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AN ASSESSMENT OF ENVIRONMENTAL SELENIUM LEVELS AROUND EMPIRE AND TILDEN MINES MARQUETTE COUNTY, MICHIGAN

Selenium Monitoring Work Group

June 2009

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Executive Summary

Cleveland Cliffs Michigan Operations (CCMOs) operates the Empire and Tilden mining facilities in the Marquette Iron Range near the town of Palmer (Marquette County). Because of concerns about selenium (Se) in facility effluents, waste rock seeps, and nearby surface waters, the Michigan Department of Environmental Quality (MDEQ) formed an internal work group in 2008 to: 1) assess Se levels and the extent and severity of associated water quality impacts; 2) determine whether additional monitoring is warranted; and 3) identify any needed facility permit modifications.

During spring 2008, primary sampling sites were selected to profile the extent of Se contamination on all named streams and lakes under the influence of mining activities. The primary sampling sites included 7 lakes/reservoirs and 13 stream locations. Most sites were near the Empire and Tilden Mine tailings basins, or the surrounding waste rock piles. A small number of "control" sites were monitored to provide background Se levels. Water and sediment were analyzed for Se at all primary stations, while fish and benthic macroinvertebrate tissues were analyzed at three locations. Based on early results from primary sites, water from a small number of secondary sites was analyzed. Secondary sites included very small streams and springs buried by waste rock piles.

Se concentrations in water at primary lake sites were always below the Michigan Water Quality Standard (WQS) of 5 micrograms per liter (ug/l). However, Se levels in all water samples from two primary stream sites (Goose Lake Inlet, mean = 9.3 ug/l; Warner Creek at the M-35 Tailings Line, mean = 11 ug/l) were greater than 5 ug/l. Two of five samples collected from Goose Lake Outlet downstream of Gribben Tailings Basin also contained Se concentrations (8.8 ug/l and 10 ug/l) which exceeded the WQS, although the mean concentration was 3 ug/l. Se concentrations at the secondary sites were extremely high, with values ranging from 15 to 68 ug/l at stations on Partridge Creek, Lost 40 Tributary, and Mary Charlotte Outlet, and seepage from the base of the waste rock piles.

Se was measured in the sediment at 19 of the 20 primary sites. Highest concentrations were found in Goose Lake (27 to 39 milligrams per kilogram [mg/kg]), Ely Creek (12 mg/kg), and Green Creek below the Empire Tailings Basin (5 mg/kg). At the other locations, sediment Se levels were less than 5 mg/kg. Except for Goose Lake, sites with high sediment concentrations do not correspond with the sites at which the highest Se levels in water were found.

Fish tissues from four locations were analyzed (wet weight) for Se. At Goose Lake Outlet, mean Se levels ranged from 8 to 17.5 parts per million (ppm) in the tissues of brook trout, white suckers, fathead minnows, and creek chubs. In Warner Creek, mean tissue Se levels for the same species ranged from 5.6 to 10.1 ppm. Se concentrations in fish from the Bear Creek control site were extremely low, never exceeding a mean of 1 ppm. Mean tissue Se levels in northern pike and white sucker from Goose Lake were 9.5 ppm and 11.6 ppm, respectively.

Benthic macroinvertebrates from Goose Lake Outlet also were analyzed. A Se concentration of 22.3 ppm was found in a composite of caddisfly tissue (greater than in fish tissue). Se was also present at lower levels in leeches, snails, mayflies, and odonates. Sufficient numbers of benthic invertebrates were not collected from Goose Lake, Warner Creek, or Bear Creek for tissue analysis.

In addition to assessing the extent and severity of WQS exceedances, this work group compared the results of tissue, water, and sediment sampling to recommended risk levels for Se. Fish tissue is considered the best risk indicator. The United States Environmental Protection Agency (USEPA) has drafted a water quality value of 7.91 ppm in fish tissue. Tissue

measurements confirm that Se is accumulating in fish at levels that may have adverse impacts on fish reproduction. Mean tissue Se concentrations of all fish species found in Goose Lake Outlet exceeded the USEPA draft water quality value, as did those in Warner Creek brook trout tissues. These elevated tissue levels are especially noteworthy considering that USEPA's draft criterion is a dry weight value while the 2008 results are wet weight. To convert the 2008 results into dry weight, the tissue concentrations have to be multiplied by approximately four.

Invertebrate tissues from Goose Lake Outlet also indicate a pattern of food chain Se bioaccumulation. The levels measured in some invertebrates (up to 22.3 mg/kg wet weight) exceeded concentrations shown to be directly toxic for other invertebrates.

Acute aquatic life toxicity concerns from water exposure appear limited to localized areas around source waters. Total Se concentrations at the primary sampling sites were well below the acute Michigan WQS of 120 ug/l. However, Se levels above the acute WQS in surface flow water from waste rock piles and associated seeps have been documented by CCMO during monthly reclamation monitoring.

Although acute water quality concerns appear limited, water data suggest a potential for bioaccumulative chronic toxicity to both aquatic and terrestrial life. The sites with samples exceeding the chronic WQS (5 ug/l) were Goose Lake Inlet, Goose Lake Outlet downstream of the Gribben Tailings, Partridge Creek, and Warner Creek.

Sediments represent a major Se sink, and therefore, a potential source for Se bioaccumulation by aquatic and terrestrial life. A maximum 2 mg/kg Se sediment concentration has been recommended in literature to protect against bioaccumulative chronic toxicity risk in aquatic life and other water-dependent biota. Comparisons of sediment Se concentrations with this risk level indicate a potential bioaccumulative toxicity concern. Se has accumulated at levels exceeding the 2 mg/kg sediment maximum in the sediments of several area water bodies. These include Green Creek, Ely Creek and its unnamed tributary, the Goose Lake Outlet downstream of the Gribben Basin, Warner Creek at the M-35 Tailings Line, and Goose Lake. Sediment Se concentrations in Goose Lake, evidently a major sink for Se, were nearly an order of magnitude greater than the 2 mg/kg risk level.

There are some gaps in the 2008 monitoring. Comprehensive wet weather sampling was not possible in 2008 because of a lack of significant precipitation events, and snowmelt-related Se transport has not been assessed. We also lack a characterization of Se speciation, because speciation analysis was not feasible for this study.

As a result of Se's complex environmental fate and toxicology, more study is needed to assess potential environmental damage. Assessment of damage to fish could be made using direct fish reproductive effects studies, while egg hatchability studies are a sensitive index of Se toxicity for birds. Additional studies could also include the biogeochemical conditions influencing Se mobility, bioaccumulation, and Se cycling in water. A better understanding of how biological, chemical, and physical conditions in waste rock piles, tailings basins, and ore processing activities impact environmental fate and impact of Se would be beneficial.

Section 1: Introduction

Cleveland Cliffs Michigan Operations (CCMO) operates the Empire and Tilden mining facilities in the Marquette Iron Range near the town of Palmer (Marquette County). The Empire Mine has operated since 1963, while the Tilden Mine began operations in 1974. Because of concerns about selenium (Se) detections in facility effluents, waste rock seeps, and nearby surface waters, the Michigan Department of Environmental Quality (MDEQ) formed an internal work group in 2008 to: 1) assess Se levels and the extent and severity of associated water quality impacts; 2) determine whether additional monitoring is warranted; and 3) identify any needed facility permit modifications.

The work group consisted of the following MDEQ, Water Bureau, staff: Steve Casey, William Dimond, Doug Knauer, Gary Kohlhepp, Alvin Lam, George Pelkola, William Taft, and Ben Thierry.

The work group decided to monitor water quality in two stages. The first consisted of sampling 20 primary sites and a few secondary sites in the vicinity of Tilden and Empire Mines. The purpose of this initial stage was to identify waters where Se levels were elevated and may be impacting chemical and/or biological integrity. Water, sediment, and fish and benthic macroinvertebrate tissue samples were collected and analyzed. The second stage, if needed, will further assess potential problem areas identified in the first sampling stage and document the extent and severity of Se impacts on affected waters. The second stage could include analysis of water, sediments, fish tissue, bird tissue (for species known to eat aquatic organisms), potential fish and bird reproductive impairment, and further biological community assessment.

This report summarizes data from the first stage of monitoring conducted in 2008 and suggests potential options for future monitoring activities.

<u>Selenium Toxicology and Environmental Fate</u>

Se is an element with a complex environmental chemistry. The primary known sources of environmental Se contamination include coal, phosphate, and metal mining; fly ash from coal combustion; the petroleum industry; natural geologic processes; municipal landfills; and irrigation drainage (Lemly, 2004). Hard rock mining can result in the transformation of insoluble reduced Se forms into the mobile, oxidized forms by exposing rock to water and oxygen. Se has a propensity to bioaccumulate in fish, other aquatic life, and water-dependent birds. Adverse effects in fish and water-dependent birds are primarily manifested as reproductive defects/failures (Spallholz and Hoffman, 2002), including teratogenesis (birth defects).

Environmental Se contamination has caused fish and wildlife injury in and around United States surface waters. For example, fish populations have been eliminated because of reproductive failures caused by Se bioaccumulation (Crutchfield and Ferson, 2000). These losses have occurred with little evidence of toxicity because early life stages were impacted while adults appeared healthy (Lemly, 1998). Birds have suffered gross teratogenic abnormalities and widespread reproductive failures. Bird populations were decimated in the early 1980s by Se poisoning and reproductive failures at California's Kesterson Wildlife Refuge (KWR). The KWR was eventually closed, partially buried, and declared a hazardous waste site (Presser, 1994).

Recent research indicates that Se speciation is a key component of Se environmental fate and toxicity. Reduced forms are not thought to be bioavailable, remaining bound up in parent rock or sediments until oxidized by chemical processes or microbial oxidation. The major oxidized forms (selenite [Se^{+4}]; selenate [Se^{+6}]), are highly soluble and mobile. Selenate and selenite acute toxicity and bioaccumulative potential differ substantially (Simmons and Wallschlager, 2005). Finally, organic Se forms are up to two orders of magnitude more bioaccumulative than inorganic forms, with some measured organic bioaccumulation factors greater than 350,000 (Besser et al, 1993).

Water Quality Standards (WQS)

The environmental fate of Se in water is complex and difficult to predict, and diet is the major exposure route for fish and wildlife. As a result, water concentrations are often not predictive of environmental consequences, except in the very rare circumstance when dissolved selenate and/or selenite concentrations are high enough to cause direct acute toxicity. Because water concentrations provide limited information, bioaccumulation is a better measure of environmental impacts. Consequently, the United States Environmental Protection Agency (USEPA) has developed a draft chronic freshwater Se water quality criterion based on winter fish tissue Se concentration (7.91 milligrams per kilogram [mg/kg]; USEPA, 2004). However, the USEPA acknowledges that fish tissue criteria do not necessarily protect water-dependent birds, and stated a need to develop criteria protective for birds. California and the United States Fish and Wildlife Service (USFWS) are working to develop Se criteria to protect water-dependent California wildlife (Renner, 2003), including water birds, aquatic and semi-aquatic mammals, reptiles, and amphibians. This broader ecosystem approach could become a model for additional national standards (Presser and Skorupa, 2006).

