RICE UNIVERSITY

The New DRET Test to Predict Metals Available during the Resuspension of Anoxic Sediments

by

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Abstract

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In industrialized countries, many aquatic environments are polluted with contaminants, such as metals. Metals can be found in the particulate matter of the sediment [1, 2]. Metals could be potentially dangerous to biota, if released. The metals can be released to the environment by oxidation due to resuspension (dredging). Neither the water column metal concentrations nor the sediment metal concentrations are good indicators of the amount of metals that will be available during a resuspension. A new method was developed, the new DRET test, to predict the amount of metals available during a six hour resuspension of anoxic sediment using an in-situ Chelex® resin as a constant adsorption-potential sink. This method was adapted from DiGiano's et al. [3] DRET test for use with metals instead of organic contaminants. The new DRET test could be used in the field to predict the possible metals available before a resuspension event occurred.
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Chapter 1

1. Introduction

In industrialized countries, many water bodies are polluted with contaminants, such as metals. And many of these contaminants are associated with particulate matter [26], which has sorptive behavior that can cause sediments to act as a sink for metals in the aquatic environment [14, 26].

In the aquatic environment, most metals are immobilized in the anoxic sediment by binding with sulfide minerals. Changing the aquatic conditions and exposing the anoxic sediment to an oxic environment can cause the sulfide minerals to be re-oxidized and metals released. The aquatic conditions can be affected by natural events such as storms or by human activity such as dredging, both of which usually cause changes in the physical and chemical properties of the environment.

At the point of dredging, the sediments are suspended in the river, which results in two changes: an immediate increase in solid surface area and a simultaneously immediate change in the physical and chemical parameters that characterize the water. Physical and chemical parameters that can change are the pH, redox conditions, and organic complexation that can cause metals to mobilize and become bioavailable [26]. Changing the physical and chemical parameters affects the kinetics and equilibrium of the environment.

The physical and chemical changes that occur during a resuspension, such as dredging, can cause the release of metals from the sediment into the aquatic environment. Released, metals can be potentially dangerous to biota. Currently, the dredge elutriate test (DRET) by DiGiano, et al.[7], is used to predict the amount of metals released from
the sediment during a resuspension. The DRET test works well in the field for PCBs and other organic contaminants during dredging, but not for metals. The limitations of the DRET test are explained by Myers et al.: “…this approach is not recommended for application for the release of dissolved metals during dredging because the rapid and pronounced change in redox and the complicated environmental chemistry of metals make equilibrium approaches highly unreliable and uncertain.” I created a new DRET test to predict the concentration of metals released during dredging or other resuspension activities since the current one does not accurately predict what is happening with metals.

1.1 Organization of Thesis

The following chapters explain the details of this research and the new DRET test that was created for predicting the amount of metals releasable. Chapter one explains the purpose of this work. Chapter two discusses what I found in the literature: dredging, metals in contaminated sediment, the metals studied, the methods available to determine metal concentrations in aquatic environments, and the Chelex 100 resin. Chapter three discusses the materials and methods: the sediments; sample collection and characterization; the new DRET test; the resuspension experiments; instrumentation, calibration, and chemicals; and Visual Minteq. Chapter four shows the results: the composition of metals in the sediment, the kinetics of metal release, the resuspension experiments, effects of parameter changes on the method, and a comparison of the new DRET test to the standard DRET test. Chapter five discusses the results and provides conclusions: a discussion about the resuspension experiments, a comparison of the new DRET test with the standard DRET test, calculations in Visual Minteq, and the
conclusion. Chapter six discusses future work that could be done on this research to expand what is currently known.

1.2 Statement of Purpose

The purpose of this study is to develop a new DRET test to predict the metals available during resuspension. The purpose is also to study the effects of resuspension variables on the release of available metals.
Chapter 2

2. Literature Review

The literature review is divided into six sections: dredging, metals in contaminated sediments, the metals, methods available to determine metal concentrations in aqueous environments, Chelex 100 resin, and a summary. Sections one and two demonstrate the importance of the research by giving background information about dredging, mobilization and chemical behavior of metals in the aquatic environment. Section three discusses in detail each of the five metals studied in the research along with iron and manganese. Section four discusses other methods that are used to find the metal concentration in aqueous environments such as the DRET test or solid phase extraction (SPE), so they later can be compared to the new DRET test. Section five discusses details about the Chelex 100 resin that was used in the new DRET test. And finally, section six summarizes the important information from each of the sections.

2.1 Dredging

Dredging uses three methods to scoop or suction materials out of waterways, creating deeper areas:

- Suction dredging removes loose materials.
  Examples of the suction dredging heads are hydraulic pipeline or hoppers.

- Mechanical dredging removes loose, hard, or compacted materials.
  Examples of mechanical dredging heads are cutterhead, clamshell, or dipper.

- Most dredges are a combination of suction and mechanical dredging.
Dredged material is disposed of in three ways: put on a barge and taken to a disposal facility, side cast to the adjacent bank, or pumped directly to another area for disposal.

Hopper and cutterhead dredges are selected based on the materials to be dredged and the conditions of the waterway. Figure 1 shows a schematic of the hopper and cutterhead dredges. The schematic shows how the two dredges are different and how they remove materials. For example, the hopper dredge drags the dredge head along the bottom of the waterway while the cutterhead dredge scoops the material.

Figure 1 Schematic of Hopper Dredge and Cutterhead Dredge [31]

Hopper dredges can self-propel themselves in rough, open waters. They are most effective in removing the materials that form shoals after an initial dredging takes place. A drawback of hopper dredges is that they discharge overboard fine-grained dredged material, which can have environmental impacts.
Cutterhead dredges are the most commonly used dredging vessels and are generally the most efficient and versatile because they can excavate a wide range of materials including clay, silt, sand, and gravel. A drawback to cutterhead dredges is that the rotation of the cutterhead produces a turbidity cloud that increases the potential for adverse environmental impacts [31].

Though dredges are useful for the removal of materials, they cause mixing of the sediment water boundary layer, which causes particulate matter to be suspended in the water. The particulate matter contains contaminants that can be moved by the water currents. Water currents during dredging can be complex due to the movement of the water and the dredge, which can affect the mobility of the contaminants. Such mobility can cause a risk to biota. Both the particulate matter and the water currents add to the difficulty of understanding contaminant behavior in the water.

2.2 Metals in Contaminated Sediments

This section is divided into four sub-sections. Sub-section one discusses how the metals move through the environment and the processes that control mobilization. Sub-section two discusses the metals species present in the environment and the binding of metals to solids. Sub-section three discusses what happens in the environment due to the oxidation of iron and metal sulfides. Sub-section four discusses the results of resuspension experiments conducted by other groups to compare with my results.
2.2.1 Mobilization of Metals in Contaminated Sediments

Storms and dredging in the aquatic environment can cause metals to mobilize from the sediment to the water column. Particulates adsorb metals and can be a sink or a source of metals in the aquatic environment [26, 32, 33] here most of the metals are bound to particulates in the sediments, so they are not immediately available to biota. Particulates in rivers and lakes consist of clay minerals, carbonates, organic matter, biota, and iron and manganese oxyhydroxides.

The main factors affecting mobility and bioavailability of metals in the environment are the type and the stability of the metal bonds to solids. Mobilization is controlled by three processes:

- physical transport such as advection, turbulent mixing, and diffusion;
- biological processes such as bioturbation; and
- geochemical processes such as adsorption/desorption and precipitation/dissolution.

Bioavailability is controlled by the degree of sorption and precipitation [29, 32]¹

One important factor in the mobility of contaminants in the aquatic environment is the settling velocities of particles, which are based on their size, shape, and density. Stokes Law is generally used to calculate the settling velocity:

\[
V_s = \frac{g \Delta \rho d^2}{18 \mu}
\]

where \( V_s \) is the settling velocity (cm/s); \( g \) is gravity (cm/s²); \( \mu \) is dynamic viscosity of water (g/cm·s); \( \rho_s \) is density of the particles (g/cm³); \( \rho \) is the density of water (g/cm³); \( d \) is

¹ Bioavailability is not discussed in further detail since bioavailability test were not conducted in this study.
the diameter of the particles (cm). Table 1 gives the size of common particles and their settling velocities.

Table 1 Size of Particles

<table>
<thead>
<tr>
<th>Particles</th>
<th>Size (cm)</th>
<th>Settling Velocity* (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel</td>
<td>&gt;0.2</td>
<td>&gt;200.6</td>
</tr>
<tr>
<td>Sand</td>
<td>0.006-0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Silt</td>
<td>4.0e^-4-0.006</td>
<td>3.92e^-4</td>
</tr>
<tr>
<td>Clay</td>
<td>&lt;4.0e^-4</td>
<td>&lt;4.09e^-5</td>
</tr>
</tbody>
</table>

* assumptions: μ is 10^-2 g/cm s at 20°C; densities and size of particles found in literature tables; calculated using Stokes Law

The settling velocities influence how far particles move in the aquatic environment.

2.2.2 Chemical Behavior of Metals in the Aquatic Environment

Because different metal species are present in the water and in the sediment, understanding the chemical behavior of metals in the aquatic environment is critical for predicting the amount released. The metal species can affect how the metal is dispersed in the environment. Metal ions can be in two states: dissolved or solid. Table 2 outlines the main metal species for the two states in the aquatic environment.

Table 2 Forms of Metal Species in the Aquatic Environment (illustrated for FeIII)

<table>
<thead>
<tr>
<th>Speciation</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolved (in pore water* or water column)</td>
</tr>
<tr>
<td>free [Fe²⁺]</td>
<td>precipitated FeOOH</td>
</tr>
<tr>
<td>complexed [FeOH²⁺]</td>
<td>adsorbed [≡SOFe²⁺]**</td>
</tr>
</tbody>
</table>

* pore water is the water filling the space between the grains of sediment
** [≡SOFe²⁺] represents Fe(III) adsorbed to a surface oxide
In the dissolved state, metal ions can be either free or complexed. Free metal ions are positively charged ions surrounded by water. They are carried with the water, can easily be taken up by biota, and can be highly toxic. Complexed metals form by a Lewis acid-base reaction with the metal ion to negatively charged ligands, such as chloride or organic matter. The ligands surround the metal ion and form a coordination sphere. The ligands can form two types of coordination spheres, outer and inner. The outer coordination sphere is ligands loosely coordinated to the metal ion. The inner sphere is ligands directly bonded to the metal ion [3].

In the solid phase, metal ions can be either precipitated or adsorbed. Precipitated metals can form an insoluble salt with counter ions such as iron sulfide or iron carbonate, which are chemically stable in anoxic conditions but can become unstable when introduced to oxic conditions [10]. Adsorbed metals are bonded to a solid surface; both physical and chemical adsorption can occur. Physical adsorption is a relatively weak bond to the surface of a solid. Chemical adsorption is an ionic or covalent bond in addition to Van der Waals interactions with a solid. Most inorganic compounds are adsorbed by chemical interactions with sediment surfaces. The interactions with the sediment surface can range from electrostatic to covalent bonds [4].

Only a small fraction of metals in the sediment are dissolved due to the tendency of metal ions to bind with particles. The redox potential and the pH both greatly affect the speciation of metals and their ability to shift between species [4, 10, 32]. Figure 2 shows how the metals can shift between species. The metals are free ions that shift back and forth between complexed metals, precipitated metals, or adsorbed metals.
Figure 2 Schematic of Possible Shifts in Speciation

Figure 2 shows possible transformations metals can go through. An important transformation is free metal ions binding with solids. Binding can occur by many different processes [5]:

- sorption and desorption (e.g., $\equiv X + M^{\cdot\cdot} \rightarrow \equiv XM$)
- formation and dissolution of carbonate bound metal, and hydroxides (e.g., $M^{\cdot\cdot} + CO_3^{2-} \rightarrow MCO_3$); (e.g., $M^{\cdot\cdot} + H_2O = MOH_2$ or $MOH^+$)
- formation and decomposition of soluble and insoluble metal organic complexes (e.g., $M^{\cdot\cdot} + HA^- = MHA^+$)
- sorption and co-precipitation of metals with Fe/Mn-oxides
\[(\text{e.g., FeOH} + \text{Cu}^{n+} = \text{FeOCu}^{+} + \text{H}^+)\]

- precipitation and dissolution of metal sulfides (e.g., \(M^{x+} + S^{-2} = MS\))

2.2.3 Oxidation of Iron and Sulfides

The oxidation of metal sulfides, oxygen, iron, and manganese causes metals to exhibit complex behavior. Most sediments are in anoxic conditions where a high concentration of dissolved \(Fe^{2+}\) exists. Mixing anoxic sediment and oxic water causes two main reactions: oxidation of the metal sulfides and oxidation of dissolved iron [5, 10, 26]. Figure 3 shows what can happen to iron and metal sulfides before, during, and after a resuspension, such as dredging. Specifically, after the iron and metal sulfides undergo oxidation causing adsorption and precipitation.

Figure 3 Schematic of Dredging [10]

The oxidation reactions of free iron and metal sulfides (shown below) are redox reactions. Redox reactions are reversible reaction in which electrons (e-) transfer from one atom to another. The key components of the reaction are the electron (e-), the
reducant, and the oxidant. The reducant is an electron donor and the oxidant is an
electron acceptor. The gain by the oxidant has to equal the loss by the reducant [28]. The
two oxidation reactions listed here are common in aquatic environments:

\[
\text{FeS} + \frac{9}{2}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} = \text{FeOOH} + \text{SO}_4^{2-} + 2\text{H}^+ \quad (2)
\]
\[
\text{ZnS} + 2\text{O}_2 + 2\text{H}_2\text{O} = \text{Zn(OH)}_2 + \text{SO}_4^{2-} + 2\text{H}^+ \quad (3)
\]

The oxidation leads to acidification of the system, which could cause the metals to
become mobile. The degree of acidification is dependent on the buffering capacity of the
sediment, which is the ability of the sediment to neutralize the acid formed. This
buffering is controlled by the carbonate system [5, 26]. An important carbonate buffer
reaction in sediments is

\[
\text{CaCO}_3 + 2\text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \quad (6)
\]

The oxidation of the sulfide is possibly the major source of metals to the oxic
water column [29]. The oxidation of the iron causes the formation of iron
oxyhydroxides. The oxyhydroxides form very adsorptive surfaces, which allow a place
for other ions to adsorb such as metals [5, 10, 33]. Pugh et al, Milero et al, and Ahmad
and Nye suggest that iron oxidation is faster than sulfide oxidation; therefore,
oxyhydroxides form before the dissolution of metal sulfides. The oxyhydroxides could
compensate for the amount of metals released into the water column by adsorbing the
metal ions that dissolve from the sulfide [29].
2.2.4 Resuspension Experiments

Many resuspension studies have been done on the release of metals from the aquatic environment. The first study was by Hirst and Anston. It is a six-hour resuspension where they observed significant release of Fe and Mn but not Cu or Zn.

In Gao’s resuspension study (7 days), Co, Ni, Zn, and Cd release are associated with Mn carbonates and oxides, which occurs when the acidity increases in the system. These metals are strongly bonded to Mn oxide [30]. In the same resuspension study, Gao observed that Pb and As have a strong affinity to FeOOH; therefore, less is released into the aqueous phase and more is sorbed onto FeOOH. Cu has a strong complexation with organic matter so it remains stable and has little release even under acidic conditions [9]. FeOOH and MnOOH have a significant role in the fate of metals in the environment. In Gao’s resuspension, the peak metal concentration was observed after two days and then became a steady concentration.

