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Sediment Toxicity from Copper in the Torch Lake (MI) Great Lakes Area of Concern

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ABSTRACT. *Torch Lake (MI) is a Federal Superfund Site and a Great Lakes Area of Concern. Torch Lake was impacted by over 200 million tons of copper rich mine tailings that were deposited in and along the shores of the lake. Twenty percent of the volume of the lake was displaced and the sediments have high concentrations of copper (1,000 mg/kg dry weight on average).*

Pore water from four sediment cores was analyzed at incremental depths for copper, total organic carbon, and toxicity using the Microtox® 90% Comparison Test. Cores were also analyzed for copper and organic matter in the dry sediments. Statistical evaluation of data indicated that the upper sediments compared to the deeper sediments: 1) were less toxic (49% light loss versus 68%); 2) contained less pore water copper (0.59 mg/L vs. 0.81 mg/L); 3) had a higher percent organic matter (2.2% vs. 1.6%); and, 4) had no difference in the solid phase copper concentrations.

Further evaluation of the sediment toxicity through direct comparison to copper chloride standards demonstrated that all pore water samples had reduced toxicity. The reduced toxicity of the pore water samples was reproduced by adding synthetic organic carbon to the copper chloride standards. These findings have implications for the EPA's No Action alternative for the sediments of Torch Lake. In making their recommendation, the EPA cites that preliminary data (believed to be obtained from nearby Portage Lake) shows that the sediments of Torch Lake are being covered and detoxified by natural sedimentation. However, total copper concentrations in the sediments from the south basin of Torch Lake do not indicate that the sediments are being covered and diluted by natural organic matter laden particles. Also, detoxification may be difficult to demonstrate without a baseline of sedimentation readings for comparison. In fact, solid phase copper concentrations may remain high due to scouring and erosion of surrounding stamp sand beaches or the steep side walls of the lake. This instability of particles has important implications for future restoration and monitoring activities in Torch Lake.

INDEX WORDS: *Sediment, toxicity, copper, Torch Lake, Lake Superior, Microtox®, porewater.*

INTRODUCTION

Torch Lake is part of the Keweenaw waterway in the Upper Peninsula of Michigan and connects to Lake Superior via Portage Lake as shown in Figure 1. Over a 100-year period from 1868 to 1968, the lake was inundated with over 200 million tons of tailings (stamp sands) from the copper industry. The stamp mills along the shores of Torch Lake used the lake water in their floatation process and deposited copper rich stamp sands into, and along the lake shore. It is estimated that the lake lost 20% of its volume to this disposal method (Leddy *et al.* 1986). Torch Lake was declared a Great Lakes Area of Concern in 1983 and a Federal Superfund Site by the United States Environmental Protection Agency (EPA) in 1984. The Torch Lake Superfund site encompasses a much larger area than just Torch Lake and includes all of Torch Lake, part of Portage Lake and the Keweenaw Waterway, and several individual sites on the Keweenaw Peninsula. Therefore, due to the immense size of the site, it was divided into three Operable Units (OU). This research addressed the lake sediments of the south basin of Torch Lake (part of OU II).

Torch Lake is oligotrophic. It has an area of 971 ha, a mean depth of 15.2 m, and a maximum depth of 37 m. The 82 square mile drainage basin is pri-