The Michigan acute Se WQS for the protection of aquatic life is 120 micrograms per liter (ug/l).

Michigan's chronic Se WQS is 5 ug/l for all surface waters and is based on the protection of aquatic life. The standard was established by the USEPA, through the Great Lakes Initiative, and subsequently adopted by Michigan. Se is not considered a human carcinogen. Accordingly, Michigan has determined a human health non-cancer protection value (2,700 ug/l) for direct contact with surface water not used for a drinking water source. Since the aquatic life protection value (5 ug/l) is lower, it is protective of human health from direct water contact.

Michigan has not calculated wildlife surface water protection values because Se bioaccumulation values are below the threshold for definition as a bioaccumulative chemical of concern. However, based on the ongoing California and USFWS wildlife protection effort, it may be appropriate in the future to develop Michigan surface water Se values for the protection of wildlife.

Se can accumulate in fish tissue at levels high enough to be harmful to humans. Some states (California, Idaho, Utah, and West Virginia) have responded to more severe instances of game fish contamination by issuing local Se fish consumption advisories.

Facility Descriptions and Monitoring

National Pollutant Discharge Elimination System (NPDES) Permit

The Tilden Mine discharges process wastewater, following physical settling in tailings basins and chemical precipitation. This facility began sampling for Se as part of its NPDES permit (report only) effective December 1, 2007. From December 2007 to December 2008, Se content of the Tilden tailings basin Outfall 002 effluent samples exceeded the WQS (5 ug/l) 13 of 16 times. Se concentrations ranged from less than quantifiable (<1 ug/l) to 50 ug/l.

Effluent from two Empire Mine NPDES process outfalls has been monitored for Se since May 2003. The Empire tailings basin (Outfall 001) contains process water. The Mary Charlotte Pit (Outfall 003) contains pit dewatering from each mine, storm water, and flow from waste rock piles. On December 1, 2011, a 5 ug/l limit goes into effect for both outfalls.

Se concentration in the Empire Mine tailings basin Outfall 001 effluent samples exceeded the future Se limit 26 of 112 times between May 2003 and December 2008, with a 7 ug/l average over that period. Se concentrations in the discharge varied between 0 and 80 ug/l; 5 samples exceeded 30 ug/l during 2006. Se levels in the Empire tailings basin discharge have not exceeded 5 ug/l since January 2008. Se in the Empire Mine-Mary Charlotte Pit Outfall 003 effluent samples has exceeded the future Se limit 93 of 112 times. Concentrations have varied between non-detect and 90 ug/l over a period between May 2003 and December 2008, with an average of 18 ug/l. The highest concentrations occurred during 2006 and 2007.

Empire and Tilden facility Discharge Monitoring Report results are summarized in Tables 1a and 1b.

Although Se concentrations in the process and storm water discharges at the Empire and Tilden Mines have been documented significantly above 5 ug/l, downstream water quality had not been fully assessed until the current study. Previous limited ambient water monitoring in these receiving streams revealed some values greater than 5 ug/l. Previous MDEQ biological monitoring in the vicinity of the mines has not documented ecological problems. However, the rapid biological survey method used is not designed to detect bioaccumulative chronic toxicity, except where such toxicity has grossly impacted populations of fish and insects.

Site Reclamation Information

Open pit mining includes the excavation of mine rock too low in iron to process. Most of the waste rock is piled hundreds of feet on the land surface. The Empire and Tilden Mines have approximately 3,000 acres of waste rock. Part 631, Reclamation of Mining Lands, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended, requires open pit iron mines to revegetate or reclaim waste rock piles prior to mine closure. The Empire and Tilden Mines have engaged in reclamation, including the use of soil and (since 2004) full scale application of pulp and paper mill residuals to facilitate revegetation of waste rock piles and control fugitive dust from tailings basins.

Paper mill residuals are applied to provide a growing medium for revegetating waste rock piles. A relatively small portion of the 3,000 acres of waste rock piles has received paper residuals. The application of paper mill residuals was preceded by a pilot study and surface water monitoring at locations where continuous seepage from stockpiles with residual applications is occurring. Monitoring locations were selected to collect data on continuously flowing seeps influence by paper mill residuals. Since September 2003, monthly monitoring of continuous seepage sites has been conducted by CCMO (except when seeps are frozen) for numerous parameters, including Se. Annual reclamation reports, including monthly monitoring data, are submitted every March.

Reclamation monitoring indicates waste rock seeps are a source of Se to receiving waters (Table 2). Results vary from month to month, and Se concentrations differ greatly among locations. However, data indicate Se concentrations in seepage water from the Empire Mine waste rock piles (3 locations) are two orders of magnitude higher (up to 450 ug/l) than in seepage water from a Tilden Mine waste rock pile (1 location).

Section 2: Methods

Study Design and Site Selection

During spring 2008, primary sampling sites were identified and evaluated in the field. Primary sites were selected to profile the extent of Se contamination on all named streams and lakes under the influence of the Empire and Tilden's mining activities. The primary sampling sites included 7 lakes/reservoirs and 13 stream locations (Figure 1, Table 3). Most sites were near the Empire and Tilden Mine tailings basins, or the surrounding waste rock piles. A small number of "control" sites in areas not expected to be affected by the mines were monitored to provide background Se levels in area waters. These include Keewaydin Lake, Bear Creek, Flopper Creek, and the most upstream Warner Creek Control (WCC) station.

Primary lake sites were sampled once during the summer. Primary stream sites were sampled four times, with the intent to sample once during spring runoff, twice during the summer, and once in the fall. Sediment samples were collected at each of the primary lake and stream locations, except for one site (Schweitzer Basin) where a suitable depositional area could not be found. In addition, fish and benthic macroinvertebrate tissues were collected for contaminant analysis at a few locations with known or suspected high Se levels.

Because monitoring data from primary sites indicated Warner Creek and the Goose Lake system (inlet, lake, and outlet) exceeded published Se toxic effect thresholds for water, sediment, and biota, these waters are central to future determinations of Se impacts. Secondary sites were added to incorporate stream and waste rock seepage sites flowing into or tributary to the Goose Lake Inlet and Warner Creek (Figure 2, Table 3). These sites included very small streams and springs, some buried by waste rock piles, as well as former subsurface mining locations. Water from secondary stream sites was sampled only one time.

Sampling Procedures

Water Collection

Water samples were collected in 16 ounce (473 milliliter [mL]) high density polyethylene bottles. In streams, the water samples were collected upstream of the collector while using latex powder-free disposable gloves. The exception was during cold weather sampling in November when insulated shoulder-length rubberized gloves were used. In lakes/reservoirs, surface samples were collected on the upwind side of the boat just under the surface using latex powder-free disposable gloves. When taking water samples from the hypolimnion, an acid-washed Teflon line with a Teflon weight and peristaltic pump was used. The bottles were rinsed three times in the field with lake/stream water. Appropriate acids were added to preserve the samples within 30 minutes for most stream samples and within 3 hours for the lakes and reservoirs. Ten drops of H_2SO_4 per bottle were added as a preservative for Kjeldahl-N, NO_3 + NO_2-N, NH_4-N, total phosphorus, and total organic carbon. In a second bottle, 5 mL of HNO_3 per bottle was added as a preservative for total metals. No preservative was added to a third bottle for pH, conductance, and SO_4. In most cases, the water samples were shipped on ice the day of collection by overnight courier to the MDEQ, Environmental Laboratory, in Lansing.

In lakes/reservoirs, depth profiles of temperature and dissolved oxygen were taken using a YSI Model 57 dissolved oxygen/temperature meter.

Sediment Collection

MDEQ staff sampled organic sediments in the streams. At each site, sediments were collected using a glass or plastic jar to scoop the sediments and place them in a stainless steel bowl.

Due to stream characteristics, the level of organics in stream sediments varied considerably from site to site. The composite sample was thoroughly mixed and put into glass jars with Teflon cap liners and kept refrigerated until shipped on ice to the MDEQ, Environmental Laboratory, in Lansing.

Lake sediments were collected by 1 of 2 methods; either a piston core sampler with an inside diameter of 3.5 inches, or a Wildco K-B core sampler with an inside diameter of 2.5 inches. The piston core was used in water depths of 20 feet or less and the K-B core was generally used in water depths greater than 20 feet. Sediment samples were extruded at 1 centimeter (cm) intervals through the first 10 cm and placed into Ziploc bags or glass jars with Teflon cap liners and kept refrigerated until shipped on ice to the MDEQ, Environmental Laboratory, in Lansing.

Fish and Benthic Macroinvertebrate Tissue Collection

On May 29, 2008, MDEQ staff (William Taft, Joseph Bohr, Randall Conroy, and Ben Thierry) met with representatives for CCMO at a bridge crossing (North Bridge) on the Goose Lake Outlet, downstream of the Tilden 002A process outfall in Marquette County for fish and macroinvertebrate collections. Two additional streams sites, Warner Creek at Tilden Tailings Pond Road and Bear Creek at County Road 565 (a site not impacted by the mines) were visited for fish monitoring on that same day. MDEQ staff selected a downstream entry point at each location to collect fish for tissue analysis and followed the fish collection procedures outlined in the Surface Water Assessment Section Procedure 51 (MDEQ, 1990). A backpack shocking unit was used and adjusted to the local water conductivity conditions for maximum performance. Fish sampling proceeded by wading in an upstream direction and all fish were collected in five gallon plastic buckets. The time of collection, along with average stream width and depth measurements, was recorded.

On June 8, 2008, Michigan Department of Natural Resources (MDNR) personnel collected northern pike and white suckers from Goose Lake with fyke nets and experimental gillnets.

Macroinvertebrate samples were collected from Goose Lake Outlet using a triangular framed 1 millimeter mesh dip net and by hand picking. Macroinvertebrate samples were sorted in plastic pans and identified to order or family.

All fish and macroinvertebrate samples for tissue analysis were put in plastic bags, placed on ice, and transported to the MDEQ, Environmental Laboratory, in Lansing, where they were frozen. Fish were identified to species, and fish weight and length (in larger individuals) were recorded.

<u>Analytical Procedures</u>

All water and sediment samples collected during this study were analyzed by the MDEQ, Environmental Laboratory, in Lansing. Se in water samples was analyzed by Inductively Coupled Plasma-Mass Spectrometry following USEPA Method 200.8. Se in sediment was analyzed according to USEPA Method 6020A. Samples were also analyzed for a suite of other parameters using USEPA-approved methods. All water samples are reported as unfiltered total Se and all sediment results are reported as dry weight.

