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**Quantifying the Cycling of Toxic Metals and Metal-Complexing Ligands in a
Major US Naval Harbor (Elizabeth River, VA)**

Final Report for ONR N00014-02-10894

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ABSTRACT

This project was a modeling and synthesis effort that examined metal and metal-complexing ligand dynamics in a major US Naval harbor, the Elizabeth River (VA). It built on our past work (funded through the ONR Harbor Processes program) studying the biogeochemical cycling of Cu, Cd, Zn, and Mn in the water column and sediments of the Elizabeth River.

INTRODUCTION

For several years, we were funded through the ONR Harbor Processes program to study the biogeochemical cycling of Cu, Cd, Zn, and Mn in the water column and sediments of a major US Naval harbor, the Elizabeth River (VA). In particular, we examined: (1) trace metal concentrations, complexation and speciation (Donat); (2) *in situ* production of Cu complexing-ligands by natural microbial populations (Gordon and Donat); (3) phytoplankton metal uptake (Donat, in collaboration with W. Sunda/S. Huntsman [NOAA]); (4) fluxes of metals and metal-complexing ligands from sediments (Donat and Burdige). This work built on past ONR-funded work by Donat and Burdige, who examined the role of sediments as sources of copper-complexing ligands to coastal waters, and studied the biogeochemical fate of these ligands in coastal waters (e.g., photochemical oxidation). In the last year of our Elizabeth River studies we were also joined by researchers from Ken Buesseler's lab (WHOI) who were studying groundwater inputs to the Elizabeth River, and from Beth Ahner's group (Cornell), who were studying the distributions of phytochelatins (algal-produced metal complexing ligands).

The individual pieces of this loose collaborative effort represented an unprecedented look at

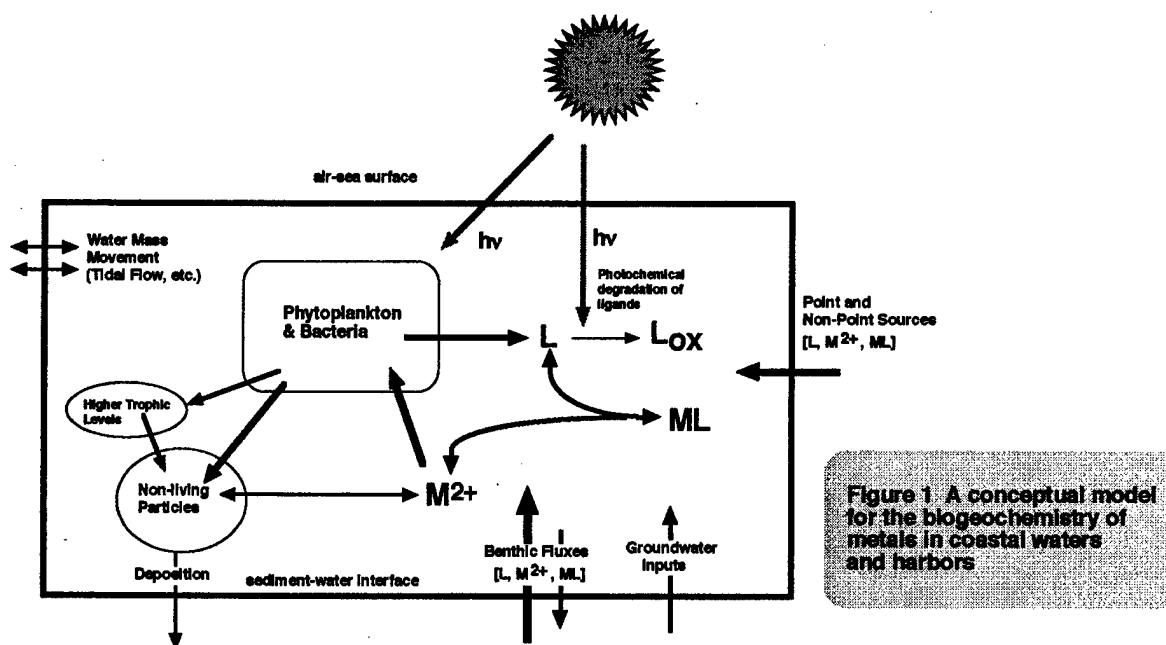
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metal and metal-complexing ligand dynamics in a coastal harbor. As a result of these efforts we were in the unique position to develop a more holistic understanding of metal and metal-ligand dynamics in the Elizabeth River and also to further our understanding, in general, of copper toxicity and bioavailability in other river-estuarine systems. Consequently, this work represented a modeling and synthesis effort that began to address these goals.