Calmano’s long-term resuspension (70 days) study showed a small release of Cd, Zn, Cu, and Pb. Simpson found that during resuspension, FeS and MnS oxidize readily and form oxyhydroxides. These oxidations were dependent on pH. To form MnO₂, the maximum oxidation occurred at a pH of 5; for Fe(OH)₃ the maximum oxidation occurred at a pH of 6.5; and for FeOOH the maximum oxidation occurred at a pH of 7 [29].

Further resuspension studies were conducted by Gao et al. to see how different conditions would affect metal release. Gao et al. compared the resuspensions (7 days) done in oxic and anoxic conditions. She found that under oxic conditions considerable release of the metals occurred; however, under anoxic conditions the release was negligible. For example, 7.3% of Zn was released after five days—that is, about 25 times
greater than under anoxic conditions. She also compared the effect of microbial activity on resuspensions by the addition and absence of sodium azide in the system. Gao et al. found after seven days that Zn, Ni, Co, and Cd had a much greater release without sodium azide in the system. For example, the Zn and Cd release was about two times greater in the presence of microbes. She found the induction of microbe activity to occur sometime between one and two days.

2.3 The Metals

The metals section is divided into seven sub-sections. Sub-sections one and two discuss the metals iron and manganese, which are not analyzed in the study but important because of their impact on the release of other metals. Sub-sections three through seven discuss the five metals (Co, Ni, Cu, Pb, and Zn) that were analyzed during the study.

2.3.1 Iron

In nature, iron exists as Fe(II) (ferrous) or Fe(III) (ferric). Iron makes up 5% of the earth’s crust by weight; therefore, it is naturally present in both freshwater and oceanic soils and sediments and its concentration ranges from 1% to 9%. In the sediment layer dissolved ferrous iron is present up to several mg/L. Even though iron is not toxic, it can affect the concentration of other metals, which are toxic.

In solution, both Fe(II) and Fe(III) undergo hydrolysis and form various hydrolysis species, which are dependent on pH. Examples of iron species formed are:
Fe(II) Hydrolysis

\[
\begin{align*}
    \text{Fe}^{+2} + \text{H}_2\text{O} &= \text{FeOH}^{+} + \text{H}^{+} \\
    \text{Fe}^{+2} + 2\text{H}_2\text{O} &= \text{Fe(OH)}_2 \text{(aq)} + 2\text{H}^{+} \\
    3\text{Fe}^{+2} + 4\text{H}_2\text{O} &= \text{Fe}_3(\text{OH})_4^{2+} + 4\text{H}^{+}
\end{align*}
\]

Log K (25°C)

-6.74

-16.04

45.39

In nature, Fe can form complexes with both organic and inorganic species in the aqueous environment. Iron reacts with sulfides and forms a variety of FeS, which is the predominant inorganic species. The sulfide species form by anaerobic bacteria reducing sulfate in the sediment.

Iron also forms iron hydroxides and oxides that can precipitate in natural waters and form colloidal particles that aggregate and settle on the bottom. Particles can adhere to surfaces, which causes coatings, granules, and nodules to form. Iron oxides absorb many elements and can attenuate most metals by scavenging. The dissolved concentrations of Cd, Cu, Pb, and Zn decrease during dredging because of the precipitation of iron oxides [3].

2.3.2 Manganese

Manganese is an essential nutrient that is found in every plant and animal and present in many minerals. It is a multi-valent element, kinetically labile, and can exist in many oxidation states. The most thermodynamically stable oxidation state is Mn(II) in reducing conditions. In natural waters, the oxidation of Mn(II) to MnOOH is usually catalyzed by microorganisms.
In nature, the redox conditions, pH, and salinity affect the speciation of manganese in water. Mn can form complexes with both inorganic and organic ligands; however, it does not form strong complexes with organic ligands.

Specific adsorption, ion exchange, and organic complexation are important mechanisms of sorption for Mn to the sediment, which mechanism is most important is unclear. The highest sorption capacity of Mn occurred in sediments with high clay content and high total organic carbon [3].

2.3.3 Cobalt

Cobalt has many uses in industry, such as a blue dye in glass and ceramics or used in a metal alloy to create strong magnets. Cobalt has two oxidation states Co(II) and Co(III), but Co(II) is generally much more stable than Co(III).

Co can form complexes with both inorganic and organic species in the aquatic environment. The main cobalt species under oxidizing and moderately reducing conditions is Co(II), in very basic conditions is Co(OH)2, and under very reducing conditions is CoS2. Cobalt can form strong complexes with organic ligands, such as humic acid, if the organic content is high in the sediment, which causes less sorption to other ligands and increased mobility of cobalt [17].

The concentration of cobalt in the sediment is controlled by adsorption and coprecipitation reactions with iron/manganese oxides. The adsorption of cobalt is strongly linked to the oxidation state and the availability of organic complexes. The adsorption of cobalt to other minerals was shown to be high in the absence of organic complexes.
2.3.4 Nickel

Ni occurs in the form of oxides, silicates, and sulfides. Much of the Ni produced is in metal alloys used for electroplating, batteries, and catalyst. The primary oxidation state is Ni(II).

Ni forms complexes with both inorganic and organic species in the aquatic environment. It forms complexes with carbonate, sulfate, and hydroxide in anaerobic condition below the pH of 9, which decreases the amount available free Ni. Predominant species are Ni(II) and NiSO₄(aq) but in very basic condition is Ni(OH)₂(aq). An important complex is nickel humic acid, which can solubilize Ni away from nickel carbonate complexes.

Specific adsorption, ion exchange, and/or co-precipitation are important mechanisms of sorption for Ni. Important sorbents are iron/manganese oxides, clay, and some types of organic matter. The competition of Ni(II) with other metals, organics, and ligands, such as SO₄²⁻ can cause Ni(II) to be mobile and reduce sorption. Table 3 shows the sorption constants of Ni to various sorbents, such as clay [3]

Table 3 Ni(II) Sorption Constants for Various Sorbents

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>S*(μmol/g)</th>
<th>Kₛ*(L/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clays</td>
<td>40</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe oxides</td>
<td>8.6</td>
<td>100</td>
</tr>
<tr>
<td>Mn oxides</td>
<td>5.6</td>
<td>40</td>
</tr>
</tbody>
</table>

* S is the moles sorbed at equilibrium per gram of solid and Kₛ is the ratio of quantity of sorbate per gram of solid to the amount of sorbate remaining in solution at equilibrium

From Table 3, the greatest specific sorption of Ni(II) occurs with clays.
2.3.5 Copper

Copper naturally occurs in the form of oxides and sulfides. It is used in wires, electronic and electrical equipment, electroplating, and construction. Copper exists as Cu(I) and Cu(II) but is commonly found as Cu(II).

Copper forms complexes with both inorganic and organic ligands in the aquatic environment. It forms strong complexes with OH\(^-\) and CO\(_3\)\(^{2-}\) and weak complexes with Cl\(^-\) and SO\(_4\)\(^{2-}\). Copper organic complexes have a high stability, which can affect the stability of other metal organic complexes.

Sorption is the most important mechanism controlling the mobility of copper in the environment along with precipitation and co-precipitation. In sediments, copper strongly sorbs to iron/manganese oxides, clay, and organic matter. The primary sorbed species to sorbents is Cu(OH\(^-\)) rather than Cu\(^{2+}\) [3]. Table 4 shows the Langmuir isotherm sorption constants of copper to various sorbents, such as clay.

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>(A_m)^* (umol/g)</th>
<th>(\log K_L)^* (log M(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Fe Oxides</td>
<td>130</td>
<td>5</td>
</tr>
<tr>
<td>Mn Oxides</td>
<td>1670</td>
<td>4</td>
</tr>
<tr>
<td>Organic Matter</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>Sediments</td>
<td>34</td>
<td>5</td>
</tr>
</tbody>
</table>

\(^*\) \(A_m\) and \(K_L\) are Langmuir constants where, \(A_m\) is maximum sorption capacity of solid and \(K_L\) is sorption constant related to the binding energy of sorbate

From Table 4, Cu has strong sorption to Mn oxides and organic matter.
2.3.6 Lead

Lead is the most abundant heavy metal, which is used in acid storage batteries, anti-knocking gasoline additives (foreign countries), and metal alloys. The oxidation states are Pb, Pb(II), Pb(IV), but Pb(II) is generally the most stable.

Lead can complex with both inorganic and organic ligands in the aquatic environment. Pb(II) forms strong complexes with OH⁻, and CO₃²⁻ and weaker complexes with Cl⁻ and other inorganic ligands. In freshwater, free Pb(II) ions are the primary species, but at higher pHs the primary complexes are carbonate and hydroxide species. Pb(II) can also form complexes with humic matter and several major anions (CO₃²⁻, OH⁻, S²⁻, PO₄³⁻) depending on the pH, redox conditions, and other ions present, which can control the amount of total dissolved lead in the environment.

Ion exchange, specific adsorption, co-precipitation with hydrous oxides, and incorporation into cationic lattice sites in crystalline sediments are the primary sorption mechanisms in the sediment. Important sorbents are organic matter, clay, and iron/manganese oxides. Lead sorption can increase by raising the pH or the presence or addition of humic acid. Table 5 shows the Langmuir isotherm sorption constants of lead to various sorbents, such as clay [3].
Table 5 of Sorption Constants for Lead

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>$A_m^*$ (umol/g)</th>
<th>Log $K_L^*$ (log M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>40</td>
<td>3.5</td>
</tr>
<tr>
<td>Fe Oxides</td>
<td>2400</td>
<td>4</td>
</tr>
<tr>
<td>Mn Oxides</td>
<td>2700</td>
<td>3.8</td>
</tr>
<tr>
<td>Organic Matter</td>
<td>300-500</td>
<td>4</td>
</tr>
<tr>
<td>Sediments</td>
<td>20</td>
<td>4.9</td>
</tr>
</tbody>
</table>

* $A_m$ and $K_L$ are Langmuir constants where, $A_m$ is maximum sorption capacity of solid and $K_L$ is sorption constant related to the binding energy of sorbate

From Table 5, lead sorption is greatest with Fe and Mn oxides.

2.3.7 Zinc

Zn, naturally occurs as sulfides, carbonates, silicate, and oxides. Zinc complexes are used in plastics, paints, cosmetics, and many other applications. The only oxidation state is Zn(II), which is also the predominate species in freshwater. Many factors affect the solubility of zinc in natural waters: the pH, the redox potential, the temperature, the presence of complexing ligands, competing ions, and precipitating reagents.

Zn forms complexes with both inorganic and organic ligands such as sulfides and hydroxides, which can be affected by the redox conditions and the amount of organic matter in the environment.

The sorption of Zn affects its mobility in the aquatic environment; if no sorbents are present it can become one of the most mobile metals. The sorbents that control the mobility are hydrous iron/manganese oxides, clay, carbonate minerals, and organic matter. Zn has an inverse correlation between sediment grain size and sorption and pH
and sorption. For example, the amount of Zn sorbed increases with smaller particles and raising the pH. Table 6 shows the Langmuir isotherm sorption constants for zinc with various sorbents, such as clay.

Table 6 Zn sorption constants

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>$A_m$ (umol/g)</th>
<th>Log $K_L$*(log M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>6.1-560</td>
<td>2.7-3.3</td>
</tr>
<tr>
<td>Fe Oxides</td>
<td>5-600</td>
<td>2.7-6.7</td>
</tr>
<tr>
<td>Mn Oxides</td>
<td>34-4650</td>
<td>3.4-6.3</td>
</tr>
<tr>
<td>Organic Matter</td>
<td>12180</td>
<td>3.4</td>
</tr>
<tr>
<td>Sediments</td>
<td>47-180</td>
<td>3.8-4.8</td>
</tr>
</tbody>
</table>

* $A_m$ and $K_L$ are Langmuir constants where, $A_m$ is maximum sorption capacity of solid and $K_L$ is sorption constant related to the binding energy of sorbate

In the sediment, 30-60% is associated with iron/manganese oxides, 20-45% with clay, and less than 5% is bound to organic matter. Specific adsorption, co-precipitation, and ion exchange can attenuate Zn in sediments. The co-precipitation of Zn during precipitation to iron/manganese oxides allows zinc to be incorporated into the crystal lattice structure of the oxides [3].

2.4 Methods Available to Determine Metal Concentrations in Aquatic Environments

There are many methods used to find metal concentrations in the aqueous environment during a resuspension or steady state. The following section discusses five methods: the standard DRET test, SEM/AVS ratio, DGT technique, SPE, and chelating resins. The standard DRET test, by DiGiano et al. is the mostly widely used test to find
contaminant concentrations during dredging. The ratio of SEM/AVS is used to indicate the sediment quality. Other recent methods are diffusive gradients in thin films (DGT), solid phase extraction (SPE), and chelating resins or fibers.

2.4.1 The Standard DRET Test

The standard DRET test simulates conditions at the point of dredging, in contrast to the original elutriate test created by Palmero and Thackston, which used a settling column test to predict contaminant release from confined disposal sites. The standard DRET test uses a simple equilibrium-partitioning model to predict contaminant release (PCBs). They created equation 7 to find the predicted soluble PCB concentration.

\[
C_e = \frac{M_s q_i}{V_i + M_s K_p}
\]  

(7)

\(C_e\) predicted soluble PCB concentration (ug/L), \(M_s\) mass of sediment added (g), \(q_i\) initial mass of PCB in sediment (ug/g), \(V_i\) volume of solution (L), \(K_p\) partition coefficient (L/g).

The standard DRET test procedure used 10g/L of sediment and mixed the solution for one hour then allows the solution to settle for one hour. After the solution settles, three analyses are done:

1. Chemical analysis of filtered samples, filtered by a 0.45um filter
2. Chemical analysis on unfiltered samples
3. Analysis of the suspend solids and particle size.

DiGiano et al. calculated the mass of PCBs sorbed per unit mass of sediment two ways:

1. Extraction and analysis of the PCBs on the filter
2. Subtracting the filtered from the unfiltered samples to find the mass of PCBs sorbed
Both ways found good agreement between the results.

The experiment stresses the importance of understanding the dependency of final TSS (total suspended solids) on initial TSS, the aeration time, and the settling time. The final TSS is important because both the model and data suggest a majority of the PCB mass is associated with the sediment rather than the water. The settling time is important in estimating the concentration of PCB, for example a settling time that is too short may over estimate the concentration. The mixing time can be affected by the extent of particle flocculation, which can then affect the settling time. Conducting the experiment with varying initial TSS, aeration times, and settling times found that the aeration time had no real effect on the final TSS. The settling time had more impact on the final TSS than the initial TSS.

The results of the standard DRET test and the sorption equilibrium model showed reasonable results for the lab, but not in field studies. The experimental results from the standard DRET test were equal to or less than the predicted results from the sorption equilibrium model for soluble PCB. The test found that unfiltered concentrations of PCBs were always much higher than those in filtered samples by three times. In field studies, the standard DRET test both over predicted and under predicted PCB release from different types of dredge heads by one order of magnitude [7].

2.4.2 SEM/AVS Ratio

The ratio of SEM/AVS (simultaneously extracted metals/ acid volatile sulfide) is used to determine the quality of sediments. The SEM/AVS ratio is an equilibrium partitioning model (EqP) that predicts the toxicity of metals in the sediment. The EqP is
a method that incorporates bioavailability into sediment criteria. The general approach was initially developed with organic chemicals. It found that the concentration response curve for the biological effect was correlated with the water concentration instead of the total chemical sediment concentration [21]. Di Toro et al. were the first to show that the toxicity of cadmium was linked to the SEM/AVS ratio, since then it has been used by the EPA as a good way to predict sediment quality [1].

