TRANSITION METALS AND HEAVY METAL SPECIATION

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Introduction

The transition metals and heavy metals (those with atomic weights greater than 20) enter the ocean via river runoff, wind-blown dust, diffusion from sediments, hydrothermal inputs resulting from reactions of sea water with newly formed ocean crust at midocean seafloor spreading centers, and from anthropogenic activities. Some of these metals (e.g., manganese, iron, cobalt, nickel, copper and zinc) are extremely important micronutrients needed by phytoplankton for various metabolic functions. Several trace metals that are nonconservative with short oceanic residence time (e.g., manganese and aluminum, though the latter is not a heavy metal) are valuable as tracers for circulation and mixing in the ocean. Micronutrient metals, as well as metals like mercury, lead, and silver, which have no biochemical role, can be toxic very low concentrations.

Until recently, marine chemists and chemical oceanographers, using sample collection and analytical techniques of the time, could not accurately measure the naturally low concentrations of these metals in unpolluted sea water because of sample contamination problems and lack of instrumental sensitivity. Development of modern techniques for collection, storage, and analysis of uncontaminated samples, plus the development of highly sensitive analytical techniques and instrumentation, have only recently enabled marine trace metal chemists to determine accurate concentrations of these elements in sea water, furthering our understanding of their distributions and chemical behavior in the oceans. These procedural, analytical, and instrumental advancements led to the discoveries that the concentrations of many of these metals were orders of magnitude lower than previously believed, and that the depth distributions ('vertical profiles') of transition and heavy metal concentrations result from biological, physical, and geochemical processes in the oceans.

We now have a basic understanding of the concentrations and distributions of nearly all the naturally occurring elements in sea water. However, it has become increasingly clear that this information alone is insufficient for providing a complete understanding of the biological and geochemical interactions of these metals in the sea. Metals in sea water can exist in different physical forms (dissolved, colloidal, particulate) and chemical forms (ions, inorganic complexes, organic complexes, organometallic compounds) and in different oxidation states (collectively termed 'species') within a given chemical form. Knowing the distribution of a metal's total concentration among these various forms ('speciation') is critically important because the different forms can have very different biological and geochemical behaviors, and thus different fates and transport.

Before considering the speciation of the transition and heavy metals, we first present a brief overview of the concentrations and distributions of these elements.

Overview: Transition Metal and Heavy Metal Concentrations and Distributions

Concentrations of the transition metals and heavy metals vary both horizontally and vertically through the world's oceans. **Table 1** lists the ranges in the oceanic concentrations of the transition metals and heavy metals. For a representation of the North Pacific depth profiles of the elements in the periodic table, including the transition metals and heavy metals (*see* **Elemental Distribution Overview**). The relative rates of supply and removal of the elements determine their horizontal and vertical distributions. These elements are supplied to the oceans primarily by riverine input, atmospheric precipitation, hydrothermal venting, and anthropogenic activities, and they are removed by adsorption onto sinking particles ('scavenging') or by incorporation into sinking biologically produced material by active uptake by phytoplankton. On the basis of their vertical profiles, these elements can be classified into one of the following categories: (1) conservative type, (2) scavenged type, (3) nutrient (recycled) type, and (4) mixed type. **Figure 1** shows the shapes of the vertical profiles for the conservative, scavenged, and nutrient (recycled) categories and lists the elements that display them.

