EXECUTIVE SUMMARY

Understanding the Relationships Among Low Level Metal Influx, Remediated Sediments, and Biological Receptors

SERDP Project ER-2427

JANUARY 2020

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ACRONYMS AND ABBREVIATIONS

As	arsenic
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
DGT	Diffusive gradients in thin films
DoD	Department of Defense
Hg	mercury
ICP-MS	inductively coupled plasma-mass spectrometry
MAAC or MC	multiple amendment active cap or mixed amendment cap
Ni	nickel
Pb	lead
Se	selenium
SFM	Sediment Flux Model
SERDP	Strategic Environmental Research and Development Program
TICKET	Tableau Input Coupled Kinetic Equilibrium Transport
Zn	zinc

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ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

Contaminated sediments are commonly remediated by environmental dredging, which involves their removal and disposal to reduce environmental risks. However, sediment capping is sometimes preferred because it is less expensive and disruptive to the benthic environment. In passive capping, contaminated sediment is covered with a layer (cap) of clean, inert material such as sand, soil, or sediment to physically isolate the contaminants. In active capping, chemically reactive amendments are applied to the sediment surface to bind contaminants, thereby reducing pore water contaminant concentrations and bioavailability (Figure 1).

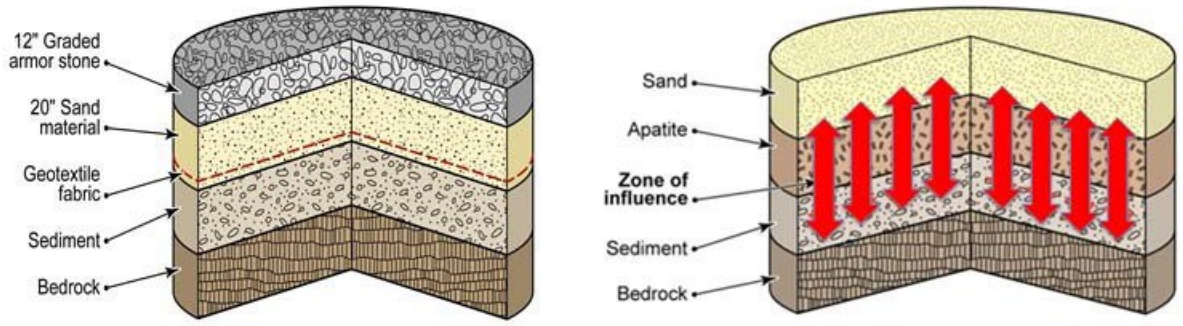

Figure 1. Passive Cap (left) and Active Cap (right).

Active caps incorporate chemically active materials that react with contaminants to reduce their bioavailability.

Remediated sediments may be exposed to continued inputs from permitted discharges, upstream contaminated sites, or stormwater discharge resulting in recontamination that can slow or reverse recovery associated with remedial efforts. The recontamination of sediments can negate expensive remedial actions by producing a polluted habitat zone that overlies the remediated sediment (Figure 2). This is a challenge to all remedial approaches, but the severity of the problem may be affected by the type of remediation that has been undertaken. Contaminant influxes can degrade the benthic environment as contaminants accumulate in areas previously remediated by environmental dredging or conventional capping with inert materials such as sand. However, remedial effectiveness may persist in areas remediated by active capping with chemically active sequestering agents because these agents interact with incoming contaminants to reduce their bioavailability and toxicity. Remedial effectiveness can be further influenced by bioturbation, the physical disturbance, restructuring, and reworking of sediments by benthic organisms. Bioturbation can mix newly deposited contaminated sediment with underlying uncontaminated sediment, which may contribute to the release of contaminants from the newly deposited contaminated sediment or, conversely, to contaminant sequestration or dilution by burial in underlying clean sediment or active capping material. In the latter case, contaminants may react with sequestering agents to reduce their toxicity and bioavailability.

