Impact of Sediment Resuspension Events on the Availability of Heavy Metals in Freshwater Sediments

By

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A project submitted in partial fulfillment of the requirements for the degree of Master of Science (Natural Resources and Environment) at the University of Michigan January 2012

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Abstract:

Release of heavy metals during sediment resuspension is an understudied problem that may be cause for environmental concern. Common activities such as shipping and dredging have the ability to resuspend large amounts of contaminated anoxic sediment into the overlying water column. Oxidation of anoxic sediment can alter metal binding, potentially releasing metals into the water column. Understanding fate, bioavailability, and transport of metals is ecologically important, and key to creating more accurate metal speciation and transport models to predict environmental impacts. A Sediment Flux Exposure Chamber (SeFEC) was used to resuspend four types of contaminated sediment to replicate different resuspension scenarios. Dissolved metal concentrations were measured to determine the percent of total metal released. AVS and SEM values were measured to gauge sediment toxicity. *Pyrocystis lunula* (dinoflagellate) Daphnia magna (zooplankton) and Hyallela azteca (amphipod) were exposed to resuspension conditions to assess biotic endpoints No significant mortality of D. magna and H. azteca was seen. P. lunula exhibited decreased bioluminescence when exposed to bedded sediments, but exhibited mixed responses with resuspended water column samples. . Release of heavy metals to the water column occurred during resuspension. Both increasing and decreasing concentrations were seen through time during consecutive resuspension events.. The findings allow for better determination of the ecological relevance of resuspension events and further the development of metal speciation models by tracing the transport of heavy metals during resuspension events.

Introduction:

Contaminated sediments are found in harbors and shipping channels, due to anthropomorphic contributions of heavy metals and other pollutants. Dredging and shipping activity resuspends large amounts of sediment, potentially mixing anoxic sediment with the water column. Physicochemical changes occur during sediment suspension, which can lead to release of contaminants. However, sediment quality guidelines are based on bedded sediment contaminant levels. Understanding the transportation of contaminants during resuspension will give us a better assessment of the ecological effects of pollutants associated with bedded sediment.

The duration, intensity, amount, and type of sediment in resuspension should determine the amount of metal potentially released. Dredging activity can create sediment plumes at a maximum total suspended solids (TSS) concentration of approximately 1 g/L (Torres, 2009) and, in shipping channels, sediment may be resuspended multiple times over a relatively short time period. Unlike dredging, which is characterized by a single large resuspension event, boat traffic in shipping harbors leads to multiple short sediment resuspensions. The varied resuspension scenarios could produce different outcomes in metal bioavailability. Biota can be negatively impacted by resuspension of sediment (Weltens, 2000; Hill, 2009; Hedge, 2009) and *Daphnia magna* have been shown to be susceptible to both physical (clogging digestive tract) and chemical stressors of resuspension conditions (Robinson, 2010).

During resuspension of polluted anoxic sediment, the physical and chemical environment surrounding sediment particles can change drastically (Saulnier,2000; Eggleton, 2004; Reible, 2010). Factors which influence heavy metal release include: pH, dissolved oxygen (DO), the sediment acid volatile sulfides (AVS) / simultaneously extracted metals (SEM) ratio, organic carbon content, sediment grain size (Bridges, 2010), salinity, and redox potential (Cantwell, 2002). Metal sulfides are the dominant solid phase

molecule controlling adsorption/desorption of metals in anoxic sediment (DiToro, 1992). During resuspension, anoxic sediments become oxic, potentially oxidizing metal sulfides and releasing dissolved heavy metals. Oxidation of metal sulfides during sediment resuspension is rapid, with 90% of the total AVS oxidized within four hours (Simpson, 2000; Reible, 2010). As metal sulfides are oxidized, water column pH declines, further increasing metal solubilization (Youssef, 1996; Chen, 2004; Bushey, 2008). Therefore, a drop in pH of the water column is one of many signals that oxidation is taking place, and metals are potentially being released. As anoxic sediment is oxidized, reduced iron and manganese can be oxidized to form Fe and Mn oxides. Metal oxide surfaces contain binding sites that are capable of removing heavy metals from the dissolved phase, reducing availability. Both sulfide oxidation and metal oxide formation can occur during sediment resuspension and the balance between the two processes influences bioavailability.

Bioavailability describes the portion of a contaminant that can be taken up by biota from the environment and subsequently metabolized, stored, or excreted (Weltens, et al. 2000). Bioavailability ranges from dissolved metal ions which are the most bioavailable form to precipitates (e.g., MeS) which are not bioavailable. The bioavailability of heavy metals is impacted by: the binding strength and partitioning behavior of sediment (Eggleton, 2004), speciation of the metal (Usero, 1998; Yuan, 2004), biological mechanisms of organisms (Robinson, 2010), and presence of ions in the water column (Chapman, 1998).

To better understand resuspension's impact on metal bioavailability and biota, I measured the resuspension of sediment in a controlled laboratory setting, which allowed for characterization of the physical, chemical, and toxicity (bioavailability) changes over time. Acute and chronic exposures to resuspended conditions allowed for a prediction of effects on biota. Four exposure scenarios were developed. 1.) A 10-day bedded sediment exposure to *D. magna* and *H. azteca.* 2.) Exposing dinoflagellates to filtered sediment

elutriate and resuspended water column sample, to measure toxicity. 3.) A four-hour continuous resuspension (press resuspension). 4.) A pulsed resuspension of four one-hour resuspensions. Through these sets of experiments, I hypothesize that the changing physiochemical conditions during resuspension should release dissolved metals from the total metals pool in the resuspended sediments. I further hypothesize sediments with more AVS-bound metals should release more metal than oxide-bound metals; and response of test organisms to released metal concentrations should be similar to other water column exposures. Additionally, I hypothesize that exposure magnitude, duration, and frequency of resuspension will influence the amount of metal released and the biotic response.

Methods:

Four sediments with a range of heavy metal contamination were evaluated including: Duck Lake sediment (Muskegon, MI), San Diego Bay sediment (San Diego, CA), Idaho river bank sediment (Blackbird Mine, ID), and Lake DePue sediment (DePue, IL) (Table 1). Root fibers and other plant debris were removed through sieving from Duck and DePue sediments. All sediments were stored at 4° C with a headspace of N₂. At time of resuspension it was thought that Duck Lake was a sediment without elevated metal contamination. Duck Lake, as a reference sediment, was used to evaluate the impact of sediment particles during resuspension. Sediment geochemistry was characterized by measuring TOC (loss-on-ignition at 450°C multiplied by the Redfield ratio of 0.36), AVS, and SEM (EPA, 1991) (Table 2). The difference between the sum of molar concentrations of SEM's (Total SEM) and AVS accurately predict whether sediment will show toxicity from present metals. If total SEM is greater than AVS, there is more metal present than can be bound by the AVS, therefore making the sediment capable of having toxicity to organisms. (EPA, 2005) In determining SEM, of

all the metals of interest, only copper, zinc, and nickel were summed. The other metals of interest form metal sulfides that are not labile in the AVS extraction method used, and therefore, not included in total SEM. Total metal concentrations were determined by microwave acid digestion (3:1 nitric: hydrochloric acid) followed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy). Resuspension samples were filtered through 0.2 um polycarbonate membrane filter, acidified with 10% nitric acid solution and analyzed on ICP-OES for dissolved metals of interest. For each ICP-OES analysis only standard curves with R² values > 0.9995 were accepted, and duplicate readings and spiked sample readings were run as QA/QC. Concentrations of dissolved metals from each triplicate set of experiments were averaged, and an one way ANOVA was run to find significant differences in metal concentration and percent total metal released between resuspensions. The mass of metal released was divided by the total metal within the sediment in the chamber to calculate a percent metal released for every resuspension.

Three sediments were used for the multiple (pulsed) resuspension experiments. Due to lack of metal released from San Diego sediment in the continuous four-hour resuspension, it was not used. The metal concentrations for the four one-hour resuspensions (prior to water exchange) were summed and compared to the total released during the four-hour pulse resuspension.

Table 1. Total metals (mg kg ⁻¹ dry weight) for all sediments used in resuspension experiments. Bold values are levels above NOAA Threshold Effect Level (TEL) for *H. azteca*

Metal	As	Cu	Zn	Со	Fe	Mn
Duck Lake	2.6	48.8	116	73	15025	668
San Diego	2.7	318	331	180	51883	308
Idaho	11.4	323	56	257	90	41197
DePue	1.0	15.6	29791	37	41340	1738

Table 2. Analysis of Total Organic Carbon (TOC), Acid Volatile Sulfides (AVS) (μ mol/g), and Simultaneously Extracted Metals (SEM) (μ mol/g) for all sediments used in experiments

Metals	Duck Lake	Idaho	San Diego	DePue	
Cu	0.71	4.10	0.11	5.96	
Ni	0.23	0.22	36.53	0.40	
Zn	1.50	0.26	0.39	434.25	
AVS	51	0.63	0.53	17	
Total SEM	2.44	4.58	37.03	440.63	
SEM-AVS	-48.56	3.95	36.5	423.63	
TOC	0.234	0.96	0.79	2.59	

A sediment flux exposure chamber (SeFEC) was created to simulate sediment resuspension caused by dredging and prop wash (Fig 1). The SeFEC was similar in design to a chamber used by Hammerschmidt and Fitzgerald (2008) but had increased power to the propeller to resuspend all bedded sediment within the chamber. The chamber (580 ml) and propeller were polycarbonate and teflon to minimize absorption and desorption of metals during resuspension. Powered by a six volt battery, a propeller is spun creating a vortex powerful enough to resuspend all sediment within the chamber. Two ports (Fig. 1A) along the side of the chamber allow for sampling of both water column and pore water within settled sediment. A smaller, mesh walled (243 nm nylon mesh), inner chamber clipped inside the SeFEC allowing test organisms to be exposed to overlying water during resuspension, while being protected from the spinning propeller and excessive turbulence.

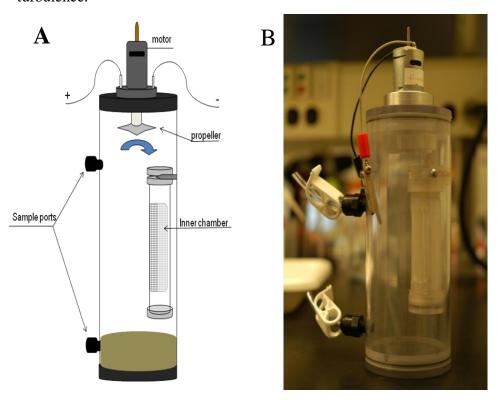


Figure 1. Schematic (A) and photograph (B) of Sediment Flux Exposure Chamber.

Preparing the SeFEC Chamber:

For all exposure scenarios, SeFECs were prepared and sampled in an identical manner. SeFECs were washed with a 15% HCl solution, triple rinsed with Milli-Q water, and allowed to air dry before each resuspension. Sediments from storage containers were stirred to homogenize, weighed, and added to the SeFEC chamber. The chamber was then carefully filled with culture water (Ann Arbor city water (hardness ~130 mg/L) passed through a carbon filter) using a syringe to avoid disturbing the sediment. When animal exposures were done, ten *D. magna* neonates (< 24 hours of age) and ten *H*. azteca neonates (< 2 weeks of age) were placed into the inner chamber with a pipette. The inner chamber was capped and air pockets were removed before begin clipped in place within the filled SeFEC. pH, DO, conductivity, and temperature, were measured pre-resuspension (time zero) and 5 mL of water was removed and filtered for initial metal concentrations. All air was removed from the chamber (Fig. 2). Physicochemical readings and water samples were taken every hour during the four-hour continuous resuspension and every three hours during the multiple resuspension. Each sediment resuspension was run in triplicate.



Figure 2. Photograph of several SeFECs during resuspension, with control chamber (no sediment) on the far right.

Exposure Scenarios:

Four exposure scenarios were conducted: a bedded sediment exposure assay in which samples were taken from a water column above non-resuspended sediment, a sediment aliquot elutriate exposure using a Qwik-lite toxicity test, an exposure to resuspension for four continuous hours (press resuspension), and finally an exposure for four separate one-hour resuspensions over a 16-hour period (pulse resuspension).