Table 1 Oceanic concentrations of transition metals and heavy metals

Element	*Concentration units*^{a}	*North Pacific*		*North Atlantic*	
		Surface	*Deep*	*Surface*	*Deep*
Sc	pmol l^{-1}	8	18	14	20
Ti	pmol l^{-1}	4–8	200–300	30–60	200
V	nmol l^{-1}	32	36	23	
Cr	nmol l^{-1}	3	5	3.5	4.5
Mn	nmol l^{-1}	0.5–3	0.08–0.5	1–3	0.25–0.5
Fe	nmol l^{-1}	0.02–0.5	0.5–1	1–3	0.25–0.5
Co	pmol l^{-1}	4–50	10–20	18–300	20–30
Ni	nmol l^{-1}	2	11–12	2	6
Cu	nmol l^{-1}	0.5–1.3	4.5	1.0–1.3	2
Zn	nmol l^{-1}	0.1–0.2	8.2	0.1–0.2	1.6
Ga	pmol l^{-1}	12	30	25–30	
Ge	pmol l^{-1}	5	100	1	20
Y	pmol l^{-1}	66–187	306–383		
Zr	pmol l^{-1}	12–95	275–325	100	
Nb	pmol l^{-1}	2.8	3.9		
Mo	nmol l^{-1}	93	105		
Rh	fmol l^{-1}	370	900		
Pd	pmol l^{-1}	0.18	0.66		
Ag	pmol l^{-1}	1–5	23	0.69–4.6	2.7–6.9
Cd	pmol l^{-1}	1–10	1000	1–10	350
In	pmol l^{-1}	0.09–1.8	0.07–0.09	2.7	0.9
Sn	pmol l^{-1}	4		10–20	8
Te	pmol l^{-1}	1.2	1	1–1.5	0.4–1
la	pmol l^{-1}	20	50–70	12–15	80–84
Hf	pmol l^{-1}	0.2–0.4	1–2	0.4	
Ta	pmol l^{-1}	0.09	0.3		
W	pmol l^{-1}	41	51		
Re	pmol l^{-1}	28–82		32–43	
Os	fmol l^{-1}		20	15	17
Ir	fmol l^{-1}	0.5	0.8		
Pt	pmol l^{-1}	0.4	0.3–1.2	0.2–0.4	0.2–0.4
Au	fmol l^{-1}	50–150		50–150	
Hg	pmol l^{-1}	0.5–10	2–10	1–7	1
Tl	pmol l^{-1}	60–80	80	60–70	60
Pb	pmol l^{-1}	14–50	3–6	100–150	20
Bi	pmol l^{-1}	0.2	0.02	0.25	

^{a}1 nmol l^{-1} = 10^{-9} mol l^{-1}; 1 pmol l^{-1} = 10^{-12} mol l^{-1}; 1 fmol l^{-1} = 10^{-15} mol l^{-1}.

Conservative Type

Owing to their low reactivity, conservative type transition metals and heavy metals (V, Mo, W, Re, and Tl) are present in sea water at relatively high concentrations that are in constant proportion to salinity. Conservative metals have long mean oceanic residence times ($\gg 10^5$ y), their distributions are considerably homogeneous throughout the ocean due to the ocean's 1000-year circulation, and their concentrations are controlled by physical processes (e.g., advection and turbulent mixing).

Scavenged Type

Scavenged type transition metals and heavy metals (Mn, Co, Ga, In, Te, Pb, Bi, Ce) typically have strong interactions with particles, short mean oceanic residence times (10^2–10^3 y), and low concentrations. Their removal from sea water is dominated by adsorption onto the surfaces of particles and transport to the sediment via interactions with large, rapidly settling particles. Their depth profiles typically show enrichment in surface waters owing to sources from rivers and atmospheric dust, and rapid depletion to low concentrations at depth.

Nutrient (Recycled) Type

Metals having nutrient type distributions (Fe, Ni, Zn, Ge, Se, Y, Ag, Cd, Ba, La) are characterized by surface water depletion and enrichment at depth. Surface depletion is caused by biological uptake, and enrichment at depth is due to regeneration of the elements from particles back into solution by

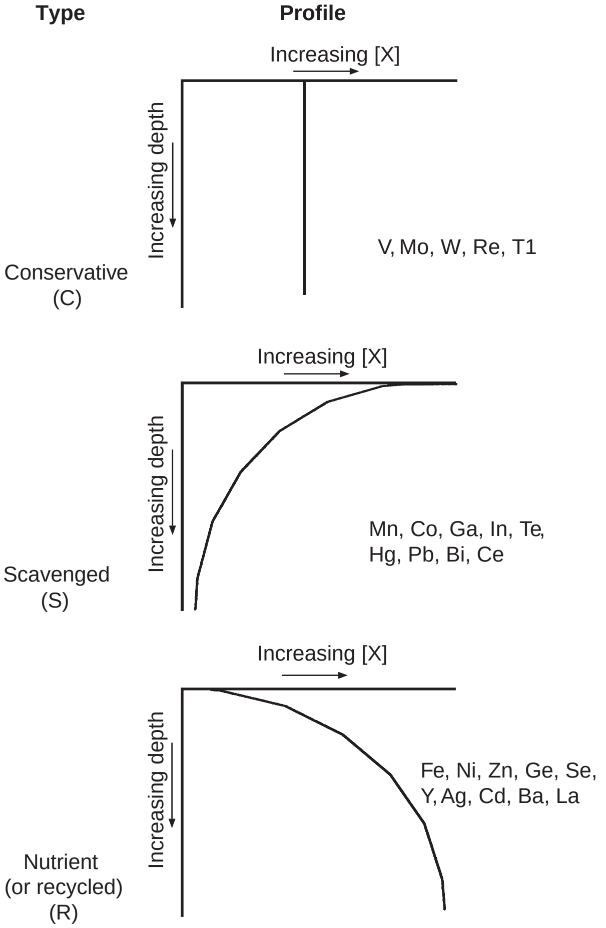

Figure 1 Oceanic profile classifications.

bacterial oxidation of the biological particulate matter. Deep waters of the North Pacific and Indian Ocean typically have higher concentrations of these elements than North Atlantic deep waters owing to biogeochemical cycles and ocean circulation.

