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Using Reference Systems and Multi-elemental Techniques**

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**Assessing Recovery of Anthropogenically Disturbed Lakes
Using Reference Systems and Multi-elemental Techniques**

By

Joel D. Fett

A THESIS

**Submitted to
Michigan State University
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Abstract

Assessing Recovery of Anthropogenically Disturbed Lakes Using Reference Systems and Multi-elemental Techniques

By

Joel D. Fett

Assessing recovery in anthropogenically disturbed lakes using sediment core chronologies can be challenging. As is the case for Torch Lake, Houghton County, Michigan, where approximately 200 million tons of heavy metal rich mine tailings were dumped from 1868 to 1968. To deal with this issue, multi-element data was collected and compared to a reference lake, Gratiot Lake, to assess how the lake has responded to lessened anthropogenic burdens. Sediment cores were collected from four depositional basins of the Torch Lake and one from Gratiot Lake, metals extracted by a microwave-assisted HNO_3 digestion and the leachates analyzed for 21 metals via ICP-HEX-MS and AAS. Sediment ages for Torch Lake were calculated using an “event dating” technique that is based on historical and geochemical data. Copper concentrations in post mine tailing dominated sediments still averaged 1,615 - 2,844 mg/kg, suggesting the little recovery of the lake has occurred since direct inputs ceased. However, other elements (e.g., Ti, Co) and elemental ratios (e.g., Co/Zn, K/V) suggest Torch Lake is responding to the cessation of mining activities and the sediments are approaching levels reflective of Gratiot Lake. This study demonstrates the importance of using reference systems and multi-element techniques when assessing recovery of anthropogenically disturbed systems.

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Assessing Recovery of Anthropogenically Disturbed Lakes Using Reference Systems and Multi-elemental Techniques

I. Introduction

General Introduction

One of the greatest concerns presently confronting the Keweenaw Peninsula of Michigan is the persistence of Cu contaminated sediments that are the result of mining practices of the past. The predominant source of Cu contamination was the direct input of heavy metal rich mining tailings into rivers, lakes and their surrounding ecosystems. Through bioaccumulation, heavy metal contaminated sediments can negatively impact the surrounding wildlife and humans, and represent a continual source of contamination in aquatic environments (Song and Breslin, 1999 and Catallo et al., 1995). As a result, several studies have focused on Cu (i.e., concentration, mobility, distribution or toxilogical effects) in numerous environments within and around the Keweenaw Peninsula, such as: Lake Superior (Smith and Moore, 1972; Kemp et al., 1978; Kerfoot et al., 1999a and Kolak et al., 1999), Portage Lake (Kerfoot and Lauster, 1994 and Kerfoot and Robbins, 1999b) and Torch Lake (Wright et al., 1973; Lopez and Lee, 1977; Charters and Derveer, 1991; EPA, 1992; Ellenberger et al., 1994; Cusack and Mihelcic, 1999; Jeong et al., 1999 and Lytle, 1999).

This study will focus on Torch Lake, a U.S. EPA Superfund site located in Houghton County, Michigan (Figure 1). Wasteful mining practices led to the

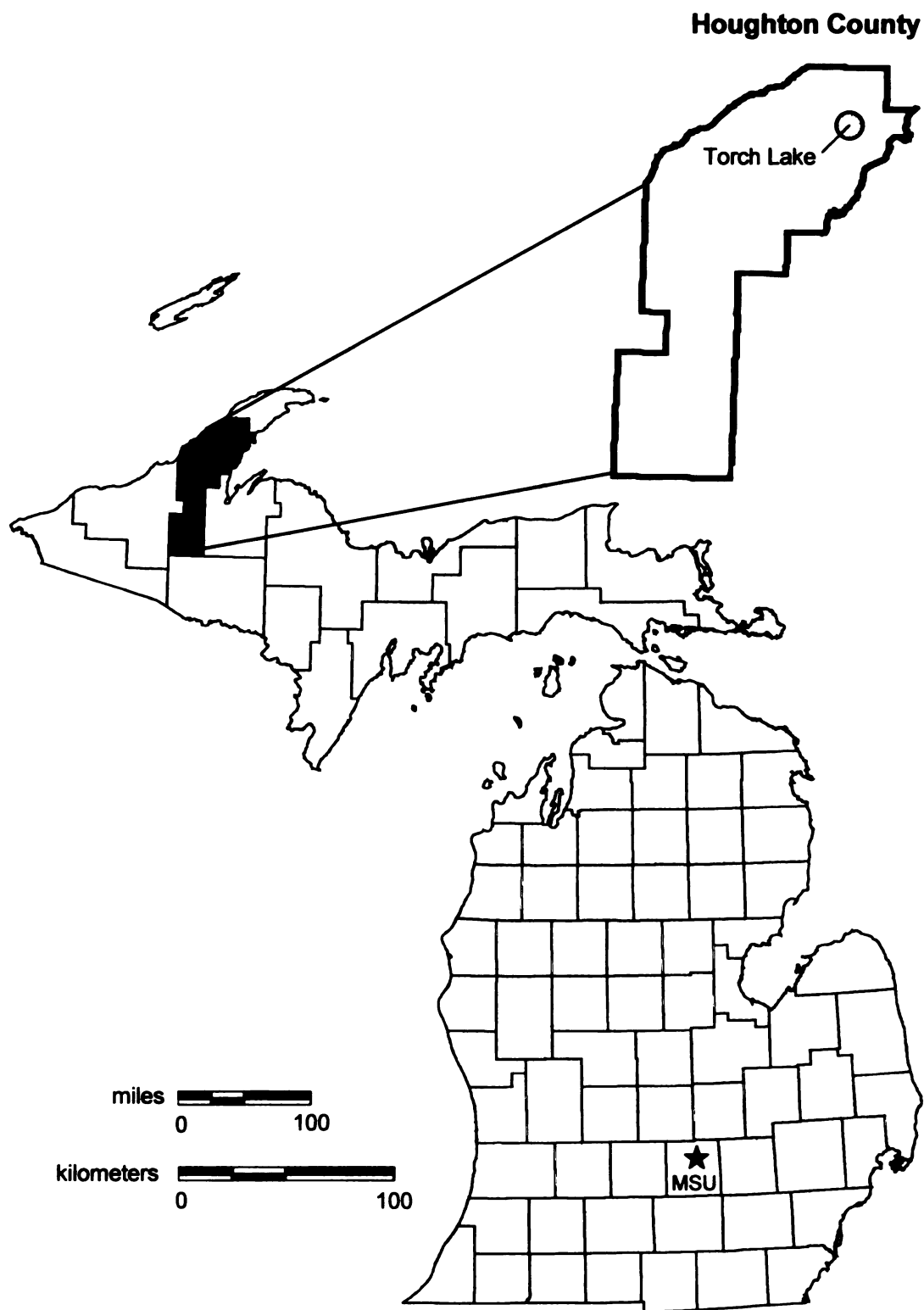


Figure 1. Map showing the location of Torch Lake, Houghton County, Michigan.

deposition of 200 million tons of heavy metal rich mine tailings into the Torch Lake basin and around its shores. Direct inputs of tailings have ceased, allowing for a more dominant natural sediment input, but millions of tons of tailings still line the shores of Torch Lake and are potentially available for erosion and re-deposition into the lake. Currently, the U.S. EPA is in the process of soil covering and revegetating the exposed tailing deposits in an attempt to control further erosional inputs, but the success of this effort is unclear.

Previous studies of Torch Lake sediments have been restricted “largely to bulk chemical analyses on sediment samples retrieved using grab samplers” (Cusack and Mihelcic, 1999), and little work has been done to determine the spatial and temporal trends of heavy metals. However, lake sediments can act as recorders of historical as well as modern inputs (Edgington and Robbins, 1976; Erten, 1997; Wakeham et al., 1979 and Mueller et al., 1989), when properly collected and analyzed (VonGunten et al., 1997). So, the main purpose of this research is assessing the recovery of Torch Lake by evaluating the spatial and temporal changes of Cu and other heavy metals (i.e., the multi-elemental approach) in the sediments of the lake. With a multi-elemental approach, the focus is not only the contaminant of interest (i.e., the target specific approach), such as Cu, but also several other non-toxic elements. This approach allows for the understanding of diagenesis and influences from terrestrial inputs from the surrounding watershed, and differentiating terrestrial inputs from anthropogenic inputs (Yohn et al., 2002).

When attempting to assess recovery of anthropogenically disturbed lake sediments, several questions should be answered such as: 1) what was the past state of the system; 2) what is the current state of the system; and 3) what is the future state of the system. These questions will be addressed in an attempt to assess the recovery of Torch Lake from past disturbances. It is hypothesized that the source for Cu and other heavy metals to Torch Lake was once dominated by anthropogenic local inputs of stamp sands and clays, but today is dominated by a more regional, watershed input.

Formation of Copper Deposits in Michigan

A “hot spot” beneath the current Lake Superior region led to doming and creation of a rift zone approximately 1.10 to 1.0 billion years ago (LaBerge, 1994). Basaltic flows spread out of the rift zone and the region was covered with lava deposits over hundreds of kilometers wide and 4 to 24 km thick (Kerfoot and Nriagu, 1999). The Cu in Michigan is thought to have been deposited by hot, briny fluids that rose up through these basaltic flows (Kerfoot and Nriagu, 1999). As the brines approached the surface, the Cu in the underlying Portage Lake Volcanic series was re-dissolved and deposited in the form of native Cu on the upper sections of these basalt flows or inter-bedded within the conglomerate and shale sequences of the Oronto Group (Kerfoot and Nriagu, 1999) (Figure 2). The two main Cu bearing rock types of the Keweenaw Peninsula of Michigan are: 1) amygdules, which contain Cu and other minerals within vesicles and fragmented surface materials, and 2) sedimentary rocks, such as conglomerate

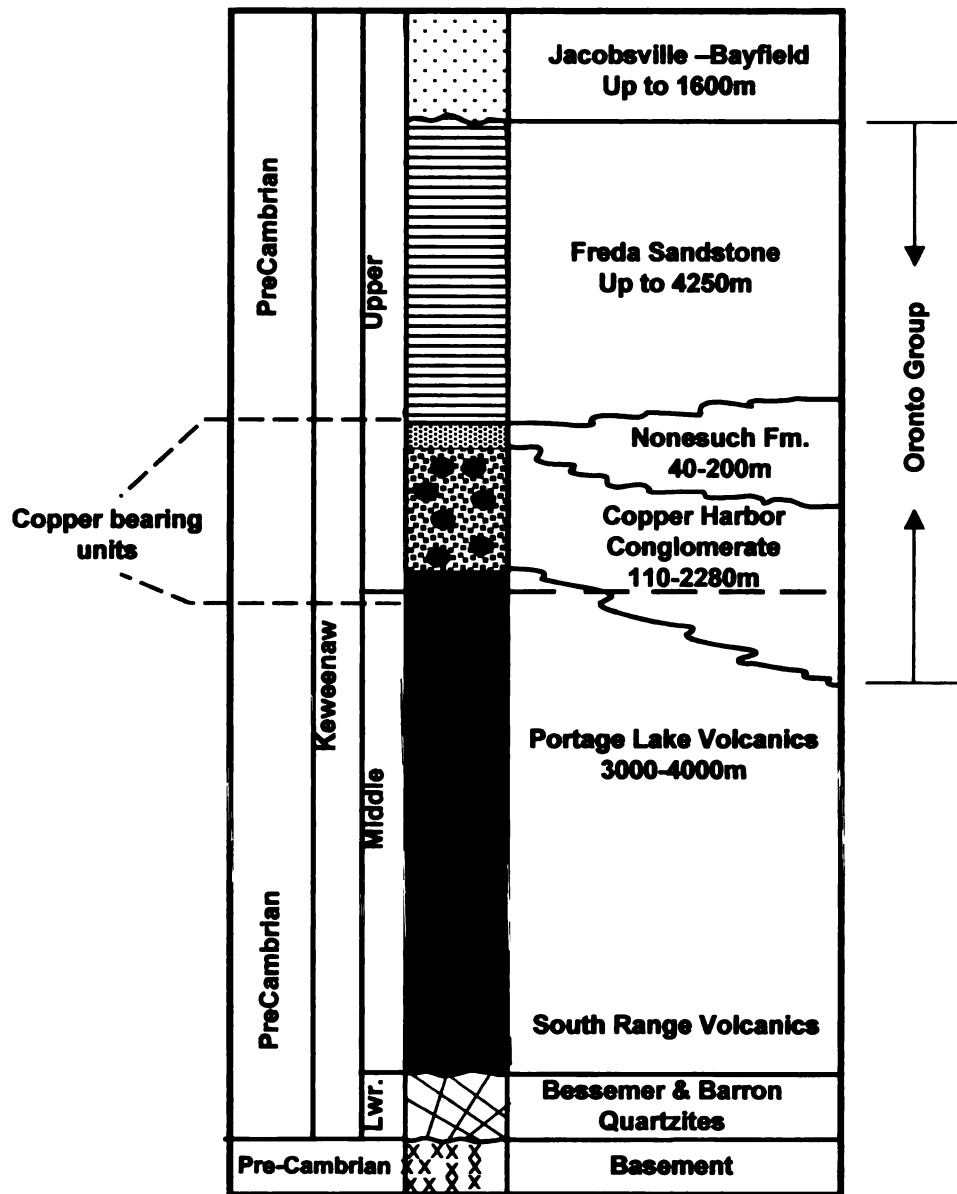


Figure 2. Generalized stratigraphic column for Keweenaw Peninsula of Michigan.

and shale, which have Cu filling pore openings or surrounding pebbles and grains of sand (Dorr and Eschman, 1977). Copper deposits of the Keweenaw consist mainly of native copper and copper sulfides (mainly chalcocite) (Kerfoot and Nriagu, 1999). Recent studies have suggested that the Cu in Michigan was formed between 1.06 and 1.05 billion years ago, which is about 20 million years after the period of volcanism in the region (Kerfoot and Nriagu, 1999).

Copper Mining in Michigan

Small-scale Cu mining in the Lake Superior region began with the Native Americans approximately 7,000 years ago, and these practices lasted for about 4,000 years. Then much later, 1844, mining of Michigan's native copper began again on an industrial scale, and between 1850 and 1929, the Keweenaw Peninsula of Michigan was the second largest producer of Cu in the world (Kerfoot and Nriagu, 1999). Productive copper-mines were mainly localized to rock formations of Precambrian age, which run the entire length of the Keweenaw and stretch from the northern tip, along the western shore, then down the center of the peninsula (Figure 3). The Portage Lake Volcanic series, Copper Harbor Conglomerate and the Nonesuch Shale, were host to the largest deposits of native copper in the world. Ninety-six percent of the native copper harvested came from a 28-mile stretch that extended southwest from the town of Pinedale to just east of Mohawk (Kerfoot and Lauster, 1994) (Figure 3).

In the early stages of Cu mining, the focus was on the easily extractable forms of Cu such as: float copper (i.e., native copper that has been relocated by

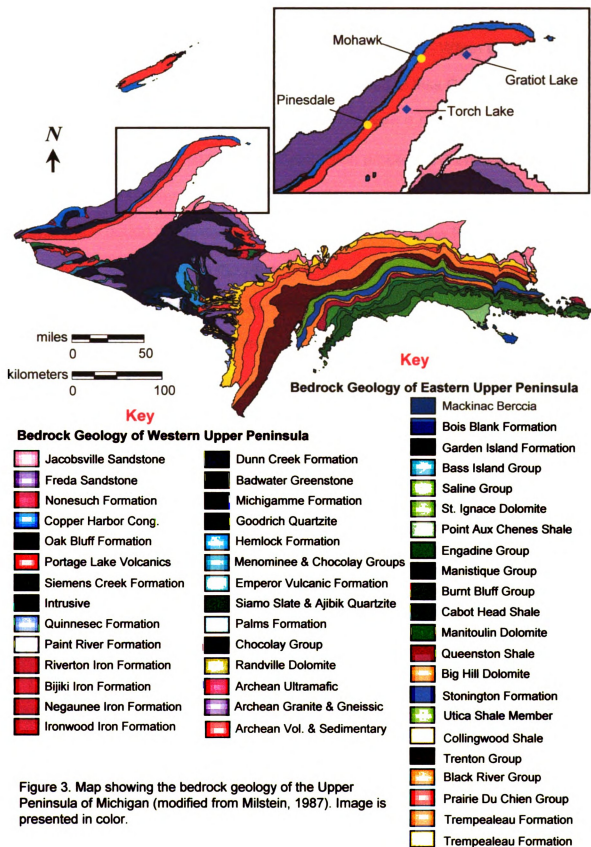


Figure 3. Map showing the bedrock geology of the Upper Peninsula of Michigan (modified from Milstein, 1987). Image is presented in color.

natural processes such as erosion or glaciation), vein copper, and mass copper (large masses of pure copper) (Kerfoot and Nriagu, 1999). When the easily extractable lodes began to be depleted, focus turned to less Cu rich ores. The concentration of Cu within these ores ranged between 0.5 and 6.1% (Kerfoot and Lauster, 1994). As part of the Cu extraction process, the ore was stamped or crushed into smaller fractions. Stamp mills were generally located in small clusters and dotted the landscape throughout the Keweenaw Peninsula. One such cluster was located on the western shore of Torch Lake, where five stamp mills operated within a 6-mile stretch (Figure 4). The shores of lakes were the preferred location of the many stamp mill operations because of the need for water to create steam for power generation and the easy disposal of mine tailings into the natural lake basins.

At the peak of the industry, there were over 140 operational Cu mines and 40 stamp mills to process the Cu rich ores (Kerfoot and Lauster, 1994). From approximately 1850 to 1960, there was an estimated 4.8 million tons of Cu harvested, with the maximum Cu production in one year being 122,000 tons. Since the percent Cu was relatively low in the ores, huge amounts of rock were extracted and stamped to yield enough Cu to be economically profitable. As a result, over 500 million tons of solid waste was also generated (Kerfoot and Lauster, 1994). There were two main types of solid waste: stamp sands and slime clays (Kolak et al., 1999). As the name suggests, stamp sands were sand sized particles generated by crushing the host rock (e.g., large pieces of crushed basalt and conglomerate). Stamp sands have elemental compositions that

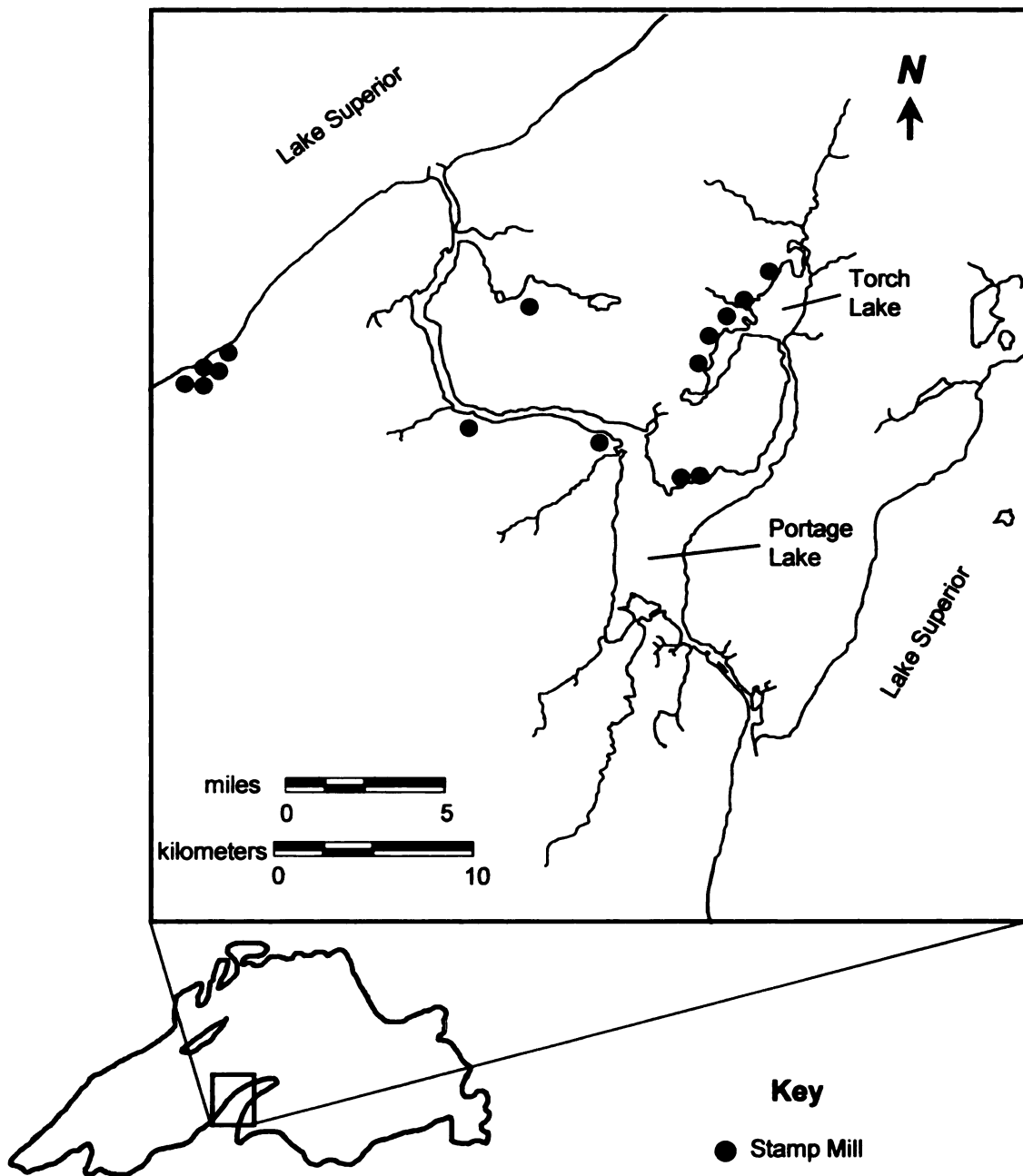


Figure 4. Map of stamp mill locations in the Keweenaw Peninsula of Michigan (modified from Wright et. al., 1973 and Kerfoot et. al., 1999).

resembled local bedrock, but also contained high concentrations of Cu and other metals such as titanium and calcium, since these elements were major constituents of the parent rock (Kerfoot et al., 1999a). Compared to natural lake sediments, stamp sands are distinctive in color, elemental composition, and have different physical characters (Kerfoot and Lauster, 1994).

Slime clays were reprocessed stamp sands that were finer grained and more mobile (Kolak et al., 1999). Copper concentrations in slimes range from 1,000 – 2,000 mg/kg (Wright et al., 1973) and are still elevated compared to the local geology. Their small size, which excluded them from gravity separation techniques, created a large surface area to volume ratio for the absorption of dissolved Cu to the sediments (Kerfoot and Lauster, 1994). Slime clays and stamp sands had three potential depositional fates: 1) upon introduction to a waterway, the particles separated out by size and the fine clay particles dispersed away from the point of injection, 2) when sluiced into plies, the grains separated naturally by density and formed layers of fine clays within the stamp sand piles, and 3) wave-action eroding and carrying the fine particles off-shore and re-deposited in the lake basin (Kerfoot and Lauster, 1994).

History of Torch Lake

Wright et al., (1973) has stated that the history of Torch Lake is one of abuse and degradation, and this can be attributed to the heavy impact from mining activities around the lake. From 1868 to 1968, Torch Lake was inundated with 200 million tons of stamp sands and slime clays (about half of the

total stamp sands produced in the Keweenaw Peninsula) (Kerfoot and Lauster, 1994). These materials were deposited directly into and around the shores of the lake, and sill are visible today (Figure 5). Assuming that the concentration of Cu in the stamp sands ranges from 0.4 to 1.7% (Kolak et al., 1999), the sediment burden of Cu to the lake during direct anthropogenic inputs (assuming 200 million tons) was on the order of 1.8×10^{10} to 7.7×10^{10} kg.

The burden of stamp sands and slime clays deposited into Lake Superior was only 1/3 of what was received by Torch Lake; and Portage Lake, a lake hydrologically connected to Torch Lake (Figure 6), had only about 1/9 the inputs of mining waste inputs. According to Wright et al., (1973), approximately 20% of the original Torch Lake basin had been filled with stamp sands between 1946 and 1968. This translates to a decrease in the depth of 7-9 meters in some locations. The total amount of lake volume filled prior to 1946 is not known (Wright et al., 1973).

New technologies after WWII allowed for the reclaiming of previously deposited stamp sands and extraction of the Cu by chemical leaching. Stamp sands were re-collected from the shores and within the lake with the use of mechanical dredges that were capable of extracting the sediments up to depths of 33.5 m (Kerfoot and Lauster, 1994). The previously discarded tailings were reclaimed using an ammonia leach, involving cupric ammonia carbonate. When the Cu was extracted from these tailings, they were once again discharged back into Torch Lake.



Figure 5. Photos from the western shore of Torch Lake along M-26. Notice the pink/purple colored stamp sands lining the shores. Image is presented in color.

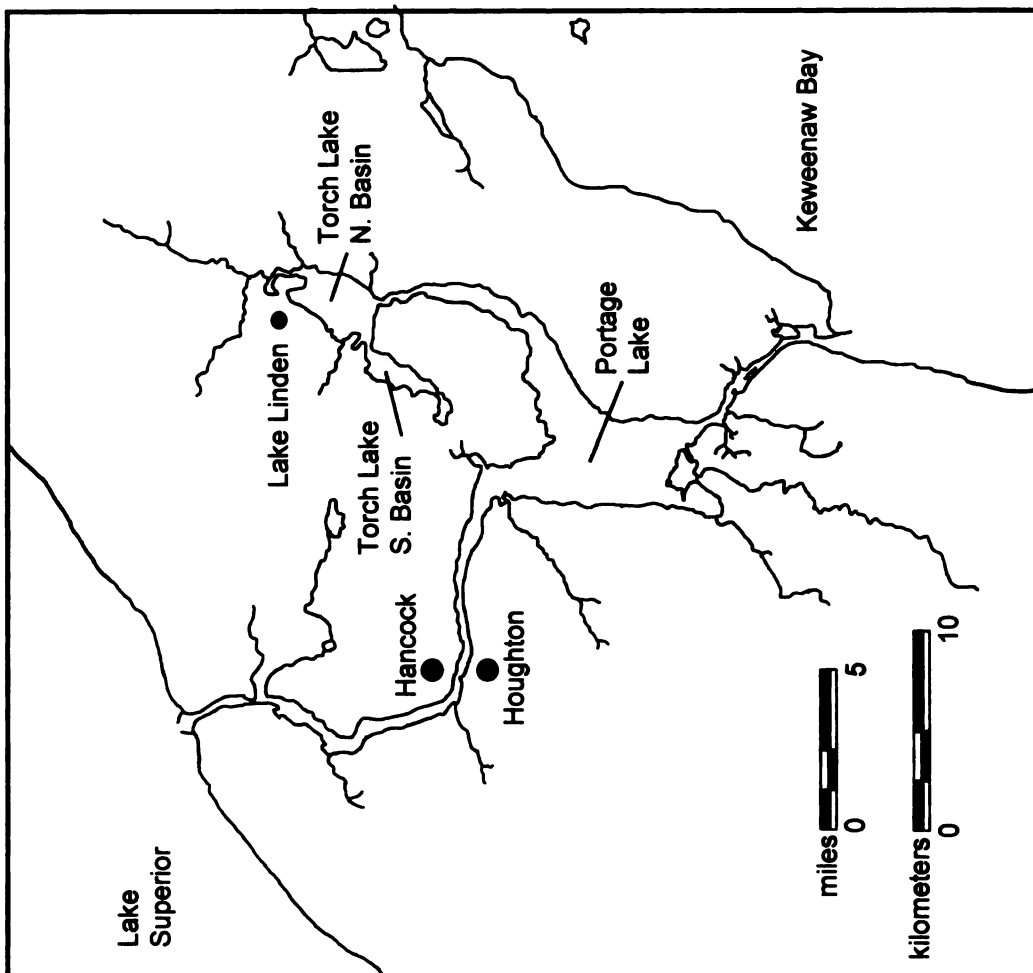


Figure 6. Map showing the location of Portage Lake, Keweenaw Peninsula, Michigan (modified from Wright et. al., 1973)

After most mining activities ceased in the Keweenaw Peninsula and around Torch Lake, there were spills of stored cupric ammonium carbonate into the lake during the late fall (October) 1971 and again in early summer (June) 1972 (Wright et al., 1973). These discharges released approximately 27,000 gallons of used leaching solution directly into the waters of Torch Lake (Wright et al., 1973). The cupric ammonium carbonate contained Cu in the concentration range of 0.07-7.8 g/L (parts per thousand) (Wright et al., 1973). Dissolved Cu concentrations of Torch Lake in 1972 ranged from 40 µg/L at the surface to 100 µg/L with depth in the water column, and were almost nine times higher near the spill location, with concentrations as high as 910 µg/L (Wright et al., 1973).

Also in 1972, it was discovered that some fish species of Torch Lake (i.e., Sauger) were beginning to develop liver tumors and fish populations were decreasing. Although not proven at the time, the higher concentrations of Cu were thought to be the cause of the tumors. The U.S. Environmental Protection Agency (EPA) classified Torch Lake as an Area of Concern in 1983 and a Super Fund site in 1984. Remediation strategies are being implemented that are attempting to control the amount of Cu rich shore tailings from entering the lake. The main action done by the U.S. EPA since 1999 was covering the stamp sands and re-vegetate the exposed piles in an attempt to control further stamp sand erosion. The success of this strategy as well as the current state of natural recovery is unclear, and remediation efforts are currently on going.

Aqueous Geochemistry & Toxicity of Copper

Copper is a chalcophile, and Cu II is the normal oxidation state for soluble Cu complexes (Nriagu, 1979). With further oxidation Cu compounds may be in the +3 oxidation state, or by reduction Cu^+ or Cu^0 can be formed, especially when sulfide is present in the system (Ellis, 1999). Available Cu in a natural system is dependent on absorption and desorption processes and precipitation of certain Cu compounds (Stumm and Morgan, 1996). The concentrations of Cu in the environment, as well as the presence of other metals may lead to a competition of the adsorption sites and lead to higher dissolved values, and Cu toxicity in aqueous systems depends on the amount of free Cu ion in the system and not total Cu (Mansilla-Rivera and Nriagu, 1999).

Living organisms need specific levels of naturally occurring elements such as Cu for sustaining biochemical processes (ATSDR, 1990). However, in high concentrations, Cu can then potentially become toxic in aquatic ecosystems (Hodson et al., 1979). Thus, Cu is a cause for concern when levels in the environment (e.g., lake sediments) greatly exceed levels sustainable for proper cell function. The toxicity of Cu to biological systems may be attributed to free ions of Cu binding to the cytoplasmic membrane of cells and halting proper cell division (Charters and Derveer, 1991). Dissolved organic matter may significantly bind to heavy metals, such as Cu. Copper is bound more strongly than any other divalent metal (McBride, 1994), and when complexed with organic matter, the Cu available in the water column is reduced, thus reducing

Cu toxicity in the system (Sprague, 1968; Lytle, 1999 and Cusack and Mihelcic, 1999).

Hypothesis

The main purpose of this research is to determine extent of recovery that Torch Lake has undergone since the cessation of mining activities around its shores. It is hypothesized that the source for Cu and other heavy metals to Torch Lake was once dominated by anthropogenic local inputs of stamp sands and clays, but today is dominated by a more regional, watershed input. If this hypothesis is true, then concentrations of heavy metals in the sediments will change from being reflective of stamp sands and slime clays to being reflective of watershed inputs controlled by the local geology. Copper concentrations should also be lower in the recent sediments compared to the mining related sediments.

Significance

Mining wastes, such as stamp sands and slime clays, represent historical and potentially continual source of Cu to the aquatic systems of the Keweenaw Peninsula, and the controls on Cu and Cu concentrations in different environments (i.e., near-shore to off-shore, lake to lake and stamp sands deposits) vary throughout the Keweenaw Peninsula (Kerfoot et al., 1999a; Kolak et al., 1999; Kerfoot and Lauster, 1994; Kerfoot and Robbins, 1999b; Wright et al., 1973; Lopez and Lee, 1977; Ellenberger et al., 1994; Cusack and Mihelcic,

1999; Jeong et al., 1999 and Lytle, 1999). This means that areas in the Cu mining region of Michigan have been affected differently, and no one ecosystem can be considered fully representative of another or the peninsula as a whole. Therefore, ecosystems in the Keweenaw must be examined as separate entities to better assess recovery of the Keweenaw area from Cu mining activities on a local scale. If the aforementioned questions about Torch Lake can be answered, then the information can be used to better determine what further remediation procedures, if any, should be undertaken.