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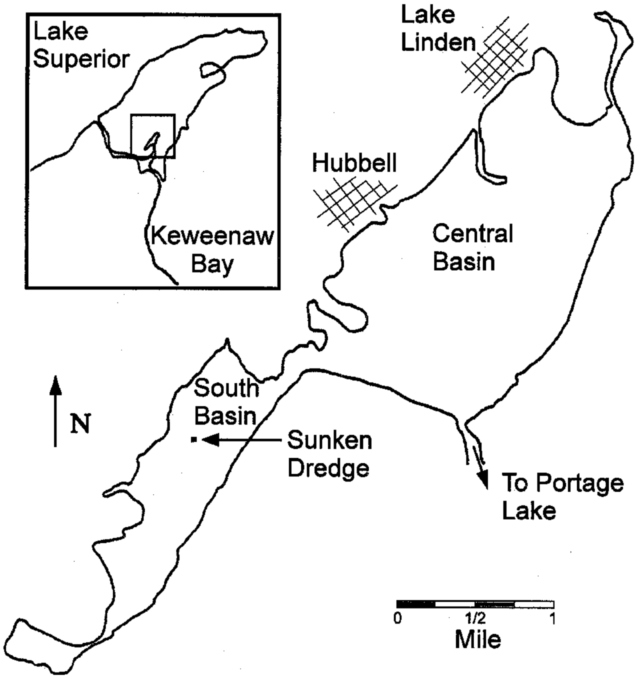

FIG. 1. Torch Lake (Upper Peninsula of MI) study site showing location of the sunken dredge in the south basin. Sample location was based on distance from the dredge. Torch Lake connects to Portage Lake and then the Keweenaw Waterway which cuts across the Keweenaw Peninsula.

marily forested and the lake has a residence time of one year (Sabol 1981). The sediments are grayish-purple in appearance and contain concentrations of total copper often exceeding 1,000 mg/L (Leddy *et al.* 1986). The sediments consist mainly of clay-sized stamp sand particles which are the smallest fractions remaining after the milling processes (Kerfoot *et al.* 1994).

Limited work has been done on the sediments of Torch Lake. Past studies have focused on risk to humans and fish because of concern about copper and floatation chemicals. Sediment analysis has been restricted largely to bulk chemical analysis on sediment samples retrieved using grab samplers. Preliminary studies measured copper in the pore water with depth in a sediment core. The pore water contained ten times more copper than the overlying water and there was no apparent pattern of pore water copper concentration with depth (Leddy *et al.* 1986, EPA 1992, Ellenberger *et al.* 1994). Published research on sediments was done in other parts of the Torch Lake Superfund Site. Research in nearby Portage Lake have documented an organic rich layer which is suspected to be capping and detoxifying the copper rich stamp sand sediments (Kerfoot *et al.* 1994). Research on sediments from the Keweenaw waterway, north of Torch Lake, determined copper toxicity to *Hyallela azteca, Chironomus tetans,* and *Lumbriculus variegatus* (Schubauer-Berigan *et al.* 1993, West *et al.* 1993) and suggested that pore water copper concentrations are a good estimate of toxicity to *H. azteca.*

The EPA has selected a remedy, *i.e.*, to cover stamp sand piles surrounding Torch Lake with soil and vegetation, but has selected the "No Action" alternative for Torch Lake OU II. The EPA stated that the only documented ecological impact was the effect on benthos due to high copper and other metal concentrations in the sediments and further noted that preliminary research showed natural processes were detoxifying and covering the sediments. However, this was never specifically confirmed in Torch Lake nor has research documenting such been published to the authors' knowledge.

High copper concentrations are a concern since copper is a known toxicant to several aquatic species. The ionic forms of copper (Cu^{2+} and $CuOH^{+}$) have been identified as the primary forms of copper controlling toxicity (Andrew *et al.* 1977, Verweij *et al.* 1989, Tubbing *et al.* 1994). Organic matter, sulfides, hydroxide, and hardness play key roles in controlling copper toxicity by decreasing the amount of the toxic form of copper through precipitation, sorption, or complexation (Di Toro *et al.* 1992, Jackson *et al.* 1992).

Copper toxicity is analyzed through the use of bio-assays, which for sediments are performed in one of three ways: bulk sediment, pore water, and elutriate testing (Burton and Scott 1992, Hill *et al.* 1993, Harkey *et al.* 1994). Bulk sediment testing is most closely related to *in situ* conditions (Giesy and Hoke 1989, Hill *et al.*1993). Pore water has been considered representative of the exposure pathway which effects many benthic organisms (Giesy and Hoke 1989, Burton and Scott 1992, Adams *et al.* 1992, Ankley *et al.* 1993). Elutriate testing has been linked to conditions of resuspension due to turbation or dredging (Giesy and Hoke 1989, Burton and Scott 1992). Traditionally, water column organisms, and less often benthic or epibenthic organisms, have been used for sediment toxicity testing (Ankley *et al.* 1993). Toxicity tests are typically expensive, time consuming, and data interpretation is often subjective (Retuna *et al.* 1989).

