

# **Mercury and Mining in Minnesota**

Minerals Coordinating Committee  
Final Report

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## Summary

Mercury is a naturally occurring element that is ubiquitous in the earth's crust. It is released to the environment by natural processes and anthropogenic activities and transported worldwide through atmospheric and aquatic reservoirs. Increased Hg loading to the environment has ultimately led to increased Hg in freshwater fish, often to levels considered unsafe for human consumption. This has, in turn, led to global, national, and statewide efforts to reduce mercury emissions. The present document summarizes mercury cycling in NE Minnesota where an economically important iron-mining district ("taconite") operates within a region prized for its many fishing lakes.

As is the case in most regions, mercury loading in NE Minnesota is dominated by atmospheric deposition. Most mercury deposited on land is revolatilized, but a significant fraction is incorporated into local soils with only a relatively small component transported to lakes. Only a tiny fraction of the mercury deposited in any region is converted to methylmercury ( $\text{CH}_3\text{Hg}^+$ ), the type of mercury that accumulates in fish. Considerable uncertainty exists concerning relationships between mercury emission, deposition, methylation, and bioaccumulation. However, recent research (METAALICUS) suggests much of the methylated mercury in a lake is generated in surface sediments but comes from "new mercury" that was recently deposited on the lake surface (e.g., precipitation within the last season) and conveyed to the bottom via particle transport.

Average mercury concentration in NE Minnesota precipitation is higher than dissolved mercury in most streams and lakes, underscoring the importance of sedimentation and uptake by soils and vegetation in regional mercury cycles. Atmospheric deposition of mercury from precipitation appears to be increasing or holding steady since 1990 despite large reductions in Minnesota's statewide emission rates. Lake sediment records indicate that mercury is being delivered to lakes at rates much greater now than in pre-industrial times, but some lakes reveal recent declines. Mercury concentrations in fish inhabiting surface waters are sufficiently high to trigger consumption advisories, but in more lakes than not, fish-Hg levels are declining.

Taconite processing in NE Minnesota potentially participates in the mercury cycle in three ways: (1) by releasing spent water that was originally obtained from precipitation and other freshwater supplies, (2) by generating tailings that interact with the environment, and (3) by emitting mercury to the atmosphere through stack emissions. Release of mercury to waters during taconite processing appears to be insignificant since the water sampled from tailings basins has mercury concentrations that are lower than local precipitation and similar to normal surface waters. Most of the dissolved mercury in taconite tailings basins may have come from atmospheric sources, rather than from mineral processing. Stack emissions are clearly the dominant pathway of mercury release from taconite processing on the iron range.  $\text{Hg(II)}$  in ore concentrate is converted to  $\text{Hg(0)}$  during the firing of pellets and released to the atmosphere in stack emissions. Emission factors reflect primary distribution of mercury in the ore body, and generally

increase in a westward direction across the district from 1 to 17 kg Hg per million long tons of pellets.

Atmospheric Hg emissions from taconite processing exceeded 100 kg/yr in the late 1960's, and have ranged between approximately 200 and 400 kg/yr ever since. The great majority of this mercury is transported out of the state and distributed globally, contributing approximately 0.24% and 0.007%, respectively, to national and global totals. No suitable technology has been found to curtail taconite mercury emissions. Regardless of whether currently active research on the iron range provides a cost efficient and effective method to limit mercury emissions from taconite processing, significant reduction of mercury deposition to Minnesota lakes will require global reductions in mercury emissions.

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## 1. Introduction

Human activities since the industrial revolution have increased atmospheric deposition of mercury to lakes compared to pre-industrial times (Swain et al., 1992; Engstrom and Swain, 1997; Engstrom et al., 1999; Fitzgerald et al., 1998). The resulting increased environmental availability of mercury has led, in turn, to increased uptake of the element by many aquatic organisms, including fish that may be consumed by humans. Mercury in fish tissue is now the leading cause for issuance of consumption advisories for fish captured in Minnesota lakes, just as it is at many localities throughout the US.

In an attempt to reduce mercury deposition to lakes, US legislation has mandated emission regulations for coal-fired power plants, previously identified as the largest anthropogenic emitter of mercury to the atmosphere (EPA, 1997). Decreased emissions from this and other sources will likely help Minnesota to reach statewide mercury emission reduction goals which were set during 1999 state legislation, and include reducing mercury emissions from 1990 levels by 60% in 2000 and 70% by 2005. Already, decreases in Hg release from industrial sectors where effective control measures are easiest to implement have led to large reductions in Minnesota statewide mercury emissions. At the same time, however, these decreases have effectively increased the proportion of current statewide Hg emissions for industries where control measures are either not available or difficult to implement. One such industry is taconite processing, which has seen its share of statewide emissions increase from 16% in 1995 to 20% in 2000, making it the second largest current source of Hg emissions in Minnesota (Table 1). As the primary domestic supplier of iron ore to US steel manufacturing companies, however, Minnesota is the only state where taconite processing is considered a major emitter of mercury. Important timelines for reduction of Hg from this source may include 2007 and 2010 when mercury “total-maximum-daily-load” (TMDL) limits must be set for the Great Lakes Basin and Minnesota (statewide), respectively (MPCA, 2001).

Northeastern Minnesota is a region prized not only for its economically important taconite mining industry, but also for its many wetlands and fishing lakes. Thus, the Minnesota Department of Natural Resources has undertaken this two-year study on mercury cycling and distribution in northeastern Minnesota, with emphasis on taconite processing. The overall goal of this study is to provide a technical foundation and background that can be used to guide mercury research and future discussions regarding the development and application of mercury regulations to Minnesota’s taconite industry.

## 2. Mercury Chemistry

Mercury occurs in the environment in two forms: zero-valent Hg(0) (or elemental mercury) and doubly charged Hg(II) (or oxidized mercury). Hg(0) is a liquid in pure form at room conditions, but vaporizes when in contact with the atmosphere. Because it has low solubility in water and does not adsorb readily to solids, Hg(0) emitted into the atmosphere generally remains there until it is oxidized to Hg(II). Hg(II) readily combines with other compounds to form non-volatile species that are both water-soluble and adsorb to solids. These properties promote a return of the element to terrestrial and aquatic environments through wet and dry deposition. While much of the mercury deposited

from the atmosphere in terrestrial environments may be revolatilized and returned to the atmosphere, a significant fraction is retained in local soils, sediments, and biota. Ultimately, only a very small fraction of mercury deposited in a region is incorporated in the tissues of fish.

Seasonal, annual, and spatial variations, as well as the high cost and technical specialization associated with low-level mercury analysis, make it difficult to determine an absolute mercury budget for any single watershed. However, based on a review of data from forested watersheds in temperate and boreal zones, Grigal (2002) provided a general description and semi-quantitative understanding of the most important processes. In detail, mercury deposition in a region can be divided into three distinct categories: that associated with litterfall (captured by and transported with falling vegetation), that in throughfall (rinsed from vegetation during precipitation), and mercury deposited in open precipitation (direct dry and wet deposition). Mean reported flux values for these three transport mechanisms for a region like NE Minnesota are approximately 21, 17, and 10  $\mu\text{g m}^{-2} \text{a}^{-1}$ , respectively. Grigal suggested that the dominance of the first two terms (21 and 17) over the last (10) indicates the relative importance of vegetative matter as a trap and transport mechanism for mercury. These data further indicate that the flux of mercury to the forested portion of a watershed can be much greater than that for open water (approximately 4x or  $(21+17+10)/10$ ).

On the other hand, most mercury deposited in a forested watershed appears to be revolatilized (e.g., mean value is 32  $\mu\text{g m}^{-2} \text{a}^{-1}$ ) by poorly understood processes. The primary step must involve reduction of Hg(II) back to Hg(0), but how this occurs is uncertain. Most of the remaining non-volatilized mercury is sequestered by soils (5  $\mu\text{g m}^{-2} \text{a}^{-1}$ ) and only a small fraction is transported out in streams (e.g., 1.7  $\mu\text{g m}^{-2} \text{a}^{-1}$ ) (Grigal, 2002). As a result, only about 5-25% of the mercury deposited on forested lands typically winds up in streams and lakes but, depending on the relative surface area of lakes and lands, this can account for between about 5 and 85% of the mercury delivered to lakes.

Mercury sequestration and transport in terrestrial and aquatic environments most commonly involves complexation with organic molecules, the most important of which appear to be fulvic and humic acids. A particularly strong affinity exists between Hg(II) and reduced-sulfur functional groups such as thiol (Skylberg et al., 2000). The capacity for organic molecules to bind with mercury in soils and streams typically exceeds mercury availability, meaning that any unbound Hg(II) is “captured” and transported with organic “captors”. As a consequence, strong correlations are often found between mercury concentration and dissolved or particulate organic carbon (Sorenson et al., 1990; Fleck, 1999; Kolka et al., 1999). The later correlation becomes more important in watersheds characterized by draining of peat lands, which, owing to slow growth and efficient adsorption of mercury, can accumulate mercury deposited from many centuries of precipitation. Groundwaters, by contrast, typically have little or no detectable mercury because nearly all of the mercury in infiltrating waters is captured by soils.

Although most terrestrial and aquatic mercury interactions involve organic compounds, one reaction that deserves special consideration is methylation, or the generation of methyl-mercury ( $\text{CH}_3\text{Hg}^+$  or “MeHg”). This species, although representing only a small fraction of dissolved mercury in lakes, accounts for nearly all of the mercury

present in the tissues of fish. MeHg is a persistent bioaccumulative compound, meaning that once formed, it can remain in the environment where, owing to a high affinity for living tissues, it accumulates up the food chain. MeHg is not “emitted” into the environment, but rather produced from Hg(II) that is present in the environment. Gilmour et al. (1992) were the first to recognize that bacterial reduction of  $\text{SO}_4^-$  to  $\text{S}^-$  is associated with increased generation of methylmercury. Benoit et al. (1999) hypothesized later that methylation of mercury occurs at the transition zone between oxidizing and reducing conditions, where dissolved neutral Hg-sulfur species, having the ability to penetrate the cell membranes of methylating bacteria, are most likely to form. Their results, which revealed a direct correlation between calculated abundances of neutral Hg-sulfide complexes and rates of mercury methylation, support this idea. Kelley et al. (2003) recently provided data disagreeing with this model, however, and suggested an alternative explanation involving an  $\text{H}^+$  facilitated mechanism for cell-uptake of mercury.

Hg(II) can also form complexes with other inorganic species (e.g.,  $\text{Cl}^-$ ), and can adsorb to solids. Indeed, most of the mercury in wet and dry precipitation is inorganically bound Hg(II), but most of this mercury quickly combines with organic carbon or sulfide in terrestrial and lake environments. Owing to the low solubility of HgS (cinnabar), dissolved Hg(II) is virtually absent from solutions when sulfide ion becomes abundant.

Although much has been learned about specific reactions that might affect mercury distribution, a more important question concerns identification of the most important pathways that exist between anthropogenically released mercury and fish uptake. The chain connecting mercury deposited from the atmosphere to mercury taken up by fish has many links, many of which are not fully understood. However, a multi-institutional collaborative study named “METAALICUS” (Mercury Experiment To Assess Atmospheric Loading In Canada and the United States, Hintelmann et al., 2002) has recently provided clues to the more important processes by introducing isotopically labeled Hg to a lake and its watershed and tracking its dispersal in the environment.

In an initial phase of the study, most of the mercury applied to a forested area surrounding a small Canadian lake (Hintelmann et al., 2002) remained bound to vegetation and soils in the application area. Less than 1% of the new mercury was rinsed into the lake and approximately 8% was revolatilized. In a more recent study phase,  $^{202}\text{Hg}$  was added directly to the lake surface and other isotopes,  $^{200}\text{Hg}$  and  $^{198}\text{Hg}$ , were added to surrounding wetland and upland areas, respectively (Krabbenhoft and Goodrich-Mahoney, 2003). The  $^{202}\text{Hg}$  isotope spike was found in sediment traps on the lake bottom within six days of application and continued to accumulate throughout the summer months. Simultaneously,  $\text{Me}^{202}\text{Hg}$  spread upward from the sediments into the water column. The isotope spikes added to the land around the lake did not contribute significantly to any of the various lake-mercury reservoirs (water column, sediments, MeHg). Although full results and discussion have not yet been published, the data provide evidence that mercury deposited on the surface of a lake is conveyed relatively rapidly to the sediments via particle transport, and it is this “new” mercury that appears to provide the dominant source of bioaccumulative MeHg to the water column.

### **3. Mercury Distribution in NE Minnesota**

As is apparent from the discussion above, concentration of mercury in a lake or stream, or in the tissues of fish or in other aquatic species that inhabit a watershed may be functions of a large number of parameters (Glass et al., 1990). Considering the seasonal and annual variations in precipitation and the fact that no two lakes are identical (e.g., underlying geology and topography, vegetation, soil development, relative distributions of forest, wetland, and open water), it is not surprising that there is considerable variation in the mercury levels of northeastern Minnesota lakes. Moreover, mercury appears to be very transient in its behavior, meaning that relatively recent effects (rainfall, enhanced sedimentation or runoff, filtration) can cause the concentration at a single location to vary, depending on when and how the sample was collected. For an organism such as a fish, mercury may accumulate through its lifetime and mercury concentration may reflect a time-integrated snapshot of mercury uptake processes.

The following brief summary of mercury distribution in NE Minnesota is meant to provide information on the quality and quantity of mercury data that exist for the region.

#### **3.1 Precipitation**

A considerable database has been developed on recent precipitation in the US, largely through efforts of the Mercury Deposition Network (MDN) which is part of the National Atmospheric Deposition Program (NADP) (Vermette et al., 1995; Glass et al., 1999; NADP, 2002). Currently, there are over fifty MDN sites nationwide that collect and report high quality mercury data for precipitation. Four of these sites are located in Minnesota: including one near Ely and another at the Marcel research center near Grand Rapids.

Both Ely and Marcel stations began reporting on mercury deposition in early spring of 1995. Additional mercury data for precipitation in NE Minnesota are reported for the period 1990 to 1995 by Glass and Sorenson (1999). In that report, data are included for stations located in or near Duluth, Finland, International Falls, and Ely. Data for 1988 and 1989 are also available for Marcel, Ely, and Duluth (Sorenson et al., 1990; Glass et al., 1991), however, the reported concentrations were conspicuously elevated compared to those in the later two datasets and compared to precipitation in many other similar stations elsewhere in the world. Noting this discrepancy, Sorenson et al. (1994) reported that the higher values for 1988 and 1989, as compared to 1990 or 1991 may have been related to either a change in sampling procedures or to changing local emissions, and did not include the data in subsequent studies. The 1988 and 1989 data are also excluded here.

Combining data from 1990 to 1995 from Glass and Sorenson (1999) and the data collected since then from northern Minnesota MDN sites (Marcel and Ely), we can evaluate trends in mercury concentration for precipitation (Figure 1a) and for wet deposition (Figure 1b) on an annualized basis for the twelve-year period extending from 1990 through 2001. Data in Figure 1a suggest that the volume-averaged concentration of mercury in regional precipitation in northern Minnesota have been relatively level or slightly rising in the last decade. Data in Figure 1b suggest that total wet deposition of

mercury is also relatively level, or slightly increasing in the region, although the dataset is noisier than that for concentration.

Because data from the beginning and end portions of the twelve-year period were generated by two different research groups, it is possible that the apparent increasing trends could be related to minor differences in sampling or analytical procedures. However, Glass and Sorenson (1999) argue that increases in wet mercury deposition for the abbreviated time period of their study (1990-1996) were already statistically meaningful. They suggested that the increasing trend is due to an increase in atmospheric mercury owing to increased coal consumption in the region.