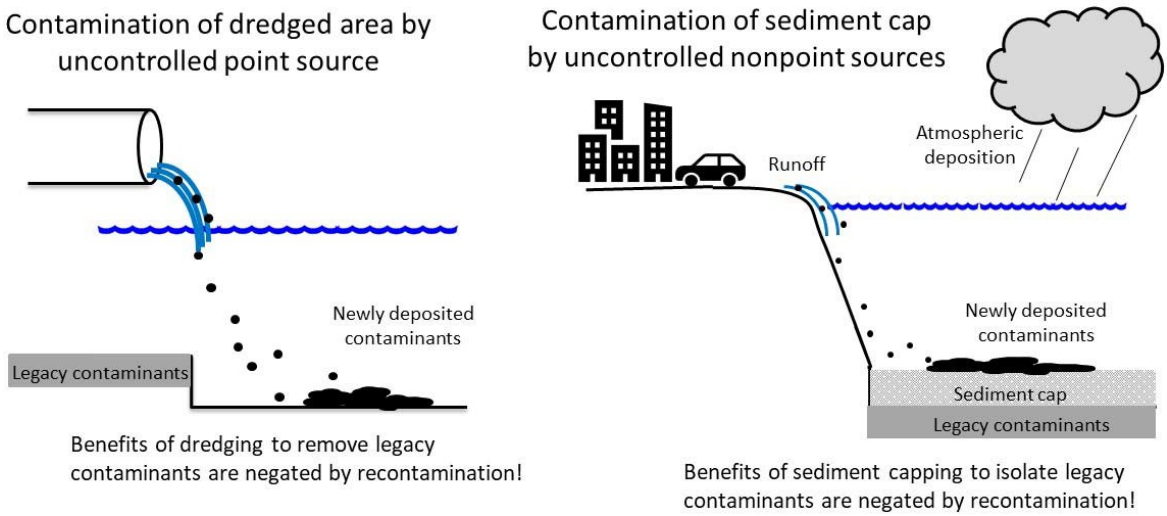

Figure 2. Remediated Sediments May Be Exposed to Contamination from Uncontrolled Point or Nonpoint Sources Resulting in Recontamination that Reverses Recovery.

The project team's research addressed the knowledge gap related to the effects of ongoing contamination on different sediment remediation technologies including active caps, passive caps, and sediment remediated by the removal of contaminants through environmental dredging (simulated by uncontaminated, uncapped sediment). None of these technologies have been evaluated for their effectiveness when confronted with ongoing contamination.

2.0 OBJECTIVES

The objectives of this project were the following:

1. Evaluate the effects of low-level metal influxes from uncontrolled sources on passive caps, active caps, and clean, uncapped sediment in a freshwater environment.
2. Assess the effects of bioturbation on an incoming particulate contaminant load deposited over underlying clean sediment or active capping material.
3. Develop numerical models for assessing the long-term effectiveness of remediated sediment subjected to recontamination.
4. Improve understanding of the relationships among surface sediment recontamination, remediated contaminated sediments, and biological receptors.

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3.0 TECHNICAL APPROACH

The research objectives were addressed in three tasks: Task 1—Linkages between contaminant loading and recontamination of remediated sediments—flow through mesocosms with continuous metal influx, Task 2—Understanding relationships among remediation methods, low level influxes of contaminants, bioturbation, and effects on biological receptors, and Task 3—Development of numerical models for predicting long-term relationships between low level contaminant influxes and remediated sediments.

Task 1 evaluated linkages between dissolved contaminant loading and recontamination of remediated sediments. Subtask 1.1 of Task 1, Dissolved Metal Influx, employed flow-through mesocosms to simulate recontamination by an inflow of dissolved contaminants. The setup included 30 flow-through mesocosms (20 x 41 x 43 cm) representing 10 treatments including uncapped sediment and different cap compositions and thicknesses (2.5 or 5.0 cm) (Figure 3). Passive caps consisted of sand. There were five types of active caps: 1) apatite; 2) organoclay (MRM from CETCO); 3) activated carbon; 4) silty clay sediment; and 5) a mixture of apatite, activated carbon, and organoclay (referred to as MAAC or MC). A single reservoir supplied a continuous inflow of spike solution with 0.5 mg L^{-1} each of arsenic (As), chromium (Cr), cadmium (Cd), cobalt (Co), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn) to each mesocosm. Pore water samplers composed of fine mesh screens were buried in the mesocosm sediments. Dissolved oxygen, temperature, electrical conductivity, pH, turbidity, and calcium hardness were measured in surface waters. Total and dissolved metals in surface and pore water were measured by inductively coupled plasma-mass spectrometry (ICP-MS). Annelid worms, *Lumbriculus variegatus*, held in plastic screened cages within the sediments of the mesocosms for 10 days were weighed in aggregate before and after exposure to assess mortality, then analyzed by ICP-MS to assess element bioaccumulation. Diffusive gradients in thin films (DGT) sediment probes were deployed for 24 h to measure potentially bioavailable metals at different depths within the caps and sediment of each mesocosm, and sediment cores were taken to measure sediment pH.

Subtask 1.2 of Task 1, Low-level Dissolved Metal Influx and Metal Interactions, used the experiment setup described for Subtask 1.1 to assess the effects of low level Cu influxes, alone and in the presence of other contaminants, on different remediation methods. Competitive interactions among metals may exist at sites with co-occurring contaminants. Experiment I included Cu with other metals, and Experiment II included only Cu. Treatments in both experiments included uncapped sediment and sediment capped with 2.5 cm of 75% apatite, 5% activated carbon, and 20% MRM organoclay. Experimental methods were as in Task 1.

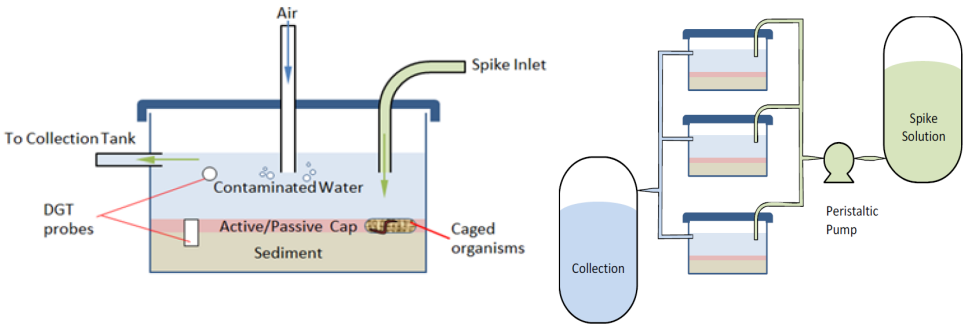

Figure 3. Experimental Mesocosms.