The rational for using the ratio is AVS reacts with SEM, which forms insoluble metal sulfides. Sulfides are believed to be the major phase that regulates the mobility of metals in the sediment. In anoxic sediment, the sulfides are stable and only become unstable when exposed to the oxic water column. The amount of AVS in the sediment will determine the metals toxicity and availability. For example, if there is an excess of AVS low metal activity occurs. If the SEM/AVS value is greater than one it means that more metals are present in the sediment relative to the AVS, which means the unbound metals have a potential to be more bioavailable than those bond to the sulfides. If the SEM/AVS value is less than one that means more AVS is present than metals and the bioavailability could possibly be decreased [9, 11, 29].

SEM/AVS ratio has restrictions; the ratio can only predict toxicity or lack of toxicity not the amount of metals released. It also is only applicable to anaerobic sediments with AVS and not aerobic sediments since other binding factors control availability.
2.4.3 DGT

A method used to find the release of contaminants during resuspension is the diffusive gradients in thin films device (DGT) by Zhang et al [36]. It uses diffusive thin films to find the kinetics of metal release from the solid phase to the solution. Understanding the exchange that occurs between the solid phase and the solution is important to understanding metal mobility and availability.

The rational for creating this method was most studies focus on equilibrium partitioning and not kinetics; that implies greater importance to metal exchange rates instead of the potential for kinetic controls on availability to biota. In sediments, it can be used to quantify the distribution coefficient of labile metals and exchanged kinetics between the solid phase and the solution.

Figure 4 shows a schematic view of the device and the layers. The method is based on the accumulation of solutes by a binding agent (Chelex 100) after diffusion through the gel. The DGT device consist of an outside layer of protecting plates, then a filter layer, a layer of Chelex 100 resin embedded in gel, and the resin layer is surrounded by diffusion layers.

Figure 4 Schematic of DGT Device

<table>
<thead>
<tr>
<th>Retaining plate</th>
<th>Millipore membrane</th>
<th>Gel Layer</th>
<th>Resin layer</th>
<th>Back plate</th>
</tr>
</thead>
</table>

DGT provides a controlled perturbation of the porewater concentration by introducing a sink for specific contaminants. The DGT device used the Chelex 100 resin
as a sink because it strongly binds labile trace metals species such as Fe, Mn, Co, Cu, and Ni.

A first order kinetic model describes the changes to the metals between the solid phase and the solution. The sorption kinetics of the metals were described using distribution coefficients. $K_{dl}$ is the distribution coefficient that expresses the ratio of the mass metal concentration found in the resin layer of the DGT device with respect to the metal concentration in the sediment solution. $K_d$ is the other distribution coefficient that expresses the ratio of the mass concentration of metals in the sediment with respect to the metal concentration in the sediment solution. The $K_d$ values for the total metals measured in the soil are higher than the $K_{dl}$ values calculated for the total metals in the device.

A problem that can arise from using this method is the time it takes for the metals to transverse through the diffusion layers. Molecular diffusion is how the metals are transported through the device. The metals that reach the resin have to be smaller than the pore size of the hydrogel that was used to make the resin/gel layer to be measured, which suggest that the metals need to be sufficiently mobile or have a diffusion coefficient that is within an order of magnitude of the free metal ion. Therefore, the device only measures a portion of the metals that are released from the sediment [8, 23].

2.4.4 SPE

Another method used to find the concentration of metals in the aqueous environment is solid phase extraction (SPE). SPE is used for isolating a target chemical species from an aqueous solution using a solid phase extraction media. The SPE method
was modeled after liquid-liquid extraction, which is a method used for pre-concentrating metal ions and/or matrix removal.

The procedure for SPE is to pass a liquid sample through a column, cartridge, or disk containing an adsorbent that holds the analytes. The analytes are recovered upon elution of a solvent through the SPE device. The metals are adsorbed onto the solid phase through hydrophobic interactions or Van der Waals forces. The most common sorbent is C18-silica. Figure 5 shows the interactions occurring at the surface of the solid sorbent. The solid sorbent can sorb functional groups, trace elements, or the matrix solvent while the matrix ligands, the matrix solvent, or the matrix ions adhere to the trace elements or functional groups sorbed to the surface.

Figure 5 Matrix Effects

F is the functional group, MI is the matrix ion, ML is the matrix ligands, MS is the matrix solvent, and TE is the trace element.
Metals cannot sorb directly with C18-silica sorbent and need an additional agent, such as a chelate because of their ionic character. The chelating agent binds with the metal, which then becomes a hydrophobic complex that can sorb onto the sorbent.

Advantages to using SPE are the ability to preserve and store samples, the high selectivity, the reduced amount of solvents, and the reduced time [6]. The disadvantages are a low capacity, breakthrough, and incomplete recovery of all the analytes. SPE seems better suited for clean water samples that do not contain particles since the columns, disk, or cartridges could become clog and total elution of the metals would not occur.

The following paragraphs outline the methods and results of three groups, which used SPE. Hou [13] used the 3M Empore chelating SPE disk for pre-concentration prior to analysis to determine the concentration of trace metals in drinking water. The disk is selective to multivalent metal cations. Results showed that for Cu, Ni, Pb, and Cd had a 93-100\% recovery.

Leekipatpiboon [18] created a chelate PAR (4-(2-pyridylazo)) that binds with metals and form complexes. The metal-PAR is trapped on a C18-silica SPE cartridge and eluted with a solvent. The results show the recovery of Ag, Cd, Cu, Ni, and Pb is between 81-96\% as a single component in the water. As a mixed component the results show Ag, Cd, Cu, Ni, and Pb recovery is 81-100\%.

Abbasse et al. [24] used 8-hydroxyquinoline (8-HQ) to chelate the metals followed by adsorption onto a C18-silica column to discriminate the metal liable form and metal organic complexes in seawater. Metals are chelated in solution then passed through a C18-silica column to retain the metal-chelate and eluted to find the metal concentration. Figure 6 shows the experimental method.
Their results show that Fe and Zn have a metal organic fraction of 70% of the total metal fraction; Ni and Cu have organic fractions of 40%, which means that for Fe and Zn 70% of the total metal fraction is complexed to organic matter.

2.4.5 Chelating Resins

Methods have been developed with resins to adsorb ions in aqueous solutions. Resins can be classified into three main groups: cation-exchangers, anion-exchangers, and chelating polymeric resins, which then can be sub-divided into strong, intermediate, or weak depending on the functional groups. Resins can have different functional groups such as carboxyl, hydroxyl, amino, etc. or synthesized with dithiocarbamate, amidoxide, iminodiacetate, and other functional groups. Figure 7 shows common chelating functional groups.
The functional groups are the following (a) iminodiacetate, (b) nitrilotriacetate, (c) poly(acrylamidoxime), (d) dithiocarbamate, (e) poly(vinylthiopropionamide).

Iminodiacetate is the most commonly used functional group in the analytical field [15].

Chelating resins are an effective technique that can be used for the adsorption of metal ions onto resin [35]. They are useful because they have high selectivity; larger adsorbing capacities than other adsorbents, such as metal oxides or activated carbon, and are easier to elute and regenerate [19]. Chelating resins are effective since they do not exhibit an affinity for alkali or alkaline earth metals, which are usually present in all aqueous solutions. Problems that occur with resins are shrinking and swelling can happen during adsorption/desorption processes, which causes channeling and formation of dead zones in the resin [35].
Chelating resin complexation behavior is similar to that of EDTA [15]. In order for the metal ions or metal complexes from an aqueous phase to be extracted into an organic phase the ionic charge needs to be neutralized, which is achieved by complexing the metal ions with the anions of the chelating agent. The anions act like a Lewis base and neutralize the ionic charge of the metal ion, which it coordinates to causing the metal chelate to become hydrophobic.

Chelating resins can be created in the lab, commercial, or commercial and modified. The resins created in the lab use polymer backbones usually polystyrene with chelating ligands such as β-diketones, dithiocarbamates, carboxylates, and Schiff bases. Examples of commercial chelating resins are Amberlite XAD-16, Chelex-100 resin, Duolite ES-346, Duolite Cs-346, and Chelilite-N, which have an affinity for a wide variety of metals ions such as Cu, Cd, Hg, Pb but not for alkali or alkaline earth metal ions [16]. Chelating resin, Chelex-100 is a widely used resin that has an affinity for many metal ions such as Hg, Cu, Pb, Ni, Cd, Zn, Co, Fe, Mn, Ca, and Mg.

The following two examples show the use of chelating resin in aqueous environments for the determination of metal concentrations. Yabutani et al. [34] used the Chelex-100 resin to monitor the dissolved and total metal concentrations of 28 metals in seawater using ICP-MS. They saw the amount of metals present in the seawater as dissolved or acid soluble fractions. They show that Mn has a large acid soluble fraction, which suggests it occurs mostly in the colloidal form of hydroxides and/or oxides.

Prabhakaran et al. [27] created a new class of resins using a modified Amberlite XAD-16 for the purpose of the extraction of transition and post transition metals (Ni, Cd, Pb, Cu, Co). Kinetics studies show that the rate of metal ion uptake was less then five
minutes except for cobalt which took 20 minutes. Their results show a 99.4-100.8% recovery of the metals from synthetic seawater. Samples were also done for river water and show R.S.D values less than 2.5%.

Expanding on forming metal chelates with resins, chelating fibers have been created, which are polymer fibers that have functional groups attached to complex the metal ions. Interest has increased in fibers because they can be used in many places such as in situ; and they have larger specific areas, which mean they have the potential to have more adsorption capacity and a higher absorption rate. The problem with chelating fibers is their high cost, the complicated process of preparation, and difficulty in keeping mechanical properties during preparation [19].

2.5 Chelex 100 Resin

Chelex 100 resin is made by BioRad Laboratories, which is a chelating ion exchange resin. Chelex 100 is a styrene divinylbenzene copolymer containing a paired iminodiacetate ion, which acts as the chelating group in binding metal ions. It has a high selectivity for divalent over monovalent ions approximately 5000:1 and a very strong attraction to transition metals.

The resin is an ion exchanger and a chelating resin; therefore, the metal exchanges with the sodium and forms a chelate. Once the metal ions complex with the resin they are relatively stable. The metal-chelate is stable due to the hydrophobic interactions between the functional group of the resin and the metal ion. Figure 8 shows the exchange that takes place between the resin and the metal ion.

Figure 8 Schematic of Ion Exchange
The actual selectivity of the metals is dependent on the systems pH, ionic strength, and the presence of other complex forming species. The following is the approximate order of selectivity of cations in a nitrate or chloride solution at a pH of about 7 [2]:

\[
\begin{align*}
\text{Cu}^{2+} & \gg \text{Pb}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Ag}^{+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \\
\text{Mn}^{2+} & > \text{Ba}^{2+} > \text{Ca}^{2+} >>> \text{Na}^{+}
\end{align*}
\]

The pH does not only affect the metal selectivity but also the functional group on the resin. Figure 9 shows how the iminodiacetate functional group changes with increasing pH.

Figure 9 Change in the Chelex 100 functional group structure with increasing pH

The Chelex resin is usually used in a column or a batch method to retain metal ions, hydrated metal ions, and weakly complexed or bound metal species that dissociate and can complex with the resin. It does not retain stable metal complexes with humic
acid or metals strongly associated with (e.g. complexed by or adsorbed on or occluded in colloidal particles [20]. Metal concentrations can be found as low as 1 ppb (ug/L).

Many procedures have been developed using Chelex 100 resin to find the metal concentration in aqueous solutions such as natural waters both salt and fresh, biological materials, and industrial. Pakalns et al conducted a column experiment were the resin was hydrated, packed, and conditioned so that the resin pH was at 4.6. The samples were filtered before they were run through the column with a 0.45um filter. The column was rinsed with nitric acid to release the metals off the resin for analysis. The metal of interest was uranium, which had a 90% recovery. They found that the type of water (saline or fresh) did not affect the recovery of the metal [25].

Greenberg and Kingston also used the resin in a column experiment with a metal standard reference solution, which was used to check the analytical procedures of their method. The resin was hydrated and packed into the column. The metal ions present in the solution complexed with the resin and the rest of the solution eluted out. Then the metals were eluted off the column by washing it with nitric acid and collecting the effluent. The certified values of the standard reference solution matched with the values obtained with the Chelex resin within 2 standard deviations. The metals that were measured were Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, V, and Zn [12].

2.6 Summary

The chemical and physical properties of the aquatic environment control the mobility of metals. Problems arise when the chemical and physical properties undergo
changes due to resuspension. These changes can cause the oxidation of metal sulfides or the oxidation of dissolved iron and manganese into iron/manganese oxyhydroxides. Therefore, after oxidation the metals release and become free ions in the water, which then can precipitate onto iron/manganese oxyhydroxides, form other metal complexes, or stay free ions. Pugh et al, Milero et al, and Ahmad and Nye suggested that the iron oxidation occurs faster than sulfide oxidation.

Many methods have been developed to predict the concentration of metals in aqueous solutions, such as the standard DRET test, SEM/AVS ratio, DGT, SPE, and chelating resins. The most widely used method to predict contaminant concentration during resuspension (dredging) is the standard DRET test. This test was developed using organics as the contaminants. It is used to determine the concentrations at the point of dredging and has been an effective method for organics, but not for metals.

Another method is the ratio of SEM/AVS. The EPA suggested using this method as a way to determine the quality of sediments and the toxicity of the sediment based on the amount of AVS to the amount of SEM metals in the sediment.

Another method is the DGT device. This method uses the accumulation of solutes by a binding agent after diffusion through a gel and placed in the sediment water interface. The method provides kinetics of metal release between the solid phase and the solution.

Another method is SPE, which isolates a target chemical species from an aqueous solution onto the solid phase that can later be eluted. It can be performed in a column, disk, or cartridge usually with a C18-silica as the sorbent. This method is better suited for cleaner systems where the devices cannot get clog with particles.
Finally, chelating resins have been used to find metal concentrations in aqueous samples due to their high selectivity and large adsorbing capacities. They are commercially made or created in a lab. The most common functional group used on chelating resins is iminodiacetate, but many others can be used.

A common chelating resin is Chelex 100 made by BioRad Laboratories. It is a styrene divinylbenzene copolymer containing a paired iminodiacetate ion, which is the chelating group used to bind the metal ions. It has a strong selectivity with divalent ions and transition metals.
Chapter 3

3 Materials and Method

The materials and method is divided into six sections: sediments; sample collection and characterization; new DRET test; resuspension experiments; instrumentation, calibration, and chemicals; and Visual Minteq. Sections one describes the sediments that were used in the study. Section two discusses how the sample sediments were collected and the methods used to characterize them. Section three discusses the method developed for the new DRET test. Section four discusses the procedure of the five resuspension experiments conducted in the study. Section five discusses the instrumentation used, how it was calibrated, and the chemicals that were used in the study. Section six discusses details about the program Visual Minteq.

3.1 Sediments

Two sediments were used: Tre pangier Bayou sediment from Norco, LA and Anacostia River sediment from Washington D.C. Tre pangier and Anacostia sediments were chosen because of their potential for serious metal contamination.