Increasing mercury in precipitation is in direct contrast to global atmospheric data (Slemr et al., 2003) and also to data from 1994 through 1999 generated at the Trout Lake station in northern Wisconsin. Atmospheric mercury as measured at various stations in the Northern Hemisphere appears to have decreased greatly during the early 1990's and leveled off in the period since 1996 (Slemr et al., 2003). Meanwhile, mercury in both precipitation and surface waters from the precipitation-dominated Trout Lake in Northern Wisconsin appeared to be on a decreasing trend (Watras et al., 2000). Moreover, many, but not all, lakes in Minnesota record decreasing mercury accumulation in sediments following periods of peak accumulation in the 1960's and 1970's (see section 3.4 below). Spatial and temporal changes of mercury in precipitation are apparently very complicated on a regional scale, but the twelve years of continuous precipitation records in NE Minnesota suggest mercury concentrations may have been increasing, or at least not decreasing.

### **3.2 Lakes and Streams**

A search of the US EPA's "STORET" database (EPA, 2002) provided mercury concentrations for 84 lakes in NE Minnesota, nearly all of which were sampled in 1991 and referenced to the MPCA. Samples were collected just beneath the surface of the lake using clean techniques and analyzed by a sensitive technique (cold vapor atomic fluorescence spectroscopy or "CVAFS") (Swain, E., MPCA, personal communication). Additional data for approximately 80 lakes sampled in 1996 were found in a recent report by Glass et al. (1999). Samples for this study were also collected using clean techniques, but from a 1-meter depth and then analyzed using a less sensitive, but widely accepted method (Cold vapor atomic absorption spectroscopy or "CVAAS"). Finally, data from an additional 80 lakes in NE Minnesota sampled in 1988 were found in Sorenson et al. (1989, 1990). Hg data from the lakes where samples were analyzed by the more sensitive CVAFS technique are shown in Figure 2. As can be seen, considerable variability exists for lake mercury, but the values are all less than that of average precipitation.

The most striking difference between the different datasets is they had greatly different ranges in mercury concentration. The STORET database values range up to 10 ng/L while mercury concentrations reported by Glass et al. (1999) are all less than 3 ng/L for a similar set of lakes. Hg concentrations in the Sorenson et al. study are similar to the 1991 STORET data, ranging in concentration up to 7 ng/L. In that study, a significant positive correlation was found for total Hg and total organic carbon (TOC), consistent with the general consensus that most mercury in lakes is associated with organic carbon. Similar correlations and concentration ranges have been reported elsewhere, including

New York (Driscoll et al., 1995) and Wisconsin (Watras et al., 1995). The reason for the different ranges in mercury concentrations is unknown.

There is a near complete absence of readily available information on mercury concentrations in lake waters for the region extending southeastward from the iron range to the Lake Superior shoreline. Some indication of mercury levels in that area can also be found in stream data. The EPA's STORET database reported mercury concentration data for six rivers draining into Lake Superior from NE, Minnesota. Samples were collected on monthly intervals during the summer of 1996 (Figure 3). Again, the data were collected and analyzed using clean techniques by the MPCA. Concentrations generally varied from 2 to 6 ng/L (reported as total mercury recovered), but two concentrations reported for the Knife River were well above these values (9 and 14). With the exception of those two higher values the concentrations are similar to those reported for area lakes in the STORET database.

Abundant stream data has also been reported from the Marcel research station near Grand Rapids, MN, for an area characterized by upland forests and bogs (Kolka et al., 1999). Mercury concentrations up to 50 ng/L were reported for streams draining bogs during periods of high flow, and most of this mercury was bound to particulate organic carbon. Because this form of carbon settles from the water column under calmer conditions, streams often have much higher total mercury concentrations than lakes.

### **3.3 Fish**

Fish have many orders of magnitude higher mercury concentrations than the waters they grow in. The concentration varies among lakes and species, but within a single lake, mercury in fish tends to increase with size and age. In order to compare mercury concentrations in fish from different lakes, therefore, it is important to compare similar sized fish of the same species.

Two of the largest databases on Minnesota fish mercury levels were generated by Glass et al (1999) and Sorenson et al. (1990). Jeremiason (2002) combined these data with other fish mercury data collected by Minnesota state agencies through 1999 and produced an extensive database of normalized fish-mercury concentrations which allowed assessment of spatial and temporal trends. Empirical relationships were developed to estimate mercury concentrations for a 55 cm northern pike (NP<sub>55</sub>) using mercury concentrations measured in northern pike of other sizes or fish of other species (Sorenson et al., 1990; Jeremiason, 2002).

Recent NP<sub>55</sub> fish mercury concentrations in NE Minnesota range up to approximately 2 µg/g (Fig. 4). For comparison, recent fish consumption advisories began to take effect at a level of 0.038 µg/g Hg, but fish containing 2 µg/g Hg were to be consumed no more than once per month by most people, and no more than approximately once per year by young children or by women of child-bearing age (Table 2). These levels are subject to change as more becomes known about health effects of Hg consumption.

A number of lakes in extreme northern Minnesota have relatively high fish-mercury concentrations, as do some located near the iron range but none of these appear to be close to the highest level for fish consumption advisories. The highest Np<sub>55</sub> mercury

concentrations near the iron range are in Wynne (Np55= 0.60 and 1.11 µg/g in 1996), Esquagama (0.64 and 0.66 µg/g in 1999), Colby (0.82 µg/g in 2000), and Embarrass Lakes (0.64 and 0.94 µg/g in 1999) located on or just south of the eastern side of the Mesabi Iron Range. These values are for a standard sized northern pike of 55 cm as reported by Jeremiason (2002 and personal communication).

Determining whether fish mercury is increasing or decreasing in Minnesota is a difficult task owing to the slow rate at which changes take place and to a relatively sparse dataset for lakes that have had fish measured at least twice over a long period of time. Statewide, Jeremiason (2002) found 114 lakes that had fish mercury data available for 1995 and later and which had been sampled at least 5 years previous. Of these, fish-Hg declined in 63 cases, increased in 22 cases, and stayed approximately the same for 29 lakes, suggesting that fish mercury levels, on average, may be declining. On the other hand, when measurements of fish mercury were grouped according to year, regardless of which lakes were sampled, a regression of fish mercury levels versus time resulted in no significant change with time. Likely, it is too early to tell whether state, national, and international efforts to reduce mercury emissions are having a direct impact on the mercury levels in Minnesota fish.

### **3.4 Historical Deposition**

Much of the mercury delivered to a lake in the form of precipitation or runoff is deposited and stored permanently in sediments. Thus, coring and age-dating the sediments from a lake make it possible to evaluate historical changes in Hg deposition and to evaluate changing mercury transport characteristics for a watershed. Two recent lake sediment studies conducted on lakes in Minnesota include Swain et al. (1992) and Engstrom and Swain (1997), who reported age-dated sediment data from 12 lakes including four in NE Minnesota, and Engstrom et al. (1999) who report data from 50 Minnesota lakes including 20 in NE Minnesota. Actual mercury accumulation rates are highly variable owing to geographic and geologic differences, but cores consistently record increasing mercury accumulation rates since pre-industrial times (Figure 5). These increases can be attributed to increased erosion of soils within disturbed watersheds and to increased global and regional atmospheric deposition.

Not surprisingly, the greatest changes in Hg fluxes to lakes in Minnesota occur in the east central part of the state, near Minneapolis and St. Paul, where watersheds are most likely to have been disturbed and where lakes are located closest to a number of potential mercury sources (e.g., coal combustion, waste incinerators). As is the case for Hg data from lakes and rivers, however, few cores exist to evaluate changes in Hg accumulation rates on or near the iron range. A group of lakes cored near Grand Rapids is well west, and generally “upwind” of the areas currently being mined. Another group of lakes cored near Silver Bay, meanwhile, are relatively close to Northshore mining’s processing plant, but as will be discussed later, the ore processed at this site has much lower mercury concentration than ore mined by the other companies on the iron range.

## 4. Iron Mining in Minnesota

### 4.1 Introduction

The iron mining industry in Minnesota began with discoveries of iron ore in the late 1860's, production on the Vermilion Range in the 1880's, and rapid expansion to the Mesabi Iron Range in the early 1890's and Cuyuna Range in the early 1910's (Emmons and Grout, 1943; Hatcher, 1950; Engesser and Niles, 1997). The so called "natural ore" mined during the first half of the 20th century was high grade, having been oxidized and enriched by extensive weathering near the surface. Most ore of this type required little or no processing before being shipped through the Great Lakes to iron and steel manufacturing facilities in the eastern United States, but beneficiation increased gradually during the early part of the 1900's. From 1906 to 1936, the percentage of ore beneficiated increased in five-year periods as follows: 0.6, 8.9, 9.6, 18.3, 36.3, 35, and 42.0, and increasing to over 50% by 1940 (Emmons and Grout, 1943). Most beneficiation in these early periods involved simple crushing, screening, washing, and drying of the ore, all processes that likely did not result in release of significant mercury.

Mining and beneficiation of taconite, a very hard, relatively low grade, siliceous ore that forms the basis of the iron industry in Minnesota today, began in 1949 after years of research determined how best to utilize this large resource. While the "natural" direct-shipment ore has been largely mined out, it is estimated that there may still be over 200 years of taconite reserves remaining in Minnesota (Ojakangas and Matsch, 1982). Taconite production involves the fine grinding and magnetic separation of ore, and importantly, the conversion of concentrate into pellets. Because, as will be discussed later, Hg release is intrinsically linked to the firing of pellets, airborne Hg emissions from Minnesota's iron industry effectively began with taconite processing in 1949.

In 2003, at the beginning of the year, six active taconite companies remained, all of which mine on the Mesabi Iron Range (Fig. 6). These include, from west to east: National Steel Pellet Company (NSPC) near Keewatin (recently purchased by US-Steel and called Keewatin Taconite Minnesota Ore Operations), Hibbing Taconite (HibTac) near Hibbing, US Steel-Minntac (Minntac), near Mountain Iron, EVTAC Mining (EVTAC), near Eveleth, Ispat-Inland Mining Company (IIMC), near Virginia, and, finally, Northshore (NS) Mining, with mines located near Babbitt and ore processing facility located on the shore of Lake Superior in Silver Bay. EVTAC was in a temporary shut down mode at the time this document was prepared. LTV-Steel Mining company (LTVSMC) is a Cliffs-Erie facility that mined and processed ore on the iron range until 2001, at a site near Hoyt Lakes and located between IIMC and Northshore. In more recent developments on the iron range, newer Direct-Reduction-Iron (DRI) and pig-iron nugget technologies are being considered for mining operations near Nashwauk (the former Butler mine site) and Northshore, respectively. These and similar products, with their higher iron contents, may represent the future of mining production in Minnesota and elsewhere in the world.

## 4.2 Taconite and the Biwabik Iron Formation

All taconite companies in Minnesota currently mine ore from the Biwabik Iron Formation. This formation is similar to banded iron formations found throughout the world, all of which were deposited primarily from 1.8 to 2.6 billion years ago, during a period of time when oxygen in the Earth's atmosphere was becoming more available. This oxidation led to world-wide deposition of iron from seawater. In Minnesota, near-surface exposure of the Biwabik Iron Formation strikes east-northeast in a continuous band extending approximately 120 miles from a location southeast of Grand Rapids to a point near Babbitt, where it is truncated by the Duluth Complex. Sandwiched between the Pokegama Quartzite below and the Virginia Formation above, the Biwabik Iron Formation ranges in thickness from about 200 to 750 feet, and dips approximate 5 to 15° towards the southeast (Morey, 1972). The relatively planar feature is interrupted by several major structural features, the most prominent of which is the so-called "Virginia Horn". This feature, consisting of the Virginia syncline and parallel Eveleth anticline, produces, in surface expression, a seven-mile curved offset of the formation between EVTAC and Minntac (Fig. 6). The crest of the Eveleth anticline, traced using geophysical methods, plunges into the subsurface in a southwesterly direction (Morey, 1972).

Taconite is a sedimentary rock, probably deposited originally as a mixture of  $\text{Fe}(\text{OH})_3$  and varying proportions of other common material (silica, carbonates, organic carbon, iron-sulfides, clays) and converted to present form during diagenesis or low-grade regional metamorphism (Morey, 1972; Perry et al., 1983; Thode and Goodwin, 1983; Bauer et al., 1985). Eastern sections of the formation have been subjected to thermal metamorphism, especially near Babbitt, where intense heating occurred during intrusion of the Duluth Complex (Morey, 1972; Ojakangas and Matsch, 1982). Although the metamorphism in that area has not seriously affected the major element geochemistry, it has certainly affected mineralogy, as the primary low temperature silicate phases (minnesotaite, greenalite, stilpnomelane, and chamosite) have been replaced by a compositionally equivalent high temperature phase assemblage (quartz, amphibole, magnetite, pyroxene, fayalite, cummingtonite). By comparison, isotopic data on minerals recovered from the western side of the district suggest peak "metamorphic" temperatures were less than 100 or 150° C (Morey, 1972).

## 5. Mercury Release from Taconite Processing

There are two potential primary sources of mercury during taconite processing: (1) mercury released from processing of the ore and (2) mercury released from fuels used when processing the ore. Of these two categories, the first is clearly dominant and will be discussed in detail below. Coal is the primary source of mercury in fuels used by mining companies, but only Minntac and EVTAC commonly use coal to fire their pellets. However, it takes only about 20 to 30 lbs of coal to fire one long ton of pellets (Engesser, personal communication), so for this to be a significant source of mercury compared to pellets, the concentration would have to be much higher. Mercury concentrations for coal used by mining companies (included in the appendix) are similar to those in the unprocessed ore, so this report focuses on mercury distribution in the ore.

## 5.1 Mercury in Taconite Ore

Mercury concentrations in the Biwabik Iron Formation reflect concentrations of the element deposited with the original sediment as modified by diagenetic, metamorphic, and weathering processes. Despite a significant amount of chemical work on the Biwabik Iron Formation, relatively few data exist which can be used to confidently quantify the abundance and distribution of mercury in taconite ore. Data from the most extensive study of mercury distributions in the Biwabik Iron Formation (Morey and Lively, 1999) cannot be easily reconciled with data from numerous other studies conducted on samples collected from mineral processing facilities (Appendix I). Both datasets are described here along with possible explanations for observed discrepancies.

Morey and Lively (1999) reported mercury concentrations for approximately 200 samples collected from drill core at three sites south of the present area of mining. Collectively, the samples had a mean value of 79.2 ng/g (ppb) for mercury concentration, but the ore zone had slightly lower mercury concentrations near Biwabik (56.82 ppb, n=13) and Keewatin (70.9 ppb, n=12) and slightly higher near Buhl (90.2 ppb, n=10). Replicate analyses were made at three other laboratories. Results from Frontier Geosciences, Seattle Washington, who employed a more sensitive technique (cold-vapor atomic fluorescence spectrometry, or CVAFS with detection limit of approximately 0.5 ppb) than that used in the rest of the study (cold vapor atomic *absorption* spectroscopy or CVAAS; detection limit about 5 to 10 ppb) proved to be systematically lower than values obtained from the other three labs, sometimes by more than 70%. Morey and Lively noted this, as well as the large differences between concentrations they measured and those reported for materials presently being mined (Engesser and Niles, 1997). Further research and appropriate iron formation standards were needed to explain the disparate results.

As a result of limitations in the above data, mercury measurements from a large number of studies conducted at taconite processing facilities (Engesser and Niles, 1997; Engesser, 1998a,b, 2000; Monson et al., 2000; Lapakko and Jakel, 2000; Benner, 2001a,b) were compiled (Appendix 1) and summarized in Table 3 and Figure 7. Mercury concentrations from freshly crushed, non-beneficiated ore samples ranged in value from 0.6 up to a maximum of only 32 ppb, well below the values reported by Morey and Lively (including the subset of samples analyzed by Frontier Geosciences). Moreover, there is general agreement among data collected in various studies, providing evidence of a relatively clear trend in mercury concentration for unprocessed ore. Mercury concentration at the west end of the district is only about 20 ppb but increases gradually eastward to a maximum of 32 ppb and then decreases gradually again to a value less than 1 ppb in thermally metamorphosed ore at Northshore. A similar geographic trend is present in the Morey and Lively data, but their reported concentrations are elevated over those at the present mining surface by approximately 50 ppb.

