Chapter 11

Trace Elements in the Oceans

John R. Donat and Kenneth W. Bruland

CONTENTS

I. INTRODUCTION

Over the past 15 years a revolution has occurred in marine and environmental chemistry regarding our knowledge of the distributions and chemical behavior of trace elements in natural waters, particularly seawater. Important factors initiating this revolution were the development and adoption of noncontaminating or "clean" techniques for collection, preservation, storage, and analysis of seawater samples, and major advances in modern analytical methods and instruments. As a result, seawater concentrations of many trace elements have been shown to be factors of 10 to 1000 lower than those previously accepted. Vertical concentration profiles have been found to be consistent with known biological, physical, and/or geochemical processes operating within the ocean. As the oceanic concentrations of most of the trace elements have been determined, the oxidation states and chemical forms or speciation of certain trace elements in the oceans have been identified. Complexation of certain trace

metals with inorganic and organic ligands has been demonstrated. Organometallic forms of certain trace elements have been identified and their concentrations determined. Thus, a new picture of the trace element composition of seawater has developed.

The progress made in advancing our understanding of trace element chemistry in seawater up through the early 1980s was demonstrated in the major collection of papers edited by Wong et al.[1] Thorough reviews of this field have been prepared by Burton and Statham,[2-4] Bruland,[5] and Whitfield and Turner.[6] We refer the reader to these sources and the references cited within them for detailed information. In this chapter, we do not attempt a comprehensive survey of the elements for which reliable data are now available. Rather, we concentrate on presenting recent highlights regarding some of the more interesting aspects of oceanic trace element chemistry, and we summarize background information on input and removal processes, and sampling, preanalysis, and analytical considerations.

II. CONTRIBUTING AND REMOVAL PROCESSES

Trace elements in seawater have two major external sources: (1) atmospheric or riverine inputs of weathering products of the exposed continents; and (2) inputs resulting from the interactions of seawater with newly formed oceanic crustal basalt at ridge-crest spreading centers via both high temperature hydrothermal activity and low temperature interactions with newly formed oceanic crust.

While the riverine inputs of the major elements to the oceans are known fairly accurately, those of the majority of the trace metals are not, primarily because the concentrations of many of the trace elements in rivers are not known reliably. This situation results most likely from insufficient control of sample contamination and lack of validation of the data obtained. Examples of reliable studies that have been performed include those of Shiller and Boyle[7] and Trefrey et al.[8] who, using sampling and analytical methods proven to eliminate or reduce trace element contamination of natural water samples, determined concentrations of Cu, Ni, Cd, Fe, and Zn in the Mississippi River that were much lower than those for the same region published annually in the U.S. Geological Survey Water Data Reports. Shiller and Boyle[9] demonstrated that dissolved Zn concentrations commonly quoted as typical in rivers are as much as a factor of 100 too high. Table 1 presents the most recent reliable data on world average riverine trace element concentrations and fluxes to ocean margins.[10] Martin and Windom[10] state that a need still exists for additional reliable data from river systems draining geologically, climatologically, and physiologically diverse watersheds.

Chester and Murphy[11] and Buat-Ménard[12] have recently reviewed the literature regarding the geochemical significance of atmospheric inputs of trace elements to the oceans. Arimoto et al.[13] have provided a similar review specific to the Pacific Ocean. Chester and Murphy[11] compiled reports showing that the atmospheric flux of some metals, especially Pb, Zn, and Cd, to surface coastal waters can equal or exceed their riverine flux. They also attempted to illustrate the relative importance of atmospheric and riverine inputs of various trace metals to individual ocean basins such as the North and South Pacific and the North Atlantic (Table 2). Their estimates indicate that atmospheric deposition has the most influence on the surface waters of the North Atlantic and the least on those of the South Pacific. In addition, they estimate that, averaged over an entire ocean basin, the atmospheric dissolved fluxes for Mn, Ni, Co, Cr, V, and Cu are an order of magnitude less than their riverine dissolved fluxes; the two fluxes are the same order of magnitude for Al, Fe, and Cd, but the atmospheric fluxes are dominant for Zn and Pb. If, however, just open ocean regimes are examined, atmospheric inputs overwhelmingly predominate for particle reactive elements such as Fe and Al because the riverine inputs of these elements are largely removed by intense particle scavenging in the coastal ocean.

The estimates made by Chester and Murphy[11] required estimates of the solubility of aerosol-associated trace metals in seawater. Such solubilities are experimentally difficult to obtain and the values are the subject of much discussion. For example, the wide variability in the estimates of the solubility of Fe(III) in surface seawater, and their dependence upon the pore size of the filter used, provide a striking example of our lack of definition of this process. In the first study to examine aerosol dissolution using sufficiently high dilution factors such that the solubility of Fe was not exceeded, Zhuang et al.[14] found the "saturated concentration" of dissolved atmospheric Fe passing through a 0.4-μm filter to be 10 to 17 nM, while that passing through a 0.05-μm filter was 5 to 8 nM. Sunda[15] estimated the solubility of truly dissolved Fe(III) to be 1.5 nM at pH 8.2 and 20 to 25°C. In a review of Fe biogeochemistry in seawater, Wells[16] argues for a maximum solubility of 0.1 nM. Wells[16] suggests that the discrepancy in the different values is due to the existence of colloidal Fe. Reliable estimates of the soluble fractions of trace metals such as Fe in seawater and data on colloidal metals in the open ocean are still needed.

Table 1 Atmospheric dissolved vs. fluvial dissolved inputs to regions of the world ocean (μg/cm^2/year)

| | Oceanic Region | | | | | |
| | North Atlantic | | North Pacific | | South Pacific | |
Element	Fluvial Dissolved Flux[a]	Atmospheric Dissolved Flux	Fluvial Dissolved Flux	Atmospheric Dissolved Flux	Fluvial Dissolved Flux	Atmospheric Dissolved Flux
Al	0.56	0.25	0.24	0.09	0.12	0.0066
Fe	0.18	0.24	0.076	0.062	0.038	0.0035
Mn	0.18	0.025	0.076	0.004	0.038	0.0013
Ni	0.017	0.008	0.0074	—	0.0037	—
Co	0.0044	0.00061	0.0019	0.00004	0.0009	0.000006
Cr	0.011	0.0014	0.0047	—	0.0023	—
V	0.022	0.0043	0.0094	0.0017	0.0047	—
Cu	0.037	0.0075	0.016	0.0021	0.0079	0.0013
Pb	0.0022	0.093	0.0009	0.0022	0.0005	0.0004
Zn	0.016	0.059	0.0071	0.029	0.0035	0.0026
Cd	0.0018	0.0016	0.0008	0.00023	0.0004	—

[a] No attempt has been made to adjust the North Atlantic fluvial flux for European and North American anthropogenic inputs.

From Chester, R. and Murphy, K. J. T., Metals in the marine atmosphere, in *Heavy Metals in the Marine Environment*, Rainbow, P. S. and Furness, R. W., Eds., CRC Press, Boca Raton, Florida, 1990, 27. With permission.

Hydrothermal activity associated with the formation of a new oceanic crust exerts a major influence on the composition of seawater. High temperature systems, such as the "black smokers" on the East Pacific Rise in which hot (~350°C), acidic (pH ~3.5), sulfide-, and metal-rich solutions emerge directly into surrounding seawater, are major oceanic sources of the trace elements Fe and Mn, and the minor elements Li and Rb, and the major oceanic sinks for Mg and SO_4^{2-}. More detailed discussions of the trace element solution chemistry of hydrothermal systems can be found in the literature reviewed by Thompson[17] and Edmond,[18] in the NATO Advanced Research Institute volume edited by Rona et al.,[19] and in papers by Von Damm et al.[20,21]

Most dissolved trace elements are ultimately removed from seawater to marine sediments primarily by adsorption onto sinking particles ("scavenging") or by incorporation into biological phases via active uptake by phytoplankton followed by sinking of biological detritus. However, prior to their ultimate removal, trace elements may undergo various degrees of recycling which can involve chemical desorption reactions or redissolution from particles ("regeneration") as the particle carrier phases oxidize and/or dissolve. Regeneration may occur within the water column, and within surficial sediments followed by diffusion of the dissolved trace elements back into the water column, allowing these elements to participate again in their internal cycling within the oceans.

III. SAMPLING AND PREANALYSIS HANDLING

The recent revolution in our knowledge of the distributions and forms of trace elements in seawater results primarily from major advances in the development of: (1) "clean techniques" to eliminate or control contamination during sampling, storage, and analysis, (2) preconcentration and separation techniques, and (3) extremely sensitive analytical instruments.[5] These major advances in sampling and preanalysis handling techniques are reviewed below; the advances in analytical techniques and instruments are presented in the subsequent section.

A. GENERAL CONTAMINATION CONTROL CONSIDERATIONS

The importance of using clean, noncontaminating methods in all stages of trace element determinations was emphasized by Moody and Beary:[22]

Table 2 Riverine trace element concentrations and fluxes
to ocean margins

	Concentrations		Fluxes	
	Dissolved µg/l	Particulate µg/g	Dissolved kg/yr	Particulate kg/yr
Metalloids				
As	1.7	5	65	75
Nutrient-type				
Cd	0.01	1.2	0.4	18
Cu	1.5	100	58	1,500
Ni	0.5	90	19	1,350
Zn	0.6	250	23	3,750
Geochemically controlled				
Al	50	94,000	1,925	1,410,000
Co	0.1	20	3.8	300
Fe	40	48,000	1,540	720,000
Mn	8.2	1,050	320	15,750
Pb	0.03	35	1.1	525
U	0.24	3	9.2	45
Rare earth elements				
Ce	0.08	80	3.1	1,200
Eu	0.001	1.5	0.04	23
La	0.05	45	1.9	675
Sm	0.008	7	0.31	105

From Martin, J.-M. and Windom, H. L., Present and future roles of ocean margins in regulating marine biogeochemical cycles of trace elements, in *Ocean Margin Processes in Global Change,* Mantoura, R. F. C., Martin, J.-M., and Wollast, R., Eds., John Wiley & Sons, New York, 1991, 45. With permission.

"In the present-day real world of trace element analyses, the theoretical or even practical sensitivity limit of the instrument is very often not the limiting factor in the accuracy of an analysis. Instead the size and variability of the analytical blank is the principal limitation."

Trace element analysts must be concerned with the reduction and control of this blank through all steps of the analysis, from choosing containers to making the final quantitative measurement. Sample contamination can be caused by the method of handling or containment, by apparatus, by the use of analytical reagents, by the environment in which the sampling or analysis is performed, and even by the presence and influence of the analyst.

The specific means used to reduce the analytical blank may vary from element to element, but use of Class 100, clean-air work spaces, and purified reagents has become common for present day trace element analysis of natural waters. For most laboratories involved with the analysis of trace elements in seawater, the cost of a complete Class 100 laminar-flow laboratory is prohibitive. Instead, a more pragmatic and less stringent approach is adopted whereby the laboratory is flushed with a nonlaminar flow of filtered air, and within this "clean" area, several Class 100, laminar-flow work benches provide dust-free conditions for all critical manipulations.[23] Additional precautions include elimination of corroding metal components (or those with the potential to corrode) and unnecessary instrumentation, and covering walls and ceilings with nonshedding paint or plastic.

Reduction of blanks can be extremely difficult during work at sea aboard a research vessel because the ambient laboratory air and work area can be severely contaminated with high trace element levels. However, clean-air work areas can be arranged by mounting a portable clean-room container or van onto the research vessel's deck or by constructing a clean room within the vessel's laboratory space from heavyweight polyethylene sheeting. These options have worked very effectively for a number of different research groups.

High purity water, acids, and reagents are essential for a trace element analytical scheme. Although Milli-Q systems (Millipore) appear adequate to produce high purity water, the method of subboiling distillation has been the primary means to prepare purified acids and many other reagents (see Moody and Beary[22]).

Bottles for sample storage should, in general, be Teflon or polyethylene because of their inherent cleanliness as well as their ability to be cleaned further of any trace element content by acid leaching. Cleaning procedures can vary from lab to lab, but generally involve the initial use of detergents and/or solvents (e.g., ethanol, acetone), extended strong-acid cleaning with or without heating and/or ultrasonification, with repeated rinses with successively cleaner water between soak solutions, and final storage in ultraclean weak acids and/or water. The final stages of cleaning and handling of the sample bottles are performed within a Class 100 clean bench. The cleaned bottles are sealed in multiple polyethylene bags to protect them from dust during storage and transport.

B. SAMPLING

The requirements for contamination control during sampling vary tremendously from one trace element to another, dependent primarily upon the concentration of the element or species in seawater and its ubiquity. For example, a research vessel can be a significant source of contamination (e.g., from stack dust, steel hydrowire, paint, brass fittings, galvanized materials, sacrificial Zn anodes, bilge and holding tank discharges, etc.) for many trace elements during collection of the water samples. For some trace elements (e.g., Ba, V, As, and Se) contamination is relatively easy to control, whereas for other elements (e.g., Pb, Zn, Fe, Hg, and Sn) more painstaking procedures are required to collect uncontaminated samples.

The requirement for clean procedures can best be appreciated by reviewing C.C. Patterson's zealous and successful efforts to determine common Pb accurately in seawater. The decrease of three orders of magnitude in the accepted concentration of Pb in seawater over the last four decades is not a real oceanographic effect, but rather an artifact of successive improvements in reduction and control of the level of contamination introduced during sampling, storage, and analysis.[34] Although Patterson had at his disposal an elegant analytical technique, isotope dilution mass spectrometry, the problems of field contamination in collecting a deep seawater sample with a Pb concentration of only 5 pM (one part per trillion) had to be overcome.

Schaule and Patterson[34] developed their own exotic deep water sampler in order to collect samples uncontaminated with Pb. Subsequently, Martin and co-workers[35] showed that commercially available, Teflon-coated GO-Flo (General Oceanics) samplers mounted on nonmetallic (Kevlar) hydroline[26] enabled them to produce a large set of accurate and precise Pb concentration data. The use of Teflon-coated GO-Flo sampling bottles mounted on a nonmetallic hydroline was developed and first reported by Bruland and co-workers.[24] This sampling system is currently the most commonly used for obtaining deep water profiles of trace metals. Recently, researchers at Moss Landing Marine Laboratories have designed and assembled a Nylon-II coated, stainless steel rosette system which holds eight 30-liter, Teflon-coated and modified GO-Flo bottles. This system is deployed on a polyurethane-coated Kevlar conducting cable, and was used to collect uncontaminated water samples during the recent IronEx experiments near the Galapagos Islands.[36a]

Consistent data for open-ocean surface waters for elements such as Pb, Hg, Cd, Cu, and Zn have been obtained from samples either collected by hand from rafts rowed well away from the research vessel,[26,37] collected by extending a pole over the side of the ship while the ship is steaming at approximately 2 knots,[28] or pumped while underway from a towed "fish".[29]

C. FILTRATION AND STORAGE

The definition of "dissolved" trace metals is operational and is dependent upon the filter pore size used. Nuclepore polycarbonate filters of either 0.3- or 0.4-μm pore size have been utilized for the vast majority of trace metal studies, although some researchers have recently switched to using 0.2 μm pore size filters to ensure removal of all microorganisms. After capturing the sample, the GO-Flo sampler is usually pressurized with filtered, high-purity nitrogen through a Swagelok fitting at the top of the sampler. The water sample is then pushed out of a Teflon stopcock at the bottom of the sampler, through Teflon tubing to the filtration system. A commonly used filtration system consists of precleaned, 142-mm, 0.4-μm pore size Nuclepore polycarbonate filters contained in Teflon filter holders. Water samples for dissolved trace metal assays are then collected from the filter effluent line within a clean environment.

There is considerable variety among investigators on the method chosen to preserve samples for later analysis. Ideally, the analysis would occur *in situ*. However, the bulk of the studies that have been performed to date have involved sample analysis back in the home laboratory of the investigator or, at best, aboard the research vessel. Depending upon the analysis to be performed, samples have been preserved by acidification to pH values between 1 and 2 with either ultrapure nitric or hydrochloric acid, by storing the unacidified sample in the dark at temperatures from 1 to 4°C, or by storing the sample frozen. Certain analyses preclude some of the above preservation methods. For example, samples for metal speciation determinations should not be acidified.

D. PRECONCENTRATION STEPS

Because most of the instrumental analytical methods currently available do not have the requisite selectivity, sensitivity, or freedom from matrix interferences despite great advances in sensitivity made recently, trace elements in natural waters, particularly seawater, must be concentrated (and separated from the matrix for some techniques) prior to assay. The majority of the oceanographically consistent trace element results have been obtained using a wide variety of selective preconcentration steps prior to the analysis: hydride generation techniques for the determination of the trace metalloids, electrochemical preconcentration in anodic stripping voltammetry, adsorptive electrochemical preconcentration in cathodic stripping voltammetry, liquid-liquid extraction with chelating agents such as dithiocarbamates, chelating cation exchange with resins such as Chelex-100, and coprecipitation methods using, for example, Co pyrrolidine dithiocarbamate as a carrier.

These preconcentration techniques also serve to minimize matrix effects which can cause difficulties when nanomolar and picomolar levels of trace elements are being determined in a solution that is roughly 0.5 M NaCl. In general, the use of various chemical methods of concentration, matrix alteration, and species isolation is an essential supplement to the powerful instrumental techniques available. Many of the concentration steps would provide a sample amenable to analysis by a variety of detection techniques. Radioactive isotopes of the elements of interest have proven to be invaluable as yield tracers in developing these various preconcentration methods.

IV. ANALYTICAL CONSIDERATIONS

The sensitivity of a number of instrumental techniques has improved dramatically over the last 15 years. For example, there has been the development of graphite-furnace atomic absorption spectrometry and inductively coupled plasma emission spectrometry, as well as major advances in the areas of anodic stripping voltammetry, cathodic stripping voltammetry (preceded by a metal-chelate adsorption step), gas and liquid chromatography, mass spectrometry, etc. In the following sections, selected applications of these various approaches are presented.

