



Trade Science Inc.

# Environmental Science

*An Indian Journal*

*Current Research Paper*

ESAIJ, 6(6), 2011 [320-328]

## Total levels and equilibrium-based phyto- and bioaccessibility of heavy metals as tools to assess sediment quality in recreational waterways

Tsanangurayi Tongesayi\*, Ester Booth, Sade Stevens, Eric Winter

Department of Chemistry Medical Technology and Physics, Monmouth University, 400 Cedar Avenue, West Long Branch, NJ 07764, (USA)

ttongesa@monmouth.edu

Received: 8<sup>th</sup> July, 2011 ; Accepted: 8<sup>th</sup> August, 2011

### ABSTRACT

Deal Lake is one of the major recreation sites in the state of New Jersey, and its vitality is restored by periodic dredging. The quality of the Lake's sediments is extremely crucial for the health of its ecosystem and human health. Dredged sediments are often used for land reclamation and beach restoration, which potentially expose humans to chemical hazards. We assessed the quality of the Lake's sediments by determining heavy metal(loid) concentrations, and the phytoaccessibility and bioaccessibility of the metals. A certified reference material, Ref1944, was used to validate the analytical measurement. Total metal levels of As, Cd, Cr, Pb and Zn were significantly higher than the National Oceanic and Atmospheric Administration's Probable Effects Levels. Arsenic level was highest at the site closest to the Power and Light Plant, probably due to effluent from arsenic-containing wood preservatives, and was lowest at the site which had an overgrowth of weeds, probably due to uptake by weeds in place of phosphorus. Phytoaccessibility and bioaccessibility showed dependence on binding preferences and binding strengths. We proposed equilibrium-based availability models that depict the 24-hour phytoaccessibility and the 60-minute bioaccessibility as equilibrium concentrations. Uptake by cells shifts the equilibria towards dissolution, meaning that larger proportions of metals can become available than predicted.

© 2011 Trade Science Inc. - INDIA

### KEYWORDS

Dredging;  
Sediment quality;  
Phytoaccessibility;  
Bioaccessibility.

### INTRODUCTION

Deal Lake, the largest freshwater coastal lake in New Jersey, hosts recreational activities like sport fishing, boating, canoeing, kayaking, wildlife watching and surfing<sup>[1]</sup>. The long history of Deal Lake includes name,

role and pollution. Centuries ago, it used to be called Lake Uliquecks by the Lelane Indians, then it became the White's Pond, the Hogs Swamp Pond, the Boylston Great Pond and in the late 1800s, the Deal Lake. During the Revolutionary War, the British soldiers used to gather fish, clams, and oysters from the lake to feed

## Current Research Paper

people back in England. The Lake, then, had an inlet to the ocean which facilitated a self purifying mechanism, ensuring that fish and other seafood it nourishes were safe for human consumption. However, a land developer who named it Deal Lake in the late 1800s sealed off the lake's ocean inlet, effectively turning it into an effluent, storm water, trash, silt, and waste collecting pond<sup>[1]</sup>.

The increase in pollution prompted the seven towns surrounding the lake to launch the Deal Lake Commission in 1974<sup>[1]</sup>. The mission of the commission is to restore and preserve the lake and its watershed by undertaking activities that decontaminate and reduce water pollution. Decontamination and pollution reduction activities include dredging; seaweed eradication; picking of litter; community education on problems associated with water quality, siltation, lake restoration and the benefits of preserving the natural environment of the lake; and liaising with the NJ department of environmental protection (NJ DEP) for the efficient implementation of a Regional Storm Water Management Plan. Dredged material is generally sediment that has collected into waterways through erosion. Its management can be costly, especially if it is contaminated with chemicals. Relatively uncontaminated dredged material can be used for beach replenishment, land reclamation, and soil conditioning among other beneficial uses<sup>[2-4]</sup>. Regardless of the extent of contamination of the dredged sediments, their use on land and beaches present a source of environmental contamination<sup>[5,6]</sup>.

The use of dredged contaminated sediments in land reclamation and beach restorations, among other uses, potentially expose humans to toxic metals during normal daily activities<sup>[7-10]</sup>. The oral route remains one of the major routes of exposure of sediment/soil-bound metals to humans. The low pH in the stomach will result in the dissolution of sediment/soil-bound metals, rendering them bioavailable<sup>[11-14]</sup>. Bioaccessibility is routinely used to determine bioavailability of metals from the inadvertent ingestion of contaminated soils and sediments. It involves extraction of metals from the solid matrices using artificial gastrointestinal fluid. Simulated gastric fluids used in bioaccessibility studies can be a simple HCl solution (0.1M HCl) or complex mixtures that gastrointestinal fluids and nonacidic constituents that include enzymes, lipids, or mucins, whose pH is adjusted to gastric pH using HCl<sup>[10]</sup>. Some researchers

have used the US Pharmacopoeia formula which is commonly used to simulate drug dissolution in the stomach<sup>[11, 13]</sup>, used the simplified physiological-based extraction technique (SBET), a solution of glycine (0.4M) adjusted to pH 1.5 using HCl, to determine bioaccessibility of heavy metals in soils.

