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Trace Elements in Estuarine and Coastal Waters - U.S. Studies from 1986-1990

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The use of specialized analytical techniques, field studies, controlled laboratory experiments, and geochemical modeling have allowed U.S. investigators to expand our understanding of trace element cycling in coastal waters and estuaries. Considerable emphasis has been placed on quantifying the flux of trace elements within and through the coastal zone. In addition, substantial progress has been made in identifying the chemical speciation of many trace elements, providing a linkage between the geochemical and biochemical behavior of these elements. Another significant advance has been the use of trace elements as tracers of geochemical processes and water masses in the coastal environment.

INTRODUCTION

Estuaries and coastal waters are sites of biogeochemical processes that modify the fluxes of trace elements between the continents and the open ocean. Thus, it is not surprising that considerable efforts in the U.S. have been devoted to examining trace elements in the coastal environment (i.e., estuaries, embayments, continental shelf). These studies have utilized a variety of specialized analytical techniques, controlled laboratory experiments, and modeling approaches to quantitatively describe the cycling of trace elements such as the transition metals, rare earths, and metalloids. This report will provide an overview of U.S. research since 1986 on trace elements in the coastal environment, with particular emphasis on dissolved elements in the water column; sediments and suspended matter will only be discussed if they relate to elemental fluxes. For the purposes of this review, trace elements will be defined as those having concentrations in the nanomolar to sub-nanomolar range [*Bruland, 1983*]. However, some elements such as iron or manganese have micromolar concentrations in the upper portion of an estuary, but decrease to nanomolar levels before the mouth of the estuary is reached; these elements will also be discussed. To provide a "chemical" orientation to this review, trace elements will be examined according to groups on the Periodic Table (if published results are available).

DISCUSSION

Group IIIa - Al, Ga

Aluminum. In the dissolved state aluminum can be considered a trace element, but particulate aluminum concentrations in coastal waters are in the micromolar range [*Windom and Gross*, 1989]. Within the Geum Estuary, Korea, *Byrd et al.* [1990] found that dissolved aluminum behaves non-conservatively, with apparent inputs in the upper and lower estuary. Since the estuarine profiles of dissolved and particulate aluminum parallel each other, *Byrd et al.* [1990] attributed the inputs to the dissolution of alumino-silicate

phases. These alumino-silicate minerals (e.g., clays) are a major fraction of inorganic particles in coastal waters and account for the high particulate aluminum concentrations. *Windom and Gross* [1989] exploited this feature in order to use aluminum as a tracer of inorganic particles on the continental shelf off the southeastern U.S. Aluminum may also be scavenged onto biogenic particles, as suggested by the dissolved aluminum profile obtained by *Measures et al.* [1986] on the New England shelf. At this site dissolved aluminum concentrations range from 12 to 34 nmol/L.

Gallium. *Shiller* [1988] reported a value of 11 pmol/L for "dissolvable" gallium in the shelf waters off New England and in waters near the California coast. By comparing these concentrations to those of aluminum and to the Ga/Al ratios in crustal rocks, *Shiller* [1988] found gallium to be enriched. He postulated that this enrichment is due to the preferential dissolution of solid phase gallium and the higher reactivity of aluminum in seawater.

Group IVa - Ge, Sn, Pb

Germanium. Until the discovery of organic germanium compounds (i.e., monomethylgermanium, MMGe; dimethylgermanium, DMGe), the cycling of germanium in the coastal environment was largely thought to parallel that of silicon [*Froelich et al., 1985*]. These methylated germanium compounds are at picomolar concentrations and display conservative behavior in the water column [*Lewis et al., 1985*]; as a consequence, their sources and sinks are difficult to identify. Using a variety of coastal regimes *Lewis et al.* [1989] further examined methylgermanium cycling. In Skan Bay (Alaska), which is seasonally anoxic, MMGe and DMGe show conservative behavior, but in the permanently anoxic Framvaren Fjord (Norway), removal below the oxic/anoxic interface is apparent. Along with similar data from the Black Sea, *Lewis et al.* [1989] suggested that methylgermanium compounds may be consumed in anoxic environments, presumably by demethylation.

