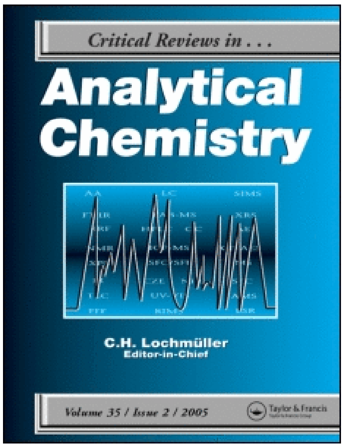

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CHEMICAL SPECIATION IN NATURAL WATERS

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I. INTRODUCTION

Chemical speciation may be defined as the determination of the individual concentrations of the various chemical forms of an element which together make up the total concentration of that element in a sample. The next decade will certainly see a blossoming of interest from chemists, biochemists, and biologists in techniques for chemical speciation. This is because it is becoming more and more apparent that both bioavailability and toxicity are critically dependent on the chemical form of the substance under test. Measurement of the total concentration of a nutrient or a trace element provides very little information about the bioavailability of the substance, since many vitamins and essential elements are now known to exist in a variety of chemical forms, the assimilability of which vary greatly.[1-3] For example, niacin and folic acid exist in some foods in bound forms which are unavailable to many species,[4] and the same is true of a whole range of essential metals, including iron, zinc, cobalt, and chromium. For man, the most assimilable form of iron is heme iron from meat. Inorganic iron salts and simple organic complexes are far less available. The group of chromium-amino-acid complexes known as the glucose tolerance factor[1,5] provides most of the usable chromium, while cobalamin (vitamin B_{12}) is the only essential chemical form of cobalt.[6] It has also been suggested that zinc-amino-acid complexes are more available than inorganic zinc.[2,7] Analysis of a diet for total iron, chromium, cobalt, or zinc, without some information about their chemical forms, is therefore almost worthless because a nutritional deficiency of these elements could exist despite their widespread distribution.

In the case of metal toxicity, it is generally accepted that the free (hydrated) metal ion is the form most toxic to aquatic life. Strongly complexed metal, or metal associated with colloidal particles, is much less toxic.[3,8-12] For this reason, the determination of the total concentration (e.g., by atomic absorption spectrophotometry) of a heavy metal in a water sample provides very little information about the toxicity of that water. Depending on the chemical forms of the metal, a water with a high total metal concentration may, in fact, be less toxic than another water with a lower total metal concentration. To obtain meaningful data on either bioavailability or toxicity, it is essential that chemical speciation techniques be applied.

The development of analytical techniques which can reliably measure the concentration of the various chemical forms of a trace metal in a water sample is one of the most challenging problems at present facing analytical chemists. In the case of natural waters, even the total concentrations of metals such as copper, lead, cadmium, and zinc are exceedingly low, and few laboratories are competent to work in this area of subtrace analysis.[13] The problem is obviously much more difficult if each total-metal measurement has then to be divided into the several different chemical forms which contribute to the total. Great analytical sensitivity is required, and the whole analytical procedure must be designed to keep blanks and contamination to an absolute minimum. In addition, any preliminary separation steps, and the analytical measurement itself, must be chosen to avoid, as far as possible, altering the equilibria between the various chemical species in the sample. However in a dynamic system such as a natural water, some disruption of the chemical equilibria is inevitable, although it can be minimized by using rapid separation procedures.

The problems involved in developing an analytical scheme to measure all the specific metal species present in a natural water sample seem insurmountable with techniques now available. Nevertheless, even the ability to classify dissolved metal concentrations into groups of species is a most important contribution to the study of water chemistry, metal transport, and trace-metal toxicity. For both biological and geochemical pur-

Table 1
POSSIBLE CHEMICAL FORMS (SPECIATION) OF METALS IN NATURAL WATERS

Chemical form	Possible examples	Approximate diameter (nm)
Particulate	Retained by 0.45 μm filter	>450
Simple hydrated metal ion	$Zn(H_2O)_6^{2+}$	0.8
Simple inorganic complexes	$Zn(H_2O)_5Cl^+$	1
Simple organic complexes	Cu-glycinate	1—2
Stable inorganic complexes	PbS, $ZnCO_3$	1—2
Stable organic complexes	Cu-fulvate	2—4
Adsorbed on inorganic colloids	Cu^{2+}-Fe_2O_3,Cd^{2+}-MnO_2	10—500
Adsorbed on organic colloids	Pb^{2+}-humic acid, Zn^{2+}-organic detritus	10—500

poses, it would be desirable, as a minimum requirement, to be able to divide dissolved metal into seven classes (Table 1): free (hydrated) metal ion, labile metal complexes (organic and inorganic), inert metal complexes (organic and inorganic), and metal associated with colloidal particles (organic and inorganic). No speciation scheme yet published completely fulfills this requirement, although some approach it.

In this review, all the important speciation techniques are considered, and the results which have been obtained for several important elements are critically discussed. The many problems involved in this exacting area of trace analysis are enumerated, and recommendations are made for future research.

II. CHEMICAL FORMS OF METALS IN NATURAL WATERS

The most recent results obtained in our laboratory for total dissolved Cu, Pb, Cd, and Zn in unpolluted streams near Sydney and in the Northern Territory and in nearshore surface Pacific Ocean water off Sydney are summarized in Table 2. The measurements were made using anodic stripping voltammetry (ASV) and were obtained as part of routine environmental surveys. It is interesting to note that in unpolluted freshwater streams around the globe the concentrations of these trace heavy metals are very similar.[3] Gardiner[14] has suggested that, at least in the case of cadmium, humic substances in river sediments act as a buffer by absorbing heavy metals and maintaining a constant dissolved-metal level.

Although the total concentrations of a dissolved metal may be similar in two water systems, the chemical forms of that metal may be quite different. Some of the possible dissolved forms of a divalent trace metal present in a natural water are listed in Table 1. Note that, by convention, "dissolved" metal is all metal species which pass through a 0.45 μm filter. Most colloidal particles will, therefore, be included in the dissolved fraction.

Salinity and pH will obviously have a significant effect on the speciation of trace heavy metals.[15] In seawater, chloro complexes may be an important species, and because of the relatively high pH, adsorption of metal ions onto organic and inorganic colloids may occur. In freshwaters, which generally have a lower pH, but higher organic content, than seawater, carbonate is usually more important than chloride as a ligand. Metal-organic interactions may dominate the speciation.

There has been considerable controversy over the existence of dissolved, molecular (i.e., nonpolymeric and noncolloidal) organic complexes of trace heavy metals in seawater. Organic complexing is often invoked as a means of explaining a lack of behavior according to simple mass-action relationships. However, Duursma and Sevenhuysen[16]

Table 2
AVERAGE TOTAL CONCENTRATIONS OF Cu, Pb, Cd, AND Zn FOUND IN UNPOLLUTED FRESHWATER STREAMS AND IN NEAR-SHORE SURFACE PACIFIC OCEAN WATER USING ANODIC STRIPPING VOLTAMMETRY

	Concentration ($\mu g\ l^{-1}$)	
Metal	Pacific Ocean[a]	Freshwater Streams[b]
Cu	0.28	0.40
Pb	0.15	0.20
Cd	0.10	0.15
Zn	1.5	1.8

[a] Sampled near Sydney, Australia.
[b] Streams near Sydney and in the Northern Territory, Australia.

concluded from solubility measurements that for ions such as Fe^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} no formation of molecular organic complexes would take place. Their experiments, using EDTA, isoleucine, and arabinose as model complexing agents, indicated that natural chelators would be present in seawater at concentrations too low to compete with inorganic ligands for the metal ion. Florence and Batley[17] found that a mixture of organic complexing agents, including several amino acids and humic acid, had no effect on the ASV waves of Cu, Pb, Cd, and Zn in either natural or synthetic seawater. Also, a computer model of seawater showed that at the natural pH of 8.1, very little of these metals would be complexed by EDTA at concentrations below 2×10^{-8} *M* (Table 3).[17] It is unlikely that any natural chelator exists which forms stronger complexes with the transition metals than does EDTA. For example, humic and fulvic acids form much weaker complexes than EDTA.[15,18,19]

Pocklington[20] summarized the evidence for and against the presence of organic complexes in seawater. He pointed out that no one as yet has isolated and characterized a metal-organic complex from seawater. He believes that until such direct evidence is forthcoming, the whole concept of seawater metal-organic complexes should be viewed with suspicion. Sanchez and Lee[21] found little evidence of soluble organic complexes of copper in Lake Monona, Wis., even though the lake has received nearly one million kg of copper sulfate over the past 50 years for algae control. The added copper has become incorporated in the sediments.

Many of the apparently conflicting results on dissolved organometallic complexes in seawater could be reconciled if it were assumed that the concentration of molecular organic complexes was negligible, and that all metal-organic interaction takes place between metals and organic colloids.[3,22,23] Breger[24] and Sharp[25] have pointed out that much of the organic matter in natural waters is in colloidal form. This organic colloidal matter has a widely varying origin and composition,[26,27] but is likely to be a powerful agent for the adsorption and occlusion of trace heavy metals.[28,29] These colloids are, in effect, much stronger "ligands" than any simple complexing agent.[20,23] Depending on their composition, partial extraction of the organic colloids into solvents such as

Table 3
CALCULATED EFFECT OF EDTA ON THE DISTRIBUTION OF Cu, Pb, Cd, AND Zn IN SEAWATER (pH 8.1)

EDTA (*M*)	Percentage of total metal as EDTA complex			
	Cu	Pb	Cd	Zn
2×10^{-9}	0.3	0.3	< 0.1	0.2
2×10^{-8}	4.8	5.2	0.7	2.9
2×10^{-7}	35.1	36.9	6.8	24.3

Seawater contained 2×10^{-9} *M* and 1×10^{-9} *M* of soluble iron(III) and chromium(III), respectively.

From Florence, T. M. and Batley, G. E., *Talanta*, 23, 179 (1976). With permission.

chloroform and carbon tetrachloride may take place, which could account for the presence of extractable copper in seawater.[30] When oxidized by UV irradiation or chemical oxidants, the organic colloids would decompose and release the associated metal. Batley and Florence[31] and Batley and Gardner[32] found that a significant fraction of the copper, lead, and cadmium in seawater was associated with colloidal organic matter. Florence[33] reported that in a low pH, low hardness freshwater up to 59% of the total dissolved copper was adsorbed on organic colloids.

In the freshwater-seawater mixing zone of estuaries, the precipitation and flocculation of humic substances and hydrous oxides of iron and manganese results in the transfer of most of the dissolved heavy metals from the riverwater to the precipitated phase.[14,22,23] In this way, the water is effectively scavenged of dissolved heavy metals. This continuous scavenging by organic and inorganic particulate matter accounts for the very low concentrations of heavy metals in seawater.[23,34] Most of the metal-laden particulates will eventually find their way to the sediment, but some will remain in solution as colloidal particles, and so contribute to the analytical result for dissolved metal. Turekian[23] and Bruland et al.[35] have pointed out that the concentration-depth profiles of many essential metals in seawater bear conservative relationships to the concentrations of nutrient components such as phosphate, nitrate, and silicate. Because both essential metals and nutrients are concentrated by aquatic organisms such as plankton, this may seem reasonable, but if most of the essential metals (e.g., Cu, Zn, and Mn) in seawater indeed exist as species adsorbed on particles, colloidal and larger, it is rather remarkable that they maintain a conservative relationship to the nutrients, which are mainly in true solution.

Most freshwaters have a pH which is in the critical range for adsorption of heavy metals onto particles. Since as small a decrease as 0.5 pH unit can cause the difference between complete adsorption and complete desorption (Figure 1), the extent of trace metal adsorption on particles in freshwater is largely pH dependent.[36] It is possible that the greatly increased fish mortalities which have been observed[37,38] when some soft freshwater lakes were acidified by atmospheric SO_2 pollution, may be partly the result of the release of ionic copper, lead, and other heavy metals from colloidal particles and sediments (Figure 2).

A great deal more data have been accumulated for the adsorption of metals from

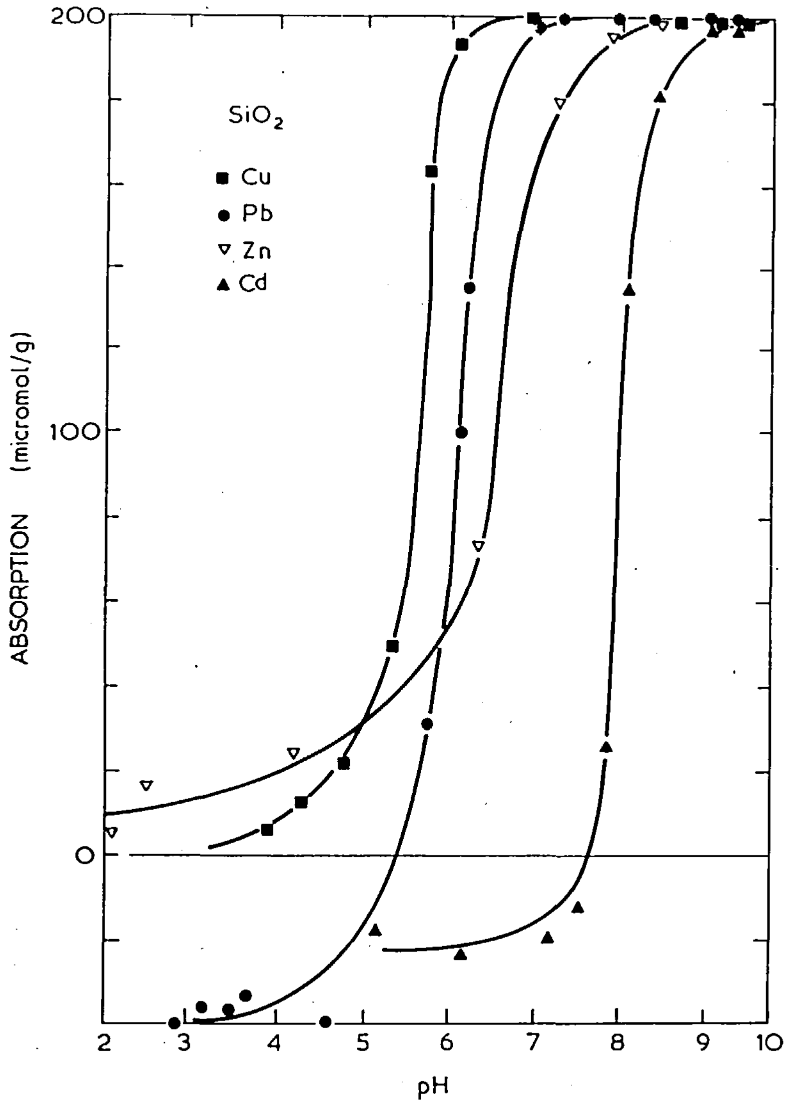


FIGURE 1. Adsorption of metals on silica. (From Huang, C. P., Elliott, H. A., and Ashmead, R. M., *J. Water Pollut. Control Fed.*, 49, 745 (1977). With permission.)

natural waters onto inorganic particles[39-51] than for adsorption by organic particles or organically coated minerals.[20] Even so, most of the laboratory studies used model adsorbents, and it is unlikely that the model compounds have chemical or physical properties which duplicate naturally occurring particles. In addition, Morgan[52] has pointed out that thermodynamic equilibrium for particle adsorption may not always be achieved in natural waters, especially freshwaters.

Gilbert et al.[34] and James and McNaughton[43] have discussed the different interfacial models used to describe metal ion adsorption onto inorganic particles. The James and Healy[53] hydrolysis-adsorption model is most often used. It predicts that at constant pH fractional adsorption should increase with increasing $\log{}^*\beta_1$, the hydrolysis constant for addition of the first $-OH$ to the metal ion. Thus, adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} should decrease in that order, as was shown by Huang et al.[36] to be

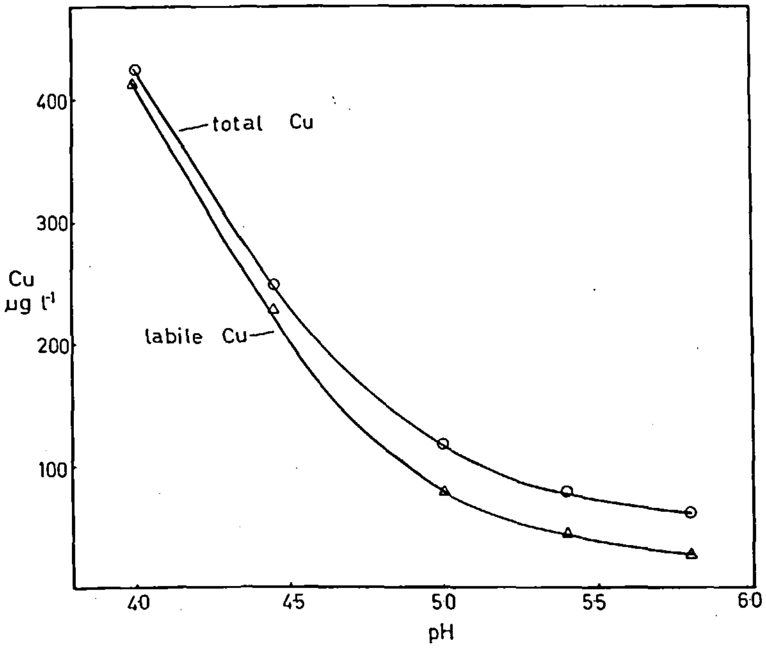


FIGURE 2. Effect of pH change on the speciation of dissolved copper (measured by anodic stripping voltammetry) released from a mineralised sediment. The sediment was from Captains Flat, A.C.T. (Australia) and had a total copper concentration of 156 $\mu g\ g^{-1}$. (From Rendell, P. S. and Batley, G. E., unpublished results, 1978.)

true for silica, alumina, and some soil minerals. In the case of silica, significant adsorption of the metal ion begins to occur at the pH value corresponding approximately to $\log{}^*\beta_1$ -1.5 (Table 4, Figure 1). This empirical approximation also applies to adsorption onto hydrous ferric oxide (Figure 3) and illite.[46] Huang et al.[36] found that adsorption was not related to the zero point of charge of the adsorbent. In general, α-Al_2O_3 showed the smallest adsorption capacity. They also found that in the presence of certain anions, adsorption of heavy metals is more pronounced. Adsorption of Cu, Pb, Cd, and Zn decreased in the order, humic acid > NTA > glycine = tartrate > phosphate. Jenne[54] has suggested that whereas clay mineral particles, because of their low ion-exchange capacity,[22,29] are unlikely to play a significant role in heavy metal transport, clay minerals coated with iron or manganese hydrous oxides would allow the hydrous oxides to present a large surface area for adsorption, and so exert a far greater chemical activity.

Colloidal organic matter present in natural waters may be able to compete successfully with hydrous metal oxides for the adsorption of trace heavy metals. Florence,[33] in a study of some soft riverwaters of pH 6.0 to 6.1, found that over 50% of the copper was adsorbed on organic colloids with no measurable adsorption on inorganic colloidal particles, even though some adsorption by inorganic substrates would be expected in this pH range (Table 4). In organic-rich freshwaters[55] or in sewage effluents,[56] metal-organic complexes may also be an important solution species.

Krauskopf[47] made a comprehensive study of the adsorption of 13 metals from seawater onto a variety of adsorbents, including hydrated ferric oxide, manganese dioxide, clay, plankton, and peat moss. Copper, zinc, and lead were the metals most effectively scavenged. Of the adsorbents, MnO_2 and peat moss were the best, followed by hydrated ferric oxide. Hem[48] calculated that very stable spinel structures such as

Table 4
HYDROLYSIS OF METAL IONS

	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}
$p^*\beta_1$	7.0	7.5	8.5	9.5
$p^*\beta_1 - 1.5$	5.5	6.0	7.0	8.0

Note: $M^{2+} + H_2O \rightleftharpoons M(OH)^+ + H^+$; $^*\beta_1 = [M(OH)^+][H^+]/[M^{2+}]$

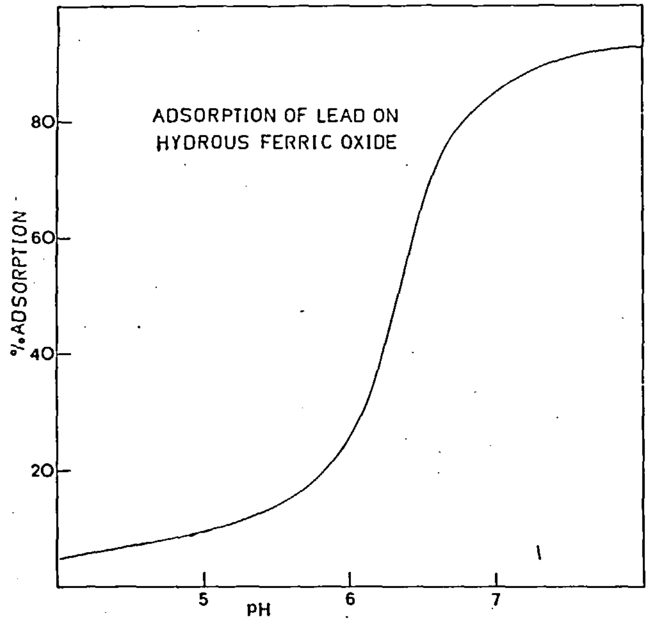


FIGURE 3. Adsorption of lead on hydrated ferric oxide. (From Gadde, R. R. and Laitinen, H. A., *Anal. Chem.*, 46, 2022 (1974). With permission.)

chromites or ferrites of Cu, Ni, and Zn could form on the surface of hydrous ferric oxide at pH 8 and would result in equilibrium concentrations well below 10^{-9} *M* for these divalent metal ions. Such processes could be very important for solubility control in some natural waters.

For cobalt and nickel[47] and a range of other metal ions,[29,40,43,45] MnO_2 is a very efficient collector in seawater. Also, Bacsó et al.[42] reported that iron-manganese deposits in the water-supply pipelines of several Hungarian cities had accumulated high concentrations of Pb, Cu, Zn, and As. Krauskopf[47] suggested that adsorption onto metal sulfides (e.g., FeS) may be an important factor in establishing the equilibrium solubilities of some heavy metals in seawater, although there is no apparent correlation between the existing metal concentrations and metal sulfide solubility products, an observation also made by Elderfield and Hepworth for sediment-pore waters.[44]

The interaction between organic matter and iron in freshwaters is likely to produce colloidal particles with a high affinity for heavy metals. Hall and Lee[55] concluded from a gel filtration study that much of the organic matter in Lake Mary, a highly colored meromictic lake in Wisconsin, is in true solution. However, when ferric iron was added to the system, the organics and iron became associated to form larger, colloidal particles.

Many other types of organic matter in natural waters are important collectors of trace heavy metals. Ferguson and Bubela[28] showed that algae can effectively concentrate Cu, Pb, and Zn from solution, and Pocklington[20] suggested that organically coated mineral particles are common in seawater. Guy and Chakrabarti[18] showed that Cu^{2+}, Zn^{2+}, and Cd^{2+} are strongly adsorbed by humic acid, although MnO_2 is an even stronger adsorbent.[29] Relatively few reliable data are available on metal-organic interactions in natural waters, and the field is ripe for study using modern chromatographic and analytical techniques.