Plants are the primary producers in ecological food chains and represent one of the exposure routes of heavy metals to organisms up the food chain. Humans can access metals from contaminated sediments through consumption of contaminated agricultural products, if the dredged sediment-reclaimed land is used for agricultural activities<sup>[15-18]</sup>. Total metal concentration is not a measure of the phytoavailability of trace heavy metals because not all forms of the metal will be available for uptake. Metals can also be phytotoxic, depending on metal load and form, so use of contaminated sediments can potentially eradicate vegetation. Without vegetation, the land is exposed to erosion, increasing chances of siltation and contaminating nearby water systems. Solutions that are routinely used to extract phytoavailable metals pools include aqueous solutions of salts such as sodium chloride (NaCl), calcium chloride (CaCl<sub>2</sub>), calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>), ammonium chloride (NH<sub>4</sub>Cl), and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>)<sup>[13, 16]</sup>. Chelating ligands such as diethylenetriaminepentaacetic acid (PTPA) have also been used<sup>[16]</sup>. According to literature, these solutions seem to yield satisfactory results, but solutions containing the chloride (Cl<sup>-</sup>) may give an underestimate of the phytoavailable Cd due to the formation of stable Cd-Chlorocomplexes<sup>[13]</sup>.

To assess the potential health risk posed by Deal Lake sediments, we determined the total metal concentration, bioaccessibility and phytoavailability of selected heavy metals in the sediments. The bioaccessibility fraction, which is the maximal amount of contaminant in a particular environmental matrix that can be absorbed by an organism, was extracted using SBET. In this study, 1M NH<sub>4</sub>NO<sub>3</sub> was used to extract the phytoavailable fraction of each metal from accurately measured sediment samples.

## EXPERIMENTAL

### Study area

Deal Lake<sup>[1]</sup>, shown in Figure 1, is the largest freshwater coastal lake in the state of New Jersey located

## Current Research Paper

and is located in the middle of Monmouth County. It covers about 158 acres and has an average depth of 5 to 6 feet. It is made of a number of shallow ponds and channels clustered together. Its long, thin tentacles reach municipalities of the Allenhurst, Deal, and Interlaken boroughs; Loch Arbour Village; the City of Asbury Park, and Neptune and Ocean townships. The main activities on the lake include sport fishing, boating (unlimited horsepower), Canoeing, kayaking, wildlife watching (raccoons, osprey, herons, chipmunks, egrets, mallards, loons, painted turtles, and snapping turtles), surfing on the waves of the Atlantic.

### Samples collection and total organic carbon (TOC) analysis

Samples were collected from the Lake at 4 sites shown in Figure 1 into polyethylene bags using a 500-mL Fisherbrand PTFE Dipper (Fisher Scientific, Pittsburgh, PA, USA). At each site, three samples were collected from a depth of about 10-20 cm. The samples were not mixed, but were treated and analyzed separately. Levels of metals from the three samples collected from each site were computed to give the average concentration for the site. Sampling site directions and bear-

ings were measured using the boat compass. The depth and temperature at the sampling sites were measured using the boat's inbuilt devices, while the pH was measured using a portable pH meter (VWR Scientific Products, West Chester, PA). In the laboratory, the collected sediment samples were transferred to Fisherbrand PTFE evaporating dishes and dried in an oven at 95°C. The dried samples were ground into powder using an Agate mortar and pestle (Fisher Scientific, Pittsburgh, PA, USA) and stored in polyethylene bags under moisture-free conditions until analysis. Total Organic carbon was determined using the loss-on ignition method<sup>[19]</sup>.

### Equipment

A handheld X-Ray Fluorescence Spectrometer (XRF; Innov-X Systems) was used for total metal analysis while an Atomic Absorption Spectrometer (AAS; Varian AA240FS) was used for the analysis of samples following digestions. A rugged rotator was used to mix the samples during extractions. An Isotemp Immersion Circulator (Fisher Scientific) was used for digestions that required controlled temperatures above ambient conditions. Microwave assisted digestions were carried out in a SEM MARSXpress microwave digester.