Recently, the Microtox® bioassay has become popular as a rapid, reproducible, and reliable bioassay that takes 30 minutes for test results and exposes samples to statistically significant numbers of organisms (Retuna *et al.* 1989, Ross 1992). Microtox® utilizes the bio- luminescent bacteria, *Photobacterium phosphoreum* (NRRL B-11177), which luminesce as a by- product of their metabolism. Toxicity is indicated by a decrease in metabolism which is measured as a decrease in luminescence. Microtox® was chosen for this research since it has been shown to be sensitive to copper, is simple to operate, can be used for small sample volumes, and utilizes statistically significant numbers of organisms.

Accordingly, the overall objective of this research was to determine if the copper rich sediments of Torch Lake are being detoxified by burial or dilution from natural sedimentation, which in turn would support the recommended management plan for Torch Lake. To accomplish this a Microtox® test protocol was chosen to evaluate the depth dependence of the toxicity found in the pore water.

METHODS

Study Site and Sampling Location

Torch Lake has two distinct settling basins. The central basin has high copper concentrations and an area near the town of Hubbell has been identified as a “hot spot” because of additional concentrations of metals (As, Cd, Cr, Pb). The basin to the south is smaller and contamination consists primarily of copper. Both basins are bathtub-shaped with steep sides and a deep settling basin. The south basin was chosen as the sampling site because within the scope of this research it was not feasible to deal with multiple toxicants.

Cores 1 through 3 were collected on 15 August 1994, approximately 200 yards NE of the sunken dredge (Fig. 1) and cores 4 and 5 were collected on 27 October 1994 approximately 300 yards east of the dredge. The five sediment cores were analyzed with depth for toxicity, pH, and dissolved copper in the pore water. The solid phase of these five cores was analyzed for copper and percent organic matter (dry weight). The pore water of cores 4 and 5 was analyzed for dissolved organic and inorganic carbon (alkalinity).

Equipment Cleaning

All glassware and polyethylene containers were washed in 50% HCl and rinsed repeatedly with distilled water followed by three rinses with Milli-Q deionized water. Borosilicate vials were washed, ethanol rinsed, Milli-Q rinsed, and heated for 1 hour at 500°C to remove organic contaminants.

Sample Collection and Analysis

A KB gravity corer with a 48-inch stainless steel barrel (2 inch diameter Phleger-type) was used to retrieve cores. The cores, contained in polyethylene sleeves, were transported back to the laboratory within 4 hours of retrieval and stored in the dark at 4°C until extruded (ASTM 1992). Cores 1, 2, and 4 were extruded within several days after collection while cores 3 and 5 were extruded 3 weeks after collection. The Microtox® assay was performed on the same day of extrusion and all other analyses were performed within allowable holding times. The cores were extruded and sliced in 2 cm sections to provide enough recoverable pore water for the battery of tests. Sections were placed in 50-mL polyethylene centrifuge tubes then centrifuged at 2,000 rpm and 4°C for 30 minutes. The 12 to 15 mL of pore water recovered from each section was then filtered through a 0.45 µm filter.

Three mL of pore water were stored in 30-mL polyethylene bottles at 4°C in the dark for the Microtox® assay. Another 3 mL were placed in borosilicate TOC vials, combined with 27 mL of Milli-Q water, and stored at 4°C in the dark for TOC on a Seives 800 TOC analyzer. The remaining 4 to 6 mL of pore water were acidified below a pH of 2 with 0.02 mL concentrated HNO_3 and stored in polyethylene bottles at room temperature. The acidified samples were analyzed for copper on a Perkin Elmer 3100 Atomic Absorption Spectrophotometer (AA) at a wavelength of 324 nm using flame technique (sensitivity 0.077 mg/L).