Task 2 investigated how bioturbation affected the recontamination of uncapped clean sediments (simulating dredged sediment) and sediment remediated by apatite caps. Contaminated sediment was deposited directly over the remediated sediment to simulate the influx of contaminants bound to particulates. There were 12 mesocosms divided into four groups: apatite caps with bioturbation, apatite caps without bioturbation, uncapped sediment with bioturbation, and uncapped sediment without bioturbation. Contaminated sediment was manually added to produce a 1.5 cm thick top layer over a bottom layer of uncontaminated sediment or uncontaminated sediment with an overlying apatite cap. Levels of Cu, As, Ni, and Cd in the contaminated sediment were typical of polluted sediments; levels of Zn, and Pb were above those in the uncontaminated layer. The bioturbating organisms, Asian clams *Corbicula fluminea*, burrowed to a depth of about 2.5 cm and remained in the mesocosms for 28 days. Other experimental methods were as described previously.

Task 3 evaluated the long-term effectiveness of remedial methods through modeling that synthesized results from Task 1. It developed numerical models for the prediction of long-term relationships among low level influxes of metals and remediated sediments, thereby providing a basis for the selection of remediation strategies that exhibit long-term effectiveness in the face of ongoing contaminant influxes.

4.0 RESULTS AND DISCUSSION

Task 1, Subtask 1.1

The concentrations of most elements in surface water remained significantly lower in mesocosms with apatite and mixed amendment active caps than mesocosms with passive caps (sand) or uncapped sediment. By the end of the 2520 h experiment, average Cd concentrations in surface water were 100 µg L^{-1} in the mesocosms with active caps compared with 300 µg L^{-1}in mesocosms with passive caps, and 500 µg L^{-1} in control mesocosms (Figure 4). Like Cd, average dissolved Zn increased over time in the control mesocosms and mesocosms with passive caps, reaching 500 µg L^{-1} in the former and nearly 200 µg L^{-1} in the latter, but remained under 10 µg L^{-1} in most active cap treatments (Figure 4). Similar results were observed for other elements, especially divalent metals.