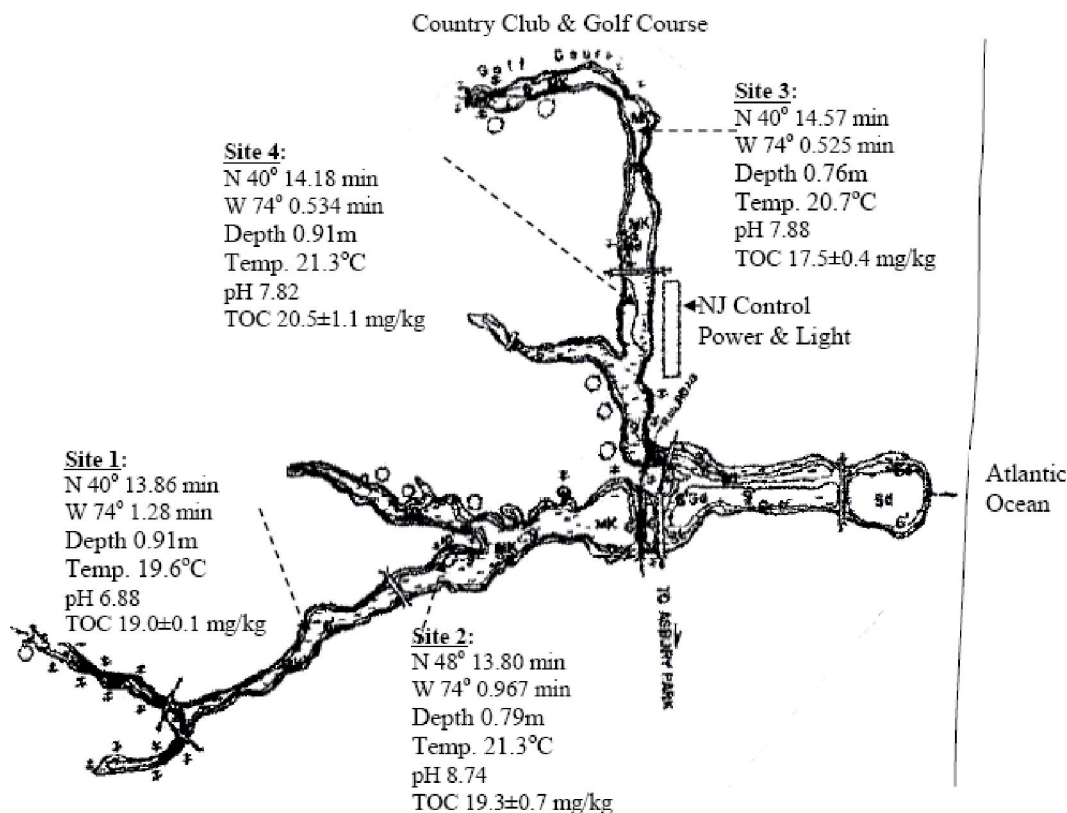


Figure 1 : Map of the Deal Lake showing the sampling sites and their characteristics.

All glassware and other reaction utensils were soaked in 10% nitric acid overnight, washed thoroughly with water and then rinsed with deionized water before use. All glassware was dried in an oven and, together with other reaction utensils, was kept under dust-free conditions. A model 2100 pH/Temp/mV meter (VWR Scientific Products, West Chester, PA) was used to measure the pH of the solutions. PTFE Whatman Autovial Syringeless Filters (0.45  $\mu\text{m}$ ) were used to filter the samples before analysis using flame atomic absorption spectroscopy (FAAS).

### Reagents

All standards used for the analysis of metals were plasma grade SPEX CertiPrep standards (Fisher Scientific, Pittsburgh, PA, USA). Nitric acid optima and hydrochloric acid optima (Fisher Scientific, Pittsburgh, PA, USA) were used for acid digestions. All other reagents were analytical reagent grade, and Millipore Milli-Q deionized water was used to prepare all solutions.

### XRF Analysis for total metal concentration

Most chemical digestions for total metal analysis use procedures that simulate EPA3051/3051A methods<sup>[20, 21]</sup>. These EPA methods are applicable to the microwave assisted acid digestion of sludge, sediments, soils, and oils for metals and other elements. They are not intended to extract total analyte from the sample but to provide a quick multielement acid digestion prior to analysis of metals and other elements to enable faster decision making regarding site cleanup levels. They provide pseudo-total metal concentrations. However, our preliminary experiments with reference standards and similar samples showed that the EPA methods, particularly the EPA3051 method which extracts using concentrated HCl, gave results that were statistically comparable to the XRF data. We then decided to use XRF for total metal analysis because it is faster and precision is better.

Finely ground and thoroughly mixed sediment samples and the reference samples (Ref 1944 and Ref 1646a) were transferred to small plastic bags and then analyzed using an Innov-X Systems handheld XRF instrument. The analysis was done in triplicate.

### Bioaccessibility

The method used to determine the bioaccessible pool was the simplified physiological-based extraction test (SBET), which simulates gastrointestinal conditions<sup>[13]</sup>. Sediment samples (0.1 g) were extracted as a function of time for one using a simulated gastric solution (10 mL, 0.4 M glycine adjusted to pH  $1.5 \pm 0.01$  using HCl optima) previously equilibrated at  $37 \pm 2^\circ\text{C}$  in an isotemp immersion circulator. The samples were filtered through 0.45  $\mu\text{m}$  PTFE Whatman Autovial Syringeless Filters and analyzed using FAAS. The extractions were done in triplicate each by three independent analysts, so each data value reported represents an average of nine individual results.