Fish and benthic macroinvertebrate tissue samples were prepared for laboratory analysis on June 11, 2008. Fish were analyzed as individual whole samples if a minimum of 2 grams of tissue was available. Smaller fish were randomly divided into composite samples of whole fish. Macroinvertebrates were analyzed by taxon as composite samples of whole individuals. Trichoptera (Limnephilidae) larvae were removed from larval cases before samples were composited.

Samples were delivered to the Michigan Department of Community Health, Analytical Chemistry Laboratory (MDCH-AC), for analysis of Se content. The MDCH-AC followed standard operating procedures for tissue homogenization prior to analyzing the samples for Se using techniques based on USEPA Method 200.11. All fish and benthic macroinvertebrate tissues were analyzed as wet weight. Analytical results were reported to the MDEQ electronically and were added to the Fish Contaminant Monitoring database.

Quality Assurance/Quality Control

Split water and sediment samples were taken at all primary sites and usually delivered on site to the CCMO consultants (White Water Associates, Amasa, Michigan). On one occasion (October 27-28, 2008), samples were collected at the primary stream sites using White Water Associates' sample bottles. On another occasion (November 13, 2008), samples were collected for White Water Associates in MDEQ sample bottles and delivered on site to them. We hope to compare split sample results, but it is unclear whether CCMO will share its results.

Some duplicate samples were collected using trace metal clean sampling protocols and sent to an ultra-clean laboratory at the United States Geological Survey (USGS) Laboratory (Dr. Howard Taylor) in Boulder, Colorado. The data were compared to those generated by the MDEQ, Environmental Laboratory, (see Results section).

Three field blanks (deionized water) were analyzed to assess the potential for external contamination of samples. In addition, the MDEQ, Environmental Laboratory, routinely conducts internal quality assurance/quality control assessment, including instrument calibration, sample custody and recordkeeping, matrix spikes, surrogate recoveries, method blanks, and laboratory duplicates, among other controls.

Section 3: Results

Water

Se concentrations at primary surface water lake/reservoir sites were generally low (Figure 3a, Table 4). Four of seven primary lake/reservoir sites had Se concentrations below the level of quantitation (1 ug/l). The Lake Sally epilimnetic sample contained 1.1 ug/l Se, while the Se concentration in Gunpowder Lake water was 1.2 ug/l. The Goose Lake water sample contained 4.8 ug/l Se, just below the Michigan WQS of 5 ug/l. Goose Lake is fed by Goose Lake Inlet, which is characterized by elevated Se levels (see below).

Some primary stream site Se concentrations were greater than the Michigan WQS of 5 ug/l. Mean Se concentrations for Goose Lake Inlet (9.3 ug/l) and Warner Creek at the Tilden Tailings Line (11 ug/l) exceeded the WQS. In addition, the Se concentration of each individual sample from these two sites exceeded the WQS, indicating that exceedances were frequent during 2008. Se concentrations in two of five samples collected from Goose Lake Outlet downstream of Gribben Tailings basin (8.8 ug/l and 10 ug/l) also exceeded the WQS. However, other samples at this location contained less Se, resulting in a geometric mean of 3 ug/l. Further upstream, Goose Lake Outlet sample Se concentrations were lower (mean = 2.4 ug/l), and the Se concentrations of individual samples did not exceed the WQS. Se concentrations at other primary stream sites were not elevated.

Se concentrations at the secondary sites were extremely high. Values ranged from 15 to 68 ug/l at stations on Partridge Creek, Lost 40 Tributary, and Mary Charlotte Outlet, and seepage from the base of the waste rock pile (Figure 3b, Table 4). All exceeded the Se WQS.

Sediment

Se was measured in the sediment at 19 of the 20 primary sites in 2008, and results were compared with published sediment risk levels and previous studies of area lakes (Figure 4, Tables 5 and 6; Fett et al, 2000; MDNR, 1991). The only site with a Se concentration below quantitation (0.2 mg/kg) was the Middle Branch Escanaba River. The highest concentrations were found in Goose Lake (27 to 39 mg/kg) and Ely Creek (12 mg/kg). Other locations with elevated levels included Green Creek below the tailings pond (5 mg/kg), Gunpowder Lake (4.1 mg/kg), Lake Sally and Lake Ogden (both 4 mg/kg), and a small unnamed tributary to Ely Creek (3.2 mg/kg). Se was usually above quantitation levels in the water at these locations, but below 5 ug/l. At the other locations, sediment Se levels were low. Except for Goose Lake, sites with high sediment concentrations do not correspond with the sites with the highest Se levels in water.

Core samples from several lakes indicated very low Se levels throughout the top 10 cm of sediment (Table 7). The exception was Goose Lake sediment, in which Se levels were elevated throughout the core. In one Goose Lake core, Se concentration increased from approximately 20 mg/kg at 10 cm to almost 40 mg/kg at 6 cm. The concentration was relatively steady (near 40 mg/kg) from 6 cm to the sediment surface.

Fish and Benthic Macroinvertebrate Tissue

Fish were collected from four locations for analysis of whole-body tissue Se concentrations, and all tissue results are reported as wet weight. At Goose Lake Outlet, mean Se levels ranged from 8 to 17.5 parts per million (ppm) in the tissues of brook trout, white suckers, fathead minnows, and creek chubs (Figures 5 and 6). Concentrations were highest in creek chubs and lowest in white sucker. In addition to the fish, several benthic macroinvertebrates were collected from Goose Lake Outlet (Figure 6). The concentration of Se in a composite of caddisfly (Limniphilidae) tissue was 22.3 ppm, greater than was found in the fish at this location. Se was also present in leeches, snails, mayflies, and odonates, although at levels generally lower than in any of the fish tissues.

The same fish species collected at Goose Lake Outlet were present at the Warner Creek and Bear Creek locations, except for the absence of fathead minnows at the latter site (Figures 5 and 7). In Warner Creek, mean tissue Se levels ranged from 5.6 ppm (fathead minnows) to 10.1 ppm (brook trout), substantially lower than levels in Goose Lake Outlet fish. As expected, Se levels in fish from the Bear Creek control site were extremely low, ranging from 0.7 ppm in creek chub and white sucker to 1 ppm in brook trout (Figure 5). We were not able to collect a sufficient quantity of benthic invertebrates from Warner Creek or Bear Creek for tissue analysis.

Mean fish tissue Se concentrations were 9.5 ppm for walleye and 11.7 ppm for white sucker collected from Goose Lake (Figure 5).

Because the 2008 fish and benthic macroinvertebrate tissue results are reported as wet weight while the draft USEPA fish selenium criterion is dry weight, the 2008 data must be multiplied by a factor based on the moisture percentage in the tissues. The moisture content was determined for selected ground and homogenized tissue samples by weighing the samples before and after drying (48 hours at 90 degrees Celsius) in May 2009. The results for Goose Lake are shown in Table 8. The wet weight concentrations should be multiplied by a factor of approximately four to calculate the corresponding dry weight concentration.

Quality Assurance/Quality Control Results

Se concentrations of all three field blank samples were less than quantitation (1 ug/l).

A comparative Se analytical study at three locations was conducted with the USGS in Boulder, Colorado. The USGS method for preparing the glass bottles uses only high purity acids; the MDEQ uses the trace metal protocols for sampling. The USGS results are derived from filtered samples while the MDEQ results are based on unfiltered samples. The results were essentially equivalent, indicating that the water sampling and analytical procedures generated reliable data:

Goose Lake Inlet:	MDEQ = 6 ug/l;	USGS = 5.4 ug/l
Warner Creek Tilden Tailings Basin:	MDEQ = 11 ug/l;	USGS = 11 ug/l
Bear Creek:	MDEQ <1 ug/l;	USGS = 0.1 ug/l

Some split samples collected by the MDEQ were provided to CCMO for independent analyses.

Section 4: Discussion

Although acute Se WQS exceedances (>120 ug/l) were not found in primary site surface water samples, high concentrations in source waters (i.e., secondary locations) suggest localized acute water quality concerns. The maximum value detected at a surface water site was 68 ug/l, in a sample from a waste rock pile seep to Partridge Creek. However, data submitted in CCMO's Annual Reclamation Report identify waste rock seepage up to 450 ug/l. The regulatory status of many waste rock pile seeps has not been determined.

Se analysis indicates chronic WQS exceedances were limited in the surface waters sampled. Although water Se concentrations were often elevated (up to 16 ug/l) above background levels found at control sites, most surface water Se concentrations were below the chronic WQS (5 ug/l). However, the Se concentrations of samples from some waters frequently exceeded the chronic WQS. Water bodies of concern for chronic WQS exceedances included Goose Lake Inlet, Goose Lake Outlet downstream of the Gribben Tailings, Partridge Creek, and Warner Creek.

There are some gaps in the 2008 monitoring effort that may warrant additional sampling. First, comprehensive wet weather sampling was not possible in 2008 because of a lack of significant precipitation events. In addition, snowmelt-related Se transport has not been assessed. We also lack a characterization of Se speciation, because speciation analysis was not feasible for this study. Finally, additional source waters in the study area could be monitored.

In addition to assessing the extent and severity of WQS exceedances, this work group was charged with providing adequate information to make scientifically defensible decisions related to permits and potential enforcement actions. The work group is also charged with determining whether additional monitoring is needed to evaluate potential natural resource damages in the vicinity of the Tilden and Empire Mines. To address these additional charges, we compared the results of tissue, water, and sediment sampling to recommended risk levels for Se.

Fish tissue is considered the best risk indicator (USEPA, 2004). If Se is not elevated in representative fish tissue, adverse effects are unlikely. There has been some controversy about acceptable fish tissue concentrations. Because of the bioaccumulative nature of Se toxicity, the USEPA (2004) has drafted a water quality value of 7.91 mg/kg in fish tissue (**dry weight**, whole body).

Tissue measurements in 2008 confirm that Se is accumulating in fish at levels that may have adverse impacts. Wet weight mean tissue Se concentrations of all fish species sampled from the Goose Lake Outlet and Goose Lake exceeded the USEPA draft water quality value. Se concentrations in Warner Creek brook trout tissue samples also exceeded the USEPA value. These elevated tissue levels are especially noteworthy considering that USEPA's draft criterion is a dry weight value while the results reported here are based on wet weight. Dry weight conversions require multiplying wet weight levels by a factor of approximately 4 (Table 8). In contrast, Se levels were low in Bear Creek (control site) fish tissue samples; even with a wet weight/dry weight conversion, Bear Creek fish would be below the draft criterion.

