Research Brief #21

1999

Assessing The Toxicity of Southeastern Coastal Sediments With Heavy-Metal And Total-Sulfide Measurements

Introduction

The U.S. Environmental Protection Agency (EPA) is developing sediment quality criteria, and one proposed method of assessing toxicity is with heavy-metal and total-sulfide measurements. Acidification of a sediment releases heavy-metal sulfide precipitates, allowing acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM). SEM includes cadmium (Cd), nickel (Ni), zinc (Zn), lead (Pb), mercury (Hg), and copper (Cu). Because metals bind with AVS, it has been proposed that a SEM: AVS ratio serve as an indicator of metal toxicity in sediments. If a sediment has higher SEM levels than AVS, then a sediment is considered toxic; if this SEM:AVS ratio is less than one, it is deemed to be nontoxic. The SEM: AVS ratio has worked well for predicting toxicity in laboratory experiments; however, its value in the field is unproved, especially in cases where sediments are polluted with multiple metals. Furthermore, research has not established whether the typical breakdown patterns of metals differ by sediment type.

To assess the value of the SEM: AVS ratio as an indicator of metal toxicity, researchers from Georgia Tech's School of Civil and Environmental Engineering and the Skidaway Institute of Oceanography (SKIO) studied sediments from several field sites in the southeastern United States to determine how metals were bound to AVS. They examined the respective importance to metal binding of AVS and other possible contributors, including carbonates, organic carbon, and sediment grain size. They also determined kinetic rates for metal binding as a means of further clarifying the indicators of toxicity in sediments and finally examined metal competition effects. Specifically, they wanted to understand if AVS accounted for all metal binding in sediments or if other factors shared responsibility. They were also able to examine the influence of sediment type on metal binding patterns, by comparing data gathered in this study with SEM: AVS data collected from sediments originating in the northeast United States.

Research Study

The project's main goal has been to study how heavy metals competed to bind with acid volatile sulfides and re-enter water as trace metals. To this end, the researchers studied:

- whether a sediment's AVS binding capacity could be used to predict the metals likely to remain bound given a certain mix of metal types;
- how a metal's sulfide solubility products (high or low) influence its ability to compete for AVS binding sites;
- whether a metal with a lower sulfide solubility product would completely displace a metal with a higher sulfide solubility product in binding with AVS.

The Georgia Tech/SKIO group used a batch test method to study sediment samples from coastal areas in the U.S. Southeast: the Pensacola and St. Andrews Bay regions of Florida, the Louisiana and Texas coast, Skidaway Island in Georgia, and the Florida Keys.

Initially, cadmium ions were chosen as a representative heavy metal because:

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Summary of the Problem

When heavy metals are released into water by natural processes or industrial activities, most of them end up in sediments of rivers, coasts or wetlands. Research monitoring studies have shown that heavy metals are among the most frequently reported contaminants found in sediments along the Atlantic or Gulf coasts.

At toxic levels, these pollutants can degrade important ecological processes in coastal wetlands and undermine the quality of ocean fishing harvests. As a result, the U.S. Environmental Protection Agency (EPA) is establishing a framework of regulations to control heavy metal contamination in sediments.

As part of this process, EPA is developing sediment quality criteria (SQC) to define the concentration threshold at which certain substances start to harm benthic organisms and water-column aquatic life. Before establishing new standards, research is needed to determine accurate indicators of metal toxicity in sediments.

An indicator has been proposed based on the level of metals that are simultaneously extracted (SEM) when acid volatile sulfides (AVS) are released by laboratory acidification of sediments. Because heavy metals bind with sulfide, it has been proposed that the SEM: AVS ratio can serve as an indicator of sediment toxicity. A research group from Georgia Tech and the Skidaway Institute of Oceanography (SKIO) has investigated the appropriateness of this ratio as such an indicator by studying the behavior of mixed metals in sediments collected in the U.S. Southeast.

- use of a single metal ion with a low incidence of interference provided a quick, easy and accurate method to determine aqueous metal concentrations;
- cadmium had been used extensively in past research, with its AVS appearing to offer a one-for-one match for the sediment's binding capacity;
- cadmium did not undergo major pH changes in the form of an ion-specific electrode;
- cadmium is soluble in seawater over the ranges tested in the research.

The metal binding capacities and kinetics of the samples were determined, and binding capacities and AVS levels were compared. The researchers also ran batch tests to determine how sediment-sea water slurries spiked with aqueous cadmium, nickel and zinc competed for AVS binding sites.

Research Results

According to study results, cadmium (Cd) titration of AVS levels appears to offer an effective indicator for estimating a sediment's metal-binding capacity; however, in cases where AVS content is low, binding capacity may be underestimated through use of this metric alone. Researchers reinforced earlier findings that fresh water sediments with low AVS content appear dominated by other binding mechanisms, such as organic carbon content. But the higher the AVS content, the greater the chances it can predict total binding capacity.

The researchers found strong evidence to support the claim that overall AVS content is the most important influence on the kinetic rate of metal binding. In general, kinetic rates will increase as AVS levels rise.

Another finding was that significant AVS losses in sample sediments occurred during storage. The reductions appear to reflect an instability of AVS in sediments likely to take place in the natural environment during storms or dredging operations.

In experimental systems with additions of equimolar levels of Ni, Zn, and Cd, nickel was the most soluble and was outcompeted for sulfide binding by Cd and Zn. Zinc was complexed by sulfide until Cd levels saturated available sulfide. In addition, zinc was competitively bound by non-sulfide sites. Finally, cadmium was excellent for assessing sulfide binding capacity because it had the lowest metal-sulfide solubility product and was not reactive with other sites in the sediments examined.

This study demonstrates that AVS does not account for all of the metal-binding capacities or the concentrations of metal in the aqueous phase. While the SEM:AVS ratio is useful in the laboratory and in sediments containing only a single metal contaminant, it does not perform effectively in the much more common case where several metals are mixed in a single sediment layer. When other metals are present, the sediment-binding characteristics of nickel and zinc are due to factors in addition to AVS. Cadmium, however, acts more in accordance with the hypothesis that AVS removal determines metal-binding behavior. The Georgia Tech/ SKIO researchers also found evidence that a sediment's metal-binding capacity rises as its AVS concentration increases.

Future Research Directions

The SEM: AVS ratio is a promising tool for investigating the correlations between heavy metals and sediment toxicity to benthic organisms, but the SKIO/Georgia Tech study shows more research is needed before this indicator can be made part of the sediment quality criteria proposed by EPA.

The study lays a foundation for a more comprehensive investigation of how heavy metals compete for AVS binding sites. This research should focus on determining the total metal-binding capacities for a wide range of sediments.

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