II. Methods and Materials

Study Area

Torch Lake is an oligotrophic lacustrine system located on the eastern side of the Keweenaw Peninsula in Houghton County, Michigan. The lake has a surface area of 20.5 km² (approximately 2.2 km wide and 9.3 km long), with a maximum depth of 36 m and average depth of 17 m (Ellenberger et al., 1994). The southern extent of the lake is about 8 km WNW of Houghton and its northern extent is adjacent to the town of Lake Linden (Figure 6). There are two distinct basins within Torch Lake, a north and south basin (Cusack and Mihelcic, 1999). Discharge from Torch Lake flows south into Portage Lake, eventually reaching Lake Superior via the Keweenaw waterway. Residence time of the water is approximately 1 year (Cusack and Mihelcic, 1999).

Sample collection

Sediment cores were collected from four sites within Torch Lake in late July 1999. The locations of each sample site are shown in Figure 7. Sample sites were located in both the north and south basins. It must be noted that initially more sites were chosen for sampling, however after several uses of the multi-corer, the fine-grained nature of the sediments caused the multi-corer to malfunction, and only four sites were collected. Sites were chosen based on

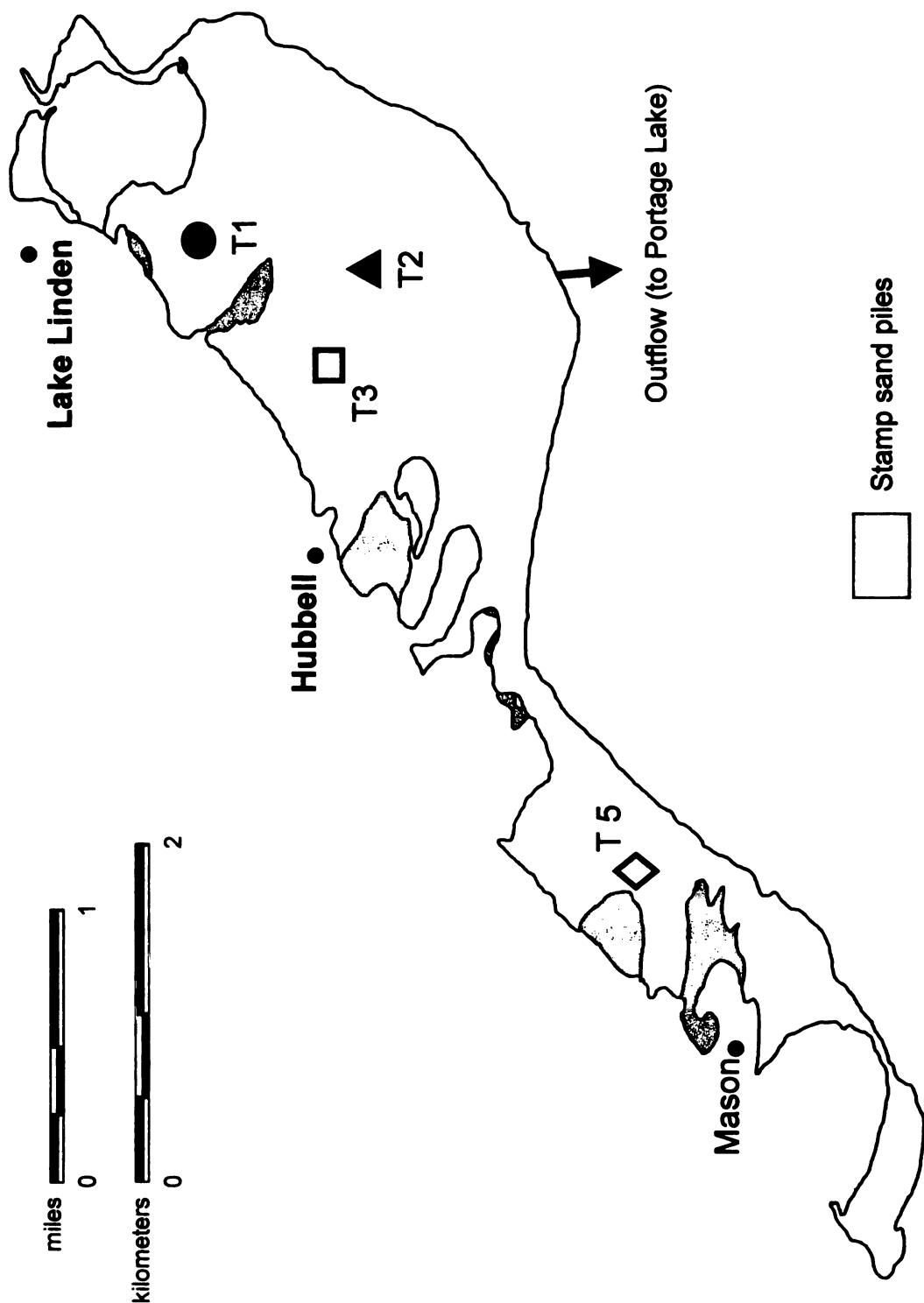


Figure 7. Map of sample sites within Torch Lake, Upper Peninsula, Michigan. Image is presented in color.

depth, and assumed to be depositional areas of the lake based on the classification scheme of Hakason (1977). This classification scheme uses the percent water content of surficial sediments (0-1 cm) to predict sedimentation zones (erosional, transitional or depositional) by assuming that there is a relationship between grain size and percent water in lake sediments. For example, if the percent water in the surficial sediments is greater than 75%, the sediments will be composed of silts and clays, and represent a depositional area of the lake (Hakason, 1977). Percent water in the surficial sediments (0-5 cm) of sites T1, T2 and T5 was greater than 75% (Table 1), so these sites were considered to be depositional zones of the lake. Site T3 sediments were not analyzed for porosity, however site T3 is assumed to be a depositional zone of the lake based on depth, which is similar to sites T1 and T2.

Cores were taken using an Ocean Instruments MC-400 Lake/Shelf Multi-corer. The multi-corer is based on the principle of the box corer, but slightly different from a box-corer, the multi-corer retrieves four individual core samples at one time, and sub-coring of the sample is not necessary (Figure 8). The multi-corer was deployed from the U.S. Environmental Protection Agency R/V *Mudpuppy*. Core tubes measure 64 cm in length and 10 cm in diameter, but the actual sediment lengths collected were between 30 and 40 cm.

After retrieval, the sediment cores were inspected on the boat to insure good quality cores were taken. A core was considered good quality and undisturbed if: 1) the water above the sediment column was clear and free of

Table 1. Percent water in the surficial sediments from three sampling sites of Torch Lake: T1, T2 and T5. Site T3 sediments were not analyzed for porosity

Sample	Depth (cm)	% water
T1-1	0.0-0.5	92.6
T1-2	0.5-1.0	89.9
T1-3	1.0-1.5	84.5
T1-4	1.5-2.0	83.7
T1-5	2.0-2.5	82.4
T1-6	2.5-3.0	81.5
T1-7	3.0-4.0	80.5
T1-8	4.0-5.0	80.2
T1-9	5.0-6.0	78.2
T1-10	6.0-7.0	78.9
T2-1	0.0-0.5	92.7
T2-2	0.5-1.0	88.9
T2-3	1.0-1.5	90.8
T2-4	1.5-2.0	88.3
T2-5	2.0-2.5	88.3
T2-6	2.5-3.0	84.0
T2-7	3.0-4.0	82.7
T2-8	4.0-5.0	82.7
T2-9	5.0-6.0	81.2
T2-10	6.0-7.0	76.4
T5-1	0.0-.5	94.5
T5-2	.5-1.0	92.3
T5-3	1.0-1.5	87.2
T5-4	1.5-2.0	87.9
T5-5	2.0-2.5	83.7
T5-6	2.5-3.0	84.0
T5-7	3.0-4.0	81.5
T5-8	4.0-5.0	76.9
T5-9	5.0-6.0	75.3
T5-10	6.0-7.0	77.2

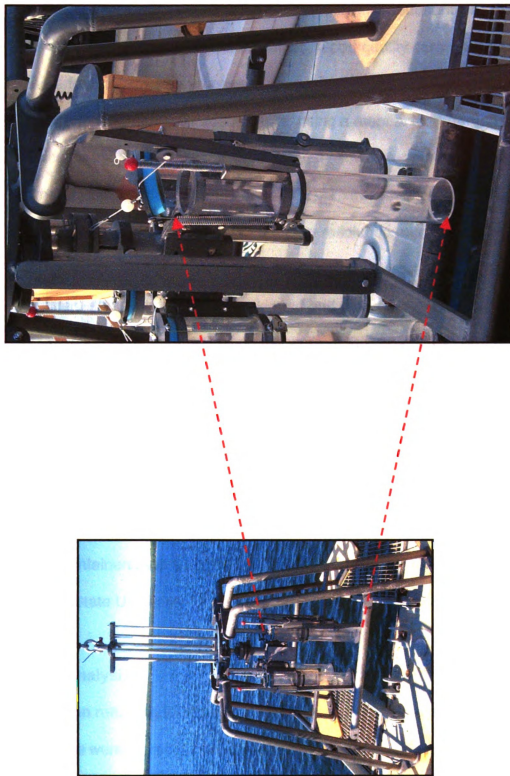


Figure 8. Photos of the Ocean Instruments MC-400 Lake/Shelf Multi-corer on the deck of the R/V *Mudpuppy*. Image is presented in color.

sediment, and 2) the sediment at the sediment/water interface was horizontal. If the cores were considered not to be good quality, the sediment was discarded and new samples were immediately taken. Good quality core were transported to shore for the extrusion process.

Sediments were extruded on-site, using a manual extruder (i.e., no electrical or hydrologic power is needed) that allowed for precise sampling of the sediment/water interface (Yohn et al., 2002). Extrusion intervals were 0.5 cm for the top 2.5 cm, in an attempt to get a higher resolution record of recent loading histories, and 1 cm below the 2.5 cm depth. At depths greater than 20 cm, intermittent sample intervals were skipped and discarded. To prevent contamination from smearing along the walls of the core-tubes, sediment that was in contact with the sides of the core tube (outer rind sediments) were scrapped away using a Teflon coated spatula (Kolak et al., 1998). Sectioned slices were also described on-site in terms of color, texture, and evidence of zoobenthos disturbances. Sample descriptions for each slice are summarized in Appendix A. Extruded sample intervals were placed into acid washed plastic sample containers, stored in ice packed coolers and transported back to Michigan State University for metal analysis.

Sample Analysis

Upon returning to Michigan State University, sediment samples from Torch Lake were stored, frozen and then freeze-dried in preparation for metals extraction. For the metals extraction, 10 ml of concentrated, trace metal grade

nitric acid was added to ~0.5g of sediment, sealed in Teflon vessels and digested by microwave assistance in a CEM-MDS-81D microwave (Hewitt and Reynolds, 1990). The concentrated leachates were diluted to 100mL with distilled-deionized water (DDW) and filtered through acid washed; DDW rinsed, Nucleopore® 0.40 µm polycarbonate filters. The samples were then separated into a total extractable metal fraction and a Hg sample by filtering the solutions into separate 60mL, HCl acid, washed Nalgene® bottles. The 40 mL of digest solution for Hg analysis was preserved by adding 200 µL of a 100 µg/mL gold chloride (AuCl) solution (EPA, 1998). The Hg samples were not analyzed as part of this study.

The prepared digested fluids were then analyzed using a Micromass Platform inductively coupled plasma mass-spectrometer with hexapole technology (ICP-HEX-MS) at a 1:10 or 1:100 dilution, depending on the concentration of the element. All standards were spiked with 30 µg/mL Ca in an attempt to match the matrix of the samples. Bismuth and In were used as internal standards. Sediments were analyzed for a suite of metals and metalloids including Mg, Al, K, Ti, V, Cu, Mn, Se, Co, Ni, Sc, Zn, As, Cd, Ba, Pb and U. Between the analyses of each sample, there was a three minute rinse period of 2.5% HNO₃ + 2.5% HCl + 10 µg/mL AuCl to minimize memory effects of the previous sample before the next is analyzed. Due to high concentrations within the digestive fluids, Fe and Ca were analyzed on Perkin-Elmer Zeeman 5100 PC Atomic Absorption Spectrometer (AAS) at dilutions of 1:3 to 1:20 depending on the concentration in the sample.

^{210}Pb and ^{137}Cs analyses were performed on a sub-core from sites T1 and T2 and ^{210}Pb only was measured for site T5 to determine accumulation rates, sedimentation rates, and sediment ages. Samples were sent to The Freshwater Institute in Winnipeg, Manitoba, Canada for radionuclide analyses. Porosity measurements were also done at the Freshwater Institute for sites T1, T2 and T5.

Quality Assurance/Quality Control

See Appendix B.

Reference Systems

Torch Lake offered additional challenges not encountered in most other relatively disturbed or undisturbed lake systems. Direct anthropogenic inputs buried the older, natural sediments with up to 9 meters of stamp sands and slime clays (Wright et al., 1973). Due to these inputs, the 30 - 40 cm sediment cores from Torch Lake didn't penetrate deep enough to reach non-mining deposited/impacted sediments. So, for lake systems that have been severally anthropogenically disturbed, reference systems provide the data for comparing impacted and non-impacted sediments in a lake. The baseline or anthropogenically undisturbed concentration value from the reference system will be known as a "background concentration". In order to better understand chemical concentration versus depth profiles, some terms will be defined.

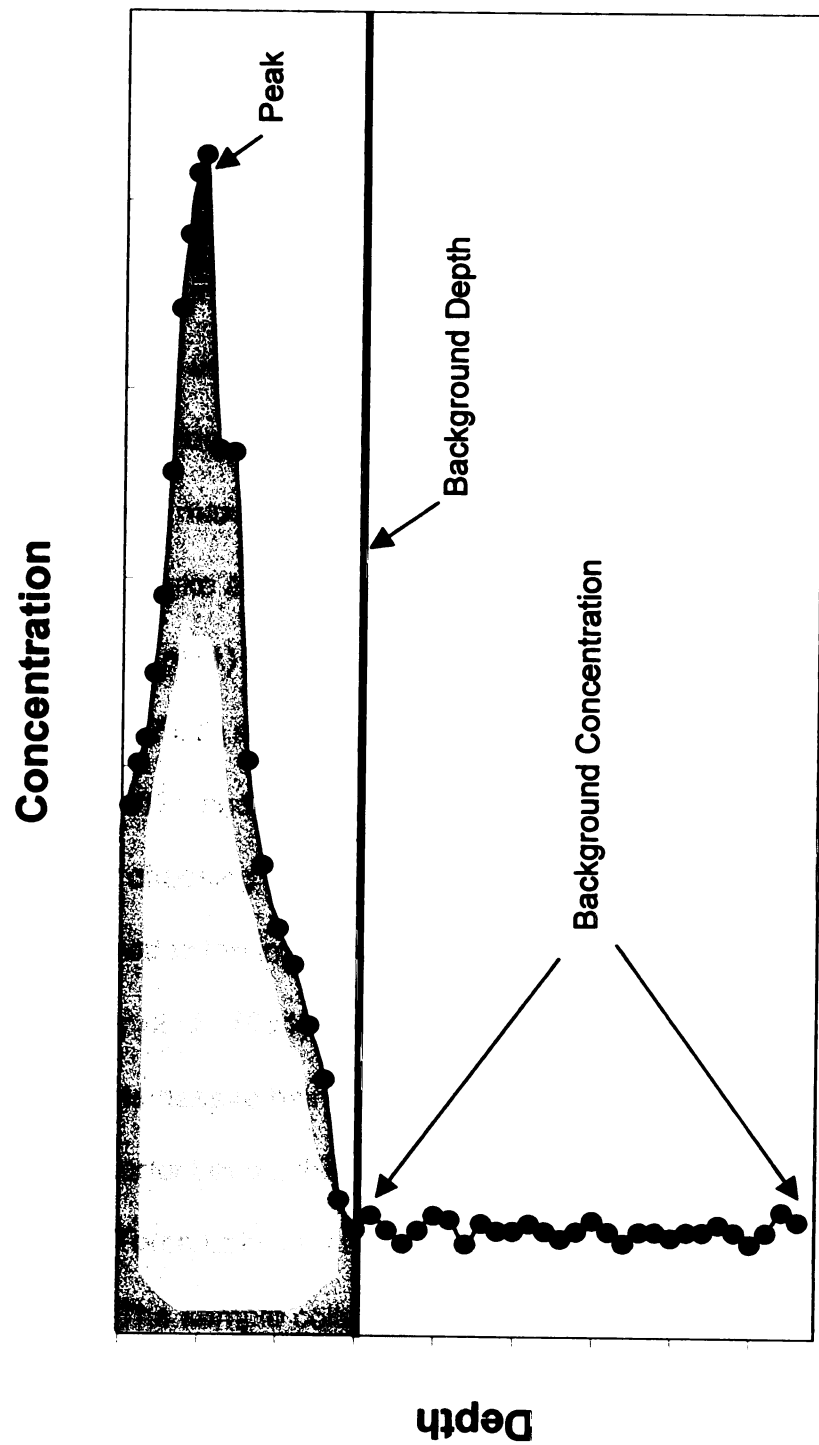


Figure 9. Diagram of terms used in profile descriptions.

Figure 9 is a generalized sediment core profile of an element concentration versus depth. Background concentrations at a given site are calculated by averaging the concentrations below a certain background depth, and this is the depth in the core at which the element concentration reaches a steady-state (Kolak et al., 1999). Peak concentrations are the highest concentrations in the core.

The system chosen to represent background heavy metal concentrations (i.e., sediments unaffected by mining inputs) in Torch Lake is Gratiot Lake. Gratiot Lake is located on the eastern side of the Keweenaw Peninsula (Figure 10), and has a maximum depth of 24 m and area of 5.82 km². The factors for choosing this lake as a reference lake in this study were its similarities to Torch Lake in terms of: 1) bedrock geology (e.g., Jacobsville Sandstone) (Figure 3) (Milstein, 1987), 2) surficial geology (e.g., coarse textured glacial till) (Figure 11) (Farrand, 1982), and 3) land cover (e.g., deciduous forest) (Figure 12). Other reasons for choosing Gratiot Lake were that no mining or processing activities have occurred in the immediate vicinity (i.e., not in the watershed) of the lake (Ellenberger et al., 1994), and Gratiot Lake has a low anthropogenic inventory of contaminants despite being in close proximity to the Cu deposits and mining activities (Kerfoot et al., 1999a). Gratiot Lake has also been used as a reference system for Torch Lake in a fish reproduction assessment done by Ellenberger et al. (1994). The sample collection (depth of 24 m), sample preparation and chemical analysis of Gratiot Lake were performed using the same methods as

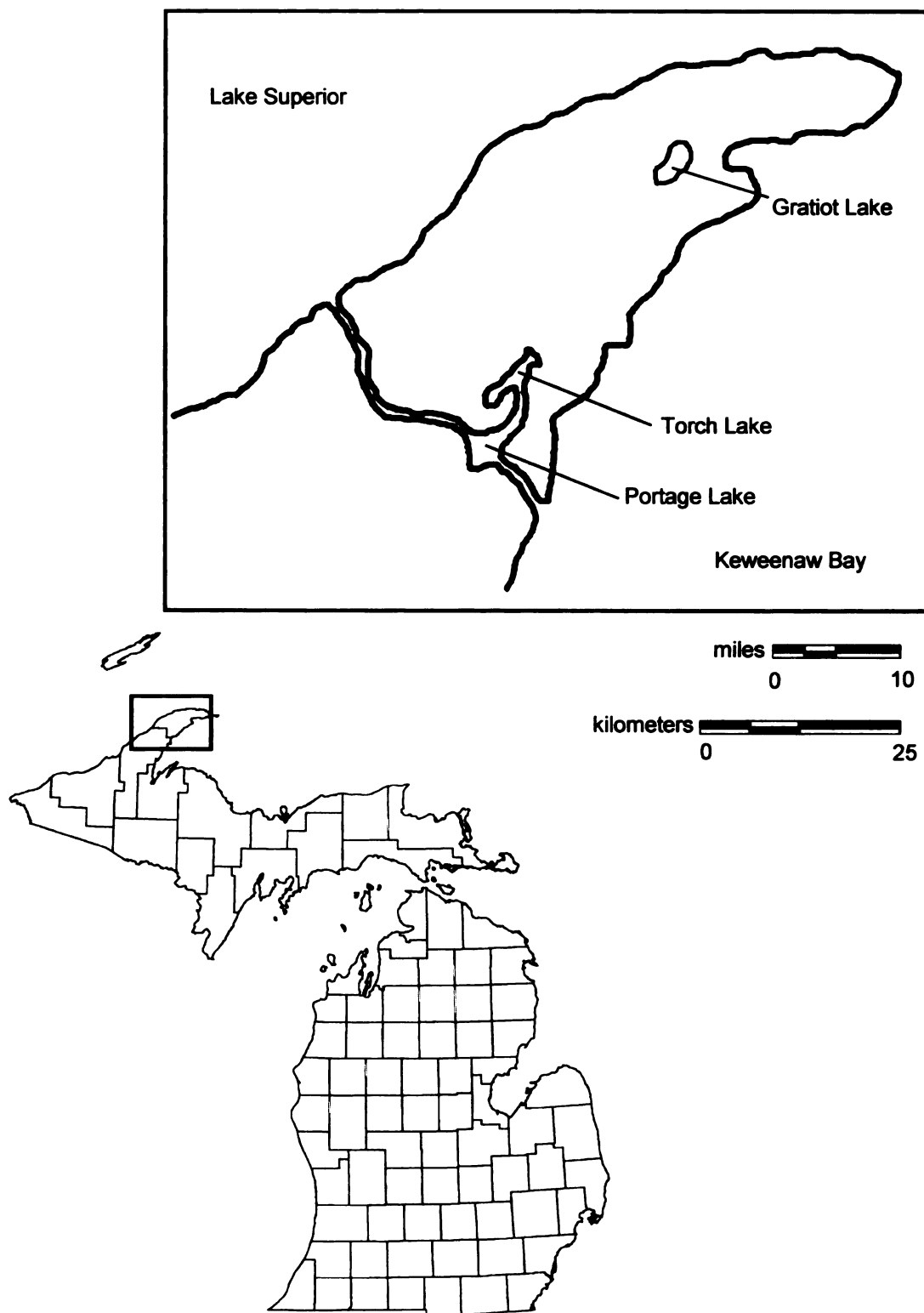


Figure 10. Map showing the location of Gratiot Lake, Portage Lake and Torch Lake in the Keweenaw Peninsula of Michigan (modified from Ellinger et. al., 1994).

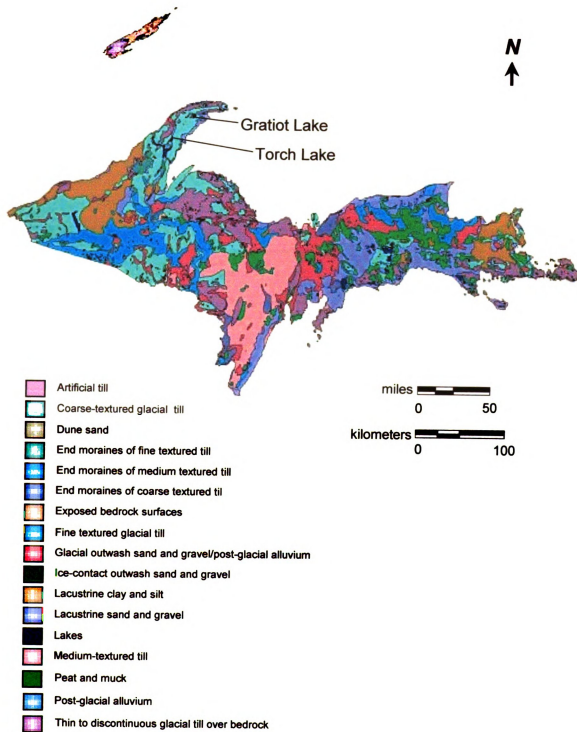


Figure 11. Surficial geology map of the Upper Peninsula of Michigan (modified from Farrand, 1982). Image is presented in color.

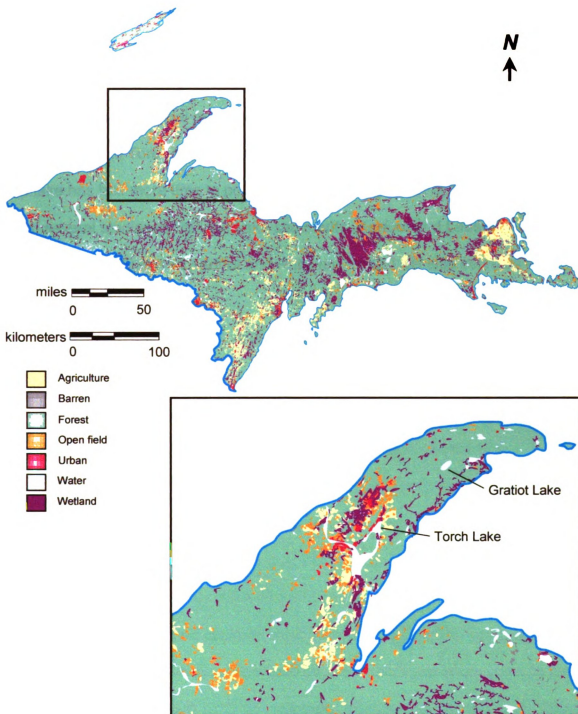


Figure 12. Land cover/land use map for the Upper Peninsula of Michigan (modified from Center for Remote Sensing & Geographic Information Science, Michigan State University). Image is presented in color.

discussed earlier. Studies on Portage Lake have documented different sediment types coming into the lake since the cessation of mining activities. Portage Lake is hydrologically connected to Torch Lake (Figure 4) with the same bedrock geology, surficial geology and current land use. Portage Lake had a similar history to Torch Lake, but stamping operations ceased around 1920 and the lake has had more time to potentially recover from past disturbances. Data from several studies of Portage Lake sediments (Kerfoot and Lauster, 1994; Kerfoot et al., 1999a and Kerfoot and Robbins, 1999b) will also serve as a reference for Torch Lake

III. Results and Discussion

Nature of Sediments

Sediment cores from Torch Lake could be separated into two distinct layers based on color. The top 8-10 cm of sediment from each sample location was either a light brown or brownish/red color, and the remaining length of sediment (23-39 cm depending on the site) was a pink/purple color (Figure 13). On-site descriptions are summarized in Appendix A. Sediment analyses done by Kerfoot and Lauster (1994) on Portage Lake documented a similar difference in sediment color, and these results will be used to help interpret the shift in color of sediments documented in the Torch Lake cores. On average, the top 15-22 cm of sediment from Portage Lake was reported to consist of a brown/light brown color, then there was a middle region that was a pinkish/purple color, and the remaining length of the sediment core was a red to purple color with thin, regular bands (Kerfoot and Lauster, 1994). These observations were related to three different depositional histories: 1) sediments deposited after mining had ceased, which have a higher organic content, 2) stamp sands and slime clays which were the dominant input of sediment to the lake after 1900 until about 1920, 3) sediments deposited when early (pre-1900) mining activities were ongoing.

In Torch Lake, organic rich sediments near the sediment/water interface are watery, then grade to thicker clay like sediments with depth until the

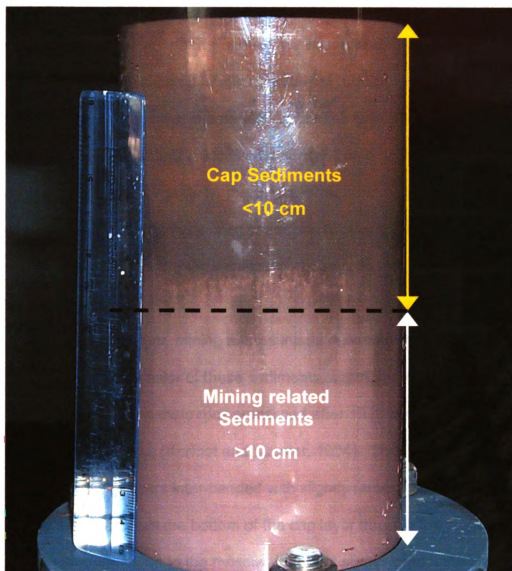


Figure 13. Photo of a sediment core from Torch Lake, Site T1. Sediments are labeled by depositional history and the dashed line represents a depth of 10 cm. Image is presented in color.

pink/purple sediments are reached. This organic rich layer will be referred to as the “cap layer”. Cap layer sediments are as thick as 10 cm and varied in color from light brown to brownish-red (Figure 13). These sediments were deposited in the years after the cessation of mining activities around the lake. Although organic content analyses was not performed in this study, Jeong et. al., (1999) found organic matter content in top 5 cm of Torch Lake, near MSU site T3 (Figure 7), to be 7.7%. A study by the U.S. EPA in 1992 also found a similar dark brown layer overlying the mining sediments that varied in thickness and between 1.0 and 2.5 cm, these samples were also collected near MSU site T3 (Figure 7).

Below the cap layer, mining related inputs dominate the sediment make-up. The pinkish-purple color of these sediments is attributed to tailings from the Allouez Conglomerate, a main rock processed after 1920 in stamp mills along the shores of Torch Lake (Kerfoot and Lauster, 1994). These sediments are fine grained, with watery layers inter-bedded with slightly firmer layers. Pink/purple sediments extended from the bottom of the cap layer through the remaining length of each core. Due to the massive inputs of stamp sands and slime clays to the lake, it was observed that the coring device didn't penetrate deep enough to encounter background sediments in Torch Lake or a third (pre-1900) layer as documented in Portage Lake by Kerfoot and Lauster (1994).

^{210}Pb and ^{137}Cs

In an attempt to document temporal changes, sediments from Torch Lake were dated using ^{210}Pb and ^{137}Cs . Age dating of lake sediments via the radionuclide ^{210}Pb has been a successful method used in numerous studies (Robbins and Edgington, 1975; Edgington and Robbins, 1976; Hilton et al., 1986; McKee et al., 1989; Appleby and Oldfield, 1983 and Golden et al., 1993). In soils, ^{226}Rn decays to ^{222}Rn , which eventually decays to ^{210}Pb . This ^{210}Pb is known as “supported ^{210}Pb ”. During decay, some of the ^{222}Rn gas escapes to the atmosphere, where it eventually decays to ^{210}Pb and gets re-deposited onto the earth’s surface (e.g., depositional basins of lakes) (Wetzel, 2001). This ^{210}Pb is known as “unsupported ^{210}Pb ”. Sediment ages are calculated by subtracting the supported ^{210}Pb (^{210}Pb resulting from the presence of ^{226}Rn in the sediment) from the total ^{210}Pb , yielding the unsupported ^{210}Pb (Wetzel, 2001). Knowing the half-life of ^{210}Pb (~22.3 years) and activity of unsupported ^{210}Pb relative to the surface, age calculations are made based on the decay constant of ^{210}Pb and the slope of the regression line of excess ^{210}Pb (Bq/g) vs. accumulated dry mass (g/cm^2).

Interpretations of sediment ages via ^{210}Pb are strengthened with the use of fallout horizons (nuclear testing, pollen, etc.), which are recorded in the lakes sediments (Robbins, 1978). The fallout horizon chosen for this study was the radionuclide ^{137}Cs . This isotope is produced during nuclear reactions (i.e., power generation, nuclear bombs, etc.). The concept of using ^{137}Cs for an age marker is that the first appearance of ^{137}Cs can be traced to the early 1950’s,

and the peak fallout occurred during the span of 1963-1964, when nuclear bomb testing was at its peak (Robbins and Edgington, 1975; Mueller et al., 1989 and Walling and Qingping, 1992). Assuming that the ^{137}Cs peak recorded in the lake sediments is 1963-1964 and dates calculated via ^{210}Pb are similar, then the calculated sediment ages will be considered valid. Lead-210 analysis was performed on three cores, T1, T2 and T5, and ^{137}Cs analysis was performed on two cores, T1 and T2.

