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13. ABSTRACT (Maximum 200 words) The objective of this research was to determine the influences of metal speciation on the kinetics of toxic metal solid phase transitions and interactions between solid phases and natural waters. Primary emphasis was on sulfidization-desulfidization reactions associated with near interfacial anoxic sediments. The approach utilized both the collection and analysis of natural samples and laboratory experiments. Samples from Chesapeake Bay were studied from organic matter rich and poor sites on a time-dependent basis in collaboration with the ONR-sponsored research of Drs. Donat and Burdige. A time-dependent field study was also conducted in Offatts Bayou, Texas, which is particularly well suited to our objectives because of the major redox changes that occur on a seasonal basis to the deeper basin waters. Sediments in these areas are more spatially heterogeneous in composition than anticipated and can also undergo seasonal variations in their trace metal chemistry. These results, coupled with those of the laboratory experiments, demonstrated the very dynamic nature of toxic metal speciation in sediments during early diagenesis. They point to the need to use considerable caution in the application of limited data bases and simple time-independent models for predicting potential bioavailability of toxic metals.			
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Objectives

The primary objective of the proposed research was to investigate the influences of metal speciation on the kinetics of toxic metal solid phase transitions and interactions between solid phases and natural waters. Primary emphasis was on sulfidization-desulfidization reactions associated with near interfacial anoxic sediments and overlying waters.

Within this general objective specific sub-objectives were: 1) to experimentally determine the rates at which different chemical species of metals react under conditions approximating those found in anoxic sediments; 3) to determine the extent that metals have become associated with authigenic pyrite and the time variability of this process; 4) to determine the rate of metal release to oxic waters when near-interfacial anoxic sediments are resuspended.

Field-Related Activities

We have collaborated with Drs. Donat and Burdige at Old Dominion University, in the study of metal chemistry in sediments from the Chesapeake Bay area. We have also devoted extensive efforts to the study of Offatts Bayou in Galveston, Texas, which is a seasonally highly anoxic human-made basin. Trace metal concentrations and speciation variation with time were determined in Chesapeake Bay and Offatts Bayou (adjacent to Galveston) TX. Two sites with anoxic sediments containing high (Site M ~3 wt.%) and low (Site S ~0.5 wt.%) organic carbon concentrations were studied in Chesapeake Bay in collaboration with Drs. Burdige's and Donat's MEQ program grant to determine dissolved Cu species fluxes across the sediment-water interface. They have provided us with multiple cores from these sites on a seasonal basis. We observed large variations in the fraction of total reduced sulfur present as AVS and reactive Fe (cold HCl leachable) at site M where these parameters co-vary, whereas they are close to constant and very low at site S. Very interestingly, pyrite-Hg also shows a similar trend, whereas the extent of reactive Cu in the pyrite fraction behaves very differently with time. Offatts Bayou was studied because of the major variations that occur in its bottom water redox states between winter (well mixed and oxic) and summer (stratified and highly sulfidic) conditions. Field data from Offatts Bayou indicate that sedimentary trace metal concentrations in both total metals and operationally defined metal fractions change dramatically on a seasonal basis. Higher levels are seen in the late summer and lower levels are found in early spring, supporting the theory that AVS minerals act as a sink for trace metals. However the ratio of reactive-metal:AVS was always less than one, indicating that the cation exchange model does not provide a sufficient mechanism to drive these variations in trace metals. One possible explanation is that rapid oxidation of sulfide minerals, such as mackinawite, greigite, and pyrite, can lead to release of associated trace metals, which could then associate with colloids or organic ligands and be transported out of sediments before the AVS minerals could reprecipitate. In this way, sedimentary trace metal concentrations would be controlled by degree of iron sulfidization, rather than simply by the ratio of HCl-extractable metal to AVS. This work is complimented by Sea Grant support in which the water column chemistry is being monitored.

Experimental Studies

Experimental tracer work has shown that sulfide-associated trace metals tend to stay associated with the particulate phase upon rapid oxidation of the synthetic mackinawite ($\sim\text{FeS}_2$) carrier. As metal solubility depends upon concentration, pH, and redox state, it became necessary to measure the oxidation rate of mackinawite as a function of oxidant concentration, pH, and ionic strength. Using a chemostat oxidation reactor, initial estimates of mackinawite oxidation rate in dilute solution have been made on the basis of AVS loss. Results indicate that 100% oxidation occurs within 4-48 hours. These results agree with previous estimates and point to the potential for highly dynamic processes influencing toxic metal speciation near the sediment-water interface. The oxidation rate of mackinawite and analogous trace metal sulfides depends, to a large part, on the surface area of the particles available for reaction with the solution. It is therefore necessary to obtain a reliable estimate of the surface area of different batches of synthetic mackinawite, or other metal sulfides of interest, so that oxidation rates may be normalized to this parameter. Arakaki and Morse demonstrated that standard gas adsorption methods (BET) are inadequate for determination of mackinawite surface areas because the drying stage leads to oxidation and vacuum welding of very fine particles leads to loss of surface area. Consequently, we have developed a dye (methylene blue)-adsorption technique that does not require the removal of mackinawite from deaerated water. Using this method, we have determined that our synthetic mackinawite typically has a surface area of about $200 \text{ m}^2/\text{g}$. We also constructed two chemostat systems for studying the oxidation rate of metal sulfides under carefully controlled conditions (e.g., constant P_{O_2} and pH).

Laboratory experiments were carried out to identify the structure, relative oxidation rates, and general chemical behavior of synthetic mackinawite and the metastable sulfide minerals. Sequential XRD spectra demonstrate that iron sulfide minerals undergo radically different diagenetic sequences under different ratios of aqueous iron to aqueous sulfide. Results indicate that the FeS minerals formed when aqueous sulfide is in excess oxidize more slowly than FeS minerals formed when the molar concentration of aqueous sulfide is equal to that of aqueous iron. This work indicates that mackinawite is not always the most common metastable iron sulfide mineral, and has broad implications toward our understanding of the iron-sulfur cycle in estuarine sediments.

Products

Reviewed Papers

- Morse, J.W., 1995, Dynamics of trace metal interactions with authigenic sulfide minerals in anoxic sediments. p. 187-200, *In Metal Contaminated Aquatic Sediments*, H.E. Allen (ed.), Ann Arbor Press, Chelsea, MI.
- Cooper, D.C. and J.W. Morse, 1996, The chemistry of Offatts Bayou, Texas: A seasonally highly sulfidic basin. *Estuaries* (in press).

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Talks and Presentations

Morse, J.W., 1995, Seasonal variation of sediment geochemistry and toxic metal speciation in organic carbon rich and poor Chesapeake Bay sediments. Estuarine Research Federation Conf. Abstracts.

Cooper, D.C. and J.W. Morse, 1995, Speciation and geochemistry of toxic metals in the sediments of Offatts Bayou, TX- A seasonally highly euxinic basin. Estuarine Research Federation Conf. Abstracts.

Seminars at:

Rice University

Northwestern University

Texas A&M University

Presentation at ONR MEQ meeting in San Diego.

Invited talk at Washington, D.C. meeting on silver in the environment, 1995.

In Preparation or Planned

D.C. Cooper's Ph.D. dissertation will be completed in about 9 months. Much of the work in this dissertation will have been supported by this grant. Probably at least 2 more reviewed papers will result as well.

A paper is being discussed with Jeff Cornwell which will combine his and our Chesapeake Bay trace metal data.

Another paper will be written on trace metals in Offatts Bayou after we complete this summer's sampling and analysis under Sea Grant support.