Mixed Type

Some transition metals and heavy metals, such as Cu, Fe, Ga, Zr, Ti, La and other rare earths, have distributions that are influenced by both recycling and scavenging processes. For example, copper displays the characteristic surface depletion and deep-sea enrichment of the recycled element type; however, its concentration increases only gradually (almost linearly) with depth, indicating the effects of scavenging.

Modern Advances

Development of new analytical techniques, especially those that can be used at sea aboard ship, have enabled oceanographers to make large numbers of measurements of the concentration of a few transition metals across some ocean basins to construct two- and three-dimensional horizontal profiles, instead of just presenting an element's vertical profile. For example, two-dimensional ocean basin-scale distribution maps have been produced for aluminum and iron. These two-dimensional distribution maps can help identify the input and distribution mechanisms of an element and can be useful as tracers of water mass movements.

Although such detailed information has been obtained for a few transition metals and heavy metals, initial measurements of the oceanic concentrations and distributions need to be made for elements such as Ti, Ga, Ru, Pd, Ir, Pt, Au, Re Te, Zr, and Hf in many ocean basins before simple vertical and horizontal profiles can be constructed. Using newly developed analytical techniques, researchers have begun to obtain initial data on these metals. For example, the first concentration data on iridium in sea water (North Pacific) have been reported. Iridium concentrations ranged from $0.5 \times 10^{-15}\,\mathrm{mol\,l^{-1}}$ in North Pacific surface waters and increased with depth to a maximum of $0.8 \times 10^{-15}\,\mathrm{mol\,l^{-1}}$ near the bottom.

Speciation

Introduction

Knowing the oceanic concentrations and distributions is only part of the picture in understanding the biological and geochemical interactions of transition metals and heavy metals. Dissolved metals can exist in different oxidation states and chemical forms ('species'). These forms include free solvated ions, organometallic compounds, organic complexes (e.g., metals bound to proteins or humic substances), and inorganic complexes (e.g., metals bound to Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, etc.). Knowledge of the concentrations of these various species of a transition metal or a heavy metal, in conjunction with its distribution and concentration, is critical to understanding how the various chemical species interact biologically and geochemically. For example, the nutrient availability and toxicity of several transition metals have been found to be proportional to the concentrations of their free metal ions and not their total concentrations. Complexation of a metal by an organic ligand will decrease the concentration of the free ion form of the metal, thereby decreasing its toxicity or bioavailability. Organic complexation may also decrease or increase adsorption of metals onto metal oxide particles. These examples illustrate the importance of speciation information for fully understanding a metal's oceanic biogeochemical cycle.

Inorganic Speciation

Inorganic forms of the transition metals and heavy metals in sea water include hydrated metal ions, complexes with inorganic ligands, and species with different oxidation states. Transition metals and heavy metals with different oxidation states can exist in sea water when the potential required to change valence states falls within the range of the sea water's oxidizing/reducing potentials. Examples of transition metals and heavy metals having multiple oxidation states in sea water include Fe(II)/Fe(III), Mn(II)/Mn(IV), Cr(III)/Cr(VI), and Cu(I)/Cu(II). In oxygenated sea water, the thermodynamically stable form is usually the higher of the two oxidation states. However, species whose existence is thermodynamically unfavorable (i.e., usually the lower oxidation states) can be produced biochemically (e.g., by photosynthesis) and/or chemically (e.g., by photochemistry), as a result of the input of solar energy.