The results from the ^{210}Pb and ^{137}Cs analyses are summarized in Tables 2a, 2b & 2c. The ^{210}Pb ages for site T1 were determined using a constant flux, constant sedimentation rate model (CF:CS). The CF:CS method assumes that there is a constant flux of ^{210}Pb with a constant sediment input into the lake over a given time (Robbins, 1978 and Golden et al., 1993). The equation for the CF:CS model is:

$$A_{(z)} = A_s \exp ((-k z) / W)$$

Where:

$A_{(z)}$ = the unsupported ^{210}Pb activity at mass depth z

A_s = unsupported ^{210}Pb activity at the sediment-water interface

W = sedimentation rate ($\text{g}/\text{cm}^2/\text{yr}$)

z = mass depth (g/cm^2)

k = decay constant 0.0311/yr

A modification to the CF:CS model was proposed by Heyvaert et al. (2000) where the slope of ^{210}Pb vs. accumulated dry mass was segmented into different sedimentation rates. This method is known as SCF:CS. The equation for the SCF:CS method is the same as the CF:CS method with the exception of

Table 2a. Data from the ^{210}Pb and ^{137}Cs analysis of Torch Lake sediments, site T1

Sample	Depth (cm)	Acc. Dry wt. (g/cm ²)	Porosity	Excess ^{210}Pb (Bq/g)	^{137}Cs (Bq/g)	Age Date
T1-1	0.25	0.0911	0.97	7.26E-01		1999
T1-2	0.75	0.0632	0.96	8.07E-01		1996
T1-3	1.25	0.0564	0.94	8.39E-01		1994
T1-4	1.75	0.0663	0.94	7.25E-01		1992
T1-5	2.25	0.0804	0.93	5.70E-01	3.47E-02	1990
T1-6	3	0.1985	0.93	5.12E-01	4.00E-02	1985
T1-7	4	0.2061	0.92	4.54E-01	5.60E-02	1978
T1-8	5	0.2179	0.92	3.92E-01	6.82E-02	1972
T1-9	6	0.2292	0.91	3.10E-01	6.80E-02	1964
T1-10	7	0.1762	0.92	2.52E-01	5.51E-02	1958
T1-11	8	0.5334	0.82	1.14E-01	4.82E-02	1946
T1-12	9	0.6921	0.76	3.83E-02	1.94E-02	1926
T1-13	10	0.6220	0.79	2.65E-02		1905
T1-14	11	0.6454	0.78	2.25E-02		1884
T1-15	12	0.5884	0.80	1.17E-02		1864
T1-16	13	0.4317	0.85	7.82E-03		1847
T1-17	14	0.6031	0.79	3.55E-03		1830
T1-18	15	0.5883	0.80	1.28E-02		
T1-19	16	0.5403	0.81	4.50E-03		
T1-20	17	0.6153	0.79	1.58E-02		
T1-21	18	0.6766	0.77	1.45E-02		
T1-22	19	0.5802	0.80	1.02E-02		
T1-23	20	0.4874	0.83			
T1-24	21	0.5011	0.83			
T1-25	22	0.4991	0.83			
T1-26	23	0.6020	0.79			
T1-27	24	0.6164	0.79			
T1-28	25	0.5458	0.81			
T1-29	26	0.4091	0.86			
T1-30	27	0.4513	0.84			
T1-31	28	0.5245	0.82			
T1-32	29	0.5251	0.82			
T1-33	30	0.5399	0.81			
T1-34	31	0.6105	0.79			

Table 2b. Data from the ^{210}Pb and ^{137}Cs analysis of Torch Lake sediments, site T2

Sample	Depth (cm)	Acc. Dry wt. (g/cm ²)	Porosity	Excess ^{210}Pb (Bq/g)	^{137}Cs (Bq/g)	Age Date
T2-1	0.25	0.0336	0.97	1.06E+00		1999
T2-2	0.75	0.0690	0.96	1.11E+00		1997
T2-3	1.25	0.1045	0.97	1.12E+00		1996
T2-4	1.75	0.1532	0.96	1.14E+00		1993
T2-5	2.25	0.2022	0.96	9.93E-01	1.84E-02	1991
T2-6	3	0.3561	0.94	7.65E-01	2.72E-02	1986
T2-7	4	0.5288	0.93	5.90E-01	3.73E-02	1979
T2-8	5	0.7326	0.93	5.01E-01	4.80E-02	1972
T2-9	6	0.9237	0.93	4.26E-01	5.08E-02	1965
T2-10	7	1.1409	0.90	3.08E-01	4.63E-02	1958
T2-11	8	1.9682	0.71	6.04E-02	1.60E-02	1928
T2-12	9	2.7852	0.72	2.61E-02		
T2-13	10	3.6257	0.71	1.90E-02		
T2-14	11	4.3676	0.74	1.67E-02		
T2-15	12	5.1547	0.73	1.64E-02		
T2-16	13	5.8128	0.77	1.49E-02		
T2-17	14	6.4973	0.76	1.12E-02		
T2-18	15	7.0862	0.80	9.32E-03		
T2-19	16	7.6106	0.82	8.44E-03		
T2-20	17	8.1048	0.83	9.28E-03		
T2-21	18	8.6566	0.81	3.36E-03		
T2-22	19	9.0672	0.86	5.29E-03		
T2-23	20	9.6217	0.81			
T2-24	21	10.3541	0.75			
T2-25	22	11.5824	0.58			
T2-26	23	12.5748	0.66			
T2-27	24	13.1077	0.82			
T2-28	25	13.6902	0.80			
T2-29	26	14.2351	0.81			
T2-30	27	14.7679	0.82			
T2-31	28	15.3023	0.82			
T2-32	29	15.8402	0.81			
T2-33	30	16.3961	0.81			
T2-34	31	16.9636	0.80			

Table 2c. Data from the ^{210}Pb analysis of Torch Lake sediments, site T1

Sample	Depth (cm)	Acc. Dry wt. (g/cm²)	Porosity	Excess ^{210}Pb (Bq/g)	Age Date
T5-1	0.25	0.0420	0.98	1.19E+00	1998
T5-2	0.75	0.0312	0.97	1.18E+00	1995
T5-3	1.25	0.0550	0.95	1.17E+00	1993
T5-4	1.75	0.0566	0.95	1.23E+00	1991
T5-5	2.25	0.0772	0.94	8.94E-01	1989
T5-6	3	0.0849	0.94	7.34E-01	1988
T5-7	4	0.1061	0.93	5.70E-01	1985
T5-8	5	0.1034	0.91	4.94E-01	1983
T5-9	6	0.1213	0.90	3.80E-01	1983
T5-10	7	0.2592	0.91	2.80E-01	1979
T5-11	8	0.4592	0.84	1.30E-01	1964
T5-12	9	0.7238	0.75	1.16E-02	1937
T5-13	10	0.6152	0.79	4.41E-03	1912
T5-14	11	0.5989	0.79	1.97E-03	1907
T5-15	12	0.5166	0.82		
T5-16	13	0.5566	0.81		
T5-17	14	0.5738	0.80		
T5-18	15	0.5573	0.81		
T5-19	16	0.6184	0.79		
T-20	17	0.6828	0.76		
T5-21	18	0.6902	0.76		
T5-22	19	0.6282	0.78		
T5-23	20	0.5776	0.80		
T5-24	21	0.6528	0.77		
T5-25	22	0.5678	0.80		
T5-26	23	0.6908	0.76		
T5-27	24	0.5808	0.80		
T5-28	25	0.6355	0.78		
T5-29	26	0.5810	0.80		
T5-30	27	0.5962	0.79		
T5-31	28	0.6436	0.78		
T5-32	29	0.6886	0.76		
T5-33	30	0.6248	0.78		
T5-34	31	0.6743	0.77		
T5-35	32	0.7200	0.75		

varying sedimentation rates for different segments of the core. The SCF:CS method was used in cores T2 and T5. Plots of excess ^{210}Pb vs. accumulated dry weight are shown in Figures 14 and 15.

One assumption when using ^{210}Pb for dating sediments is that there has been very little or no re-suspension of sediments or migration of the ^{210}Pb . This assumption is usually valid for depositional basins, however the aforementioned dredging of previously deposited stamp sands seriously disturbed the historical record in the sediments (Kerfoot and Lauster, 1994). Large mechanical dredges were capable of extracting the sediments up to depths of 33.5 m in Torch Lake, so even the deep basin of the lake (32 m) could have been affected. Also, below the cap layer, the excess ^{210}Pb rapidly approach supported levels of ^{210}Pb , due to the substantial contribution of ^{210}Pb deficient stamp sands entering the lake with the ^{210}Pb from the atmosphere and natural sediments. These factors caused ^{210}Pb dates to approach the 1800's at depths below 10 cm (Tables 2a, 2b & 2c). Based on historic data of lake basin fill, 7-9 m, these dates could not be valid. So, dates in the cap sediments (<10 cm) might be considered valid, but below the cap sediments, age dates were not considered valid.

However, the ^{210}Pb dates in the cap sediments were also considered to be not valid, even though peaks in ^{137}Cs activity corresponded to a ^{210}Pb date of 1964 and 1965 for sites T1 and T2 respectively (Figure 16). Peak activities of ^{137}Cs are at the 6 cm depth for both sites T1 and T2, and based on sediment composition, sediments at the 6 cm depth are still within the cap sediments

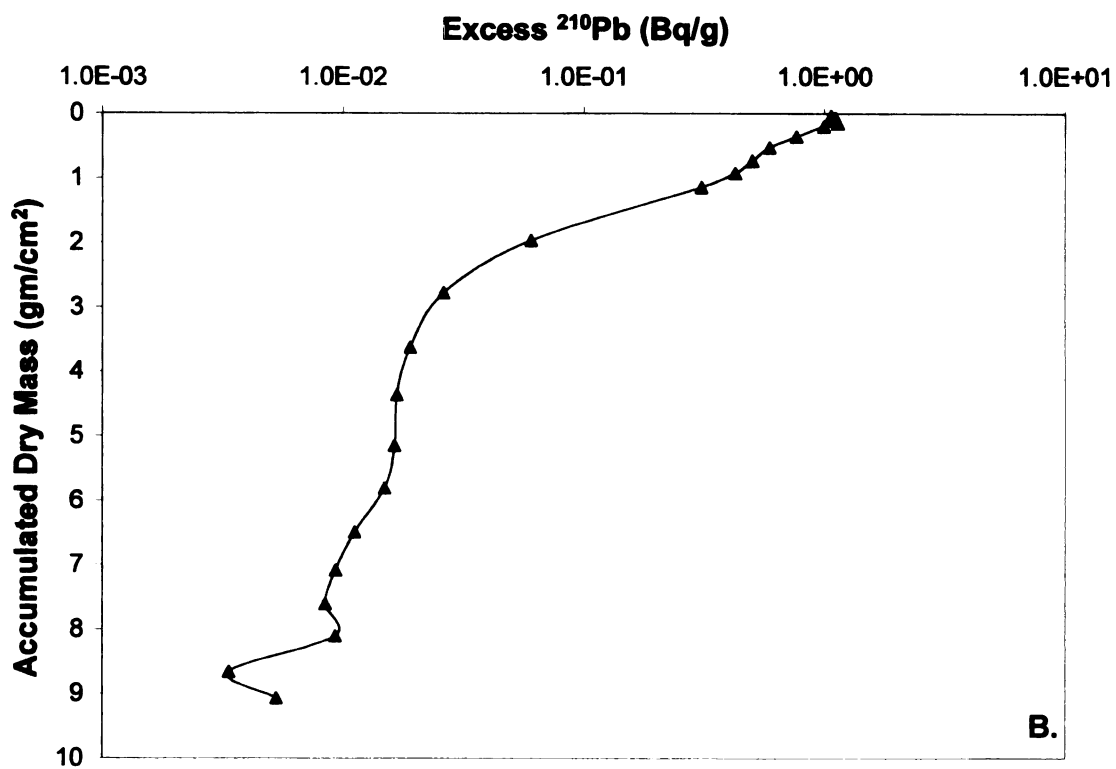
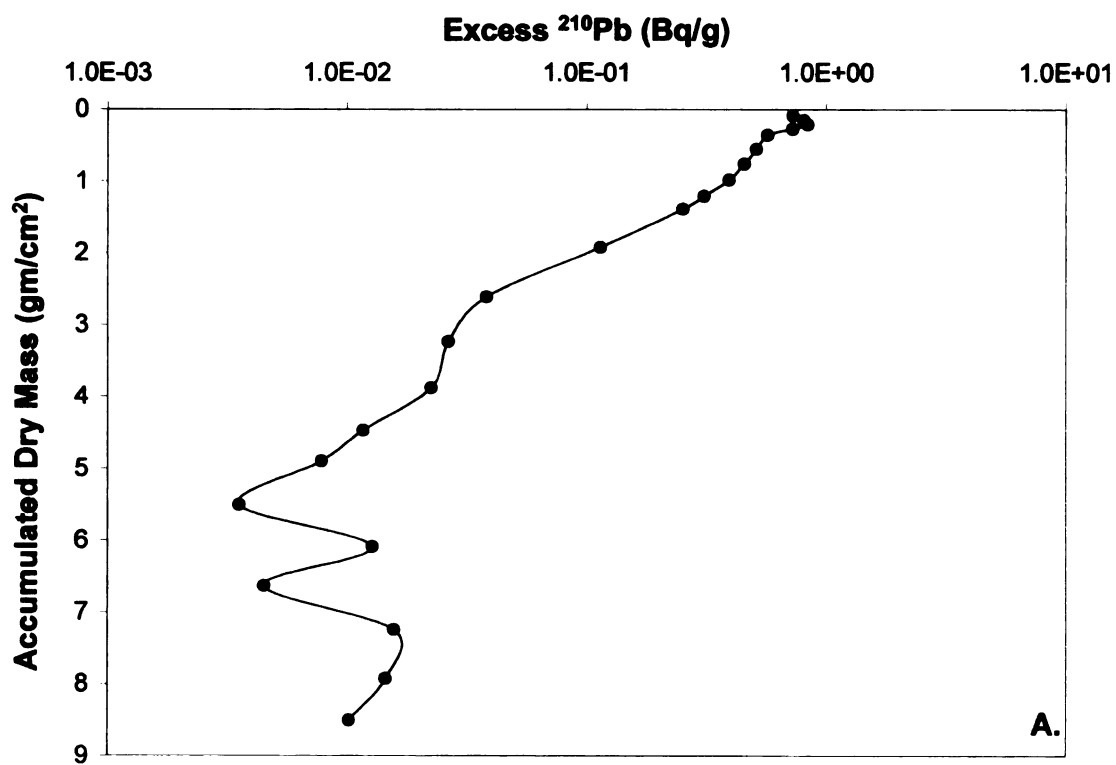


Figure 14. Profile of excess ^{210}Pb (Bq/g) vs. accumulated dry mass in Torch Lake sediments. A) Site T1 and B) Site T2.

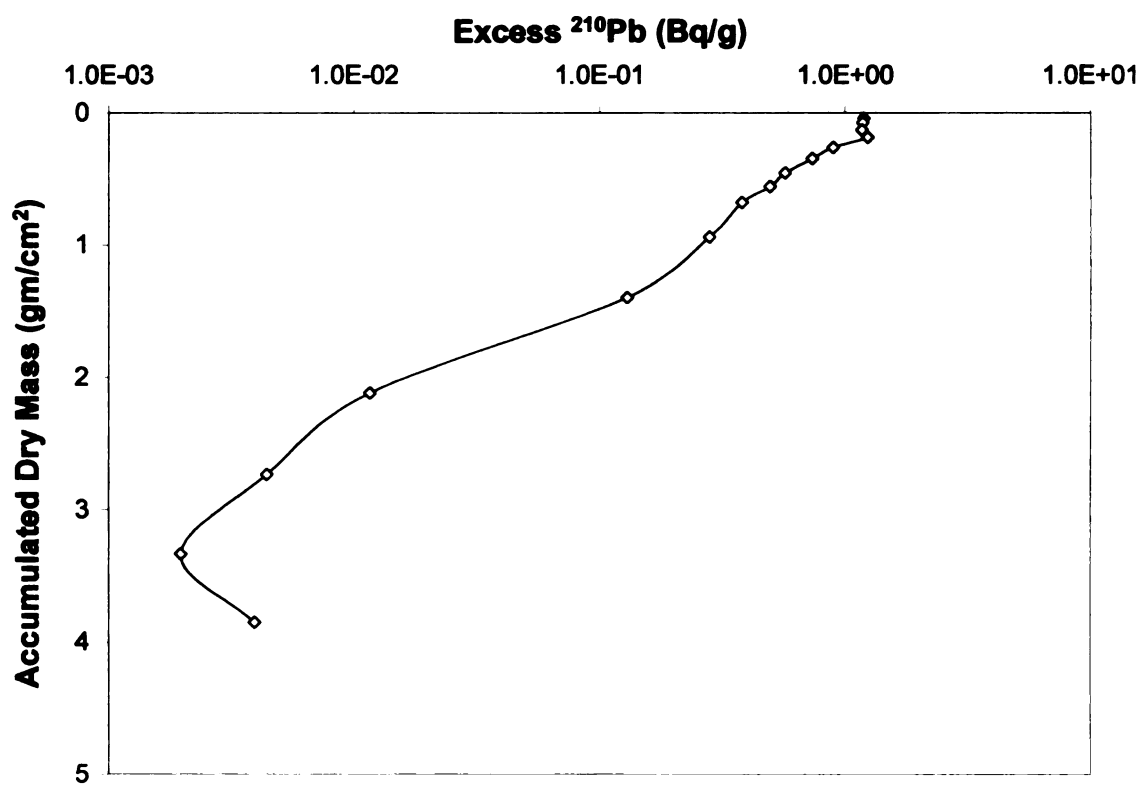


Figure 15. Profile of excess ^{210}Pb (Bq/g) vs. accumulated dry mass in Torch Lake sediments, site T5.

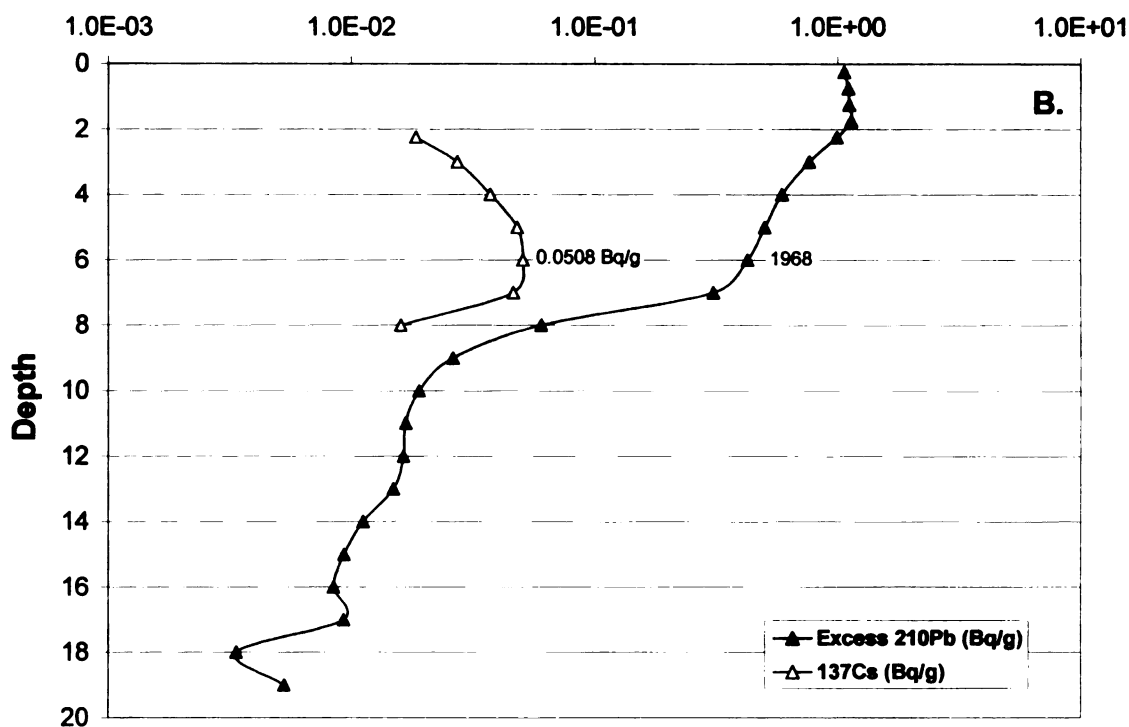
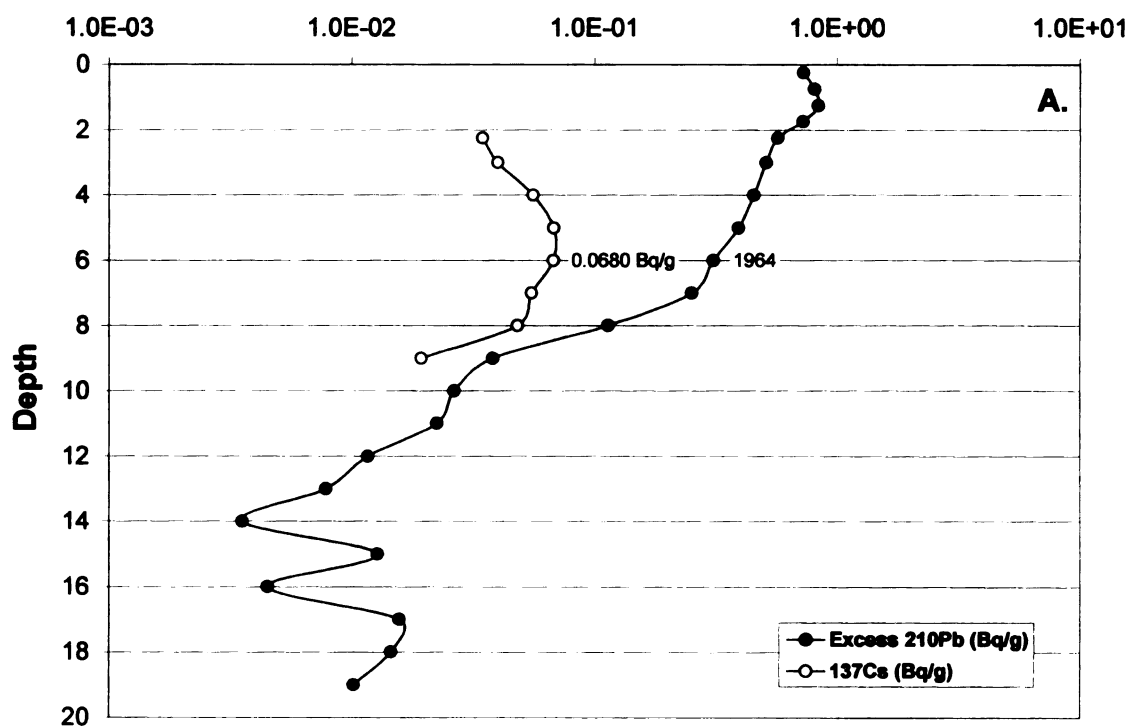


Figure 16. Profile of excess ^{210}Pb (Bq/g) vs. depth and ^{137}Cs (Bq/g) vs. depth in Torch Lake sediments. A) Site T1 and B) Site T2.

(Appendix A). If stamp sand inputs ceased the final time in 1968, than the ^{137}Cs was most likely not captured in the cap sediments. Dating of Torch Lake sediments is further explored in the “event dating” section.

Extractable Copper Concentrations

Copper concentrations were anticipated to be lower in the cap sediments, because of the cessation of direct inputs of mine tailings, however this was not observed. The vertical profiles of Cu concentrations versus depth are shown in Figures 17 and 18. At sites T1, T2, T3 and T5, the average concentration of Cu in the cap sediments was 2,752, 2,044, 2,262 and 1,551 mg/kg respectively. Below the cap sediments (total depth varied with sample site), average Cu concentrations were slightly lower at 1,746, 1,063, 1,120 and 1,442 for sites T1, T2, T3 and T5 respectively. Copper concentrations in the north basin peak in the cap sediments, with site T1 had the largest peak concentration at 5,472 mg/kg, correlating to a depth of 9.0 cm. This peak is most likely attributed to the spill of stored cupric ammonium carbonate solution that occurred from October 1971 to June 1972. Average Cu concentrations within both the cap sediments and mining related sediments of site T1 were the highest of the four sites sampled. In the south basin of the lake, site T5, the highest concentration of Cu (2,132 mg/kg) was measured in the mining related sediments, at a depth of 39 cm. Both basins show an overall increase in Cu concentrations from the bottom of the cap layer to the sediment/water interface.

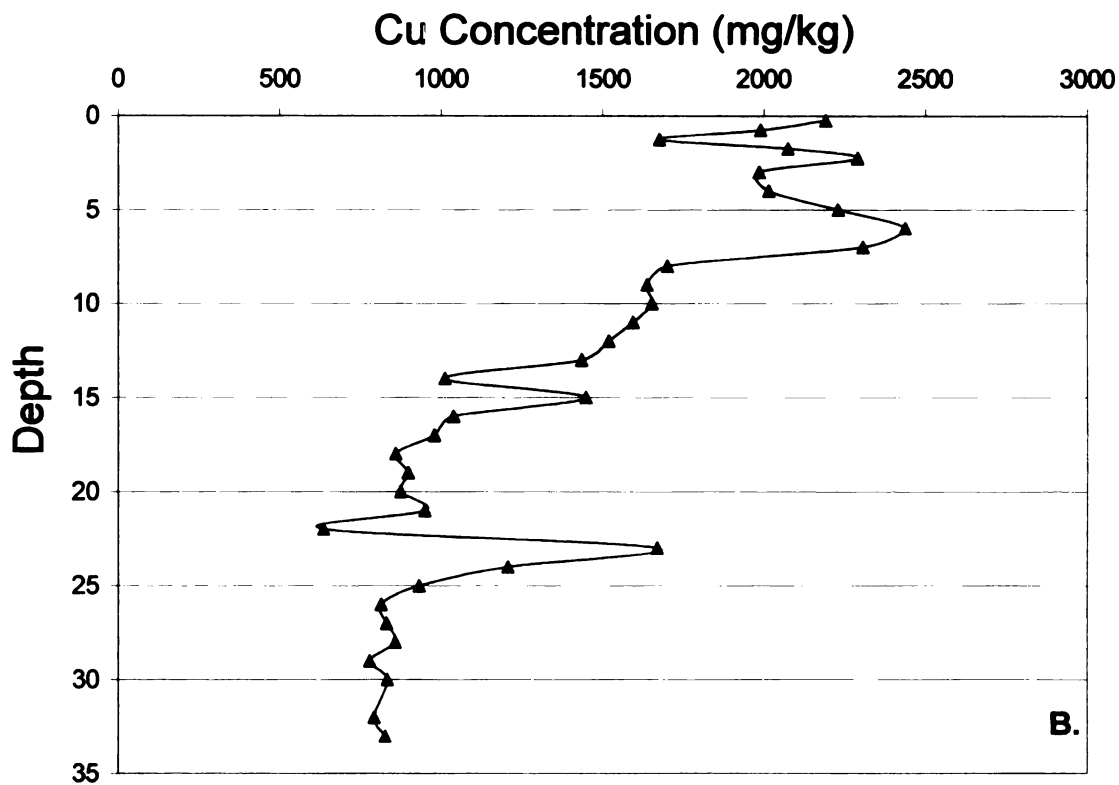
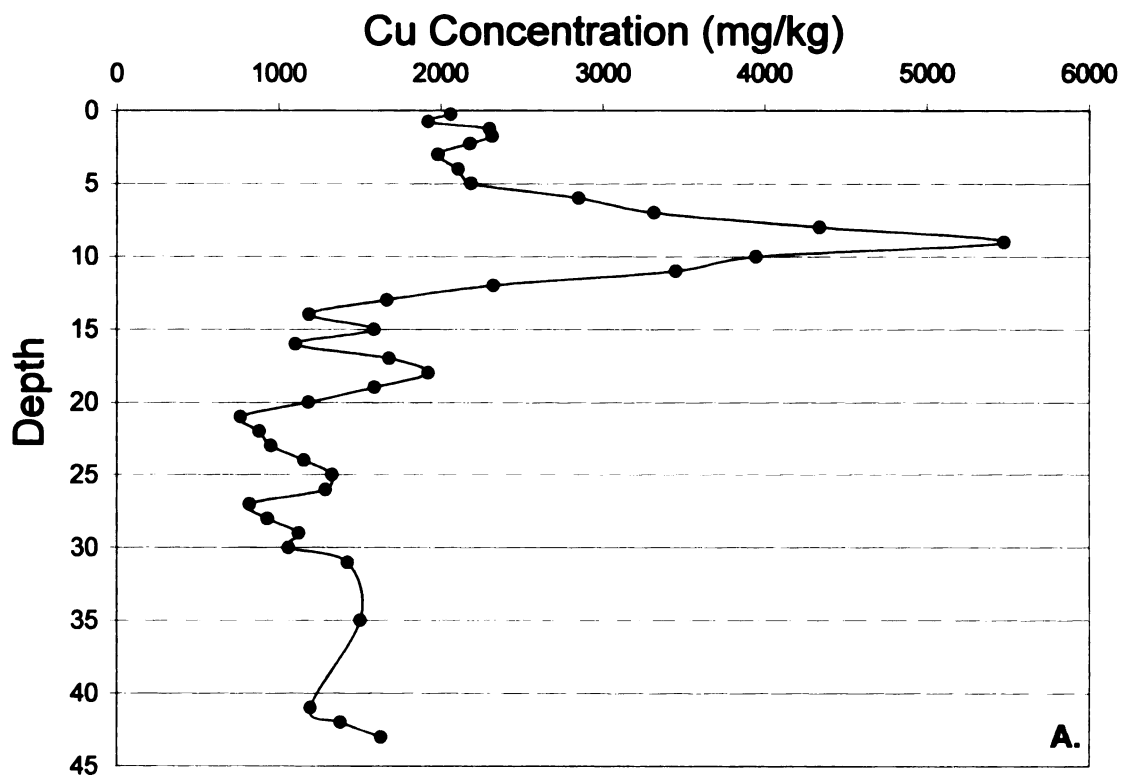


Figure 17. Vertical profiles of copper concentrations in Torch Lake sediments. A) Site T1 and B) Site T2.

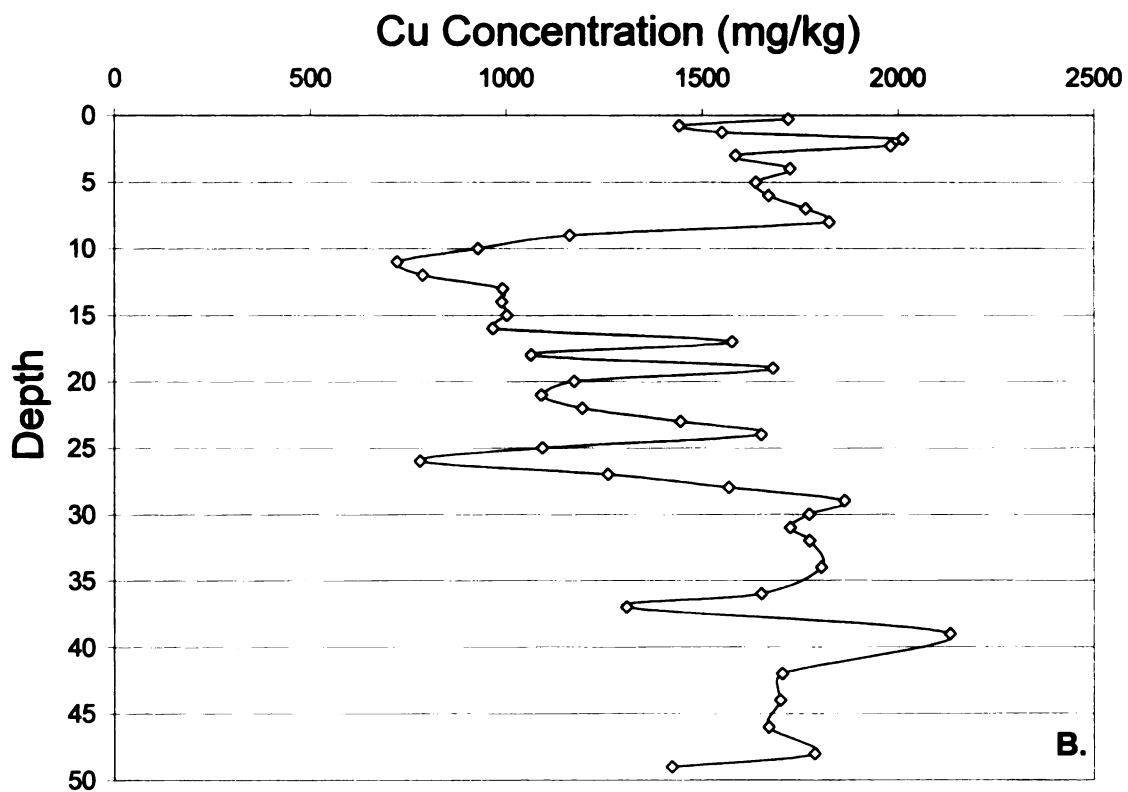
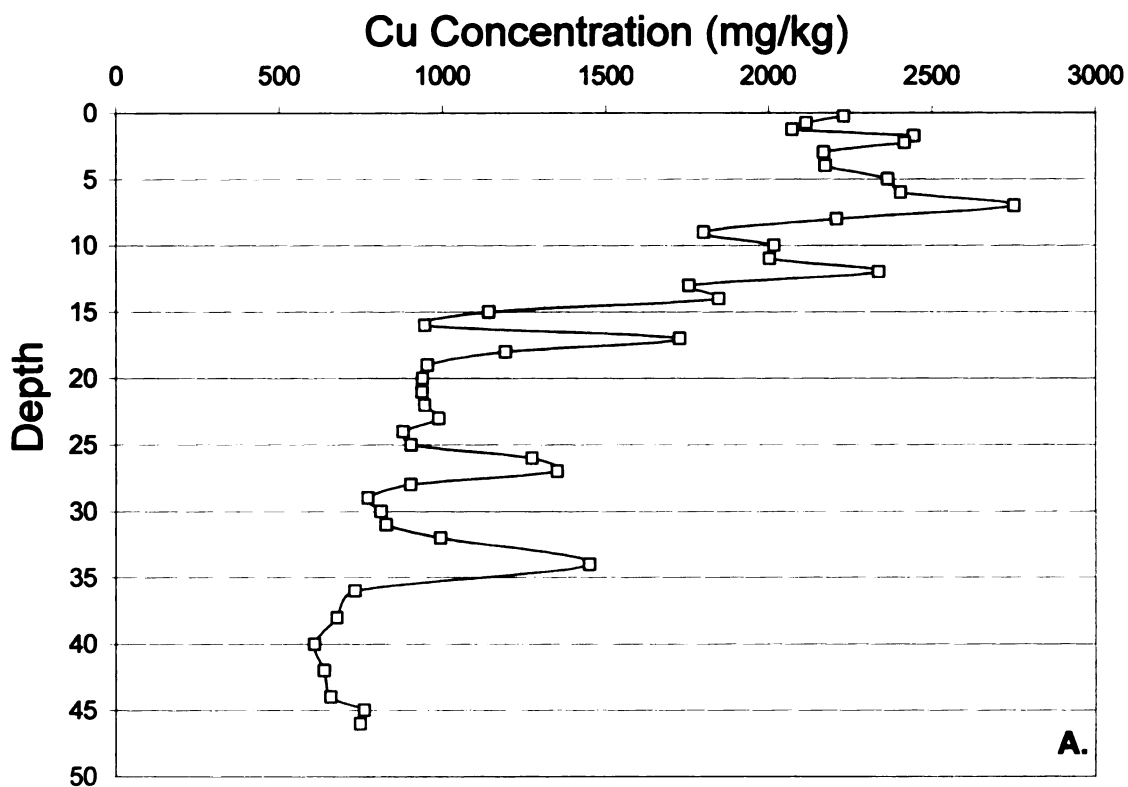


Figure 18. Vertical profiles of copper concentrations in Torch Lake sediments. A) Site T3 and B) Site T5.

