

Existing mine pit and natural lakes in northern Minnesota as predictors of total mercury concentration of a mine pit at closure

C.J. Twaroski *Barr Engineering Company, USA*

L.I. Segroves *Barr Engineering Company, USA*

Abstract

Open pit mining of taconite ore has been ongoing in northern Minnesota since the early 1900s and mine pit lakes are a common feature on the Mesabi Iron Range. The approximate western half of the Iron Range is within the Mississippi River watershed and the approximate eastern half is within the Lake Superior Basin watershed. In the Lake Superior Basin the outflow water from pit lakes is required to meet a standard of 1.3 nanograms per litre (ng/L) for total mercury concentration. The average concentration of mercury in precipitation in northern Minnesota is approximately 12 to 13 ng/L (1996–2009 time period). Available surface water chemistry data indicate that a number of existing mine pit lakes on the eastern end of Minnesota's Iron Range and several remote lakes in Voyageurs National Park (located about 50 km to the north of the Iron Range) have annual average total mercury concentration in the water column or outflow water that is less than 1.3 ng/L. Characteristics of pit lakes and natural lakes set in bedrock, when compared to other lake-specific research findings in the Upper Midwest, suggest that atmospheric mercury deposited to these water bodies is likely removed from the water column by volatilisation back to the atmosphere and by sedimentation and burial in the bottom sediments.

As part of the environmental review and permitting process in Minnesota, mining companies with projects in the Lake Superior Basin watershed are asked to demonstrate that the potential total mercury concentration in the outflow from the closed mine pit will comply with the 1.3 ng/L standard for total mercury. Using data from existing mine pit lakes and natural lakes in northern Minnesota as predictors of future conditions it is likely that a mine pit at closure will comply with the total mercury water quality standard.

1 Introduction

Recently proposed mining projects in northeast Minnesota (Figure 1) will have one or more pit lakes at closure. Water balance calculations indicate that the respective pits will be filled within 30 to 45 years after mining is completed and have a surface water discharge. Because several of the pit lakes are within the Lake Superior watershed, the respective water discharges will be required to meet a total mercury concentration limit of 1.3 nanograms per litre (ng/L).

2 Mass balance approach

The proposed future pit lakes are predicted to fill primarily with water from precipitation and runoff of precipitation from the watershed i.e. stormwater runoff. For one project, some of the runoff water is expected to be channelled flow from a nearby second pit that will have been filled in and converted to a shallow water wetland.

Regulatory agencies in Minnesota have asked the respective project proposers to demonstrate that all proposed pit lake discharges will meet the surface water quality standard of 1.3 ng/L of total mercury. Screening-level mass balance calculations and data from existing pit lakes and precipitation-dominated natural lakes provide preliminary indications that the proposed future pit lakes will likely meet the 1.3 ng/L standard.



Figure 1 Location of the Mesabi Iron Range in northeast Minnesota

3 Background data and considerations

3.1 Estimated total mercury deposition in northern Minnesota

Annual precipitation in northern Minnesota ranges from approximately 61 cm near International Falls (western edge of Voyageurs National Park) to approximately 76 cm on the eastern end of the Iron Range (USDA, data from 1971 through 2000).

The background concentration of total mercury in precipitation averages 12 to 13 ng/L (National Atmospheric Deposition Program, Fernberg Road Site, MN18, 1996–2009). For open areas, wet deposition of mercury in northeast Minnesota is estimated to be about 8.5 to 9 micrograms per square metre per year ($\mu\text{g}/\text{m}^2/\text{yr}$) (National Atmospheric Deposition Program, Fernberg Road Monitoring Site, MN18).

Grigal (2002) identified that atmospheric deposition of mercury to forests is about 4 times open precipitation because of additions from throughfall, washoff of dry deposition and litterfall (dropping of senescent leaves that accumulated atmospheric mercury). Wiener et al. (2006) estimated that deposition to forest canopies in northern Minnesota ranged from 290 to 390% of direct wet deposition, with total deposition for northern Minnesota ranging from about 25 to 33 $\mu\text{g}/\text{m}^2/\text{yr}$. Chen et al. (2008) estimated dry deposition for the Western Lake Superior Basin watershed to be approximately 16 to 17 $\mu\text{g}/\text{m}^2/\text{yr}$. Overall in northern Minnesota, total deposition of mercury (wet + dry) could be as high as 25 to 33 $\mu\text{g}/\text{m}^2/\text{yr}$, with dry deposition being approximately 60% of total deposition.