Tin. The use of clean sampling techniques and determinations employing selective hydride generation/atomic absorption methods have allowed the geochemistry of tin to be examined in coastal waters. Concerns over the toxicity of tin compounds, particularly tributyltin used in antifouling paints, has heightened interest in this element. In their stud-

ies of estuaries in the U.S., England, and Spain, *Byrd and Andreae* [1986a] reported concentrations ranging from 1 to 15 pmol/L and found that removal processes have little effect on dissolved, inorganic tin (i.e., dissolved tin behaves conservatively). In addition, the transport of tin to the coastal ocean is dominated by particulate fluxes. In polluted estuaries *Byrd and Andreae* [1986a] found concentrations of inorganic tin up to 60 pmol/L, and also detected monobutyltin, a degradation product of tributyltin. In coastal waters off the eastern U.S. dissolved tin concentrations are approximately 5 pmol/L [*Byrd and Andreae*, 1986b], in agreement with the apparent seawater end-member predicted from their estuarine profiles.

Lead. The anthropogenic mobilization of lead and its potential toxicity have created considerable interest in this element. In a Texas estuary, *Keeney-Kennicutt and Presley* [1986] found that dissolved lead has mid-estuarine maxima (up to 900 pmol/L), which they attributed to inputs from sediments. However, most of the lead in this estuary is bound in suspended particles. Dissolved lead in the Geum Estuary (Korea) also displays input, although the maximum (ca. 160 pmol/L) is at a lower salinity [*Byrd et al.*, 1990]. In a small estuary near Seattle, Washington (Elliott Bay), dissolved lead (ca. 200 pmol/L) displays conservative behavior, and particulate lead represents the largest fraction of the total [*Paulson et al.*, 1989]. In contrast to the North American estuaries, *Windom et al.* [1988] found lower concentrations (25-300 pmol/L) and apparent removal of dissolved lead in a tropical estuary in Thailand. They ascribed this removal to particulate scavenging.

Group Va - As

Like the other metalloid elements (e.g., Sb, Se), dissolved arsenic is found in a variety of chemical forms, primarily arsenite [As(III)], arsenate [As(V)], and the methylated arsenicals (monomethylarsonate and dimethylarsinate). *Andreae and Andreae* [1989] examined the behavior of dissolved arsenic in the Schelde Estuary, situated in a highly industrialized region of Belgium. Estuarine profiles of arsenic show concentrations ranging from 28 to 60 nmol/L and suggest input in the low salinity region of the estuary. However, using a numerical model with varying river end-member composition and discharge rate, the observed arsenic distributions can be explained by mixing processes alone (i.e., conservative behavior). The primary form of arsenic in the estuary is arsenate, but in some of the Schelde's tributaries where anoxic conditions exist, the As(III)/As(V) ratios are elevated.

Byrd [1988] examined the seasonal behavior of arsenic in waters of the continental shelf off the southeastern U.S. and in several adjacent estuaries. In the winter and spring, sediment resuspension and planktonic uptake in shelf waters appear to lower the concentrations of inorganic arsenic (2-8 nmol/L), but in the fall, regeneration from the sediments substantially elevates the arsenic concentrations (15-30 nmol/L). During all periods the methylated arsenicals are less than 10% of the inorganic concentrations. In the adjacent estuaries, arsenic behaves conservatively (concentrations of total dissolved arsenic from 2-30 nmol/L), with the only seasonal variations largely due to the varying seawater end-member (i.e., shelf waters).

Group VIa - Se

Dissolved selenium can exist as selenate [Se(VI)], selenite [Se(IV)] and organic selenides [Se(-II)] such as seleno-amino acids. The estuarine geochemistry of selenium was examined by *Cutter* [1989] in the North and South San Francisco Bay during periods of high and low river discharge. In the South Bay dissolved selenium shows conservative behavior (1.0-4.0 nmol/L for total selenium), and the primary input appears to be effluents from sewage treatment plants. In the northern Bay, dissolved selenium shows input and removal depending on the chemical form and river discharge rate; generally selenate is the predominant form of dissolved selenium (total dissolved concentration of 0.5-4.0 nmol/L), with particulate selenium never more than 10% of the total. Monitoring of the river end-members reveals that their variability can not account for selenium's apparent non-conservative behavior. However, the selenium concentration (up to 1900 nmol/L) and chemical form (>80% selenite) in effluents from oil refineries that discharge into northern San Francisco Bay suggest that these sources can account for the input of selenium to the estuary. Selenium fluxes from rivers, refineries, and sewage treatment plants to the San Francisco Bay were examined by *Cutter and San Diego-McGlone* [1990]. These investigators showed that the riverine selenium flux varies considerably with time, but fluxes from industrial and municipal sources are relatively constant. Overall, the anthropogenic sources account for 52-90% of the total selenium input to San Francisco Bay.