### Phytoavailability

The phytoavailable fraction was extracted using a method described by<sup>[13]</sup>. Sediment samples (1 g) were extracted with  $\text{NH}_4\text{NO}_3$  (10 mL, 1M) as a function of time, centrifuged and then filtered through 0.45  $\mu\text{m}$  PTFE Whatman Autovial Syringeless Filters. The extractions were done in triplicate. The filtered samples were analyzed using FAAS.

## RESULTS AND DISCUSSION

The TOC levels at the four sampling sites are shown in Figure 1. A Q-test analysis showed that the TOC level at site 3, which is slightly lower than levels at the other three sites, is not statistically different from TOC values at the other sites, at 90% confidence level ( $t_{\text{calc}} = 0.50$ ;  $t_{\text{table}} = 0.76$ ). Natural organic matter (NOM) in sediments and soils plays a crucial role in the speciation, mobility, bioaccessibility and phytoaccessibility of heavy metals and other chemical species. NOM can bind metals, and compete with metals and other chemical species for sorption sites in soils and sediments<sup>[22, 23]</sup>. The form of each metal that associate with NOM constitutes the oxidizable fraction, and can only be available when NOM is oxidized. Most metals associate with NOM on a one-to-one ratio, implying that about a fifth of each of the heavy metals in the Lake, particularly those that have high affinities for organic carbon like copper, could be in the oxidizable fraction. The first three speciation fractions, i.e., the exchangeable, the bound to carbonates and the Mn/Fe oxides-bound

## Current Research Paper

(reducible fraction), constitute the forms of metals that are readily available fractions (Hseu, 2006; Intawongse and Dean, 2008). This means that the oxidizable fraction will not be readily available, provided the soil/sediment conditions remain reducing. In well aerated soils, the oxidizable fraction will be more available compared to the reducible fraction. Dredging and the subsequent use of the sediments for beneficial uses such as beach restorations will make the sediment conditions oxidizing, which will make the oxidizable metal forms readily available. Regardless of the sediment/soil conditions, NOM will make those metals that form weak or no associations with NOM, and those metals that are out competed by NOM for sorption sites readily available.

TABLE 1 shows total metal concentrations of selected metals in the certified reference sample, Ref 1944, as determined by XRF. The reference sample was used to validate the analytical measurement, and as shown in the TABLE, there was at least 90% recovery for each metal in the reference, and the certified levels of the metals were within the 98 % confidence intervals (95 % confidence level for As) obtained from the XRF analysis of the reference sample. Recoveries were calculated using the following formula:

$\% \text{ Recovery} = (\text{Avg conc. of metal in ref. sample by XRF} / \text{Certified value}) \times 100$

TABLE 2 shows the XRF-determined total metal distribution of the selected metals(loids) in the Lake. As shown in the TABLE, the order of abundance of the selected metals(loids) was Fe>Ti>Zn>Co>Pb>Zr>Mn>As>Cr>Cu>Cd. Site 3, which is close to a golf course, was the shallowest of all the four sampling sites and had the lowest levels of Fe, Zn, Co and Pb. It, however, had the highest levels of Zr. Sites 1 and 4 were the deepest, with the major difference between the two sites being that Site 1 was overpopulated by weeds during the time of sampling while site 4 is close to New Jersey Power and Light plant. Site 1 had the highest levels of Ti, Zn, Pb, Mn, and Cd, while Site 4 had highest levels of Cu and As. Arsenic is used in the treatment of

wooden electric poles while Cu is used in electric wires, implying that the New Jersey Power and Light could be the source of the elevated levels of As and Cu found at site 4. The golf course may not be as contaminated as the other catchment areas around the Lake,

**TABLE 1 : Analysis of the certified reference sample (Ref 1944) using XRF. Units of concentration are mg/kg.**

Metal	XRF	98% Conf. Interval	Certified Value	Recovery
Ti	4140±180	3420 to 4860	*4300±300	96.3±7.9%
Cr	240±23	206 to 274	266±24	90.2±11.8%
Fe	31500±300	30300 to 32700	35000±1600	90.0±4.2%
Zn	676±12	627 to 725	656±75	103±12%
As	17±5	**5 to 29	18.9±2.8	89.9±29.6%
Pb	306±6	303 to 327	330±48	92.7±13.6%

Percentages represent recoveries. \*Reference values. \*\*95 % confidence interval

which may explain the lower levels of some of the metals at site 3. The shallowness at Site 3 could be a result of siltation from the golf course area, with the silt covering or burying the contaminated sediments. Site 1, which had an overgrowth of weeds, had the lowest levels of As compared to the other sites. Phosphate, which is a structural analogue of arsenate, is a micronutrient that is associated with algal blooms and excessive growth of other sea weeds in freshwater. Arsenate and phosphate compete for the same binding sites in sediments/soils and can be interchangeably taken up by plants. This implies that the low levels As at site 1, despite the site having higher levels of most other metals, could be due to uptake of As by the sea weeds in place of phosphorus. The levels of arsenic and copper in soils around the New Jersey Power and Light and other sites around the Lake, including the golf course, need to be determined to establish the anthropogenic sources of metals and metalloids studied. It is a known fact that plants can take up arsenate in place of phosphate but the levels of phosphate at all the sites, as well as the amounts of phosphorus and arsenic in the Lake weeds, need to be determined to establish if the competitive uptake of the two chemical analogs is the mechanism that explains the disparities in arsenic levels at the sites investigated.