A. GRAPHITE-FURNACE ATOMIC ABSORPTION SPECTROMETRIC METHODS

With regard to the transition metals, graphite-furnace atomic absorption spectrometry has been the single most important instrumental technique used in advancing our knowledge of the dissolved metal distributions in seawater. It has primarily been used on samples that have been preconcentrated by solvent-solvent extractions using chelating agents such as dithiocarbamates,[26,30-33] 8-hydroxyquinoline,[34,35] and dithizone;[36,37] by chelating ion-exchange resins such as Chelex-100[26,31,38] and immobilized 8-hydroxyquinoline resins;[39,40] and by coprecipitations of metal chelates such as Co dithiocarbamates.[41] Van Geen and Boyle[42] developed an automated preconcentration method based on adsorption of the metal complexes of sodium bis(2-hydroxyethyl) dithiocarbamate onto a hydrophobic resin. Graphite-furnace atomization has the advantage of being highly sensitive and using only a small sample size (e.g., 10 to 100 μl). This makes the method amenable to sequential multielement analysis. For example, Boyle and Edmond,[41] Kingston et al.,[38] Bruland et al.,[26] Smith and Windom,[37] Sturgeon et al.,[33] and van Geen and Boyle[42] used various preconcentration techniques and GFAAS to determine Co, Cu, Cd, Fe, Mn, Ni, Pb, and Zn in seawater. The recent use of atomization platforms within the graphite furnace has been a substantial advance to minimize matrix effects and ensure uniform atomization from sample to sample.

B. VOLTAMMETRIC STRIPPING METHODS

The attributes of voltammetric methods and their applications to trace element analysis of seawater have been reviewed by Nürnberg[43] and more recently by van den Berg.[44] Advantages of voltammetric methods

include their sensitivity, small sample volume requirement, amenability towards real-time shipboard analysis, and speciation determination capability.

Differential pulse anodic stripping voltammetry (DPASV) using a rotating, glassy carbon, mercury film electrode under conditions developed to minimize contamination sources and to enhance sensitivity for seawater matrices[31,45] has been effectively utilized for determining both the concentrations and speciation of Cu, Pb, Cd, and Zn in seawater. In DPASV, preconcentration is achieved electrochemically and as an integral (i.e., not separate) part of the determination, typically for deposition periods of 5 to 30 min.

Recently, sensitive techniques based on cathodic stripping voltammetry (CSV) have been developed by van den Berg and co-workers (see review by van den Berg[44] and references cited therein) and others[46-48] that preconcentrate the trace metal-of-interest by adsorption of surface-active complexes onto a hanging mercury drop electrode (HMDE) followed by a reductive stripping step producing a cathodic current. The advantage of CSV is the wide applicability of the technique. Unlike DPASV, amalgamation of the trace metal-of-interest with the mercury electrode is not required for preconcentration, thus essentially opening up the periodic table for analysis by this method. Trace metals determined in seawater by this approach to date include Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, Pt, Sb, Se, Sn, Ti, V, and Zn. Detection limits by this approach are typically in the subnanomolar and picomolar range.

C. GAS CHROMATOGRAPHIC METHODS

Measures and co-workers have developed electron capture/gas chromatographic methods for the determination of $Se(IV)$,[49] Be,[50] and Al[51] in seawater. The methods are based upon forming a volatile organic chelate or derivative of the trace element in the sample, extraction into a small volume of organic solvent, and determination by electron capture gas chromatography. These techniques are extremely sensitive, and detection limits in the picomolar range can be achieved. In addition, they use small sample volumes, the instrumentation costs are low, and the methods have been used at sea to obtain large sets of near-real-time data. Surprisingly, these methods have not caught on in popularity amongst other trace element labs. A liability of the methods is that many metal chelates are unstable at the high temperatures required for sufficient volatility.

D. MASS SPECTROMETRIC METHODS

Historically, isotope dilution mass spectrometry (IDMS) has played an important role in trace element determinations in natural waters. Patterson and co-workers[24,52,53] used this elegant instrumental technique to achieve the first accurate Pb concentrations in ocean waters. Stukas and Wong[54] used thermal source IDMS to determine Cu, Cd, Pb, Zn, Ni, and Fe concentrations simultaneously in seawater in a single experiment. Berman, Sturgeon, and co-workers at the National Research Council of Canada have used it to put confidence limits on their reported values for their seawater standard reference materials.[33,55,56] It has been used for the bulk of the studies on rare earth elements in seawater.[57-61] However, the liabilities of this approach are the initial cost of instrumentation and relatively slow sample throughput. On the other hand, the power of the technique lies in measurement of the isotopic ratios of those elements with geochemically interesting signatures or fingerprints, such as Pb. Currently, there is a great deal of interest on the potential of inductively coupled plasma emission mass spectrometry (ICPMS). This technique is proving particularly useful for refractory elements such as Ti[62] and Au.[63,64]

E. CHEMILUMINESCENCE DETECTION METHODS

Recently, chemiluminescence methods for the determination of Co, Cu, Mn, and Fe with detection limits in the picomolar and nanomolar ranges have been introduced. Boyle et al.[65] developed a method for the analysis of Co in natural waters by cation-exchange liquid chromatography using luminol chemiluminescence detection (LC/CL). Johnson and co-workers have developed methods for the determination of picomolar levels of Co[66] and nanomolar levels of Cu,[67] Mn,[68] and Fe(II)[69] in seawater by flow injection analysis with chemiluminescence detection (FIA/CL). Obata et al.[69a] developed an automated shipboard method for determining Fe(III) in seawater which couples chelating resin column preconcentration with chemiluminescence detection. These techniques are sensitive, rapid, require small sample volumes, and are particularly amenable to shipboard and even *in situ* analyses.

F. MISCELLANEOUS METHODS

In addition to the methods discussed above, a variety of other methods have been developed for various elements as we show in the following examples. Cutter[70,71] developed a selective hydride generation

method for the determination of Se in seawater involving cryogenic trapping of the hydride, followed by thermal desorption and determination by atomic absorption spectrometry using a quartz cuvette burner with an air-hydrogen flame (quartz burner/AAS). Andreae[72] described the development and application of hydride generation techniques for determination of As, Sb, Ge, and Sn species in seawater. The hydrides of these elements were quantified by a variety of detection systems: quartz burner/AAS for As and Sb species, electron capture detection for some methylarsines, flame photometric detection for Sn species, and graphite-furnace atomic absorption detection for Ge and Sn species. Gill and Bruland[73] measured Hg concentrations and speciation in natural waters using a selective sample reduction method and detection via two-stage Au amalgamation to introduce gas-phase Hg° into the cell of a nondispersive atomic fluorescence system (AFS). The AFS system is markedly more sensitive than similar systems using atomic absorption spectrometric detection.[74] Cutter et al.[75] developed a selective hydride generation, gas chromatographic/photoionization detection method for the simultaneous determination of inorganic As and Sb species (As (III) + Sb(III) and As (III + V) + Sb(III + V)) in natural waters.

V. CONCENTRATION LEVELS

The advances in analytical chemistry and instrumentation and control of potential contamination have enabled corresponding advances in our knowledge of the true oceanic concentrations of dissolved metals and their distributions. Since the review by Bruland,[3] the seawater concentrations of Ti, Ga, the Pt group metals, Re, Te, Au, Zr, and Hf have been determined. Thus, we now know reliably the concentrations and distributions of most of the elements in the periodic table. The surface and deepwater concentrations of the trace elements in open North Atlantic and North Pacific Ocean waters are presented in Table 3. Whitfield and Turner[6] have grouped the trace elements into three principal categories reflecting their biogeochemical interactions with particles: conservative, recycled, and scavenged.

A. CONSERVATIVE ELEMENTS

The conservative trace elements interact weakly with particles, have long residence times ($> 10^5$ yr) relative to the mixing time of the oceans, and have concentrations that maintain a constant ratio to one another, varying only as a result of water mass mixing. Trace elements in this category include the monovalent cations Li^+, Rb^+, and Cs^+, Tl^+, the negatively charged carbonato complex ($UO_2(CO_3)_3^{4-}$) of the oxy-cation UO_2^{2+}, the oxy-anion MoO_4^{2-}, and, interestingly, the methylated forms of Ge monomethylgermanic acid ($CH_3Ge(OH)_3^0$) and dimethylgermanic acid ($(CH_3)_2Ge(OH)_2^0$).

B. RECYCLED ELEMENTS

Recycled (or nutrient-type) elements appear to be involved with the internal cycles of biologically derived particulate material. Consequently, their concentrations are depleted in surface waters by direct uptake by phytoplankton and/or adsorption onto biogenic particles, and increase with depth as sinking detrital particles undergo microbial decomposition of their organic phases, and/or dissolution of their inorganic mineral phases (e.g., opal, calcium carbonate). In addition, the concentrations of the recycled elements in deep waters increase along the direction of the main advective flow of deep water in the world ocean. Consequently, their concentrations in deep North Pacific waters are higher than in deep North Atlantic waters. The residence times of the recycled elements are intermediate (10^3 to 10^5 yr) to those of the conservative and scavenged elements.

Two of the most striking examples of recycled elements are $Cd^{26,76-79}$ and $Zn.^{78-80}$ The vertical distribution of Cd correlates closely with that of phosphate, suggesting that Cd is cycled with the formation and decomposition of organic soft tissues, while the vertical distribution of Zn correlates most closely with that of silicate (Figure 1). Depletion of these elements in surface waters and their regeneration at depth causes deep waters to be enriched relative to surface waters by up to 1000-fold for Cd and 180-fold for Zn. Deepwater enrichment of these metals and the deepwater flow pattern results in substantial fractionation between ocean basins; deep North Pacific Cd and Zn concentrations are 3 and 5 times greater, respectively, than the concentrations at comparable depths in the North Atlantic.

C. SCAVENGED ELEMENTS

Because of their strong interactions with particles, the scavenged elements have very short oceanic residence times ($<10^3$ yr). Their concentrations are maximum near, and decrease with distance from, their sources which include rivers, atmospheric dust, hydrothermal sources, and bottom sediments. In general,

Table 3 Concentrations and distribution types of the trace elements
in ocean waters

Element	Concentration Units	North Pacific		North Atlantic		Distribution Type
		Surface	Deep	Surface	Deep	
Be	pM	4–6	28–32	10	20	R + S
Al	nM	0.3–5	0.5–2	30–43	15–35	S
Sc	pM	8	18	14	20	R
Tl	pM	4–8	200–300	30–60	200	R + S
V	nM	32	36	23		R
Cr	nM	3	5	3.5	4.5	R
Mn	nM	0.5–3	0.08–0.5	1–3	0.25–0.5	S
Fe	nM	0.02–0.5	0.5–1	0.05–1	0.6–1	R + S
Co	pM	4–50	10–20	18–300	20–30	S
Ni	nM	2	11–12	2	6	R
Cu	nM	0.5–1.3	4.5	1.0–1.3	2	R + S
Zn	nM	0.1–0.2	8.2	0.1–0.2	1.6	R
Ga	pM	12	30	25–30	?	S
Ge	pM	5	100	1	20	R
As	nM	20	24	20	21	S
Se	nM	0.5	2.3	0.5	1.5	R
Y	nM				(0.15)	?
Zr	pM	12–95	275–325	100	(150)ᶜ	R + S
Nb	pM		(<50)			?
Ru	fM		(<50)			?
Rh			(?)			?
Pd	pM	0.18	0.66			
Ag	pM	1–5	23			R
Cd	pM	1–10	1000	1–10	350	R
In	pM	<0.5–1.8		2.7	0.9	S?
Sn	pM	4		10–20	8	?
Sb	nM	(0.74–1.13)		1.7		?
Te	pM	1.2	1	1–1.5	0.4–1	S
Cs	nM	2.3	—	—	—	C
La	pM	20	50–70	12–15	80–84	S + R
Ce	pM	10	3	80	40–60	S
Pr	pM	3–4	7–9	3–4	10	S + R
Nd	pM	13–16	40–50	12.8	24.9	S + R
Sm	pM	2.6–2.8	8–9	3–4	7.6–8.0	S + R
Eu	pM	0.73	2.3	0.6–0.8	1.6–1.8	S + R
Gd	pM	3.8	12–13			S + R
Tb	pM	0.56	1.8–2.1	0.73	1.4–1.6	S + R
Dy	pM		6.1	4.8	5.1	?
Ho	pM	0.7–1.0	4–5	1.5–1.8	2.5–2.7	S + R
Er	pM		5.8	4.1	5.1	?
Tm	pM	0.3–0.5	2.0–2.5	0.7–1.0	1.1–1.3	S + R
Yb	pM	1.9–2.8	13–17	3.8–5.1	7.0–7.4	S + R
Lu	pM	0.3–0.4	2.3–3.1	0.7–0.8	1.5–1.6	S + R
Hf	pM	0.2–0.4	1–2	0.4	(0.8)ᶜ	?
Ta	pM		(<14)			?
W	nM		(0.6)			?
Re	pM	28–82		32–43		?
Os				(?)		?
Ir	fM	(5–30)ᵃ				?
Pt	pM	0.4	0.3,1.2	0.2–0.4ᵇ	0.2–0.4ᵇ	?ᵈ
Au	fM	50–150		50–150		?

256

Table 3 (Continued) Concentrations and distribution types of the trace elements in ocean waters

Element	Concentration Units	North Pacific		North Atlantic		Distribution Type
		Surface	Deep	Surface	Deep	
Hg	pM	0.5–10	2–10	1–7	1	S
Tl	pM	60–80	80	60–70	60	C
Pb	pM	14–50	3–6	100–150	20	S
Bi	pM	0.2	0.02	0.25		S

Note: R, Recycled type; S, Scavenged type; C, Conservative type.

[a] SIO Pier sample; [b] Indian Ocean concentrations; [c] depth = 1250 m; [d] R, S, and C distributions have been reported.
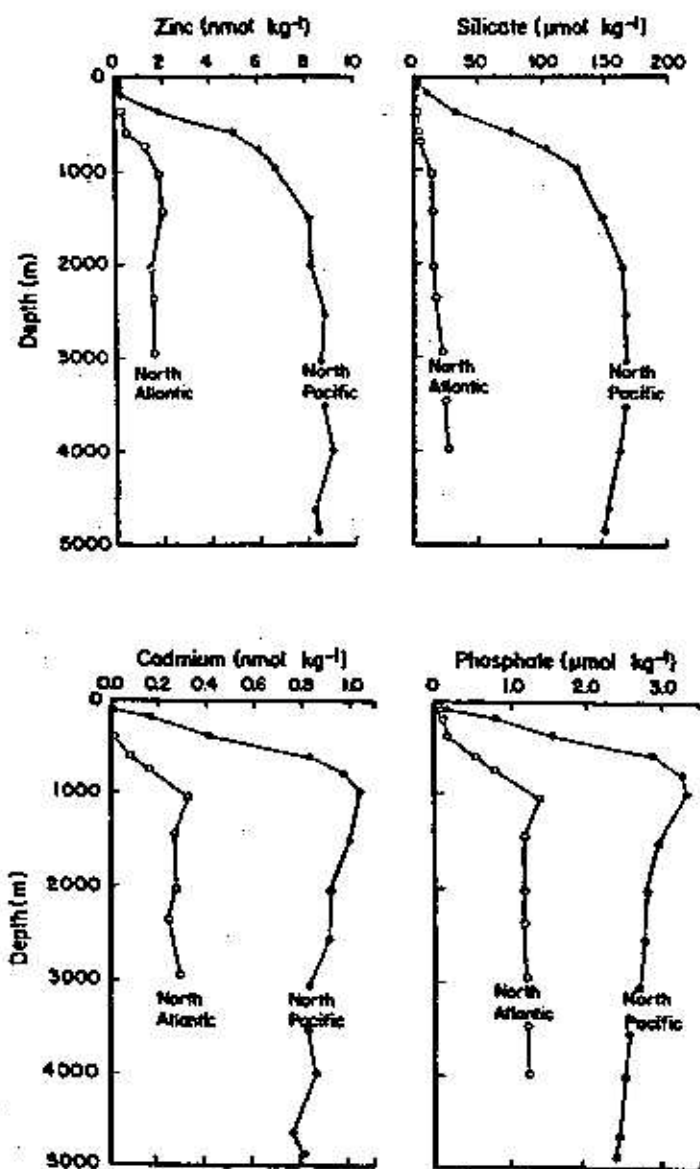

Figure 1 Vertical concentration profiles of dissolved cadmium, phosphate, zinc, and silicic acid in the North Pacific and North Atlantic Oceans. (From Bruland, K.W., *Chemical Oceanography*, Vol. 8, Riley, J.P. and Chester, R., Eds., Academic Press, 1983; and Bruland, K.W. and Franks, R.P., *Trace Metals in Seawater*, Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., and Goldberg, E.D., Eds., Plenum Press, 1983. With permission.)
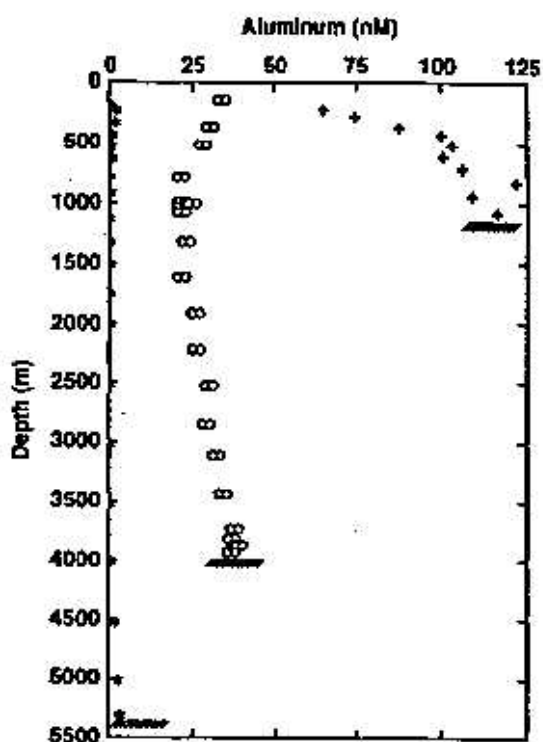
Aluminum (nM)

Figure 2 Vertical concentration profiles of dissolved aluminum: (*) North Pacific;[86,87] (o) North Atlantic;[81] (+) Mediterranean (From Orians, K.J. and Bruland, K.W., *Nature*, 316, 427, 1985; Orians, K.J. and Bruland, K.W., *Earth. Planet. Sci. Letts.*, 78, 402, 1986; Hydes, D.J., *Science*, 205, 1261, 1979; and Measures, C.I. and Edmond, J.M., *J. Geophys. Res.*, 93, 591, 1988. With permission.)

concentrations of the scavenged elements decrease along the direction of deepwater flow due to continuing particle scavenging. Thus, concentrations in the North Pacific are lower than in the North Atlantic.

