ESTUARINE COLLOIDS: SORPTION CAPACITY, COLLOID FACILITATED TRANSPORT AND BIOAVAILABILITY

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LONG-TERM GOALS

To gain a better understanding of the role of colloidal organic macromolecules and inorganic colloidal microparticles in the cycling, speciation and bioavailability of trace elements in coastal waters.

SCIENTIFIC OBJECTIVES

1. Critically evaluate ultra-filtration methodology for the collection of colloidal matter from fresh, estuarine and sea water.
2. Investigate changes in the the phase distribution of selected trace metals and metalloids in estuarine water along salinity transects.
3. Determine the importance of coagulation of colloidally bound trace metals (e.g., Ag, Hg, Se, As, Sb, Cd, Cu, Co, Ni, Pb, Zn, Fe) in estuarine waters.
4. Determine the bioavailability of colloidally bound trace elements and metalloids to penaeid shrimp.
5. Develop new analytical methods to establish binding of trace elements (e.g., Ag) with natural organic macromolecules and colloidal organic matter in the estuarine environment.
6. Evaluate microscopy imaging approaches to determine forms, shapes and sizes of natural organic macromolecules and inorganic microparticles (i.e., colloids).

APPROACH

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1) Colloid collection methodology: The cross-flow ultrafiltration technique (CFUF) for preconcentration and isolation of colloidal organic matter (COM) from 1 - 100 L of river, estuarine and sea water samples has been evaluated with regards to blank, speed of processing, mass balance, diafiltration effectiveness and retention of standard macromolecules to determine nominal molecular weight cut-offs of ultrafilters.
2) Colloidal trace element distribution: Salinity transects of the phase speciation distribution of trace metals and metalloids in Galveston Bay and other Texas estuaries have been conducted with regards to fluxes, geochemical behavior, and importance of colloidal forms of trace metals and metalloids in different molecular weight categories (i.e., 1kDa to 0.2µm, 3 to 0.2 µm, or 10kDa to 0.2µm).
3) Coagulation rates of colloidally bound trace metals: Radiotracer experiments using colloids isolated through CFUF and dialysis have been conducted in the laboratory to investigate coagulation rates of colloidally bound trace metals to colloids and suspended particles (_0.4µm).
4) Bioavailability of Colloidally Bound Trace Metals to Penaeid Shrimp: A number of laboratory uptake (14 days) and depuration (14 days) experiments have been conducted using penaeid shrimp, exposed to radioactive trace metals in colloidal or free-ionic forms.
5) Binding of selected trace metals to organic macromolecules: HPLC separation with thiol detection after addition of Ag and fluorescent tag to colloids was evaluated through collaboration with Dr. John Contois.
6) Forms, sizes and shapes of colloids: Atomic Force Microscopy (AFM) and Transmission Electrom Microscopy (TEM) of natural colloids was evaluated through collaboration with the group of Drs. Jacques Buffle, University of Geneva, Switzerland.

WORK COMPLETED

Objective 1 has been completed, as far as the CFUF methodology for the collection and analysis of bulk organic carbon and a number of trace metals is concerned. Results from calibration and other test experiments, which were part of 3 Ph.D dissertations (i.e., Mary Stordal, Liang-Saw Wen, supported by ONR, and Laodong Guo, supported by DOE) have been published. Radiotracer experiments on colloidal trace metals are currently being conducted to investigate complicating effects arising from sorption kinetics in ultrafilters, as part of a new Ph.D thesis (Degui Tang) on colloids. Preliminary results have been presented at the annual ACS symposium in Las Vegas (Tang et al., 1997; Santschi, 1997).
Objective 2 has been completed, and results are described in 5 publications. Reviews of the subject have also been presented at a number of national and international meetings.
Objective 3 has been completed and published over the last year.
Objective 4. Considerable work has been completed. Initial results are described in a master thesis (R. Carvalho, 1996) and in a manuscript which is currently in review.
Objective 5 has been initiated, and preliminary results have been obtained using HPLC and voltammetry techniques.
Objective 6 has been partly completed, and results are currently being written up for publication.