The total metal levels are not a measure of the fraction of each metal that is available, but may be indicative of potential availability. As shown in TABLE 2, the National Oceanic and Atmospheric Administration's *Probable Effects Levels* for As, Cd, Cr, Pb and Zn for freshwater sediments are lower than the respective concentrations of the metals found in the sediments. Probable Effects Levels (PEL) represent upper thresh-

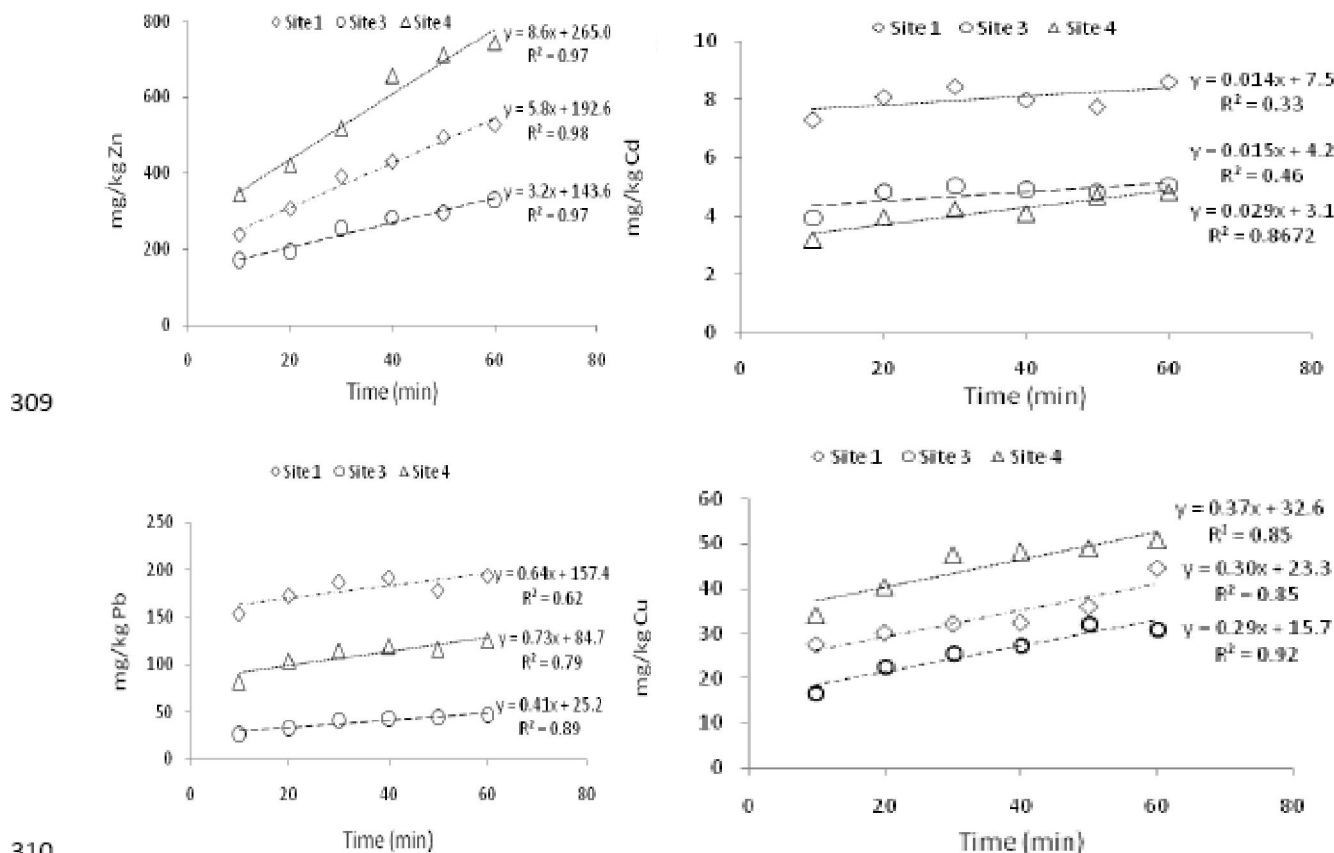
**TABLE 2 : Total metal levels in Deal Lake sediments by XRF.**