The average Cu concentration from all four basins in the cap sediments was 2,197 mg/kg and in the average in the mining related sediments was 1,232 mg/kg. These results are consistent with previous studies (Jeong et al., 1999; Cusack and Mihelcic, 1999 and EPA, 1992), and still remain high compared to other sediments in the Keweenaw Peninsula that are relatively anthropogenically undisturbed (Table 3). For example, in deep basins of Lake Superior Cu concentrations have been reported at 57 mg/kg (Kolak et al., 1998) and 60 mg/kg (Kemp et al., 1978), dry weight. Background Cu concentrations in sediments of Gratiot Lake averaged 61 mg/kg (this study). Cu in sediments of the Keweenaw Peninsula, not adjacent to any Cu mining activities, averaged 70 mg/kg (Jeong et al., 1999). Cu concentrations in unaffected sediments of the Keweenaw Peninsula region are approximately 38 times lower than Cu concentrations in the cap sediments and 21 times lower than the mining related sediments of Torch Lake. The average sediment-copper concentrations for Torch Lake and other selected sediments and soils within and around the Keweenaw Peninsula are summarized in Table 3.

Table 3. Copper concentrations in Torch Lake sediments, Gratiot Lake sediments, Lake Superior sediments and soils around the Keweenaw Peninsula.

Location	Average (mg/kg)	Std. Dev.
Torch Lake – Cap sediments (this study)	2,197	518
Torch Lake – Mining related sediments (this study)	1,232	197
Torch Lake – Tailings (EPA, 1992)	2,330-18,500	ND
Torch Lake – Organic Layer(EPA, 1992)	10,100-24,100	ND
Torch Lake – S. Basin(Cusack and Mihelcic, 1999)	976	365
Torch Lake – N. Basin(Jeong et al., 1999)	4,200	200
Gratiot Lake (this study)	61	8
Lake Superior (Kolak et al., 1999)	57	ND
Lake Superior (Kemp et al., 1978)	60	ND
Keweenaw Peninsula soils (Jeong et al., 1999)	70	ND

Cu/Zn Ratios

Copper ores mined the Keweenaw Peninsula have a unique signal of Zn depletion relative to Cu, and this depletion is preserved in lake sediments that have been affected by mining inputs (Kerfoot and Lauster, 1994; Kerfoot and Robbins, 1999b; Kerfoot et al., 1999a and Kolak et al., 1999). Copper is normally less abundant in lake sediments due to geology, greater solubility of Zn and higher concentrations of Zn in living matter (Kerfoot et al., 1999a). Therefore, Cu/Zn ratios can be used to correlate total Cu within the sediments to a source such as stamp sands (Kerfoot et al., 1999a; Kerfoot and Lauster, 1994 and Kolak et al., 1999). For example, Cu/Zn ratios in some Lake Superior sediments are <1 and fairly constant when concentrations of Cu are below 100 mg/kg, which is near background concentrations for the region (57-61 mg/kg). However, once the Cu/Zn ratio is > 1, Cu concentrations often exceed background, implying that the sediment-copper concentrations are dominated by

inputs from stamp sands and slime clays (Kolak et al., 1999). At all sample depths from each of the four sites, the Cu/Zn ratio is greater than 1. Site T1 had the highest Cu/Zn ratio with a value 16.5 at 9 cm depth, and site T5 had the highest Cu/Zn ratio in the mining related sediments at a value of 12.3. Site T1 had the highest average Cu/Zn ratio in the cap sediments at 10.9, and site T5 had the highest Cu/Zn ratio for mining sediments at 7.9. Ratios of Cu/Zn versus depth for all four sediment cores of Torch Lake are shown in Figure 19. Overall, the Cu/Zn ratio in the cap sediments (<10 cm) averaged 9.4 and the mining related sediments (>10 cm) averaged 5.8 for all four sites. The Cu/Zn ratios from Torch Lake and other sediments and soils around the Keweenaw Peninsula are summarized in Table 4.

When the Cu/Zn ratios from the mining related sediments and cap sediments are plotted with Lake Superior, Gratiot Lake and stamp sands, Torch Lake sediments plot in the same cluster as stamp sands for the region (Figure 20). These data suggest that the Cu/Zn ratios measured in this study are the most reflective of stamp sand ratios, especially in the cap sediments. This suggests that there is a continual, dominant input of stamp sands from the shoreline erosion of tailing deposits.

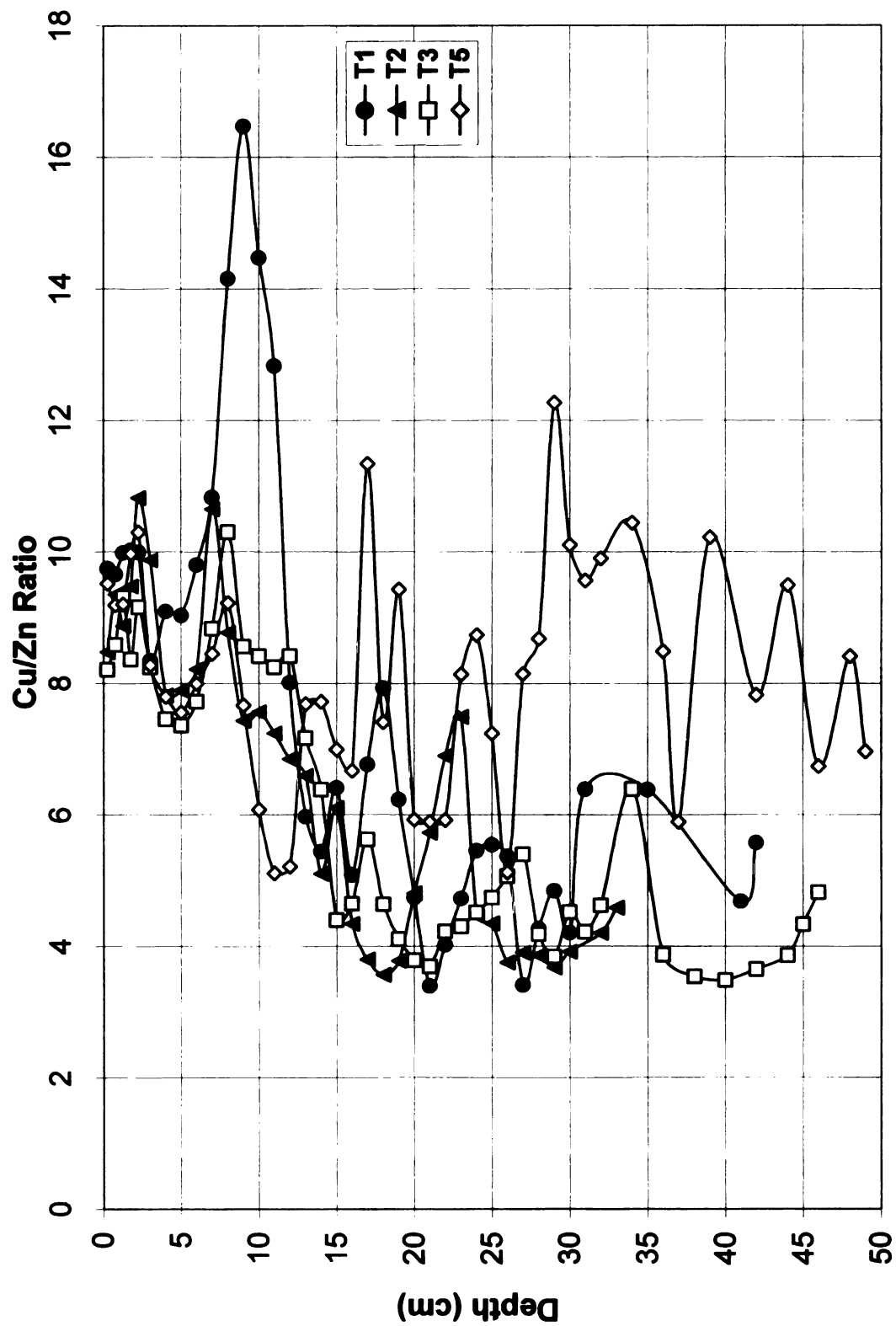


Figure 19. Cu/Zn vs. depth profiles in Torch Lake sediments.

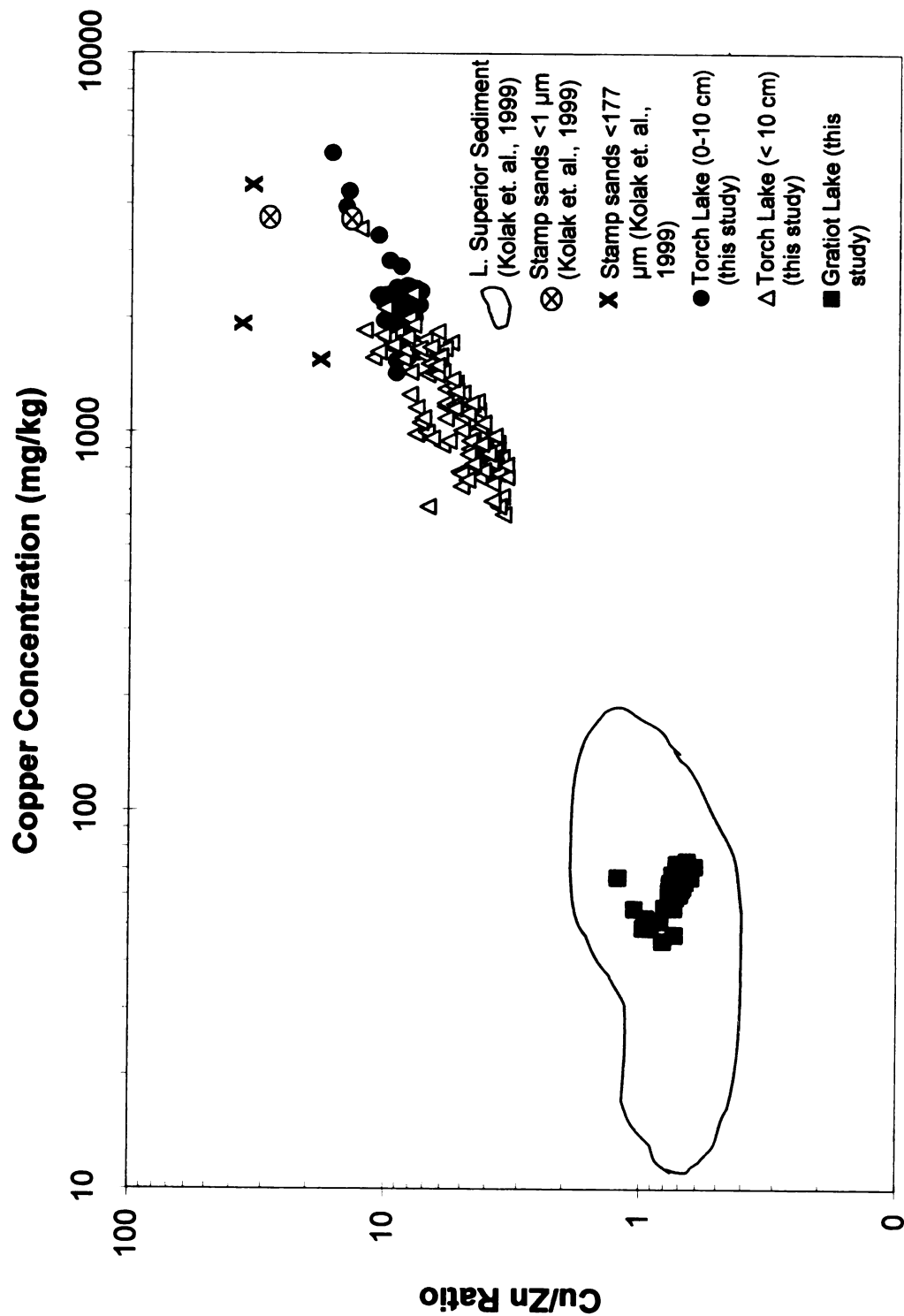


Figure 20. Cu/Zn vs. copper concentration profiles for selected sediments in and around the Keweenaw Peninsula of Michigan, including Torch Lake.

Table 4. Average ratios for Cu/Zn in the cap sediments and mining related sediments of Torch Lake and several other sediments from within and around the Keweenaw Peninsula, Michigan.

Cu/Zn Ratio		
Location (study)	Average	Std. Dev.
Stamp Sands (Kerfoot and Nriagu, 1999)	23.4	15.83
Torch Lake (Kerfoot and Nriagu, 1999)	9.97	2.53
Torch Lake (Cap Sediments) (This Study)	9.4	1.2
Portage Lake (Kerfoot and Nriagu, 1999)	9.00	5.33
Torch Lake (Bottom Sediments) (This Study)	5.8	1.4
Keweenaw Waterway (Kerfoot and Nriagu, 1999)	5.49	4.06
S. Lake Superior (Kerfoot and Nriagu, 1999)	1.95	1.66
S. Lake Superior (Kerfoot and Nriagu, 1999)	1.64	1.45
N. Lake Superior (Kerfoot and Nriagu, 1999)	1.06	0.76
N. Lake Superior (Kerfoot and Nriagu, 1999)	0.92	0.58
Inland Lakes (Kerfoot and Nriagu, 1999)	0.79	0.71
Gratiot Lake – Average (This Study)	0.76	0.12
South Portage Lake (Kerfoot and Nriagu, 1999)	0.37	0.07

Multi-elemental Results

Results from the Cu analysis and Cu/Zn ratios suggest that even though direct anthropogenic sediment inputs have ceased, Cu concentrations still remain high throughout the core, perhaps due to the continual input of stamp sands eroding from shoreline deposits (Kerfoot and Lauster, 1994). However, there is a visible shift in color of the sediments when mining activities ceased. To further examine the nature of these observations, the trends of 20 other elements were examined as part of the multi-elemental approach. For several elements (e.g., Ba, Ca, Co, K, Mg, Ti, U) there is a shift in concentration at the same depth as the change in color of sediment. These elements have concentration trends that both increase (e.g., U and K), and decrease (e.g., Ti, Co and Ca) in the cap sediments towards the sediment/water interface. To better visualize the trend in concentration shifts for Ba, Ca, Co, K, Mg, Ti and U,

the concentrations determined at each increment were normalized to the highest concentration in a particular core. These results are plotted in Figure 21 and 22. Since elemental concentrations both decrease and increase in the cap sediments, dilution of materials via intra-lake production of organic matter (that is visible in the cap sediments) cannot account for the differences in elemental concentrations from mining related sediments to cap sediments.

Average mining related and cap sediment concentrations of U, K, Ti, Co and Ca and their trends from mining related sediments to cap sediments are summarized in Table 5. The overall trends of U, K, Ti, Co and Ca concentrations versus depth are consistent with an overall shift from basaltic rocks (e.g., Portage lake Volcanics) to sandstones (e.g., the Jacobsville Sandstone) based on world averages from Reimann and Caritat (1998) (Table 6). These trends are also consistent with a change in dominant sediment input from mine tailings to more natural, watershed inputs dominated by the local bedrock geology of Torch Lake.

Table 5. Concentrations (mg/kg) and trend shifts of U, Ti, K, Co, and Ca from the cap sediments to the mining related sediments in Torch Lake, MI.

Element (mg/kg)	Mining Related Sediments	Cap Sediments	Trend from Mining Related sediments to Cap Sediments
U	0.65	2.14	Increase
Ti	6,425	3,259	Decrease
K	289	1,019	Increase
Co	60.41	34.81	Decrease
Ca	40,085	22,639	Decrease

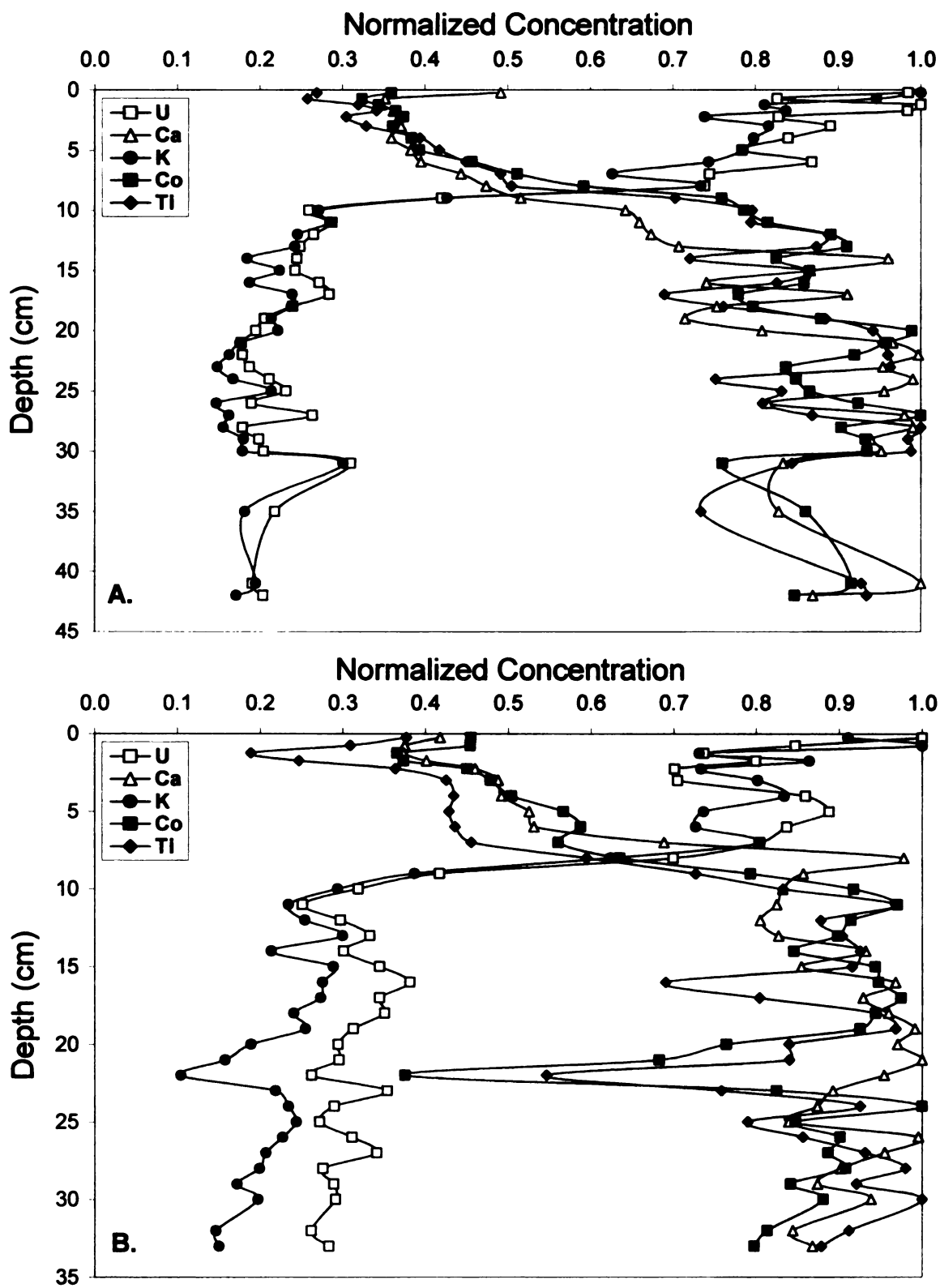


Figure 21. Normalized concentrations of uranium, calcium, potassium, cobalt and titanium in Torch Lake sediments. A) Site T1 and B) Site T2.

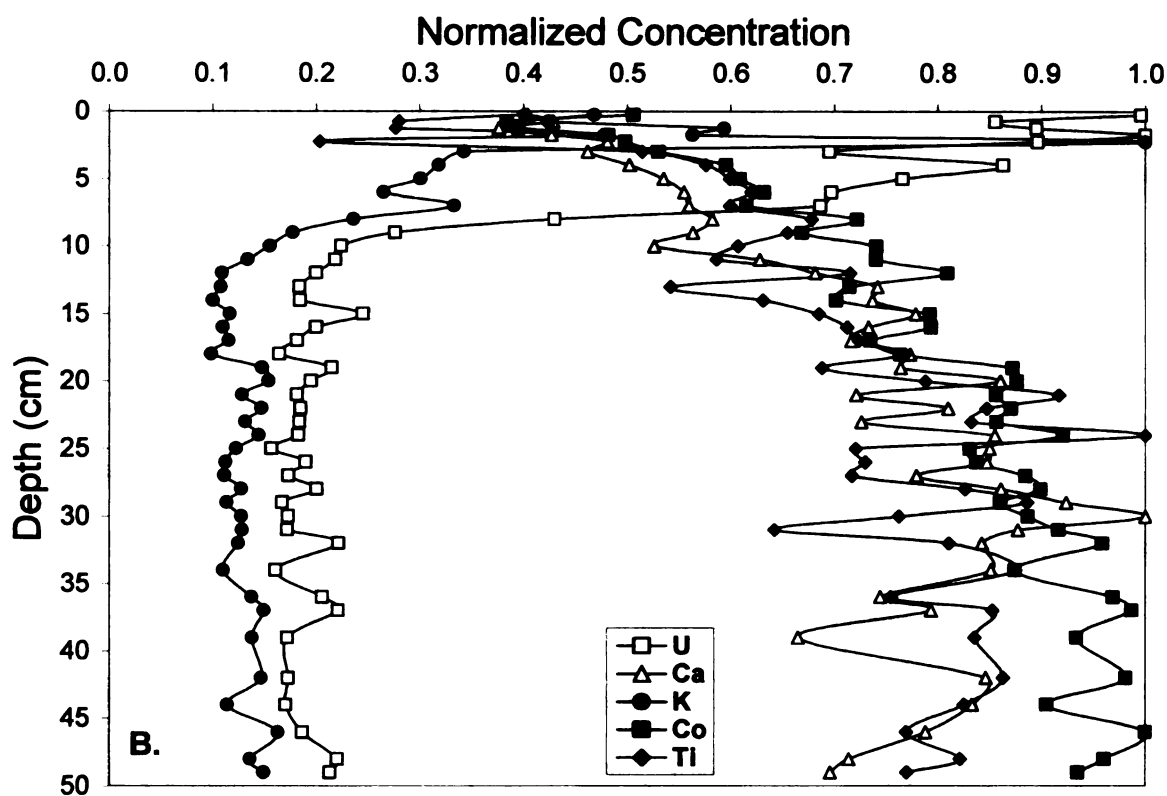
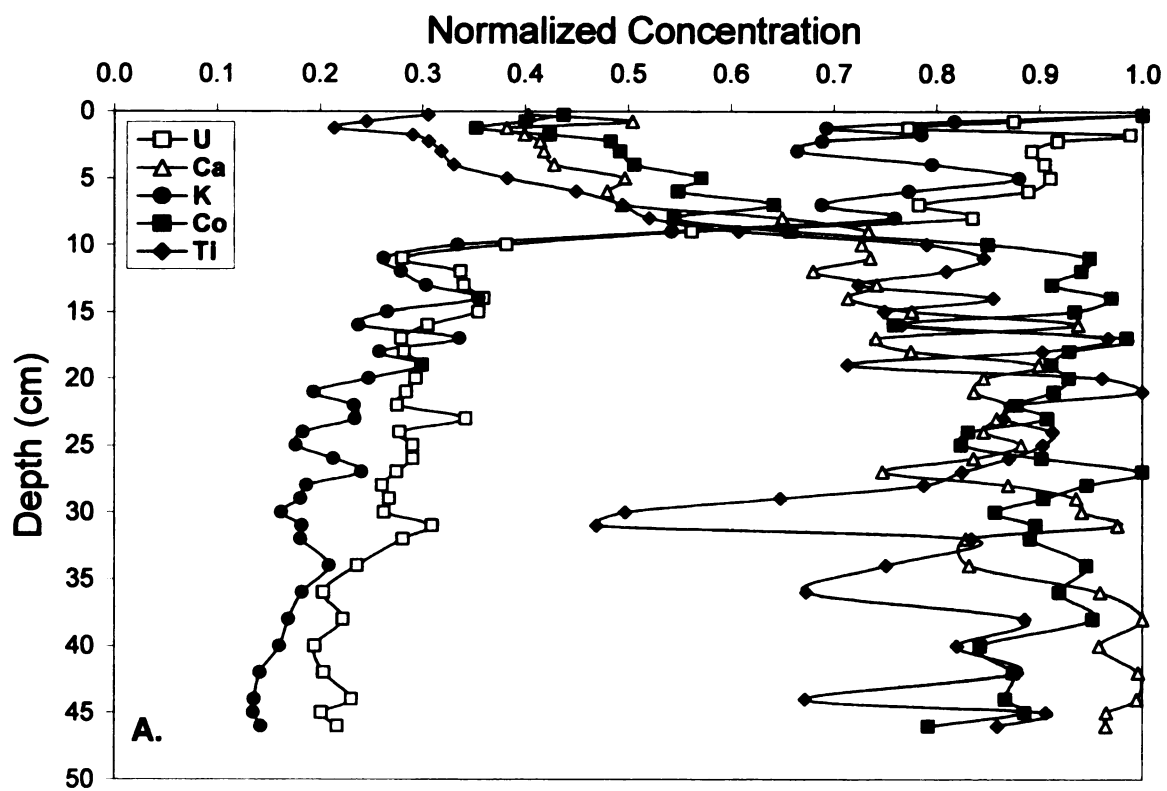


Figure 22. Normalized concentrations of uranium, calcium, potassium, cobalt and titanium in Torch Lake sediments. A) Site T3 and B) Site T5.

Table 6. Average concentrations (mg/kg) and trend shifts of U, Ti, K, Co, and Ca from basalts to sandstones. Averages based on data from Reimann and Caritat, (1998).

Element (mg/kg)	Basalt	Sandstone	Trend from Basalt to Sandstone
U	0.5	1.3	Increase
Ti	10,000	1,500	Decrease
K	8,000	11,000	Increase
Co	45	0.3	Decrease
Ca	74,000	13,000	Decrease

Even with the overall change in dominant sediment input, there are still local heavy metal inputs. Lead concentrations in the sediments near MSU sites T2 and T3 were reported as high as 18,400 mg/kg and As concentrations were as high as 494 mg/kg (Charters and Derveer, 1991). Slag piles on the grounds of the Peninsula Cu Industry (PCI), the former Calumet and Hecla Smelter facility have been identified by the U.S. EPA as the potential source for heavy metal contamination (EPA, 1992). The PCI building is located on-shore of sites T2 and T3. Arsenic and Pb concentrations in the cap sediments from the northern basin were elevated with respect to the southern basin (Figure 23). Arsenic also has two distinct peaks, one at 7 cm for sites T1, T2 and T3 and 5 cm at site T5 and another at the surface (Figure 23). The surface peak is related to early diagenesis (i.e., redox) processes, but the lower peak represents an anthropogenic input of arsenic. This conclusion is further supported by the fact that both As and Pb peak at the 7 cm depth, because Pb is not influenced by redox processes. At site T5 (south basin), the As and Pb concentrations versus depth profiles are similar to those from sites T1, T2 and T3 (north basin),

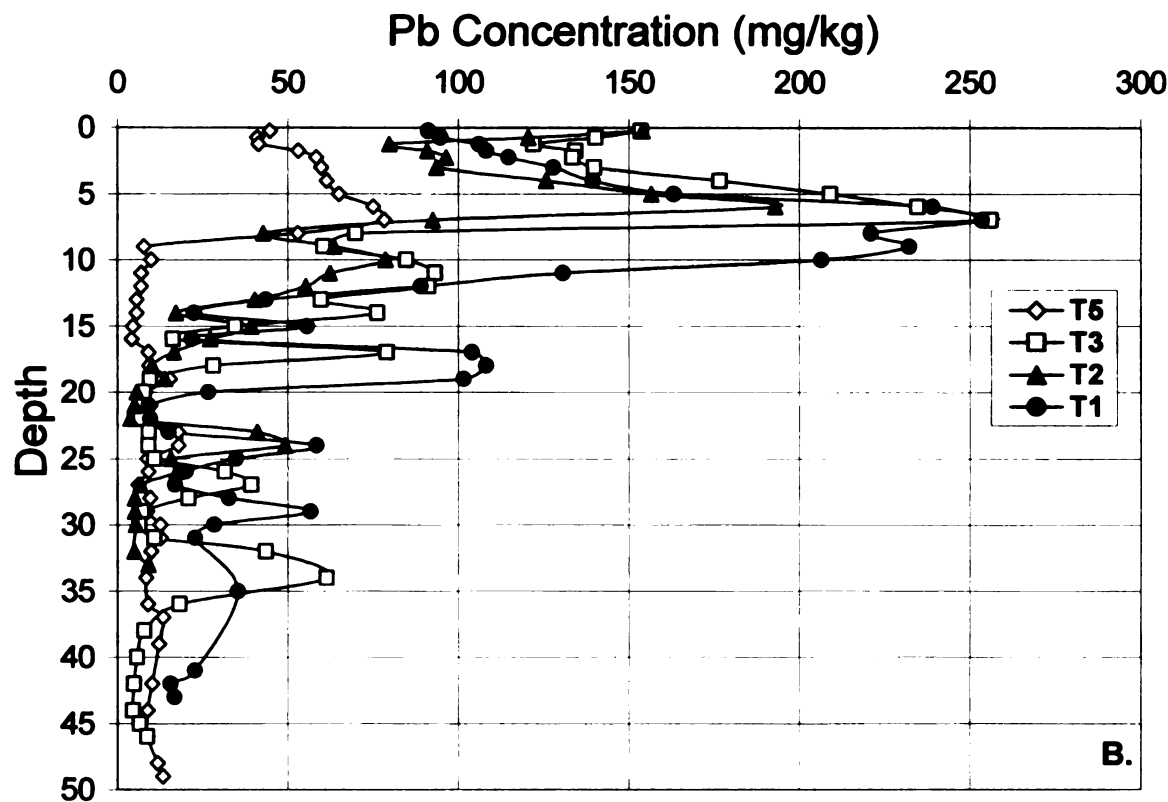
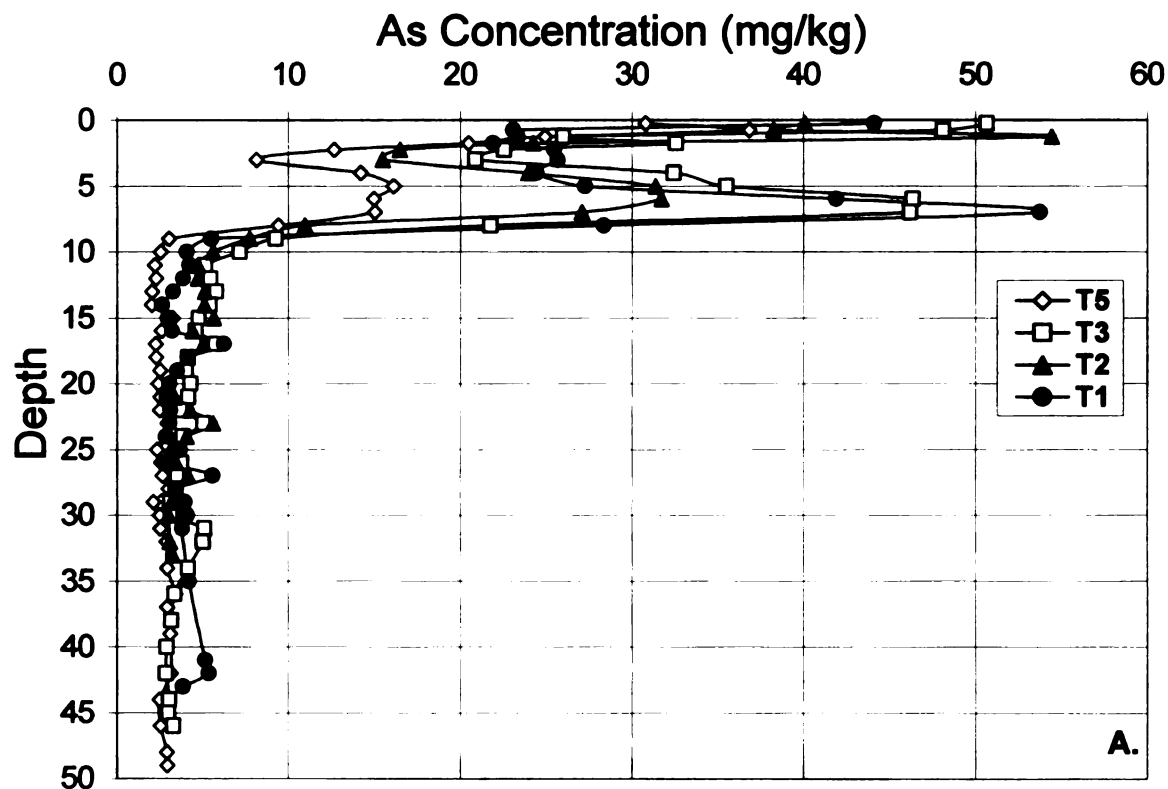


Figure 23. Concentration vs. depth profiles in Torch Lake sediments. A) arsenic and B) lead.

but the absolute concentrations for these elements in the south basin are lower by 2.8 and 3.0 times for As and Pb, respectively. Site T5 may not have been as anthropogenically influenced by inputs from the PCI. From these data, it is clear that the two basins of Torch Lake have been affected differently by past, local anthropogenic inputs.