3.2 Surface water total mercury concentrations and water body and watershed characteristics

Relatively recent data from a number of streams in northeast Minnesota indicate that total mercury concentrations ranged from 0.9 to 10 ng/L (MDNR, 2009). Total mercury concentrations in lakes tend to be lower than in streams, ranging from less than 1 to about 4 ng/L, but generally being 2 ng/L or lower (Brigham et al., 1999; Goldstein et al., 2003; MPCA, 2008).

Data from Goldstein et al. (2003) indicate that several lakes in Voyageurs National Park, located on the Minnesota–Canada border in northeast Minnesota approximately due north of the Iron Range (Figure 1), have total mercury concentrations less than 1 ng/L. As described by Wiener et al. (2006), Voyageurs National Park is an 886 km² park along the Minnesota–Ontario border, east of International Falls, MN. The Park contains many small interior lakes and wetlands, principally on the Kabetogama Peninsula, which is surrounded by three larger lakes: Rainy, Kabetogama, and Namakan. Watersheds in the park are largely forest-covered and characterised by thin soils and abundant outcrops of Precambrian bedrock. Annual precipitation averages about 68 cm, and lakes are typically ice covered for 5–6 months of the year. The lakes with total mercury concentrations less than 1.3 ng/L tend to be small and receive most of their water from direct precipitation i.e. precipitation-dominated lakes. Concentrations of total mercury in these lakes range from approximately 0.3 to 1.7 ng/L, with most concentrations for individual samples being less than 1.3 ng/L (Table 1).

For the lakes studied in Voyageurs National Park, total mercury concentrations in unfiltered samples were highly correlated with total organic carbon (TOC), with TOC used as an indicator of wetland influence (Goldstein et al., 2003; Wiener et al., 2006). The more wetland influence, the higher the concentration of TOC; the less wetland influence, the lower the concentration of TOC. When comparing the total mercury concentrations reported by Goldstein et al. (2003) with the TOC concentrations reported by Wiener et al. (2006), the lakes with the lowest total mercury concentrations have the lowest TOC concentrations, indicating very little watershed influence in these lakes. These same lakes were found by Goldstein et al. (2003) to have low dissolved silica which can be used as an indicator of a lake's landscape position; lower silica indicates a position high in the landscape with the lake receiving a greater proportion of their input waters from precipitation than lakes lower in the landscape (Webster et al., 1996; Kratz et al., 1997).

Watras and Morrison (2008) provided data for precipitation-dominated lakes in north central Wisconsin that indicated water falling on the terrestrial watershed short-circuited the watershed i.e. water delivered to the lake as overland flow, and was delivered to the surface water relatively unchanged. Total mercury concentration in runoff ranged from 7 to 12 ng/L, similar to the total mercury concentration in rainfall. This short-circuiting of precipitation from the watershed adds to the influence of precipitation on the characteristics of the surface water.

Mine pit lakes are common on Minnesota's Iron Range and according to Axler et al. (1992) have been filled primarily from groundwater. However, recent mass balance calculations for several mining projects indicate that precipitation and surface runoff from the watershed are likely to be the major contributors to pit filling, with groundwater contributing from 10 to 30% of the water (Barr Engineering Company, unpublished data). When precipitation and surface runoff are the primary contributors to mine pit water, these mine pit lakes can be considered precipitation-dominated systems.