Engesser and Niles (1997) noted an association between mercury and sulfur concentrations at Minntac and LTVSMC's facilities. This introduces the possibility that higher Hg concentrations reported by Morey and Lively (1999) for deep drill core might be related to the presence of higher sulfur concentrations than near the surface. Thus, mercury concentrations from Morey and Lively (1999) were plotted as a function of

sulfur concentration (for the same core intervals as reported earlier by Morey, 1992) and compared to similar data for presently mined ore from Engesser and Niles (1997) (Fig. 8). The mercury values reported by Morey and Lively (1999) are clearly elevated for samples having similar sulfur as reported by Engesser and Niles (1997), indicating that the high mercury cannot be attributed to increased sulfur.

Another possibility to consider is that of Hg contamination for the dataset reporting the higher numbers: Morey and Lively (1999). In this regard, the potential for significant mercury contamination in powdered samples is demonstrated by the results of mercury adsorption experiments conducted by Fang (1978). This study found that 2.0 gram powdered mineralogical samples adsorbed up to 5  $\mu\text{g}$  of Hg from air containing 79.2  $\mu\text{g}/\text{m}^3$  Hg(0) in a few weeks. Furthermore, mercury was still rapidly adsorbing to the solids when the experiments ended and the adsorbed mercury was not later released when samples were placed into a vacuum. These data indicate that powders exposed to air for long periods of time could experience increasing concentrations of mercury.

Of relevance to the contamination question, in this case, is the fact that samples collected by Morey and Lively (1999) were garnered from a previous study (Pfleider et al., 1968), and had been stored as powders for approximately 30 years prior to being analyzed for mercury. Although Hg concentrations typical for indoor air are three orders of magnitude less than those used in Fang's experiments (Carpi and Chen, 2001), the powders analyzed by Morey and Lively were exposed for a much longer period of time than that used in the experiments. Furthermore, because the samples analyzed by Morey and Lively (1999) were stored in cardboard boxes, rather than in air-tight glass or plastic containers, temporary exposure to air containing high levels of Hg from common products, such as latex paints, pesticides, fungicides, or detergents or from the accidental breakage of Hg-containing devices (fluorescent lights, tilt switches, thermostats), cannot be ruled out. Because of the possibility of mercury adsorption from air, data from Morey and Lively (1999) are not considered further in the present study. Distribution of mercury in ores deep in the subsurface may well be similar to those in ore presently being mined today (See Fig. 7), but the possibility of elevated Hg values should not be ignored. Conducting further analyses on fresh core samples could potentially clarify this issue.

Perhaps more significant than bulk mercury concentration, especially regarding atmospheric emissions, is the concentration of mercury in magnetite, the primary ore mineral from which iron is derived. During processing, magnetite is magnetically separated from other solids in the composite ore and the resulting concentrate is rolled with other minor components (fluxing agents, binders) into balls (greenballs). It is the magnetite dominated "greenballs" that are introduced into the indurating furnaces where mercury emissions are generated. Mercury concentrations in "concentrate" and "greenball" were found to be statistically similar to each other, and these concentrations were almost always lower than concentrations in the bulk ore, especially at IIMC and Minntac (Fig. 7). Because magnetite is, by far and away, the dominant mineral in concentrate and greenballs, these concentrations probably represent mercury associated with magnetite in the primary ore. Correspondingly, tailings from Minntac, EVTAC, and IIMC have the highest mercury of all samples collected (averages of 39.5, 40.2, and 35.4 ppb, respectively), consistent with the idea that selective removal of low-Hg magnetite from the bulk ore results in selective enrichment of mercury in tailings (Fig. 7).

Engesser and Niles (1997) noted mercury concentrations at some facilities (Minntac and LTVSMC) were closely associated to sulfur concentrations. In these cases, a relatively small percentage of the mercury in the primary ore was routed into the pelletizing plant. Apparently, pyrite, which is non-magnetic and is sent, therefore, to tailings basins, provides an important host for the trace mercury at Minntac and LTVSMC. Little correlation was observed by Engesser and Niles between mercury and sulfur at HibTac and Northshore mining, however, and the result was that a higher percentage of the mercury was routed with concentrate into the pellet plant at those facilities. Nevertheless, significant mercury was routed into the tailings basins when no correlation with sulfur could be made. This indicates that, in addition to magnetite and sulfide minerals, some mercury resides in other phases in the ore matrix (non-magnetite iron oxides, silicates, and carbonates). No attempt has been made to establish the distribution of mercury among these other minerals.

Other sample types were collected at some of the processing sites, including dust from scrubbers and various filtrates. Values are reported in the appendix, but have little application to the present study, which focused on the broader question of mercury distribution in the Biwabik Iron Formation and release during mineral processing.

## 5.2 Tailings Basins

Fine tailings generated at most mining operations are slurried with processing waters and pumped into large man-made impoundments called tailings basins. There, the tailings settle from the discharged waters, and most of the water is recycled to the plant for reuse. IIMC previously disposed tailings in a tailings basin but in December, 2001, began disposing tailings and recycling water in an abandoned open-pit mine located near their processing facility (Minorca Pit). An important question for all of these operations relates to the effect of tailings disposal on mercury distributions in NE Minnesota.

As discussed previously, and shown in Figure 7, the concentration of mercury in tailings is usually greater than the concentration of mercury in the concentrate. Furthermore, the mass of tailings released to tailings basins is typically two to three times the mass of pellets generated (Engesser and Niles, 1997, Skillings, 2001). Thus, the total mass of mercury that reports to tailings basins must be larger than that which is emitted to the atmosphere. At least two pathways need to be considered for release of mercury from tailings basins: (1) transport out of the system in waters that leak or are intentionally discharged from the tailings basin and (2) direct release of mercury to the atmosphere as Hg(0).

Averaged mercury concentrations for tailings basin waters are compiled in Table 4. The averaged values range from 1.23 to 3.48 ng/L for basin waters and from 0.72 to 2.44 ng/L for seeps. These values are similar to those measured in lakes and streams (see above), but much less than that of recent precipitation (most recently about 12 ng/L). In fact, calculations suggest that a relatively large fraction of the mercury present in tailings basins waters may have been supplied by precipitation. According to Cl concentration data available in Berndt et al. (1999), it can be shown that water discharged to tailings basin at NSPC from 1996 to 1999 was diluted by an average 21% by precipitation falling on the basin. Assuming 21% dilution in 1999 when mercury concentrations were measured in NSPC's basin, and considering that precipitation contained an average 12

ng/L in the area for that year, precipitation alone would account for at least 2.54 ng/L mercury. Although this calculation does not take into account mercury added by dry deposition or further concentration of dissolved elements by evaporation, the average value of dissolved mercury in NSPC's tailings basin was 2.52 ng/L. Thus, wet and dry precipitation alone, combined with evaporative increase, more than accounts for all of the dissolved mercury in tailings basins. This is not particularly surprising, as the same can be said for many lakes in NE Minnesota. However, it does demonstrate that tailings are not a significant source of dissolved mercury.

Minntac performed a study to evaluate mercury released during seepage from tailings basins (US Steel, 2000) (See Table 4 and Appendix 1). Water within the tailings basin had an average of 1.1 ng/L Hg during the study in 1999. This is considerably less than the single value of 4.23 ng/L reported by Engesser and Niles (1997) for a sample collected in 1996. Seepage during 1999 averaged only 0.73 ng/L, indicating that reaction of water with tailings does not result in an increase in the concentration of mercury and may, in fact, result in a decrease in concentration. The mercury concentrations in waters seeping from the tailings basins were found to be lower than concentrations in surrounding surface waters. Similar findings were made at Northshore by Monson et al. (2000) who determined that the net effect of discharge from the tailings basin was to decrease the concentration of mercury in the river receiving the discharge.

It is important to note that just because an industry discharges water with a concentration that is less than that of the water it takes in does not mean it will meet water quality standards. Currently, two major water quality standards are in effect, depending on which drainage basin the discharge is located. Tailings basins for Northshore, Evtac, and the former LTVSMC as well as Ispat-Inland's Minorca Pit disposal facility are all located in the Lake Superior watershed, which currently has a Class 2B mercury discharge standard for mercury of 1.3 ng/L. The current standard for IIMC's inactive tailings basin and for Hibbtac, National, and Minntac, all of which have tailings basins located in the Red and Mississippi River watersheds, is 6.9 ng/L. Currently, it appears that all of the mining companies meet the higher water quality standard, but water in some tailings basins and seepages are above the stricter 1.3 ng/L water standard.

Finally, volatilization is an important natural process in forested watersheds where it has been estimated that a mean value of 32 ug of mercury is volatilized (or deposited and revolatilized) per square meter per year (Grigal, 2002). Thus, a screening study was conducted to evaluate mercury volatilization rates from taconite tailings basins (Swain, 2002). Rates of measurement for the 20 minute intervals used in the study, which was conducted in the fall under daylight conditions, cannot be extrapolated for the year nor can it be applied to nighttime conditions. Nevertheless, the data suggest that some mercury does appear to volatilize from unvegetated tailings, and that this amount is different for different tailings. Rates of volatilization ranged from 24 to 44 ng/m<sup>2</sup>/hr at Evtac, 29 to 34 ng/m<sup>2</sup>/hr at Minntac, and were indistinguishable from the control at Northshore. No volatilization was detected above ponded water in the tailings basin. If tailings volatilized approximately 30 ng/m<sup>2</sup>/hr for a full year, then a total of 263 ug m<sup>-2</sup> a<sup>-1</sup> would be released. Although this is greater than that estimated for natural background volatilization (32 ug m<sup>-2</sup> a<sup>-1</sup>), extrapolating this rate to a tailings basin having a size of

300 hectares (Evtac's tailings basin area), results in an estimate of approximately 0.8 kg a<sup>-1</sup>. This would represent a relatively small addition to EVTAC's mercury emissions, which as will be shown in the next section, already commonly exceed 50 kg a<sup>-1</sup>. Moreover, closure of tailings basins involves a revegetation of the surface. It is unknown, what effect this will have on mercury volatilization.

### 5.3 Stack Emissions

Engesser and Niles (1997) realized that emission rates (per ton of ore produced) increased in a westward direction across the Mesabi Iron Range. This trend can be attributed to a combination of effects including low levels of mercury in ore from the eastern side of the district and sulfide enhanced mercury levels in the center of the district. Highest mercury emission rates were found on the western side of the district, where the mercury was neither diminished by metamorphism nor sequestered into easily separable sulfide minerals. However, because stack emissions weren't measured directly by Engesser and Niles (1997), they had to be estimated by difference and by assuming a value for scrubber efficiency for mercury removal from stack effluents. Stack emissions have since been measured directly at all taconite facilities on the Iron Range and results have been compiled and summarized by Jiang et al. (2000). In general, these stack emission tests have corroborated and better refined the trends noticed by Engesser and Niles.

An important parameter for estimating emissions from taconite companies is the "emission factor", which represents the mass of mercury released divided by the mass of pellets produced. Probably the most convenient unit for presenting emission factors is kg mercury per million long tons of pellets produced (kg/10<sup>6</sup>LT). Not only are taconite production figures often provided in units of long tons, but one long ton of solid containing 1 ppb (or 1 µg/kg) mercury is capable of releasing a numerically similar amount of mercury in kg (1.016 kg) (1 ppb = 1.016 kg/10<sup>6</sup>LT).

Emission factors reported by Jiang et al. (2000) are listed in Table 5 and plotted with concentration data as a function of distance from Northshore's mine in Figure 7, a procedure first adopted by Engesser and Niles (1997). Several important observations can be made, including: (1) emission factors and concentrations are extremely low on the eastern side of the district (Northshore); (2) mercury in the concentrate and/or green ball generally increases westward across the district; and (3) despite its location at the center of the district, EVTAC's emissions and mercury levels in concentrate or greenball are closer to values characteristic of facilities on the western side of the district (NSPC and HibTac).

It is generally recognized that low mercury in Northshore ore is related to past geological processes, whereby mercury was expelled during intense heating associated with emplacement of the Duluth Complex. A possibility to account for the other noted trends might involve heating to lesser degrees due to (1) increasing distance from the Duluth Complex or (2) range-wide differences in the peak depth of burial. Indeed, ore across the district exhibits increasing metamorphism and recrystallization from west to east on the iron range (Morey, 1972). Increasing recrystallization of magnetite may have systematically released a greater percentage of mercury from the magnetite.

The portion of the Biwabik Iron Formation currently mined by EVTAC, is somewhat unique compared to other parts of the formation because it is positioned at the top of the Eveleth anticline. Whether this ultimately affected the depth to which this section of the formation was buried, or whether it affected the degree to which it was affected by igneous intrusion during emplacement of the Duluth Complex, is beyond the scope of this paper. Indeed, with the collection of more data, it may turn out that the higher mercury at EVTAC relative to other nearby operations is a statistical anomaly, or may be rooted in differences in mineral processing technique (IIMC and Minntac use flotation to refine their concentrate, while EVTAC does not).

Whatever the cause of the mercury emission trends, it is generally assumed that the mercury that is emitted from stacks is predominantly in elemental form. Although this has not been verified at every plant, a study conducted at HibTac indicated that an average of 93.3% of mercury emissions were in Hg(0) form, with almost all of the remainder emitted as Hg(II) (Jiang et al., 2000). Very little particulate mercury was emitted. The form of mercury is important for determining where the element is deposited. Elemental mercury can be transported in the atmosphere for years prior to being deposited, while particulate and charged forms may be deposited much more locally.

### *5.3.1 Historical stack emissions*

Because mining companies keep relatively complete production records, and because mercury stack emissions are believed to be directly proportional to mining production, it is possible to estimate historical mercury release levels for taconite mining operations since the industry began. Such records may have value for evaluating links between mercury emissions and local mercury accumulation.

Records of annual concentrate production were compiled for Minnesota taconite mining companies through 1995 by Engesser and Niles (1997). Similar data were also obtained for the present study for the years 1995 through 2003 (estimated) in Skillings (2003). All concentrate production data were converted to pellet production numbers using recent conversion factors (pellet mass/ concentrate mass) and are plotted as a function of time for individual mining companies in Figure 9. Resulting values were multiplied by emission factors from 1995 to 1997 reported by Jiang et al. (2000) (Table 5) to provide estimates of annual atmospheric emission since initiation of taconite mining in 1949. Prior to this, nearly all ore and concentrate shipped to ports in the eastern US were mined and processed using techniques involving little or no intense heating. While emission factors may have varied through time, data presented in Figure 7 suggest that emissions are closely linked to concentration of mercury in the concentrate, which appears to be closely related to geographic location of the mine. Thus, by multiplying geographically appropriate emission factors by production figures for individual taconite plants, reasonable estimates of historical atmospheric emissions can be achieved (Appendix 3).

No mercury data are available for the former Butler site, so production at this site was assumed to have an emission factor similar to that of NSPC, the nearest site. LTVSMC operated the Dunka mine, which, with its location immediately adjacent to the

Duluth Complex, probably contained very little mercury. IIMC, meanwhile, extracted ore from the Minorca pit, located near Virginia Minnesota (on the Virginia anticline) between Minntac and EVTAC until 1993, but has since switched to its current mine location, between EVTAC and LTVSMC. These and other possible geographic shifts in mining operations were not taken into account here.