Group VIIa - I

The geochemistry of iodine was examined in the Chesapeake Bay by *Luther and Cole* [1988]. The profile of total iodine shows conservative behavior throughout the estuary (50-400 nmol/L). Iodate is only detectable in the lower estuary (salinity >20°/oo), with the presumed source being coastal waters. The primary iodate sinks were postulated to be reduction to iodide in the anoxic bottom waters of the estuary, and uptake by phytoplankton. Most of the dissolved iodine in the Chesapeake Bay is present as iodide. *Luther and Cole* [1988] suggested that biotic production in surface waters and iodate reduction in anoxic bottom waters are the sources of this reduced iodine. *Ullman et al.* [1988] also examined iodine in several estuaries in the eastern U.S. In this study, iodine was found to display some non-conservative behavior, and the authors used organic matter remineralization (sediment and water column), anthropogenic inputs, sediment resuspension, and physical processes (estuarine mixing) to explain the behavior and speciation of iodine.

Group IIb - Zn, Cd, Hg

Zinc. The behavior of zinc has been examined in a number of estuaries and coastal environments. Plots of dissolved zinc (15-230 nmol/L) versus salinity in the Delaware Bay [*Church*, 1986] indicate some non-conservative behavior, and laboratory mixing studies (i.e., similar to those described by *Sholkovitz* [1976]) demonstrate desorption from particles at low salinity (<5°/oo). In the South San Francisco Bay [*Kuwabara et al.*, 1989] and Elliott Bay near Seattle [*Paulson et al.*, 1989], zinc shows conservative mixing behavior (Elliott Bay, 15-45 nmol/L; S.F. Bay, 20-100 nmol/L). These

North American results contrast sharply with those of the Bang Pakong Estuary (Thailand), where zinc concentrations (2-10 nmol/L) displayed pronounced mid- estuarine maxima [*Windom et al.,* 1988]. The co-occurrence of nutrient maxima with zinc suggests that this element is being regenerated from organic matter. In the Geum Estuary (Korea) *Byrd et al.* [1990] found both low salinity removal and mid-estuarine input for dissolved zinc. These workers attributed the removal to particle scavenging and the input to sedimentary fluxes.

In the western Mediterranean Sea, *Sherrell and Boyle* [1988] found concentrations of dissolved zinc (0.5-4.5 nmol/L) that are elevated relative to those in the open Atlantic Ocean. They speculated that this enrichment occurs as surface water travels through coastal regions outside the Strait of Gibraltar. Using data obtained on the Spanish shelf and a four end-member mixing model, *van Geen et al.* [1988] confirmed that the shelf region is the most likely source of excess zinc to the Mediterranean.

Cadmium. The estuarine behavior of cadmium has been examined in the Delaware Bay [*Church,* 1986], where removal is apparent, particularly in the low salinity portion of the estuary (dissolved concentrations of 0.4-3.0 nmol/L). This removal parallels that of phosphate, and the observed cadmium/phosphate ratio is very similar to those found in the open ocean. Although no nutrient data were presented, dissolved cadmium (1.2-4.7 nmol/L) also displays non-conservative behavior (removal) in the South San Francisco Bay [*Kuwabara et al.,* 1989]. Like the observations in the Delaware Bay, *Windom et al.* [1988] found dissolved cadmium distributions (20-150 pmol/L) in the Bang Pakong Estuary are similar to those of phosphate and nitrate. Perhaps the most atypical behavior for cadmium was found in Korea's Geum Estuary [*Byrd et al.,* 1990]. In this system a maximum in dissolved cadmium (150 pmol/L) is found near the mouth of the estuary. *Byrd et al.* [1990] speculated that sediment fluxes can account for the input, but phosphate data that would enable comparisons with the other estuarine studies are not given. Dissolved cadmium concentrations were also determined in the western Mediterranean and Spanish shelf by *van Geen et al.* [1988]. Highest concentrations (up to 0.7 nmol/L) are found near the Spanish coast, and these waters may strongly influence cadmium concentrations in the Mediterranean.