	Metal Concentration (mg/kg)				
	Site 1	Site 2	Site 3	Site 4	*PEL <sup>[24]</sup>
Fe	81700± 500 (0.6%)	86300± 600 (0.7%)	67800± 400 (0.6%)	81300± 500 (0.6%)	
Ti	4710± 80 (2%)	3590± 330 (9%)	4130± 80 (2%)	3840± 90 (2%)	
Zn	1080± 10 (0.9%)	763± 2 (0.3%)	563± 5 (0.9%)	741± 6 (0.8%)	315
Co	1040± 22 (2%)	1190± 70 (6%)	699± 15 (2%)	920± 19 (2%)	
Pb	486± 5 (1%)	414± 6 (1%)	249± 3 (1%)	420± 4 (1%)	91.3
Zr	241± 2 (0.8%)	241± 2 (0.8%)	337± 2 (0.6%)	183± 1 (0.5%)	
Mn	164± 5 (3%)	119± 34 (29%)	143± 4 (3%)	150± 4 (3%)	
As	101± 11 (1%)	120± 6 (5%)	126± 5 (4%)	195± 3 (2%)	17
Cr	90± 3 (3%)	88± 4 (5%)	101± 11(11%)	93± 0 (0%)	90
Cu	88± 2 (2%)	86± 5 (6%)	69± 1 (1%)	128± 2 (2%)	197
Cd	17± 1 (6%)	10± 2 (20%)	11 ± 5 (45%)	14± 0 (0%)	3.5

\*PEL: Probable Effects Level. NOAA Screening Quick Reference Tables for Inorganics in Sediments (values are for freshwater sediments). Percentages in paranthesis represent relative uncertainties (% relative standard deviations). Relative uncertainty = [standard deviation/mean]x100.

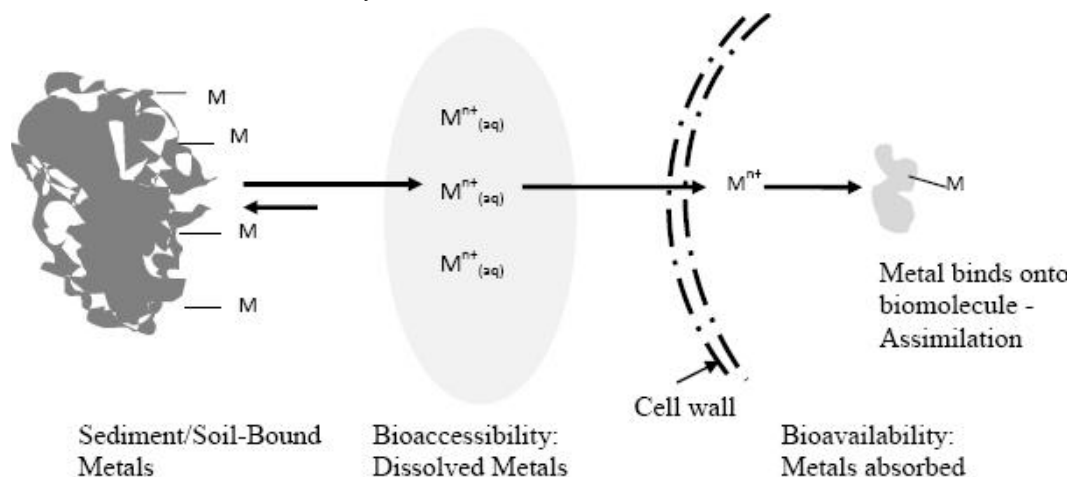
old and identify chemical substances that are more probably elevated to toxic levels. They are based on dose-response studies and can be used to predict toxicity of a chemical substance. It can, therefore, be concluded that the Deal Lake sediments are toxic with respect to

As, Cd, Cr, Pb and Zn the metals with given PEL values except Cu. Bioavailability is dependent on chemical load, chemical form and mobility of the chemical species among other factors<sup>[13, 16, 25-27]</sup>. An increase in the loading of metals will saturate specific natural sorp-



**Figure 2 : Bioaccessible levels of selected heavy metals at sites 1, 3 and 4 as a function of time.**

## Current Research Paper



**Figure 3 : Simplified schematic that depicts bioaccessibility and bioavailability of metals following inadvertent ingestion of contaminated soil or sediment by a human being.**

tion sites for the metals in the sediment/soil, increasing the mobility, and hence availability of the metals.

To estimate bioavailability, we used SBET to determine the bioaccessible fraction of each of the selected metals. Figure 2 shows the dissolution of metals in the simulated gastric solution as a function of time, with the total amount dissolved after 60 minutes representing the bioaccessible fraction. The 60-minute bioaccessibility represents the equilibrium concentration of a metal in the simulated gastric solution. As shown in Figure 2, a significantly large proportion of the bioaccessible fraction of each of Cd and Pb was in solution after just 10 minutes, with the graphs almost horizontal, compared to that of Cu and Zn. This implies that the residence time in the gastrointestinal tract of inadvertently ingested contaminated sediment may not be a factor in determining bioavailability of Ca and Pb. The bioaccessible fraction of such metals will go into solution almost instantly.