The press and pulse resuspensions were done using the SeFEC. In the pulse exposure, a water exchange was conducted to simulate a more natural flow-through system after each three-hour settling period. Each water exchange reduced the TSS value for the chamber, as not 100 percent of the sediment had settled in the three-hour settling time. Dissolved metal samples were taken during both resuspended and settled periods. Samples were taken after the first water exchange and measured for TSS. A lower TSS decreased the total metal within the chamber, therefore total metal remaining in the

SeFEC was adjusted to the new TSS concentration, in determining the percent of total metal released during each sampling period. The decrease in TSS was minimal, therefore the metal removed during each water exchange were not corrected for. The four-hour continuous scenario was designed to replicate a single intensive dredging event and the pulse resuspension replicated intermittent ship traffic. DO, pH, and conductivity were measured hourly using handheld probes.

Organism exposures for resuspension tests included *D. magna* and *H. azteca* neonates, as well as adult *D. magna*. Neonates and adults were exposed to bedded sediment, press and pulse resuspension conditions and observed for mortality and reproduction (adults only). Following resuspension, organisms were carefully removed from the inner chamber, placed in clean culture water (50 ml beakers), and survival was immediately determined by hand counting surviving and dead organisms. Survival was indicated by movement of individuals, after gentle prodding with pipette. Surviving *D. magna* and *H. azteca* neonates were held for 7 and 10 days, respectively, to monitor longterm survival. *D. magna* of reproducing age (two weeks) were exposed to a press resuspension, then placed in clean culture water and number of neonates produced was recorded over seven days by counting and removing neonates by pipette on a daily basis. Reproduction of adult *D. magna* was used to determine sub-lethal effects.

Organisms were also exposed to bedded sediment without resuspension. *D.magna* and *H.azteca* neonates were placed in the water column above bedded sediment for the 7-day and 10-day exposure tests. Fifty ml of sediment was placed in 300 ml beakers and 200 ml of culture water was added slowly, to minimize sediment resuspension. After a 24-hour equilibration period, ten *D. magna* and ten *H. azteca* were added to each beaker. pH, DO, temperature, and mortality were recorded each day for the seven day *D. magna* exposure test, and ten day *H. azteca* exposure test. A full water exchange was done every other day. Prior to each water exchange,

water column samples were collected and analyzed for dissolved metals as described above.

Qwik-lite is a toxicity assessment test, using bioluminescence of dinoflagellates (*Pyrocystis lunula*) to determine toxicity. Sediment Qwik-lite testing was conducted on sediment aliquot samples to observe basic whole sediment toxicity for each sediment type and press and pulse resuspended water samples. For sediment aliquots, a mixture of 1:4 whole sediment to artificial seawater was stirred for one hour, and then allowed to settle to produce the aliquot elutriate. Elutriate was then filtered to remove suspended solids (similar to resuspension samples), and prepped for Qwik-lite testing. Prepping included adjustment of pH (8.0-8.2) and salinity (32-34%) of a sample to create optimum survival conditions for the dinoflagellate. Optimum conditions insured any reduction in bioluminescence was due only to contaminants from the sample. Dinoflagellates were exposed to samples for 24 hours in a cuvette, while on a 12-12 light-dark cycle. Afterwards, the cuvette was loaded into Qwik-lite testing chamber, sample was agitated by bubbling air, and bioluminescence was measured.

In press and pulse resuspensions, 50 mL of sample was removed from the water column after completion of the press resuspension, and after each 3-hour settling period for pulse resuspensions. Samples were filtered (0.4 µm isopore membrane filter) to remove any particulates, adjusted for pH (8.0-8.2) and salinity (32-34%) to provide optimum conditions. Dinflagellates were exposed to the sample for 24 hours, on a 12-12 light-dark cycle. The endpoint of this assay was percent bioluminescence as compared to an artificial seawater control. A control sample is included in each individual Qwik-lite sample run. The toxicity value for each sample was determined by taking the inverse of the percent bioluminescence produced, for example if a sample produced thirty percent of the control bioluminescence, the inverse out of ten would be seventy, which on a scale of one to ten, would give a toxicity value of seven. The toxicity range is from one to ten with ten being highly toxic. Toxicity of a sample was determined by taking 10 times the percentage of

bioluminescence compared to the control, subtracted from 10. For example, if a sample only produced 10 percent (value of 0.1 (times 10) value of 1) of the bioluminescence when compared to the control, that sample would receive a toxicity rating of 9. Each Qwik-lite value was an average of six replicates from one sample.

An one-sided ANOVA was run to determine significant differences between the amount of metals released during the two different resuspension scenarios (press and pulse). Error bars on resuspension and reproduction graphs represent a 95% confidence interval, to determine significant differences between sediment types. Each 95% confidence interval was determined from running each exposure scenario in triplicate.

Results:

Sediment Toxicity:

AVS and SEM were measured in each sediment type (Table 2). In all sediments except Duck Lake the summed molar concentration of SEM's was higher than the molar concentration of the AVS. When SEM-AVS is >0, there are more metals than the present sulfide could bind, resulting in metals in the dissolved phase, or in another metal-bound phase of the sediment. Therefore metal toxicity was likely in San Diego, Idaho, and DePue sediments. DePue sediment had an extremely high SEM value for zinc. In the environment, it is likely that all copper and nickel would be bound to the available AVS, and only a small portion of zinc would be bound. Therefore, zinc would be the most likely metal to cause any observed toxicity. The same situation can be said for San Diego sediment where zinc and copper would likely be bound to the available AVS, and the excess nickel would cause any toxicity observed.

4-Hour Resuspension:

Press resuspensions were monitored for changes in physicochemical parameters, and sampled for dissolved metal concentrations throughout the resuspension. An average decrease of pH (0.14) and DO (0.24 mg/L) (appendix) was observed in the press resuspensions of all sediment types. A general decrease of pH and DO were seen during the beginning of each press resuspension, shown most dramatically by the press resuspension of Idaho sediment (Fig. 3). Larger declines of pH and DO were seen in TSS resuspensions above 1g/L.

Metals were released from all sediments during four-hour continuous resuspension. Metal concentrations remained constant after the resuspension began. Less than 2% of total metal was released into the water column for the majority of runs (Table 3).

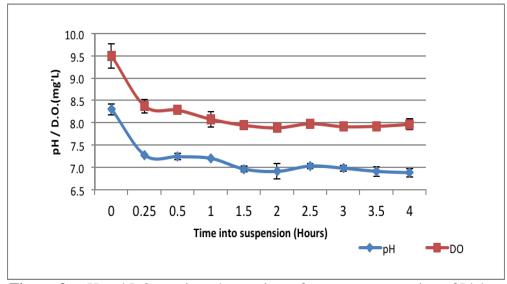


Figure 3. pH and DO monitored over time of a press resuspension of Idaho sediment

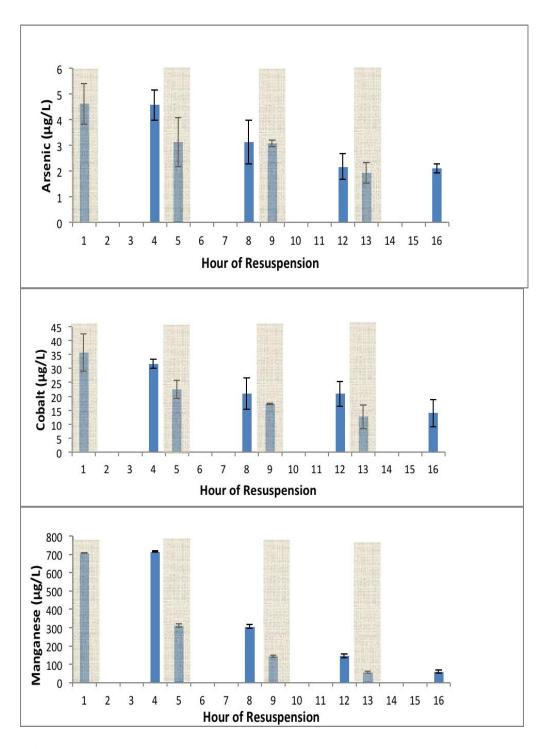


Figure 4. Concentrations of dissolved manganese, arsenic, and cobalt (ug/L) after four one-hour resuspension periods (shaded) over a 16-hour time frame beginning at 1g/L for Idaho sediment

16 Hour Pulse Resuspension:

Dissolved metal concentrations were measured prior to resuspension, after each one-hour resuspension, and after each three-hour settling period for the pulsed scenarioAfter each water exchange, a new TSS value was calculated due to loss of sediment. TSS values ranged from 1 - 0.7 g/L. When corrected for decline in TSS, the slight decline in nickel, copper, and iron released overtime was no longer evident.

Table 3. Percent of total metal dissolved during press and pulse (hourly and total) resuspension events. Percent adjusted for sediment loss during water exchange. Each hourly percent is determined from total sediment present at start of resuspension (B.D. = Below Detection on ICP-OES, * signifies significant difference between press and pulse, arrows signify percent released trend through time (increasing or decreasing))

Sediment	Resuspension	As	Cu	Zn	Co	Fe	Mn
	1						
Duck Lake	4-hour Press	B.D.	1.53	0.08	0.87	B.D.	0.17
Duck Lake	Pulse 1-hour	B.D.	0.01	0.39	0.76	B.D.	0.34
Duck Lake	Pulse 2-hour	B.D.	0.14	1.35	0.92	B.D.	0.08
Duck Lake	Pulse 3-hour	B.D.	0.24	2.47	1.68	0.01	0.06
Duck Lake	Pulse 4-hour	B.D.	1.08	2.07	2.60	0.04	0.12
Duck Lake	Total Pulse	B.D.	1.47	6.28	5.96	0.05	0.6*
San Diego	4-hour Press	B.D.	0.77	0.10	0.87	B.D.	0.07
Idaho	4-hour Press	5.40	0.42	0.97	1.06	0.02	12.01
Idaho	Pulse 1-hour	3.58	0.12	1.22	1.23	0.01	14.23
Idaho	Pulse 2-hour	2.60	0.25	5.37	0.83	0.01	6.78
Idaho	Pulse 3-hour	3.00	0.38	6.32	0.75	0.01	3.65
Idaho	Pulse 4-hour	2.89	0.27	6.24	0.85 ♥	0.01	2.16 ♥
Idaho	Total Pulse	12.07*	1.02*	19.15*	3.66*	0.04	26.82*
DePue	4-hour Press	B.D.	0.05	0.15	14.38	0.03	2.68
DePue	Pulse 1-hour	B.D.	0.10	0.22	15.92♠	0.01	4.18
DePue	Pulse 2-hour	B.D.	0.15	0.36	14.52	0.07	2.68
DePue	Pulse 3-hour	B.D.	0.11	0.33	16.24	0.05	1.41
DePue	Pulse 4-hour	B.D.	0.17	0.34	17.94	0.07	1.01♥
DePue	Total Pulse	B.D.	0.53*	1.25*	64.62*	0.20	9.28*

Percent Metal Comparison:

The percent of total metal released as dissolved ions in the chamber during resuspension were compared between the two resuspension scenarios. Overall, all metals, except copper from Duck sediment, showed a higher average amount released during summed pulse resuspensions than the continuous resuspension (Table 3). Three metals (Cu, Zn, and Co) increased through time during pulsed resuspension of Duck Lake sediment. Zinc percent released increased through time during Idaho resuspension, but manganese and arsenic decreased through time during resuspension of Idaho sediment. Cobalt showed an increase while again manganese showed a decrease during the DePue pulse resuspension. A one way Analysis of Variance (ANOVA) test revealed which pairs of resuspension scenarios showed significant (p > 0.05) difference between the amounts of metal released. In resuspension of Idaho and DePue sediments; zinc, cobalt, manganese, and arsenic (Idaho only), showed significant differences between press and pulse resuspensions, while iron did not. Duck sediment was found to have the significant differences in released copper, zinc, and cobalt. When looking at percent metal release, sediment type may be an overlying factor, considering Idaho and DePue were both low organic, small particle sediments, while Duck sediment had high organic content. Metal concentrations of manganese, cobalt, and arsenic in the water column decreased over time in pulse resuspension scenario. The decrease between the first and fourth resuspension metal concentration for manganese, cobalt, and arsenic (Fig. 4) was found to be significantly different (ANOVA, p<0.005). The pulse resuspension released a higher percentage of total metal when summed over four hours except for copper release from Duck sediment. Total metal released each individual hour of the pulse resuspension varied over time.