Mercury. Few quality data are available for mercury in the coastal environment, in part because of its ultratrace concentrations (picomolar) and resultant contamination problems. In the Gulf of Maine, *Gill and Fitzgerald* [1988] found total (unfiltered) mercury concentrations ranging from 1.6 to 7.6 pmol/L, while a vertical profile from the Peru shelf shows a concentration of 0.5 pmol/L at the surface and 2.6 pmol/L at 195 m (bottom depth of 215 m). Due to the high reactivity of mercury in seawater, these investigators hypothesized that the behavior of mercury is primarily controlled by the strength of its sources, atmospheric input and fluxes from coastal sediments.

Transition Metals - V, Cr, Mn, Fe, Co, Ni, Cu

Because of their diverse chemical properties (i.e., multiple oxidation states), participation in major geochemical cycles (i.e., redox processes), biochemical importance as micronutrients and potential role as anthropogenic contaminants in the marine environment, the transition metals continue to receive considerable attention by U.S. scientists.

Vanadium. Shiller and Boyle [1987] examined the biogeochemistry of vanadium in three estuarine systems (Amazon, Connecticut, and Mississippi Rivers). Vanadium-salinity plots show conservative behavior in the Connecticut (8-22 nmol/L), non-conservative behavior in the Mississippi (2-40 nmol/L), and a mixture of behaviors depending on the season in the Amazon (8-35 nmol/L). Results from laboratory mixing experiments using filtered and unfiltered Mississippi waters from the riverine and marine end-members do not display input or removal of dissolved vanadium, eliminating abiotic flocculation or adsorption as important processes affecting vanadium distributions. However in the Mississippi, vanadium concentrations followed those of phosphate, indicating that biotic processes such as uptake and remineralization affect vanadium. Similarly, *Sherrell and Boyle* [1988] invoked biotic removal to explain the apparent depletion of vanadium in the western Mediterranean (25-30 nmol/L) relative to waters near the Strait of Gibraltar (35 nmol/L).

Chromium. Sherrell and Boyle [1988] determined chromium concentrations in the western Mediterranean (3.4-5.0 nmol/L) and in coastal waters outside the Strait of Gibraltar (3.0 nmol/L). They found that some chromium input occurs during water transport from the eastern Atlantic to the Mediterranean. Although the source remains unidentified, it appears to be within the western Mediterranean rather than outside the Strait (as observed with zinc).

Manganese. A substantial number of U.S. investigators have examined manganese cycling in estuarine and coastal environments. The aqueous species of manganese are the soluble ions of Mn(II) and insoluble manganese oxides (e.g., MnO_2). *Tebo and Emerson* [1986] examined the bacterially catalyzed oxidation of Mn(II) above the oxic/anoxic interface of the Saanich Inlet. While the abiotic oxidation rate is slow (residence time of months to years), this study demonstrates that biotic catalysis reduces the residence time of Mn(II) to approximately one day. *Sunda and Huntsman* [1987] examined whether bacterially-mediated oxidation can affect manganese cycling in an oxic estuary. These workers found oxidation rates equivalent to those in the Saanich Inlet and suggested that the estuarine removal of manganese can be controlled by bacterial oxidation, rather than by abiotic scavenging to particles.

In the Delaware Bay, *Church* [1986] reported that the behavior of dissolved manganese (3,500-90 nmol/L) varies seasonally, with minor input during the winter and removal dominating the summer profiles. Dissolved manganese removal was generically ascribed to "flocculation processes," but considering the later studies of *Sunda and Huntsman* [1987], this presumed removal process may be mechanistically incorrect. Manganese behavior in the Geum Estuary (Korea) is dominated by removal at low salinities (140 to 20 nmol/L), although some sediment input was suggested by *Byrd et al.* [1990]. In the small Yaquina Estuary in Oregon [*Callaway et al.,* 1988], manganese is released from particles in the upper estuary, leading to dissolved maxima (up to 1,200 nmol/L). However, *Callaway et al.* [1988] noted that this input is a function of the estuarine residence time, a factor that is also used to explain the conservative behavior of manganese in Elliott Bay in the northwestern U.S. [*Paulson et al.,* 1989].