The seawater distribution of Al best illustrates the general characteristics of the scavenged elements (Figure 2). Seawater concentrations of dissolved Al are maximal in surface waters due to atmospheric input, minimal at middepths due to particle scavenging, and increase toward the seafloor.[81-87] North Pacific deepwater Al concentrations[86,87] are 8- to 40-fold lower than those in the North Atlantic[81,82,85,88,89] and about 100-fold lower than those in the Mediterranean.[90-93] This marked interocean fractionation is the reverse of that shown by the recycled elements and the greatest yet observed for any element in seawater.

D. ELEMENTS SHOWING HYBRID DISTRIBUTIONS

Some trace elements, such as Cu and Fe, have distributions that are influenced by both recycling and scavenging processes. Like recycled elements, dissolved Cu[78,94,95] and Fe[96-98] are often depleted in surface waters in areas of high productivity and regenerated at depth. In less productive waters or in areas with higher external aeolian inputs, these elements can exhibit surface maxima more indicative of scavenged elements.

Instead of the rapid increase in concentration with depth shown by recycled elements, dissolved Cu concentrations increase only gradually with depth, due to the combined effects of regeneration and scavenging in deep waters. Also consistent with the recycled nature of its behavior, dissolved Cu concentrations in Atlantic deep waters are one half to two thirds of those in the deep Pacific.[78,99] The oceanic residence time of Cu is about 1000 years.

Seawater constituents showing recycled behavior like nitrate, phosphate, and Cd are assimilated primarily in surface waters, are regenerated with depth, and have long oceanic residence times. Unlike these elements, regenerated Fe is scavenged relatively intensely throughout the oceans, including deep waters. The short oceanic residence time of Fe (thought to be less than 100 years) reflects this scavenging. Thus, the oceanic concentrations of Fe result from a balance between regeneration from the "rain" of particulate matter and scavenging.

E. RECENT ADVANCES

The recent advances in our knowledge of the trace elements in the oceans can be placed into two general categories: (1) concentrations and distributions and (2) biogeochemical processes.

1. Concentrations and Distributions

Through the use of the newer analytical techniques mentioned in previous sections, especially those amenable to shipboard analyses, several researchers have gone beyond producing single vertical or horizontal profiles. These researchers have made large numbers of measurements allowing construction of 2- and even 3-dimensional ocean basin-scale distribution maps for certain elements (e.g., Al and Fe).

Using electron capture gas chromatography, Measures and Edmond[100] determined dissolved Al concentrations in water samples from 18 vertical profiles and 35 surface samples aboard ship during the South Atlantic Ventilation Experiment. The data coverage provided by the shipboard analyses allowed vertical sections of Al concentrations in the South Atlantic to be constructed (Figure 3) which were useful in examining the input and distribution mechanisms of Al in a region of the Atlantic for which no previous information existed. Subsurface Al distributions were used to examine the evolution of the enriched Al signal of recently descended North Atlantic Deep Water propagating through the South Atlantic.

Martin et al.[101] reported a dissolved Fe section in the Northeast Pacific from 25°N, 137°W north to Alaska (Figure 4), obtained by APDC/DDDC-chloroform organic extraction preconcentration and GFAAS detection. This section shows general surface depletion and enrichment with depth above 500 m for all stations. Inputs of Fe along the continental margin in the near-surface waters at Stn T-9 and in the oxygen-minimum zones (800 to 1000 m) at offshore Stns T-2 to T-6 and nearshore Stn T-8 are also evident. The small maximum at T-4 was suggested to result from water flowing offshore from California 1500 km to the east, whereas the relatively Fe-poor waters at Stn T-6 are thought to be flowing towards California from the central Pacific.

In addition to obtaining basin-wide distributions of the trace elements in the oceans, researchers continue to develop and apply new analytical techniques to obtain zero- and first-order understandings of the oceanic concentrations and distributions of the remaining elements in the periodic table (e.g., Ti, Ga, Ru, Pd, Ir, Pt, Au, Re, Te, Zr, and Hf).

Dissolved Ti have been determined concentrations in North Pacific[61] and North Atlantic[62,101a] waters. Although the inorganic speciation of Ti is predicted to be dominated by particle reactive hydrolysis species (predominantly $TiO(OH)_3^-$), dissolved Ti shows a recycled-type profile with surface water depletion and deep water enrichment (Figure 5). However, indications of scavenging behavior also exist. North Pacific surface water concentrations range from 4 to 8 pM and increase linearly with depth to maximum concentrations of 200 to 300 pM near the bottom. North Atlantic surface concentrations are ~60 pM and increase linearly with depth to ~200 pM at 2000 m. In the northwest Atlantic, Skrabal[101a] reported that dissolved Ti concentrations decrease from 390 pM off the mouth of Delaware Bay to ~30 to 60 pM in the outer shelf and slope waters. Locally-high Ti concentrations of 90 to 140 pM were determined at the dynamic shelf/slope boundary, due perhaps to shallow upwelling. Orians et al.[62] estimated residence times of Ti in the deep waters of the relatively highly productive North Pacific Sub-Arctic gyre of 100 to 200 years, and they speculated that the residence time of Ti in the deep waters of the North Pacific central gyre (lower productivity) might be longer, about 800 to 900 years.

Orians and Bruland[102] reported the vertical distribution of dissolved Ga in the North Pacific and down to 1000 m in the Gulf Stream. They determined Ga concentrations after preconcentrating their filtered samples using the chelating ion-exchange resin Chelex-100 and evaporation (North Pacific) or using an 8-hydroxyquinoline resin (Gulf Stream), followed by detection by GFAAS. North Pacific concentrations increase from surface values of 12 to 18 pM near 300 m, decrease to 7 to 10 pM between 500 to 1000 m, and increase to 30 pM from 1000 m to the bottom. Gulf Stream concentrations are approximately three times higher than those at comparable depths in the North Pacific. The vertical distribution of dissolved Ga reflects surface, subsurface, and deep water sources combined with particle scavenging throughout the water column. Thus, Ga appears to show a hybrid oceanic distribution; its moderately short deep water residence time of 750 years and interocean fractionation (concentrations in North Atlantic > North Pacific) reflect scavenging behavior, while its vertical distribution reflects recycling behavior. Shiller[103] observed that the Ga/Al ratios of seawater are distinctly greater than that in crustal rocks and suggested that the Ga enrichment could be due to anthropogenic input or, more likely, due to preferential dissolution of solid phase Ga and preferential removal of dissolved Al.

Results of the first analyses of the trace metals Ru,[104] Ir,[105] Pd,[106] and Re[107,107a] in Pacific Ocean waters have been reported. Pacific Ocean seawater appears to have Ru[104] and Ir[105] concentrations in the low femtomolar range. Pd concentrations in Pacific surface waters are 0.18 pM and deep water concentrations are 0.66 pM.[106] The vertical distribution of Re in Pacific Ocean waters shows no consistent trend; dissolved concentrations range from 28 to 82 nM.[107]
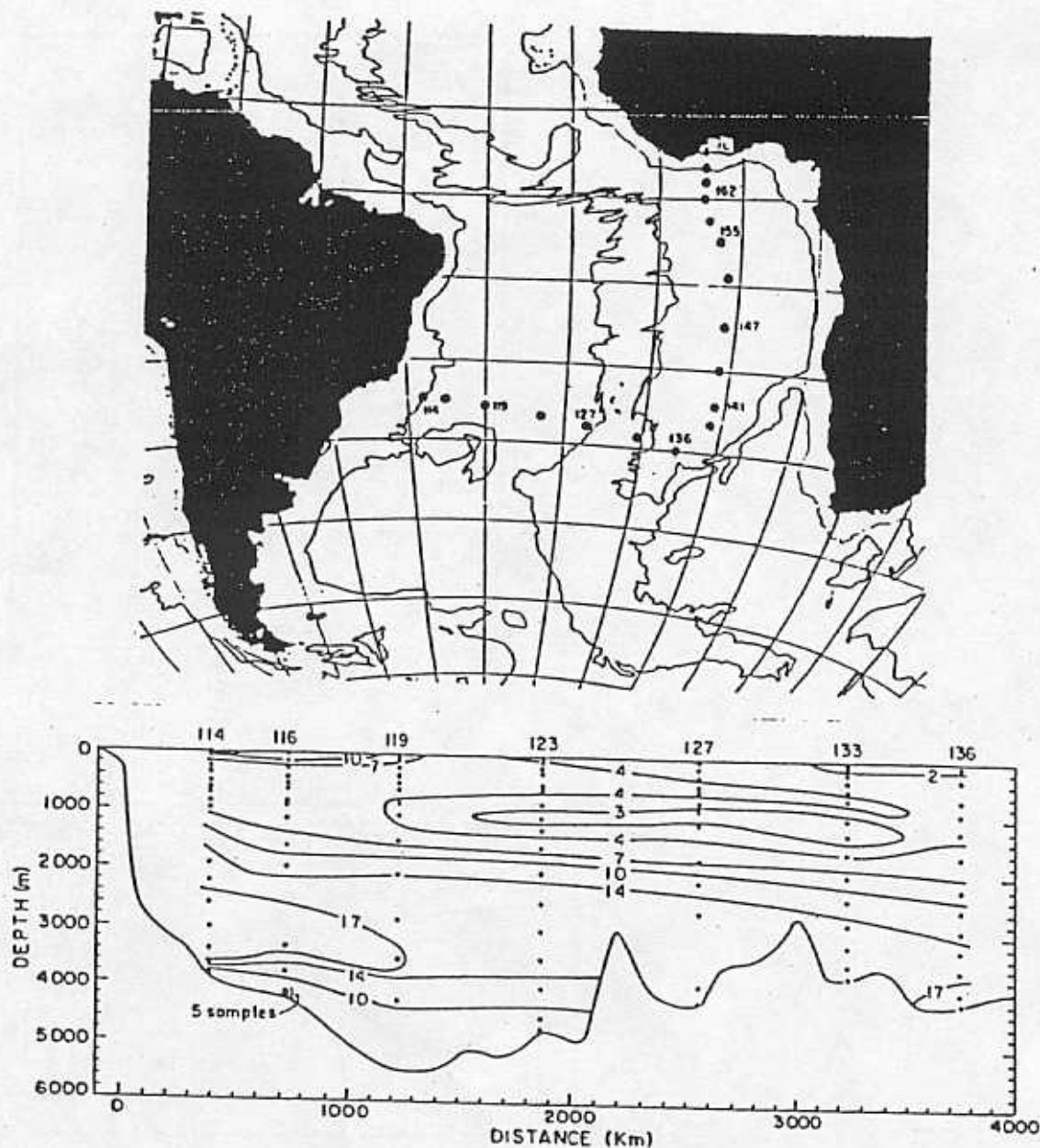
Figure 3 (Upper) Station positions for leg III of the South Atlantic Ventilation Experiment (SAVE) cruise. (Lower) Vertical cross-section of dissolved aluminum concentrations (nM) in the western basin of the South Atlantic, SAVE Stns 114 to 136. (From Measures, C.I. and Edmond, J.M., *J. Geophys. Res.*, 95, C4, 5331, 1990. With permission.)

Falkner and Edmond[64] reported vertical profiles of Au from the Atlantic, Pacific, and Mediterranean determined using anion exchange preconcentration and ICPMS detection.[63] Atlantic and Pacific concentrations were similar (~50 fM to 150 fM) with Au concentrations appearing fairly uniform with depth. Mediterranean deep water concentrations are higher, ranging from 100 to 150 fM.

Lee and Edmond[108] have recently determined the seawater concentrations of Te for the first time. Te exists in two oxidation states in seawater, (IV) and (VI). The distributions of both oxidation states reflect surface enrichment and strong scavenging at depth. Total Te concentrations appear to average about 1.2 to 1.3 pM in surface waters and ~0.5 to 0.6 pM at depths below 2500 m.
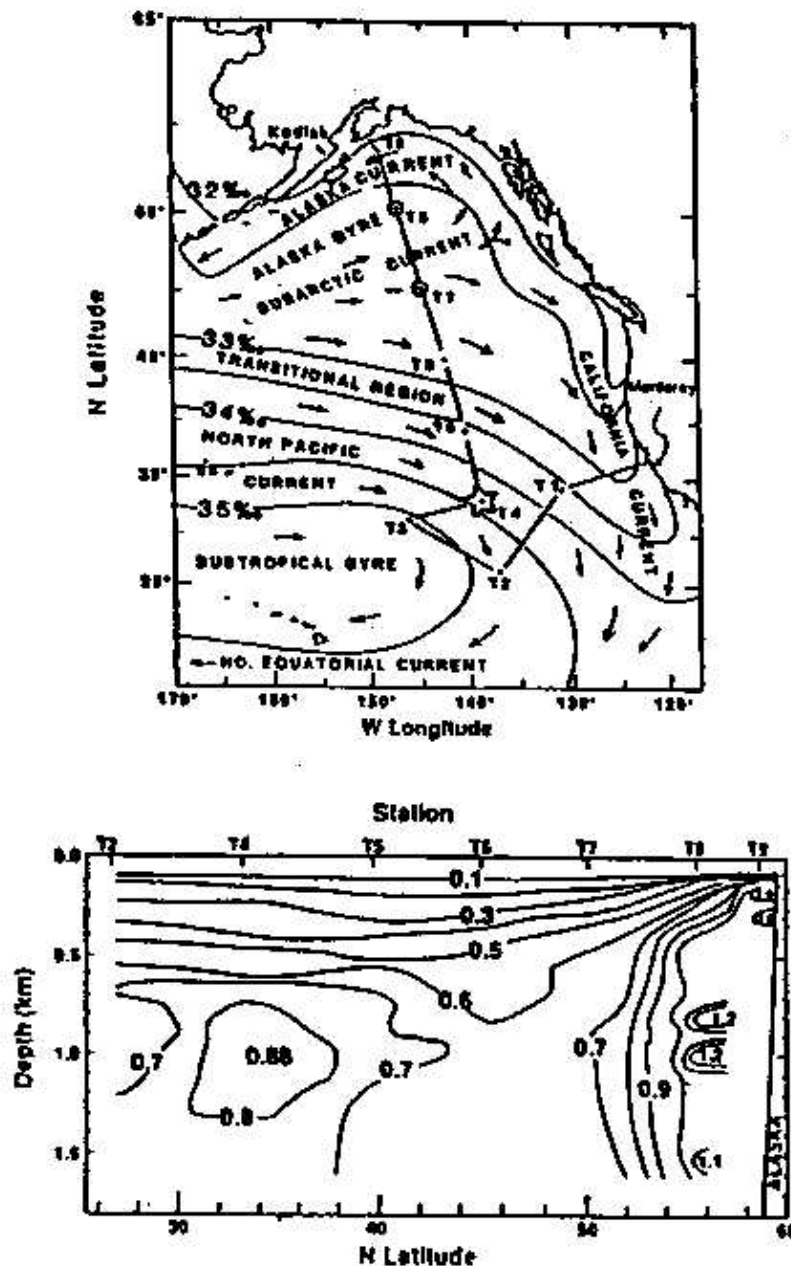
Figure 4 (Upper) Station positions, surface current systems, and surface isohalines for Vertical Transport and Exchange (VERTEX) seasonal and Alaska transect cruises in the Northeast Pacific. (Lower) Vertical cross-section of dissolved iron concentrations in the Northeast Pacific, VERTEX Stns T2 to T9. (From Martin, J.H., Gordon, R.M., Fitzwater, S.E., and Broenkow, W.W., *Deep-Sea Res.*, 36, 649, 1989. With permission.)

Concentrations of Pt have been determined in Pacific,[107a,109,110] Atlantic,[107a] and Indian Ocean waters.[112] However, the distributions reported in these studies sharply contrast each other. In the Pacific, Hodge et al.[109,110] and Goldberg[111] reported a recycled-type profile for Pt, while in Indian Ocean waters Jacinto and van den Berg[112] reported a scavenged-type profile (Figure 6). Most recently, Colodner's[107a] observations agree with neither of the previous reports: she measured Pt concentrations in both Pacific and Atlantic waters that were invariant with depth! Although the vertical profiles of dissolved Pt show smooth variation with depth (one criterion for "oceanographic consistency"), the data presently available
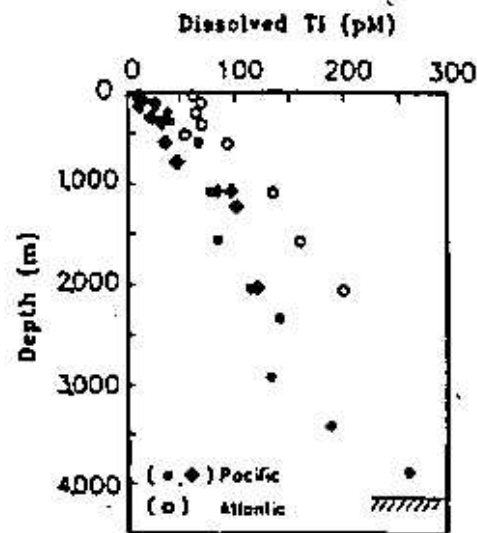
Figure 5 Vertical concentration profiles of dissolved titanium in the North Pacific: 50°N, 145°W (o), and 33°N, 139°W (♦); and in the North Atlantic: 32°N, 64°W (o). (From Orians, K.J., et al., *Nature*, 348, 323, 1990. With permission.)
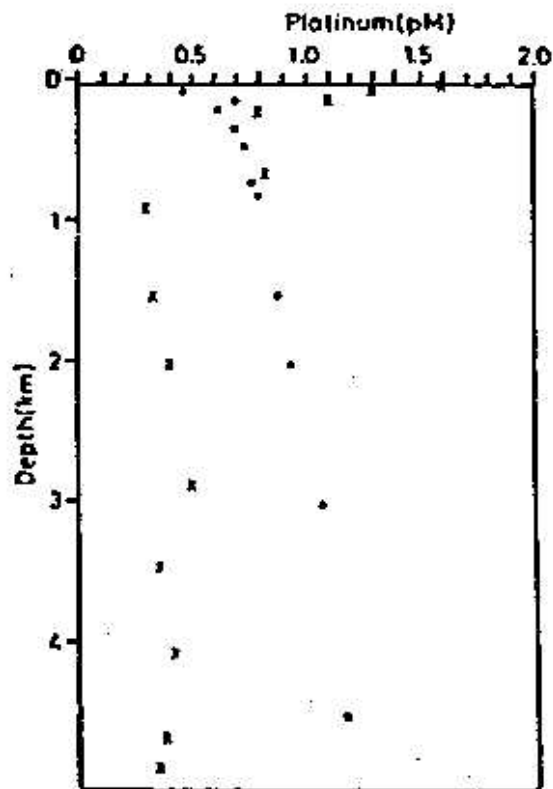

Figure 6 Vertical concentration profiles of dissolved platinum: (o) North Pacific;[110] (x) western Indian Ocean. (From Jacinto, G.S. and van den Berg, C.M.G., *Nature*, 338, 333, 1989. With permission.)

for Pt are not "oceanographically consistent" with respect to their basin-to-basin variation. More information is required to settle this apparent discrepancy.

