Real Tradeoffs” Drs. Phillips and Alkire describe the key indicators of transition and economic growth in the diversifying and more stable modern economy that exists in the three-county Arrowhead Region, which has developed in the years since the start of mining’s decline in the early 1980s. In the modern Arrowhead economy, amenity-based development has taken the place of mining as the engine of development in the region. The authors describe amenity based development as:

economic activity connected to a region’s scenic, recreational, environmental (clean air, clean water), and other quality-of-life assets. Amenity-based development extends far beyond the recreation and tourism industries to any good- or service-producing industry that sells homes, cars, personal or professional services, food, etc. to people who move to, or stay in, a region because of its scenic beauty, quality of life, and in the case of the Boundary Waters, unique, world-renowned recreational opportunities.

The authors further describe how a mineral withdrawal of 234,328 acres in the Superior National Forest (Withdrawal Study area) would avoid economic costs associated with actual and potential sulfide-ore copper mining that, absent the withdrawal, could proceed in the Withdrawal Study area. These estimated costs include:

- an annual loss of \$288 million in regional spending that would otherwise support 4,490 local jobs, \$76 million in residents’ income, \$31 million in state and local taxes, and \$181 million in proprietors’ income and business-to-business transactions;
- 5,066 to 22,791 lost jobs, and between \$402 million and \$1.6 billion in lost income in the rest of the economy if sulfide-ore copper mining suppresses or reverses growth in the amenity-based economy that has been the backbone of the region’s economy since the early 1980s; and
- \$344 million to \$480 million in lost property value (a one-time drop in asset value) that will spur annual reductions in local property tax revenue throughout the region.

The authors also recommend a set of studies, valuations, and surveys that the U.S. Forest Service should include in the economics section of the Environmental Impact Statement. These include:

- a systemic survey of business owners and managers in all sectors to estimate the effect of potential sulfide-ore copper mining on the outlook for Minnesota, and especially the Arrowhead Region;
- a thorough, statistically valid survey of residents, visitors, vacation and second homeowners, and other stakeholders decisions about whether to vacation, retire, locate, or stay in the region under alternative scenarios;
- a hedonic price survey of residential, commercial, and other property values in areas where similar mining operations have occurred;
- an examination of the extent to which forecasted mining employment at lower- and higher-wage positions would be available to and occupied by current Arrowhead residents;
- an evaluation of the proposed action’s avoided effects on all ecosystem services (timber production, fish and game and plant foods, water for drinking, recreational opportunities as valued by impacts and benefits, and other ecosystem benefits); and
- an estimate of impacts to passive-use value.

S. Phillips, Ph.D. 2014. "The Boundary Waters Canoe Area...Wealth Generator."

Dr. Spencer Phillips sought to characterize the existing economy in the Boundary Waters Region, defined as the three counties surrounding the Boundary Waters Canoe Area Wilderness. He found that the Boundary Waters is an important driver of wealth, and supports the local and regional economy. Specifically, the report states that the natural amenities of the Boundary Waters and surrounding Superior National Forest provide a critical component to a thriving rural economy, and that property values increase with proximity to a wilderness area. Dr. Phillips also examined likely negative economic impacts from allowing sulfide-ore copper mining to proceed within the Boundary Waters watershed, including displacing the existing economy supported by natural amenities, tourism, forestry, and recreation. Erratic boom and bust cycles associated with mining would have economic costs, as well, as they would create instability in the labor markets and increase strain on public services.

T. Power, Ph.D. 2007. "The Economic Role of Metal Mining in Minnesota: Past, Present, and Future."

Dr. Thomas Power's report investigates the economic role of metal mining in Minnesota within the context of metal mining across the country and over time. He found that economic benefits of proposed sulfide-ore copper mining would be uncertain at best. Automation and other laborsaving technology have greatly reduced the need for workers in new sulfide-ore mines. From 1972 to 2007, while US copper production fluctuated above and below 1.5 million metric tons, the number of copper-mining jobs dropped by 71%. Similar trends occurred in the Minnesota taconite-mining sector between 1979 and 2005, where labor productivity tripled and production declined modestly, resulting in 73% fewer Minnesota taconite-mining jobs. Employment would still have declined by 67% even if production had remained constant. Of special concern to the Boundary Waters region is Power's statement, "For adjacent communities that do not have diversified economies and rely heavily on mining, this pattern of labor-displacing technological change means regular layoffs and relatively high unemployment rates, even when high levels of production are maintained" (p. 6).