Calculational estimates of the inorganic speciation of many of the transition metals and heavy metals in sea water have been given in two landmark papers by Turner *et al.* and Byrne *et al.* (see Further Reading). The extent to which a metal is complexed by inorganic ligands is expressed by the inorganic side-reaction coefficient, α. This, in turn, is calculated from eqn [1] where β is the overall conditional stability constant for the inorganic complex MX_i of the transition or heavy metal M with the inorganic ligand X_i, and $[X_i']$ is the concentration of uncomplexed X_i.

$$\alpha = 1 + \sum_i \beta_{MX_i}[X_i'] \qquad [1]$$

The inorganic side-reaction coefficient, α, is also equal to the ratio of the sum of the concentrations of all inorganic species of the metal M ([M′]) to the concentration of its free hydrated cation M $[M^{n+}]$ (eqn [2]).

$$\alpha = \frac{[M']}{[M^{n+}]} \qquad [2]$$

For zinc and the first transition series metals manganese, iron, cobalt, and nickel, the free hydrated divalent cation form dominates the dissolved inorganic speciation. The trivalent metal cations Al^{3+}, Ga^{3+}, Tl^{3+}, Fe^{3+}, and Bi^{3+} are strongly hydrolyzed (i.e., they form strong complexes with OH^-). With respect to complexation by OH^-, the inorganic side-reaction coefficients of the strongly hydrolyzed metals range from $10^{5.76}$ for Al^{3+} to $10^{20.4}$ for Tl^{3+}, and their inorganic speciation is strongly influenced by pH and temperature. For example, at a pH of 7.6, α for Al^{3+} increases 300-fold as the temperature is increased from 5 to 25°C; and at a temperature of 5°C, α for Al^{3+} increases 4000-fold as the pH increases from 7.6 to 8.2 (**Table 2**).

Table 2 Influence of pH and temperature on the α of Al^{3+}

pH	*Temperature (°C)*	*α*
7.6	5	$10^{5.76}$
7.6	25	$10^{7.23}$
8.2	5	$10^{9.39}$

Source: Byrne *et al.* (1988).

Other important inorganic species are the chloride and carbonate complexes. Chloride complexes are important in the inorganic speciation of Ag^+, Cd^{2+}, and Hg^{2+}. Unlike the strongly hydrolyzed metals, chloride dominated metals are 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 is $10^{15.10}$ at 5°C. Carbonate complexes dominate the inorganic speciation of the lanthanides and some actinides (e.g., U(VI) and La(III)). These carbonate complexes are considerably influenced by temperature and pH, although less than the strongly hydrolyzed metal cations.

Organic Speciation

Organic forms of the transition metals and heavy metals in sea water include complexes with organic ligands (e.g., metals bound to proteins or humic substances) and organometallic compounds in which the metal is covalently bound to carbon (e.g., methyl forms of As, Ge, Hg, Sb, Se, Sn, and Te; ethyl-Pb forms; butyl-Sn forms). A most interesting discovery is that 90% of the germanium in open-ocean sea water exists in methylated forms so stable to degradation that they have been called the 'Teflon of the sea.' Methyl forms of metals are generally highly toxic because these compounds are soluble in cell walls and accumulate in cells. This accumulation is one example of how a nonessential metal can become biologically available.

The organically complexed fraction of certain transition metals and heavy metals in sea water has been reliably estimated only relatively recently, and attempts have been made to characterize the nature of these complexes. Early studies of metal complexation showed little agreement between values for ligand concentrations, conditional stability constants, and the extent to which copper was organically complexed, which ranged from 0 to 100%. Organic speciation work on copper, zinc, and iron shows that the organically complexed fraction dominates the dissolved speciation of these metals in oceanic surface waters and is critically important in controlling the free metal ion concentrations of these metals. Although the chemical nature and complete chemical characteristics of the complexing ligands remains unknown, preliminary investigations have shown that the ligands are generally hydrophillic and of low molecular weight.

Methods for determining the speciation of transition metals and heavy metals in natural waters include fixed-potential amperometry (FPA), ion-selective electrodes (ISE), biological assays, solid-phase extraction (SPE), competitive equilibration with $MnO_2(s)$, differential pulse anodic stripping voltammetry (DPASV), and competitive ligand equilibration with adsorptive cathodic stripping voltammetric detection (CLE/CSV). **Table 3** lists the methods utilized for copper speciation with pertinent limitations and considerations. These techniques involve physical isolation or detection of one of the metal's species, or of a metal species not originally present in the sample but created for the speciation determination by introduction of a competing ligand. The speciation methods must operate under some general constraints: (1) samples must be at equilibrium, and (2) the technique must detect only the species intended.