The solids remaining after centrifugation were dried at 65°C in aluminum drying dishes, crushed with a ceramic mortar and pestle, and redried to a constant weight. Copper was extracted by placing 1 g dried sediment in 15 mL aqua regia (3:3:1 $HCl:H_2O:HNO_3$) for 12 hours, shaking occasionally, heating to 90°C for 2 hours, centrifuging at 2,000 rpm for 30 minutes to remove solids, and bringing to a 50 mL total volume with Milli-Q water (Jackson *et al.* 1992). The extract was then prepared as a 1:10 dilution in order to be in the linear range of the AA. Volatile solids were measured by igniting 1 g of dry sediment at 500°C to determine the percent organic matter.

Microtox® 90% Comparison Test

The "Microtox® 90% Comparison Test" was performed using a 50T007T Standard Desktop Microtox® Toxicity Test System (Cusack 1995). Solid NaCl in the ratio of 0.2 g per 10 mL sample was used for osmotic adjustment of samples. Diluent (2% NaCl ultra-pure water) was used as a reference sample. The "90% Comparison Test" consists of exposing test samples and diluent (or reference sample) to photoluminescent bacteria for a predetermined exposure time (15 minutes for this research) and then determining the light loss in the test sample relative to the light loss in the reference sample. Unlike the Basic Test Protocol, this protocol does not provide an EC_{50}. Instead, by comparing samples and blanks, a percent light loss is calculated for each sample. The advantage of this test is that it is reproducible and can distinguish as low as a 3% light change in the test sample.

Modifications were made to the 90% Comparison Test. The test usually analyzes five identical test samples and compares the results to five reference samples. Due to the limited volume of pore water available, the test samples were analyzed in duplicate and compared to four reference samples. Also, since the test samples were analyzed in duplicates the spectrophotometer could accommodate five test samples in each run. The samples were randomly placed in the spectrophotometer to account for any variations in temperature within the instrument. Temperature variations are important if one is trying to measure a 3% light loss but not as critical with the 20% to 80% light loss measured in the pore water samples from Torch Lake.

Quality Assurance/Quality Control

Solids Digestion

Digestions in triplicate were performed on sediments taken from the same 2-cm sections. Following digestion, centrifugation, dilution, and analysis by AA, the concentration of copper (mg/kg dry wt) in the triplicate samples agreed within 8%.

AA Analysis

*E*ach sample was aspirated three times. The mean and standard deviation for the three aspirations was determined. A 1 mg/L copper standard was analyzed after every third to fifth sample to determine accuracy. The 1 mg/L standard was accurate within 3% of the concentration.

Microtox®

To verify that the reagent (*P. Phosphoreum*) was performing properly, a 100 mg/L $ZnSO_4$ standard was analyzed using the Microtox® Basic Test Protocol as recommended by Microbics. For a vial of reagent to be used, the $ZnSO_4$ had to have an EC_{50} between 5 and 12 mg/L. Duplicate samples analyzed using the "90% Comparison Test" as modified for this research, agreed within a 6% light loss.

Laboratory Standards

For comparison to toxicity of Torch Lake samples, $CuCl_2$ standards ranging in concentration from 0.1 to 2.0 mg/L Cu (pH 8.0 ± 0.3) were prepared by dissolving $CuCl_2$ in Milli- Q water and adjusting the pH with NaOH. Standards were filtered through 0.45 μm filters. The standards were then bioassayed using the 90% Comparison Test and total copper was measured by AA.

Later, $CuCl_2$ standards were prepared in the same manner (pH 8.0 ± 0.3) with either 3.4, 10, or 17 mg/L TOC added as Aldrich Humic Acid. First, humic acid standards were bio-assayed without copper added, to determine the light loss due to the humic acid alone. The light loss was found to be significant (20%) in the 17 mg/L TOC sample and therefore, all samples with copper and humic acid were compared to a control which contained the same concentration of humic acid as the samples. Therefore, the only variable being tested was the copper toxicity.