With the exception of a few subtle differences, the historical patterns of mercury emission (Fig. 9) are, of course, similar to historical patterns of taconite production (Fig. 10). Because early pellet production was concentrated on the east end of the range (Northshore and LTVSMC) where emission factors are low, initial mercury emission rates were also initially low relative to production. In contrast, a peak in taconite production that occurred from 1979 to 1981 involved the opening and rapid expansion of companies on the western side of the district, where mercury emission factors are comparatively high. This westward shift in mining lead to an acceleration of mercury emissions relative to production. Annual mercury emissions exceeded the 100 kg mark in 1967, leveled off at approximately 200 kg at the end of the 1970's, and then abruptly and temporarily increased to the 350 kg range from 1978 through 1981. Following that, annual mercury emissions abruptly decreased to 200 kg but then increased gradually through the 1980's and eventually leveled off between 300 and 350 kg/year through the 1990's.

The closing of LTVSMC, and production decreases in 2001 at other companies, have resulted in a correspondingly large reduction in mercury emissions from taconite companies in recent years. If other companies on the western side of the district had picked up the reduced pellet production caused by LTVSMC's closing, then emissions would likely have increased slightly owing to the higher emission factors for those companies. However, LTVSMC's closing does not appear to have bolstered pellet production at other Minnesota companies. Hg emissions have, therefore, decreased substantially.

Based on the most recent precipitation records available from the National Atmospheric Deposition Program (NADP, 2002; Vermette et al., 1995), the annual atmospheric Hg release from taconite mining is approximately two to three times that deposited from precipitation over an area the size of St. Louis County in NE Minnesota. Thus, if only a fraction of the Hg released by taconite processing were deposited locally, it should be recorded in Hg distributions in sediments from nearby lakes. Because of the global nature of mercury dispersal, a link between mercury emission and deposition is not always established in an area. This appears also to be the case here, where an assessment of Minnesota lake sediment data by Engstrom et al. (1999) found that mercury accumulation rates for lakes closest to the iron range (e.g., near Silver Bay) did not obviously reflect taconite emission data. This is consistent with the notion that most Hg emissions from taconite companies are airborne and not deposited locally. Because Hg(0) released to the atmosphere remains in the atmosphere for a long period of time before being precipitated (approximately half will be oxidized and precipitated out every 1 to 3.5 yrs; Mason et al., 1994, Pirrone et al., 2000), mercury in Minnesota taconite stack emissions is probably dispersed globally before being deposited.

### *5.3.2 Comparison to other sources*

While the amount of mercury released to the atmosphere by taconite mining companies is second (in Minnesota) to that of power companies, the total is relatively small compared to emissions from other national and international sources (Table 6). An estimated maximum of 388 kg of mercury was released by the taconite industry in 1979. Mercury emission data from other iron producers world-wide was not readily available, except for an estimate of 4360 kg released annually by the steel and iron industry in the Mediterranean area of Europe (Pirrone et al., 2001). The later number, which may include mercury released by scrap iron processing (a considerable source due to presence of mercury bearing equipment in scrapped automobiles), is similar to Minnesota's entire 1990 annual output of 5,305 kg, but much higher than Minnesota's entire annual output in 2000, estimated at 1720 kg (MPCA, 2002).

US emissions were estimated to be approximately 144,000 kg in 1994 to 1995 (EPA, 1997), less than half of North America's estimated 1992 total of 301,000 kg. Global anthropogenic emissions are approximately 1,450,000 to 2,000,000 kg, which is less than half of the estimated total global Hg emissions to the atmosphere (anthropogenic + natural) of 5,000,000 kg/yr (EPA, 1997). Based on these figures, taconite emissions represent about 0.24% of the US anthropogenic releases in 1994/1995, 0.1% of North American anthropogenic Hg emissions to the atmosphere, and about 0.007 % of total global emissions (anthropogenic plus natural).

### *5.3.2 Potential control*

As part of a statewide plan to reach emission reduction goals, many taconite companies have entered into voluntary mercury reduction agreements with the MPCA. Although significant steps have indeed been taken by all of the taconite companies to eliminate and/or control use of Hg bearing chemicals and equipment (IMA, 2001), these sources were not even considered in the MPCA's prior assessment of taconite companies, which focused exclusively on mercury in stack emissions (Engesser and Niles, 1997; Jiang et al, 2000). As discussed above, mercury present in taconite occurs as a trace element, and cannot be eliminated by simply using a different fuel source or by eliminating mercury-bearing components from material to be combusted.

A recent study by the Coleraine Minerals Research Laboratory (CMRL-NRRI), University of Minnesota, suggested that some emission control may be obtained by modifying the current practice of recycling the dust from wet scrubbers into the indurating furnaces (Benner, 2001b). Benner (2001b) found that this dust contains extremely high mercury concentrations, and if this material, particularly the fine fraction, was channeled into the waste stream (rather than recycled to the indurator), mercury emissions could be cut. Estimated savings in terms of mercury release to the environment are shown in Table 7, but it is important to note that these estimates are based on one time measurements, and are based on many assumptions.

For example, Berndt et al. (2003) showed that considerable mercury is present in dissolved form in plant scrubber systems and that with passage of time this mercury adsorbs to the suspended dust. The concentration of mercury measured on dust, therefore, can vary considerably depending on when the filtration was performed.

Because most previous studies collected samples at the plant and processed them at the laboratory (after adsorption occurred), the amount of mercury adsorbed to dust has probably been previously over-estimated.

In addition, Berndt et al. (2003) found that the amount of mercury captured in wet scrubbers depends greatly on whether the processing facility is producing fluxed or acid pellets. At Minntac, mercury capture by the plant scrubber system was nearly an order of magnitude greater when the company was producing acid pellets compared to fluxed pellets. Thus, the combined mercury captured by scrubber waters and suspended solids can, at times, represent a significant fraction of the mercury released during taconite processing. This is a continuing area of active research on the iron range (see section 7 below) and may potentially lead to re-estimates of taconite plant emissions (taking into account increased capture during acid pellet production) and/or more cost effective means to eliminate at least some of the mercury from taconite air emissions.

## **6. Cost and Benefit**

Cost-benefit analyses attempt to weigh the costs of implementing control measures against the benefit in terms of environmental and public health. Technologies to reduce mercury emission from taconite processing have only recently begun to be addressed (see above) so the cost of reducing mercury from emissions is unknown.

Hagen et al. (1999) surveyed and interviewed Minnesota residents to help arrive at a dollar figure for the value of reduced mercury deposition to Minnesotans. They first educated a large number of Minnesota residents on mercury issues, and then asked how much they would be willing to pay for mercury reductions. 2500 Minnesotans were surveyed and an additional 250 were interviewed. For a 12% reduction in mercury deposition, the surveyed households were willing to pay an average of \$118.91 per year while those interviewed were willing to pay an average \$198.03 per year. The lower figure translates to a value of approximately 212 million dollars for Minnesota as a whole.

Lutter and Irwin (2002) reviewed literature on health effects and mercury exposure and estimated the cost per child of controlling mercury from coal burning power plants. They claim that “approximately 6000 children in the US would experience improvements in specific, narrow measures of neurological performance (between 13 and 22 percent of a standard deviation)” upon the complete elimination of mercury from fish. The authors noted that even sharp cuts to the power industry would not achieve such improvements owing to the fact that many other industries and activities emit mercury to the atmosphere. Using what the authors claimed to be conservative choices, the cost of implementing mercury control on coal-fired power plants (\$1.1 billion to \$1.7 billion per year) amounted to spending approximately \$10,000.00 per affected US child. The authors indicated, however, that the positive effects of reduced mercury exposure would likely be hard to measure or detect.

The taconite industry emits much less mercury to the atmosphere than coal-fired power plants and, in fact, it is clear from data in Table 6 that cutting even 100% of the mercury from taconite stack emissions would have only a small impact on the national and world inventories of mercury. If mercury in the environment is to be controlled, it

must involve a global effort, placing emphasis on curtailing emissions from the largest sources that are easiest to control. Mercury control methods and costs are only beginning to be established for taconite processing companies, but even if an economic means is found to remove this source of mercury, continued efforts will be needed to reduce mercury emissions elsewhere to have significant impact on mercury deposited in Minnesota.

## **7. Additional Studies**

Studies are being conducted at Coleraine Minerals Research Laboratory and by the Department of Natural Resources which could help to improve our understanding of mercury concentrations and distribution in taconite ore and also help to control emissions. Funding from the Minerals Coordinating Committee (MCC), the Iron Ore Cooperative Research Fund (IOCR), and the Permanent University Trust Fund (PUTF) is being used for conducting mercury balance studies around the concentrators at EVTAC, IIMC, Minntac, and HibTac. Results from this study are due out shortly. CMRL is also studying removal of elemental mercury from flue gases using a copper-coated magnetite injection process at Clay-Boswell, using funding from PUTF and the Federal Government Economic Development Administration (EDA).

Other studies are being conducted by the Minnesota Department of Natural Resources to evaluate mercury exchange between water and solids in processing lines and to determine if minor processing changes can lower mercury emissions to the atmosphere. This work is funded partially by IOCR, Environmental Cooperative Research (ECR), and the Great Lakes Nation Program Office (GLNPO-EPA). The idea is to maximize mercury oxidation in processing lines, eliminate recycling of oxidized mercury captured by plant scrubbers (to the induration furnace), and to ensure permanent disposal of the mercury in tailings basins. A secondary objective is to better evaluate the relative sources of mercury in tailings basin water (precipitation?). These studies are expected to take two years, with start times ranging from July to October, 2003.

## 8. Summary

This study summarizes and presents available data on mercury distributions in and around the taconite mining region in Minnesota. Twelve years of deposition records suggest a stable to increasing trend of mercury concentration in precipitation and mercury deposition, while sediment records indicate a recent decreasing trend for selected localities within NE Minnesota. Two large datasets on the total mercury concentration in lakes yield conflicting results, one suggesting much higher concentrations than the other. Neither dataset provide concentration of mercury for lakes in a large region extending from the iron range southeastward to Lake Superior. Fish mercury is decreasing in more lakes than it is increasing in, but the overall record is insufficient to prove a declining trend in fish mercury levels. Recent research reveals that the mercury in precipitation that falls directly on a lake is much more available for methylation than that which falls on (and runs off from) land.

Mercury is present in small quantities in primary taconite ore, ranging in concentrations from approximately 20 ppb on the western edge of the active area, up to approximate 32 ppb at Minntac, near the center of the mining district, and decreasing again eastward to approximately 1 ppb in Northshore's ore. Mercury in Northshore's ore is low owing to effects of extensive thermal metamorphism that occurred during intrusion of the Duluth Complex. Data from a study on drill core suggest that mercury concentration increases by approximately 50 ppb down-dip in the iron formation, however, the possibility that samples analyzed in that study were affected by Hg-adsorption from air makes this an unresolved issue.

Waters existing in and being discharged or seeping from tailings basins have mercury concentrations similar to and possibly lower than rivers and lakes in the region and much lower than local precipitation. Class 2b water quality standards for total mercury in NE Minnesota are 6.9 ng/L for waters discharged into the Red and Mississippi River Drainage basins and 1.3 ng/L total mercury for waters discharged into the Lake Superior basin. All tailings basin waters and seeps have concentrations less than the higher standard, and a few have concentrations that are below the much stricter Lake Superior basin standard. No mercury appears to be volatilized from tailings basin ponds, but small amounts are volatilized from the tailings themselves.

The primary source of mercury from taconite mining are stack emissions. The amount of mercury released per kg of pellets produced is a plant-specific quantity related more to the distribution of mercury within the primary ore than to bulk concentration in the ore, itself. Mercury release to the atmosphere increases westward across the range from a value less than 1.0 kg per million long tons at the eastern edge of the mined area to about 15 to 17 kg per million long tons on the western side of the district. The exception to this trend is EVTAC, located in the center of the district at the top of a prominent geologic feature (the Eveleth anticline). This company releases mercury at a rate similar to taconite producers located on the western side of the district. The notion that most mercury emitted is in elemental form, Hg(0), has been tested and confirmed by stack emission measurements at HibTac. Most mercury emitted in this form would be dispersed worldwide.

Present day emission factors were combined with past production records to estimate annual Hg release since taconite mining began in NE Minnesota (1949). Results suggest that atmospheric Hg emissions exceeded 100 kg/yr in the late 1960s, and have ranged between approximately 200 and 350 kg/yr ever since, with a peak occurring from 1979 to 1981, corresponding to a peak in taconite pellet production. Taconite emissions represent about 0.24% of the US anthropogenic releases (1994-1995), 0.1% of North American anthropogenic Hg emissions to the atmosphere, and about 0.007% of estimated total annual global emissions (anthropogenic plus natural). Thus, although taconite processing is a sufficiently large industry that it is one of the biggest emitters of mercury in the state of Minnesota and to the Lake Superior Basin, it is not so large as to significantly impact national and international mercury atmospheric budgets. Current efforts to reduce mercury emissions from taconite processing reflect Minnesota's desire and commitment to reach state-wide reduction goals as a part of national and international cooperative efforts to reduce mercury in the environment.

## 9. References

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## 10. Tables

Table 1. Estimates of Minnesota mercury emissions for 1990, 1995, and 2000 (MPCA, 2002).

Source	1990		1995		2000	
	Kg	%	Kg	%	Kg	%
Coal-fired power plants	711	13.4	737	34.6	820	47.7
Latex Paint	1725	32.5	0	0.0	0	0.0
Municipal Solid Waste Combustion	820	15.4	288	13.5	73	4.3
Household Waste Incineration	302	5.7	123	5.8	82	4.8
Taconite Processing	333	6.3	352	16.5	342	19.9
Volatilization from Solid Waste	592	11.1	196	9.2	131	7.6
Medical Waste Combustion	234	4.4	16	0.8	4	0.2
All Other	594	11.2	419	19.7	268	15.6
<b>Total</b>	<b>5312</b>	<b>100.0</b>	<b>2131</b>	<b>100.0</b>	<b>1719</b>	<b>100.0</b>

Table 2. Fish consumption advisories for Minnesota. Advisories vary by group depending on susceptibility and how often fish are eaten (e.g., only on vacation, only during fishing season, or year round. “Susceptible groups” in this table refers to young children and women of child-bearing age. Data on Minnesota lakes is from Jeremiason (2002). Fish advisories are subject to change as more data become available. Up-to-date fish advisories can be found on the internet at <http://www.health.state.mn.us/divs/eh/fish/safeeating/safeeating.html>.

Mercury Level	Advisory	% MN Lakes (1998/1999)
0-0.038	Unlimited consumption for all groups	2.4
0.038-0.16	Vacation: Unlimited Seasonal: Unlimited for most, 2 meals/wk for susceptible groups Annual: 2 meals/wk for most, 1 meal/wk for susceptible groups	35.2
0.16-0.65	Vacation: Unlimited for most, 1 meal/wk for susceptible groups Seasonal: 2 meals/wk for most, 2 meals/mo for susceptible groups Annual: 1 meal/wk for most, 1 meal/mo for susceptible groups	54.1
0.65-2.8	Vacation: 1 meal/wk for most, 1 meal/year for susceptible groups Seasonal: 2 meals/mo for most, 1 meal/2 mo for suscept. groups Annual: 1 meal/mo for most, none for suscept. groups	8.1
>2.8	Vacation: 1 meal/yr for most, none for suscept. groups Seasonal: 1 meal/mo for most, none for suscept, groups Annual: do not eat	0.2

Table 3. Summarized data for Hg concentrations (ppb or ng/g) and number of samples analyzed (n) from taconite mining operations in Minnesota. Full data set is included in the appendix.

Company	Miles from Northshore	Raw ore	n	Concentrate or "greenball"	n	Tailings	n
NSPC	51	21	3	15.2	3	20.4	6
HibTac	46	24	4	16.6	7	26.0	6
Minntac	30	32	2	8.2	7	39.5	7
EVTAC <sup>1</sup>	29	32	0	11.4	3	40.2	3 <sup>2</sup>
IIMC	23	27	1	7.8	1	35.4	1
LTVSMC	12	11	2	4.0	3	12.2	3
Northshore	0	0.6	3	1.1	5	1.1	8

<sup>1</sup> No estimated or measured value was available for raw ore from EVTAC so a value was calculated using reported values for "greenball" and tailings and assuming 31.5 % recovery rate (Skillings, 2003).