Tre pangier Bayou is part of a larger watershed called LaBranche Bayou. It is a tidal wetland stream characterized by a mixed hardwood forest with a substantial overhanging canopy, slow flow, and a clay bottom. Tre pangier Bayou received effluents from a nearby refinery for over 70 years, which resulted in chemical deposition into the sediment. Figure 10 shows a map of Tre pangier Bayou.
Anacostia River is one of the most endangered rivers in America. It is a sub-watershed within the Potomac River Drainage Basin, which in turn empties into the Chesapeake Bay. The composition of the sediment is a medium silty clay to a fine sand. The river is relatively flat and tidal; therefore, it moves and flushes itself very slowly giving it a chance for greater contamination. Long-term military use and industrial activity have contaminated the sediment with significant amounts of heavy metals, PCBs, hydrocarbons, and chlordane. Figure 11 shows a map of the Anacostia River.
3.2 Sample Collection and Characterization

Trepanier sediment samples were collected from a soft-bottom shallow water area of the bayou by Louis Thibodeaux's group from Louisiana State University. Anacostia River sediment samples were collected by partners in Hazardous Substance Research Centers-South/Southwest (HSRC). Both sediment samples anoxic character were maintained by storing them in a glove box under N₂ conditions.

The water content was found for both sediments by recording the empty weight of a 50ml glass beaker and weighing into it, 2-5g of the wet sediment and recording the weight. Then it was dried in an oven at 105°C for 48hrs. The sample was then cooled and weighed again. The difference in the weight before and after drying gave the water content of the sediment. The water content for Trepanier sediment was 84.84% and for Anacostia sediment was 42.76%.
The total metal concentrations of each sediment was determined by using EPA report # SW-846 Chapter 3.2 method 3050B, which is acid digestion of sediments, sludges, and soils. EPA states, "… that the method is a very strong acid digestion that dissolves almost all elements that could become environmentally available". The rational for using this method is that it is recognized as a robust, standard method to determine metal concentrations in sediments and soils by both industry and academics.

The procedure was

- To mix the sediment sample (to achieve homogeneity) and weigh 1.0g of sediment into a polypropylene digestion vessel to the nearest 0.01g.
- 5mL of concentrated nitric acid and 5ml of DI water were added to the vessel. The vessel was then covered with a ribbed watchglass and heated in the HotBlock™ at 95°C for 15minutes, without boiling the solution.
- The sample was then cooled and another 5mL of concentrated nitric acid was added. The sample was then heated for 30mins at 95°C. An addition 5mL of concentrated nitric acid was added and heated for 2hrs.
- After heating, the sample was completely cooled, then 2mL of DI water and 0.5mL of 30% hydrogen peroxide was added to the sample. 5-10mins passed to allow the exothermic reaction to take place before placing the sample back in the HotBlock™ with a ribbed watchglass over it at 95°C. This step was repeated two more times. The sample was heated for a total of 2hrs after the initial addition of 30% hydrogen peroxide.
- After the sample cooled, 5mL of concentrated hydrochloric acid was added. The sample was covered with a ribbed watchglass and heated at 95°C for 15mins.
- The sample was then cooled and diluted to 50ml with DI water. After dilution the sample was filtered through a 0.45um Nalgene™ syringe filter (SFCA).

After digestion, the total metal concentration was determined by ICP and ICP-MS. Treangier bayou sediments contain many metals, such as Zn, Cu, Pb, Co, As, Ni, and Cd. Table 7 shows the total metal concentration in the sediment along with other parameters.

Table 7 Total Metal Concentrations and Other Parameters of Treangier Bayou Sediment

<table>
<thead>
<tr>
<th>Metals and other parameters</th>
<th>Treangier</th>
<th>Sediment Quality Guideline (ug/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ions</td>
<td>Conc. (ug/g)</td>
<td>Conc. (umol/g)</td>
</tr>
<tr>
<td>Fe</td>
<td>88296.5</td>
<td>1582.4</td>
</tr>
<tr>
<td>Mn</td>
<td>862.2</td>
<td>15.7</td>
</tr>
<tr>
<td>Zn</td>
<td>196.4</td>
<td>3</td>
</tr>
<tr>
<td>Co</td>
<td>7.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>17</td>
<td>0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>23</td>
<td>0.4</td>
</tr>
<tr>
<td>Pb</td>
<td>281.37</td>
<td>1.4</td>
</tr>
<tr>
<td>As</td>
<td>22.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Cd</td>
<td>0.96</td>
<td>0.0086</td>
</tr>
<tr>
<td>SEMb</td>
<td></td>
<td>5.2</td>
</tr>
<tr>
<td>AVS</td>
<td></td>
<td>130</td>
</tr>
<tr>
<td>OC (%)</td>
<td></td>
<td>8.1</td>
</tr>
</tbody>
</table>

a the values are sediment quality guidelines determined by EPA that reflect probably effect concentrations
b the SEM is calculated by adding the sum of the Co,Ni,Cu,Pb,Cd,Zn ions
Anacostia River sediment contains the following metals: Fe, Mn, Zn, Cr, Co, Ni, Cu, As, and Pb. Table 8 shows the metal concentration in the Anacostia River sediment along with other parameters.

Table 8 Metal Concentrations and Other Parameters in Anacostia River Sediment

<table>
<thead>
<tr>
<th>Metals and other parameters</th>
<th>Anacostia</th>
<th>Sediment Quality Guideline (ug/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. (ug/g)</td>
<td>Conc. (umol/g)</td>
</tr>
<tr>
<td>Ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>16647.4</td>
<td>298.3</td>
</tr>
<tr>
<td>Mn</td>
<td>252.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Zn</td>
<td>336.6</td>
<td>5.15</td>
</tr>
<tr>
<td>Co</td>
<td>16.9</td>
<td>0.29</td>
</tr>
<tr>
<td>Ni</td>
<td>31.8</td>
<td>0.54</td>
</tr>
<tr>
<td>Cu</td>
<td>79</td>
<td>1.24</td>
</tr>
<tr>
<td>Pb</td>
<td>116.3</td>
<td>0.56</td>
</tr>
<tr>
<td>As</td>
<td>1.5</td>
<td>0.02</td>
</tr>
<tr>
<td>Cd</td>
<td>1.65</td>
<td>0.015</td>
</tr>
<tr>
<td>SEM&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>7.795</td>
</tr>
<tr>
<td>AVS</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>OC (%)</td>
<td></td>
<td>3.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> the values are sediment quality guidelines determined by EPA that reflect probably effect concentrations
<sup>b</sup> the SEM is calculated by adding the sum of the Co, Ni, Cu, Pb, Cd, Zn ions
3.3 New DRET Test

Laboratory scaled resuspension events were done on the Anacostia and Trepanier sediments with the pH monitored. Figure 12 is a schematic of the new DRET test.

Figure 12 Schematic of New DRET Test

- **Background Water**
  - 250mL (0.01M NaCl, 0.86 mM NaHCO₃, 0.33 mM CaCl₂)

- **Resin** (12.5g Chelex 100)
- **Sediment** (2.5g wet sediment)

  - Mix sediment, resin, and water together in a 300mL beaker with an overhead stirrer
  - Resuspend the solution for a total of 6hrs taking 20mL samples in a syringe at 10, 20, 30min followed by 1, 2, 4, 6hr
  - Push the 20mL sample through 2 sieves that are positioned above a 100mL beaker to catch the water effluent.

  - **Resin is trapped on this sieve (149um)**

  - Filter water effluent solution with 0.45um filter into 15mL centrifuge tube and acidify w/ HNO₃ by 1% volume
  - Analyze samples on ICP and ICP-MS

  - Scrape resin into a 50mL centrifuge tube add 2mL HNO₃ to resin to release the absorbed metals and heat for 30mins at 85°C. Then cool solution and dilute to 50mL.
  - Analyze samples on ICP and ICP-MS
Trepanier or Anacostia sediment slurries (2.5g) were resuspended with 12.5g of Chelex 100 resin in 250ml of artificial river water (0.01M NaCl, 0.86mM NaHCO3, 0.33mM CaCl2) by an overhead propeller stirrer. The solution was sampled as a function of time (10, 20, 30min followed by 1, 2, 4, 6hr). The pH of the solution was taken before each sampling and recorded. An Orion-Ross combination glass electrode was used to measure the pH of the solution. The glass electrode was calibrated at 25°C using pH buffers 4, 7, and 10. Samples were obtained by taking 20ml of the resuspension solution by a BD polypropylene 10ml syringe. The sample was then passed through two screen sieves and the effluent solution was captured in a beaker under the sieves. The first sieve is approximately 500um and the second 149um openings both made out of polypropylene. The large particles in the sediment are caught on the first sieve and the resin was captured on the second sieve. The resin was scraped off the screen into a 50ml polypropylene centrifuge vessel. Then 2ml of concentrated nitric acid was added to the resin and it was heated for 30mins at 85°C in a hot block to release the metals absorbed to the resin. Once the resin solution was cooled it was diluted to 50ml with de-ionized water and ICP-MS samples were prepared. The effluent that was captured in the beaker was filtered by 0.45um Nalgene™ syringe filter (SFLCA). After filtration the samples were acidified with 1% nitric acid and prepared for the ICP-MS. Samples of the resin and effluents were analyzed on the ICP-MS for Pb, Co, Cu, Ni, and Zn.

The sampling times were chosen to study the kinetics of the resuspension. Multiple sample times were needed to see if the release of the metals occurs quickly and reaches a steady concentration or if a slow release occurs. The resuspension time of six hours was chosen because dredging usually is done within an eight hour work day. The
dredging can take place for multiple days, but not for a constant amount of time, such as 24 hours.

ICP-MS samples were prepared by putting 10ml of each sample into a polypropylene centrifuge tube. The ICP-MS is equipped with a mixing block that mixes the internal standard (Ge) with the sample, so no internal standard was added to the sample.

3.4 Resuspension Experiments

Five different resuspension experiments were conducted: aerated, anoxic, microbial activity, twelve hour, and the standard DRET test. The new DRET test was used during each of the four resuspension experiments to analyze the amount of metal released.

The aerated resuspension was conducted by adding 2.5g of anoxic sediment and 12.5g of resin in 250ml of artificial river water. The resuspension solution was mixed with an overhead propeller stirrer for six hours. The samples were taken according to the new DRET test method 10min, 20min, 30min, 1hr, 2hr, 4hr, and 6hr. The samples were collected and analyzed according to the new DRET test.

The anoxic resuspension was conducted by adding 2.5g of anoxic sediment, 12.5g of resin, and 250mL of anoxic artificial river water. The artificial river water was purged with nitrogen before the resuspension and the DO was at least 1ppm. The resuspension was mixed with the overhead propeller stirrer for six hours and pumped with N₂. The sample times, the samples, and the analysis were all conducted according to the new DRET test.
The microbial activity resuspension conducted in the presence of microbes was done by adding 2.5g of anoxic sediment, 12.5g of resin, and 250mL of artificial river water. The resuspension was mixed by and overhead propeller stirrer for six hours. The sampling time, the samples, and the analysis were conducted according to the new DRET test.

The resuspension conducted in the absence of microbes was done by adding 2.5g of anoxic sediment, 12.5g of resin, and 250ml of artificial river water including 0.01M NaN3. The resuspension solution was mixed by the overhead propeller stirrer for six hours. The sampling times, samples, and analysis were conducted according to the new DRET test.

The twelve hour resuspension can be divided into two parts, though the whole resuspension took place over twelve hours. 2.5g of anoxic sediment, 12.5g of resin, and 250ml of artificial river water were resuspended by mixing the resuspension solution with the overhead propeller stirrer for six hours. A sample was taken at six hours according to the new DRET test. Then all the resin in the resuspension solution was removed by the sieves. The effluent solution (sediment slurry and artificial river water) was collected, another 12.5g of resin was added, and mixing of the resuspension solution resumed. The sampling times were 6hr10min, 6hr20min, 6hr30min, 7hr, 8hr, 10hr, and 12hr. The samples were collected and analyzed according to the new DRET test.

The standard DRET test resuspension was conducted in the following way: 2.5g of anoxic sediment and 250mL of artificial river water were mixed by the overhead propeller stirrer. The solution was resuspended for an hour in atmospheric conditions, and then the resuspension solution was allowed to settle for one hour. Samples were
taken after the resuspension settled. Two different samples were taken, first was 10mL, which was filtered by 0.45um Nalgene™ syringe filter (SFCA) and then acidified by volume to 1% nitric acid. The second was 10mL unfiltered and acidified by volume to 1% nitric acid. Both samples were analyzed by ICP-MS for Co, Ni, Cu, Pb, and Zn.

3.5 Instrumentation, Calibration, and Chemicals

An ICP-MS instrument (Perkin Elmer Sciex Elan 900) having a quadrupole type mass spectrometer was used to determine metal concentrations in the range of ppb. ICP-OES (Perkin Elmer Optima 4300DV) was also used to determine metals and other major elements in the ppm range. The ICP-MS and ICP-OES operating conditions are listed in the following table.

Table 9: ICP-MS and ICP-OES Operating conditions

<table>
<thead>
<tr>
<th>ICP-MS Perkin Elmer Elan 900</th>
<th>ICP-OES Perkin Elmer Optima 4300DV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>Plasma</td>
</tr>
<tr>
<td>Ar Gas</td>
<td>Ar Gas</td>
</tr>
<tr>
<td>Nebulizer Gas Flow</td>
<td>Nebulizer Gas Flow</td>
</tr>
<tr>
<td>0.96 L/min</td>
<td>1 L/min</td>
</tr>
<tr>
<td>Lens Voltage</td>
<td>Lens Voltage</td>
</tr>
<tr>
<td>7.50V</td>
<td>6V</td>
</tr>
<tr>
<td>ICP RF Power</td>
<td>ICP RF Power</td>
</tr>
<tr>
<td>1400W</td>
<td>750-1400W</td>
</tr>
<tr>
<td>Auto Sampler Timing</td>
<td>Auto Sampler Timing</td>
</tr>
<tr>
<td>30s wash, 40s reading</td>
<td>30s wash, 40s reading</td>
</tr>
<tr>
<td>Replicate Readings</td>
<td>Replicate Readings</td>
</tr>
<tr>
<td>3 readings</td>
<td>3 readings</td>
</tr>
</tbody>
</table>

The standards were prepared for the ICP-MS with VHG Labs multi-element environmental calibration standard containing Pb, Co, Cu, Ni, and Zn. The standard obtained from VHG Lab was a 100mg/L multi-element solution in a 5% nitric acid matrix. The standards were made by making a 0.01ppm standard stock solution of 100mL from the VHG Lab standard. Then the stock solution was diluted accordingly with DI water to 50mL solution with the desired calibration standard concentrations of 0.2, 1, 10, and 50ppb. The calibration standards were acidified to 1% nitric acid by
volume. The ICP standards were made from the same VHG Lab standard to the desired concentrations of 0.1, 10, 100ppm and also acidified to 1% nitric acid by volume. The concentrations for the calibration standards were chosen, so the standards would be above and below the concentrations of the samples.

Calibration curves were created from the standards. They always had an R value of 0.9999 or greater from the line of best fit and were determined by the Elan software program. The calibration curve was found by graphing the measured mean intensity (found by the ICP-MS) versus the concentrations of the standards. The graph was fitted with a linear line of best fit and an equation was produced. The equation was used to find the concentrations of the samples, by taking the measured intensity for the sample inserting it into the calibration equation to give the concentrations, which is done by the software. The measured intensity RSD values and the concentration RSD values for the samples were always below 5%.

The internal standard solution was prepared with a Peak Performance Ge standard at 1000ppm ± 3ppm in 2% nitric acid solution. The internal standard solution was made by diluting the original standard by Peak Performance to 40ppb using DI water. The internal standard was then acidified in 1% nitric acid by volume.