Statistical Analysis

The upper and lower sediments were averaged and their means were compared using a 95% confidence interval. Since dredging has made correlation of depth with time difficult, an arbitrary depth "X" was selected as the interface between upper and lower sediments. The interface was moved from X = 2 cm to X = 28 cm to determine the effect of the location of X on the mean concentrations of the upper and lower sediments. The upper sediment mean was calculated by averaging the 2 cm to the X cm depth intervals data points from all five cores and determining one mean. Then, the X + 2 cm to 30 cm data points were averaged together and the lower mean was determined.

TABLE 1. Compilation of data from the five cores retrieved from Torch Lake. TOC was only determined in cores 4 and 5.

Chemical parameters	n	mean	S.D.	high	low
pH (pore water)	74	8.2	0.22	8.6	7.2
Copper mg/L (pore water)	74	0.71	0.43	2.16	0.06
Copper mg/kg dry wt. (solid phase)	74	976	365	1,876	464
Organic matter % dry wt. (solid phase)	74	1.81	1.2	7.09	0.77
TOC mg/L (pore water)	28	39.7	11.7	67	16.0

TABLE 2. Average concentrations of parameters which were statistically different in the upper and lower sediments of Torch Lake. The solid phase copper concentration showed no statistical difference with depth.

Parameters which are statistically different with depth	Depth range over which the parameters are statistically different:	Average concentration in the upper sediment column-2 depths	Average concentration in the deeper sediment column-2 depths
Pore water copper	8–18 cm	0.59 ± 0.02 mg/L	0.81 ± 0.04 mg/L
Toxicity (% light loss)	4–20 cm	49 ± 3.9%	68 ± 2.8%
% organic matter (% VSS dry wt.)	8–14 cm	2.2 ± 0.09%	1.6 ± 0.05%

RESULTS

Analysis of Sediment Profiles

Table 1 lists the means and standard deviations for all pH, pore water copper, solid phase copper, solid phase organic matter, and pore water total carbon measurements made in the five cores. The five cores were first analyzed to determine if there were any similarities between individual cores. A mean was calculated for each individual core for each variable tested (toxicity, pore water copper, solid phase copper, solid phase copper). Next, using a t-test for comparison of means, with a 95% confidence interval, the means were compared to determine if they were statistically different. Following analysis, the means of the cores could not be shown to be statistically different with regards to all variables.

Next, the mean toxicity, pore water copper, solid phase copper, and solid phase organic matter of the upper and deeper sediments were compared. Since the five cores could not be shown to be statistically different, the data from all five cores were combined. For the solid phase copper concentrations, regardless of the depth chosen as the interface between the upper and lower sediments, the upper and lower sediments could not be shown to be statistically different (the 95% confidence interval was larger than the difference of the means).

Table 2 shows the mean concentration of pore water copper, toxicity, and % VSS in the upper and lower sediments. For toxicity, pore water copper, and organic matter a statistical difference was found between the means of the upper and lower sediments. However, a single depth (X) was not found which could justifiably be chosen as the optimal interface depth between the upper and lower regions. Instead, a range of depths for each variable which resulted in a statistical difference at a 95% confidence level between the upper and lower sediments could be chosen as the interface as listed in Column 2 of Table 2.