III. SAMPLING, FILTRATION, AND STORAGE OF WATER SAMPLES

The sampling, filtration, and storage of natural water samples are the most critical stages in the whole trace-metal analysis procedure. These operations should be performed either directly by, or under the supervision of, qualified personnel, with an acute awareness of all possible sources of error. Lack of care, especially in the sampling and filtration operations, will negate the many hours of tedious and expensive chemical analysis, while leading to unjustified conclusions as to the environmental threats or possible toxicity of trace metals should such data be accepted.

Techniques for the collection of samples free of trace-metal contamination are now well established.[57-61] These involve the use of a wide range of Teflon®, Perspex® (plexiglas), and polypropylene bottle samplers, polyethylene bag samplers, polyethylene bottles or jerry cans, and pumping systems.

The absence of established sources of contamination, such as rubbers, springs, metal surfaces, and grease, is imperative. Care should be given to the cleaning of the container material. For this purpose, 1:1 HCl has been shown to be the most effective.[62]

Zinc is probably the most ubiquitous trace-metal contaminant, being present in rubber, galvanized retort stands, talcum powder, paper (including filter papers), paint, dust, and human skin, all of which can be found in the laboratory. Zinc stearate is used as a lubricant in the manufacture of some plastics and can be present as a surface contaminant. Potential sources of other trace-metal contaminants have been well documented in the literature.[61,63-65]

The use of "clean" laboratories has been advocated for most trace-analysis studies. It is, of course, impossible in an instrumental laboratory to eliminate all metal components, but an essential prerequisite is a dust-free working environment, established either in a laminar-flow clean hood or using a filtered air supply to the laboratory. The extremes to which precautions need be taken when setting up a clean laboratory are debatable. An important advantage of an ultra-clean laboratory is that it establishes in the minds of the users the need for extreme care to be exercised to avoid contamination.

As soon as possible after its collection, the sample should be filtered if metal speciation is to be studied. Many oceanographic laboratories choose not to filter their samples. Common shipboard practice is to acidify after collection, but acidification is obviously undesirable in speciation studies. It is possible, however, that speciation studies could be performed for seawater on unfiltered, unacidified samples. With fresh water and some estuarine water samples, the suspended load will contribute significantly to the total metal concentrations,[66] and filtration is essential. Membrane filters need to be thoroughly washed with acid, distilled water, and sample before use. From our experience, polycarbonate filter flasks are the most readily decontaminated. They are preferred to those having sintered-glass filter supports. Measurement of labile metals by anodic stripping voltammetry on filtered and unfiltered samples can be used as a useful test for contamination during filtration.

Pressure filtration offers advantages in terms of speed of filtration[67] and is preferable with freshwater samples having a high suspended sediment load, where filtration rates using vacuum may be as low as 100 mℓ h^{-1} using 47 mm diameter 0.45 μm filters. A serious disadvantage, however, is the problem of rupture of phytoplankton cells which will occur at pressures greater than 25 kPa. At the high pressures (700 kPa) attainable under pressure filtration, ruptured cells will contribute soluble organic matter, nutrients, and heavy metals, which could significantly affect speciation studies. Martin and Knauer[68] have reported concentration factors of 3×10^4 for zinc, lead, and copper in phytoplankton.

The many studies of storage losses of heavy metal have been comprehensively reviewed by Rattonetti[66] and Batley and Gardner.[61] Moody and Lindstrom[62] reported a detailed examination of commercially available plastic containers for use in trace-metal analysis which showed that conventional polyethylene and the various teflons (TFE, FEP, and PFA) were best in terms of trace-metal content and rate of transpiration of water. Conventional polyethylene is now preferred in most laboratories, both from a cost consideration and for the greater ease of removing leachable metal contaminants.

While the acid-leaching of sample containers is essential to remove surface contamination from container materials, this treatment may lead to the activation of adsorption sites capable of removing trace metal from solution. For this reason, it is essential that, after acid treatment, the container be well rinsed with sample. Nurnberg et al.[69] use conditioning salt solutions containing calcium and magnesium sulfates for inland water sampling, and a mixture of sodium chloride, calcium sulfate, and magnesium sulfate for seawater. For the collection of unpolluted seawater samples, we reuse the same aged containers, with sample, but not acid, rinsing between samples, so that the surfaces are well equilibrated with natural levels of heavy metals.

Care must be taken in the interpretation of the results of storage experiments using either radiotracer or ionic metal spikes, since these give no information about the adsorptive behavior of naturally present trace-metal species. The only satisfactory test for storage losses is to perform direct analyses on the untreated sample after various storage periods. The number of published results based on this type of experiment is, however, limited. For zinc analysis, Fukai et al.[70] and Florence[33] have shown that the chemical speciation of dissolved zinc in estuarine and river waters, respectively, did not change significantly over 1 to 2 months when the samples were stored at 4°C in polythene containers. Storage at 25°C produced no changes after 27 days, but freezing to −20°C brought about significant irreversible changes. Similar results were obtained for cadmium, lead, and copper in both marine and freshwaters.[32,33,70]

For mercury analysis, losses on storage of unacidified samples have been shown to be significant for freshwaters, but not for seawater.[61] Adsorptive losses can be reduced if polyethylene containers are leached before use with hot, concentrated nitric acid.[71] For speciation studies, it is nevertheless important in the case of mercury, and indeed for all other metals, that the analyses be performed as soon as possible after collection. Otherwise, storage at 4°C appears to be the best alternative. The effectiveness of freezing in speciation studies has yet to be disputed for seawater samples.[32] However, results for freshwater samples are not encouraging.[33]

There is a paucity of information on the storage losses of other heavy metals. Data for iron suggest that it is unstable in unacidified solution, being readily adsorbed as hydrolyzed species on the container walls.[61] It is likely that if this is correct, then manganese (II), chromium (III), and possibly cobalt (II) behave similarly. There is a real need for further experimentation for these and other metals before definitive judgments can be made.

IV. SPECIATION TECHNIQUES

Two basically different approaches have been used to determine the chemical speciation of trace metals in natural water samples. The first involves calculation of the equilibrium concentrations of all the metal-ligand species using known values for total metal and ligand concentrations and published values of the relevant metal-ligand stability constants. The second approach is experimental and attempts to place the various metal species in experimentally defined "boxes" based on their behavior during separation and chemical analysis.

A. Calculation Methods

There is a rapidly increasing interest in the use of computer modeling for the determination of trace-metal species distribution in natural waters.[72] This is a very tempting approach to the measurement of speciation because all the problems of sample collection and contamination immediately disappear. Many hours of careful, exacting, and tedious laboratory work are eliminated. Until recently, most workers used stability constants singly or in pairs to calculate the equilibrium concentration of a particular metal-ligand species. This procedure is invalid because any natural water contains many metals capable of reacting with each ligand, and many ligands which can react with each metal. The correct equilibrium concentration of any species can be computed only by simultaneously taking into account all the competing equilibria. This task is too laborious for manual calculation, and excellent computer programs are now available for application to the problem. Some programs designed for the calculation of equilibrium concentrations in solution (rather than for the determination of stability constants from experimental data) are HALTAFALL,[73] REDEQL,[74] WATEQ,[75] REDEQL2 and GEOCHEM,[76] COMICS,[77] and SIAS.[78,79] A symposium on chemical modeling was recently held in Miami, Fla., where the advantages and disadvantages of the various programs were discussed.[80] REDEQL2 and GEOCHEM are more complicated, but more comprehensive than SIAS, and can take into account adsorption and redox equilibria as well as complexing reactions. REDEQL2 has been applied to the calculation of speciation in freshwater,[81] seawater,[82] and freshwater-seawater mixtures.[83] COMICS has been used for freshwater speciation by Pagenkopf[84] and Lerman and Childs,[85] and SIAS for seawater modeling.[17,79] Typical SIAS output data for the speciation of copper, magnesium, and calcium in seawater are shown in Figure 4.

Comparisions of some recent computer-modeling results for zinc and copper in seawater[15,86-89] are shown in Tables 5 and 6. The wide variation in these calculations is the result of using different published stability constants and the inclusion of additional complex species (e.g., Zn(OH)Cl).[87,90] Published data on stability constants vary greatly,[91] even for such simple, but important, species as the chloro complexes. Smith and Martell[92] have published a compilation of selected (or "best") values for metal-ligand stability constants, which is very useful, although the criteria for selecting the best values from the mass of data are necessarily somewhat subjective. A Commission on Equilibrium Data has been set up by the International Union of Pure and Applied Chemistry to attempt to evaluate published thermodynamic equilibrium data critically. The first report of this Commission has now been published,[93] and the case of the $Ni(CN)_4^{-2}$ complex is quoted as an example (albeit extreme) of the gross variations in values that exist in tne literature for the stability constant of the one complex (Table 7).

Although variations in published stability constant data and, to a lesser extent, problems with activity coefficient corrections seriously compromise the accuracy of computer modeling of dissolved trace elements in natural waters, far more important errors

```
Number of iterations = 29

                 C1          C2          C3          C4          C5          C6          C7          C8          C9

Free Metals      8.747D-03   4.393D-02   2.636D-10   2.086D-12   2.480D-11   2.043D-08   1.467D-08   1.284D-10
Free Ligands     5.590D-01   1.893D-02   3.115D-06   6.107D-11   8.602D-04   3.877D-05
% Free Metals    8.331D+01   8.075D+01   2.333D+00   8.444D-01   2.732D+00   2.663D+01   4.955D+01   1.477D+01

                 Distribution of Metal 1                          %           CONC

                                   1  CASO4             1  1.577D+01   1.656D-03
                                   2  CACO3             2  4.113D-01   4.319D-05
                                   3  CAHCO3            3  4.945D-01   5.192D-05
                                   4  CAHPO4            4  4.859D-04   5.102D-08
                                   5  CABR              5  2.853D-03   2.995D-07
                                   6  CAF               6  1.286D-02   1.350D-06
                                   7  CAOH              7  2.759D-03   2.896D-07
                                                   FREE M  8.331D+01   8.747D-03

                                                    TOTAL 1.000D+02   1.050D-02

                 Distribution of Metal 2                          %           CONC

                                   8  MGSO4             8  1.528D+01   8.315D-03
                                   9  MGCO3             9  3.987D-02   2.169D-05
                                  10  MGHCO3           10  3.807D+00   2.071D-03
                                  11  MGHPO4           11  7.464D-04   4.061D-07
                                  12  MGBR             12  2.765D-03   1.504D-06
                                  13  MGF              13  6.393D-02   3.478D-05
                                  14  MGOH             14  5.335D-02   2.902D-05
                                                   FREE M  8.075D+01   4.393D-02

                                                    TOTAL 1.000D+02   5.440D-02

                 Distribution of Metal 3                          %           CONC

                                  15  CUCL             15  2.067D+00   2.336D-10
                                  16  CU(CL)2          16  3.654D-01   4.129D-11
                                  17  CU(CL)3          17  6.459D-02   7.299D-12
                                  18  CU(CL)4          18  1.437D-02   1.624D-12
                                  19  CUSO4            19  4.416D-01   4.991D-11
                                  20  CU(SO4)2         20  5.275D-03   5.961D-13
                                  21  CUCO3            21  4.586D+01   5.182D-09
                                  22  CU(CO3)2         22  2.264D-01   2.559D-11
                                  23  CUHCO3           23  3.479D-01   3.931D-11
                                  24  CUHPO4           24  6.820D-04   7.707D-14
                                  25  CUBR             25  1.789D-03   2.021D-13
                                  26  CUF              26  4.534D-04   5.123D-14
                                  27  CUOH             27  7.726D+00   8.730D-10
                                  28  CU(OH)2          28  4.054D+01   4.582D-09

                                                   FREE M  2.333D+00   2.636D-10
```

FIGURE 4. Typical output data for the speciation of metals in seawater using the computer program SIAS.[78,79]

are introduced by failure to include in the calculations all metal-binding species, especially colloidal particles. In seawater at least, it is unlikely that soluble complexing agents such as amino acids, citrate, nitrilotriacetic acid (NTA), and even EDTA would complex copper, lead, cadmium, and zinc to a significant extent unless the ligands were present at, for natural waters, unrealistically high concentrations[17] (Table 3). However, adsorption of trace metals onto organic and inorganic colloidal particles is certainly important in natural waters. Unfortunately very few quantitative data are available to "plug into" the computer programs for speciation calculations. Not only are the adsorption isotherm parameters unknown for most of the colloidal adsorbents, but even the nature and concentration of these adsorbents is usually unknown. This is especially true for organic adsorbents. The problem cannot be minimized by proposing that, for toxicity studies, metal species adsorbed on particles can be ignored because they are unlikely to be toxic. In this case, before the computer calculations could be made, an analytical measurement of total dissolved metal in true solution (as opposed to metal adsorbed on colloids) would be required. Even then, the modeling results would lack credibility because the various inorganic complexes show different degrees of adsorption. It would be difficult to include this effect in the computer program.

Chemical modeling results for light, conservative elements such as calcium and mag-

Table 5
COMPUTER MODELING RESULTS FOR THE SPECIATION OF ZINC IN SEAWATER AND FRESHWATER

Zinc species	Species (%)			
	Seawater			Freshwater[a]
	Ref. 83	Ref. 86	Ref. 79	Ref. 83
Zn^{2+}	14.1	17.2	26.6	50.2
Zn-chloro	79.5	10.6	47.0	0.3
$ZnSO_4^0$	1.7	3.5	4.3	0.7
$ZnOH^+$	0.9	0.2	4.4	7.1
$Zn(OH)_2^0$	0.9	62.8	—	7.1
$ZnHCO_3^+$	3.8	0.7	1.0	38.1[b]
$ZnCO_3^0$	3.8	5.0	16.7	38.1[b]

[a] pH 8.0.

[b] Inorganic particulates were found to have adsorbed 3.6%.

Table 6
COMPUTER MODELING RESULTS FOR THE SPECIATION OF COPPER IN SEAWATER AND FRESHWATER

Copper species	Species (%)			
	Seawater			Freshwater[a]
	Ref. 83	Ref. 86	Ref. 79	Ref. 83
Cu^{2+}	0.6	0.9	2.3	2.7
Cu-chloro	95.5	0.1	2.5	0.6
$CuSO_4^0$	0.1	0.2	0.4	—
$CuOH^+$	0.3	1.0	7.7	3.2
$Cu(OH)_2^0$	0.3	90.0	40.7	3.2
$CuHCO_3^+$	3.5	0.1	0.3	47.9[b]
$CuCO_3^0$	3.5	7.7	46.1	47.9[b]

[a] pH 8.0.

[b] Inorganic particulates were found to have adsorbed 45.6%.

nesium which are present at relatively high concentrations may be quite accurate, but calculations of trace heavy-metal speciation in natural waters are unlikely to even approximate the true situation because of inaccurate stability-constant data, lack of information about particle adsorption, and nonequilibrium conditions which exist in many natural waters. Unfortunately, the development of modeling programs has far outstripped the supply of reliable thermodynamic data. It may perhaps be more profitable if most of the effort now expended on obtaining doubtful modeling results was applied to the measurement of the equilibrium constants which are necessary for meaningful calculations.

Table 7
LITERATURE VALUES FOR THE STABILITY CONSTANT OF THE TETRACYANONICKELATE II COMPLEX

Method	Log β_4
Potentiometry	12.5
Potentiometry	22.2
Polarography	>24.0
Polarography	15.5
Spectrophotometry	31.1
Spectrophotometry	31.5

From Beck, M. T., *Pure Appl. Chem.*, 49, 129 (1977). With permission.

B. Experimental Methods

Few analytical techniques are "species-specific", i.e., respond to only one particular chemical form of an element in solution. Perhaps the best example of a species-specific technique is ion selective electrode potentiometry because metal ion-selective electrodes (ISE) respond only to the activity of the free (hydrated) metal ion. Unfortunately in natural waters, the concentrations of even the most common toxic heavy metals (Cu, Pb, Cd, and Zn) are usually too low for determination by ISE. The copper ISE has been used[94] to measure free cupric ion activity down to 0.6 $\mu g\ \ell^{-1}$ in seawater, but the use of these electrodes at such low concentrations is fraught with problems, and the potential readings are difficult to interpret.[95] Many highly sensitive analytical techniques such as atomic absorption spectrophotometry, spark-source mass spectrometry, and neutron activation analysis cannot be used directly for speciation measurements because they are, in general, insensitive to the chemical form of the element. Atomic absorption spectrophotometry, although not inherently capable of differentiating metal species, can be used as a sensitive detector if species separation is first carried out chromatographically.[96] In some instances, neutron activation analysis can be used for speciation, provided it can be shown that neutron irradiation of the sample does not cause scrambling of the chemical species.[97]

Anodic stripping voltammetry (ASV) is one highly sensitive technique which can be used directly to distinguish between "labile" and "bound" metal species.[98] Labile species are free metal ion plus metal complexes which will dissociate in the diffusion layer to liberate metal ion. As shown by Davison,[99] the important parameter in ASV lability, in addition to the rate constants for the formation and dissociation of the metal complex, is the effective thickness of the diffusion layer. The degree of dissociation of a metal complex at the electrode surface is independent of deposition time and sample volume. The thickness of the diffusion layer is controlled by the rate of rotation of the electrode (or rate of stirring of the solution) and determines the "residence time" of the complex in the diffusion layer. Bound metal is metal combined in relatively inert complexes and is defined as total metal minus labile metal.[100] Although the labile-bound discrimination cannot be related to specific chemical forms of the metal, it nevertheless gives important information about speciation, particularly if the ASV measurements are combined with chemical separations.

Preliminary chemical separations may be used to separate metal associated with colloidal particles or with organic ligands from other forms of metal. The characteristics of some separation techniques commonly applied in speciation measurements are summarized below.

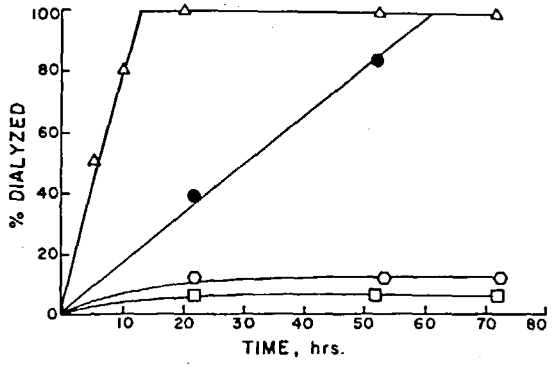


FIGURE 5. Dialysis of 5 μg ml^{-1} copper; △ 10^{-3} *M* $NaHCO_3$; ● 10^{-3} *M* $NaHCO_3$ + 10^{-3} *M* EDTA; ○ 20μg ml^{-1} humic acid; □ 20 μg ml^{-1} tannic acid. (From Guy, R. D. and Chakrabarti, C. L., in *Proc. Int. Conf. Heavy Metals Environ.*, Vol. 1, Hutchinson, T., Ed., University of Toronto, Ontario, 1975, 275. With permission.)

1. Liquid-Liquid Extraction

Solvent extraction of seawater with chloroform or carbon tetrachloride has been used in an attempt to measure organically associated copper. Slowey et al.[30] found that when filtered seawater was extracted with chloroform, 10 to 60% of the total copper present was transferred to the organic phase. This technique probably gives low results for organically bound copper. Charged copper complexes would not be extracted, and copper adsorbed on organic colloids may be only partially extracted. On the other hand, some of the copper adsorbed on inorganic particles may be included in the measurement since these colloids tend to accumulate at the phase interface.

Chelation-solvent extraction methods have also been used in an attempt to determine organically complexed metal in seawater. The usual procedure is to extract the seawater with diethyldithiocarbamate or dithizone before and after an oxidation procedure to destroy organic matter and then equate the difference in extractable metal to organically bound metal.[101] These methods generally showed that 5 to 30% of copper in seawater was present in an organic form. However, as pointed out by Kamp-Nielsen,[102] the chelation-extraction methods probably seriously underestimate the percentage of organic copper in the waters. Dithizone, diethyldithiocarbamate, and ammonium pyrrolidinedithiocarbamate (APDC) form exceptionally strong complexes with copper and would decompose most, if not all, copper complexes with natural ligands. Kamp-Nielsen calculated that the stability constant of a natural copper complex would have to be greater than 10^{30} to avoid decomposition by diethyldithiocarbamate. Perhaps the only form of organic copper that would partially escape extraction would be that which is occluded in, or adsorbed on, colloidal organic particles.[17]

2. Dialysis, Electrophoresis, Ultrafiltration, and Centrifugation

These techniques have all been used to separate metal associated with colloidal particles from ionic metal species. The ability to distinguish between colloidal and ionic metal is important because heavy metal adsorbed on colloids probably has low toxicity. Yet, for some metals, it may account for most of the dissolved species in natural waters.

Dialysis membranes commonly have pore diameters of 1 to 5 nm, whereas ultrafiltration membranes are available with apparent pore diameters of 1 to 15 nm. Both types of membrane should provide a fairly efficient separation of colloidal and molecular species (Table 1). There are serious problems, however, with the use of dialysis and ultrafiltration membranes for the determination of trace metals and metal speciation in natural waters. The diffusion of negatively charged complexes through some dialysis membranes may be very slow[103,104] (Figure 5). In addition, considerable dissociation of some metal complexes may occur at the membrane surface, and the Donnan effect can complicate interpretation of results.[103] Elimination of metal contamination is also very difficult. Dialysis membranes need to be washed for an exceptionally long time before acceptable blanks are obtained. Ultrafiltration cells are likewise liable to introduce serious contamination, both organic and inorganic,[105] especially since the volume of sample filtered is small. A further complication is that once these membranes have been freed of metal contamination, they show a tendency to strongly adsorb trace metals from solution.[13,104,105] The *in situ* dialysis technique of Benes and Steinnes[104] may minimize many of these difficulties.

Benes, Steinnes, and co-workers have carried out much of the pioneering work on the application of dialysis and ultrafiltration to natural water analysis.[104,106-108] Benes and Steinnes[104] studied 20 elements in river water using a dialysis bag immersed for 1 to 4 weeks in the river. They found that most of the light, mono- or divalent elements existed primarily as low-molecular-weight species, whereas heavy, or multivalent ions (e.g., Al(III), Sc(III), Th(IV), Fe(III)) were present mainly in colloidal or particulate form. Similar results were obtained by Benes et al.[106] for 18 elements in a freshwater lake. In this study, a comparison was made of the percentages of metals which could be removed by centrifugation and by ultrafiltration. In general, a far higher percentage of metal was removed by ultrafiltration than by centrifugation. Benes and Steinnes, in another paper,[107] used a variety of techniques, including electrophoresis, to measure the migration forms of trace elements in freshwaters and the effect of water storage on speciation. The electrophoretic behavior of the alkali and alkaline earth elements was as expected for simple hydrated cations, with strong mobility towards the cathode, whereas trivalent metals such as Sc, Ce, and Fe migrated to both the cathode and anode, suggesting that positively and negatively charged colloidal particles of trivalent trace elements can co-exist.[108] Zinc showed anomalous behavior in that it had low retention on a cation exchange resin. It also had a tendency to migrate to the anode. It is possible that basic carbonates (e.g., $Zn_2(OH)_2CO_3$) are significant forms of zinc in some freshwaters.[13]

Hart and Davies[109] minimized the problem of long equilibration times in dialysis by continuously pumping the dialyzate through a column of chelating resin so as to remove dialyzed metal and maintain a maximum concentration gradient across the membrane (Figure 6). In this manner, complete dialysis was achieved in 6 hr compared with the normal period of at least 24 hr.

3. Ion Exchange

Conventional cation and anion exchange resins have been used to study trace-metal speciation. Filby et al.[110] passed filtered riverwaters sequentially through anion- and cation-exchange resins. In this way, they divided dissolved metal into anionic, cationic, or neutral (adsorbed by neither resin) species. In three rivers studied, most of the zinc present was adsorbed by the cation exchanger, but in a fourth river 87% of the zinc was retained by the anion-exchange resin.