E. Hjerpe, Ph.D. 2017. "Regional Economic Impacts of Boundary Waters Wilderness Visitors."

This study quantified out-of-region Boundary Waters visitor spending in summer 2016 created nearly 1,000 full and part-time jobs in the three county Boundary Waters Region. These visitors spent nearly \$57 million in the three counties, generating \$77 million in economic output.

Timberjay. 2017. An economic analysis published by the Timberjay on August 3, 2017 provides an in-depth look at some of the potential economic costs associated with a proposed sulfide-ore copper mine in the Ely area.

This conservative analysis is a case study of one specific mine proposal, the Twin Metals mine, and the economic impact it would have on income generated by local residents in the Ely area (Ely and the four neighboring townships). The study concludes that the opening of a Twin Metals mine could lead to an initial loss of anywhere from \$22.9 million to \$28.6 million in local income, a figure that will likely increase over time. This economic loss of local income would exceed any gain in local income from a Twin Metals mine.

Sun, B. 2013. "Land use conflict in an iron range community: an econometric analysis of the effect of mining on local real estate values and real estate tax collections." Oral Presentation, University of Minnesota-Morris.

An econometric study of a gold and silver mine's effect on local real estate values in Fairfield County, South Carolina, showed that property sale prices decreased with increasing proximity to the mine.

E. Hjerpe, Ph.D. and S. Phillips, Ph.D. 2013. A Review of “The Economic Impact of Ferrous and Non-Ferrous Mining on the State of Minnesota and the Arrowhead Region.”

An expert critique of an industry-funded economic study that is widely used to promote positive economic impact from bringing every single proposed sulfide-ore copper mine in northeastern Minnesota online. Drs. Hjerpe and Phillips (natural resource economists) reviewed the study and found that it inappropriately included all ongoing ferrous and non-ferrous mining operations in addition to future construction and operation, resulting in an overstated total economic impact. Additionally, they found, “Inclusion of existing operations indicates a lack of understanding economic impact analysis and grossly exaggerates impacts. In reality, such rapid mining expansion would come at the loss of existing mining industry due to increased cost of supply inputs and decreased market prices of final products from flooded local markets” (p. 7). Finally, the job increases projected in the study were to be realized by 2016 (instead mining jobs declined). Over 90% of the projected job gains were to be in the taconite industry; less than 10% were projected for the copper industry.

Assumptions for the assessments by Dr. Myers, Dr. Baker, Dr. Frelich, Dr. Chambers, Dr. Venturelli, Dr. Vondracek, Dr. Powell, and Dr. Fitzpatrick:

- Twin Metals Minnesota deposits would be developed in accordance with the 2014 Technical Report 43-101, Duluth Metals, Inc., with state-of-the-art methods, facilities, and management practices.
- Studies addressed impacts and risks that are likely to occur regardless of changes in mine plans.

Performance Record of Hardrock Mining and Potential Impacts to the Boundary Waters Region

Earthworks summarized the state of current US copper mining environmental impacts in its peer-reviewed report “U.S. Copper Porphyry Mines: The Track Record of Water Quality Impacts Resulting from Pipeline Spills, Tailings Failures, and Water Collection and Treatment Failures” (July 2012, revised November 2012). Earthworks found:

- Of fourteen sulfide-ore copper mines representing 89% of U.S. copper production found that 100% of the mines studied had experienced pipeline spills or other accidental releases, and 92% (13 of 14) had experienced water collection and treatment failures resulting in significant effects on water quality.
- Leaks occur at all mines.
- Although the likelihood of a particular type of leak cannot be predetermined (and this is true even with a detailed, comprehensive mine plan), the probability of some type of leak is high.