Figure 2 also shows that bioaccessibility was positively correlated with total metal levels, except for Zn (site 1). This shows that, as reported the literature<sup>[13, 16, 25-27]</sup> bioaccessibility is dependent on chemical load among other factors. This implies that more polluted sediments and soils pose a more health hazard than less polluted ones in the event of inadvertent ingestion. The same Figure also shows that the rate of bioaccessibility (mg/kg.min) was positively correlated with TOC levels. NOM (TOC) binds metals, influences mobility of chemical species, and competes for binding sites with metals among other chemical species<sup>[22, 23]</sup>. This means

that metals bound onto soluble NOM, under bioaccessible simulation solution conditions, will be bioaccessible, as well as those metals that are out competed by NOM, soluble or insoluble, for binding sites.

Figure 3 shows a simplified schematic that depicts bioaccessibility and bioavailability of metals following inadvertent ingestion of contaminated soil or sediment by a human being. Inadvertent ingestion of contaminated soil or sediment will result in the dissolution of metals in the gastric solution, mainly because of the low pH in the stomach. The presence of equilibrium between soil-bound metal and the dissolved metal and the simultaneous dissolution and uptake will increase bioaccessibility beyond that estimated by simulated gastric solution. Increasing bioaccessibility will increase bioavailability. The amount that is absorbed by human cells represents the bioavailable fraction. Bioavailability may be negatively impacted by the low pH in the stomach because receptor ligands may be protonated, reducing their capacity to transport metals across the cell membrane.

TABLE 3 shows the 24-hour phytoaccessible fractions of the selected metals in Deal Lake sediments. The 24-hour phytoaccessible fraction represents the amount of metal that is mobile (dissolved) in the soil. It represents the equilibrium concentration of a metal at a given time. It is this form of metal that can be absorbed by plant cells. The amount that is eventually absorbed represents the phytoavailable fraction. Because of the equilibrium that exists between the dissolved metal and the soil-bound metal, metal uptake and assimilation by

**TABLE 3 : 24-hr phytoaccessible levels (mg/kg) of selected metals in Deal Lake sediments.**

	Site 1	Site 2	Site 3	Site 4
Cu	0.190 ± 0.011 (6%)	0.342 ± 0.007 (2%)	0.342 ± 0.007 (2%)	0.309 ± 0.025 (8%)
	0.216 ± 0.013% (6%)	0.398 ± 0.025% (6%)	0.496 ± 0.012% (2%)	0.241 ± 0.020% (8%)
Pb	0.688 ± 0.014 (2%)	0.653 ± 0.012 (2%)	0.693 ± 0.064 (9%)	0.636 ± 0.084 (13%)
	0.142 ± 0.003% (2%)	0.158 ± 0.004% (3%)	0.278 ± 0.026% (9%)	0.151 ± 0.020% (13%)
Zn	35.4 ± 0.6 (2%)	8.35 ± 1.04 (12%)	28.2 ± 2.1 (7%)	35.7 ± 1.4 (4%)
	3.28 ± 0.06% (2%)	1.09 ± 0.14% (13%)	5.01 ± 0.38% (8%)	4.82 ± 0.19% (4%)
Cd	0.644 ± 0.072 (11%)	0.406 ± 0.080 (20%)	0.486 ± 0.015 (3%)	0.609 ± 0.005 (1%)
	3.79 ± 0.48% (13%)	4.06 ± 0.8% (20%)	4.42 ± 0.20% (5%)	4.35 ± 0.04% (1%)

Percentages outside the brackets represent the phytoaccessible fraction (compared to the total) at each site and those in parenthesis are relative uncertainties (% relative standard deviations). % phytoaccessibility = {[mean accessibility ± standard deviation]/ [mean total metal ± standard deviation]} x100; Relative uncertainty = [standard deviation/mean]x100.

plant cells will increase solubility (phytoaccessibility), and hence phytoavailability of the metal. This means that all forms of a metal, except the residual form, are potentially phytoavailable. Figure 4 shows a simplified schematic that summarizes the envisaged processes of phytoaccessibility and phytoavailability of metals in plants exposed to contaminated soils or sediments.

As shown in TABLE 3, the order of proportional phytoaccessibility (% phytoaccessibility) was Cd > Zn > Cu > Pb. The % phytoaccessibility of Zn was slightly greater than that of Cd at Sites 3 and 4. This order agrees with the Irvin-Williams order of heavy metal competition for limited binding sites in the soil is as follows: Hg<sup>2+</sup> > Pb<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Cd<sup>2+</sup>[13]. Other studies have also reported higher availabilities for Zn and Cd than that for Pb and Cu[13].