Allen[111] used the measurement of the concentration of free metal in equilibrium with a cation-exchange resin to determine the stability constants of some copper complexes with ligands of environmental significance. He proposed that an ion-exchange technique could be used to measure labile (or "available") metal in water samples.

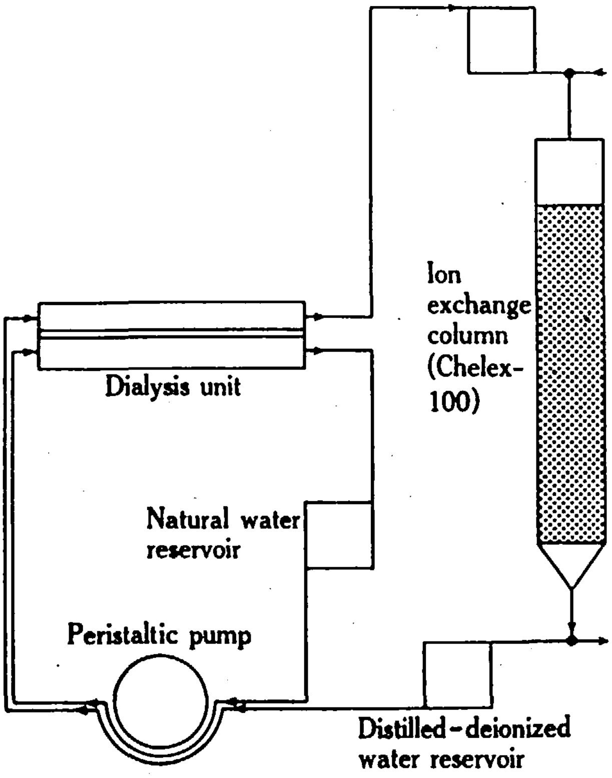


FIGURE 6. Dialysis-ion exchange apparatus. (From Hart, B. T. and Davies, S. H., *Aust. J. Mar. Freshwater Res.*, 28, 105 (1977). With permission.)

Benes and Steinnes[107] and Benes et al.[106] used strongly acidic cation-exchange membranes through which lake and river water was forced to measure cation-exchangable metal. The percentage of metal retained by the resin was compared with results obtained by dialysis and ultrafiltration on the same water samples. They suggested that the cation-exchange membrane may retain not only positively charged species, but also particulate metal forms (filtering action) and some neutral species by adsorption. However, as will be shown later, this latter error should be very small.

Marchand[112] used a strongly acidic cation-exchange resin to divide Co, Mn, Zn, Cr, and Fe radiotracers added to seawater into anionic, cationic, neutral, and colloidal species. An aliquot of seawater, spiked with the radionuclide under study, was added to the top of a cation-exchange column, then eluted with seawater. Marchand assigned neutral and negative charges to metal species which were rapidly eluted and positive charges to slowly eluted species. Metal which could be eluted only by 3 M HNO_3 was called colloidal. Marchand conceded that the results obtained by this procedure may not reflect the situation extant in seawater because the radiotracer and metal naturally present in seawater may not have reached chemical equilibrium. This is particularly likely in the case of iron and chromium.

Riley and co-workers introduced the use of chelating resins for the concentration and determination of trace metals in seawater.[113-115] Chelating resins are simpler to use and less time consuming than solvent extraction. They allow much higher concentration factors to be attained. In addition, the sample is not contaminated by heavy-metal impurities from buffers and organic reagents.

Riley and Taylor[113] showed that many metals, when added as ionic spikes to seawater at the natural pH (pH 8.2), were quantitatively retained by a column of Chelex-100[116] chelating resin. This is not the case, however, with metals which are naturally present in seawater. Riley and Taylor[114] reported that there was some initial leakage of zinc when a seawater sample was passed through a Chelex-100 column, and Muzzarelli and Rocchetti[117] found that the chelating resin removed only a small fraction of the total copper present in seawater. Florence and Batley[17,118] made a thorough study of the effects of pH and the ionic form of the resin on the retention of ASV-labile and ASV-bound species of Cu, Pb, Cd, and Zn naturally present in seawater. If the resin was initially in the H^+-form, very little metal was retained until 1 *l* of seawater had passed through, and the pH had risen to above 6.0 as a result of replacement of H^+ by Na^+, Mg^{2+}, and Ca^{2+}. When the resin was used in the Na^+- or NH_4^+-form, almost complete retention of ASV-labile metal was achieved immediately, although ASV-bound species still showed little adsorption.[17] Florence and Batley[17] suggested that most of the metal, which is electroinactive and not retained by a chelating resin column, is present in seawater as species adsorbed on, or occluded in, colloidal particles. Chelex resin has a pore size of about 1.5 nm.[33] Therefore, large molecules and colloidal particles are excluded from the resin beads and are not retained on the column. Florence[33] showed that solutions of colloidal hydrated ferric oxide and large organic dyes are quantitatively rejected by the resin. The possibility remains that some colloidal species may be adsorbed on the surface of the resin beads,[112] although this did not occur with Cu, Pb, Cd, and Zn in several fresh waters. The external surface area of a resin bead is very small compared with the internal surface area, and consequently, the adsorptive capacity of the external surface is only a small fraction of the total capacity of the resin.[119]

Figura and McDuffie,[120] using the calcium form of Chelex-100 resin, found that 22, 67, 94, and 34% of Cu, Pb, Cd, and Zn, respectively, in Susquehanna River water (pH 6.5) was retained by Chelex-100 resin, even though quantitative recovery of these metals was obtained from synthetic river water. These authors raised the possibility that slow dissociation of metal complexes in solution, rather than molecular exclusion, may be the cause of incomplete retention by chelating resins of some trace metals in natural waters. However, this cannot be the case with metal-NTA complexes because NTA complexes of Cu, Pb, Cd, and Zn are known to be very labile.[121,122] There is no doubt, though, that NTA and several other ligands, whose metal complexes should be dissociated by the iminoacetate groups of Chelex-100, do prevent uptake of the metal.[123] The explanation may lie in slow resin kinetics, although Hart and Davies,[124] using a batch-equilibration technique with Chelex-100 resin and river water, found no difference in ion-exchangeable metal (Cu, Pb, Cd, Zn, Fe) using 16 and 168 hr equilibration time.

Other chelating resins, e.g., an oxine resin,[125] have been proposed for the separation of trace metal ions, but Chelex-100 appears to be the most suitable resin for the concentration of a variety of ions over a wide pH range. The chelating ion-exchange-resin technique for the separation of ionic and colloidally associated metal has many advantages over dialysis and ultrafiltration. The procedure is simple and rapid, the equipment inexpensive, and the results are less ambiguous than those obtained using the other methods. The most important advantage, however, of the Chelex-100 technique is that there is very little likelihood of contamination of the sample. In addition, if the column effluent (i.e., colloidally associated metal) is analyzed for metal, and metal adsorbed on the resin is obtained by difference between total metal and effluent metal, then blank values are close to zero. When analyzing natural waters with very low metal concentrations, this is a most important consideration.

4. Anodic Stripping Voltammetry

ASV has been used in three distinct ways to study trace-metal speciation in natural waters. The first is where the technique is used simply as a highly sensitive analytical method for measuring total metal in various fractions of the water obtained by separation procedures such as solvent extraction[17,126,127] or ion exchange.[31] The second discriminates labile and bound metal species by taking advantage of the property of ASV that it will respond only to metal complexes which dissociate in the diffusion layer and liberate free metal ion. Labile metal is measured at either the natural pH of the sample, or after making it weakly acidic (pH 5) with CO_2 or acetate buffer. Total metal (bound metal = total minus labile) is determined after acid oxidation[3,100] or UV irradiation in acid media.[128] UV irradiation in acid media[128] is the preferred technique for destroying organic matter and liberating total metal because it avoids the high blanks associated with the use of persulfate or perchloric acid and, unlike ozone,[129] oxidizes all organic matter present. The effect of deposition potential on the labile-metal ASV peak height ("pseudopolarograms")[69] and the variation in peak height with electrode rotation speed[99,130] can be used to provide information about the dissociation kinetics of the electroactive metal complexes.

The third way in which ASV has been used to study speciation is to observe the effect of pH on peak potential and peak height.[3,131-133] From the results, estimated values can be calculated for the stability constants of the metal complexes present. ASV peak-potential shifts and pH-peak potential relationships may be useful for theoretical calculations in ideal, synthetic solutions, but it is doubtful of these methods can be extended to trace metals in natural waters. Besides having very low concentrations of the metal under study, the natural systems contain a wide variety of complexing agents so that any change in peak potential or peak current may be the result of a combined effect from several ligands. Adsorption of organic compounds on the electrode surface[134,135] and liberation of ligand in the diffusion layer[136] may also complicate interpretation of results.

ASV can be carried out using a hanging mercury drop electrode (HMDE) or a thin mercury-film electrode (TFE).[137-139] The relative advantages of these different electrode systems have been discussed by Batley and Florence.[140] In general, the TFE is more sensitive than the HMDE, but suffers more from interference effects. The use of a high-frequency technique, such as differential pulse voltammetry, is essential with the HMDE, but is optional with a TFE. A simple, rapid, d.c. scan gives excellent results with a glassy-carbon TFE,[141] but for glassy-carbon electrodes which have a high residual current because of inadequate polishing, the differential pulse mode provides flatter base lines and higher sensitivity.[142] The very slow scan rate, which must be used with commercial differential pulse instruments, is time consuming when a large number of samples must be handled. In the differential pulse mode, surface-active organic substances can produce tensammetric waves which may interfere with, or be mistaken for, metal stripping peaks.[135,143]

Although ASV is perhaps the most important analytical tool presently available for studying trace-metal speciation, its major limitation is that it can be applied to only a small number of metals, viz, Cu, Pb, Cd, Zn, and Bi, in natural waters. Some information can be obtained about the chemical states of a few other metals (e.g., Tl and Sb), but in general, speciation cannot be carried out on the full list of elements accessible by ASV[98] because their concentrations are usually too low in natural systems. Nevertheless, it is fortunate that the four toxic heavy metals of the most environmental concern, i.e., Cu, Pb, Cd, and Zn, are readily amenable to the ASV technique.[144]

V. SPECIATION RESULTS FOR SELECTED ELEMENTS

In this section, the literature on the speciation of selected elements is reviewed and discussed. Most of the important elements are covered, but no attempt was made to include an exhaustive list of references. Emphasis is on those elements which are the prime research interest of the authors, i.e., copper, lead, cadmium, and zinc.

A. Copper

Copper is naturally present in basaltic rocks, shales, clays, and to a lesser extent, in limestone, from which it is released through leaching and weathering into the aquatic environment. Copper will be transported both as dissolved species and associated with solid phases. Mobilization of copper from the latter can occur through interaction with dissolved organic matter, or, after sedimentation, as a result of changes in Eh and pH.

Man-made sources can be significant inputs in the case of copper, and not the least of these arises from copper roofing and plumbing materials. Sewage, mine waste, metallurgical processing (cyanide plating baths), together with the widespread use of copper as an algicide, pesticide, fungicide, and in marine antifouling paints, represent major inputs of copper.

The toxicity of copper to aquatic biota has been well established.[145] These studies clearly demonstrate the need for measurement of metal speciation in natural waters. There is now a weight of evidence to show the ability of organic chelators to detoxify ionic copper species.[146-148] Humic acids, glutamic acid, and EDTA, for example, were found to significantly reduce the toxicity of copper to marine bacteria,[148] while Gnassia-Barelli et al.[148] showed that natural organic substances liberated into a culture medium by certain phytoplankton species were able to complex and detoxify copper. Recent studies by Magnuson et al.[149] on the toxicity of copper to *Daphnia magna* suggest that the carbonato copper complexes were not toxic, anionic hydroxy copper complexes contributed 15 to 18% to the observed toxicity, while free copper plus neutral and cationic hydroxy complexes were responsible for 60 to 70% of the toxicity observed.

Numerous attempts have been made to model copper equilibria in natural waters using the programs described earlier.[15,17,74,83,86,150-153] Soluble copper concentrations have been assumed to be regulated by either tenorite CuO, azurite $Cu(OH)_2$, or malachite $(Cu_2(OH)_2CO_3)$. Adsorption and organic complexation, however, significantly reduce "free" copper concentrations to below those calculated on the basis of solubility data. The limitations of speciation models are best illustrated by the results for inorganic copper species in seawater summarized in Table 6. The considerable disagreement in predictions concerning the major inorganic species arises in this instance from a lack of reliable equilibrium constant data[154] and the failure to account for all competing equilibria. The model of Sibley and Morgan[83] considered SiO_2 as a typical adsorbing species and treated adsorption in the same manner as complex formation. No significant adsorption was predicted in seawater. Attempts have also been made to consider equilibria with organic species,[17,89,153] but these have usually been limited to one or two compounds either poorly representative of seawater or for which equilibrium data are suspect. Figure 7 shows the equilibrium speciation of copper as a function of salinity in a model estuary using calculations by Mantoura et al.[15] Complexation with humic substances is seen to be significant in freshwater, but with increasing salinity, competition for the humic ligand by calcium and magnesium present in high concentrations becomes significant, and the predicted copper humate species concentration decreases to 10%. Paulsen,[152] using the $K_{Cu\text{-}organic}$ data from the paper of Mantoura et al.,[15] predicted that as much as 72% of copper would be organically bound at pH 8.2 in seawater, which agrees well with experimental findings.[31,32]

Speciation models for copper in freshwater generally concur that the carbonate complex is the dominant solution species (Table 6), although Sibley and Morgan[83] predicted

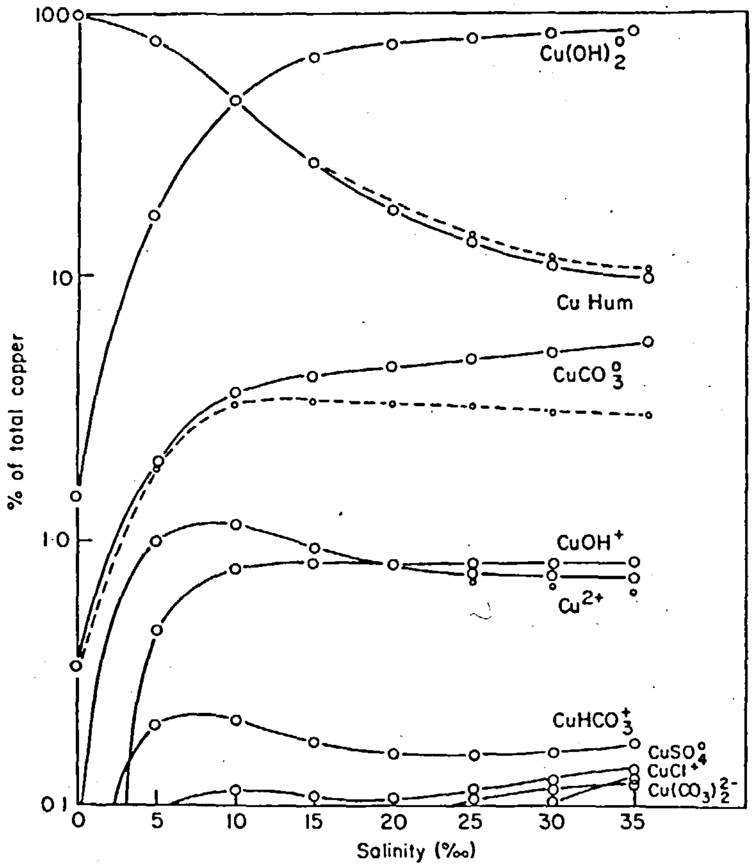


FIGURE 7. The equilibrium speciation of copper(II) as a function of salinity along a model estuary. (From Mantoura, R. F., Dickson, A., and Riley, J. P., *Estuarine Coastal Mar. Sci.*, 6, 387 (1978). With permission.)

that copper adsorbed on inorganic substances such as SiO_2 would be equally important. Adsorbed species have indeed been found experimentally as major species in freshwaters, although organic adsorbing species were more significant than inorganic species.[33]

There are still uncertainties concerning the total concentration of dissolved copper in open ocean waters. Much of the data accumulated before 1952 can be discounted because of the lack of sufficiently sensitive analytical techniques. In the ensuing 20 years, extensive measurements of near-shore and open ocean regions gave values between 0.3 and 1.7 $\mu g\ l^{-1}$.[115,155,156] More recently, the extra care needed to avoid contamination at these concentrations has been fully realized. Improved samplers and sampling techniques have been applied, and consistently lower figures are being reported.[61] Moore and Burton[157] reported values in the range 0.09 to 0.23 $\mu g\ l^{-1}$ for the Eastern Atlantic Ocean, using preconcentration of copper on Chelex-100 resin after acidification of the sample to pH 5. The inability of this procedure to recover total dissolved copper has been discussed previously.[17] Boyle and Edmond[158] obtained values of 0.07 to 0.21 $\mu g\ l^{-1}$ for waters south of New Zealand using the cobalt pyrrolidinedithiocarbamate coprecipitation method. Bender and Gagner[57] reported similar values for the Sargasso Sea. A study by Boyle et al.[159] of the North Pacific showed a decrease in copper with depth from a surface maximum of about 0.19 $\mu g\ l^{-1}$ to 0.10 $\mu g\ l^{-1}$ in the

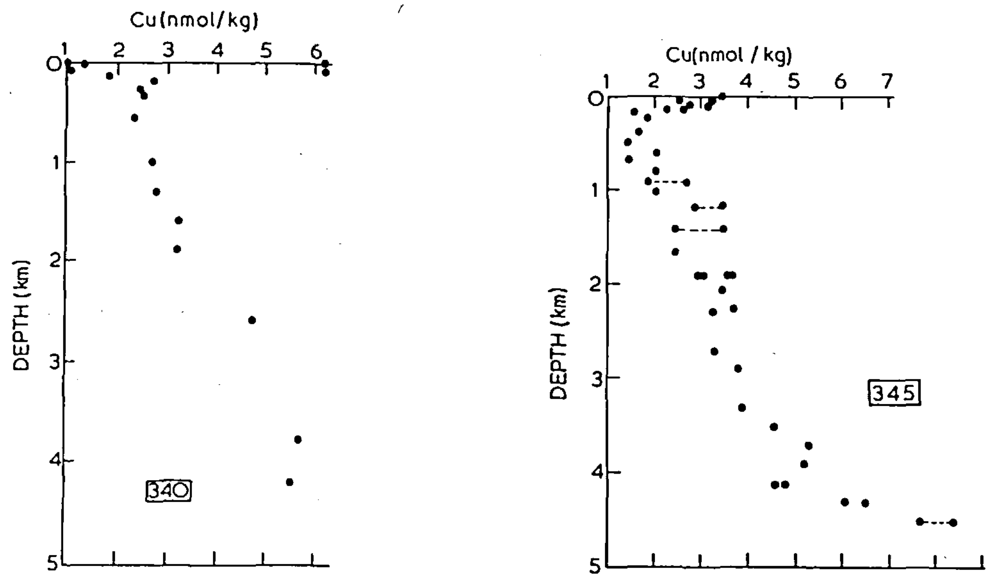


FIGURE 8. Depth profiles of dissolved copper at several Geosecs Pacific Stations. (From Boyle, E., Sclater, F. R., and Edmond, J. M., *Earth Planet. Sci. Lett.*, 37, 38 (1977). With permission.)

upper thermocline, then increasing below 750 m to over 0.40 $\mu g\ \ell^{-1}$ in bottom waters (Figure 8). The results indicate an aeolean input to surface waters, scavenging by sinking particles in subsurface and deeper waters, but a strong source of copper near the sediment surface.

There have been many attempts to measure copper species in waters, the simplest distinction being that between dissolved ionic and organically associated copper, the latter measured after UV irradiation by the same procedure used to measure ionic copper, i.e., diethyldithiocarbamate or ammonium pyrrolidinedithiocarbamate extraction. However, it should be remembered that these extractants will also dissociate weakly bound complexes.[160] Williams[101] reported increases of between 0 and 28% in extractable copper released as a result of UV irradiation. There is now increasing evidence to demonstrate that a significant proportion of the total dissolved copper in seawater is associated with organic matter.[30-32,101,126,160,161] There are still, however, no precise data on the nature of these organic species. The main source of dissolved organic matter in the oceans is considered to be phytoplankton,[162] with many of these species able to complex copper.[148] Foster and Morris[160] found bound copper in water from the Menai Straits amounting to 6 to 40% of total copper. There was no correlation with dissolved organic carbon content, but the variations were attributed at least partially to active marine production. Slowey et al.[30] showed that up to 60% of copper was extracted with chloroform from filtered seawater. This technique probably gives low results for organically bound copper since charged copper complexes would not be extracted, while copper adsorbed on colloids would only partially extract. Complexes were assumed to involve phospholipids, amino lipids, or the porphyrin fraction of lipids.

Possibly the simplest, and indeed most useful, method of speciation is the discrimination between labile- and bound-metal species as measured by anodic stripping voltammetry. Labile metal will include free ionic copper, simple inorganic or organic complexes, such as carbonate or citrate complexes of copper, together with labile copper associated with colloidal species, such as hydrated ferric oxide, clays, or humic acids. These species will dissociate and deposit during electrolysis. It is likely that this

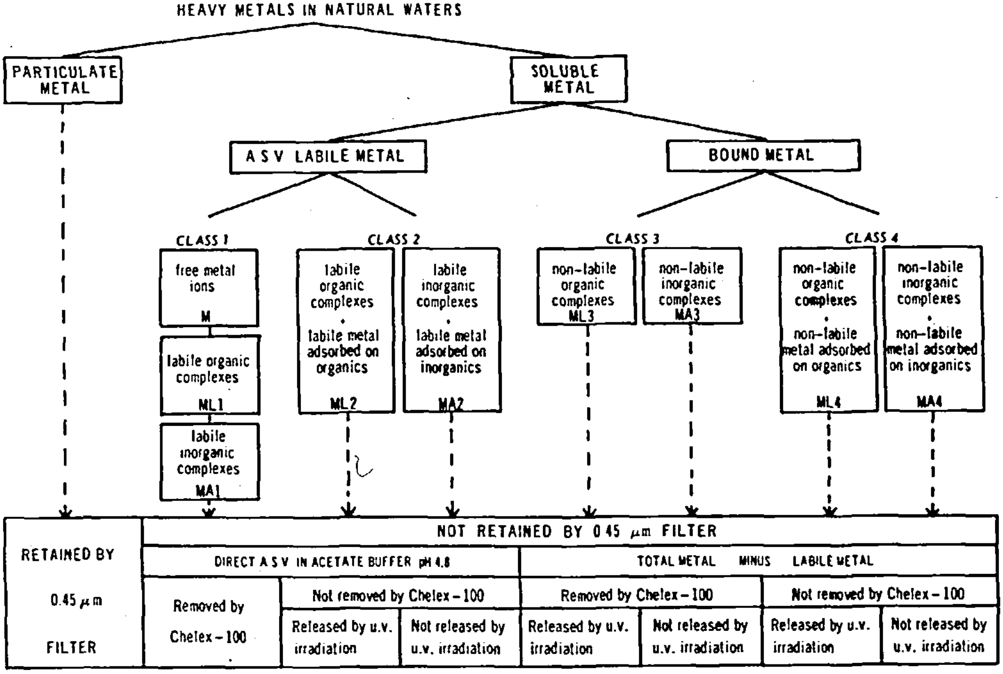


FIGURE 9. Analytical scheme for chemical speciation of trace metals in natural waters. (From Batley, G. E. and Florence, T. M., *Anal. Lett.*, 9, 379 (1976). With permission.)

labile class could prove to be a more reliable index of toxicity than copper activity measured by an ion-selective electrode since it more closely represents available metal. The labile fraction is, however, an operationally defined parameter.[17,100] Most workers choose to measure labile species in the presence of an added acetate buffer of pH 5 when the sensitivity and resolution of the stripping peaks is greatest. Above this pH, the loss in sensitivity is due to the presence of electroinactive species, such as metal carbonate species which are dissociated at pH 5. In freshwater samples, some electrolyte addition is essential to increase the solution conductivity. At pH 5, however, dissociation of some weak metal complexes will occur, although this is the optimum pH for formation of many complexes. In addition, there may be slow desorption of adsorbed zinc or cadmium, but not copper, lead, iron or chromium (Figure 1), while the added acetate will complex free metal ions. Gaseous carbon dioxide has been used as an alternative buffering system by some workers.[163] Total metal is measured after either acid digestion or, preferably, UV irradiation of the acidified sample.