Before, each sample is analyzed by the ICP-MS or the ICP a forty second wash with 1% nitric acid by volume occurs. Then the machine flushes the sample through the line for 30 seconds before it begins to read the sample to eliminate cross contamination.

The screens that were placed in the sieves were from Small Parts Inc. They were polypropylene sheets cut to fit the diameter of the sieves. The sieves were from Bel Art Products under Scienceware® and also made of polypropylene.
Chemicals such as nitric acid and hydrochloric acid were reagent grade and purchased from Fisher Scientific. The multi element standard solutions used to make the calibration curves were prepared from VHG Labs Environmental Calibration Standard at 100ppm for ICP and ICP-MS. The chelating resin Chelex 100 was in 100-200mesh sodium form and purchased from Bio-Rad Laboratories in Hercules, California. The resin was prepared by washing it with 5L of DI water to lower its pH to 8.5.

Water used in this research was prepared by passing de-ionized water (Continental Water Co., Bedford, MA) through a Barnstead Ultrapure Mixed Bed Cartridge (Barnstead Co., Boston, MA) to remove silica and CO₂. The water was further purified with an Amberlite XAD-2 resin (Rohm & Hass Co., Philadelphia, PA) column to remove trace organic materials. Solution metal concentrations were measured on a Perkin Elmer Optima 4000 DV ICP-OES or an Elan 9000 ICP-MS. The RSD of three replicate analyses was generally below 5%.

3.6 Visual Minteq

Visual Minteq is the windows version of MinteqAQ, which was released by the U.S. EPA in 1999. It is a chemical equilibrium model that calculates metal speciation, solubility equilibria, acid and base reaction, redox reaction, adsorption modelling, etc. for natural waters. A comprehensive data base is included that is adequate for solving a broad range of problems without need for additional constants added by the user. The model has a set of pre-defined components that includes free ions (K⁺), neutral (ex., NaCl), and charged complexes (ex. Co(OH)²⁺). The data base of reactions is written in terms of the components as reactants similar to the Tableau method. The program is
supported by two Swedish research councils VR and MISTRA. Examples of calculations that Visual Minteq can do (KTH Royal Institute of Technology):

- Ion speciation using equilibrium constants
- Solubility calculations involving solid phases
- Adsorption calculations with adsorption isotherms, five surface complexation models (Diffuse Layer, Constant Capacitance, Triple Layer, Basic Stern and Three Plane), with the 1-pK or 2-pK formalisms,
- Ion-exchange calculations using the Gaines-Thomas formalism
- Metal-humic complexation can be simulated using the Gaussian DOM, the Stockholm Humic Model, or the NICA-Donnan model.
- Calculations with redox couples and gases
- Sweep runs in which one parameter is varied, e.g. pH or the total concentration of a component.
- Titrations in which a titrant with a given composition is added in steps to the original solution.
Chapter 4

4 Results and Comments

Results and comments is divided into seven sections: composition of metals in the sediment; kinetics of metal release; resuspension experiments; effects of parameter changes on the new DRET test; new DRET test vs. standard DRET test; comparison of metal concentrations for the water column, available metals, and sediment; and a summary. Section one shows the elements found in the Tre pangier and Anacostia sediments. Section two shows the amount of available metals released as a function of time. Section three shows the metal concentrations for the three resuspensions. Section four shows the affects of two parameter changes on the new DRET test. Section five shows the difference in the metal concentrations between the new DRET test and the old DRET test. Section six shows a comparison of the metal concentrations found in the water column, by the new DRET test, and in the sediment.

4.1 Composition of Metals in the Sediment

Both, the Anacostia and Tre pangier sediments have received metal contamination for many years from industry or military. These sources have caused some of the metal concentrations to be over sediment quality guidelines. Figure 13 shows the composition of the metals and other parameters in the sediments.
Figure 13 Composition of Metals in Trengangier and Anacostia Sediments

Pb in the Trengangier sediment is the only metal higher than the SQG; however, in the Anacostia sediment Pb is the same concentration as the SQG. Ni, Cu, and Zn (Anacostia sediment) and As (Trengangier sediment) also have a comparable value to the SQG. Trengangier has a higher concentration of S than Anacostia; however, Trengangier has a higher organic content (OC) than Anacostia.
Figure 13b shows the composition of elements in the water of Anacostia and Tre pangier.

**Figure 13b Composition of Water in Anacostia and Tre pangier**

Other parameters for Tre pangier were a pH of 7.08, conductivity of 5870μS/cm, chloride 1760 mg/L, and alkalinity of 447mg/L CaCO₃. Other parameters for Anacostia were a pH of 8.50, conductivity of 525μS/cm, chloride 25mg/L, and alkalinity of 125mg/L CaCO₃.

### 4.2 Kinetics of Metal Release

The resuspension experiments had samples taken as a function of time, which allowed the kinetics of the available metal concentration to be studied. The available metal concentration is the total amount of metal released into the water column and onto the resin per gram of sediment. Equation 8 is used to calculate the available metal concentration

\[
\text{Available Metal Conc (ug / g)} = \frac{(w \times V_s) + (r \times Vr)}{M \times \% \text{solid} \times \frac{V}{V_s}}
\]  

(8)
w is the metal concentration in the water by ICP-MS(ug/L), r is the metal concentration on the resin by ICP-MS(ug/L), Vs is the sample volume(0.02L), Vr is the volume of the resin solution(0.05L), M is the mass of wet sediment used in the resuspension(2.5g), %solid is the amount solid in the sediment slurry, and V is the volume of the resuspension solution(0.25L). The resuspensions sampling times were 10mins, 20mins, 30mins, 1hr, 2hr, 4hr, 6hr. Figure 14 shows the changes that occurred in the available metal concentrations over the six hour resuspension for the Anacostia sediment.

Figure 14 Anacostia Sediment Kinetic Release

![Graph](image1)

![Graph](image2)
The release profile of each metal is different, especially in the first hour. Co, Pb, and Cu concentrations at 10mins are the highest in the first hour and slowly decrease as they approach an hour. The available metal concentrations of Zn and Ni increase from time zero to 20 minutes and then decrease through the rest of the first hour. For all of the metals, except Zn, the concentrations begin to increase again at one hour and become steady by the fourth hour until the end of the resuspension. Zn increases again at two hours and continues to increase till the end of the resuspension; it does not appear to become steady.

Figure 15 Trepangier Kinetic Metal Release

For Co, Ni, Pb, and Cu, at ten minutes the available metal concentrations are the highest then slightly decrease and reach a steady state concentration by one hour. For Zn, the available metal concentration is the highest at ten minutes then decreases and becomes steady at thirty minutes. The highest concentration for Pb is the initial concentration at ten minutes then the concentration fluctuates throughout the resuspension.
Figure 14 shows an initial burst within the first ten minutes of the resuspension and the available metal concentration becomes relatively steady by two hours. Figure 15 also shows and initial burst within the first ten minutes but the available metal concentrations become relatively steady by the first hour in the Trengangier sediment. These observations suggest that an initial release occurs when the anoxic sediment is introduced into oxic conditions. Since, the new DRET test resin is in-situ it allows the available metal concentration to be observed over time and the impact of changing conditions during the resuspension.

4.3 Resuspension Experiments

Four types of resuspension experiments were conducted to see how different parameters would affect the metal release. They were aerated conditions; anoxic conditions; microbial activity; and twelve hour resuspension. The experiments compare the available metal concentration and the concentration of metals in the water column. The available metal concentration is defined in equation 8. The water concentration is reported in ug/g instead of ug/L, so it can be compared to the sediment concentrations.
The pH of the resuspensions ranged from a starting value of about 9.7 and fell to about 9.08 after six hours. The motivation for doing the resuspension experiments with the new DRET test was to later compare the available metal results with the standard DRET test, metal concentrations in the sediment, and metal concentrations in the water.

4.3.1 Aerated vs. Anoxic

Aerated and anoxic resuspension experiments were done to see if the presence or absence of oxygen in the system affects the available metal concentrations. The experiments were conducted for six hours by stirring the solution with the overhead propeller under atmospheric conditions. The anoxic resuspension experiments were done by stirring the solution with the overhead propeller and sparging the system with nitrogen gas to remove the oxygen. The DO was checked periodically to make sure the oxygen was removed from the system. The average DO concentration during the resuspensions was 2mg/L.

Figure 16 shows the concentrations of available metal during the aerated and anoxic resuspension of Anacostia sediment.
Figure 16 Anacostia Sediment Resuspension of Aerated vs. Anoxic

The aerated concentration is always higher than the anoxic (P-value = 0.038 by paired t-test). For Co, the aerated and anoxic resuspension available metal concentrations are similar (aerated 0.79ug/g and anoxic 0.70ug/g). Ni, Cu, Pb and Zn available metal concentrations are comparable between the aerated and anoxic resuspension. The difference is about 2ug/g. Zn is the most available and also the most abundant metal out of the five tested (refer to table 7 and figure 13). The standard error replicate determinations for the metals under aerated conditions is Co 0.0295, Ni 0.6, Zn 2.055, Pb 0.725, and Cu 0.051.

The P-value for figure 16 shows the aerated and anoxic available metal concentrations are not similar, which is to be expected. These resuspensions were conducted using the new DRET test. The aerated available metal concentrations are later compared with the standard DRET test, the total metal concentrations in the sediment, and the metal concentrations in the water. The comparison of the new DRET test aerated
available metal concentration with metal concentrations from the other procedure is discussed in more detail in sections 4.5 and 4.6.

Figure 17 shows the concentrations of the metals in the water column during the aerated and anoxic resuspension.

Figure 17 Anacostia Sediment Water Column Concentrations

<table>
<thead>
<tr>
<th>Available Metal Conc µg/g</th>
<th>aerated</th>
<th>anoxic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Pb</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Co and Pb concentrations are about the same in both the aerated and anoxic resuspensions. For Ni and Cu, and Zn, the metal concentrations in aerated conditions are approximately 0.4µg/g higher than in the anoxic conditions. The P-value is 0.078 between the aerated and anoxic concentrations of the metals by paired t-test. The standard error for the metals under aerated conditions is Co 0.019, Ni 0.177, Zn 0.0435, Pb 0.071, and Cu 0.11.

Figure 17 shows that there is a similarity between the aerated and anoxic available metal concentrations in the water. The similarity may be due to the small amount of metals that is found in the water during the resuspension, which might be due to the length of the resuspension. A six hour resuspension may not be long enough to be able to
see the difference in the concentrations. The aerated available metal concentrations are later compared to the standard DRET test in section 4.5.

Figure 18 shows the available metal concentrations in Tre pangier sediment for the aerated and anoxic resuspensions.

Figure 18 Tre pangier Sediment Resuspension of Aerated vs. Anoxic

![Tre pangier Sediment](image)

The aerated concentration is higher than the anoxic concentration, except for lead. The P-value is 0.364 between the aerated and anoxic metal concentrations by paired t-test. The aerated available metal concentrations for Ni, Zn, and Cu are about two times higher than the anoxic available metal concentrations. For Co the aerated concentration is about three times higher than the anoxic concentration. Pb has the highest available metal concentration out of the five metals tested and also the highest metal composition in the Tre pangier sediment (refers to figure 13 and table 7). The standard error for the metals under aerated conditions is Co 0.155, Ni 0.885, Zn 9.11, Pb 1.5, and Cu 2.46.

Figure 18 shows that the aerated and anoxic available metal concentrations are very similar in the Tre pangier sediment. The concentrations could be similar because
Tre pangier sediment has a high sulfide concentration and since the pH does not drop close to acidic conditions, the metal release may be limited and cause the concentrations to be similar. Gao et al. observed peak concentrations occurring after 1 to 2 days were pH conditions were around 4.3. The aerated available metal concentrations are compared later with other metal concentrations in section 4.5 and 4.6.

Figure 19 shows the metal concentration in the water column of Tre pangier sediment for both the aerated and anoxic resuspension.

Figure 19 Tre pangier Sediment Metal Concentration in the Water Column

![Tre pangier Water Concentration Graph]

For Co and Ni, little variation exists between the aerated and anoxic metal concentrations, about 0.3ug/g. For the remaining metals, Cu, Pb, and Zn, about 2ug/g difference exists between the aerated and the anoxic metal concentrations. The P-value is 0.50 between the aerated and anoxic metal concentrations by paired t-test. For Cu, Co, and Zn, the metal concentration is higher in aerated conditions than anoxic conditions; however, for Pb and Ni the opposite is true. The standard error for the metals under aerated conditions is Co 0.011, Ni 0.0063, Zn 0.033, Pb 0.331, and Cu 0.487.
Figure 19 shows the aerated and anoxic available metal concentrations are similar. The reason for this might be due to pH and the length of the resuspension. Since the pH does not decrease a lot during the length of the resuspension this may cause the available metal concentrations to be similar. The aerated available metal concentration is used for comparison later in section 4.5 with the standard DRET test.

Figure 20 shows a comparison of the aerated and anoxic resuspensions of the two sediments.

Figure 20 Aerated vs. Anoxic for Anacostia and Tre pangier Sediments

The available concentrations of Co are nearly identical for both sediments in all conditions except in Tre pangier aerated. For the rest of the metals the available metal concentrations are not comparable between the two sediments. Tre pangier sediment release has significantly more metal ions than Anacostia sediments. The P-value for Anacostia versus Tre pangier paired samples is 0.043, suggesting that Tre pangier sediment releases more metals than Anacostia sediment. This is surprising because the Tre pangier sediment has more AVS than the Anacostia sediment and AVS is proposed as
a strong heavy metal sink. The greater release of metals from Trepanier sediment might be related to the lower pH values of the original porewater even though the pH during the resuspensions is similar.

Figure 21 shows a comparison of the metal concentrations in the water column in aerated and anoxic conditions between Anacostia and Trepanier sediments.

For Co, the metal concentration did not vary much between the two resuspensions or the sediments except for Trepanier aerated. For the other metals, variation exists in the metal concentration depending on the resuspension condition and the sediment. For Cu and Zn, the aerated resuspension had higher concentrations than the anoxic resuspension for both sediments. The P-value is 0.0083 between the Trepanier and Anacostia available metal concentrations, using a paired t-test. Therefore, there is no similarity in available metal concentrations between Trepanier and Anacostia. Trepanier releases more metal ions than Anacostia even though its AVS/SEM ratio is greater than 1. The metal concentrations in the water column are considerably lower than the available metal concentrations seen in Figure 20.
4.3.2 Microbial Activity

Resuspension experiments were done to see the effect of microbial activity on the available metal concentration in Anacostia and Trengangier sediments. The resuspension experiments conducted in the presence of microbes were done by stirring the resuspension solutions with the overhead propeller in atmospheric conditions. The resuspension experiments conducted in the absence of microbes were done by using 0.01M NaN₃ as part of the artificial river water solution to quench microbial activity. Figure 22 shows the available metal concentrations for Anacostia sediment with and without the addition of sodium azide.

Figure 22 Anacostia Sediment Microbial Activity

The available metal concentration is higher with NaN₃ in the solution. For Co and Ni the concentrations are comparable with and without NaN₃. The Pb available metal concentration is about 1.5 times larger with NaN₃. The Cu available metal concentration with NaN₃ is about two times larger than without NaN₃. The P-value is 0.178 between available metal concentration with or without NaN₃ by paired t-test.
Figure 23 shows the metal concentration in the water column during resuspension with and without NaN₃.