Elemental ratios

To better determine the source for the cap sediments, elemental ratios were examined and compared to Gratiot Lake. Ratios are used and not absolute concentrations, because there are two main sources of sediment input into a lake: watershed (terrestrial) inputs and intra-lake production (i.e., organic matter or carbonate production), and these factors can vary greatly from lake to lake (Yohn et al., 2002). This makes absolute concentrations vary from lake to lake, and direct comparisons of two different lake systems is not often possible. However, by using ratios of one element to another or to organic matter, and not absolute values, comparisons between lakes can be made. For example, it is believed that geochemically similar terrestrial inputs are entering both Gratiot and Torch Lakes, but organic material produced in the eutrophic Gratiot Lake has “diluted” the elemental signatures within the sediments. Ratios to organic matter in the samples could correct for this anomaly, however sediment samples were not analyzed for organic content. So, elemental ratios (e.g., Cu/Zn, Ti/Zn, Co/Zn) in the sediments of Torch Lake were compared to ratios in sediments from Gratiot Lake. Assuming that pre-mining related sediments in Torch Lake

are geochemically similar to Gratiot Lake (based on their geologies), and the current sediments entering Torch Lake have similar ratios as Gratiot Lake, it will be assumed that the sediments currently entering Torch Lake are reflective of watershed-dominated inputs.

Co/Zn, Ti/Zn, K/V, Co/V, U/Zn and Ti/Ba

Changes in the Cu/Zn ratios with depth do not indicate a change from stamp sand dominated inputs to natural inputs, but the physical nature (e.g., color, texture) of the cap sediments compared to the bottom sediments, as well as the total elemental concentrations, indicate that a change in dominant sediment input to Torch Lake has occurred. To determine if this is any indication that the Torch Lake system is beginning to again come into equilibrium with its watershed, several other elemental ratios of Torch Lake sediments were compared to Gratiot Lake sediments. When the Co/Zn, Ti/Zn, K/V, Co/V, U/Zn and Ti/Ba ratios are plotted, there is a trend from mining related sediments to cap sediments that are more reflective of Gratiot Lake. Sediments from the cap layer of Torch Lake plot between the lower sediments of Torch Lake and sediments of Gratiot Lake, which implies that the cap sediments of Torch lake are being influence by a different sediment input than the mining related sediments (Figures 24, 25 and 26). These data may suggest that sediments currently entering Torch Lake are more representative of a terrestrial, watershed dominated input as opposed to an input dominated by erosion of stamp sands surrounding the lake, which is consistent with visual interpretations

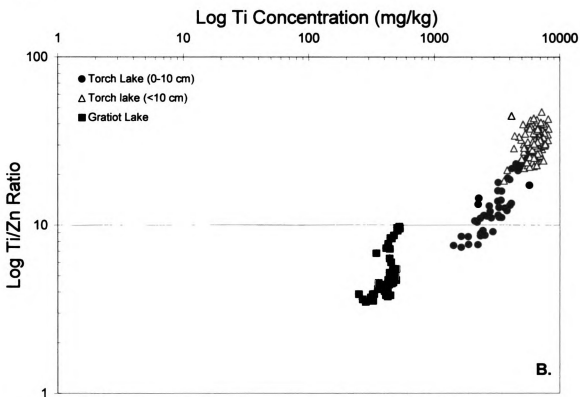
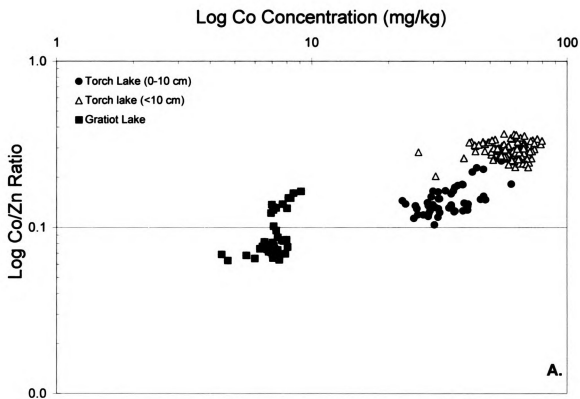


Figure 24. A) Log Co/Zn vs. log cobalt concentration and B) Log Ti/Zn vs. log titanium concentration for the cap sediments and mining related sediments of Torch Lake and Gratiot Lake.

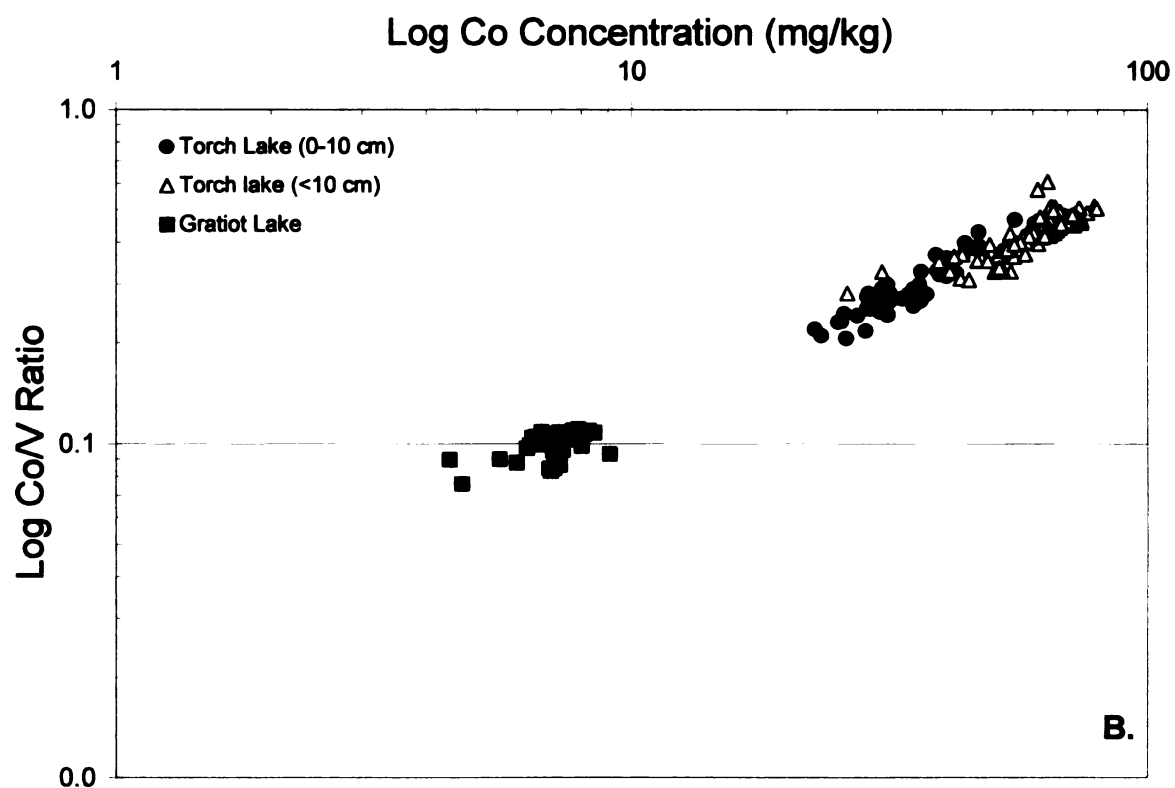
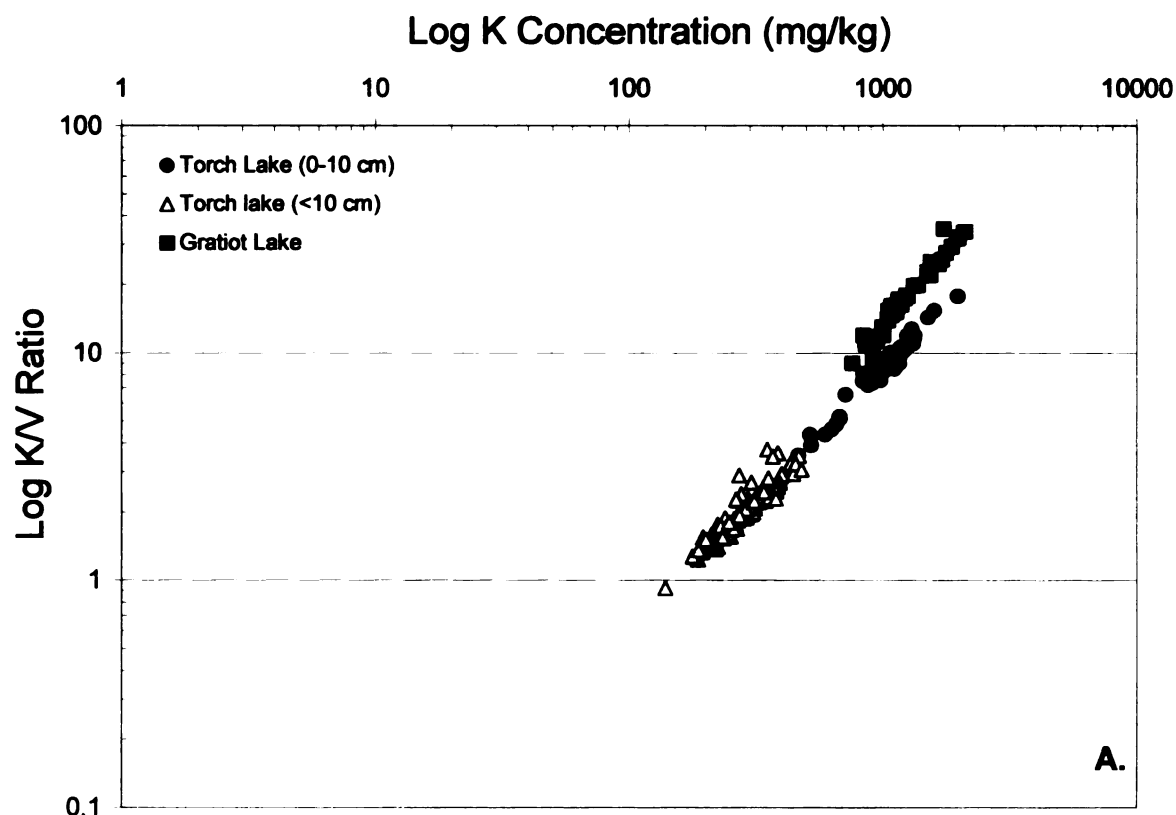


Figure 25. A) Log K/V vs. log potassium concentration and B) Log Co/V vs. log cobalt concentration for the cap sediments and mining related sediments of Torch Lake and Gratiot Lake.

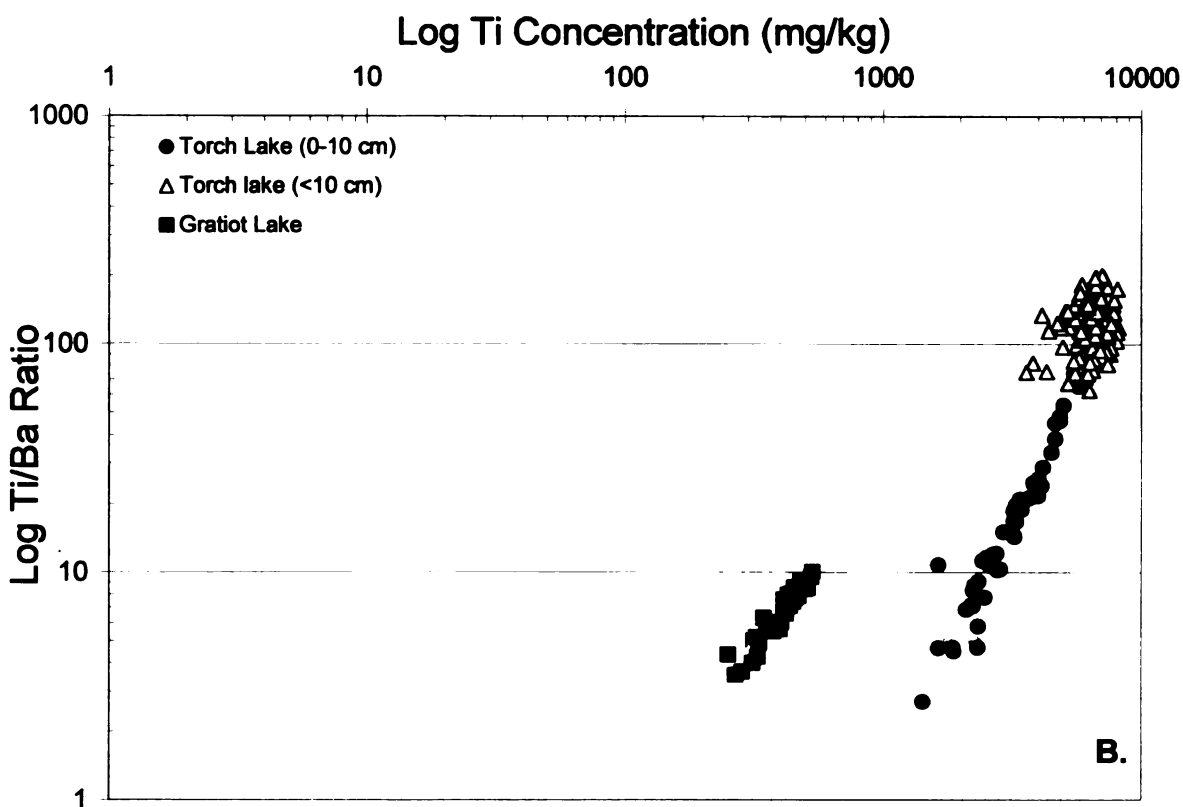
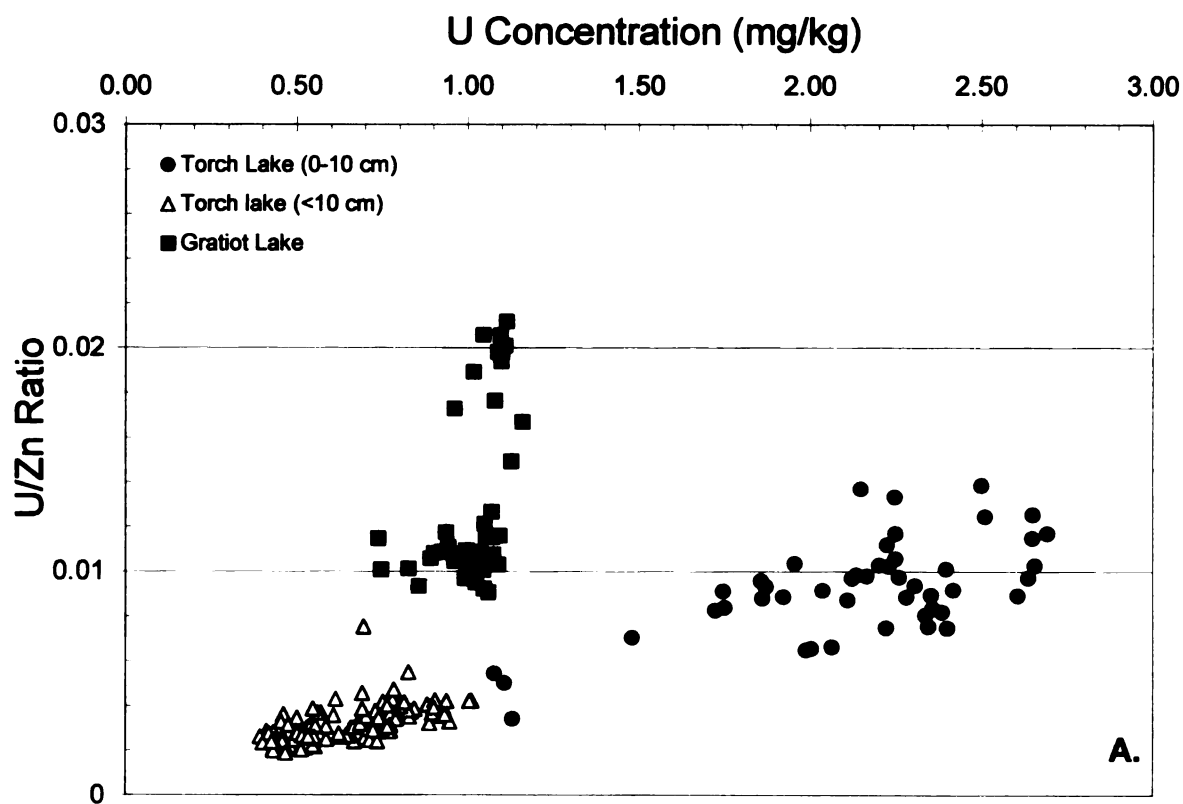


Figure 26. A) Log U/Zn vs. uranium concentration and B) Log Ti/Ba vs. log titanium concentration for the cap sediments and mining related sediments of Torch Lake and Gratiot Lake.

of changes in dominant sediment input (Figure 13). These data are summarized in Table 7.

Table 7. Selected elemental ratios in the sediments of Torch and Gratiot Lakes.

Ratio	Torch Lake (<10 cm)	Torch Lake (0-10 cm)	Gratiot Lake
Co/Zn	0.29	0.15	0.091
Ti/Zn	31.6	14.1	5.40
K/V	2.1	9.8	18.2
Co/V	0.42	0.29	0.09
U/Zn	0.0032	0.0093	0.0131
Ti/Ba	122.7	21.1	7.1

Based on elemental ratios, there seems to be a shift in sediment input since the cessation of mining activities around Torch Lake. At depth, <10 cm, the dominant control on sediment chemistry was the direct inputs of stamp sands and slime clays, based on historical records and distinct elemental ratios. In the cap sediments, there seems to be a switch in the dominant sediment input from stamp sands to inputs that are reflective of a watershed signature (i.e., sediments more geochemically similar to those from Gratiot Lake). These conclusions would not have been made if only Cu concentrations were studied (i.e., the target specific approach), demonstrating the need for multi-elemental data when assessing recovery of anthropogenically disturbed systems.

Controls on Copper in the Cap Sediments

Results from the copper and Cu/Zn data from Torch Lake suggest continual inputs of stamp sands dominating the recent sediment geochemistry. However, multi-elemental data suggests that recent sediments entering Torch Lake are beginning to reflect watershed dominated sediments (e.g., Gratiot Lake). With several elements and elemental ratios showing a new, dominant watershed source for recent Torch Lake sediments, several possibilities are explored to explain the anomalous copper and Cu/Zn trends in the cap sediments.

Grain Size

Kerfoot and Robbins (1994) found that Cu concentrations in stamp sands increase with decreasing grain size. For example, the authors found that tailings from the Point Mills stamp mill (located on Portage Lake) had more Cu associated with the clay fraction than the sand or silt sized fraction. Particles <53 μm contained 0.46% (4,600 mg/kg) Cu and particles >53 μm contained 0.32% (3,200 mg/kg) Cu (Kerfoot and lauster, 1994). Prior to the cessation of direct anthropogenic inputs, the bottom sediments of Torch Lake primarily consisted of tailings (Lopez and Lee, 1977). If the finer, more Cu enriched particles are now accumulating in the deep depositional basins of Torch Lake, the increase in copper may be a shift of grain sizes from larger, stamp sands and silts to smaller, wave-eroded clays size materials.

Pore-water Diffusion

Enrichments of trace metals such as Cu have been attributed to near-surface oxic precipitation of Fe and Mn metals that are mobilized under reducing conditions (Kerfoot et al., 1999a). Below the redox horizon in lake sediments, iron and manganese oxides dissolve and release Fe and Mn into the pore-waters, which then can diffuse upward towards oxic waters (Berner, 1980). In Torch Lake there is a sharp redox horizon in the top 2 cm, and this process is capable of concentrating trace elements (e.g., AS, Cu, Ba) at the redox boundary (Belzile and Tessier, 1990). Iron and Mn appear to be significantly affected by redox, but Cu did not appear to be significantly affected by the redox characteristics of Torch Lake (Figures 27 and 28). The profiles of Fe and Mn are much sharper than the Cu profile that is gradually increasing from the 10 cm depth towards the surface. These results are consistent with other studies that have shown that Cu is relatively unaffected by changes in redox conditions (Kolak et al., 1998 and Shaw et al., 1990).

However, Cu in the sediments of Torch Lake may be migrating up the core via sediment pore-water and being sequestered in the organic rich cap sediments. In a study by Cusack (1995), pore-water samples were retrieved from Portage Lake that contained both an organic rich top layer (>10% organic matter) and mining related sediments. Pore-water Cu concentrations in the organic rich top sediments were reported at 0.077 mg/L and when the organic matter decreased in the mining related sediments, the pore-water Cu concentrations increased to 0.20 mg/L (Cusack, 1995). These results suggest

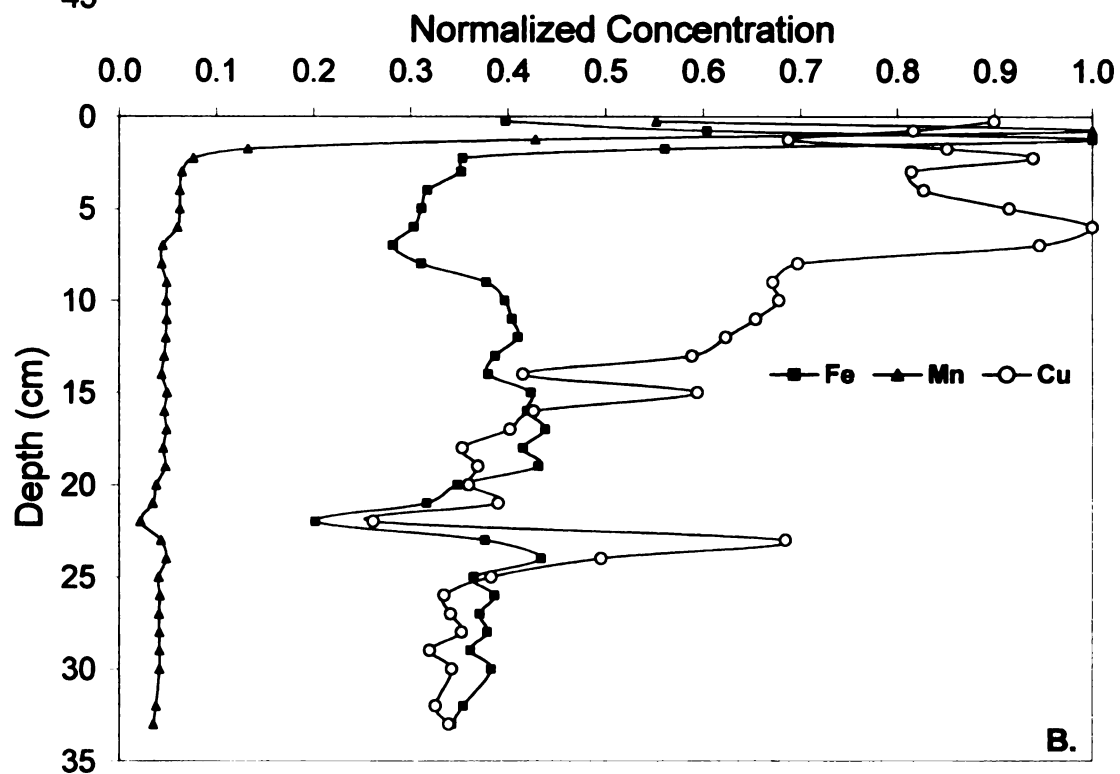
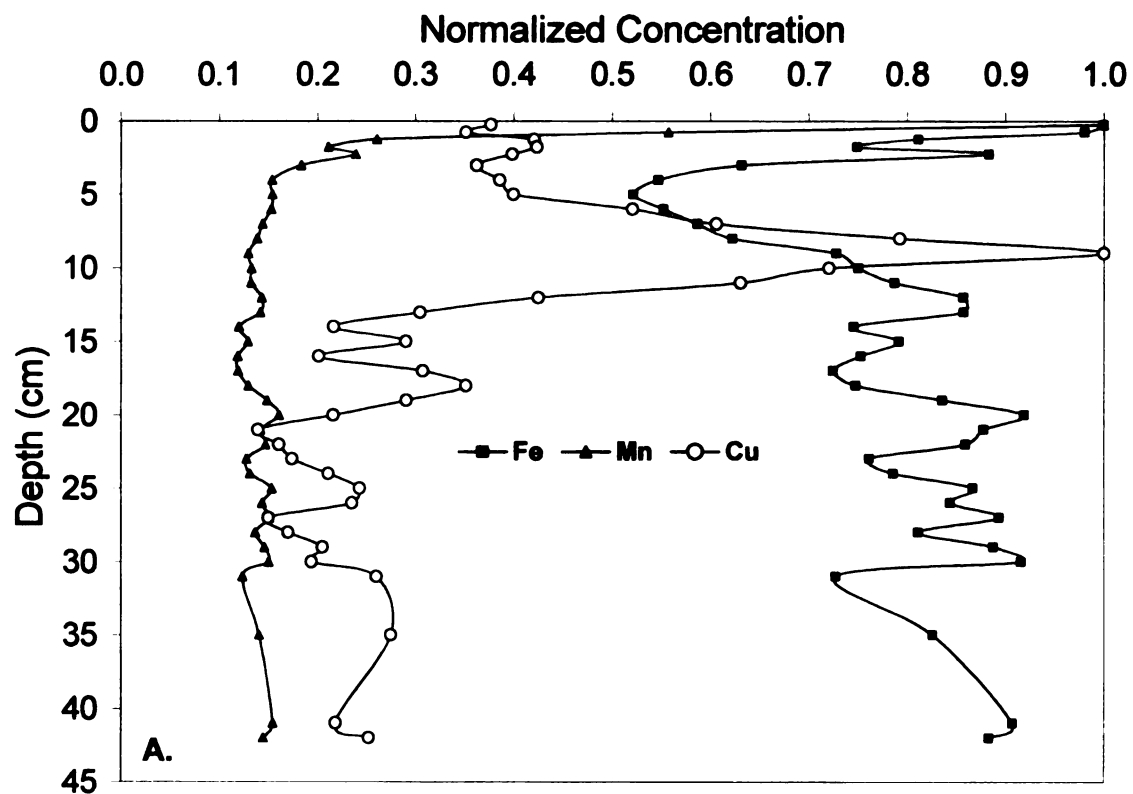


Figure 27. Normalized iron, manganese and copper concentrations vs. depth. A) Site T1 and B) Site T2.

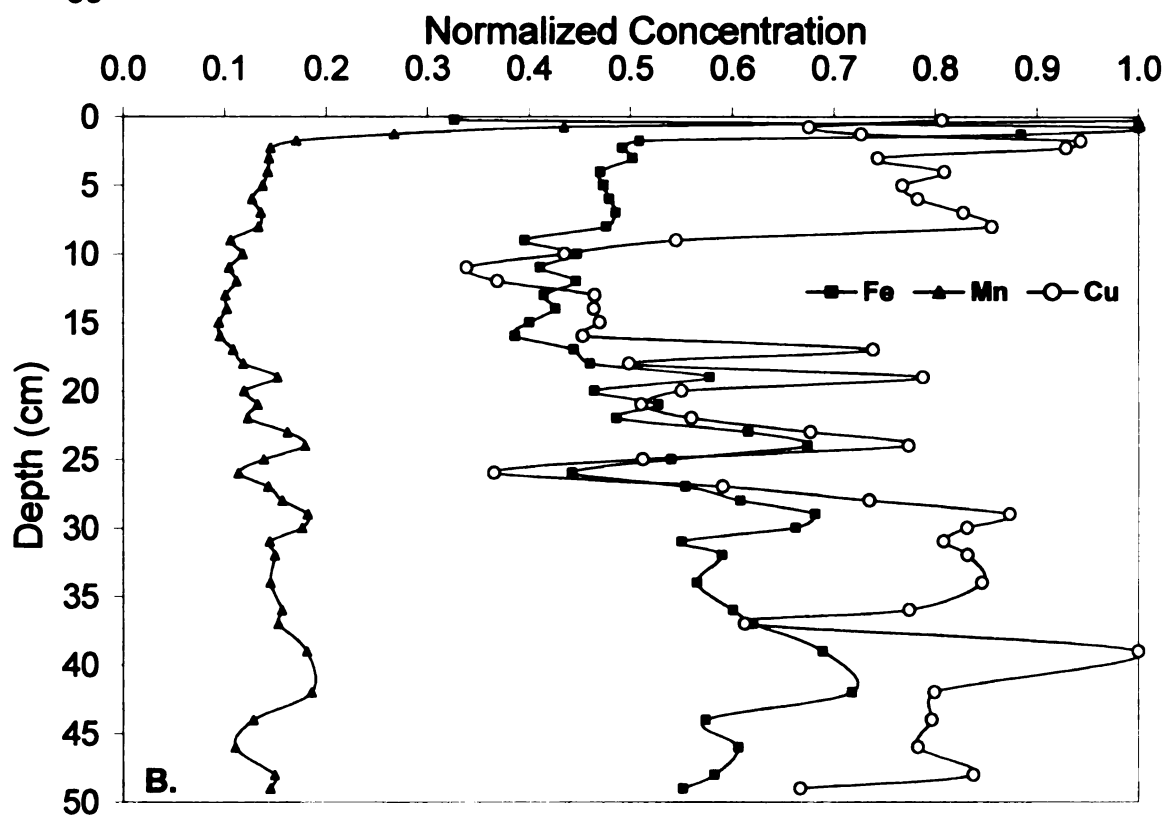
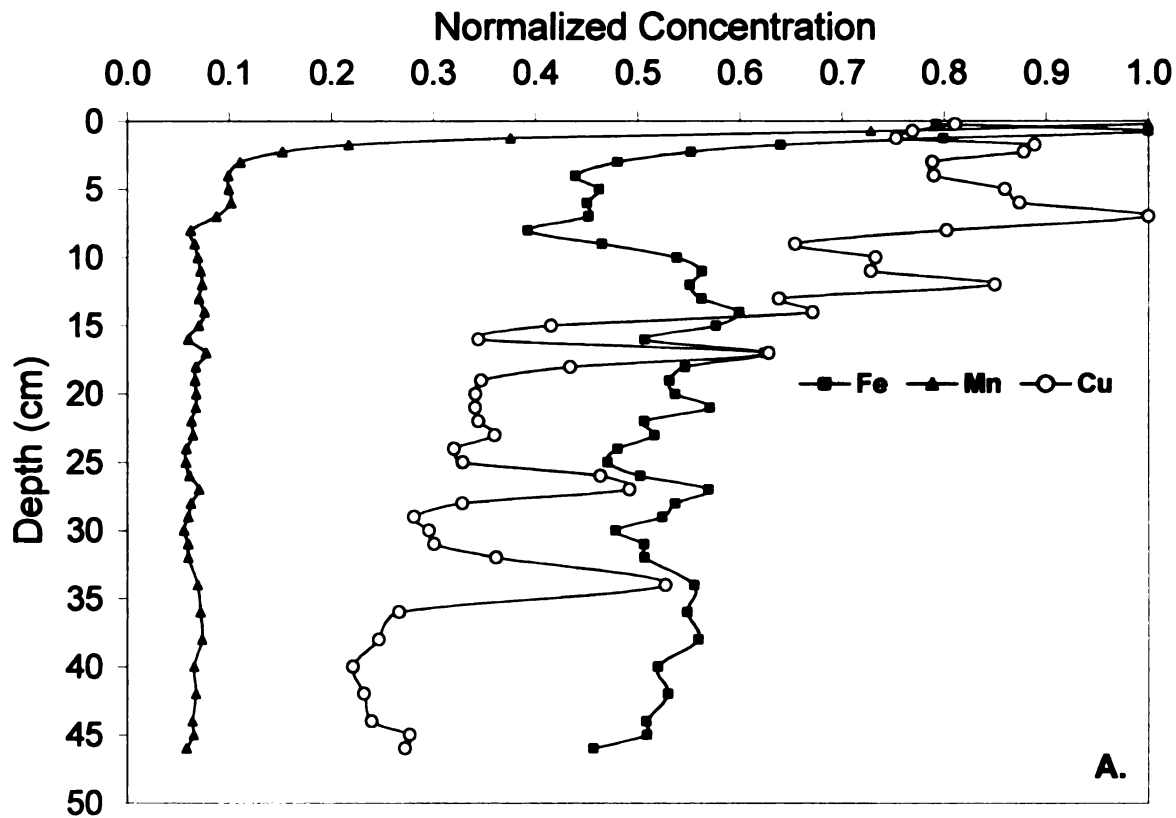


Figure 28. Normalized iron, manganese and copper concentrations with depth. A) Site T3 and B) Site T5.

that Cu is being scavenged out of the pore-water by complexing with the solid organic matter. Similar results were also documented in Torch Lake by Cusack and Mihelcic (1999). Samples from Torch Lake with higher organic matter had lower aqueous Cu concentrations (Cusack and Mihelcic, 1999). In the Keweenaw Waterway, at least 50% of the dissolved Cu is bound to the organic fraction (Kerfoot et. al., 1999c). If Cu were available in the pore-waters in high enough concentrations, then complexes formed by the interactions with organic matter might account for the observed copper enrichment in the cap sediments of Torch Lake.