In more acid solutions, the dissociation of organic complexes will occur more readily. Duinker and Kramer[126] and Fukai and Huynh-Ngoc[127] have used the difference between ASV measurements at pH 2 to 3 and pH 8.1 in studies of metal speciation in seawater. The assumption was that measurements at pH 8.1 include all inorganic complexes, whereas the increase in the labile fraction produced on acidification arises from organic complexes which will be completely dissociated. Studies by Batley and Florence,[31] Florence,[33] and Batley and Gardner[32] illustrate the shortcomings of these assumptions, since not only are many organic metal species labile at pH 8.1, but many inorganic metal species are made labile at pH 2 to 3.

The use of the labile-bound metal discrimination at pH 4.8 has been combined with a number of separations and solution treatments to provide a more comprehensive breakdown of metal species in a scheme described by Batley and Florence[31,164] (Figure 9).

Table 8
SCHEME FOR HEAVY METAL SPECIATION

		Measured in solution after treatment	
Treatment	Effect of treatment	a. Labile metal	b. Total metal
Measurements			
1. Filtration (0.45 μm)	Removes particulate metal	M, ML_1, ML_2, MA_1, MA_2	M, ML_1, ML_2, ML_3, ML_4 MA_1, MA_2, MA_3, MA_4
2. Chelex-100	Removes M, ML_1, ML_3, MA_1, MA_3	ML_2 MA_2	ML_2, ML_4 MA_2, MA_4
3. UV	Releases metal from ML_1, ML_2, ML_3, ML_4	M, ML_1, ML_2, ML_3, ML_4 MA_1, MA_2	M, ML_1, ML_2, ML_3, ML_4 MA_1, MA_2, MA_3, MA_4
4. UV, Chelex-100	Removes metal released from ML_1, ML_2, ML_3, ML_4	MA_2	MA_2, MA_4

Note: Calculations:

$$M + ML_1 + MA_1 = 1a - 2a$$

$$MA_2 = 4a$$

$$MA_4 = 4b - 4a$$

$$ML_2 = 2a - 4a$$

$$ML_4 = 2b - 2a - [MA_4]$$

$$MA_3 = 1b - 3a - [MA_4]$$

$$ML_3 = 3a - 1a - [ML_4]$$

From Batley, G. E. and Gardner, D., *Estuarine Coastal Mar. Sci.*, 7, 59 (1978). With permission.

Measurements were made of (1) ASV labile and (2) total metal. Each was performed (1) before treatment, (2) after passage through a Chelex-100 column, (3) after UV irradiation, and (4) after passage of the UV irradiated sample through the Chelex-100 column.[31] From these eight measurements, metal concentrations were obtained, each of which included different combinations of seven heavy metal species as shown in Table 8. These operationally defined species are as follows (where the suffixes L and A refer, respectively, to organic or inorganic species).

1. M + ML1 + MA1 — Free metal ions and inorganic or organic complexes which are readily dissociated, i.e., ASV labile, under the measurement conditions. In seawater at natural pH, this group will consist principally of simple inorganic complexes such as chloride, sulfate, and hydroxide. In freshwater, citrate and amino-acid complexes may be present.
2. MA2, MA4, ML2, ML4 — Since significant concentrations of metal complexes stronger than the corresponding metal-Chelex-100 complexes are unlikely to be present in seawater, these species would be mainly metal adsorbed on, or oc-

cluded in, organic and inorganic colloidal particles. The situation may be different in freshwater, which generally has a higher organic content, and hence, possibly higher concentrations of strongly chelating organic ligands such as humic and fulvic acids.

3. **MA3, ML3** — Nonlabile organic and inorganic complexes which are dissociated on passage through Chelex-100. These could include metal complexes of cysteine, nitrilotriacetic acid, soluble metal sulfides, or silicates.

There is undoubtedly some overlap between the experimental classes determined in this speciation scheme. The MA3 and ML3 species may also include some metal dissociated from colloids and retained by the resin. This group could also include some of the humic and fulvic acid complexes, which should be at least partially dissociated by Chelex-100 resin.

Data obtained using this scheme indicated that between 30 and 80% of total copper in a coastal seawater sample was organically associated. Up to half of this was present as soluble nonlabile complexes, while the remainder was associated with colloidal organic species such as humates and organic detritus.[32] These results are supported by the findings of Slowey and Hood[165] that high percentages of copper in seawater are nondialyzable.

The isolation of humic materials from sea, river, and lake waters has been achieved by Mantoura et al.[15] by adsorption at pH 2.2 onto Amberlite XAD-2 resin. This technique formed the basis of the scheme used by Montgomery and co-workers[166,167] to separate copper species in tropical rivers of western Puerto Rico. An ionic fraction was retained on Chelex-100, while organic complexes collected on the XAD-2 column. The per cent coefficient of variation in the latter step was high (21%), most likely as a result of the high blanks associated with the wet-ashing treatment of the resin needed to remove adsorbed organic complexes. The means of results for the Guanagibo River were 0.5 $\mu g\ \ell^{-1}$ for ionic copper and 0.4 $\mu g\ \ell^{-1}$ for organic copper. It is unlikely that either resin would remove colloidally associated copper species, either organic or inorganic, on the basis of results of Batley and Gardner[32] and Florence[33] for Chelex-100.

Studies of other estuarine samples indicate a similar high organic species concentration. Blutstein and Smith[168] found up to 74% of total copper from the Yarra River (Australia) in an organically bound form. In surface waters above the halocline, bound copper figures correlated well with organic carbon. For the same river, Hart and Davies[109] reported a large nondialyzable component.

Changes in species distribution at sampling sites within the Port Hacking Estuary (Australia) were studied by Batley and Gardner.[32] While in marine-dominated stations, copper was distributed principally between inorganic and organic colloidal species, in a low-salinity area the concentrations of soluble and colloidal inorganic species were significantly higher. Samples from an anoxic basin showed lowered total copper with high colloidal inorganic species, possibly copper sulfide, and high soluble organic complexes attributed to organosulfides released from sediment. High concentrations of soluble inorganic complexes were attributed to antifouling paints in water from a marina.

In freshwater rivers and reservoirs, Florence,[33] using the same scheme, observed high levels of copper associated with organic colloids. In these systems, humic, fulvic, and tannic acids, comprising the bulk of organic matter in soils and sediments, are particularly important as metal complexing agents, as shown by Mantoura et al.[15] Their molecular weight fractions, as separated by ultrafiltration, can be tested for copper complexing capacity. Giesy and Briese[169] observed an even distribution of copper complexing humates over molecular weights up to 300,000 for some soft, high-organic waters. The removal of metal species by cation exchange, anion exchange, and chelat-

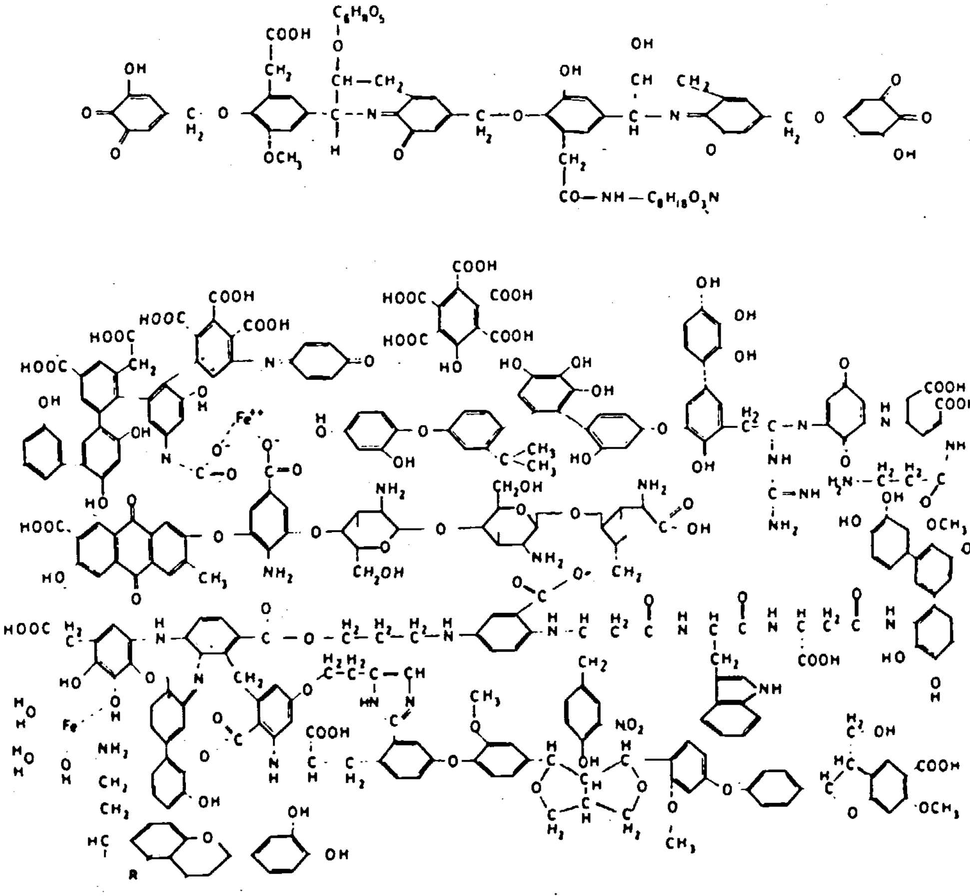


FIGURE 10. Proposed structures of humic acids. (From Rook, J. J., *Environ. Sci. Tech.*, 11, 478 (1977). With permission.)

ing resins was also studied.[169] However, the interpretation of these results in terms of metal species is extremely tenuous. The authors attributed the large anion-exchangeable copper concentration to organically bound species since it was assumed that anionic inorganic species would be absent at the low pH of the samples studied. Smaller, but similar, concentrations were removed by both the chelating and cation exchange resins, possibly representing only inorganic species. Some organic complexes are presumably too large to enter the pore network of the chelating resin. Humic acid-type molecules containing a multiplicity of binding sites[170]would fit into this category (Figure 10), and the bonding may vary between pure electrostatic and covalent bonds. As with other organic ligands, humic acid complexes of copper will be more stable than those of other transition metals.

Smith[105] used ultrafiltration to measure copper complexing capacity of samples from a Georgia estuary. The concentration of dissolved organic matter decreased with increasing salinity. In the higher salinity stations, a greater proportion of organic matter was associated with low molecular weight species (<100,000). These species also had the highest copper complexing capacity. The measurement of complexing capacity can provide useful information about the ability of a water body to accept and detoxify added ionic copper.

In freshwater systems, the suspended load can also contain high concentrations of inorganic species. These will comprise mainly clay minerals (gypsum, dolomite, illite, and kaolinite) together with colloidal iron and manganese oxides. Colloidal species will be present in the fraction which passes a 0.45 μm filter. Florence,[33] however, reported no copper associated with inorganic colloidal species, although in estuarine samples up to 40% of the total copper was so combined.[32] Considerable flocculation of dissolved iron, manganese, phosphorus, and aluminum takes place in the estuarine zone.[51] These precipitating species will almost certainly be ideal adsorption sites for charged chloro and hydroxy copper species, thus facilitating their removal from solution, and will include a range of particle sizes including a colloidal fraction.

Stiff[171] presented a comprehensive scheme for the chemical speciation of dissolved copper in polluted freshwater. The analysis scheme involves the following operations:

1. Measurement of the free cupric ion activity with a copper ion-selective electrode.
2. After measurement of the pH and bicarbonate concentrations, calculation of the concentration of $CuCO_3$ from the known equilibrium constant.
3. Determination of copper complexed by "cyanide-like" ligands from the difference between spectrophotometric copper determinations using neocuproine after nitric acid digestion, and the reagent 3-propyl-5-hydroxy-5-D-arabino-tetrahydroxybutyl-3-thiazolidine-2-thione (PHTTT) directly. Cyanide and other powerful ligands interfere quantitatively in the reaction between copper and PHTTT, whereas neocuproine, after acid digestion, gives total copper.
4. Extraction of the water with hexanol. Hexanol-soluble copper was assumed to be associated with humic substances.
5. Ascription of the difference between total copper and Cu^{2+} + $CuCO_3$ + Cu-cyanide complexes + Cu-humic complexes to copper present as amino and polypeptide complexes, and carbonate complexes other than $CuCO_3$.

Stiff[171] applied this scheme only to polluted waters containing 100 to 1000 μg ℓ^{-1} levels of copper, i.e., copper concentrations two orders of magnitude higher than those found in most natural waters. Considerable modification would be necessary before it could be used at natural levels of copper. Also, several questionable assumptions were made, e.g., in the calculation of $CuCO_3$ concentration, in the description of all hexanol soluble copper as being complexed by humic substances, and in assigning all remaining copper to amino and polypeptide complexes.

B. Lead

Lead is toxic towards aquatic life, although its toxicity is less than that of copper. Lead produces structural alterations in chromosomes and binds strongly to mitochondrial membranes.[172] Davies et al.[9] found that lead was toxic to rainbow trout in both soft and hard water. The maximum acceptable lead concentration for chronic exposure in soft water was found to be 4 to 8 μg ℓ^{-1} when lead exposure was initiated at the eyed-egg stage of development. Acute toxicity was caused by 1.0 to 1.5 mg ℓ^{-1} of dissolved lead. Ionic lead (measured polarographically) was the active form of the element. Colloidal lead species were innocuous and caused no fish mortalities during an 8-day bioassay procedure. In the hard-water experiments, Davies et al.[9] calculated that the solubility of lead would be 30 μg ℓ^{-1}, in approximate agreement with Hem and Durum,[173] and assumed that higher concentrations would exist as colloidal and precipitated forms. Atomic absorption spectrophotometric analysis of the waters measured dissolved plus a fraction of the colloidal and precipitated lead forms present

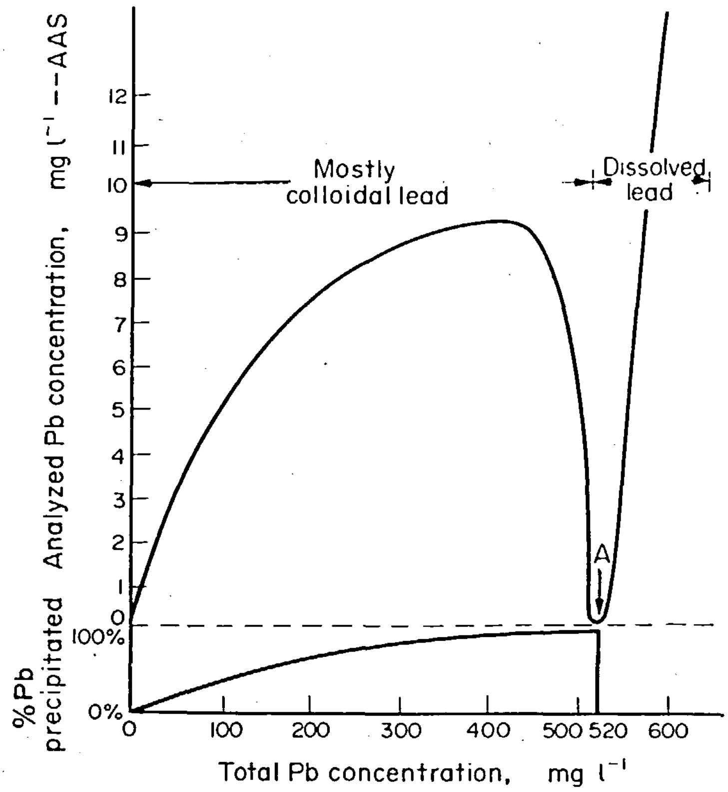


FIGURE 11. Determination of synthetic solutions of lead in a hard water using atomic absorption spectrophotometry. Point "A" indicates the lead concentration at which the carbonate buffering system of the water is essentially eliminated. (From Davies, P. H., Goettl, J. P., Sinley, J. R., and Smith, N. F., *Water Res.*, 10, 199 (1976). With permission.)

(Figure 11). The 520 mg l^{-1} concentration, shown as point A in Figure 11 (Davies et al.[9]) corresponds approximately to that concentration at which sufficient lead was added to eliminate the carbonate buffering capacity of the water.

Merlini and Pozzi studied the effect of lead on sunfish[174] and immature goldfish[8] using an ion-selective electrode to determine ionic lead. They found that total lead concentrations of 40 and 500 $\mu g\ l^{-1}$, when added to Lake Maggiore (North Italy) water, were nontoxic to sunfish and goldfish, respectively. However, only 8% of the 500 $\mu g\ l^{-1}$ total lead (added as nitrate) remained in the ionic state. The remainder was converted to unreactive chemical forms. It was shown that the fish accumulate only ionic lead, and that as the pH of the lake water was lowered and the fraction of ionic lead increased, the lead concentration factors in the fish also increased. Merlini and Pozzi[174] showed that greatest lead accumulation occurred in the gills, fins, and liver of the fish, with the lowest concentration being in the edible portion, the muscle.

Accepted values for the total concentration of lead in natural waters have changed dramatically as a result of the meticulous and painstaking work of Patterson and coworkers.[60,175-181] Using stable-isotope dilution-spark-source mass spectrometry, Patterson showed that all results previously reported for the concentration of lead in seawater and marine organisms were high, often by orders of magnitude. These high results were caused by gross contamination with industrial lead during sampling and/or analysis.[60] Failure to understand the basic principles of atomic absorption spectrophoto-

Table 9
LEAD IN CANNED TUNA. COMPARISON OF RESULTS FROM CALIFORNIA INSTITUTE OF TECHNOLOGY (CIT) AND FEDERAL SURVEILLANCE LABORATORY (FSL)

Type of tuna muscle	Reported lead content (μg kg^{-1} fresh weight)
Prehistoric tuna in sea	0.07 (estimated)
Present-day tuna in sea	0.3 (CIT)
Present-day tuna in sea	400 (FSL)
Tuna in Pb-soldered can	1400 (CIT)
Tuna in Pb-soldered can	700 (FSL)

From Burnett, M. and Patterson, C., in *Proceedings of an International Experts Discussion on Lead: Occurrence, Fate and Pollution in the Marine Environment,* Branica, M., Ed., Pergamon Press, Oxford, in press. With permission.

metry still occasionally leads to the publication of high results for lead and other trace metals when water samples are aspirated directly into the flame and adsorption readings are not corrected for nonatomic absorption.[182,183] Because of its apparent simplicity, atomic absorption spectrophotometry can be a dangerous tool in the hands of operators who are not professional analytical chemists.

Burnett and Patterson[181] pointed out one example where analytical contamination can lead to dangerously incorrect conclusions. A study was carried out by a U.S. Federal Surveillance Laboratory on behalf of the U.S. Food and Drug Administration to determine the extent of contamination of canned tuna by lead from the solder used in the cans. Because the laboratory carrying out the analyses badly contaminated the fresh, uncanned tuna used as a comparison sample, it was concluded that lead-soldered cans increase the lead content of tuna by a factor of less than 2 (Table 9). In fact, canning the tuna increases its lead concentration from 0.0003 μg g^{-1} (fresh weight) to 1.4 μg g^{-1}, an increase of 5000 fold (Table 9). Burnett and Patterson concluded that fish muscle is one of the purest foods available with respect to lead content.

Schaule and Patterson[179] showed that the concentration of lead in seawater decreases sharply at depths below 400 m (Figure 12), in contrast to metals such as barium, cadmium, and zinc which follow the concentration of certain nutrients and increase with depth. Schaule and Patterson believe that the high concentration of lead in surface waters is a result of industrial pollution, originating principally from the combustion of leaded gasoline fuels.

Errors caused by contamination during sampling and analysis throw serious doubt on results so far reported for lead speciation in natural waters. The possibility exists that many of the studies reported in the literature are invalid because the results relate not to the speciation of lead naturally present in the waters, but to the speciation of industrial lead inadvertently added to the sample as contamination. This possibility must be kept in mind when considering the results reviewed in this Section.

Many computer models have been designed for the speciation of lead in both seawater and freshwater.[17,80-83,86-88,184] In seawater, $PbCO_3$ (83%) and lead chloro com-

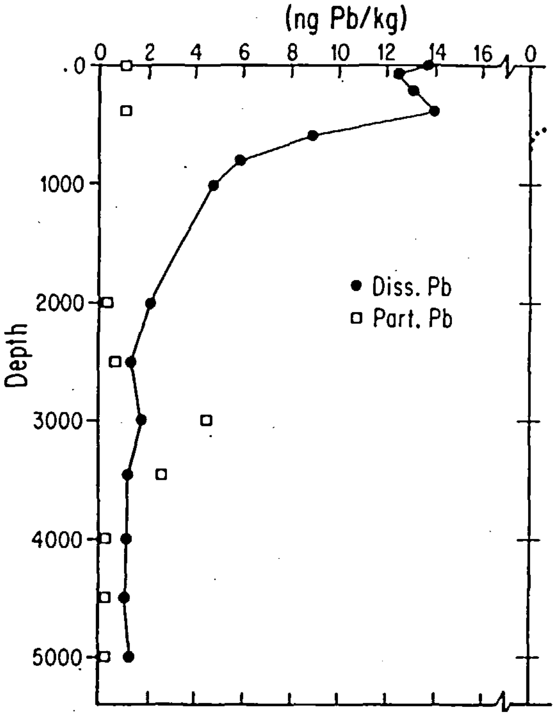


FIGURE 12. Concentration-depth profile for lead in central northeast Pacific Ocean. (From Schaule, B. and Patterson, C., in *Proceedings of an International Experts Discussion on Lead: Occurrence, Fate, and Pollution in the Marine Environment*, Branica, M., Ed., Pergamon Press, Oxford, in press. With permission.)

plexes are computed to be the predominant inorganic complexes, while in a typical freshwater (oxidizing conditions, pH 8) the major form is $PbCO_3$ with 1 to 2% of Pb^{2+} and $PbOH^{+}$[81,83] (Table 10). Lead carbonate is, therefore, considered to predominate in all natural waters,[69] with the exception of anoxic waters where lead sulfide may exist.[81] These calculations do not take into account the possibility that other, more complex inorganic forms of lead, e.g., $Pb_2(OH)_2CO_3$, may be present. Only lead complexes whose thermodynamic stability constants are known are included in the calculations. The presence of powerful organic complexing agents in a freshwater could alter the speciation considerably.[28,29] Morel et al.[81] showed that 1×10^{-5} *M* NTA added to a typical freshwater (pH 7) would complex essentially all the lead present. Cornroot exudate can form strong soluble complexes with lead,[185] and may by solubilizing lead, promote its uptake by the plant and produce detrimental effects. Inorganic lead, like mercury, can be methylated by microorganisms in sediments to form compounds such as Me_3Pb^+ and Me_4Pb,[186] although the biological conversion to alkyl compounds is apparently a more difficult process for lead than for mercury. The toxicity of Me_4Pb is about 20 times that of Pb^{2+}.