The means of the upper and lower sediments remained fairly constant over the range of depths at which the means were determined to be statistically different. To demonstrate how constant the mean concentrations for the upper and lower sediments remained, the means found for each interface depth

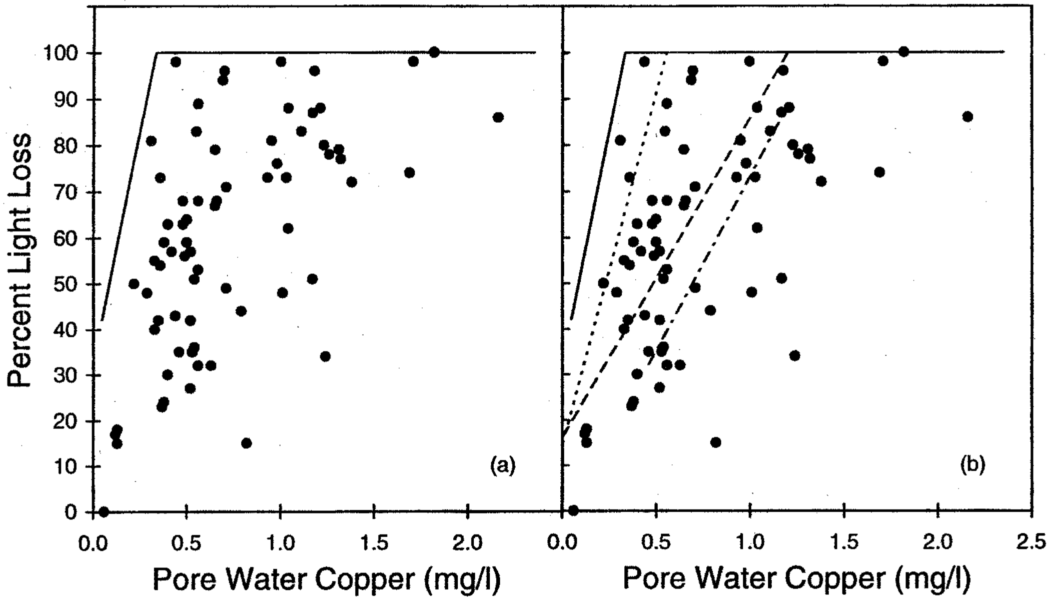

FIG. 2. The dependence of toxicity as measured by light loss in the sediment pore water of the south basin of Torch Lake on the total pore water copper concentration. [2a] Toxicity is compared to laboratory standards of similar copper concentrations showing reduction in toxicity observed in field samples. [2b] Effect of Aldrich humic acid on the toxicity of copper chloride standards. The lines are linear regressions of toxicity determined on samples with constant TOC (as Aldrich humic acid) and different copper concentrations. Field data (•); $CuCl_2$ chloride standards___; 3.4 mg/L TOC ------; 10 mg/L TOC _ _ _ _ ; 17 mg/L TOC___ _ ___.

were averaged and a mean and standard deviation were determined for the means. As shown in Table 2, regardless of where the interface (X) was placed over the depths showing statistical difference, the pore water copper concentration in the upper sediments was 0.59 ± 0.02 mg/L and in the lower sediments was 0.81 ± 0.04 mg/L. For toxicity the percent light loss in the upper and lower sediments was quite constant at 49% ± 3.9% and 68% ± 2.8%, respectively. For organic matter, the upper and lower sediments were 2.2% ± 0.09% and 1.6% ± 0.05%, respectively. This suggests that solid phase copper concentration is relatively constant with depth while the percent organic matter is greater in the upper levels of the sediments and toxicity and pore water copper are lower in the upper sediment levels.

Toxicity Dependence on Total Aqueous Copper

It is generally agreed that total metal concentrations in sediments are not an accurate determination of toxicity and some researchers have suggested that total dissolved copper in the pore water is a better determinant of toxicity (Ankley *et al.* 1993). Figure 2a shows the toxicity of the pore water relative to the dissolved copper for all field samples. As can be seen from the field samples, there is a general trend of increasing toxicity with increasing copper. However, aqueous copper alone cannot account for toxicity variations among samples since pore waters with the same aqueous copper concentration have strikingly different toxicities.