<sup>2</sup> A single sample with a high value of 130 was not included in the average.

Table 4. Averaged mercury concentrations in tailings basin waters and seeps. The full data set can be found in the appendix.

Site	Hg (Total) (ng/L)	Hg (Filtered) (ng/L)	MeHg (ng/L)
NSPC: Basin	2.52 (n=3)		
Monitoring well	2.69 (n=1)		
Hibbing Taconite: Basin	2.24 (n=1)		
US Steel (Minntac): Basin	1.72 (n=5)	0.42 (n=4)	<0.008 (n=4)
Seep	0.72 (n=3)	0.77 (n=3)	<0.016 (n=3)
EVTAC			
IIMC: Seeps and wells	2.9 (n=3)		
LTV: Basin	3.48 (n=1)		
Seep	2.44 (n=1)		
Northshore: Basin	1.23 (n=5)		

Table 5. Air emission factors for taconite production from Jiang et al. (2000). These factors have been multiplied by production figures to estimate yearly mercury emissions to air in Minnesota since taconite mining began in 1949. Hg values measured for greenball and concentrate from Table 3 are provided for direct comparison.

Company	Air Emission Factor (kg Hg/10 <sup>6</sup> LT pellet) Jiang et al (2000)	Hg (ppb) in “greenball” or concentrate Average value
National Steel Pellet Company (NSPC)	10.1	15.2
Hibbing Taconite	12.6	16.6
U.S. Steel (Minntac)	5.3	8.2
EVTAC	11.4	11.4
Inland Steel (IIMC)	5.4	7.8
LTVSMC Steel	5.1	4.0
Northshore Mining Company	1.8	1.1

Table 6: Comparison of taconite stack air emissions with emissions from other sources and regions throughout the world. It is important to note that emission records for mercury are uncertain and subject to change with increasing information. These data are presented for relative comparison purposes only.

Source	Hg Emission (kg/yr)	Reference
MN Taconite industry <sup>1</sup> : peak (1979)	388	This report
1995-1997	347	Jiang et al. (2000)
2000	342	This report
Steel and Iron Industry in Mediterranean Area (1995)	4,360	Pirrone et al. (2001)
Minnesota anthropogenic 1990	5,305	MPCA (2002)
1995	2,120	MPCA (2002)
2000 (est.)	1,720	MPCA (2002)
US total anthropogenic emissions (1990)	144,000	EPA (1997)
North America anthropogenic Emissions (1992)	301,000	Pirrone et al. (1998)
Global emissions (anthropogenic)	1,450,000	Pacyna and Pacyna (1996)
	2,000,000	Pirrone et al. (1996)
Global total Hg emissions (anthropogenic + natural)	5,000,000	EPA (1997)

<sup>1</sup>Taconite values are for air emissions only. Hg reductions relating to recycling or discontinued use of Hg-bearing equipment and chemicals are reported in IMA (2001) but have not been factored in here.

Table 7. Cost estimate figures for mercury reduction from stack emissions. Estimates were made by John Engessor (MnDNR, personal communication), using data in the listed references, extrapolated from one time results to a full year of production.

<b>Taconite company:</b> Reference	Recycled dust (lt/yr)	Value of recycled dust assuming \$25/lt	Hg saved (lbs/yr) by discarding rather than recycling the dust	Cost of technology (\$ per lb Hg)
<b>EVTAC:</b>				
Benner (2001b)	8343	\$208,575.00	15	\$13,905.00
Engesser and Niles (1998b)	27600	\$690,000.00	19	\$36,315.79
<b>Minntac:</b>				
Benner (2001b)	11231	\$280,775.00	2.2	\$127,625.00
Engesser (1998a)	39900	\$997,500.00	22.6	\$44,137.17

## 11. Figures

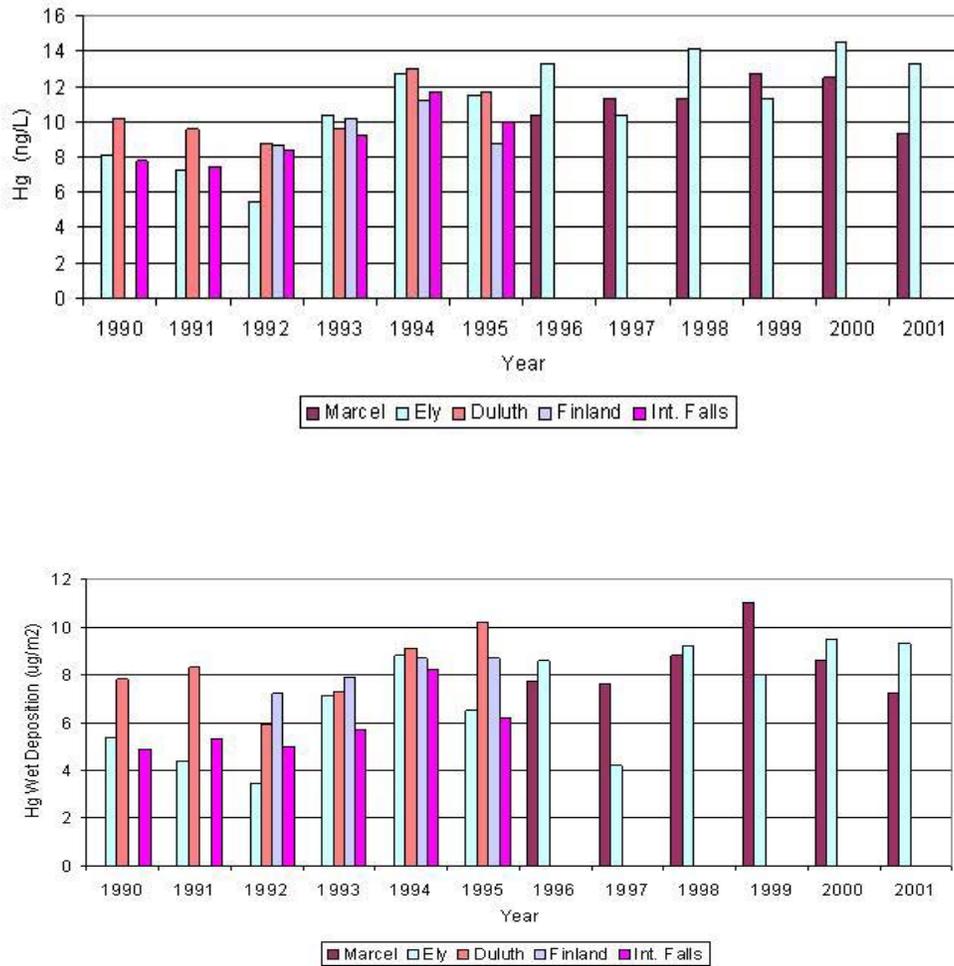


Figure 1. (A) Concentration and (B) annual deposition rate (wet) of Hg in precipitation in NE Minnesota. 1990-1995 data from Glass et al. (1999); 1996-2001 data from NADP (2002). The data appear to reveal a trend of increasing mercury concentration and mercury deposition in NE Minnesota over the last twelve years.

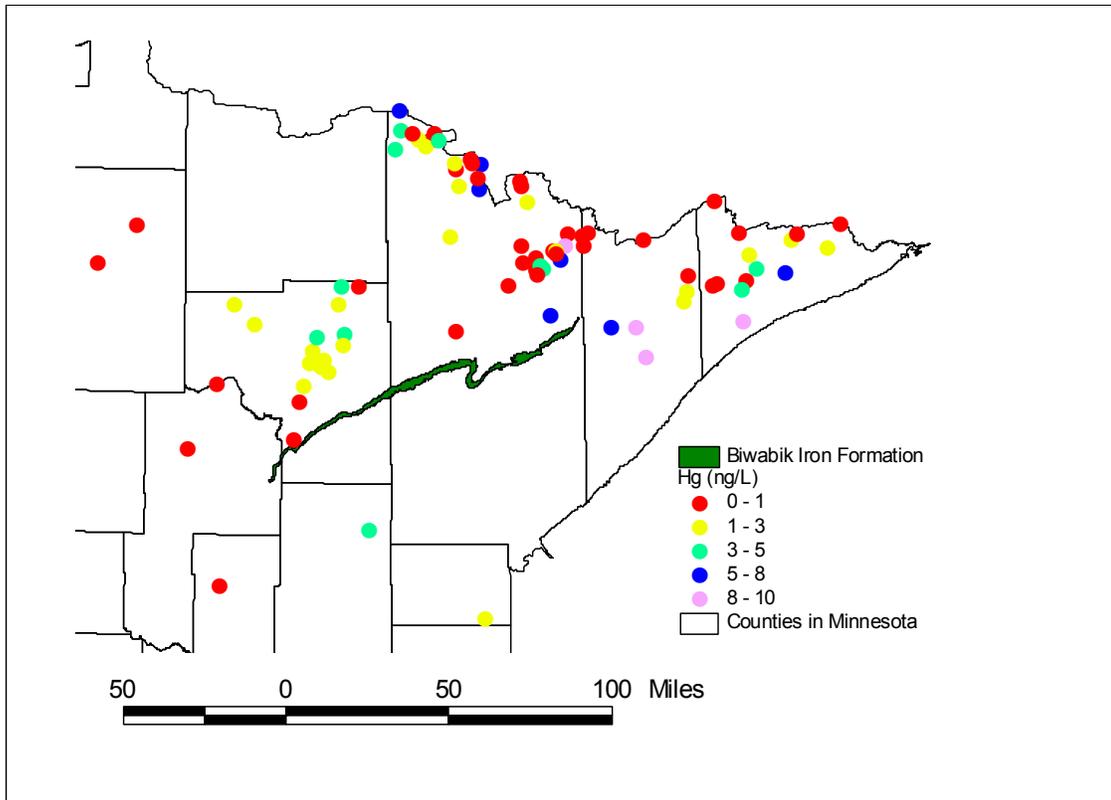


Figure 2. Total Hg in water from lakes in Northeastern Minnesota. Data are from STORET database that for this region consisted almost exclusively of 1991 values.

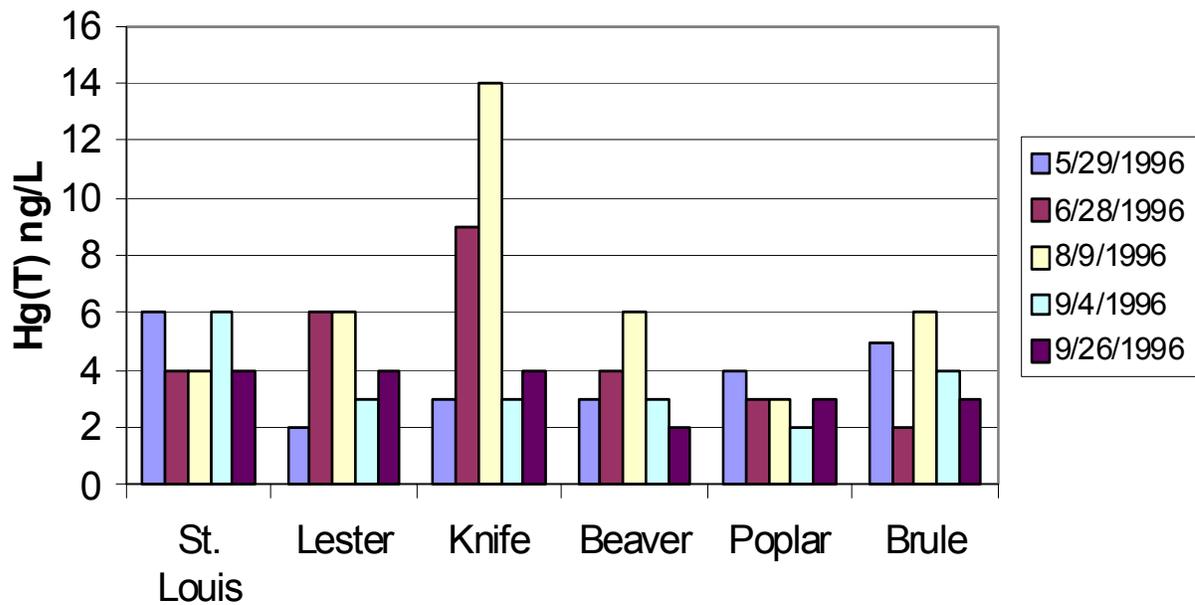


Figure 3. Mercury concentrations for rivers entering Lake Superior from NE Minnesota. Average value for all measured concentrations is  $4.3 \pm 2.8$ . Data are from MPCA STORET database. Dates of sample collection are  $\pm 1$  day.

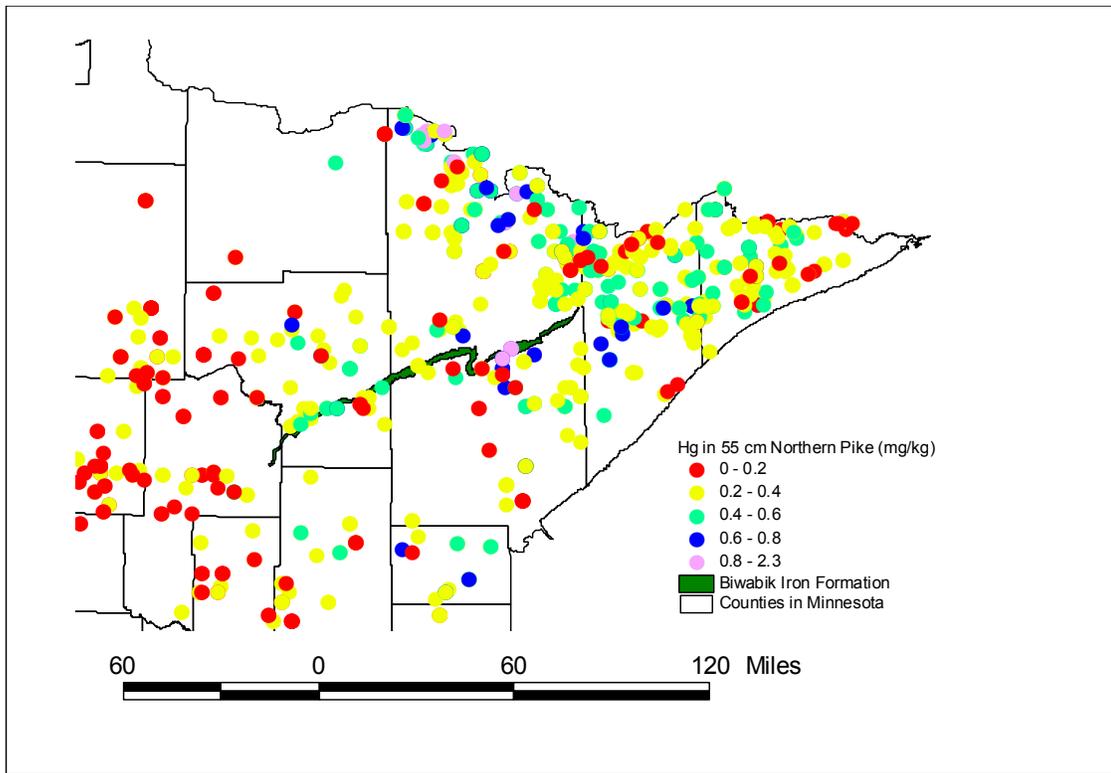


Figure 4. Mercury levels in standard sized (55 cm) Northern Pike Fish. Data are from samples collected in the 1990's as compiled by Jeremiason (2002). The database for fish mercury is considerably larger than that for lake water chemistry.