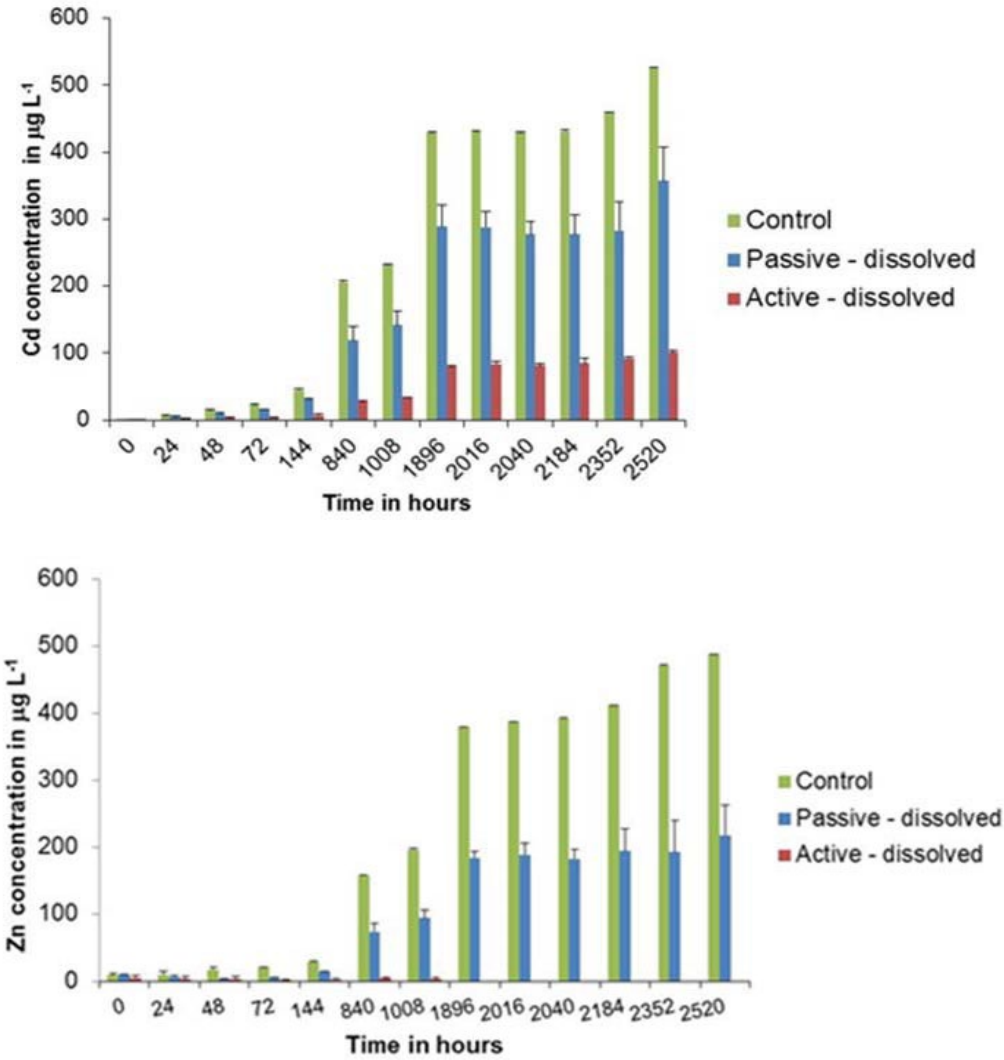

Figure 4. Average Surface Water Concentrations of Dissolved Cd and Zn in Mesocosms with Active Caps, Passive Caps, and Controls (i.e., Multiple Element Spike Solution).

Average percent survival of *Lumbriculus* was higher in mesocosms with active caps (65-80%) than mesocosms with uncapped sediment and sand caps (0-10%). Higher water hardness in the active cap mesocosm likely contributed to this higher survival because the acute toxicity of many metals diminishes as hardness increases. Whole-body concentrations of most metals in surviving *Lumbriculus* differed significantly among mesocosms, with lower concentrations in mesocosms with active caps (Figure 5). Although all active caps reduced metal uptake, there were differences among cap types, with the most effective caps varying among metals.

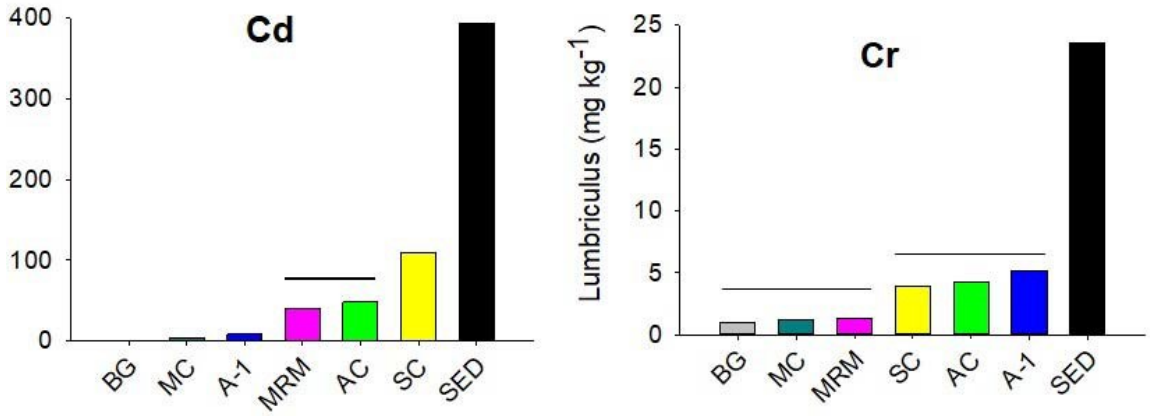

Figure 5. *Lumbriculus* Metal Concentrations Among Sediment Treatments for Cd and Cr (BG=Background, AC=Activated Carbon, SC=Silty Clay Cap, A-1=Apatite Cap, MRM=Organoclay MRM Cap, MC=Mixture of Active Amendments, and SED=Untreated Sediment.

Means connected by the same line are not significantly different at $p \leq 0.05$.

The bioavailable pool of metals assessed by sediment DGT was lower in apatite caps, MC caps, and sediment treated with activated carbon than in passive sand caps, silty clay caps, and uncapped sediment. Pearson correlations between metal concentrations in *Lumbriculus* and DGT metal concentrations in the top 2.5 cm of sediment or cap were generally strong (up to 0.98) and significant ($p \leq 0.05$) for all metals except zinc (example for Co in Figure 6). These results indicated that metal concentrations in *Lumbriculus* were the result of uptake from the surrounding sediment or cap and possibly overlying water and the bioavailable pool of metals was lower in mesocosms with active caps than mesocosms with uncapped sediment or passive caps.

Task 1, Subtask 1.2

This task investigated the effects of Cu influxes on sediment remediated by different treatments, alone and in the presence of other elements to investigate potential competitive interactions between Cu and co-occurring contaminants. The behavior of Cu was generally similar in Experiments I (multiple metals) and II (Cu only); i.e., surface water Cu concentrations were higher in mesocosms with passive sand caps or uncapped sediment than mesocosms with apatite and mixed amendment caps. However, slightly lower surface water concentrations of Cu in Experiment I than II were visible after 528 h in mesocosms with mixed amendment caps, likely because Cd and Zn precipitated Cu and lowered average total Cu concentrations. The most effective amendment for controlling metal influxes in Experiment I was apatite, which reduced concentrations of Pb, Cu, Cd, As, and Zn by 96, 90, 89, 76, and 63%, respectively.