Lead adsorbed on inorganic colloidal particles should be an important dissolved species of lead, since, at the pH of natural waters, Pb^{2+} is strongly adsorbed on hydrated ferric oxide,[40] manganese dioxide,[45] silica,[36] alumina,[36] and soil minerals.[36] Lead carbonato complexes are adsorbed even more strongly than Pb^{2+}.[187] The computer model of Sibley and Morgan,[83] which used silica as a model adsorbent, plus the James and Healy[53] treatment of adsorption, predicted that in a typical freshwater (pH 8)

Table 10
COMPUTER MODELING RESULTS FOR THE SPECIATION OF LEAD IN SEAWATER AND FRESHWATER

Lead species	Species (%)			
	Seawater			Freshwater[a]
	Ref. 83	Ref. 86	Ref. 79	Ref. 83
Pb^{2+}	1.6	1.7	0.8	1.0
Pb-chloro	51.4	18	13	—
$PbSO_4^0$	0.6	0.7	1.3	—
$PbOH^+$	1.6	1.5	1.4	1.9
$Pb(OH)_2^0$	1.6	—	0.1	1.9
$PbHCO_3^+$	44.8	0.5	0.2	91.1
$PbCO_3^0$	44.8	77.6	83.2	91.1[b]

pH 8.0.

Inorganic colloids showed 6% adsorbed.

about 6% of total lead would be adsorbed on inorganic particles, whereas in seawater, because of chloride complexing of lead and competition by Na^+, Ca^{2+}, and Mg^{2+} for adsorption sites, no adsorption of lead would take place.

Florence and Batley[17,118] used a chelating resin column to distinguish between lead species in seawater. In four samples of seawater studied, 16, 20, 52, and 53% of total lead present was not adsorbed by the resin and passed through the column. It was suggested that this inactive lead was associated with organic and inorganic colloidal particles. Florence and Batley[17] also found that APDC extraction of seawater at pH 4.5 extracted only 35 to 65% of total lead, but when the sample was first heated at pH 0.7, then adjusted to pH 4.5, complete extraction of lead was achieved.

The ASV speciation scheme devised by Batley and Florence,[31] involving preliminary UV irradiation and chelating resin steps (Section 5.1), was applied to the speciation of lead in seawater[32,188] and freshwater.[33] In seawater and estuarine water a high proportion of dissolved lead (40 to 80%) with colloidal inorganic particles, while a smaller fraction (10 to 35%) was adsorbed on organic colloids. Labile (ionic) lead represented 10 to 40% of the total, while molecular organic and inorganic lead complexes accounted for 0 to 20% and 0 to 30%, respectively. Seawater samples taken in the vicinity of a marina showed a high total lead concentration which was associated principally with colloidal organic matter, possibly from oil or gasoline pollution.[32]

For a series of low-pH (pH 6.0), low-hardness lake and river waters, Florence[33] found that the predominant form of lead was an MA3 form, i.e., an inorganic molecular lead species which is electroinactive, but which is dissociated and adsorbed on a chelating resin column. It is possible that this MA3 lead species is a basic carbonate, e.g., $Pb_3(OH)_2CO_3$. In these low pH waters, no lead was present as species adsorbed on inorganic colloids (Table 10). This result was expected, because adsorption of lead onto most inorganic adsorbents only occurs at pH values above 6.0 (Table 4).

Florence and Batley[17,118] and Batley and Florence[31] found that ionic lead spikes added to seawater at the natural pH did not equilibrate immediately with the pool of natural lead species present in seawater. After 3 days, only 20 to 50% of the added spike had chemically exchanged. Matson et al.[189] found that even at pH 2 ionic lead added to a sample of rainwater (containing 40 μg Pb l^{-1}) from urban Chicago took 40 to 50 min to reach chemical equilibrium. Catanzaro[190] used isotope-dilution mass spectrometry to study the chemical exchange of copper and lead in samples of Hudson River water. He found that the copper spike achieved equilibrium after 20 days, but that lead was still exchanging after 30 days. Analytical chemists should always be aware that the recovery of trace metals from natural waters cannot be determined by measuring the recovery of an ionic spike unless the water has first been treated to convert all forms of the metal to ionic metal.

The ASV wave for lead in seawater of natural pH (pH 8.2) is very small compared with the wave obtained at a pH less than 4,[17] and Petrie and Baier[191] concluded that this effect was due principally to the electroinactivity of the $PbOH^+$ species, since their simple speciation model for lead in seawater indicated that over 90% would be present as $PbOH^+$ at pH 8.2. However, recent computer models of seawater and freshwater show that the predominant lead species is in fact $PbCO_3$ (Table 10). Reinterpretation of Petrie and Baier's results suggests that the electroinactive form of lead is $PbCO_3$, or possibly $Pb_2(OH)_2CO_3$.

Chau and Lum-Shue-Chan[100] carried out a simple ASV labile-bound discrimination for Cu, Pb, Cd, and Zn in lake waters. Labile metal was determined in acetate solution, and total metal after persulfate oxidation. In all but one of the 17 lakes studied, all the lead was present in bound form. The lakes had relatively low pH (pH 4.4 to 6.9), but a high complexing capacity (about 0.4 μmol Cu^{2+} ℓ^{-1}) This is indicative of strong metal binding agents present in the samples.

Duinker and Kramer[126] analyzed seawater samples from the North Sea and seawater/freshwater mixtures from the Rhine River for several metals, including lead, using ASV and APDC-MIBK extraction followed by atomic absorption spectrophotometry. The results are shown in Figure 13. The high lead concentrations found in acidified North Sea samples (2 to 3 μg ℓ^{-1}) seem very doubtful. Duinker and Kramer discounted the possibility of contamination and suggested that the acid-soluble lead may be colloidal lead oxide. It seems more likely, however, that in some way or other the seawater samples were contaminated with lead.

Hart and Davies[124] and Blutstein and Smith[168] studied the chemical forms of some trace metals in the Yarra River and its estuary. The Yarra River is fairly polluted, and Hart and Davies found total dissolved lead concentrations as high as 17 μg ℓ^{-1}. Approximately 43% of this lead did not adsorb on Chelex-100 chelating resin and was recorded as bound lead. Blutstein and Smith measured lead by ASV before and after UV irradiation. They found that in samples of high salinity, lead gave normal ASV waves, and increased lead peak heights were obtained after irradiation. In the low-salinity samples, however, no lead waves appeared unless the samples were acidified after UV irradiation. It is probable that at the natural pH of the samples, lead is adsorbed on colloidal inorganic material (e.g., hydrated ferric oxide) and requires acidification to be released.

C. Cadmium

The occurrence, distribution, and toxicity of cadmium have been well documented.[192] An EIFAC Working Party on Water Quality Criteria has reviewed the literature on cadmium toxicity to freshwater fish and has recommended maximum concentrations of total soluble cadmium for rainbow trout and perch.[193] This working party stated that a substantial proportion of the cadmium in river water is adsorbed on suspended solids, but that only the soluble forms of cadmium are toxic to fish. Giesy et al.[10] studied the toxicity of soft well water and highly organic pond water to zooplankton and fish. In addition, organic matter from the pond water was separated into molecular weight fractions by ultrafiltration, and its effect on toxicity was determined when it was added to well water. Giesy et al.[10] found that cadmium toxicity

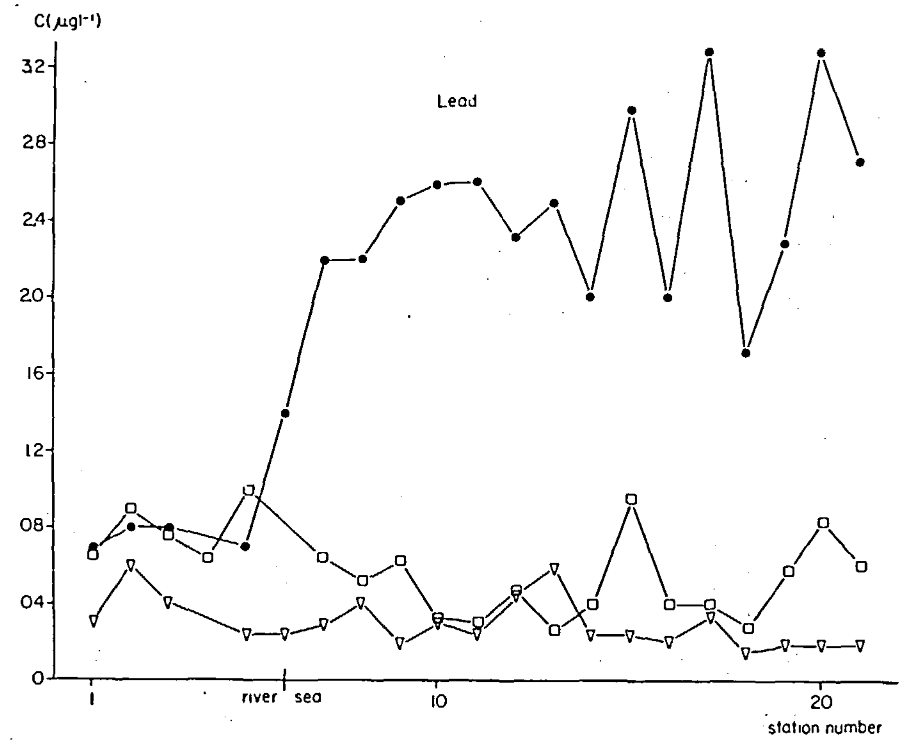


FIGURE 13. Concentrations of dissovled lead in Rhine River and North Sea waters. Increasing salinity from station 1 to 20. Station 1 essentially freshwater, stations 7 to 20 essentially seawater. •, Differential pulse anodic stripping voltammetry (DPASV) at pH 2.7; ∇, DPASV at pH 8.1 (seawater) or pH 7.0 (riverwater); □, atomic absorption spectrophotometry after APDC-MIBK extraction. (From Duinker, J. C. and Kramer, C. J., *Mar. Chem.*, 5, 207 (1977). With permission.)

cannot be predicted from ion-selective electrode measurements of free Cd^{2+} activity, and that the larger molecular weight fractions of organic matter from pond water reduced the toxicity of cadmium to zooplankton, but had little effect on the fish. The toxicity of cadmium to aquatic organisms appears to be more complicated than some other metals.[193;194]

The distribution of cadmium in the open Pacific Ocean has been investigated by Boyle et al.[195] and Martin et al.[196] Cadmium concentrations increase from about 0.01 $\mu g\ l^{-1}$ at the surface to 0.1 $\mu g\ l^{-1}$ below 1 km. They bear a conservative relationship to phosphate and nitrate concentrations. In a single sample taken from the Amazon River, Boyle et al.[195] found 0.07 $\mu g\ l^{-1}$.

Computer modeling results for cadmium speciation in seawater and in a typical freshwater are shown in Table 11. Cadmium forms relatively strong chloro complexes which predominate in seawater. In freshwater, cadmium is predicted to exist principally as the free Cd^{2+} ion and carbonato complexes. Sibley and Morgan[83] calculated that in seawater no cadmium would be adsorbed on inorganic colloids and that less than 1% would be adsorbed in a freshwater of pH 8 (Table 11).

Raspor et al.,[197] using pulse polarography, showed that NTA concentrations in seawater would have to be above 10^{-5} *M* before a significant percentage of the cadmium would exist as NTA complexes. Gardiner,[14,198] on the other hand, demonstrated that in fresh waters, humic compounds and suspended muds have the ability to adsorb ionic cadmium strongly. Under certain circumstances, calcium carbonate was also

Table 11
COMPUTER MODELING RESULTS FOR THE SPECIATION OF CADMIUM IN SEAWATER AND FRESHWATER

Cadmium species	Species (%) Seawater Ref. 83	Ref. 86	Ref. 79	Freshwater[a] Ref. 83
Cd^{2+}	2.6	2.5	0.7	7.8
Cd-chloro	96.3	95.8	94.8	0.3
$CdSO_4^0$	0.3	0.5	0.6	0.1
$CdOH^+$	—	0.1	0.1	—
$Cd(OH)_2^0$	—	—	—	—
$CdHCO_3^+$	0.8	0.1	0.1	91.8
$CdCO_3^0$	0.8	1.0	1.7	91.8

[a] pH 8.0.

found to coprecipitate cadmium. Gardiner found rapid adsorption of cadmium onto mud solids with concentration factors of 5,000 to 50,000. He suggested that it is humic substances in mud which bind cadmium and that adsorption onto suspended mud is a major factor in controlling cadmium concentrations in fresh waters.[29,199] Mantoura et al.[15] measured the stability constants of cadmium with humic acid from a variety of sources and, although the complexes were quite strong ($\log K_o = 4.6$ to 5.1), a computer model of a typical lake water predicted that only 2.7% of cadmium would exist as a humic complex. In seawater, less than 0.1% of total cadmium should be present as humates. These models did not, however, take into account possible adsorption of cadmium onto humic material existing as a colloidal suspension, which, in view of Gardiner's work[14] may be an important sink for cadmium. Martin et al.[196] showed that plankton also strongly adsorbs cadmium in seawater.

Benes and Kopicka[200] investigated the state of cadmium in aqueous solution using dialysis, centrifugation, and electrophoresis. Because the experiments were carried out in triply distilled water, the results are not necessarily directly applicable to natural waters. They found that 5×10^{-7} *M* cadmium was completely dialyzable as long as the pH of the solution was less than 7. However, the experiments were complicated by the strong adsorption of cadmium on the dialysis membranes and the walls of the cell. Centrifugation and electrophoresis showed that pseudocolloids (cadmium adsorbed on colloidal impurities) may form at pH values as low as 5. These colloids are positively charged below pH 10.5, and their abundance and properties depend on the age and concentration of the solution. Cadmium may be desorbed from these colloids at a dialysis membrane surface and pass through the membrane. Adsorption onto glass and plexiglass at pH 7 to 8.5 was rapid when no electrolyte was present, but in 0.1 *M* $NaNO_3$, no adsorption took place below pH 8.5 for glass and pH 7.5 for plexiglass. In the pH range of 9.5 to 13, strong adsorption occurred in all solutions.

Baric and Branica[201] and Bubić and Branica[202] studied the ionic state of cadmium in seawater using electrochemical techniques. Baric and Branica made use of polarography with a dropping mercury electrode and a cadmium amalgam electrode to deduce that the principal cadmium ion in seawater is $CdCl^+$. Bubić and Branica constructed "pseudopolarograms", i.e., plots of ASV peak current vs. deposition potential, of cadmium in chloride media. They showed that in 0.55 *M* NaCl (equivalent to seawater) and in waters with chloride higher than 3×10^{-2} *M*, $CdCl^+$ is a major species. The interpretation of pseudopolarograms is, however, not straightforward, and the electrode reactions involved should be thoroughly understood before conclusions are drawn from the curves.[69]

The experimental determination of cadmium speciation in natural waters is made very difficult by the exceptionally low total concentrations of cadmium in unpolluted sea and freshwaters (Table 2). For example, Chau and Lum-Shue-Chan[100] were able to detect cadmium in only four of 17 lakes studied. Using their labile-bound ASV technique, all the cadmium in a low-pH (pH 4.4) lake was labile, while in the remaining three (pH 5.9 to 6.5) all cadmium was in a bound form. In the Yarra River, which had total cadmium concentrations from 2 to 12 $\mu g\ \ell^{-1}$, a high proportion (up to 65%) was found to be associated with organic matter.[168] Also in the Yarra River, Hart and Davies[124] found that over 90% of total dissolved cadmium was adsorbed by a chelating resin column.

Batley and Florence[31] found that ionic ^{109}Cd added to seawater was removed to the extent of 99.9% by a chelating resin column, even after 5 days equilibration. This result suggests that bound forms of cadmium in seawater must be absent, or extremely inert. Batley and Gardner,[32] studying the speciation of cadmium in the Pacific Ocean and an estuary, found that, in general, free metal and labile complexes are the predominant forms of cadmium, although in a deep, anoxic region of the estuary, 44% of the cadmium existed as ML3 species, i.e., electroinactive organic complexes which are dissociated by Chelex-100 resin. Florence[33] reported that 70 to 90% of cadmium in low-hardness, low-pH (pH 6.0 to 6.1) freshwaters was in the form of free hydrated ion or labile complexes.

Because of contamination during collection and analysis of natural waters, and because of analytical difficulties involved in measuring the very low levels of cadmium in natural waters, some doubt still exists about the predominant forms of cadmium. It appears, however, that in the absence of organic adsorbents, most dissolved cadmium is present as the free metal ion in freshwaters and as chloro complexes in seawater. Colloidal organic matter (e.g., humus and plankton) can adsorb cadmium and alter the speciation dramatically.[14,106]

D. Zinc

The speciation of zinc in natural waters has recently been comprehensively reviewed by Florence.[13]

Zinc is one of the most ubiquitous of the essential trace metals, and its bioavailability is critically dependent on its chemical form. Zinc is a component of many enzymes. It is involved in the synthesis of RNA and DNA (and hence in the healing process). It acts to diminish the toxicity of cadmium and copper. The epidermis contains a high proportion of the total amount of zinc in the body, and a zinc deficiency can result in skin diseases.[7] It has been suggested that skin problems common in vegetarians are caused not by a dietary deficiency of total zinc, but a deficiency of the bioavailable zinc-methionine complex, which is at a higher concentration in meat than in plants.[1]

Many marine organisms, particularly filter-feeders, can accumulate very large concentrations of zinc, apparently without ill effect.[203] Live oysters collected near a zinc refinery in the Derwent Estuary (Tasmania) contained 10% by weight of zinc on a dry basis.[204] Because of this biomagnification of zinc, radioecologists have shown considerable interest in the accumulation of the fission product ^{65}Zn ($t_{1/2}$ = 244 days) in marine organisms.[205] The total amount of zinc in even unpolluted oysters far exceeds the amount which can be attributed to the measured concentration of zinc-dependent enzymes. Coombs[206] found that zinc in the European flat oyster *Ostrea edulis* can be divided into a soluble component and a tissue-bound component, both of which are

Table 12
SOME RECENT MEASUREMENTS ON THE TOTAL CONCENTRATION OF DISSOLVED ZINC IN SURFACE SEAWATER

Source	Method*	Soluble Zinc ($\mu g\ l^{-1}$) Range	Mean	Ref.
Mediterranean	ASV	2—11	5	218
North Sea	ASV	2—8	4	126
Baltic Sea	ASV	4—6	5	208
Pacific	ASV	3—5	4	163
Pacific	ASV	3—6	4	17
Atlantic	NAA	1—5	2	209
Mediterranean	SE	1—7	4	214
Pacific	SE	—	0.0085	35

ASV = anodic stripping voltammetry; SE = complexation-solvent extraction; NAA = neutron activation analysis.

readily exchangeable with $^{65}Zn^{2+}$. The soluble component (40% of total zinc) was found to consist of zinc complexes of taurine, lysine, and ATP. It is believed that these soluble complexes act as a mobile reserve of metal to ensure a constant saturation of zinc enzyme systems.

Zinc has a relatively low toxicity towards aquatic organisms,[84,207] and its toxicity diminishes with increasing hardness and increasing pH of the water. Solbé[207] found that the 48-hr LC_{50} of zinc to rainbow trout in water of pH 7.8 and hardness 500 mg $l^{-1}CaCO_3$ was 4.7 mg l^{-1}. With a water hardness of 50 mg l^{-1}, the fish survived for less than half the time they did at 500 mg $l^{-1}CaCO_3$. Since many of his experiments were carried out under conditions where the theoretical solubility of zinc carbonate was exceeded by factors of up to 30, Solbé, concluded that solid (perhaps colloidal?) forms of zinc may contribute to the toxicity of the water.

Some recent results for the total concentration of zinc in seawater[208,163,209] are shown in Table 12. The most common range of 0.5 to 10 μg Zn l^{-1} is similar to that found for soft, unpolluted freshwaters (Table 2). Recently, however, Bruland et al.[35] found an average value of only 0.0085 $\mu g\ l^{-1}$ for surface waters collected off the central California coast. The zinc concentration increased to 0.6 $\mu g\ l^{-1}$ at a depth of 3 km, and the concentration-depth profile of zinc paralleled that of silicon (Figure 14). Bruland et al. believed that all earlier results are high as a result of gross contamination during sampling and/or analysis. If this conclusion is correct, then laboratories all over the world are contaminating their samples in a remarkably uniform manner (Table 12). In our own laboratory, we commonly find 0.5 to 3 $\mu g\ l^{-1}$ of zinc from routine, direct ASV analysis of surface seawater samples taken 0 to 10 km off Sydney. We checked one of these samples by an independent method, using chelating resin separation followed by neutron activation analysis and radiochemical separation of the active zinc.[210] The surface sample was collected in a polythene bottle which had been acid-washed and treated as recommended by Patterson and Settle[60] using great care to avoid contamination during and after collection of the sample. To avoid the serious loss of trace metals to the container walls, which can occur with plastic bottles which have been soaked in strong acid,[69] a sample was collected, stored overnight at 25°C, then emptied next day and a fresh sample taken (after several rinsings of the bottle with the sample water) from the same location. Aliquots of seawater (1l) were passed

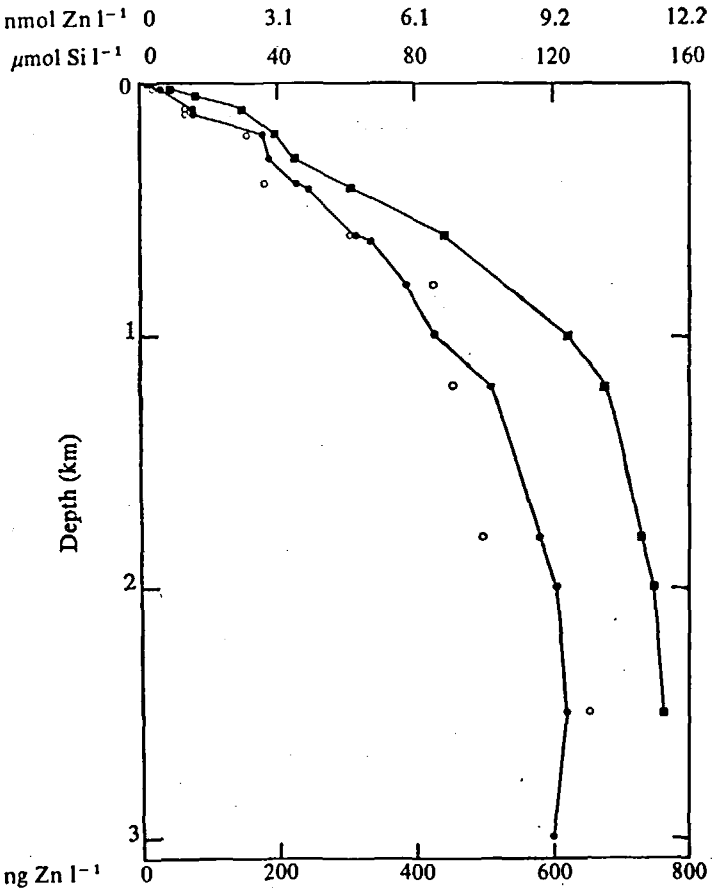


FIGURE 14. Depth profiles of Zn and Si (■) off the central California coast. The Zn profile line was drawn using average organic extraction data (●). Chelex values are indicated by (O). (From Bruland, K. W., Knauer, G. A., and Martin, J. H., *Nature (London)*, 271, 741 (1978). With permission.)

through 1-m*l* columns of Chelex-100 resin (NH_4^+-form) under class-100 clean room conditions, and a blank was carried out under the same conditions. The resin was immediately transferred to sealed irradiation capsules for neutron activation. The resin blank was 0.02 µg l^{-1} Zn, and the seawater was found to contain 0.7 ± 0.1 µg l^{-1}. This figure would not represent total zinc because zinc adsorbed on colloidal particles would pass through the resin column. On the basis of previous work,[17] total zinc is usually about twice the zinc removed by chelating resin, so the total zinc concentration in the sample analyzed by NAA was probably close to 1.4 µg l^{-1}. This is within the range normally found by ASV for the sampling location.