Figure 23 Effect of Microbial Activity on Metal Concentration in Anacostia Water Column

![Anacostia Microbial Activity Water Concentration](chart)

For Co and Cu, the metal concentration is comparable with or without NaN₃. For Ni the concentration is approximately 1.5 times higher without the addition of NaN₃. For Pb the concentration is about 2 times higher with NaN₃ in the solution. NaN₃ has a greater effect on the Pb concentration than Co, or Cu concentration. The P-value is 0.592 between available metal concentration with or without NaN₃ by paired t-test.

Figures 22 and 23 show the available metal concentrations with and without NaN₃ are similar, which suggest that oxidation is not increased by microbes during the six hour resuspension.
Figure 24 shows the available metal concentration for Treangenier sediment with
the addition or absence of NaN₃ in the solution.

Figure 24 Treangenier Sediment Microbial Activity

For Co, the available metal concentration is not affected by the addition or absence of
sodium azide in the solution. For Ni and Cu, the concentrations are comparable with or
without NaN₃. For Pb, the difference in the available metal concentration is about 15ug/g
higher with NaN₃. The P-value is 0.328 between available metal concentration with or
without NaN₃ by paired t-test.
Figure 25 shows the effect of NaN$_3$ on the metal concentration in the water column for Trengangier sediment.

Figure 25 Effect of Microbial Activity on Metal Concentration in Trengangier Water Column

![Graph showing metal concentration](image)

For all the metals the concentration is the same with or without NaN$_3$. The addition or absence of sodium azide does not effect the metal concentrations in the water column. The P-value is 0.442 between available metal concentration with or without NaN$_3$ by paired t-test.

Figures 24 and 25 show the addition or absence of NaN$_3$ does not seem to affect the available metal concentrations, which are very similar. The similarity in available metal concentrations maybe due to the fact, that within a six hour resuspension the microbes do not increase the sulfide oxidation that occurs in Trengangier sediment [9].
Figure 26 compares the two sediments and the influence of microbial activity on the available metal concentration.

Figure 26 Microbial Activity in Anacostia and Tre pangier Sediment

For Co, the available metal concentration was not affected by the presence or absence of sodium azide for both sediments, the concentrations are comparable. For the rest of the metals the concentrations are not comparable between the sediments. Tre pangier has higher metal concentrations, especially for Pb. The P-value is 0.092 between the available metal concentrations of Tre pangier and Anacostia sediment with and without NaN3 by the paired t-test. The P-value suggests there is some similarity in the available metal concentrations between the Tre pangier and Anacostia sediment. This is surprising since the Tre pangier sediment seems to release more metal ions than the Anacostia sediment.
Figure 27 shows the effect of sodium azide on the metal concentrations in the water column between the two sediments.

Figure 27 Microbial Activity Resuspension of Metal Concentrations in the Water Column

The available metal concentrations are not comparable for any of the metals between the sediments (P-value = 0.025 by paired t-test). The P-value suggests there is no similarity in the available metal concentrations between Trepanier and Anacostia, since Trepanier releases more metal ions than Anacostia.

4.3.3 12hr. Resuspension

Twelve hour resuspension experiments were conducted on both Anacostia and Trepanier sediments. The reason they were conducted was to see what happened to the available metal concentration after six hours. Figures 28 and 29, shows the available metal concentrations for the last six hours of the twelve hour resuspension. The available metal concentration for the twelve hour resuspension was found by taking the concentration at six hours and adding the concentrations found at each time interval.
For all of the metals, the pattern of release for the available metal concentration is the same. Within the first hour the concentration peaks at 6hr10mins then decreases slightly and begins to increase again. The concentrations continue to increase gradually almost reaching a steady concentration by the twelfth hour.

For Pb and Zn, the pattern of release is the same. The Pb and Zn concentration from six hours to seven hours makes two humps as the concentration increases and decreases. After seven hours the concentration gradually increases and reaches a steady
concentration. Cu and Ni also follow the same release pattern. The concentration increases from the sixth hour then slightly decreases and remains relatively steady till the end of the resuspension. For Co, the available metal concentration stays relatively the same throughout the resuspension.

For figures 28 and 29 the similar release pattern for the available metals is unique and it is not certain why this occurs. It could be due to the resuspension being stopped and started again or that the metals are undergoing similar re-adsorption or co-precipitation. The new DRET test allows measurements of the kinetics that are occurring in-situ. The resin does not appear to reach its maximum adsorption capacity by six hours so new resin may not need to be put into the solution to observe resuspension effects for twelve hours.

4.4 Effects of Parameter Changes on the New DRET Test

Different parameters of the new DRET test were changed to see the effect on the available metal concentrations and if certain steps were necessary. The first parameter changed was to eliminate heating the resin and nitric acid solution. The purpose of heating was to have a complete release of the metals from the resin. Figure 30 shows a comparison of the available metal concentration with heating and without heating.
For Co and Ni the effect of not heating the resin and nitric acid solution is almost negligible on the available metal concentration. For Pb and Zn the available metal concentrations 15ug/g higher with heating but for Cu it is only 3ug/g. The P-value is 0.11 between the available metal concentration for heating and not heating the resin solution by the paired t-test, which suggest the available metal concentrations are similar. This is mostly likely due to the fact that nitric is strong enough to release the metals from the resin and the extra heating does not do anything to increase the amount of metals released.

The second parameter that was changed was the amount of resin that was initially added to the resuspension solution. Initially, the amount was 12.5g and changed to 10g. The reason for changing the amount of resin was to see if 12.5g was needed or could a smaller amount be used and give the same available metal concentrations. 10g of resin was chosen because 10g was a smaller amount but still enough for seven samples to be
collected. Figure 31 compares Trepagier sediment resuspension with 10g of resin to 12.5g.

Figure 31 Trepagier Sediment Effect of Resin Mass

For Co and Ni changing the amount of resin had a small affect on the available metal concentration. For Zn and Pb the metal concentrations are different by about 20ug/g and for Cu about 6ug/g. The P-value is 0.671 between the available metal concentration for 12.5g and 10g of resin in the solution by the paired t-test, which suggest the concentrations are very similar.

4.5 New DRET Test vs. DRET Test

Resuspensions were done using both the new DRET test and the standard DRET test. The resuspensions were both aerated resuspensions of Anacostia and Trepagier sediments. Figure 32 compares the available metal concentrations found by the new DRET test versus the standard DRET test for Anacostia sediment.
The filtered samples by the standard DRET test do not give significant available metal concentrations, for example, the lead concentration is only 0.06ug/g. The new DRET test water column metal concentrations are quite small compared to the unfiltered samples of the standard DRET test and the available metal concentration of the new DRET test, though they are larger than the metal concentrations in the filtered samples of the standard DRET test. The unfiltered samples by the standard DRET test have higher available metal concentrations than the new DRET test, except for Ni. For Zn and Pb, the available metal concentrations are larger especially for the unfiltered standard DRET test. The unfiltered standard DRET test available metal concentrations are 1.7 to 2 times higher compared to the new DRET test, except for nickel.

Figure 33 compares the standard DRET test versus the new DRET available metal concentration in Trepaniguer sediment.
Figure 33 Comparison of new DRET vs. standard DRET test Tre pangier Sediment

The available metal concentration in the filtered sample of the standard DRET test is insignificant, for example, the copper concentration is only 0.031ug/g. The water column metal concentrations from the new DRET test are small, especially for Co and Ni. For Cu, the water column metal concentrations by the new DRET test are larger than from the standard DRET test unfiltered. The new DRET test has higher available metal concentrations than the standard DRET test unfiltered samples. The available Pb concentration for the new DRET test is about four times larger than standard DRET test. The available Ni concentration for the new DRET test is about 20 times larger than the standard DRET test; for example Ni is 0.143ug/g in the unfiltered DRET and 2.944ug/g in the new DRET.

The standard DRET test has inconsistencies in predicting the amount of metals that might be available to biota; it allows the resuspension solution to settle after it has been mixed to simulate a resuspension. The standard DRET test is a short term test, 1 hr, and may not accurately simulate what occurs during a long term resuspension. The
standard DRET test was shown by DiGiano et al. [7] to overestimate expected release of contaminants.

The inconsistencies in the standard DRET test can be seen in figures 32 and 33. It would be expected that the standard DRET unfiltered would be higher than the nDRET available but this is not true. The reason why it would be expected that the standard DRET unfiltered would have a higher concentration than the nDRET available is because the standard DRET test has been shown to overestimate the contaminants release and also because it is an unfiltered sample so it would be assumed that the concentration would be closer to what the sediment metal concentration is. However, with Trepanier sediment the nDRET available metal concentration is higher than the standard DRET unfiltered for all the metals. In Anacostia sediment the standard DRET unfiltered is higher than the nDRET available, except Ni. Therefore, the standard DRET test does not always overestimate expected metal release as claimed by DiGiano et al [7].

The standard DRET filtered and the nDRET water column concentrations should be very similar since both samples were filtered by a 0.45um filter taken from the resuspension solution. The only difference in the samples is that the standard DRET filtered was allowed to settle before a sample was taken and the nDRET water column was taken during the resuspension. However, the standard DRET filtered and the nDRET water column do not have similar metal concentrations, the standard DRET filtered metal concentration is much lower than the nDRET water column metal concentration, which suggests that allowing the resuspension solution to settle according to the standard DRET test affects the observed concentration of metals released and does not express a true picture of the available metals to the biota.
The variation between the Anacostia and Treponger sediment standard DRET concentrations suggests that the standard DRET test is not a reliable test to predict the amount of available metals released. The new DRET test mixes the resuspension solution to simulate a resuspension event and takes the samples while the solution is mixing. Chelex 100 resin is put in the resuspension solution. Having the resin in the resuspension solution might simulate what the biota could come in contact with and what is available to the biota. The new DRET test allows for the varying properties of the sediment to be reflected by the resin adsorbing what is released by the specific sediment, which is the available metal concentration.

4.6 Comparison of Metal Concentrations in the Water Column, Available Metals, and Sediment

Tables 10 and 11 compare the different concentrations of the metals based on where the sediment sample is taken. The water column and the sediment metal concentrations are both used to predict the amount of metals released. The available metal concentration is what is used in the new DRET test to predict the available metal concentrations during resuspension.

<table>
<thead>
<tr>
<th></th>
<th>Concentrations (μg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water Column</td>
</tr>
<tr>
<td>Co</td>
<td>0.065</td>
</tr>
<tr>
<td>Ni</td>
<td>0.48</td>
</tr>
<tr>
<td>Cu</td>
<td>1.025</td>
</tr>
<tr>
<td>Pb</td>
<td>0.415</td>
</tr>
<tr>
<td>Zn</td>
<td>0.65</td>
</tr>
</tbody>
</table>
The metal concentrations are quite different between the water column, available metals, and the sediment. The sediment has the highest concentration and the water column has the lowest concentration. The available metal concentration is between the two. For example, the available metal concentration of Co is 12 times larger than the water column concentration, while the sediment is 21 times larger than the available metals concentration.

Table 11 Trepangier Bayou Comparison of Metal Concentration

<table>
<thead>
<tr>
<th></th>
<th>Concentrations (ug/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water Column</td>
</tr>
<tr>
<td>Co</td>
<td>0.066</td>
</tr>
<tr>
<td>Ni</td>
<td>0.161</td>
</tr>
<tr>
<td>Cu</td>
<td>0.925</td>
</tr>
<tr>
<td>Pb</td>
<td>1.025</td>
</tr>
<tr>
<td>Zn</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Again the concentrations are different between the water column, available metal, and the sediment concentrations. The water column has the lowest concentration of metals and the sediment has the highest metal concentration. The available metal concentration lies between the two. For example, Cu has an available metal concentration about 19 times larger than the water column concentration, while the sediment concentration is about 1.3 times larger than the available metals concentration.

There are shortcomings in using the sediment metal concentration and the water column metal concentration as indicators of the amount of metals that may be released and available to biota. This can be seen in tables 10 and 11. According to Berry et al. [1], “Numerous studies have shown that dry weight concentrations of metals in sediments cannot be used to predict toxicity across sediments.” The sediment metal concentration is
not a realistic indicator of the available metals, since it considers the total amount of metals in the sediment. During a resuspension the total amount of metals in the sediment will not be released so this is not a reflection of what is available to biota.

Also the water column metal concentration is also not a realistic predictor for the amount of metals available to biota. The water column metal concentration is usually filtered so only free metal ions are considered in the metal concentration and not metal complexes or particles that might also be available. It is usually an underestimate of the amount of metals released during a resuspension. When metals are released during a resuspension they can re-adsorb onto other particles and complexes, which still might be available, but the water column metal concentration does not consider this.

As seen in tables 10 and 11 the sediment metal concentration is higher than the available metal concentration and the water column metal concentration is lower. Both the sediment and water column metal concentration over an underestimate what could be available to biota during a resuspension. The available metal concentration that is gotten from the new DRET test considers metal ions, hydrated metal ions, and weakly complexed and bound metal species; therefore the available metal concentration more realistically express what is available to biota by considering many metal ions and metal species but not everything. The available metal concentration by the new DRET test might be a good predictor of the amount of metals that will be available to biota because the resin simulates what the biota could come in contact with by retaining the metals that are released. Therefore, the new DRET test provides realistic metal concentrations that can be released and might be available to biota.
4.7 Summary

The results were divided into five major areas: the metal composition in the sediment, kinetics of metal release, the resuspension experiments, the effects of changing parameters on the new DRET test, and a comparison of the new DRET test versus the standard DRET test. The composition of the metals in the sediment showed Pb was above the SQG for Tre pangier and the same for Anacostia. The composition of the sediments showed that Tre pangier had a much higher sulfur concentration than Anacostia and for the OC the opposite was true.

The kinetics of metal release showed repeatable release patterns among the metals. For Anacostia all of the metals seemed to reach a steady concentration as they reached the sixth hour of the resuspension, except for zinc, which kept increasing. In Tre pangier sediment, a similar pattern of release was exhibited and all the metals reached a steady concentration by the sixth hour, except Pb. Pb had more variation in its release.

Five types of resuspension experiments were conducted: aerated resuspension, anoxic resuspension, resuspension without sodium azide, resuspension with sodium azide, and a twelve hour resuspension. The aerated and anoxic resuspensions did not have a significant difference in the available metal concentrations between the sediments. The metals that seemed to vary the most in their concentrations were Pb and Zn. The resuspensions done dealing with microbial activity; the available metal concentrations were not significantly different in the presence or absence of NaN₃, except for Cu and Pb. The twelve hour resuspension experiment showed similar patterns of release for the metals.
Two parameters were changed in the test: using heat to release the metals from the resin and the amount of resin used. Not heating the sample and reducing the amount of resin used had no significant affect on the available metal concentration.

The comparison of the DRET tests showed the standard DRET test had higher available metal concentrations for the unfiltered samples than the new DRET test for Anacostia sediment. For Trenganger sediment, the new DRET test’s available metal concentrations were higher than the filtered and unfiltered samples of the standard DRET test. For Trenganger and Anacostia sediments, the filtered standard DRET test concentrations were insignificant.
Chapter 5

5 Discussion and Conclusion

The discussion and conclusion chapter is divided into six sections: resuspension experiments; comparison of metal concentrations in the water column, available metals, and sediment; comparison of the new DRET test to the standard DRET test; comparison of new DRET test with other methods; Visual Minteq calculations; and the conclusion. Section one discusses the kinetics of metal release, the aerated vs. anoxic resuspension, the microbial activity, and the twelve hour resuspension. Section two compares the concentrations of the metals in the water column, available metals, and the sediment. Section three discusses the results obtained from the two DRET tests. Section four compares the new DRET test with other methods used to find the metal concentration in aqueous environments. Section five illustrates using Visual Minteq to model the resuspension experiments and then comparing them to experimental results. Section six discusses the conclusions drawn from the results.