DGT water probes showed that concentrations of potentially bioavailable Cu, Cd and Pb were lower ($p \leq 0.05$) in apatite, activated carbon, and MC treatments than in the control and passive sand cap treatments. However, there were no significant differences in DGT Cu concentrations between Experiments I and II for mesocosms with MC caps indicating that the presence of other elements did not influence the effectiveness of MC caps for remediating Cu. Cu concentrations in *Lumbriculus* were significantly higher in mesocosms with untreated sediment than with active caps and related to element concentrations in sediment measured by DGT probes (Figure 7).

Although Cu uptake by *Lumbriculus* (indicated by tissue concentrations) differed little between Experiments I and II, the toxicity of Cu mixed with other elements (indicated by mortality) was greater than the toxicity of Cu alone in treatments with uncapped sediment (Figure 8). This was not observed in treatments with mixed amendment active caps indicating that active caps can protect remediated sediments by reducing metal toxicity in ongoing contamination by multiple metals (Figure 8).

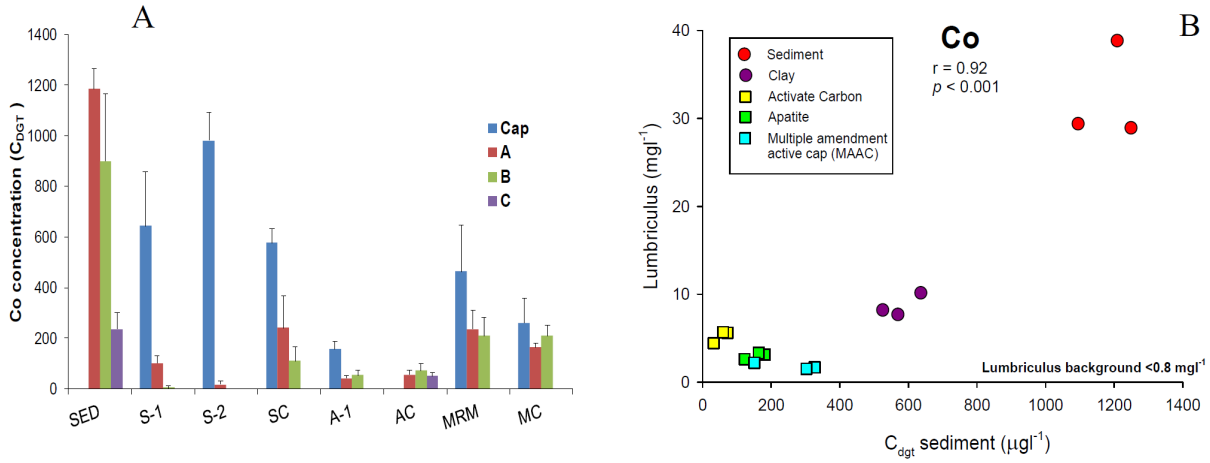

Figure 6. Graph A Depicts Co Concentrations (µg kg^{-1}) Measured by Sediment DGT Probes (C_{DGT}) in Cap Materials and Sediment Beneath the Cap (Layer A, 0–2.5 cm; Layer B, 2.5–5.0 cm; Layer C, 5–7.5 cm).

Treatments include uncapped sediment (SED), sediment with passive sand caps (S-1=2.5 cm thick cap and S-2=5 cm thick cap) and sediment with active caps (apatite=A-1; silty clay=SC; activated carbon= AC; organoclay=MRM; mixture of active amendments=MC). Graph B depicts Pearson correlations between metal concentrations in Lumbriculus and metal concentrations in sediment measured by DGT.

Task 2

A layer of sediment contaminated with As, Cd, Cu, Ni, Pb, and Zn was deposited over clean sediment capped with apatite, and clean uncapped sediment to simulate influxes of particle- bound contaminants on sediments remediated by active capping and dredging. The bioturbating organism, *Corbicula fluminea*, was added to half of the mesocosm to assess the effects of bioturbation on remedial effectiveness as measured by metal fluxes to sediment pore water and surface water, the distribution of mobile contaminants in surface water and sediment measured by DGT, and contaminant bioaccumulation by *Lumbriculus variegatus*.