The first goal of this effort was to quantify the various metal and metal-ligand fluxes and transformations shown in the conceptual model in Fig. 1. Such an effort has never been undertaken in the Elizabeth River nor in any other estuarine system, and represented an important first step in the development of predictive biogeochemical models for such systems. This effort has also helped us more critically determine the gaps in our knowledge about metal and metal-ligand cycling in estuaries, for future field work and more detailed model development. At the same time, additional, more general, synthesis efforts were carried out here, again building on our past studies of copper toxicity and bioavailability in estuarine and harbor waters.

RESULTS

Rather than repeat here the results in our published papers and abstracts funded by this proposal, listed below are the citations to the publications, abstracts and presentations that addressed the goals of this project. Furthermore, this project provided support for one Ph.D. dissertation (Christina Dryden, 2004) and also provided support and research opportunities to several other M.S. and Ph.D. students.

Modeling copper fluxes and dynamics in the Elizabeth River

Dryden, C.L. 2004. Organic Copper Binding Ligands and Thiol Compounds Produced by Bacteria and in the Elizabeth River, Virginia. Ph.D. dissertation, Old Dominion University.

Dryden, C.L., and D.J. Burdige. A box model study of dissolved copper in the Elizabeth River, Virginia. ms. in prep. for Estuaries.

Additional synthesis efforts (publications)

Dryden, C.L. 2004. Organic Copper Binding Ligands and Thiol Compounds Produced by Bacteria and in the Elizabeth River, Virginia. Ph.D. dissertation, Old Dominion University.

Dryden, C., Gordon, A.S. and Donat, J.R. 2004. Interactive regulation of dissolved copper toxicity by an estuarine microbial community. *Limnology & Oceanography*. 49(4):1115-1122.

Wei, L., J.R. Donat, G. Fones, and B.A. Ahner. 2003. Interactions between Cd, Cu, and Zn influence particulate phytochelatin concentrations in marine phytoplankton: Laboratory results and preliminary field data. *Environmental Science and Technology*, 37(16): 3609-3618.

Additional synthesis efforts (abstracts and presentations)

Carrasco, G.G., J.R. Donat, and D.J. Burdige. 2002. Benthic fluxes of copper, zinc, and cadmium and their complexing ligands in the Elizabeth River, Virginia. Abstract OS21O-08: The American Society of Limnology and Oceanography/ American Geophysical Union Ocean Sciences Meeting, Honolulu, HI.

Donat, J.R., G.G. Carrasco, and J.A. Consolvo III. 2002. Water column trace metal concentrations and speciation in the Elizabeth River, Virginia. Abstract OS21O-07: The American Society of Limnology and Oceanography/ American Geophysical Union Ocean Sciences Meeting, Honolulu, HI.

Dryden, C.L., A.S. Gordon, J.R. Donat, and A.J. Ericsson. 2002. Copper-responsive production of copper-complexing ligands by estuarine microbial communities. Abstract OS21O-09: The American Society of Limnology and Oceanography/ American Geophysical Union Ocean Sciences Meeting, Honolulu, HI.

Dryden, C., A.S. Gordon, and J.R. Donat. 2004. Interactive regulation of dissolved copper toxicity by an estuarine microbial community. 9th FECS Conference on Chemistry and the Environment and 2nd SFC Meeting on Environmental Chemistry Behaviour of Chemicals in the Environment. Bordeaux, France, Aug. 29– Sept. 1.

Poorvin, L., J.R. Donat, and S.W. Wilhelm. 2002. The fate of intracellular Fe from marine microbes following viral lysis. Abstract OS12T-01: The American Society of Limnology and

Oceanography/ American Geophysical Union Ocean Sciences Meeting, Honolulu.