Brook trout tissue Se concentrations are of the greatest concern. Holm et al. (2003) estimated a chronic value (geometric mean between no effect concentration and effect concentration) of 12.4 mg/kg brook trout parental tissue (whole body). Higher concentrations induced significant rates of embryo-larval deformities. Larval effects were severe, including gross craniofacial deformities. Goose Lake Outlet brook trout Se concentrations exceeded 12.4 mg/kg in 4 of 6 individuals sampled, and averaged 12.9 mg/kg. Warner Creek brook trout Se concentrations were lower on average (10.1 mg/kg), but Se concentration of one individual was 19.9 mg/kg. The elevated Se concentrations in Goose Lake, Goose Lake Outlet, and Warner Creek fish tissue are consistent with elevated water and sediment Se measurements in those or nearby waters. Goose Lake is shallow, eutrophic, relatively warm, and contains substantial organic sediments. Lakes with these characteristics are primary sinks for environmental Se (Lemly, 1997), but may serve as secondary sources via Se cycling.

Potential reproductive effects have apparently not eliminated Goose Lake fish populations. An October 2008 fisheries survey (Richard Harrison, MDNR, Fisheries Division, personal communication) indicated that abundance of pike and bullheads were similar to previous years. Golden shiners were very abundant. However, perch and walleye abundances were greatly reduced. Recent fish population changes are more likely the result of dry weather and resultant low groundwater flow and low dissolved oxygen concentrations (William Taft, personal communication).

Invertebrate tissue Se measurements also indicate a pattern of food chain Se bioaccumulation toxicity risk, and perhaps direct chronic toxicity risk to invertebrates. Tissue from Limnephilid caddisflies, leeches, and snails collected in Goose Lake Outlet contained elevated Se. These concentrations (up to 22.3 mg/kg) are potentially toxic to fish reproduction via bioaccumulation (5 to 15 mg/kg; Lemly, 1998). In addition, the levels detected in some invertebrate tissues exceeded concentrations shown to be directly toxic for other invertebrates (3 mg/kg; Debruyn and Chapman, 2007).

Acute aquatic life toxicity concerns from water exposure appear limited to localized areas around highly contaminated source waters. Total Se concentrations at the primary sampling sites were uniformly well below the Michigan WQS of 120 ug/l. In addition, recent research indicates the acute toxicity of one of the major dissolved forms of Se, selenate, is reduced by sulfate (Brix et al., 2001). Sulfate concentrations were often elevated in these waters, ranging from 2 to 152 mg/l. The elevated sulfate concentrations suggest the potential for acute toxicity mitigation. However, Se levels well above the acute WQS from waste rock piles and associated seeps have been documented by CCMO during monthly reclamation monitoring.

Water is often a key transport medium for the soluble Se forms. However, sediments represent a major Se sink for insoluble and organic forms, and therefore, a potential perennial source for bioaccumulation of Se by aquatic and terrestrial life (Lemly, 1997). Because of the propensity of Se to accumulate in sediment, sediment Se concentrations may be elevated when water Se concentrations are very low, even below a level of quantitation (Lemly, 2002).

A maximum 2 mg/kg Se sediment concentration has been recommended in literature (Lemly, 2002) to protect against bioaccumulative chronic toxicity risk in aquatic life and other water-dependent biota. In addition, Lemly characterizes sediment Se concentrations >4 mg/kg as having a high risk of bioaccumulative toxicity.

Comparisons of sediment Se concentrations with the Lemly risk levels further indicate a potential bioaccumulative toxicity concern. Se has accumulated at levels exceeding the 2 mg/kg maximum in the sediments of several area water bodies. These include Green Creek, Ely Creek and its unnamed tributary, the Goose Lake Outlet downstream of the Gribben Basin, Warner Creek at the Tilden Tailings Line, Goose Lake, Lake Ogden, Lake Sally, and Gunpowder Lake. In addition, Se levels in sediments in 3 streams and 4 lakes exceeded the 4 mg/kg high risk level. Sediment Se concentrations in Goose Lake, evidently a major sink for Se, were nearly an order of magnitude greater than the high risk level.

The elevated Goose Lake water and sediment Se concentrations suggest a potential risk to water-dependent birds. However, habitat restrictions limit bird use (William Taft, personal communication). The lake is divided by a railroad grade, and waterfowl use is largely limited to brief migratory stopovers. Impacts on other water-dependent birds are unknown.

Site Se environmental concentrations are elevated, but at this time appear less than those that resulted in the decimation of fish and bird populations at California's KWR. Goose Lake Outlet fish whole body tissue Se concentrations (maximum 20 mg/kg, wet weight) were substantially lower than KWR tissue Se concentrations (up to 290 mg/kg, dry weight). In addition, surface water Se concentrations were much less at the Empire and Tilden mining site (maximum mean 9.3 ug/l) than at KWR (maximum 430 ug/l). However, Goose Lake sediment Se concentrations (27 to 39 mg/kg) approached KWR sediment Se values (up to 67 mg/kg).

In summary, analysis of water, sediment, and aquatic animal tissue samples suggest the potential for aquatic life and water-dependent wildlife injury due to Se in the study area. Goose Lake appears to be particularly at risk among the water bodies sampled. However, it must be emphasized that actual environmental damage has not been documented.

Because of Se's complex environmental fate and toxicology, more study is needed to assess potential environmental damage. Since larval fish teratogenesis is a clear marker of a cause-effect relationship, final assessment of damage to fish would best be made using direct fish reproductive effects studies (Lemly, 1998; and personal communication). For birds, egg hatchability studies are recommended as a sensitive index of Se toxicosis (O'Toole and Raisbeck, 1998).

Additional assessment could include examining the biogeochemical conditions influencing Se mobility in surface water and groundwater, Se speciation, bioaccumulation, and Se cycling in water. An improved understanding of biological, chemical, and physical conditions in waste rock piles, tailings basins, and ore processing activities would allow for a better assessment of sources and potential control/treatment efforts. Because of laboratory limitations, this study did not include analysis of Se speciation (e.g., organic vs. inorganic), which greatly affects mobility of Se and its uptake by aquatic life via bioaccumulation and bioconcentration. Detailed speciation would allow better delineation of sites contributing the greatest risk to the surrounding environment.

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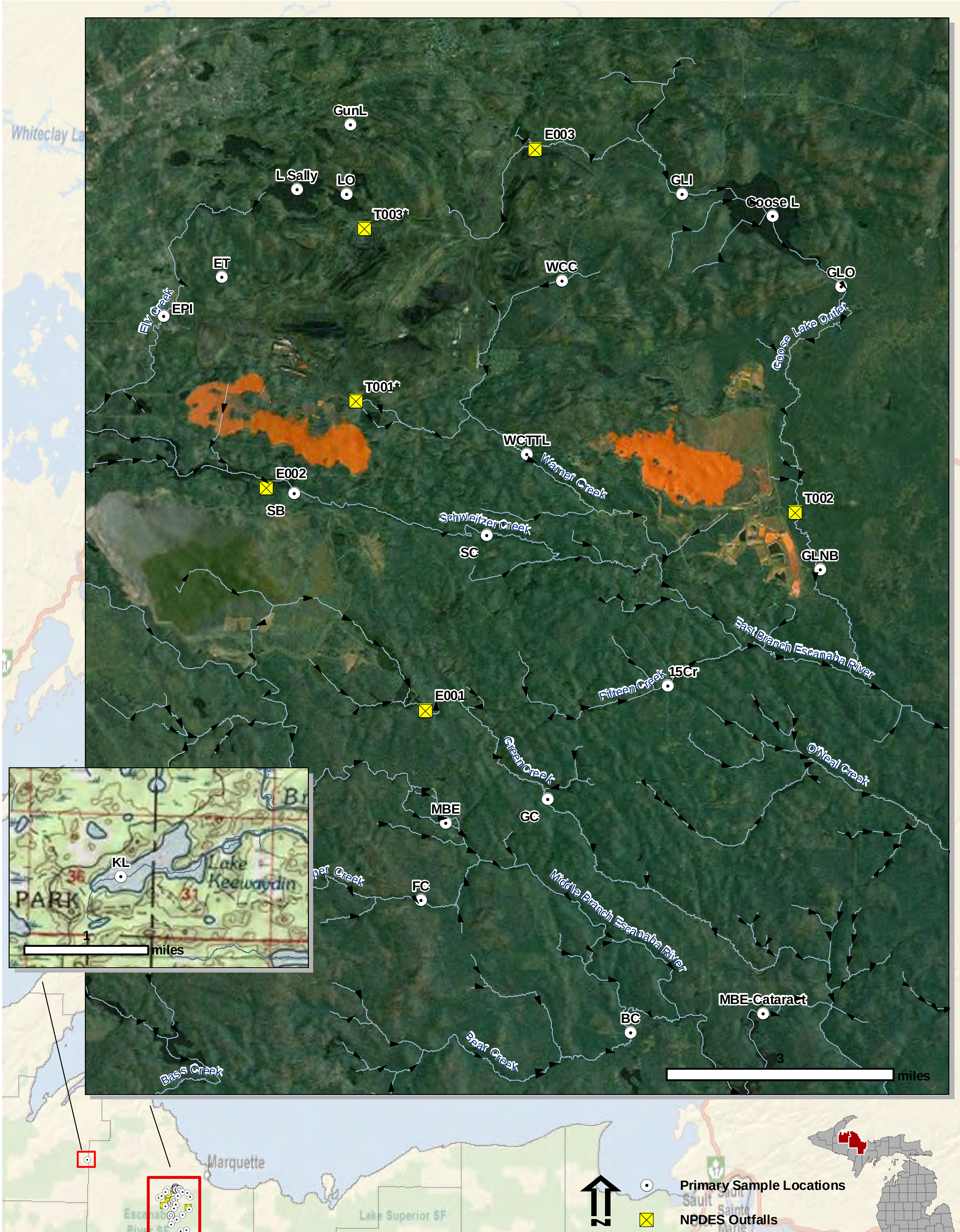

Figure 1: Primary Selenium Sample and NPDES Outfall Locations Near Empire and Tildens Mines, Marquette County, Michigan, 2008.
***rarely used or emergency outfalls**

Figure 2: Secondary Sample and NPDES Outfall Locations Near Empire and Tildens Mines, Marquette County, Michigan, 2008.

Figure 3A: Mean Selenium Concentrations at Primary Sites Near Empire and Tilden Mines, Marquette County, Michigan, 2008.
All values are in ug/L.