L.N. Bowker and D.M. Chambers. 2015. “The Risk, Public Liability, & Economics of Tailings Storage Facility Failures.” Bowker Associates, Science and Research in the Public Interest, Stonington, ME, and Center for Science in Public Participation, Bozeman, MT.

Lindsay Newland Bowker, CPCU, ARM, and Dr. David Chambers, professional engineer, examined 100 years of tailings storage facility failures and found that despite industry assurances to the contrary, the risk of serious and very serious failures is increasing. While technological advances have allowed miners to economically recover increasingly lower grade ore, the design of storage facilities for waste rock, tailings and waste water has not kept pace with the increasing volume of waste that must be stored in perpetuity. Additionally, the tight bottom lines faced by companies extracting poor quality ore at low metal prices contributes to the challenge of maintaining tailings storage facility integrity since the techniques that reduce risk are often prohibitively expensive. Bowker and Chambers found that 49% of all recorded “serious” and “very serious” failures between 1940-2010 occurred since 1990. Included were failures at operating mines and mines in the U.S. and Europe. These failures are large enough to cause serious damage, involve loss of life, or contribute other types of significant social or economic damage, which can be non remediable. They project that with increasing numbers

of mining projects extracting increasingly low-grade ore the rate of serious or very serious tailings storage facility failures will increase, which will carry catastrophic results.

D.M. Chambers. 2015. A Review of the “Report on Mount Polley Tailings Storage Facility Breach, Independent Expert Engineering Investigation and Review Panel.” Center for Science in Public Participation, Bozeman, MT.

Dr. Dave Chambers of the Center for Science in Public Participation reviewed the report on the 2014 tailings storage facility failure at the Mount Polley copper mine. Dr. Chambers summarized the causes of the dam failure and the ineffective monitoring technologies that failed to warn anyone that a catastrophic failure was about to occur. Dr. Chambers also emphasizes the panel’s conclusion that the industry must work toward a goal of zero tailings dam failures, which is not currently the industry’s goal.

D.M. Chambers, and B. Higman. 2011. “Long Term Risks of Tailings Dam Failure.” Center for Science in Public Participation, Bozeman, MT, and Ground Truth Trekking, Seldovia, AK.

Report describing the high risks of long-term storage of tailings using large dams since they must remain intact forever, and yet have a higher incidence of failure than water reservoir dams. The authors argue that since technology and science have limits, policy makers should use a more conservative approach to making decisions about long-term risk than currently used.

Earthworks. 2013. “Polluting the Future: How mining companies are contaminating our nation’s waters in perpetuity.”

This report from Earthworks documents the extent to which perpetual pollution from hard rock mining in the United States has contaminated vast amounts of the nation’s fresh ground – an increasingly valuable and scarce essential resource. An estimated 17 to 27 billion gallons of water will be polluted by just 40 mines every year in perpetuity, and yet no open pit hard rock mine in existence today has demonstrated the ability to stop acid mine drainage once it has begun on a large scale.

D. Giurco, and J.G. Petrie. 2007. “Strategies for reducing the carbon footprint of copper: New technologies, more recycling or demand management?” *Minerals Engineering* 20: 842-853. doi:10.1016/j.mineng.2007.04.014

In this peer-reviewed journal article, the authors conducted a life-cycle analysis of mined copper to estimate the copper industry’s CO₂ contribution and climate change impacts. The carbon emissions from primary mined copper is expected to increase over time, due to the decreasing quality of ore and increasing amount of industrial effort and energy necessary to extract and process the ore. A case study of US copper production demonstrates the importance of improving recycling techniques and share of the copper market to reduce the industry’s carbon impact.

J.R. Kuipers, Maest, A.S., MacHardy, K.A., and Lawson, G. 2006. “Comparison of Predicted and Actual Water Quality at Hardrock Mines: The reliability of predictions in Environmental Impact Statements.” Kuipers & Associates, Butte, MT, and Buka Environmental, Boulder, CO.