Samples of sediment aliquot elutirate, press, and pulse resuspensions were tested for toxicity using the Qwik-lite toxicity assessment. Higher toxicity was observed in sediment aliquot elutriate than the press and pulse

resuspended water columns. Qwik-lite testing revealed that aliquots from DePue and Idaho sediments had relatively high toxicity, while Duck and San Diego had low toxicity levels (Fig. 5). Press resuspension of Idaho sediment had high toxicity; press resuspension of other sediments had generally lower toxicity. Toxicity was observed over time for water column samples from pulsed resuspensions of all sediments. The interesting trend of decreasing toxicity over time was seen in the pulsed resuspension of Idaho and DePue sediment, but not in resuspension of Duck sediment (Fig. 6). Duck Lake toxicity increased from the third to fourth resuspension. From Table 3, copper, zinc, and cobalt increased over time during this resuspension, which could have caused the increase in toxicity. For pulsed exposure, the water column was sampled during resuspension and settling periods. Toxicity decline was seen in both water column circumstances of over time.

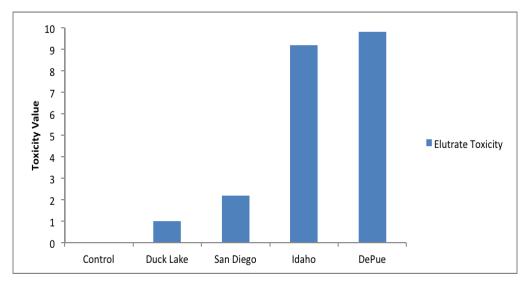


Figure 5. Qwik-lite toxicity values of elutriates(1:4 sediment /seawater) compared to controls for each sediment. Toxicity range 1 to 10. Less than 3 is considered low toxicity, greater than 7 high toxicity.

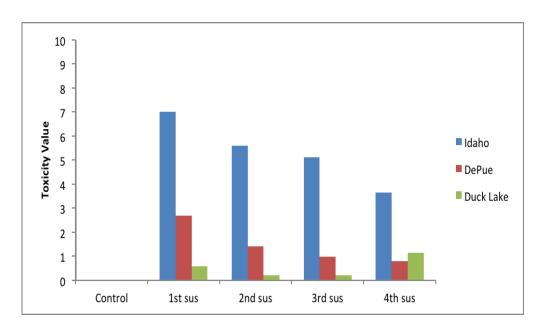
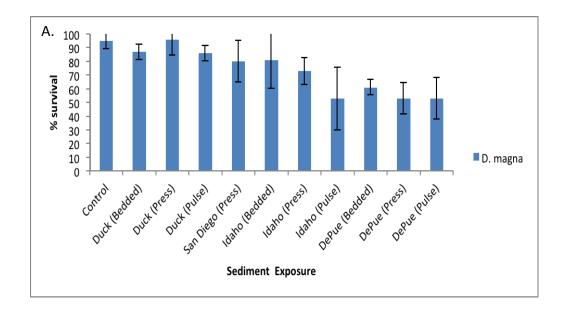


Figure 6. Level of Qwik-lite toxicity for suspended water column of 16-hour multiple resuspension experiment using Duck, Idaho and DePue sediments



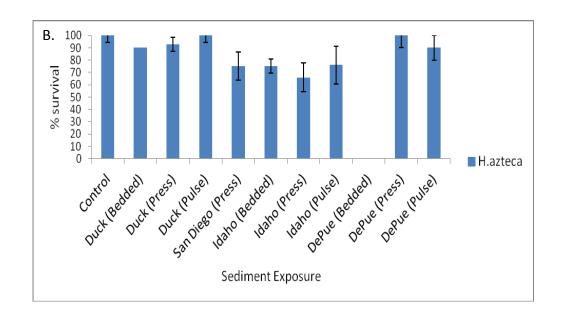


Figure 7. Survival of *D. magna* (A) and *H. azteca* (B) for all exposure scenarios

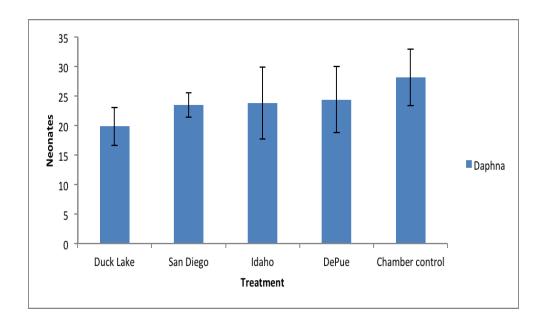


Figure 8. Average number of neonates per female *D. magna* after press exposure resuspension

Survival of *D.magna* and *H.azteca* were measured following bedded, press, and pulse exposures. Overall, survival was higher in Duck sediment, followed by Idaho and DePue, but no significant differences were found. Survival was generally less during resuspended exposure of Idaho and DePue sediments than bedded sediment exposure for *D. magna* (Fig. 7A). San Diego bedded sediment exposure results are not applicable for survival, as it was a marine sediment. Reproduction averages of adult *D. magna* after exposure to resuspension also showed no significant difference between sediment types (Fig. 8). However, on average *D. magna* exposed to resuspension conditions had a significantly decreased neonate production when compared to the control. This sub-lethal effect over a longer period of time could lead to negative population effects.

Discussion:

Physicochemical changes of the water column during resuspension signify chemical and physical shifts that aid in release of heavy metal contaminants. pH decline has been directly related to the oxidation of metal sulfides, which in turn releases metals into the dissolved phase. The observed pH decline along with an initial drop of DO suggests oxidation of metal sulfides did occur, however changes were slight due to low TSS values. Metals could have been from desorption of easily exchangeable sediment particles, rather than released by metal sulfides, or a combination of the two processes.

In bedded sediment, metals tend to accumulate in porewater due to reductive dissolution of iron and manganese oxyhydroxides in anoxic conditions (Saulnier, 2000). The metals residing in the porewater could then be scavenged by metal oxides, or remain in the dissolved phase during sediment resuspension. Very little pore water was present prior to resuspension, due to low TSS concentrations tested. Metal concentrations where sediment with pore water was resuspended would potentially have higher metal concentrations than what has been shown here (Saulnier, 2000).

In waterways, during resuspension, porewater is highly diluted in the water column, a reason why metal concentrations in the SeFEC water column may appear lower than if bedded sediment including pore water was used for resuspension. Further research should be conducted in a chamber which includes bedded sediment with pore water during resuspension.

Decreased survival was seen in both D. magna and H. azteca neonates, but survival was higher than other studies with TSS concentrations between 250-500g/L (Weltens, 2000). The conditions of the resuspension at TSS at 1g/L were considered a worst case scenario for sediment resuspension caused by dredging. As 1g/L is at the high end of the range of suspended solids measured during dredging activity (700-1000mg/L). The near fifty percent survival seen in D.magna exposed to DePue sediment may be due to the increased dissolved metals concentration of the water columns. However, given the acute exposure time and the fact that not all dissolved metal concentrations reached levels that would cause acute harm to test organisms; increased turbidity could be an additional reason for reduced survival (Robinson, 2010). No survival of *H. azteca* was observed when they were exposed to bedded DePue sediment. This significant difference was thought to not be caused by metal concentrations in the water column. H. azteca mainly resides in the sediment and not solely in the water column, like D. magna. The zero survival rate was probably due to high metal contamination or low DO within the sediment and not from metal contamination of the water column, since at least half of the *D.magna* from the same exposure test survived in the water column.

Through use of controls, I showed that the turbulence of the water column within the SeFEC had no effect on the organisms. In the acute exposures conducted here, I expected to see higher survival and effects than traditional 96-hour water quality guideline tests, due to the shorter exposure time. The linear relationship between length of exposure and toxic results, support the finding of effects from acute exposure would not be as intense as longer exposure scenarios.

Metal concentrations released through time during the pulsed resuspension showed both increasing and decreasing trends (Table 3). During the resuspension of Duck Lake sediment copper, zinc, and cobalt increased in concentration through time, having a slow release time throughout the 16-hour resuspsion. It has been shown that the oxidation of metal sulfides occurs rather quickly, taking approximately 4 hours for 90% of the sulfide to oxidize (Simpson, 2000; Reible, 2010). The increasing concentration trend suggests that these metals may not have been bound to metal sulfide, or the majority of the metal would have been released during the first resuspension. The slower release time suggests that another solid-binding phase held the metals before resuspension such as organic carbon. Resuspension of Idaho sediment showed a decrease through time of manganese. A rapid released of a large percentage of manganese at the beginning of the resuspension suggests that it was bound to sulfide. Manganese and cobalt also showed a decreasing trend during the resuspension of DePue sediment. However, cobalt increased throughout the Idaho resuspension. Cobalt showed increasing and decreasing trends during resuspension of different sediments, this suggested that sediment factors (particle size, number of available binding sites,) influence metal partioning and therefore how rapid a metal was released over time. The timing of metal release is critical in predicting toxicity of resuspended sediment. If metals are mainly sulfide bound, they may release relatively quickly posing an immediate toxic threat, whereas if metals are bound in another solid phase, release and toxicity may be delayed.

Biases and Assumptions:

Properties of culture water used in this set of experiments were not identical to properties of a water column which would be found above contaminated sediment in the environment. Factors such as hardness, alkalinity, nutrients, TSS, and pre-resuspension concentration of heavy metals within the water column impact the chemical shifts that occur during a resuspension event (Cantwell, 2004). Being a lab based set of experiments; a

single, readily available, water source was used throughout all resuspensions for experimental consistency.

The SeFEC was not capable or replicating a flow-through system where the water column is continually being exchanged throughout the resuspension event, as in a river channel or canal. In between multiple resuspensions of the pulse experiment, the water was exchanged in an attempt to create a more realistic system; however, this was not an ideal solution. The small size of the SeFEC restricted the volume of water column that could be used during resuspensions. In a river or canal a large dilution gradient would occur as the resuspended sediment plume moved downstream. This dilution was not replicated in resuspensions using the SeFEC.

Within these experiments, I could not assume the toxicity observed was due entirely to metal release in the water column. Many factors such as nutrients, sediment particles, and physicochemical shifts could cause negative effects on the test organisms used. The addition of salt to the filtered samples of the Qwik-lite toxicity assay may have also affected the toxic effects of the metals within samples. Most likely, a combination of these factors was the cause of the negative impacts viewed in these resuspension experiments. Determining which factors most strongly affected metal release and toxicity of sediment resuspension should be a focus of future work.

In order to gain a more in-depth understanding of the physical and chemical shifts that occurred during sediment resuspension, a more complete design should be used. The SeFEC provides a solid representation of the mixed water column during sediment resuspension. However, the bedded sediment and pore water were not represented well in the SeFEC, but should be studied. Within the SeFEC, an accurate measurement of the TSS concentration was achieved since all of the sediment within the SeFEC was resuspended, but because of total resuspension no measurements could be taken on the sediment which lies below a resuspension event. In order to allow metal speciation models to accurately model sediment resuspension,

metal release and transport, a more complete look at the environment surrounding a resuspension event would be beneficial.

Near completion of the study, I discovered that Duck Lake sediment was in fact not reliable as an uncontaminated reference sediment, due to heavy metals found at the collection site (Nelson, 2011). Even being used as a questionable reference sediment, it was still valuable, in adding to the understanding the transport and movement of heavy metals during resuspension over a range of sediment types.

I hypothesized that sediment with more AVS would release the greatest amount of metals. However, the sediment with the highest AVS, Duck Lake, did not release the highest percentage of metals among the four sediments tested. Duck Lake sediment had nearly 4 times the AVS than the other sediments; but, Idaho and DePue sediments released twice as much metal, percentage wise. This suggests that there are a multitude of other factors influencing metal sulfide release of metals.

Summary:

Release of heavy metals from sediments has been documented in many works (Saulnier, 2000; Eggleton, 2004; Reible, 2010) making heavy metals one of many stressors present in aquatic environments (Burton, 2010). As I hypothesized, increased water column concentration of heavy metals was observed during anoxic sediment resuspension at TSS of 1 g/L inside a SeFEC. Metals from contaminated anoxic sediment were released into the water column and remained in the dissolved phase after resuspension had subsided. As in other studies, the percent to total metal released into a dissolved phase was low, between 2-10 percent (Salunier, 2008). Significant differences between resuspension scenarios (press and pulse) were found, but not in all metals or sediment types. Variation in metal speciation and sediment partitioning behavior may be cause for these mixed results. Cantwell, (2004) also found variation in release between different metals. These results suggest that the duration of a resuspension may influence the

release of heavy metals. Contaminated sediment resuspension at 1g/L does not appear to be a high enough concentration to create negative ecological impacts. Although decreased survival and reproduction was seen, given the initial heavy metal concentrations of the sediments used, I expected the negative effects to be much more severe. The contamination of the sediments used here was high, while strong negative effects were not observed, most likely due to the low percentage of total metals released. In smaller scale, as in SeFECs, this concentration did not appear to be an acute environmental stressor.

