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STAMP SAND ALONG THE KEWEENAW SHORELINE: SOLID AND DISSOLVED COPPER & EFFECTS ON BIOTA

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By

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Author Contribution Statement

The data in this paper comes from a combination of previous work I have done for Charles Kerfoot on the Saving Buffalo Reef project, some data from Charles' previous students, and additional data from AEM and MDEQ. Credit is given in the references to published works where we compared our data to in the Discussion section.

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Abstract

Stamps sand refers to the regional colloquialism for the mine-tailing byproducts generated from copper (Cu) ore processing mills located in Michigan's Keweenaw Peninsula. In the Keweenaw region, copper extracted from basalt ores resulted in a legacy of 100's of millions of metric tonnes of stamp sand wastes, including 22.7 million metric tonnes at Gay, MI. Trace amounts of Cu persist in stamp sands and when leached have toxic enough concentrations to influence aquatic biota. To better understand stamp sands' properties, we ran experiments and compiled data about the solid and dissolved phases of Cu. Solid phase concentration of Cu was assumed to be 2863 mg/kg from MDEQ's previous studies of Gay's tailings pile and was compared to Cu concentration data from AEM and other published works. Dissolved Cu concentrations were determined through leaching experiments, measured in stamp sand ponds, and compared to other literature/published results. The physical properties of mean density (2.88g/cm^3), grain sizes, and mean percentage stamp sand were also determined. Both field and laboratory studies on the chronic effects of stamp sands were done using native *Daphnia* species. Acute toxicity for *Daphnia* was determined through an LD50 test for Cu (8.89 µg/L). Laboratory chronic toxicity studies tested local waters with low dissolved organic carbon (DOC) and neutral pH against those with high DOC and lower pH. These experiments demonstrate that lower pH and higher DOC may lead to higher rates of Cu leaching from stamp sands, compromising complexation of Cu. The chemistry of overlying water plays a significant role in the leaching of Cu from stamp sand deposits, and the particle size on dispersal and Cu concentration.

1 Introduction

1.1 Worldwide Copper Scarcity

Worldwide, copper (Cu) is the 25th most abundant element, which is about 0.01% of all naturally occurring elements, (Barberá et al., 2003). Usually found in natural isotopes of ^{63}Cu and ^{65}Cu (11 total known), Cu's native state tends to be in components of sulfides, oxides, and carbonates (Barberá et al., 2003). Otherwise, dissolved Cu naturally occurs in aquatic environments in low concentrations (Nriagu, 1979; Davis et al., 2000; Woody and O'Neal, 2012). Elevated aquatic Cu concentrations primarily occur near Cu mining and smelting facilities and in urbanized areas (Davis et al., 2000; Eisler, 2000). Aquatic environments are susceptible to Cu primarily as receptors of industrial mine tailings discharges, urban and industrial wastewater release, stormwater runoff, and industrial-era atmospheric deposition (Nriagu, 1979; Davis et al., 2000). Major lakes and reservoirs in the U.S. have concentrations of total Cu less than 10 µg/L (Lee and Helsel, 2005). Canadian waters have 1-8 µg/L Cu (ATSDR, 1990), whereas seawater concentrations generally exceed 1 µg/L (Ellingsen et al., 2007). Concentrations of dissolved Cu out in central Lake Superior are as low as 0.7 µg/L (Weiler, 1978). Because of natural ore deposits, background Cu in Lake Superior sediments can range from 21-75 mg/kg (Kerfoot et al., 1999). However, serious Cu enrichments in nearshore sediments are found primarily close to regions of mining activities and exceed 200 mg/kg, especially around the Keweenaw Peninsula (Kerfoot et al., 2002).

1.2 History of the Keweenaw

Keweenaw means Portage in the Ojibwe language (Anishinaabe), emphasizing safe passage through a natural waterway. The north end of the Keweenaw Waterway canal was opened in the late 1800s, creating a shipping route that no longer required ships to travel around the entire Keweenaw Peninsula. This also made a port of refuge from Lake Superior's harsh storms.

Historically, the indigenous people of the area traded Cu from the Keweenaw through the Mississippi River before European settlement. There are traces of Cu mining activity that date back to over 4,500 years ago within this area of indigenous people (Rakestraw, 1965). From 1850 to 1929, mining operations from east coast enterprises exploited the vast abundance of Cu in the Keweenaw, leading the region to become the second-largest Cu producer in the world (Bornhorst and Barron, 2011; Babcock and Spiroff, 1970). However, the effects of this industry left a legacy of mine tailings and several million tonnes of mine tailings, locally known as stamp sands, deposited inland and along several coastlines of the Keweenaw Peninsula (Kerfoot et al., 2009; 2012).

1.3 What are Stamp Sands?

Stamp sands are byproducts of crushed basalt rock from stamp mills, released during mining. The primary deposits are a series of billion-year-old lava flows, termed the Portage Lake Volcanic deposits. Original mining operations concentrated on removing large masses of Cu, known as barrel copper (Lankton, 1993), whereas later operations shifted to extracting Cu through stamping ore. After stamping, particles were sorted by water-borne gravity separation, using jigs and tables (Benedict, 1955). The denser particles formed a concentrate shipped off to smelters, whereas the lighter fractions, often around 98% of the mass, were sluiced out of the mill into rivers or along lake shorelines. Unfortunately, the early mill extraction was not very efficient, as around 25% of the Cu was lost in the tailings (Benedict, 1955; Babcock and Spiroff, 1970). Thus, stamp sands also became a contaminant along beaches and in water, as they contained high concentrations of Cu plus a suite of accessory metals, including aluminum, arsenic, silver, chromium, cobalt, lead, manganese, nickel, and zinc (Kerfoot and Robbins, 1999).

Under natural light conditions (Figure 1.1), the various grains in stamp sand deposits appear very heterogeneous and colorful, because of various gangue minerals. These include calcite, epidote, chlorite, prehnite, pumpellyite, microcline, and K-feldspar (Bornhorst et al., 1988). However, once you step back, the fine-grain sands appear to be dark gray to blackish beach sand deposit (Figure 1.1; Figure 1.2). When observed using light microscopy, most particles appear dark or translucent under transmitted light, whereas they vary in dark reds, greens, oranges, grays, and black under reflected light (Figure 1.3). We expect stamp sands, much like basalts, are composed of approximately 50% SiO_2 (Philpotts and Ague, 2009). After basalts are sorted through the stamping process resulting in the byproduct of stamp sands, heavy metals such as lead along with Al, As, Au, Ag, Ba, Ca, Co, Cr, Cu, Fe, Hg, K, Mn, Na, and Zn are still detectable as some of the components (Kerfoot and Robbins, 1999).

The stamp mills in the Keweenaw released millions of tonnes of stamp sands along the coastlines of Lake Superior and inland lakes and rivers. There are several notable areas in the Keweenaw where amounts of stamp sands are quantified. For example, the Mohawk and Wolverine Mills in Gay released 22.7 million metric tonnes of stamp sands, whereas the Champion Mill along with four other Mills in the Freda and Redridge area accumulatively released around 45.5 million metric tonnes. Around Portage Lake in Houghton/Hancock, a total of eleven mills released 10.1 million metric tonnes; while six mills at Torch Lake released 178.5 million metric tonnes (Kerfoot, et al., 1994; 2019; Kerfoot and Robbins 1999). Of the stamp sands released, much of the coarse material ended up as beach deposits or sand bars, while the copper-enriched slime clays (7-14% of discharge; Babcock and Spiroff 1970; Lankton and Hyde, 1982) ended up dispersed much further from their original dumping sites, depositing across deep water sediments in lakes and along deeper underwater troughs in Keweenaw Bay (Kerfoot and Robbins 1999). Stamp sands were moved along shorelines by wave and current action. This is especially the case as stamp sands from the original pile in Gay, MI, eroded and moved southwestward to encroach onto Buffalo Reef.

1.4 Saving Buffalo Reef Initiative

Buffalo Reef is a cobblestone reef off the shore of Gay in Grand (Big) Traverse Bay, MI. A LiDAR bathymetric plot from 2010 provides the underwater details of Buffalo Reef (Figure 1.4). The reef is a major spawning ground for lake trout and whitefish, accounting for 32% of commercial fishing in Keweenaw Bay, and 22% caught along the southern Lake Superior shoreline (Chiriboga and Mattes, 2008; Kerfoot et al., 2019a). The coastal bay is both environmentally and economically important due to historic commercial and recreational fishing. Fisheries have been showing recent declines in lake whitefish populations in Buffalo Reef through surveys (Chiriboga and Mattes, 2008). Encroaching stamp sands from the eroding Gay Pile are threatening the mid-bay reef. Stamp sands have migrated down-drift from the pile and filled up the northern stretches of an ancient riverbed (termed the Trough). The stamp sands are now moving out of the filled the Trough into cobble beds on the northeastern edge of Buffalo Reef. Stamp sand encroachment from the Trough and nearby shorelines is suspected to correlate with the declining whitefish population (Chiriboga and Mattes, 2008).

The reef is shown to be already 35% covered by stamp sands, using 2016 LiDAR/MSS images (Kerfoot et al., 2019). Within the next ten years, the Army Corps of Engineering hydrodynamic models predict cover will increase to 60% (Hayter et al., 2015). The impending risk to lake trout and whitefish populations and consequent economic loss have led to the formation of the Buffalo Reef Task Force. The task force intends to investigate the environmental damages caused by stamp sands and to orchestrate the removal of stamp sands. Environmental Protection Agency's (EPA) Great Lakes National Program Office, Michigan Department of Natural Resources (MDNR), the Army Corps of Engineering (Operations, Detroit Office), and the Keweenaw Bay Indian Community (KBIC) have collectively provided around $14M in funding since 2017 for remediation and planning efforts (see MDNR Saving Buffalo Reef Website, 2022). Michigan Technological University (MTU), the Great Lakes Indian Fish and Wildlife Commission (GLIFWC), the U.S. Army Corps ERDC-EL lab at Vicksburg, MS, and the U.S Geological Survey (USGS) have conducted research activities at the site.

Here the concentrations of Cu in the shoreline beach deposits, underwater sediments, and interstitial and standing waters are discussed relative to ecotoxicology. In the ecosystem, we determine and discuss the spatial concentrations of Cu in the dispersing stamp sands, known as solid phase Cu. Then we look at Cu leaching from stamp sands into the water, the dissolved phase, and its potential effects on organisms. Initial EPA studies of copper-laden sediments around the Keweenaw suggest that dissolved Cu is central to local organism toxicity (Malueg et al., 1984; Ankley et al., 1993).

1.5 AEM Surveys: Determining Copper Concentrations in Beach Stamp Sands and Underwater Sediments

In 2021, Dr. Kerfoot and I were involved in an attempt to determine the abundance of Cu in both beach deposits and underwater sediments. Using aerial surveys, LiDAR over-flights, and bathymetric maps, the volume of stamp sands along the pile and beach was previously estimated. However, only the surface area of stamp sands had been estimated underwater using Multispectral sensors (MSS) color techniques (Kerfoot et al., 2012; Yousef et al., 2013) and surface Ponar sediment samples. Sediment core profiles would determine the extent of underwater deposits, providing a mass balance for the underwater portion of the Bay. The Army Corps conducted new surface and sediment core sampling in 2021 along the beach and underwater to determine the extent of bay Cu contamination around Buffalo Reef. Sediment and core sampling were conducted by AEM (Advanced Environmental Management Group; Environmental Services, Plymouth, MI; under Contract With USACE). Sediment subsamples from Ponar surveys and core slices were shipped to MTU for percentage stamp sand (%SS) grain counts

(Kerfoot et al., 2021), while replicate subsamples were sent for Cu concentration determinations. The separate data sets allowed direct comparisons of our %SS values against corresponding solid phase Cu determinations. Our method of determining %SS grain counts in sand mixtures from particles under transmitted light, and its checks, is discussed further in the Methods section.

1.6 *Daphnia's* use As an Indicator Organism

Daphnia spp., also known as Water Fleas, are a common zooplankton genus in freshwater ecosystems like Lake Superior. In Lake Superior around the Keweenaw Peninsula, the common native species found are *Daphnia pulex*, *D. retrocurva*, *D. dentifera* (formerly *rosea*)*,* and *D. mendotae* (Kerfoot et al., 1999). Hence, when referring to native *Daphnia*, it is in reference to these four native species. Due to their abundance, sensitivity to ecosystem changes, and ease of culturing in laboratories, they are the standard aquatic invertebrate for aquatic toxicity testing (Siciliano et al., 2015). There has also been expressed interest in the chemical toxicological effects of stamp sands on the benthos (Kerfoot et al., 2021). The effects of stamp sands on coastal stamp sand ponds and nearby native wetland ponds were checked in preliminary 1990s experiments with native *Daphnia* species (Kerfoot et al., 1999; Lytle, 1999). Our experiments with pond waters can be cross-compared with those earlier results, to see if circumstances have changed. Insight into benthic and water column biota potentially relates to the issue of declining whitefish populations, as population density declines of benthic species and zooplankton can influence food available to young of the year (YOY) and whitefish populations (Müller, Breitenstein and Bia, 2007). For this reason, we used the same native *Daphnia* species (Kerfoot et al., 1999) to evaluate the extent to which Cu can leach from stamp sand deposits and if toxic responses can be observed.

1.7 Experimental Purpose and Hypotheses

Using laboratory experiments with *Daphnia*, and data from AEM, we characterize both the solid phase and dissolved phase of Cu in and around stamp sands. The solid phase part of our research determines the abundance of Cu in stamp sand deposits across the bay, from above-water beach sands to underwater sediments. Although our earlier investigations attempted to predict Cu concentrations using %SS in beach sands and sediments, a large number of direct determinations in data from the AEM study allowed further, more direct, cross-comparisons. We checked our indirect predictions of Cu concentration from %SS calculations, against the directly determined Cu concentrations. Additionally, a leaching study was conducted using agitated stamp sand in the laboratory, to determine the extent of Cu release from the solid phase into the surrounding waters. We then compared the correlations and calculations with previously mapped spatial 1) Percentages of Stamp Sand, 2) Solid phase Cu concentrations in sediments (mostly predicted), and 3) Effects on bay benthic organisms.

To address the toxicity of stamp sands in Keweenaw Peninsula freshwater ecosystems, our main experiments used native *Daphnia* as an *in situ* indicator species. First, we conducted incubation experiments with native *Daphnia* in stamp sand coastal ponds. A stamp sands agitation experiment quantified the extent to which Cu can leach from stamp sands and into surface waters of varying chemical composition. We also compared dissolved Cu in various beach stamp sand ponds with leached concentrations.

In the laboratory, we determined a standard acute toxicity tests to determine how sensitive *Daphnia* were to observed ranges of dissolved Cu in the ponds, interstitial (groundwater), and stream waters. Recognizing the importance of dissolved organic carbon (DOC) and humic substances in normally reducing Cu toxicity in natural environments, we then conducted more complex chronic toxicity tests, using the same experimental design as in the field tests, but in the lab with different kinds of local waters. In these tests, multiple water samples were collected. This includes tannin-stained waters from a wetland riparian zone off the side of Coal Dock Road, water upstream from the boat launch in Traverse River, water from Portage Lake, and Lake Superior water near the Traverse River seawall and from Bete Grise nature preserve. These areas were chosen to: 1) represent a pond surrounded by, and subjected to seepage from, beach stamp sands, 2) shallow clear coastal waters from Lake Superior with low DOC, and 3) tannin-stained waters (high DOC, low pH) from the river and wetland swales. The tannin-stained waters contain humic substances and were chosen as they have the potential to chelate Cu, thereby binding Cu^{2+} ions in a form unable to interact with aquatic biota as easily. However, evidence shows that low-pH tannin-stained groundwater which moves through stamp sands may also mobilize metals and lead to higher dissolved concentrations in ponds (Jeong, Urban, and Green, 1999). In other words, local interactions with humic substances may have contradictory or opposite effects. Our long-term chronic experiments should aid in clarifying the extent of positive and negative effects of DOC on Cu availability and potential toxicity. The lab chronic experiment characterized and used freshwater from each site and stamp sands at different 10% concentration increments (ratio of stamp sands to natural sands, to simulate both beach and underwater particle mixtures), in a survival and reproduction toxicity test on native *Daphnia*. We predicted survival of *Daphnia* would differ based on the relative abundance of stamp sand and the water source used. We also expected that increased DOC (humic substances) concentrations, and introduced food (as TOC) would lower observed toxic effects.

Figure 1.1. Close-up (A) and wide angle (B) images of Gay, MI stamp sand deposits

Images were taken under natural light conditions. The lens cap in (B) has a diameter of 56 mm.

Figure 1.2. Image of stamp sands from Gay, MI beach overtopping seawall

At Traverse River, Grand Traverse Bay, Lake Superior, MI. Date of photograph May 11, 2020.

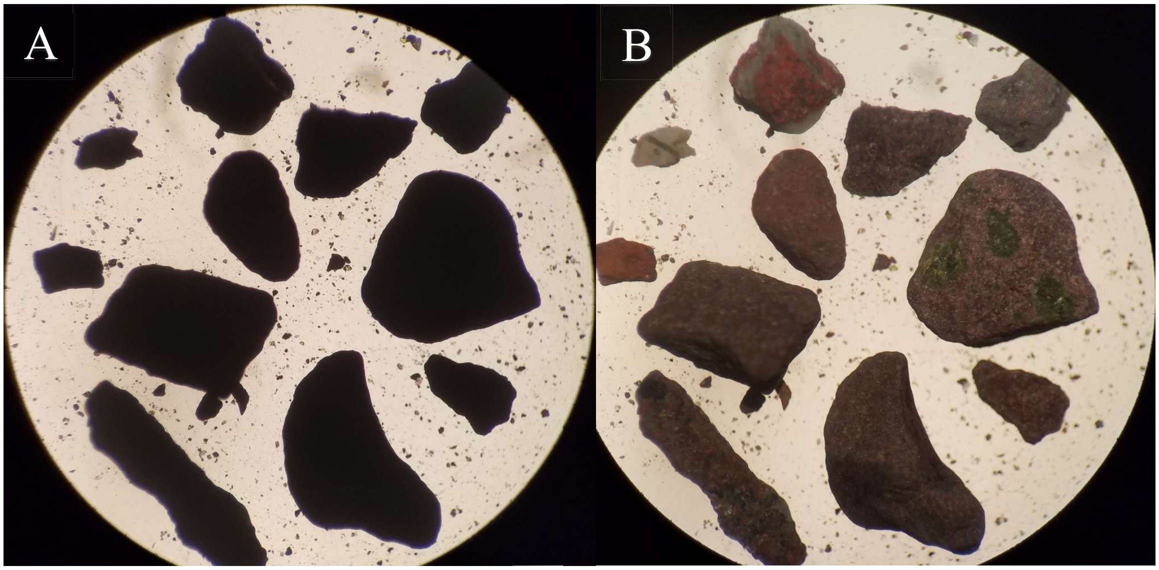

Figure 1.3. Stamp sand under 40x magnification

In the laboratory, the rough, irregular particle sizes of stamped basalt are evident. Both images are stamp sands photographed under a binocular microscope at around 40x. In the photos the sizes of stamp sands range from 200-2000 µm. Picture (A) is taken under transmitted light, whereas (B) is under reflected light and shows more colors.

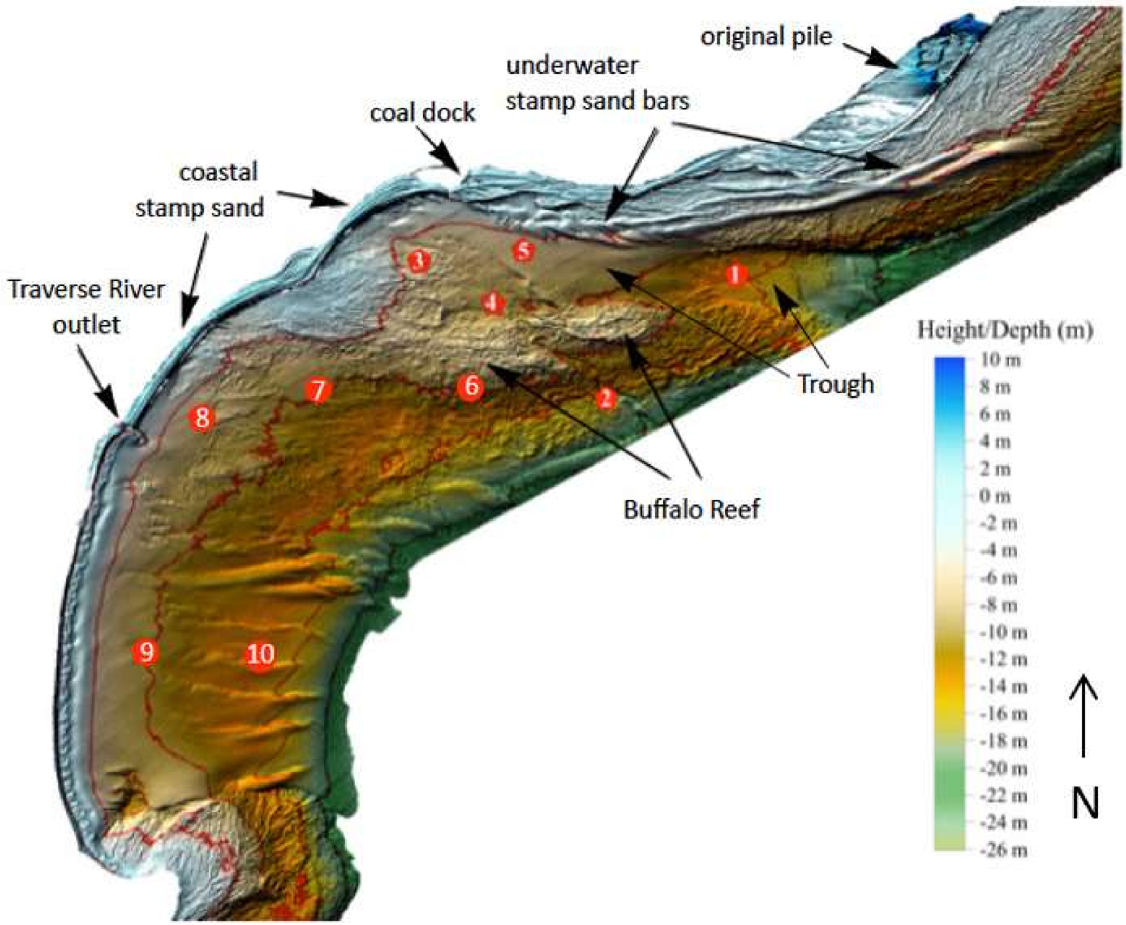

Figure 1.4. NOAA 2010 LiDAR DEM of Grand (Big) Traverse Bay

This map is color-coded by elevation and water depth (right depth scale). It is off the coast near Gay, MI. Red horizontal contour lines are at 5m depth intervals (modified from Kerfoot et al., 2014). Notice the position of the Gay tailings pile, migrating underwater stamp sand bars dropping into an ancient river channel (the Trough; at locations #1, and #5). Stamp sands have migrated as a beach deposit to the Traverse River Seawall (#8) and have moved into cobble/boulder fields along the eastern (#3, #4) and western (#6, #7) edges of Buffalo Reef. The southern bay has a natural white (quartz grain) beach with natural sand (#9, #10) moving into deeper waters.

2 Data Collection and Methods

2.1 Archimedes Experiment: Determining Stamp Sand Specific Gravity & Density

To characterize the specific gravity and density of the different sands used, an Archimedes-style test was performed. Specific gravity is defined as the density of a substance relative to a given standard substance, usually water. One cm^3 of water under standard temperature and pressure (1 atm, 298 K) is defined as one gram. The setup used a 2000 mL graduated cylinder filled with 1000 mL of distilled water. For both the natural sands and stamp sands, ten trials were done, and the average density for all ten was calculated to obtain the average density. The samples were air dried on the benchtop until there was no visible moisture and weighed before each trial. Additionally, clay and silt size particles (<63 μm) were removed from the samples by sieving. Samples were weighted between 200 to 400 grams to demonstrate the independence between sample mass and specific gravity. With the 2000 mL graduated cylinder used, as it was enough sample to visualize the water displaced, but not too much to cause splashing and loss of sediment samples or water in the graduated cylinder. A total of 1000 mL of distilled water was put into the 2000 mL graduated cylinder, along with the known mass of sediments and the displacement of the water was recorded. Using known mass and displacement, the density (g/cm^3) of particles could be calculated (Table 3.1).

For reference, natural sands are primarily mixtures of quartz (eroding from the Jacobsville Sandstone), whereas stamp sands are basalt. The mean densities of both pure quartz (2.65 g/cm^3) and pure basalt (2.9 g/cm^3) (Hamilton, 1978; Stolper and Walker, 1980) were used as a standard to check the results obtained for the Archimedes experiment. An additional note, the specific gravity of pure Cu is around 8.95 g/cm^3, although ores generally only consist of 1-2% Cu. This means the expected difference in specific gravity between natural sand and stamp sand (basalt) is around 9%, which is a relatively small value. The use of specific gravity to determine %SS in a mixed sample is one option to determine the percentage of stamp sand (Kerfoot et al., 2017), but because of the relatively slight differences, we devised a different and more precise method using grain counts.

2.2 Percentage Stamp Sand (%SS) Determinations from Microscopic Grain Counts

2.2.1 Microscopic Determination of %SS In Sand Mixtures

As mentioned earlier, the two major sand types in the bay come from different sources. The crushed Portage Lake Volcanic rock, locally known as stamp sands, are basalts (K, Fe, Mg plagioclase silicates; augite, and minor olivine), whereas the coastal bedrock (Jacobsville Sandstone) and glacial till produces rounded quartz sands that make up the white beach sands. Under a microscope (Figure 2.1; Olympus LMS225R, 40-80X), particle grains from the Ponar samplings could be separated into crushed opaque (dark) basalt versus rounded, transparent quartz grain components, allowing calculation of %SS particles in particle (sand) mixtures. Percentage stamp sand values were based on means of randomly selected subsamples, with 3-4 replicate counts, around 300 total grains in each sub-count. Around 300 gains were used to lower variance between subsamples, while still being practical to count under a microscope with assistance from a hand held tally counter. Standard deviations and errors were calculated for individual samples and the means were used to calculate confidence intervals for typical counts (Figure 2.2).

Technically, mixed grain counts follow a binomial distribution, where there is an inverse relationship between the coefficient of variation (CV = SD/mean) and the mean %SS (Figure 2.2). That is, from Figure 2.2, if the mean %SS is high (>50%), the coefficient of variation (CV = SD/mean) is relatively low (3.1%, n = 12), but if mean %SS is low (<10%), the value could be much higher (mean = 25.3%, n = 30).

The inadvertent inclusion (misidentification) of natural manganese sands (Johnson, 1984), which are present, but scarce, could also influence low-end calculations, but generally to only a small extent. We found that under the microscope, reflected light could be used to distinguish natural manganese sand (gray metallic color) from basalt particles (dark brown, greenish). Values in direct determinations show some Mn corrections are important for beach samples but rather low in underwater samples (underwater samples averaged only 1.8% Mn grains). See Appendix Table A.2, obtained from Kerfoot et al. 2021 supplementary tables, which gives examples of Mn counts and corrections.

2.2.2 Determining Particle Sizes

For selected standard Ponar samples, we sieved sediments for various particle size classes in the second set of measurements. Six Wildco Stainless Steel Sieves of 4000 µm (#5 Mesh), 2000 µm (#10 Mesh), 500 µm (#35 Mesh), 250 µm (#60 Mesh), 125 µm (#120 Mesh), and 63 µm (#230 Mesh) were used on a Cenco-Meinzer Sieve Shaker

Table (Central Scientific), or, after 2022 sampling, a Gilson 8-inch Sieve Shaker w/ Mechanical Timer (115V, 60Hz) model SS-15 to separate particles into specific size classes. See Appendix Table A.3 for locations and particle size distributions.

Another method we did for determining particle size was direct diameter measurements of particles of sand under the microscope. The microscope's reticule (scale) tick marks at 40x magnification were calibrated using a stage micrometer graduated scale which was subdivided into units of one-tenth millimeter in length. The distance from tick mark to tick mark at 40x magnification for the microscope (Olympus LMS225R, 40-80X) is 25.64 μm. Only particle sizes two tick marks (51.28 μm) or higher were measured as these smaller clay and silt particles were not easily identifiable as stamp sand or natural quartz sand. Notice only five samples with determined %SS and mean particle size (μm) were used due to how time consuming this method is compared to sieving (20 minutes compared to 6 hours per sample). Two samples were beach samples from the main tailings pile, and three were underwater samples with %SS mixtures around 50% throughout the Grand Traverse Bay area. This was done under transmitted light in a petri dish to distinguish the natural quartz particles from stamp sand particles. Much like the %SS determinations, a subsample was used, but it contained about 600 particles of half natural quartz and half stamp sands. In the beach samples with higher %SS, sorting was done under the microscope in the petri dish until there was about 300 particles of stamp sands and 300 particles of natural quartz. These amounts were chosen to mirror what the subsamples appear like in the %SS determinations.

2.2.3 Observed vs. Predicted Copper Concentrations in Gay Stamp Sand Bay Deposits and Dispersal Samples

There were previous studies done by MDNR on the stamp sand tailings pile in Gay where they tested for Cu concentrations from multiple stamp sand samples, which led to them determining the mean concentration of Cu in the tailings pile as 0.2863 % Cu, or 2863 mg/kg Cu (MDEQ, 2006). Using this as a standard, we can predict Cu concentration in any mixed particle sample, if we know the %SS. For example, a 50%SS mixture would have a 1,432 mg/kg Cu concentration, a 25%SS mixture would have a 716 mg/kg, and a 10% would be 286 mg/kg. Notice, even the 10% exceeds EPA and Michigan probable effects levels (around 149 mg/kg; MacDonald et. al. 2000). The MDEQ 2006 value of 2863 mg/kg for Cu in stamp sands was used initially throughout our project to predict Cu concentrations at any given %SS value, but with checks.

To check the %SS predicted Cu concentrations directly against observed Cu concentration, we determined Cu concentrations on several Ponar samples, then constructed a calibration curve of predicted Cu concentration against observed Cu concentration (Kerfoot et al., 2019; 2021). For direct Cu determinations, Ponar sediments were digested at MTU in a microwave (CEM MDS-2100) using EPA method 3051A. Solutions were shipped to White Water Associates Laboratory for final analysis. Cu was measured using a Perkin-Elmer model 3100 spectrophotometer. Digestion efficiencies were verified using NIST standard reference material Buffalo River Sediments (SRM 2704), and instrument calibration was checked using the Plasma-Pure standard from Leeman Labs, Inc. Digestion efficiencies averaged 104%, and the calibration standard was, on average, measured as 101% of the certified value. Despite minor deviations at both the high and low ends of the index, there was a good overall fit between %SS predicted Cu concentration and analytically measured Cu concentrations (see regression, $R^2 = 0.911$, Kerfoot et al., 2019b).

During the summer of 2021, we had the opportunity to cooperate with the Army Corps on the AEM Project. We conducted an independent check on our microscope %SS method to estimate Cu concentrations from %SS composition with the sediment samples collected from both underwater and on shore deposits in Grand (Big) Traverse Bay. These sediment samples had their Cu concentration determined at Trace Analytical Laboratories in Muskegon, MI. Additionally, the Cu concentration data of the AEM Project provides a check for the MDEQ predicted Cu concentration value (2863 mg/kg) in the main tailings pile near Gay's shoreline, and also allows us to see how that compares to stamp sands in other parts of the by and further south the shoreline up to the Traverse River seawall.

2.3 AEM Solid Phase Analysis

The AEM Project allowed a direct comparison of Cu concentrations in beach stamp sands and bay sediments that had our %SS measurements. The set includes Ponar and core samples from three different locations: deep water (DW; 7 samples), over water (OW; 52 samples), and on land (OL, beach; 104 samples). The data for sample depths was not provided, but from comparing the NOAA 2010 LiDAR map to our map of Cu concentration of Grand Traverse Bay using AEM data (Figure 1.3 compared to Figure 3.5), we know the deep water samples are deeper than 20 meters and are around 1 mile from the shoreline. The over water samples depths range from 1 meter to 20 meters, and are up to a mile from shoreline. Normally we would not use our technique on deep-water samples because they are dominated by silt and clay-sized particles (62.5 µm - 0.98 µm; Wentworth, 1922), so some grain sieving was necessary to remove sand-size particles for counting under the microscope. The over water samples were from the shelf region, generally dominated by medium to fine sand-sized particles (0.5 mm – 125 µm; Wentworth, 1922). The on land sites were all beach deposits with medium sands to fine gravel (0.25 mm - 8 mm; Wentworth, 1922). The 164 samples are dominated by beach samples (see Appendix Table A.1), largely because beach cores were sliced into sections, moving from top stamp sands into original quartz sand bottom deposits.

With the AEM Project, when we started comparing our %SS values with the Cu concentration, there were complications. One issue with the tabulated data from AEM Cu determinations was the great variability in Cu concentrations beyond 50%SS mixtures, especially in the beach core studies. To better handle the variation, we considered the data sets as independent runs and dealt with the scatter by a variety of conventional statistical methods. Due to heteroskedasticity, fitting a regression line to the entire set was not appropriate, since the variance around a regression line increased with %SS and Cu Concentration plots (especially >50% SS), leading to inappropriate regression fits. These heteroskedastic effects could be reduced by a variety of statistical methods: 1) log transforming the data, 2) plotting grand mean values of Cu concentrations at intervals of % SS, or 3) looking at only a portion of the set (lower end, 0-50% SS) where there is less heteroskedasticity. We utilized options 2 and 3. In addition, a table was constructed which summarized the previous %SS vs Cu determinations (Kerfoot et al. 2021), and the three various AEM regression equation intercepts (Table 3.2). From that table, we were able to cross-compare the regressions with one another, and with the previous Cu concentration value for the Gay tailings pile (2863 mg/kg; MDEQ, 2006).