McKelvey and Orians have measured the first vertical profiles of Zr[112a,b] and Hf[112b] in the North Pacific and North Atlantic. Both elements show surface depletion and deep water enrichment, and evidence of coastal and bottom sources. North Pacific Zr and Hf concentrations range, respectively, from 12 to 95 pM and 0.2 to 0.4 pM in surface waters, to 275 to 325 pM and 1 to 2 pM in deep waters. A single North Atlantic profile showed surface Zr and Hf concentrations, respectively, of ~100 pM and ~0.4 pM, and concentrations of ~150 pM and ~0.8 pM at 1250 m depth.

2. Trace Element Biogeochemical Processes

Recent highlights regarding biogeochemical processes involving trace elements include photomediated processes such as photochemical control of Mn, Fe, and Cu redox cycling, and the formation of, and interactions of dissolved trace elements with, colloids.

Calculations for oxygenated seawater based on the redox couple between $MnO_2(s)$ or $MnOOH(s)$ and Mn^{2+} suggest that the equilibrium concentration of dissolved Mn should be much less than 1 nM, possibly less than 1 pM, depending on the oxide mineral phase with which it is in equilibrium. The observed values for dissolved Mn in open ocean waters are normally between 0.1 and 3 nM,[97,98,101] and a maximum in the dissolved Mn concentration is a prominent feature in surface waters of the oceans. Sunda and Huntsman[113,114] have presented evidence that the higher-than-expected concentrations and the surface maximum of dissolved Mn may be maintained by photoreduction of Mn oxides and by photoinhibition of Mn oxidizing microorganisms. Sunda and Huntsman[114] observed pronounced diel cycles in the formation rates of particulate Mn in coastal surface waters of the Bahama Islands which, they suggest, is caused by nightly removal of dissolved Mn^{2+} by Mn-oxidizing bacteria, followed by its daily regeneration and maintenance by reductive photodissolution processes and photoinhibition of the Mn-oxidizing bacteria. Reductive photodissolution of Mn oxides may have important implications for organic matter in seawater because this process may involve light-activated ligand-to-metal charge transfer reactions between Mn oxides and bacterial extracellular organic polymers associated with them or from photochemical production of reductants such as O_2^- and H_2O_2 in seawater or within bacterial MnO_x aggregates.[115]

Fe may be the most important of all the trace elements essential to phytoplankton, and evidence exists that Fe may limit primary production in nutrient-rich, oligotrophic open ocean regimes having low atmospheric Fe inputs.[98,101,116,117] Photoreductive dissolution of Fe(III)-oxides and Fe colloids, and photoreduction of organically chelated Fe may be a major mechanism influencing the availability of Fe to phytoplankton. Waite and Morel[118] and Rich and Morel[119] demonstrated the importance of photoreductive dissolution of particulate and colloidal Fe in seawater. The photoreaction does not appear to proceed in the absence of organics in synthetic seawater[119] or in UV-irradiated coastal seawater.[118] Although no evidence exists for complexation of Fe by organic ligands in oceanic waters, the photoreduction of particulate and colloidal Fe may have potentially important implications for the concomitant photooxidation of organic matter associated with Fe in seawater.

Thermodynamic equilibrium considerations predict that nearly all of the dissolved Cu in seawater should exist as Cu(II). However, Cu(II) may be reduced to Cu(I) in seawater by a number of potentially important reactions, many of which are photochemically induced.[120] For example, Cu(I) may be produced by direct photoreduction of Cu(II) organic complexes (with simultaneous oxidation of the organic ligand via Cu catalysis) and/or by reduction of Cu(II) by photochemically produced reductants. Moffett and Zika[121] and Moffett et al.[122] have provided evidence for these mechanisms operating in surface seawaters. Vertical profiles of Cu(I) in surface seawaters are consistent with a photochemical production mechanism: concentrations show a surface maximum and a decrease with depth.[121] The vertical concentration profile of L_1, the stronger of two Cu-complexing organic ligands whose complexes dominate the speciation of dissolved Cu(II) in oceanic surface waters, in the Sargasso Sea shows concentrations decreasing toward the surface, possibly due to photochemical decomposition potentially involving Cu-catalyzed photooxidation.[122]

As mentioned previously, removal of most trace elements from seawater is controlled by the oceanic cycle of particulate matter, through reactions in the water column and at the sediment interface. For particle reactive metals that have no biological function, partitioning onto marine particulate material is the dominant removal process. Partitioning onto particles controls the dissolved concentration of many trace elements in the oceans. Several recent studies have focused on the role of colloids (particles in the 0.5 nm to 0.4μm range) in particle sedimentation[123] and in particle scavenging of trace elements in seawater (e.g., Honeyman and Santschi[124] and references cited therein; Moran and Moore[125]).

Farley and Morel[123] studied the dynamics of coagulation and settling of particles in well-mixed systems for wastewater discharge. In analytical, numerical, and laboratory studies, they observed that during the initial period of sedimentation a characteristic particle size distribution develops as smaller particles are aggregated into larger particles through coagulation, resulting in an increased rate of solids removal but relatively constant particle mass concentrations. After this initial period, the rate of particle removal (via sedimentation) becomes characteristic of the particle mass concentration, regardless of the initial particle concentration. Farley and Morel[123] determined that the characteristic rate of solids removal as a function of particle mass concentration appears to be described by the summation of three power laws

corresponding to particular coagulation mechanisms including differential settling, shear, and Brownian motion.

Honeyman and Santschi[124] used the same form of Farley and Morel's[123] equation describing the particle-concentration-dependent particle removal rate in establishing their conceptual and mathematical "Brownian-pumping" model. The "Brownian-pumping" model describes the transfer of truly dissolved metal species to larger, filterable particles through a colloidal intermediate emphasizing Brownian motion as the coagulation mechanism. In this model, the transfer consists of two rate steps: (1) rapid formation of metal/colloid surface site complexes, and (2) slow coagulation of colloids with filterable particles. This model indicates that trace element behavior in natural waters results from the tight coupling of chemical equilibrium and physico-chemical interactions between particles. It also provides a framework for interpreting the behavior of the particle reactive trace element Th and perhaps other trace elements prone to adsorptive particulate scavenging.

Moran and Moore[125] used cross-flow filtration to study the size distribution of Al and organic carbon in an operationally defined colloidal size range (1 nm to 0.45μm) in coastal and open ocean waters off Nova Scotia. They determined that colloidal Al was <5 to 15% of the dissolved Al. Colloidal organic carbon was < 10 to 15% of the dissolved organic carbon (measured using UV-photooxidation).

VI. SPECIATION

A. INTRODUCTION AND BACKGROUND

Although our knowledge of the oceanic concentrations and distributions of the trace metals has advanced dramatically, it has become increasingly clear that this information alone is insufficient for providing a complete understanding of a trace metal's biological and geochemical interactions. Trace metals dissolved in seawater can exist in different oxidation states and chemical forms (species) including free solvated ions, inorganic complexes (e.g., with Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, etc.), organometallic compounds, and organic complexes (e.g., with phytoplankton metabolites, proteins, humic substances).

Knowledge of the distribution of a trace metal's total dissolved concentration amongst its various forms (speciation) is extremely important because the different oxidation states and chemical forms undergo very different biological and geochemical interactions. For example, Fe(III) and Mn(IV) are much less soluble than their reduced forms (Fe(II) and Mn(II)). The toxicity and nutrient availability of several transition metals to phytoplankton have been shown to decrease as a result of complexation with ligands such as EDTA, indicating that the toxicity and availability of these metals are proportional to their free metal ion activities (see Sunda[15] for a recent review). Organic complexation may greatly decrease[126,127] or, in some cases, even increase[127-129] adsorption of metals onto metal oxide particles. Thus, speciation information is necessary to attempt to fully understand a trace metal's marine biogeochemical cycle.

B. INORGANIC SPECIATION

Inorganic forms of the trace elements in seawater include hydrated metal ions and complexes with inorganic ligands. These inorganic forms can also include trace elements in different oxidation states because the potential required for the elements to change valence states falls within the range of the oxidizing/reducing potentials developed in the elements' immediate environment. Important examples of trace elements exhibiting redox changes in seawater include Fe (Fe(II)/Fe(III)),[130-132] Mn (Mn(II)/Mn(IV)),[130-132] Se (Se(IV)/Se(VI)),[49,133-134] Cr (Cr(III)/Cr(VI)),[137] and Cu (Cu(I)/Cu(II)).[130-132] The higher of the two oxidation states mentioned are the thermodynamically stable forms of these elements in oxidizing seawater. However, most natural waters, especially surface waters, never attain complete chemical equilibrium due to the relatively steady input of solar energy, some of which can cause production, either biochemically (e.g., photosynthesis) or chemically (e.g., photochemistry), of species that are out of thermodynamic equilibrium with their environment.

The theoretical inorganic speciation of the trace metals in seawater has been summarized in two landmark papers by Turner et al.[134] and Byrne et al.[179] Turner et al.[138] used a database of stability constants for more than 500 metal complexes to calculate the inorganic speciation for 58 trace elements in model seawater at pH 8.2, 25°C, and 1 atm. Byrne et al.[179] extended the models of Turner et al.[134] by considering the results of recent metal-ligand equilibrium studies and by considering the influence of temperature and pH on speciation. In this section, we only briefly summarize the inorganic speciation of the trace metals in seawater described in these two papers.

The extent to which a trace element is complexed by inorganic ligands is given by α, the element's inorganic side reaction coefficient:[140]

$$\alpha = 1 + \Sigma\beta_{MX_i}\left[X_i'\right] \tag{1}$$

where β is the overall conditional stability constant for the inorganic complex MX_i of the trace element M with the inorganic ligand X_i, and $[X_i']$ is the concentration of uncomplexed X_i. The inorganic side reaction coefficient α is also equal to the ratio of the sum of the concentrations of all inorganic species of the trace element M ($[M']$) to the concentration of its free hydrated cation $[M^{n+}]$:

$$\alpha = [M']/[M^{n+}] \tag{2}$$

The free hydrated divalent cation form dominates the dissolved inorganic speciation of Zn and the first transition series metals Mn, Fe, Co, and Ni. Strongly hydrolyzed trace metals include the trivalent trace metal cations Al^{3+}, Ga^{3+}, Tl^{3+}, Fe^{3+}, and Bi^{3+}. The inorganic side reaction coefficients of this group of strongly hydrolyzed trace elements with respect to complexation by OH^- range from $10^{5.76}$ for Al^{3+} to $10^{20.47}$ for Tl^{3+}. The inorganic speciation of the hydrolyzed trace metals is strongly influenced by pH and temperature. For example, at a constant temperature of 5°C, the side reaction coefficient of Al^{3+} varies from $10^{5.76}$ at pH 7.6 to $10^{9.39}$ at pH 8.2, and at a constant pH of 7.6, it ranges from $10^{5.76}$ at 5°C to $10^{7.23}$ at 25°C.[138]

The inorganic speciation of Fe is complex and still not adequately understood. The literature reviews by Turner et al.[138] and Byrne et al.[139] indicate that the hydrolysis species $Fe(OH)_3^0$ is the dominant species of dissolved Fe(III) in surface seawater. In contrast, Zafiriou and True[141] and Hudson and Morel[142] discounted the importance of the neutral $Fe(OH)_3^0$ hydrolysis species and argued that the $Fe(OH)_2^+$ species is dominant. The different assumptions used by these authors concerning which thermodynamic data are correct, and thus, which hydrolysis species is predominant, result in nearly a two order-of-magnitude difference in the estimates of the inorganic side reaction coefficient for Fe(III). This discrepancy needs to be resolved particularly because Fe may be the most important biologically essential trace metal, and potential differences in the reactivity and behavior of hydrolysis species such as $Fe(OH)_2^+$ and $Fe(OH)_3^0$ may influence the bioavailability of Fe.

Trace metals whose dissolved speciation is dominated by chloride complexation include the noble metal cations Ag^+ (predominantly as $AgCl_2^-$), Au^+ (as $AuCl_2^-$), Pd^{2+} (as $PdCl_4^{2-}$), and Pt^{2+} (as $PtCl_4^{2-}$), and Cu^+ (as $CuCl_2^-$), Cd^{2+} (as $CdCl_2^0$ and $CdCl_3^-$), and Hg^{2+} (as $HgCl_4^{2-}$). The dissolved speciation of these metals is only moderately affected by temperature and pH. Of this group, Hg^{2+} is complexed by chloride to the greatest extent. The side reaction coefficient of Hg^{2+} with respect to chloride complexation is $10^{15.10}$ at 5°C, which, for a typical Hg concentration of 5 pM, represents an average of only 1 free Hg^{2+} ion for every 400 l of seawater!

The dissolved speciation of most of the lanthanides and some of the actinides is dominated by carbonate complexes, and is influenced considerably by temperature and pH, although less than the strongly hydrolyzed metal cations.

C. ORGANIC SPECIATION

Organic forms of the trace elements in seawater can include organometallic compounds in which the trace element is covalently bound to carbon (e.g., methyl forms of As, Ge, Hg, Sb, Se, Sn, and Te; ethyl-Pb forms; butyl-Sn forms), and complexes with organic ligands (e.g., with phytoplankton metabolites and proteins, humic substances). The concentrations of naturally occurring methylated forms of As,[143,144] Ge,[145,146] Hg,[147] Sb,[148] and Sn[72,149,150] have been determined in seawater. A most astonishing discovery is that 90% of the oceanic Ge exists as methylated forms ($CH_3Ge(OH)_3^0$ and $(CH_3)_2Ge(OH)_2^0$) that are so stable to degradation that they have been called the "Teflon of the sea". The remarkable stability of these species is reflected in their conservative vertical profiles, which markedly contrast those of other methylated metal species and with the recycled behavior of inorganic H_4GeO_4.

Even though the existence of organic trace metal complexes in seawater had been postulated as much as 60 years ago,[151,152] and subsequent attempts were made to demonstrate the presence and characterize the nature of these complexes, the organically complexed fraction of the total concentration of certain trace metals in seawater has been reliably estimated only recently. Previous literature reviews (e.g., Mantoura[153] and van den Berg et al.[154]) of metal complexation determinations in seawater indicated little

Table 4 Determinations of the fraction of organically complexed copper in seawater

Location	Percent Organic Cu	Technique	Reference
San Francisco Bay	80–92	CLE/DPCSV DPASV CRCP/GFAAS	Donat et al.[161b]
Indian Ocean	>99.7	CLE/DPCSV	Donat & van den Berg[48]
North Sea	>99.9	CLE/DPCSV	Donat & van den Berg[48]
Sargasso Sea	98.8	CLE/LP/GFAAS	Moffett et al.[122]
Sargasso Sea	93	CLE/DPCSV DPASV	Donat & Bruland[161a]
North Pacific	99.4–99.8	DPASV	Coale & Bruland[160,161]
New York coast	99.8	FPA	Hering et al.[208]
Biscayne Bay	99.6	CLE/LP/GFAAS	Moffett & Zika[159]
Narragansett Bay	99.9	CLE/SPE/GFAAS	Sunda & Hanson[158]
Coastal Peru	98	CLE/SPE/GFAAS	Sunda & Hanson[158]
North Atlantic	89–99.8	MnO$_2$ ads.	Buckley & van den Berg[157]
North Atlantic	98.8–99.4	CLE/DPCSV	Buckley & van den Berg[157]
South Atlantic	99.9	CLE/DPCSV	van den Berg[156]
Coastal Florida	98.7	Bioassay	Sunda & Ferguson[155]
Mississippi Plume	99.1	Bioassay	Sunda & Ferguson[155]
New York Bight	>95	DPASV	Huizenga & Kester[209]
Irish Sea	94–98	MnO$_2$ ads.	Van den Berg[126]

Note: CLE/DPCSV = Competitive ligand equilibration/differential pulse cathodic stripping voltammetry; CRCP/GFAAS = Chelating resin column partitioning/graphite furnace atomic absorption spectrometry; CLE/LP/GFAAS = Competitive ligand equilibration/liquid partitioning/graphite-furnace atomic absorption spectrometry; DPASV = Differential pulse anodic stripping voltammetry; FPA = Fixed potential amperometry; CLE/SPE/GFAAS = Competitive ligand equilibration/solid phase extraction/graphite-furnace atomic absorption spectrometry; MnO$_2$ ads. = Manganese dioxide adsorption.

agreement between values for ligand concentrations, conditional stability constants, and the overall extent of organic complexation for Cu — in fact, previous estimates of the organically complexed fraction for Cu ranged from 0 to 100%. However, recent work shows that this fraction dominates the dissolved speciation of Cu[48,122,155–161a,b] (Table 4) and Zn[162–164] in oceanic surface water and is, therefore, of utmost importance in calculating the free metal ion concentrations of these two trace metals. These observations differ markedly from frequently cited model predictions by Mantoura et al.[165] that, of all the transition metals, only Cu should be complexed significantly (~10%) with organic ligands, and that dissolved humic substances (as well as dissolved organic compounds in general) should not substantially influence the speciation of Zn in seawater.