5.1 Resuspension Experiments

Section one is divided into four sub sections: kinetics of metal release, aerated vs. anoxic resuspension, microbial activity, and twelve hour resuspension. Sub-section one discusses the amount of available metals released and the impact of time on the release. Sub-section two compares the amount of available metals released under each resuspension condition. Sub-section three discusses the affect of microbial activity on
the amount of metals released. Sub-section four discusses the amount of metals released in 12 hours and the impact of time on the release.

5.1.1 Kinetics of Metal Release

The reason for studying the kinetics of metal release is to see how the metal concentrations change over time and are affected by changing conditions, such as exposing an anoxic system to an oxic system. The sampling times were chosen to cover the entire resuspension with an emphasis on the first hour to be able to see the initial affects of changing conditions on the metals release. Anacostia and Tre pangier sediments kinetics were studied to see the impact of time and conditions on release.

In Anacostia sediment, the pattern of metal release is very similar. A slow release does not appear to occur, the metals release within the first ten minutes and stay relatively close to that concentration, which suggests an initial release occurs when the anoxic sediment is exposed to the oxic water column. The reason for the relatively stable concentrations could be the available metal concentration considers both the free metal ions and weakly bonded metal complexes, so a steady concentration is seen as metals release, become free, or re-absorb or co-precipitate to particulate matter. Zn is the only metal that does not appear to reach a steady concentration. The Zn concentration decreases from its initial burst, but increases when the other metals are reaching a steady concentration. It can be strongly affected by the presence of complexing ligands and competing ions; therefore, when the other metals reach a steady release its concentration increases, since it does not have to compete with other ions or ligands.
In the Trepanier sediment, the kinetics of the metals release shows it reaches a relatively stable concentration after the initial burst. For Pb and Zn, the initial concentration at ten minutes is the highest concentration over the six hour resuspension. For Co, Ni, Cu, and Zn, the concentration becomes steady by thirty minutes. The available metal concentrations do not increase slowly, within the first ten minutes they have reached a moderate concentration and remain there. Like in the Anacostia sediment, the initial burst suggests metals are being released when exposed to the oxic conditions. A reason the metal concentration may become stable is the iron and manganese oxyhydroxides are oxidizing faster than the metal sulfides; therefore, when the metals become free they complex to the oxyhydroxides or re-absorb to particulate matter after their initial release due to the oxidation.

Pb is the only metal that does not reach a steady concentration, but fluctuates throughout the resuspension. A reason for the fluctuation could be Pb specifically adsorbs to oxides or the lattice structure of the sediment. Specific adsorption is a stronger interaction than electrostatic interactions.

5.1.2 Aerated vs. Anoxic Resuspension

Two resuspension experiments compared whether aerated or anoxic conditions affect the amount of metals released. The aerated resuspension mixes the solution in contact with air. The anoxic resuspension mixes the solution keeping it under nitrogen conditions. The expected results, based on literature [9], show the aerated resuspension concentration is much greater than the anoxic resuspension concentration. However, the
results showed the available metal concentrations were similar between the aerated and anoxic resuspension but the aerated available metal concentration is higher.

For Co, Ni, Pb, and Zn, the concentrations of the metals are strongly controlled by the adsorption and co-precipitation reactions with the iron/manganese oxyhydroxides and clay. Cu is impacted by its complexation to organic matter. The re-adsorption of metals could be occurring rapidly because of the formation to oxyhydroxides and clay particles that no difference is seen between what is sorb during anoxic conditions compared to what is being re-adsorbed during aerated condition. The Cu concentrations remain the same, since the predominate complexation of Cu is to organic matter.

Gao et al. found that during a seven day resuspension the peak metal concentration was observed between one and two days. Therefore, a six hour resuspension may not reveal the maximum amount of metal that can be released, which is supported by the twelve hour resuspension. The concentrations between the two resuspensions are similar, which suggests the length of the resuspension is important to the amount of metals released into the environment.

The pH remained stable throughout both resuspensions, above 8.5; therefore, acidic conditions, which could cause more metals to be released, did not occur. Trepanier sediment has a high sulfide concentration and since the pH did not drop substantially, the metal release may be limited and cause the concentrations to look similar to concentrations found during the anoxic resuspension.

An explanation for the Zn concentration being higher in the aerated resuspension is that Zn sorption is dependent on the size of the particles and adsorbs more to smaller particles. During the aerated resuspension, larger particles can form since
iron/manganese hydroxides form large aggregates, other metals sorb to the aggregates causing more zinc to be released.

The available metal concentrations and the water column concentrations between the two resuspension were not drastically different due to the length of time of the resuspension, complexation, adsorption of ions, and no acidic conditions. Also, the concentrations being similar between the two resuspensions suggest mixing may have an affect on the release of metals.

5.1.3 Microbial Activity

The effect of microbial activity was studied by conducting two experiments with and without NaN₃ in the solution; NaN₃ is a bacterial inhibitor. The available metal concentrations for Anacostia and Trepanier sediments are not significantly different with or without NaN₃ in the solution. The addition of NaN₃ does not seem to have a strong affect on the concentrations but the concentrations are higher with the addition of NaN₃.

In the Anacostia sediment, the available metal concentrations are the same for Co and Ni, but for Pb and Cu the concentration is higher in the resuspension with NaN₃. A reason the metals could be unaffected by the addition of NaN₃ is the re-adsorption that can occur to iron/manganese oxyhydroxides or the strong complexation to other species, such as clays or organic matter. Another reason the concentrations could be similar is that six hours might not be long enough to see increased sulfide oxidation from the enhancement of microbial activity for Co, Ni, Pb, and Zn. This occurs when microbes are exposed to oxic conditions incubation can improve and enhance the microbial
activity, which is believed to help in the oxidation of metal sulfides. Microbes are believed to stimulate the oxidation of AVS, which then causes metals (Co, Ni, Zn) to release since the metals dissociate from the sulfide. But, the results show that increased oxidation of AVS by microbes is not occurring in the six hour resuspension since the concentrations of the metals are not higher without NaN₃ then with NaN₃.

The Cu concentration is higher with the addition of NaN₃ in the Anacostia sediment. Cu is known to form strong complexes with dissolved organic matter. Dissolved organic matter (DOM) is produced by the decomposition of high molecular weight organic matter and is consumed by microbes. Gao showed during a resuspension that both the Cu and DOM concentration increase without microbes and with microbes the Cu concentration increases as the DOM concentration decreases. The addition of NaN₃ causes greater release of Cu due to its complexation with dissolved organic matter.

In Trepanier sediment, the available metal concentrations are very similar for Co, Ni, and Cu with and without NaN₃. The Pb concentration with NaN₃ is slightly higher than without NaN₃ in solution. Trepanier sediment has a higher sulfide concentration than Anacostia; therefore, oxidation of the AVS should cause a greater release of metals. However, the available metal concentration was not affected by the presence or absence of microbes but remained the same. The available metal concentration does not change, which suggests increased oxidation of AVS by microbes is not occurring during the six hour resuspension. Gao’s resuspension experiments with microbial activity showed affects at one to two days.

The metal concentration in the water column seemed to be unaffected by the presence or absence of microbes, except for Pb in the Anacostia sediment. The increased
oxidation that is supposed to occur due to microbial activity does not appear to be happening at least in the six hour resuspension. The release of metals is occurring most likely due to the oxidation of sulfides but does not appear to be increased by the presence of microbes in the environment. The Pb concentration can be affected by the formation of complexes with organic matter especially humic acid, which has been shown to increase the sorption of Pb to sediments.

5.1.4 12 hour Resuspension

The twelve hour resuspension experiment shows the impact of time on metal release and shows the resin does not always get the same concentration, but reflects the concentration in the solution. In the Anacostia and Trepanier sediment, the available metal concentration only increased by a factor of approximately 1.5 by the end of twelve hour resuspension. Most of the metals reached a steady concentration by the seventh hour. The results were unique and showed similar release patterns for all the available metal concentrations. The reason the same release pattern is occurring during the last 6 hours of the resuspension is not completely understood. One reason could be the resuspension was stopped for a few minutes and restarted causing a similar release to occur. Another reason could be for all the metals similar re-adsorption or co-precipitation may be occurring.
5.2 Comparison of Metal Concentrations in the Water Column, Available Metals, and Sediment

The comparison of the water column, available metals, and the sediment concentrations showed the traditional methods of testing metal release are insufficient. The water column concentration is significantly lower than the other two concentrations and only considers the free metal ions or small complexes that are less than 0.45μm. The sediment concentration is significantly higher than the other two concentrations and it is the dissolution of all elements in the sediment showing a total elemental concentration. The available metal concentration is between the water column and the sediment concentrations and suggests a more realistic picture of the metals concentration; it is the total amount of metals released into the water column and onto the resin. The water column and sediment concentrations seem to be an under and over estimate of the amount of metals released during a resuspension.

The water column concentration does not consider metal complexes, which could still be available to biota or have the potential for release later, depending on the length of time they remain in the oxic conditions. The problem with the sediment concentration is it is a robust acid digestion that does not distinguish what is and is not released during a resuspension.

The available metal concentration shows the metal ions, hydrated metal ions, and weakly bounded metal species, which have the potential to be available to biota. The ability of the resin to show bounded metal species allows it to show what could possibly be released later based on how long the species are in an oxic environment. The resin does not scavenge for metals but exchanges the sodium on the resin for a metal it comes
in contact with, which allows the resin to simulate the behavior of particulate matter resuspended in solution. Unfortunately, the resin does not show metals strongly associated with colloid particles or humic acid, though strongly bonded metal species may not have the potential to be available to biota. The available metal concentration gives a reasonable picture of the amount of metals released unlike the water column concentration or the sediment concentration.

5.3 Comparison of New DRET Test to the Standard DRET Test

The new DRET test was modified from the standard DRET test to make it more applicable to metals. In Anacostia sediment, the standard DRET metal concentration for the unfiltered samples was higher than what was reported by the new DRET test. For Trepanier sediment, the new DRET test had higher available metal concentrations than the standard DRET test filtered metal concentrations. It would have been expected that the standard DRET test unfiltered sample metal concentrations would have been higher in both sediments since it gives the total metal concentration. Therefore, the standard DRET test is not a good predictor of the amount of metals released.

There are four major similarities between the two tests; one similarity is they both consider the contaminant concentrations at the point of dredging. Both tests used the same total suspend solid, 10g/L, and mix the resuspension solution in atmospheric conditions. Both tests also used the same size filter (0.45μm) for the filtered samples.

There are three major differences between the two tests. One difference is the standard DRET test resuspends the solution for one hour and then the solution settles for one hour before taking a sample, while the new DRET test resuspends the solution for 6
hours and does not let the solution settle before sampling. Results showed that the settling done in the standard DRET test affects the metal concentrations reported. The new DRET test filtered concentration has a much higher concentration than the standard DRET test filtered concentration, which supports settling decreases the concentrations observed. Observations taken during the standard DRET test showed a clear liquid on top of the sediment particles that had settled and the samples were much easier to push through the filter than in the new DRET test. Therefore, allowing the solution to settle before taking samples does not give a realistic picture of what concentration the metals are during a resuspension, since the particulates are suspended throughout the water column and not settled. Settling simulates undisturbed sediments, which is not what occurs during a resuspension.

Another difference between the two tests is the sample concentrations show different information about the metals. The standard DRET test has two concentrations: the filtered and the unfiltered. The filtered concentration gives the free metal ions in the solution and other complexes that can pass through the 0.45um filter. The unfiltered concentration gives the possible total metal concentration in the solution, except the sample is allowed to settle; therefore, all the possible metals may not be reflected in the sample concentration. The new DRET test also has two concentrations: the available metal concentration and the metal concentration in the water column. The available metal concentration is the total amount of metal released into the water column and onto the resin per gram of sediment. The resin can form complexes with free metal ions, weakly complexed metals, or weakly bound metals. The second concentration is the free
metal ions or any metal complex that can pass through the 0.45um filter used during sampling.

Another difference between the two tests is the sorption model the two tests are based on. The standard DRET test was modeled after equilibrium sorption of PCBs, which PCBs have strong binding to sediment particles and most of the PCBs remain bound to the sediment. It does not adequately capture all the process that can occur during a resuspension and assumes equilibrium and does not consider the kinetics that may affect metal release during a resuspension. The standard DRET test breaks the resuspension down into two simple phases: free ions or the total contaminant concentration. The difference between the two phases is assumed to be the fraction adsorb to the sediment, which is not entirely true for metals. The difference could be sorption to oxyhydroxides or speciation with other ligands.

The standard DRET test under or over estimates the metal concentration during resuspension. The under and over estimate also occurred in field studies using the standard DRET test, where the predicted PCB concentrations were lower and higher than the actual concentration. The resin used in the new DRET test allows it to capture metal concentrations that are free or weakly complexed or bound to other ions or particles without dissociating strong complexes that may not be available or become available.

5.3.1 Comparison of C_e between the New DRET Test and the Standard DRET Test

The standard DRET test used equation 7

\[
C_e = \frac{(M_s^*q_i)}{(V_i + M_s^*K_p)}
\]
to predict the soluble concentration of PCBs (ug/L) in the system. Equation 7 was created from a sorption equilibrium model to predict the soluble PCBs in suspension from the result of a resuspension. Di Giano et al. comparison of the calculated soluble PCB and the experimental showed the calculated was higher or equal to the experimental value. They state, “This equation can be an alternative to doing the test to predict the contaminant concentration at the point of dredging as long as the values for the variables are known”. This equation was used on the Anacostia and Trepangier sediment resuspension to see if the calculated values were comparable to the experimental values found by the new DRET test. Instead of using $K_p$, which is a partitioning coefficient usually used for organics, $K_d$ (L/g) was used, which is the total mass concentration of metal in the sediment (ug/g) to the metal concentration in the solution (ug/L). The $K_d$ values used in equation 7 to find the calculated $C_e$ came from the literature [3]; they can be seen in table 13. A literature $K_d$ value could not be found for Co. The experimental $C_e$ is the metal concentration found in the water from the resuspension experiments by ICP-MS. Table 12 compares the calculated and experimental $C_e$ values.

<table>
<thead>
<tr>
<th></th>
<th>Anacostia Sediment</th>
<th>Trepangier Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated $C_e$</td>
<td>Experimental $C_e$</td>
</tr>
<tr>
<td>Co</td>
<td>NA</td>
<td>0.649</td>
</tr>
<tr>
<td>Ni</td>
<td>27.03333</td>
<td>4.613</td>
</tr>
<tr>
<td>Zn</td>
<td>7.879581</td>
<td>6.31</td>
</tr>
<tr>
<td>Pb</td>
<td>20.04142</td>
<td>4.172</td>
</tr>
<tr>
<td>Cu</td>
<td>8.622857</td>
<td>10.267</td>
</tr>
</tbody>
</table>

In the Anacostia sediment the calculated Zn and Cu concentrations are similar to the experimental concentrations. For Ni and Pb, the calculated concentration is much higher than the experimental, while Cu has a higher experimental concentration. The
variation illustrates that the supplement, equation 7, to the standard DRET test should not be used.

For Trepanier sediment, the calculated Cu concentration is similar to the experimental concentration. The Pb, Ni, Zn have much higher calculated concentrations than experimental concentrations. Pb is about 16 times higher, while Ni is about 35 times higher.