2.4 Leaching Studies of Stamp Sands with Various Water Samples

The water samples collected for the leaching studies, acute toxicity studies, and chronic studies are of waters which represent a local inland lake water, river water, riparian zone water, and Lake Superior water. Each water sample varied in DOC (humic) concentrations. The inland lake water came from Portage Lake at Houghton, MI, and was taken at 47.12061667 ºN, -88.54543333 ºW. The river water came from Traverse River at Gay, MI, and was taken at 47.19583333 ºN, -88.23943333 ºW. Tannic-stained water from the Traverse River with heightened amounts of humic substances can be shown contrasting with the clear water south of the harbor in Figure 2.4. The riparian zone water comes from the riparian zone next to Coal Dock Road at Gay, MI, at 47.21518333 ºN, -88.2071 ºW. The original Lake Superior water sample came from 47.1894 ºN, -88.23598333 ºW, which is by the Traverse River seawall. Another Lake Superior sample came from Bete Grise bay, and was collected at 47.384900 ºN, -87.958933 ºW. This served as a control and medium for the LD50 test, as this coastal area is a Nature Conservancy wetland preserve. Several liters of water (18~36 L) were collected at each site in high density polyethylene (HDPE) containers rinsed with distilled water, to be used throughout all of these experiments.

A 140 mL polyethylene bottle of water was collected at the five different sites in additional to the normal water samples. These were filtered of sediments and debris of over 100 μm by a mesh netting, but not through a 0.45 μm filter. The implications of this will be discussed in the discussion section. Added to each was 1% nitric acid (138.6 mL sample water: 1.4 mL nitric acid). These were cold-stored (5-10°C) until sent for metals analysis at the MTU School of Forestry Laboratory for Environmental Analysis of Forests (LEAF) for Cu, Al, Co, and Fe using a Perkin Elmer Optima 7000DV ICP-OES. Additionally, for each water sample, a vial was prepared to contain 5g of 100%SS and 25 mL of water (1:5 solid to liquid ratio). The 25 mL of sample water put into each vial was filtered through a 0.45 μm filter using a gravity filtration apparatus. These were agitated periodically over one week. A glass stir rod was used to stir the sediment, with this being done three times throughout the week. The water collected from these vials were not filtered again. These too were sent to MTU School of Forestry Laboratory LEAF for metals analysis of Cu, Al, Co, and Fe. Comparing the metal concentrations of each water sample with and without 100%SS was used to determine the amount of metals leached given each type of water over a week. This data would be used along with pH, DOC, and TOC to determine the effects of humic substances in the water causing leaching from stamp sands.

2.5 Stamp Sand Ponds

2.5.1 Field Experimental Setup

A *Daphnia* survivorship and fecundity experiment was done in the stamp sand ponds at Gay, MI, main stamp sand pile and off of the GLRC docks (control) at the MTU campus in 2019. The field tests used the same set-up and served as a precursor of the acute LD50 and long-term chronic lab toxicity experiments. Water exchange rates in the net-covered vials had been tested in pond placements previously, using blue dye (Lytle 1999; Kerfoot et al. 1999). The native *Daphnia* (*Daphnia pulex, D. retrocurva, D. dentifera, and D. mendotae*) were collected using a 180 micron mesh plankton net from two small ponds several miles south-west of Gay, MI. The exact locations were not recorded due to lack of equipment and foresight. These native *Daphnia* were sorted from the small pond water samples, and a stock of them grown for at least three months. To start the survivorship and fecundity experiments we filled forty 40mL vials with Portage Lake water filtered through a 0.45 µm filter using a gravity filtration apparatus, added one adult *Daphnia spp*. to each, covered each vial a 100 µm mesh nitex netting, secured the mesh using rubber bands, and deployed by submerging the vials in a vial rack at four different stamp sand ponds and the GLRC docks at MTU. A small rope was tied to the vial rack at the GLRC docks to secure the vial rack and vials. At the ponds the racks were secured by anchoring them with a small stick and nearby sediment to prevent the racks from moving. Every two to three days on a Monday, Wednesday, and Friday cycle, the *Daphnia* were retrieved and the survivorship of adults and number of offspring produced were counted. These experiments lasted the full 14 days or until survivorship reached zero.

2.5.2 Ponds Metals Analysis

To better understand the results in the 2019 stamp sand ponds study, in 2022 we collected 14 water samples from 13 different stamp sand ponds in the main stamp sand piles south of Gay, MI (Table 3.7 for locations). Collection was done using 140 mL polyethylene bottles with a 100 µm mesh net to prevent larger particles from entering into the bottles. Important note, however, is no additional filtering was done, meaning all reported metal concentration values may not be biologically available. These water samples had a metals analysis done on them for Cu, Al, and Co by MTU School of Forestry Laboratory LEAF. These stamp sand pond water samples do not exactly correlate with the 2019 pond experiment locations due to the artificial movement of sediment in this area by the Army Corps for the construction of a berm. This was constructed to dump the dredged tailings from Traverse River seawall in 2019 (Figure 1.2). Though the metals analysis of the ponds was done in 2022 after the construction of the berm, these ponds still look the same as they did in 2019 with the bottoms filled with stamp sands. We can still make cross-comparisons with our Cu concentration data, along with our other metals, to the 2019 survival studies. We can also report a mean value for Cu concentration and other metals in the stamp sand ponds.

2.6 *Daphnia magna* Acute LD50 Test in The Laboratory

2.6.1 Preparation of Cupric Sulfate Stock Solution and Set-up of Lab LD50 Test

To perform an LD50 test for Cu, a stock solution was prepared. Our source of Cu came from dissolving Cupric Sulfate ($CuSO_45H_2O$) salt in Bete Grise water (Lake Superior water), which was filtered through a 0.45 µm filter using a gravity filtration apparatus. The stock solution consisted of 1L of the filtered Bete Grise water with 1mg of dissolved Cu, creating a stock solution of 1,000 µg/L Cu. The amount of Cupric Sulfate needed was determined from the molar mass of cupric sulfate (249.685 g/mol) and Cu (63.546 g/mol), since Cu makes up 25.45% of the molar weight of the crystal Cupric Sulfate hydrate. The resulting stock solution would theoretically contain 1000 µg/L of

Cu. A subsample of this stock solution along with a subsample of a preliminary, more concentrated stock solution was sent to MTU School of Forestry Laboratory LEAF to confirm initial Cu concentrations.

2.6.2 Acute LD50 Experiment

An LD50 test for Cu was performed using live *Daphnia magna* stock ordered from Carolina™. The *Daphnia magna* were placed in 40 mL vials (the same as used in the pond experiments) filled with 40 mL of 0.45 µm filtered Bete Grise water and stock Cu solution in a dilution sequence to generate nominal exposure concentrations from 0 µg/L to 1000 µg/L. Using the known stock concentration (c_1), our dilution sequence concentration (c_2), and the volume of the vials (v_2), we could calculate the volume of stock solution (v_1) needed for each vial using the formula $c_1v_1=c_2v_2$ (Table 2.1). The sequence used ten replicate vials at each Cu concentration marked as 1000 µg/L, 500 µg/L, 250 µg/L, 100 µg/L, 50 µg/L, 25 µg/L, 10 µg/L, 5 µg/L, and 0 µg/L. The survival of adults was recorded at 24hrs, 48hrs, and 72hrs for each vial at each Cu concentration sequence. A probit test was done at 24hr to calculate the LD50 value. The value was then compared to other literature values (Long et al., 2009; Guilhermino et al., 2000).

2.7 *Daphnia* Laboratory Chronic Survival & Reproduction Toxicity Tests using Stamp Sands

2.7.1 Water and Sediment Collection Locations for Long-term Chronic Toxicity Test

To begin the chronic toxicity experiment, two different beach sediment samples and five different water samples were collected (see Appendix Figure A.1). Each sediment samples were collected using a trowel and bucket, which were rinsed and dried with tap water prior to use in the field. The trowel was rinsed between sites by lake water from Lake Superior. For the beach samples, one represented a sediment sample containing only stamp sands (100% SS), and the other represents sediments with only natural quartz sand (0% SS). The only stamp sands sample was collected from the main stamp sand piles near Gay, MI at 47.21428333 ºN, -88.17016667 ºW. The only natural quartz sand was collected from Schoolcraft Township Park on the bay's southern shoreline, the natural beach region, west of the Traverse River, at 47.17926667 ºN, -88.24096667 ºW.

Several liters of water (18~36 L) were collected at each site. Containers were cleaned prior and rinsed with the water from the site location before collection. After collection, over half of the unfiltered water from each water sample was filtered through a 0.45µm filter. Filtered water for each of the five locations was sent in five different 140 mL polyethylene bottles to have total organic carbon (TOC) and total nitrogen (TN) analyzed using a Shimadzu TOC-LCPH analyzer with TNM-L at the AQUatic Analysis (AQUA) Laboratory in the GLRC at MTU.

2.7.2 Water Filtration and Sediment Sieving and %SS Determination

Water filtration was done using a pump filtration apparatus. The filter used was the Pall Corporation Supor®-450 0.45 µm 90 mm 100/PK. Filtered water was put into the same containers after those containers were rinsed with distilled water. A ~25 mL subsample of water from each water sample had its pH measured using Fisher Scientific Accumet® AE150. A 4 pH, 7 pH, and 10 pH buffer was prepared and used as a standard.

If pH was lower than 5, humic acid was isolated and quantified using the IHSS method (Aiken, 1985), however, this was generally not needed for this experiment.

The collected sediment samples representing only stamp sands (100%SS) and only natural quartz sands (0%SS) were allowed to air-dry overnight on the benchtop before sieving. Sieving was done using the Gilson 8-inch Sieve Shaker w/ Mechanical Timer (115V, 60Hz) model SS-15, and three Wildco Stainless Steel Sieves at sizes 2000 µm, 500 µm, and 250 µm. These sizes ensure sediments used to determine %SS and used in the survival and reproduction toxicity test are too large for *Daphnia* to ingest. Between 100-500 grams of dry sediment could be sieved on the sieve shaker before clogging was an issue. Sieving was done in 10-minute intervals. The sieves were cleaned, rinsed, and allowed to air dry as needed to prevent clogs and maintain efficiency. This was done until there were a few thousand grams of both the sediments representing only stamp sands (100%SS) and only natural quartz sands (0%SS).

Using the %SS determination method outlined earlier in the methods section, the actual %SS value for the beach sediment samples which represent only stamp sands and only natural quartz sands were determined. These actuals were close to the our expected %SS values (Table 3.9). Using these %SS values multiplied with the predicted Gay Pile standard Cu concentration (at 100%SS = 2863 mg/kg), we could estimate the Cu concentration of any given sediment sample (MDEQ, 2006; Kerfoot et al., 2021).

2.7.3 Establishing *Daphnia* Stock Populations

The *Daphnia* used in the field pond and long-term chronic experiments were hatched and raised from local (Keweenaw County) resting eggs (Kerfoot et al., 1999). Some were additionally collected from inland ponds using a plankton net to maintain stock populations. They were raised in pump-filtered water from Portage Lake. The filter used was the Pall Corporation Supor®-450 0.45 µm 90 mm 100/PK. The feed used was Carolina®*Daphnia* Food, 4 oz. The standards of cultivating *Daphnia* come from USEPA (2002) method guidelines.

2.7.4 *Daphnia* Chronic Survival & Reproduction Toxicity Test

The 40 mL vials used for the exposure experiments were pre-cleaned with 10% nitric acid (HNO_3) and rinsed with distilled then deionized water. One hundred twenty 40 mL vials would be used in each experiment using water from four different sources (480 vials total). The water sources were Lake Superior, Portage Lake, Coal Dock Road riparian zone, and Traverse River. Each setup consisted of twelve rows of ten vials. The rows were labeled Control(C), 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%. The control represented the water sample without sediment. 0%-100% had 5 grams(g) of sediment with a stamp sand concentration corresponding to the percentages (0%= no SS, 100%= only SS). Stamp sand concentrations were made through a weight ratio with natural sands and stamp sands. For example, 50% had 2.5g of stamp sand and 2.5g of natural sand. After the 5g of sediment and 35 mL of water were added to each vial, particles were allowed to settle for one week, and the sediment was stirred every few days to ensure leaching occurred.

One adult native *Daphnia* was put into each vial on the same day for an experiment to begin. The chronic experiment ran for twenty-one days. At 24hrs, 48hrs, and 72hrs the survivorship of the adult *Daphnia ssp.* was recorded, along with the number of offspring. Afterward, adult survivorship and the number of offspring produced were only recorded every two to three days at Monday, Wednesday, and Friday intervals. During the experiment, *Daphnia spp.* were regularly fed, resting eggs collected, and vials carefully refilled to 35 mL of water. On day 14 for each experiment, offspring were counted and collected to mitigate the effects of resource competition on survivorship. This experimental setup was adopted from USEPA (2002) guidelines.

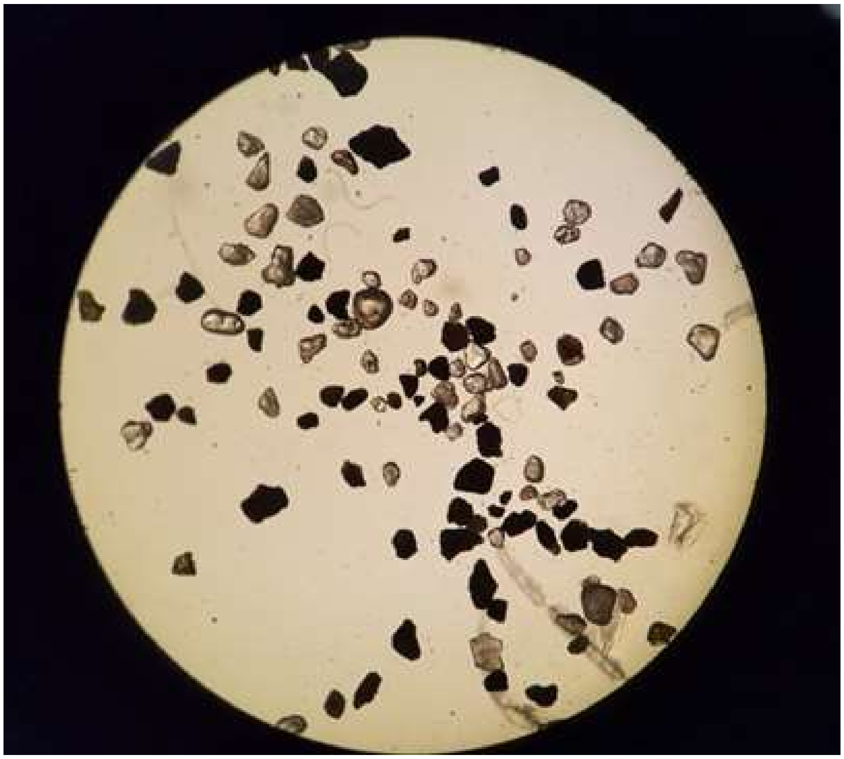

Figure 2.1. Sand grains from Sand Point 30x magnification

Sample is a 55% stamp sands mixture under transmitted light. Shows the contrast between rounded natural sand (transparent quartz) and dark stamp sand grains (dark, irregular, slightly larger).

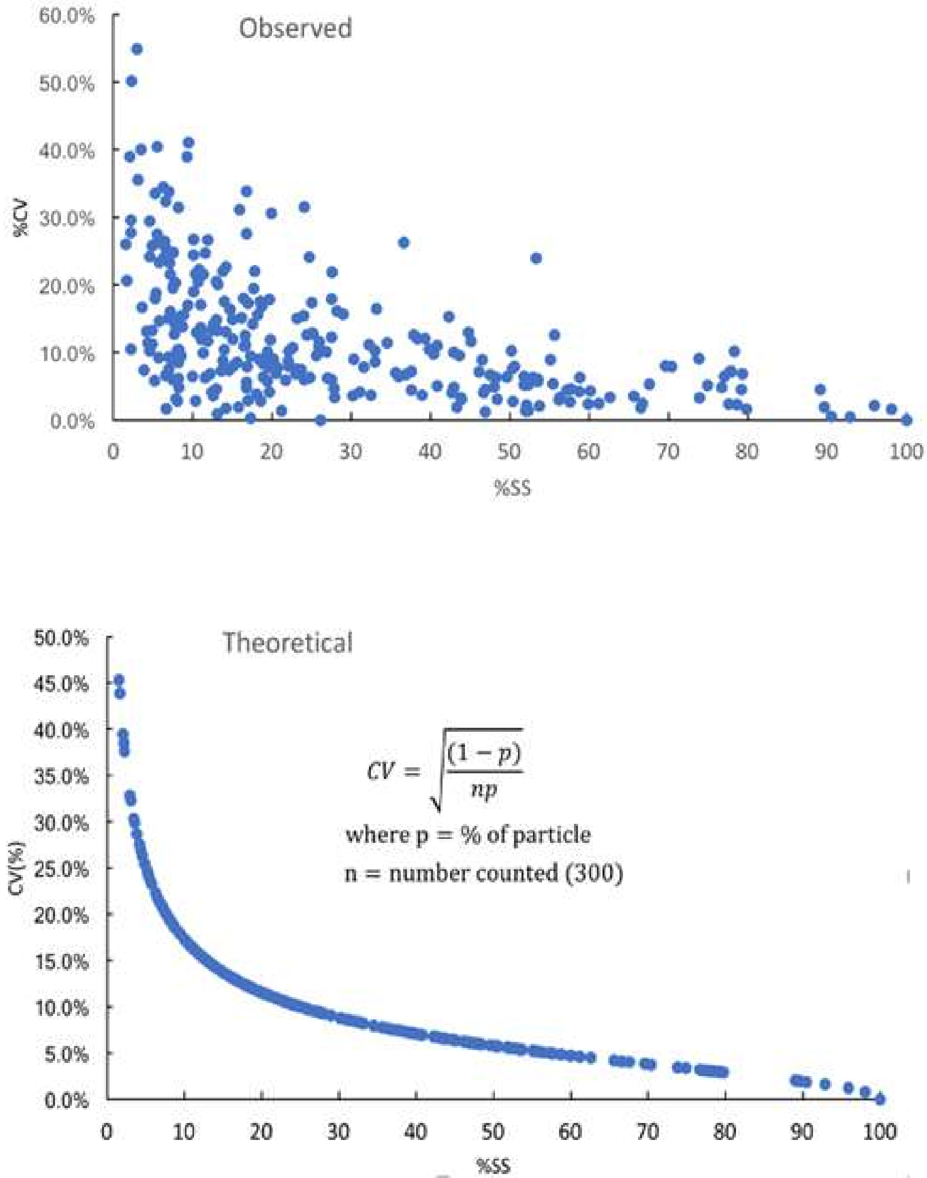

Figure 2.2. Observed vs. theoretical grain counts

Observed graph shows grain count method data (%SS) against calculated coefficient of variation (%CV). Theoretical graph shows grain counts (%SS) against coefficient of variation (%CV) set as a binomial distribution.

Figure 2.3. Stamp sand pond experiment set up

A vial rack, with vials covered by mesh net and one adult *Daphnia spp.* placed in them. Picture taken in early June, 2019 of the stamp sand ponds on the tailings pile at Gay, MI.

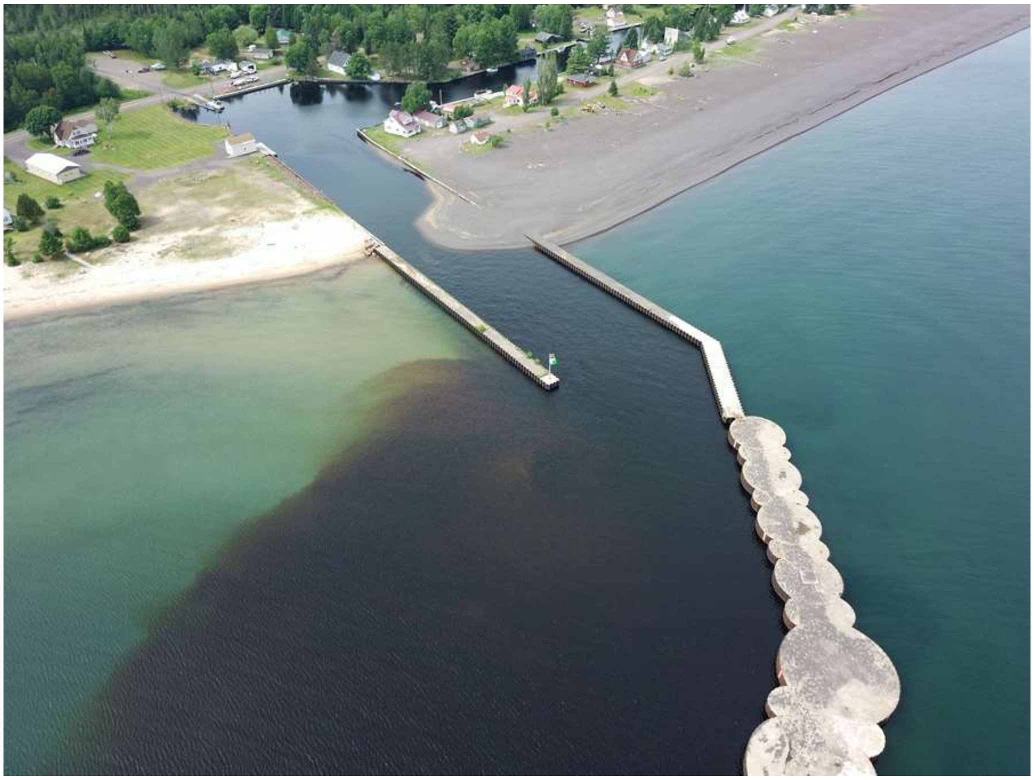

Figure 2.4. Image drone shot of Traverse River seawall

By Colin Brooks at Travers River, Grand Traverse Bay, Lake Superior, MI. Date early summer of 2019.

Table 2.1. Cu concentration for acute experiment vials

Calculations for the needed volume of stock solution (v_1) using the Cu concentration of the stock solution (c_1), our desired Cu concentration in a vial (c_2), and the volume of a vial (v_2). Calculations follow the formula $c_1v_1=c_2v_2$ or $v_2=(c_1v_1)/c_2$.

c_1 (mg/L)	c_2 (mg/L)	v_2 (L)	v_1 (L)
1	1	0.04	0.04
1	0.5	0.04	0.02
1	0.25	0.04	0.01
1	0.1	0.04	0.004
1	0.05	0.04	0.002
1	0.025	0.04	0.001
1	0.01	0.04	0.0004
1	0.005	0.04	0.0002
1	0	0.04	0

3 Results

3.1 Physical Properties of Stamp Sands

3.1.1 Density and Specific Gravity of Stamp Sands: Archimedes Experiment Results

At both sites, the determined density of sediment using an Archimedes experimental design is shown in Table 3.1. At the Gay stamp sand Pile, our mean density was 2.88g/cm^3, whereas at Schoolcraft Beach the mean density was 2.55g/cm^3. These differences were very similar to expected density differences between stamp sand basalt and natural beach quartz grains (pure basalt = 2.9g/cm^3; pure quartz = 2.65g/cm^3). Based on 10 measurements, the mean difference was 0.33, or a mean difference of 12.2% mass between the two types. For the basalt/quartz standards, the mean difference was 9.0%. Based on the 10 measurements of each type, the relative uncertainty as measured by the CV (SD/mean) was 3.8-4.9%.

3.1.2 Characterization of Percentage Stamp Sand (%SS) Around Buffalo Reef and Nearby Shores

To better understand where stamp sands from the main pile near Gay, MI have dispersed to, offshore sediment samples were taken using Ponar in the surrounding area (Figure 3.1), including in Buffalo Reef, by Dr. Kerfoot and I since 2019 (Kerfoot et al., 2021). The %SS data used in the creation of the figure was generated by us using the microscopic determination of %SS in sand mixtures method outlined earlier in this paper. The highest mixtures of stamp sands are found closest to the shore of the main pile, which is not surprising, and some higher %SS values have been detected in the trough, north of the reef. Some medium values of stamp sand (40-60%) have also been detected North of the Traverse River Seawall, as this seawall acts as a barrier for the migrating stamp sands. Lower values of stamp sands are detected past the seawall in the Lower Bay and quartz shoreline nearby, giving rise to the concern that stamp sands are beginning to move into the lower portion of the bay.

When interpreting Figure 2.2, the grain count method to determine %SS is shown to follow a binomial distribution. The coefficient of variation (%CV) can be determined using the equation under the theoretical graph (Figure 2.2). It shows observed values have a close correspondence to expected values. Notice in the theoretical graph %SS values under 10%SS the coefficient of variation spans from about 15 – 50 %, and %SS values between 10%SS to 90%SS have coefficient of variation values between 15 – 2%.

3.1.3 Mean and Direct Particle Size Determinations

Using the location and particle size data compiled from Appendix Table A.3 data and Kerfoot et al. 2021, the Grand Traverse Bay area could be split into four regions for the purpose of reporting mean particle size. These regions are on shore stamp sands beach deposits north of Traverse River seawall (SS GTB-N), natural quartz sands beach south of the Traverse River seawall (Q GTB-S), Grand Traverse Bay shelf (GTB Shelf) with depths no greater than 22 meters, and deep water (GTB- DW) samples from Kerfoot et al. 2021 data which exceed depths of 22 meters. Shown in Table 3.11, the results for mean particle size is as follows: SS GTB-N is 2081 µm (n = 9), Q GTB-S is 932 µm (n = 20), GTB Shelf is 417 µm (n = 83, and GTB-DW is 252 µm (n = 10). These results show particle sizes are the largest on the shore, especially north of the seawall on the stamp sand beaches, particle size decreases out into the shelf area of Grand Traverse Bay, and decreases even further in the deeper waters.

Particle sizes for natural quartz sand and stamp sands were determined for three underwater samples (labeled A3, Sta #5, and Gay 13) in Grand Traverse Bay and two beach samples (labeled #64 and #2) on the main tailings pile at Gay, MI (Appendix Figure A.2) The beach samples mean particle sizes are 1555 µm for #64 and 1877 µm for #2. The underwater samples mean particle sizes are 198 µm for A3, 185 µm for Sta #5, and 349 µm for Gay 13. From these samples the distribution of particle sizes of stamp sands compared to natural quartz show at particle size values of between 50 µm to 500 µm, both have similar distributions. In the case of both beach samples and the underwater sample of Gay 13 however, particle sizes above 500 µm were often dominated by only stamp sand grains, though the majority of measured particles in all samples were between the 50 µm to 500 µm size categories. For these samples it shows the particle sizes of natural quartz sand and stamp sands are similar in size in 50%SS mixtures underwater. In higher %SS mixtures on the main tailings pile at Gay, MI, stamp sands have a larger size range of 50 µm to 3000 µm, with the majority of stamp sand particles in the 50 µm to 500 µm range along with natural quartz sand.

3.2 AEM Solid Phase Analysis Results

The AEM Project gave us an excellent opportunity to see if Cu concentrations remained similar in stamp sands across the bay, as particles were dispersed by waves and currents. However, for regression analysis of the data, there were some issues with heteroskedasticity (see Methods) that required statistical techniques. For the entire data set (n = 132), to avoid heteroscedasticity, we plotted our mean %SS values against the corresponding AEM mean Cu Concentrations at 10%SS counting intervals (0-10%, 10-20%, 20-30%, and so on up to 90-100% on the x-axis). As shown in Figure 3.2, there was an excellent correspondence between the two measures (R^2= 0.812, r =0.901; regression equation y = 17.838X + 272). There was reduced variance around regression, with little evidence of heteroscedasticity. Moreover, the predicted 100%SS value was at 2056 mg/kg (Figure 3.2). The intercept value was a bit on the low side, but close to the 2863 mg/kg for the Gay pile mean Cu concentration (MDEQ, 2006). MDEQ found a lower value at the Traverse River Seawall (1,443 mg/kg Cu), suggesting some loss of Cu in southern stamp sand beach sands. An average of the two values would be around 2153 mg/kg, close to our AEM regression. Other regressions can be plotted with the AEM data, which allows additional estimates of Cu concentrations in 100% SS.

For example, looking at individual points in some of the data sets, we reduced heteroskedasticity by plotting only the points between 0-50% Stamp Sand percentages. We also found relatively high and significant correlations. Plotting the original data points just between 0-50%SS, the correlation is not bad (R^2 = 0.475, r = 0.689) and the regression is y = 28.699x - 17.965 (Figure 3.4). The regression intercept at 50% is 1,417 mg/kg. Extending the regression to 100%SS gives an intercept of 2,852 mg/kg, very close to the MDEQ Gay pile value of 2863 mg/kg. The other regression, Cu concentrations for on land (beach) values only, between 0-50%, also gives a decent correlation (R^2 = 0.610, r = 0.781) and a regression of Y= 33.019X +37.744. At 50%SS, the intercept is 1,689 mg/kg Cu, whereas extending the regression to 100% stamp sand, the Cu concentration is 3,340 mg/kg, slightly above the Gay pile value (Figure 3.3). The latter set incorporates core samples punched down into underlying beach sands. Overall, the predicted regression values are close to Gay pile values, and probably within confidence limits for the intercept values (Table 3.2). These comparisons are across the entire bay region and suggest that Cu concentration values are widely retained by particles at different sites, hence our predicted Cu values from %SS calculations correlate well. However, the closer to the main tailings pile, the better the correspondence.

A plot of AEM determined solid phase Cu concentrations in beach and underwater sediments (Figure 3.5) shows the very high concentrations along the beach from the Gay pile to the Traverse River Seawall. Cu concentrations are also high immediately offshore, in the Trough, and in NE cobble fields of Buffalo Reef. Intermediate concentrations are present across the shelf region, with some evidence of leakage around the Seawall area into the southern bay. Concentrations drop to relatively low values in deep water off the shelf region. Our particle counting technique overestimated Cu concentrations in deep-water (DW) samples, as the ratio of observed to predicted ranged from only 0.04-0.33, with a mean ratio of 0.16. Shelf (OW) and beach (OL) sediments had much closer ratios, but with variance (Figures 3.3-3.4).

3.3 Leaching Studies: Transfer of Copper from the Solid to The Dissolved Stage

3.3.1 Simple Leaching Tests with Stamp Sands

Metal concentrations in stamp sands can be derived from the extensive MDEQ studies of metal concentrations in the Gay pile stamp sands (MDEQ 2004; n = 274 samples). Relevant concentrations of metals in stamp sands for the leaching tests were aluminum (Al) = 15,872 mg/kg; copper (Cu) = 2863 mg/kg, iron (Fe)= 7,950 mg/kg, and cobalt (Co) = 22.9 mg/kg (Gay Fe results from Kerfoot et al. 2020).

Leaching results from shaken stamp sands are presented for these selected metals: Cobalt (Co), Aluminum (Al), Copper (Cu), and Iron (Fe) in Table 3.3. Values were reported in mg/L and converted to µg/L (1000 µg/L = 1 mg/L). Iron (Fe) was the most prevalent cation leached in all water samples subjected to stamp sands except in Bete Grise water, where it was second to Al. Aluminum (Al) was the second highest in most samples with stamp sands and Cu third. Only in the Bete Grise water sample with stamp sands was Co in high enough concentrations to be detected (Co 0.4 µg/L). Our highest concentrations of Al (770 µg/L), Cu (610 µg/L), and Fe (1546 µg/L) were in Coal Dock Road water with stamp sands. The difference in metal concentrations between each water sample with and without stamp sands (Table 3.4) shows how much metal leached from the stamp sands into each water sample over one week.

Iron leached the most from the stamp sands when compared to the other metal concentrations in each water sample. However, concentrations of Cu were also very high (330-590 µg/L) relative to potential toxic effects. Of additional importance is that all coastal waters had some dissolved Cu, although the values were much lower (10-30 µg/L) than the amounts released into the dissolved state when stamp sands were present and shaken.

Leaching here was from a one-time agitation, rather than from sequential leaching to see if Cu concentration values decline with time. The total amount of dissolved Cu leached is much less than the estimated total amount of Cu in the bulk stamp sands (330-

590 µg/L leached into dissolved phase compared with 2863 mg/kg in solid phase within stamp sand particles; that is, around only 0.16% of total mass). This suggests that most Cu remains in the particles. The latter finding is important for our %SS assays of stamp sand and using these percentages to estimate Cu concentrations in sand mixtures. The observations suggest that little Cu will be removed from stamp sand grains from dissolution as they disperse under wave action across Grand (Big) Traverse Bay. Yet the amount released into the dissolved phase of surrounding boundary phase waters could very well be high enough to be important for toxic effects.

3.3.2 Complexing Interactions in Nature: Total Organic Carbon and Total Nitrogen

Results for Total Organic Carbon (TOC) and Total Nitrogen (TN) are shown in Table 3.5 and come from the MTU Biological Sciences AQUatic Analysis (AQUA) lab. The highest TOC and TN values come from the Coal Dock Road water samples (TOC = 21.2mg-C/L, TN = 0.5264mg-N/L). The samples from Lake Superior, Bete Grise, and Portage lake have very similar low TOC values (1.5-1.8 mg-C/L). Traverse River water samples were the second highest TOC and TN (TOC = 13.9mg-C/L, TN = 0.5264 mg-N/L). The higher values of TOC from the Coal Dock Road and Traverse River probably indicate the much higher concentrations of humic substances and suspended compounds in these waters (see Figure 2.3). High levels of humic substances are evident in the stream (Coal Dock Stream) and river waters (Traverse River, Tobacco River) draining into Grand (Big) Traverse Bay. Of importance here is that humic substances can complex dissolved Cu and potentially greatly modify toxicity. Concerns about DOC led to the use of these multiple water sources in the chronic toxicity tests with *Daphnia.*

3.3.3 Resulting pH of Water Samples

The resulting pH values for the water samples are shown in Table 3.6. The Lake Superior sample, Bete Grise, and Portage Lake were all close in pH (7.3-7.36) and essentially neutral. The lowest pH was Coal Dock (5.43), the second lowest being Traverse River (6.4). Based on the brownish-yellow colors of the Traverse River water (Figure 2.3) and brownish-red colors of the Coal Dock waters, the lower pH values likely contain high levels of humic acids. However, the IHSS method (Aiken, 1985) for isolated humic acid was not performed since the pH values were not lower than 5. Note, pH values can also influence both mobilization and complexation of Cu, influencing toxicity. The presence of high levels of humic acids in wetland and river samples may complex dissolved Cu, lowering toxicity and lower pH values, or can lead to accelerated leaching if the waters percolate through stamp sands (Jeong et al. 1999).