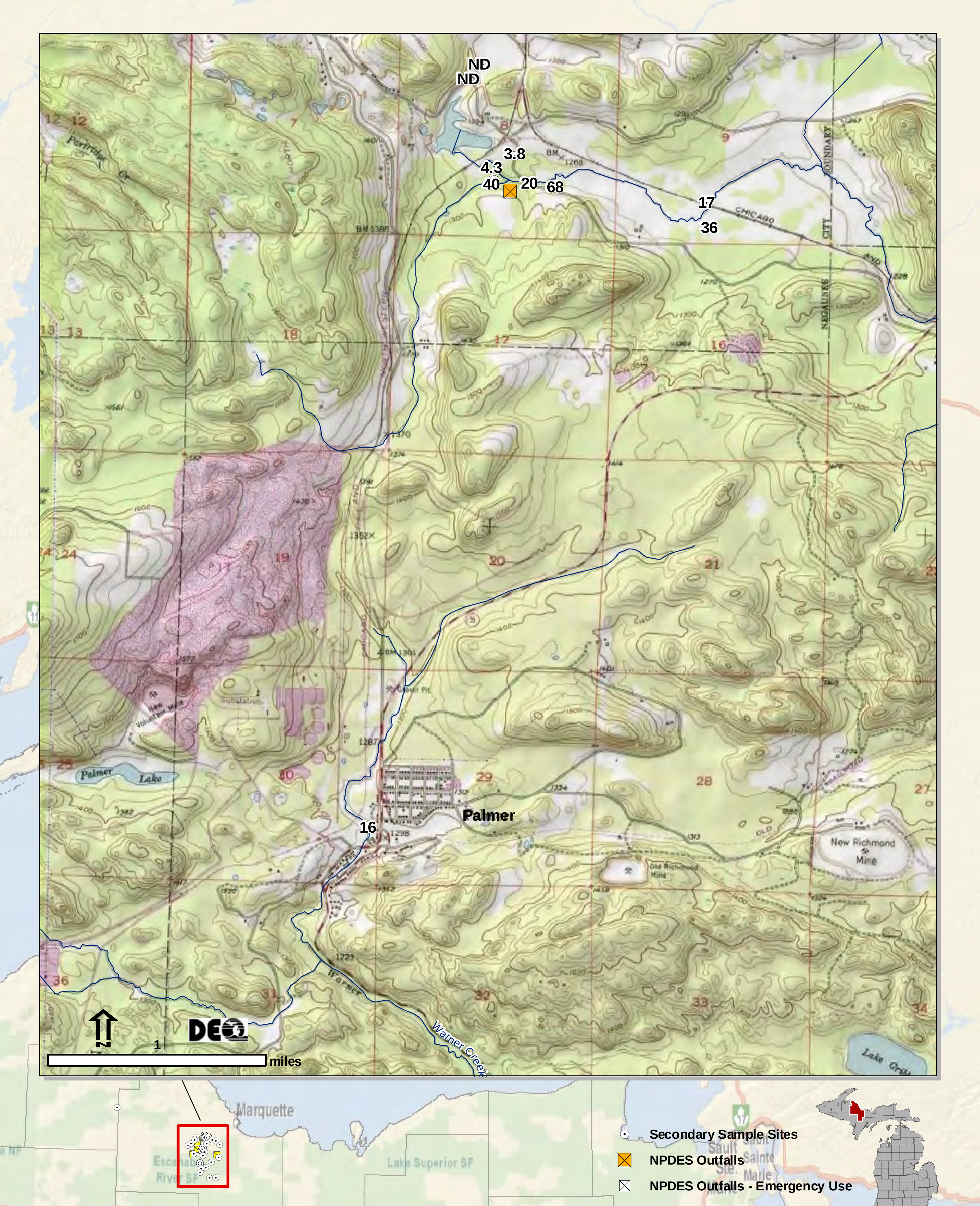

Figure 3B: Mean Selenium Concentrations at Secondary Sites Near Empire and Tilden Mines, Marquette County, Michigan, 2008.
All values are in ug/L.

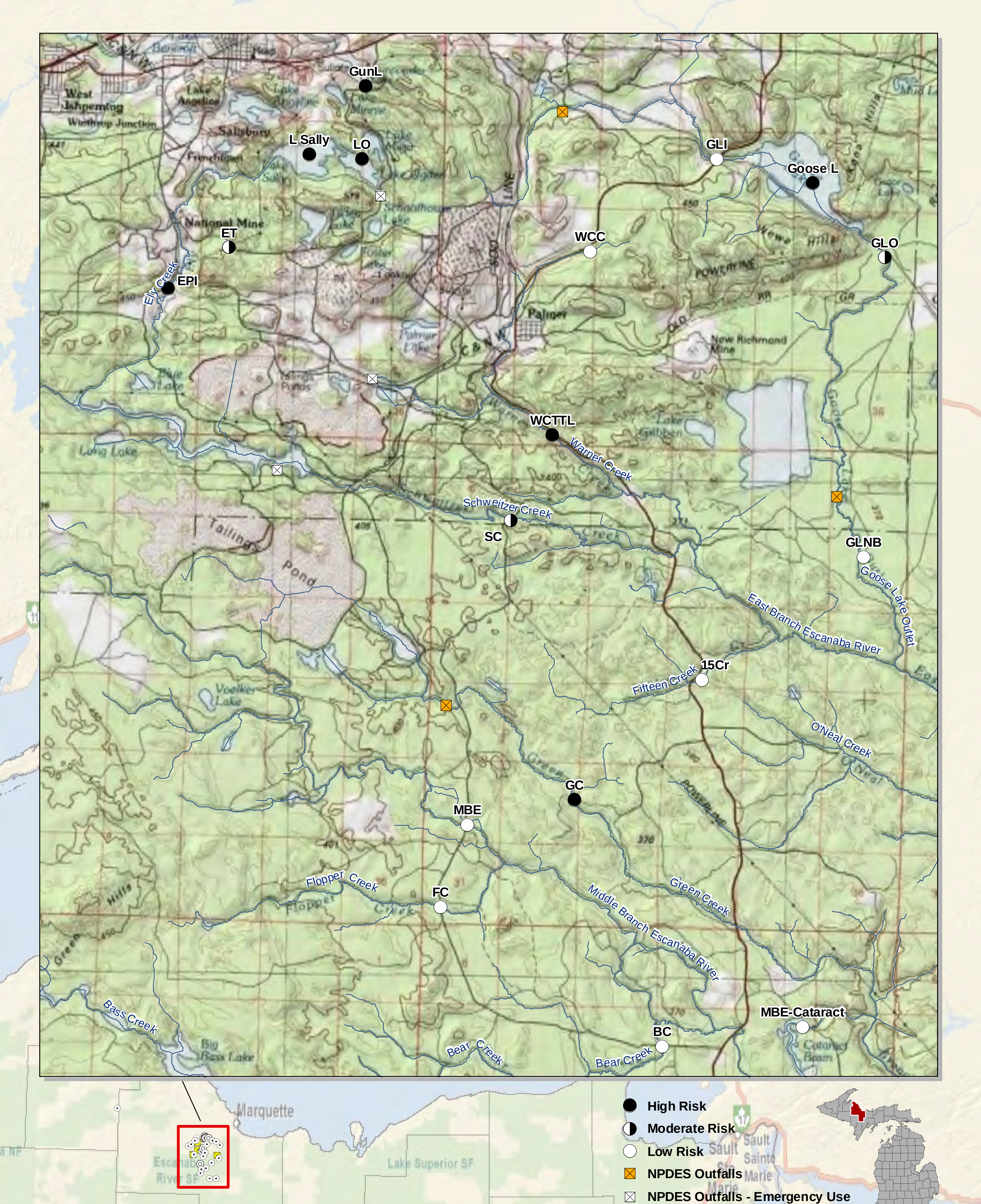

Figure 4: Selenium Concentration Levels in Sediment at Primary Sites Near Empire and Tilden Mines, Marquette County, Michigan, 2008.

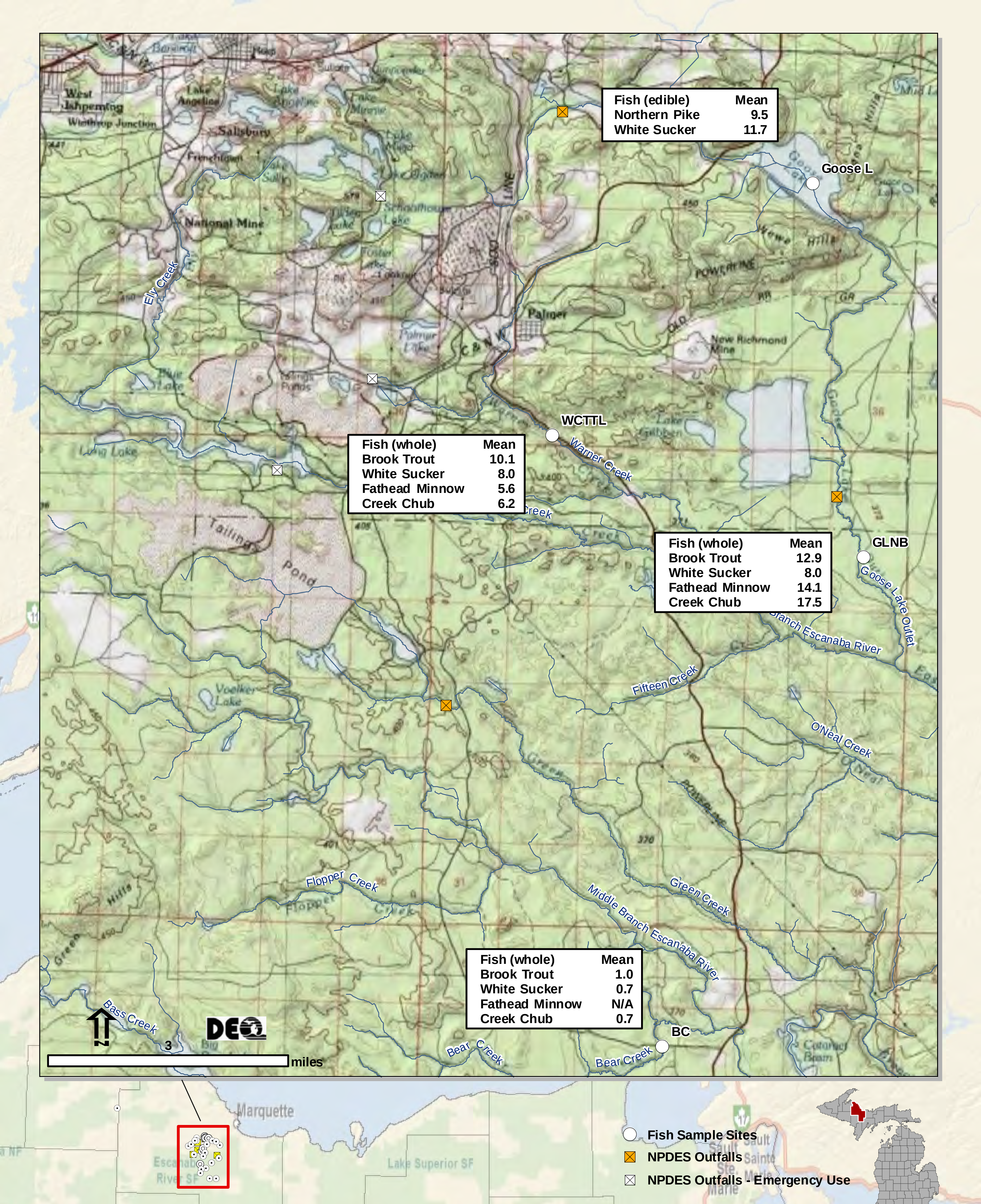

Figure 5: Selenium Concentration Levels in Fish (wet weight) From Goose Lake, Goose Lake Outlet, Warner Creek, and Bear Creek (control site) Near Empire and Tilden Mines, Marquette County, Michigan, 2008.