Microbial Processes

Konstantinidis et. al. (2003), examined the microbial resistance to Cu and other heavy metals (Ni, Zn and Cd) in the sediments of Torch Lake. In particular, two isolates harvested from sediments of sites T1 and T2, *Ralslonia* and *Arthrobacter* were resistant to elevated levels of Cu, at least to 200 mg/L CuSO₄. Scanning electron microscopy showed changes in the outer envelope of cells when they were grown in the presence of Cu (Konstantinidis et al., 2003). The microbe *Ralslonia* was resistant up to 1,200 mg/L CuSO₄ and produced green colonies when grown in the presence of CuSO₄. A green “coating” on the microbe *Ralslonia* suggests that Cu sequestration is a mechanism of resistance (Konstantinidis et al., 2003). Sequestering of CuSO₄ from the pore-water in Torch Lake may also be a mechanism of Cu enrichment in the cap sediments.

Event Dating

Since the ^{210}Pb and ^{137}Cs data from Torch Lake are unreliable due to past disturbances, a different approach was taken to date the sediment cores. This approach, called “event dating” is based on historical and geochemical data from Torch Lake. There is a well documented history of mining activity around the lake, and having a good history of anthropogenic activities for disturbed lakes can be used to deduce a history when their radionuclide records are questioned (Kerfoot and Lauster, 1994). In an attempt to event date the sediments, the transition of pink, mining related inputs to brown, watershed inputs (a depth of ~10 cm) was set to be 1968, the year of the cessation of mining inputs. This shift also corresponded to shifts in elemental concentrations of Ba, Ca, Co, K, Mg, Ti and in particular U.

To calculate an age, a sedimentation rate has to be established at each sample location. By assuming that the sedimentation rate since the cessation of mining activities has been constant, sedimentation rates were calculated based on the total accumulated dry mass (g/cm^2) and number of years of accumulation (31 years, 1968-1999). The method for calculating the sedimentation rate was:

$$W = \sum A_{(m)} / n$$

Where:

W = sedimentation rate ($\text{gm}/\text{cm}^2/\text{yr}$)

$A_{(m)}$ = accumulated dry mass at depth z (g/cm^2)

n = number of years from depth z to the sediment/water interface (31 yrs)

The method for age calculation was based on the previously calculated sedimentation rate and was as follows:

$$X = Y_{(s)} - C_{(y)} - y/2$$

Where:

X= date of sectioned slice

Y(s)= year sample was taken (1999)

C(y)= cumulative years to depth z (acc. dry mass to z / sedimentation rate)

y/2= years per section / 2

Results of event dating are summarized in Tables 8a, 8b and 8c.

Table 8a. Data from the event dating method of age calculation for site T1.

Acc. Dry Mass (g/cm²)	Depth (cm)	Years/Slice	Cumulative years	Years/2	Date
0.0911	.25	0.8736	0.874	0.437	1999
0.0632	.75	0.6057	1.479	0.303	1998
0.0564	1.25	0.5406	2.020	0.270	1997
0.0663	1.75	0.6355	2.655	0.318	1997
0.0804	2.25	0.7710	3.426	0.385	1996
0.1985	3	1.9037	5.330	0.952	1995
0.2061	4	1.9769	7.307	0.988	1993
0.2179	5	2.0893	9.396	1.045	1991
0.2292	6	2.1977	11.594	1.099	1989
0.1762	7	1.6896	13.284	0.845	1987
0.5334	8	5.1151	18.399	2.558	1983
0.6921	9	6.6368	25.035	3.318	1977
0.6220	10	5.9644	31.000	2.982	1971

Sedimentation Rate = 0.1043 g/cm²/yr

Table 8b. Data from the event dating method of age calculation for site T2.

Acc. Dry Mass (g/cm²)	Depth (cm)	Years/Slice	Cumulative years	Years/2	Date
0.0336	.25	0.2873	0.287	0.144	1999
0.0354	.75	0.3028	0.590	0.151	1999
0.0356	1.25	0.3040	0.894	0.152	1998
0.0487	1.75	0.4162	1.310	0.208	1998
0.0490	2.25	0.4186	1.729	0.209	1997
0.1539	3	1.3161	3.045	0.658	1997
0.1727	4	1.4765	4.521	0.738	1995
0.2039	5	1.7431	6.264	0.872	1994
0.1910	6	1.6333	7.898	0.817	1992
0.2173	7	1.8577	9.755	0.929	1990
0.8272	8	7.0730	16.828	3.537	1986
0.8171	9	6.9860	23.814	3.493	1979
0.8404	10	7.1857	31.000	3.593	1972

Sedimentation Rate = 0.1170 g/cm²/yr

Table 8c. Data from the event dating method of age calculation for site T5.

Acc. Dry Mass (g/cm²)	Depth (cm)	Years/Slice	Cumulative years	Years/2	Date
0.0420	.25	0.4760	0.476	0.238	1999
0.0732	.75	0.3534	0.829	0.177	1998
0.1282	1.25	0.6236	1.453	0.312	1998
0.1848	1.75	0.6412	2.094	0.321	1997
0.2620	2.25	0.8746	2.969	0.437	1996
0.3469	3	0.9626	3.931	0.481	1996
0.4530	4	1.2024	5.134	0.601	1994
0.5564	5	1.1721	6.306	0.586	1993
0.6778	6	1.3751	7.681	0.688	1992
0.9369	7	2.9373	10.618	1.469	1990
1.3962	8	5.2047	15.823	2.602	1986
2.1200	9	8.2038	24.027	4.102	1979
2.7352	10	6.9726	31.000	3.486	1971

Sedimentation Rate = .0882 g/cm²/yr

Using the dates calculated via event dating, the spike in the Cu concentration at site T1 corresponded to an age date of 1971-1977. A spill of cupric ammonium carbonate occurred in Torch Lake during the span of 1971-1972, and a date of 1977 calculated by event dating techniques is much more accurate, based on historical data, than the date calculated via ^{210}Pb , which was 1926 (Figure 29). There is a gap in time of six years from the known data to the calculated date of the spill because of the 1 cm sampling interval. The results from the two dating techniques, ^{210}Pb and event dating are summarized in Table 9.

Table 9. Comparison of dates using the ^{210}Pb event dating methods from site T1.

Depth (cm)	^{210}Pb Dates	Event Dating
.25	1999	1999
.75	1996	1998
1.25	1994	1997
1.75	1992	1997
2.25	1990	1996
3	1985	1995
4	1979	1993
5	1972	1991
*6	1964	1989
7	1958	1987
8	1946	1983
9	1926	1977
10	1905	1971

*peak in ^{137}Cs .

Lead-210 and ^{137}Cs analyses are proven methods to date lakes that have not been disturbed (Kemp et al., 1978; Kada and Heit, 1992; Robbins and Edgington, 1975; Golden et al., 1993 and Yohn et al., 2002), however in systems such as Torch Lake with a disturbed history, the data must be carefully

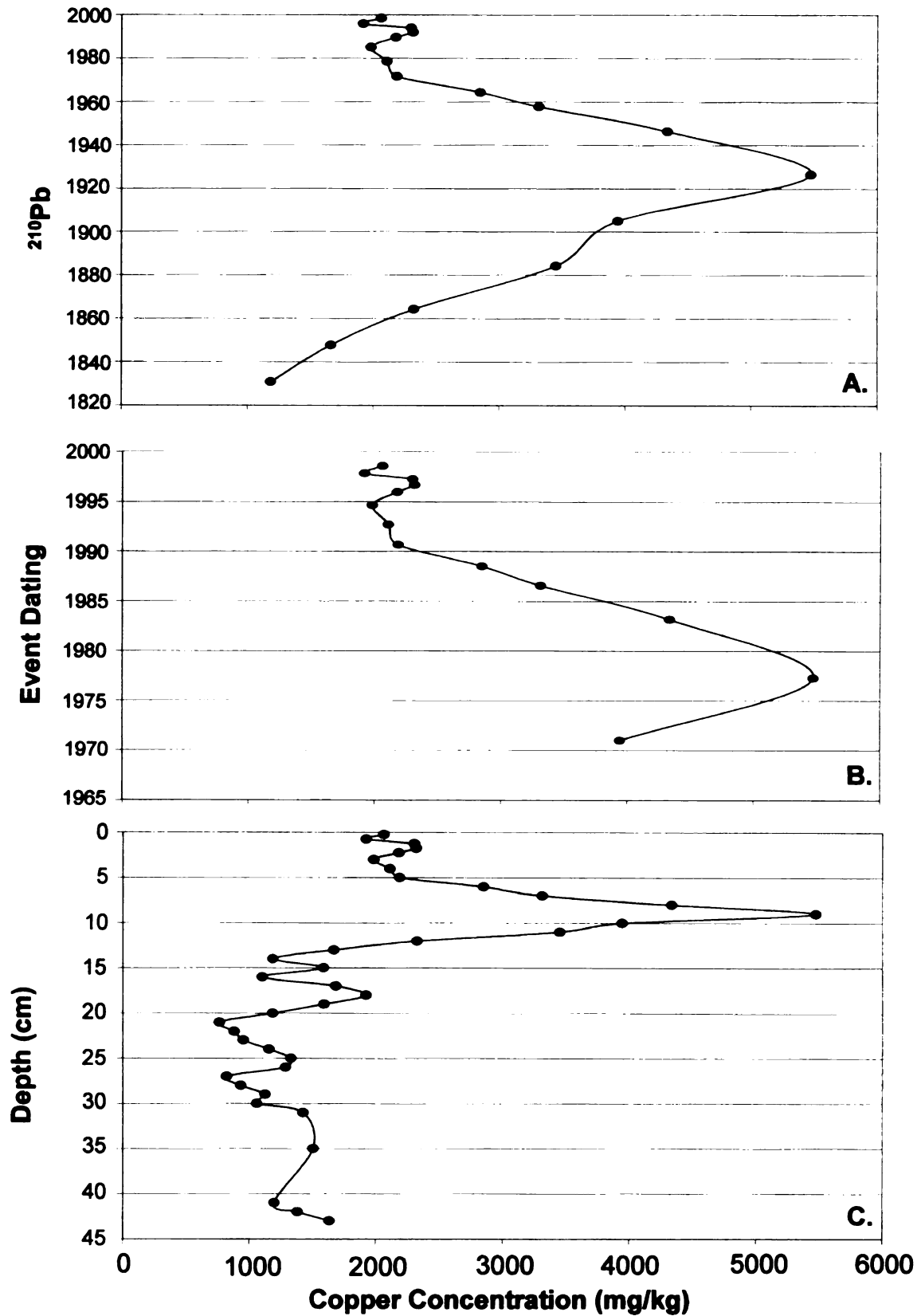


Figure 29. Copper concentrations in Torch Lake sediments from site T1, as a function of: A) the ^{210}Pb dating method, B) the event dating method and C) depth.

examined to assess the accuracy of the data. Age dating of sediment cores based on historical in geochemical records has proven to be useful in anthropogenically disturbed systems.

Estimating Recovery Rates

In order to manage a changing system such as Torch Lake, it is necessary to calculate its rate of change. Using the age dates calculated by event dating, it might be possible to predict recovery rates for the sediments of Torch Lake. Recovery will be defined as changing element ratios in the sediments of Torch Lake to ratios reflective of Gratiot Lake. A recovery rate per year was calculated as follows:

$$\text{Recovery rate} = A_{(z)} - A_{(S)} / n$$

Where:

$A_{(z)}$ = element ratio at depth z

$A_{(S)}$ = ratio at sediment/water interface

n = number of years from depth z to the sediment/water interface

From that data, an estimate of recovery in years was calculated. The equation for calculating recovery is as follows:

$$\text{Recovery in Years} = (G - TS) / Rr$$

Where:

G = Gratiot Lake average

TS = elemental ratio for the top sample of cap sediments in Torch Lake

RR = recovery rate / yr

Results from the recovery analysis are summarized in Table 10.

Although recovery time varies depending on the elements chosen, sediments of the north basin show very similar average estimates of recovery, ~10-12 years. In the south basin, site T5 is slightly longer than the others at ~23 years. This is possibly due to the slower sedimentation rate in the south basin.

Table 10. Number of years to reach ratios reflective of average Gratiot Lake ratios for Co/Zn, Ti/Zn, K/V, Co/V, U/Zn and Ti/Ba at each sampling site.

Ratio	T1	T2	T3	T5
Co/Zn	13	5	5	21
Ti/Zn	10	9	5	12
K/V	6	27	22	51
Co/V	31	23	23	51
U/Zn	2	8	9	0
Ti/Ba	0	1	0	2
Average time to Gratiot Lake ratios	10.3	12.1	10.6	22.8

The recent temporal trends indicate some decline in recent Cu loadings Cu concentrations, but the trends are quite noisy. There is enough data however to estimate the possible rates of decline of Cu loadings to compare to the other geochemical indicators of recovery (Table 10). Therefore, estimated time to recovery was also calculated using absolute Cu concentrations (Table 11). Recovery rates were calculated based on a segment of decreasing trends in the cap sediments. The decreasing trend was determined from these intervals: Site T1, sample 2 to 8; site T2, sample 2 to 9; site T3, sample 2 to 9 and site T5, sample 2 to 11 (Figures 17 and 18). The target Cu concentrations representing recovery was estimated to be 61 mg/kg of Gratiot Lake which is

similar to average Great Lakes sediments (Kolak et al., 1999). Even though there is possibly significant error in the calculations, estimated time for Cu loadings to return to inferred watershed values are similar for all four basins around 50 years. Because of the potential for error, the value of 50 years should not be used for any lake management decisions, and further monitoring to better define the trend is needed. However, the values are longer than what is predicted from some elemental ratio analysis, which further supports the observation that recent Cu loadings in Torch Lake are not related to watershed processes.

Table 11. Recovery time in years for Torch Lake sediments to get to a concentration of 61 mg/kg (Gratiot Lake average) based on patterns of Cu concentrations in the cap sediments.

Site	T1	T2	T3	T5
	49	56	49	47

Conclusions

Sediment cores were collected from Torch Lake, Upper Peninsula, Michigan to assess the recovery of the lake from past anthropogenic disturbances related to the copper mining industry. This was done by determining the spatial and temporal trends of heavy metals in the sediments and comparing these data to a reference lake and the local geology. A multi-element approach of assessing recovery in Torch Lake was undertaken, where several other elements, many non-toxic, were measured as well as the chemical

of interest (i.e., Cu). Sediment ages were calculated based on historical and geochemical data by a process known as event dating.

It was hypothesized that Cu concentrations in recent sediments would be lower compared to the mining related stamp sands and slime clays, however this trend was not observed. Copper concentrations in the top 10 cm of sediments in Torch Lake still remain elevated at an average of 2,197 mg/kg. This suggested that Torch Lake is not responding to the cessation of mining operations, possibly due to continued inputs of tailings eroding from shoreline deposits and post-depositional processes (e.g., porewater diffusion and microbial processes). However, results from other elements (Ti, Co, K, etc.) and elemental ratios (Ti/Zn, Co/Zn, K/V, etc.) suggest the lake is responding to the cessation of mining activities and the sediments are approaching levels reflective of a reference system (i.e., Gratiot Lake) and expected levels based on the local geology of the region. If the re-vegetation of the shoreline controls new inputs, there is little re-mobilization of previously deposited stamp sands and local inputs cease, Torch Lake may continue to recover from the heavy anthropogenic disturbances of the past. Torch Lake sediments will have elemental ratios in the surface sediments similar to ratios in Gratiot Lake sediments in from 10 to 12 years in the north basin and ~23 years for the south basin. However, the estimates for copper recovery are longer than what is predicted from some elemental ratios at ~50 years, which further supports the observation that recent Cu loadings in Torch Lake are not related to watershed processes. This study not only demonstrates the importance of using reference systems and multi-

element techniques when assessing environmental remediation, but also of event based sediment chronologies.

Future Work

I would propose that the lake be sampled in ~10 years at approximately the same location as this study, using the same equipment and methods. It seems that there is natural attenuation processes at work in Torch Lake and new samples could document further change from a geochemical signature dominated by mining inputs to one the is dominated by a more watershed input consistent with ratios similar to Gratiot Lake. Also, to better characterize Torch Lake sediments and possible sources of copper enrichment in the cap sediments, pore-water samples should be collected and analyzed for the same suite of metals as the sediments and organic carbon analyses should also be done.

Appendices

Appendix A. Sediment-Core Descriptions

Table A-1. Sediment description from Torch Lake, site T1.

Torch Lake - T1

Sample Date: 7/26/1999

Water Depth: 28 m (89 ft)

Location/Description: **Latitude:** 47°10.989' N **Longitude:** 88°24.528' W

Core description: ~ 44 cm long, sediment color changes from brown to purple, many copepods in surface water

Sample #	Thickness (cm)	Depth (cm)	Description
1	0.5	.25	Red/light brown
2	0.5	.75	Red/light brown
3	0.5	1.25	Brown and dark grains
4	0.5	1.75	Brown, dark speck, rust specks
5	0.5	2.25	Brown in color
6	1.0	3.0	Brown in color
7	1.0	4.0	Brown in color
8	1.0	5.0	Brown/red
9	1.0	6.0	Darker red/brown
10	1.0	7.0	Darker red/brown
11	1.0	8.0	Darker red/brown
12	1.0	9.0	Dark red at the top and pink/purple at bottom
13	1.0	10.0	Solid pink with dark streaks
14	1.0	11.0	Becoming more watery
15	1.0	12.0	Watery
16	1.0	13.0	Watery
17	1.0	14.0	Watery
18	1.0	15.0	Watery
19	1.0	16.0	Very watery
20	1.0	17.0	More firm
21	1.0	18.0	Pinkish in color
22	1.0	19.0	Pinkish in color
23	1.0	20.0	Watery
24	1.0	21.0	Watery
25	1.0	22.0	Less watery
26	1.0	23.0	Evidence of sand
27	1.0	24.0	Evidence of sand

28	1.0	25.0	Evidence of sand
29	1.0	26.0	More watery
30	1.0	27.0	Pink/purple in color
31	1.0	28.0	Pink/purple in color
32	1.0	29.0	Pink/purple in color
33	1.0	30.0	Pink/purple in color
34	1.0	31.0	Pink/purple in color, piece of leaf stem
Skip	1.0	32.0	Pink/purple in color
35	1.0	33.0	Pink/purple in color
Skip	1.0	34.0	Pink/purple in color
36	1.0	35.0	Pink/purple in color
Skip	1.0	36.0	Pink/purple in color
37	1.0	37.0	Pink/purple in color
Skip	1.0	38.0	Pink/purple in color
38	1.0	39.0	Pink/purple in color
Skip	1.0	40.0	Pink/purple in color
39	1.0	41.0	Pink/purple in color
40	1.0	42.0	Pink/purple in color
41	1.0	43.0	Hit extruder piston

Table A-2. Sediment description from Torch Lake, site T2.

Torch Lake - T2

Sample Date: 7/26/1999

Water Depth: 33 m (105 ft)

Location/Description: Latitude: 47°10.285' N Longitude: 88°24.826' W

Core description: ~41 cm, at 10 cm the brown sediment changes to purple; ~ 24 cm down, a darker (black) layer present

Sample #	Thickness (cm)	Depth (cm)	Description
1	0.5	.25	Light brown, very watery, top very crooked
2	0.5	.75	Light brown, very watery, dark brown mixed in
3	0.5	1.25	Light brown, watery, dark brown mixed in, slightly thicker
4	0.5	1.75	Light brown, thicker
5	0.5	2.25	Light brown, thicker
6	1.0	3.0	Thick brown sediment
7	1.0	4.0	Dark reddish brown, thicker
8	1.0	5.0	Dark reddish brown, thicker
9	1.0	6.0	Dark brown, thick
10	1.0	7.0	Dark brown, some purple, very thick, clayey
11	1.0	8.0	Dark brown, some purple, very thick, clayey
12	1.0	9.0	Brown -> purple, very thick -> wetter
13	1.0	10.0	Purple, pudding like
14	1.0	11.0	Purple, thick
15	1.0	12.0	Purple, thick
16	1.0	13.0	Purple, less thick
17	1.0	14.0	Purple, watery, thinner
18	1.0	15.0	Watery, moving into thicker
19	1.0	16.0	Purple, still watery
20	1.0	17.0	Purple, more watery
21	1.0	18.0	Purple, even more watery
22	1.0	19.0	Purple, very watery
23	1.0	20.0	Purple, very watery
24	1.0	21.0	Purple, very watery
25	1.0	22.0	Purple, watery, bottom suddenly very thick

26	1.0	23.0	Purple, very thick top 0.5 cm, bottom more watery
27	1.0	24.0	Purple, still thick, some gray streaking
28	1.0	25.0	Purple, more watery, little gray streaking
29	1.0	26.0	Purple, watery
30	1.0	27.0	Purple, watery
31	1.0	28.0	Purple, watery
32	1.0	29.0	Purple, watery
33	1.0	30.0	Purple, watery
34	1.0	31.0	Purple, gooey
Skip	1.0	32.0	Purple, gooey
35	1.0	33.0	Purple, gooey
Skip	1.0	34.0	Purple, gooey
36	1.0	35.0	Purple, gooey
Skip	1.0	36.0	Purple, gooey
37	1.0	37.0	Purple, gooey
Skip	1.0	38.0	Purple, gooey
38	1.0	39.0	Purple, gooey

Table A-3. Sediment description from Torch Lake, site T3.

Torch Lake - T3

Sample Date: 7/27/1999

Water Depth: 32 m (100 ft)

Location/Description: Latitude: 47°10.436 'N Longitude: 88°24.024' W

Core description: ~51 cm long. 4.5 cm light brown; 5.5 cm dark brown changing to purple

Sample #	Thickness (cm)	Depth (cm)	Description
1	0.5	.25	Lt brown, v. fluffy, sediment probably suspended in water removed
2	0.5	.75	Light brown, black, gray, and lighter brown specks
3	0.5	1.25	Light brown, black, gray, and lighter brown specks, thicker
4	0.5	1.75	Light brown, black, gray, and lighter brown specks
5	0.5	2.25	Light brown, black, gray, and lighter brown specks
6	1.0	3.0	Darker brown, still mixed with gray, black and lighter brown
7	1.0	4.0	Dark brown, mixed w/ a little back, much thicker
8	1.0	5.0	Dark brown, thick
9	1.0	6.0	Brown/purple, gray streaks, thick
10	1.0	7.0	Brown/purple, gray streaks, thick, bottom very thick and clayey
11	1.0	8.0	Brown/purple, very thick, clayey
12	1.0	9.0	Thin layer of brown and gray in purple
13	1.0	10.0	Purple, thick, stick
14	1.0	11.0	Thin line of brown and gray
15	1.0	12.0	Purple, thin brown line
16	1.0	13.0	Thick on top of watery, gray layer
17	1.0	14.0	Purple, somewhat watery, swirled with lighter purple
18	1.0	15.0	Above on much more watery layer, gray brown streaking
19	1.0	16.0	Purple w/ gray, watery
20	1.0	17.0	Purple w/ gray, watery, thicker
21	1.0	18.0	Purple w/ gray, watery
22	1.0	19.0	Purple w/ gray, watery
23	1.0	20.0	Purple w/ gray, watery

24	1.0	21.0	Purple w/ gray, watery
25	1.0	22.0	Purple w/ gray, watery
26	1.0	23.0	Purple, gray line
27	1.0	24.0	Purple w/ gray, little thicker
28	1.0	25.0	Purple w/ gray, thicker
29	1.0	26.0	Purple, gray layering
30	1.0	27.0	Purple, gray layering
31	1.0	28.0	Purple w/ gray, thinner
32	1.0	29.0	Purple w/ gray
33	1.0	30.0	Purple w/ gray, gray layer
34	1.0	31.0	Purple w/ gray, thicker
35	1.0	32.0	Purple w/ gray, thicker
Skip	1.0	33.0	Purple w/ gray, thick on more watery
36	1.0	34.0	Purple, thick layer on thinner
Skip	1.0	35.0	Medium thickness
37	1.0	36.0	Medium thickness
Skip	1.0	37.0	Medium thickness
38	1.0	38.0	Purple, med thick
Skip	1.0	39.0	Purple, thinner
39	1.0	40.0	Purple
Skip	1.0	41.0	Purple
40	1.0	42.0	Gray streaking
Skip	2.0	44.0	Thick brown/ gray layer, ~ 1 mm
41	1.0	45.0	Purple, some gray
Skip	2.0	47.0	Purple w/ some gray
42	1.0	48.0	Purple w/ some gray
43	1.0	49.0	Purple into a thick clayey brown

Table A-4. Sediment description from Torch Lake, site T5.

Torch Lake - T5

Sample Date: 7/27/1999

Water Depth: 21 m (66 ft)

Location/Description: **Latitude:** 47°08.823' N **Longitude:** 88°26.944' W

Core description: ~ 42 cm total; top ~8 cm brown; 0.5 cm pink below; some mottling

Sample #	Thickness (cm)	Depth (cm)	Description
1	0.5	.25	Brown/red
2	0.5	.75	Brown/red
3	0.5	1.25	Brown/red
4	0.5	1.75	Brown/red
5	0.5	2.25	Brown/red
6	0.5	3.0	Brown/red
7	0.5	4.0	Brown
8	0.5	5.0	Brown
9	0.5	6.0	Brown
10	1.0	7.0	Brown w/ layers of black coal?
11	1.0	8.0	Brown/red
12	1.0	9.0	Brown/red, transition to pink/purple
13	1.0	10.0	Pink/purple in color Very wet
14	1.0	11.0	Pink/purple in color
15	1.0	12.0	Pink/purple in color
16	1.0	13.0	Pink/purple in color
17	1.0	14.0	Pink/purple in color
18	1.0	15.0	Pink/purple in color
19	1.0	16.0	Pink/purple in color
20	1.0	17.0	Pink/purple in color
21	1.0	18.0	Pink/purple in color
22	1.0	19.0	Pink/purple in color
23	1.0	20.0	Pink/purple in color
24	1.0	21.0	Pink/purple in color
25	1.0	22.0	Pink/purple in color
26	1.0	23.0	Pink/purple in color
27	1.0	24.0	Pink/purple in color
28	1.0	25.0	Pink/purple in color
29	1.0	26.0	Pink/purple in color
30	1.0	27.0	Pink/purple in color

31	1.0	28.0	Pink/purple in color
32	1.0	29.0	Pink/purple in color
33	1.0	30.0	Pink/purple in color
34	1.0	31.0	Pink/purple in color
35	1.0	32.0	Pink/purple in color
Skip	1.0	33.0	Pink/purple in color
36	1.0	34.0	Pink/purple in color
Skip	1.0	35.0	Pink/purple in color
37	1.0	36.0	Pink/purple in color
38	1.0	37.0	Pink/purple in color
Skip	1.0	38.0	Pink/purple in color
39	1.0	39.0	Pink/purple in color
Skip	1.0	40.0	Pink/purple in color
40	1.0	41.0	Pink/purple in color
Skip	1.0	42.0	Pink/purple in color
41	1.0	43.0	Pink/purple in color
Skip	1.0	44.0	Pink/purple in color
42	1.0	45.0	Pink/purple in color
Skip	1.0	46.0	Pink/purple in color
43	1.0	47.0	Pink/purple in color
Skip	1.0	48.0	Pink/purple in color
44	1.0	49.0	Hit piston

Appendix B. Quality Assurance / Quality Control

Solids digestion

The method of digestion via microwave-nitric acid has been shown to be effective for sediment chemical extractions (Hewitt and Reynolds, 1990). This method is not a total extraction (i.e. aluminosilicates are not digested), but is a method used to extract metals that are potentially available to natural leaching and biological processes (e.g. copper, mercury, lead, etc) (Hewitt and Reynolds, 1990). A total digestion is not the goal of this research, since the majority of anthropogenic metals in soils and sediments are associated with the organic matter or absorbed onto clay particles.

After each use, the Teflon[®] digestion vessels were rinsed with DDW, subjected to a 10% HCL bath for 24-hours, soaked in DDW for 24-hours and set to air dry in a class 100 hood. Digestions in duplicate and triplicate were performed on at least one sample per core. A procedural blank and a standard reference material (SRM #2704, Buffalo River Sediment, New York) were also processed with each set of ten samples.

Duplicates & Triplicates of samples

Results from the ICP-HEX-MS and AAS analysis of sediments are summarized in Table B-2.