To better analyze toxicity variations between samples, copper chloride standards were prepared at concentrations of 0.1 mg/L to 2 mg/L copper, and bio-assayed using the Microtox® 90% Comparison Test. The percent light loss was calculated and graphed versus the aqueous copper concentration. Figure 2a shows that the standards have a linear increase of light loss (toxicity) with increasing dissolved copper concentrations until approximately 0.3 mg/L beyond which point the toxicity remains at 100% light loss. The field data lie below the standard line showing that there is measurable toxicity reduction in the pore water. From this and bulk chemical analysis on the sediments showing that copper was the primary contaminant as well as observations made by others in the Keweenaw waterway (Leddy *et al.*1986, West *et al.* 1993), it was concluded that the toxicity observed was primarily due to copper, and variations were due to the removal of ionic copper in solution. Microtox® profiles were constructed for samples containing 3.4 mg/L TOC, 10 mg/L TOC, and 17 mg/L TOC with varying copper chloride standard concentrations. As can be seen in Figure 2b, as the TOC increases, the toxicity response shifts to the right or regions of less toxicity for a given copper concentration.

DISCUSSION

Microtox

The modified Microtox 90% Comparison Test used in the test proved very successful at measuring differences in toxicity in the Torch Lake sediments. Ankley and Schubaruer-Berigan (1994) have determined that centrifugation is an acceptable method to recover pore water for toxicity testing; however, high speed centrifugation will provide a greater proportion of bioavailable metals and filtration during sample preparation can result in a loss of toxicity. None the less, the sample preparation used in this study combined with the Microtox 90% comparison test proved very sound for distinguishing differences in sediment toxicity with depth.

Sediment Copper Profiles

The solid phase copper concentrations which showed no statistical difference between the upper and lower sediments has implications for the recovery of the lake. Discharges of copper rich stamp sands to Torch Lake ended in 1968 with the close of the last stamp mill. However, over 25 years later, the concentration of copper in the sediments is still on average 1,000 mg/kg in the south basin and does not statistically change with depth. This indicates continual inputs of copper rich particles into the lake. These copper rich particles could be attributed to erosion from tailings on the shore (OU I) or scouring and remixing of particles from the shallow regions of the lake. In fact, it is estimated that erosion from all the exposed stamp sands located near the lake is 19 to 25 tons/acre/yr (Gary Aho, National Resources Conservation Service, 13 June 1997).

The EPA has recommended that the tailings along the shore be covered and revegetated to eliminate erosion. Covering the erosion prone stamp sands may decrease the mass percent of copper rich particles settling into the south basin. However, if the predominant source of copper is from the shallow regions of the lake, the revegetation may have an insignificant effect on the sediments. In addition, the south and central basins are shaped similarly and if the beach sands are covered, there still might be scouring from the deep side walls of the lake.

A constant solid phase copper concentration may provide a continual source of pore water copper and thereby, the potential for aqueous copper toxicity. However, the greatest amount of sediment copper is probably not readily released from the sediments. The pore water copper concentrations did not correlate to the solid phase copper concentrations which may be the result of limited solubility of the solid phase. In support of this theory is a study that determined only a limited amount of the copper (0.03 to 0.32 mg/L) could be leached from the tailings in and around Torch Lake with 0.01 M KNO_3 at a pH of 5.70 (Zahl 1990). However, Jeong *et al.* (1999) have recently determined that 70% of copper, from a limited number of Torch Lake sediment samples collected from the central basin, is labile and the largest copper reservoir consists primarily of copper carbonate and copper-organic complexes.

It is unlikely that copper precipitates could account for the low solubility in Zahl (1990). At a pH of 5.70, copper hydroxide has an estimated solubility of 500 mg/L, and copper carbonate has a solubility of about 250 mg/L. Sulfide precipitates would be stable as well. However, work in the Keweenaw waterway has shown the copper-to-AVS (acid volatile sulfide) ratio is generally greater than 100 meaning that sulfides are not present in abundant enough concentrations to control aqueous copper concentrations (Ankley *et al.* 1993).

