The Role of Chemical Speciation in Processes Governing the Environmental Fate and Effects of Trace Metals in Estuarine and Coastal Environments

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LONG-TERM GOALS

The long-term goals of our research have been to:

1) Continue to develop and evaluate highly sensitive analytical techniques for determining the concentrations of bioactive trace metals in seawater and the extent of their complexation or chelation by natural organic ligands.

2) Further our basic understanding of the role of chemical speciation with respect to both trace metal toxicity and bio-limitation of phytoplankton within coastal and estuarine environments for a suite of bio-active trace metals - Mn, Fe, Ni, Cu, Zn, Cd and Pb. This includes the influence of organic complexation on the reactivity of these trace metals, as well as gaining insight into the production and fate of the metal chelating organic ligands.

This research has been particularly complementary to that of Bill Sunda, another Harbor Processes PI, by providing the field data needed to evaluate the applicability of his laboratory studies examining the effects of these trace metals.

OBJECTIVES

A free ion concentration model has evolved as a result of numerous well-defined laboratory studies which characterizes the toxicity or availability of these metals to microorganisms as a function of their free metal ion concentration in seawater. Our primary objective is to characterize the extent of organic complexation of these dissolved trace metals in coastal and estuarine waters and to determine their respective ambient free metal ion concentrations.

Specific tasks are to:

1) Measure concentrations of trace metals and specific metal-complexing organic ligands and determine the conditional stability constants of their respective complexes. These values allow the calculation of ambient free metal ion concentrations and provide a basis to estimate free metal ion concentrations given variable metal inputs.

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2) Investigate competitive interactions among metals for binding to various classes of metal-binding organic ligands present in seawater.

3) Collaborate with Mark Wells to determine what fractions of the organically bound trace metal species exist as “truly dissolved” species (e.g., <1000 NMW) or are associated with colloidal material, and to characterize the affinity of marine colloids for binding trace metals.

Our secondary objective is to examine the interactive effects of trace metal concentrations and speciation on phytoplankton growth rates, phytoplankton species composition, community structure, and bio-accumulation of trace metals. We carry out our field research to be highly complementary with the laboratory studies of Bill Sunda.

APPROACH

We have taken a multi-technique approach to our studies of dissolved metal concentrations and speciation. Over the years, we have developed many of the analytical techniques ourselves. The techniques include:

1) Chelation/solvent extraction/graphite furnace atomic absorption spectroscopy (GFAAS) for the determination of total dissolved metal concentrations.

2) Chelation/solid phase extraction/high resolution inductively coupled plasma mass spectrometry (ICP/MS) for the determination of total dissolved metal concentrations.

3) Anodic stripping voltammetry (ASV) at a thin mercury film (TMF), rotating glassy carbon disk electrode (RGCDE) for speciation studies of Cu, Zn, Cd and Pb.

4) Competitive ligand equilibration (CLE) coupled with adsorptive cathodic stripping voltammetry (ACSV) for speciation studies of Fe, Ni, Cu, and Zn.

5) Cathodic stripping voltammetry (CSV) for the determination of the concentration and speciation of Mn.

We have applied these various analytical methods in a series of field studies to determine the partitioning of trace metals among their various physico-chemical forms, and provide basic thermodynamic data needed to predict the environmental fate and effects of these metals. Such field data are sorely lacking, particularly in estuarine and coastal areas influenced by marine, terrigenous and anthropogenic inputs. The major field efforts of this study have been in Narragansett Bay, Rhode Island, and in the South San Francisco Bay. Both of these sites have substantial anthropogenic inputs of trace metals, but differ in that they have either a relatively permanent phytoplankton bloom (upper parts of Narragansett Bay) or a pronounced spring phytoplankton bloom (South San Francisco Bay).

WORK COMPLETED

Our tasks completed this past year include:

1) Publication of “The complexation of ‘dissolved’ Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, RI.” 1998. Marine Chemistry, 62: 203-218 (Wells, Kozelka and Bruland).
2) Publication of “Chemical speciation of dissolved Cu, Zn, Cd and Pb in Narragansett Bay, RI.” 1998. Marine Chemistry, 60: 267-282 (Kozelka and Bruland).
3) Publication of “Physico-chemical speciation of lead in South San Francisco Bay.” 1997. Estuarine, Coastal and Shelf Science, 44: 649-658 (Kozelka and Bruland).
4) Publication of “Determination of dissolved manganese(II) in coastal and estuarine waters by differential pulse cathodic stripping voltammetry.” 1997. Analytica Chimica Acta, 344: 175-180 (Roitz and Bruland).
5) Publication of “Trace metal exchange in solution by the fungicides ziram and maneb (dithiocarbamates) and subsequent uptake of lipophilic organic zinc, copper and lead complexes into phytoplankton cells. 1997. Environmental Toxicology and Chemistry, 16: 2046-2053 (Phinney and Bruland).
6) Publication of “Effects of diethyldithiocarbamate and 8-hydroxyquinoline additions on algal uptake of ambient Cu and Ni in South San Francisco Bay water.” 1997. Estuaries, 20: 66-76 (Phinney and Bruland).
7) Publication of “Competitive equilibration techniques for determining transition metal speciation in natural waters: Evaluation using model data.” 1997. Analytica Chimica Acta, 343: 161-181 (Miller and Bruland).
8) Revision of “An improved method for rapid preconcentration and determination of bioactive trace metals in seawater using solid phase extraction and high resolution inductively coupled mass spectrometry.” In press. Marine Chemistry (Wells and Bruland).
9) Revision of “An iron limitation mosaic in the California Current upwelling regime. In press. Limnology and Oceanography (Hutchins, DiTullio, Zhang and Bruland).
10) Submission of a manuscript “An Intercomparison of Voltammetric Approaches to Determine the Chemical Speciation of Dissolved Cu in an Estuarine Sample from Narragansett Bay, RI. Submitted to Analytica Chimica Acta (Bruland, Rue, Kozelka, Donat, Skrabal, and Moffett).