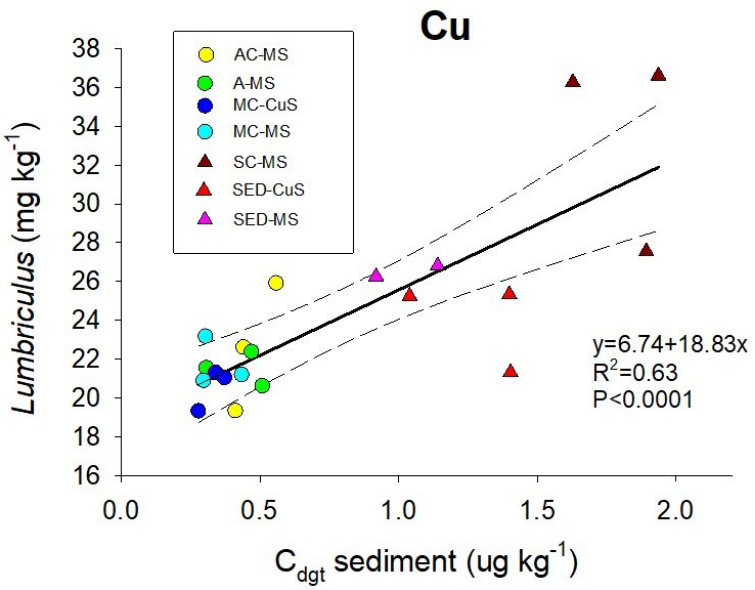

Figure 7. Regression of Cu in *Lumbriculus* on DGT Cu in Sediments (see Figure 8 for Explanation of Legend).

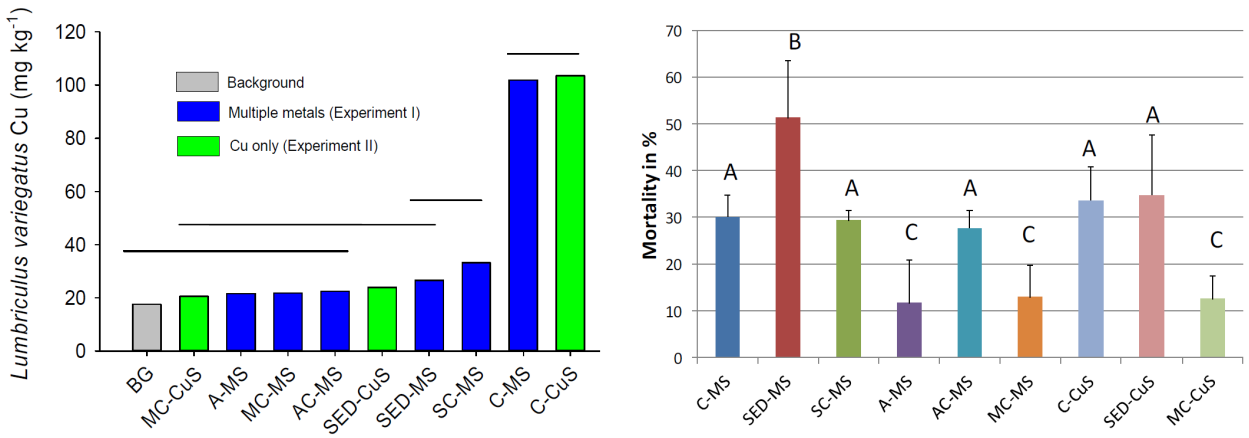

Figure 8. *Lumbriculus* Cu Concentrations (left) and Mortality (right) in Experiments I and II.

Experiment I (multiple element): control with no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated in situ with activated carbon (AC-MS). Experiment II (Cu only): control with no sediment (C-CuS), uncapped sediment (SED-CuS), sediment with mixed amendment active caps (MC-CuS), and background (BG). Means connected by the same line or indicated by the same letter are not significantly different (α=0.05).

Bioturbation strongly affected the vertical distribution of the layer of contaminated sediment, which was initially well-consolidated and distinct but thoroughly mixed with apatite and underlying sediment after 28 days of bioturbation (Figure 9). However, the metal sequestration capacity of the apatite caps was unaffected or improved by bioturbation for all elements except As, as shown by DGT metal concentrations in sediment and metal uptake by *Lumbriculus* (Cd example in Figure 10), probably because bioturbation mixed apatite with the incoming sediment thereby enhancing chemical sequestration of the metals. Effects with uncapped sediment were metal-specific including reductions in the bioavailable pool for Ni, Cd, and to a lesser extent, Pb, increases in the bioavailable pool for As and Cu, and little effect for Zn. It is likely that the reductions observed for some metals in uncapped sediment were the result of burial and dilution of the contaminated sediment combined with chemical processes such as sequestration by iron and other minerals in the clean sediment. These results show what can occur when newly dredged, uncapped sediment is challenged by a combination of recontamination and bioturbation.

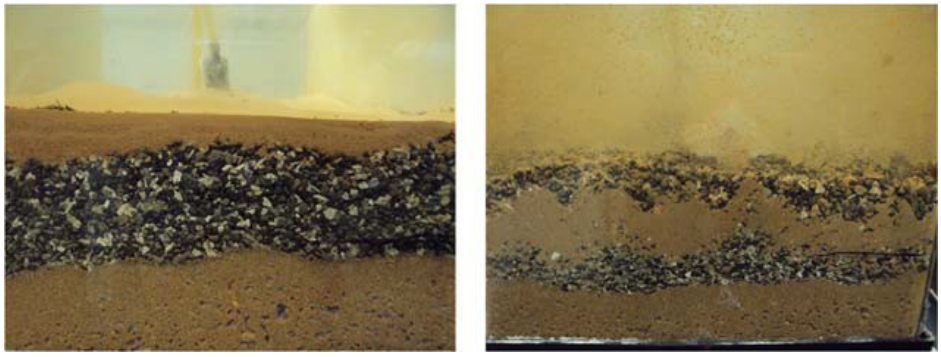

Figure 9. Before and After Bioturbation of Contaminated Sediment Deposited Over an Apatite Cap.