In the southern U.S., *Keeney-Kennicutt and Presley* [1986] found mid-estuarine maxima for manganese in the Brazos River system (200-300 nmol/L). They attributed this input to manganese diffusion from the underlying, anoxic sediments. When a portion of the water column in an estuary is anoxic, the effects on manganese are dramatic. *Gavis and Grant* [1986] showed that concentrations of dissolved manganese in anoxic portions of the mid-Chesapeake Bay approach 10,000 nmol/L, and attributed this to the reductive dissolution of manganese oxides. Finally, in the tropical Bang Pakong Estuary, *Windom et al.* [1988] found manganese removal in the upper estuary, and some input from suspended particles and sediments in the lower estuary. The actual magnitudes of these input and removal processes are modified by the river discharge (i.e., fresh water residence time).

Manganese has also been examined on the continental shelf of the Bering Sea [*Heggie et al.,* 1987]. Dissolved concentrations range from 2 to 30 nmol/L, with the highest values found just above the bottom (50 to 200 m). In combination with pore water data, *Heggie et al.* [1987] quantitatively showed that the source of this near-bottom manganese is flux from the underlying sediments. Furthermore, the shelf sediments can act as a manganese source to deep waters of the ocean.

Iron. Like manganese, iron has also received considerable attention in recent years. In anoxic waters dissolved Fe(II) is the stable species of iron, but in oxygenated waters Fe(II) is oxidized to colloidal Fe(III) oxides. These colloids can pass through many filters and thus appear to be "dissolved." *Church* [1986] reported that manganese and iron profiles for the Delaware Bay are quite similar, with iron removal via colloid flocculation occurring in the upper estuary. Colloid flocculation also removes phosphate, as shown by the strong positive correlation between concentrations of dissolved iron (30-400 nmol/L) and phosphate (0.5-3.0 μmol/L). The net effect of this removal process can be modified by the estuarine residence time. As an example, iron behaves conservatively in Elliott Bay [*Paulson et al.,* 1989], which at the time of sampling had a residence time on the order of 24 hours. In the Brazos River Estuary, iron input is minor in comparison to that for manganese [*Keeney-Kennicutt and Presley,* 1986], while in the Bang Pakong Estuary [*Windom et al.,* 1988], iron is efficiently removed in the low salinity portion of this system (from 400 nmol/L to 20 nmol/L).

In the *Windom et al.* [1988] study, the simple salinity-driven flocculation mechanism is questioned since a corresponding pH gradient also exists in the estuary. In this case, it is argued that the solubility of Fe(OH)$_3$ is responding to the ambient pH, and as the pH increases with salinity, iron is precipitated. *Byrd et al.* [1990] also examined the pH effect on iron removal, but concluded that colloid flocculation largely removes iron in the Geum Estuary. A few coastal iron data were obtained by *Sherrell and Boyle* [1988] for the western Mediterranean. Since the samples were not filtered, particulate "contamination" was likely, but the iron concentrations range from 5 to 50 nmol/L. *Sherrell and Boyle* [1988] speculated that eolian input is the likely source of iron in this region.

Iron has also been examined in a number of anoxic coastal environments. In the mid-Chesapeake Bay, anoxic conditions develop in the summer, and dissolved iron(II) concentrations up to 5000 nmol/L can be found in bottom waters [*Gavis and Grant,* 1986]. Presumably such high concentrations can increase iron fluxes out of this portion of the estuary. Iron cycling was also examined in the anoxic Framvaren Fjord (Norway) by *Landing and Westerlund* [1988]. Within the oxic portion of the fjord, dissolved Fe(II) concentrations are approximately 20 nmol/L, and rise just below the oxic/anoxic interface to a maximum of 890 nmol/L. In the deepest samples (170 m), Fe(II) concentrations drop to 26 nmol/L. Using thermodynamic calculations, *Landing and Westerlund* [1988] proposed that dissolved Fe(II) in the anoxic zone is controlled by the solubility of the iron-sulfide minerals mackinawite (FeS) and greigite (Fe$_3$S$_4$).