The US EPA recommends that assessments of the effects of aqueous metals on aquatic organisms be based upon the dissolved metal concentration (EPA, 2005). This is due to the fact that the dissolved fraction of metals is believed to be the most bioavailable to organisms, and therefore the biggest toxic threat. The dissolved metal fraction in bedded sediments is not a good indication of the bioavailability of metals if the sediment is resuspended due to the chemical and physiochemical changes that occur. Presently there are very few federal regulations on suspended sediments. As of 2001, only 32 of 53 states and territories had numerical criteria for suspended sediments. Although sediment resuspensions are not a constant threat, as metal in bedded sediments may be, they are still important when considering potential exposure to sediment contaminants. It is difficult to understand the extent of risk associated with resuspended sediment, without taking into account the variables that were studied here.

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A Literary review on resuspension of sediment, and the release, transport and fate of heavy metals.

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Introduction:

Resuspended sediments can act as both physical and chemical stressors in aquatic ecosystems. Physical impacts include increased turbidity, abrasion, burial, and transportation of sediment downstream, as well as reduced visibility. Contaminated sediments pose a chemical impairment of water quality and aquatic organisms, due to potential release and transport of contaminants and removal of oxygen from the water column during resuspension. Contaminants found in anoxic sediments include: polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and heavy metals.

Metals of most concern are copper, cadmium, iron, manganese, nickel, lead, zinc, and arsenic. The focus of this literature review will be on sediment resuspension and heavy metal release. It should be recognized that other contaminants are likely to be present during resuspension. I focus on metals because of their abundance in ecosystems and their ability to accumulate within the food web, and become more concentrated in higher trophic levels.

Sediment resuspensions can be caused by a number of different natural and anthropogenic activities: dredging (Eggleton 2004; Hedge 2009; Torres 2009), high winds (Chen 2004; Rao, 2004; Vanderploeg, 2007), stormwater runoff (Birch, 2007; Wilber, 2001), coastal upwelling, soil erosion, wave and current action, bioturbation/bioirrigation (Sutherland, 1998; Ciarelli et al. 2000), shipping traffic, and vertical mixing/convection (Porter, 2010). For the purpose of this literature review sediment resuspension caused

by dredging activity and its potential for heavy metal release will be the focus because dredging most often occurs in areas with contaminated sediment where there is a great potential for aquatic biota to be exposed to heavy metals during resuspension.

During resuspension of anoxic sediment, the physical and chemical environment surrounding sediment bound metals will change. Bedded sediment is drawn up into the water column which is often fully saturated with dissolved oxygen (DO). Exposure to oxygen can result in oxidation / precipitation and transformation of metals into more bioavailable chemical forms (Zhuang, 2004.) The degree of oxidation depends upon the rate, magnitude, and duration of the event. Besides DO, other factors which impact heavy metal release are salinity, pH, acid volatile sulfide (AVS), organic carbon content, sediment grain size (Bridges, 2010), and redox potential (Cantwell, 2002). Understanding the physiochemical and chemical changes that occur during sediment resuspension is vital to accurately predict the environmental risk that a resuspension event will have on the surrounding area. A more complete understanding of potential partitioning, toxicity, and bioavailability of the sediment contaminants when resuspended is important when determining environmental risk. If accurately predicted, measures can be taken to prevent or reduce these negative impacts. Resuspension models, to more accurately predict transport and fate of metals, will also gain from more thorough understanding.

Sediment Properties:

The composition of resuspended sediment during dredging greatly influences the release of heavy metals. Sediment grain size, phosphorous concentration, organic compounds, and extent of contamination are all key factors (Torres, 2009). The magnitude of physical and chemical change in the overlying water is influenced by the amount of sediment which is suspended (Cantwell, 2004). Aqueous heavy metals bind most easily to fine particles (Vincente et al. 2009), due to metal oxide binding sites on silt and clay particles (Ciutat et al. 2003) and a small surface area to volume ratio.

Differences between metal affinity towards oxides have been researched.

Copper has been found to bind to sulfide and organic matter most readily, whereas zinc binds to hydroxides more often than sulfide or organic matter (Kelderman and Osman, 2007). Yet, lead has shown an even distribution between all available binding sites.

A strong gradient in redox conditions control partitioning of heavy metals in bedded sediment. In the anoxic layer the majority of heavy metals are partitioned onto sulfides, carbonates, and organic substances (Calmano, 1993). Bedded sediments with an excess of sulfide have low pore water concentrations of dissolved metals, due to availability of sulfide binding sites and low solubility of metal sulfide compounds (Simpson, 2000). In the aerobic layer, heavy metals are likely to be bound to particulate organic carbon (POC) in the form of humic compounds (Reible, 2010; Chapman, 1998) or iron and manganese oxides (Singh et al. 1984). During resuspension,

there is little chemical change expected for sediments previously within the aerobic layer because of previous exposure to the oxygenated water column. However, for deeper anaerobic sediments large physical and chemical changes may occur during resuspension which may promote release of heavy metals.

Bioavailability:

Bioavailability is the portion of a contaminant that can be taken up by an organism from its environment and is subsequently metabolized and transported. (Weltens et al. 2000). The bioavailability of a metal depends on binding strength and partitioning behavior to the geochemical components of the sediment (Eggleton, 2004, Usero 1998; Yuan, 2004), and other ions present in the water column. Metal bioavailability is often affected by particle size, pH, redox, salinity, temperature, organic carbon content, and molecular structure. AVS, manganese and iron oxides, and dissolved organic carbon also affect the bioavailability of metals. In anoxic conditions metals sulfides are strong scavengers of metal ions, decreasing bioavailability. In oxic conditions metal oxides and DOC replace sulfides in binding to metal ions, making it difficult for metals to be metabolized by present organisms, reducing metal toxicity. Resuspension promotes availability of metals, deep in anoxic sediment, that previously were physically and chemically not bioavailable to most biota.

Metal Release / AVS:

Total recoverable metal concentrations allow for estimation of how much actual contaminant is at a specific site, however, are poor estimates of potential toxicity. The aqueous phase of metals is most important when trying to determine biota toxicity and total metal in sediment is often unrelated to dissolved metal concentrations (Chapman, 1998). Metals in the dissolved phase are most bioavailable to biota; however, metals in the solid phase bound to sediment particles have shown more toxicity than originally thought. Sulfide, a reduced form of sulfur, is the dominant solid phase molecule controlling the sorption of metals in anoxic sediments (Burton, 2010). The portion of heavy metal which is assumed to be bound to AVS are known as simultaneously extractable metals (SEM). The difference between AVS and SEM levels is a metric used to determine how much, if any, heavy metals are potentially bioavailable. In bedded sediments where the SEM-AVS ratio is greater than one, it is unlikely that the sediment will cause toxic effects in its anoxic state, because all available metals are bound to sulfides (Chapman, 1998). In bedded sediment where the SEM-AVS ratio is less than one, metals will accumulate in porewater (Saulnier and Mucchi, 2000). The SEM-AVS model (Di Toro, 1992) is based on field and experimental evidence, that no sediment toxicity is typically observed when the molar concentration of AVS is greater than SEM.

Numerous studies show a decrease in sediment and water column AVS as resuspension occurs (Reible, 2010; Chapman, 1998; Simpson, 1998).

During resuspension, reduced sediment is brought into contact with dissolved oxygen in the overlying water column oxidizing the metal sulfides, which produces oxidized sulfur species SO₄-2 (sulfate), and elemental sulfur S⁰. When oxidation occurs, the metals bound to sulfides will be released into the water column, becoming bioavailable (Simpson, 1998). Saulnier and Mucchi (2000) suggested the amount of metal released into the water column is strongly correlated to the amount of AVS in resuspended sediment. In some cases, minimal resolubilization of metals and organic compounds from highly contaminated sediment has occurred (Ludwing, 1988). However, in many environmental risk assessments, porewater is sampled to determine the toxicity of bedded sediments. It is thought contaminant concentrations in pore water are closely related to the toxicity of the bulk sediment (Ma, 2000). If sulfide rich sediments are resuspended and all metal sulfides are oxidized, this may cause an underestimate of potential toxicity. Although contaminants released from sediments through the process of dredging resuspension have been shown to have minimal impact in most cases, other reports have shown affects on aquatic biota due to physical changes in the environment.

The oxidation of AVS during sediment resuspension can be rapid, taking only approximately 4 hours for 90% of the total AVS to oxidize (Simpson, 2000; Reible, 2010). The process has been observed to occur in two steps. Initially, a transformation of AVS to elemental sulfur (S^0) occurs. Secondly, a slower paced oxidation of S^0 to SO_4^{-2} takes place. The second process is associated with pH decline (Youssef, 1996), due to the oxidation of

FeS to S⁰ and Fe⁺². The relatively quick chemical shift promotes release of metals from resuspended sediments to occur soon after resuspension (Saulnier and Mucchi 2000).

Metal sulfides that are oxidized during resuspension have been directly connected to a decline in pH and increased metal solubilization (Chen, 2004). As pH is lowered, an increase in the number of free hydrogen ions in the water column occurs and fewer binding sites are available for heavy metals (Bushey et al. 2008). Reible (2010) found that pH was the most important parameter for metal release when looking at sensitivity analysis. The effect of pH buffers can have a substantial impact on shift of pH during sediment resuspension (Cantwell 2008). The full potential release of heavy metals may not occur in the overlying water column if there is high buffering capacity. In the overlying water, calcium carbonate in an aqueous phase, can act as a buffer which prevents decrease in pH, reducing the amount of metals released during resuspension (Reible, 2010).

No significant decrease of pH over a 6 hour resuspension was seen using a Particle Entrainment Simulator (PES) (Cantwell, 2008). This is not typical of most studies which have shown a decrease in pH over time caused by oxidation of metal sulfides (Youssef, 1996; Eggleton, 2004; Reible, 2010; Chen, 2004). No decrease in pH was an indication of the buffering capacity of the sediment and seawater was large enough to absorb any measureable decline in pH due to oxidation of metal sulfides (Simpson, 2000). The low variability in pH may also indicate an absence of large scale oxidation of

metal sulfides if present. If conditions in the water column and surface sediment are favorable for metal adsorption, dissolved metal concentrations could be lower after resuspension than before (Forstner, 1995).

Release of metals by sulfide bonds is accompanied by the oxidation or reduced iron and manganese during sediment resuspension, creating binding sites for free metal ions. As soon as a free metal ion is released from a sulfide bond, it may be re-bound or scavenged by present metal oxides and/or organic matter (Simpson, 1998; Singh, 1984). This released re-capture of metals during resuspension makes it difficult to pre-determine how much metal will be made available during a resuspension event.

Metal Release / Transport:

Metals released from sulfides do not all operate identically in the aqueous phase. Differences among metal desorption / re-adsorption have been observed during controlled resuspensions (Caetano, 2002; Cantwell, 2004). Zinc was found to re-adsorb to particulates very rapidly upon oxidation, whereas cadmium and arsenic have been shown to remain in solution much longer. These variations are due to chemical interactions with chlorides and other anions which can limit sorption of metals onto iron and manganese oxides (Caetano, 2002). A long residence time in the dissolved phase signifies a threat to the surrounding environment even after dredging activity has been completed (Saulnier and Mucchi, 2000). Variation in binding site preference and release has been observed among different heavy

metals. It is important to consider which type of binding site heavy metals prefer when sediment is resuspended and determining where the most toxic sediment may be found at a restoration site. The transport and fate of heavy metal contaminants is largely site specific, but Connolly, 2007 suggests that impacts can occur not only at the dredging site, but miles downstream.

Dredging:

Dredging is the removal or relocation of sediment and debris from bodies of water either for navigation or removal of contaminated sediments from an impacted location as part of a restoration project. Most environmental dredging uses a cutter dredging technique along with silt curtains (Hedge, 2009). Environmental dredging is usually done with a self propelled ship equipped with a hydraulic suction system, a cutterhead bit for loosening the sediment, and a self contained hopper to transport sediment to a disposal site (Torres, 2009). Silt curtains are used to contain resuspended sediment to a small area around the dredging activity. This type of dredging is one of many ways to remove contaminated sediments from an area. However, the dredging process is usually more costly and complex then other sediment restoration methods (Bridges, 2010).