Table 1 Total mercury concentration data for selected mine pit lakes and natural lakes in northeast Minnesota

Pit or Lake Name	Sample Number	Average (ng/L)	Range (ng/L)
Cruiser Lake [1]	3	0.43	0.39–0.46
Fishmouth Lake [1]	5	1.25	0.97–1.73
Little Trout Lake [1]	5	0.52	0.38–0.86
Mukooda Lake [1]	5	0.44	0.34–0.55
O’Leary Lake [1]	5	0.64	0.47–0.78
Pit 1	6	0.95	0.5–2.3
Pit 1 [2]		1.13	
Pit 2/2E	1	0.87	N/a
Pit 2W	3	1.61	0.99–2.55
Pit 2WX	2	1.19	1.18–1.19
Pit 2WX [2]		0.97	
Pit 3	2	1.16	0.65–1.66
Pit 5N	1	0.74	N/a
Pit 5N (East)	1	1.08	N/a
Pit 5S	2	0.55	0.52–0.58
Pit 6	9	1.0	0.5–2.11
Pit 6 [2]		0.9	
Pit 9	2	1.02	0.86–1.18
Pit 9 [2]		0.7	
Pit 9S	2	1.87	1.49–2.24
Pit 9S [2]		0.9	
Knox Pit [2]		1.2	
Stephens Pit [2]		0.4	
Dunka South [3]	2	0.75	0.7–0.8
Dunka Middle [3]	2	0.80	0.6–1.0
Dunka North [3]	2	0.65	0.6–0.7

[1] Data from Goldstein et al., 2003, for lakes in Voyageurs National Park. Selected precipitation-dominated lakes with minimal wetlands in the watershed; surface water samples collected in 2001 and 2002.

[2] Baseline monitoring data for mine pits in the Aurora and Hoyt Lakes area of northeast Minnesota submitted to the Minnesota Department of Natural Resources and the Minnesota Pollution Control Agency.

[3] Data reflects intersection of portions of the Dunka Pit with the Duluth Complex in northeast Minnesota.

Mercury concentrations in the mine pit lakes are similar to the concentrations found for precipitation-dominated lakes in Voyageurs National Park. Total mercury concentration data from several mine pit lakes in the Hoyt Lakes area of northeast Minnesota are provided in Table 1 and indicate that average total mercury concentrations in surface water are generally less than 1.3 ng/L.

Recently proposed copper-nickel mining in the Duluth Complex is a new development for northeast Minnesota and concerns have been raised about potential differences in the mercury concentration of surface

water exposed to rock formations associated with taconite mining versus copper-nickel mining. The Dunka Pit is of interest because a portion of the pit intersects with the Duluth Complex. For the respective portions of the Dunka Pit (south, middle, north), total mercury concentrations in the surface water are below 1.3 ng/L (Table 1). Because the Dunka Pit intersects the Duluth Complex, and it has been present on the landscape for a number of decades, these data are considered an important indicator of potential total mercury concentrations for any proposed mine pits at closure.

3.3 Mercury removal processes in water bodies and implications for mine pit lakes

For drainage lakes that receive water and chemical contributions from their watersheds via tributary streams/rivers, the watershed is an important source of mercury loading (Grigal, 2002; Watras and Morrison, 2008). As indicated by the data from Goldstein et al. (2003) and Wiener et al. (2006), lakes in Voyageurs National Park that have higher TOC concentrations that indicate more watershed influence tend to have higher total mercury concentrations. In contrast, available data for precipitation-dominated lakes in Minnesota e.g. Voyageurs National Park, and Wisconsin indicate these systems tend to have lower total mercury concentrations, generally on the lower end of the range and often less than 1.3 ng/L.

Research on mercury cycling in the environment indicates that about 90% of total mercury input to a water body is removed from the system either through sedimentation (i.e. burial) or volatilisation back to the atmosphere (i.e. evasion) (Porcella, 1994; Watras and Morrison, 2008). Table 2 summarises information from selected lakes investigated by various researchers in Wisconsin.

Table 3 indicates that burial rates for mercury in smaller precipitation-dominated lakes in Minnesota and Wisconsin are estimated to range from 17 to 33 $\mu\text{g}/\text{m}^2/\text{yr}$. The estimated burial rate represents approximately 60 to 95% of total mercury inputs from the atmosphere. The average estimated burial rate of 22.6 $\mu\text{g}/\text{m}^2/\text{yr}$ represents about 80% of the estimated average background deposition of total mercury in northern Minnesota.