3.4 Stamp Sand Ponds Experiment

The field Stamp Sand Pond experiments allowed us to check the survival of native *Daphnia* in a set of ponds that were solely surrounded by beach stamp sand deposits. That is, where interstitial waters seep into depressions and maintain dissolved Cu concentrations. A total of four racks of forty *Daphnia* were collected and deployed in ponds located at the stamp sand beach field south of the Gay tailings pile (Figure 3.7). For the Control, one rack set was deployed from MTU's dock at the GLRC (Figure 3.6).

Results at the two sites (Control, Stamp Sand Field Ponds) could not have been more different. Survivorship reached zero within two days at each stamp sand pond, so those experiments ended early (Figure 3.7). Only one pond had a survival rate above zero after the first count which was pond #1, with that rate being 2.5% (1 of 40 survival). Pond #1 had zero survival after the second count. At each pond, no offspring were produced. In marked contrast, the control site MTU dock experiment lasted the full two weeks with five counts done. The survival rate ended at 97.5% (39 of 40 *Daphnia* survived), and the number of offspring was a total of 295 juveniles (Figure 3.6).

Measurements of dissolved Cu along with Al and Co in various ponds from the Stamp Sand Pond region are found in Table 3.7. The values range from a low of 50 µg/L to a high of 2,580 µg/L, and have a mean value of 602 µg/L. Many of the ponds have mean concentrations in the hundreds of µg/L Cu. In contrast, the concentration of dissolved Cu in Portage Lake water at the GLRC Control site is around 20 µg/L. These preliminary field results prompted a set of acute and chronic laboratory experiments with *Daphnia*. Note water samples of these ponds were taken in 2022 and are similar in location and appearance, but do not fully correspond to the ponds used in the 2019 stamp sands pond experiments. This is due to the activities of the Army Corps moving sediment in the area.

3.5 Copper Cupric (Copper (II) Sulfate) LD50 with *Daphnia magna* Results

Subsamples of our theoretical 1000 µg/L Cu stock solution after being run by MTU School of Forestry Laboratory LEAF turned out to be 790 µg/L. This means Cu from the cupric sulfate either did not fully dissolve into the stock solution or Cu adsorbed to beaker walls in the three days before use. As for the results of the LD50 Cu test for the *Daphnia magna*, percentage survival at 24hr, 48hr, and 72hr are shown in Table 3.8

below. The expected Cu concentrations were adjusted slightly down from our original 1,000 µg/L, 500 µg/L, 250 µg/L, 100 µg/L, 50 µg/L, 25 µg/L, 10 µg/L, 5 µg/L, and 0 µg/L sequence (Appendix Table A.4) using reported Cu concentrations of the Bete Grise water (9.9 µg/L) and Cu concentration of the stock solution (790 µg/L). This slight change caused no difficulties with the application of the regression approach for determining an LD50 value.

The results for the LD50 Cu test on *Daphnia magna* show all adults dead within 48hrs. A regression and probit test to calculate LD50 was only done using 24hr survival data. The resulting regression was $y=3.469x+1.708$ (Appendix Table A.5). Using the regression, the LD50 Cu concentration for *Daphnia magna* in our experiment was 8.89 µg/L. In the Discussion, we compare this value with other published values and find it very close to recognized toxic levels.

3.6 Laboratory *Daphnia* Chronic Toxicity Test Results

3.6.1 Percentage Stamp Sand (%SS) In Sand Mixtures for Sediment in Chronic Toxicity Tests

The chronic toxicity test results of both Gay, MI tailings pile and Schoolcraft Beach sands %SS grain counts are shown in Table 3.9. The tailings pile sample has a mean %SS of 97.8%, and our Schoolcraft Beach sample a mean %SS of 1.5%. Given we chose the tailings pile sample to represent a 100%SS field sample and the Schoolcraft Beach sample to represent a 0%SS sample, the determined values are acceptable for use as representations.

3.6.2 Results of Chronic Toxicity of *Daphnia* in Stamp Sands

In contrast to the Control incubation in Portage Lake for the field pond stamp sand field experiments, where survival was very high with lots of young produced, *Daphnia* survival was only moderate in all chronic toxicity experiments. However, throughout the lab chronic toxicity experiment there was a trend of the longer the experiments ran, the less likely *Daphnia* survived, especially at a higher %SS (Figure 3.8, Appendix Figure A.3). Over the entire chronic test, a span of 21 days, especially with Portage Lake water, significant negative results were more consistent with exposure to stamp sand (Appendix Table A.6). In Portage Lake water, the *Daphnia* which remained at the end of 21 days were in stamp sand concentrations of NA%SS, 0%SS, and 10%SS at a survival rate of 40%, 60%, and 30% (4 of 10, 6 of 10, and 3 of 10) respectively, much above the average. Moreover, fecundity differences between control (NA%SS) and stamp sands were significantly different ($p<0.05$, t-test), which showed a negative effect (Table 3.10).

In other water treatments, differences between control and stamp sand presence were less variable. In Traverse River water the *Daphnia* which remained were in 0%SS and 10%SS at survival rates of 10% each, again above the average. In Lake Superior water the *Daphnia* which remained were in 0%SS and 20%SS at survival rates of 10% each, again above the mean. In the Coal Dock Road riparian zone, the *Daphnia* which remained were only in NA%SS at survival rates of 40%, a good value for the control situation, but low and high stamp sand treatments showed insignificant differences. We suspect that the Coal Dock's high DOC and low pH might have influenced differences, but the food chosen to feed *Daphnia* might have had negative effects on survivorship and fecundity, relative to the excellent control results when vials were suspended in natural waters.

The pattern for juvenile production, of course, depends partly upon survivorship. Note on day 14, to mitigate the effects of resource competition, all juveniles were removed from vials, but any new juveniles afterward were still recorded (Appendix Table A.7). The highest cumulative total number of juveniles was 361 in the Portage Lake samples on day 14. The day 14 total number of juveniles for Traverse River, Lake Superior, and Coal Dock Road were 31, 19, and 17 respectively. The highest number of juveniles in a single vial was 182 in Portage Lake NA%SS on day 14, which is also our control. After day 14, no juveniles were found in the Lake Superior water samples. In Portage Lake, after day 14 juveniles were only detected in %SS concentrations below 50%. For Traverse River, after day 14 juveniles were only detected in %SS concentrations below 20%. Coal Dock Road after day 14 only detected juveniles in NA%SS. The number of juveniles were usually higher below 50%SS concentrations in all water samples at any given time. The only exception was in Portage Lake day 7 50%SS where 34 juveniles were detected, which was the highest number of juveniles detected that day. This value decreased to 10 juveniles by day 14.

For the juveniles, the significance of natality was tested using a series of T-tests (Table 3.10). Data was tested from both the chronic toxicity tests and the 2019 stamp sand ponds experiment. The vials with Portage Lake water without sediment (NA%SS; PL *ex situ*) were used as a control for the T-tests on data from the lab chronic experiment, and MTU Docks (Portage Lake water, PL *in situ*) was the control for the T-tests with the stamp sand ponds data. Both Portage Lake water *in situ* and *ex situ* were compared for significance using a T-test as well (0.118, non-significant).

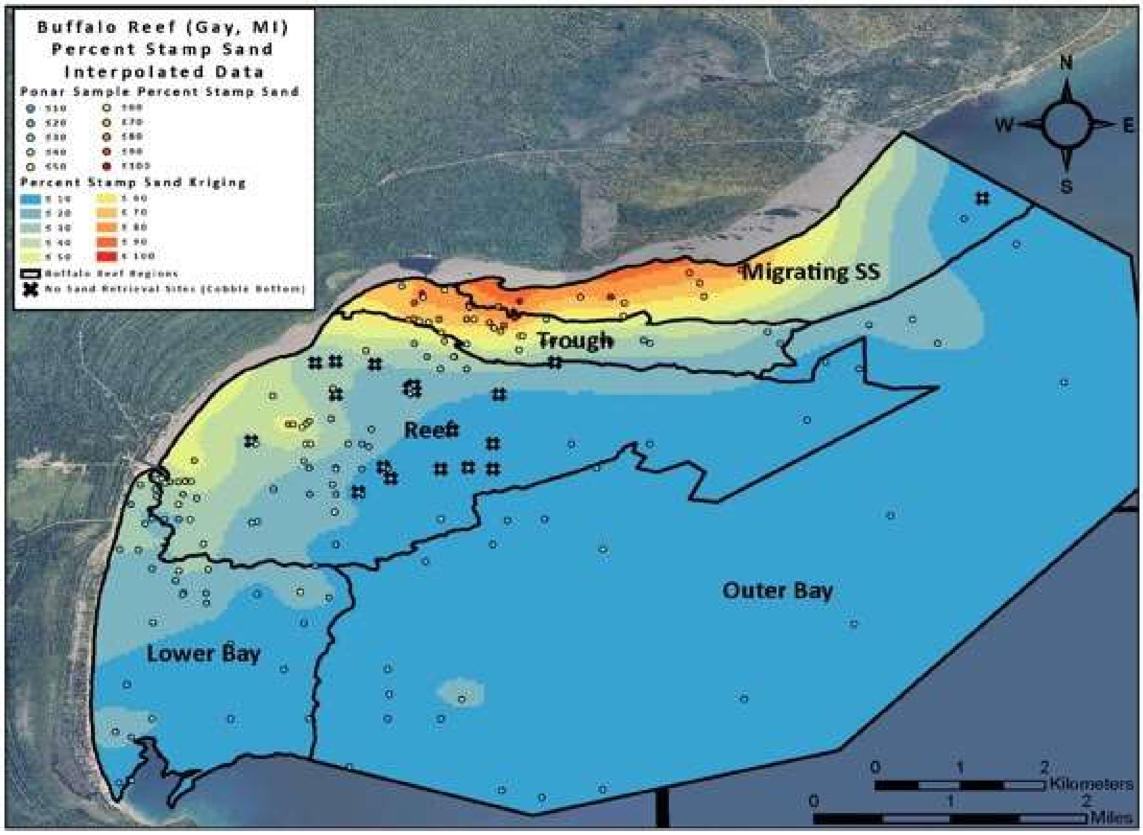

Figure 3.1. Buffalo Reef percentage stamp sand interpolated data

Example of GIS map for variables in Grand (Big) Traverse Bay (legends in the upper left). This shows the percentage stamp sand (%SS) in underwater sand mixtures across the bay. Densities are most impacted by high %SS and Cu-rich regions near the pile and shoreline down to the Traverse River (after Kerfoot et al., 2021). Major effects are near the Coal Dock, where nearshore stamp sand percentages are highest. Map by MTRI, based on counts by Swain and Kerfoot.

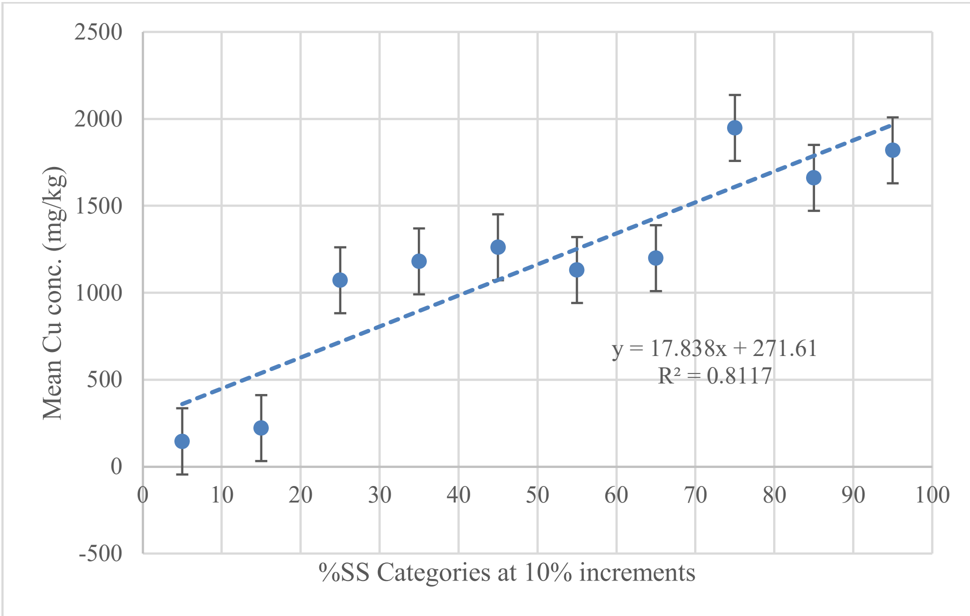

Figure 3.2. AEM mean Cu concentration regression at %SS categories at 10% increments

The entire AEM set was divide into %SS categories at 10% increments (10 categories plotted). The mean Cu concentration (mg/kg) from all samples at each 10% increment %SS categories (between 0%SS - 10%SS, 10%SS – 20%SS, 90%SS – 100%SS, etc.) were calculated and plotted. The 100%SS intercept is 2056 mg/kg.

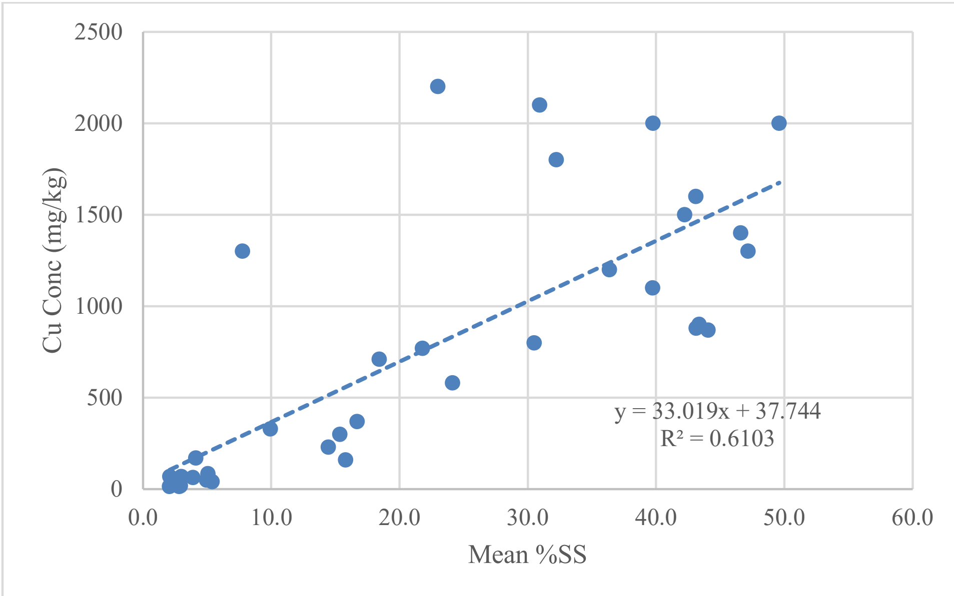

Figure 3.3. Mean %SS vs. actual Cu concentration for on land samples under 50%SS

Data was taken from all on land samples under 50%SS in the AEM data set (n = 36). The 100%SS intercept is 3340 mg/kg.

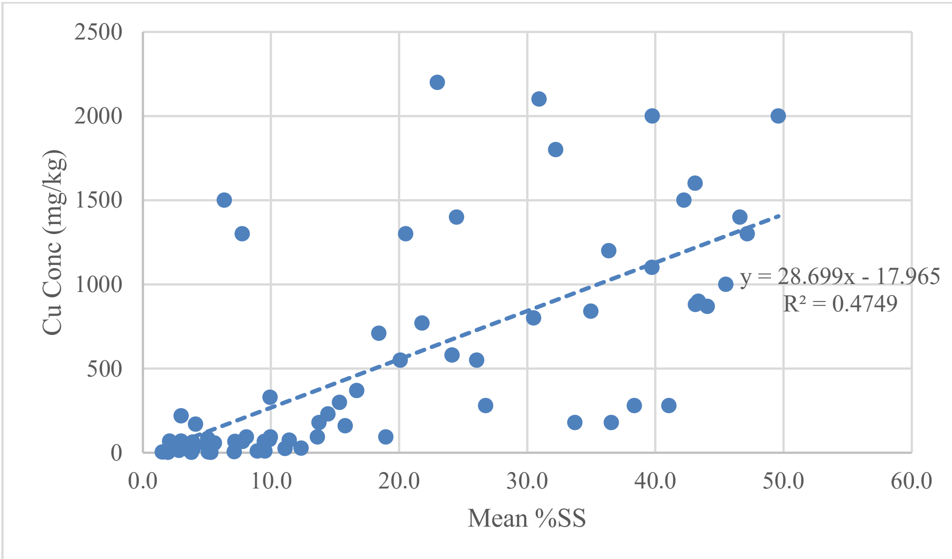

Figure 3.4. Mean %SS vs. actual Cu concentration for all samples under 50%SS

Data taken from all samples (on land, over water, deep water) under 50%SS in the AEM data set (n = 72). The 100%SS intercept is 2,852 mg/kg.

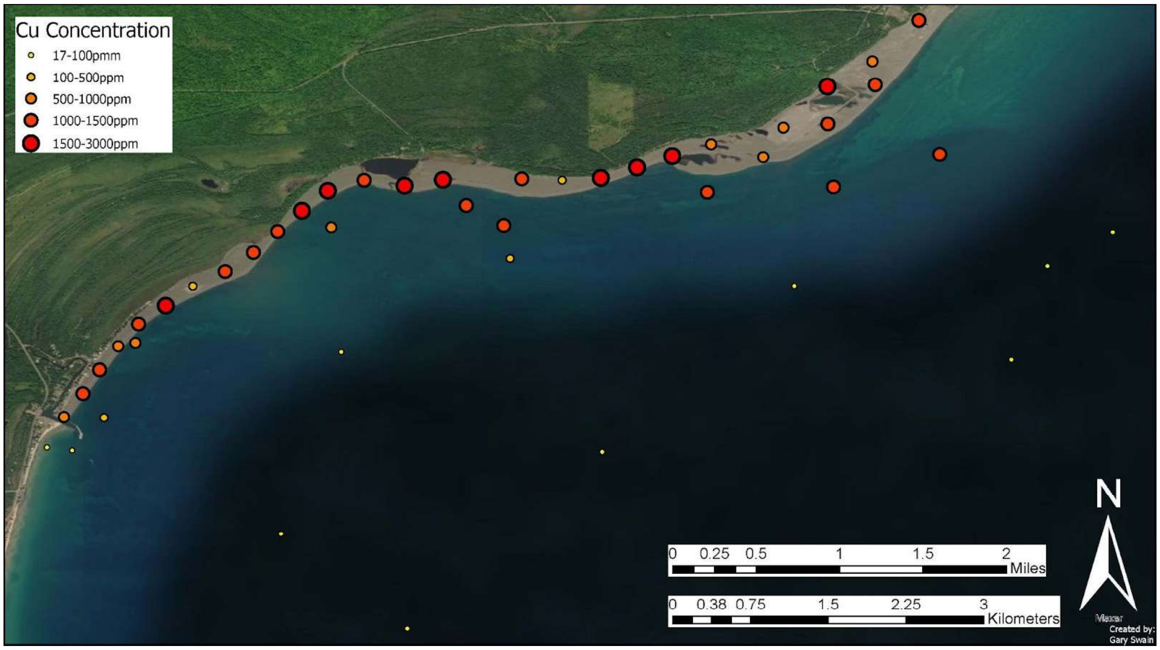

Figure 3.5. Grand Traverse Bay AEM Data Cu Concentration

Grand Traverse Bay Cu concentration (mg/kg = ppm; legend in upper left) of AEM Project 2021 top layer sediment samples. Samples include on land beach samples, nearshore underwater samples, and deep-water samples.

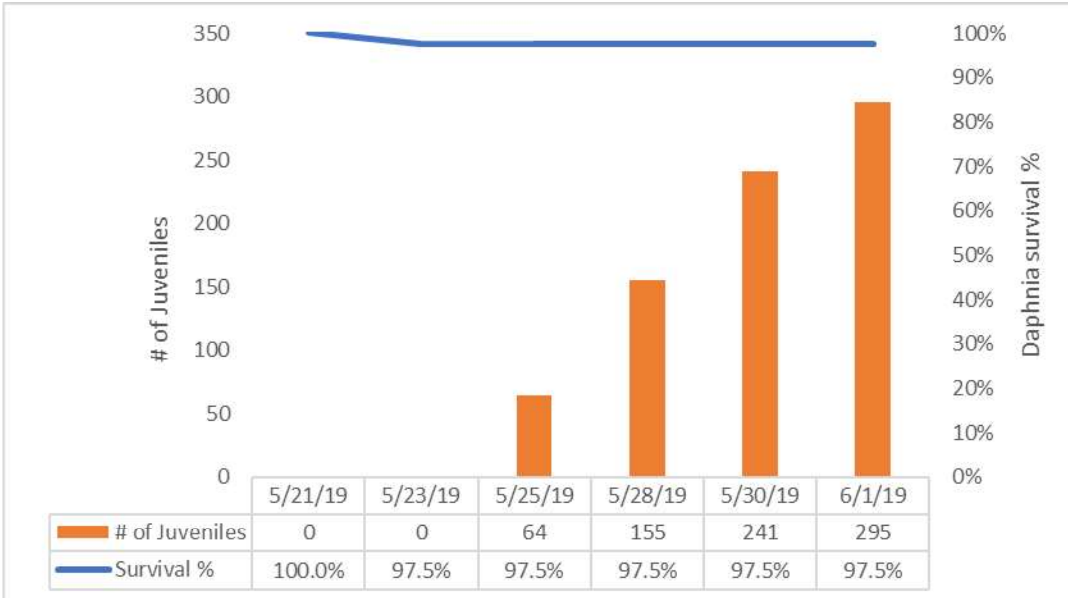

Figure 3.6. Stamp sand ponds experimental control: *Daphnia spp.* survival and fecundity

Experiment done off of the docks of Michigan Technological University (MTU) by the Great Lake Research Center (GLRC) in 2019 from 5/21/19 – 6/1/19. Survival % is out of forty adults, represented by the blue line. The number of Juveniles is represented by the orange bars.

Figure 3.7. Stamp sand ponds experimental results: *Daphnia spp.* survival and fecundity

Experiments were done in four different ponds on the stamp sand tailings pile at Gay, MI in 2019 from 5/22/19 – 6/7/19. Survival % is out of forty adults, represented by the blue line. Number of Juveniles is represented by the orange bars (hence no juveniles).

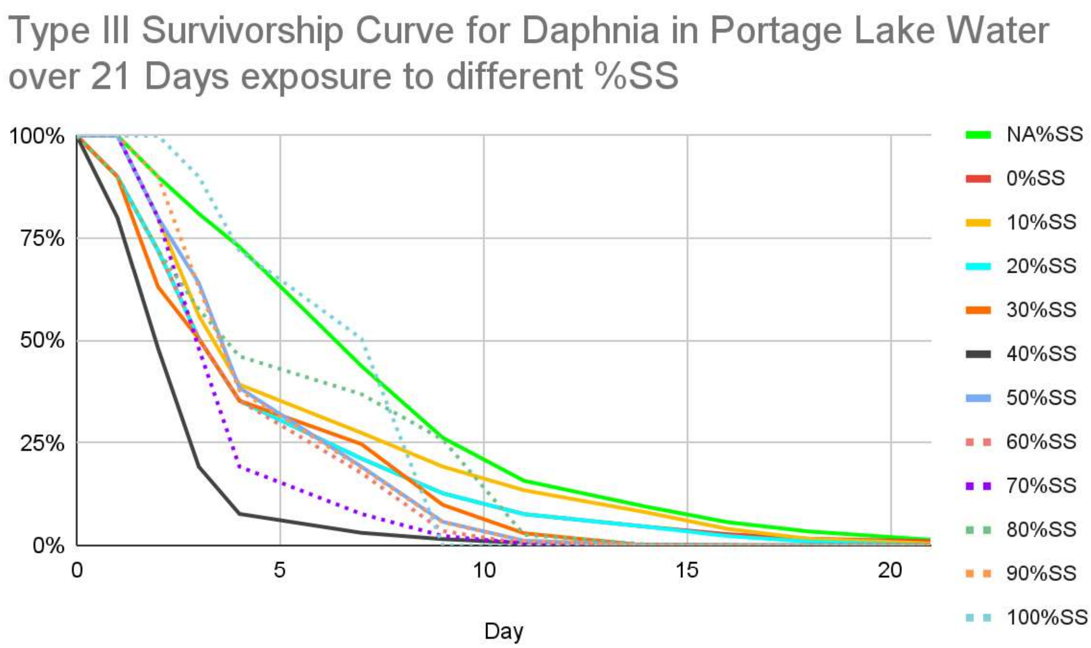

Figure 3.8. *Daphnia* survivorship probability curve

Portage Lake (PL) *Daphnia* survivorship probability curve at various %SS concentrations over 21 days. Survivorship results using waters from Traverse River (TR), Lake Superior (LS), and Coal Dock Road riparian zone (CDR) are provided in the appendix. NA%SS data was water without the presence of any sediment.

Table 3.1. Archimedes experiment results

Archimedes experiments on sediments from Gay, MI, main stamp sand pile, and Schoolcraft Township beach. Ten subsamples were used to obtain mean density. Also calculated were standard deviation (SD), standard error (SE), and error of mean value.

Archimedes Experiment Schoolcraft Beach Sands (Natural Sands)					
Trial	Starting V (mL)	Dry weight (g)	End V (mL)	End V - Start V	Density (g/cm^3)
1	1000	161.52	1065	65	2.48
2	1000	312.34	1135	135	2.31
3	1000	217	1090	90	2.41
4	1000	306.91	1120	120	2.56
5	1000	225.51	1090	90	2.51
6	1000	280.52	1105	105	2.67
7	1000	259.22	1100	100	2.59
8	1000	204.37	1075	75	2.72
9	1000	363.68	1140	140	2.60
10	1000	290.27	1110	110	2.64
SD	CV	SE	Error		Avg Density
0.124	4.870	0.039	0.087		**2.55**
Archimedes Experiment Main SS Pile Gay (stamp sands)					
Trial	Starting V (mL)	Dry weight (g)	End V (mL)	End V - Start V	Density (g/cm^3)
1	1000	307.37	1105	105	2.93
2	1000	204.91	1072	72	2.85
3	1000	303.14	1100	100	3.03
4	1000	253.12	1085	85	2.98
5	1000	434.8	1152	152	2.86
6	1000	236.99	1090	90	2.63
7	1000	296.08	1100	100	2.96
8	1000	283.83	1100	100	2.84
9	1000	287.38	1100	100	2.87
10	1000	228.36	1080	80	2.85
SD	CV	SE	Error		Avg Density
0.109	3.770	0.034	0.077		**2.88**

Table 3.2. Cross comparisons of regression lines Cu concentrations at 100% stamp sand

MDEQ standard for Gay tailings Pile is 2863 mg/kg (n = 247) for 100% Stamp Sand (100%SS). The first regression is the original calibration curve regression from Kerfoot et al. 2021; the rest are derived from the AEM Project.

Source	n	R^2	Equation	100%SS Intercept
Initial Cu Calibration Kerfoot 2021	40	0.867	Y = 25.066X - 156.43	2350 mg/kg
AEM Mean Cu Concentration Regression	10	0.812	Y = 17.838X + 271.61	2055 mg/kg
AEM, All Under 50% SS	72	0.475	Y = 28.699X - 17.965	2852 mg/kg
AEM, On Land Under 50% SS	36	0.61	Y = 33.019X + 37.744	3340 mg/kg

Table 3.3. Metals analysis of local waters

Metals analysis results from Perkin Elmer Optima 7000DV ICP-OES and converted from mg/L to µg/L. Labels are as follows: TR for Traverse River, LS for Lake Superior, CDR Coal Dock Road, PL for Portage Lake, and BG for Bete Grise. Values contrast with 100% stamp sands (SS) and without (NA) stamp sands exposures.

Sample ID	Co conc. (µg/L)	Al conc. (µg/L)	Cu conc. (µg/L)	Fe conc. (µg/L)
TR NA SS	0	290	10	547.5
TR 100SS	0	720	560	1400
LS NA SS	0	70	30	71.7
LS 100 SS	0	550	360	1065
CDR NA SS	0	250	20	807.2
CDR 100SS	0	770	610	1546
PL NA SS	0	30	10	323.8
PL 100 SS	0	540	340	1084
BG NA SS	0	9	9.9	4.4
BG 100 SS	0.4	534	524.6	531.1

Table 3.4. Leached metals from stamp sand in local waters

Metals leached from stamp sands over one week in five different water samples. Stamp sands came from Gay, MI, main tailings pile. Labels are as follows: TR for Traverse River, LS for Lake Superior, CDR Coal Dock Road, PL for Portage Lake, and BG for Bete Grise.

Samples	Co conc. (µg/L)	Al conc. (µg/L)	Cu conc. (µg/L)	Fe conc. (µg/L)
TR	0.0	430.0	550.0	852.5
LS	0.0	480.0	330.0	993.3
CDR	0.0	520.0	590.0	738.8
PL	0.0	510.0	330.0	760.2
BG	0.4	525.0	514.7	526.7

Table 3.5. TOC and TN of local waters

Total Organic Carbon (TOC) and Total Nitrogen (TN) from the five water samples around the Keweenaw Peninsula. Data was collected using a Shimadzu TOC-LCPH analyzer with TNM-L from Michigan Technological University's AQUA Lab.

Sample ID	TOC (mg-C/L)	TN (mg-N/L)
Lake Superior	1.798	0.4022
Bete Grise	1.468	0.4769
Portage Lake	1.480	0.5022
Traverse River	13.90	0.5264
Coal Dock	21.20	0.5847

Table 3.6. Local waters pH

The pH of five water samples around the Keweenaw Peninsula. Data was collected using Fisher Scientific Accumet® AE150.

Sample	pH
Lake Superior	7.3
Bete Grise	7.36
Portage Lake	7.34
Traverse River	6.4
Coal Dock	5.43

Table 3.7. Metals analysis of stamp sand ponds

Metals analysis of Co, Al, and Cu reported in µg/L from several ponds in the stamp sand main pile below Gay, MI. Metals analysis was done using Perkin Elmer Optima 7000DV ICP-OES.

Sample ID	Lat	Long	Co conc. (µg/L)	Al conc. (µg/L)	Cu conc. (µg/L)
P1	47.16781667	-88.17075000	0.0	70.0	990.0
P2	47.21850000	-88.17008333	0.0	50.0	270.0
P3	47.21896667	-88.16863333	0.0	40.0	120.0
P4	47.21825000	-88.16753333	0.0	50.0	80.0
P5	47.21736667	-88.16800000	0.0	10.0	70.0
P5B	47.21653333	-88.16900000	0.0	10.0	60.0
P6	47.21605000	-88.16833333	0.0	20.0	50.0
P7	47.21551667	-88.17040000	0.0	20.0	90.0
P8	47.21671667	-88.16781667	0.0	130.0	200.0
P9	47.21713333	-88.17045000	0.0	150.0	2580.0
P10	47.21441667	-88.17800000	0.0	80.0	950.0
P11	47.21463333	-88.17698333	0.0	290.0	940.0
P12	47.21346667	-88.17868333	0.0	30.0	860.0
P13	47.21398333	-88.17888333	0.0	30.0	790.0
		Average Conc.	0.0	77.3	602.0

Table 3.8. Cu LD50 results for *Daphnia magna*

Results of the Cu LD50 test for *Daphnia magna* while correcting for the actual Cu concentration reported by MTU School of Forestry Laboratory LEAF for both the stock solution (790 µg/L) and Cu in Bete Grise (BG; 9.9 µg/L) water. Survival rates of adult *Daphnia magna* were given at 24hr, 48hr, and 72hr intervals. All adult *Daphnia magna* were dead after 48hrs.

Cu conc. (µg/L)	24hr	48hr	72hr
9.9	60%	0%	0%
13.85	30%	0%	0%
17.8	20%	0%	0%
29.65	20%	0%	0%
49.4	10%	0%	0%
88.9	0%	0%	0%
207.4	0%	0%	0%
404.9	0%	0%	0%
799.9	0%	0%	0%

Table 3.9. Grain counts for Gay, MI tailings pile and Schoolcraft Beach sands

Beach sediment samples from Gay, MI, main stamp sand (SS) pile, are compared with Schoolcraft Township beach (natural quartz sands). Percentage stamp sand (%SS) grain count is done to determine the mean %SS for each sample. Also determined were standard deviation (SD), standard error (SE), percent error of mean value (E), and coefficient of variation (CV). Cu concentrations were predicted using the Gay Pile standard (100%SS = 2863 mg/kg Cu).