Recent vertical profiles obtained in the central northeast Pacific for the speciation of at least two trace elements, Cu and Zn, demonstrate progress made in determining that the chemical speciation of these two trace elements is dominated by organic complexation, although the chemical nature of the complexing ligands remains unknown.

1. Copper

Recent anodic stripping voltammetric measurements reported by Coale and Bruland[160,161] indicate that greater than 99.7% of total dissolved Cu(II) in central northeast Pacific surface waters shallower than 200 m is bound in strong organic complexes, primarily with the stronger (L$_1$) of two Cu-complexing ligands which has an average concentration of ~1.8 nM in the upper 100 m (Figure 7a). The concentration of this ligand exceeds the concentration of dissolved Cu from the surface down to ~200 m which, in concert with the strength of its Cu complexes, causes the high degree of organic complexation observed in the upper 200 m (Figure 7b). Because the concentration of dissolved Cu in these surface waters is only ~0.5 to 1.0 nM, the high extent of organic complexation reduces the fraction of inorganic Cu species to
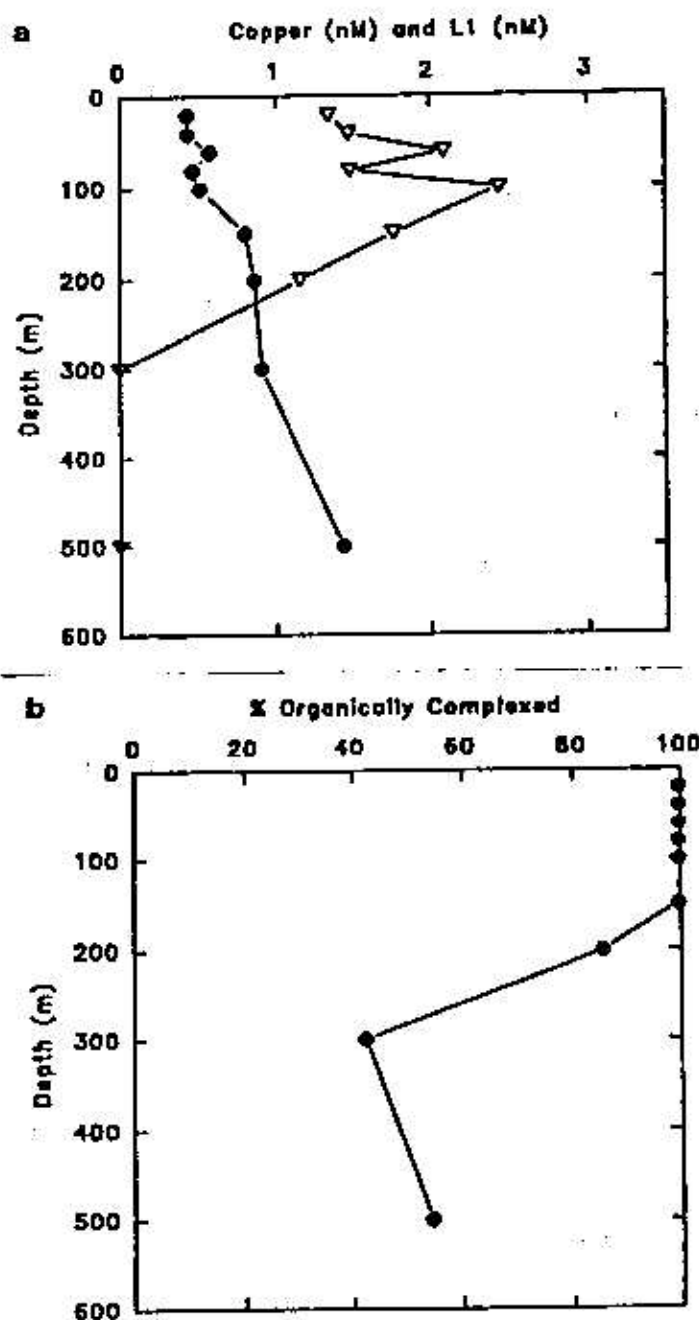
a

b

Figure 7 Dissolved copper (II) speciation vs. depth in central Northeast Pacific surface waters: (a) Dissolved Cu(II) concentrations; (b) concentrations of L_1, the stronger copper-complexing organic ligand; (c) log concentration values of free Cu^{2+} ion. (From Coale, K.H. and Bruland, K.W., *Deep-Sea Research*, 47(2), 317, 1990. With permission.)

less than 0.3% of the total dissolved Cu, and free hydrated Cu^{2+} amounts to only ~4% of this inorganic fraction. Whereas total dissolved Cu concentrations in the central northeast Pacific increase by approximately 3-fold from the surface to middepths, complexation of Cu by strong organic ligands causes the free hydrated Cu^{2+} concentration to vary from approximately $10^{-13.1}$ M at the surface to approximately $10^{-9.9}$ M at 300 m (Figure 7c), approximately a *2000-fold* increase!

In surface waters of the Sargasso sea[122,161a] and south San Francisco Bay,[161b] the concentrations of the strongest Cu-complexing ligand have been determined to be equal to or less than the dissolved Cu concentration. The weaker ligand can then dominate Cu speciation, slightly decreasing the overall extent of organic complexation, and increasing the inorganic Cu fraction and free Cu^{2+} concentrations. Some evidence exists that the ligand concentrations and extent of organic complexation can vary seasonally.
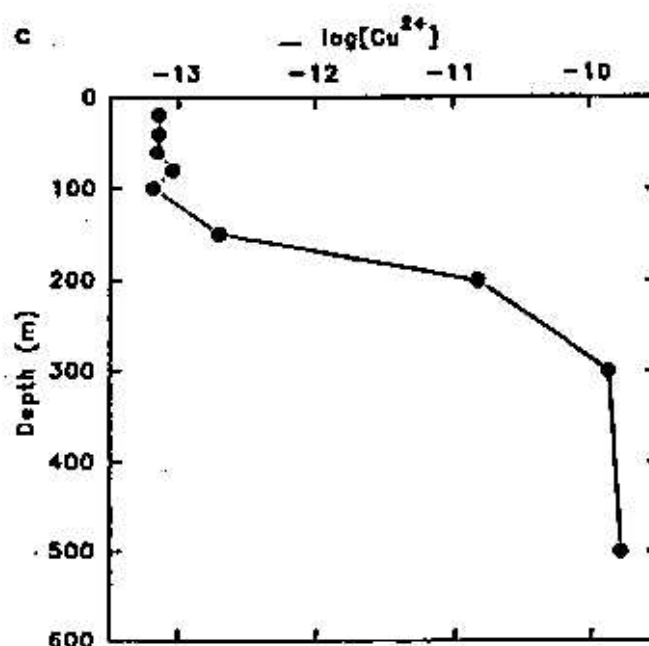
Figure 7 (continued).

2. Zinc

Recent anodic stripping voltammetry measurements in central North Pacific waters reported by Bruland[163] indicate that an average of 98.7% of the Zn in surface waters shallower than 200 m is complexed with a relatively Zn-specific organic ligand (or ligand class). Using two independent voltammetric techniques, Donat and Bruland[164] confirmed that strong organic complexes dominate the dissolved speciation of Zn in Northeast Pacific surface waters. Bruland[163] determined that the concentration of the Zn-complexing organic ligand or ligand class averages ~1.2 nM in the upper 200 m and exceeds the concentration of dissolved Zn from the surface down to ~350 m (Figure 8a). This excess in the ligand's concentration relative to that of dissolved Zn, and the strength of its Zn complexes, causes the high degree of organic complexation in the upper 300 m (Figure 8b). The free Zn^{2+} concentration varies from ~$10^{-11.1}M$ at depths shallower than 200 m, to ~$10^{-8.6}$ M at 600 m (Figure 8c) — approximately a *1400-fold* increase! The high degree of organic complexation for Zn reduces the concentration of inorganic Zn species to ~2 pM (2 × 10^{-12} M) and the free Zn^{2+} ion concentration to values as low as 1 pM (1 × 10^{-12} M; pZn = 12).

3. Other Metals

Only a few initial reports exist on the importance of organic complexation to the dissolved speciation of other metals in the open ocean, including Cd, Pb, Co, and Ni. Bruland[166] reported results of anodic stripping voltammetric measurements indicating that 70% of the dissolved Cd in central North Pacific surface waters was bound in strong complexes by relatively Cd-specific organic ligands existing at low concentrations (~0.1 nM). Bruland[166] found this ligand class only within the surface 175 m, and it had a concentration maximum at depths between 40 and 100 m. Bruland[166] determined that the concentration of inorganic forms of Cd varied from ~0.7 pM in surface waters to 800 pM at 600 m. Considering both organic and inorganic complexation, the concentration of free Cd^{2+} ranged from 20 fM in surface waters to 22 pM at 600 m — a 1000-fold variation! Chlorocomplexes appear to dominate the inorganic speciation of dissolved Cd in intermediate and deep waters, while organic complexation is important in influencing Cd speciation within oceanic surface waters.

Capodaglio et al.[167] determined the organically complexed fraction of dissolved Pb in surface waters of the eastern North Pacific by anodic stripping voltammetry. Approximately 50% of the dissolved Pb appeared to complexed by one class of strong organic ligands existing at concentrations between 0.2 and 0.5 nM. Inorganic and organic complexation of Pb in eastern North Pacific surface waters results in a free Pb^{2+} concentration of ~0.4 pM.

Organic complexation of dissolved Co and Ni in oceanic waters has not been reported; however, a few reports exist on the concentrations of organically complexed Co and Ni in estuarine and coastal samples.

a

Zinc (nM) and L (nM)
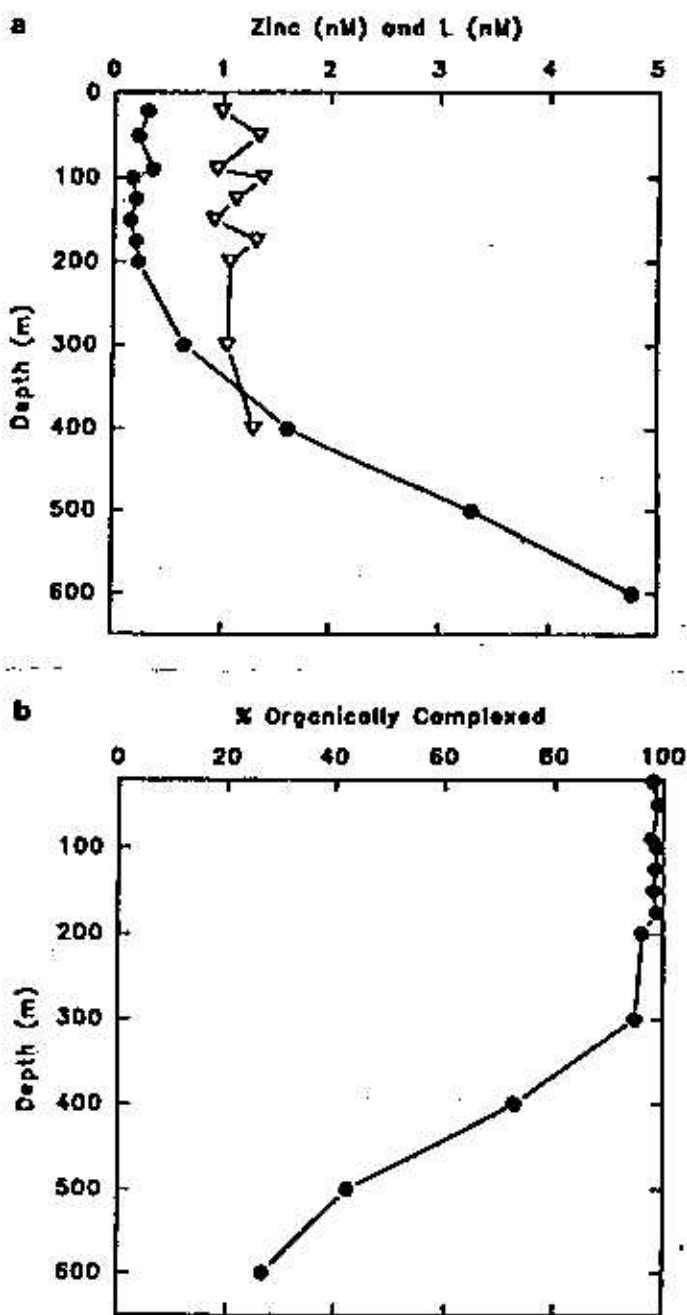

b

% Organically Complexed

Figure 8   Dissolved zinc speciation vs. depth in central Northeast Pacific surface waters: (a) Dissolved Zn concentrations; (b) concentrations of the strong zinc-complexing organic ligand; (c) log concentration values of free Zn^{2+} ion. (After Bruland, K.W., *Limnol. Oceanogr.*, 34, 267, 1989. With permission.)

Zhang et al.[168] determined that a variable fraction (45 to 100%; average 73%) of dissolved Co was very strongly complexed in the Scheldt River Estuary and the Irish Sea. Donat and Bruland[47] found evidence that ~50% of dissolved Co in coastal and open ocean seawater reference materials (CASS-1 and NASS-1) was bound in strong organic complexes, after adjustment of the pH from 1.6 to 7.6. Van den Berg and Nimmo[169] and Nimmo et al.[170] found that ~30 to 50% of dissolved Ni in the U.K. coastal waters was bound in extremely strong organic complexes. Donat et al.[161b] determined the same extent of organic complexation for Ni in south San Francisco Bay.

Fe^{3+} has a great tendency to form complexes with natural organic ligands (i.e., dissolved humic substances; see Sholkovitz[171] and references cited therein), and organic complexation is probably responsible for elevated concentrations of dissolved Fe in many estuarine and coastal waters.[171-173] Recent reviews by Sunda[15] and Wells[16] point out that most researchers have either ignored the possibility of organic complexation of Fe in the open ocean, or have argued that it is not significant. However, Gledhill
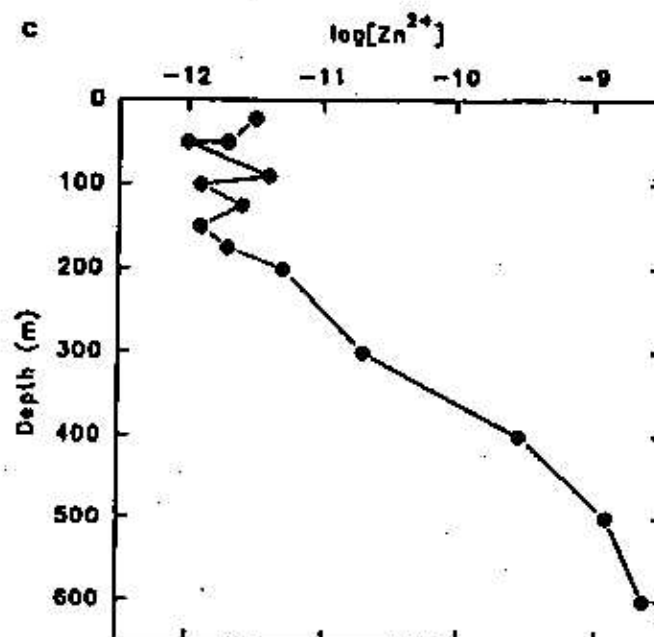
c

$\log[Zn^{2+}]$

Figure 8 (continued).

and van den Berg[174] (North Sea) and Rue and Bruland[175b] (North Pacific) have recently determined that >99% of dissolved Fe(III) is bound in strong complexes by a ligand class having a concentration of 1 to 5 nM in excess of the ambient dissolved Fe concentration. Although siderophore complexes are probably important to Fe speciation in some freshwater systems, no convincing evidence yet exists for their existence in the oceans.

Although the actual chemical structures of the trace metal complexing organic ligands are still unknown, the data presented in the preceding sections demonstrate the importance of complexation of certain trace metals with organic ligands which exist at low concentrations yet form very strong complexes (i.e., have high conditional stability constants). The recent accumulation of evidence indicating complexation of trace metals by naturally occurring organic ligands in the open ocean represents revolutionary progress beyond the previous status of this research field.

4. Biological Implications of Organic Complexation and Speciation of Trace Elements in Seawater

Almost three decades ago, Johnston[174,175] proposed that certain organic compounds present in seawater in trace quantities may exert an important influence on the primary production of marine communities. Barber and Ryther[176] suggested:

"in recently upwelled water phytoplankton growth is initially limited not by inorganic nutrients, trace metals, nor vitamin deficiencies, but rather by the absence of certain chelating substances. As the upwelling water ages, the organisms apparently gradually enrich the water with organic compounds some of which may be effective chelators."

Barber and Ryther[176] proposed that these chelators might be effective at reducing to nontoxic levels, the toxic free Cu^{2+} concentration thought to exist in freshly upwelled waters.

Compelling indications of biological sources for the Cu complexing ligands are provided by field data indicating that organic complexation of Cu is most pronounced in the surface euphotic zone, in general being highest at depths near the productivity maximum, and decreasing by one to three orders of magnitude below the vernal mixed layer in both the central northeast Pacific[160,161] and in the Sargasso Sea.[122]

The domination of the speciation of dissolved Zn by organic complexes may suggest a biological influence, as discussed above for Cu. However, the biological advantage of organic complexation of this essential and potentially biolimiting element is not readily apparent. Bruland[163] made the following speculations: (1) perhaps organic complexation may help keep Zn in solution, thereby preventing or retarding its adsorption onto particles; (2) perhaps some phytoplankton may be able to assimilate

organically complexed Zn to the exclusion of other phytoplankton; and/or (3) perhaps complexation of Zn first occurs inside a cell with intracellular ligands such as phytochelatins, the cytoplasmic detoxifying metal chelators found in higher plants and at least some algae,[177-179] followed by release of the chelators through phytoplankton DOC leakage and/or zooplankton grazing.