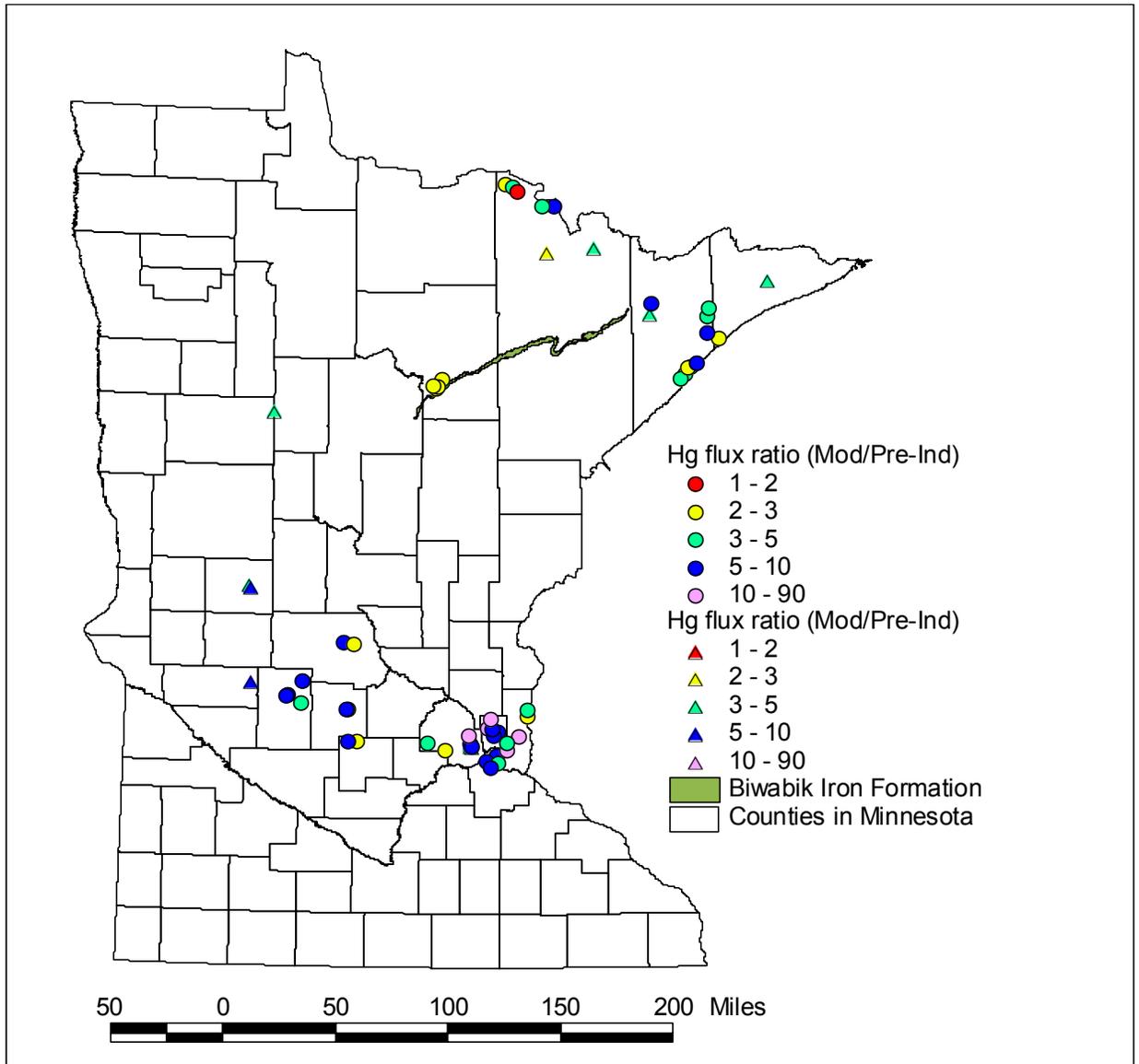


Figure 5. Ratio of Hg flux (modern versus pre-industrial) as estimated from age-dated lake sediment cores. Circles are data from Engstrom et al. (1999) and triangles are data from Engstrom and Swain (1997). As is the case for most lakes world-wide, the current mercury flux to lakes is much greater than in pre-industrial times. In Minnesota, greater increases in mercury flux have occurred near heavily populated and agricultural regions, owing most likely to increased erosion of soils. An approximate three to four-fold increase in Hg in precipitation since pre-industrial times has also caused mercury fluxes to increase to lakes in remote areas.

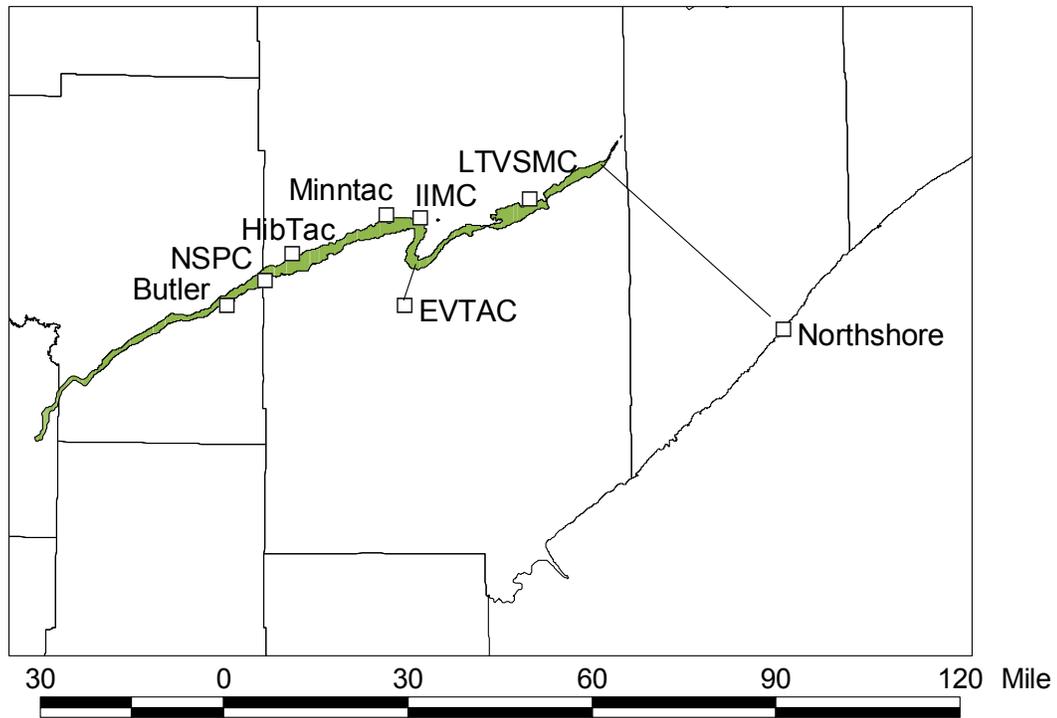


Figure 6. Location map showing location of the Mesabi Iron Range and taconite processing plants in northern Minnesota. Butler and LTVSMC plants are not currently operational, but are included for completeness. EVTAC was temporarily shut down beginning in May, 2003. The Biwabik Iron formation, which is currently the source of all iron mined in Minnesota, is shown for comparison. The formation is a broad planar feature, dipping 5 to 15 degrees to the southeast, but interrupted near the center of the district by a large fold structure known as the Virginia Horn, which is itself, composed of the Virginia syncline and Eveleth anticline. EVTAC's ore bodies are located on the Eveleth anticline.

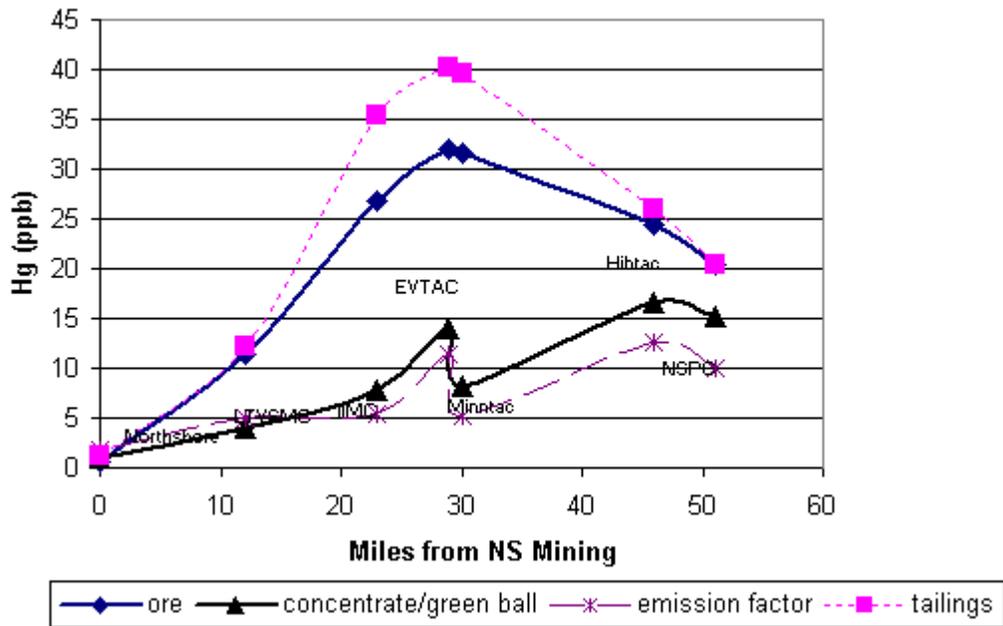


Figure 7. Mercury concentration in ore, concentrate, and tailings as a function of distance from Northshore (located on the east edge of the district). The concentration of mercury in “green ball” was considered to be within the error of measurement for mercury concentration in “concentrate” and the two were combined to provide better statistics. In addition, emission factors (in units  $\text{kg}/10^6\text{LT}$ ) are similar to concentration units presented in ppb ( $1 \text{ ppb} = 1.016 \text{ kg}/10^6\text{LT}$ ), so these parameters can be compared directly. No data were available for raw ore or tailings at EVTAC. The concentration of mercury approaches zero at Northshore where the ore has been thermally metamorphosed, but increases to highest values in the center of the mining district. Emissions and concentrations of mercury in the concentrate (and “greenball”) generally increase with distance from Northshore mine pits, with the exception of EVTAC.

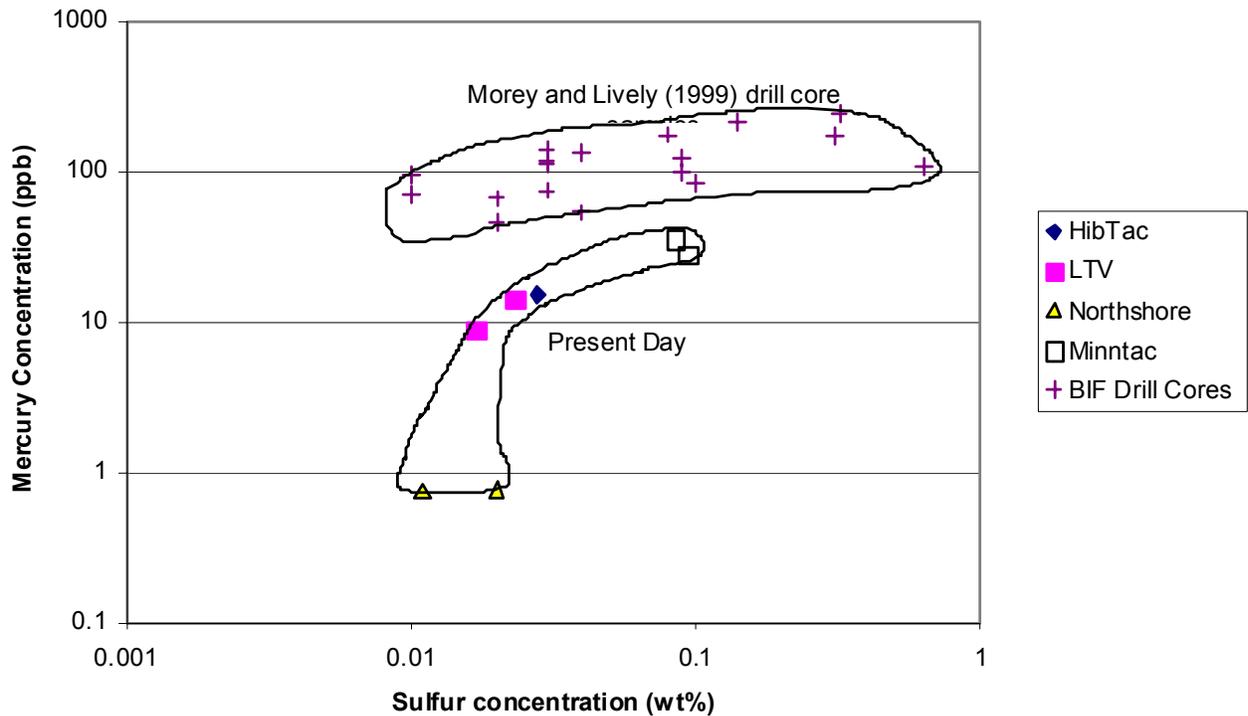


Figure 8. Mercury concentration as a function of total sulfur in Biwabik Iron Formation rocks. “Present day” samples represent ore mined at the surface and processed at the listed facility. Morey and Lively’s samples were collected from drill core locations down dip from the current mining horizon, but were powdered and stored in cardboard boxes for thirty years prior to analysis for mercury. If mercury concentration in the Biwabik Iron Formation actually does increase down dip from the current mining horizon, it is not related to increased presence of sulfur (or pyrite). Alternatively, the long-term storage of the powdered drill core samples might have led to inadvertent contamination by Hg adsorbed from air as demonstrated by experiments on other mineralogical powders by Fang (1978).

### Minnesota Historical Taconite Production

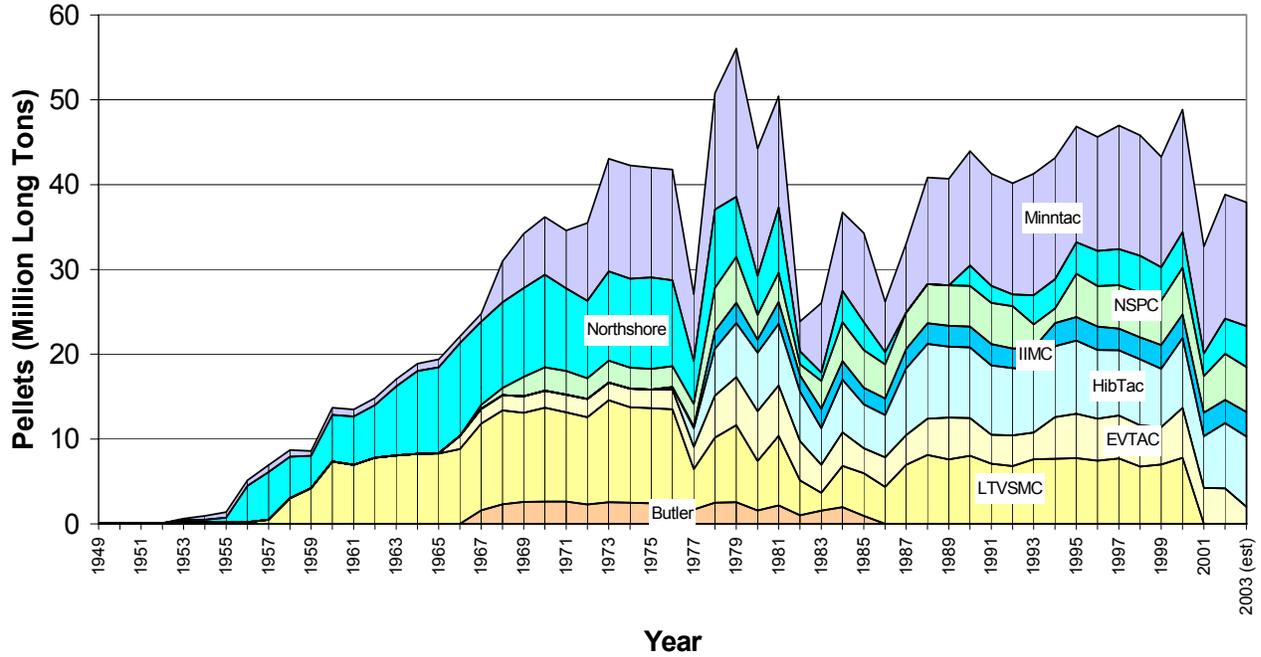


Figure 9. Taconite pellet production by Minnesota taconite companies since 1949. Production reached a peak in the late 1970's, declined sharply, in the early 1980's, but then increased gradually again, leveling off in the 1990's. After a major decline in 2001 when LTV closed, pellet production rebounded slightly in 2002 and 2003.