Station	**Latitude**	**Longitude**	**Date**	**Depth**	**Mean %SS**	**%SS1**	**%SS2**	**%SS3**
Gay SS Pile	47.214283	-88.170167	5/14/22	Beach	**97.8**	98.3	96.8	98.4
				Cu Conc. (100% = 2863 mg/kg)	SD	SE	E	CV
				2800.014	0.896	0.517	1.647	0.916
Schoolcraft Beach	47.179267	-88.240967	5/14/22	Beach	**1.5**	1.1	2.1	1.4
				Cu Conc. (100% = 2863 mg/kg)	SD	SE	E	CV
				42.945	0.513	0.296	0.943	34.211

Table 3.10. T-test *Daphnia* natality

Significance testing on the fecundity of *Daphnia* in pond experiments and chronic lab experiments, using t-tests (unequal variance); p values are given. Labels are as follows: SS for stamp sands, TR for Traverse River, LS for Lake Superior, CDR Coal Dock Road, PL for Portage Lake, and BG for Bete Grise.

T-Tests being test	T-test unequal
PL 10-40% SS	0.047
PL 50-100% SS	0.033
TR 10-40% SS	0.417
TR 50-100% SS	0.172
LS 10-40% SS	0.045
LS 50-100% SS	Na
CDR 10-40% SS	0.078
CDR 50-100% SS	0.078
SS pond 1	3.7E-5
SS pond 2	3.7E-5
SS pond 3	3.7E-5
SS pond 4	3.7E-5
PL C vs TR C	0.033
PL C vs LS C	0.030
PL C vs CDR C	0.042
PL *in situ* vs *ex situ*	0.118

Table 3.11. Mean particle sizes throughout Grand Traverse Bay

Labels are as follows: SS GTB-N stand for stamp sand beaches north of the Traverse River seawall, Q GTB-S stands for natural quart sand beaches south of the Traverse River seawall, GTB Shelf are Grand Traverse Bay underwater samples on the shelf which do not exceed 22 meters in depth, and GTB-DW are Grand Traverse Bay deep underwater samples which exceed 22 meters in depth. The n stands for the number of samples used to determine the mean. Data derives from Appendix Table A.3 and the deep water sample data from Kerfoot et al. 2021.

Region	**Mean size (µm)**	**Range (µm)**	**n**
SS GTB-N	2081	1242 - 3233	9
Q GTB-S	932	469 - 1356	20
GTB Shelf	417	108 - 2257	83
GTB-DW	252	94 - 408	10

4 Discussion

4.1 Solid Phase Determination of Percentage Stamp Sand (%SS)

4.1.1 The Implications of Stamp Sand vs. Natural Sand Specific Gravity and Particle Sizes

Our density/specific gravity calculations showed that particles of stamp sands, which are pulverized basalt, were slightly more dense than natural beach grains. The latter largely rounded quartz grains eroded from the Jacobsville sandstone. The specific gravity differences (2.88 g/cm^3 vs. 2.55g/cm^3) were significant, yet mixtures of stamp sand and natural sand along shorelines show very little sorting, as the two types of grains are about the same size (Figure 2.1). As mentioned earlier, part of this is that the density of the two types are very similar (see Archimedes Experiment). Studies at the USACE ERDC-EL lab in Vicksburg found the specific gravity of stamp sands to vary between 2.7 g/cm^3 - 2.83 g/cm^3 at three stamp sand beach sites, with low organic content (0.33-0.35 %). While they found a greater variety of size fractions and nearly 10% slime clays at the original Gay Tailings pile (< No. 200 sieve, 9.3%), wave-worked beach sands had much lower clay content, and greater size sorting (Schroeder and Ruiz, 2021).

The difference in specific gravities between stamp sands and natural sands comes from the variety of elements in basalt versus pure silicate because the Cu concentrations in stamp sands are very low, around 0.2% to 0.3% Cu. MDEQ, 2006 toxicological studies done at the Gay Pile and along the beach argue strongly for biotic effects from Cu, but also include some of the secondary suite metals. At a Gay tailings pile site sampling in

2003, several metals were found to exceed the State of Michigan Groundwater Surface Water Interface Criteria (GSWIC) levels (MDEQ, 2004). The sampling included 274 soil samples. Aluminum exceeded levels in 271 samples, chromium in 265, cobalt in 271, copper in 274, manganese in 159, nickel in 168, silver in 216, and zinc in 242. In ten groundwater samples, the number of metals exceeding GSWIC risk criteria for dissolved metals included: chromium 5, copper 10, manganese 5, nickel 8, silver 8, and zinc 8. In 2003, MDEQ also collected stamp sands from a southern redeposited stamp sand beach site, north of the Traverse River Seawall (n = 24 samples). Here MDEQ showed copper averaged lower, 710-5300 $\mu g\ g^{-1}$ (mean = 1443 $\mu g\ g^{-1}$). But in the 25 samples, various other metals again exceeded GSWIC levels: aluminum in 20 samples, chromium in 19, cobalt in 24, copper in 24, manganese in 7, nickel in 8, silver in 9, and zinc in 10 (MDEQ, 2004). However, Weston Solutions testing showed that only copper (total concentrations) exceeded surface water quality criteria in both porewater and pond water. Total metal concentrations of chromium, lead, manganese, nickel, silver, and zinc in porewater exceeded the surface water criteria, however, their dissolved concentrations did not exceed criteria. Recent USACE ERDC-EL studies have looked at elemental concentrations within stamp sand beach deposits, at three separate sites (Schroeder and Ruiz, 2021). A variety of elements showed the following ranges: Aluminum (12,700-14,700 mg/kg); Arsenic (5.52-6.39 mg/kg); Cadmium (0.405-0.544 mg/kg); Calcium (18,100-32,200 mg/kg); Chromium (15.8-24.0 mg/kg); Cobalt (26.4-31.3 mg/kg); Copper (2,470-3,460 mg/kg); Lead (2,39-3.68 mg/kg); Lithium (5.59-6.23 mg/kg); Magnesium (16,100-17,800 mg/kg); Manganese (389-459 mg/kg); Nickel (24.4-26.0 mg/kg); Selenium (1.90-2.76 mg/kg); Strontium (11.6-21.6 mg/kg); Zinc (57.9-68.7 mg/kg).

ERDC-EL conducted runoff tests following USACE Upland Testing Manual (2003) techniques, using an agitated solids concentration of 5000 mg/kg. The simulated runoff water exceeded both acute and chronic water quality criteria for copper with a maximum dissolved mean concentration of 206 μg/L. Over the range of pH conditions, the maximum total copper concentration was released at pH 4.2, and lowest at pH 7. Of the other metals, only cadmium, selenium, and silver exceeded chronic toxicity criteria (Schroeder and Ruiz, 2021).

In the USACE studies, runoff water quality was evaluated for three size fractions and solids concentrations of 250, 500, 1500, 5,000 15,000, and 50,000 mg/kg with challenge waters of pH 4.2, pH 7, and saline pH 7. The runoff water exceeded both the acute and chronic water quality criteria for copper in the pH 4.2 and saline pH 7 challenge waters. Median dissolved Cu concentrations released were similar (146-430 μg/L). Multiple leaching (rinsing) tests showed that dissolved copper concentrations generally decreased for stamp sand samples with multiple rinses, however, challenge waters remained greater than the water quality criteria (WQC) for chronic toxicity. Of the other elements, although lead and zinc also decreased throughout leaching cycles, both elements occasionally exceeded WQC levels for chronic toxicity. One interesting result was that in the presence of reasonable concentrations of DOC (20 mg/L), DOC presence increased the leachability of Cu in stamp sand by about a factor of 25, and increased the partitioning coefficient by about a factor of 18. Consequently, multiple leaching of copper in the presence of DOC is likely to increase the amount of copper released and the persistence of copper about 20 times longer, then in the absence of DOC (Schroeder and Ruiz, 2021). This result supports the findings of Jeong et al., 1999, that when forest groundwater moves through stamp sand, it accelerates the leaching of dissolved Cu into ponds.

Another feature checked by USACE ERDC-EL was the transport of Cu during the process of dredging. Concentrations in the dredging slurry released into the receiving berm pond complex were sampled, as well as seepage through berm walls into outlying ponds. Total Cu concentrations in elutriates, berm, and pond waters were around 234-2,120 µg/L total Cu and 24-117 µg/L dissolved Cu; whereas total concentrations for aluminum were 1.81-4.73 mg/kg, with 53-251 µg/L dissolved. The Cu concentrations were all above acute and chronic toxicity values, whereas the aluminum total concentrations were also over acute and chronic toxicity levels. For copper, acute and chronic toxicity levels were 13.0 µg/L and 9.0 µg/L. For aluminum, they were 87 µg/L and 750 µg/L. Manganese and selenium also flagged chronic toxicity levels (Schroeder and Ruiz, 2021).

Our leaching experiments also confirm that most of the mass of copper is retained within the stamp sand particles, a finding also from USACE ERDC-EL leaching studies. This is why particles that are widely dispersed across the bay retain the ability to remain toxic, and why the %SS prediction of solid phase copper is useful. The issue of Cu concentration along beaches and in sediments required checks, and testing for particle sorting during bay dispersal, as particles moved away from the eroding Gay tailings pile; hence the AEM studies.

4.1.2 What Stamp Sand Size Distribution Implies

Throughout this thesis we assume both our and MDEQ's Cu concentration values are representative of all stamp sands. In reality, an assumption is made as these values are actually calculating Cu concentration for the mean size of stamp sands, which varies depending on where in Grand Traverse Bay samples are collected. As shown in Table 3.11, throughout the Grand Traverse Bay area the particles can range in sizes from 3233 µm to 94 µm. The lower end of that range can even go lower into silt and clay sized particles (>63 µm), as these ranges are the highest mean and lowest mean size values for these sediment samples. Particles below 63 µm are lumped together in our calculations due to the smallest Wildco Stainless Steel Sieves being 63 µm (#230 Mesh). This is an important note as silt and clay sized particles, or fine fraction, have the potential to contain even higher amounts of Cu (Kerfoot et al., 2020). In the AEM project when calculating Cu concentrations at 100%SS intercepts (Table 3.2), we noticed our Cu concentration determinations are highest when focusing on data of only 50%SS and under, which coincide with smaller particle sizes in those areas (Appendix Table A.3).

An important note from the Archimedes experiment results shows natural quartz sand and stamps sands having similar density (2.55 and 2.88 g/cm^3). Due to similar densities, the wave and wind action in Grand Traverse Bay disperse natural quartz and stamp sands at similar rates when both have similar sizes. Waves and wind action also disperse smaller particles faster and further from the main tailings pile. In Table 3.11 we notice the mean sizes of sediment decrease the further away underwater sediments are collected from the main tailings pile. At the main pile there are elevated Cu concentrations in the silt and clay sized particles of stamp sand (Kerfoot et al., 2020), and Cu concentrations decline in these smaller particles the further dispersed they are underwater from the pile. In short, the further away from the main tailings pile stamp sands are, the smaller and lower Cu concentrated stamp sand particles appear to be.

4.1.3 Predicted Copper Concentrations from %SS Vs. Directly Determined Copper Concentrations

A few questions arose throughout our studies on stamp sand. While the microscope method establishes the %SS in mixtures of natural sand and stamp sand across the shelf of the bay and beach, one important issue relative to toxicity is: What are the corresponding copper concentrations in the stamp sands? Can the Gay tailings pile standard be used to calculate Cu concentrations in the solid phase across the bay, or is there a differential dispersal of particles based on specific gravity?

As a first approximation, we assumed the MDEQ mean Cu value for the Gay Pile was constant across the bay so that solid phase Cu could be determined by multiplying the %SS by the standard pile value of 2863 mg/kg (See Figures 3.1 and 3.2; and Appendix Table A.9). The %SS calculation for samples across the entire bay assumed no differential sorting of particles by waves or current. However, copper-rich particles might remain around the site of the original pile because of density differences. Accurate determinations of %SS in mixtures were very important for initial Cu calculations, because of the importance of Cu in toxicity and any interactions with the suite of metals that accompany it potentially causing additive effects.

Direct solid phase calculations of Cu concentrations were important across the bay. However, the leaching of Cu into the dissolved phase was also a major consideration, as well as ameliorating effects of DOC (humic substance) chelation or pH. The abundance of Cu^{2+} ions in solution is key to toxicity, including interactions with alkalinity, pH, and DOC, all of which will alter toxicity levels in nature.

4.2 Determining Solid Phase Copper Concentrations from Percentage Stamp Sand (%SS)

As mentioned earlier, of the three ways to estimate %SS in sand mixtures across the shoreline shelf deposits (specific gravity, reflectance color, grain counts), we choose to devise a grain counting technique under the microscope. We utilized a two-end source component model (stamp sand, natural quartz) under the microscope. Most mixtures from the beach and shelf sites were composed of sand-sized particles. Moreover, the two principle types of particles were similar-sized, though particle size varied with water depth. In our initial surveys, particles were counted to determine the %SS in sand mixtures across the bay, producing GIS maps of %SS (Figure 3.1).

However, we did encounter some issues. In the initial sampling of natural beach sands before 2021, we discovered that natural magnesium grains would be erroneously recorded as stamp sand. Fortunately, under reflected light, we found that these grains have a distinctive color (metallic dark-gray) which could be identified. Magnesium grains ended up being only a small fraction of grains in sediments and were corrected directly or by using a magnesium mean value of 1.6%, determined from thirty samples, and subtracting that value form mean %SS (Table A.2). Unfortunately, some natural quartz sand beaches are showing slight (up to 10%SS) stamp sand contamination. For example, the slight incidence of stamp sand at the Schoolcraft Beach site (1.5%SS) was probably due to stamp sands leaking around the Traverse River Seawall and becoming more prevalent around the southern natural beach region of Grand (Big) Traverse Bay (see the plot of Cu concentrations, Figure 3.5).

Another more recent consideration has come from restoration procedures at the bay site and Cu concentration discrepancies in Appendix Table A.9. The high AEM variance for on land (beach) Cu samples falling between 50-100% stamp sand, may relate to the recent mixing of Traverse River dredged sediments with the original Gay pile beach stamp sands. Traverse River sediments include glacial till sediments. Unfortunately, glacial till could constitute a third end member that has low Cu, and would confound our initial two-end member (natural quartz sand, basalt stamp sand) analysis, if the till sediments are in abundance. Looking at the size distributions of particles, we were able to identify this smaller-size particle component earlier in recent beach samples (see lighter sediments in the berm region, southwest of the Gay Pile; Figure 4.1). Our %SS index will tend to overestimate Cu concentrations of beach sites when there is a high component of dredged river sediments added to the original stamp sands at the site because numerous opaque grains are found in glacial till sediments. These grains do not contain Cu. The places where this anomaly now occurs include near the Traverse River, where river sediments and shoreline stamp sands have been mixed, and the berm region where dredged material was mixed with stamp sands. The original shoreline is now disturbed by these sediments moving down-current. Some of this can be shown by contrasting original beach stamp sand samples (taken around 2010-2013), with the AEM samples (taken in 2021; Appendix Table A.10).

In general, we conclude that our Stamp Sand Percentage Index seems to have good value, especially when there are only two principle end members (stamp sand, natural quartz sand). It was vastly more efficient than trying to estimate %SS based on specific gravity differences, like from our Archimedes Experiment, as was attempted by the Army Corps study of Sand Point (USACE Detroit 2001; Kerfoot et al., 2017). That method requires a lot of additional work and has questionable validity in mixed deeper sediments, due to confidence limits around values and the heterogeneous nature of opaque biotic and additional inorganic particles. In preliminary work with sand mixtures (natural sands and stamp sands), we find that the density method has low correlation ($R^2 = 0.42$) with precise percentages of stamp sands (Figure 4.2).

4.3 Direct Copper Determinations, Leaching Experiments, The Acute Toxicity Tests, and Pond *Daphnia* Experiments

4.3.1 Results of Direct Copper Determinations and Leaching Studies of Copper from Stamp Sand

Maps of %SS across the bay (Figure 3.1), constructed from our original counts, before the AEM studies, show high concentrations of stamp sands from the original tailings pile shoreline location near Gay down to the Army Corps Seawall on the Traverse River harbor (Figure 1.2, Figure 2.4; Kerfoot et al. 2021). Stamp sands have eroded from the original Gay pile and moved southward to cover the entire shoreline. The stamp sand beach shoreline amounts are estimated at around 10 million metric tonnes (Kerfoot et al. 2012; 2019a). Around an equal amount has eroded into the bay and dispersed underwater as migrating bars (Figure 1.4), filled an underwater ancient river bed (the Trough), accumulated around Buffalo Reef, and moved into northern and western cobble beds. Plots of %SS (Figure 3.1) suggest that the highest %SS in mixtures across the coastal shelf are immediately off the shore stamp sand beaches. Hardly any vegetation grows on the shoreline stamp sand deposits.

There are several small ponds on stamp sand stretches south of Gay. At present, a berm complex (Figure 4.1) has been constructed in the middle of the northern pond complex to receive dredged material from both the Traverse River and from the Trough. Our leaching experiments with stamp sands suggested an initial release of around 300-600 µg/L dissolved Cu into waters when stamp sands are agitated with water (Table 3.4; range 330-590 µg/L, mean 463 µg/L). This value is close to direct measures of dissolved Cu in 13 ponds (Table 3.7; range 50-2,580 µg/L; mean 602 µg/L). When *Daphnia* were submersed in stamp sand pond waters at 4 sites, they died within 48 hours and produced no young. Our acute toxicity tests suggested that values as low as 8.6 µg/L would kill *Daphnia* (LD50%). The rapid death of *Daphni*a in waters that range from 50 to over 2,000 µg/L dissolved Cu is therefore expected unless there are additional mitigating measures. Moreover, our acute toxicity results for *Daphnia* also closely resemble literature values for different *Daphnia* species (Table 4.1).

Previously, in Kerfoot's lab around the late 1990s (Lyttle 1999; Kerfoot et al. 1999), students performed LD50% tests in the lab on *Daphnia pulex*. They also ran comparable immersion experiments in the Gay stamp sand ponds and measured dissolved Cu in pond waters. In the lab, three separate experiments with *D. pulex* gave results of 9.4+/-0.1 µg/L, 3.6+/-0.5 µg/L, and 10.4+/-2.0 dissolved Cu for LD50% levels. Moreover, dissolved Cu measured in several of the then 26 stamp sand ponds ranged from 45-1,712 µg/L, with a mean of around 440 µg/L. *Daphnia pulex* placed in submersed vials again died rapidly relative to control vials (forest pond waters; Appendix Figure A.5). If anything, survival back in the late 1990s was slightly better. An additional review of published Cu LC50 toxicity tests on invertebrates and vertebrates suggests great sensitivity to the relatively high concentrations of dissolved Cu released by stamp sands (Table 4.1). Observed concentration levels should be toxic to a variety of benthic invertebrates and YOY fishes. Not surprisingly, pond environments were lethal to invertebrates like *Daphnia*.

4.3.2 Chronic Toxicity Results and the Ameliorating Effects of DOM, pH, and Alkalinity

From the literature, acute toxicity tests run on *Daphnia* with increasing DOM clearly show increased survival (Scannell, 2009). DOM will complex with dissolved Cu, reducing the relative abundance of Cu^{2+} anions, the primary source of toxicity. Notice that in our chronic long-term experiments, in addition to DOC in the medium, feeding *Daphnia* required an additional introduction of TOC. Over 21 days of the experiment, the food resulted in an increase of TOC by around 18.27mg/L for each vial assuming the food fully dissolved (~0.14g of feed containing yeast added to 120 vials). Unfortunately, feeding could not be avoided as long-term durations (weeks) would have caused *Daphnia* to starve. In these EPA-designed protocols, some Cu must adsorb onto introduced organic pellets. Perhaps ingestion of adsorbed Cu contributed to toxicity? Of course, in natural ponds, there is also circulating TOC in waters. Thus, the conditions are not as severe as the set-up in the standard (24-72hr) *Daphnia* acute toxicity tests, where Cu is dissolved in nearly pure water with a little buffer. *Daphnia* did react to the increasing presence of stamp sand in Portage Lake water experiments. Survivorship and fecundity levels were intermediate, less than the Portage Lake control incubations with vials in the pond experiments. The complete reasons for reduced survivorship and fecundity in the chronic tests, covering lab controls without stamp sands, is not clear.

4.3.3 Cross-comparison: Our Toxicity Findings of Stamp Sands with Other Published Agency Studies

Overall there appears to be a consensus by agencies and academics on the seriousness of stamp sands as a contaminant threat to shoreline communities. In a later sampling of shoreline sediments and near offshore water subject to water leaching from stamp sand beaches, high levels were reported (MDEQ, 2006). Concentrations of copper detected in elutriates (interstitial water) of Lake Superior nearshore sediments off the tailings pile and southward along the stamp sands shoreline plus from stamp sand pond water samples were above both acute and chronic Rule 57 Water Quality Values (MDEQ, 2006). Thus, stamp sand releases metals, especially Cu, at concentrations expected to have acute and chronic effects on aquatic organisms in water column boundary layers and in the small, shoreline-enclosed ponds. Recall that earlier experiments in the stamp sand ponds in the late 1990s showed dissolved copper concentrations ranging from 50 to over 1,200 µg/L, with rapid death of submersed *Daphnia* (Lyttle 1999; Kerfoot et al. 1999).

Our recent findings are strongly similar, as dissolved Cu in ponds ranged from 50 to over 2,500 µg/L, with a mean concentration of 604 µg/L, way above expected *Daphnia* acute and chronic toxicity levels. It is not surprising that *Daphnia* died shortly after suspension, quite in contrast to control immersions in nearby natural waters. Thus, the wide band of stamp sands that stretches from the original tailings pile location at Gay down to the Traverse River Seawall seems highly toxic to aquatic organisms.

A variety of agency tests of stamp sand contaminated underwater sediments from the Keweenaw, as well as specific tests with Grand (Big) Traverse Bay sediments, have also demonstrated toxic effects. Here the test results include not only crustaceans but a variety of benthic invertebrates. Freshly worked stamp sand in lake sediments was toxic to *Daphnia* and mayflies (*Hexagenia*) because they release Cu across the pore-water gradient (Malueg et. al. 1984). Additional laboratory toxicity experiments with stamp sand-sediment mixtures at EPA-Duluth (Ankley et al. 1993; Schubuer-Berigan et al. 1993; West et al. 1993) showed that solid phase sediments and aqueous fractions (interstitial water) were lethal to several taxa of freshwater macroinvertebrates: chironomids (*Chironomus tentans*), oligochaetes (*Lumbriculus variegatus*), amphipods (*Hyalella azteca*) and cladocerans (*Ceriodaphnia dubia*). In the latter studies, the observed toxicity was almost exclusively due to copper, not other metals in the secondary suite (principally zinc and lead). Weston's (MDEQ, 2006) toxicity studies in Grand (Big) Traverse Bay utilized *Ceriodaphnia dubia*, *Hyalella azteca,* and *Chironomus*. They utilized dilutes (interstitial waters) with five sediment samples from the Gay pile and the southward stamp sand shoreline. All sediment samples showed acute and chronic effects (growth, reproduction) on benthic organisms.

In even more recent MDEQ investigations (MDEQ, 2012), six sediment locations were sampled along the Gay to Traverse River shoreline transect. Copper concentrations varied between 1500-8500 µg g^{-1} (mean 2,967 µg g^{-1}), whereas the secondary suite had: Ag 1.2–1.7 µg g^{-1} (mean 1.5 µg g^{-1}), As 1.7–3.1 µg g^{-1} (mean 2.2 µg g^{-1}), Ba 6.6–8.6 µg g^{-1} (mean 7.7 µg g^{-1}), Cr 31–39 µg g^{-1} (mean 35 µg g^{-1}), Pb 2.1–2.9 µg g^{-1} (mean 2.6 µg g^{-1}) and Zn 62–79 µg g^{-1} (mean 72 µg g^{-1}). Bulk sediment toxicity testing showed that all six sediment samples from the shoreline were acutely toxic to both *Chironomus dilutes* and *Hyalella azteca*. Two samples were taken just south of the Traverse River harbor in a largely white sand bottom with a little stamp sand that also had excessive copper concentrations (300-400 µg g^{-1}), whereas one sample further down the white beach had expected much lower concentrations (79 µg g^{-1}). Even more recently, USACE ERDC-EL ran additional suspended phase toxicity tests on supernatants from each of their elutriate tests concerning dredging material released into the berm complex. Both acute (48- and 96-hr) and chronic (7-day) toxicity tests were run using the daphnid *Ceriodaphnia dubia* and the fathead minnow (*Pimephales promelas*). Additional tests were run on filtered elutriates of the original Gay pile stamp sand and unfiltered pond water from the berm dredging ponds. The results showed that untreated and undiluted effluent was likely to be acutely toxic and would require great dilution to eliminate toxicity. Disposal pond water (often with suspended clay) had a total Cu concentration of 2,850 µg/L compared to 1,710 µg/L in elutriation (dredged) water. Effluent water LC50 acute toxicity values ranged between 1.5-14.9 µg/L for *Ceriodaphnia* and 28-55 µg/L for *Pimephales*, whereas chronic toxicity values ranged between 1.5-12.5 µg/L for *Ceriodaphni*a and 28-55 for

Pimephales. Site cross-comparisons suggested that stamp sand from the original pile had much greater toxicity than stamp sands that migrated down the shoreline.

The consensus from the three-agency (MDEQ, EPA, USGS) and MTU experiments are that stamp sands are highly toxic to aquatic organisms. Not only do the migrating stamp sand beach deposits retain and release toxic amounts of dissolved copper, but nearshore sediments contain high enough concentrations of copper that they also provide risk for a variety of benthic organisms and YOY fishes.

Lidar and ROV imagery, and Ponar sampling have permitted the construction of maps in the bay that show %SS, Cu concentrations, and effects upon benthic biota (Appendix Figure A.4; Kerfoot et al. 2021). Ponar invertebrate sampling surveys over the past 10 years have demonstrated a severe reduction of benthic taxa where %SS and Cu concentrations were elevated (Kerfoot et al. 2019b; 2021). Maps of %SS versus benthic species abundance clearly show negative effects associated with stamp sand abundance in bay sediments, especially along stamp sand beaches and into NE portions of Buffalo Reef cobble fields (Appendix Figure A.4). Using beach seine techniques, GLIFWC (the tribal consortium) has also documented that eight young of the year (YOY) fish species remain relatively abundant in shallow waters off the lower white beach, including lake whitefish, whereas there is a virtual absence of all YOY fishes along the stamp sand beaches from the Gay pile to the Traverse River (Michaels, 2016). The lack of benthic organisms where stamp sand concentrations are high or high concentrations of copper could both be contributing to YOY fish absence. The severe effects on fish are not unexpected, given published reviews of the effects of copper concentrations on pelagic and benthic invertebrates and how fishes respond (Table 4.2).

Stamp sand tailings migrating underwater can have multiple effects on Buffalo Reef fishes. Given the massive amounts (10 million metric tonnes) migrating along the shoreline, the tailings can simply bury cobble fields where lake trout and whitefish drop their eggs. Toxic effects can kill eggs and larvae in boundary waters between boulders. Likewise, toxic effects can kill living benthos or organisms around cobbles and boulders, depriving YOY fishes of their normal food. Fish that do not like the color or Cu smell of stamp sands, or that do not find forage, may simply move elsewhere.

4.3.4 Reviewing Methodologies of Dissolved Phase Experiments

Throughout the methodologies and setup of the dissolved phase experiments, there are several improvements which can be made if they were done again. For starters for the leaching studies the waters sent for metals analysis should have been filtered through a 0.45 µm filter again. This is to insure the metals report given would be of concentrations biologically available to biota. Without this additional filtering, it may be more accurate to state our results for our Cu concentrations showed total Cu and not dissolved Cu.

Figure 4.1. Gay stamp sand berm

Drone photo of the berm made by MDNR in the shoreline stamp sands at Gay, MI. The darker sediments are stamp sands, and the lighter smaller-sized sediments are dredged mixtures from the Traverse River harbor and the Trough being released into berm ponds. Notice water percolating through berm walls into surrounding ponds.

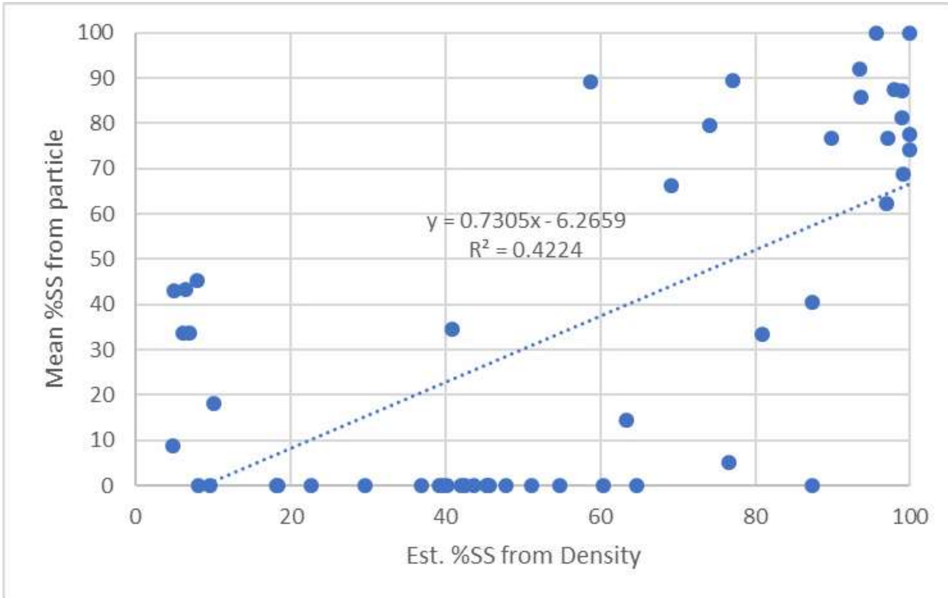

Figure 4.2. Percentage stamp sand particle counting technique compared with estimated stamp sand determinations through densities determined from Archimedes experiments

Mean percentage stamp sand (%SS) from particle counts (microscope) method is compared to percentage stamp sand (%SS) estimated (est.) from Archimedes experiments.

Table 4.1. Acute toxicity tests of Cu on Pelagic Cladocerans

Results of Acute Toxicity Tests of Cu (48hr LD50) on Pelagic Cladocerans. Compiled by Brix et al. 2001.

Species	**N**	**LD50 (µg/L Cu)**
Ceriodaphnia reticulata	1	5.2
Daphnia ambigua	1	24.8
Daphnia magna	12	18.1
Daphnia parvula	1	26.4
Daphnia pulex	2	8.8
Daphnia pulicaria	8	9.3

Table 4.2. Acute Toxicity Tests of Cu on Benthic Invertebrates and YOY fishes

Acute Toxicity of Cu results (ug/L) on benthic invertebrates and YOY fishes (from Brix et al. 2001 review of literature).

Benthic Invertebrates		48hr
Species	N (cases)	LD50 (µg/L)
Alona affinis (cladoceran)	1	386.3
Simocephalus serralatus (cladoceran)	3	95.9
Acroncyria lycorias (stonefly)	1	10,242
Chironomus deorus (midge)	1	833.6
Chironomus riparius (midge)	1	247.1
Cranconyx pseudogracilis (amphipod)	1	1290
Echinogammarus berilloni (amphipod)	1	69
Gammarus pseudolinnaeus	1	22.1
Gammarus pulex	7	31
Fish (salmonid)		
Species	N (cases)	48hr LD50
Oncorhynchus clarki (cutthroat trout)	9	66.6
Oncorhynchus kisutch (coho salmon)	3	87
Oncorhynchus mykiss (rainbow trout)	39	38.9
Oncorhynchus tsawytscha (sockeye salmon)	10	42.3
Salvelinus fontinalis (brook trout)	1	110.4

5 Conclusion

Around 22.7 million metric tonnes of copper-rich stamp sand tailings were discharged into Grand (Big) Traverse Bay by two Stamp Mills over a century ago. With the eroding of that original tailings pile, stamp sand deposits now cover beaches from the Gay pile site down to the Traverse River Seawall, with half of the original pile moving underwater towards Buffalo Reef and the bay's center. The stamp sands in the original Gay tailings pile contained about 0.28% copper (2,800 mg/kg). Our studies show that stamp sands along the shoreline and in sediments contain about 2,100 to 3,400 mg/kg Cu and are clustered along the shoreline and shallow-water shelf. In water, stamp sands leach concentrations of dissolved Cu between 150-600 μg/L. These values greatly exceed the acute water quality criteria for the protection of aquatic life and are over twenty-fold our LD50 value (8.89 μg/L) for native *Daphnia spp.* Stamp sands also contain an additional suite of metals, with aluminum able to exceed chronic water quality criteria as well.

The original pile of stamp sands have higher Cu concentrations from the 10% Cu-rich slime clay (clay and silt sized particles, <63μm) fraction, adding additional concerns (Kerfoot and Robbins, 1999). Modern interstitial beach and pond waters often range between 50-2,500 μg/L dissolved Cu (mean 602 μg/L). Unfortunately, lower pH and higher DOM waters, like those from shoreline rivers and streams (Traverse River, Tobacco River, Coal Dock Stream), leach higher amounts of dissolved Cu from the stamp sands. Recently, Traverse River water with dredged tailings was released into the berm complex, adding even more concerns. These high levels are toxic for aquatic pelagic invertebrates, benthic invertebrates, and YOY fish. Fortunately, the Buffalo Reef

Task Force has advocated the removal of stamp sand to a landfill north of Gay. Among agencies and academics, there is a consensus that stamp sands are toxic to a great variety of aquatic life and should be removed from Grand (Big) Traverse Bay.