Moffett et al.[122] provided direct laboratory evidence for production of a strong Cu-binding ligand by a marine photoautotroph. This ligand has Cu-complexing strength identical to that of the stronger ligand observed by these same researchers in the Sargasso Sea and by Coale and Bruland[161] in the central northeast Pacific. The laboratory results Moffett and co-workers[122] obtained from a preliminary survey of four marine phytoplankton species (three species of eukaryotes and one prokaryote) indicated that only the cyanobacterial species *Synechococcus* produced a chelator forming Cu complexes of the same strength as those observed in the Sargasso Sea. These observations are consistent with earlier work in freshwater systems by McKnight and Morel,[180] who reported that among freshwater phytoplankton taxa, only the cyanobacteria appear to produce strong Cu-binding organic ligands. Because *Synechococcus* appear to be widespread in the surface waters of the open ocean,[181] and can account for as much as 50% of the primary productivity in some regions,[182,183] chelators produced by this genus might have a major influence on Cu speciation in many oceanic regions.

Production of a strong Cu-complexing ligand like L_1 may reflect strong selective pressure to detoxify Cu by lowering its free ion concentration. Evidence for this includes the work of Brand et al.[184] who examined the reproduction rates of clone cultures of 38 marine phytoplankton species in media containing different free Cu^{2+} activities. The Cu toxicity responses among the various species showed a phylogenetic trend: cyanobacteria were the most sensitive, diatoms were the least sensitive, and coccolithophores and dinoflagellates showed intermediate sensitivity. The reproduction rates of most of the cyanobacteria were reduced at Cu^{2+} concentrations above 10^{-12} M, while most eukaryotic algae maintained maximum reproduction rates at Cu^{2+} activities as high as 10^{-11} M. If cyanobacteria produced an organic ligand of the same concentration and binding strength as the stronger ligand L_1, it would complex Cu and lower the free Cu^{2+} concentration in oceanic surface waters to levels noninhibitory to their growth. However, intense upwelling could bring water having Cu^{2+} concentrations approaching 10^{-11} M into the surface photic zone — concentrations potentially high enough to limit reproduction of some phytoplankton species, especially cyanobacteria.[185] Cu^{2+} toxicity due to high Cu^{2+} concentrations in upwellings was speculated to cause a decline in cyanobacterial abundance after a vertical mixing event in the North Pacific Central Gyre.[186] Thus, free Cu^{2+} may influence species composition and seasonal species succession within local phytoplankton communities, and enough evidence exists to suggest that Cu^{2+} concentrations may influence picoplankton (cyanobacteria) production in high nutrient-low chlorophyll areas.

Brand et al.[187] examined the potential limitation of marine phytoplankton reproductive rates by Zn, Mn, and Fe, and suggested that differences among species in their abilities to reproduce in the presence of low free ion activities of these nutrient trace metals could result in species shifts in phytoplankton communities subjected to changes in trace metal or organic complexation regimes. For example, the reproductive rates of neritic species were generally limited by free Zn^{2+} concentrations below $10^{-11.5}$ M, while those of oceanic species were either not limited or only slightly limited at the lowest Zn^{2+} concentration set in the experiment, about 10^{-13} M. The habitat-related patterns in Zn^{2+} requirements of oceanic and neritic species are consistent with the oceanic-neritic distributions of free Zn^{2+} concentration.[143] The low surface water free Zn^{2+} concentration of $10^{-12.5}$ M may be low enough to limit the growth rate of many neritic phytoplankton species, but generally not that of oceanic species. However, intense upwelling could bring water into the surface layer whose free Zn^{2+} concentration would be high enough to support reproduction of more neritic-type species. Thus, the similarity between the nutritional requirement for Zn^{2+} and its distributional patterns has important implications for phytoplankton community species composition and species succession.

Fe may be the most important trace element nutrient to phytoplankton, and its deficiency may limit primary production in certain oceanic areas characterized by high nutrient and low chlorophyll concentrations such as the subarctic and equatorial Pacific and the Southern Ocean.[101,116,117] Fe also influences algal nitrogen metabolism in the ocean because it is required for nitrate reduction and nitrogen fixation. Price et al.[118] determined that additions of Fe caused the indigenous phytoplankton in the equatorial Pacific to switch from using primarily NH_4^+ for growth to using NO_3^-, and that this switch in nitrogenous nutrition was accompanied by a shift in the phytoplankton community composition. Although the speciation of dissolved Fe is extremely complex and presently unknown with any reliability, it has very important biological implications. For example, photoreduction of organic Fe(III) complexes and Fe(III) oxides, and the presence of Fe(III)-siderophore complexes, could enhance Fe's biological availability.

Brand et al.[184] examined the sensitivity of 20 species of marine phytoplankton to free Cd^{2+}. Cd toxicity for even the most sensitive species in their experiments occurred only at free Cd^{2+} exceeding $10^{-10} M$, well outside the range of Cd^{2+} concentrations determined by Bruland[166] in the central North Pacific. This comparison led Bruland[166] to suggest that Cd toxicity is probably not an important selective factor to phytoplankton growth or ecology in oceanic waters. However, Brand et al.[184] stated that Cd toxicity could still be a selective factor in estuaries due to increases in Cd concentrations from riverine and anthropogenic sources.

Price and Morel[189] recently hypothesized that Cd might promote growth of Zn-limited oceanic phytoplankton. Phytoplankton can exhibit substantially reduced growth rates due to Zn limitation at a free Zn^{2+} concentration of $10^{-12} M$, a concentration identical to that determined by Bruland[163] in oceanic surface waters. This low free Zn^{2+} concentration results from both the low concentration of total dissolved Zn and its high degree of organic complexation in the surface ocean. Price and Morel[189] reported that, in laboratory experiments using seawater with low free Zn^{2+} concentrations mimicking oceanic surface water conditions, Cd stimulates the growth of the marine diatom *Thalassiosira weissflogii* by substituting for Zn in certain macromolecules. The substitution appears to be highly effective, allowing Zn-deficient cells to grow at 90% of their maximum rate when supplied with Cd. Price and Morel[189] suggest that this biochemical metal substitution of Cd for Zn by phytoplankton could account for the pronounced nutrient-type oceanographic distribution of Cd.

Dissolved Co exists at concentrations of only 4 to 50 pM in the North Pacific.[98,101] These low values suggest a potential role of Co as a biolimiting element in seawater. Co is the central metal atom in the corrin ring core of vitamin B_{12} (cobalamin), and is one of the two metals for which organic complexation is known to enhance uptake by phytoplankton; siderophore-bound Fe is the other metal. Vitamin B_{12} is a required growth factor for many algal species, particularly some diatoms, chrysophytes, and dinoflagellates.[190] Some phytoplankton have been observed to produce a glycoprotein that binds to vitamin B_{12} making it unavailable to other species,[191] supporting the idea that this form of organically complexed Co may be important in interspecies competitive interactions.

Dissolved Ni exhibits a nutrient-type distribution in the oceans and its concentration ranges from 2 to 12 nM.[74,192] Price and Morel[193] have provided evidence indicating a potential biochemical role for Ni in urea assimilation by marine phytoplankton. They observed that phytoplankton growing on urea as a sole nitrogen source are limited by low free Ni^{2+} concentrations, but those growing on nitrate or ammonium are not. Ni is known to be an essential cofactor in the enzyme urease. Price and Morel's[193] results indicate that the concentration of dissolved Ni present in oceanic surface waters would not limit urea assimilation if all of the dissolved Ni was biologically available. However, if a substantial amount of the Ni present in oceanic surface waters is rendered unavailable by complexation with organic ligands, the resulting low free Ni^{2+} concentrations could potentially limit urea assimilation. This may be important in areas in which production is supported largely through regeneration, since urea is a common waste product of zooplankton.

Most field investigations of trace metal/phytoplankton interactions have focused on the effects of a single metal, largely ignoring the effects of metal ion ratios on algal growth.[185] However, laboratory culture studies clearly show that many metals may act synergistically and antagonistically to influence growth limitation or toxicity. Thus, it is necessary to quantify and experimentally control the availability of all combinations of potentially antagonistic metals in order to accurately describe metal/biota interactions. Brand et al.[187] have argued that simultaneous limitation by Zn, Mn, and Fe may be more severe than limitation by any one of these metals alone (i.e., synergism). Even more significantly, culture studies have repeatedly demonstrated that the uptake and metabolism of nutrient metal ions is a function of the concentration of other metals, which often act in a competitive or antagonistic manner. In phytoplankton, such metal antagonisms have been reported for Cu and Mn;[115,194-196] Cu and Fe;[195] Cu and Zn;[197] Cd and Fe;[198,199] Mn and Fe;[195,200] and Mn and Zn.[196]

Because antagonistic effects have been reported between Fe and toxic metals,[195,196,199] low $[Fe^{3+}]$ to $[Cu^{2+}]$ ratios in seawater, for instance, could plausibly explain the growth stimulation observed in Fe addition experiments, such as those reported by Martin et al.[101] Some cases of primary production limitation, apparently due to Fe alone, could actually be due to antagonistic effects of Cu and Fe. This explanation is especially difficult to dismiss in incubation experiments in which relatively high Fe concentrations (>10 nM) have been added (i.e., Menzel et al.;[201] Barber;[202] deBaar et al.;[203] Buma et al.[204]). In these cases, hydrous ferric oxides may form and adsorb Cu^{2+} ions, resulting in substantially lowered free Cu^{2+} ion concentrations.[205-207] Any observed growth stimulation could be due to alleviation of Cu toxic effects by purely abiotic, chemical adsorption processes occurring in the incubation bottles.

Although this is not a true case of biological metal antagonism, it again emphasizes that metal ratios are critical and must be closely monitored in this type of experiment. Even in cases where the soluble concentration of Fe has apparently not been exceeded (e.g., Martin et al.[101,117]), relatively low Fe additions (1 nM) could cause a substantial favorable shift in the $[Fe^{3+}]$ to $[Cu^{2+}]$ ratio. Proper interpretation of the results of metal addition experiments demands that all potentially interacting trace metals be considered and quantified.

More field data on metal antagonisms are necessary to support or negate hypotheses which have been formed primarily from laboratory studies. The artifacts in this type of study can be fiendishly cunning, and correct interpretation of their results requires a thorough understanding of both the oceanic chemistry of trace metals and their potential interactions with the biota. Thus, the advancement of our understanding of trace metal influences on oceanic productivity will require a unified collaboration between clever biologists and clever chemists.

VII. SUMMARY

As a result of major advances made since 1975 in analytical techniques and instrumentation and in the elimination or control of contamination during sample collection, storage, and analysis, our knowledge of the concentrations, distributions, speciation, and, therefore, our understanding of the biogeochemical cycling of the trace elements in the oceans has progressed dramatically. We now have a first-order understanding of the distributions of most of the trace elements in the oceans. The development of extremely sensitive analytical techniques amenable to obtaining measurements at sea have provided basin-wide cross sections of the distributions of some of the trace elements (e.g., Al, Mn, and Fe), allowing their use as sensitive and important oceanographic tracers. The biogeochemical cycling of certain trace elements like Cu, Fe, and Mn have been found to involve mediation by light and microorganisms. Our knowledge of the inorganic speciation of the trace elements in seawater has progressed to include estimations of the influences of temperature and pH. Convincing evidence has accrued demonstrating not just the presence of organically complexed metals in seawater, but the overwhelmingly dominant role of organic complexation in the speciation of dissolved Cu and Zn in surface seawater. Organic complexation of certain trace elements seems to have important biological implications to phytoplankton in the sea, as it may dominate the speciation of these elements and control their availability as nutrients and toxicants.

REFERENCES

1. Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., *Trace Metals in Seawater*, Plenum Press, New York, 1983.
2. Burton, J. D. and Statham, P. J., Occurrence, distribution, and chemical speciation of some minor dissolved constituents in ocean waters, in *Environmental Chemistry*, Vol. 2, Specialist Periodical Report, Royal Society of Chemistry, London, 1982, 234.
3. Burton, J. D. and Statham, P. J., Trace metals as tracers in the ocean, *Philos. Trans. R. Soc. London Ser. A*, 325, 127, 1988.
4. Burton, J. D. and Statham, P. J., Trace metals in seawater, in *Heavy Metals in the Marine Environment*, Rainbow, P. S. and Furness, R. W., Eds., CRC Press, Boca Raton, FL, 1990, 5.
5. Bruland, K. W., Trace elements in sea-water, in *Chemical Oceanography*, Vol. 8, Riley, J. P. and Chester, R., Eds., Academic Press, London, 1983, 157.
6. Whitfield, M. and Turner, D. R., The role of particles in regulating the composition of seawater, in *Aquatic Surface Chemistry*, Stumm, W., Ed., John Wiley & Sons, New York, 1987, 457.
7. Shiller, A. M. and Boyle, E. A., Variability of dissolved trace metals in the Mississippi River, *Geochim. Cosmochim. Acta*, 51, 3273, 1987.
8. Trefrey, J. H., Nelson, T. A., Trocine, R. P., Metz, S., and Vetter, T., Trace metal fluxes through the Mississippi River delta system, in *Contaminant Fluxes Through the Coastal Zone*, Kullenberg, G., Ed., Rapp. P.-v. Reun. Const. Int. Explor. Mer., 1986, 277.
9. Shiller, A. M. and Boyle, E., Dissolved zinc in rivers, *Nature*, 317, 49, 1985.
10. Martin, J.-M. and Windom, H. L., Present and future roles of ocean margins in regulating marine biogeochemical cycles of trace elements, in *Ocean Margin Processes in Global Change*, Mantoura, R. F. C., Martin, J.-M., and Wollast, R., Eds., John Wiley & Sons, New York, 1991, 45.

11. Chester, R. and Murphy, K. J. T., Metals in the marine atmosphere, in *Heavy Metals in the Marine Environment*, Rainbow, P. S. and Furness, R. W., Eds., CRC Press, Boca Raton, FL, 1990, 27.

12. Buat-Ménard, P., Air to sea transfer of anthropogenic trace metals, in *The Role of Air-Sea Exchange in Geochemical Cycling*, Buat-Ménard, P., Ed., NATO ASI Series, D. Reidel Pub. Co., 1985, 477.

13. Arimoto, R., Duce, R. A., and Ray, B. J., Concentrations, sources and air-sea exchange of trace elements in the atmosphere over the Pacific Ocean, in *Chemical Oceanography*, Vol. 10, SEAREX: The Sea/Air Exchange Program, Riley, J. P., Chester, R., and Duce, R. A., Eds., Academic Press, London, 1989, 27.

14. Zhuang, G., Duce, R. A., and Kester, D. R., The dississolution of atmospheric iron in surface seawater of the open ocean, *J. Geophys. Res.-Oceans*, 95(C9), 6207, 1990.

15. Sunda, W. G., Trace metal interactions with marine phytoplankton, *Biol. Oceanogr.*, 6, 411, 1991.

16. Wells, M. L., The availability of iron in seawater: a perspective, *Biol. Oceanogr.*, 6, 463, 1991.

17. Thompson, G., Hydrothermal fluxes in the ocean, in *Chemical Oceanography*, Vol. 8, Riley, J. P. and Chester, R., Eds., Academic Press, London, 1983, 272.

18. Edmond, J. M., U.S. research on oceanic hydrothermal chemistry: 1987–1990, in *Rev. Geophysics, Supp.*, 645, 1991.

19. Rona, P. A., Boström, K., Laubier, L., and Smith, K. L., Jr., Eds., *Hydrothermal Processes at Seafloor Spreading Centers*, Plenum Press, New York, 1983.

20. von Damm, K. L., Edmond, J. M., Grant, B., Measures, C. L, Walden, B., and Weiss, R. F., Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise, *Geochim. Cosmochim. Acta*, 49, 2197, 1985.

21. von Damm, K. L., Edmond, J. M., Measures, C. L, and Grant, B., Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California, *Geochim. Cosmochim. Acta*, 49, 2221, 1985.

22. Moody, J. R. and Beary, E. S., Purified reagents for trace metal analysis, *Talanta*, 29, 1003, 1982.

23. Mart, L., Minimization of accuracy risks in voltammetric ultratrace determination of heavy metals in natural waters, *Talanta*, 29, 1035, 1982.

24. Schaule, B. K. and Patterson, C. C., Lead concentration in the Northeast Pacific: evidence for global anthropogenic perturbations, *Earth Planet. Sci. Lett.*, 54, 97, 1981.

25. Martin, J. H., Knauer, G. A., and Broenkow, W. W., VERTEX: the lateral transport of manganese in the northeast Pacific, *Deep-Sea Res.*, 32, 1405, 1986.

26. Bruland, K. W., Franks, R. P., Knauer, G. A., and Martin, J. H., Sampling and analytical methods for the determination of Cu, Cd, Zn, and Ni at the nanogram per liter level in seawater, *Anal. Chim. Acta*, 105, 233, 1979.

26a. Hunter, C., Gordon, M., Fitzwater, S., and Johnson, K., A rosette/winch system for the collection of trace metal clean, large volume, discrete seawater samples, *EOS*, 75(3), 150, 1994.

27. Mart, L., Prevention of contamination and other accuracy risks in voltammetric trace metal analysis of natural waters. II. Collection of surface water samples, *Fresenius Z. Anal. Chem.*, 299, 97, 1979.

28. Boyle, E. A., Huested, S. S., and Jones, S. P., On the distribution of Cu, Ni, and Cd in the surface waters of the North Atlantic and North Pacific Ocean, *J. Geophys. Res.*, 86, 8048, 1981.

29. Kremling, K., The distribution of Cd, Cu, Ni, Mn, and Al in surface waters of the open Atlantic and European shelf areas, *Deep-Sea Res.*, 32, 531, 1985.

30. Danielsson, L. G., Magnusson, B., and Westerlund, S., An improved metal extraction procedure for the determination of trace metals in seawater by atomic absorption spectrometry with electrothermal atomization, *Anal. Chim. Acta*, 98, 47, 1978.

31. Bruland, K. W., Coale, K. H., and Mart, L., Analysis of seawater for dissolved Cd, Cu, and Pb: an intercomparison of voltammetric and atomic absorption methods, *Mar. Chem.*, 17, 285, 1985.