The amount of sediment that is suspended during dredging is dependent upon water depth, currents, and surrounding bathymetry. The rate of resuspended particle generation can be represented by the rate of sediment removal (kg/day) multiplied by the dredge efficiency (kg suspended / kg

extracted) (Wu and Wang, 2006). The majority of resuspension is caused by removal of bedded sediment by the dredger head. Propeller wash and overflow from the hopper may also cause resuspension (Bridges, 2010). Very fine sediment particles are capable of binding to contaminants, and have a longer suspension time in the water column, creating plumes that stay suspended after dredging activity is completed (McAnnally, 2007).

Completion of dredging activity may take hours or days to several months.

For even the most careful dredging operations, there will still be some amount of sediment resuspended into the water column. Sediment plumes have been shown to extend as far as 1000 meters from an active dredging site (Wilber, 2001). Under these conditions, benthic organisms on the sediment surface can be exposed to turbid conditions for days (Wilber 2001), even if the dredging activity only lasts a few hours. Large plumes not only create an extended exposure period, but also act to transport contaminated sediment to locations further downstream. If heavy metals had not been released at the dredged site, due to physicochemical conditions, they may be released downstream if conditions of the plume are changed. These factors must be measured and understood to conduct dredging in a way that is most efficient in reducing potential toxic effects (Torres, 2009). However, in most cases these factors are not taken into account due to time and cost.

The length of time sediments are resuspended is one factor which determines the impact resuspension has on the water column and present biota (Tomson, 2003), the other factors being contamination level and amount of

sediment resuspended. In New York State, along the upper Hudson River, approximately 300,000 cubic yards of sediment was removed in a single restoration project. Active dredging continued for 24 hours a day, 6 days a week for a 6 month period (Bridges, 2010). If only a small percentage of metal per unit of sediment was released, from such a massive operation, significant amounts of metals may be released in the water column. However based on flow rate and dilution factor of the area toxicity may or may not be seen. The transport of contaminants should also be considered when looking at toxicity. Increase of heavy metal concentrations in fish tissue have been found 6 miles downstream of the dredging site after dredging activity (Connolly, 2007).

The other factors determining impact are contaminate concentration and amount of sediment resuspended (TSS concentration). A variable range of TSS concentrations have been reported in the literature. In shipping channels, TSS concentrations have been measured at 150mg/L during dredging activity (Torres, 2009). During active dredging elsewhere TSS values have been recorded as high as 1,300mg/L at a distance of 15 meters from active dredging. Fifty meters away TSS values were approximately 356mg/L (Torres, 2009). This rapid dilution factor creates issues when determining sustained TSS values caused by dredging activity. In general, a 1g/L suspended solids concentration is thought to best represent dredging activity.

Resuspension of sediment also occurs from shipping traffic.

Resuspension of sediment may lead to erosion, internal nutrient loading, elevated turbidity, and heavy metals in the water column (Beachler, 2003).

Spikes of deposition over time have been seen to correlate with ferry schedule, and other heavy ship movement (Michelsen, 1998). Contamination has been discovered up to 20 feet deep in core sediment samples (Michelsen, 1998). Sediment traps have been used to observe if recontamination, due to prop wash resuspension, occurs after a site has been restored. Sediment found in traps was similar to contaminant concentrations of buried sediment. This signifies that resuspension of bottom sediments in heavy traffic areas is a primary source of contaminants entering the water column, and recontaminating a site. This study concluded that anthropogenic influences, such as ship traffic and dredging, can be at least as important in transport of contaminated sediments as natural processes.

Laboratory Resuspensions:

Replication of sediment resuspension in a lab setting can be used to carefully monitor chemical and physiological changes that occur often in the water column to advance metal partitioning models. Experiments range from acute exposure (4-12 hours) to chronic week long exposure, with the majority using anoxic marine sediment, and falling within a 24-96 hour range. Given the complexity and many unknowns of sediment resuspension and its effect on metal availability, toxicity, and transport many models need more data

specific to accurately predict potential metal transformation and release. Creating the dynamic, shifting chemical equilibrium in resuspension models is another key motivator for this area of research. This type of research highlights the importance of understanding mechanisms of metal bioavailability during sediment resuspension.

Numerous types of laboratory apparati have been used in an attempt to recreate sediment resuspension, including: mesocosoms (Kim, 2006), particle entrainment simulators (PES) (Cantwell, 2004), sediment flux chambers (SeFEC) (Hammerschmidt and Fitzgerald, 2008), modified larva mixers (Hill, 2009), and beakers on stir plates (Robinson, 2010). All resuspension techniques allow for through monitoring of physicochemical parameters and sampling during resuspension. However, most resuspensions in a lab do not use a flow through system, which is unrealistic of real world scenarios. A sediment flux chamber (SeFEC) has been used in the past to continuously circulate the water column over bedded sediment (Hammerschmidt and Fitzgerald, 2008) and has more recently been used to resuspend sediment, in replicating dredging activity.

As discussed about with field measured resuspension, two important variables to be controlled and manipulated in a lab resuspension are concentration of TSS and the duration of resuspension. Laboratory sediment resuspensions have a broad range of TSS, ranging from 20,000 - >60,000mg/L (Cantwell, 2008), and duration from a few hours to days (Hammerschmidt and Fitzgerald, 2008; Weltens, 2000). The majority of

experiments conducted in lab have been within the average dredging activity range for suspended solids (100-1000mg/L). It should be noted that higher suspended solid levels may be observed in the environment, but for short periods of time. Comparisons and predictions for field resuspension events can only be made if environmentally realistic resuspension times and TSS concentrations are used.

Sediment resuspensions conducted in the lab are limited by small volume and small sediment to volume ratio, when compared to actual environmental situations. The reduced scale of lab resuspensions have caused issues with dissolved oxygen levels within resuspension chambers. Sharp and unrealistic declines in DO can occur if the sediment to water ratio is too high, which can cause negative impacts to organisms unrelated to contaminant The presence of oxygen and the chemical changes that occur exposure. during oxidation of anoxic sediment are extremely important when determining potential release of heavy metals. Therefore, it is important to control the drop of DO and make it as realistic as possible. Experiments that resuspended aerobic sediment taken from surface sediment, revealed no significant metal remobilization throughout the entire resuspension (3 weeks) (Saulnier and Mucchi, 2000). Resuspension of anoxic sediment, collected from the same area, had significant release of iron and manganese to the dissolved phase. The bulk of metals release occurred during the first 15 minutes of resuspension (Saulnier and Mucchi, 2000). A small percentage of the total metals present has been observed to be desorbed and released into the

water column during a resuspension. An arsenic contaminated sediment resuspension had only 4% of Fe and 6-12% of Mn from the solid phase released to the water column (Saulnier and Mucchi, 2000).

Within the research of lab sediment resuspension, progress has been made to better understand specific reactions and conditions that occur during a sediment resuspension. These works will continue to aid in modeling metal partitioning and gaining a more thorough understanding of heavy metal release during sediment resuspension events.

Impact on Organisms:

The bulk of observed effects on organisms have been sub-lethal, during resuspensions at TSS values that generally occur during dredging operations. However, results vary from no toxic effect to significant mortality. The re-adsorption of heavy metals by sediment particles and organic compounds, and large dilution factor are most likely responsible for this result. (Urban, 2010). The intensity of the impacts of resuspension to organisms depends greatly on the parameters of the environment and biology of the organism. A range of test organisms have been used in resuspension studies, including: bacteria (Chen, 2004), algae, zooplankton (Urban, 2010), numerous species of macroinvertebrates (*Daphnia magna, Hyalella azteca, Chironomus tentans*), mussels, oysters (Hedge, 2009), and fish (Bridges, 2010).

Urban (2010) studied ecotoxicological impact of resuspended sediments on organisms living in the water column. In all organisms tested; a bacterium (Vibrio fischeri), an algae (Skeletonema costatum), and a zooplankton (Daphnia magna), no acute toxicity was observed. Results from this study confirmed the desorption of heavy metals occurring from resuspended sediment particles. However, the contamination did not produce significant acute toxicity on test organisms. Elevated accumulation of metals in tissues of oysters has also been observed, when compared to a reference site, but no mortality was seen (Hedge, 2009). These results support the idea that sediment resuspension caused by a single dredging event may not be lethal to biota. However, if sustained over a period of time, dredging could have impacts at the population level. Sub-lethal effects have also been Exposure to resuspended contaminated observed in Daphnia magna. sediment has been shown to negatively affect the growth and reproduction of Daphnia magna (Robinson, 2010). Ingestion of suspended clay particles clogged the digestive tract, reduced feeding rates, food consumption, and decreased size at maturity which resulted in a dose-dependent decline in survival (Kirk, 1992). The effects appear to be caused by sediment particles digested, not bioavailable metals.

Duration of resuspension has also been determined as an impact factor. At multiple TSS levels, 0-734mg/L, a 24-hour exposure, caused a decline in growth compared to controls, but no decline was seen in *Daphnia* exposed for only 12 hours. Results suggest that the duration of exposure to resuspended

sediment may be a more prominent factor than TSS concentration, when determining severity of impacts (Robinson, 2010).

Daphnia exposed to multiple "pulses" of resuspended sediment, which had 48 hours to recover (clean water) had enough time to purge and feed normally. Daphnia required approximately 40 minutes purging their digestive tract (Robinson, 2010). This prevented the accumulation of impacts from multiple exposures. Heavy metal tissue concentrations suggested that heavy metals were digested but not purged as rapidly as sediment particles. This pulse study suggests that even when significant mortality is not seen, metal accumulation is still occurring, which could have larger affects if conditions were sustained. In similar studies, mortality has been observed (Cloran, 2010). At TSS values between 0-249mg/L, Daphnia were uninhibited by clean sediment but had reduced survival when exposed to nickel spiked sediment. (Cloran, 2010). Reduced survival was attributed to nickel being in the aqueous phase, and easily accumulated. From these results we can conclude that suspended solids have an important function in affecting bioavailability and toxicity of nickel to aquatic organisms (Cloran, 2010).

Aquatic organisms are rarely exposed to a single contaminant, especially during sediment resuspension. Hence, single-metal exposure can be considered inadequate when trying to determine effects of multiple toxicants available during resuspension. Less than combined toxicity was seen, when looking at the impacts on organisms compared to metal concentration. This may be explained by similar metals competing with one another in passing

through a cell membrane, and for binding sites (Hill, 2009). Overall, duration and sediment concentration both play leading roles in determining impact on test organisms. When resuspending sediment well above threshold levels, the availability of metals to the biota is much less, resulting in little mortality.

Summary:

Anoxic, contaminated sediment resuspension has been shown to increase the amount of dissolved heavy metals in the water column. Heavy metals are likely to be released due to chemical shifts in both sediment and water column, which occur during dredging activity and prop wash. Of the total amount of heavy metals present at a contaminated site, only a small percentage is released, and even a smaller percentage remains in the dissolved phase. Once desorbed from sulfide bonds, to an aqueous phase, free metals are available to be scavenged by iron and manganese oxides, and other available binding sites, making them once again unavailable to aquatic biota. Depending upon conditions, not all metals may be re-adsorbed, making them available to accumulate in organisms, potentially causing toxic effects.

From studies conducted on-site during active dredging, it has been shown that metals released during dredging have the potential to accumulate in present organisms. The rate of accumulation is increased during dredging activity, compared to background conditions. Tissue samples show increased in heavy metal adsorption, but not to a level that causes toxicity and mortality

to organisms. Test organisms exposed to conditions of contaminated sediment resuspensions caused by dredging activity have most often shown sub-lethal effects. From these results I can conclude that in the high range of TSS found during active dredging (1g/L), heavy metals, if present, may be released, but will not cause severe, acute impacts on the surrounding environment and the biota that live there. However, results discussed here, as with all dredging observations, are extremely site specific.

The US EPA recommends that assessments of the effects of aqueous metals on aquatic organisms be based upon dissolved metal concentration, which is the most bioavailable and potentially toxic fraction. However, dissolved metal fraction in bedded sediments is not a good indicator of the bioavailability of metals if sediment should become resuspended. Multiple factors such as; presence of metal sulfides, metal oxides, calcium carbonate, oxygen, pH, salinity, sediment grain size, and redox potential, should be determined to properly assess the potential toxicity of bedded sediment, and release of metals during resuspension. Presently there are very few federal regulations on suspended sediments. As of 2001, set criteria for the amount of total suspended sediments were allowed in only 32 of 53 states and territories. Although sediment resuspensions are not a constant threat, as metal in bedded sediments may be, they are still very important when considering potential exposure to sediment contaminants. It is difficult to understand the extent of risk associated with resuspended sediment, without taking into account variables considered in this review.