RESULTS

In order to model the behavior and effects of trace metals in coastal waters, it is essential to quantify their solution speciation *in situ* and characterize the major biological, chemical and geological processes that influence their chemical speciation. We have developed a variety of analytical approaches which allow us to examine the speciation of a suite of bio-active trace metals — including Mn, Fe, Ni, Cu, Zn, Cd and Pb — within the water column of estuarine and coastal environments and their interaction with plankton. We are making excellent progress in quantifying the concentrations and conditional stability constants of the metal-binding organic ligands in estuarine and coastal waters. These advances are providing key insights to the role of natural organic ligands in chelating these metals and controlling their free metal ion concentrations.

IMPACT/APPLICATIONS

The chemical speciation or form of trace metals in estuarine and coastal waters is the critical parameter governing their fate, bio-accumulation and toxicity to aquatic micro-organisms. The measurement of total dissolved concentrations of potentially toxic trace metals tells us very little about metal toxicity in coastal ecosystems. In order to understand and model the behavior and effects of trace metals in coastal waters it is essential to quantify their solution speciation *in situ* and characterize the major processes that influence their chemical speciation. There are field data indicating many bio-active trace metals exist predominantly as organic complexes or chelates in coastal waters. It appears that low concentrations of relatively strong and metal specific organic ligands play an important role in the chemical speciation of metals such as Cu and Zn. The bulk of these metal chelates appear to be relatively low molecular weight (less than 1000 Daltons NMW) and appear to be anionic and hydrophilic in character. Speciation studies carried out in coastal waters with dissolved Cu generally show that greater than 99% of the Cu is strongly bound or chelated with organic ligands. These studies also show that the concentration of free Cu^{2+} in coastal waters is usually found to be less than 10^{-11} M — a concentration that is non-toxic to most phytoplankton. There are cases, however, such as in the South San Francisco Bay where only ~80% of the Cu is chelated with these organic ligands. In these cases the free Cu^{2+} approaches 10^{-9} M and can be toxic to many phytoplankton species. The EPA currently sets a concentration of approximately 3.3 ug/L of dissolved Cu as being the allowable concentration in coastal waters. If organic complexation was minimal, the free Cu^{2+} concentration would exceed 10^{-9} M, a concentration toxic to most coastal species. However, in many coastal waters, higher concentrations of total dissolved Cu can be present yet be largely non-toxic if sufficiently high levels of natural organic chelators are present. Therefore, assessing the environmental impact of elevated trace metals in coastal systems is critically dependent on understanding the chemical speciation of these metals.

TRANSITIONS

The PI attended an ONR-sponsored Copper Workshop held in San Diego in June 1997. The major objective of the workshop was to gain a better understanding of the scientific and regulatory issues concerning copper toxicity with respect to Navy operations. The PI attended the NSF-funded Workshop on Research Needs for Coastal Pollution in Urban Areas and made a presentation on toxic metals in coastal waters. The PI also attended a November 1997 EPRI-sponsored Workshop on Paradigms of Metal Bio-accumulation in Aquatic Ecosystems where he participated in the Metal Bio-availability and Uptake Mechanisms Working Group. These are all examples of attempts at making our research results and expertise available to a broader group of users.

RELATED PROJECTS

We have a number of collaborations with various groups within this program. First, we have had an ongoing collaborative effort with Mark Wells here at UCSC in studying the role of colloids in the marine environment. This has been fruitful and is now yielding a series of papers. Second, we have had an informal collaboration with Bill Sunda where our field efforts complement his laboratory studies. Finally, we have been involved in inter-comparison studies of our methods with various groups within the Harbor Processes program. Our research group and those of Moffett and Donat have all analyzed a common sample for copper speciation. The results of this inter-comparison study are in manuscript form and being revised at this time.

PUBLICATIONS

Bruland, K.W., E.L. Rue, P.Kozelka, J. Donat, S. Skrabal, and J. Moffett (submitted).

An Intercomparison of Voltammetric Approaches to Determine the Chemical Speciation of Dissolved Cu in an Estuarine Sample from Narragansett Bay, RI. Submitted to Marine Chemistry.

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Rue, E.L. and K.W. Bruland (1997). The role of organic complexation on ambient iron chemistry in the equatorial Pacific Ocean and the response of a mesoscale iron addition experiment. Limnology and Oceanography, 42: 000.

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