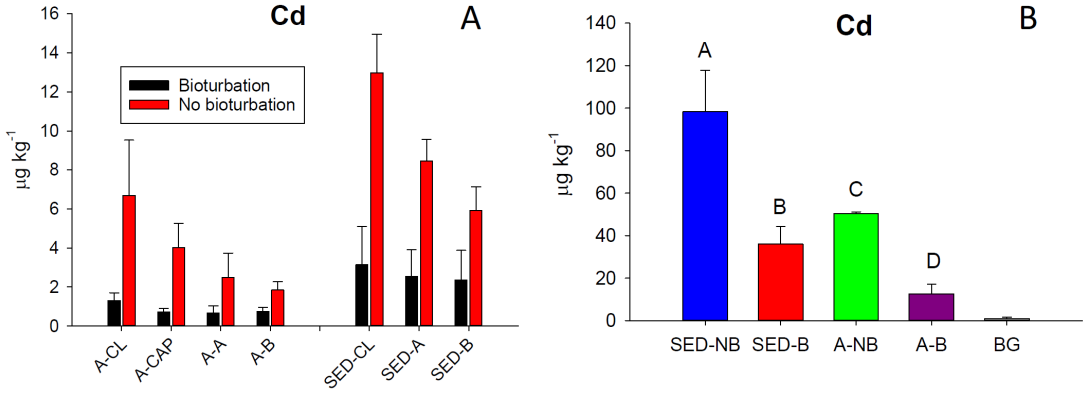

Figure 10. A) Cadmium Concentrations Measured by DGT in the Sediment of Mesocosms with Untreated Sediment (SED) and with Apatite Active Caps (A).

Three sediment layers are represented: surficial contaminated layer (CL), cap layer for mesocosms with cap (CAP), sediment layer beneath the cap or surficial layer (A), and deeper sediment (B). B) Mean element concentrations in Lumbriculus variegatus from experimental mesocosms with apatite caps (A) and uncapped sediment (SED) and bioturbation (B) or no bioturbation (NB). Means with different letters are significantly ($p<0.05$) different. Background concentrations in Lumbriculus (BG) are shown for comparison. Error bars are standard deviations.

Task 3

The Sediment Flux Model (SFM) and Tableau Input Coupled Kinetic Equilibrium Transport (TICKET) model were evaluated and compared for their ability to represent metal transport and speciation in a capped environment. The SFM provides a robust representation of transport within the sediment bed and exchange processes between the bed and the water column.

However, the representation of chemical dynamics is limited to equilibrium partitioning between the dissolved phase and the particulate organic fraction. In contrast, the TICKET model contains detailed algorithms for simulating metal speciation and precipitation via the tableau approach, but it has not been extensively used for modeling active cap performance.

Task 3 developed a modeling approach for forecasting long-term sediment conditions under different sediment treatment scenarios. It involved enhancing the SFM code by incorporating the tableau approach used in TICKET and other chemical equilibrium models into SFM producing a new framework, the SFM-TICKET, able to represent the speciation of metals and other chemicals while retaining the vertical transport capability of the SFM. The SFM-TICKET simulation of uncapped sediment reproduced both total and dissolved concentrations of the metals used in Task 1 (Zn example in Figure 10). The SFM-TICKET simulation of capped sediment differed from the uncapped sediment simulation by representing a 2.5 cm apatite cap at the top of the sediment bed. Maximum total and dissolved concentrations of Cu, Cd, and Zn observed in the experimental mesocosms with active caps were also reproduced reasonably well by SFM-TICKET (Figure 11). These and other results showed that the integrated transport- equilibrium SFM-TICKET model can simulate the effect of pH on free metal activity, adsorption to representative sequestering components, and competition between metal and hardness cations for ligand binding sites.

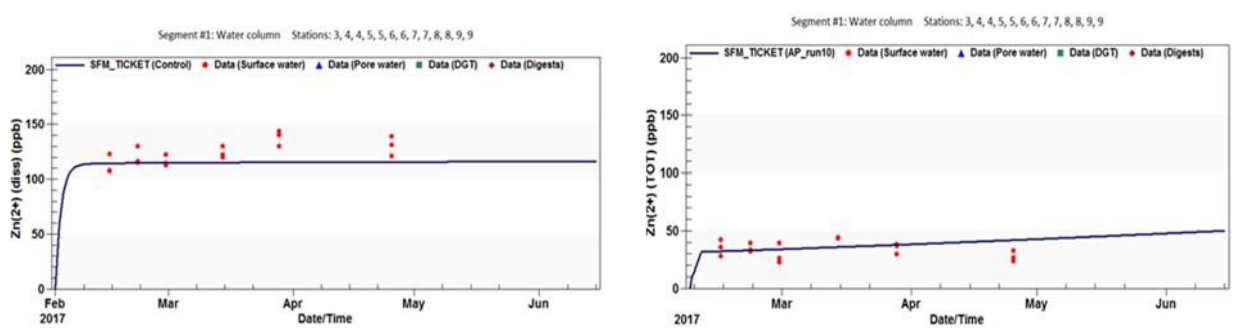

Figure 11. Time Series of Total Metal Concentrations in Surface Water Simulated by SFM-TICKET Model for Uncapped Sediment (left) and Apatite Cap (right).