Copper The fraction of organically complexed copper in sea water has been determined throughout many of the world's oceans including the Pacific, Atlantic, and Indian. The percentage of organic copper found in these oceans ranges from 89% to 99.9%. In the surface waters of the North Pacific (i.e., the upper 200 m), more than 99.7% of total dissolved Cu(II) is organically complexed (**Figure 2A**). The organic complexation is dominated by two copper-complexing ligands (or classes of ligands), L_1 and L_2. The stronger L_1 ligand class has an average concentration of $\sim 1.8\,\mathrm{nmol\,l^{-1}}$ in the upper 100 m and from the surface down to 200 m and its concentration exceeds that of dissolved copper (**Figure 2B**). The great strength of the L_1 class and its excess concentration relative to dissolved copper causes the inorganic copper fraction to account for less than 0.3% of total dissolved copper, and causes the free hydrated Cu^{2+} to account for only about 0.012% of total dissolved copper. A comparison of **Figure 2C** with **Figure 2B** shows that while dissolved copper ranges only from 0.3 to $1.5\,\mathrm{nmol\,l^{-1}}$ (a factor of 5), the Cu^{2+} concentration ranges from 10^{-13} to 10^{-10} (a thousand-fold)!

Measurements made in the Sargasso Sea revealed concentrations of the stronger L_1 copper-complexing ligand class to be equal to or less than the dissolved copper concentration, causing the weaker L_2 ligand class to dominate organic copper speciation, with a concomitant increase in the inorganic copper fraction and free Cu^{2+} concentration. Some evidence exists that the ligand concentrations and extent of organic complexation can vary seasonally.

Table 3 Techniques used to determine the speciation of copper in natural waters

Technique	*Limitations/considerations*	*References*[a]
Fixed-potential amperometry (FPA)	Applicable to high $[Cl^-]$ solutions only and low organic ligand concentrations ($\leq 1000\,\mathrm{mol\,l^{-1}}$)	Waite and Morel (1983); Hering *et al.* (1987)
Copper ion-selective electrode (ISE)	Limited sensitivity and chloride interferences	Belli and Zirino (1993); Zirino *et al.*, 1998
Biological assays	Assumes only free metal ion activity causes biological inhibition	Sunda and Ferguson (1983); Hering *et al.* (1987)
Solid-phase extraction (SPE)	May underestimate the extent of organically complexed copper in oceanic surface waters	Mills and Quinn (1981); Hanson and Quinn (1983); Donat *et al.* (1986)
Competitive equilibration with MnO_2	Assumes only Cu^{2+} adsorbs to MnO_2	van den Berg (1982)
Differential pulse anodic stripping voltammetry (DPASV)	Assumes only inorganic copper is detected and that natural copper complexes dissociate too slowly to be detected	Coale and Bruland (1988); Donat *et al.* (1994)
Competitive ligand equilibration/adsorptive cathodic stripping voltammetry (CLE/CSV)	Assumes that samples at equilibrium during measurement and that natural copper complexes are not detected (i.e., not electroactive)	van den Berg (1985); Donat and Bruland (1990)

[a] See Further Reading list.

Zinc The fraction of organically complexed zinc found in North Pacific waters averages 98.7% (**Figure 3A**). As with copper, organic complexation of zinc is dominated by a relatively zinc-specific