For some of the metals the calculated and experimental concentrations are similar, but for other metals the experimental concentration is higher or lower. Equation 7 is not a good predictor of the metal concentrations during a resuspension and could not be used as an alternative to the new DRET test, because the metal concentration would be an under or over estimate, depending on the calculated concentration, which may not be close to the actual metal concentration of the resuspension.

5.4 Comparison of New DRET Test with Other Methods

The new DRET test has similarities and differences with other methods (DGT, SPE, SEM/AVS ratio) that are used to find the concentration of metals in aqueous solutions. The DGT technique uses the Chelex 100 resin, like the new DRET test, in its device to form complexes with metals that release and diffuse through the device. Another similarity is it is an in situ device, like the new DRET test that is placed in the sediment water boundary layer, so during a resuspension the metals can diffuse through the device and complex with the resin to find the concentration of metals released. The problem with this technique is the metal concentration that is reported is limited by diffusion and size. The size of the pores the metals enter the device in are limited to the
size of the hydrogels pores. Exclusion could occur causing the metal concentration to be misrepresented, unlike the new DRET test were exclusion does not appear to occur.

The actual method of the new DRET test is not similar to SPE but both methods use similar sorbents to chelate the metals. SPE is difficult to do with a resuspension solution because both the metals and sediment particles are retained in the SPE device as a result the sorbent and the sediment particles are washed with acid, which releases the metals. The method then becomes similar to what occurs during an acid digestion because everything is washed with a strong acid.

SEM/AVS ratio is not similar to the new DRET test, it only considers metals associated with sulfides; while sulfides may be important in metal release other compounds also have an influence. The SEM/AVS ratio also only gives a value that states whether the sediment is toxic or not toxic based on the ratio being greater than or less than one. It can not give the amount of metals released.

5.5 Visual Minteq Calculations

Visual Minteq was used to illustrate a chemical equilibrium model and to show what the model could do to simulate a resuspension. The base parameters values put into the model were very simplified compared to the actual complexity and heterogeneity of the systems studied. Both sediments contain multiple layers including sands, clays, organic matter, oxides, etc. In the model only one surface reaction was used, which was HFO. The model was used to see $K_d$ values and the total sorbed and dissolved metal concentrations in the simulated system. $K_d$ is a partitioning coefficient that is used to represent the ratio of the metal concentration in mass to the metal concentration in
solution. $K_d$ can be simplified as the ratio of the mass sorbed to the dissolved concentration of the contaminant. The $K_d$ values were found using Visual Minteq and compared to the $K_d$ values found experimentally and in the literature [3].

The parameters values chosen to input into the model are not all realistic system values, though the outputted values are comparable to experimental and literature values. This could be due to the inefficiency of the model or the inefficiency of the parameter values inputted. The concentration used for the components is the concentrations used in the resuspension experiments. The pH value is the approximate value that was reported at the end of the six hour resuspension experiments. The ionic strength (IS) was calculated from the artificial river water used in the resuspension experiments. The site density value used in the adsorption model came from literature values [22]. The solid concentration is what was used during the resuspension experiments. The specific surface area was a value that was simplified and randomly chosen due to the complexity of the sediments surfaces. Visual Minteq calculated the site concentration by using the other parameters inputted into the model. The FeO reaction was used because values can be found and it is substantially sited in the literature. The model was run and the $K_d$ values were calculated from the results given by Visual Minteq. In Visual Minteq, the following parameters were inputted before conducting the adsorption model to simulate the Anacostia sediment.

<table>
<thead>
<tr>
<th>pH</th>
<th>IS</th>
<th>Temperature</th>
<th>Component Concentrations (M):</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.01185</td>
<td>25°C</td>
<td>$Ca^{2+} = 3.3 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Na^+ = 0.0109$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$CO_3^{2-} = 8.6 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Cl^- = 0.0107$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Zn^{2+} = 2.87 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Fe^{2+} = 0.0029$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Co^{2+} = 1.01 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Ni^{2+} = 1.94 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Cu^{2+} = 6.48 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Pb^{2+} = 2.28 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Mn^{2+} = 8.16 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
The adsorption model was DLM with surface reaction with FeO and entered was
10 solid concentration (g/L)
105 Specific surface area (m²/g)
3.48663 site concentration (mmol/L)
2 site density (#sites/nm²)

The following parameters were inputted to simulate Trengangier sediment.

<table>
<thead>
<tr>
<th>pH</th>
<th>IS</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.01185</td>
<td>25°C</td>
</tr>
</tbody>
</table>

**Component Concentrations (M):**

- Ca²⁺ = 3.3x10⁻⁴
- Na⁺ = 0.0109
- CO₃²⁻ = 8.6x10⁻⁴
- Cl⁻ = 0.0107
- Zn²⁺ = 4.83x10⁻⁵
- Fe²⁺ = 0.0312
- Co²⁺ = 2.55x10⁻⁶
- Ni²⁺ = 5.72x10⁻⁶
- Cu²⁺ = 7.13x10⁻⁶
- Pb²⁺ = 2.66x10⁻⁵
- Mn²⁺ = 3.097x10⁻⁵

The adsorption model was DLM with surface reaction with FeO and entered was
10 solid concentration (g/L)
1000 Specific surface area (m²/g)
33.206 site concentration (mmol/L)
2 site density (#sites/nm²)

Table 13 shows a comparison between the $K_d$ values calculated through Visual Minteq, the values calculated experimentally, and literature values.

### Table 13 Comparison of $K_d$ values

<table>
<thead>
<tr>
<th></th>
<th>Anacostia Log $K_d$</th>
<th>V-Minteq Model Log $K_d$ Anacostia</th>
<th>Trengangier Log $K_d$</th>
<th>V-Minteq Model Log $K_d$ Trengangier</th>
<th>Literature Log $K_d$ (SETAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>3.82</td>
<td>3.15</td>
<td>4.04</td>
<td>3.30</td>
<td>NA</td>
</tr>
<tr>
<td>Ni</td>
<td>3.51</td>
<td>3.60</td>
<td>4.03</td>
<td>3.75</td>
<td>2.3</td>
</tr>
<tr>
<td>Cu</td>
<td>3.57</td>
<td>4.7</td>
<td>3.47</td>
<td>4.88</td>
<td>3.53</td>
</tr>
<tr>
<td>Pb</td>
<td>3.91</td>
<td>4.68</td>
<td>4.60</td>
<td>4.87</td>
<td>3.2</td>
</tr>
<tr>
<td>Zn</td>
<td>4.41</td>
<td>3.35</td>
<td>4.39</td>
<td>3.50</td>
<td>4.06</td>
</tr>
</tbody>
</table>

First the $K_d$ values between the two sediments are similar, but the $K_d$ values for Trengangier are slightly higher than the values calculated for the Anacostia sediment. The slight difference could be due to the differences in the physical parameters of the sediments, such as the amount of metals, the organic carbon content, and the AVS.

For Anacostia sediment, the $K_d$ values are similar between Visual Minteq calculations, the calculated $K_d$ values, and the literature values. The Ni literature value is
lower than the value found experimentally or by Visual Minteq. For Cu, the literature and experimental value are very comparable. The Cu and Pb Visual Minteq \( K_d \) values are about one time larger than the experimental \( K_d \) values. Visual Minteq illustrates its ability to find \( K_d \) values though it is not a direct comparison to the values found in literature or experimentally.

For the Tre pangier sediment, Ni and Pb have similar \( K_d \) values between the calculated and Visual Minteq values. Cu and Zn have similar literature and experimental values. Again, the model illustrates its ability to find \( K_d \), but the model is only as good as the information put into it; therefore, insufficient information can predict unreasonable results.

The final item done in Visual Minteq is to illustrate the total dissolved and total sorbed concentration found by the model based on the input values listed above. On top of the basic inputs of components and the adsorption model, a pH sweep was added and an average pE value, which is about -5.86. Redox of Fe, Mn, and S was not included in the model along with precipitation. These items were not included because the output was very unrealistic. Again, this could be because of inefficiencies in the model or inefficiencies in values and parameters entered.
Figure 34 shows the concentration of total sorbed and dissolved metals versus the pH.

Figure 34 DLM Model of Anacostia sediment

The graph shows as the total dissolved concentration decreases the total sorbed concentration increases. This occurs mainly between the pH of 7 to 10. Above the pH of 12 the sorbed concentration begins to decrease again and the total dissolved concentration returns to what it was at a pH of 5 and below. Most sorption seems to occur between the pH of 6 to 12.
Figure 35 shows the concentration of total sorbed and dissolved metals vs. pH.

Figure 35 DLM Model of Trepanier sediment

As the total dissolved concentration decreases the total sorbed concentration increases. This occurs between the pH of 6 to 11. The total dissolved concentration returns to a similar concentration found at pH 6 and below after it decreases. Most sorption occurs during the pH range of 6 to 11.

5.6 Conclusion

"The need to consider bioavailability of metals in sediments was motivated by the common observation that similar dry weight metal concentrations (e.g. μg metal/g dry sediment) exhibit a wide range of effects on sediment organisms when the sediments are from different locations and have varying properties. The challenge...is to devise a method that accounts for these differences" [21].
The new DRET test does this by placing the Chelex 100 resin in situ without membranes or other devices that can delay the metals adsorption to the resin because of diffusion or size exclusion. The resin simulates what the biota could come in contact with during a resuspension. The metals that sorb to the resin during the resuspension reflect the amount of metals released during the resuspension. The resin can retain metal ions, hydrated metal ions, and weakly bound or complexed metal species, which is less than the total metal concentration in the sediment but more than the free metal ions suspended in solution. The new DRET test can account for the differences in each sediment because the available metal concentration reflects what is released by the sediment during a resuspension. The resin allows for the varying properties of the sediment to be reflected in available metal concentration by adsorbing what is released by the specific sediment. The resin also simulates other particles and complexes that are suspended and how the free metals can re-adsorb to them during the resuspension. Unlike the standard DRET test the new DRET test simulates mixing during a resuspension and does not assume equilibrium. The new DRET test is a good predictor of the metal concentrations that are released during a resuspension, which might be a better prediction of the amount of metals available to biota.

Neither the aqueous phase nor the sediment phase metal concentrations are a good indicator of the amount of metals available during a resuspension. Another method was needed to better simulate and predict the amount of metals released during a resuspension. The new DRET accomplishes that.

The kinetics experiments showed an initial burst of metal release occurs. The metal concentration slightly increases in the first hour or two and remains a steady
concentration till the end of the six hour resuspension. The conclusion from the kinetics study is that what happens in the initial minutes of the resuspension indicates where the metal concentration is throughout the resuspension.

The twelve hour resuspension shows that the metal concentration does not increase much more after the six hours. The release pattern of the metals is similar, which is unique but not easily explained. The similar release pattern may be due to stopping the resuspension for a few minutes and restarting the resuspension again.

The results showed little difference in the aerated and anoxic available metal concentrations during a six hour resuspension. One reason for the small difference in concentrations is due to the length of time of the resuspension. Other literature showed a peak in the metal concentration occurring between one to two days; therefore, enough time may not have lapsed to see a difference in the concentrations for the aerated and anoxic resuspensions. Another reason for the similarity in metal concentrations is in aerated conditions the oxyhydroxides formation rate is faster than sulfides oxidation, so the metals sorb quickly onto the oxyhydroxides after being released from the metal sulfide. Also, mixing could still have an effect on the metal concentration even if in anoxic conditions.

During the microbial activity resuspensions, the metal concentration was not affected by the presence or absence of microbes. In fact, the concentrations were similar to the concentrations found in the aerated and anoxic resuspension. The similar concentrations suggest that during the six hour resuspension the microbes did not increase the oxidation already occurring. The literature found that microbial induction did not begin until one to two days into a resuspension. During the six hour
resuspension, significant metal release was exhibited higher than what is found in aqueous phase concentrations, but the metal concentrations were not impacted by microbial activity.

The results showed that the standard DRET test is not a good indicator for the amount of metals released. The test shows very variable results in predicting the metal concentration during a resuspension. The settling time also has an affect on the concentrations that are reported and gives and inaccurate results. The new DRET test was shown to be very reproducible each time and considers both equilibrium and kinetics, which have an impact on metal release.

The calculations and modeling done by Visual Minteq show that computer modeling can be used to predict metal release and the speciation of metals during a resuspension. Visual Minteq allowed experimental data to be entered along with providing literature accepted constants to find the speciation and adsorption that can occur.

The results show that much more work needs to be done to understand what happens to metals during a resuspension, which is a very complex process. But overall, the results show the new DRET test is a better test to predict the metal concentrations during a resuspension from other methods, specifically the standard DRET test. The new DRET test could be conducted relatively easy by other people and in the field to predict the amount of metals released.
The new DRET test recommended procedure is:

1. In a 300mL beaker mix 2.5g wet sediment, 250mL artificial river water solution (0.01M NaCl, 0.86mM NaHCO₃, 0.33mM CaCl₂), and 12.5g Chelex 100 resin with an overhead propeller stirrer.
2. Measure the pH at time zero and every sampling time. Calibrate the pH meter with 4, 7, and 10 buffers.
3. Collect 20ml sample in a syringe at 10min, 20min, 30min, 1hr, 2hr, 4hr, and 6hr while the solution is mixing.

4. Put the 500um and 149um sieve above a 100mL beaker than push the sample in the syringe onto the sieves, collecting the water solution effluent.
5. The resin is then trapped on the bottom sieve. Transport the resin into a 50ml centrifuge container.
6. To the resin add 2mL of concentrated HNO₃.

7. While the resin solution is cooling, filter 10mL of the water solution effluent through a 0.45µm filter into a 15mL centrifuge tube and acidify sample by adding 1% by volume HNO₃ for analysis.

8. The cooled resin solution is diluted to 50ml with DI water; then a 10mL sample is taken from the diluted resin solution and put into a 15mL centrifuge tube for analysis.

9. Samples are analyzed on the ICP-MS for Co, Ni, Cu, Pb, and Zn.
Chapter 6

6 Future Work

Many more experiments could be done on this research, which could give more information and a better understanding of metal release during resuspension and the effect on biota in the environment. The New DRET test needs continued refinement to predict the fate and amount of metals releasable, which could be done by testing the method with more sediments that have a variation in sediment characteristics. Different characteristics could be AVS, carbonate content, organic carbon content, iron content, composition of the sediment, etc. Testing with more sediments leads to better reproducibility of the method and a better understanding of the sediment characteristics impact on metal release. More metals need to be tested using this method other than the five studied here; the metals need to have environmental significance, such as impact on biota.

Another aspect that can be done would be to do bioavailability tests on biota during resuspension to see the uptake of metals into their systems and would these metal concentrations be comparable to the available metal concentration found during a resuspension.

Resuspensions also need to be conducted that simulate multiple day dredging. For example, doing a resuspension for six hours then letting it sit for eighteen hours and doing a six hour resuspension again and repeating this process over several days to see the impact on metal release. The final phase would be to take this test out of the lab and into the field to test the viability of the test on metal release during a resuspension.
Other future work that could be done would be to establish if a few predominant mechanisms exist, which control metal release during resuspension. Then those mechanisms could be used to model the metal release during resuspension and the mobility of metal release. A model could be created from this work to predict the metal release during a resuspension.

More experimental and theoretical modeling could be done by examining the impact of biological processes and films on the availability of metals. More work could be done on characterizing the sediments and the metal complexes; this can be done by modern surface methods, such as atomic force microscopy (AFM) and extended range XAFS (EXAFS). Also, more work is needed to determine the generality of the metal classifications and binding.
List of References