Table B-1. Data from the replicate sample analyses

Sample Replicate Results											
Units (Mg/kg)											
Sample	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	Pb
T3-6	6.45	2,440	121	58.72	35.19	71.81	2,168	20.87	0.51	0.71	140
T3-6R2	6.88	2,643	125	62.70	35.16	73.49	2,239	21.13	0.60	0.77	133
T3-6R3	7.05	2,637	127	64.05	36.40	74.62	2,191	21.69	0.61	0.81	134
Mean	6.79	2,573	124	61.83	35.58	73.31	2,200	21.23	0.57	0.76	136
Std. Dev	0.31	115	2.73	2.77	0.70	1.42	35.79	0.42	0.06	0.05	3.53
% RSD	4.5%	4.5%	2.2%	4.5%	2.0%	1.9%	1.6%	2.0%	10.1%	6.9%	2.6%
T3-36	7.04	5,762	146	84.43	67.61	132	1,450	4.14	0.44	0.20	61.39
T3-36R2	6.76	6,029	150	83.03	67.18	131	1,433	3.94	0.48	0.21	60.51
T3-36R3	6.96	6,367	151	85.23	68.74	133	1,481	4.36	0.57	0.23	61.38
Mean	6.92	6,053	149	84.23	67.84	132	1,455	4.15	0.50	0.22	61.09
Std. Dev	0.15	303	2.54	1.11	0.81	0.92	24.53	0.21	0.07	0.02	0.51
% RSD	2.1%	5.0%	1.7%	1.3%	1.2%	0.7%	1.7%	5.1%	13.5%	7.9%	0.8%
T2M-14	4.91	6,293	133	82.41	64.06	143	1,653	5.59	0.29	0.38	78.67
T2M-14R2	4.70	6,424	135	83.01	65.07	145	1,681	6.06	0.27	0.37	78.85
T2M-14R3	4.53	6,719	135	80.80	63.52	142	1,680	6.25	0.32	0.42	77.81
Mean	4.71	6,479	134	82.07	64.22	143	1,671	5.97	0.29	0.39	78.44
Std. Dev	0.19	218	1.29	1.14	0.79	1.06	16.12	0.34	0.02	0.03	0.55
% RSD	4.1%	3.4%	1.0%	1.4%	1.2%	0.7%	1.0%	5.7%	8.3%	7.0%	0.7%
T1T-22	6.90	7,219	146	86.80	70.12	139	1,590	3.51	0.51	0.16	102
T1T-22a	7.07	7,078	144	84.14	69.33	134	1,612	3.43	0.40	0.12	100
Mean	6.98	7,149	145	85.47	69.72	137	1,601	3.47	0.45	0.14	101
Std. Dev	0.12	100	1.39	1.88	0.56	3.01	15.32	0.06	0.08	0.03	0.94
% RSD	1.7%	1.4%	1.0%	2.2%	0.8%	2.2%	1.0%	1.7%	18.2%	22.7%	0.9%
T1T-31	7.27	8,158	160	86.43	72.05	129	931	3.43	0.30	0.22	32.77
T1T-31a	7.48	8,242	160	89.38	72.26	134	933	3.84	0.44	0.20	32.34
Mean	7.37	8,200	160	87.90	72.15	131	932	3.64	0.37	0.21	32.56
Std. Dev	0.15	59.57	0.17	2.09	0.15	3.52	1.33	0.29	0.10	0.01	0.30
% RSD	2.0%	0.7%	0.1%	2.4%	0.2%	2.7%	0.1%	7.9%	26.5%	7.0%	0.9%
T5-20	7.21	5,851	139	64.57	43.41	92.75	1,575	2.26	0.28	0.12	9.15
T5-20a	6.99	5,835	138	63.66	42.90	82.99	1,573	2.03	0.30	0.20	7.58
Mean	7.10	5,843	139	64.12	43.15	87.87	1,574	2.14	0.29	0.16	8.37
Std. Dev	0.15	11.25	1.30	0.65	0.36	6.90	1.34	0.16	0.01	0.06	1.11
% RSD	2.2%	0.2%	0.9%	1.0%	0.8%	7.9%	0.1%	7.6%	5.0%	37.5%	13.2%

Table B-1 Continued

Sample Replicate Results

Units (Mg/kg)										
Sample	Al	Zn	Sr	Mg	K	Mn	Ba	Fe *	Ca *	U
T3-6	13,269	263	30.77	12,551	875	1,511	217	18,621	31,846	2.35
T3-6R2	13,458	265	34.90	12,729	1,001	1,566	223	19,859	32,944	2.44
T3-6R3	13,335	269	36.50	12,614	1,023	1,573	226	19,695	33,483	2.44
Mean	13,354	266	34.06	12,631	966	1,550	222	19,391	32,757	2.41
Std. Dev	95.91	3.24	2.95	90.60	79.83	33.92	4.41	672	834	0.05
% RSD	0.7%	1.2%	8.7%	0.7%	8.3%	2.2%	2.0%	3.5%	2.5%	2.1%
T3-36	13,762	227	38.79	12,833	275	1,008	50.26	37,042	36,821	0.62
T3-36R2	14,445	232	37.03	13,470	284	1,008	50.51	36,547	36,463	0.61
T3-36R3	14,616	233	35.21	13,630	268	1,025	51.09	37,277	35,809	0.64
Mean	14,274	230	37.01	13,311	276	1,014	50.62	36,955	36,364	0.62
Std. Dev	452	3.16	1.79	422	7.81	9.79	0.42	372	513	0.01
% RSD	3.2%	1.4%	4.8%	3.2%	2.8%	1.0%	0.8%	1.0%	1.4%	2.2%
T2M-14	12,703	219	38.40	12,111	392	984	100	37,273	35,162	0.85
T2M-14R2	14,451	222	40.25	13,777	407	1,002	100	38,625	35,588	0.87
T2M-14R3	14,630	219	35.14	13,947	391	990	100	37,493	35,137	0.86
Mean	13,928	220	37.93	13,278	397	992	100	37,797	35,295	0.86
Std. Dev	1,064	1.95	2.59	1,015	8.67	9.07	0.08	725	253	0.01
% RSD	7.6%	0.9%	6.8%	7.6%	2.2%	0.9%	0.1%	1.9%	0.7%	1.3%
T1T-22	9,158	255	35.93	9,231	340	1,170	57.82	33,796	41,889	0.55
T1T-22a	8,884	258	37.80	8,955	356	1,185	57.64	38,357	41,149	0.55
Mean	9,021	257	36.87	9,093	348	1,178	57.73	36,077	41,519	0.55
Std. Dev	194	2.26	1.32	195	11.05	10.01	0.13	3,225	524	0.00
% RSD	2.1%	0.9%	3.6%	2.1%	3.2%	0.9%	0.2%	8.9%	1.3%	0.0%
T1T-31	10,059	218	39.42	9,995	248	1,086	68.92	46,860	40,663	0.48
T1T-31a	9,984	218	37.62	9,921	241	1,091	69.48	45,020	41,120	0.50
Mean	10,021	218	38.52	9,958	245	1,089	69.20	45,940	40,891	0.49
Std. Dev	52.68	0.13	1.27	52.31	4.75	3.50	0.40	1,301	323	0.01
% RSD	0.5%	0.1%	3.3%	0.5%	1.9%	0.3%	0.6%	2.8%	0.8%	2.6%
T5-20	10,919	139	23.03	10,722	228	812	51.52	37,816	30,614	0.46
T5-20a	10,295	133	21.21	10,109	192	813	33.92	41,861	29,294	0.45
Mean	10,607	136	22.12	10,415	210	813	42.72	39,839	29,954	0.45
Std. Dev	441	4.42	1.29	433	25.12	0.16	12.45	2,861	934	0.01
% RSD	4.2%	3.3%	5.8%	4.2%	12.0%	0.0%	29.1%	7.2%	3.1%	1.5%

* Analyzed by AAS

Procedural Blanks

Results from the ICP-HEX-MS and AAS analysis of the blanks are summarized in Table B-2.

Standard Reference Material Accuracy & Reproducibility

The certified elemental concentrations of the SRM were determined by the NIST via Instrumental Neutron Activation and Direct-Current Plasma Emission Spectrometry. The extracted values of several elements from this study were in some cases much lower than the certified values, due to the use of partial digestions. Recoveries of elements from the SRM ranged from 1% to 109% for titanium and copper, respectively. Although the digestion method chosen was not a total digestion of the sediment, the SRM could still be used to evaluate the precision of digestion method via microwave assistance. Reproducibility of the standard reference material was better than 15% relative standard deviation for all elements except for selenium. Results are summarized in Table B-3.

Table B-2. ICP-HEX-MS and AAS results from blanks processed with each digestion run.

	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	Pb	Al	Zn	Se	Sr	Mg	K	Mn	Ba	Ca*	Fe*	U
BLANK 1	0.0	17.6	0.04	0.2	0.0	1.2	0.04	0.04	0.00	0.00	0.26	31.0	11.9	0.00	0.0	12.5	20.1	1.07	1.23	20	200	0.0
BLANK 2	0.0	14.7	0.07	1.0	0.0	1.8	0.68	0.10	0.00	0.03	0.26	25.4	4.1	0.00	0.0	9.9	20.2	1.21	0.35	20	200	0.0
BLANK 3	0.0	2.0	0.09	3.4	0.0	10.4	13.85	0.00	0.11	0.00	0.75	51.6	4.8	0.01	0.0	11.7	19.5	0.92	0.41	20	200	0.0
BLANK 4	0.0	9.1	0.22	1.4	0.0	2.2	2.31	0.02	0.09	0.15	0.68	39.9	5.1	0.00	0.0	23.3	26.6	4.55	0.48	20	200	0.0
BLANK 5	0.0	0.0	0.00	1.3	0.0	1.2	0.00	0.00	0.00	0.00	0.26	5.7	1.4	0.00	0.0	0.0	14.9	0.28	0.32	30	230	0.0
BLANK 6	0.0	1.7	0.14	3.1	0.0	0.8	0.31	0.00	0.00	0.00	0.28	74.5	3.4	0.10	0.0	4.9	47.6	0.56	0.56	20	160	0.0
BLANK 7	0.0	0.9	0.05	2.2	0.0	0.0	0.00	0.00	0.00	0.00	0.09	26.8	0.0	0.00	0.0	2.5	6.5	0.61	0.54	20	200	0.0
BLANK 8	0.0	0.0	0.03	2.4	0.0	0.5	0.12	0.00	0.00	0.02	0.15	17.0	5.8	0.00	0.0	2.3	6.5	0.70	0.60	20	180	0.0
BLANK 9	0.0	1.3	0.02	0.3	0.0	0.8	0.00	0.00	0.00	0.01	0.14	17.7	1.6	0.00	0.0	2.9	2.9	0.98	0.45	20	180	0.0
BLANK 10	0.0	0.0	0.03	1.9	0.0	3.2	0.22	0.00	0.01	0.00	0.31	9.7	2.8	0.00	0.0	0.0	2.9	0.62	2.00	20	190	0.0
BLANK 11	0.0	3.6	0.14	0.4	0.0	4.8	1.70	0.00	0.00	0.04	0.47	16.9	4.6	0.04	0.0	7.2	1.9	0.81	0.74	20	160	0.0
BLANK 12	0.0	5.0	0.09	0.8	0.0	1.3	0.18	0.00	0.00	0.00	0.02	19.9	2.5	0.00	0.0	7.4	0.0	0.66	0.50	20	200	0.0
BLANK 13	0.0	22.5	0.21	8.7	0.0	1.3	0.43	0.00	0.84	0.00	0.34	36.5	8.2	0.00	0.0	0.0	8.0	0.71	0.25	20	200	0.0
BLANK 14	0.0	38.1	0.35	1.9	0.0	5.7	1.81	0.00	0.02	0.00	0.36	12.2	3.0	0.00	0.0	4.2	0.0	0.60	0.38	20	220	0.0
BLANK 15	0.0	16.5	0.12	4.2	0.0	0.7	2.16	0.00	0.01	0.02	0.85	27.0	10.9	0.00	0.0	10.9	0.0	0.72	27.22	20	210	0.0
BLANK 16	0.0	12.7	0.88	0.7	0.0	0.4	0.00	0.02	0.02	0.00	0.26	4.2	2.1	0.00	0.0	1.8	0.0	0.53	0.71	20	250	0.0
BLANK 17	0.0	23.3	0.21	1.1	0.0	0.9	10.25	0.01	0.00	0.01	2.62	52.1	16.5	0.01	0.0	5.9	0.0	1.81	2.33	20	190	0.0
Median	0.0	5.0	0.09	1.4	0.0	1.2	0.31	0.00	0.00	0.00	0.28	25.4	4.1	0.00	0.0	4.9	6.5	0.71	0.54	20.0	200	0.0
Mean	0.0	9.9	0.16	2.1	0.0	2.2	2.00	0.01	0.06	0.02	0.48	27.5	5.2	0.01	0.0	6.3	10.5	1.02	2.30	20.6	198	0.0
STDev	0.0	10.9	0.21	2.1	0.0	2.6	3.92	0.03	0.20	0.04	0.60	18.7	4.3	0.03	0.0	6.0	13.0	0.97	6.45	2.43	22.43	0.0

* Analyzed by AAS

Table B-3. Results from the ICP-HEX-MS and AAS analysis of SRM 2704 (Buffalo River Sediment).

Sample	Mg/Kg											
	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	Hg	Pb
SRM 2704 T1	2.15	33.96	23.68	92.96	10.77	43.47	114	15.74	2.19	3.27	0.70	160
SRM 2704 T2	2.19	35.59	23.94	87.12	10.13	35.85	102	15.32	2.07	2.91	0.74	149
SRM 2704 T3	2.00	28.56	23.55	89.35	10.37	36.60	110	16.09	2.24	2.92	0.84	163
SRM 2704 T4	2.16	31.37	24.44	91.24	10.68	35.76	111	17.09	2.27	3.20	0.97	160
SRM 2704 T5	2.18	29.53	23.41	89.96	10.92	36.51	110	16.90	2.29	3.31	1.00	160
SRM 2704 T6	2.08	34.86	24.51	88.05	10.50	35.18	107	17.13	2.39	3.14	0.90	154
SRM 2704 T7	2.02	27.56	22.10	87.39	10.25	34.48	105	16.17	2.19	2.99	0.90	155
SRM 2704 T8	2.11	27.39	21.95	88.72	10.64	36.13	113	16.58	2.21	3.23	0.91	164
SRM 2704 T9	1.95	29.67	22.58	87.11	10.06	35.83	105	15.31	2.24	3.15	0.94	149
SRM 2704 T10	2.08	28.17	22.26	88.22	10.62	36.66	108	16.81	2.34	3.09	0.97	161
SRM 2704 T11	2.27	37.67	26.55	91.08	10.90	34.41	104	16.71	2.41	3.14	0.92	151
SRM 2704 T12	1.97	30.37	22.51	88.59	10.60	35.94	115	16.49	2.31	3.03	0.92	164
SRM 2704 T13	2.46	39.87	23.12	85.78	11.13	39.20	109	18.94	2.61	3.58	1.06	160
SRM 2704 T14	2.13	37.53	23.73	86.69	10.14	34.64	106	15.60	2.31	2.99	0.84	160
SRM 2704 T15	1.67	26.39	19.75	78.53	9.16	31.53	95	14.24	1.96	2.67	0.82	130
SRM 2704 T16	2.02	29.96	22.22	85.85	10.38	34.47	113	16.01	2.10	2.93	0.80	153
SRM 2704 T17	1.99	30.65	21.01	82.31	10.08	34.42	107	15.76	2.29	3.02	0.98	151
SRM 2704 T18	2.10	34.57	22.78	82.10	9.98	34.63	104	15.61	2.22	3.08	0.88	158
Certified	12	4,570	95	135	14	44.1	98.6	23.4	NA	3.45	1.44	161
Average	2.08	31.87	23.00	87.28	10.41	35.87	108	16.25	2.26	3.09	0.89	156
% Recovery	17%	1%	24%	65%	74%	81%	109%	69%	NA	90%	62%	97%
STDev	0.16	4.03	1.48	3.53	0.46	2.44	4.90	1.00	0.14	0.20	0.09	8.10
% RSD	8%	13%	6%	4%	4%	7%	5%	6%	6%	6%	10%	5%

* Analyzed by AAS

Table B-3 continued.

Sample	Al	Zn	Se	Sr	Mg	K	Mn	Ba	Ca*	Fe*	U
SRM Torch 1	12,918	454	0.34	27.15	9,364	1,881	540	101	37,576	32,509	0.83
SRM Torch 2	12,489	420	0.29	26.55	8,702	2,148	492	93.63	26,151	30,450	0.88
SRM Torch 3	13,860	432	0.28	25.20	9,081	1,969	521	89.66	24,137	31,849	0.86
SRM Torch 4	14,259	448	0.53	25.47	9,374	2,078	527	93.05	31,849	33,091	0.91
SRM Torch 5	13,382	447	0.49	26.27	9,126	1,910	530	92.88	25,916	32,571	0.92
SRM Torch 6	13,631	424	0.36	25.39	8,903	2,153	512	92.87	26,184	32,432	0.92
SRM Torch 7	12,486	428	0.30	25.22	8,794	1,745	508	87.01	25,073	31,162	0.84
SRM Torch 8	12,536	434	0.62	26.09	8,874	1,647	522	87.72	25,276	32,205	0.85
SRM Torch 9	12,935	425	0.51	26.22	8,864	1,988	504	94.70	26,170	31,102	0.85
SRM Torch 10	12,449	431	0.64	26.20	8,869	1,759	516	91.91	24,941	31,544	0.85
SRM Torch 11	13,581	428	0.24	26.14	8,925	2,589	506	94.94	25,579	32,347	0.96
SRM Torch 12	13,049	452	0.40	26.99	9,279	1,802	532	91.61	25,245	32,671	0.86
SRM Torch 13	11,914	420	0.48	25.95	8,643	1,799	497	85.58	26,205	32,099	0.95
SRM Torch 14	12,847	425	0.28	24.80	8,821	2,070	497	90.16	25,602	32,669	0.90
SRM Torch 15	11,326	367	0.33	20.92	7,785	1,530	439	76.14	25,359	31,765	0.75
SRM Torch 16	12,585	427	0.34	25.99	8,760	1,794	505	87.19	26,020	32,894	0.84
SRM Torch 17	11,896	411	0.57	24.59	8,503	1,581	495	86.60	25,749	31,644	0.80
SRM Torch 18	12,559	402	0.37	25.45	8,633	1,980	492	86.31	25,602	31,980	0.88
Certified	61,100	438	1.1	130	12,000	20,000	555	414	26,000	41,100	3.13
Average	12,817	426	0.41	26	8,850	1,912	508	90	26,591	32,055	0.87
% Recovery	21%	97%	37%	20%	74%	10%	91%	22%	102%	78%	28%
STDev	737	20.06	0.13	1.35	362	249	22.44	5.26	3,159	690	0.05
% RSD	6%	5%	30%	5%	4%	13%	4%	6%	12%	2%	6%

* Analyzed by AAS

Detection and Quantification Limits

Detection limits (DLs) are the concentration or response that is considered the lowest reliably detectible level for a particular instrument.

Detection limits (DLs) for the ICP-HEX-MS were determined by calculating the standard deviation of the count response of each element from ten replicates of a Nanopure® blank. Detection limits for the ICP-HEX-MS were determined by this equation:

$$\frac{\text{conc. of known standard } X}{\text{counts for standard } X} * 3 \text{ standard deviations of } 10 \text{ readings of the blank count for } X$$

Quantification limits (QLs) of an instrument differ from the detection limits in that QLs are based on the concentration and accuracy of the prepared standards. Therefore, the concentration of a sample may be higher than the detection limits of the machine, but may not be quantifiable based on the QL. The quantification limits for each element were calculated using a method from Miller and Miller (1993). Results are summarized in Table B-4.

Table B-4. Detection limit and the quantification limit of the Torch Lake sample analyzed via ICP-MS and AAS.

Element	Detection Limit µg/L	Quantification Limit µg/L
As	.0650	2.73
Al	NA	87.52
Ba	.0014	4.22
Ca*	NA	3.9 (mg/l)
Cd	.0170	.109
Co	.0150	4.70
Cr	NA	5.31
Cu	.0690	77.35
Fe*	NA	3.8 (mg/l)
Hg	.1300	ND
K	.2000	110
Mg	NA	177
Mn	.0036	25.99
Mo	NA	0.092
Ni	.4600	10.88
Pb	.0012	4.50
Sc	.0130	3.97
Se	.07902	0.82
Sr	NA	6.86
Ti	NA	66.12
U	.0003	.10
V	.0077	4.29
Zn	.0560	5.84

* Elements analyzed via AAS.

Appendix C.

Results from ICP-HEX-MS and AAS analysis

The Results from the ICP-HEX-MS, AAS and event dating technique are summarized in tables C-1 through C-4. The values shaded in gray are lower than the quantification limit and greater than the detection limit. Even though some of the concentration values are higher than the QL in the table, the QL is based on the concentration of the digested leachate and not the representative sediment concentrations. The reported sediment concentrations are calculated by this equation:

$$C(f) * D(f) * S(v) / W$$

Where:

$C(f)$ = conc. of fluid ($\mu\text{g/L}$)

$D(f)$ = dilution factor

$S(v)$ = volume of initial sample (0.1L)

W = weight of sediment digested

Table C-1. Results of ICP-HEX-MS and AAS analysis and event dating, site T1.

Units (mg/kg)

Sample	Date	Depth (cm)	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	Pb
T1-1	1999	0.25	7.15	2,196	104	54	29	67	2,062	44	1.33	0.70	91
T1-2	1998	0.75	5.82	2,102	105	52	26	57	1,921	23	0.43	0.25	95
T1-3	1997	1.25	6.23	2,605	113	54	27	55	2,301	23	0.43	0.43	106
T1-4	1997	1.75	6.81	2,785	115	55	29	63	2,317	22	0.40	0.42	108
T1-5	1996	2.25	6.30	2,486	114	52	30	60	2,179	25	0.45	0.43	115
T1-6	1995	3	6.03	2,682	102	48	29	59	1,982	26	0.57	1.90	128
T1-7	1993	4	6.55	3,212	105	54	31	66	2,109	24	0.57	0.56	139
T1-8	1991	5	6.55	3,402	105	51	31	65	2,187	27	0.65	0.69	163
T1-9	1989	6	7.01	3,667	111	66	36	95	2,849	42	1.36	0.89	239
T1-10	1987	7	6.70	4,010	114	63	41	97	3,315	54	2.93	0.90	254
T1-11	1983	8	7.89	4,118	121	80	47	127	4,336	28	0.77	0.79	221
T1-12	1977	9	6.42	5,734	132	86	60	149	5,472	5.49	0.34	0.91	232
T1-13	1971	10	5.19	6,495	139	80	63	139	3,942	4.05	0.30	0.48	206
T1-14		11	5.92	6,482	141	81	65	110	3,450	4.22	0.26	0.24	131
T1-15		12	6.43	7,247	150	85	71	118	2,324	3.85	0.32	0.16	89
T1-16		13	6.47	7,128	149	84	73	108	1,666	3.27	0.26	0.06	44
T1-17		14	5.51	5,880	133	84	66	108	1,186	2.62	0.18	0.05	22
T1-18		15	5.63	7,051	144	80	69	106	1,587	2.96	0.27	0.08	56
T1-19		16	5.40	6,738	142	73	68	90	1,102	3.20	0.20	0.08	22
T1-20		17	5.90	5,625	133	73	62	102	1,681	6.24	0.30	0.14	104
T1-21		18	6.46	6,210	138	80	64	118	1,923	4.11	0.31	0.10	108
T1-22		19	6.90	7,219	146	87	70	139	1,590	3.51	0.51	0.16	102
T1-23		20	7.20	7,688	154	93	79	147	1,184	3.05	0.39	0.31	27
T1-24		21	6.85	7,784	156	94	76	142	763	2.93	0.32	0.00	9.22
T1-25		22	6.75	7,835	151	88	73	130	880	3.09	0.32	0.00	10
T1-26		23	6.83	7,855	153	83	67	123	952	3.05	0.36	0.08	15
T1-27		24	7.39	6,133	140	83	68	122	1,155	2.85	0.22	0.06	58
T1-28		25	7.62	6,785	148	84	69	122	1,331	3.66	0.35	0.14	35
T1-29		26	6.91	6,596	145	88	74	127	1,288	2.86	0.25	0.02	20
T1-30		27	9.07	7,087	157	94	80	148	820	5.57	0.39	0.26	17
T1-31		28	7.27	8,158	160	86	72	129	931	3.43	0.30	0.22	33
T1-32		29	8.33	8,030	162	97	74	137	1,124	3.95	0.32	0.22	57
T1-33		30	8.10	8,060	160	91	75	136	1,061	4.08	0.47	0.20	28
T1-34		31	7.68	6,887	148	80	61	109	1,424	3.79	0.39	0.26	23
T1-36		35	8.77	5,987	144	85	69	124	1,504	4.19	0.16	0.16	35
T1-39		41	8.00	7,571	153	91	73	139	1,196	5.14	0.45	0.16	23
T1-40		42	7.76	7,625	152	84	68	127	1,380	5.37	0.39	0.16	16

 Below QL above DL

Table C-1. Continued

Units (mg/kg)

Sample	Date	Depth (cm)	Al	Zn	Se	Sr	Mg	K	Mn	Ba	Ca*	Fe*	U
T1-1	1999	0.25	21,382	211	2.13	43	16,032	1,591	7,864	309	35,347	50,120	2.65
T1-2	1998	0.75	22,643	199	0.00	43	16,719	1,506	4,384	308	16,647	49,146	2.22
T1-3	1997	1.25	24,175	230	0.00	37	19,174	1,290	2,050	244	16,423	40,648	2.69
T1-4	1997	1.75	25,612	231	0.00	39	20,196	1,331	1,660	273	17,105	37,530	2.65
T1-5	1996	2.25	25,340	218	0.06	42	21,283	1,174	1,879	321	17,450	44,274	2.23
T1-6	1995	3	24,806	237	0.00	37	20,002	1,298	1,441	224	17,546	31,664	2.40
T1-7	1993	4	26,199	232	0.08	38	21,246	1,270	1,208	172	16,995	27,395	2.26
T1-8	1991	5	26,758	242	0.06	40	22,200	1,248	1,212	163	18,103	26,134	2.11
T1-9	1989	6	28,319	291	0.08	45	24,150	1,182	1,205	174	18,679	27,683	2.34
T1-10	1987	7	28,162	306	0.12	45	25,728	996	1,133	156	20,976	29,391	2.00
T1-11	1983	8	30,991	306	0.00	65	31,931	1,167	1,089	172	22,436	31,181	1.99
T1-12	1977	9	35,598	332	0.00	45	39,706	679	1,020	87	24,409	36,485	1.13
T1-13	1971	10	37,128	272	0.00	39	44,520	432	1,044	71	30,404	37,585	0.70
T1-14		11	36,967	269	0.00	48	46,560	454	1,040	66	31,198	39,438	0.84
T1-15		12	38,785	290	0.00	43	51,471	391	1,128	67	31,867	42,956	0.71
T1-16		13	38,165	279	0.00	45	52,386	385	1,114	64	33,452	42,982	0.67
T1-17		14	34,572	218	0.00	53	45,372	294	942	53	45,436	37,381	0.66
T1-18		15	37,370	247	0.00	47	48,881	356	1,017	64	40,989	39,673	0.65
T1-19		16	35,326	216	0.00	50	46,582	298	934	50	35,041	37,727	0.73
T1-20		17	34,723	248	0.00	50	44,652	381	938	57	43,103	36,318	0.76
T1-21		18	36,845	242	0.00	41	46,910	379	1,019	55	35,634	37,476	0.65
T1-22		19	41,514	255	0.00	36	53,993	340	1,170	58	33,796	41,889	0.55
T1-23		20	43,796	250	0.00	36	59,445	353	1,265	52	38,218	46,070	0.53
T1-24		21	40,102	224	0.00	37	53,319	280	1,118	52	45,700	43,984	0.48
T1-25		22	41,592	219	0.00	35	55,445	259	1,158	57	47,171	43,072	0.48
T1-26		23	37,494	201	0.00	34	47,421	236	1,004	50	45,141	38,162	0.51
T1-27		24	39,329	212	0.00	43	49,510	267	1,031	48	46,848	39,391	0.57
T1-28		25	43,223	240	0.00	37	54,319	340	1,205	63	45,206	43,450	0.62
T1-29		26	41,968	240	0.00	42	56,207	234	1,131	54	38,577	42,292	0.51
T1-30		27	45,529	240	0.17	47	58,983	259	1,189	70	46,364	44,766	0.71
T1-31		28	39,796	218	0.00	39	52,316	248	1,074	69	46,860	40,663	0.48
T1-32		29	43,677	232	0.00	44	54,716	287	1,149	78	44,440	44,484	0.54
T1-33		30	44,874	252	0.00	39	55,950	285	1,181	71	45,040	45,898	0.55
T1-34		31	37,277	223	0.00	42	45,526	479	974	74	39,429	36,456	0.84
T1-36		35	41,280	236	0.00	51	52,244	289	1,107	76	39,185	41,397	0.59
T1-39		41	45,145	255	0.00	37	58,256	310	1,215	83	47,308	45,453	0.51
T1-40		42	42,650	247	0.00	36	54,880	272	1,140	79	41,132	44,268	0.55

☐ Below QL above DL

* Analyzed by AAS

Table C-2. Results of ICP-HEX-MS and AAS analysis and event dating, site T2.

Units (mg/kg)

Sample	Age	Depth	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	Pb
T2-1	1999	0.25	7.04	2,849	118	57	32	74	2,192	40	1.41	1.39	154
T2-2	1999	0.75	5.40	2,335	113	50	32	50	1,989	38	1.08	0.42	121
T2-3	1998	1.25	3.87	1,428	110	45	26	36	1,676	54	0.94	0.24	80
T2-4	1998	1.75	5.06	1,866	126	52	26	47	2,074	24	0.47	0.45	91
T2-5	1997	2.25	7.93	2,751	130	55	31	64	2,290	16	0.45	0.59	96
T2-6	1997	3	8.05	3,212	123	55	33	71	1,984	15	0.48	0.58	94
T2-7	1995	4	6.05	3,284	121	58	35	71	2,015	24	0.73	0.48	126
T2-8	1994	5	6.83	3,238	124	62	40	82	2,229	31	1.43	1.00	157
T2-9	1992	6	6.67	3,293	122	61	41	87	2,437	32	2.24	1.05	193
T2-10	1990	7	6.80	3,441	107	74	39	117	2,306	27	1.30	0.43	92
T2-11	1986	8	7.04	4,494	111	85	44	138	1,700	11	0.43	0.33	43
T2-12	1979	9	5.75	5,495	118	82	55	140	1,638	7.73	0.33	0.42	64
T2-14	1972	10	4.91	6,293	133	82	64	143	1,653	5.59	0.29	0.38	79
T2-15		11	4.16	7,322	144	80	68	136	1,594	4.71	0.33	0.37	62
T2-16		12	5.29	6,638	142	82	64	122	1,519	4.71	0.30	0.27	55
T2-17		13	5.80	6,833	142	77	63	110	1,435	5.12	0.33	0.10	40
T2-18		14	5.34	6,998	145	75	59	98	1,012	5.09	0.35	0.04	17
T2-19		15	5.47	6,924	146	79	66	105	1,448	5.64	0.28	0.11	39
T2-20		16	5.35	5,218	129	78	66	94	1,038	4.40	0.04	0.02	27
T2-21		17	5.78	6,078	142	79	68	100	980	5.04	0.16	0.02	17
T2-22		18	5.31	7,142	154	79	66	93	859	4.14	0.28	0.00	10
T2-23		19	5.77	7,320	154	79	65	94	898	3.44	0.28	0.00	14
T2-24		20	5.37	6,348	136	69	53	77	876	2.97	0.23	0.00	5.61
T2-25		21	5.33	6,350	132	66	48	70	950	3.33	0.31	0.02	4.94
T2-26		22	4.25	4,131	93	45	26	43	636	4.27	0.26	0.00	3.76
T2-27		23	6.24	5,733	138	75	58	93	1,669	5.59	0.47	0.16	41
T2-28		24	6.03	7,000	151	83	70	109	1,207	4.05	0.38	0.06	49
T2-29		25	5.46	5,971	134	71	59	81	932	3.13	0.30	0.00	16
T2-30		26	6.18	6,475	138	71	63	87	815	3.41	0.24	0.02	17
T2-31		27	6.89	7,042	146	73	62	96	831	4.13	0.49	0.11	6.66
T2-32		28	5.88	7,413	151	73	63	85	858	3.37	0.42	0.04	5.15
T2-33		29	6.34	6,964	147	72	59	82	778	3.17	0.38	0.04	5.07
T2-34		30	6.77	7,564	155	75	62	83	833	3.00	0.38	0.04	5.38
T2-35		32	5.21	6,894	145	67	57	77	793	3.07	0.41	0.06	4.94
T2-36		33	5.09	6,642	140	69	56	83	826	3.23	0.32	0.06	9.05

 Below QL above DL

Table C-2. Continued

Units (mg/kg)

Sample	Age	Depth	Al	Zn	Se	Sr	Mg	K	Mn	Ba	Ca*	Fe*	U
T2-1	1999	0.25	25,184	259	3.36	43	20,347	1,216	11,457	278	18,712	35,231	2.66
T2-2	1999	0.75	24,350	213	0.74	49	17,846	1,336	20,767	502	16,787	53,594	2.25
T2-3	1998	1.25	21,840	189	0.12	56	15,848	976	8,887	530	16,721	88,717	1.96
T2-4	1998	1.75	26,456	219	0.14	46	20,335	1,154	2,746	401	17,980	49,755	2.12
T2-5	1997	2.25	29,045	212	0.67	44	23,656	979	1,585	228	20,605	31,329	1.86
T2-6	1997	3	29,311	201	0.50	47	24,788	1,071	1,340	192	21,845	31,207	1.87
T2-7	1995	4	29,247	258	0.24	40	25,203	1,113	1,297	197	22,044	28,115	2.28
T2-8	1994	5	30,128	283	0.70	42	26,310	983	1,298	173	23,536	27,585	2.36
T2-9	1992	6	28,578	297	0.89	44	25,486	970	1,242	167	23,790	26,865	2.22
T2-10	1990	7	25,908	217	0.40	64	25,471	1,074	929	175	30,848	24,980	2.13
T2-11	1986	8	28,180	194	0.16	57	32,232	833	905	134	43,820	27,551	1.86
T2-12	1979	9	34,341	221	0.00	31	39,846	516	1,007	78	38,394	33,462	1.11
T2-14	1972	10	36,703	219	0.00	38	42,095	392	1,002	100	37,273	35,162	0.85
T2-15		11	37,384	220	0.00	32	45,459	313	1,012	77	36,947	35,824	0.67
T2-16		12	36,412	222	0.00	39	44,078	339	999	73	36,056	36,362	0.79
T2-17		13	35,464	218	0.00	43	43,603	400	962	77	37,054	34,319	0.88
T2-18		14	33,106	198	0.00	37	41,789	285	907	62	41,770	33,665	0.80
T2-19		15	37,069	237	0.00	48	47,611	385	1,017	81	38,289	37,553	0.91
T2-20		16	35,861	239	0.00	59	46,271	368	963	77	43,386	37,211	1.01
T2-21		17	38,015	258	0.00	58	49,215	365	1,009	74	41,625	38,852	0.91
T2-22		18	35,167	241	0.00	52	45,855	322	935	71	42,998	36,812	0.93
T2-23		19	36,453	238	0.00	49	46,194	341	984	79	44,423	38,239	0.83
T2-24		20	29,942	182	0.00	44	36,753	252	791	63	43,484	30,879	0.78
T2-25		21	27,885	166	0.00	36	33,605	211	720	50	44,820	28,059	0.78
T2-26		22	19,591	92	0.00	27	18,664	139	456	31	42,753	17,893	0.70
T2-27		23	33,622	223	0.00	40	40,158	292	891	69	39,982	33,367	0.94
T2-28		24	37,521	270	0.00	41	49,061	313	1,002	79	39,146	38,482	0.77
T2-29		25	31,505	214	0.00	43	42,173	326	838	74	37,594	32,349	0.72
T2-30		26	32,644	217	0.00	49	43,241	304	868	67	44,606	34,232	0.83
T2-31		27	31,510	213	0.11	45	41,969	277	851	67	42,796	32,887	0.91
T2-32		28	31,747	222	0.00	42	42,654	266	858	68	40,406	33,584	0.73
T2-33		29	30,460	212	0.00	42	42,299	230	857	64	39,156	32,040	0.77
T2-34		30	32,283	213	0.00	47	43,325	264	861	66	42,058	33,909	0.77
T2-35		32	30,159	189	0.00	37	40,242	196	781	57	37,820	31,371	0.69
T2-36		33	29,407	180	0.00	47	37,235	201	728	56	38,881	30,337	0.75

Below QL above DL

* Analyzed by AAS

Table C-3. Results of ICP-HEX-MS and AAS analysis and event dating, site T3. Event dates from site T2 are reported as site T3 due to their close proximity to each other.