Cobalt. The estuarine biogeochemistry of cobalt has been examined in the Delaware Bay by *Church* [1986], in the Bang Pakong Estuary by *Windom et al.* [1988], and in the Geum Estuary by *Byrd et al.* [1990]. In the Delaware Bay, the distribution of dissolved cobalt (14-1.7 nmol/L) is very much like those of manganese and iron, with removal in the low salinity ($<10\%_{oo}$) region. In contrast, the distribution of cobalt in the Bang Pakong [*Windom et al.,* 1988] parallels those of the nutrients, with mid-estuarine maxima (up to 0.8 nmol/L) characteristic of organic matter regeneration. This input occurs at both high and low river discharge periods, so the process of regeneration must be rapid relative to the mixing time (i.e., the behavior of cobalt does not become conservative as the residence time decreases). In the Geum Estuary cobalt displays a mixture of behaviors, with low salinity removal and mid-estuarine input [*Byrd et al.,* 1990]. Cobalt input in this estuary may be due to sediment fluxes or anthropogenic sources (a smelter is near the region of apparent input).

Nickel. Studies examining the estuarine behavior of nickel have also been conducted in the Delaware Bay, Geum Estuary, and Bang Pakong Estuary. *Church* [1986] found that nickel has nearly conservative behavior in the Delaware Bay (85-17 nmol/L), with some minor input in the upper estuary during the winter. Similarly, *Windom et al.* [1988] showed that nickel mixes conservatively in the Bang Pakong (18-5.0 nmol/L). In contrast, *Byrd et al.* [1990] found that the behavior of dissolved nickel is dominated by mid-estuarine input (from 5 to 13 nmol/L). These workers speculated that nickel is introduced via sediment fluxes or anthropogenic contamination (like cobalt).

Copper. Along with manganese and iron, copper has been extensively studied by U.S. scientists in recent years. Some of this attention may be due to the element's participation in biochemical reactions, and because of its role as both a nutrient and a toxic substance to organisms. In addition, copper can be complexed by organic ligands, thus affecting its bioavailability and geochemistry. Studies in the western U.S. found that copper generally behaves conservatively in the South San Francisco Bay [*Kuwabara et al.,* 1989] and Elliott Bay [*Paulson et al.,* 1989]. Using thermodynamic calculations in conjunction with data for copper and DOC, *Kuwabara et al.* [1989] estimated that most of the dissolved copper in the South San Francisco Bay (24-66 nmol/L) is complexed with organic ligands. In the Brazos River Estuary (Texas), copper shows input within the estuary (concentrations of 10-40 nmol/L), but end-member mixing experiments could not duplicate this feature [*Keeney-Kennicutt and Presley,* 1986]; the input of copper is thus presumed to be from sediment fluxes. Unlike the work of *Kuwabara et al.* [1989], *Keeney-Kennicutt and Presley* [1986] calculated that

copper speciation is dominated by carbonate complexes in this estuary. These calculations are probably in error since organic complexation was overlooked (see below). Data for copper in the Delaware Bay [*Church*, 1986] and Bang Pakong Estuary in Thailand [*Windom et al.*, 1988] indicate nearly conservative behavior for copper during estuarine mixing (15-50 nmol/L in the Delaware; 5-25 nmol/L in the Bang Pakong). In contrast, *Byrd et al.* [1990] found copper input in the Geum Estuary (10-30 nmol/L) and attributed it to sedimentary fluxes.

Copper biogeochemistry has also been examined in other coastal waters, including the western Mediterranean and the continental shelf of the eastern Bering Sea. In the Mediterranean, *van Geen et al.* [1988] found copper concentrations ranging up to 40 nmol/L. As these values are significantly above those in the eastern Atlantic, *van Geen et al.* [1988] proposed that waters entering the Mediterranean through the Strait of Gibraltar entrain high-copper waters from the coast near Spain. In the eastern Bering Sea [*Heggie et al.*, 1987], dissolved copper concentrations increase as one moves up the shelf (from 2.0 to 6.0 nmol/L). Porewater data indicate that shelf sediments are a likely source for the higher copper concentrations. The higher concentrations on the shelf can also act as a source of copper to the deep sea.