Figure 6. Mean Selenium Concentrations In Fish From Goose Lake Outlet (May 2008)

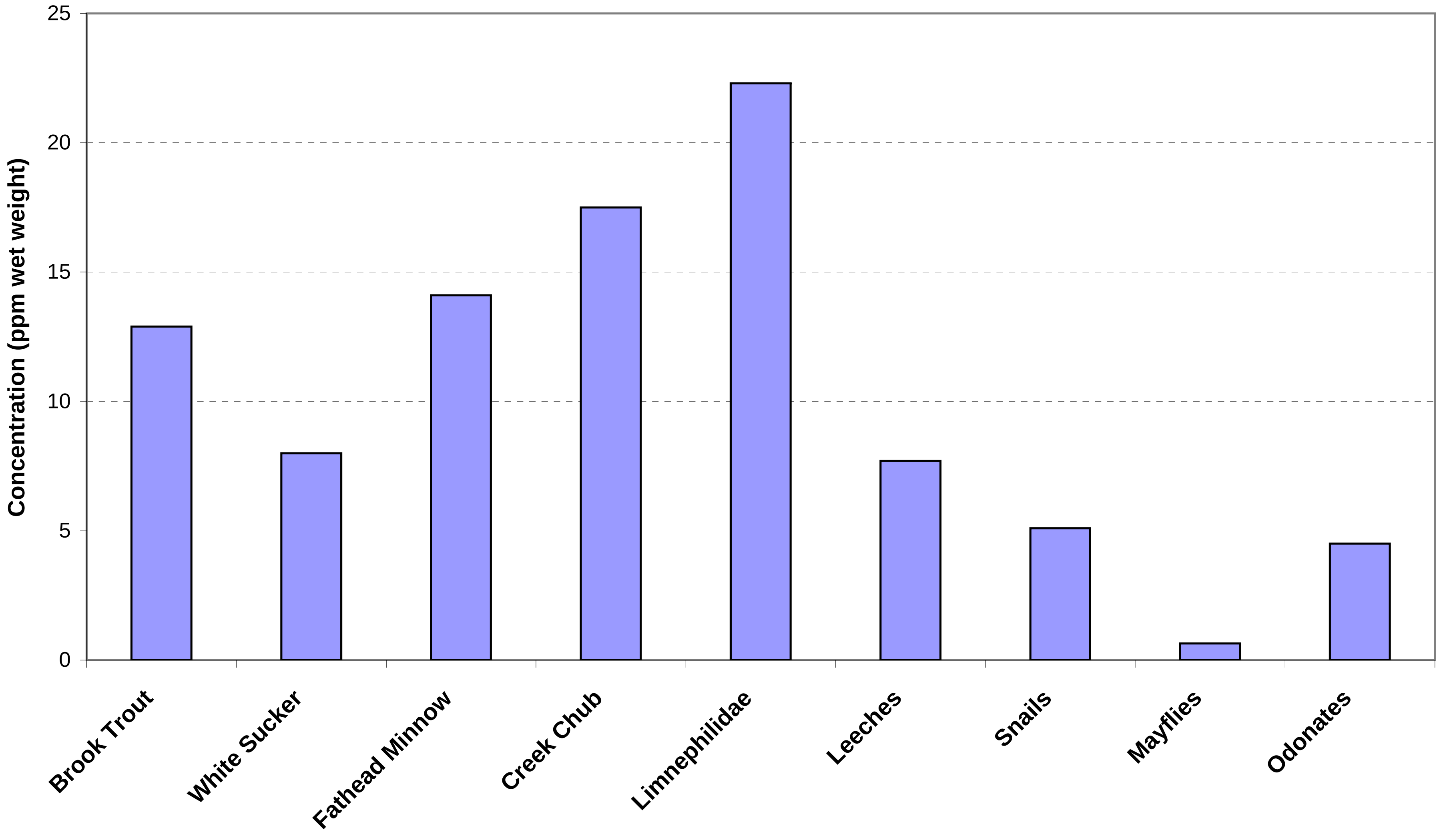

Figure 7. Mean Selenium Concentrations In Fish From Goose Lake Outlet, Warner Creek, and Bear Creek (control site)

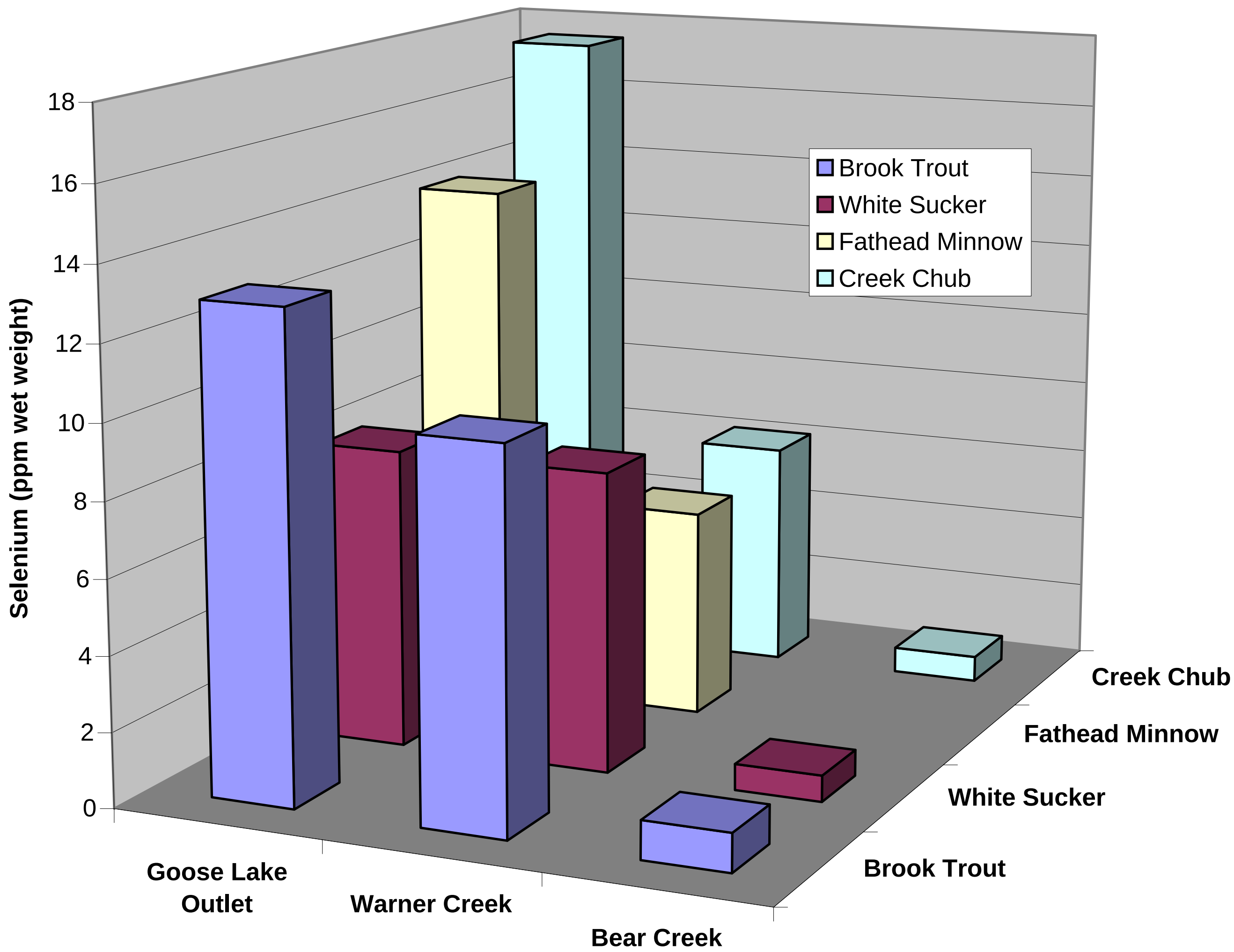

Table 1a. Empire Mine total Se discharge monitoring results.

Sample Date	Outfall 001	Outfall 003
	Se (ug/l)	Se (ug/l)
5/1/2003	7	16
6/12/2003	3	14
7/3/2003	4	15
8/7/2003	4	15
9/4/2003	4	14
10/2/2003	0	11
11/7/2003	3	10
12/4/2003	4	10
2/6/2004	6	8
3/4/2004	6	8
4/1/2004	6	---
4/8/2004	---	13
5/6/2004	3	8
6/7/2004	3	12
6/10/2004	4	12
7/1/2004	0	10
8/5/2004	5	21
9/2/2004	0	---
9/3/2004	---	9
10/7/2004	4	15
11/5/2004	4	17
12/2/2004	3	27
1/6/2005	3	12
2/3/2005	5	---
3/3/2005	9	---
3/10/2005	---	10
4/7/2005	6	11
5/5/2005	4	12
6/2/2005	3	16
7/7/2005	17	33
8/4/2005	0	13
9/1/2005	15	---
9/29/2005	---	0
10/6/2005	10	10
11/3/2005	16	22
12/1/2005	0	30
1/5/2006	0	20
2/2/2006	20	40
3/2/2006	30	50
4/6/2006	13	22
5/4/2006	13	40
6/1/2006	30	50
6/8/2006	---	20
7/6/2006	0	0
8/3/2006	70	90
9/7/2006	0	40

Table 1a (cont).

Sample Date	Outfall 001	Outfall 003
	Se (ug/l)	Se (ug/l)
10/5/2006	50	70
11/2/2006	80	90
12/7/2006	40	50
1/4/2007	60	60
2/1/2007	0	80
3/1/2007	21	20
4/5/2007	0	30
5/3/2007	0	20
6/7/2007	0	20
7/5/2007	0	0
8/2/2007	20	30
9/6/2007	0	50
10/4/2007	20	50
11/1/2007	0	60
12/6/2007	0	0
12/13/2007	30	40
12/20/2007	0	40
12/27/2007	0	0
1/3/2008	20	0
1/10/2008	0	30
1/17/2008	0	0
1/24/2008	30	40
1/31/2008	30	30
2/7/2008	0	30
2/14/2008	0	20
2/21/2008	0	0
2/28/2008	0	10
3/6/2008	0	20
3/13/2008	3	6
3/20/2008	2	8
3/27/2008	2	6
4/3/2008	3	5
4/10/2008	2	6
4/17/2008	2	6
4/24/2008	---	7
4/25/2008	3	---
5/1/2008	0	6
5/8/2008	3	9
5/15/2008	3	9
5/22/2008	1	7
5/29/2008	0	7
6/5/2008	3	8
6/12/2008	4	9
6/19/2008	4	8
6/26/2008	3	9

Table 1b. Tilden Mine total Se discharge monitoring results.