## CONCLUSION

Based on NOAA's Probable Effects Levels, Deal Lake sediments can be regarded as toxic with respect to As, Cd, Cr, Pb and Zn. Our data confirmed that indeed bioaccessibility is positively correlated with chemical load and have shown that TOC increases the bioaccessibility rate of the metals analyzed. The proposed equilibria-based bioaccessibility and

phytoaccessibility models suggest that larger proportions of metals can be accessible than predicted by the simulated 60-minute bioaccessibility and 24-hour phytoavailability respectively. Dredging is necessary to ensure that waterways are navigable and also to avoid flooding, but the dredged material should be properly managed to avoid unnecessary human exposure to chemical contaminants.

## ACKNOWLEDGEMENTS

We want to thank the School of Science and the Department of Chemistry, Medical Technology at Monmouth University for financial support. We also want to acknowledge Sarah Keysper, a former student, for helping with sample collection, and Mr. Keysper for providing the boat.

## REFERENCES

- [1] Deal Lake, Official Website of the Deal Lake Commission, <http://www.deallake.org/index.html>, (2011).
- [2] S.Brakni, N.E.Abriak, A.Hequette; Environ.Technol., **30**, 849 (2009).
- [3] Y.Yamagata, H.Kokubu; Mizu Kankyo Gakkaishi., **31**, 236 (2008).
- [4] R.Zentar, N.E.Abriak, V.Dubois, M.Miraoui; Environ.Technol., **30**, 841 (2009).
- [5] V.Cappuyns, R.Swennen, J.Verhulst; Sci.Total Environ., **333**, 233 (2004).
- [6] P.Van Den Hurk, R.H.M.Eertman, J.Stronkhorst; Mar.Pollut.Bull., **34**, 244 (1997).
- [7] C.F.Calasons, O.Malm; Science of the Total Environment, **208**, 165 (1997).
- [8] E.J.Stanek III, E.J.Calabrese, R.Barnes, P.Pekow; Ecotoxicol.Environ.Saf., **36**, 249 (1997).
- [9] E.J.Stanek III, E.J.Calabrese, M.Zorn; Hum.Ecol.Risk Assess., **7**, 357 (2001).
- [10] J.Twining, P.McGlenn, E.Loi, K.Smith, R.Giere; Environ.Sci.Technol., **39**, 7749-7756 (2005).
- [11] S.C.Hamel, K.M.Ellickson, P.J.Lioy; Sci.Total Environ., **243/244**, 273 (1999).
- [12] S.C.Hamel, B.Buckley, P.J.Lioy; Environ.Sci.Technol., **32**, 358 (1998).
- [13] K.R.Kim, G.Owens, R.Naidu; Aust.J.Soil Res., **47**, 166 (2009).
- [14] C.H.Yu, L.Yiin, P.J.Lioy; Risk Anal., **26**, 125 (2006).



## Current Research Paper

---

- [15] E.I.Bertoncini, M.E.Mattiazzi, R.Rossetto; *J.Plant Nutr.*, **27**, 1243 (2004).
- [16] Z.Y.Hseu; *Chemosphere*, **63**, 762-771 (2006).
- [17] M.Intawongse, J.R.Dean; *Environ.Pollut.* (Amsterdam, Neth.), **152**, 60 (2008).
- [18] R.W.Mullen, W.R.Raun, N.T.Basta, J.L.Schroder, K.W.Freeman; *J.Plant Nutr.*, **28**, 405 (2005).
- [19] B.A.Schumacher; *Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments*, EPA/600/R-02/069 (NTIS PB2003-100822), U.S. Environmental Protection Agency, Washington, DC, (2002).
- [20] U.S.Environmental Protection Agency (EPA); *Test Methods for Evaluating Solid Waste, SW-846*, 3<sup>rd</sup> Edition, Office of Solid Waste and Emergency Response, Washington, D.C., November 1986; Update II, (1994).
- [21] U.S.Environmental Protection Agency (EPA); *Method 3051a: Microwave Assisted Acid Dissolution of Sediments, Sludges, Soils and Oils*. 2<sup>nd</sup> Edition U.S.Gov.Print.Office, Washington, DC, (1997).
- [22] T.Tongesayi, E.J.Byam, S.B.Keyser, M.J.Crounce; *Environmental Chemistry*, **5**, 161 (2008).
- [23] T.Tongesayi, R.B.Smart; *Water SA.*, **33**, 615 (2007).
- [24] M.F.Buchman; *NOAA Screening Quick Reference Tables*, NOAA HAXMAT Report 99-1, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, Seattle WA. **12**, (1999).
- [25] G.Ho, L.Qiao; *Water Sci.Technol.*, **38**, 17 (1998).
- [26] X.L.Qiao, Y.M.Luo, P.Christie, M.H.Wong; *Chemosphere*, **50**, 823 (2003).
- [27] B.F.Sukkariyah, G.Evanylo, L.Zelazny, R.L.Chaney; *J.Environ.Qual.*, **34**, 2255 (2005).