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Appendix:

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- **Table A5:** Physicochemical (ph, DO, conductivity) monitoring of control chamber and Duck Lake sediment during 4-hour resuspension
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- **Table A20:** Conversion of dissolved metal concentration found in the water column during resuspension of Duck Lake sediment to the percent of total metal found dissolved in the water column. Concentration (ug/L) is converted to a weight (mg/L) then divided by the total amount (mg) of metal in the chamber, determined by the amount of sediment added for that run.
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- **Table A22:** Conversion of dissolved metal concentration found in the water column during resuspension of DePue sediment to the percent of total metal found dissolved in the water column. Concentration (ug/L) is converted to a weight (mg/L) then divided by the total amount (mg) of metal in the chamber, determined by the amount of sediment added for that run.
- **Table A23:** *D. magna* reproduction (number of neonates) produced over 10 day chronic exposure experiment for each of the 8 replicates.
- **Table A24:** Statistic testing of difference of metal concentrations between press and pulse resuspension.

Table A1. pH readings of water column over control beaker, Duck Lake, and San Diego 10 day bedded exposure test.

Table A2. pH readings of water column over Idaho and DePue 10 day bedded exposure test.

control:						
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	7.19	8.66	7.78	7.71	7.3	7.86
2	7.22	8.13	7.74	7.76	8.02	8.19
3	7.27	8.74	7.79	7.8	8.02	8.26
Duck Lal	lzot					
		D 2	D 5	D 7	D 0	D 10
Beaker	Day 1	Day 3	Day 5	Day 7	•	Day 10
1	7.31	7.37	7.82	7.68	7.62	7.71
2	7.38	7.41	7.85	7.74	7.66	7.46
3	7.38	7.43	7.8	7.77	7.48	7.73
4	7.4	7.44	7.8	7.86	7.81	7.57
5	7.41	7.62	7.84	7.9	8.13	7.98
6	7.41	7.44	7.81	7.86	7.7	7.65
7	7.42	7.43	7.81	7.81	7.73	7.79
8	7.4	7.42	7.81	7.86	8.16	7.63
Son Diog						
San Dieg		D 2	D 5	D 7	D 0	D 10
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	7	6.82	7.01	7.25	7.31	7.61
2	7.12	7.09	7.25	7.49	7.64	7.83
3	6.99	7.33	7.12	7.51	7.7	7.89
4	7.02	7.08	7.33	7.48	7.55	7.94
5	7.2	7.27	7.49	7.74	7.7	8.04
6	7.27	7.28	7.68	7.76	7.79	8.19
7	7.17	7.47	7.72	7.82	7.77	8.14
8	7.29	7.57	7.66	7.73	7.86	8.01

Idaho:						
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	6.52	7.07	7.31	7.23	7.24	7.25
2	6.59	7.07	7.27	7.29	7.29	7.24
3	6.55	7.1	7.31	7.29	7.32	7.23
4	6.55	7.05	7.3	7.24	7.28	7.21
5	6.58	7.12	7.35	7.24	7.31	7.2
6	6.59	7.1	7.33	7.34	7.32	7.2
7	6.61	7.08	7.42	7.21	7.32	7.21
8	6.61	7	7.44	7.13	7.33	7.18
DePue:						
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	7.37	7.37	7.55	7.24	7.62	8.09
2	7.37	7.41	7.68	7.65	8.34	8.59
3	7.41	7.43	7.63	7.68	8.46	8.67
4	7.39	7.44	7.67	7.84	8.6	8.68
5	7.43	7.62	8.26	8.75	8.92	8.93
6	7.43	7.44	7.79	7.99	8.76	8.77
7	7.47	7.43	7.75	7.87	8.67	8.73
8	7.45	7.42	7.7	7.86	8.64	8.67
	* notice sedimen		rowing or	surface	of	

Table A3: Dissolved Oxygen measurements (mg/L) of water column over control beaker, Duck Lake, and San Diego bedded sediment exposure.

Table A4: Dissolved Oxygen measurements (mg/L) of water column over Idaho and DePue 10 day bedded sediment exposure.

control:						
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	6.21	7.38	7.74	8.28	8.94	9.52
2	6.18	7.46	7.93	8.33	10.84	10.06
3	6.27	7.6	8.12	8.33	9.66	10.05
Duck La	ke:					
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	5.74	6.81	6.99	6.94	7.37	8.21
2	5.56	7.18	7.12	7.32	7.6	6.53
3	5.78	7.08	7.38	7.32	7.1	7.49
4	5.81	7.1	7.37	7.78	8.53	6.82
5	5.31	7.14	7.25	7.94	7.68	7.95
6	5.76	6.71	7.17	7.65	7.01	6.84
7	5.82	6.55	7.16	7.4	7.89	6.67
8	5.98	7.02	7.16	7.64	9.52	6.63
San Dieg	go:					
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	6.63	8.34	6.65	5.17	8.3	8.51
2	7.63	5.25	5.92	7.66	8.93	9.1
3	6.7	5.09	6.89	8.09	9	9.21
4	5.47	5.9	6.24	8.11	9	10.06
5	5.42	6.01	6.77	7.56	8.95	9.34
6	5.28	6.63	6.54	7.88	8.93	9.21
7	5.78	5.17	6.93	8.13	8.6	9.17
8	5.38	4.53	6.45	7.93	9.16	9.27

Idaho:						
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	5.93	6.05	4.42	4.86	4.04	4.48
2	5.94	5.29	4.21	4.34	4.07	4.59
3	6.17	6.42	4.2	4.4	4.62	4.85
4	5.88	5.6	4.24	4.07	3.56	4.2
5	5.95	5.59	4.31	4.01	3.91	4.29
6	6.23	5.87	4.19	4.02	4.33	4.48
7	6.01	6.93	4.17	4.13	4.76	4.39
8	5.86	6.34	4.41	4.07	5.16	4.98
DePue:						
Beaker	Day 1	Day 3	Day 5	Day 7	Day 9	Day 10
1	5.98	6.4	6.26	6.46	8.44	8.93
2	5.97	6.82	6.47	8.55	11.98	11.4
3	5.99	6.73	6.74	8.56	12.05	11.71
4	6.01	6.77	7.03	9.44	13.2	12.2
5	6.08	8.42	11.07	13.46	14.79	12.92
6	5.91	6.61	7.36	9.33	13.41	12.91
7	5.95	6.69	6.82	8.8	12.68	12.59
8	5.91	6.62	6.67	8.3	12.36	12.51
* notice algae growing on surface of sediment						

Table A5: Physicochemical (pH, DO, conductivity) monitoring of control chamber and Duck Lake 4-hour resuspension

Duck Lake Control Beaker: Initial 1hr 2hr 3hr 4hr pН 7.28 7.26 7.29 7.28 7.28 D.O. 6.84 6.89 6.92 6.95 7.04 Cond. 792 793 790 792 794 Duck Lake (1) Initial 1hr 2hr 3hr 4hr pН 7.37 7.22 7.27 7.25 7.28 D.O. 7.04 6.4 6.73 6.94 7.21 Cond. 831 828 828 827 828 Duck Lake (2) Initial 1hr 2hr 3hr 4hr pН 7.4 7.37 7.29 7.26 7.28 D.O. 6.99 6.55 6.83 7.16 7.22 Cond. 830 827 829 828 826 Duck Lake (3) Initial 1hr 2hr 3hr 4hr 7.44 7.25 7.24 7.28 7.29 pН D.O. 6.94 6.59 6.78 6.83 7.1 Cond. 829 828 828 830 828

Table A6: Physicochemical (pH, DO, conductivity) monitorin of control chamber and San Diego 4-hour resuspension.

San Diego					
Control					
Beaker:	Initial	1hr	2hr	3hr	4hr
pН	7.38	7.43	7.44	7.46	7.42
D.O.	7.12	7.14	7.15	7.15	7.18
Cond.	780	782	782	785	783
San Diego (1)	Initial	1hr	2hr	3hr	4hr
рН	7.64	7.43	7.44	7.44	7.49
D.O.	7.47	7.72	7.81	7.82	7.87
Cond.	1018	1099	1092	1080	1067
San Diego (2)	Initial	1hr	2hr	3hr	4hr
pH	7.64	7.51	7.52	7.47	7.5
D.O.	7.47	7.74	7.88	7.91	7.9
Cond.	1029	1098	1091	1077	1067
Cond.	1029	1070	1071	10//	1007
SanDiego (3)	Initial	1hr	2hr	3hr	4hr
pН	7.67	7.55	7.49	7.53	7.55
D.O.	7.48	7.86	7.89	7.83	7.85
Cond.	1061	1095	1096	1075	1065

Table A7: Physicochemical (pH, DO, conductivity) monitoring of control chamber and Idaho sediment 4-hour resuspension.

					1
Idaho					
Control					
Beaker:	Initial	1hr	2hr	3hr	4hr
pН	7.23	7.27	7.28	7.3	7.28
D.O.	6.84	6.89	6.92	6.96	6.99
Cond.	778	781	780	782	783
Idaho (1)	Initial	1hr	2hr	3hr	4hr
pН	6.88	6.76	6.76	6.78	6.81
D.O.	6.74	6.02	6.32	6.9	7
Cond.	786	805	818	807	798
Idaho (2)	Initial	1hr	2hr	3hr	4hr
рН	6.91	6.76	6.76	6.82	6.89
D.O.	6.19	6.09	6.47	6.97	7.12
Cond.	792	807	816	806	800
Idaho(3)	Initial	1hr	2hr	3hr	4hr
pH	6.91	6.74	6.76	6.78	6.83
D.O.	6.18	6.04	6.41	6.92	7.02
Cond.	799	812	814	809	792

Table A8: Physicochemical (pH, DO, conductivity) monitoring of control chamber and DePue sediment for 4-hour resuspension, 2 trials.

DePue Trial 1					
Control					
Beaker:	Initial	1hr	2hr	3hr	4hr
pН	7.73	7.67	7.68	7.68	7.67
D.O.	7.21	7.12	7.15	7.21	7.21
Cond.					
DePue (1)	Initial	1hr	2hr	3hr	4hr
рН	7.72	7.53	7.56	7.54	7.54
D.O.	7.03	6.56	6.58	6.68	6.79
Cond.					
DePue (2)	Initial	1hr	2hr	3hr	4hr
pН	7.73	7.48	7.54	7.55	7.56
D.O.	7.10	6.68	6.45	6.63	6.80
Cond.					
DePue (3)	Initial	1hr	2hr	3hr	4hr
pН	7.73	7.56	7.60	7.60	7.64
D.O.	7.02	6.59	6.57	6.70	6.83
Cond.					