Several other major conclusions come from this thesis. We constructed maps of both where the stamp sands and Cu concentrations are the highest throughout the Grand Traverse Bay. When asked the density of stamp sands a value of 2.88 g/cm^3 can be given. Based on similar densities (2.88 vs. 2.55 g/cm^3) of stamp sands and natural quartz sands, there are similar particle sizes in mixed sediment samples. Through the AEM Project data we can say with confidence stamp sands in Grand Traverse Bay area contain between 0.2 – 0.3 % Cu. Additionally, as stamp sands migrate further away from the main pile, they become more sorted and the average Cu concentrations decline. We noticed lower pH waters lead to increased leeching of heavy metals, and when combined with higher levels of DOC, total Cu concentrations increased within waters. Lastly, our acute toxicity experiments showed that even native *Daphnia* species (*Daphnia pulex*, *D. retrocurva*, *D. dentifera*, and *D. mendotae*) in the Keweenaw are very sensitive to elevated levels of Cu.

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A Appendix Tables

Table A.1. Mean percentage stamp sand from AEM data

Mean percentage stamp sand (%SS) calculation using sand mixtures obtained by AEM surveys. The sample number and type represent the type of sample obtained. The labels are as follows: DW is deep water, OW is over water, and OL is on land (beach). Surface refers to sediment mixtures obtained from the surface of deep water samples. The numbers (ex. 00-03, 06-12) refer to the depth in inches of the core sample sediment obtained. Mean %SS is the mean of 3-4 individual stamp sand counts. SD is the standard deviation and CV is the coefficient of variation.

#	Sample Number & Type	Date	Time	%SS1	%SS2	%SS3	%SS4	**Mean %SS**	SD	CV
1	GT21-DW-01-Surface	6/3/2021	12:15	11.6	9	9.1		**9.9**	1.5	14.90%
2	GT21-DW-02-Surface	6/3/2021	13:30	9.2	9.9	10.8		**10**	0.8	8.00%
3	GT21-DW-03-Surface	6/3/2021	11:25	5.6	14.3	9.1	6.8	**9**	3.9	43.00%
4	GT21-DW-04-Surface	6/3/2021	16:15	11.8	13.3	12		**12.4**	0.8	6.60%
5	GT21-DW-05-Surface	6/3/2021	9:00	11	12.5	9.8		**11.1**	1.4	12.20%
6	GT21-DW-06-Surface	6/3/2021	10:15	9.6	12	12.7		**11.4**	1.6	14.20%
7	GT21-DW-07-Surface	6/3/2021	10:45	11.1	5.3	12.2		**9.5**	3.7	38.90%
8	GT21-OW-02-00-03	6/7/2021	12:00	81.5	84.2	84.9		**83.5**	1.8	2.10%
9	GT21-OW-02-03-06	6/7/2021	12:00	81.5	84.5	86		**84**	2.3	2.70%
10	GT21-OW-02-06-12	6/7/2021	12:00	88.4	84.4	88.1		**87**	2.2	2.60%
11	GT21-OW-02-12-72	6/7/2021	12:00	71.8	71.8	68.9		**70.8**	1.7	2.40%
12	GT21-OW-02-72-132	6/7/2021	12:00	73.6	75.2	77.9		**75.6**	2.2	2.90%
13	GT21-OW-03-00-03	6/7/2021	10:00	83.5	88.8	87.3		**86.5**	2.7	3.20%
14	GT21-OW-03-03-06	6/7/2021	10:00	80.1	85.9	83.3		**83.1**	2.9	3.50%
15	GT21-OW-03-06-12	6/7/2021	10:00	84.2	76.8	82		**81**	3.8	4.70%

16	GT21-OW-03-12-61	6/7/2021	10:00	83.4	88	86.2	**85.9**	2.3	2.70%
17	GT21-OW-07-00-03	6/5/2021	8:40	55.2	52.4	53.5	**53.7**	1.4	2.60%
18	GT21-OW-07-03-06	6/5/2021	8:40	24.6	26.8	26.8	**26.1**	1.3	4.90%
19	GT21-OW-07-00-12	6/5/2021	8:40	20.6	21.8	17.9	**20.1**	2	9.90%
20	GT21-OW-07-14-38	6/5/2021	8:40	6.6	5.4	4	**5.3**	1.3	24.40%
21	GT21-OW-10-06-12	6/14/2021	11:40	1.6	2.2	2.1	**2**	0.3	16.30%
22	GT21-OW-10-12-24	6/14/2021	11:40	2.2	1.2	1.2	**1.5**	0.6	37.70%
23	GT21-OW-11-00-03	6/4/2021	8:40	42.9	38.8	41.5	**41.1**	2.1	5.10%
24	GT21-OW-11-03-06	6/4/2021	8:40	40.5	39.9	34.7	**38.4**	3.2	8.30%
25	GT21-OW-11-06-14	6/4/2021	8:40	23.7	29.6	27	**26.8**	3	11.00%
26	GT21-OW-11-14-34	6/4/2021	8:40	6.6	6.7	8.1	**7.1**	0.8	11.80%
27	GT21-OW-01-00-03	6/8/2021	9:50	81	84.6	85.3	**83.6**	2.3	2.80%
28	GT21-OW-01-03-06	6/8/2021	9:50	88.2	87.5	84.7	**86.8**	1.9	2.10%
29	GT21-OW-01-06-12	6/8/2021	9:50	79.6	76.7	77.9	**78.1**	1.5	1.90%
30	GT21-OW-01-12-72	6/8/2021	9:50	78.8	77.8	78	**78.2**	0.5	0.70%
31	GT21-OW-01-72-126	6/8/2021	9:50	62	65.1	67.9	**65**	3	4.50%
32	GT21-OW-01-126-140	6/8/2021	9:50	48.4	44.9	43.2	**45.5**	2.7	5.80%
33	GT21-OW-04-00-03	6/8/2021	14:30	64.8	63.8	61.4	**63.3**	1.7	2.80%
34	GT21-OW-04-03-06	6/8/2021	14:30	59.7	63.4	64.5	**62.5**	2.5	4.00%
35	GT21-OW-04-06-12	6/8/2021	14:30	59.1	57.5	63.8	**60.1**	3.3	5.40%
36	GT21-OW-04-12-72	6/8/2021	14:30	48.8	53.8	49.3	**50.6**	2.8	5.40%
37	GT21-OW-04-72-120	6/8/2021	14:30	29.6	22.5	21.4	**24.5**	4.5	18.20%
38	GT21-OW-04-120-148	6/8/2021	14:30	3.6	4.9	3.3	**3.9**	0.9	21.60%
39	GT21-OW-05-00-03	6/2/2021	8:30	71.1	68.6	67.8	**69.2**	1.7	2.50%
40	GT21-OW-05-03-06	6/2/2021	8:30	77.1	71.7	67.8	**72.2**	4.7	6.50%
41	GT21-OW-05-06-12	6/2/2021	8:30	64.9	64	64.5	**64.5**	0.5	0.70%
42	GT21-OW-05-12-72	6/2/2021	8:30	60.8	67.4	66.6	**64.9**	3.6	5.50%
43	GT21-OW-05-72-120	6/2/2021	8:30	33	35	36.9	**35**	2	5.60%
44	GT21-OW-05-120-180	6/2/2021	8:30	19.3	20.2	22.1	**20.5**	1.4	7.00%

45	GT21-OW-05-180-193	6/2/2021	8:30	4.9	8.4	5.8	**6.4**	1.8	28.50%
46	GT21-OW-05-193-253	6/2/2021	8:30	1.4	1.4	2.3	**1.7**	0.5	30.60%
47	GT21-OW-06-00-04	6/9/2021	13:00	35.9	40.5	33.3	**36.6**	3.6	10.00%
48	GT21-OW-06-04-07	6/9/2021	13:00	30.5	37.4	33.3	**33.7**	3.5	10.30%
49	GT21-OW-06-07-12	6/9/2021	13:00	10.8	16.8	13.7	**13.8**	3	21.80%
50	GT21-OW-06-12-72	6/9/2021	13:00	5.2	6.1	4.1	**5.1**	1	19.50%
51	GT21-OW-09-Surface	6/17/2021	16:00	61.1	59.9	64	**61.7**	2.1	3.40%
52	GT21-OW-13-00-03	6/10/2021	12:50	19.7	18.1	19.1	**19**	0.8	4.30%
53	GT21-OW-13-03-06	6/10/2021	12:50	12.8	15.1	13	**13.6**	1.3	9.30%
54	GT21-OW-13-06-12	6/10/2021	12:50	9.3	7.3	7.7	**8.1**	1.1	13.10%
55	GT21-OW-13-12-60	6/10/2021	12:50	4.1	3	4.3	**3.8**	0.7	18.40%
56	GT21-OW-12-00-03	6/10/2021	14:45	9.3	8.3	10.9	**9.5**	1.3	13.80%
57	GT21-OW-12-03-06	6/10/2021	14:45	6	6.6	9	**7.2**	1.6	22.00%
58	GT21-OW-12-06-12	6/10/2021	14:45	8.1	7.5	7.8	**7.8**	0.3	3.80%
59	GT21-OW-12-12-24	6/10/2021	14:45	4.4	5.7	6.7	**5.6**	1.2	20.60%
60	GT21-OW-12-24-60	6/10/2021	14:45	2.5	3.3	3.2	**3**	0.4	14.50%
61	GT21-OL-01-00-60	6/15/0821	11:30	80.3	82.5	87.9	**83.6**	3.9	4.70%
62	GT21-OL-01-60-96	6/15/0821	11:30	16.2	12.9	17	**15.4**	2.2	14.10%
63	GT21-OL-02-00-60	6/15/0821	13:15	36.9	39.8	42.5	**39.7**	2.8	7.00%
64	GT21-OL-02-60-120	6/15/0821	13:15	46.4	35.4	47.6	**43.1**	6.7	15.60%
65	GT21-OL-02-120-180	6/15/0821	13:15	20.2	21.5	23.7	**21.8**	1.8	8.10%
66	GT21-OL-02-180-204	6/15/0821	13:15	5.4	2.7	3.6	**3.9**	1.4	35.30%
67	GT21-OL-03-00-60	6/15/0821	15:05	38.5	33.6	37	**36.4**	2.5	6.90%
68	GT21-OL-03-60-120	6/15/0821	15:05	20	27.2	21.8	**23**	3.7	16.30%
69	GT21-OL-03-120-129	6/15/0821	15:05	18.9	17.8	18.6	**18.4**	0.6	3.10%
70	GT21-OL-03-129-153	6/15/0821	15:05	10.3	9.5	10	**9.9**	0.4	4.10%
71	GT21-OL-04-00-60	6/16/2021	8:00	53.5	49.4	58.8	**53.9**	4.7	8.70%
72	GT21-OL-04-60-120	6/16/2021	8:00	32.5	27.3	33	**30.9**	3.2	10.20%
73	GT21-OL-04-120-150	6/16/2021	8:00	24	23.3	25.1	**24.1**	0.9	3.80%

74	GT21-OL-04-150-174	6/16/2021	8:00	15.8	15.8	11.8	**14.5**	2.3	16.00%
75	GT21-OL-05-00-60	6/16/2021	10:00	62.8	75.3	68.7	**68.9**	6.3	9.10%
76	GT21-OL-05-60-120	6/16/2021	10:00	60.2	60.5	71	**63.9**	6.2	9.60%
77	GT21-OL-05-120-180	6/16/2021	10:00	43.5	42.2	44.4	**43.4**	1.1	2.60%
78	GT21-OL-05-180-195	6/16/2021	10:00	27.9	32.7	30.9	**30.5**	2.4	8.00%
79	GT21-OL-05-195-219	6/16/2021	10:00	3.3	2.5	3	**2.9**	0.4	13.80%
80	GT21-OL-06-00-60	6/16/2021	12:30	77.7	79.8	79	**78.8**	1.1	1.30%
81	GT21-OL-06-60-120	6/16/2021	12:30	61	68.9	69.3	**66.4**	4.7	7.00%
82	GT21-OL-06-120-180	6/16/2021	12:30	92	89.6	90.6	**90.7**	1.2	1.30%
83	GT21-OL-06-180-240	6/16/2021	12:30	49.8	46.6	45.1	**47.2**	2.4	5.10%
84	GT21-OL-06-240-264	6/16/2021	12:30	3	2.5	3.5	**3**	0.5	16.70%
85	GT21-OL-07-00-03	6/17/2021	8:00	14.6	19.2	16.3	**16.7**	2.3	13.90%
86	GT21-OL-07-03-60	6/17/2021	8:00	89.4	95.1	92	**92.2**	2.9	3.10%
87	GT21-OL-07-60-120	6/17/2021	8:00	59.5	63.4	69.5	**64.1**	5	7.90%
88	GT21-OL-07-120-180	6/17/2021	8:00	90.9	92.7	92.2	**91.9**	0.9	1.00%
89	GT21-OL-07-180-190	6/17/2021	8:00	81.9	84	90.3	**85.4**	4.4	5.10%
90	GT21-OL-07-190-214	6/17/2021	8:00	2.4	3.3	2.8	**2.8**	0.5	15.90%
91	GT21-OL-08-00-60	6/17/2021	9:30	10.7	4.1	8.5	**7.8**	3.4	43.30%
92	GT21-OL-08-60-90	6/17/2021	9:30	73.4	77.4	75.4	**75.4**	2	2.70%
93	GT21-OL-08-90-114	6/17/2021	9:30	5.2	4.9	4.8	**5**	0.2	4.20%
94	GT21-OL-09-00-60	6/17/2021	11:00	44.2	43.2	52.4	**46.6**	5	10.80%
95	GT21-OL-09-60-115	6/17/2021	11:00	100	98.6	98.5	**99**	0.8	0.80%
96	GT21-OL-09-115-139	6/17/2021	11:00	2.8	3.3	1.8	**2.6**	0.8	29.00%
97	GT21-OL-10-00-60	6/17/2021	12:10	77	75.6	76.7	**76.4**	0.7	1.00%
98	GT21-OL-10-60-116	6/17/2021	12:10	48.2	45.3	38.7	**44.1**	4.9	11.00%
99	GT21-OL-11-00-60	6/17/2021	13:00	73.2	74.6	82.4	**76.7**	5	6.50%
100	GT21-OL-11-60-120	6/17/2021	13:00	95.5	99.2	92.5	**95.7**	3.4	3.50%
101	GT21-OL-11-120-183	6/17/2021	13:00	96.4	98	97.3	**97.2**	0.8	0.80%
102	GT21-OL-11-183-207	6/17/2021	13:00	1.2	2.7	2.3	**2.1**	0.8	37.60%

103	GT21-OL-12-00-60	6/17/2021	14:10	93.5	93.9	96	**94.5**	1.3	1.40%
104	GT21-OL-12-60-120	6/17/2021	14:10	98.2	100	95.6	**97.9**	2.2	2.30%
105	GT21-OL-12-120-180	6/17/2021	14:10	81.8	81.5	76.6	**80**	2.9	3.70%
106	GT21-OL-12-180-203	6/17/2021	14:10	67.3	66.9	64.6	**66.3**	1.5	2.20%
107	GT21-OL-12-203-227	6/17/2021	14:10	2.9	3.1	2.7	**2.9**	0.2	6.90%
108	GT21-OL-13-00-60	6/17/2021	15:30	84	84	85.5	**84.5**	0.9	1.00%
109	GT21-OL-13-60-120	6/17/2021	15:30	96.1	96.1	96.2	**96.1**	0.1	0.10%
110	GT21-OL-13-120-180	6/17/2021	15:30	56.5	60.9	64.6	**60.7**	4.1	6.70%
111	GT21-OL-13-180-204	6/17/2021	15:30	2	1.9	2.4	**2.1**	0.3	12.60%
112	GT21-OL-14-00-60	6/18/2021	7:20	73.1	75.1	77.8	**75.3**	2.4	3.10%
113	GT21-OL-14-60-120	6/18/2021	7:20	83.9	80.4	77.6	**80.6**	3.2	3.90%
114	GT21-OL-14-120-180	6/18/2021	7:20	97.9	97.9	96.9	**97.6**	0.6	0.60%
115	GT21-OL-14-180-242	6/18/2021	7:20	97.9	96	98.5	**97.5**	1.3	1.30%
116	GT21-OL-14-242-266	6/18/2021	7:20	3.4	4.8	4.2	**4.1**	0.7	17.00%
117	GT21-OL-15-00-60	6/18/2021	9:00	88	86	89.7	**87.9**	1.9	2.10%
118	GT21-OL-15-60-120	6/18/2021	9:00	46.4	43.2	39.7	**43.1**	3.4	7.80%
119	GT21-OL-15-120-144	6/18/2021	9:00	43.2	46.1	37.4	**42.2**	4.4	10.50%
120	GT21-OL-15-144-168	6/18/2021	9:00	6.1	4.4	5.7	**5.4**	0.9	16.50%
121	GT21-OL-16-00-60	6/18/2021	10:00	89.2	83.6	86.8	**86.5**	2.8	3.20%
122	GT21-OL-16-60-124	6/18/2021	10:00	70	65.2	70.2	**68.5**	2.8	4.10%
123	GT21-OL-16-124-148	6/18/2021	10:00	6.8	4.6	3.8	**5.1**	1.6	30.70%
124	GT21-OL-17-00-60	6/18/2021	11:00	86.2	85.2	87.4	**86.3**	1.1	1.30%
125	GT21-OL-17-60-114	6/18/2021	11:00	100	100	100	**100**	0	0.00%
126	GT21-OL-18-00-60	6/18/2021	11:45	87.6	81	82.3	**83.6**	3.5	4.20%
127	GT21-OL-18-60-88	6/18/2021	11:45	67.6	61.8	60.3	**63.2**	3.9	6.10%
128	GT21-OL-19-00-60	6/18/2021	12:25	83.7	86.5	86	**85.4**	1.5	1.70%
129	GT21-OL-19-60-84	6/18/2021	12:25	90.7	92.7	91.3	**91.6**	1	1.10%
130	GT21-OL-20-00-60	6/21/2021	12:00	90.4	88.6	91	**90**	1.2	1.40%
131	GT21-OL-20-60-102	6/21/2021	12:00	96.5	96.6	98.8	**97.3**	1.3	1.30%

132	GT21-OL-21-00-60	6/21/2021	12:45	83.1	80	79.2		**80.8**	2.1	2.60%
133	GT21-OL-21-60-120	6/21/2021	12:45	73.4	77.6	77.6		**76.2**	2.4	3.20%
134	GT21-OL-21-120-149	6/21/2021	12:45	69.5	71	67.2		**69.2**	1.9	2.80%
135	GT21-OL-22-00-60	6/21/2021	13:50	95	94.3	94.7		**94.7**	0.4	0.40%
136	GT21-OL-22-60-94	6/21/2021	13:50	96.7	98.9	96.7		**97.4**	1.3	1.30%
137	GT21-OL-23-00-60	6/21/2021	14:30	86.8	92.6	90.5		**90**	2.9	3.30%
138	GT21-OL-23-60-125	6/21/2021	14:30	76	75.2	78.2		**76.5**	1.6	2.00%
139	GT21-OL-24-00-42	6/21/2021	15:40	58.4	62	65.1		**61.8**	3.4	5.40%
140	GT21-OL-24-42-51	6/21/2021	15:40	10.3	15	22.1		**15.8**	5.9	37.60%
141	GT21-OL-24-51-111	6/21/2021	15:40	84.1	87	94.7		**88.6**	5.5	6.20%
142	GT21-OL-24-111-171	6/21/2021	15:40	97.9	97.7	96.5		**97.4**	0.8	0.80%
143	GT21-OL-24-171-220	6/21/2021	15:40	62.3	62	59.8		**61.4**	1.4	2.20%
144	GT21-OL-25-00-60	6/21/2021	17:30	92	92.9	91.8		**92.2**	0.6	0.60%
145	GT21-OL-25-60-120	6/21/2021	17:30	92.7	92.7	91.8		**92.4**	0.5	0.60%
146	GT21-OL-25-120-164	6/21/2021	17:30	98.9	95.6	97.4		**97.3**	1.7	1.70%
147	GT21-OL-26-00-60	6/22/2021	10:10	95.9	95.2	97		**96**	0.9	0.90%
148	GT21-OL-26-60-120	6/22/2021	10:10	77	81.4	82.8		**80.4**	3	3.80%
149	GT21-OL-27-00-60	6/22/2021	11:00	96	97.5	96.2		**96.6**	0.8	0.80%
150	GT21-OL-27-60-120	6/22/2021	11:00	63.5	66.1	66.5		**65.4**	1.6	2.50%
151	GT21-OL-27-120-134	6/22/2021	11:00	25.7	35.9	35.1		**32.2**	5.7	17.60%
152	GT21-OL-28-00-60	6/22/2021	12:00	97.3	95.9	96.4		**96.5**	0.7	0.70%
153	GT21-OL-28-60-120	6/22/2021	12:00	98.6	96.8	95.9		**97.1**	1.4	1.40%
154	GT21-OL-29-120-180	6/22/2021	12:00	34.5	39.5	45.3		**39.8**	5.4	13.60%
155	GT21-OL-29-00-60	6/22/2021	13:10	73.3	84.7	98.1	86	**85.5**	10.1	11.90%
156	GT21-OL-29-60-120	6/22/2021	13:10	92.8	91.7	91.7		**92.1**	0.6	0.70%
157	GT21-OL-29-120-180	6/22/2021	13:10	84.3	90.2	86.6		**87**	3	3.40%
158	GT21-OL-29-180-238	6/22/2021	13:10	50.5	49.8	48.5		**49.6**	1	2.00%
159	GT21-OL-30-00-60	6/22/2021	14:30	70.4	70.4	72		**70.9**	0.9	1.30%
160	GT21-OL-30-60-120	6/22/2021	14:30	95.8	95.9	96.8		**96.2**	0.6	0.60%

161	GT21-OL-30-120-180	6/22/2021	14:30	96.5	96.4	97	**96.6**	0.3	0.30%
162	GT21-OL-30-180-240	6/22/2021	14:30	98.4	96.1	98.1	**97.5**	1.3	1.30%
163	GT21-OL-30-240-300	6/22/2021	14:30	93.7	96	94.8	**94.8**	1.2	1.20%
164	GT21-OL-30-300-360	6/22/2021	14:30	73.7	78.9	76.2	**76.3**	2.6	3.40%
165	GT21-OL-30-360-404	6/22/2021	14:30	76.7	75.1	68.6	**73.5**	4.3	5.80%

Table A.2. Mean percentage stamp sand Mn adjustments

Adapted from Kerfoot et al., 2021 Supplemental Table 2. This is a Manganese (Mn) correction table. %SS values are corrected for Mn, and Cu concentrations are estimated with and without the Mn correction. Cu concentration calculated using 100%SS=2863 mg/kg (MDEQ, 2006). The asterisks represent: * No Mn correction since value=0, ** Mean Mn assumed 1.6% and subtracted from %SS value, and *** Mn directly calculated and %SS value corrected.

Latitude North	Longitude West	Date collected	Depth (m)	Station	% SS	%SS adj Mn Mean	Est. Cu con	Cu Con not adj for Mn	
47° 13.000	88° 09.000	7/11/2013	10.4		0	0	0	0	*
47° 12.830	88° 08.670	7/11/2013	10.2		0	0	0	0	*
47°12.660	88°10.420	5/29/2013	1.6		90	88.4	2531	2577	**
47°12.640	88°10.750	5/29/2013	2		75	73.4	2101	2147	**
47°12.571	88°10.682	7/17/2019	3	GP049	65.5	63.9	1829	1875	***
47° 12.550	88° 12.580	8/23/2013	5		30	28.4	813	859	**
47°12.526	88°12.307	7/17/2019	3.6	GP053	57.7	56.1	1606	1652	***
47°12.500	88°12.450	5/29/2013	3.5		100	98.4	2817	2863	**
47°12.481	88°10.657	7/17/2019	5.6	GP048	64.9	63.3	1812	1858	***
47°12.480	88°11.250	5/29/2013	2.3		100	98.4	2817	2863	**
47°12.477	88°11.443	8/15/2012	4.2	Gay 13	62.6	61	1746	1792	***
47°12.477	88°12.443	8/15/2012	3.5	Gay 13	58.9	57.3	1640	1686	**
47°12.450	88°11.830	5/29/2013	2.2		100	98.4	2817	2863	**
47° 12.440	88° 12.500	8/23/2013	5.1		90	88.4	2531	2577	**
47° 12.440	88° 11.164	8/22/2016	8.7	Gay-10	62.8	61.2	1752	1798	**
47° 12.424	88° 12.152	9/20/2016	7.3	B-2	77.9	76.3	2184	2230	**
47° 12.416	88° 11.965	8/22/2016	4.2	BRB-005	76.7	75.1	2150	2196	**

47° 12.4124	88° 12.1516	9/9/2016	7.3	station B(2)	77.9	76.3	2184	2230	***
47°12.352	88°11.169	8/15/2012	6.4	Gay 14	52.9	51.3	1469	1515	***
47°12.340	88°11.860	5/29/2013	3.3		100	98.4	2817	2863	**
47° 12.333	88° 12.500	9/9/2016	8	station D	77.8	76.2	2182	2227	***
47° 12.333	88° 12.1667	9/9/2016	7.9	station G	74.9	73.3	2099	2144	***
47° 12.3312	88° 12.3418	9/9/2016	8.5	station 1(A)	79.3	77.7	2225	2270	***
47°12.330	88°12.120	5/29/2013	6.1		55	53.4	1529	1575	**
47°12.330	88°11.660	5/29/2013	5.3		25	23.4	670	716	**
47°12.330	88°09.330	5/29/2013	29.8		30	28.4	813	859	**
47°12.327	88° 12.537	6/18/2013	6.2		75	73.4	2101	2147	**
47° 12.318	88° 12.468	6/18/2013	6.5		50	48.4	1386	1432	**
47° 12.310	88° 12.410	8/23/2013	7.9		50	48.4	1386	1432	**
47° 12.308	88° 12.022	6/18/2013	6.3		75	73.4	2101	2147	**
47° 12.293	88° 9.605	8/22/2016	25	Gay-25	6.8	5.2	149	195	**
47°12.290	88°11.930	5/29/2013	7.9		90	88.4	2531	2577	**
47° 12.273	88° 11.993	9/20/2016	8.5	station H-2	50.6	49	1403	1449	***
47°12.250	88°11.950	5/29/2013	6.3		65	63.4	1815	1861	**
47° 12.246	88° 10.252	8/22/2016	10.7	station ?	13.2	11.6	332	378	**
47° 12.243	88° 12.328	8/22/2016	6	station 3	60.1	58.5	1675	1721	**
47°12.220	88°11.830	5/29/2013	7.9		60	58.4	1672	1718	**
47° 12.219	88° 11.810	8/22/2016	7.3	station 2	55.6	54	1546	1592	***
47° 12.196	88° 5.861	8/22/2016	49.8	Gay-50	3.7	2.1	60	106	**
47°12.190	88°11.300	5/29/2013	10.6		25	23.4	670	716	**
47°12.190	88°11.040	5/29/2013	12.9		10	8.4	240	286	**
47° 12.1854	88° 12.3077	9/20/2016	8.5	station B	67	65.4	1872	1918	**
47°12.180	88°11.620	5/29/2013	7.5		50	48.4	1386	1432	**
47°12.180	88°11.250	5/29/2013	8.6		25	23.4	670	716	**
47° 12.177	88° 11.676	9/20/2016	9.3	station J	35.6	34	973	1019	***
47°12.170	88°11.000	5/29/2013	13.4		25	23.4	670	716	**

47° 12.170	88° 11.000	6/22/2013	13.2		30	28.4	813	859	**
47°12.170	88°10.170	5/29/2013	20		10	8.4	240	286	**
47° 12.170	88° 09.170	6/22/2013	39.7	USB002	10.4	8.8	252	298	***
47° 12.167	88° 11.500	6/11/2018	13	T-4	27.5	25.9	742	787	***
47° 12.1667	88° 12.500	9/9/2016	7.8	station E	19.9	18.3	524	570	***
47° 12.1667	88°12.1667	9/9/2016	9.7	station H	39.3	37.7	1079	1125	***
47° 12.126	88° 11.834	8/22/2016	10.5	BRB-10	38.5	36.9	1056	1102	**
47°12.122	88°12.808	8/15/2012	3.4	Sta 3	63.5	61.9	1772	1818	**
47° 12.114	88° 4.173	8/22/2016	75	Gay-75	3.8	2.2	63	109	**
47°12.081	88°12.248	8/15/2012	8.8	Gay 4	20.5	18.9	541	587	**
47°12.081	88°12.245	8/15/2012	8.5	Sta 4	17.4	15.8	452	498	**
47°12.080	88°12.250	5/29/2013	8.6		40	38.4	1099	1145	**
47° 12.080	88° 12.420	8/23/2013	7.4		10	8.4	240	286	**
47° 12.046	88° 9.882	9/23/2017	24.3	BRB-25	5	3.4	97	143	**
47° 12.00	88° 12.333	9/9/2016	10.7	station C	27.6	26	744	790	***
47° 12.00	88° 12.1667	9/9/2016	9.2	station F	19.8	18.2	521	567	***
47° 12.000	88° 09.670	7/11/2013	28.8		0	0	0	0	*
47°11.944	88°11.147	8/15/2012	4.1	Sta 10	73.1	71.5	2047	2093	**
47° 11.910	88° 8.367	9/23/2017	48.7	BRB-50	6.7	5.1	146	192	**
47°11.880	88°12.520	5/29/2013	7		30	28.4	813	859	**
47°11.870	88°13.017	8/15/2012	3.7	Sta 2	64.3	62.7	1795	1841	**
47°11.836	88°12.525	8/15/2012	9.8	Sta 5	54.4	52.8	1512	1557	**
47° 11.820	88° 13.400	8/23/2013	5.2	T07W01	29.2	27.6	790	836	**
47° 11.667	88° 13.031	8/22/2016	11	BR2-10	11.8	10.2	292	338	**
47°11.660	88°10.000	5/29/2013	22		10	8.4	240	286	**
47 11.650	88°13.170	5/29/2013	7.5		30	28.4	813	859	**
47° 11.630	88° 13.300	8/23/2013	3.6		75	73.4	2101	2147	**
47° 11.630	88° 13.270	8/23/2013	8.6		60	58.4	1672	1718	**
47° 11.630	88° 13.190	8/23/2013	3.7		70	68.4	1958	2004	**

47°11.611	88°13.214	8/15/2012	8.9	Gay 1	51.4	49.8	1426	1472	**
47°11.611	88°13.214	8/15/2012	8.9	Sta 1	51.5	49.9	1429	1474	**
47°11.598	88°12.774	8/15/2012	11.5	Gay 6	19.6	18	515	561	***
47°11.598	88°12.774	8/15/2012	13.4	Sta 6	10.1	8.5	243	289	**
47°11.598	88°12.261	8/15/2012	6	Sta 7	74.3	72.7	2081	2127	**
47°11.500	88°13.510	5/29/2013	8.8		50	48.4	1386	1432	**
47° 11.500	88° 13.190	8/23/2013	10.1		40	38.4	1099	1145	**
47° 11.500	88° 13.160	8/23/2013	10.3		45	43.4	1243	1288	**
47°11.500	88°12.920	5/29/2013	8.5		30	28.4	813	859	**
47° 11.500	88° 12.833	5/26/2017	9.1	S12	9.4	7.8	223	269	**
47° 11.500	88° 12.833	5/26/2017	9.1	S13	7.3	5.7	163	209	**
47° 11.500	88° 12.500	5/26/2017	9.1	S14	12.1	10.5	301	346	**
47° 11.500	88° 11.500	5/26/2017	11.2	S18	9	7.4	212	258	**
47° 11.500	88° 11.000	6/22/2013	22		5	3.4	97	143	**
47° 11.480	88° 12.790	8/23/2013	12.7		20	18.4	527	573	**
47°11.390	88°13.900	5/29/2013	4.7		65	63.4	1815	1861	**
47° 11.386	88° 13.203	8/22/2016	11	station 5	23	21.4	613	658	***
47° 11.340	88° 13.170	6/22/2013	11.8		10	8.4	240	286	**
47° 11.340	88° 13.000	6/22/2013	12.5		10	8.4	240	286	**
47° 11.340	88° 12.670	6/22/2013	13.8		10	8.4	240	286	**
47° 11.340	88° 11.340	6/22/2013	20		10	8.4	240	286	**
47° 11.333	88° 13.00	5/26/2017	10.9	S1	15	13.4	384	429	**
47° 11.333	88° 12.833	5/26/2017	10.9	S2	6	4.4	126	172	**
47° 11.333	88° 12.666	5/26/2017	10.3	S3	7.1	5.5	157	203	**
47° 11.333	88° 12.166	5/26/2017	11.2	S6	10.2	8.6	246	292	***
47° 11.296	88° 14.149	7/31/2017	2	OP 8	26.4	24.8	710	756	**
47° 11.27	88° 14.106	7/31/2017	4.2	OP 7	31.9	30.3	867	913	**
47° 11.253	88° 13.958	7/31/2017	6.5	OP 3	44.9	43.3	1240	1285	**
47°11.250	88°13.960	5/29/2013	4.7		50	48.4	1386	1432	**