Sample Date	Outfall 001
	Se (ug/l)
12/31/2007	40
1/31/2008	0
2/29/2008	50
3/31/2008	30
4/30/2008	14
5/31/2008	6
6/30/2008	9

Table 2. Monthly water monitoring data (annual ranges) associated with reclamation and paper residuals application.

Location	Selenium Concentrations (ug/l)			
	Sept 2003-2004	2005	2006	2007
Palmer Lake Road	220-510	360-450	340-460	265-460
West Plant Storm Water	160-490	106-354	100-340	140-300
Empire/Tilden Access Road	230-510	284-456	240-510	300-470
Hoover Pond	ND-20	ND-30	ND-60	4-50
M-1 Stockpile (Warner Creek Tributary)	32-67	38-84	40-90	53-90
Warner Creek (Section 20)	5-34	ND-46	ND-40	20-60
Warner Creek Tributary	4-23	ND-41	ND-30	20-60
Ely Creek Tributary	ND-16	ND-26	ND-30	17-50
Grass Lake Outflow	ND	ND-17	ND	ND
Lost 40 Pond				40-100

Table 3. Primary and secondary site locations.

Primary Sites	Field ID	GPS Coordinates
Goose Lake Inlet	GLI	46.47254, -87.54144
Goose Lake Outlet	GLO	46.45542, -87.49695
Goose Lake Outlet downstream Gribben Basin	GLNB	46.40116, -87.50121
Ely Creek	EPI	46.44712, -87.68422
Tributary to Ely Creek	ET	46.45491, -87.66852
Warner Creek Control	WCC	46.45539, -87.57420
Warner Creek at Tilden Tailing Line	WCTTL	46.42207, -87.58305
Green Creek	GC	46.35614, -87.57535
Schweitzer Creek	SC	46.40656, -87.59354
Fifteen Creek	15Cr	46.37837, -87.54277
Middle Branch Escanaba River	MBE	46.35127, -87.60330
Flopper Creek	FC	46.33632, -87.60978
Bear Creek	BC	46.31192, -87.55115
Goose Lake	Goose L	46.46861, -87.51637
Keewaydin Lake	KL	46.59917, -88.12184
Cataract Basin	MBE-Cat	46.31594, -87.51463
Gunpowder Lake	GunL	46.48450, -87.63382
Lake Ogden	LO	46.47127, -87.63439
Lake Sally	L Sally	46.47191, -87.64815
Schweitzer Basin	SB	46.41373, -87.64725

Secondary Sites	Field ID	GPS Coordinates
Tributary to Warner Creek	WCTr565	46.42571, -87.60261
Warner Creek at Palmer	WCRR	46.438284, -87.5946372
Partridge Creek Outlet Tracy Mine	Pck-Tracy	46.48881, -87.58533
Mary Charlotte Inflow	MCI	46.48793, -87.58640
Mary Charlotte Outflow	MCO	46.48139, -87.58379 (1)
Rolling Mill Road at CCI Gate	MCO2	46.48293, -87.58182
Rolling Mill Road South Culvert	PC3B	46.48117, -87.58033
Partridge Creek between Two Waste Rock Piles	PC3	46.48131, -87.58373 (1)
Seepage under Waste Rock Pile	PC3A	46.48091, -87.57784
Lost 40 Outlet	Lost40 trib	46.47856, -87.56299
Confluence of Lost 40 and MC Outlet	MCC	46.48004, -87.56333

(1) GPS unit was not working in the field. Sample coordinates were generated by computer.

Table 4. Selenium concentrations in water at primary and secondary sampling sites during 2008.

Water Body	Location	Field ID	STORET ID #	Date	Selenium (ug/l)	Geometric Mean (ug/l) [1]
Goose Lake	Near Lake Center	Goose L.	520325	7/10/2008	4.8	NA
Goose Lake Inlet	CR 35	GLI	520326	6/12/2008	12	
Goose Lake Inlet	CR 35	GLI	520326	7/15/2008	11	
Goose Lake Inlet	CR 35	GLI	520326	8/27/2008	9.1	9.3
Goose Lake Inlet	CR 35	GLI	520326	9/16/2008	6	
Goose Lake Inlet	CR 35	GLI	520326	10/28/2008	9.5	
Goose Lake Inlet	CR 35	GLI-MC		10/28/2008	15	
Goose Lake Outlet	u/s Gribben Tailings	GLO	520475	6/12/2008	4.7	
Goose Lake Outlet	u/s Gribben Tailings	GLO	520475	7/15/2008	4.1	2.4
Goose Lake Outlet	u/s Gribben Tailings	GLO	520475	8/27/2008	3.2	
Goose Lake Outlet	u/s Gribben Tailings	GLO	520475	10/28/2008	ND	
Goose Lake Outlet	d/s Gribben Tailings	GLNB	520379	5/29/2008	2.2	
Goose Lake Outlet	d/s Gribben Tailings (dup)	GLNB	520379	5/29/2008	2.3	
Goose Lake Outlet	d/s Gribben Tailings	GLNB	520379	7/16/2008	8.9	3.0
Goose Lake Outlet	d/s Gribben Tailings	GLNB	520379	8/27/2008	10	
Goose Lake Outlet	d/s Gribben Tailings	GLNB	520379	10/28/2008	ND	
Gunpowder Lake	Center of Lake	GunL	520488	10/28/2008	1.2	NA
Lake Ogden	North Central of Lake (Surface)	LO	520476	9/3/2008	ND	NA
Lake Sally	Center of Lake-Epi	L. Sally	520477	7/9/2008	1.1	NA
Lake Sally	Center of Lake-Hypo	L. Sally	520477	7/9/2008	ND	NA
Cataract Basin	near Dam	MBE-Cataract	520478	7/8/2008	ND	NA
Ely Creek	off CR 476	EPI	520479	6/13/2008	ND	
Ely Creek	off CR 476	EPI	520479	7/16/2008	3.5	1.5
Ely Creek	off CR 476	EPI	520479	8/27/2008	2.3	
Ely Creek	off CR 476	EPI	520479	10/28/2008	1.4	
Tributary To Ely Creek	East of National Mine	ET	520307	6/13/2008	2.8	

ND = < Quantitation Limit (1.0 ug/l for Se)
NA = Not Applicable (too few samples to calculate a geometric mean)
[1] To calculate geometric means, ND values were set equal to 0.5 ug/l

Table 4 (cont.). Selenium concentrations in water at primary and secondary sampling sites during 2008.

Water Body	Location	Field ID	STORET ID #	Date	Selenium (ug/l)	Geometric Mean (ug/l) [1]
Tributary To Ely Creek	East of National Mine	ET	520307	7/16/2008	ND	0.8
Tributary To Ely Creek	East of National Mine	ET	520307	8/27/2008	ND	
Tributary To Ely Creek	East of National Mine	ET	520307	10/28/2008	ND	
Warner Creek	M-35-Tailings Line	WCTTL	520380	5/29/2008	9.8	
Warner Creek	M-35-Tailings Line	WCTTL	520380	7/15/2008	8.7	
Warner Creek	M-35-Tailings Line	WCTTL	520380	8/27/2008	13	11.0
Warner Creek	M-35-Tailings Line	WCTTL	520380	9/16/2008	11	
Warner Creek	M-35-Tailings Line	WCTTL	520380	9/16/2008	13	
Warner Creek at Palmer	Old RR Crossing in Palmer	WCRR	520483	5/29/2008	16	NA
Warner Creek Control	Headwaters	WCC	520481	6/12/2008	ND	ND
Warner Creek Control	Headwaters	WCC	520481	7/15/2008	ND	
Warner Creek Control	Headwaters	WCC	520481	8/27/2008	ND	
Warner Creek Control	Headwaters	WCC	520481	10/28/2008	ND	
Green Creek	Below Tailings Pond	GC	520378	6/12/2008	2	
Green Creek	Below Tailings Pond	GC	520378	7/15/2008	2.3	1.4
Green Creek	Below Tailings Pond	GC	520378	8/27/2008	ND	
Green Creek	Below Tailings Pond	GC	520378	10/29/2008	1.9	
Schweitzer Creek	CR 565 Crossing	SC	520385	6/12/2008	ND	
Schweitzer Creek	CR 565 Crossing	SC	520385	7/15/2008	ND	ND
Schweitzer Creek	CR 565 Crossing	SC	520385	8/27/2008	ND	
Schweitzer Creek	CR 565 Crossing	SC	520385	10/29/2008	ND	
Fifteen Creek	CR 35 Crossing	15Cr	520484	6/12/2008	ND	
Fifteen Creek	CR 35 Crossing	15Cr	520484	7/15/2008	ND	ND
Fifteen Creek	CR 35 Crossing	15Cr	520484	8/27/2008	ND	
Fifteen Creek	CR 35 Crossing	15Cr	520484	10/29/2008	ND	

ND = < Quantitation Limit (1.0 ug/l for Se)
NA = Not Applicable (too few samples to calculate a geometric mean)
[1] To calculate geometric means, ND values were set equal to 0.5 ug/l

Table 4 (cont.). Selenium concentrations in water at primary and secondary sampling sites during 2008.