RESULTS

1) We showed that it is possible to reproducibly determine the phase speciation of COM and selected trace metals (e.g., Cd, Cu, Ni, Pb, Mn, Fe, Zn, Hg), and to collect COM for elemental and isotopic characterization, using blanks, mass balance and molecular weight cut-off calibrations as a guide. Furthermore, DOC and some trace metals in the permeate conformed with predictions by a permeation model with constant coefficients (Wen et al., 1997. Mar.Chem., 55, 129; Guo and Santschi, 1996. Mar.Chem., 55, 113).
2) The colloidal (1kDa to 0.4µm) fraction in Galveston Bay waters in the filter-passing pool averaged 57%, for Hg, 45% for Cd, 55% for Cu, 19% for Co, 36% for Ni, 64% for Pb, 91% for Zn, 79% for Fe and 35% for Se. Colloidal metal concentrations, in general, correlated significantly with colloidal organic carbon, COC, concentrations, suggesting that colloidal metals resulted from metal-organic complexation. Furthermore, ratios of colloidal metal (e.g., Ag, Cu and Hg) to 0.4µm filter-passing metal correlated with the ratios of COC to total DOC, suggesting that functional groups with high affinity for these metals were relatively evenly distributed over the different molecular weight fractions (Wen et al., 1997, Mar.Chem, in press; Stordal et al., 1996. L&O 41, 52).
3) When COM was labeled with various trace metals in radioactive form, coagulation with natural suspended matter occurred over the course of hours, while slower uptake was observed over the course of days. Results, which indicated that colloids can serve as intermediaries in the transfer and removal of trace metals in estuarine systems, could be explained by postulating two major groups of surface active trace metal complexants, which complex and coagulate different trace metals at different rates (Stordal et al., 1996. ES&T 30, 3335; Wen et al., 1997, GCA, 61, 2867).
4) Radiotracer experiments to compare bioaccumulation and bioavailability to penaeid shrimp, sites of accumulation and depuration of trace metals in colloidally complexed and free-ionic forms demonstrated that colloidally bound metals are bioavailable to shrimp. Differences were noted in the rates and extent of uptake and depuration between the colloidal and free-ionic treatments for whole body and individual tissues. Depuration of metals was noted for both treatment regimes, with metals introduced as free ionic species showing greater retention in shrimp than metals introduced as colloidally bound species. Results were consistent with the hypothesis that colloidally bound metals entered the body through the gills (Carvalho et al., 1997, L&O, submitted).
5) Preliminary evidence suggests that silver in Galveston Bay colloids is complexed to sulfhydril groups (Santschi et al., 1997, Proc. of Argentum Conf., Hamilton, Ontario).
6) Colloidal organic matter, isolated by cross-flow ultrafiltration, was imaged by a new technique, Atomic Force Microscopy, and compared to Transmission Electron Microscopy. Preliminary results suggest that polysaccharide rich fibrils are a major component of COM (Santschi et al., in preparation, for submission to L&O).

IMPACTS

1) Proper adaptation of CFUF using clean technique make it suitable for isolating organic carbon and selected trace metals. 2) We established using CFUF that colloidal forms of

many trace metals are important in estuaries, including Ag, for which previous measurements have shown no organic complexation in San Francisco Bay (Miller and Bruland, 1995. ES&T 29, 2626). 3) We have shown that colloidal forms of trace metals are bioavailable to Penaeid shrimp. 4) We demonstrated that metal-organic complexes can coagulate and become part of the particulate fraction within days. 5) We showed that selected thiol groups of COM complex all the Ag in the water of Galveston Bay. 6) We determined that polysaccharide-rich fibrils are major components of COM in Galveston Bay, Gulf of Mexico and in Middle Atlantic Bight waters.

TRANSITIONS

In addition to the PIs, Assistant Research Scientist, Dr. Liang-Saw Wen, graduate student Dequi Tang, and research assistant Susan Gonzalez have been supported on this project. Over the next calender year, we expect that two new PhD and/or master students will conduct their thesis or dissertation research on topics related to this project.

RELATED PROJECTS

This project benefited from other programs which investigated marine colloids. 1) DOE, - Ocean Margins Program, “Carbon transport in the benthic boundary layer”: Investigation of the importance of benthic boundary layer processes in ocean margins for COM export to open ocean. Determination of isotopic and elemental composition of marine colloids. 2) NSF - OCE, “Relationship of Th(IV) speciation to scavenging in marine environments”: Investigation of the importance of parallel reactions for Th(IV) sorption to colloidal matter of all sizes. This project benefited also from collaborations with Drs. J. Buffle, K. Wilkinson, and E. Balnois, Dept. of Analytical Chemistry, University of Geneva, Switzerland, for the AFM and TEM work on COM, and with Dr. John Cantois, Specells, Inc., Houston, TX, for the HPLC work of Ag-thiols.

REFERENCES AND WEB ADDRESS

References are given in the text, and more information can be found at http://loer.tamug.tamu.edu