47° 11.250	88° 13.919	7/31/2017	7.4	OP 2	49.2	47.6	1363	1409	**
47° 11.248	88° 14.002	7/31/2017	5.8	OP 4	37.5	35.9	1028	1074	**
47° 11.247	88° 14.053	7/31/2017	5.1	OP 5	21	19.4	555	601	**
47° 11.241	88° 14.086	7/31/2017	5	OP 6	34.1	32.5	930	976	**
47° 11.23	88° 14.244	7/31/2017	2.1	OP 9	23.4	21.8	624	670	**
47° 11.230	88° 13.020	8/23/2013	12.3		20	18.4	527	573	**
47° 11.199	88° 14.148	7/31/2017	4.5	OP 19	12	10.4	298	344	**
47° 11.1975	88° 13.3958	6/11/2018	13	C1	11.6	10	286	332	***
47° 11.166	88° 13.166	5/26/2017	10.3	S16	8.1	6.5	186	232	**
47° 11.166	88° 13.00	5/26/2017	10.3	S17	7.9	6.3	180	226	**
47° 11.166	88° 12.833	5/26/2017	10.3	S9	8.9	7.3	209	255	***
47° 11.165	88° 13.972	7/31/2017	7.8	OP 18	18.8	17.2	492	538	**
47° 11.15	88° 14.141	7/31/2017	5.1	OP 10	17.2	15.6	447	492	**
47° 11.137	88° 13.885	7/31/2017	9.2	OP 17	29.8	28.2	807	853	**
47° 11.097	88° 14.303	7/31/2017	2.1	OP 11	9.7	8.1	232	278	**
47° 11.0971	88° 14.0010	6/11/2018	7.5	A2	43.2	41.6	1191	1237	***
47° 11.047	88° 13.008	8/22/2016	11	station 4	36.6	35	1002	1048	***
47° 11.022	88° 9.470	8/22/2016	51	BR2-50	3.7	2.1	60	106	**
47° 11.000	88° 14.170	6/22/2013	4.5		10	8.4	240	286	**
47°11.000	88°14.090	5/29/2013	5.6		10	8.4	240	286	**
47° 11.000	88° 14.000	6/22/2013	7.9		5	3.4	97	143	**
47°11.000	88°12.330	5/29/2013	18		25	23.4	670	716	**
47° 11.000	88° 11.670	7/11/2013	25.5		0	0	0	0	*
47°10.9970	88°13.9272	6/11/2018	10.5	A3	42.9	41.3	1182	1228	***
47° 10.991	88° 11.908	8/22/2016	24.5	BR-2-25	7.9	6.3	180	226	**
47°10.9822	88°13.4975	6/11/2018	14	B3	15.6	14	401	447	**
47° 10.986	88° 5.861	8/22/2016	101	BR2-100	2.4	0.8	23	69	**
47° 10.9759	88° 13.5337	9/20/2016	10.8	station N	11.3	9.7	278	324	**
47° 10.968	88° 14.213	7/31/2017	4.5	OP 12	18.6	17	487	533	**

47°10.834	88°13.842	9/24/2019	10.7	ES.T01	34.5	32.9	942	988	***
47° 10.830	88° 13.000	7/11/2013	15.5		0	0	0	0	*
47° 10.830	88° 12.000	7/11/2013	26.4		0	0	0	0	*
47°10.800	88°11.300	7/29/2010	28	GA0018	25	23.4	670	716	**
47° 10.799	88° 14.376	7/31/2017	1.9	OP 14	14.3	12.7	364	409	**
47° 10.794	88° 14.257	7/31/2017	4.8	OP 13	24.9	23.3	667	713	**
47°10.717	88° 12.428	6/18/2013	22.7		0	0	0	0	*
47° 10.688	88° 13.130	6/18/2013	22.5		10	8.4	240	286	**
47° 10.670	88° 14.170	6/22/2013	6.9		0	0	0	0	*
47°10.665	88°13.811	9/24/2019	11.3	ES.T03	32.2	30.6	876	922	***
47°10.656	88°14.000	9/24/2019	10.3	ES.T02	37.6	36	1031	1076	***
47° 10.590	88° 14.019	9/20/2016	9.1	station O	15.9	14.3	409	455	***
47°10.5153	88°13.224	8/15/2012	11	BGT 2	46.5	44.9	1285	1331	**
47° 10.510	88° 13.968	6/11/2018	13.5	A-4	6.6	5	143	189	**
47°10.506	88°13.826	9/24/2019	11.5	ES.T06	8.1	6.5	186	232	**
47° 10.50	88° 13.380	6/11/2018	10.8	C-4	24.1	22.5	644	690	***
47° 10.500	88° 13.500	7/11/2013	11.9	WSB010	0	0	0	0	*
47°10.497	88°13.976	9/24/2019	11.4	ES.T05	11.9	10.3	295	341	***
47°10.478	88°13.043	8/15/2012	15	BGT 1	14.2	12.6	361	407	***
47° 10.440	88° 13.822	8/22/2016	10.6	station 7	18.2	16.6	475	521	***
47°10.311	88°14.163	9/24/2019	9.5	ES.T04	10.5	8.9	255	301	***
47° 10.308	88° 13.203	6/18/2013	14.6		5	3.4	97	143	**
47°10.300	88°09.700	7/29/2010	35		10	8.4	240	286	**
47° 10.170	88° 13.670	6/22/2013	12.8		5	3.4	97	143	**
47° 10.000	88° 13.330	7/11/2013	15.6		5	3.4	97	143	**
47° 10.000	88° 12.670	7/11/2013	29.3		15	13.4	384	429	**
47°09.897	88° 14.330	6/18/2013	6.1		5	3.4	97	143	**
47° 9.833	88° 12.66	8/22/2016	29.1	station 8	16.8	15.2	435	481	***
47°09.800	88°12.200	7/29/2010	20		25	23.4	670	716	**

47°09.800	88°10.400	7/29/2010	35		0	0	0	0	*
47° 09.670	88° 14.170	6/22/2013	9.4		15	13.4	384	429	**
47° 09.670	88° 13.670	6/22/2013	12.1		0	0	0	0	*
47° 09.670	88° 13.170	6/22/2013	19.6		5	3.4	97	143	**
47° 09.670	88° 12.670	7/11/2013	31.1		5	3.4	97	143	**
47° 09.670	88° 12.670	6/22/2013	20		0	0	0	0	*
47° 09.670	88° 12.330	7/11/2013	35.6		5	3.4	97	143	**
47° 9.582	88° 14.402	8/22/2016	6.3	CSI-5	17.2	15.6	447	492	**
47° 09.547	88° 14.300	6/18/2013	9.4		10	8.4	240	286	**
47° 9.351	88° 12.913	10/17/2017	24.7	CSI-25	7.3	5.7	163	209	**
47° 9.192	88° 11.945	10/17/2017	55.9	CSI-50	6.1	4.5	129	175	**
47° 9.259	88° 14.298	7/31/2017	4.9	OP 15	14.5	12.9	369	415	**
47° 9.244	88° 14.379	7/31/2017	2	OP 16	7.9	6.3	180	226	**
47°09.200	88°11.300	7/29/2010	25		0	0	0	0	*
47° 9.146	88° 11.689	10/17/2017	72.2	CSI-75	6.2	4.6	132	178	**
47° 7.695	88° 16.823	10/10/2017	9	LTB 010	7.1	5.5	157	203	**

*No correction, 0 value **Mean Mn subtracted (1.6%) and SS% corrected ***Mn determined and %SS corrected

Table A.3. Sieved Ponar sediment samples

Sieved Ponar sediment samples from on shore (depth=0) and offshore in the Grand Traverse Bay area. Table lists station names, position (latitude & longitude), depth (m), percentage stamp sand in sample (%SS), mean particle size (µm), and % mass at each sieved size class (screen size). Size classes are determined from averages between Wildco Stainless Steel Sieves of 4000 µm (#5 Mesh), 2000 µm (#10 Mesh), 500 µm (#35 Mesh), 250 µm (#60 Mesh), 125 µm (#120 Mesh), and 63 µm (#230 Mesh). Sieves done on a Cenco-Meinzer Sieve Shaker Table (Central Scientific).

							% Mass at Each Screen Size						
Station	Date	Latitude N	Long W	Depth (m)	% SS	Mean size (µm)	5.3 mm	3 mm	1.25 mm	0.375 mm	0.188 mm	0.094 mm	0.047 mm
SMP004	7/11/2013	47° 12.830	88° 08.670	10.2	0	761.4	0.01	0.06	0.25	0.4	0.25	0.02	0
GP049	7/17/2019	47° 12.571	88° 10.682	3	66.5	230.7	0	0	0.01	0.19	0.78	0.02	0
T10-W08	8/23/2013	47° 12.550	88° 12.580	5	30	107.7	0	0	0	0.01	0.18	0.71	0.1
GP053	7/17/2019	47° 12.526	88° 12.307	3.6	57.7	178.8	0	0	0.01	0.04	0.65	0.28	0.01
GP048	7/17/2019	47° 12.481	88° 10.657	5.6	66.7	374.8	0	0	0.08	0.52	0.39	0	0
Gay 13	8/15/2012	47° 12.477	88° 11.443	4.2	62.6	138.1	0	0	0	0	0.43	0.51	0.05
Gay 13	8/15/2012	47° 12.477	88° 12.443	3.5	74.3	348.9	0.01	0.01	0.06	0.24	0.4	0.27	0
T10-W01	8/23/2013	47° 12.440	88° 12.500	5.1	90	132.6	0	0	0.01	0.01	0.36	0.57	0.05
B-2	9/20/2016	47° 12.424	88° 12.152	7.3	77.9	917.7	0	0	0.64	0.28	0.07	0	0
station B	9/9/2016	47° 12.4124	88° 12.1516	7.3	77.9	192.6	0	0	0.02	0.11	0.51	0.35	0.01
Gay 14	8/15/2012	47° 12.352	88° 11.169	6.4	52.9	176.5	0	0	0	0.02	0.77	0.2	0
station D	9/9/2016	47° 12.333	88° 12.500	8	77.8	150.9	0	0	0.01	0.01	0.52	0.44	0.02
station G(7)	9/9/2016	47° 12.333	88° 12.1667	7.9	74.9	142.4	0	0	0	0	0.52	0.46	0.02
station 1(A)	9/9/2016	47° 12.3312	88° 12.3418	8.5	79.3	126.6	0	0	0	0.01	0.36	0.59	0.04

T10-W02	8/23/2013	47° 12.310	88° 12.410	7.9	50	178.9	0	0	0.02	0.04	0.46	0.46	0.01
station H-2	9/20/2016	47° 12.273	88° 11.993	8.5	50.6	185.7	0	0	0.01	0.08	0.59	0.32	0
station ?	8/22/2016	47° 12.246	88° 10.252	10.7	13.2	344.5	0	0	0.07	0.45	0.44	0.04	0
station 3	8/22/2016	47° 12.243	88° 12.328	6	60.1	172.5	0	0	0.02	0.07	0.42	0.47	0.02
station 2	8/22/2016	47° 12.219	88° 11.810	7.3	55.6	181.2	0	0	0.01	0.08	0.59	0.33	0
station 2(B)	9/20/2016	47° 12.1854	88° 12.3077	8.5	67	148.6	0	0	0	0.01	0.58	0.4	0.02
station J	9/20/2016	47° 12.177	88° 11.676	9.3	35.6	232.2	0	0	0.02	0.2	0.67	0.11	0
SST002	6/22/2013	47° 12.170	88° 11.000	13.2	30	196.7	0	0	0	0.11	0.77	0.12	0
USB002	6/22/2013	47° 12.170	88° 09.170	39.7	10.4	210.9	0	0	0.01	0.21	0.46	0.3	0.01
T-4	6/11/2018	47° 12.167	88° 11.500	13	27.5	394.9	0	0	0.11	0.44	0.4	0.05	0
station E	9/9/2016	47° 12.1667	88° 12.500	7.8	19.9	1368.3	0.05	0.11	0.53	0.22	0.07	0.01	0
station H	9/9/2016	47° 12.1667	88° 12.1667	9.7	39.3	196.9	0	0	0.01	0.11	0.68	0.2	0
Sta 3	8/15/2012	47° 12.122	88° 12.808	3.4	17.4	142.8	0	0	0	0	0.51	0.48	0.01
Gay 004	8/15/2012	47° 12.081	88° 12.248	8.8	20.5	305.6	0	0	0.05	0.36	0.55	0.05	0
Sta 4	8/15/2012	47° 12.081	88°12.245	8.5	73.1	688.1	0.01	0.01	0.33	0.43	0.2	0.02	0
TRB006	8/23/2013	47° 12.080	88° 12.420	7.4	10	258.8	0	0	0.04	0.22	0.65	0.1	0
station 3(C)	9/9/2016	47° 12.00	88° 12.333	10.7	27.6	638.1	0	0	0.34	0.45	0.17	0.03	0
station F	9/9/2016	47° 12.00	88° 12.1667	9.2	19.8	530	0	0.01	0.22	0.43	0.31	0.03	0
Sta 10	8/15/2012	47° 11.944	88° 11.147	4.1	10.1	322	0	0	0.04	0.43	0.52	0	0
Sta 2	8/15/2012	47° 11.870	88° 13.017	3.7	63.5	164.6	0	0	0	0.01	0.63	0.34	0.01
Sta 5	8/15/2012	47° 11.836	88° 12.525	9.8	64.3	185.3	0	0	0.02	0.06	0.47	0.45	0
T07W01	8/23/2013	47° 11.820	88° 13.400	5.2	29.2	365.7	0	0	0.06	0.61	0.31	0.02	0
T06-W03	8/23/2013	47° 11.630	88° 13.190	3.7	70	353.3	0	0.03	0.08	0.07	0.65	0.17	0
T07W06	8/23/2013	47° 11.630	88° 13.270	8.6	60	140.5	0	0	0	0	0.49	0.5	0.01
Gay 001	8/15/2012	47° 11.611	88° 13.214	8.9	51.4	133.3	0	0	0	0.01	0.32	0.63	0.03

Sta 1	8/15/ 2012	47° 11.611	88° 13.214	8.9	58.9	1012. 9	0	0	0.74	0.19	0.07	0	0
Gay 6	8/15/ 2012	47° 11.598	88° 12.774	11.5	19.6	439.8	0	0	0.13	0.57	0.28	0.01	0
Sta 6	8/15/ 2012	47° 11.598	88° 12.774	13.4	54.4	320.4	0	0	0.08	0.3	0.56	0.06	0
Sta 7	8/15/ 2012	47°11.59 8	88° 12.261	6	51.5	373.5	0	0	0.07	0.59	0.33	0	0
T07W0 2	8/23/ 2013	47° 11.500	88° 13.190	10.1	40	131.3	0	0	0	0.01	0.37	0.62	0.01
TRC00 2	8/23/ 2013	47° 11.500	88° 13.160	10.3	45	175.5	0	0	0.01	0.09	0.38	0.51	0
SST00 4	6/22/ 2013	47° 11.500	88° 11.000	22	5	305.9	0	0	0.02	0.56	0.41	0.02	0
S12	5/26/ 2017	47° 11.500	88° 12.833	9.1	9.4	535.3	0	0.01	0.21	0.58	0.2	0.01	0
S18	5/26/ 2017	47° 11.500	88° 11.500	11.2	9	542.5	0	0.01	0.21	0.39	0.36	0.01	0
T08W0 3	8/23/ 2013	47° 11.480	88° 12.790	12.7	20	292.2	0	0	0.05	0.26	0.66	0.03	0
station 5	8/22/ 2016	47° 11.386	88° 13.203	11	23	814.1	0	0	0.51	0.43	0.05	0	0
SBR00 5	6/22/ 2013	47° 11.340	88° 13.170	11.8	10	305.6	0	0	0.03	0.49	0.46	0.02	0
SBR00 7	6/22/ 2013	47° 11.340	88° 13.000	12.5	10	357	0	0.01	0.05	0.55	0.35	0.03	0.01
SBR00 8	6/22/ 2013	47° 11.340	88° 11.340	20	10	289.5	0	0	0.03	0.36	0.56	0.04	0
S1	5/26/ 2017	47° 11.333	88° 13.00	10.9	15	2257. 3	0.21	0.17	0.44	0.12	0.05	0.01	0
S2	5/26/ 2017	47° 11.333	88° 12.833	10.9	6	1362. 5	0.05	0.03	0.78	0.11	0.02	0	0
S3	5/26/ 2017	47° 11.333	88° 12.666	10.3	7.1	776.3	0	0	0.47	0.43	0.1	0	0
S6	5/26/ 2017	47° 11.333	88° 12.166	11.2	10.2	596.9	0	0.01	0.28	0.44	0.26	0.01	0
T07W0 3	8/23/ 2013	47° 11.230	88° 13.020	12.3	20	1421. 1	0.03	0.11	0.74	0.11	0.02	0	0
C1	6/11/ 2018	47° 11.1975	88° 13.3958	13	11.6	667.3	0	0.01	0.35	0.5	0.14	0	0
S16	5/26/ 2017	47° 11.166	88° 13.166	10.3	8.1	1207. 2	0.02	0.07	0.66	0.22	0.04	0	0
S17	5/26/ 2017	47° 11.166	88° 13.00	10.3	7.9	904.5	0	0.04	0.52	0.29	0.14	0.01	0
S9	5/26/ 2017	47° 11.166	88° 12.833	10.3	8.9	1557. 6	0.05	0.17	0.59	0.13	0.06	0	0
A2	6/11/ 2018	47° 11.0971	88° 14.0010	7.5	43.2	132.9	0	0	0	0	0.26	0.69	0.04
station 4	8/22/ 2016	47° 11.047	88° 13.008	11	36.6	196.7	0	0	0.01	0.09	0.74	0.16	0

WSB001	6/22/2013	47° 11.000	88° 14.170	4.5	10	179.5	0	0	0	0.06	0.75	0.2	0
WSB002	6/22/2013	47° 11.000	88° 14.000	7.9	5	297.4	0	0	0.01	0.53	0.43	0.02	0
CDW002	7/11/2013	47° 11.000	88° 11.670	25.5	0	238.8	0	0	0.04	0.11	0.69	0.16	0
A3	6/11/2018	47° 10.9970	88° 13.9272	10.5	42.9	197.7	0	0	0.01	0.06	0.72	0.2	0.01
station N	9/20/2016	47° 10.9759	88° 13.5337	10.8	11.3	1217.4	0	0.05	0.8	0.11	0.03	0	0
ES.T01	9/24/2019	47° 10.834	88° 13.842	10.7	34.5	177.6	0	0	0	0.04	0.71	0.24	0.01
WSB011	7/11/2013	47° 10.830	88° 13.000	15.5	0	255	0	0	0.01	0.31	0.61	0.06	0
CDW001	7/11/2013	47° 10.830	88° 12.000	26.4	0	599.3	0	0.01	0.3	0.43	0.25	0.01	0
GA0018	7/29/2010	47° 10.800	88° 11.300	28	25	276.7	0	0	0.03	0.27	0.66	0.03	0
WSB003	6/22/2013	47° 10.670	88° 14.170	6.9	0	171.8	0	0	0	0.07	0.62	0.31	0
ES.T02	9/24/2019	47° 10.656	88° 14.000	10.3	37.6	148.7	0	0	0	0.01	0.39	0.57	0.02
ES.T03	9/24/2019	47° 10.665	88° 13.811	11.3	32.2	156.2	0	0	0.01	0.03	0.44	0.49	0.03
station O	9/20/2016	47° 10.590	88° 14.019	9.1	15.9	439.5	0	0	0.16	0.43	0.37	0.03	0
BGT 002	8/15/2012	47° 10.5153	88° 13.224	11	46.5	218.2	0	0	0.02	0.14	0.68	0.15	0.01
A4	6/11/2018	47° 10.510	88° 13.968	13.5	6.6	357.3	0	0	0.08	0.45	0.45	0.01	0
ES.T06	9/24/2019	47° 10.506	88° 13.826	11.5	8.1	540.2	0	0.01	0.23	0.52	0.24	0.01	0
C-4	6/11/2018	47° 10.50	88° 13.380	10.8	24.1	229.7	0	0	0.04	0.08	0.68	0.2	0
WSB010	7/11/2013	47° 10.500	88° 13.500	11.9	0	206.1	0	0	0.01	0.09	0.84	0.07	0
ES.T05	9/24/2019	47° 10.497	88° 13.976	11.4	11.9	262	0	0	0.02	0.33	0.61	0.04	0
BGT 001	8/15/2012	47° 10.478	88° 13.043	15	14.2	192.3	0	0	0.01	0.07	0.77	0.15	0.01
station 7	8/22/2016	47° 10.440	88° 13.822	10.6	18.2	230.6	0	0	0.02	0.2	0.67	0.11	0
ES.T04	9/24/2019	47° 10.311	88° 14.163	9.5	10.5	280.7	0	0	0.02	0.42	0.51	0.05	0
GA0011	7/29/2010	47° 10.300	88° 09.700	35	10	289.7	0	0	0.07	0.28	0.35	0.19	0.1
WSB004	6/22/2013	47° 10.170	88° 13.670	12.8	5	174.6	0	0	0	0.05	0.7	0.25	0
WSB009	7/11/2013	47° 10.000	88° 13.330	15.6	5	202.9	0	0	0.02	0.05	0.77	0.16	0

SDW003	7/11/2013	47° 10.000	88° 12.670	29.3	15	267.1	0	0.01	0.07	0.11	0.33	0.42	0.06
station 8	8/22/2016	47° 9.833	88° 12.66	29.1	16.8	281.3	0	0	0.04	0.31	0.59	0.06	0
GA0009	7/29/2010	47° 09.800	88° 10.400	35	0	282.5	0	0	0.07	0.28	0.34	0.2	0.11
SDW002	7/11/2013	47° 09.670	88° 12.670	31.1	5	289.2	0	0.01	0.09	0.17	0.4	0.21	0.13
SDW001	7/11/2013	47° 09.670	88° 12.330	35.6	5	324.2	0	0.01	0.09	0.23	0.48	0.18	0.01
GA0003	7/29/2010	47° 09.200	88° 11.300	25	0	329.4	0.01	0.01	0.07	0.22	0.47	0.16	0.06
Bob Regis House	Na	47° 11.969	88° 13.755	0	89.1	1285.8	0	0.05	0.88	0.06	0.01	0	0
#6	4/5/2019	47° 11.882	88° 13.764	0	77	1242.4	0	0.01	0.96	0.03	0	0	0
#5	4/5/2019	47° 11.640	88° 13.968	0	73.8	2102.1	0.04	0.4	0.56	0	0	0	0
#4	4/5/2019	47° 11.583	88° 14.008	0	92.9	1877.5	0.04	0.27	0.69	0	0	0	0
#3	4/5/2019	47° 11.468	88° 14.089	0	98.1	2357.1	0.04	0.54	0.42	0	0	0	0
#2	4/5/2019	47° 11.421	88° 14.161	0	90.5	2320.4	0.01	0.59	0.4	0	0	0	0
#1	4/5/2019	47° 11.380	88° 14.220	0	100	3233.8	0.1	0.89	0	0	0	0	0
N. Traverse R (TR)	3/29/2019	47° 11.374	88° 14.152	0	76.7	2554.3	0.04	0.66	0.31	0	0	0	0
Overtopping TR	3/29/2019	47° 11.350	88° 14.113	0	89.6	1754.9	0	0.28	0.71	0	0	0	0
#7	4/5/2019	47° 11.340	88° 14.195	0	8.3	810.2	0	0	0.5	0.49	0.01	0	0
#8	4/5/2019	47° 11.327	88° 14.221	0	9.5	469.1	0	0	0.12	0.82	0.06	0	0
#9	4/5/2019	47° 11.310	88° 14.251	0	6.7	622.7	0	0	0.29	0.66	0.05	0	0
#10	4/5/2019	47° 11.288	88° 14.275	0	7.9	831.8	0	0	0.52	0.47	0.01	0	0
#11	4/5/2019	47° 11.273	88° 14.289	0	9.4	849.5	0	0	0.54	0.45	0.01	0	0
#15	4/5/2019	47° 10.908	88° 14.414	0	6.3	973.6	0	0	0.67	0.32	0.01	0	0
#18	4/30/2019	47° 10.907	88° 14.414	0	4.9	1070.9	0	0	0.8	0.2	0	0	0
#14	4/5/2019	47° 10.877	88° 14.421	0	5.8	710.2	0	0	0.38	0.58	0.03	0	0
#13	4/5/2019	47° 10.853	88° 14.433	0	6.7	811.4	0	0	0.49	0.49	0.01	0	0

#12	4/5/2019	47° 10.839	88° 14.431	0	7	1134	0	0	0.87	0.13	0	0	0
#19	4/30/2019	47° 10.751	88° 14.455	0	6.6	1019.5	0	0	0.74	0.26	0	0	0
#20	4/30/2019	47° 10.706	88° 14.466	0	6.5	1356.2	0	0.07	0.93	0	0.01	0	0
#21	4/30/2019	47° 10.683	88° 14.474	0	11.1	729	0	0	0.42	0.53	0.06	0	0
#23	4/30/2019	47° 10.637	88° 14.490	0	4.9	1047.2	0	0	0.76	0.24	0	0	0
#22	4/30/2019	47° 10.637	88° 14.485	0	33.2	859.6	0	0	0.56	0.44	0.01	0	0
#24	4/30/2019	47° 10.579	88° 14.499	0	5.2	1012.5	0	0	0.73	0.27	0	0	0
#25	4/30/2019	47° 10.552	88° 14.511	0	5.5	1016.2	0	0	0.73	0.27	0	0	0
#26	4/30/2019	47° 10.520	88° 14.517	0	6.3	1048.8	0	0	0.76	0.24	0	0	0
#27	4/30/2019	47° 10.474	88° 14.523	0	7.6	1015.1	0	0	0.73	0.27	0	0	0
#28	4/30/2019	47° 10.440	88° 14.530	0	3.1	1243.4	0	0	0.99	0.01	0	0	0
#36	5/3/2019	47° 08.340	88° 16.844	0	2.1	528.6	0	0	0.18	0.77	0.04	0	0
#35	5/3/2019	47° 08.302	88° 16.895	0	3.9	475.1	0	0	0.12	0.84	0.04	0	0
#34	5/3/2019	47° 08.241	88° 16.967	0	7.4	532.4	0	0	0.19	0.78	0.03	0	0
#33	5/3/2019	47° 08.202	88° 17.011	0	4.4	429.4	0	0	0.08	0.83	0.09	0	0
#32	5/3/2019	47° 08.113	88° 17.107	0	3.5	472.2	0	0	0.12	0.81	0.06	0	0
#31	5/3/2019	47° 08.045	88° 17.173	0	2.2	707.6	0	0	0.38	0.62	0	0	0
#30	5/3/2019	47° 07.989	88° 17.221	0	1.7	999.3	0	0	0.71	0.29	0	0	0
#37	5/3/2019	47° 07.938	88° 17.265	0	2.2	1106.8	0	0	0.84	0.16	0	0	0
#38	5/3/2019	47° 07.898	88° 17.297	0	2.2	947.2	0	0	0.65	0.34	0	0	0
#39	5/3/2019	47° 07.824	88° 17.328	0	3	856.3	0	0	0.55	0.44	0	0	0
#40	5/3/2019	47° 07.767	88° 17.352	0	1.7	1195.4	0	0	0.94	0.06	0	0	0
#41	5/3/2019	47° 07.720	88° 17.362	0	2.3	911.1	0	0	0.61	0.39	0	0	0
#42	5/3/2019	47° 07.689	88° 17.375	0	1.6	1185.6	0	0	0.93	0.07	0	0	0
#43	5/3/2019	47° 07.618	88° 17.387	0	3.6	1080.5	0	0	0.81	0.19	0	0	0

Table A.4. Cu concentration corrections for LD50 test

Corrections for Cu concentration in LD50 test based on Cu concentration results from MTU School of Forestry Laboratory LEAF for both Bete Grise water sample and amount of Cu dissolved into a stock solution. Cu concentration for Bete Grise (Cu conc of BG) water sample was 9.9 µg/L and Cu concentration of the stock solution (LEAF correction) is 790 µg/L. All Cu concentrations are in the units of µg/L.

Theoretical	**LEAF correction**	**Cu conc of BG** (µg/L)	**Actual and BG correction** (µg/L)
0	0	9.9	9.9
5	3.95	9.8505	13.8005
10	7.9	9.801	17.701
25	19.75	9.6525	29.4025
50	39.5	9.405	48.905
100	79	8.91	87.91
250	197.5	7.425	204.925
500	395	4.95	399.95
1000	790	0	790

Table A.5. Probit test for determining Cu LD50 for *Daphnia magna*

This table used the results of our acute toxicity test (% Dead at a known concentration), calculated a probit value, and ran an Excel Regression. Statistical results such as Significance F and ANOVA are reported below along with the regression. LD50 was for *Daphnia magna* Cu concentration reported as 8.89 µg/L

Probit test using LD50 24hr				**LD50 Results**
Cu conc. (µg/L)	log10(conc.)	% Dead	Probit	y=ax+b
9.9	0.995635195	40	4.75	y=3.469x+(1.708)
13.8	1.139894821	70	5.52	5=3.469x+1.708
17.7	1.247997802	80	5.84	5-1.708=3.469x
29.4	1.468384259	80	8.84	x=(5-1.708)/3.469
48.91	1.689353263	90	6.28	x=0.949
87.91	1.94403828	100		LD50= antilog x
204.93	2.311594944	100		LD50= antilog 0.949
399.95	2.602005701	100		**LD50=8.89**
790	2.897627091	100		

Excel Regression SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.611915893
R Square	0.37444106
Adjusted R Square	0.165921414
Standard Error	1.419254418
Observations	5

ANOVA

	SS	**df**	**MS**	**F**	**Significance F**
Regression	3.617070688	1	3.617070688	1.795711179	0.272688052
Residual	6.042849312	3	2.014283104		
Total	9.65992	4			

	Coefficients	**SE**	**t Stat**	**P-value**	**Lower 95%**	**Upper 95%**
Intercept	1.707765034	3.44560173	0.495636224	0.654184932	-9.257677476	12.67320754
X Variable 1	3.46892744	2.58867168	1.340041484	0.272688052	-4.769381184	11.70723606

Table A.6. Chronic test adult survival data

In Portage Lake (PL), Traverse River (TR), Lake Superior (LS) and Coal Dock Road riparian zone (CDR), *Daphnia* were counted at various %SS concentrations over 21 days. The survival rate of adult *Daphnia* was determined out of 10 individuals (ex. 50% survival means 5 of 10 survived). On day 14, juveniles were removed after counting to reduce the effects of resource competition. NA%SS data was water without the presence of any sediment. Green is high survival or density, yellow is medium, and red is low to no survival.

PL Adults Survival	Day 0	Day 1	Day 2	Day 3	Day 5	Day 7	Day 9	Day 12	Day 14	Day 16	Day 19	Day 21
NA%SS	100%	100%	90%	90%	90%	60%	60%	60%	60%	60%	60%	40%
0%SS	100%	90%	80%	70%	70%	60%	60%	60%	60%	60%	60%	60%
10%SS	100%	100%	80%	70%	70%	70%	70%	70%	60%	50%	40%	30%
20%SS	100%	90%	80%	70%	70%	60%	60%	60%	60%	50%	40%	0%
30%SS	100%	90%	70%	80%	70%	70%	40%	30%	0%	0%	0%	0%
40%SS	100%	80%	60%	40%	40%	40%	50%	40%	30%	30%	20%	0%
50%SS	100%	100%	80%	80%	60%	50%	30%	20%	10%	0%	0%	0%
60%SS	100%	90%	80%	70%	70%	50%	20%	10%	10%	10%	10%	0%
70%SS	100%	100%	80%	60%	40%	40%	30%	20%	0%	0%	0%	0%
80%SS	100%	90%	80%	80%	80%	80%	70%	10%	10%	10%	10%	0%
90%SS	100%	100%	90%	70%	60%	50%	30%	20%	0%	0%	0%	0%
100%SS	100%	100%	100%	90%	80%	70%	0%	0%	0%	0%	0%	0%

TR Adults Counts	Day 0	Day 1	Day 2	Day 3	Day 4	Day 7	Day 9	Day 11	Day 14	Day 16	Day 18	Day 21
NA%SS	100%	60%	50%	50%	40%	20%	20%	20%	10%	10%	0%	0%
0%SS	100%	60%	50%	40%	40%	30%	30%	30%	20%	20%	10%	10%
10%SS	100%	90%	60%	60%	60%	40%	20%	20%	10%	10%	10%	10%
20%SS	100%	60%	40%	40%	30%	30%	30%	0%	0%	0%	0%	0%
30%SS	100%	100%	80%	70%	50%	10%	0%	0%	0%	0%	0%	0%
40%SS	100%	50%	40%	40%	30%	10%	0%	0%	0%	0%	0%	0%
50%SS	100%	100%	90%	40%	40%	10%	0%	0%	0%	0%	0%	0%
60%SS	100%	90%	50%	50%	40%	0%	0%	0%	0%	0%	0%	0%
70%SS	100%	100%	100%	100%	90%	60%	30%	20%	10%	10%	0%	0%
80%SS	100%	90%	80%	80%	80%	70%	40%	10%	0%	0%	0%	0%
90%SS	100%	80%	70%	60%	60%	30%	20%	10%	0%	0%	0%	0%
100%SS	100%	90%	70%	60%	60%	40%	10%	10%	0%	0%	0%	0%

LS Adults Counts	Day 0	Day 1	Day 2	Day 3	Day 5	Day 7	Day 10	Day 12	Day 14	Day 17	Day 19	Day 21
NA%SS	100%	100%	90%	40%	10%	10%	0%	0%	0%	0%	0%	0%
0%SS	100%	100%	90%	80%	40%	40%	20%	20%	20%	20%	10%	10%
10%SS	100%	100%	80%	80%	50%	40%	20%	20%	20%	10%	0%	0%
20%SS	100%	100%	90%	90%	50%	40%	10%	10%	10%	10%	10%	10%
30%SS	100%	80%	70%	60%	20%	20%	20%	20%	20%	10%	0%	0%
40%SS	100%	90%	70%	60%	40%	30%	10%	10%	0%	0%	0%	0%
50%SS	100%	100%	80%	70%	30%	20%	10%	10%	0%	0%	0%	0%
60%SS	100%	80%	60%	40%	20%	10%	0%	0%	0%	0%	0%	0%
70%SS	100%	100%	80%	70%	30%	10%	0%	0%	0%	0%	0%	0%
80%SS	100%	90%	50%	20%	10%	0%	0%	0%	0%	0%	0%	0%
90%SS	100%	80%	40%	10%	0%	0%	0%	0%	0%	0%	0%	0%
100%SS	100%	100%	50%	10%	0%	0%	0%	0%	0%	0%	0%	0%

CDR Adults Counts	Day 0	Day 1	Day 2	Day 3	Day 5	Day 7	Day 9	Day 12	Day 14	Day 16	Day 19	Day 21
NA%SS	100%	60%	60%	60%	60%	50%	50%	50%	50%	40%	40%	40%
0%SS	100%	50%	30%	20%	0%	0%	0%	0%	0%	0%	0%	0%
10%SS	100%	90%	60%	40%	20%	20%	10%	10%	10%	0%	0%	0%
20%SS	100%	50%	30%	30%	30%	10%	10%	0%	0%	0%	0%	0%
30%SS	100%	90%	60%	60%	50%	40%	10%	0%	0%	0%	0%	0%
40%SS	100%	90%	60%	40%	20%	10%	0%	0%	0%	0%	0%	0%
50%SS	100%	90%	40%	40%	40%	30%	0%	0%	0%	0%	0%	0%
60%SS	100%	70%	20%	10%	10%	0%	0%	0%	0%	0%	0%	0%
70%SS	100%	80%	20%	20%	0%	0%	0%	0%	0%	0%	0%	0%
80%SS	100%	60%	50%	20%	0%	0%	0%	0%	0%	0%	0%	0%
90%SS	100%	80%	50%	40%	10%	0%	0%	0%	0%	0%	0%	0%
100%SS	100%	70%	50%	40%	10%	0%	0%	0%	0%	0%	0%	0%

Table A.7. Chronic test juvenile counts

Portage Lake (PL), Traverse River (TR), Lake Superior (LS) and Coal Dock Road riparian zone (CDR) *Daphnia* juveniles were counted at various %SS concentrations over a 21 days period. On day 14, juveniles were removed after counting to reduce the effects of resource competition. Na%SS data was water without the presence of any sediment. Green is high juvenile density, yellow is medium, and red is few to no juveniles.

