Research Brief #26

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Fate of Heavy Metals and Inorganic Compounds During Sediment Resuspension

Introduction and Objectives

Rice University and the Lousiana State University (LSU) are conducting a two-year study to understand the dynamics and kinetics of heavy-metal release processes in sediments and develop methods for reducing heavy-metal release in dredging and resuspension. The research is necessary because of the inability of conventional methods to assess the resuspension behavior of heavy-metal contaminants such as lead, arsenic, copper, and cadmium during sediment dredging operations. This *Research Brief* summarizes the accomplishments of year one.

The study's specific objectives are to:

- test the hypothesis that sorption and desorption of heavy metals from natural sediments are not the reverse of each other;
- simulate resuspension in the laboratory and test the hypothesis that a few key parameters can effectively predict heavy-metal release;
- study the multiphasic nature of heavy-metal release, in which one set of processes controls early resuspension and a completely different set of processes governs later resuspension events;
- give special priority to understanding the dynamics governing the release of sediment fines—that is, particles in sediments that do not resettle rapidly during resuspension events. Scientists have found that fines contain many times the heavy-metal load of other types of sediment particles; and
- identify a potential remediation plan for preventing heavy-metal release during resuspension events, including dredging.

Sediment Desorption Study

During year one, researchers at Rice University studied the adsorption and desorption of cadmium (Cd), lead (Pb) and zinc (Zn) in sediments from Utica, NY, and Lula, OK. They also determined levels of heavy-metal binding in laboratory sediments using a sequential extraction method. They conducted resuspension experiments on sediment samples from Trepangier Bayou and Lake Charles, both in Louisiana. In addition, they observed the effect of polyacrylic acid on heavy-metal desorption in natural sediments from Utica and Trepangier Bayou.

These experiments allowed the group to demonstrate:

• *The reversibility of heavy-metal adsorption* Researchers found that desorption in Cd, Pb, and Zn in Utica sediments is minimal at neutral pH but significantly increases at low pH. This finding suggests heavy metal adsorption could be completely reversible in the Utica sediments by lowering pH. However, desorption hysteresis was observed in sediments at neutral pH, and the desorption hysteresis appeared to increase with aging time. The result suggests that desorption hysteresis may play an important role in inhibiting heavy-metal mobility in sediments.

• *The impact of dredging on anaerobic sediments*. The researchers demonstrated that resuspension changes solution pH and redox potential in sediment particles. In experiments with samples from Trepangier Bayou, they found that exposure of anaerobic sediments to the normal atmosphere for four weeks increased redox potential from -240 to +560 mV and decreased solution pH from 7.3 to 1.8. The dra-

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Summary of the Problem

When contaminated sediments are removed from waterways for treatment or disposal, some particles are always stirred up and resuspended in the surrounding water. This process brings about changes in physical and chemical conditions that cause contaminants to break free (desorb) from their bonds with sediment particles. The result is that dangerous contaminants are able to enter the food chain, where they eventually may threaten human health.

Resuspension of sediments that are contaminated with heavy metals, such as lead, cadmium, copper and arsenic, pose special challenges. These pollutants not only are highly toxic and resistant to breakdown, but the likelihood and impact of their release cannot be estimated by conventional diagnostic tests used to assess other types of pollutants in sediments. Heavy metals released from sediment bonds undergo rapid, pronounced and complex chemical changes that can't be picked up by established assessment methods.

In the project described in this *Research Brief*, engineers and scientists at Rice University and the Louisiana State University are conducting an in-depth study to understand the dynamics and kinetics of heavy-metal release processes. Once they determine the key parameters at work in resuspension, they plan to develop simplified assays or predictors for routine use. The ultimate goal of the research is to enable regulators and field practitioners to use only a few key sediment/water parameters for predicting the environmental risk of specific dredging operations.

matic decrease in solution pH was mainly due to the oxidation of sulfide and increased the mobility of heavy metals. Thus, metal concentrations in solution increased 200 fold. After five days of resuspension, the water became highly contaminated with Cd, Pb, Zn, Cu and As. Release rates slowed down when observed over weeks instead of hours.

The study determined that the addition of calcite does not have a strong impact on short-term heavy-metal release but does have a large stabilization effect on sediment desorption over the long term.

• *The effect of polyelectrolyte on sediment resuspension and heavy-metal desorption*. Heavy-metal release during dredging and resuspension is largely due to the resuspension of fine colloidal particles. Polyelectrolytes are widely used as flocculants and are strong adsorbents for heavy metals. They may be useful in dredging or capping to aid both the dewatering and settling of sediments and also to slow the release of heavy metals. Preliminary data from the Rice study indicate that polyelectrolyte may significantly reduce heavy-metal desorption.; however, the application of the polymer must be carefully designed.

First-year research provided the following general conclusions:

- Adsorption of Cd, Pb and Zn in natural sediments appears reversible;
- Washed sediments appear more effective than unwashed sediments in adsorbing heavy metals; and
- Solution pH strongly affects of mobility of heavy metals in contaminated sediments.

In the second year, the Rice researchers are conducting resuspension experiments on fresh sediments with distinct variations in character. They are also modeling the mobility of heavy metal release using a few principal mechanisms and investigating the potential of polymers for reducing the desorption of heavy metals from sediments.

Kinetic Modeling Study

Researchers at LSU are developing a theoretical kinetic model to describe the organic and metal desorption of contaminants in sediment particles during resuspension. The aim of this study is to provide a practical tool for understanding the likely release characteristics of heavy metals during dredging or other remediation activities.

The model depicts particles as having adsorptive patches within and on their outer surfaces. The external patches adsorb contaminants into compartments that hold them in either tight or loose bonds. The internal patches allow contaminants to migrate from one particle or another. Desorption of particle compartments takes place either: 1) in parallel by disconnected compartments; 2) in series when a loosely bound compartment completely surrounds a tightly bound one; or 3) in parallel-series when a loosely bound compartment completely surrounds a tightly bound one.

In the first year of the study, the researchers developed a theoretical model that is consistent with the empirical model used by many investigators to correlate the desorption behavior of organic chemicals. They began preliminary testing of the mathematical model to examine its congruence with existing data from sites where PAH's and chlorinated solvents have resuspended during bioremediation.

During the second year, they are refining their understanding of the two-compartment model of contaminated sediment particle desorption. They plan to apply this model to metal desorption data when it becomes available or when appropriate data sets are located in the literature. They also will perform additional numerical simulations of three-compartment arrangements.

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