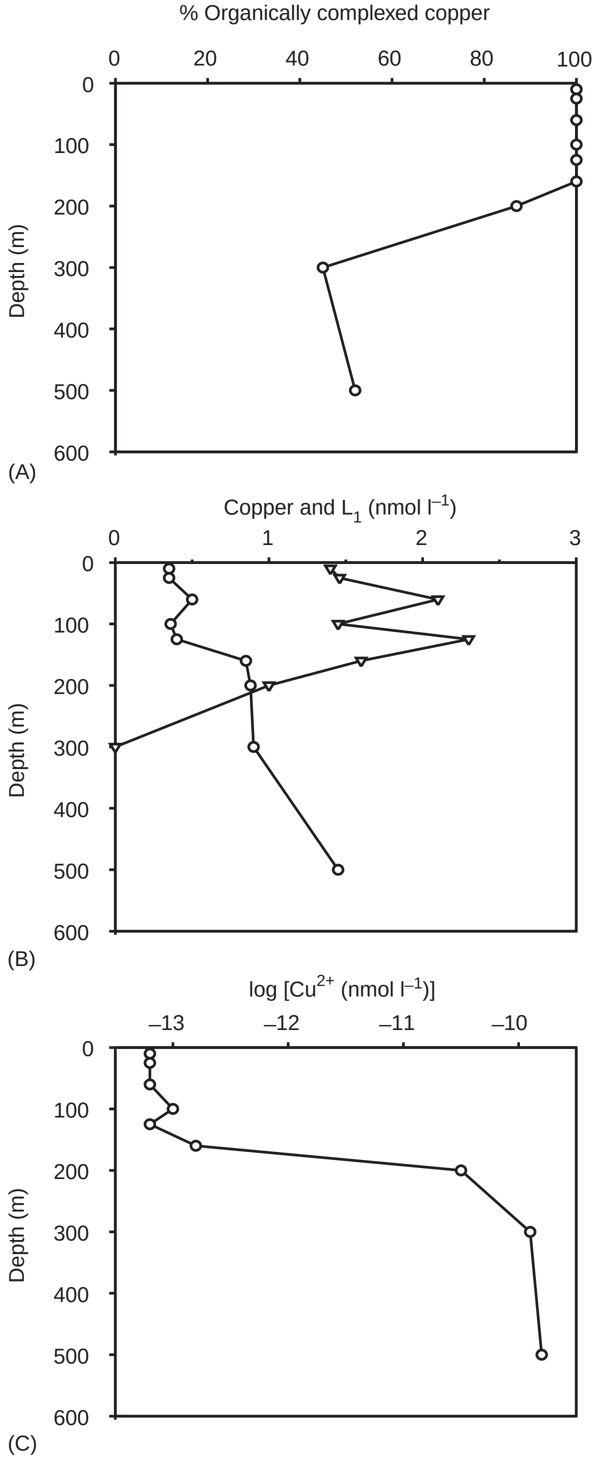

Figure 2 North Pacific surface waters dissolved Cu(II) speciation: (A) depth profile of L_1, the stronger copper-complexing organic ligand; (B) dissolved Cu(II) depth profile; (C) depth profile of free Cu^{2+} ion as logarithmic concentration values.

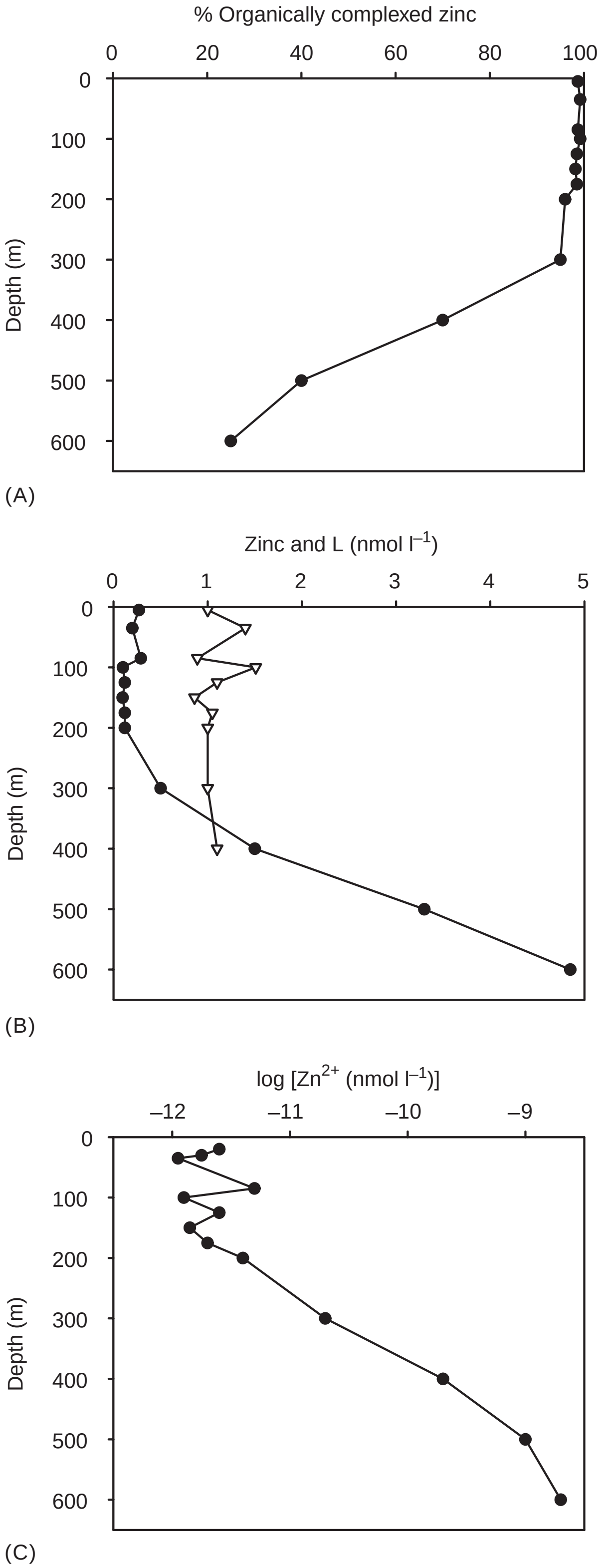

Figure 3 North Pacific zinc speciation: (A) depth profile of zinc-complexing organic ligand presented as percentage of organically complexed zinc; (B) dissovled zinc depth profile; (C) Zn^{2+} ion depth profile as logarithmic concentration values.