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

The project team used mesocosms to investigate the effects of continuing metal influxes over uncapped sediment and sediments remediated by different types of active and passive caps, investigated competitive interactions between Cu and other elements to better understand remedial processes when contaminants co-occur, and studied the effects of bioturbation on contaminated sediment deposited over underlying clean sediment and sediment remediated by active caps. The project team's overarching hypothesis was that the sequestering agents in active caps can bind metals introduced from uncontrolled sources of ongoing contamination, thereby reducing their bioavailability and protecting underlying, previously remediated sediments from recontamination (Figure 12). In contrast, metals from ongoing sources have greater potential to contaminate passive caps and uncapped sediment remediated by environmental dredging.

The project team's results supported the preceding hypothesis. They showed that concentrations of most metals in surface waters were significantly lower in mesocosms with apatite caps, mixed amendment caps, and activated carbon treatments than mesocosms with passive sand caps and uncapped sediment. Survival was higher for Lumbriculus in mesocosms with active caps than passive caps or uncapped sediment, and whole-body concentrations of most metals were lower. Regressions of metal concentrations in Lumbriculus on metal concentrations in sediment or cap measured by DGT were generally strong and showed reduced metal bioavailability in active cap mesocosms. Similarly, sediment DGT probes showed that ongoing contamination increased bioavailable metals in the top layer of uncapped sediment but not sediment treated with active amendments. Comparing results between multi-metal experiments and Cu-only experiments showed that the ability of active caps to control Cu contamination was not affected by the presence of other elements. Lastly, the ability of apatite active caps to reduce the bioavailability of most metals in incoming contaminated sediment was unaffected or even enhanced by bioturbation, probably because bioturbation mixed apatite with the incoming sediment, thereby enhancing sequestration of the metals. In contrast, bioturbation reduced the bioavailable pool of some metals in contaminated sediment that was deposited over uncapped clean sediment but contributed to the release of others.

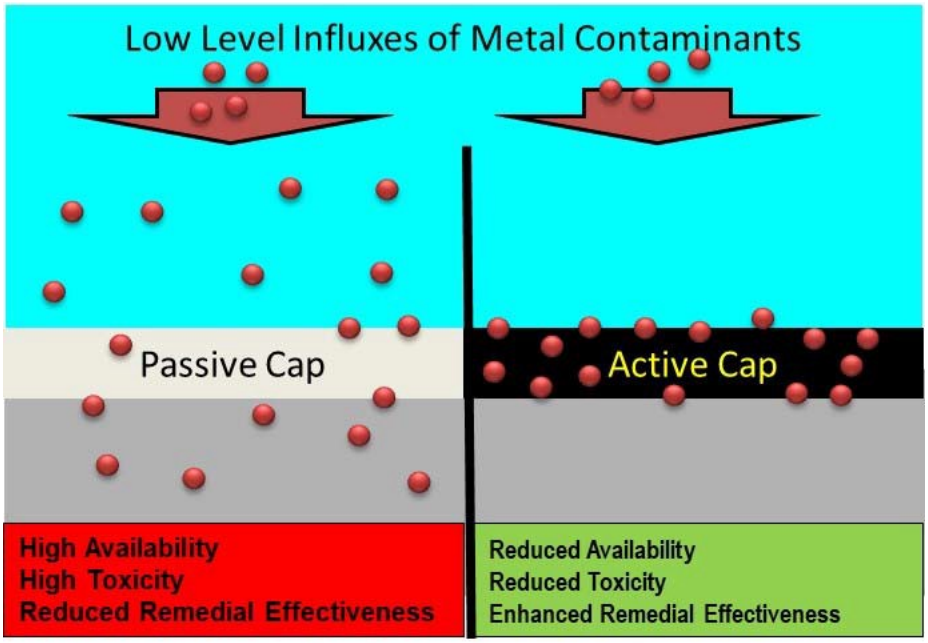

Figure 12. Conventional Methods of Remediating Contaminated Sediments May Be Inadequate for the Protection of Benthic Organisms when Ongoing Sources of Contamination Exist.

However, sediment caps with chemically active sequestering agents can reduce the pool of bioavailable metals in ongoing contamination (red dots), reduce toxicity, and enhance remedial effectiveness.

The remediation of contaminated sediments is an expensive process that can be negated by the continued influx of contaminants from uncontrolled sources. However, the results of this study indicate that apatite and other types of active amendments can protect remediated sediments by reducing the bioavailable pool of metals in ongoing sources of contamination. They also indicate that this ability is not affected by competitive interactions among elements nor by bioturbating organisms. This knowledge will contribute to more rigorous risk management that incorporates the resilience of remedies in the face of ongoing contamination into criteria for remedy selection.