Since the complexation of copper has important ramifications to its biogeochemical cycle, several U.S. investigators have examined this topic in the coastal environment. A variety of analytical techniques have been used to quantify copper complexation by organic ligands, including C_{18} reverse phase liquid chromatography [*Mills et al.*, 1987], the ligand competition method [*Sunda and Huntsman*, 1987], bacterial bioassay [*Hering et al.*, 1987], ligand exchange/solvent extraction [*Moffett and Zika*, 1987a], and fixed-potential amperometry [*Hering et al.*, 1987]. As will be seen below, all of the methods except the C_{18} technique indicate that >95% of the dissolved copper in coastal waters is complexed by organic ligands. *Donat et al.* [1986] examined the performance of C_{18} columns for isolating copper-organic complexes, and found that the recoveries vary with the type of organic ligands. Thus, the C_{18} method likely underestimates the amount of organically complexed copper. Nevertheless, *Mills et al.* [1989] used C_{18} reverse-phase liquid chromatography to examine organic copper complexes in an anoxic basin of the Pettaquamscutt Estuary. Their results show that total dissolved copper ranges from 8 nmol/L in the oxic water column to 2 nmol/L in the anoxic zone. Organic copper is 42-60% of the total in oxic waters and less than 1% of the total in the deepest samples from the anoxic zone. *Mills et al.* [1989] concluded that the organic copper complexes are replaced by sulfide complexes in the anoxic water column. However, potential analytical artifacts suggest that their estimates of organic copper concentrations are lower limits.

Using a ligand competition method, *Sunda and Hanson* [1987] determined copper complexation in Narragansett Bay (Rhode Island) and in the coastal waters of Peru. In these waters, total copper ranges from 3.7 to 27 nmol/L, but 98 to 99.97% of the total is complexed by organic ligands. *Moffett and Zika* [1987a] also examined copper complexation in Biscayne Bay and at two stations off the Florida coast. Interestingly, greater than 99% of the total copper is organically complexed, but depth profiles at the coastal stations show a minimum in complexation at the surface (maximum free

copper) and an increase in copper complexation with depth. *Moffett and Zika* [1987b] experimentally demonstrated that this behavior can be due to the photolytic degradation of copper-ligand complexes.

Rare Earth Elements

The aquatic chemistries of the rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu) show trends consistent with periodic properties, and these elements are affected by adsorption/desorption, complexation, and oxidation-reduction reactions (Ce only). *Sholkovitz and Elderfield* [1988] presented a detailed examination of rare earth cycling in the Chesapeake Bay. Concentrations of the dissolved rare earths are in the picomolar range, and all show removal in the low salinity region (<10‰). However, this low salinity removal is more rapid for the light rare earths (La to Gd) compared to the heavy rare earths (Dy to Lu). Similar behavior during estuarine mixing was found in the Great Whale River estuary (Quebec) by *Goldstein and Jacobsen* [1988]. These investigators attributed the removal of dissolved rare earths to a pH-controlled adsorption to suspended particles.

In addition to surface waters, *Sholkovitz and Elderfield* [1988] examined rare earth elements in the low oxygen bottom waters of the Chesapeake Bay. Under oxygen-depleted conditions, concentrations of the light rare earths are 2-9 times higher than those in the upper, oxygenated water column; the heavy rare earths do not display this enrichment. Moreover, the concentrations of all rare earths in the sediment porewaters are substantially above those in the overlying water column (i.e., net flux into the water column). To explain the differential behavior of light and heavy rare earths, *Sholkovitz and Elderfield* [1988] suggested that light rare earths are selectively scavenged by iron and manganese oxides. This results in the rapid removal of light rare earths in the upper estuary and enrichment in the low oxygen waters where oxide dissolution occurs. Rare earth elements were studied by *Elderfield et al.* [1990] in three other North American estuaries, the Connecticut, Delaware, and Mullica, as well the the Tamar in the United Kingdom. All show low salinity removal, with the light rare earths generally removed to a greater extent than the heavy rare earths. Concentrations of rare earths in the coastal waters outside these estuaries are a factor of 2-3 higher than typical open ocean values. Additionally, the shale-normalized patterns for the rare earths are intermediate between those of the rivers and oceanic surface waters [*Elderfield et al.*, 1990].