It is possible that the concentration of zinc in surface waters close to shore is much higher than in the open ocean. More work is necessary to resolve this problem and to decide whether most of the reported zinc analyses in seawater are high as a result of contamination, or whether the results of Bruland et al.[35] are low because of losses of zinc during sampling or analysis. In the meantime, as in the case of lead, all published work on the speciation of zinc in natural waters must be viewed with suspicion.

Some computer modeling results for zinc in natural waters are shown in Table 5. In seawater, inorganic zinc is divided between free metal ion, chloro complexes, and the carbonato complex. In a typical freshwater, free metal ion, carbonato, and hydroxy

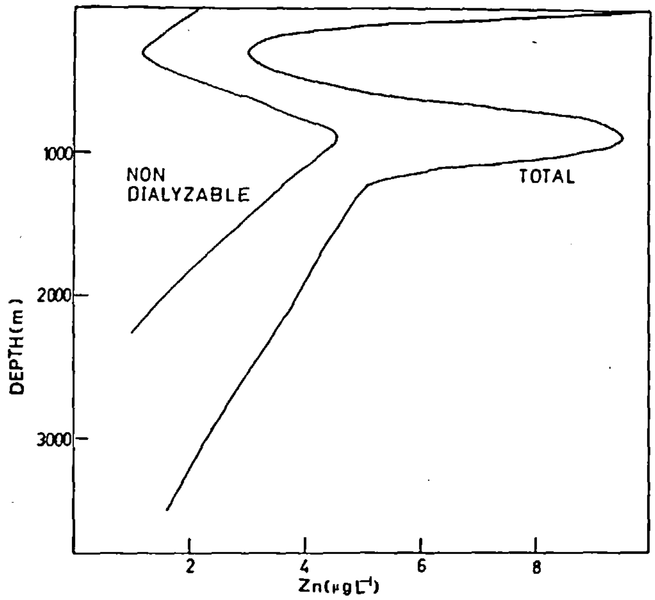


FIGURE 15. Vertical profile for zinc in the Gulf of Mexico. (From Slowey, J. F. and Hood, D. W., *Geochim. Cosmo Chim. Acta*, 35, 121 (1971). With permission.)

complexes would predominate. Using the computer program REDEQL2 and silica as a model inorganic adsorbent, Sibley and Morgan[83] calculated that 4% of total zinc would be adsorbed in a freshwater of pH 8, whereas in seawater less than 0.1% of zinc would be adsorbed.

Dialysis, centrifugation, and ultrafiltration have been used by several workers to separate ionic and colloidal zinc in natural waters. Rona et al.[211] carried out the earliest studies on the chemical forms of zinc in seawater. In a sample taken from a closed bay and containing 33 μg Zn l^{-1}, 38% of the zinc passed a 10 nm ultrafilter, but none of this zinc was dialyzable (membrane pore size 4.8 nm). Slowey and Hood[165] applied dialysis and solvent extraction to the separation of different forms of zinc in seawater. They found that not all the zinc was dialyzable and concluded that the nondialyzable zinc was associated with organic matter (Figure 15). Guy and Chakrabarti[18] studied the effect of pH on the dialysis of zinc in the presence of humic and tannic acids. Below pH 5.5 all the zinc in a humic acid solution was dialyzable, but at pH 7 only 45% of zinc passed through the membrane.

Benes and Steinnes,[104] using their *in situ* dialysis technique in the Glomma River, showed that 54% of the total zinc was dialyzable, a result which was confirmed by ultrafiltration. In a later paper,[107] these authors reported that 90% of zinc in the Glomma River was dialyzable. Approximately 20% of the zinc in this river could be removed by centrifugation, and 80% by a cation exchange resin. No zinc was adsorbed on the walls of the polythene sample containers until the samples had stood for over 30 hr. Benes and Steinnes[107] found that the non-ion exchangeable fraction of zinc in the Glomma River did not equilibrate with $^{65}Zn^{2+}$, indicating that it was in a very inert chemical form. Benes et al.[106]obtained results which suggested that in a freshwater lake some zinc is strongly associated with humic materials.[18]

Florence and Batley[17] found that approximately 50% of the total zinc in four samples of surface seawater was not retained by a column of Chelex-100 chelating resin. ASV-labile zinc was almost completely adsorbed by the column, but bound forms

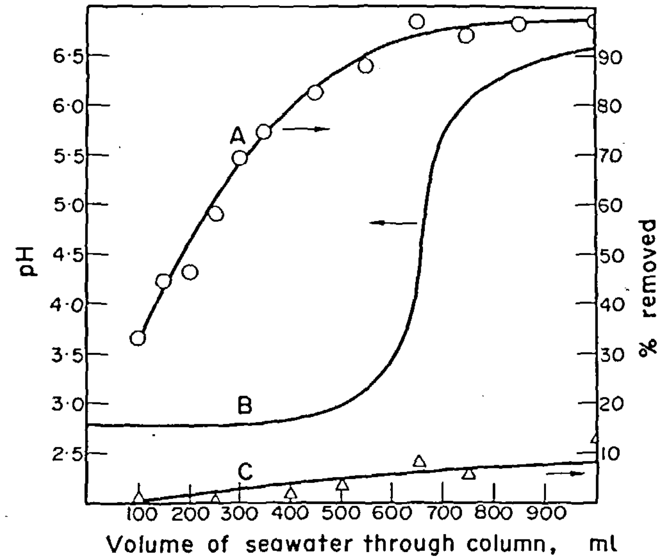


FIGURE 16. Effect of volume of seawater passed through column of Chelex-100 chelating resin (H^+-form) on pH of effluent and on removal of zinc. (A) Removal of labile zinc. (B) pH of effluent. (C) Removal of bound zinc. (From Florence, T. M. and Batley, G. E., *Talanta*, 23, 179 (1976). With permission.)

passed through unchanged (Figure 16). Fukai and Huynh-Ngoc,[127] on the other hand, reported an average of 80% retention of zinc from seawater by the calcium form of Chelex-100, and Abdullah et al.[212] found retentions exceeding 95% for samples from Oslofjord. The total zinc in the seawater used in this latter study was, however, unusually high (20 to 40 μg l^{-1}), and may have been largely ionic as a result of pollution or contamination. Bruland et al.[35] found that Chelex-100 extracted less zinc from seawater than did solvent extraction with APDC.

Florence[33] reported that when three samples of unpolluted, soft freshwaters (pH 6.0 to 6.1) containing 2 to 6 μg l^{-1} of total zinc were passed through a column of NH_4^+-Chelex-100, complete adsorption of zinc took place. Hart and Davies,[124] using a batch equilibration technique with Chelex-100 resin found that 50% of the total of 65 μg l^{-1} in the polluted Yarra River was exchangeable. Figura and McDuffie[120] found that only 34% of the zinc (7.4 μg l^{-1} total) in a sample of Susquehanna River water was removed by Ca^{2+}-Chelex-100, even though ionic zinc was completely removed under the same conditions.

Conventional cation and anion exchange resins have also been used to study zinc speciation. Filby et al.[110] passed filtered riverwater through anion and cation exchange resins. In three rivers studied, most of the zinc was adsorbed on the cation exchanger, but in a fourth river, 87% was retained by the anion exchange resin. Marchand,[112] using his radiotracer cation exchange technique, obtained results which indicated that most zinc in seawater is cationic with 5 to 10% possibly existing as $ZnCO_3$.

Several workers have studied the extraction of zinc from natural waters using chelating agents such as APDC. Hood[213] reported that organic-extractable zinc in seawater from the Gulf of Mexico was much lower than total zinc. For samples collected below 2 km, less than 1% of zinc was extractable. Slowey and Hood,[165] however, found higher concentrations of extractable zinc. Florence and Batley[17] found that for surface Pacific Ocean seawater only 23 to 59% of zinc was extractable by APDC at pH 4.5, even though ionic zinc spikes gave 98% extraction in the pH range 3.5 to 8.1. When the seawater was acidified to pH 0.7, heated, cooled, and adjusted to pH 4.5, all the zinc could be extracted. Fukai et al.[214] studied the extraction of zinc from Mediterranean coastal seawater by dithizone at pH 7. The extractable zinc ranged from 13 to 90% cent of total zinc, depending on the time of year. Fukai et al.[70] carried out a similar study on the Var River. In this river (pH 8), dithizone-extractable zinc varied from 9 to 20% of total soluble zinc, and most of the zinc was adsorbed on suspended sediment particles. Fukai and Huynh-Ngoc[127] found that 30, 56, and 56% of total zinc in three seawater samples was extracted by dithizone-CCl_4 at pH 7. Duinker and Kramer[126] found that an average of 40% of zinc in seawater was extracted by APDC.

Although there is a considerable variation in the results, it appears as if about 50% of the zinc in unpolluted seawater is extractable by APDC, and a similar fraction by Chelex-100 chelating resin. For freshwaters, extraction of zinc may vary from 10 to 100% depending on the pH of the water and its organic content.

Barić and Branica[201] used polarography with a zinc amalgam electrode to investigate the possible ionic forms of zinc in seawater. Their results suggested that zinc should exist predominantly as Zn^{2+} with a smaller fraction as $Zn(OH)^+$. Piro et al.[215] and Bernhard et al.[154] described an ASV technique for differentiating between ionic, particulate, and complexed zinc in seawater. The first ASV measurement at the natural pH (pH 8.1) gave ionic zinc. The pH was then lowered to 6, and the increase in peak height taken to represent particulate zinc. Finally, the pH was lowered to 2, and the increase over the pH 6 result was attributed to complexed zinc. In one sample of seawater, this method indicated that 40% of total zinc was complexed and 42% associated with particulate matter. In the Gulf of Taranto,[154] an average of less than 10% was ionic. Small et al.[216] used this technique to determine the chemical forms of zinc excreted by prawns. The procedure of Piro et al.[215] has the virtue of simplicity, and because the only modification of the sample is the addition of small amounts of acid, there are no blank complications and little likelihood of contamination. However, the assigning of ionic, particulate, and complexed zinc to the three pH ranges is somewhat arbitrary. There are likely to be some particulate forms, e.g., organic matter, from which zinc is not released at pH 6. Also, adjusting seawater to pH 2 at room temperature does not yield total zinc.[17,214] Additionally, the ASV measurement of zinc at pH 2, even using differential pulse mode, is difficult because of hydrogen ion reduction.

Total zinc in lake water was determined by Chau and Lum-Shue Chan[100] by ASV after oxidation with persulfate-H_2SO_4 mixture, and labile zinc was measured at pH 7. Labile zinc in 17 lakes studied varied from 100 to 11% of total zinc. It did not, as might have been expected, increase with decreasing pH of the water. Bradford[217] studied the distribution of zinc species in Chesapeake Bay water by ASV before and after destruction of organic matter. Except in late summer when dissolved organic matter was very high, most of the zinc was ASV-labile. Fukai and Huynh-Ngoc[218] measured zinc in the N.W. Mediterranean by ASV at pH 8 as well as at pH 4. It was assumed that the results at pH 8 represented ionic zinc or simple zinc complexes, whereas those at pH 4 included adsorbed plus strongly complexed zinc. The zinc found at pH 4 ranged from 1 to 3 times that measured at pH 8. In a comprehensive review of the speciation of zinc in seawater, Fukai and Huynh-Ngoc[127] reported that only about 80% of total dissolved zinc in seawater is measured by ASV at pH 4. The zinc measured by ASV at pH 8 corresponds to about 90% of zinc extractable by dithizone, whereas the pH 4 reading is approximately equivalent to the fraction of zinc adsorbed by Chelex-100 chelating resin.

Application of the Batley and Florence[31] speciation scheme (Section V.A , Figure 9) to three unpolluted freshwater samples (pH 6.0 to 6.1) showed[33] that the speciation of zinc was very simple, being divided approximately equally between (M + MA1 +

ML1), i.e., simple ionic species, and MA3, or strong inorganic complexes (possibly basic carbonates). No evidence was found for organic complexes or for zinc adsorbed on organic or inorganic colloidal particles. However, in freshwaters of higher pH or higher organic content, the speciation may be quite different.

There are some problems in the determination of zinc by ASV.[13] The precision of zinc results is usually less than that for the determination of similar concentrations of copper, lead, or cadmium. This lower precision may be because of random contamination by zinc, variation in hydrogen overpotential, or interferences by copper, nickel, and other metals. The hanging-mercury-drop electrode, although less sensitive than thin-film electrodes, usually provides more reproducible results for zinc.[98,140] Zinc is electrodeposited between −1.2 and −1.3 V vs. SCE, and at this potential, many other metals are also deposited. Of the metals which are codeposited with zinc, copper and nickel are particularly important because at high concentrations they form intermetallic compounds with zinc in the mercury phase and interfere with the stripping process, especially at the TFE. This problem can be overcome by dilution of the sample[203] or by addition of gallium ions.[219] However, in unpolluted natural waters the concentrations of copper and nickel are normally too low to cause interference.

E. Iron

Iron is a particularly important metal in all natural water systems. It is a nutrient for algae, higher plants, and many other forms of aquatic life. It has unique biological significance because of its inclusion in porphyrin molecules and proteins which act as oxygen carriers and participate in biochemical oxidation-reduction reactions.[220] Heme iron is the most bioavailable form of iron to mammals. The iron proteins ferritin and transferrin are absorbed by the common mussel, *Mytilus edulis,* 20 and 35 times more efficiently, respectively, than is hydrated ferric oxide.[221]

A completely different, but nonetheless vital, role is played by iron in the freshwater-seawater mixing zone of estuaries where a variety of drastic chemical reactions occur. River water contains a high concentration of dissolved iron which consists almost entirely of negatively charged iron oxide-organic matter colloids.[104,106,107,109,124] On contacting the saline water, the colloids are neutralized and flocculated. As they precipitate, they carry with them most of the other dissolved heavy metals, plus some of the river humic material.[50,222] The heavy metals which escape this estuarine scavenging process enter the oceans principally as species adsorbed on low-molecular-weight colloidal particles of humic acid, hydrated iron oxide, or humic-stabilized iron oxide.

The concentration of total dissolved iron in riverwater varies greatly, but is often in the vicinity of 200 $\mu g\ \ell^{-1}$,[107,223] with particulate iron as high as several mg/ℓ.[222] However, because most of the iron is in colloidal form, the concentration of iron in the "dissolved" fraction depends on the extent to which clogging of the filter paper during filtration changes the effective pore size of the 0.45 μm membrane filter. Seawater contains 2 to 5 $\mu g\ \ell^{-1}$ of dissolved iron and a similar concentration of particulate iron.[224,225] The concentration of dissolved iron in estuarine water decreases progressively as the salinity increases, until, at salinities above 20‰, no additional flocculation of iron or humic substances occurs.[51] Sholkovitz et al.[226] showed that only 3 to 6% of river-dissolved organic matter is removed during estuarine mixing, but that 60 to 80% of the dissolved humic acid flocculates. Most of the flocculating humic acid is in the high-molecular-weight fraction (0.45 to 0.1 μm filtered). Less than 10% of the humic acid which passes a 0.01 μm filter is removed.

The chemical form of iron in all oxygenated natural waters is highly complex. Boyle et al.[50] and Sholkovitz[51] proved that dissolved iron in riverwater exists as negatively charged colloids stabilized by natural organic matter. Organic stabilization is possibly

Table 13
SPECIATION OF IRON IN SEAWATER AND RIVERWATER

Salinity $(^{\circ}/_{oo})^{*}$	Total iron ($\mu g\ l^{-1}$)	Total dissolved iron ($\mu g\ l^{-1}$)	Dissolved organic iron ($\mu g\ l^{-1}$)
0	28	14	2.0
5	17	8	1.5
15	15	4	2.5
23	15	2.5	2.0
30	10	2.5	2.0
33	7	2.5	2.0

Coastal waters off Taokai-mura, Japan.

From Sugimura, Y., Suzuki, Y., and Miyake, Y. *Deep Sea Res.*, *25*, 309 (1978). With permission.

effected by the colloid having an exterior sheath of ionized carboxyl groups.[227] In the estuary, the iron-organic colloid is neutralized by the cations of seawater (Mg^{2+} and Ca^{2+} are more effective than Na^{+}) and precipitates, carrying with it elements such as Mn, Al, and P, as well as additional organic matter. A small fraction of this complex precipitate doubtlessly remains in colloidal suspension, possibly stabilized by humic substances,[16,23] and constitutes the dissolved iron component of seawater.

Sugimura et al.[224] used the macroreticular resin Amberlite XAD-2 to show that 80 to 90% of dissolved iron in the open ocean is combined with organic matter. Only organic iron is retained by the XAD-2 resin at pH 3, and it can be eluted from the column with dilute ammonia. Sugimura et al. found that total dissolved iron decreased with increasing salinity, but that organic iron was relatively constant from river to the open ocean (Table 13). In the North Pacific Ocean, only minor variations in dissolved organic iron occurred to depths of 5 km, although larger differences were found in total dissolved iron (Figure 17).

The observation of Sugimura et al.[224] that the concentration of dissolved organic iron was relatively constant in a river, its estuary, and the open ocean, implies that a particular fraction of dissolved riverwater iron escapes the estuarine flocculation process and enters the sea. This special fraction probably consists of low-molecular-weight[226] organo-iron colloids. It is unlikely to be true molecular complexes of iron with an organic ligand because, as pointed out by Kester et al.,[223] such complexes would need to have unrealistically high stability constants to exist in seawater. The complex of ferric iron with fulvic acid,[228,229] for example, appears to be too weak to be stable in seawater because of the extensive hydrolysis of Fe(III) at pH 8 (>95% of iron is computed to exist as $Fe(OH)_3$ at pH 8 and $35^{\circ}/_{oo}$ salinity[83,133,223,230]) and competition for the ligand by magnesium and calcium ions (Figure 18).

Marchand,[112] using his cation exchange procedure, obtained evidence that the addition of algal matter to seawater increased the concentration of anionic forms of iron, and at the same time decreased the percentage of insoluble iron. However, Marchand's experiments involved spiking seawater with ionic radiotracer iron. It is unlikely that the physicochemical forms of iron produced by this procedure would be in any way similar to the forms naturally present in seawater. This same criticism would apply to any iron spiking procedure in seawater.

The oxidation of iron(II) to iron(III) is important to the precipitation of the iron and its bioavailability. Thermodynamic calculations show that in all oxygenated natural waters, ferric iron should predominate at pH values above 6.[223] Stumm and Lee[231]

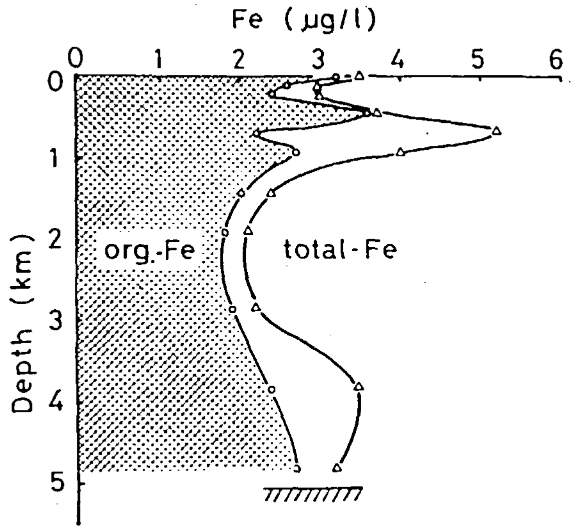


FIGURE 17. Concentration-depth profile for total dissolved and organic dissolved iron in the western North Pacific. (From Sugimura, Y., Suzuki, Y., and Miyake, Y., *Deep Sea Res.*, 25, 309 (1978). With permission.)

found that the rate of oxygenation of Fe(II) in simple aqueous media is given by:

$$-\frac{d\,[\mathrm{Fe(II)}]}{dt} = k\,[\mathrm{Fe(II)}]\,(P_{O_2})\,[OH^-]^2 \qquad (1)$$

where k = 1.36 × 10^{14} mole^{-2} atm^{-1} min^{-1} at 25°C. At pH 7 and 0.21 atm. of O_2, the half-time of the reaction is 4 min. Iron(II) should, therefore, be rapidly oxidized in most surface waters, providing a simple process for iron removal and limiting its availability as a nutrient. In natural waters, however, the rate of oxidation of Fe(II) is, in fact, much slower than predicted by theory. Kester et al.[223] reported that in Narragansett Bay (pH 7.9 to 8.3) and the Sargasso Sea (pH 8.2), $t_{1/2}$ values were 550 and 330 min, respectively. The stabilization of the ferrous state is believed to be achieved by naturally occurring organic compounds. Theis and Singer[232] found that many organic compounds, including tannic acid, glutamine, and vanillic acid, prevented oxidation of Fe(II) either by complexation, or by acting as reducing agents, or both. Tannic acid was especially effective and stabilized ferrous solutions (pH 6 to 7) for several weeks. Langford et al.[229] found that fulvic acid rapidly reduced Fe(III) and dissolved particulate iron. Despite this organic protection of the ferrous state, Boyle et al.[50] found that less than 10% of total iron in estuary water was present as Fe(II). Senesi et al.[233] reported that all the iron in humic material in soil extract was in the ferric state. Acid bog lakes, however, do contain high concentrations of iron(II).[234]

A very sensitive ASV procedure for determining labile and total iron in waters was described by Florence.[235] The sample solution is reacted with bismuth-EDTA complex, and Fe(III) selectively liberates Bi(III) from the complex:

$$\mathrm{BiY^-} + \mathrm{Fe^{3+}} \rightleftarrows \mathrm{FeY^-} + \mathrm{Bi^{3+}} \qquad (2)$$

The liberated Bi(III) is then determined by ASV. This method requires only a 25-mℓ sample and is almost specific for iron. Labile iron is determined by direct measurement, and total iron after fuming the sample with acid. In a sample of tap water, labile iron was found to be 11% of total.