PL # Juveniles	Day 0	Day 1	Day 2	Day 3	Day 4	Day 7	Day 9	Day 11	Day 14	Day 16	Day 18	Day 21
NA%SS	0	0	1	1	0	21	71	110	182	6	7	7
0%SS	0	0	0	0	0	7	13	26	49	1	4	10
10%SS	0	4	3	3	3	16	31	42	52	4	13	14
20%SS	0	0	7	10	12	24	47	33	34	0	0	0
30%SS	0	10	0	4	3	14	13	14	5	0	0	0
40%SS	0	11	9	11	8	10	20	6	5	0	2	0
50%SS	0	1	1	1	1	34	33	24	10	0	0	0
60%SS	0	3	2	2	2	8	2	6	2	0	0	0
70%SS	0	0	0	0	0	0	13	0	0	0	0	0
80%SS	0	17	11	12	9	17	38	21	20	0	0	0
90%SS	0	0	0	3	0	1	20	12	0	0	0	0
100%SS	0	14	14	0	0	11	23	3	2	0	0	0

TR # Juveniles	Day 0	Day 1	Day 2	Day 3	Day 4	Day 7	Day 9	Day 11	Day 14	Day 16	Day 18	Day 21
NA%SS	0	0	0	0	0	0	0	6	6	0	0	0
0%SS	0	0	0	0	11	15	5	9	7	3	2	6
10%SS	0	0	0	0	5	15	16	11	14	0	2	2
20%SS	0	0	0	0	0	0	5	5	4	0	0	0
30%SS	0	0	0	0	0	0	0	0	0	0	0	0
40%SS	0	0	0	0	0	0	0	0	0	0	0	0
50%SS	0	6	13	18	11	0	0	0	0	0	0	0
60%SS	0	0	0	0	0	0	0	0	0	0	0	0
70%SS	0	0	0	0	0	0	0	0	0	0	0	0
80%SS	0	0	1	0	0	0	2	2	0	0	0	0
90%SS	0	0	0	0	0	1	3	0	0	0	0	0
100%SS	0	0	0	0	0	0	8	0	0	0	0	0

LS # Juvenile	Day 0	Day 1	Day 2	Day 3	Day 5	Day 7	Day 10	Day 12	Day 14	Day 17	Day 19	Day 21
NA%SS	0	0	0	0	0	0	0	0	0	0	0	0
0%SS	0	0	0	0	0	0	0	0	0	0	0	0
10%SS	0	0	0	0	0	0	0	0	6	0	0	0
20%SS	0	0	0	0	0	0	0	0	0	0	0	0
30%SS	0	1	7	17	9	9	9	9	8	0	0	0
40%SS	0	0	2	4	0	3	0	0	5	0	0	0
50%SS	0	0	0	0	0	0	0	0	0	0	0	0
60%SS	0	0	0	0	0	0	0	0	0	0	0	0
70%SS	0	1	0	0	0	0	0	0	0	0	0	0
80%SS	0	0	1	2	3	0	0	0	0	0	0	0
90%SS	0	0	1	1	0	0	0	0	0	0	0	0
100%SS	0	6	6	4	0	0	0	0	0	0	0	0

CDR # Juvenile	Day 0	Day 1	Day 2	Day 3	Day 5	Day 7	Day 9	Day 12	Day 14	Day 16	Day 19	Day 21
NA%SS	0	0	0	0	0	0	0	11	17	5	14	16
0%SS	0	0	0	0	0	0	0	0	0	0	0	0
10%SS	0	0	0	0	0	0	0	0	0	0	0	0
20%SS	0	0	0	0	0	0	0	0	0	0	0	0
30%SS	0	1	4	4	4	0	0	0	0	0	0	0
40%SS	0	0	0	0	0	0	0	0	0	0	0	0
50%SS	0	0	0	0	0	0	0	0	0	0	0	0
60%SS	0	0	0	0	0	0	0	0	0	0	0	0
70%SS	0	0	0	0	0	0	0	0	0	0	0	0
80%SS	0	0	0	0	0	0	0	0	0	0	0	0
90%SS	0	0	0	0	0	0	0	0	0	0	0	0
100%SS	0	0	0	0	0	0	0	0	0	0	0	0

Table A.8. Chronic test survivorship probability

Portage Lake (PL), Traverse River (TR), Lake Superior (LS) and Coal Dock Road riparian zone (CDR) *Daphnia* survivorship probability at various %SS concentrations over a 21 days period. On day 14, juveniles were removed after counting to reduce the effects of resource competition. Na%SS data was water without the presence of any sediment. Green has a high survivorship probability, yellow is medium, and red is close to or zero chance for survival.

PL Survivorship Probability

Day	NA% SS	0% SS	10% SS	20% SS	30% SS	40% SS	50% SS	60% SS	70% SS	80% SS	90% SS	100% SS
0	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
1	100%	90%	100%	90%	90%	80%	100%	90%	100%	90%	100%	100%
2	90%	72%	80%	72%	63%	48%	80%	72%	80%	72%	90%	100%
3	81%	50%	56%	50%	50%	19%	64%	50%	48%	58%	63%	90%
4	73%	35%	39%	35%	35%	8%	38%	35%	19%	46%	38%	72%
7	44%	21%	27%	21%	25%	3%	19%	18%	8%	37%	19%	50%
9	26%	13%	19%	13%	10%	2%	6%	4%	2%	26%	6%	0%
11	16%	8%	13%	8%	3%	1%	1%	0%	0%	3%	1%	0%
14	9%	5%	8%	5%	0%	0%	0%	0%	0%	0%	0%	0%
16	6%	3%	4%	2%	0%	0%	0%	0%	0%	0%	0%	0%
18	3%	2%	2%	1%	0%	0%	0%	0%	0%	0%	0%	0%
21	1%	1%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

TR Survivorship Probability

Day	NA% SS	0% SS	10% SS	20% SS	30% SS	40% SS	50% SS	60% SS	70% SS	80% SS	90% SS	100% SS
0	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
1	60%	60%	90%	60%	100%	50%	100%	90%	100%	90%	80%	90%
2	30%	30%	54%	24%	80%	20%	90%	45%	100%	72%	56%	63%
3	15%	12%	32%	10%	56%	8%	36%	23%	100%	58%	34%	38%
4	6%	5%	19%	3%	28%	2%	14%	9%	90%	46%	20%	23%
7	1%	1%	8%	1%	3%	0%	1%	0%	54%	32%	6%	9%
9	0%	0%	2%	0%	0%	0%	0%	0%	16%	13%	1%	1%
11	0%	0%	0%	0%	0%	0%	0%	0%	3%	1%	0%	0%
14	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
16	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
18	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
21	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

LS Survivorship Probability

Day	NA% SS	0% SS	10% SS	20% SS	30% SS	40% SS	50% SS	60% SS	70% SS	80% SS	90% SS	100% SS
0	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
1	100%	100%	100%	100%	80%	90%	100%	80%	100%	90%	80%	100%
2	90%	90%	80%	90%	56%	63%	80%	48%	80%	45%	32%	50%
3	36%	72%	64%	81%	34%	38%	56%	19%	56%	9%	3%	5%
4	4%	29%	32%	41%	7%	15%	17%	4%	17%	1%	0%	0%
7	0%	12%	13%	16%	1%	5%	3%	0%	2%	0%	0%	0%
9	0%	2%	3%	2%	0%	0%	0%	0%	0%	0%	0%	0%
11	0%	0%	1%	0%	0%	0%	0%	0%	0%	0%	0%	0%
14	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
16	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
18	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
21	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

	CDR Survivorship Probability											
Day	NA% SS	0% SS	10% SS	20% SS	30% SS	40% SS	50% SS	60% SS	70% SS	80% SS	90% SS	100% SS
0	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
1	60%	50%	90%	50%	90%	90%	90%	70%	80%	60%	80%	70%
2	36%	15%	54%	15%	54%	54%	36%	14%	16%	30%	40%	35%
3	22%	3%	22%	5%	32%	22%	14%	1%	3%	6%	16%	14%
4	13%	0%	4%	1%	16%	4%	6%	0%	0%	0%	2%	1%
7	6%	0%	1%	0%	6%	0%	2%	0%	0%	0%	0%	0%
9	3%	0%	0%	0%	1%	0%	0%	0%	0%	0%	0%	0%
11	2%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
14	1%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
16	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
18	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
21	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

Table A.9. Actual Cu concentration vs estimated Cu concentration AEM data

Comparing estimated (est.) Cu concentration using MDEQ mean Cu value (2863 mg/kg) and actual recorded Cu concentration (conc) by AEM. Sediment samples were obtained by AEM from the Grand Traverse Bay area in deep water (DW), in open water (OW), and on land (OL). Mean %SS was determined using the grain count method, and the mean %SS was multiplied by MDEQ mean Cu value to get an estimated Cu concentration value.

#	Sample Number & Type	Core Depth (in)	Date	Time	Lat	Long	Mean %SS	Actual Cu Conc (mg/kg)	Est. Cu Conc (100%=2863 mg/kg)
1	GT21-DW-01-Surface		6/3/2021	12:15	47.20594	-88.145222	9.9	78	283
2	GT21-DW-02-Surface		6/3/2021	13:30	47.202971	-88.150887	10	93	285
3	GT21-DW-03-Surface		6/3/2021	11:25	47.201224	-88.172822	9	10	256
4	GT21-DW-04-Surface		6/3/2021	16:15	47.19477	-88.154013	12.4	28	354
5	GT21-DW-05-Surface		6/3/2021	9:00	47.179537	-88.217309	11.1	26	318
6	GT21-DW-06-Surface		6/3/2021	10:15	47.171237	-88.206369	11.4	75	327
7	GT21-DW-07-Surface		6/3/2021	10:45	47.186742	-88.189472	9.5	11	273
8		00-03	6/8/2021	9:50	47.212765	-88.160218			
9	GT21-OW-01-00-12	03-06	6/8/2021	9:50	"	"	82.8	1400	2372
10		06-12	6/8/2021	9:50	"	"			
11	GT21-OW-01-12-72		6/8/2021	9:50	"		78.2	1300	2239
12	GT21-OW-01-72-126		6/8/2021	9:50	"	"	65	1200	1861
13	GT21-OW-01-126-140		6/8/2021	9:50	"	"	45.5	1000	1303
14		00-03	6/7/2021	12:00	47.209899	-88.169425			
15	GT21-OW-02-00-12	03-06	6/7/2021	12:00	"	"	84.8	1300	2429
16		06-12	6/7/2021	12:00	"	"			
17	GT21-OW-02-12-72		6/7/2021	12:00	"	"	70.8	1200	2028
18	GT21-OW-02-72-132		6/7/2021	12:00	"	"	75.6	1300	2163

19		00-03	6/7/2021	10:00	47.20943	-88.180361			
20	GT21-OW-03-00-12	03-06	6/7/2021	10:00	"	"	83.5	1400	2392
21		06-12	6/7/2021	10:00	"	"			
22	GT21-OW-03-12-61		6/7/2021	10:00	"	"	85.9	1300	2458
23		00-03	6/8/2021	14:30	47.208268	-88.201257			
24	GT21-OW-04-00-12	03-06	6/8/2021	14:30	"	"	62	1100	1775
25		06-12	6/8/2021	14:30	"	"			
26	GT21-OW-04-12-72		6/8/2021	14:30	"	"	50.6	1300	1450
27	GT21-OW-04-72-120		6/8/2021	14:30	"	"	24.5	1400	701
28	GT21-OW-04-120-148		6/8/2021	14:30	"	"	3.9	22	113
29		00-03	6/2/2021	8:30	47.206528	-88.198004			
30	GT21-OW-05-00-12	03-06	6/2/2021	8:30	"	"	68.6	1100	1964
31		06-12	6/2/2021	8:30	"	"			
32	GT21-OW-05-12-72		6/2/2021	8:30	"	"	64.9	1300	1859
33	GT21-OW-05-72-120		6/2/2021	8:30	"	"	35	840	1001
34	GT21-OW-05-120-180		6/2/2021	8:30	"	"	20.5	1300	588
35	GT21-OW-05-180-193		6/2/2021	8:30	"	"	6.4	1500	182
36	GT21-OW-05-193-253		6/2/2021	8:30	"	"	1.7	6	49
37		00-04	6/9/2021	13:00	47.203638	-88.197455			
38	GT21-OW-06-00-12	04-07	6/9/2021	13:00	"	"	28	180	802
39		07-12	6/9/2021	13:00	"	"			
40	GT21-OW-06-12-72		6/9/2021	13:00	"	"	5.1	3.7	147
41		00-03	6/5/2021	8:40	47.206364	-88.212951			
42	GT21-OW-07-00-14	03-06	6/5/2021	8:40	"	"	33.3	550	953
43		00-12	6/5/2021	8:40	"	"			
44	GT21-OW-07-14-38		6/5/2021	8:40	"	"	5.3	2.3	153
45	GT21-OW-09-Surface		6/17/2021	16:00	47.196231	-88.229932	61.7	870	1766
46	GT21-OW-10-00-12		6/14/2021	11:40	47.195438	-88.212093	2	3.5	56
47	GT21-OW-10-12-24		6/14/2021	11:40	"	"	1.5	4.5	44

48		00-03	6/4/2021	8:40	47.189684	-88.232649			
49	GT21-OW-11-00-14	03-06	6/4/2021	8:40	"	"	35.4	280	1014
50		06-14	6/4/2021	8:40	"	"			
51	GT21-OW-11-14-34		6/4/2021	8:40	"	"	7.1	6	204
52		00-03	6/10/2021	14:45	47.187127	-88.237594			
53	GT21-OW-12-00-12	03-06	6/10/2021	14:45	"	"	8.2	67	234
54		06-12	6/10/2021	14:45	"	"			
55	GT21-OW-12-12-24		6/10/2021	14:45	"	"	5.6	58	160
56	GT21-OW-12-24-60		6/10/2021	14:45	"	"	3	220	86
57		00-03	6/10/2021	12:50	47.18687	-88.235413			
58	GT21-OW-13-00-12	03-06	6/10/2021	12:50	"	"	13.6	94	388
59		06-12	6/10/2021	12:50	"	"			
60	GT21-OW-13-12-60		6/10/2021	12:50	"	"	3.8	2.3	109
61	GT21-OL-01-00-60		6/15/0821	11:30	47.189737	-88.236116	83.6	600	2393
62	GT21-OL-01-60-96		6/15/0821	11:30	"	"	15.4	300	440
63	GT21-OL-02-00-60		6/15/0821	13:15	47.191788	-88.234476	39.7	1100	1138
64	GT21-OL-02-60-120		6/15/0821	13:15	"	"	43.1	880	1235
65	GT21-OL-02-120-180		6/15/0821	13:15	"	"	21.8	770	624
66	GT21-OL-02-180-204		6/15/0821	13:15	"	"	3.9	63	112
67	GT21-OL-03-00-60		6/15/0821	15:05	47.193893	-88.233033	36.4	1200	1041
68	GT21-OL-03-60-120		6/15/0821	15:05	"	"	23	2200	658
69	GT21-OL-03-120-129		6/15/0821	15:05	"	"	18.4	710	528
70	GT21-OL-03-129-153		6/15/0821	15:05	"	"	9.9	330	284
71	GT21-OL-04-00-60		6/16/2021	8:00	47.195944	-88.231418	53.9	960	1543
72	GT21-OL-04-60-120		6/16/2021	8:00	"	"	30.9	2100	886
73	GT21-OL-04-120-150		6/16/2021	8:00	"	"	24.1	580	691
74	GT21-OL-04-150-174		6/16/2021	8:00	"	"	14.5	230	414
75	GT21-OL-05-00-60		6/16/2021	10:00	47.197891	-88.229655	68.9	1200	1974
76	GT21-OL-05-60-120		6/16/2021	10:00	"	"	63.9	2100	1829

77	GT21-OL-05-120-180	6/16/2021	10:00	"	"	43.4	900	1242
78	GT21-OL-05-180-195	6/16/2021	10:00	"	"	30.5	800	873
79	GT21-OL-05-195-219	6/16/2021	10:00	"	"	2.9	19	84
80	GT21-OL-06-00-60	6/16/2021	12:30	47.199511	-88.227295	78.8	2500	2257
81	GT21-OL-06-60-120	6/16/2021	12:30	"	"	66.4	2100	1901
82	GT21-OL-06-120-180	6/16/2021	12:30	"	"	90.7	1200	2598
83	GT21-OL-06-180-240	6/16/2021	12:30	"	"	47.2	1300	1350
84	GT21-OL-06-240-264	6/16/2021	12:30	"	"	3	69	86
85	GT21-OL-07-00-03	6/17/2021	8:00	47.201201	-88.224948	16.7	370	478
86	GT21-OL-07-03-60	6/17/2021	8:00	"	"	92.2	1000	2639
87	GT21-OL-07-60-120	6/17/2021	8:00	"	"	64.1	850	1836
88	GT21-OL-07-120-180	6/17/2021	8:00	"	"	91.9	1200	2632
89	GT21-OL-07-180-190	6/17/2021	8:00	"	"	85.4	1400	2445
90	GT21-OL-07-190-214	6/17/2021	8:00	"	"	2.8	15	81
91	GT21-OL-08-00-60	6/17/2021	9:30	47.202486	-88.222149	7.8	1300	222
92	GT21-OL-08-60-90	6/17/2021	9:30	"	"	75.4	4800	2159
93	GT21-OL-08-90-114	6/17/2021	9:30	"	"	5	49	142
94	GT21-OL-09-00-60	6/17/2021	11:00	47.204165	-88.219699	46.6	1400	1334
95	GT21-OL-09-60-115	6/17/2021	11:00	"	"	99	630	2835
96	GT21-OL-09-115-139	6/17/2021	11:00	"	"	2.6	36	75
97	GT21-OL-10-00-60	6/17/2021	12:10	47.206	-88.217595	76.4	1500	2188
98	GT21-OL-10-60-116	6/17/2021	12:10	"	"	44.1	870	1262
99	GT21-OL-11-00-60	6/17/2021	13:00	47.207809	-88.215498	76.7	2700	2197
100	GT21-OL-11-60-120	6/17/2021	13:00	"	"	95.7	1200	2741
101	GT21-OL-11-120-183	6/17/2021	13:00	"	"	97.2	830	2784
102	GT21-OL-11-183-207	6/17/2021	13:00	"	"	2.1	15	59
103	GT21-OL-12-00-60	6/17/2021	14:10	47.209561	-88.213251	94.5	2600	2705
104	GT21-OL-12-60-120	6/17/2021	14:10	"	"	97.9	910	2804

105	GT21-OL-12-120-180	6/17/2021	14:10	"	"	80	910	2289
106	GT21-OL-12-180-203	6/17/2021	14:10	"	"	66.3	1400	1897
107	GT21-OL-12-203-227	6/17/2021	14:10	"	"	2.9	22	83
108	GT21-OL-13-00-60	6/17/2021	15:30	47.210486	-88.210111	84.5	1200	2419
109	GT21-OL-13-60-120	6/17/2021	15:30	"	"	96.1	940	2752
110	GT21-OL-13-120-180	6/17/2021	15:30	"	"	60.7	1500	1737
111	GT21-OL-13-180-204	6/17/2021	15:30	"	"	2.1	69	60
112	GT21-OL-14-00-60	6/18/2021	7:20	47.210009	-88.206599	75.3	2300	2157
113	GT21-OL-14-60-120	6/18/2021	7:20	"	"	80.6	1500	2309
114	GT21-OL-14-120-180	6/18/2021	7:20	"	"	97.6	800	2793
115	GT21-OL-14-180-242	6/18/2021	7:20	"	"	97.5	700	2790
116	GT21-OL-14-242-266	6/18/2021	7:20	"	"	4.1	170	118
117	GT21-OL-15-00-60	6/18/2021	9:00	47.210533	-88.203285	87.9	2500	2517
118	GT21-OL-15-60-120	6/18/2021	9:00	"	"	43.1	1600	1234
119	GT21-OL-15-120-144	6/18/2021	9:00	"	"	42.2	1500	1209
120	GT21-OL-15-144-168	6/18/2021	9:00	"	"	5.4	41	155
121	GT21-OL-16-00-60	6/18/2021	10:00	47.210577	-88.199839	86.5	4500	2477
122	GT21-OL-16-60-124	6/18/2021	10:00	"	"	68.5	1400	1960
123	GT21-OL-16-124-148	6/18/2021	10:00	"	"	5.1	84	145
124	GT21-OL-17-00-60	6/18/2021	11:00	47.210615	-88.196442	86.3	1400	2470
125	GT21-OL-17-60-114	6/18/2021	11:00	"	"	100	1200	2863
126	GT21-OL-18-00-60	6/18/2021	11:45	47.210493	-88.192941	83.6	350	2394
127	GT21-OL-18-60-88	6/18/2021	11:45	"	"	63.2	1300	1810
128	GT21-OL-19-00-60	6/18/2021	12:25	47.210697	-88.189593	85.4	1700	2445
129	GT21-OL-19-60-84	6/18/2021	12:25	"	"	91.6	1600	2622
130	GT21-OL-20-00-60	6/21/2021	12:00	47.211619	-88.186449	90	2500	2577
131	GT21-OL-20-60-102	6/21/2021	12:00	"	"	97.3	750	2786
132	GT21-OL-21-00-60	6/21/2021	12:45	47.212618	-88.183401	80.8	2500	2312

133	GT21-OL-21-60-120	6/21/2021	12:45	"	"	76.2	2800	2182
134	GT21-OL-21-120-149	6/21/2021	12:45	"	"	69.2	790	1982
135	GT21-OL-22-00-60	6/21/2021	13:50	47.213644	-88.180033	94.7	1000	2710
136	GT21-OL-22-60-94	6/21/2021	13:50	"	"	97.4	1400	2790
137	GT21-OL-23-00-60	6/21/2021	14:30	47.212524	-88.17552	90	890	2576
138	GT21-OL-23-60-125	6/21/2021	14:30	"	"	76.5	950	2189
139	GT21-OL-24-00-42	6/21/2021	15:40	47.215091	-88.17377	61.8	780	1770
140	GT21-OL-24-42-51	6/21/2021	15:40	"	"	15.8	160	452
141	GT21-OL-24-51-111	6/21/2021	15:40	"	"	88.6	1900	2537
142	GT21-OL-24-111-171	6/21/2021	15:40	"	"	97.4	830	2788
143	GT21-OL-24-171-220	6/21/2021	15:40	"	"	61.4	540	1757
144	GT21-OL-25-00-60	6/21/2021	17:30	47.215415	-88.169913	92.2	1100	2641
145	GT21-OL-25-60-120	6/21/2021	17:30	"	"	92.4	480	2645
146	GT21-OL-25-120-164	6/21/2021	17:30	"	"	97.3	2400	2786
147	GT21-OL-26-00-60	6/22/2021	10:10	47.218687	-88.169957	96	1600	2749
148	GT21-OL-26-60-120	6/22/2021	10:10	"	"	80.4	1500	2302
149	GT21-OL-27-00-60	6/22/2021	11:00	47.218836	-88.16581	96.6	1500	2765
150	GT21-OL-27-60-120	6/22/2021	11:00	"	"	65.4	860	1871
151	GT21-OL-27-120-134	6/22/2021	11:00	"	"	32.2	1800	923
152	GT21-OL-28-00-60	6/22/2021	12:00	47.220872	-88.166056	96.5	680	2764
153	GT21-OL-28-60-120	6/22/2021	12:00	"	"	97.1	910	2780
154	GT21-OL-28-120-180	6/22/2021	12:00	"	"	39.8	2000	1139
155	GT21-OL-29-00-60	6/22/2021	13:10	47.222414	88.162468	85.5	3500	2449
156	GT21-OL-29-60-120	6/22/2021	13:10	"	"	92.1	2400	2636
157	GT21-OL-29-120-180	6/22/2021	13:10	"	"	87	1400	2492
158	GT21-OL-29-180-238	6/22/2021	13:10	"	"	49.6	2000	1420
159	GT21-OL-30-00-60	6/22/2021	14:30	47.224469	-88.162026	70.9	1400	2031
160	GT21-OL-30-60-120	6/22/2021	14:30	"	"	96.2	1800	2753

161	GT21-OL-30-120-180	6/22/2021	14:30	"	"	96.6	1700	2767
162	GT21-OL-30-180-240	6/22/2021	14:30	"	"	97.5	1700	2792
163	GT21-OL-30-240-300	6/22/2021	14:30	"	"	94.8	1800	2715
164	GT21-OL-30-300-360	6/22/2021	14:30	"	"	76.3	1500	2184
165	GT21-OL-30-360-404	6/22/2021	14:30	"	"	73.5	2100	2103

Table A.10. Older mean %SS values compared to AEM mean %SS values

A general comparison of Mean %SS data collected from the Grand Traverse Bay area. The older data was collected and processed between 2010-2013 by MTU and the newer data was collected in 2021 by AEM and processed at MTU.

Sample Name	Date	Lat	Long	Mean %SS	Sample Number & Type	Date	Lat	Long	Mean %SS
	7/11/2013	47.21667	-88.15	0	GT21-OL-30-00-60	6/22/2021	47.224469	-88.162026	70.9
	7/11/2013	47.21383	-88.1445	0	GT21-OL-30-60-120	6/22/2021	47.224469	-88.162026	96.2
	5/29/2013	47.211	-88.17367	90	GT21-OL-30-120-180	6/22/2021	47.224469	-88.162026	96.6
	5/29/2013	47.21067	-88.17917	75	GT21-OL-30-180-240	6/22/2021	47.224469	-88.162026	97.5
	8/23/2013	47.20917	-88.20967	30	GT21-OL-30-240-300	6/22/2021	47.224469	-88.162026	94.8
	5/29/2013	47.20833	-88.2075	100	GT21-OL-30-300-360	6/22/2021	47.224469	-88.162026	76.3
	5/29/2013	47.208	-88.1875	100	GT21-OL-30-360-404	6/22/2021	47.224469	-88.162026	73.5
Gay 13	8/15/2012	47.20795	-88.19072	62.6	GT21-OL-29-00-60	6/22/2021	47.222414	88.16247	85.5
Gay 13	8/15/2012	47.20795	-88.20738	58.9	GT21-OL-29-60-120	6/22/2021	47.222414	88.16247	92.1
	5/29/2013	47.2075	-88.19717	100	GT21-OL-29-120-180	6/22/2021	47.222414	88.16247	87
	8/23/2013	47.20733	-88.20833	90	GT21-OL-29-180-238	6/22/2021	47.222414	88.16247	49.6
Gay 14	8/15/2012	47.20587	-88.18615	52.9	GT21-OL-28-00-60	6/22/2021	47.220872	-88.166056	96.5
	5/29/2013	47.20567	-88.19767	100	GT21-OL-28-60-120	6/22/2021	47.220872	-88.166056	97.1
	5/29/2013	47.2055	-88.202	55	GT21-OL-28-120-180	6/22/2021	47.220872	-88.166056	39.8
	5/29/2013	47.2055	-88.19433	25	GT21-OL-27-00-60	6/22/2021	47.218836	-88.16581	96.6
	5/29/2013	47.2055	-88.1555	30	GT21-OL-27-60-120	6/22/2021	47.218836	-88.16581	65.4
	6/18/2013	47.20545	-88.20895	75	GT21-OL-27-120-134	6/22/2021	47.218836	-88.16581	32.2
	6/18/2013	47.2053	-88.2078	50	GT21-OL-26-00-60	6/22/2021	47.218687	-88.169957	96
	8/23/2013	47.20517	-88.20683	50	GT21-OL-26-60-120	6/22/2021	47.218687	-88.169957	80.4
	6/18/2013	47.20513	-88.20037	75	GT21-OL-25-00-60	6/21/2021	47.215415	-88.169913	92.2
	5/29/2013	47.20483	-88.19883	90	GT21-OL-25-60-120	6/21/2021	47.215415	-88.169913	92.4
	5/29/2013	47.20417	-88.19917	65	GT21-OL-25-120-164	6/21/2021	47.215415	-88.169913	97.3
	5/29/2013	47.20367	-88.19717	60	GT21-OL-24-00-42	6/21/2021	47.215091	-88.17377	61.8
	5/29/2013	47.20317	-88.18833	25	GT21-OL-24-42-51	6/21/2021	47.215091	-88.17377	15.8
	5/29/2013	47.20317	-88.184	10	GT21-OL-24-51-111	6/21/2021	47.215091	-88.17377	88.6

	5/29/2013	47.203	-88.19367	50
	5/29/2013	47.203	-88.1875	25
	5/29/2013	47.20283	-88.18333	25
	5/29/2013	47.20283	-88.1695	10
	6/22/2013	47.20283	-88.18333	30
USB002	6/22/2013	47.20283	-88.15283	10.4
Sta 3	8/15/2012	47.20203	-88.21347	63.5
Gay 4	8/15/2012	47.20135	-88.20413	20.5
Sta 4	8/15/2012	47.20135	-88.20408	17.4
	5/29/2013	47.20133	-88.20417	40
	8/23/2013	47.20133	-88.207	10
	7/11/2013	47.2	-88.16117	0
Sta 10	8/15/2012	47.19907	-88.18578	73.1
	5/29/2013	47.198	-88.20867	30
Sta 2	8/15/2012	47.19783	-88.21695	64.3
Sta 5	8/15/2012	47.19727	-88.20875	54.4
Sta 5	8/15/2012	47.19727	-88.20875	54.4
T07W01	8/23/2013	47.197	-88.22333	29.2
	5/29/2013	47.19433	-88.16667	10
	5/29/2013	47.19417	-88.2195	30
	8/23/2013	47.19383	-88.22167	75
	8/23/2013	47.19383	-88.22117	60
	8/23/2013	47.19383	-88.21983	70
Gay 1	8/15/2012	47.19352	-88.22023	51.4
Sta 1	8/15/2012	47.19352	-88.22023	51.5
Gay 6	8/15/2012	47.1933	-88.2129	19.6
Sta 6	8/15/2012	47.1933	-88.2129	10.1
	5/29/2013	47.19167	-88.22517	50
	5/29/2013	47.19167	-88.21533	30
	6/22/2013	47.19167	-88.18333	5
	8/23/2013	47.19167	-88.21983	40
	8/23/2013	47.19167	-88.21933	45
	8/23/2013	47.19133	-88.21317	20
	5/29/2013	47.18983	-88.23167	65

GT21-OL-24-111-171	6/21/2021	47.215091	-88.17377	97.4
GT21-OL-24-171-220	6/21/2021	47.215091	-88.17377	61.4
GT21-OL-22-00-60	6/21/2021	47.213644	-88.180033	94.7
GT21-OL-22-60-94	6/21/2021	47.213644	-88.180033	97.4
GT21-OW-01-00-03	6/8/2021	47.212765	-88.160218	83.6
GT21-OW-01-03-06	6/8/2021	47.212765	-88.160218	86.8
GT21-OW-01-06-12	6/8/2021	47.212765	-88.160218	78.1
GT21-OW-01-12-72	6/8/2021	47.212765	-88.160218	78.2
GT21-OW-01-72-126	6/8/2021	47.212765	-88.160218	65
GT21-OW-01-126-140	6/8/2021	47.212765	-88.160218	45.5
GT21-OL-21-00-60	6/21/2021	47.212618	-88.183401	80.8
GT21-OL-21-60-120	6/21/2021	47.212618	-88.183401	76.2
GT21-OL-21-120-149	6/21/2021	47.212618	-88.183401	69.2
GT21-OL-23-00-60	6/21/2021	47.212524	-88.17552	90
GT21-OL-23-60-125	6/21/2021	47.212524	-88.17552	76.5
GT21-OL-20-00-60	6/21/2021	47.211619	-88.186449	90
GT21-OL-20-60-102	6/21/2021	47.211619	-88.186449	97.3
GT21-OL-19-00-60	6/18/2021	47.210697	-88.189593	85.4
GT21-OL-19-60-84	6/18/2021	47.210697	-88.189593	91.6
GT21-OL-17-00-60	6/18/2021	47.210615	-88.196442	86.3
GT21-OL-17-60-114	6/18/2021	47.210615	-88.196442	100
GT21-OL-16-00-60	6/18/2021	47.210577	-88.199839	86.5
GT21-OL-16-60-124	6/18/2021	47.210577	-88.199839	68.5
GT21-OL-16-124-148	6/18/2021	47.210577	-88.199839	5.1
GT21-OL-15-00-60	6/18/2021	47.210533	-88.203285	87.9
GT21-OL-15-60-120	6/18/2021	47.210533	-88.203285	43.1
GT21-OL-15-120-144	6/18/2021	47.210533	-88.203285	42.2
GT21-OL-15-144-168	6/18/2021	47.210533	-88.203285	5.4
GT21-OL-18-00-60	6/18/2021	47.210493	-88.192941	83.6
GT21-OL-18-60-88	6/18/2021	47.210493	-88.192941	63.2
GT21-OL-13-00-60	6/17/2021	47.210486	-88.210111	84.5
GT21-OL-13-60-120	6/17/2021	47.210486	-88.210111	96.1
GT21-OL-13-120-180	6/17/2021	47.210486	-88.210111	60.7
GT21-OL-13-180-204	6/17/2021	47.210486	-88.210111	2.1