organic ligand (or ligand class) in surface waters shallower than 200 m (**Figure 3B**). In this upper 200 m, the zinc-complexing ligand averages 1.2 nmol l^{-1} and exceeds the concentration of dissolved zinc at depths above 300 m (**Figure 3B**). The high degree of organic complexation of zinc in the upper 300 m is caused by the excess in ligand relative to that of dissolved zinc and the strength of its zinc complexes. Organic complexation of zinc reduces the concentration of inorganic zinc species to 2×10^{-12} mol l^{-1}. Concentrations of free Zn^{2+} vary with depth from $\sim10^{-11.8}$ mol l^{-1}, at depths less than 200 m, increasing to $\sim10^{-8.6}$ mol l^{-1} at a depth of 600 m.

Iron Fe^{3+} forms complexes with natural organic ligands (like humic substances) that help keep this very insoluble cation in solution at elevated levels in estuarine and coastal waters. In the North Pacific and in the North Sea, researchers have determined that more than 99% of dissolved Fe(II) is bound with an extremely strong ligand class whose concentration ranges from 1 to 5 nmol l^{-1} and is in excess of the ambient dissolved iron concentration. These ligands have conditional stability constants consistent with low molecular weight organic substances called siderophores, which are produced by bacteria to specifically obtain iron. The availability of iron to aquatic primary producers has become the focus of many research projects since experiments have shown that in certain areas of the world's oceans iron availability is very low and may regulate productivity and perhaps influence atmospheric levels of carbon dioxide.

Other metals Organic complexation of other dissolved transition metals and heavy metals (i.e., Cd, Pb, Co, Ni, and Fe) has been investigated only much more recently and the information on these metals is not as defined or as extensive as for copper, iron and zinc. Recent measurements of dissolved cadmium in the North Pacific revealed that 70% was bound by cadmium-specific organic ligands found only at depths less than 175 m. Inorganic cadmium concentrations varied from 0.7×10^{-12} mol l^{-1} in surface waters to 800×10^{-12} mol l^{-1} at 600 m. The free Cd^{2+} concentration ranged from 20×10^{-15} mol l^{-1} in the surface, where organic complexation dominates the speciation, to 22×10^{-12} mol l^{-1} at 600 m where chloro complexes appear to dominate the inorganic speciation.

In the North Pacific, measurements of dissolved lead in the surface waters revealed that 50% was organically complexed by one class of strong organic ligands found to have concentrations between 0.2 and 0.5 nmol l^{-1}. The free Pb^{2+} surface water concentration as a result of inorganic and organic complexation was $\sim0.4\times10^{-12}$ mol l^{-1}.

Organic complexation of dissolved cobalt and nickel in the open ocean has not been reported; however, organically complexed cobalt and nickel in estuarine and coastal samples have been found. The fraction of organic complexation is highly variable from estuary to coastal ocean. About 50% of the dissolved cobalt in coastal sea water was found to be organically complexed. In UK coastal waters and south San Francisco Bay, 30–50% of the nickel was bound in extremely strong organic complexes.

The information presented in this section demonstrates the importance of organic complexation of several transition metals and heavy metals. These organic ligands exist at low concentrations and form very strong complexes (i.e., they have high conditional stability constants). Although the actual chemical structures of these complexing organic ligands are still unknown, new analytical techniques may soon uncover their structure.

How Speciation Relates to Biology

Early researchers suggested that some organic compounds present in sea water in trace quantities may influence the primary production of marine communities by reducing toxic free metal concentrations (especially Cu^{2+}) to nontoxic levels. Data show that maximum levels of organically complexed copper occur in the surface euphotic zone at depths near the productivity maximum, and decrease dramatically below the vernal mixed layer in the North Pacific. The speciation of dissolved zinc is dominated by organic complexes and it may suggest a biological influence, as discussed for copper. Yet, the reasons for organic zinc speciation are not completely understood and only speculations exist.