Water Body	Location	Field ID	STORET ID #	Date	Selenium (ug/l)	Geometric Mean (ug/l) [1]
M.B. Escanaba River	CR 565 Crossing	MBE	520485	6/12/2008	ND	
M.B. Escanaba River	CR 565 Crossing	MBE	520485	7/15/2008	ND	ND
M.B. Escanaba River	CR 565 Crossing	MBE	520485	8/27/2008	ND	
M.B. Escanaba River	CR 565 Crossing	MBE	520485	10/29/2008	ND	
Flopper Creek Control	CR 565 Crossing	FC	520486	6/12/2008	ND	
Flopper Creek Control	CR 565 Crossing	FC	520486	7/15/2008	ND	ND
Flopper Creek Control	CR 565 Crossing	FC	520486	8/27/2008	ND	
Flopper Creek Control	CR 565 Crossing	FC	520486	10/29/2008	ND	
Bear Creek Control	CR 565 Crossing	BC	520263	5/29/2008	ND	
Bear Creek Control	CR 565 Crossing	BC	520263	7/15/2008	ND	
Bear Creek Control	CR 565 Crossing	BC	520263	8/27/2008	ND	ND
Bear Creek Control	CR 565 Crossing	BC	520263	9/16/2008	ND	
Bear Creek Control	CR 565 Crossing	BC	520263	10/29/2008	ND	
Keewaydin Lake Control	Western Basin	KL	070038	6/4/2008	ND	NA
Schweitzer Basin	Surface	SB		9/4/2008	ND	NA
Mary Charlotte Inlet		MCI		9/3/2008	ND	NA
Mary Charlotte Outlet		MCO		11/13/2008	4.3	NA
Mary Charlotte Outlet	Rolling Mill Road	MCO2		11/13/2008	3.8	NA
Mary Charlotte Confluence	Confluence of Lost 40/MC at RR Bridge	MCC (1)		11/13/2008	17	NA
Lost 40 Tributary		Lost 40 Tributary		11/13/2008	36	NA
Partridge Creek	Tracy Mine Works	PCK-TRACY		9/3/2008	ND	NA
Partridge Creek	Valley between pore rock piles	PC3		11/13/2008	40	NA
Partridge Creek	Seepage from rock pile	PC3A		11/13/2008	68	NA
Partridge Creek	Rolling Mill rd culvert	PC3B		11/13/2008	20	NA

ND = < Quantitation Limit (1.0 ug/l for Se)

NA = Not Applicable (too few samples to calculate a geometric mean)

[1] To calculate geometric means, ND values were set equal to 0.5 ug/l

(1) Note: MCC, GLC, and GLI-MC are the same locations with the same GPS coordinates (46.48004, -87.56333) and had Se results of 16 ug/l on 10/2/08 (GLC) and 15 ug/l on 10/28/08 (GLI-MC).

Table 5. Selenium concentrations in sediment at primary and secondary sampling sites during 2008.

Water Body	Location	Field ID	STORET ID #	Date	Selenium (mg/kg) dry
Goose Lake	Near Lake Center	Goose L.	520325	7/10/2008	39 (0-1 cm)
Goose Lake	Near Lake Center	Goose L.	520325	7/10/2008	38 (1-2 cm)
Goose Lake	Near Lake Center	Goose L.	520325	5/29/2008	27 (0-1 cm)
Goose Lake Inlet	CR 35	GLI	520326	6/12/2008	1.7
Goose Lake Inlet	CR 35	GLI	520326	7/15/2008	0.65
Goose Lake Outlet	u/s Gribben Tailings	GLO	520475	6/12/2008	2.2
Goose Lake Outlet	d/s Gribben Tailings	GLNB	520379	5/29/2008	0.67
Goose Lake Outlet	d/s Gribben Tailings (dup)	GLNB	520379	5/29/2008	0.87
Goose Lake Outlet	d/s Gribben Tailings	GLNB	520379	7/16/2008	0.56
Lake Sally	Center of Lake	L. Sally	520477	7/9/2008	4 (0-1 cm)
Lake Sally	Center of Lake	L. Sally	520477	7/9/2008	3.9 (0-2 cm)
Lake Ogden	Center of Lake	LO	520476	9/3/2008	4.0 (0-1 cm)
Lake Ogden	Center of Lake	LO	520476	9/3/2008	4.1 (1-2 cm)
Gunpowder Lake	Center of Lake	GunL	520488	10/2/2008	4.1 (1-2 cm)
Cataract Basin	near Dam	MBE-Cataract	520478	7/8/2008	1.5 (0-1 cm)
Ely Creek	off CR 476	EPI	520479	6/12/2008	12
Ely Creek	off CR 476	EPI	520479	7/16/2008	14
Tributary To Ely Creek	East of National Mine	ET	520307	6/12/2008	3.2
Tributary To Ely Creek	East of National Mine	ET	520307	7/16/2008	2.8
Warner Creek	M-35-Tailings Line	WCTTL	520380	5/29/2008	1.5
Warner Creek	M-35-Tailings Line	WCTTL	520380	7/15/2008	7.6
Warner Creek Control	Headwaters	WCC	520481	6/12/2008	0.64
Warner Creek Control	Headwaters	WCC	520481	7/15/2008	0.76
Green Creek	Below Tailings Pond	GC	520378	6/12/2008	5
Green Creek	Below Tailings Pond	GC	520378	7/15/2008	0.57
Schweitzer Creek	CR 565 Crossing	SC	520385	6/12/2008	2
Schweitzer Creek	CR 565 Crossing	SC	520385	7/15/2008	0.3
Fifteen Creek	CR 35 Crossing	15Cr	520484	6/12/2008	0.75
Fifteen Creek	CR 35 Crossing	15Cr	520484	7/15/2008	0.43
M.B. Escanaba River	CR 565 Crossing	MBE	520485	6/12/2008	ND
M.B. Escanaba River	CR 565 Crossing	MBE	520485	7/15/2008	ND
Flopper Creek Control	CR 565 Crossing	FC	520486	6/12/2008	0.5
Flopper Creek Control	CR 565 Crossing	FC	520486	7/15/2008	0.32
Bear Creek Control	CR 565 Crossing	BC	520263	5/29/2008	0.48
Bear Creek Control	CR 565 Crossing	BC	520263	7/15/2008	0.45
Keewaydin Lake Control	Western Basin	KL	70038	6/4/2008	2.2 (0-1 cm)
Keewaydin Lake Control	Western Basin	KL	70038	6/4/2008	2.2 (1-2 cm)

Table 6. Surficial sediment concentrations from Upper Peninsula lakes.

Lake	**County**	**Surficial Se (ug/g) dry weight**	**Source**
Grand Sable	Alger	<0.82	MI/DNR/SWQ-91/106
Keewaydin	Baraga	2.2	2008 Se Project MDEQ
Beaufort	Baraga	1-2	MI/DNR/SWQ-91/106
Carp	Chippewa	<0.82	MI/DNR/SWQ-91/106
Round	Delta	<0.82	MI/DNR/SWQ-91/106
Pickerel	Dickinson	2-3	MI/DNR/SWQ-91/106
Silver	Dickinson	1-2	MI/DNR/SWQ-91/106
Beaton	Gogebic	2-3	MI/DNR/SWQ-91/106
Emily	Houghton	<0.82	MI/DNR/SWQ-91/106
Rice	Houghton	1-2	MI/DNR/SWQ-91/106
Roland	Houghton	<0.82	MI/DNR/SWQ-91/106
Ottawa	Iron	2-3	MI/DNR/SWQ-91/106
Chicagon	Iron	2-3	MI/DNR/SWQ-91/106
Gratiot	Keewenaw	1-2	MI/DNR/SWQ-91/106
Lac LaBelle	Keewenaw	1-2	MI/DNR/SWQ-91/106
Medora	Keewenaw	<0.82	MI/DNR/SWQ-91/106
Bodi	Luce	1-2	MI/DNR/SWQ-91/106
North Manistique	Luce	<0.82	MI/DNR/SWQ-91/106
Deer	Marquette	0.8-1.0	MI/DNR/SWQ-91/106
Deer	Marquette	3.1-4.3	Fett et al., 2000
Goose	Marquette	27-39	2008 Se Project MDEQ
Independence	Marquette	<0.82	MI/DNR/SWQ-91/106
Michigamme	Baraga	1-2	MI/DNR/SWQ-91/106
Squaw	Marquette	2-3	MI/DNR/SWQ-91/106
Sally	Marquette	4.0	2008 Se Project MDEQ
Cataract Basin	Marquette	1.5	2008 Se Project MDEQ
Ogden	Marquette	4.0	2008 Se Project MDEQ
Gunpowder	Marquette	4.1	2008 Se Project MDEQ

Table 7. Selenium concentrations by depth in lake sediments.

LAKE	Date	Depth (cm)	Piston Corer[1] Se (mg/kg)	Date	K-B Corer[1] Se (mg/kg)
Goose Lake-Middle	5-29-08	0-1	27	7-10-08	39
		1-2	11		38
		2-3	4.6		37
		3-4	4		36
		4-5	2.8		38
		5-6	3		38
		6-7	3		38
		7-8	2.8		32
		8-9	2.9		28
		9-10	3.1		22
Goose Lake-Shallow	4-3-08	0-1	11		
		1-2	4.7		
		2-3	2.8		
		3-4	1.9		
		4-5	1.6		
		5-6	1.9		
		6-7	1.5		
		7-8	1.6		
		8-9	1.6		
		9-10	1.5		
Goose Lake-Inlet	5-29-08	0-1	6.1		
		1-2	2.5		
		2-3	3		
		3-4	2.4		
		4-5	3.1		
		5-6	3.4		
		6-7	3.7		
		7-8	2.6		
		8-9	1.8		
		9-10	2.3		
Lake Sally-Middle	7-9-08	0-1		7-9-08	4.0
		1-2			3.9
		2-3			4.1
		3-4			3.8
		4-5			3.2
		5-6			3.4
		6-7			3.6
		7-8			3.3
		8-9			2.8
		9-10			3.5

Table 7 (cont).

LAKE	Date	Depth (cm)	Piston Corer[1] Se (mg/kg)
Lake Ogden-Middle	9-3-08	0-1	4.0
		1-2	4.1
		2-3	3.8
		3-4	3.6
		4-5	2.9
		5-6	2.6
		6-7	2.9
		7-8	3.2
		8-9	2.9
		9-10	2.7
Cataract Basin	7-8-08	0-1	1.5
		1-2	1.6
		2-3	1.4
		3-4	1.1
		4-5	1.1
		5-6	0.98
		6-7	1.0
		7-8	1.1
		8-9	1.0
		9-10	1.1
Keewaydin Lake	6-4-08	0-1	2.2
		1-2	2.2
		2-3	2.1
		3-4	1.9
		4-5	1.7
		5-6	1.6
		6-7	1.8
		7-8	1.6
		8-9	1.6
		9-10	1.7
Gunpowder Lake	10-2-08	0-1	
		1-2	4.1
		2-3	4.2
		3-4	3.8
		4-5	3.3
		5-6	2.4
		6-7	1.5
		7-8	0.9
		8-9	0.5
		9-10	0.6

[1] The piston corer was used in water depths of 20 feet or less and the K-B corer was used in water depth greater than 20 feet.

Table 8. Wet weight vs. dry weight tissue comparison from fish and benthic invertebrates in Goose Lake.

Sample #	**% Moisture**	**x Wet = Dry**	**Taxa**
Goose Lake			
1	77.8	4.5	Northern pike
2	78.2	4.6	Northern pike
3	75.9	4.2	Northern pike
4	76.6	4.3	Northern pike
5	76.6	4.3	Northern pike
6	77.0	4.3	White sucker
7	75.4	4.1	White sucker
8	79.1	4.8	White sucker
9	78.0	4.6	White sucker
10	74.8	4.0	White sucker