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FINAL REPORT

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THE VOLTAMMETRIC DETERMINATION OF TRACE METAL CONCENTRATIONS AND ORGANIC COMPLEXATION IN SEAWATER

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INTRODUCTION

Biological processes can strongly influence the oceanic chemistries of trace metals and, in turn, trace metals can influence plankton production and community structure. Our knowledge of the oceanic concentrations, distributions, and cycles of trace metals has advanced significantly (see Bruland 1983; Whitfield and Turner 1987). We now know the bioactive trace metals exist at nanomolar (10^{-9} M) to picomolar (10^{-12} M) concentrations in oceanic waters. In addition, marine chemists have recently advanced their ability to characterize the chemical speciation of these bioactive trace metals in the sea; that is, we can now determine their free ion concentrations and the extent to which certain trace metals interact with organic and inorganic ligands naturally present in oceanic surface waters.

In 1983 in his excellent text book Principles of Aquatic Chemistry, Francois Morel stated that "The subject of coordination of trace elements in natural waters is probably the greatest remaining challenge to analytical chemists; the objective is to demonstrate and quantify the existence of fractions of chemical constituents as picomolar concentrations of perhaps ephemeral species." Bruland et al.(1991) argue that "Recent results for Cu and Zn demonstrate that marine chemists have begun to meet the "challenge" and "objective" described by Morel. We now know that the chemical speciation of these two trace metals is largely dominated by organic complexation..." A substantial portion of the convincing evidence derives from results of the P.I.'s research funded by ONR.

ACCOMPLISHMENTS

The primary goals of our research in this field are to: 1) develop voltammetric techniques for determining the concentrations and extent of organic complexation of various

trace metals in seawater, 2) use the results of these determinations to estimate the organic and inorganic solution speciation of trace metals in seawater, and 3) to interpret the significance of strong trace metal-organic ligand interactions with respect to trace metal toxicity and bioavailability to phytoplankton, and with respect to biogeochemical cycling of dissolved trace metals in the oceans.

Much of our research in technique development has been strongly influenced by the work of two research groups. Our applications of differential pulse anodic stripping voltammetry (DPASV) at a thin mercury film (TMF), rotating glassy carbon disk (RGCD) electrode built upon the expertise of the late Professor H.W. Nurnberg and Leon Mart at KFA, Julich, FRG; while our use of differential pulse cathodic stripping voltammetry (DPCSV) with interfacial adsorption of metal chelates onto a hanging mercury-drop (HMD) electrode has built upon the expertise of Stan van den Berg, in the Dept. of Oceanography at The University of Liverpool, UK.

Our ONR-funded research efforts over the past 5 years have resulted in the continuation of a series of advancements in development of techniques based on DPASV and DPCSV for determining concentrations and speciation of trace metals in seawater, and to our understanding of the significance, distribution, and variability of organic-trace metal complexation in seawater. Perhaps the best indicator of our accomplishments is that of our publications and manuscripts in press. A chronological listing of these refereed publications and manuscripts for the period of this award (since 1989) is presented below:

1) Bruland, K.W., 1989. Complexation of zinc by natural organic ligands in the central North Pacific. Limnology and Oceanography, vol. 34, p. 269-285.

2) Donat, J.R. and K.W. Bruland, 1989. A comparison of two voltammetric techniques for determining zinc speciation in Northeast Pacific Ocean waters. Marine Chemistry, vol. 28, p. 301-323.

3) Coale, K.H. and K.W. Bruland, 1990. Spatial and temporal variability in copper complexation in the North Pacific. Deep Sea Research, vol. 47, p. 317-336.

4) Capodaglio, G., K.H. Coale, and K.W. Bruland, 1990. Lead speciation in surface waters of the eastern North Pacific. Marine Chemistry, vol. 29, p. 221-233.

5) Bruland, K.W., J.R. Donat, and D.A. Hutchins, 1991. Interactive influences of bioactive trace metals on biological production in oceanic waters. Limnology and Oceanography, vol. 36, p. 1555-1577.

6) van den Berg, C.M.G. and J.R. Donat, 1992. Determination and

data evaluation of copper complexation by organic ligands in sea water using cathodic stripping voltammetry at varying detection windows. Analytica Chimica Acta, vol. 257, p. 281-291.

7) Donat, J.R. and C.M.G. van den Berg, 1992. A new cathodic stripping voltammetric method for determining organic copper complexation in seawater. Marine Chemistry, in Press.

8) Bruland, K.W., 1992. Complexation of cadmium by natural organic ligands in the central North Pacific. Limnology and Oceanography, in Press.

9) Donat, J.R. and K.W. Bruland, 1992. Trace elements in the oceans (Chapter 12), in Trace Elements in Natural Waters, Eds. Steinnes and Salbu, CRC Press.

10) Coale, K.H., 1991. Effects of iron, manganese, copper and zinc enrichments on productivity and biomass in the subarctic Pacific. Limnology and Oceanography, vol. 36, p. 1851-1864.

In addition to the above publications which attest to our productivity, a number of post docs and graduate students received valuable training. Dr. John Donat was a post doc on much of this grant and received approximately 50% of his funding from ONR. He has now taken an Assistant Professor position at Old Dominion University in the Department of Chemistry and Biochemistry. He will also act as a liaison between the Chemistry and Biochemistry Department and the Oceanography Department. Dave Hutchins, Jonathon Phinney and Edie Rue have all received partial support from this ONR grant. Dave and Jonathon are graduate students in the Biology Ph.D. program working on trace metal phytoplankton interactions, while Edie is a graduate student in the Chemistry Ph.D. program working on the chemistry and speciation of bioactive trace metals. They have all received valuable training and are beginning to be productive scientists. Both Kenneth Coale and John Donat were former students who were funded partially by ONR.

Statement A per telecon Edward Green
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