Laboratory evidence exists for production of a strong copper-binding ligand by four marine phytoplankton (three species of eukaryotes and one prokaryote). The ligand that was produced has identical copper-complexing strength (i.e., similar conditional stability constants) to that of the stronger ligand observed in surface waters of the North Pacific and Sargasso Sea. The production of this L_1-like ligand may demonstrate a detoxification mechanism used by phytoplankton to lower the free Cu^{2+} concentration. Laboratory studies of the sensitivity of phytoplankton to varying Cu^{2+} concentrations revealed the following trend: cyanobacteria were the most sensitive; diatoms were the least sensitive; and coccolithophores and dinoflagellates showed intermediate sensitivity. Using this laboratory work, researchers are theorizing how cyanobacteria might produce strong L_1 ligands to lower the free Cu^{2+} concentration in oceanic surface waters to levels at which their growth would not be impacted ($< 10^{-12}\,\mathrm{mol\,l^{-1}}$). During an upwelling event, cyanobacterial production of the L_1 ligand might not exceed the newly upwelled Cu^{2+}, therefore cyanobacteria abundance would decline. Actual field evidence is supporting the speculation that species composition and seasonal species successions of phytoplankton are influenced by Cu^{2+} concentrations, especially in high-nutrient–low-chlorophyll areas.

Growth limitation experiments, like those for copper, have also been performed for iron, zinc, and manganese. These experiments showed that sufficiently low free ion activities of these nutrient metals could result in species shifts in phytoplankton communities. Iron is perhaps the most important nutrient transition metal to phytoplankton and its speciation is extremely complex and is not known with any reliability. Forms of iron that are speculated to have biological importance are organic Fe(III) complexes, Fe(III) oxides, and Fe(III)–siderophore complexes. Unlike Cu^{2+} which acts as a toxin, increased free Zn^{2+} concentrations in upwelled water could enhance reproduction of phytoplankton communities. Manganese in sea water, which shows no evidence of any organic complexation, appears to be maintained by photochemical reduction processes and photoinhibition of microbial oxidation of Mn^{2+}. Low manganese concentrations could potentially limit oceanic productivity if not supplied in sufficient quantities by atmosphere or horizontal mixing. Therefore, the distributions of Zn^{2+}, Mn^{2+}, and dissolved iron have important consequences for species composition and species succession of a phytoplankton community.

Oceanic concentrations of dissolved cadmium may be outside the range causing cadmium toxicity. However, in estuarine and riverine areas, anthropogenic sources could supply excessive cadmium inputs, leading to cadmium toxicity in aquatic phytoplankton. On the other hand, some researchers have shown that cadmium can promote growth of zinc-limited oceanic phytoplankton by substituting for zinc in certain macromolecules, thereby causing growth at lower than expected free Zn^{2+} concentrations. It has been speculated that this biochemical substitution of cadmium for zinc by phytoplankton could account for the nutrient-type oceanic distribution of cadmium.

Summary

Major advances in procedural, analytical, and instrumental techniques have advanced our knowledge of the concentrations, distributions, and speciation of the transition metals and heavy metals in the oceans, and therefore our understanding of their biogeochemical cycling. For most of the transition metals and heavy metals we have a first-order understanding of their oceanic distributions, and now with more data and better sea-going analytical techniques, basin-wide cross-sections of the distributions of some metals (e.g., aluminum, manganese, and iron) are becoming available. These basin-wide distributions allow more interpretation of sources and fates of these metals. Mediation by light and microorganisms dominates the biogeochemical cycling of certain metals such as copper, iron, and manganese. Organic complexation has come into the forefront of metal speciation research. Not only has the evidence for the existence of organic complexation been overwhelming, but organic ligands dominate the speciation of copper, zinc, and iron in oceanic surface waters. Organic complexation of certain metals in the oceans has important biological implications (i.e., controlling availability of metals as nutrients and toxicants) for phytoplankton.

See also

Bacterioplankton. Carbon Cycle. Metal Pollution. Tracers of Ocean Productivity.

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TRANSMISSOMETRY AND NEPHELOMETRY

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Introduction

Transmissometry and nephelometry are two of the most common optical metrics used in research and monitoring of the Earth's oceans, lakes, and streams. Both of these measurements relate to what we perceive as the clarity of the water, and both provide vital information in numerous studies of natural processes and human activities' impact upon water bodies. Applications involving these measurements range from monitoring drinking water suitability to understanding how carbon is transferred into and transported within ocean waters.