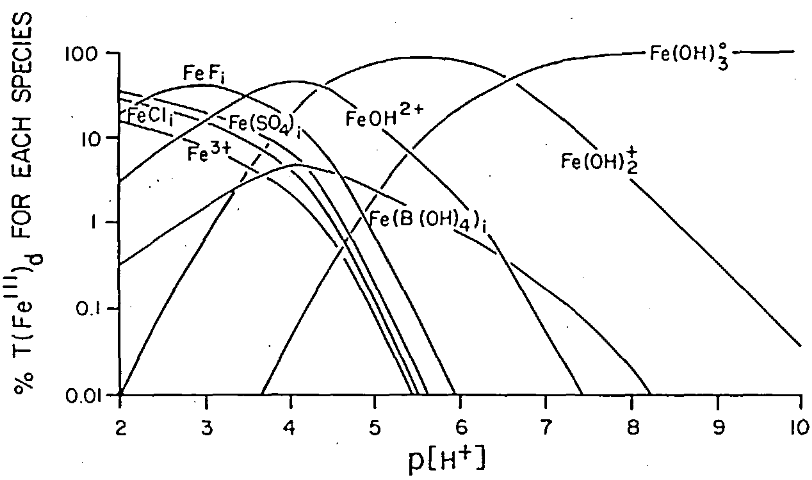


FIGURE 18. Calculated speciation of dissolved iron in seawater as a function of pH. (From Byrne, R. H. and Kester, D. R., *Mar. Chem.*, 4, 255 (1976). With permission.)

F. Chromium

Chromium occurs principally in nature as the mineral chromite, $FeO \cdot Cr_2O_3$, in which form it is extremely stable. In most soils and bedrocks, it is similarly immobilized in the trivalent state. The biological and geochemical cycling of chromium has been thoroughly discussed in monographs by the National Research Council of Canada[5] and the U.S. National Academy of Sciences.[236] Chromium is found at low levels in most biological materials with no evidence of accumulation at any point in the cycle. Chromium(III) has the ability to form strong, inert complexes with a wide range of naturally occurring organic and inorganic ligands.

Environmental pollution by chromium has been shown to be significantly in excess of the natural mobilization of chromium by weathering processes. While in most atmospheric emissions chromium is in the trivalent state, aqueous emissions resulting from such activities as metal dipping, pickling, electroplating, animal glue manufacture, and sewage treatment are principally as hexavalent chromiun.

The study of the chemical speciation of chromium in natural waters has been a topic of increasing research interest over the past decade. Almost exclusively, these studies have been concerned with the distribution of chromium between the two common oxidation states, +6 and +3. Trivalent chromium has been shown to function as an essential element in mammals where it maintains efficient glucose, lipid, and protein metabolism. In biological systems, hexavalent chromium is extremely mobile, being able to diffuse as anionic CrO_4^{2-} through negatively charged cell membranes and to oxidize, and then be bound to, other important biological molecules with toxic results.

Elderfield[237] *in 1970 predicted that, on the basis of equilibrium data for possible* chromium species present in seawater at pH 8.1, chromium should exist almost exclusively as chromium(VI). He calculated that at this pH hexavalent chromium should be mainly as the chromate ion CrO_4^{2-}, with minor amounts as $HCrO_4^-$, H_2CrO_4, and $Cr_2O_7^{2-}$, while chromium(III) should be present to 85% as $Cr(H_2O)_4(OH)_2^+$, 13.5% as CrO_2^-, and $Cr(H_2O)_5OH^{2+}$ as a minor species. Considering only the dominant species, the redox equilibrium is assumed to be controlled by:

$$Cr(H_2O)_4(OH)_2^+ \rightleftarrows CrO_4^{2-} + 6H^+ + 2H_2O + 3e \qquad (3)$$

and theoretically, log Cr(VI)/Cr(III) = 9.7 at pH 8.1, and pE = 8.7.

In practice, Elderfield[237] measured an excess of chromium(III), in most instances exceeding chromium(VI) by 10:1. He rationalized these results on the basis of either poor stability-constant data, the failure to consider some relevant equilibrium species such as organic complexes, the kinetics being such that equilibrium is not attained, or analytical data not truly reflecting the species present.

Sibley and Morgan[83] considered equilibrium models for chromium speciation in both freshwater and seawater, taking into account pH, pE, and simple adsorption processes. Their calculations showed that the majority of chromium should be present in both seawater and freshwater as $Cr(OH)_4^-$, with minor amounts as $Cr(OH)_2^+$ and $Cr(OH)^{2+}$. Adsorbed Cr is the dominant species in freshwater, but decreases significantly in seawater as a result of displacement by Na^+. They, however, assumed chromium to exist entirely as Cr(III) despite the equilibrium redox potential being in favor of Cr(VI). This they supported by the fact that Cr(III) oxidation is kinetically very slow, while Cr(VI) would be removed by reaction with organic matter. In a concurrent paper, however,[82] the same authors stated that oxidation causes CrO_4^{2-} to be the major equilibrium form of chromium in seawater.

Chromium(VI) is often mistakenly referred to as a powerful oxidant in seawater, when, in fact, at pH 8.1 it has a redox potential lower than that of seawater. Studies of ^{51}Cr transport in natural waters[238] have shown that in a well-aerated riverwater under slightly alkaline conditions trivalent chromium tended to be reoxidized to Cr(VI).

In polluted river systems, lowered oxygen concentrations favor reduction of Cr(VI) to Cr(III), which is readily adsorbed by suspended particulates, aquatic plants, or by bottom sediments.[238] Release of sorbed Cr(III) was slow and incomplete, but occurred as trivalent chromium. Chromium(VI) is only weakly adsorbed on these media, which can often bring about chromium reduction, the kinetics being more favorable than for its oxidation by dissolved oxygen. Morgan and Sibley[82] have theoretically modeled the chromium speciation in sewage diluted with seawater. Again, $Cr(OH)_4^-$ is the favored Cr(III) species, with adsorbed chromium(III) contributing significantly at high sewage concentrations (1:10) in seawater. The dominant form of Cr(VI) will be CrO_4^{2-}, which is favored at pE values greater than 6. Dilution of sewage was predicted to result in reduced adsorption of Cr(III).

In addition to its occurrence in polluted waters, localized reduction of Cr(VI) can occur in any natural waters where the oxygen concentrations are depleted, as in anoxic basins or in some upwelled water.[239,240] The ability of organic matter associated with sediments and soils to bring about reduction of Cr(VI) has been discussed by Nelson et al.[241] and Bartlett and Kimble.[242]

On the basis of the above theoretical treatments and tracer experiments it is evident that the valency-state distribution of dissolved chromium in nat
on the following important factors:

1. The oxygen content and redox potential of the water
2. The presence of dissolved or particulate organic matter
3. The presence of suspended inorganic matter

Where the natural levels are perturbed by either atmospheric or aqueous inputs, the distance from the input and time of mixing with the sampled water mass will also be important. A large number of results have now been accumulated (Table 14) where Cr(III)/total Cr ratios range from 0.02 to 0.99.

In discussing these results, it is important to consider the analytical method used and its specificity for the particular valency state. A number of these are based on the

Table 14
LITERATURE DATA FOR CHROMIUM SPECIES IN SEAWATER

Sample	Depth	Cr-(VI) (μg l^{-1})	Cr-(III) (μg l^{-1})	Ref.
Irish Sea	S[•]	0	0.46	243
Monaco coast	S	0.29	0.14	245
Cap d'Ail coast	S	0.28	<0.02	245
Roquebrune Bay	S	0.22	0.25	245
	35 m	0.34	0.10	245
Conway Bay, Wales	S	<0.01	0.45	237
Menai Straits, Wales	S	0.05	0.52	237
Caernarvon Bay, Wales	S	0.16	0.30	237
Tremadoc Bay, Wales	S	<0.01	0.50	237
		0.45	0.06	237
Hamada, Japan	S	0.45	—	252
Kure, Japan	S	1.3	—	252
Nishinomiya, Japan	S	0.91	0.39	252
	S	1.3	—	252
Pacific Ocean	S	0.16	0.23	246
	3800 m	0.005	0.35	246
	S	0.11	0.25	246
	3900 m	0.04	0.51	246
North Sea, Holland	S	0.24—0.92	0.13—0.50	254
		0.30—0.60	0.16—0.32	254
Zandvoort Beach, Holland	S	1.0—1.5	0.05—1.0	255
N. W. Pacific Ocean	5—100 m	0.10	0.002	240
	>100 m	0.15	0.004	240
Columbia River, Canada	S	0.17	0.005	240
Columbia River Estuary, Canada	S	0.12	0.017	240
Saanich Inlet	S	0.08	0.004	240
Saanich Inlet (anoxic)	S	0.01	0.004	240

[•] S = surface.

iron(III) hydroxide coprecipitation technique developed by Chuecas and Riley.[243] This method selectively carries down Cr(III), with Cr(VI) being measured only after reduction with sulfur dioxide or some other reductant. For a surface Irish Sea sample, Chuecas and Riley[243] reported an absence of Cr(VI) in a Cr(III) content of 0.46 μg l^{-1}. Using a radiotracer spike, they reported less than 1.2% of Cr(VI) being coprecipitated. Cutshall et al.[244] observed substantial carrying of Cr(VI), and Fukai and Vas[245] showed that for 5, 4, 2, and 1 μg additions of Cr(VI) to 10 l of seawater, recoveries of 0.4, 3, 10, and 22%, respectively, were obtained. In a recent study, Cranston and Murray[240] found only 1% recovery of added Cr(VI) spikes using iron(III) hydroxide, while iron(II) hydroxide quantitatively reduced and coprecipitated Cr(VI). Clearly, the method will be sensitive to oxidizable impurities, and the differences observed reinforce the need for ultrapure reagents and the minimum of sample manipulation to avoid any changes in speciation.

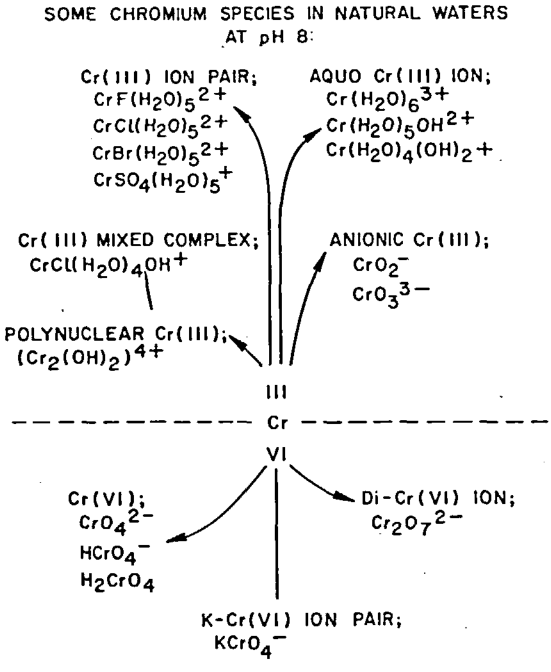


FIGURE 19. Some chromium species in natural waters at pH 8. (From Pankow, J. F., Leta, D. P., Lin, J. W., Ohl, S. E., Shum, W. P., and Janauer, G. E., *Sci. Total Environ.*, 7, 17 (1977). With permission.)

The predictions of Elderfield[237] are supported by the results for the large number of samples analyzed by Cranston and Murray[240] and those reported by Fukai and Vas[245] for open ocean seawater. Grimaud and Michard's data[246] for Pacific Ocean waters measured by isotope dilution mass spectrometry show 30 to 40% Cr(VI) in surface samples reducing to 1 to 7% at a depth of 3800 m.

It would be easy to dismiss the data of Elderfield[237] and Chuecas and Riley[243] as coming from polluted near-shore waters. However, such differences may be the result of one or more of the factors listed earlier. Natural levels for total chromium in open seawater appear to lie in the range 0.1 to 0.5 $\mu g\ l^{-1}$, with the Cr(III) content being 0.001 to 0.36 $\mu g\ l^{-1}$. The relative proportions of each valency state appear to be controlled by *in situ* redox processes. The separation of Cr(VI) and Cr(III) by ion exchange has been investigated by several authors.[112,247] Pankow and Janauer[247] showed that chromate was quantitatively preconcentrated from natural waters by an anion exchange resin and expanded this into a procedure for chromium speciation to quantify anionic, cationic, and nonionic forms.[248] Figure 19 lists the possible inorganic species of chromium in natural waters. With one exception, the only anionic species which will, therefore, be retained by the anion exchange resin, contain hexavalent chromium. The exception, $Cr(OH)_4^-$, cannot be lightly dismissed since in seawater it was estimated by Elderfield[237] to account for 13.5% of the total Cr(III). Sibley and Morgan[83] considered it to be the principal Cr(III) species. All other Cr(III) species will be either cationic or neutral and will, therefore, be retained by a cation exchange resin, or in the fraction not retained by either resin.

Results for the Susquehanna River Basin area[248] indicate that as much as 50% of the total chromium is in a cationic form (Table 15), with a lesser amount of soluble nonionic, presumably Cr(III), species. The concentration of soluble anionic species

Table 15
RESIN-SEPARATED CHROMIUM SPECIES IN RIVER WATERS (μg Cr l^{-1})

Sample		Cationic species	Anionic species	Nonionic species[a]	Ref.
Cape Fear River, U.S.	↓	0.8	7.9	nm	249
		0.4	1.5	nm	249
		0.3	1.9	nm	249
		0.3	0.7	nm	249
		0.3	0.4	nm	249
	Mouth	0.2	0.1	nm	249
Susquehanna River		1.2	0.6	0.8	248
		0.9	0.4	0.5	248
		1.3	1.6	0.7	248

[a] nm, not measured.

was modified in certain areas by sewage input of chromate. These results appear inconsistent with thermodynamic predictions, and this points out the shortcomings of attempts to treat, by equilibrium methods, a situation in which equilibrium is not attained. Pankow et al.[248] reasoned that Cr(III) should be present as $Cr(OH)_2^+$ together with cationic polynuclear species, if originating from a Cr(III)-containing solid. No cognizance was taken of Cr(III) species formed by Cr(VI) reduction.

Shuman and Dempsey[249] applied the ion-exchange method in a field technique to separate cation- and anion-exchangeable chromium. Particulate Cr was retained by a 0.2 μm membrane filter. Colloidal particles (0.02 to 0.2 μm) which are unable to enter the pore network of the resin will, in their system, pass to waste. Their measurement in the waste stream should be possible, although no data were reported. A major problem with resin techniques can be the high blanks of the resin columns. Cowell[250] measured Cr levels from 1 to 4 μg g^{-1} in analytical grade resins. Results for the Cape Fear river system[249] showed that a detectable input of CrO_4^{2-} waste was significantly reduced towards the river mouth to a figure close to the detection limit. Somewhat higher concentrations of cationic species were measured. Rapid association of Cr with particulate and colloidal matter was apparent.

Benes and Steinnes[107] applied dialysis and centrifugation to the separation of chromium species in lake and river waters. A high percentage of dialyzable metal resulted from the high CrO_4^{2-} concentration of the less-polluted Glomma River. Lake Trehorningen water was high in organics and, in keeping with the expected Cr(III) concentrations had a high proportion separable by centrifugation. Other separation processes used include the use of activated carbon and selective solvent extractions. In the former case, van der Sloot[251] observed adsorption of CrO_4^{2-} at pH values below 5, while above pH 4, Cr(III) was measured. High blank values precluded speciation studies on natural samples. Hiiro et al.[252] extracted CrO_4^{2-} with sodium diethyldithiocarbamate in methylisobutylketone at pH 4 with no interference from Cr(III), and the method was applied to the analysis of Japanese seawater samples.

A more recent attempt to separate Cr species into meaningful fractions has been reported by Batley and Matousek.[253] Using an electrodeposition technique, they were able to separate labile and bound Cr(VI) and Cr(III) species. With a deposition potential of −0.3 V vs. SCE, it was possible to selectively reduce chromium(VI) on a graphite-tube electrode at pH 4.8 in the presence of added mercuric ions. This resulted in the formation of an adsorbed film of chromium(III) hydroxide. The amount of chromium hydroxide formed is a function of electrolysis time and of chromium(VI) and mercuric ion concentrations. Reduction at −1.8 V vs. SCE deposits chromium metal from both chromium(VI) and chromium(III). The deposited chromium is then analyzed by atomization from the tube in an atomic absorption spectrometer. The electrochemical discrimination between labile and bound metal has been applied to the selective determination of chromium species in each oxidation state.

G. Manganese

The chemistry of manganese in natural waters parallels that of chromium in many respects, in that it is dominated by redox changes. Manganese exists in two common oxidation states, as manganese (II) and manganese (IV). In oxygenated waters, the former is unstable being readily oxidized to Mn(IV), when as manganese dioxide it precipitates from solution to be transported to the sediment load. Manganese (VII), as MnO_4^- is a powerful oxidant, is used in water technology, but is unstable in natural waters, being reduced to MnO_2.

Manganese comprises approximately 0.1% of the earth's crust. It is found in rivers, lakes, and ocean waters originating both through erosion and transportation of particulate mineral species and through biological and chemical processes. It is present in all plant and animal tissue where it is an essential nutritional element. In the oceans, manganese deposits on the ocean floors as ferromanganese minerals containing manganese in both common oxidation states. Similar deposits have been reported in freshwaters.[256] Hydrothermal activity has been postulated as a major source of manganese in the oceans.[257] A second source involves transportation of sedimentary manganese deposits which in the absence of oxygen are reduced to divalent manganese and dissolved in the sediment interstitial waters.[258] Reprecipitation can occur as MnO_2 in the upper or oxidizing layers.

As with iron, the cycling of manganese in natural waters has been extensively investigated. The precipitation and dissolution of hydrated manganese and iron oxides as a result of changes in pH is believed to be an important buffer mechanism for regulating the levels of phosphorus and trace metals. Krauskopf[47] has pointed out that since it is easier to reduce manganese oxides than iron oxides in natural waters under increasingly depleted oxygen concentrations, dissolution of manganese from lake and river sediments will occur preferentially to that of iron. Burns and Nriagu,[259] examining manganese and iron forms in Lake Erie, observed a seasonal variation. There was conversion of a highly soluble Mn in the hypolimnion in August, changing with disturbances of the sediments and reoxygenation in the September-October overturn, to an increasing particulate manganese which is slowly reprecipitated at the sediment interface. Predicted species are shown in Figure 20.

Evans et al.[260] examined the cycling of manganese in the Newport River Estuary. Contrary to the findings of Holliday and Liss[261] in the Beaulieu Estuary, they reported nonconservative behavior of manganese. They postulated that manganese is carried in suspension or as traction load by the river and deposited in, or transported through, the estuary. In the high-salinity environment, desorption of manganese will occur, while the dissolved concentration will be further augmented from interstitial-water exchange or by release through decomposition of manganese-containing organic matter. Dissolved manganese will be carried downstream where it is oxidized and deposited as particulate MnO_2. The cycle is completed by an upstream flow of particulate manganese.

Data for Narragansett Bay[262] suggest that riverine manganese is predominantly particulate, but in the bay it is dissolved, the soluble concentration being greater at depth than at the surface. There is considerable evidence to suggest that desorption of activated manganese occurs at the freshwater-seawater interface.[263, 264] In organically rich

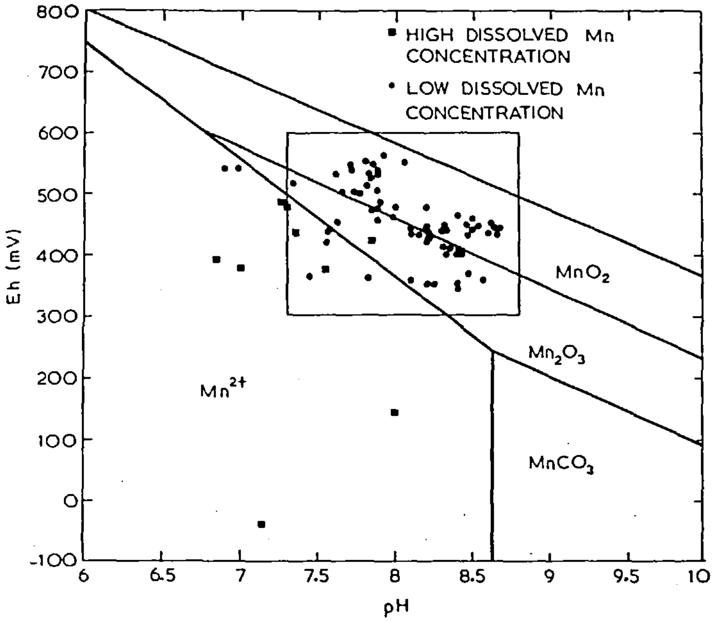


FIGURE 20. Eh-pH distribution of manganese species in Lake Erie. (From Burns, N. M. and Nriagu, J. O., *J. Fish. Res. Board Can.*, 33, 463 (1976). With permission.)

rivers, organic complexes of manganese are formed which flocculate on entering saline waters.[265] The major changes in manganese speciation are brought about by increases in pH, resulting in an overall increase in particulate manganese. This stems principally from the more facile oxidation of manganese at higher pH values.[262]

In marine anoxic basins, Spencer and co-workers[266, 267] have shown that at the zero-oxygen boundary, the equilibrium solubility of manganese is greatly increased from below 2 $\mu g\ l^{-1}$ in oxygenated waters to as high as 450 $\mu g\ l^{-1}$. The upper limit in solubility is believed to be controlled by the formation of $MnCO_3$.

In oxygenated ocean waters, typical dissolved manganese concentrations lie in the range 0.2 to 5 $\mu g\ l^{-1}$. There have been no attempts to determine the proportions of this as divalent manganese or as colloidal MnO_2.

The existence of stable organic complexes of manganese in solution is also highly probable. Manganese is important in the biological functions of marine plants and organisms in which it is likely to exist as complexed species.[268] Experiments by Rona et al.[211] on seawater indicated the presence of a nondialyzable, soluble manganese species, most probably colloidal forms.

Inorganic speciation models have predicted that in seawater the chloro complex is the dominant manganese species with lesser amounts as the free ion and sulfate complex.[83] In freshwater, the free ion is calculated to predominate with minor amounts of carbonate and sulfate complexes and adsorbed species.[8] An equilibrium model of Stumm and Brauner[89] predicted no significant organic complexation.

Data for manganese in Norwegian rivers[107] showed that up to 40% was dialyzable, while nearly 90% was removed by a cation exchange resin. The former observation suggests a high concentration associated as organic complexes or with nondialyzable species. Studies by Zajicek and Pojasek[269] on manganese transport have shown that naturally occurring organic ligands, such as fulvic acids, enhance the solubility of manganese oxides by reduction and subsequent complexation. It is, therefore, likely that, in both freshwater and seawater, organic complexes could account for significant manganese concentrations.

Inorganic colloidal species, such as iron and manganese oxides, are also capable of adsorbing divalent manganese.[54] No attempts have been made to measure manganese so combined. Giesy and Briese[270] examined ultrafiltration to separate manganese fractions in organic-rich swamp water. The major metal percentage was associated with the fraction below 0.0009 μm (<500 mol wt). Delfino,[271] examining lake waters, showed the principal form of manganese to be Mn(II). In periods of thermal stratification, Mn(II) was the only form in anoxic waters, with both Mn(II) and Mn oxides present in oxygenated waters. Sorption on manganese and iron oxides was considerable, and diminished the rates of oxidation of Mn(II). These rates were generally slow at pH values below 8.5.

H. Cobalt

Very little is known about the speciation of cobalt in natural waters. The open-ocean concentration of dissolved cobalt is also uncertain. Values between 0.01 and 0.6 $\mu g\ \ell^{-1}$ have been reported.[272-274] Modeling studies of cobalt speciation, as in the case of the other metals, has led to widely differing predictions concerning the major species present in natural waters. Sibley and Morgan,[83] for example, predicted a high proportion of chloro complexes in seawater, while Stumm and Brauner[89] calculated free cobalt(II) as the major species with lesser amounts of chloro and sulfate complexes. Mantoura et al.[15] predicted the carbonate complex, $CoCO_3$, as the major species, with slightly lesser amounts of the free ion, these species being reversed in abundance in low salinity waters. Calculations indicated less than 1% of organic complexes in freshwaters with insignificant complexation in seawater.[15]

The work of Lowman and Ting[6] in estuarine waters of Puerto Rico showed soluble cobalt in the range 2 to 5 $\mu g\ \ell^{-1}$. Between 50 and 65% of the total was present as ionic species, while the remainder was in complexed forms. The behavior of these two groups of species in a number of typical preconcentration methods was also investigated using radiotracers (Table 16), and a method was devised to separate the two.[6] These results illustrate the pitfall in making the assumption of complete and exclusive removal of a species by accepted procedures.