Since chemical precipitation does not appear to control the solubility of the solid phase copper concentrations, other mechanisms should be examined. Complexation by organic matter was shown to be somewhat influential in that the only five samples with pore water copper less than 0.25 mg/L corresponded to the only five samples with solid phase organic matter greater than 4.3% dry weight (Cusack 1995). The results showing that the upper sediments had statistically higher organic matter and statistically lower aqueous copper concentrations, as compared to the lower sediments, supports the theory that solid phase organic matter may be reducing the concentration of copper in the pore water.

In addition to these results from Torch Lake, similar results were found on one core collected from Portage Lake (Cusack 1995). That sediment core had a relatively constant average solid phase copper concentration of 780 mg/kg down to a depth of 29 cm which is similar to the cores taken from Torch Lake. However, the Portage Lake core had an organic rich cap with greater than 10% organic matter down to 8 cm and greater than 6% organic matter down to 20 cm. This same organic rich cap in Portage Lake has been identified by others (Kerfoot *et al.* 1994). The pore water samples taken from the sections of the Portage Lake core had pore water copper concentrations less than 0.077 mg/L down to 10 cm and less than 0.20 mg/L down to 29 cm. Similar to samples taken from Torch Lake, samples with high solid phase organic matter had correspondingly low pore water copper concentrations.

Effect of Aldrich Humic Acid on Copper Toxicity

Vertical profiles of total organic carbon in the sediments were fairly constant with depth. However, constant organic carbon concentration profiles are not necessarily representative of constant complexation ability. Rather, to test the hypothesis that organic carbon was complexing copper, standards using Aldrich humic acid were prepared to determine if a synthetic humic acid would reduce toxicity similar to the observed field data.

As shown in Figure 2b, the addition of organic carbon produced a shift in copper toxicity similar to that found in the pore water samples taken from the sediments of Torch Lake. This suggests that the mechanism reducing toxicity in the pore water of Torch Lake may be complexation by dissolved organic matter. The concentrations of dissolved TOC in the sediment samples ranged from 16.1 to 67 mg/L C as compared to 3.4 to 17 mg/L C of Aldrich humic acid. Less Aldrich humic acid may have been necessary because it probably has a higher stability constant with copper than natural organic matter.

CONCLUSIONS

The Microtox® 90% Comparison Test worked well for measuring the toxicity found in Torch Lake sediments. Statistically, a difference between mean solid phase copper concentrations in the upper and lower sediments could not be determined when combining data from the five cores. However, there was a statistical difference between the mean of the upper and lower sediments with regard to toxicity (percent light loss), pore water copper, and percent organic matter. The upper sediments had a lower mean toxicity and pore water copper concentration and a higher mean percent organic matter.

The pore water samples showed toxicity reduction relative to laboratory standards at similar copper concentrations and pH. Upon examining aqueous chemistry in an attempt to determine the cause of the toxicity reduction, it was concluded that complexation by dissolved organic matter could best explain the variations observed in toxicity. In addition, copper toxicity reduction found in the pore water, was well simulated by the addition of Aldrich humic acid to the laboratory copper standards.

In regards to the management of Torch Lake, the EPA has chosen the No Action alternative for remediation and has stated that “some very preliminary research information seems to suggest that Torch Lake may be undergoing a recovery in those deeper areas which are not directly subject to the sands eroded from the shoreline (EPA 1994).” This study suggests a need for further research to determine to what extent the sediments of Torch Lake are recovering and to initially determine a sedimentation baseline for comparison after the surrounding tailings have been covered and revegetated.

Past work has noted a significant organic cap of 15 to 22 cm in Portage Lake (Kerfoot *et al.* 1994). However, such an organic cap was not found in any of the samples collected in this study from the south basin of Torch Lake. Even though both lakes were affected similarly by the mining industry, the higher productivity of Portage Lake (the lake is mesotrophic) and flushing by Lake Superior compared to the lower productivity of Torch Lake (the lake is oligotrophic) and 1 year residence time may account for a slower recovery in Torch Lake. Therefore, monitoring of both water bodies and data analysis should be separated with the knowledge that they are two distinct systems.

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