The research team compared the predictions of water quality impacts from hardrock mines made during the environmental review phase to actual water quality impacts that occurred at hardrock mines once they were built. They studied a representational sample of hardrock mines subject to environmental review under the National Environmental Policy Act in order to create a comprehensive picture of the predicted versus actual water quality impacts. Of the case study mines, sixty percent caused surface water quality exceedances, and at the majority of the mines, impacts occurred despite predictions that no impacts would occur after mitigation efforts were put in place. Of the case study mines, most mines predicted no groundwater quality impacts after

mitigation was in place, but impacts occurred in a majority of the cases. The effectiveness levels of mitigation measures were consistently overestimated, leading to unexpected surface water and groundwater impacts. Finally, “nearly all of the mines (8/9) that developed acid mine drainage either underestimated or ignored the potential for acid drainage in their EISs” (p. ES-8).

B. Loechel, J. Hodgkinson, and K. Moffat. 2013. “Climate change adaptation in Australian mining communities: Comparing mining company and local government views and activities.” *Climatic Change* 119(2): 465-477. doi:10.1007/s10584-013-0721-8

Future climate change impacts will increase the uncertainty around whether mining infrastructure, including tailings storage facilities and process water ponds, will retain their structural integrity over time. To avoid catastrophic failure, mining companies must plan for an uncertain future that includes increased severity and frequency of extreme weather events. This study surveyed mining companies and local governments in Australia to assess the mining companies’ and governments’ perception of future impacts from climate change. The authors found a striking lack of concern for future impacts, “suggesting discounting of risks due to climate change skepticism.” While specific to Australia, this study demonstrates how personal and industry attitudes toward climate change can increase the risk of catastrophic impacts from mines built without considering necessary adaptation techniques.

M. Rico, G. Benito, A.R. Salgueiro, A. Díez-Herrero, and H.G. Pereira. 2008. “Reported tailings dam failures: A review of the European incidences in the worldwide context.” *Journal of Hazardous Materials* 152: 846-852. doi:10.1016/j.jhazmat.2007.07.050

The research team compiled records for European tailings dam failures within the context of tailings dam failures around the world in an effort to describe the distribution of tailings dam failures and identify risk factors. Out of 147 identified tailings dam failures around the world during an unspecified period of time, 57 occurred in the United States. The paper reports another index of tailings dam incidents that recorded 185 tailings dam incidents in the United States between 1917-1989, and many additional tailings dam incidents were known to occur after 1990.

E.J. Sherlock. 1995. “Evaluation of Static and Kinetic Prediction Test Data and Comparison with Field Monitoring Data” (MAS thesis). Retrieved from MEND database. MEND Project 1.16.4.

This master’s thesis compared methods of predicting acid mine drainage potential with actual field data for a tailings impoundment once it was developed. Sherlock found that there can be great variability in acid generation predictions, and that the predictions depend on many factors that can lead to incorrect predictions. For instance, sites predicted to have “no acid generating potential” often use short-term studies that do not consider the extended length of time material will be exposed to oxidizing conditions. In one case, it took three years of continued kinetic testing of tailings in humidity cells for acid rock drainage conditions to manifest, and many kinetic tests during environmental review processes do not allow such long-term testing.

Related Ecological Studies and Potential Impacts to the Boundary Waters Region

W.M. Daniel, D.M. Infante, R.M. Hughes, Y.P. Tsang, P.C. Esselman, D. Wieferich, K. Herreman, A.R. Cooper, L. Wang, and W.W. Taylor. 2014. “Characterizing coal and mineral mines as a regional source of stress to stream fish assemblages.” *Ecological Indicators* 50: 50-61.

In 2014, a team of researchers from Michigan State University, Oregon State University, the USGS Great Lakes Science Center, and the International Joint Commission Great Lakes Regional Office published a study in the

peer-reviewed *Ecological Indicators* journal that showed the potential for mines to be sources of regional stress on fish assemblages (groups of fish that co-occur in an ecosystem) over large spatial scales. Daniel et al. built on an established body of research showing local negative impacts to fish habitats, fish species diversity, and fish size and survival in streams and their immediate basins in close proximity to coal and mineral mines. This team, however, broadened their inquiry to assess relationships between mine density and indicators of fish assemblage health on a regional scale, across multiple streams and catchments. While this study did not address mines in northern Minnesota, it did look at three broad ecoregions (Northern Appalachian Ecoregion, Southern Appalachian Ecoregion, and Temperate Plains Ecoregion) and showed consistent trends of negative, cumulative impact from mines to fish assemblages across all of them at the regional/multi-catchment scale.