32. Sturgeon, R. E., Berman, S. S., Desaulniers, A., and D. S. Russell, Pre-concentration of trace metals from sea-water for determination by graphite-furnace atomic-absorption spectrometry, *Talanta*, 27, 85, 1980.

33. Sturgeon, R. E., Berman, S. S., Desaulniers, J. A. H., Mykytiuk, A. P., McLaren, J. W., and Russell, D. S., Comparison of methods for the determination of trace elements in seawater, *Anal. Chem.*, 52, 1585, 1980.

34. Klinkhammer, G., Determination of manganese in seawater by flameless atomic absorption spectrometry after pre-concentration with 8-hydroxyquinoline in chloroform, *Anal. Chem.*, 52, 117, 1980.

35. Landing, W. M. and Bruland, K. W., Manganese in the North Pacific, *Earth Planet. Sci. Lett.*, 49, 45, 1980.

36. Armannsson, H., Dithizone extraction and flame atomic absorption spectrometry for the determination of cadmium, zinc, lead, copper, nickel, cobalt, and silver in sea water and biological tissues, *Anal. Chim. Acta*, 110, 21, 1979.

37. Smith, R. G., Jr. and Windom, H. L., A solvent extraction technique for determining nanogram per liter concentrations of cadmium, copper, nickel, and zinc in sea water, *Anal. Chim. Acta*, 113, 39, 1980.

38. Kingston, H. M., Barnes, I. L., Brady, T. J., and Rains, T. C., Separation of eight transition elements from alkali and alkaline earth elements in estuarine and sea water with chelating resin and their determination by graphite furnace atomic absorption spectrometry, *Anal. Chem.*, 50, 2064, 1978.

39. Sturgeon, R. E., Berman, S. S., Willie, S. N., and Desaulniers, J. A. H., Pre-concentration of trace metals from seawater with silica-immobilized 8-hydroxyquinoline, *Anal. Chem.*, 53, 2337, 1981.

40. Landing, W. M., Haraldsson, C., and Paxéus, N., Vinyl polymer agglomerate based transition metal cation chelating ion-exchange resin containing the 8-hydroxyquinoline functional group, *Anal. Chem.*, 58, 3031, 1986.

41. Boyle, E. A. and Edmond, J. M., Determination of copper, nickel, and cadmium in sea water by APDC chelate coprecipitation and flameless atomic absorption spectrometry, *Anal. Chim. Acta*, 91, 189, 1977.

42. van Geen, A. and Boyle, E., Automated preconcentration of trace metals from seawater and freshwater, *Anal. Chem.*, 62, 1705, 1990.

43. Nürnberg, H. W., Trace analytical procedures with modern voltammetric determination methods for the investigation and monitoring of ecotoxic heavy metals in natural waters and atmospheric precipitates, *Sci. Tot. Environ.*, 37, 9, 1984.

44. van den Berg, C. M. G., The electroanalytical chemistry of sea water, in *Chemical Oceanography*, Vol. 9, Riley, J. P. and Chester, Eds., Academic Press, London, 1988, 197.

45. Mart, L. Nürnberg, H. W., and Rutzel, H., Comparative studies on cadmium levels in the North Sea, Norwegian Sea, Barents Sea, and the Eastern Arctic Ocean. *Fresenius Z. Anal. Chem.*, 317, 201, 1984.

46. Pihlar, B., Valenta, P., and Nürnberg, H. W., New high-performance analytical procedure for the voltammetric determination of nickel in routine analysis of waters, biological materials and food, *Fresenius Z. Anal. Chem.*, 307, 337, 1981.

47. Donat, J. R. and Bruland, K. W., Direct determination of dissolved cobalt and nickel in seawater by cathodic stripping voltammetry preceeded by collection of cyclohexane-1,2-dione dioxime complexes, *Anal. Chem.*, 60, 240, 1988.

48. Donat, J. R. and van den Berg, C. M. G., A new cathodic stripping voltammetric method for determining organic copper complexation in seawater, *Mar. Chem.*, 38(1-2), 69, 1992.

49. Measures, C. I. and Burton, J. D., Gas chromatographic method for the determination of selenite and total selenium in sea water, *Anal. Chim. Acta.*, 120, 177, 1980.

50. Measures, C. I. and Edmond, J. M., Determination of beryllium in natural waters in real time using electron capture detection gas chromatography, *Anal. Chem.*, 58, 2065, 1986.

51. Measures, C. I. and Edmond, J. M., Shipboard determination of aluminum in seawater at the nanomolar level by electron capture detection gas chromatography, *Anal. Chem.*, 61, 544, 1989.

52. Schaule, B. K. and Patterson, C. C., Perturbations of the natural lead depth profile in the Sargasso Sea by industrial lead, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 487.

53. Flegal, A. R. and Patterson, C. C., Vertical concentration profiles of lead in the central Pacific at 15°N and 20°S, *Earth Planet. Sci. Lett.*, 64, 19, 1983.

54. Stukas, V. J. and Wong, C. S., Accurate and precise analysis of trace levels of Cu, Cd, Pb, Zn, Fe, and Ni in sea water by isotope dilution mass spectrometry, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 513.

55. Berman, S. S., Sturgeon, R. E., Desaulniers, J. A. H., and Mykytiuk, A. P., Preparation of the sea water reference material for trace metals, NASS-1, *J. Mar. Pollut. Bull.*, 14, 69, 1983.

56. Beauchemin, D. and Berman, S. S., Determination of trace metals in reference water standards by inductively coupled plasma mass spectrometry with on-line preconcentration, *Anal. Chem.*, 61, 1857, 1989.

57. Piepgras, D. J. and Wasserburg, G. J., Neodymium isotopic variations in sea water, *Earth Planet. Sci. Lett.*, 50, 128, 1980.

58. Elderfield, H. and Greaves, M. J., The rare earth elements in seawater, *Nature*, 296, 214, 1982.

59. Elderfield, H. and Greaves, M. J., Determination of the rare earth elements in sea water, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 427.

60. German, C. R. and Elderfield, H., Rare earth elements in Saanich Inlet, British Columbia, a seasonally anoxic basin, *Geochim. Cosmochim. Acta*, 53, 2561, 1989.

61. German, C. R. and Elderfield, H., Rare earth elements in the NW Indian Ocean, *Geochim. Cosmochim. Acta*, 54, 1929, 1990.

62. Orians, K. J., Boyle, E. A., and Bruland, K. W., Dissolved titanium in the open ocean, *Nature*, 348, 322, 1990.

63. Falkner, K. K. and Edmond, J. M., Determination of gold at femtomolar levels in natural waters by flow injection inductively coupled plasma quadrupole mass spectrometry, *Anal. Chem.*, 62, 1477, 1990.

64. Falkner, K. K. and Edmond, J. M., Gold in seawater, *Earth Planet. Sci. Lett.*, 98, 208, 1990.

65. Boyle, E. A., Handy, B., and van Geen, A., Cobalt determination in natural waters using cation-exchange liquid chromatography with luminol chemiluminescence detection, *Anal. Chem.*, 59, 1499, 1987.

66. Sakamoto-Arnold, C. M. and Johnson, K. S., Determination of picomolar levels of cobalt in seawater by flow injection analysis with chemiluminescence detection, *Anal. Chem.*, 59, 1789, 1987.

67. Coale, K. H., Stout, P. M., Johnson, K. S., and Sakamoto, C. M., Determination of copper in seawater using a flow injection method with chemiluminescence detection, *Anal. Chim. Acta*, 266, 345, 1992.

68. Chapin, T. P., Johnson, K. S., and Coale, K. H., Rapid determination of manganese in sea water by flow injection analysis with chemiluminescence detection, *Anal. Chim. Acta*, 249, 469, 1991.

69. Elrod, V. A., Johnson, K. S., and Coale, K. H., Determination of subnanomolar levels of iron(II) and total dissolved iron in seawater by flow injection analysis with chemiluminescence detection, *Anal. Chem.*, 63, 893, 1991.

69a. Obata, H., Karatani, H., and Nakayama, E., Automated determin of iron in seawater by chelating resin concentration and chemiluminescence detection, *Anal. Chem.*, 65, 1524, 1993.

70. Cutter, G. A., Species determination of selenium in natural waters, *Anal. Chim. Acta*, 98, 59, 1978.

71. Cutter, G. A., Elimination of nitrite interference in the determination of Se by hydride generation, *Anal. Chim. Acta*, 149, 391, 1983.

72. Andreae, M. O., The determination of the chemical species of some of the "hydride elements" (arsenic, antimony, tin and germanium) in seawater: methodology and results, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 1.

73. Gill, G. A. and Bruland, K. W., Mercury speciation in surface freshwater systems in California and other areas, *Environ. Sci. Technol.*, 24, 1392, 1990.

74. Gill, G. A. and Fitzgerald, W., Picomolar mercury measurements in seawater and other materials using stannous chloride reduction and two-stage gold amalgamation with gas phase detection, *Mar. Chem.*, 20, 227, 1987.

75. Cutter, L. S., Cutter, G. A., and San Diego-McGlone, M. L. C., Simultaneous determination of inorganic arsenic and antimony species in natural waters using selective hydride generation with gas chromatography/photoionization detection, *Anal. Chem.*, 63, 1138, 1991.

76. Boyle, E. A., Sclater, F., and Edmond, J. M., On the marine chemistry of cadmium, *Nature*, 263, 42, 1976.

77. Martin, J. H., Bruland, K. W., and Broenkow, W. W., Cadmium transport in the California Current, in *Marine Pollutant Transfer*, Windom, H. and Duce, R., Eds., D.C. Heath, Lexington, MA, 1976, 159.

78. Bruland, K. W., Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific, *Earth Planet. Sci. Lett.*, 47, 176, 1980.

79. Bruland, K. W. and Franks, R. P., Mn, Ni, Cu, Zn and Cd in the western north Atlantic, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 395.

80. Bruland, K. W., Knauer, G. A., and Martin, J. H., Zinc in north-east Pacific water, *Nature*, 271, 741, 1978.

81. Hydes, D. J., Aluminium in seawater: control by inorganic processes, *Science*, 205, 1260, 1979.

82. Hydes, D. J., Distribution of aluminium in waters of the North East Atlantic 25°N to 35°N, *Geochim. Cosmochim. Acta*, 47, 967, 1983.

83. Moore, R. M., Oceanographic distributions of zinc, cadmium, copper and aluminum in waters of the central Arctic, *Geochim. Cosmochim. Acta*, 45, 2475, 1981.

84. Olafsson, J., Mercury concentrations in the North Atlantic in relation to cadmium, aluminium, and oceanographic parameters, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 475.

85. Measures, C. I., Grant, B., Khadem, M., Lee, D. S., and Edmond, J. M., Distribution of Be, Al, Se, and Bi in the surface waters of the western North Atlantic and Caribbean, *Earth. Planet. Sci. Lett.*, 71, 1, 1984.

86. Orians, K. J. and Bruland, K. W., Dissolved aluminum in the central North Pacific, *Nature*, 316, 427, 1985.

87. Orians, K. J. and Bruland, K. W., The biogeochemistry of aluminum in the Pacific Ocean, *Earth Planet. Sci. Lett.*, 78, 397, 1986.

88. Moore, R. M., and Millward, G. E., Dissolved-particulate interactions of aluminium in ocean waters, *Geochim. Cosmochim. Acta*, 48, 235, 1984.

89. Measures, C. I., Edmond, J. M., and Jickells, T. D., Aluminium in the northwest Atlantic, *Geochim. Cosmochim. Acta*, 50, 1423, 1986.

90. MacKenzie, F. T., Stoffyn, M., and Wollast, R., Aluminum in seawater: control by biological activity, *Science*, 199, 680, 1978.

91. Caschetto, S. and Wollast, R., Vertical distribution of dissolved aluminum in the Mediterranean Sea, *Mar. Chem.*, 7, 141, 1979.

92. Hydes, D. J., De Lange, G. J., and De Baar, H. J. W., Dissolved aluminium in the Mediterranean, *Geochim. Cosmochim. Acta*, 52, 2107, 1988.

93. Measures, C. I. and Edmond, J. M., Aluminium as a tracer of the deep outflow from the Mediterranean, *J. Geophys. Res.*, 93, 591, 1988.

94. Boyle, E. A. and Edmond, J. M., Copper in surface waters south of New Zealand, *Nature*, 253, 107, 1975.

95. Boyle, E. A., Sclater, F., and Edmond, J. M., The distribution of dissolved copper in the Pacific, *Earth Planet. Sci. Lett.*, 37, 38, 1977.

96. Gordon, R. M., Martin, J. H., and Knauer, G. A., Iron in northeast Pacific waters, *Nature*, 299, 611, 1982.

97. Landing, W. M. and Bruland, K. W., The contrasting biogeochemistry of iron and manganese in the Pacific Ocean, *Geochim. Cosmochim. Acta*, 51, 29, 1987.

98. Martin, J. H. and Gordon, R. M., Northeast Pacific iron distributions in relation to phytoplankton productivity. *Deep-Sea Res.*, 35, 177, 1988.

99. Moore, R. M., The distribution of dissolved copper in the eastern Atlantic Ocean, *Earth Planet. Sci. Lett.*, 41, 461, 1978.

100. Measures, C. I. and Edmond, J. M., Aluminium in the South Atlantic: steady state distribution of a short residence time element, *J. Geophys. Res.*, 95 C4, 5331, 1990.

101. Martin, J. H., Gordon, R. M., Fitzwater, S., and Broenkow, W. W., VERTEX: phytoplankton/iron studies in the Gulf of Alaska, *Deep-Sea Res.*, 36, 649, 1989.

101a. Skrabad, S. A., The estuarine and marine geochemistry of titanium, Ph.D. thesis, University of Delaware, Newark, 1993.

102. Orians, K. J. and Bruland, K. W., Dissolved gallium in the open ocean, *Nature*, 332, 717, 1988.

103. Shiller, A. M., Enrichment of dissolved gallium relative to aluminum in natural waters, *Geochim. Cosmochim. Acta*, 52, 1879, 1988.

104. Koide, M., Stallard, M., Hodge, V., and Goldberg, E. D., Preliminary studies on the marine chemistry of ruthenium, *Neth. J. Sea Res.*, 1986.

105. Goldberg, E. D., Hodge, V. F., Kay, P., Stallard, M., and Koide, M., Some comparative marine chemistries of platinum and iridium, *Appl. Geochem.*, 1, 227, 1986.

106. Lee, D. S., Palladium and nickel in northeast Pacific waters, *Nature*, 305, 5929, 1983.

107. Koide M., Hodge, V., Yang, J. S., and Goldberg, E. D., Determination of rhenium in marine waters and sediments by graphite furnace atomic absorption spectrophotometry, *Anal. Chem.*, 59, 1802, 1987.

107a. Colodner, D. C., Boyle, E. A., and Edmond, J. M., Determination of rhenium and platinum in natural waters and sediments, and iridium in sediments by flow injection isotope dilution inductively coupled plasma mass spectrometry, *Anal. Chem.*, 65, 1419, 1993.

108. Lee, D. S. and Edmond, J. M., Tellurium species in seawater, *Nature*, 313, 782, 1985.

109. Hodge, V. F., Stallard, M., Koide, M., and Goldberg, E. D., Platinum and the platinum anomaly in the marine environment, *Earth Planet. Sci. Lett.*, 72, 158, 1985.

110. Hodge, V. F., Stallard, M., Koide, M., and Goldberg, E. D., Determination of platinum and iridium in marine waters, sediments, and organisms, *Anal. Chem.*, 58, 616, 1986.

111. Goldberg, E. D., Comparative chemistry of the platinum and other heavy metals in the marine environment, *Pure Appl. Chem.*, 59, 565, 1987.

112. Jacinto, G. S. and van den Berg, C. M. G., Different behavior of platinum in the Indian and Pacific Oceans, *Nature*, 338, 332, 1989.

112a. McKelvey, B. A. and Orians, K. J., Dissolved zirconium in the North Pacific Ocean, *Geochim. Cosmochim. Acta*, 57, 3801, 1993.

112b. McKelvey, B. A. and Orians, K. J., The marine geochemistry of zirconium and hafnium, *EOS*, 75(3), 78, 1994.

113. Sunda, W. G. and Huntsman, S. A. Effect of sunlight on redox cycles of manganese in the southwestern Sargasso Sea, *Deep-Sea Res.*, 35, 1297, 1988.

114. Sunda, W. G. and Huntsman, S. A., Diel cycles in microbial manganese oxidation and manganese redox speciation in coastal waters of the Bahama Islands, *Limnol. Oceanogr.*, 35, 325, 1990.

115. Sunda, W. G. and Huntsman, S. A., Effect of competitive interactions between manganese and copper on cellular manganese and growth in estuarine and oceanic species of the diatom *Thalassiosira*, *Limnol. Oceanogr.*, 28, 924, 1983.

116. Martin, J. H. and Fitzwater, S. E., Iron deficiency limits phytoplankton growth in the northeast Pacific subarctic, *Nature*, 331, 341, 1988.

117. Martin, J. H., Gordon, R. M., and Fitzwater, S., Iron in Antarctic waters, *Nature*, 345, 156, 1990.

118. Waite, T. D. and Morel, F. M. M., Photoreductive dissolution of colloidal iron oxides in natural waters, *Environ. Sci. Technol.*, 18, 860, 1984.

119. Rich, H. W. and Morel, F. M. M., Availability of well-defined iron colloids to the marine diatom *Thalassiosira weissflogii*, *Limnol. Oceanogr.*, 35, 652, 1990.

120. Moffett, J. W. and Zika, R. G., Oxidation kinetics of Cu(I) in seawater: implications for its existence in the marine environment, *Mar. Chem.*, 13, 239, 1983.

121. Moffett, J. W. and Zika, R. G., Measurement of copper(I) in surface waters of the subtropical Atlantic and Gulf of Mexico, *Geochim. Cosmochim. Acta*, 52, 1849, 1988.

122. Moffett, J. W., Zika, R. G., and Brand, L. E., Distribution and potential sources and sinks of copper chelators in the Sargasso Sea, *Deep-Sea Res.*, 37, 27, 1990.