Units (mg/kg)

Sample	Age	Depth	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	Pb
T3-1	1999	0.25	6.73	2,342	120	52	31	61	2,230	51	1.64	0.97	154
T3-2	1999	0.75	5.46	1,882	113	49	29	48	2,115	48	0.97	0.58	140
T3-3	1998	1.25	4.54	1,641	109	46	25	46	2,072	26	0.44	0.48	122
T3-4	1998	1.75	6.38	2,230	122	52	30	59	2,444	33	0.59	0.69	134
T3-5	1997	2.25	6.77	2,346	123	56	35	71	2,415	23	0.47	0.59	133
T3-6	1997	3	6.45	2,440	121	59	35	72	2,168	21	0.51	0.71	140
T3-7	1995	4	6.76	2,533	121	59	36	76	2,173	32	1.00	0.85	177
T3-8	1994	5	7.78	2,934	129	64	41	84	2,364	36	1.51	1.07	209
T3-9	1992	6	6.73	3,446	119	62	39	77	2,403	46	2.38	1.20	235
T3-10	1990	7	6.92	3,795	119	69	46	112	2,750	46	3.23	1.03	256
T3-11	1986	8	7.24	3,993	106	79	39	121	2,207	22	0.81	0.42	70
T3-12	1979	9	6.59	4,659	109	80	47	137	1,799	9.26	0.33	0.47	60
T3-13	1972	10	5.34	6,064	131	84	61	145	2,016	7.17	0.41	0.49	85
T3-14		11	5.28	6,488	137	81	68	141	2,002	5.14	0.34	0.60	93
T3-15		12	5.39	6,211	142	83	67	130	2,336	5.43	0.31	0.60	91
T3-16		13	5.63	5,553	135	80	65	111	1,755	5.79	0.21	0.39	60
T3-17		14	5.88	6,561	144	79	69	108	1,846	5.40	0.31	0.43	76
T3-18		15	5.75	5,747	136	76	67	98	1,142	4.76	0.16	0.26	35
T3-19		16	5.88	5,879	127	69	54	79	946	4.60	0.10	0.27	16
T3-20		17	6.53	7,416	147	79	70	111	1,727	5.74	0.35	0.43	79
T3-21		18	6.04	6,928	141	73	66	93	1,193	4.14	0.24	0.22	28
T3-22		19	6.56	5,473	127	73	65	90	954	4.03	0.12	0.24	9.66
T3-23		20	6.48	7,374	147	75	66	89	938	4.30	0.31	0.18	7.74
T3-24		21	6.07	7,672	152	77	65	87	937	4.16	0.45	0.20	6.94
T3-25		22	7.07	6,689	141	75	63	85	945	3.67	0.20	0.18	6.74
T3-26		23	6.90	6,639	140	76	65	102	989	5.04	0.37	0.51	9.22
T3-27		24	5.66	7,002	138	74	59	88	880	3.84	0.39	0.16	9.09
T3-28		25	5.46	6,929	143	75	59	87	904	3.58	0.33	0.22	11
T3-29		26	5.16	6,677	147	78	64	129	1,274	3.73	0.50	0.20	31
T3-30		27	6.15	6,326	148	84	71	106	1,352	3.50	0.35	0.25	39
T3-31		28	5.61	6,042	137	74	68	93	903	3.40	0.32	0.19	21
T3-32		29	5.58	4,975	128	70	65	97	772	3.10	0.15	0.35	7.27
T3-33		30	5.40	3,815	106	144	61	104	813	3.13	0.63	0.13	6.38
T3-34		31	6.06	3,600	105	74	64	89	827	5.09	0.31	0.17	11
T3-35		32	5.02	6,397	148	74	64	92	994	5.02	0.68	0.21	44
T3-36		34	7.04	5,762	146	84	68	132	1,450	4.14	0.44	0.20	61
T3-37		36	7.63	5,165	132	79	66	128	732	3.35	0.15	0.17	18
T3-38		38	7.13	6,794	150	83	68	129	678	3.17	0.36	0.17	7.90
T3-39		40	6.88	6,288	141	72	60	113	608	2.90	0.38	0.13	5.81
T3-40		42	6.98	6,737	151	78	63	118	639	2.86	0.46	0.12	4.87
T3-41		44	7.41	5,157	130	76	62	115	658	3.04	0.17	0.13	4.52
T3-42		45	6.89	6,952	151	78	63	115	761	3.00	0.49	0.17	6.57
T3-43		46	6.89	6,591	147	74	57	100	749	3.28	0.47	0.15	8.75

☐ Below QL above DL

Table C-3. Continued

Units (mg/kg)

Sample	Age	Depth	Al	Zn	Se	Sr	Mg	K	Mn	Ba	Ca*	Fe*	U
T3-1	1999	0.25	25,844	272	2.13	51	19,215	1,317	14,242	407	17,951	52,515	2.64
T3-2	1999	0.75	24,023	246	0.74	52	18,208	1,076	10,374	419	22,447	66,303	2.31
T3-3	1998	1.25	25,615	222	0.24	36	20,253	912	5,346	354	17,016	53,004	2.04
T3-4	1998	1.75	27,241	292	1.17	40	21,645	1,034	3,088	316	17,778	42,424	2.61
T3-5	1997	2.25	29,139	264	1.30	32	25,276	907	2,163	259	18,455	36,606	2.42
T3-6	1997	3	28,877	263	0.59	31	25,953	875	1,575	217	18,621	31,846	2.35
T3-7	1995	4	29,633	292	0.60	36	25,311	1,047	1,408	218	19,066	29,087	2.39
T3-8	1994	5	31,014	321	0.91	48	26,533	1,159	1,413	195	22,123	30,635	2.40
T3-9	1992	6	29,267	311	0.82	44	24,534	1,018	1,446	183	21,363	29,840	2.34
T3-10	1990	7	29,071	311	0.84	50	27,580	906	1,240	176	21,989	29,944	2.06
T3-11	1986	8	25,262	214	0.10	70	26,673	1,000	883	184	28,948	25,992	2.20
T3-12	1979	9	30,072	210	0.00	48	33,747	714	935	103	32,690	30,819	1.48
T3-13	1972	10	34,469	240	0.00	33	39,475	440	984	84	32,382	35,688	1.01
T3-14		11	37,688	243	0.00	35	43,974	345	1,023	84	32,760	37,320	0.74
T3-15		12	38,135	278	0.00	41	45,938	367	1,044	83	30,272	36,534	0.89
T3-16		13	36,921	245	0.00	53	46,138	400	1,001	74	33,041	37,271	0.90
T3-17		14	37,784	289	0.00	48	48,469	467	1,077	76	31,799	39,729	0.95
T3-18		15	36,408	259	0.00	54	47,095	350	1,001	66	34,560	38,242	0.93
T3-19		16	31,199	204	0.00	51	37,563	313	850	56	41,773	33,588	0.80
T3-20		17	38,097	307	0.00	45	48,851	443	1,098	91	33,004	41,376	0.74
T3-21		18	34,262	257	0.00	44	45,356	340	952	74	34,517	36,227	0.74
T3-22		19	33,378	232	0.00	57	44,414	394	942	65	40,059	35,198	0.79
T3-23		20	33,133	248	0.00	45	46,026	326	959	66	37,678	35,580	0.77
T3-24		21	33,999	254	0.00	40	46,024	256	952	62	37,258	37,830	0.75
T3-25		22	32,858	223	0.00	46	43,004	307	893	59	38,802	33,576	0.73
T3-26		23	34,109	230	0.10	46	45,521	308	914	61	38,235	34,235	0.90
T3-27		24	31,228	195	0.00	38	40,325	242	818	51	37,679	31,839	0.73
T3-28		25	31,669	191	0.00	46	40,391	233	817	50	39,293	31,198	0.77
T3-29		26	34,405	251	0.00	42	42,794	281	868	56	37,238	33,306	0.77
T3-30		27	37,648	250	0.00	48	49,008	317	998	76	33,292	37,743	0.72
T3-31		28	35,012	216	0.00	51	45,923	246	888	57	38,740	35,573	0.69
T3-32		29	34,122	201	0.00	57	44,656	239	851	51	41,688	34,750	0.71
T3-33		30	31,936	180	0.00	49	40,477	214	787	46	41,923	31,712	0.69
T3-34		31	35,244	196	0.00	56	43,564	240	851	48	43,476	33,573	0.82
T3-35		32	33,352	215	0.00	38	44,166	239	849	49	36,914	33,601	0.74
T3-36		34	38,094	227	0.00	39	46,975	275	979	50	37,042	36,821	0.62
T3-37		36	37,535	189	0.00	40	46,806	241	1,023	43	42,722	36,389	0.54
T3-38		38	38,142	191	0.00	39	48,682	223	1,042	43	44,549	37,107	0.59
T3-39		40	34,923	174	0.00	31	43,373	212	930	37	42,667	34,457	0.51
T3-40		42	35,957	175	0.00	30	45,155	187	962	38	44,369	35,135	0.54
T3-41		44	34,602	170	0.00	39	42,350	179	909	37	44,297	33,707	0.61
T3-42		45	35,089	175	0.00	29	44,236	178	926	39	42,979	33,766	0.53
T3-43		46	33,411	155	0.00	29	39,986	188	828	36	42,966	30,297	0.57

□ Below QL above DL

* Analyzed by AAS

Table C-4. Results of ICP-HEX-MS and AAS analysis and event dating, site T5.

Units (mg/kg)

Sample	Age	Depth	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	Pb
T5-1	1999	0.25	7.76	3,238	115	64	30	57	1,719	30.79	1.19	0.69	45
T5-2	1998	0.75	5.97	2,264	103	47	23	36	1,441	36.83	0.63	0.35	41
T5-3	1998	1.25	7.23	2,238	111	49	23	40	1,550	24.94	0.47	0.43	41
T5-4	1997	1.75	9.00	3,847	131	53	28	50	2,011	20.49	0.39	0.51	53
T5-5	1996	2.25	9.12	1,644	112	51	29	59	1,981	12.68	0.10	1.02	58
T5-6	1996	3	8.34	4,162	129	52	31	59	1,585	8.13	0.35	0.41	60
T5-7	1994	4	8.60	4,660	137	54	35	66	1,724	14.21	0.53	0.71	61
T5-8	1993	5	8.47	4,849	136	53	36	64	1,637	16.11	1.00	0.67	65
T5-9	1992	6	8.33	5,017	133	54	37	71	1,669	14.97	1.09	0.68	75
T5-10	1990	7	8.84	4,848	136	52	36	63	1,764	15.03	1.22	0.64	78
T5-11	1986	8	7.78	5,487	132	62	43	86	1,824	9.41	1.90	0.41	53
T5-12	1979	9	6.10	5,298	113	67	39	75	1,162	3.01	0.32	0.18	7.76
T5-13	1971	10	6.35	4,911	116	67	44	89	928	2.55	0.20	0.28	9.90
T5-14		11	5.54	4,742	118	71	44	103	722	2.21	0.23	0.98	6.99
T5-15		12	5.95	5,788	133	71	48	103	786	2.28	0.34	0.26	7.03
T5-16		13	5.67	4,383	116	62	42	73	990	2.04	0.15	0.21	5.62
T5-17		14	6.32	5,106	126	64	41	77	989	2.00	0.17	0.19	5.66
T5-18		15	6.52	5,542	133	73	47	99	1,001	3.24	0.33	0.08	4.55
T5-19		16	5.65	5,761	133	78	47	107	965	2.59	0.38	0.02	4.17
T5-20		17	7.21	5,851	139	65	43	93	1,575	2.26	0.28	0.12	9.15
T5-21		18	7.41	6,213	146	60	45	78	1,063	2.28	0.33	0.06	9.27
T5-22		19	9.71	5,567	149	59	52	82	1,680	2.52	0.25	0.12	15.38
T5-23		20	6.52	6,375	138	59	52	79	1,173	2.42	0.20	0.00	8.13
T5-24		21	8.18	7,416	155	59	51	80	1,089	2.52	0.34	0.08	9.62
T5-25		22	6.29	6,851	140	59	51	83	1,194	2.48	0.32	0.00	8.33
T5-26		23	9.66	6,732	155	65	51	88	1,444	2.95	0.28	0.12	18
T5-27		24	9.94	8,090	166	65	54	85	1,650	3.00	0.35	0.13	18
T5-28		25	8.31	5,830	139	59	49	81	1,091	2.32	0.17	0.07	8.82
T5-29		26	5.99	5,903	126	68	49	94	779	2.56	0.22	0.10	9.15
T5-30		27	8.28	5,800	138	66	52	106	1,259	2.64	0.18	0.04	6.19
T5-31		28	7.10	6,686	140	70	53	127	1,568	3.00	0.35	0.04	9.67
T5-32		29	9.62	7,168	154	58	51	86	1,862	2.13	0.23	0.06	8.74
T5-33		30	11.89	6,168	158	58	52	79	1,772	2.48	0.14	0.12	13
T5-34		31	9.72	5,197	139	64	54	89	1,724	2.51	0.11	0.09	13
T5-35		32	8.69	6,557	151	70	57	106	1,774	2.90	0.22	0.14	9.94
T5-36		34	8.79	7,079	154	66	52	94	1,804	2.92	0.34	0.06	8.41
T5-37		36	7.95	6,106	138	75	57	123	1,651	3.40	0.23	0.40	9.04
T5-38		37	7.53	6,898	145	68	58	102	1,306	2.93	0.33	0.67	13
T5-39		39	9.42	6,758	152	64	55	88	2,132	3.10	0.23	0.04	12
T5-40		42	9.91	6,981	157	68	58	89	1,705	3.13	0.28	0.08	10
T5-41		44	7.53	6,676	141	70	53	102	1,699	2.49	0.26	0.02	8.81
T5-42		46	8.32	6,222	141	72	59	86	1,669	2.53	0.27	0.00	8.91
T5-43		48	7.73	6,645	142	67	57	92	1,786	2.93	0.48	0.63	12
T5-44		49	7.46	6,225	140	65	55	92	1,422	2.94	0.38	0.04	13

☐ Below QL above DL

Table C-4. Continued

Units (mg/kg)

Sample	Age	Depth	Al	Zn	Se	Sr	Mg	K	Mn	Ba	Ca*	Fe*	U
T5-1	1999	0.25	26,670	181	1.11	33	18,218	924	6,991	227	44,058	22,500	2.50
T5-2	1998	0.75	24,259	157	0.00	37	15,328	837	3,038	260	22,641	68,957	2.15
T5-3	1998	1.25	28,222	169	0.00	41	16,958	1,172	1,869	270	19,857	60,972	2.25
T5-4	1997	1.75	31,527	202	0.00	35	21,427	1,111	1,192	156	22,551	35,061	2.51
T5-5	1996	2.25	34,491	192	0.00	36	22,226	1,974	1,014	153	25,408	33,926	2.25
T5-6	1996	3	31,261	192	0.02	26	23,720	676	1,005	144	24,397	34,620	1.75
T5-7	1994	4	32,157	221	0.00	27	25,447	628	997	121	26,509	32,409	2.17
T5-8	1993	5	32,672	217	0.06	26	26,282	593	962	105	28,239	32,638	1.92
T5-9	1992	6	30,615	209	0.00	23	25,496	523	888	93	29,305	33,038	1.75
T5-10	1990	7	33,344	209	0.00	28	25,642	657	947	101	29,537	33,467	1.72
T5-11	1986	8	32,555	198	0.00	29	30,686	466	930	74	30,741	32,824	1.08
T5-12	1979	9	25,986	152	0.00	31	30,575	350	740	45	29,745	27,287	0.69
T5-13	1971	10	30,529	153	0.00	29	34,400	306	821	42	27,782	30,823	0.56
T5-14		11	29,483	141	0.00	26	30,803	264	729	38	33,153	28,337	0.55
T5-15		12	32,120	151	0.00	24	33,353	215	782	40	35,988	30,762	0.50
T5-16		13	29,695	129	0.00	37	29,046	212	703	38	39,158	28,558	0.46
T5-17		14	30,073	128	0.00	32	28,229	197	713	37	38,904	29,383	0.46
T5-18		15	28,420	143	0.00	36	29,531	230	660	38	41,098	27,602	0.61
T5-19		16	28,309	145	0.00	29	30,583	216	667	35	38,689	26,633	0.50
T5-20		17	29,942	139	0.00	23	28,020	228	758	52	37,816	30,614	0.46
T5-21		18	32,201	144	0.00	18	29,738	194	827	36	40,818	31,709	0.41
T5-22		19	37,946	178	0.00	24	35,083	291	1,061	43	40,334	39,846	0.54
T5-23		20	31,770	198	0.00	28	35,843	304	833	42	45,423	32,016	0.49
T5-24		21	35,120	185	0.00	24	33,948	253	926	42	38,065	36,395	0.46
T5-25		22	32,520	202	0.00	24	36,356	290	857	41	42,751	33,508	0.46
T5-26		23	39,242	177	0.00	26	35,965	259	1,133	42	38,327	42,465	0.46
T5-27		24	42,818	189	0.00	26	39,004	285	1,252	46	45,150	46,521	0.46
T5-28		25	37,882	151	0.00	26	32,894	242	968	37	44,875	37,247	0.39
T5-29		26	33,407	152	0.00	30	34,394	221	795	32	44,738	30,516	0.48
T5-30		27	38,368	155	0.00	27	37,080	219	998	34	41,151	38,205	0.43
T5-31		28	41,102	181	0.00	27	35,761	252	1,097	34	45,444	41,934	0.50
T5-32		29	45,113	152	0.00	21	37,221	224	1,272	37	48,762	47,010	0.42
T5-33		30	45,447	175	0.00	24	41,829	251	1,232	42	52,800	45,709	0.43
T5-34		31	39,306	180	0.00	29	38,037	253	1,009	37	46,319	37,955	0.43
T5-35		32	39,390	179	0.00	29	37,134	245	1,046	37	44,465	40,694	0.56
T5-36		34	39,251	173	0.00	23	42,159	217	1,014	35	44,940	38,994	0.40
T5-37		36	39,926	195	0.00	34	43,745	271	1,095	40	39,300	41,434	0.52
T5-38		37	38,764	222	0.00	32	44,099	295	1,070	42	41,893	42,811	0.55
T5-39		39	43,081	209	0.00	27	42,702	272	1,266	49	35,105	47,542	0.43
T5-40		42	44,706	218	0.00	27	46,673	289	1,298	44	44,672	49,529	0.43
T5-41		44	34,015	179	0.00	31	35,474	224	898	37	43,992	39,572	0.43
T5-42		46	27,400	248	0.00	31	35,816	321	773	43	41,599	41,793	0.47
T5-43		48	38,136	212	0.00	28	45,366	268	1,045	34	37,680	40,166	0.55
T5-44		49	37,123	204	0.00	29	43,169	294	1,016	42	36,740	38,015	0.53

 Below QL above DL

* Analyzed by AAS

Appendix D.

Table D-1. Results of ICP-HEX-MS, AAS analysis and ^{210}Pb dating of Gratiot Lake sediments.

Units (mg/kg)													
Sample	Age	Depth (cm)	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	Pb
Gratiot-1	1999	0.5	5.57	325	68.1	20.9	5.98	20.55	68.21	7.19	0.40	0.79	43.2
Gratiot-2	1998	1.0	4.81	268	62.0	14.6	4.69	13.4	55.5	5.89	0.44	0.75	34.8
Gratiot-3	1998	1.5	5.06	284	61.6	18.7	5.54	17.2	59.1	6.83	0.48	0.93	40.5
Gratiot-4	1997	2.0	5.26	312	64.6	20.2	6.26	19.7	62.6	6.41	0.48	0.93	47.9
Gratiot-5	1997	2.5	3.98	250	49.5	15.3	4.43	14.1	47.2	5.73	0.38	0.72	37.1
Gratiot-6	1996	3.0	5.41	377	64.3	20.6	6.52	20.3	62.5	6.56	0.44	0.89	48.7
Gratiot-7	1995	3.5	5.87	397	70.3	22.9	6.98	21.3	68.0	7.57	0.51	1.02	55.8
Gratiot-8	1994	4.0	5.72	389	66.1	23.7	7.08	22.3	66.5	6.97	0.46	1.00	53.9
Gratiot-9	1993	4.5	5.27	323	61.6	22.0	6.41	19.7	63.5	6.37	0.45	0.92	50.2
Gratiot-10	1992	5.0	5.62	354	64.1	29.3	6.35	20.1	64.7	6.43	0.44	0.94	51.1
Gratiot-11	1990	6.0	5.59	331	61.5	22.0	6.68	20.6	63.6	5.69	0.42	0.91	47.5
Gratiot-12	1987	7.0	5.45	360	62.1	19.9	6.53	20.1	61.3	6.04	0.43	1.00	48.1
Gratiot-13	1985	8.0	6.06	401	66.7	23.2	7.22	22.9	67.3	7.99	0.46	1.09	60.4
Gratiot-14	1982	9.0	5.87	420	69.6	21.2	7.27	23.1	67.4	8.54	0.45	1.07	67.4
Gratiot-15	1979	10.0	5.63	435	67.3	43.4	6.95	22.2	65.1	8.56	0.48	1.04	67.7
Gratiot-16	1975	11.0	5.87	417	69.0	26.3	7.34	23.3	68.5	9.49	0.49	1.06	71.5
Gratiot-17	1972	12.0	5.69	426	67.5	30.6	7.03	22.8	67.5	9.59	0.53	1.10	71.4
Gratiot-18	1968	13.0	5.89	470	70.9	22.5	7.29	22.8	69.1	10.06	0.51	1.10	72.1
Gratiot-19	1965	14.0	5.70	412	69.8	27.5	7.05	23.1	69.1	9.86	0.52	1.08	70.8
Gratiot-20	1961	15.0	6.55	426	71.2	23.2	7.86	26.4	74.1	11.93	0.51	1.27	70.5
Gratiot-21	1957	16.0	6.08	456	70.6	22.0	7.20	23.4	72.9	10.27	0.54	1.11	62.9
Gratiot-22	1954	17.0	5.87	443	67.4	23.2	6.95	22.8	67.4	9.64	0.52	1.12	58.5
Gratiot-23	1950	18.0	6.20	447	71.7	22.6	7.46	24.2	71.7	9.88	0.52	1.19	60.1
Gratiot-24	1946	19.0	5.79	418	68.3	20.5	6.78	22.5	67.0	9.84	0.51	1.09	53.6
Gratiot-25	1943	20.0	6.34	463	73.0	22.0	7.33	24.2	69.5	10.43	0.56	1.16	52.5
Gratiot-26	1939	21.0	5.72	429	67.0	21.6	6.70	22.2	63.3	8.95	0.47	1.09	47.8
Gratiot-27	1935	22.0	6.06	433	68.4	21.6	7.12	23.8	65.3	8.92	0.45	1.20	48.2
Gratiot-28	1932	23.0	7.16	497	74.8	29.1	8.04	25.8	66.9	9.19	0.48	1.21	46.8
Gratiot-29	1928	24.0	6.22	485	74.3	22.7	7.74	24.1	63.1	8.77	0.44	1.13	40.8
Gratiot-30	1924	25.0	6.15	498	74.2	29.3	7.63	24.4	62.4	8.72	0.47	1.15	38.2
Gratiot-31	1920	26.0	6.44	489	75.5	23.6	7.95	25.5	64.3	8.98	0.44	1.23	38.8
Gratiot-32	1916	27.0	6.11	468	73.8	22.8	7.03	22.9	60.3	7.88	0.42	1.09	35.3
Gratiot-33	1912	28.0	6.16	440	76.7	28.9	7.36	22.9	60.1	7.80	0.44	1.17	33.7
Gratiot-34	1909	29.0	6.37	452	79.5	21.0	7.25	22.9	55.5	7.60	0.49	1.05	29.4
Gratiot-35	1905	30.0	6.56	440	82.8	23.9	7.08	23.1	55.7	6.04	0.50	0.88	25.2
Gratiot-36	1901	31.0	6.76	413	82.1	28.0	6.92	23.8	51.0	3.89	0.48	0.66	16.6
Gratiot-37	1896	32.0	7.07	429	83.9	24.4	7.07	22.9	50.7	3.18	0.47	0.61	15.4
Gratiot-38	1892	33.0	7.08	446	83.2	23.3	7.06	22.9	49.8	2.63	0.46	0.60	11.9
Gratiot-39	1888	34.0	7.23	459	83.9	23.6	7.25	23.5	51.3	2.54	0.50	0.55	10.3
Gratiot-40	1883	35.0	6.79	345	84.1	22.1	6.98	23.2	49.1	2.37	0.43	0.56	9.91
Gratiot-41	1879	36.0	7.10	442	81.2	26.1	7.99	23.4	51.1	2.39	0.45	0.44	8.01
Gratiot-42	1873	37.0	6.86	526	75.7	23.5	8.09	24.0	49.0	2.03	0.38	0.57	6.46
Gratiot-43	1867	38.0	6.50	531	70.1	22.2	7.69	22.8	45.3	1.98	0.37	0.56	5.44
Gratiot-44	1854	40.0	7.45	509	75.6	26.3	8.25	26.2	52.2	2.14	0.39	0.55	6.65
Gratiot-45	1839	42.0	7.22	506	78.5	25.8	8.47	26.9	55.2	2.23	0.40	0.56	3.10
Gratiot-46	1823	44.0	7.93	477	97.3	27.1	9.07	29.1	66.9	2.79	0.48	0.64	3.09

Table D-1 Continued

Units (mg/kg)

Sample	Age	Depth (cm)	Al	Zn	Se	Sr	Mg	K	Mn	Ba	Ca*	Fe *	U
Gratiot-1	1999	0.5	12,555	91.7	4.07	15.6	4,408	1,332	716	76.4	2,645	19,476	0.86
Gratiot-2	1998	1.0	11,505	74.0	1.85	13.0	3,606	2,110	772	75.4	2,280	19,087	0.75
Gratiot-3	1998	1.5	12,290	81.6	2.48	12.8	4,078	2,090	617	77.5	2,236	17,520	0.83
Gratiot-4	1997	2.0	13,009	84.1	3.15	12.8	4,548	1,774	622	77.7	2,352	17,043	0.89
Gratiot-5	1997	2.5	10,569	64.4	1.86	10.0	3,445	1,735	476	57.4	1,921	13,459	0.74
Gratiot-6	1996	3.0	13,715	85.0	2.45	13.3	4,674	1,616	526	68.4	2,449	17,022	0.93
Gratiot-7	1995	3.5	14,636	92.2	2.27	14.3	4,928	1,543	516	70.2	2,596	17,660	0.99
Gratiot-8	1994	4.0	14,032	91.5	2.45	14.5	5,008	1,499	484	66.6	2,557	17,454	0.96
Gratiot-9	1993	4.5	13,381	83.3	3.31	13.7	4,714	1,549	463	62.2	2,657	16,588	0.90
Gratiot-10	1992	5.0	15,145	85.1	2.11	14.2	4,701	1,867	472	64.4	2,627	17,229	0.94
Gratiot-11	1990	6.0	14,128	84.8	2.84	14.3	4,820	1,983	470	67.6	2,630	16,137	0.93
Gratiot-12	1987	7.0	14,368	79.6	2.02	13.8	4,599	1,966	429	59.7	2,628	16,000	0.94
Gratiot-13	1985	8.0	15,050	99.0	2.30	15.7	5,208	1,709	440	66.4	2,628	17,219	1.03
Gratiot-14	1982	9.0	15,059	102	2.19	15.4	5,126	1,377	397	63.5	2,727	17,874	0.99
Gratiot-15	1979	10.0	15,240	98.0	1.88	15.5	5,005	1,324	368	60.7	2,625	17,255	1.00
Gratiot-16	1975	11.0	15,115	104	2.17	16.1	5,140	1,238	366	61.3	2,667	17,966	1.05
Gratiot-17	1972	12.0	14,782	101	1.89	15.5	5,039	1,161	346	58.5	2,707	18,071	1.02
Gratiot-18	1968	13.0	15,320	103	1.77	16.7	5,121	1,257	343	59.6	2,670	17,996	1.04
Gratiot-19	1965	14.0	15,343	108	1.85	15.9	5,130	1,134	336	58.6	2,701	17,972	1.02
Gratiot-20	1961	15.0	15,088	113	2.96	16.2	5,291	1,098	334	60.1	2,710	18,316	1.05
Gratiot-21	1957	16.0	15,296	101	2.10	16.4	5,367	1,219	330	59.2	2,678	17,485	1.03
Gratiot-22	1954	17.0	14,910	96.2	1.84	15.8	5,226	1,154	309	56.8	2,619	16,774	1.00
Gratiot-23	1950	18.0	15,163	117	2.12	16.5	5,579	1,147	327	59.9	2,813	17,505	1.06
Gratiot-24	1946	19.0	14,075	94.8	1.81	15.6	5,091	1,105	298	55.6	2,671	16,489	1.01
Gratiot-25	1943	20.0	15,429	99.7	1.90	17.1	5,444	1,186	312	58.8	2,793	17,645	1.07
Gratiot-26	1939	21.0	14,419	90.9	1.68	15.8	5,004	1,079	280	53.6	2,570	16,367	1.00
Gratiot-27	1935	22.0	14,470	95.0	1.66	16.6	5,277	1,047	291	55.7	2,702	15,862	1.03
Gratiot-28	1932	23.0	15,207	105	2.22	17.8	5,735	1,129	304	58.8	2,810	16,976	1.09
Gratiot-29	1928	24.0	15,011	92.8	1.74	17.3	5,619	1,040	293	56.2	2,889	16,707	1.07
Gratiot-30	1924	25.0	14,709	90.7	1.84	17.5	5,497	1,082	285	56.1	2,901	16,518	1.05
Gratiot-31	1920	26.0	14,472	94.0	1.74	18.1	5,608	1,047	289	56.7	2,920	16,762	1.09
Gratiot-32	1916	27.0	14,462	86.5	1.68	17.6	5,269	1,103	272	55.4	2,737	16,262	1.05
Gratiot-33	1912	28.0	14,332	84.3	1.55	17.4	5,363	994	278	54.6	2,807	15,975	1.07
Gratiot-34	1909	29.0	14,377	75.5	1.99	17.3	5,149	902	270	52.6	2,889	15,963	1.13
Gratiot-35	1905	30.0	14,255	69.5	2.00	18.3	5,164	921	277	54.6	2,954	14,900	1.16
Gratiot-36	1901	31.0	14,295	56.6	2.06	18.1	4,955	935	267	54.0	2,842	14,181	1.10
Gratiot-37	1896	32.0	14,912	55.4	1.63	19.3	5,133	946	275	56.7	2,921	13,831	1.10
Gratiot-38	1892	33.0	15,295	53.3	1.69	19.6	5,146	1,007	267	56.9	2,852	13,519	1.10
Gratiot-39	1888	34.0	15,230	55.1	1.63	20.1	5,231	1,003	271	57.4	2,891	13,786	1.11
Gratiot-40	1883	35.0	13,639	50.7	1.87	18.6	4,980	758	256	54.5	2,800	12,295	1.04
Gratiot-41	1879	36.0	14,335	61.2	2.12	20.9	5,404	635	253	54.6	2,920	13,182	1.08
Gratiot-42	1873	37.0	14,685	53.7	1.29	19.8	5,761	860	257	55.2	3,011	14,216	1.02
Gratiot-43	1867	38.0	14,604	55.6	1.37	19.5	5,465	837	244	52.7	2,913	13,904	0.96
Gratiot-44	1854	40.0	16,160	54.9	1.95	19.8	6,094	852	257	59.6	2,959	15,010	1.09
Gratiot-45	1839	42.0	15,908	52.6	1.89	19.5	6,077	855	247	56.8	2,877	15,229	1.11
Gratiot-46	1823	44.0	16,018	54.9	2.13	21.3	6,132	918	244	52.0	3,081	14,333	1.37

* Analyzed by AAS

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