DePue Trial 2					
Control					
Beaker:	Initial	1hr	2hr	3hr	4hr
pН	7.80	7.70	7.71	7.75	7.78
D.O.	8.69	8.53	8.50	8.33	8.31
Cond.	794	784	792	780	803
DePue (1)	Initial	1hr	2hr	3hr	4hr
pН	7.64	7.61	7.58	7.59	7.56
D.O.	7.96	7.69	7.66	7.77	7.88
Cond.	819	814	805	803	
DePue (2)	Initial	1hr	2hr	3hr	4hr
pH	7.65	7.58	7.64	7.63	7.63
D.O.	7.85	7.55	7.56	7.03 7.71	7.03
Cond.	7.03	1.55	804	7.71 797	809
Cond.			00-	171	007
DePue (3)	Initial	1hr	2hr	3hr	4hr
pН	7.68	7.54	7.56	7.53	7.57
D.O.	7.99	7.75	7.77	7.73	7.76
Cond.	807		808	801	795

Table A9: Physicochemical (pH, DO, conductivity) monitoring of control chamber and Duck Lake sediment during 16-hour multiple resuspension

Duck Lake									
Control		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Beaker:	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.23	7.19	7.2	7.24	7.22	7.29	7.28	7.25	7.24
D.O.	6.09	6.15	6.2	6.19	6.22	6.28	6.3	6.42	6.45
Cond.	751	755	757	762	759	754	750	752	754
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Duck Lake (1)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.52	7.34	7.37	7.44	7.38	7.47	7.36	7.43	7.45
D.O.	5.97	6.3	6.24	6.91	6.91	7.14	6.9	7.3	6.88
Cond.	829	819	821	819	817	818	818	819	812
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Duck Lake (2)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.56	7.31	7.36	7.48	7.45	7.49	7.37	7.62	7.61
D.O.	5.98	6.13	6.04	6.48	6.5	7.02	6.8	7.32	6.9
Cond.	833	818	817	823	831	829	828	831	813
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Duck Lake (3)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.49	7.37	7.41	7.49	7.5	7.54	7.43	7.63	7.6
D.O.	5.98	6.13	6.04	6.48	6.5	7.02	6.8	7.32	6.9
Cond.	833	818	817	823	831	829	828	831	813

Table A10: Physicochemical (pH, DO, conductivity) monitoring of control chamber and Idaho sediment during 16-hour multiple resuspension

Idaho									
Control		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Beaker:	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.23	7.19	7.2	7.24	7.22	7.29	7.28	7.25	7.24
D.O.	6.09	6.15	6.2	6.19	6.22	6.28	6.3	6.42	6.45
Cond.	758	756	756	753	759	752	750	752	754
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Idaho (1)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.04	6.87	7.27	7.18	7.15	7.27	7.2	7.38	7.29
D.O.	6.12	5.4	5.7	7.08	6.9	7.8	7.51	6.52	7
Cond.	817	827	837	836	828	852	854	848	848
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Idaho (2)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.07	6.77	7.17	7.19	7.14	7.29	7.24	7.59	7.6
D.O.	6.17	5.57	6.13	7.07	6.81	7.08	7.14	8.01	7.69
Cond.	814	831	834	852	831	858	856	844	844
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Idaho (3)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.11	6.71	7.17	7.21	7.2	7.28	7.22	7.62	7.6
D.O.	6.29	6.02	6.39	7.26	7.33	7.12	6.97	7.74	7.32
Cond.	819	834	832	854	834	856	858	842	844

Table A11: Physicochemical (pH, DO, conductivity) monitoring of control chamber and DePue sediment during 16-hour multiple resuspensi

D _o D _{reo}									
DePue		1 .	1 .	2 1	2 1	2 1	2 1	4.1	4.1
Control		1st	1st	2nd	2nd	3rd	3rd	4th	4th
Beaker:	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.23	7.19	7.2	7.24	7.22	7.29	7.28	7.25	7.24
D.O.	6.09	6.15	6.2	6.19	6.22	6.28	6.3	6.42	6.45
Cond.	751	755	757	762	759	754	750	752	754
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
DePue (1)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.32	7.34	7.37	7.44	7.38	7.47	7.36	7.43	7.45
D.O.	6.01	6.58	6.39	6.88	6.68	6.8	6.89	6.94	6.65
Cond.	821	846	860	862	864	866	865	869	861
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
DePue (2)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.36	7.31	7.36	7.48	7.45	7.49	7.37	7.62	7.61
D.O.	5.9	5.82	5.82	6.31	7.18	7.24	7.01	7.99	7.81
Cond.	823	847	833	850	866	865	866	864	860
		1st	1st	2nd	2nd	3rd	3rd	4th	4th
DePue (3)	Initial	susp	settle	susp	settle	susp	settle	susp	settle
pН	7.39	7.37	7.41	7.49	7.5	7.54	7.43	7.63	7.6
D.O.	6.02	5.81	6.01	6.89	6.8	7.3	7.09	7.24	7.98
Cond.	820	851	859	861	866	866	866	866	860

Dissolved Metal Concentrations (ug/L):

Table A12: Average dissolved metal concentration (ug/L), and standard deviation, of water column over bedded Duck Lake sediment during 10 day bedded exposure test

Avg	Day 1	Day 3	Day 5	Day 7	Day 9
Cu	2.69	2.47	1.88	2.28	2.38
Zn	65.42	16.71	8.27	0.19	0.15
Co	6.26	11.13	11.50	10.16	12.46
Fe	67.62	23.54	12.48	11.81	7.42
Mn	17.90	6.71	3.61	3.40	3.09
As	0.34	1.46	0.85	0.96	1.95

St. dev	Day 1	Day 3	Day 5	Day 7	Day 9
Cu	1.81	0.64	2.70	0.80	2.59
Zn	63.79	22.99	2.21	0.30	0.36
Co	7.97	4.92	2.14	3.93	2.81
Fe	63.84	8.77	2.14	3.99	2.55
Mn	16.42	1.28	1.42	0.80	0.59
As	1.05	0.77	1.55	2.12	0.46

Table A13: Average dissolved metal concentration (ug/L), and standard deviation, of water column over bedded San Diego sediment during 10 day bedded sediment exposure test

		•			
Avg	Day 1	Day 3	Day 5	Day 7	Day 9
Cu	1.98	2.49	7.43	5.89	4.54
Zn	107.30	17.00	7.45	10.32	17.22
Co	18.23	16.32	20.17	18.67	17.13
Fe	14.03	10.94	29.41	17.56	14.73
Mn	21.53	12.31	15.65	14.38	9.53
As	0.61	1.05	0.31	0.85	2.10

St. dev	Day 1	Day 3	Day 5	Day 7	Day 9
Cu	2.14	2.75	6.50	3.45	2.07
Zn	81.46	31.03	13.17	12.43	12.30
Co	2.44	11.81	5.29	4.67	1.58
Fe	5.73	2.94	12.29	9.83	11.56
Mn	3.25	2.60	8.77	6.21	2.79
As	0.63	0.89	0.29	0.48	0.88

Table A14: Average dissolved metal concentration (ug/L), and standard deviation, of water column over bedded Idaho sediment during 10 day bedded sediment exposure test

Avg	Day 1	Day 3	Day 5	Day 7	Day 9
Cu	13.95	2.27	2.10	0.26	0.41
Zn	59.76	26.67	24.49	8.61	9.47
Co	129.20	134.87	98.99	78.29	75.97
Fe	901.37	3627.78	3954.11	1168.61	2293.33
Mn	2722.33	2957.67	2089.44	2327.33	2020.67
As	14.08	33.19	35.05	14.97	14.72

St. dev	Day 1	Day 3	Day 5	Day 7	Day 9
Cu	4.61	0.71	4.19	0.28	2.15
Zn	32.22	18.98	7.35	3.17	3.80
Co	8.12	10.68	2.35	7.48	7.16
Fe	8.82	1078.11	694.94	744.84	585.46
Mn	129.11	282.57	16.10	128.63	239.37
As	0.83	2.12	0.78	6.04	0.55

Table A15: Average dissolved metal concentration (ug/L), and standard deviation, of water column over bedded DePue sediment during 10 day bedded exposure test

Avg	Day 1	Day 3	Day 5	Day 7	Day 9
Cu	8.28	12.13	20.19	20.90	17.67
Zn	115.74	598.75	918.43	719.67	232.15
Co	11.32	9.11	11.26	11.50	14.64
Fe	20.12	46.37	37.54	30.95	3.05
Mn	414.97	406.00	440.07	334.93	189.16
As	1.50	3.29	8.13	9.01	7.36

St. dev	Day 1	Day 3	Day 5	Day 7	Day 9
Cu	1.06	2.62	4.68	2.67	3.50
Zn	22.47	113.60	85.25	206.78	257.98
Co	0.65	3.42	3.41	3.14	1.80
Fe	2.06	9.33	9.41	12.12	2.27
Mn	14.22	37.06	21.08	67.54	92.56
As	0.32	1.86	1.67	1.55	3.30

4 hour Continuous Resuspension:

Table A16: Average dissolved metal concentration (ug/L), and standard deviation, of water column of resuspened Duck Lake sediment during 4 continuous hours of resuspension

Avg	1hr	2hr	3hr	4hr
Cu	12.33	11.00	14.67	12.33
Zn	5.33	0.33	0.67	0.00
Co	8.00	12.67	11.00	11.00
As	0.00	0.00	0.00	0.00
Fe	17.78	14.67	8.22	7.00
Mn	29.33	23.67	17.78	5.56

St.dev	1hr	2hr	3hr	4hr
Cu	1.53	4.36	1.53	7.09
Zn	4.16	1.53	3.21	3.00
Co	1.00	1.15	4.58	2.65
As	8.72	16.46	6.24	7.21
Fe	2.96	7.17	4.29	4.15
Mn	4.93	0.75	0.52	1.01

Table A17: Average dissolved metal concentration (ug/L), and standard deviation, of water column of resuspened San Diego sediment during 4 continuous hours of resuspension

AVG	1hr	2hr	3hr	4hr
Cu	11.33	14.33	16.67	20.00
Zn	1.33	0.00	2.67	4.33
Co	12.33	10.00	10.33	7.00
As	0.00	0.00	4.67	0.67
Fe	13.44	10.56	15.44	8.44
Mn	2.56	1.11	0.89	1.00

St.dev	1hr	2hr	3hr	4hr
Cu	6.11	4.16	4.16	4.36
Zn	2.31	2.65	3.06	3.79
Co	3.79	3.61	3.51	1.73
As	0.00	0.00	7.57	6.35
Fe	0.88	6.82	4.92	3.94
Mn	0.88	0.60	0.60	0.50

Table A18: Average dissolved metal concentration (ug/L), and standard deviation, of water column of resuspened Idaho sediment during 4 continuous hours of resuspension

	1hr	2hr	3hr	4hr
Cu	17.33	12.00	14.67	17.67
Zn	9.67	5.00	4.33	5.67
Co	30.00	32.33	32.33	29.00
As	142.33	135.33	129.67	132.33
Fe	88.44	87.89	88.00	82.11
Mn	629.56	607.33	575.11	571.44

St.dev	1hr	2hr	3hr	4hr
Cu	5.51	7.21	8.62	5.51
Zn	3.60	2.65	3.79	3.79
Co	2.65	0.58	6.51	1.73
As	14.29	15.57	10.69	15.31
Fe	1.53	0.58	1.53	0.00
Mn	14.72	9.71	1.76	15.95

Table A19: Average dissolved metal concentration (ug/L), and standard deviation, of water column of resuspened DePue sediment during 4 continuous hours of resuspension

AVG	1hr	2hr	3hr	4hr
Cu	1.6	2.9	2.4	1.7
Zn	92	99.4	117.2	147.3
Co	Below I	Detection		
As	Below I	Detection		
Fe	18.6	35.6	35.3	17
Mn	117	113.6	120.6	123.5

St.Dev	1hr	2hr	3hr	4hr
Cu	2.33	1.54	2.5	2.01
Zn	32.44	43.29	50.81	38.98
Co	Below D	Detection		
As	Below D	Detection		
Fe	10.26	15.57	16.76	4.74
Mn	19.41	15.46	19.84	16.59

Multiple Resuspension Concentration and % total metal Released:

Table A20: Conversion of dissolved metal concentration found in the water column during resuspension of Duck Lake sediment to the percent of total metal found dissolved in the water column. Concentration (ug/L) is converted to a weight (mg/L) then divided by the total amount (mg) of metal in the chamber, determined by the amount of sediment added for that run.

Metal	1st sus. ug/L	1st. sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 1st sus
As	1.615	0.002	0.001	0.026	3.589
Cu	0.096	0.000	0.000	0.478	0.012
Zn	7.631	0.008	0.004	1.133	0.391
Co	9.264	0.009	0.005	0.709	0.758
Fe	9.827	0.010	0.006	146.941	0.004
Mn	37.977	0.038	0.022	6.536	0.337
Metal	2nd sus ug/L	2nd sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 2nd sus
As	0.965	0.001	0.001	0.017	3.290
Cu	0.740	0.001	0.000	0.311	0.138
Zn	17.215	0.017	0.010	0.738	1.352
Co	7.315	0.007	0.004	0.462	0.918
Fe	7.863	0.008	0.005	95.808	0.005
Mn	5.724	0.006	0.003	4.262	0.078
Metal	3rd sus ug/L	3rd sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 3rd sus
As	1.037	0.001	0.001	0.012	5.029
Cu	0.916	0.001	0.001	0.219	0.243
Zn	22.070	0.022	0.013	0.519	2.468
Co	9.386	0.009	0.005	0.325	1.676
Fe	9.692	0.010	0.006	67.301	0.008
Mn	3.338	0.003	0.002	2.994	0.065
Metal	4th sus ug/L	4th sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 4th sus
As	0.372	0.000	0.000	0.007	3.201
Cu	2.289	0.002	0.001	0.123	1.077
Zn	10.439	0.010	0.006	0.292	2.072
Co	8.203	0.008	0.005	0.183	2.600
Fe	27.470	0.027	0.016	37.912	0.042
Mn	3.533	0.004	0.002	1.686	0.122

Table A21: Conversion of dissolved metal concentration found in the water column during resuspension of Idaho sediment to the percent of total metal found dissolved in the water column. Concentration (ug/L) is converted to a weight (mg/L) then divided by the total amount (mg) of metal in the chamber, determined by the amount of sediment added for that run.