123. Farley, K. J. and Morel, F. M. M., Role of coagulation in the kinetics of sedimentation, *Environ. Sci. Technol.*, 20, 187, 1986.

124. Honeyman, B. D. and Santschi, P. H., A Brownian-pumping model for oceanic trace metal scavenging: evidence from Th Isotopes, *J. Mar. Res.*, 47, 951, 1989.

125. Moran, S. B. and Moore, R. M., The distribution of colloidal aluminum and organic carbon in coastal and open ocean waters off Nova Scotia, *Geochim. Cosmochim. Acta*, 53, 2519, 1989.

126. van den Berg, C. M. G., Determination of copper complexation with natural organic ligands in seawater by equilibration with MnO₂. II. Experimental procedures and application to surface seawater, *Mar. Chem.*, 11, 323, 1982.

127. Davis, J. A., Complexation of trace metals by adsorbed natural organic matter, *Geochim. Cosmochim. Acta*, 48, 679, 1984.

128. Davis, J. A. and Leckie, J. O., Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides, *Environ. Sci. Technol.*, 12, 1309, 1978.

129. Bourg, A. C. M. and Schindler, P. W., Ternary surface complexes. 1. Complex formation in the system silica-Cu(II)-ethylenediamine, *Chimia*, 32, 166, 1978.

130. Spencer, D. W. and Brewer, P. G., Vertical advection diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea, *J. Geophys. Res.*, 76, 5877, 1971.

131. Emerson, S., Cranston, R. E., and Liss, P. S., Redox species in a reducing fjord: equilibrium and kinetic considerations, *Deep-Sea Res.*, 26A, 859, 1979.

132. Bacon, M. P., Brewer, P. G., Spencer, D. W., Murray, J. W., and Goddard, J., Lead-210, polonium-210, manganese, and iron in the Cariaco Trench, *Deep-Sea Res.*, 27A, 119, 1980.

133. Measures, C. I., McDuff, R. E., and Edmond, J. M., Selenium redox chemistry at GEOSECS I reoccupation, *Earth Planet. Sci. Lett.*, 49, 102, 1980.

134. Measures, C. L., Grant, B. C., Mangum, B. J., and Edmond, J. M., The relationship of the distribution of dissolved selenium IV and VI in three oceans to physical and biological processes, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 73.

135. Cutter, G. A., Selenium in reducing waters, *Science*, 217, 829, 1982.

136. Cutter, G. A. and Bruland, K. W., The marine biogeochemistry of selenium: a re-evaluation, *Limnol. Oceanogr.*, 29, 1179, 1984.

137. Murray, J. W., Spell, B., and Paul, B., The contrasting geochemistry of manganese and chromium in the eastern tropical Pacific Ocean, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 643.

138. Turner, D. R., Whitfield, M., and Dickson, A. G. The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure, *Geochim. Cosmochim. Acta*, 45, 855, 1981.

139. Byrne, R. H., Kump, L. R., and Cantrell, K. J., The influence of temperature and pH on trace metal speciation in seawater, *Mar. Chem.*, 25, 163, 1988.

140. Ringbom, A., *Complexation in Analytical Chemistry*, Wiley-Interscience, New York, 1963.

141. Zafiriou, O. C. and True, M. B., Interconversion of Fe(III) hydroxy complexes in seawater, *Mar. Chem.*, 8, 281, 1980.

142. Hudson, R. J. M. and Morel, F. M. M., Iron transport in marine phytoplankton: kinetics of cellular and medium coordination reactions, *Limnol. Oceanogr.*, 35, 1002, 1990.

143. Andreae, M. O., Determination of arsenic species in natural waters, *Anal. Chem.*, 49, 820, 1977.

144. Andreae, M. O., Arsenic speciation in seawater and interstitial waters: the influence of biological-chemical interactions on the chemistry of a trace element, *Limnol. Oceanogr.*, 24, 440, 1979.

145. Hambrick, G. A., III, Froelich, P. N., Jr., Andreae, M. O., and Lewis, B. L., Determination of methylgermanium species in natural waters by graphite furnace atomic absorption spectrometry with hydride generation, *Anal. Chem.*, 56, 421, 1984.

146. Lewis, B. L., Froelich, P. N., and Andreae, M. O., Methylgermanium in natural waters, *Nature*, 313, 303, 1985.

147. Mason, R. P. and Fitzgerald, W. F., Alkylmercury species in the equatorial Pacific, *Nature*, 347, 457, 1990

148. Andreae, M. O., Asmodé, J.-F., Foster, P., and Van't dack, L., Determination of antimony (III), antimony (V), and methylantimony species in natural waters by graphite furnace atomic absorption spectrometry with hydride generation, *Anal. Chem.*, 53, 287, 1981.

149. Byrd, J. T. and Andreae, M. T., Tin and methyltin species in seawater: concentrations and fluxes, *Science*, 218, 565, 1982.

150. Andreae, M. O. and Byrd, J. T., Determination of tin and methyltin species by hydride generation and detection with graphite-furnace atomic absorption or flame emission spectrometry, *Anal. Chim. Acta*, 156, 147, 1984.

151. Harvey, H. W., *Biological Chemistry and Physics of Sea Water*, Cambridge University Press, Cambridge, 1928.

152. Cooper, L. H. N., Some conditions governing the solubility of iron, *Proc. R. Soc. London*, B124, 299, 1937.

153. Mantoura, R. F. C., Organo-metallic interactions in natural waters, in *Marine Organic Chemistry*, Duursma, E. K. and Dawson, R., Eds., Elsevier Science Publ. Co., New York, 1981, 179.

154. van den Berg, C. M. G., Buckley, P. J. M., and Dharmvanlj, S., Determination of ligand concentrations and conditional stability constants in seawater. Comparison of the DPASV and MnO₂ adsorption techniques, in *Complexation of Trace Metals in Natural Waters*, Kramer, C. J. M. and Duinker, J. C., Eds., Nijhoff/Junk Publishers, 1984, 213.

155. Sunda, W. G. and Ferguson, R. L. Sensitivity of natural bacterial communities to additions of copper and to cupric ion activity: a bioassay of copper complexation in seawater, in *Trace Metals in Seawater*, Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D., and Goldberg, E. D., Eds., Plenum Press, New York, 1983, 871.

156. van den Berg, C. M. G., Determination of the complexing capacity and conditional stability constants of complexes of copper (II) with natural organic ligands in seawater by cathodic stripping voltammetry of copper-catechol complex ions, *Mar. Chem.*, 15, 1, 1984.

157. Buckley, P. J. M. and van den Berg, C. M. G., Copper complexation profiles in the Atlantic Ocean, *Mar. Chem.*, 19, 281, 1986.

158. Sunda, W. G. and Hanson, A. K., Jr., Measurement of free cupric ion concentration in seawater by a ligand competition technique involving copper sorption onto C_{18} Sep Pak cartridges, *Limnol. Oceanogr.*, 32, 537, 1987.

159. Moffett, J. W. and Zika, R. G., Solvent extraction of copper acetylacetonate in studies of copper (II) speciation in seawater, *Mar. Chem.*, 21, 301, 1987.

160. Coale, K. H. and Bruland, K. W., Copper complexation in the Northeast Pacific, *Limnol. Oceanogr.*, 33, 1084, 1988.

161. Coale, K. H. and Bruland, K. W., Spatial and temporal variability in copper complexation in the North Pacific, *Deep-Sea Res.*, 47, 317, 1990.

161a. Donat, J. R. and Bruland, K. W., Organic copper complexation in Sargasso Sea surface waters: comparison to the North Pacific, *EOS*, 72(51), 44, 1992.

161b. Donat, J. R., Lao, K. A., and Bruland, K. W., Speciation of dissolved copper and nickel in south San Francisco Bay: a multi-method approach, *Anal. Chim. Acta*, 284(3), 547, 1994.

162. van den Berg, C. M. G., Determination of the zinc complexing capacity in seawater by cathodic stripping voltammetry of zinc-APDC complex ions, *Mar. Chem.*, 16, 121, 1985.

163. Bruland, K. W., Oceanic zinc speciation: complexation of zinc by natural organic ligands in the central North Pacific, *Limnol. Oceanogr.*, 34, 267, 1989.

164. Donat, J. R. and Bruland, K. W., A comparison of two voltammetric techniques for determining zinc speciation in Northeast Pacific Ocean waters, *Mar. Chem.*, 28, 301, 1990.

165. Mantoura, R. F. C., Dickson, A., and Riley, J. P., The complexation of metals with humic materials in natural waters, *Estuarine Coastal Mar. Sci.*, 6, 387, 1978.

166. Bruland, K. W., Complexation of cadmium by natural organic ligands in the central North Pacific, *Limnol. Oceanogr.*, 37(5), 1008, 1992.

167. Capodaglio, G., Coale, K. H., and Bruland, K. W., Lead speciation in surface waters of the Eastern North Pacific, *Mar. Chem.*, 29, 221, 1990.

168. Zhang, H., van den Berg, C. M. G., and Wollast, R., The determination of interactions of cobalt (II) with organic compounds in seawater using cathodic stripping voltammetry, *Mar. Chem.*, 28, 285, 1990.

169. van den Berg, C. M. G. and Nimmo, M., Determination of interactions of nickel with dissolved organic material in seawater using cathodic stripping voltammetry, *Sci. Tot. Environ.*, 60, 185, 1987.

170. Nimmo, M., van den Berg, C. M. G., and Brown, J., The chemical speciation of dissolved nickel, copper, vanadium, and iron in Liverpool Bay, Irish Sea, *Estuarine Coastal Shelf Sci.*, 29, 57, 1989.

171. Sholkovitz, E. R., Boyle, E. A., and Price, N. B., The removal of dissolved humic acids and iron during estuarine mixing, *Earth Planet. Sci. Lett.*, 40, 130, 1978.

172. Boyle, E. A., Edmond, J. M., and Sholkovitz, E. R., The mechanism of iron removal in estuaries, *Geochim. Cosmochim. Acta*, 41, 1313, 1977.

173. Sholkovitz, E. R., The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co, and Cd during estuarine mixing, *Earth Planet. Sci. Lett.*, 41, 77, 1978.

173a. Gledhill, M. and van den Berg, C. M. G., Determination of complexation of Fe(III) with natural organic complexing ligands using cathodic stripping voltammetry, *Mar. Chem.*

173b. Rue, E. L. and Bruland, K. W., Complexation of Fe(III) by natural organic ligands in the central North Pacific as determined by competitive ligand equilibration/adsorptive cathodic stripping voltammetry, *Mar. Chem.*, submitted.

174. Johnston, R., Seawater, the natural medium of phytoplankton. I. General features, *J. Mar. Biol. Assoc. UK*, 43, 427, 1963.

175. Johnston, R., Seawater, the natural medium of phytoplankton. II. Trace metals and chelation, and general discussion, *J. Mar. Biol. Assoc. UK*, 44, 87, 1964.

176. Barber, R. T. and Ryther, J. H., Organic chelators: factors affecting primary production in the Cromwell Current upwelling, *J. Exp. Mar. Biol. Ecol.*, 3, 191, 1969.

177. Grill, E., Winnacker, E. L., and Zenk, M. H., Phytochelatins: the principal heavy metal-complexing peptides of higher plants, *Science*, 230, 674, 1985.

178. Grill, E., Winnacker, E. L., and Zenk, M. H., Phytochelatins, a class of heavy metal-binding peptides from plants, are functionally analogous to metallothioneins, *Proc. Natl. Acad. Sci. U.S.A.*, 84, 439, 1987.

179. Gekeler, W., Grill, E., Winnacker, E. L., and Zenk, M. H., Algae sequester heavy metals via synthesis of phytochelatin complexes, *Arch. Microbiol.*, 150, 197, 1988.

180. McKnight, D. M. and Morel, F. M. M., Release of weak and strong copper-complexing agents by algae, *Limnol. Oceanogr.*, 24, 823, 1979.

181. Waterbury, J. B., Watson, S. W., Guillard, R. R. L., and Brand, L. E., Widespread occurrence of a unicellular marine planktonic cyanobacterium, *Nature*, 277, 293, 1979.

182. Glover, H. E., Keller, M. D., and Guillard, R. R. L. Light quality and oceanic ultraphytoplankters, *Nature*, 319, 142, 1986.

183. Iturriaga, R. and Marra, J., Temporal and spatial variability of chroococcoid cyanobacteria *Synechococcus* spp. specific growth rates and their contribution to primary production in the Sargasso Sea, *Mar. Ecol. Prog. Ser.*, 44, 175, 1988.

184. Brand, L. E., Sunda, W. G., and Guillard, R. R. L., Reduction of marine phytoplankton reproduction rates by copper and cadmium, *J. Exp. Mar. Biol. Ecol.*, 96, 225, 1986.

185. Bruland, K. W., Donat, J. R., and Hutchins, D. A., Interactive influences of bioactive trace metals on biological production in oceanic waters, *Limnol. Oceanogr.*, 36(8), 1555, 1991.

186. DiTullio, G. R. and Laws, E. A., Impact of an atmospheric-oceanic disturbance on phytoplankton community dynamics in the North Pacific Central Gyre, *Deep-Sea Res.*, 38, 1305, 1991.

187. Brand, L. E., Sunda, W. G., and Guillard, R. R. L., Limitation of marine phytoplankton reproductive rates by zinc, manganese, and iron, *Limnol. Oceanogr.*, 28, 1182, 1983.

188. Price, N. M., Andersen, L. F., and Morel, F. M. M., Iron and nitrogen nutrition of equatorial Pacific plankton, *Deep-Sea Res.*, 38, 1361, 1991.

189. Price, N. M. and Morel, F. M. M., Cadmium and cobalt substitution for zinc in a zinc-deficient marine diatom, *Nature*, 344, 658, 1990.

190. Swift, D. G., Vitamins and phytoplankton growth, in *The Physiological Ecology of Phytoplankton*, Morris, I., Ed., Blackwell Scientific Publications, Oxford, 1980, 329.

191. Pitner, L. J. and Altmeyer, V. L., Vitamin B_{12} binder and other algal inhibitors, *J. Phycol.*, 15, 391, 1979.

192. Sclater, F. F., Boyle, E. A., and Edmond, J. M., On the marine geochemistry of nickel, *Earth Planet. Sci. Lett.*, 31, 119, 1976.

193. Price, N. and Morel, F. M. M., Co-limitation of phytoplankton growth by nickel and nitrogen, *Limnol. Oceanogr.*, 1991.

194. Sunda, W. G., Barber, R. T., and Huntsman, S. A., Phytoplankton growth in nutrient rich seawater; importance of copper-manganese cellular interactions, *J. Mar. Res.*, 39, 567, 1981.

195. Murphy, L. S., Guillard, R. R. L., and Brown, J. F., The effects of iron and manganese on copper sensitivity in diatoms: differences in the responses of closely related neritic oceanic species, *Biol. Oceanogr.*, 3, 187, 1984.

196. Sunda, W. G., Neritic-oceanic trends in trace-metal toxicity to phytoplankton communities, in Proceedings of the Fourth International Ocean Disposal Symposium, Plymouth, England, April 1983, 1986, 19.

197. Rueter, J. G. and Morel, F. M. M., The interaction between zinc deficiency and copper toxicity as it affects the silicic acid uptake mechanisms of *Thalassiosira pseudonana*, *Limnol. Oceanogr.*, 26, 67, 1981.

198. Foster, P. L. and Morel, F. M. M., Reversal of cadmium toxicity in a diatom: an interaction between cadmium activity and iron, *Limnol. Oceanogr.*, 27, 745, 1982.

199. Harrison, G. I. and Morel, F. M. M., Antagonism between cadmium and iron in the marine diatom *Thalassiosira weisflogii*, *J. Phycol.*, 19, 495, 1983.

200. Harrison, G. I. and Morel, F. M. M., Response of the marine diatom *Thalassiosira weissflogii* to iron stress, *Limnol. Oceanogr.*, 31, 989, 1986.

201. Menzel, D. W., Hulburt, E. M., and Ryther, J. H., The effects of enriching Sargasso Sea water on the production and species composition of phytoplankton, *Deep-Sea Res.*, 10, 209, 1963.

202. Barber, R. T., Organic ligands and phytoplankton growth in nutrient-rich seawater, in *Trace Metals and Metal-Organic Interactions in Natural Waters*, Singer, P. C., Ed., Ann Arbor Science, Ann Arbor, MI, 1973, 321.

203. deBaar, H. J. W., Buma, A. G. J., Nolting, R. F., Cadee, G. C., Jacques, G., and Treguer, P. J., On iron limitation of the Southern Ocean: experimental observations in the Weddell and Scotia Seas, *Mar. Ecol. Prog. Ser.*, 65, 105, 1990.

204. Buma, A. G. J., deBaar, H. J. W., Nolting, R. F., and van Bennekom, A. J., Metal enrichment experiments in the Weddell-Scotia Seas: effects of Fe and Mn on various plankton communities, *Limnol. Oceanogr.*, 36(8), 1865, 1991.

205. Steemann-Nielsen, E. and Wium-Anderson, S., Copper ions as poison in the sea and in fresh water, *Mar. Biol.*, 6, 93, 1970.

206. Huntsman, S. A. and Sunda, W. G., The role of trace metals in regulating phytoplankton growth, in *The Physiological Ecology of Phytoplankton*, Morris, I., Ed., Studies in Ecology, Vol. 7, Blackwell Scientific, Oxford, 1980, 285.

207. Stauben, J. L. and Florence, T. M., Interactions of copper and manganese: a mechanism by which manganese alleviates copper toxicity to the marine diatom, *Nitzschia dostenium* (Ehrenberg) W. Smith. *Aquat. Toxicol.*, 7, 241, 1985.

208. Hering, J. G., Sunda, W. G., Ferguson, R. L., and Morel, F. M. M., A field comparison of two methods for the determination of copper complexation: bacterial bioassay and fixed-potential amperometry, *Mar. Chem.*, 20, 299, 1987.

209. Huizenga, D. L. and Kester, D. R., The distribution of total and electrochemically available copper in the northwestern Atlantic Ocean, *Mar. Chem.*, 13, 281, 1983.