Rare earth concentrations were also determined in Buzzards Bay (Massachusetts) by *Sholkovitz et al.* [1989]. Water column concentrations are a factor of 2-5 higher than those found in the open North Atlantic, but the shale-normalized pattern for the rare earths at this coastal site were identical to those in the ocean. Pore water analyses indicate that diffusion from the sediments is a likely source for higher rare earth concentrations in the water column. However, by examining the shale-normalized patterns in the water column and pore waters, the preferential input of light rare earths is apparent.

Finally, the oxidation of Ce(III) to Ce(IV) was studied by *Moffett* [1990]. The negative cerium anomaly seen in shale-normalized patterns of dissolved rare earths in the ocean is typically attributed to the oxidation of soluble Ce(III) to insoluble Ce(IV). Using radiotracer and poison additions to

Element	Estuarine Concentration	Behavior	Coastal Concentration
Al	1.8-3.5 nmol/L	NC	12-34 nmol/L
As	2.0-65 nmol/L	C	0.5-15 nmol/L
Cd	0.02-0.85 nmol/L	NC	0.05-0.7 nmol/L
Ce	10-103 pmol/L	NC	82-106 pmol/L
Co	0.2-10 nmol/L	NC	
Cr			3.4-5.0 nmol/L
Cu	5.0-60 nmol/L	C&NC	2.0-40 nmol/L
Dy	6.1-33 pmol/L	NC	11-15 pmol/L
Er	6.1-24 pmol/L	NC	8.7-11 pmol/L
Eu	0.8-5.3 pmol/L	NC	1.7-2.6 pmol/L
Fe	0.5-5000 nmol/L	NC	5.0-50 nmol/L
Ga			11 pmol/L
Gd	5.3-38 pmol/L	NC	8.0-15 pmol/L
Ge (inorg.)			13-3900 pmol/L
Ge (MMGe)			86-310 pmol/L
Ge (DMGe)			45-114 pmol/L
Hg			0.5-7.6 pmol/L
I	20-500 nmol/L	C&NC	
La	6-68 pmol/L	NC	49-74 pmol/L
Lu	1.3-6.9 pmol/L	NC	1.4-1.7 pmol/L
Mn	5.0-10,000 nmol/L	NC	2.0-30 nmol/L
Nd	13-87 pmol/L	NC	45-77 pmol/L
Ni	5-85 nmol/L	C	
Pb	20-900 pmol/L	C&NC	
Se	0.6-4.5 nmol/L	C&NC	
Sm	3.0-21 pmol/L	NC	7.4-12 pmol/L
Sn	2.0-60 pmol/L	C	5 pmol/L
V	1.0-38 nmol/L	C&NC	32 nmol/L
Yb	1.5-30 pmol/L	NC	8.7-11 pmol/L
Zn	12-180 nmol/L	NC	0.5-4.5 nmol/L

C - Conservative mixing behavior
NC - Non-conservative mixing behavior
Blank entries indicate no data were published by
    U.S. scientists between 1986-1990

TABLE 1. Trace Elements in Estuaries and Coastal Waters -
U.S. Results from 1986-1990

water samples, *Moffett* [1990] demonstrated that the oxidation of Ce(III), like Mn(II), is bacterially catalyzed. However, he also showed that Ce(III) can be rapidly removed by adsorption to particle surfaces. Thus in low particle environments such as the open ocean, Ce(III) oxidation can be the dominant removal mechanism. In contrast, cerium removal by adsorption can predominate in high particle environments such as estuaries.

SUMMARY

Efforts on the part of U.S. scientists continue to broaden our knowledge of trace element cycling in the coastal environment. Not only have these studies examined the basic biogeochemical properties of the elements, but they have also begun to use trace elements as process or water mass tracers. As a summary, the concentration ranges for estuaries and near-shore waters (i.e., continental shelf) have been compiled in Table 1.

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