As described by several studies (Porcella, 1994; Watras et al., 2000; Watras and Morrison, 2008), precipitation-dominated lakes in northern Wisconsin indicate the following:

- Particulate mercury accounted for almost all of the mercury input as wet and dry deposition.
- Input of mercury from surface water and from groundwater was negligible, supporting the assumption of a system dominated by atmospheric inputs.
- Deposition input to the lakes was balanced by sedimentation plus evasion and in some lakes a small flux to the ground water.
 - For Little Rock Lake, evasion of mercury as elemental mercury from the lake to the atmosphere was about 5% of the deposited input. Others have estimated evasion as a similar percentage of atmospheric deposition for other lakes (Brigham 1992; Lorey and Driscoll 1999). Other seepage lakes that have been studied indicate evasion ranging from about 10 to 50 percent of the total deposition (Porcella, 1994).
 - Evasion rates typically have a large degree of uncertainty associated with them.
 - More than 90% of atmospheric deposition was deposited into the sediment.

Table 2 Estimated annual loss of total mercury for selected lakes in the Upper Midwest, USA

Lake	Units	Input	Evasion Rate	Percent of Input	Sedimentation Rate (net)	Percent of Input	Outflow (stream)	Percent of Input
Devils Lake, Wisconsin ^[1]	grams	3.07	N/a		2.31 [2]	75%	0.69	22%
Little Rock, Wisconsin ^[3]	µg/m ²	9.2	1.2	13%	8.1	88%	N/a	
Little Rock, Wisconsin ^[4]	µg/m ²	5.1	1.0	20%	4.2	82%	N/a	

N/a = not applicable.

Units: µg/m² = micrograms per square metre.

[1] Data from Watras and Morrison, 2008; mean values for the 2002 to 2004 time period.

[2] For Devils Lake, Watras and Morrison (2008) reported the term Sedimentation and Evasion.

[3] Data from Watras et al., 2000; estimated total mercury budget for 1995.

[4] Data from Watras et al., 2000; estimated total mercury budget for 1999.

Table 3 Estimated burial rates of mercury for selected lakes in the Upper Midwest, USA

Lake	Burial Rate (µg/m ² /yr)	Location (State, USA)	Reference
Cedar	20	Minnesota	Brigham et al., 1992
Mountain	33	Minnesota	Brigham et al., 1992
Little Rock	17	Wisconsin	Brigham et al., 1992
Kjostad	26	Minnesota	Brigham et al., 1992
Meander	23	Minnesota	Brigham et al., 1992
Meander	20	Minnesota	Engstrom and Swain, 1997
Dunnigan	17	Minnesota	Brigham et al., 1992
Thrush	25	Minnesota	Brigham et al., 1992
Average	22.6		

In those cases where mine pits receive the majority of their water from precipitation, the processes that affect mercury cycling and surface water concentrations in precipitation-dominated natural lakes likely are applicable to mine pit lakes as well. The data from Porcella (1994), Watras et al. (1994) and Watras and Morrison (2008) indicate that the predominant processes for mercury loss in a precipitation-dominated water body are sedimentation and evasion. Therefore, these two processes need to be included into any mass balance approach developed for predicting future concentrations of total mercury for a pit lake.

4 Conclusions

Preliminary water balance estimates for several proposed pit lakes indicate that precipitation and runoff from the watershed are the major inputs of water. There is a smaller contribution of groundwater to pit filling (10 to 30%), but it is considered relatively minor compared to the precipitation and runoff inputs (70% or more).

Because of the known removal of total mercury by sedimentation and evasion processes in precipitation-dominated lakes, there is a high probability that the same processes will predominate in mine pit lakes that receive most of their water from precipitation and runoff from the watershed. The available data from natural lakes that receive most of their water inputs from direct precipitation suggest that mine pit lakes that

predominantly receive their water from precipitation are likely to have surface water and discharge water total mercury concentrations less than 1.3 ng/L.