### Estimated Hg emissions from Minnesota Taconite mining operations

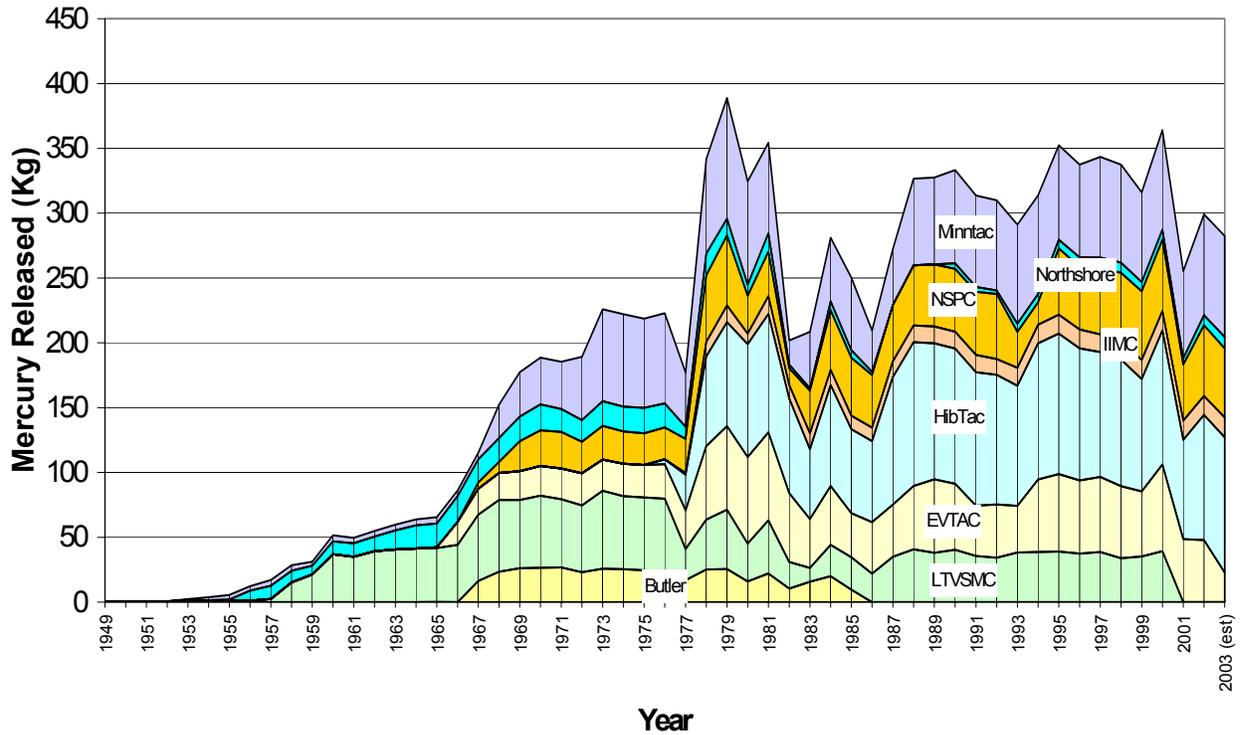


Figure 10. Estimated stack emissions of Hg from Minnesota taconite companies since 1949. Mercury emission estimates are generally similar to pellet production (Fig. 9), but with subtle differences owing to differences in mercury emission factors across the range (See Fig. 7).

## Appendices

## Appendix 1: Hg Concentrations at Taconite Plants

Compiled data on concentration of mercury in water and solids from taconite mining companies. Note: Many of the water samples collected from processing lines were apparently unfiltered. Water samples having high concentrations of mercury may have entrained solids containing adsorbed Hg.

Location	Sample Description	Source	Hg(T)	Date	Hg(TD)	MeHg
			ng/l (water)			ng/L
			ng/g (solid)			
NSPC	Tailings Basin Monitoring Well	Lapakko (2000)	2.69			
NSPC	Tailings Basin Clear Pool	Engesser (2000)	1.7	08/10/99		
NSPC	Tailings Return Water	Engesser (2000)	3.03			
NSPC	Tailings Return Water	Engesser (2000)	2.83			
Hibtac	Concentrator	Benner (2001b)	8.61	10/15/98		
Hibtac	Make-up	Benner (2001b)	5.37	10/15/98		
Hibtac	Scrubber Water	Benner (2001b)	11.96	10/15/98		
Hibtac	Scrubber Water In (average)	Engesser and Niles (1997)	2.81	02/04/97		
Hibtac	Scrubber Water Out (average)	Engesser and Niles (1997)	63.35	02/04/97		
Hibtac	Tailings Basin	Engesser and Niles (1997)	2.24	09/19/96		
Minntac	Scrubber Water Out	Benner (2001b)	66.5	07/18/01		
Minntac	Scrubber Water In	Engesser and Niles (1997)	2.05	02/04/97		
Minntac	Scrubber Water Out	Engesser and Niles (1997)	491.55	02/04/97		
Minntac	Tailings Basin Water	Engesser and Niles (1997)	4.23	09/19/96		
Minntac	Tailings Basin Water (TB1-2')	USX(2000)	1.54	09/22/99		
Minntac	Tailings Basin Water (TB1-2')	USX(2000)	1.06	09/22/99		
Minntac	Tailings Basin Water (TB1-2')	USX(2000)	0.99	Nov. 1999	0.41	<0.008
Minntac	Tailings Basin Water (TB1-27')	USX(2000)		Nov. 1999	0.36	<0.008

Minntac	Tailings Basin Water (TB2-2')	USX(2000)	0.76	Nov. 1999	0.41	<0.008
Minntac	Tailings Basin Water (TB1-32')	USX(2000)		Nov. 1999	0.51	<0.008
Minntac	West Seepage (O2O)	USX(2000)	1.17	Nov. 1999	1.33	<0.008
Minntac	Dark River (Cty Rd 668)	USX(2000)	1.12	Nov. 1999		0.091
Minntac	Dark River (US For Rd 271)	USX(2000)	1.66	Nov. 1999		0.056
Minntac	Sturgeon River (Cty Rd 107)	USX(2000)	2.77	Nov. 1999		0.128
Minntac	East Seepage (030)	USX(2000)	0.44	09/22/99	0.27	0.033
Minntac	East Seepage (030)	USX(2000)	0.54	Nov. 1999	0.7	<0.008
Minntac	Sandy River (Hwy 53)	USX(2000)	3.56	09/22/99		0.67
Minntac	Sandy River (Hwy 53)	USX(2000)	1.3	Nov. 1999		0.089
Minntac	Sandy River (Hwy 169)	USX(2000)	3.85	09/22/99		
Minntac	Sandy River (Hwy 169)	USX(2000)	2.19	Nov. 1999		0.162
Minntac	Pike River (Hwy 169)	USX(2000)	2.82	Nov. 1999		0.238
Minntac	Step III Scrubber	USX(2000)		Nov. 1999	3.42	0.288
Minntac	Step II Scrubber (L7)	USX(2000)		Nov. 1999	6.04	0.174
Minntac	Step III Loadout Discharge	USX(2000)		Nov. 1999	1.23	0.026
Minntac	Scrubber Water Rec. Pond	USX(2000)		Nov. 1999	0.8	<.02
Minntac	Scrubber Water Rec. Pond	USX(2000)		Nov. 1999	3.42	0.288
Minntac	Step I Ditch	USX(2000)		Nov. 1999	0.65	<.02
Minntac	Step II Ditch	USX(2000)		Nov. 1999	0.29	<.02
Minntac	Step III Ditch	USX(2000)		Nov. 1999	0.59	<.02
EVTAC	Thickener Underflow 2A	Benner (2001b)	15.5			
EVTAC	Thickener Overflow 2A	Benner (2001b)	82.2			
EVTAC	Thickener Underflow 2B	Benner (2001b)	18.1			
EVTAC	Thickener Overflow 2B	Benner (2001b)	24.35			
EVTAC	Slat Spray Water	Benner (2001b)	5.25			
EVTAC	Slat Spray Water	Engesser (1998b)	2.46	11/18/97		
EVTAC	Slat Spray Water	Engesser (1998b)	2.15	11/18/97		
EVTAC	Thickener overflow	Engesser (1998b)	199.6	11/18/97		
EVTAC	Thickener overflow	Engesser (1998b)	293.6	11/18/97		

IIMC	Process Water	Benner (2001b)	5.67	07/18/01		
IIMC	Scrubber Water	Benner (2001b)	112	07/18/01		
IIMC	Tailings Basin Seep	Lapakko (2000)	2.99			
IIMC	Tailings Basin monitoring well	Lapakko (2000)	2.83			
IIMC	Tailings Basin monitoring well	Lapakko (2000)	2.86			
LTVSMC	Tailings Basin Water	Engesser and Niles (1997)	3.48	09/19/96		
LTVSMC	Tailings Basin Seep	Lapakko (2000)	2.44			
Northshore	Tailings Basin Water	Swain (2002)	1.1	Sept. 2000		
Northshore	Tailings Basin Water	Swain (2002)	1.3	Sept. 2000		
Northshore	Tailings Basin Water	Swain (2002)	1.9	Sept. 2000		
Northshore	Lake Superior	Monson et al. (2000)	1.02			
Northshore	Return water	Monson et al. (2000)	0.96			0.025
Northshore	Discharge to Beaver River	Monson et al. (2000)	0.73			<0.009
Northshore	Process Water	Monson et al. (2000)	1.12			0.237
Northshore	Beaver River	Monson et al. (2000)	6.15			0.271
Northshore	Beaver River	Monson et al. (2000)	5.78			0.294
Northshore	Upstream of MP7 Discharge	Monson et al. (2000)	4.02			0.262
Northshore	Downstream of MP7 Discharge	Monson et al. (2000)	3.48			0.248
Northshore	Feedwater	Benner (2001b)	7.05			
Northshore	Hood Exhaust 11	Benner (2001b)	32.8			
Northshore	Hood Exhaust 12	Benner (2001b)	15.7			
Northshore	Waste Gas Wet 11	Benner (2001b)	29.1			
Northshore	Waste Gas Wet 12	Benner (2001b)	15.7			
Northshore	Thickener Overflow	Engesser and Niles (1997)	2.21	09/20/96		
Northshore	Hood Exhaust Out	Engesser and Niles (1997)	6.61	09/20/96		
Northshore	Waste Gas Out	Engesser and Niles (1997)	10.87	09/20/96		

Northshore	Lake Superior	Engesser and Niles (1997)	2.18	09/20/96		
Northshore	Tailings Basin Water	Engesser and Niles (1997)	0.9	09/20/96		
NSPC	Sag Mill Discharge	Benner (2001a)	20.3			
NSPC	Sag Mill Discharge	Engesser (2000)	21.5	08/10/99		
NSPC	Sag Mill Discharge	Engesser (2000)	19.7	08/10/99		
NSPC	Coarse Tailings	Engesser (2000)	17.1	08/10/99		
NSPC	Coarse Tailings	Engesser (2000)	14	08/10/99		
NSPC	Fine Tailings	Engesser (2000)	25.5	08/10/99		
NSPC	Fine Tailings	Engesser (2000)	29	08/10/99		
NSPC	Concentrate	Engesser (2000)	16.5	08/10/99		
NSPC	Concentrate	Engesser (2000)	15.2	08/10/99		
NSPC	Concentrate	Benner (2001a)	14			
NSPC	Fired Pellet	Engesser (2000)	2.85	08/10/99		
NSPC	Fired Pellet	Engesser (2000)	5.73	08/10/99		
NSPC	Tailings	Lapakko(2000)	17.1			
NSPC	Tailings	Lapakko(2000)	19.5			
Hibtac	Filter Cake	Benner (2001b)	13.9			
Hibtac	Concentrate	Benner (2001b)	18.2			
Hibtac	Limestone	Benner (2001b)	3.72			
Hibtac	Multi-tube dust	Benner (2001b)	154			
Hibtac	Greenball	Benner (2001b)	16.7			
Hibtac	Bentonite	Benner (2001b)	26.4			
Hibtac	Pellet	Benner (2001b)	<0.69			
Hibtac	Mill Feed	Engesser and Niles (1997)	14.89	07/24/96		
Hibtac	Calculated Mill Feed	Engesser and Niles (1997)	22.41	07/24/96		
Hibtac	Concentrate	Engesser and Niles (1997)	14.85	07/24/96		
Hibtac	Tailings	Engesser and Niles (1997)	25.03	07/24/96		
Hibtac	Calculated Mill Feed	Engesser and Niles (1997)	23.24	12/10/96		
Hibtac	Concentrate	Engesser and Niles	15.4	12/10/96		

		(1997)				
Hibtac	Tailings 1	Engesser and Niles (1997)	24.6	12/10/96		
Hibtac	Tailings 2	Engesser and Niles (1997)	27.5	12/10/96		
Hibtac	Calculated Mill Feed	Engesser and Niles (1997)	23.78	12/13/96		
Hibtac	Concentrate	Engesser and Niles (1997)	13.2	12/13/96		
Hibtac	Tailings 1	Engesser and Niles (1997)	22.6	12/13/96		
Hibtac	Tailings 2	Engesser and Niles (1997)	25.8	12/13/96		
Hibtac	Calculated Mill Feed	Engesser and Niles (1997)	28.3	01/28/97		
Hibtac	Final Concentrate	Engesser and Niles (1997)	21.87	01/28/97		
Hibtac	Tailings	Engesser and Niles (1997)	30.54	01/28/97		
Hibtac	Fired Pellets	Engesser and Niles (1997)	0.48	07/24/96		
Hibtac	Bentonite	Engesser and Niles (1997)	22.39	07/24/96		
Hibtac	Limestone	Engesser and Niles (1997)	5.89	07/24/96		
Hibtac	Greenball	Engesser and Niles (1997)	16.2	01/28/97		
Hibtac	Fired Pellets	Engesser and Niles (1997)	0.94	01/28/97		
Hibtac	Bentonite	Engesser and Niles (1997)	12.56	01/28/97		
Hibtac	Limestone	Engesser and Niles (1997)	91.6	01/28/97		
Minntac	Fine Tailings	Swain (2002)	29.6	Sept. 2000		
Minntac	Fine Tailings	Swain (2002)	35.1	Sept. 2000		
Minntac	Greenball	Benner (2001b)	8.1	08/31/01		
Minntac	Pellet	Benner (2001b)	<0.6	08/31/01		
Minntac	Scrubber Filtrate	Benner (2001b)	87	08/31/01		
Minntac	Coal	Benner (2001b)	25.3	08/31/01		
Minntac	Rod Mill Feed	Engesser and Niles (1997)	35.09	07/09/96		