D.C. Evers, L.J. Savoy, C.R. DeSorbo, D.E. Yates, W. Hanson, K.M. Taylor, L.S. Siegel, J.H. Cooley Jr., M.S. Bank, A. Major, K. Munney, B.F. Mower, H.S. Vogel, N. Schoch, M. Pokras, M.W. Goodale, and J. Fair. 2008. "Adverse effects from environmental mercury loads on breeding Common Loons." *Ecotoxicology* 17: 69-81. <http://dx.doi.org/10.1007/s10646-007-0168-7>

This research team studied groups of loons in New Hampshire and Maine to determine the effects of methylmercury loads on the breeding success of Common loons. They found that the loons at highest risk for environmental mercury contamination had 41% fewer fledged young than the reference group of lower risk loons, demonstrating the negative impacts methylmercury can have on loon populations.

S.R. Jennings, D.R. Neuman, and P.S. Blicher. 2008. "Acid Mine Drainage and Effects on Fish Health and Ecology: A Review." Reclamation Research Group Publication, Bozeman, MT.

This review paper describes the ways that acid mine drainage (AMD) negatively affects fish health and ecology. Oxidation and hydrolysis reactions turn formerly stable minerals into toxic materials, including acid, metals (e.g., mercury, copper, cadmium, nickel, lead, arsenic, and zinc), and sulfates (react to form sulfides). Acidic conditions further catalyze these reactions, making them proceed at faster rates than would otherwise occur. AMD can affect fish populations and aquatic ecosystems both through direct toxicity and by indirect effects on the food chain and habitat availability. For instance, high acidity (low pH) can alter gill membranes and cause hypoxia among fish, and pH below 6.5 can have negative effects on fish reproductive success. Indirect effects to fish include direct toxicity to food sources (e.g., insects and other macroinvertebrates that live in streambeds), reduction of habitat, and coating of gravel beds used for spawning. Episodes of acute toxicity can kill thousands of fish in a number of minutes, as occurred in 1989 when a thunderstorm event caused enough acidification and elevated copper concentrations within 20 minutes to kill over 5,000 salmonids in Montana's Clark Fork River.

D.C. Tozer, C.M. Falconer, and D.S. Badzinski. 2013. "Common Loon reproductive success in Canada: the west is best but not for long." *Aviation Conservation and Ecology* 8(1): 1. <http://dx.doi.org/10.5751/ACE-00569-080101>

This long-term study of loons in Canada emphasizes their importance at the top of the food chain, and the threats they face from methylmercury. The Common Loon is a "powerful indicator of local aquatic system health, especially in relation to mercury and acid precipitation" (p. 1). Elevated methylmercury levels create neurological and physiological problems for loons, including increased lethargy, reduced food-seeking behavior, and reduced ability to avoid predators (Tozer et al. 2013). Data collected over 18 years across Canada showed a relationship between smaller lakes with higher methylmercury exposure and low pH and reduced loon reproductive success, and the study suggested that "mercury and acid precipitation are among the most important drivers of Common Loon reproductive success in southern Canada" (p. 9).

Best Practices for Siting Mines in Ecologically and Culturally Significant Areas

Robert M. Hughes, Felipe Amezcua, David M. Chambers, Wesley M. Daniel, James S. Franks, William Franzin, Donald MacDonald, Eric Merriam, George Neall, Paulo dos Santos Pompeu, Lou Reynolds & Carol Ann Woody. 2016. "2016 AFS [American Fisheries Society] Position Paper and Policy on Mining and Fossil Fuel Extraction, Fisheries," 41:1, 12-15, DOI; [10.1080/03632415.1121742](https://doi.org/10.1080/03632415.1121742); <http://dx.doi.org/10.1080/03632415.2016.1121741>.

This paper recommends substantive changes in how North American governments conduct environmental assessments and permit, monitor, and regulate mine and fossil fuel development. AFS recommends that a formal environmental impact statement should be done first, and following such a study, the public should be involved in deciding whether a mine...is the most appropriate use of land and water, particularly relative to the need to preserve ecologically and culturally significant areas.