	6/22/2013	47.189	-88.2195	10	GT21-OL-14-00-60	6/18/2021	47.210009	-88.206599	75.3
	6/22/2013	47.189	-88.21667	10	GT21-OL-14-60-120	6/18/2021	47.210009	-88.206599	80.6
	6/22/2013	47.189	-88.21117	10	GT21-OL-14-120-180	6/18/2021	47.210009	-88.206599	97.6
	6/22/2013	47.189	-88.189	10	GT21-OL-14-180-242	6/18/2021	47.210009	-88.206599	97.5
	5/29/2013	47.1875	-88.23267	50	GT21-OL-14-242-266	6/18/2021	47.210009	-88.206599	4.1
	8/23/2013	47.18717	-88.217	20	GT21-OW-02-00-03	6/7/2021	47.209899	-88.169425	83.5
	5/29/2013	47.18333	-88.23483	10	GT21-OW-02-03-06	6/7/2021	47.209899	-88.169425	84
	5/29/2013	47.18333	-88.2055	25	GT21-OW-02-06-12	6/7/2021	47.209899	-88.169425	87
	6/22/2013	47.18333	-88.23617	10	GT21-OW-02-12-72	6/7/2021	47.209899	-88.169425	70.8
	6/22/2013	47.18333	-88.23333	5	GT21-OW-02-72-132	6/7/2021	47.209899	-88.169425	75.6
	7/11/2013	47.18333	-88.1945	0	GT21-OL-12-00-60	6/17/2021	47.209561	-88.213251	94.5
	7/11/2013	47.1805	-88.21667	0	GT21-OL-12-60-120	6/17/2021	47.209561	-88.213251	97.9
	7/11/2013	47.1805	-88.2	0	GT21-OL-12-120-180	6/17/2021	47.209561	-88.213251	80
GA0018	7/29/2010	47.18	-88.18833	25	GT21-OL-12-180-203	6/17/2021	47.209561	-88.213251	66.3
	6/18/2013	47.17862	-88.20713	0	GT21-OL-12-203-227	6/17/2021	47.209561	-88.213251	2.9
	6/18/2013	47.17813	-88.21883	10	GT21-OW-03-00-03	6/7/2021	47.20943	-88.180361	86.5
	6/22/2013	47.17783	-88.23617	0	GT21-OW-03-03-06	6/7/2021	47.20943	-88.180361	83.1
BGT 2	8/15/2012	47.17526	-88.2204	46.5	GT21-OW-03-06-12	6/7/2021	47.20943	-88.180361	81
	7/11/2013	47.175	-88.225	0	GT21-OW-03-12-61	6/7/2021	47.20943	-88.180361	85.9
BGT 1	8/15/2012	47.17463	-88.21738	14.2	GT21-OW-04-00-03	6/8/2021	47.208268	-88.201257	63.3
	6/18/2013	47.1718	-88.22005	5	GT21-OW-04-03-06	6/8/2021	47.208268	-88.201257	62.5
	7/29/2010	47.17167	-88.16167	10	GT21-OW-04-06-12	6/8/2021	47.208268	-88.201257	60.1
	6/22/2013	47.1695	-88.22783	5	GT21-OW-04-12-72	6/8/2021	47.208268	-88.201257	50.6
	7/11/2013	47.16667	-88.22217	5	GT21-OW-04-72-120	6/8/2021	47.208268	-88.201257	24.5
	7/11/2013	47.16667	-88.21117	15	GT21-OW-04-120-148	6/8/2021	47.208268	-88.201257	3.9
	6/18/2013	47.16495	-88.23883	5	GT21-OL-11-00-60	6/17/2021	47.207809	-88.215498	76.7
	7/29/2010	47.16333	-88.20333	25	GT21-OL-11-60-120	6/17/2021	47.207809	-88.215498	95.7
	7/29/2010	47.16333	-88.17333	0	GT21-OL-11-120-183	6/17/2021	47.207809	-88.215498	97.2
	6/22/2013	47.16117	-88.23617	15	GT21-OL-11-183-207	6/17/2021	47.207809	-88.215498	2.1
	6/22/2013	47.16117	-88.22783	0	GT21-OW-05-00-03	6/2/2021	47.206528	-88.198004	69.2
	6/22/2013	47.16117	-88.2195	5	GT21-OW-05-03-06	6/2/2021	47.206528	-88.198004	72.2
	6/22/2013	47.16117	-88.21117	0	GT21-OW-05-06-12	6/2/2021	47.206528	-88.198004	64.5
	7/11/2013	47.16117	-88.21117	5	GT21-OW-05-12-72	6/2/2021	47.206528	-88.198004	64.9
	7/11/2013	47.16117	-88.2055	5	GT21-OW-05-72-120	6/2/2021	47.206528	-88.198004	35

6/18/2013	47.15912	-88.23833	10
7/29/2010	47.15333	-88.18833	0

GT21-OW-05-120-180	6/2/2021	47.206528	-88.198004	20.5
GT21-OW-05-180-193	6/2/2021	47.206528	-88.198004	6.4
GT21-OW-05-193-253	6/2/2021	47.206528	-88.198004	1.7
GT21-OW-07-00-03	6/5/2021	47.206364	-88.212951	53.7
GT21-OW-07-03-06	6/5/2021	47.206364	-88.212951	26.1
GT21-OW-07-00-12	6/5/2021	47.206364	-88.212951	20.1
GT21-OW-07-14-38	6/5/2021	47.206364	-88.212951	5.3
GT21-OL-10-00-60	6/17/2021	47.206	-88.217595	76.4
GT21-OL-10-60-116	6/17/2021	47.206	-88.217595	44.1
GT21-DW-01-Surface	6/3/2021	47.20594	-88.145222	9.9
GT21-OL-09-00-60	6/17/2021	47.204165	-88.219699	46.6
GT21-OL-09-60-115	6/17/2021	47.204165	-88.219699	99
GT21-OL-09-115-139	6/17/2021	47.204165	-88.219699	2.6
GT21-OW-06-00-04	6/9/2021	47.203638	-88.197455	36.6
GT21-OW-06-04-07	6/9/2021	47.203638	-88.197455	33.7
GT21-OW-06-07-12	6/9/2021	47.203638	-88.197455	13.8
GT21-OW-06-12-72	6/9/2021	47.203638	-88.197455	5.1
GT21-DW-02-Surface	6/3/2021	47.202971	-88.150887	10
GT21-OL-08-00-60	6/17/2021	47.202486	-88.222149	7.8
GT21-OL-08-60-90	6/17/2021	47.202486	-88.222149	75.4
GT21-OL-08-90-114	6/17/2021	47.202486	-88.222149	5
GT21-DW-03-Surface	6/3/2021	47.201224	-88.172822	9
GT21-OL-07-00-03	6/17/2021	47.201201	-88.224948	16.7
GT21-OL-07-03-60	6/17/2021	47.201201	-88.224948	92.2
GT21-OL-07-60-120	6/17/2021	47.201201	-88.224948	64.1
GT21-OL-07-120-180	6/17/2021	47.201201	-88.224948	91.9
GT21-OL-07-180-190	6/17/2021	47.201201	-88.224948	85.4
GT21-OL-07-190-214	6/17/2021	47.201201	-88.224948	2.8
GT21-OL-06-00-60	6/16/2021	47.199511	-88.227295	78.8
GT21-OL-06-60-120	6/16/2021	47.199511	-88.227295	66.4
GT21-OL-06-120-180	6/16/2021	47.199511	-88.227295	90.7
GT21-OL-06-180-240	6/16/2021	47.199511	-88.227295	47.2
GT21-OL-06-240-264	6/16/2021	47.199511	-88.227295	3

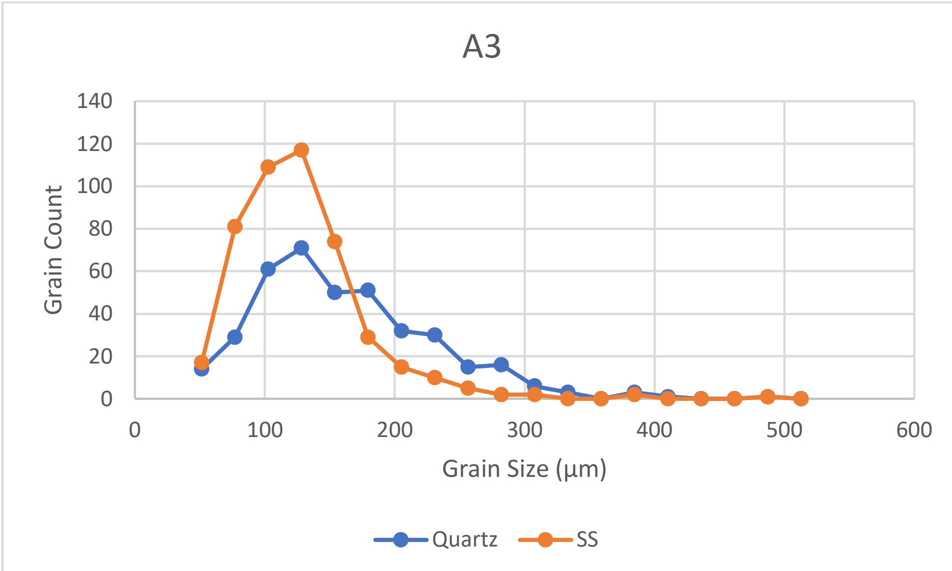
GT21-OL-05-00-60	6/16/2021	47.197891	-88.229655	68.9
GT21-OL-05-60-120	6/16/2021	47.197891	-88.229655	63.9
GT21-OL-05-120-180	6/16/2021	47.197891	-88.229655	43.4
GT21-OL-05-180-195	6/16/2021	47.197891	-88.229655	30.5
GT21-OL-05-195-219	6/16/2021	47.197891	-88.229655	2.9
GT21-OW-09-Surface	6/17/2021	47.196231	-88.229932	61.7
GT21-OL-04-00-60	6/16/2021	47.195944	-88.231418	53.9
GT21-OL-04-60-120	6/16/2021	47.195944	-88.231418	30.9
GT21-OL-04-120-150	6/16/2021	47.195944	-88.231418	24.1
GT21-OL-04-150-174	6/16/2021	47.195944	-88.231418	14.5
GT21-OW-10-06-12	6/14/2021	47.195438	-88.212093	2
GT21-OW-10-12-24	6/14/2021	47.195438	-88.212093	1.5
GT21-DW-04-Surface	6/3/2021	47.19477	-88.154013	12.4
GT21-OL-03-00-60	6/15/0821	47.193893	-88.233033	36.4
GT21-OL-03-60-120	6/15/0821	47.193893	-88.233033	23
GT21-OL-03-120-129	6/15/0821	47.193893	-88.233033	18.4
GT21-OL-03-129-153	6/15/0821	47.193893	-88.233033	9.9
GT21-OL-02-00-60	6/15/0821	47.191788	-88.234476	39.7
GT21-OL-02-60-120	6/15/0821	47.191788	-88.234476	43.1
GT21-OL-02-120-180	6/15/0821	47.191788	-88.234476	21.8
GT21-OL-02-180-204	6/15/0821	47.191788	-88.234476	3.9
GT21-OL-01-00-60	6/15/0821	47.189737	-88.236116	83.6
GT21-OL-01-60-96	6/15/0821	47.189737	-88.236116	15.4
GT21-OW-11-00-03	6/4/2021	47.189684	-88.232649	41.1
GT21-OW-11-03-06	6/4/2021	47.189684	-88.232649	38.4
GT21-OW-11-06-14	6/4/2021	47.189684	-88.232649	26.8
GT21-OW-11-14-34	6/4/2021	47.189684	-88.232649	7.1
GT21-OW-12-00-03	6/10/2021	47.187127	-88.237594	9.5
GT21-OW-12-03-06	6/10/2021	47.187127	-88.237594	7.2
GT21-OW-12-06-12	6/10/2021	47.187127	-88.237594	7.8
GT21-OW-12-12-24	6/10/2021	47.187127	-88.237594	5.6
GT21-OW-12-24-60	6/10/2021	47.187127	-88.237594	3
GT21-OW-13-00-03	6/10/2021	47.18687	-88.235413	19
GT21-OW-13-03-06	6/10/2021	47.18687	-88.235413	13.6

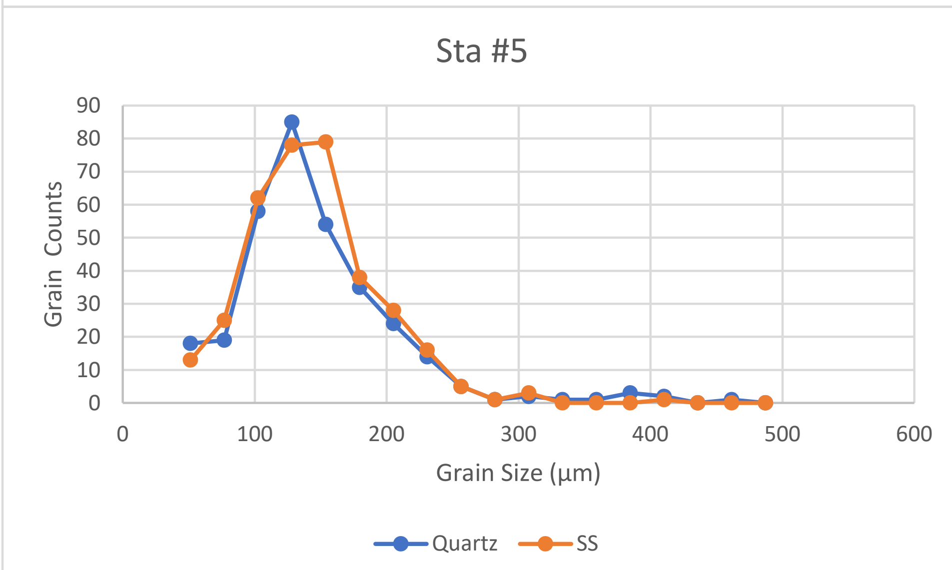
GT21-OW-13-06-12	6/10/2021	47.18687	-88.235413	8.1
GT21-OW-13-12-60	6/10/2021	47.18687	-88.235413	3.8
GT21-DW-07-Surface	6/3/2021	47.186742	-88.189472	9.5
GT21-DW-05-Surface	6/3/2021	47.179537	-88.217309	11.1
GT21-DW-06-Surface	6/3/2021	47.171237	-88.206369	11.4

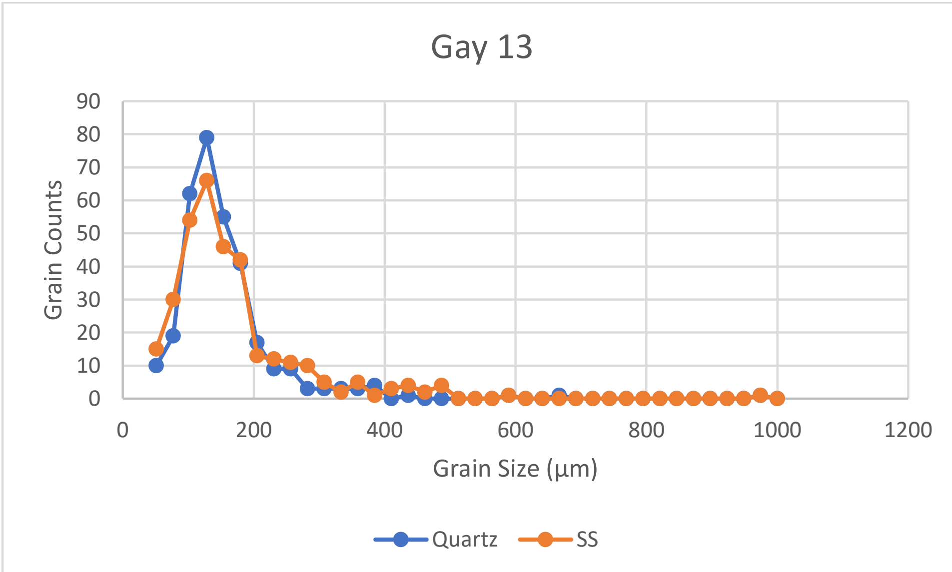
B Appendix Figures

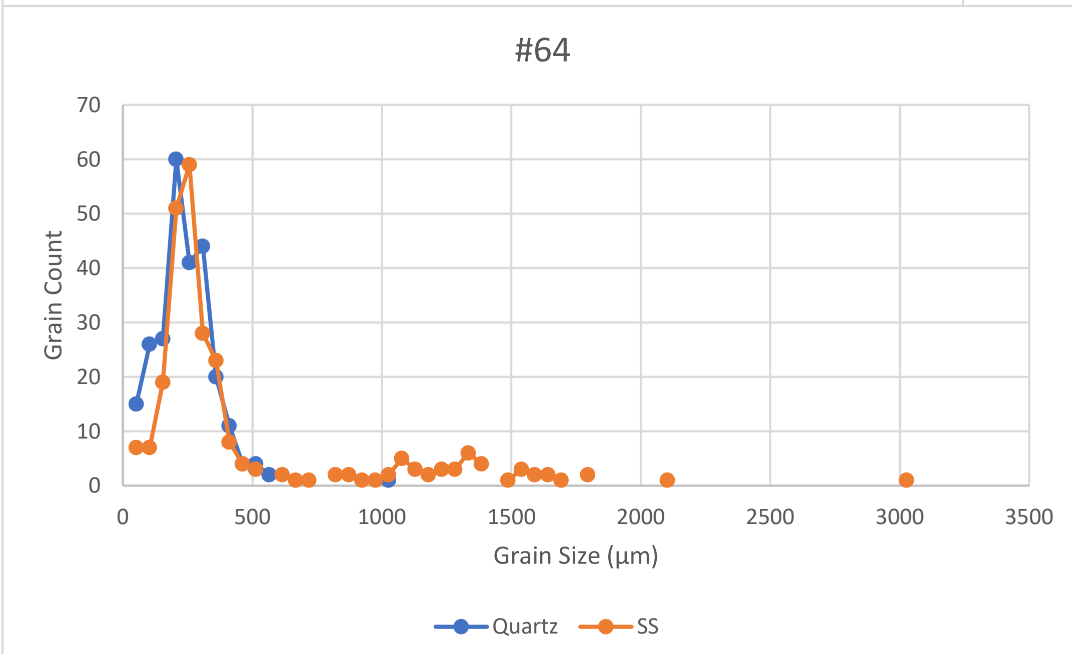
Figure A.1. Location of study sites

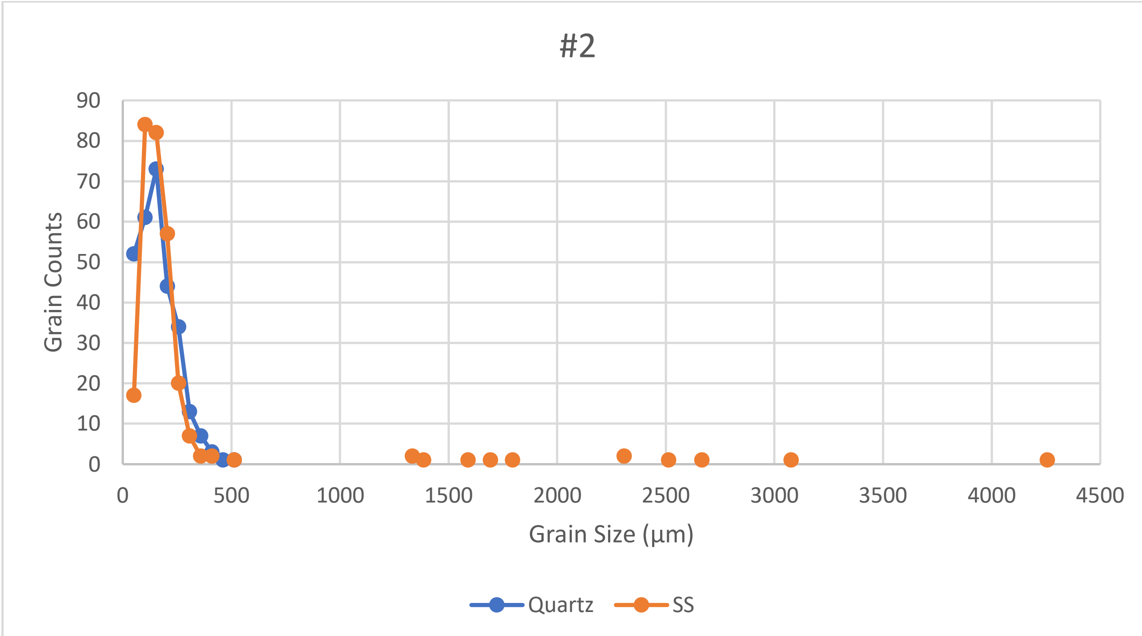
Google map image of Keweenaw Peninsula of where sediment and water samples used for the chronic toxicity test were taken from. BG is Bete Grise, CDR is Coal Dock Road, TR is Traverse River, LS is Lake Superior, and PL is Portage Lake.


A3
Grain Count
140
120
100
80
60
40
20
0
0
100
200
300
400
500
600
Grain Size (µm)
Quartz
SS


Sta #5
Grain Counts
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
Grain Size (µm)
Quartz
SS


Gay 13
Grain Counts
90
80
70
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
Grain Size (µm)
Quartz
SS


#64
Grain Count
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
3500
Grain Size (µm)
Quartz
SS



Label	Latitude	Longitude	date	depth (m)	%SS	Mean size (µm)	Total Q	Total SS
A3	47°10.9970	-88°13.9272	6/11/2018	10.5	42.9	198	383	464
Sta #5	47°11.836	-88°12.525	8/15/2012	9.8	54.4	185	323	349
Gay 13	47°12.477	-88°12.443	8/15/2012	3.5	58.9	349	321	327
#64	47° 12.087	-88°13.351	9/4/2020	B	92.3	1555	255	260
#2	47° 11.407	-88° 14.127	3/9/2020	B	93.5	1877	289	284

Figure A.2. Direct particle size distribution determination

The series of graphs and accompanying table show particle sizes (grain size) of natural quartz sands (Quartz or Q) and of stamp sand (SS) from three underwater Ponar samples (have depths) and two beach sediment samples (B) in the Grand Traverse Bay area.

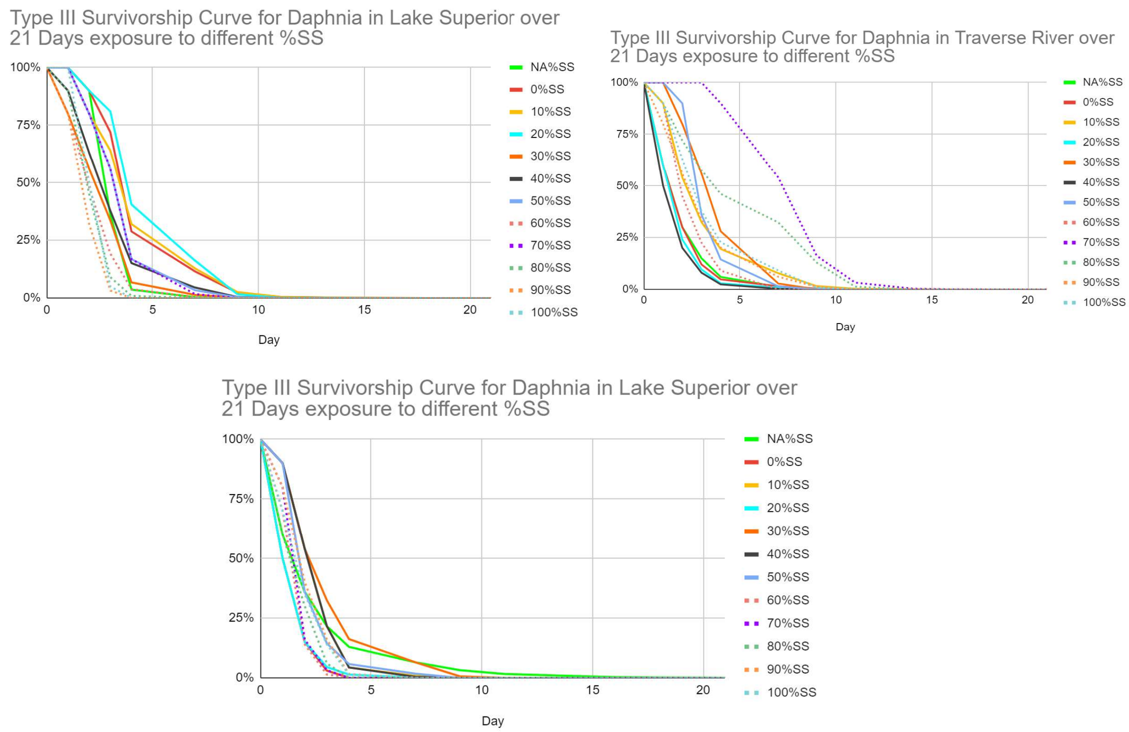


Figure A.3. Survivorship probability curves for other local waters

Traverse River (TR), Lake Superior (LS), and Coal Dock Road riparian zone (CDR) *Daphnia* survivorship probability curve at various %SS concentrations over 21 days. On day 14, juveniles were removed after counting to reduce the effects of resource competition. NA%SS data was water without the presence of any sediment. Figure derived from Appendix Table A.8 data.

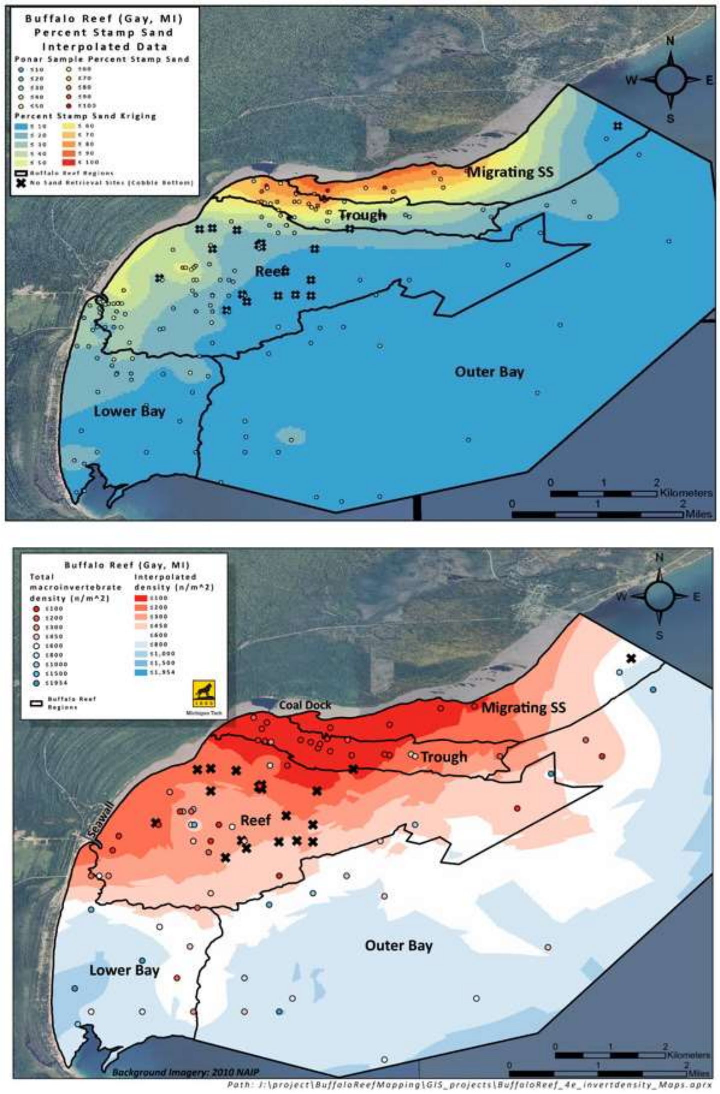


Figure A.4. Cu concentration and macroinvertebrates density maps of Grand (Big) Traverse Bay

Two examples of GIS maps for variables in Grand (Big) Traverse Bay (legends in the upper left). The top is percentage stamp sand (%SS) in underwater sand mixtures across the bay, whereas the second is the density of macroinvertebrates (low densities are in deep red). Densities are most impacted by high %SS and Cu-rich regions near the pile and shoreline down to the Traverse River (after Kerfoot et al., 2021). Major effects are near the Coal Dock, where nearshore stamp sand percentages are highest.

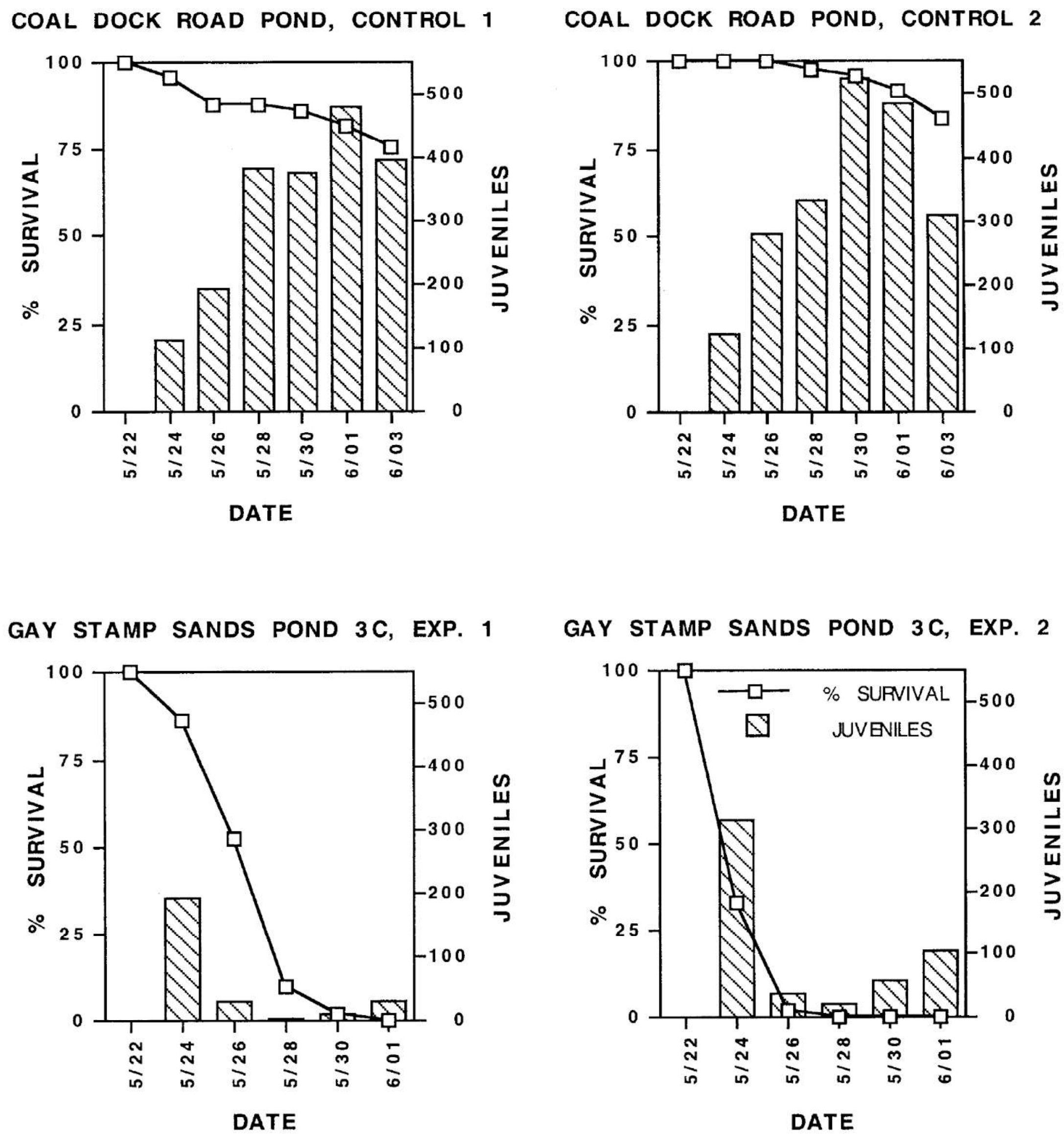


Figure A.5. Stamp sand pond previous survival experiments by Lyttle, 1999

Figure taken from Lyttle, 1999. *Daphnia* toxicity test results from Controls 1 and 2 vs Stamp Sand Pond. Percent survival was recorded, and the number of juveniles was recorded. This inspired our tests at the Gay Stamp Sand Ponds in 2019.