Metal	1st susp. ug/L	1st. Sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 1st sus
As	4.621	0.005	0.003	1.449	0.185
Cu	4.248	0.004	0.002	2.128	0.116
Zn	7.749	0.008	0.004	0.369	1.217
Co	35.753	0.036	0.021	1.691	1.226
Fe	51.532	0.052	0.030	271.024	0.011
Mn	705.944	0.706	0.409	2.878	14.225
Metal	2nd susp ug/L	2nd sus mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 2nd sus
As	3.118	0.003	0.002	0.069	2.604
Cu	8.569	0.009	0.005	1.973	0.252
Zn	31.705	0.032	0.018	0.342	5.374
Co	22.487	0.022	0.013	1.568	0.832
Fe	50.174	0.050	0.029	251.240	0.012
Mn	311.822	0.312	0.181	2.668	6.778
Metal	3rd susp ug/L	3rd sus mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 3rd sus
As	3.069	0.003	0.002	0.059	2.999
Cu	11.038	0.011	0.006	1.685	0.380
Zn	31.870	0.032	0.018	0.292	6.323
Co	17.333	0.017	0.010	1.340	0.750
Fe	39.924	0.040	0.023	214.651	0.011
Mn	143.367	0.143	0.083	2.280	3.648
Metal	4th susp ug/L	4th sus mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 4 th sus
As	1.917	0.002	0.001	0.039	2.887
Cu	5.016	0.005	0.003	1.094	0.266
Zn	20.398	0.020	0.012	0.190	6.235
Co	12.745	0.013	0.007	0.869	0.850
Fe	34.321	0.034	0.020	139.307	0.014
Mn	55.016	0.055	0.032	1.479	2.157

Table A22: Conversion of dissolved metal concentration found in the water column during resuspension of DePue sediment to the percent of total metal found dissolved in the water column. Concentration (ug/L) is converted to a weight (mg/L) then divided by the total amount (mg) of metal in the chamber, determined by the amount of sediment added for that run.

Metal	1st susp. ug/L	1st. Sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 1st sus
As	1.944	0.002	0.001	0.155	0.726
Cu	4.023	0.004	0.002	2.310	0.101
Zn	399.683	0.400	0.232	44.091	0.526
Co	15.027	0.015	0.009	0.055	15.916
Fe	11.950	0.012	0.007	61.183	0.011
Mn	185.400	0.185	0.108	2.572	4.180
Metal	1st susp. ug/L	1st. Sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 1st sus
As	1.601	0.002	0.001	0.145	0.642
Cu	5.509	0.006	0.003	2.151	0.149
Zn	252.317	0.252	0.146	41.048	0.357
Co	12.763	0.013	0.007	0.051	14.520
Fe	65.199	0.065	0.038	56.962	0.066
Mn	110.611	0.111	0.064	2.395	2.679
Metal	1st susp. ug/L	1st. Sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 1st sus
As	0.832	0.001	0.000	0.133	0.362
Cu	3.633	0.004	0.002	1.982	0.106
Zn	217.800	0.218	0.126	37.830	0.334
Co	13.153	0.013	0.008	0.047	16.237
Fe	43.650	0.044	0.025	52.495	0.048
Mn	53.463	0.053	0.031	2.207	1.405
Metal	1st susp. ug/L	1st. Sus. mg/L	mg in chamber dissolved	mg in chamber total	% metal dissolved in water column 1st sus
As	2.207	0.002	0.001	0.115	1.110
Cu	5.121	0.005	0.003	1.714	0.173
Zn	193.533	0.194	0.112	32.715	0.343
Co	12.570	0.013	0.007	0.041	17.943
Fe	52.687	0.053	0.031	45.398	0.067
Mn	33.343	0.033	0.019	1.909	1.013

Table A23: *D. magna* reproduction (number of neonates) produced over 10 day chronic exposure experiment for each of the 8 replicates.

Beaker	Duck Lake	San Diego	Idaho	DePue	Chamber control	Beaker control
1 Deaker		_				
1	19	21	30	24	27	11
2	22	27		16		12
3	19	24	28			12
4	21	22			21	
5	16	24	21	24	29	
6	15		26	25	34	
7	24		25	18		
8	23	23	13	17	30	
Average	19.88	23.50	23.83	24.45	28.20	11.67
St. Dev	3.23	2.07	6.11	5.49	4.76	0.58

Table A24: Statistical tests

t-test Normality Test: Failed (P < 0.050)Mann-Whitney Rank Sum Test

Tuesday, January 10, 2012, 4:56:34 PMData source: Data 1 in

Notebook1Group N Missing Median 25% 75%

Duck Lake: Cu 9 1 6.502 1.099 12.330 Duck Lake: Cu 9 1 6.502 1.099 12.330 Mann-Whitney U Statistic= 32.000

T = 68.000 n(small) = 8 n(big) = 8 P(est.) = 0.958 P(exact) = 1.000The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant

difference (P = 1.000)

t-test

Normality Test: Passed (P = 0.060)

Equal Variance Test:

Group Name N Missing Mean Std Dev SEM

Idaho: Cu 9 1 12.299 4.599 1.626 Idaho: Cu 9 1 12.299 4.599 1.626

Difference 0.000

t = 0.000 with 14 degrees of freedom. (P = 1.000)

95 percent confidence interval for difference of means: -4.931 to 4.931 The difference in the mean values of the two groups is not great enough to reject the possibility that the difference is due to random sampling variability. There is not a statistically significant difference between the input groups (P = 1.000).

t-test

Test execution ended by user request, Rank Sum Test begun

Mann-Whitney Rank Sum Test

Data source

Group N Missing Median 25% 75% DePue: Cu 9 1 2.451 0.950 4.433 DePue: Cu 9 1 2.451 0.950 4.433 Mann-Whitney U Statistic= 32.000

T = 68.000 n(small) = 8 n(big) = 8 P(est.) = 0.958 P(exact) = 1.000The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 1.000)

PULSE RESUSPENSIONS:

Kruskal-Wallis One Way Analysis of Variance on Ranks Tuesday, January 10, 2012, 5:09:15 PM

Data source:

Group N Missing Median 25% 75%

Idaho: Pulse Mn 2 0 710.070 705.940 714.200

Col 2 2 0 307.660 303.500 311.820

Col 3 2 0 144.230 143.360 145.100

Col 4 2 0 57.635 55.010 60.260

H = 6.667 with 3 degrees of freedom. P(est.) = 0.083 P(exact) = 0.010

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.010)

One Way Analysis of Variance

Normality Test:

Equal Variance Test:

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source:

Group N Missing Median 25% 75%

Idaho: Pulse Co 2 0 33.705 31.660 35.750

Idaho: Pulse Co 2 0 33.705 31.660 35.750

Col 2 2 0 21.755 21.030 22.480

Col 3 2 0 19.120 17.330 20.910

Col 4 2 0 13.360 12.740 13.980

H = 8.393 with 4 degrees of freedom. (P = 0.078)

The differences in the median values among the treatment groups are not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically

significant difference (P = 0.078)

Data 1 in Notebook1Tuesday, January 10, 2012, 5:13:07 PM Failed (P <

0.050) Passed (P = 0.132)Data 1 in Notebook1Data 1 in

Notebook1Tuesday, January 10, 2012, 4:58:26 PM Failed (P < 0.050)

One Way Analysis of Variance

Normality Test:

Equal Variance Test:

Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source:

Group N Missing Median 25% 75%

Idaho: Pulse Co 2 0 4.590 4.560 4.620

Col 2 2 0 3.117 3.110 3.125

Col 3 2 0 2.617 2.164 3.069

Col 4 2 0 2.000 1.910 2.090

H = 6.667 with 3 degrees of freedom. P(est.) = 0.083 P(exact) = 0.010

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.010)

Duck Lake:

Cu

Mann-Whitney Rank Sum Test

Data source:

Group N Missing Median 25% 75%

Duck lake Cu 17 9 12.330 7.810 23.166

Col 2 17 9 2.557 1.099 12.078

Mann-Whitney U Statistic= 12.000

T = 88.000 n(small) = 8 n(big) = 8 P(est.) = 0.040 P(exact) = 0.038

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.038)

Duck Lake:

Zn

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:24:36 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75% Col 1 24 12 8.165 2.615 13.500 Col 2 24 12 2.396 0.820 4.090

Mann-Whitney U Statistic= 51.000

T = 171.000 n(small) = 12 n(big) = 12 (P = 0.236)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.236)

Duck Lake

Fe

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:27:12 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 35 19 9.610 4.590 14.670 Col 2 35 19 3.117 1.229 5.458

Mann-Whitney U Statistic= 80.000

T = 312.000 n(small) = 16 n(big) = 16 (P = 0.073)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.073)

Duck Lake

Mn

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:28:35 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 41 21 11.665 4.975 17.780

Col 2 41 21 3.454 1.755 5.761

Mann-Whitney U Statistic= 118.000

T = 492.000 n(small) = 20 n(big) = 20 (P = 0.027)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.027)

IDAHO:

Cu

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:34:58 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 64 32 8.945 4.590 16.000

Col 2 64 32 3.696 1.756 5.761

Mann-Whitney U Statistic= 333.000

T = 1219.000 n(small) = 32 n(big) = 32 (P = 0.017)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.017)

IDAHO

Zn

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:34:05 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 64 32 8.945 4.590 16.000

Col 2 64 32 3.696 1.756 5.761

Mann-Whitney U Statistic= 333.000

T = 1219.000 n(small) = 32 n(big) = 32 (P = 0.017)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.017)

IDAHO:

Co

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:36:34 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 71 35 11.500 4.810 17.780

Col 2 71 35 3.833 2.117 9.589

Mann-Whitney U Statistic= 446.000

T = 1516.000 n(small) = 36 n(big) = 36 (P = 0.023)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.023)

IDAHO

As

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:38:07 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 78 38 12.330 5.165 29.165

Col 2 78 38 3.789 2.127 6.637

Mann-Whitney U Statistic= 471.500

T = 1948.500 n(small) = 40 n(big) = 40 (P = 0.002)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.002)

IDAHO:

Mn

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:39:59 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 85 41 14.670 5.330 31.996

Col 2 85 41 4.215 2.197 13.475

Mann-Whitney U Statistic= 631.500

T = 2294.500 n(small) = 44 n(big) = 44 (P = 0.005)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.005)

IDAHO

Fe

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:43:52 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 92 44 16.000 5.445 58.930

Col 2 92 44 4.812 2.508 19.540

Mann-Whitney U Statistic= 766.500

T = 2713.500 n(small) = 48 n(big) = 48 (P = 0.005)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.005)

DePue

Cu

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:45:40 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 101 49 14.670 4.810 34.040

Col 2 101 49 4.812 2.465 16.930

Mann-Whitney U Statistic= 999.500

T = 3082.500 n(small) = 52 n(big) = 52 (P = 0.022)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.022)

Zn

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:47:14 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 108 52 16.000 5.165 87.945

Col 2 108 52 5.229 2.744 21.030

Mann-Whitney U Statistic= 1214.500

T = 3517.500 n(small) = 56 n(big) = 56 (P = 0.040)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.040)

Fe

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:48:30 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 114 54 16.240 5.330 85.000

Col 2 114 54 5.706 2.787 21.755

Mann-Whitney U Statistic= 1414.500

T = 4015.500 n(small) = 60 n(big) = 60 (P = 0.043)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P=0.043)

Mn

Mann-Whitney Rank Sum Test Tuesday, January 10, 2012, 5:49:53 PM

Data source: Data 1 in Notebook1

Group N Missing Median 25% 75%

Col 1 121 57 17.725 5.445 109.055

Col 2 121 57 6.136 2.813 38.965

Mann-Whitney U Statistic= 1637.500

T = 4538.500 n(small) = 64 n(big) = 64 (P = 0.051)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P=0.051)