Low nickel prices a hurdle for new mines

Analysts see little prospect for rebound any time soon

07/26/2017 By: Marshall Helmberger

<http://timberjay.com/stories/low-nickel-prices-a-hurdle-for-new-mines.13531>

REGIONAL— Nickel prices could continue to plumb historically low levels for the foreseeable future, according to a new analysis by BMI Research, as reported by Mining.com, and that trend could complicate the economic prospects for new copper-nickel mining ventures in the region.

Nickel production is now expected to increase globally this year for the first time since 2013, due to a loosening of a nickel import ban in Indonesia and the ousting of a government minister in the Philippines who has advocated for more intensive environmental protections for mining operations there.

The increased production and availability of nickel is not presently being met by rising demand for nickel, however, which BMI projects could keep nickel prices suppressed for several years.

Goldman Sachs has also downgraded its price forecasts for nickel through at least 2018. As of Wednesday, nickel was trading at \$4.52 per pound, reflecting slight improvement over the last month.

The latest news on nickel is likely to complicate the financial picture for PolyMet's proposed NorthMet mine, although company officials note that their project remains economically viable even with lower overall metal prices than at present. The public should get a better look at PolyMet's financial picture in the months ahead as part of the permitting process for the mine.

DNR Assistant Commissioner Barb Naramore said recently that the agency will be seeking more financial details from PolyMet before making a final decision on whether to issue the company a permit to mine. "I don't have additional details at this point regarding the timing or scope of what we will require," Naramore added.

The company did produce a definitive feasibility study in 2006 and provided updates to the report in 2008 and 2013. But much of the financial data dates back to 2008, making it now nearly a decade old. While the impact of metal prices on the company's finances is relatively easy to estimate, it's less clear how the intervening years have affected projected operating costs at the mine.

The depressed state of nickel prices is likely to be offset to some extent by higher-than-projected prices for palladium and the sudden dramatic improvement in cobalt prices, but neither of those metals constitutes a significant portion of projected revenue for the project. In early projections, PolyMet had anticipated that nickel— then trading for \$10-\$12 per pound—would constitute nearly 40 percent of revenues from the project. In 2008, the company's financials pegged nickel prices at \$12.20, or roughly three times its current price.

While the project would appear to remain financially viable, relatively low metal prices do increase the level of risk, both for PolyMet investors as well as state taxpayers, who could be left on the hook for cleanup at the mine if the company were to go bankrupt, as frequently happens in the mining industry.

That's a concern raised by EOR, the financial consultant hired by the DNR to advise the state on financial assurance for the project. "The NorthMet mine economics are very sensitive to the metal commodity price assumptions," states a report issued by the consultants in December. "When metal prices are high, the revenue can generate a healthy cash flow, but when prices are low, the revenue can drop as much as \$150 million per year, thus reducing the rate of return and increasing the economic risk," the consultants conclude.

While the company continues to make progress in the permitting process, investor interest has waned in recent months, with PolyMet stock currently trading at around 60 cents per share, the lowest price range in nearly a decade.

The generally sluggish metals market is creating other financial concerns for mining ventures, such as a lack of investment interest in the sector. According to Mining.com, a new report from a London-based financial research firm provides more evidence of the current diminished interest in mining ventures from investors. The July 7 article, titled "Private capital says no to mining," highlights the research of London financial research firm, known as Preqin, which made note in a recent quarterly report that private investment in the natural resources sector was the lowest the sector has seen since 2011. "What is of more concern to the growth of the asset class is the continued lack of funds closing to pursue opportunities in industries other than energy," according to Preqin's report. "While there are many funds currently in market that are looking to focus on agriculture, timber or mining, these vehicles do not seem to be able to secure capital and hold a final close."

Tom Carr, head of real assets products at Preqin, described the current lack of fundraising for investment in metals and mining as "worrying."

Preqin tracks private investment, which includes traditional private equity, venture capital funds, turnaround funds, and direct lending. The lack of interest in the mining sector is in stark contrast to most other sectors, where private investment is at near-record levels.