References

- Axler, R., Larsen, C., Tikkanen, C. and McDonald, M. (1992) Intensive aquaculture in abandoned Minnesota iron ore pits: Environmental and regulatory perspectives. viewed 28 April 2011: http://www.techtransfer.osmre.gov/NTTMainSite/Library/proceed/asmr92/section_3e2.
- Brigham, M.E. (1992) Accumulation of mercury in Minnesota, Alaska, and Wisconsin lakes. Thesis for MS Degree in Civil Engineering, University of Minnesota. Minneapolis - St. Paul, MN.
- Brigham, M.E., Olson, M.L. and Dewild, J.F. (1999) Mercury, methylmercury, and other water-quality data from flood-control impoundments and natural waters of the Red River of the North basin, Minnesota, 1997–99. USGS Open File Report 99-273A (p 34).
- Chen, C.W., Herr, J.W. and Goldstein, R.A. (2008) Model calculations of total maximum daily loads of mercury for drainage lakes. *J. American Water Resources Assoc.*, Vol. 45, pp. 1295–1307.
- Engstrom, D.R. and Swain, E.B. (1997) Recent declines in atmospheric mercury deposition in the Upper Midwest. *Environmental Science and Technology*, 1997, Vol. 31, pp. 960–967.
- Goldstein, R.M., Brigham, M.E., Steuwe, L. and Menheer, M.A. (2003) Mercury data from small lakes in Voyageurs National Park, northern Minnesota, 2000–02. U.S. Geological Survey, Open File Report 03-480.
- Grigal, D.F. (2002) Inputs and outputs of mercury from terrestrial watersheds: A review. *Environ. Rev.*, 2002, Vol. 10, pp. 1–39.
- Kratz, T.K., Webster, K.E., Bowser, C.J., Magnuson, J.J. and Benson, B.J. (1997) The influence of landscape position on lakes in northern Wisconsin. *Freshwater Biology*, 1997, Vol. 37, pp. 209–217.
- Lorey, P. and Driscoll, C.T. (1999) Historic trends of mercury deposition in Adirondack lakes. *Environ. Sci. Technol.*, Vol. 33 (5), pp. 718–722.
- MDNR (2009) Minnesota Department of Natural Resources. Sulphate and Mercury Chemistry of the St. Louis River in Northeastern Minnesota. A Report to the Minerals Coordinating Committee. Division of Lands and Minerals, 500 Lafayette Road, St. Paul, MN 55155. Draft Report, June 2009.
- MPCA (2008) Minnesota Pollution Control Agency. MERCLKS water ecoregion data. Unpublished data from the Minnesota Pollution Control Agency Environmental Outcomes Division (St. Paul, MN); data as of 22 January 2008.
- Porcella, D.B. (1994) Mercury in the environment: Biogeochemistry in Mercury Pollution, Integration and Synthesis, C.J. Watras and J.W. Huckabee (eds), Lewis Publishers, Boca Raton, FL., pp. 3–19.
- USDA (1997–2000) U.S. Department of Agriculture. National Weather and Climate Center. Natural Resources Conservation Service. Climate information retrieval for Minnesota, by county. Viewed 26 April 2011, <http://www.wcc.nrcs.usda.gov/>
- Watras, C.J. and Morrison, K.A. (2008) The response of two remote, temperate lakes to changes in atmospheric mercury deposition, sulphate, and the water cycle. *Can. J. Fish. Aquat. Sci.*, Vol. 65, pp. 100–116.
- Watras, C.J., Morrison, K.A., Hudson, R.J.M., Frost, T.M. and Kratz, T.K. (2000) Decreasing mercury in northern Wisconsin: Temporal patterns in bulk precipitation and a precipitation-dominated Lake. *Environmental Science and Technology*, Vol 34, pp. 4051–4057.
- Webster, K.E., Kratz, T.K., Bowser, C.J., Magnuson, J.J. and Rose, W.J. (1996) The influence of landscape position on lake chemical responses to drought in northern Wisconsin. *Limnol. Oceanogr.*, Vol. 41(5), pp. 977–984.
- Wiener, J.G., Knights, B.C., Sandheinrich, M.B., Jeremiason, J.D., Brigham, M.E., Engstrom, D.R., Woodruff, L.G., Cannon, W.F. and Balogh, S.J. (2006) mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors. *Environ. Sci. Technol.* 2006, Vol. 40, pp. 6261–6268.