Minntac	Final Concentrate	Engesser and Niles (1997)	8.12	07/09/96		
Minntac	Coarse Tailings	Engesser and Niles (1997)	45.93	07/09/96		
Minntac	Fine Tailings	Engesser and Niles (1997)	38.97	07/09/96		
Minntac	Rod Mill Feed	Engesser and Niles (1997)	27.97	01/23/97		
Minntac	Final Concentrate	Engesser and Niles (1997)	8.22	01/23/97		
Minntac	Coarse Tailings	Engesser and Niles (1997)	43.54	01/23/97		
Minntac	Fine Tailings	Engesser and Niles (1997)	36.96	01/23/97		
Minntac	Filter Cake	Engesser and Niles (1997)	7.19	07/10/96		
Minntac	Greenball	Engesser and Niles (1997)	7.5	07/10/96		
Minntac	Fired Pellets	Engesser and Niles (1997)	0.65	07/10/96		
Minntac	Bentonite	Engesser and Niles (1997)	7.42	07/10/96		
Minntac	Fluxstone	Engesser and Niles (1997)	1.97	07/09/96		
Minntac	Greenball	Engesser and Niles (1997)	8.79	01/24/97		
Minntac	Fired Pellets	Engesser and Niles (1997)	0.57	01/24/97		
Minntac	Bentonite	Engesser and Niles (1997)	12.36	01/24/97		
Minntac	Fluxstone	Engesser and Niles (1997)	3.26	01/24/97		
Minntac	Wood chips	Engesser and Niles (1997)	6.01	01/24/97		
Minntac	Wood chip ash	Engesser and Niles (1997)	11.85	01/24/97		
Minntac	Greenball	Engesser (1998a)	8.62	09/03/97		
Minntac	Greenball	Engesser (1998a)	7.76	09/03/97		
Minntac	Fired Pellets	Engesser (1998a)	0.76	09/03/97		
Minntac	Fired Pellets	Engesser (1998a)	0.72	09/03/97		
Minntac	Scrubber Solids Out	Engesser (1998a)	252.7	09/03/97		
Minntac	Drying furnace solids	Engesser (1998a)	12.77	09/03/97		

Minntac	Tailings	Lapakko(2000)	46.6			
EVTAC	Coarse Tailings	Swain (2002)	24.7			
EVTAC	Coarse Tailings	Swain (2002)	130.2			
EVTAC	Fine Tailings	Swain (2002)	44			
EVTAC	Fine Tailings	Swain (2002)	51.9			
EVTAC	Greenball	Benner (2001b)	12			
EVTAC	Pellet	Benner (2001b)	<0.69			
EVTAC	Coal	Benner (2001b)	10.3			
EVTAC	Thickener underflow 2A	Benner (2001b)	527			
EVTAC	Thickener overflow 2A	Benner (2001b)	233			
EVTAC	Thickener underflow 2B	Benner (2001b)	367			
EVTAC	Thickener overflow 2B	Benner (2001b)	826			
EVTAC	Final Pellet	Engesser (1998b)	0.36	11/18/97		
EVTAC	Final Pellet	Engesser (1998b)	0.34	11/18/97		
EVTAC	Green Ball	Engesser (1998b)	17	11/18/97		
EVTAC	Green Ball	Engesser (1998b)	13	11/18/97		
EVTAC	Ball Mill	Engesser (1998b)	2.84	11/18/97		
EVTAC	Ball Mill	Engesser (1998b)	2.44	11/18/97		
EVTAC	Classifier Overflow	Engesser (1998b)	11.99	11/18/97		
EVTAC	Classifier Overflow	Engesser (1998b)	10.62	11/18/97		
EVTAC	Thickener Underflow	Engesser (1998b)	286.4	11/18/97		
EVTAC	Thickener Underflow	Engesser (1998b)	243.5	11/18/97		
IIMC	Scrubber Filtrate	Benner (2001b)	3179	08/31/01		
IIMC	Multiclone dust	Benner (2001b)	193	08/31/01		
IIMC	Greenball	Benner (2001b)	7.8	08/31/01		
IIMC	Pellet	Benner (2001b)	<0.6	08/31/01		
IIMC	Tailings	Lapakko (2000)	35.4			
LTVSMC	Rod Mill Feed	Engesser and Niles (1997)	14.05	08/06/96		
LTVSMC	Final Concentrate	Engesser and Niles (1997)	4.87	08/06/96		
LTVSMC	Total Tailings	Engesser and Niles (1997)	17.86	08/06/96		

LTVSMC	Rod Mill Feed	Engesser and Niles (1997)	8.86	02/06/96		
LTVSMC	Final Concentrate	Engesser and Niles (1997)	3.73	02/06/96		
LTVSMC	Total Tailings	Engesser and Niles (1997)	11.61	02/06/96		
LTVSMC	Fired Pellets	Engesser and Niles (1997)	0.16	08/06/96		
LTVSMC	Pellet Chips	Engesser and Niles (1997)	0.42	08/06/96		
LTVSMC	Bentonite	Engesser and Niles (1997)	9.41	08/06/96		
LTVSMC	Filter Feed	Engesser and Niles (1997)	5.72	08/06/96		
LTVSMC	Fired Pellets	Engesser and Niles (1997)	2.17	02/06/96		
LTVSMC	Pellet Chips	Engesser and Niles (1997)	2.88	02/06/96		
LTVSMC	Bentonite	Engesser and Niles (1997)	14.81	02/06/96		
LTVSMC	Green Balls	Engesser and Niles (1997)	3.49	02/06/96		
LTVSMC	Total Tailings	Lapakko (2000)	7			
Northshore	Coarse Tailings	Swain (2002)	0.43			
Northshore	Fine Tailings	Swain (2002)	1.2			
Northshore	Fine Tailings	Swain (2002)	3.2			
Northshore	Wastegas 11 filtrate	Benner (2001b)	211			
Northshore	Wastegas 12 filtrate	Benner (2001b)	110			
Northshore	Hood exhaust 11 filtrate	Benner (2001b)	26			
Northshore	Hood exhaust 12 filtrate	Benner (2001b)	26.4			
Northshore	Greenball 11	Benner (2001b)	1.44			
Northshore	Greenball 12	Benner (2001b)	1.1			
Northshore	Pellet 11	Benner (2001b)	<.69			
Northshore	Pellet 12	Benner (2001b)	1.85			
Northshore	Dry Cobber Feed	Engesser and Niles (1997)	0.75			
Northshore	Final Concentrate	Engesser and Niles (1997)	0.82			
Northshore	Dry Cobber Tailings	Engesser and Niles	0.28			

		(1997)				
Northshore	Coarse Tailings	Engesser and Niles (1997)	0.83			
Northshore	Fine Tailings	Engesser and Niles (1997)	1.07			
Northshore	Dry Cobber Feed	Engesser and Niles (1997)	0.76			
Northshore	Final Concentrate	Engesser and Niles (1997)	1.13			
Northshore	Dry Cobber Tailings	Engesser and Niles (1997)	0.77			
Northshore	Coarse Tailings	Engesser and Niles (1997)	0.54			
Northshore	Fine Tailings	Engesser and Niles (1997)	1.64			
Northshore	Acid Pellets	Engesser and Niles (1997)	0.22			
Northshore	Flux Pellets	Engesser and Niles (1997)	0.04			
Northshore	Limestone	Engesser and Niles (1997)	0.48			
Northshore	Bentonite	Engesser and Niles (1997)	19.4			
Northshore	Oriox	Engesser and Niles (1997)	1.09			
Northshore	Green Balls	Engesser and Niles (1997)	0.83			
Northshore	Fired Pellets	Engesser and Niles (1997)	0.29			
Northshore	Limestone	Engesser and Niles (1997)	0.91			
Northshore	Bentonite	Engesser and Niles (1997)	14.69			
Northshore	Oriox	Engesser and Niles (1997)	1.46			
Northshore	Coal	Engesser and Niles (1997)	15.61			
Northshore	Coal Ash	Engesser and Niles (1997)	86.76			

## Appendix 2: Historical Pellet Production

Pellets produced (Million Long Tons) by individual mining companies. Sources included compilation of concentrate produced as reported by Engesser and Niles (1997) multiplied by a conversion factor (mass pellets/mass concentrate) and direct report of pellets production as reported by Skillings (2003).

	Butler	LTVSMC	EVTAC	Hibbing	IIMC	NSPC	Northshore	Minntac
1949		0.05						
1950		0.13						
1951		0.10						
1952		0.10					0.01	0.00
1953		0.24					0.26	0.14
1954		0.19					0.32	0.43
1955		0.21					0.53	0.66
1956		0.22					4.28	0.66
1957		0.50					5.62	0.82
1958		3.04					4.89	0.80
1959		4.23					3.80	0.57
1960		7.35					5.50	0.85
1961		6.97					5.71	0.81
1962		7.82					6.21	0.82
1963		8.09					8.12	0.85
1964		8.25					9.77	0.88
1965	0.01	8.28	0.05				10.12	0.93
1966		8.81	1.56				10.94	0.81
1967	1.62	10.20	1.76			0.47	9.80	0.94
1968	2.33	11.04	1.82			0.84	10.10	4.84
1969	2.6	10.51	1.94			2.29	10.45	6.42
1970	2.64	11.06	2.01			2.73	10.94	6.82
1971	2.65	10.50	2.08			2.81	9.73	6.83
1972	2.3	10.27	2.16			2.42	9.13	9.19
1973	2.56	12.01	2.09			2.58	10.52	13.29
1974	2.52	11.23	2.19			2.48	10.47	13.38
1975	2.44	11.21	2.18			2.43	10.81	12.92
1976	2.4	11.10	2.31	0.31		2.46	10.15	13.03
1977	1.69	4.79	2.60	2.19	0.25	2.62	5.08	7.88

1978	2.51	7.64	4.97	5.52	2.08	5.10	9.24	13.71
1979	2.55	9.08	5.66	6.38	2.42	5.37	7.10	17.48
1980	1.58	5.85	5.84	6.94	1.52	2.90	4.63	15.00
1981	2.19	8.18	5.94	7.27	2.58	3.42	7.72	13.12
1982	1.04	4.08	4.66	5.81	1.93	1.29	1.54	3.51
1983	1.56	2.11	3.30	4.29	2.31	3.27	1.00	8.17
1984	1.99	4.84	3.97	6.20	2.19	4.58	3.71	9.23
1985	0.95	5.01	2.97	5.16	1.97	4.43	3.31	10.50
1986		4.36	3.49	4.98	1.95	4.02	1.44	5.96
1987		6.97	3.51	7.84	2.29	4.31	0.00	8.13
1988		8.13	4.28	8.82	2.43	4.61	0.00	12.56
1989		7.59	4.96	8.35	2.45	4.75	0.00	12.56
1990		8.03	4.46	8.30	2.45	4.81	2.40	13.47
1991		7.10	3.40	8.18	2.53	4.85	2.01	13.22
1992		6.82	3.61	7.96	2.28	5.00	1.40	13.09
1993		7.62	3.15	7.38	2.59	2.76	3.44	14.32
1994		7.69	4.91	8.35	2.71	1.73	3.46	14.28
1995		7.76	5.24	8.62	2.77	5.08	3.71	13.65
1996		7.46	4.94	8.12	2.74	4.77	4.16	13.42
1997		7.71	5.07	7.67	2.58	5.11	4.25	14.58
1998		6.75	4.87	7.78	2.58	5.28	4.35	14.19
1999		7.00	4.40	6.90	2.80	5.25	3.91	13.01
2000		7.80	5.87	8.23	2.81	5.47	4.20	14.44
2001			4.26	6.10	2.77	4.30	2.65	12.64
2002			4.19	7.70	2.73	5.44	4.14	14.64
2003 (est)			2.00	8.30	2.90	5.30	4.80	14.61

### Appendix 3: Historical Mercury Emissions

Mercury (kg) emitted from taconite mining companies. Estimates were made by multiplying past production records with present day emission factors.

kg Hg	Butler	LTVSMC	EVTAC	Hibbing	IIMC	NSPC	Northshore	Minntac	Total	Cumulative
1949		0.23							0.23	0.23
1950		0.67							0.67	0.90
1951		0.52							0.52	1.42
1952		0.52					0.02		0.54	1.96
1953		1.19					0.48	0.73	2.40	4.36
1954		0.93					0.59	2.32	3.84	8.19
1955		1.03					0.96	3.50	5.49	13.69
1956		1.09					7.79	3.50	12.38	26.07
1957		2.53					10.22	4.35	17.10	43.17
1958		15.25					8.90	4.24	28.39	71.56
1959		21.25					6.91	3.05	31.21	102.78
1960		36.92					10.02	4.52	51.46	154.23
1961		35.00					10.39	4.29	49.68	203.92
1962		39.24					11.30	4.35	54.90	258.82
1963		40.59					14.78	4.52	59.89	318.70
1964		41.42					17.78	4.69	63.88	382.59
1965	0.10	41.57	0.58				18.42	4.97	65.64	448.23
1966		44.21	17.76				19.91	4.29	86.17	534.40
1967	16.30	51.19	20.07			4.73	17.83	5.03	115.14	649.54
1968	23.44	55.43	20.76			8.45	18.38	25.82	152.28	801.82
1969	26.16	52.74	22.15			23.04	19.03	34.24	177.34	979.17
1970	26.56	55.53	22.95			27.46	19.91	36.33	188.74	1167.91
1971	26.66	52.69	23.76			28.27	17.70	36.38	185.46	1353.37
1972	23.14	51.55	24.68			24.35	16.62	48.98	189.32	1542.69
1973	25.75	60.29	23.88			25.95	19.15	70.85	225.88	1768.57
1974	25.35	56.36	25.03			24.95	19.06	71.30	222.05	1990.62
1975	24.55	56.26	24.91			24.45	19.67	68.87	218.70	2209.32
1976	24.14	55.74	26.41	3.84		24.75	18.47	69.44	222.80	2432.12
1977	17.00	24.04	29.64	27.54	1.32	26.36	9.25	41.98	177.13	2609.25
1978	25.25	38.37	56.75	69.31	11.09	51.31	16.82	73.05	341.94	2951.19

1979	25.65	45.60	64.59	80.07	12.87	54.02	12.92	93.17	388.90	3340.09
1980	15.89	29.37	66.67	87.12	8.10	29.17	8.42	79.94	324.69	3664.78
1981	22.03	41.05	67.82	91.34	13.73	34.41	14.04	69.94	354.38	4019.15
1982	10.46	20.48	53.17	73.02	10.28	12.98	2.79	18.70	201.89	4221.04
1983	15.69	10.60	37.72	53.94	12.30	32.90	1.82	43.56	208.52	4429.56
1984	20.02	24.30	45.33	77.89	11.66	46.07	6.75	49.21	281.24	4710.80
1985	9.56	25.13	33.91	64.82	10.46	44.57	6.03	55.99	250.46	4961.26
1986		21.87	39.91	62.52	10.40	40.44	2.63	31.75	209.52	5170.78
1987		35.00	40.14	98.52	12.18	43.36	0.00	43.33	272.54	5443.32
1988		40.80	48.91	110.82	12.93	46.38	0.00	66.95	326.77	5770.09
1989		38.11	56.63	104.92	13.04	47.79	0.00	66.95	327.44	6097.53
1990		40.33	50.98	104.28	13.04	48.39	4.37	71.81	333.21	6430.74
1991		35.63	38.87	102.75	13.44	48.79	3.66	70.45	313.59	6744.33
1992		34.23	41.18	99.93	12.12	50.30	2.56	69.78	310.09	7054.42
1993		38.26	35.99	92.75	13.79	27.77	6.27	76.33	291.15	7345.57
1994		38.62	56.06	104.92	14.42	17.40	6.31	76.10	313.84	7659.41
1995		38.96	59.84	108.27	14.74	51.10	6.75	72.75	352.41	8011.82
1996		37.43	56.43	101.99	14.56	47.99	7.57	71.53	337.50	8349.32
1997		38.70	57.85	96.34	13.74	51.37	7.74	77.70	343.43	8692.75
1998		33.89	55.57	97.68	13.74	53.12	7.92	75.63	337.54	9030.28
1999		35.14	50.25	86.66	14.90	52.78	7.11	69.35	316.19	9346.48
2000		39.16	67.04	103.38	14.97	55.03	7.64	76.97	364.18	9710.66
2001			48.65	76.62	14.74	43.26	4.82	67.34	255.43	9966.08
2002			47.80	96.71	14.53	54.70	7.54	78.04	299.31	10265.40
2003 (est)			22.84	104.25	15.43	53.32	8.74	77.84	282.41	10547.81