Although cobalt(II) is known to form stable complexes with organic ligands, in the presence of dissolved oxygen these will almost certainly be oxidized to their respective cobalt(III) complexes which are kinetically inert. The most common organic complex of cobalt is cobalamin, vitamin B_{12}. Measurements by Duursma[275] and Carlucci and Silbernagel[276] suggest that cobalamin is present in seawater in the range 0.03 to 10 ng ℓ^{-1}. The higher complexed-cobalt content of the Puerto Rican waters[6] is not necessarily all attributable to cobalamin, rather it is the result of the naturally high organic content of these waters arising from sugar-mill effluent and municipal sewage.

Studies by Batley and Matousek[277] on estuarine and coastal waters near Sydney, Australia, indicated that approximately 70% of the total dissolved cobalt concentration of 0.25 $\mu g\ \ell^{-1}$ was labile. These fractions were determined in water samples adjusted to pH 4.7 by electrodeposition with mercury on a tubular pyrolytic-graphite electrode followed by atomization of the deposited cobalt in an atomic absorption spectrometer.

The speciation of cobalt in seawater has been examined by Marchand[111] using the technique of cation exchange-resin chromatography. The technique, described earlier, relies upon the properties of the resin to allow rapid elution of anionic or neutral species, strong retention and hence slower elution of cationic species, and surface adsorption of insoluble, possibly colloidal, species which must be removed by acid elu-

Table 16
TESTS ON PRECONCENTRATION METHODS FOR ISOLATING ORGANICALLY BOUND AND IONIC COBALT FROM SEAWATER

Method	% Separated from the water Organically bound (^{57}Co)	Ionic (^{58}Co)
$Fe(OH)_3$[a]	0.8	83.0
MnO_2[b]	51.0	100.0
Chelex-100	0.6	91.0
MnO_2(pH 9)[c]	1.2	100.0
Saturated sodium carbonate	1.1	100.0
Dithizone extraction[d]	1.3	97.0
APDC + MIBK extraction[e]	0.5	88.0
α-nitroso-β-naphthol extraction[f]	1.8	75.0
Thioacetamide sulfide (ppt)[g]	81.0	1.0
α-nitroso-β-naphthol (ppt)	48.0	89.0
Activated charcoal	100.0	67.0

[a] Two precipitations.
[b] Potassium permanganate + ethyl alcohol + heat.
[c] Potassium permanganate + manganous sulfate.
[d] Three extractions.
[e] Two extractions.
[f] Into chloroform.
[g] Tin carrier, pH 1.5.

From Lowman, F. G. and Ting, R. Y., in *Radioactive Contamination of the Marine Environment,* International Atomic Energy Agency, Vienna, 1973, 369. With permission.

tion. Only 1% of dissolved cobalt was found in the first category, while 5.5% and 55.3% were found for two separate cationic elution peaks, possibly Co^{2+} and $CoCl^+$. A further 27.0% was attributed to unidentified cationic species. In the insoluble category, 11.1% was found as insoluble species, possibly cobalt as $CoOOH_{(s)}$ or adsorbed on colloids such as FeOOH. These results agree well with theoretical predictions for inorganic cobalt species,[83] but the scheme makes no distinction between organic and inorganic species. A more valuable extension of this exercise would be an attempt to identify the eluted species, particularly with respect to organic complexation, using larger preparative columns.

In freshwater, the adsorption of cobalt on a wide range of clays, quartz, and on hydrous metal oxides has been well demonstrated.[278, 279] Desorption is known to occur on mixing with seawater.[51] The work of Benes and Steinnes[107] has shown that in lake and river waters of Norway less than 40% of total cobalt was dialyzable, suggesting a high concentration as colloidal or particulate species. Measurements in the St. Lawrence Estuary[280] gave freshwater cobalt concentrations near 8 $\mu g\ l^{-1}$, decreasing in the mixing zone to $<1.5\ \mu g\ l^{-1}$.

I. Nickel

The literature is similarly lacking in data on nickel speciation in natural waters, although the marine geology of nickel has been extensively studied. Dissolved nickel concentrations appear to have been accurately measured. In seawater, values between 0.2 and 0.7 $\mu g\ l^{-1}$ were obtained from Geosecs profiles in both the Atlantic and Pacific Oceans.[281]

Bender and Gagner[57] reported a value of 0.1 μg ℓ^{-1} for the Sargasso Sea, using an ammonium pyrrolidinedithiocarbamate precipitation procedure. Values appeared to increase significantly with depth for the first 200 m, thereafter reaching a constant value.

Theoretical models of nickel speciation are very similar to those for cobalt. Mantoura et al.[15] predict both the carbonate complex, $NiCO_3$, and free ion, Ni^{2+}, to be present in freshwaters, with the former dominant in seawater. The same species are predicted by Sibley and Morgan[83] for freshwaters, with an added contribution from nickel adsorbed on particulate matter. Again, these models do not predict a significant contribution from organic species.

Data obtained by Batley and Matousek[277] for labile and total nickel in estuarine samples showed the former amounting to 70 to 80% of the total dissolved nickel concentration.

J. Thallium

Thallium determination in natural waters has received little attention. This is possibly because, like indium, its concentration is in the nanogram per litre range.[282] It is an element whose speciation should warrant more attention in view of its toxicity and pollution potential.[282] Thallium pollution could be a problem in the mining industry because the metal is usually not recovered. Industrial uses of thallium include alloys, electronic devices, catalysts, and rodenticides.[282] Its toxicity to mammals has been equated to that of mercury, but less than methyl mercury. To fish, it is at least as toxic as copper.[282] The first definitive figures for thallium in seawater were published by Matthews and Riley,[283-284] who found 10.1 and 18.7 ng ℓ^{-1}, respectively, for samples from the Bay of Biscay and the Irish Sea. Recently, Batley and Florence[285] published figures in the range of 10.3 to 15.3 ng ℓ^{-1} for coastal seawater near Sydney, Australia. This study considered thallium speciation in some detail.

With thallium, two common oxidation states are found, Tl(I) and Tl(III). Tl^+ is distinctly more stable than Tl^{3+} in aqueous solution, however Tl(I) forms weak complex compounds, while those of Tl(III) exhibit greater stability than those of Fe(III) and Cr(III). Equilibrium calculations showed that in natural seawater at pH 8.1, and in freshwaters at pH 6.5, trivalent thallium should predominate. These predictions were confirmed by Batley and Florence.[285] Their procedure requires oxidation of thallium species with bromine and collection on an anion exchange column prior to elution and ASV analysis. Up to 80% of the thallium in seawater was recovered, if bromine was omitted from the sample. The remaining 20% was assumed to be present as either cationic or neutral thallium(III) complexes or as thallium(I) species, none of which will be retained by the resin. For freshwaters, thallium concentrations were significantly lower, 2.8 to 5.1 ng ℓ^{-1}.

K. Aluminum

The toxicity and chemistry of aluminum in aqueous solution has been comprehensively reviewed by Burrows.[286] Very little information is available about the chemical forms of aluminum in natural waters, and most of the work reported on aluminum speciation has involved physical separation procedures such as dialysis and ultrafiltration.

The concentration of dissolved aluminum in open ocean water is about 0.5 μg ℓ^{-1},[287] but coastal seawater often contains higher concentrations (average 1.5 μg ℓ^{-1}).[288] The range of aluminum concentrations in coastal waters (1 to 5 μg ℓ^{-1}) is similar to that found when clay minerals are dissolved in seawater.[287] Particulate aluminum in seawater off the southeastern coast of the U.S. was measured as 2 to 70 μg ℓ^{-1}, with a mean of 18 μg ℓ^{-1}.[225]

Table 17
SIZE FRACTIONATION OF ALUMINUM IN NATURAL WATERS BY MEMBRANE FILTERS

Filter pore size (μm)	Aluminum measured ($\mu g\ \ell^{-1}$) Freshwater	Seawater
5.0	21.2	8.5
1.2	18.5	5.5
0.8	17.4	5.7
0.45	17.3	5.4
0.2	16.4	5.4
0.1	14.6	5.3

From Hydes, D. J. and Liss, P. S., *Estuarine Coastal Mar. Sci.*, 5, 755 (1977). With permission.

Table 18
FILTERABLE ALUMINUM VERSUS *n* IN $Al(OH)_n$[a]

n	Al in solution (%)
1.45	100
2.0	92
2.2	80
2.5	57
2.7	35
3.0	0

[a] Filter pore size, 0.10μm; 5×10^{-4} *M* Al (III) in sodium perchlorate, pH 4.5.

From Hem, J. D., *Trace Inorganics in Water*, Gould, R. F., Ed., American Chemical Society, Washington, D.C., 1968, 98. With permission.

The concentration of aluminum in freshwaters varies greatly, with reported values for dissolved aluminum ranging from 2 to 98 $\mu g\ \ell^{-1}$,[288] and particulate aluminum from 400 to 900 $\mu g\ \ell^{-1}$.[225] Although the amount of dissolved aluminum doubtlessly increases with decreasing pH, the river aluminum concentrations of several thousand micrograms per litre listed by Burrows,[286] almost certainly represent total, rather than dissolved, aluminum.

The dissolved fraction of aluminum varies considerably with the pore size of the membrane filters, both in freshwater and seawater (Table 17).[288] Hem[289] found that when 5×10^{-4} *M* aluminum perchlorate solutions (pH 4.5) which had been aged for 10 days were filtered through 0.10-μm membrane filters, significant amounts of aluminum were retained by the filter unless the value of n in $Al(OH)_n$ was less than 1.5. Where n was 3.0, all the aluminum could be filtered out (Table 18).

Many natural organic materials, e.g., humic and fulvic acids, are capable of mobilizing aluminum from soils.[286] Beck and Reuter[290] reported significant enhancement of aluminum in waters of high organic content. As in the case of iron, much of the mobilized aluminum probably consists of organo-aluminum colloids, stabilized by a negatively charged sheath of the organic matter. Hydes and Liss[288] found that 30% of the dissolved aluminum in freshwater entering the Conway estuary was removed during estuarine mixing with seawater. Removal was essentially complete at 8‰ salinity, no further precipitation occurring with increasing salinity. Hydes and Liss believed that aluminum removal involved adsorption onto very fine clay particles which are coagulated by saline water. The lumogallion fluorimetric method used for aluminum determination by Hydes and Liss[288] measured aluminum in solution plus aluminum adsorbed on the surface of clay particles, but not aluminum in clay material itself. For most of the waters studied, Hydes and Liss found that the naturally present aluminum reacted with lumogallion at a rate similar to that of an ionic aluminum standard, which suggests that the chemical forms of aluminum in the waters were fairly simple. With Conway River water, however, the reaction rate was only about 20% that of the standard, possibly indicating more complex forms of aluminum.

Benes and Steinnes[104, 107] and Benes et al.[106] used dialysis, ultrafiltration, and centrifugation to study the forms of aluminum in river and lake waters. Ultrafiltration removed 80 to 90% of total aluminum, and dialysis experiments showed that much of the aluminum was in colloidal or suspended forms.

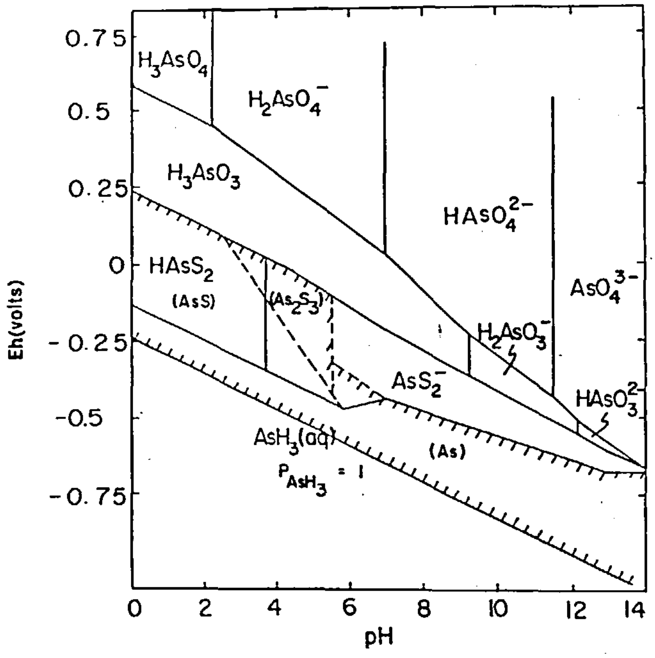


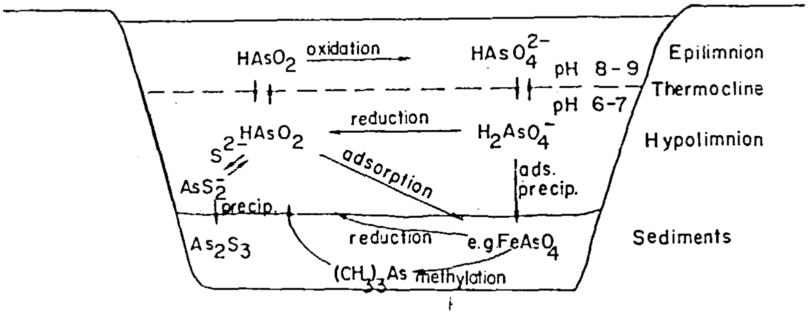
FIGURE 21. Eh-pH diagram for arsenic (10^{-5} *M*). (From Ferguson, J. F. and Gavis, J., *Water Res.*, 6, 1259 (1972). With permission.)

L. Arsenic

Arsenic occurs naturally in a wide range of minerals which, together with a once widespread use of arsenic in pigments, insecticides, and herbicides, represent the major sources of arsenic in natural waters. The chemistry of arsenic in natural waters is complex and, in many respects, parallels that of phosphorus. Much of the early analytical data for arsenic in seawater are believed to be in error because of phosphate interference. Arsenic exists naturally in four oxidation states, +5, +3, 0, and −3, the dominant species being a function of Eh and pH. In oxygenated waters at pH 8, both $HAsO_4^=$ and $Ba_3(AsO_4)_2$ have been postulated as the major species.[291,292] In less oxidizing conditions, arsenite species, e.g., H_3AsO_3, become significant. While in still more reducing conditions, AsS_2^-, As, and AsH_3 dominate (Figure 21). A typical cycle of arsenic in a stratified lake is shown in Figure 22.

The dissolved arsenate concentration measured in the Atlantic Ocean in the Geosecs program[273] was shown to be very homogeneous with an average value of 1.6 $\mu g\ l^{-1}$. Studies by Johnson and Pilson[293] found 2.1 $\mu g\ l^{-1}$ for surface ocean waters, increasing to 3.3 $\mu g\ l^{-1}$ in deep waters. There is evidence of arsenite in seawater and river water,[294] although arsenate is generally the dominant species.[295]

The distribution of inorganic species of arsenic between the two oxidation states has been studied in considerable detail using a variety of methods. Solvent extraction using complexing agents such as ammonium pyrrolidinedithiocarbamate[295, 296] or diethyldithiocarbamate[297] will selectively remove arsenic (III) from neutral solutions. Total arsenic can be measured in 1 *N* acid medium, or after reduction of arsenic (V) to arsenic (III). To separate the two oxidation states, Braman and Foreback[298] used selective reduction of arsenic(III) at pH 4 to 9 by sodium borohydride, while arsenic(V) is reduced by sodium cyanoborohydride at pH 1 to 2 to arsenic(III) and then further reduced to arsine by sodium borohydride. Although Haywood and Riley[296] could not confirm the selectivity of these reductions, it has since been verified by Shaikh and



Local cycle of arsenic in a stratified lake.

FIGURE 22. Local cycle of arsenic in a stratified lake. (From Ferguson, J. F. and Gavis, J., *Water Res.*, 6, 1259 (1972). With permission.)

Tallman[299] and Andreae[300] (Figure 23). Data obtained from the above measurements are included in Table 19. In all these examples, however, no account is taken of arsenic in colloidal species. Arsenite is known to readily adsorb onto hydrous iron oxides,[301] and although this will certainly be desorbed in acid solution, its extraction or reduction at the natural pH is uncertain.

Arsenic is also likely to be present as organo-arsenic species. Many aquatic organisms are capable of accumulating arsenic and may catalyze the oxidation of arsenite to arsenate while also promoting the formation of methylarsines through biomethylation reactions.[302] Certain diatoms are known to reduce arsenate to arsenite and dimethylarsinic acid, $(CH_3)_2AsOOH$.[303] The production of methylarsines by methogenic bacteria under anaerobic conditions has been demonstrated by McBride and Wolfe.[304] This could conceivably occur in sediments, with the species produced being subsequently released to the overlying water. McBride and Wolfe[304] showed that dimethylarsinic acid and methylarsonic acid ($CH_3AsO(OH)_2$) are intermediates in the reductive methylation of inorganic arsenic to dimethylarsine. Ridley et al.,[302] however, proposed reaction of molecular oxygen with volatile arsines as the means of formation of these acids. Organic arsenic compounds are also known to be present in marine animals, and recently, the composition and structure of one such compound, arsenobetaine, isolated from the tail muscle of a western rock lobster was described.[305] It is possible that such compounds could also find their way into natural waters.

The measurement of both organic and inorganic arsenic species in natural waters has been described by a number of authors.[299, 300, 306] They are based on modifications of the elegant selective-volatilization procedure developed by Braman and Foreback.[298] In the modification by Andreae,[300] volatile arsines such as mono-, di-, or trimethylarsine are stripped initially from the sample by a helium gas stream. Arsenic(III) is then reduced to arsine with sodium borohydride at pH 6 and is again stripped with helium. Adjustment of the pH to 1 and a second reduction with borohydride converts arsenic(V), monomethylarsenic acid, dimethylarsinic acid, and trimethylarsine oxide ($(CH_3)_3AsO$) to the corresponding arsines, to be stripped again with helium. The stripped species are separated by gas chromatography using an atomic absorption detection technique. Typical results of speciation studies of river waters, lake waters and saline waters are shown in Table 19.

Recent results of Andreae[306] show that the distribution of methylated arsenic species in seawater is almost wholly confined to the photic zone, indicating that they are produced by phytoplankton or by heterotrophs closely associated with the primary producers. At depth, arsenate was the dominant species, its total concentration differing little from surface values. Arsenite in most instances diminished with depth, although instances of high arsenite were found associated with high primary productivity.

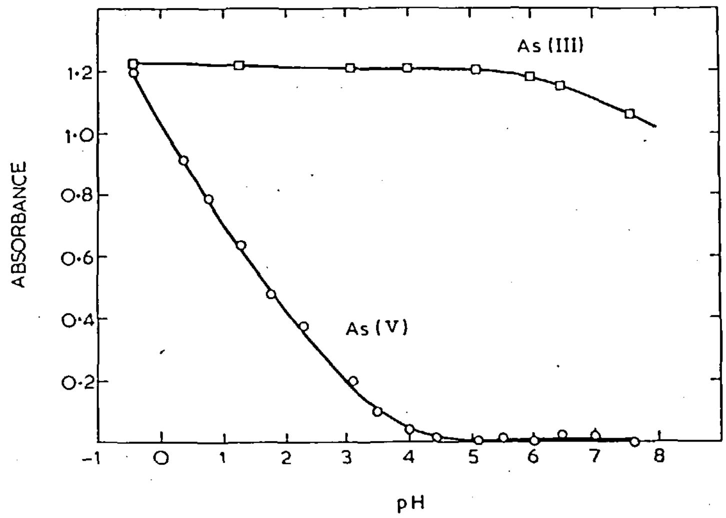


FIGURE 23. AAS response for arsenic(III) and arsenic(V) reduction at various pH values. (From Shaikh, A. V. and Tallman, D. E., *Anal. Chim. Acta,* 98, 251 (1978). With permission.)

Andreae[300] reported similar concentrations of methyl arsenicals in freshwaters to those found in seawater. However, data from Florida lakes and rivers[298] showed some instances in which dimethylarsinic acid was the major dissolved arsenic species. This could be due to the use of this material as a pesticide near the sampling site. As(V)/As(III) ratios were variable in freshwaters with instances in which As(III) was dominant. Again, this could reflect a sewage input of a low dissolved-oxygen content.

Storage data for arsenic indicate that in airtight containers arsines are stable for several days, being slowly oxidized by air to the corresponding acids.[300] The methylated acids are stable only in acidified solutions. Arsenic(III) oxidation is, however, accelerated by acidification, and samples are best stored at 4°C to prevent losses.[300]

M. Antimony

Antimony occurs in seawater in the concentration range 0.1 to 0.5 $\mu g\ \ell^{-1}$, and as with arsenic, it has been shown to occur in both the trivalent and pentavalent states. Data obtained by Gohda[297] for Japanese coastal waters showed that 70 to 94% of antimony was present as Sb(V) in the range 0.12 to 0.49 $\mu g\ \ell^{-1}$, with Sb(III) from 0.03 to 0.09 $\mu g\ \ell^{-1}$. A fraction 0.01 to 0.03 $\mu g\ \ell^{-1}$ was associated with particulate species. Kamada and Yamamoto[307] have obtained figures for Sb(III) and total Sb in river water and seawater using a solvent-extraction procedure. Antimony(III) was selectively extracted at pH 5 to 8.5 using ammonium pyrrolidinedithiocarbamate in methylisobutylketone. The same extraction at pH 1 removed both Sb(III) and Sb(V). Although the authors claim a sensitivity of 0.2 $\mu g\ \ell^{-1}$, no antimony was detectable in either sea or river waters.

Sillen[308] has suggested that antimony in seawater should be in the pentavalent state, while Gilbert and Hume[309] postulated that these species would be highly hydrolyzed, probably polymerized hydroxychloro complexes or colloidal hydrous oxides. Strohal et al.[310] suggest $Sb(OH)_4^-$ or the dimer $Sb_2O(OH)_4$, while high antimony concentrations associated with humic acids suggest that organic chelation may account for portion of the dissolved antimony concentration in seawater. No definitive data are, however, available on antimony speciation.

A potential method for the measurement of antimony speciation has been discussed

Table 19
ARSENIC SPECIES CONCENTRATIONS IN NATURAL WATERS ($\mu g\ l^{-1}$)

Sample	As(V)	As(III)	Methylarsonic acid	Dimethylarsinic acid	Ref.
		Freshwater			
Hillsborough River, Fla.	0.25	<0.02	<0.02	<0.02	298
Withlacoochee River, Fla.	0.16	<0.02	0.06	0.30	298
Lake Echols, Fla.	0.41	2.74	0.11	0.32	298
Sacramento River, Calif.	1.08	0.040	0.021	<0.004	300
Colorado River, Calif.	2.25	0.085	0.13	0.31	300
Silver Lake, Minn.	1.47	1.27	0.2	2.0	299
		Seawater			
McKay Bay, Fla.	0.35	0.06	0.07	1.00	298
Scripps Pier, Calif.	1.75	0.019	0.017	0.12	300
Southern Calif. Bight (1 m)	1.08	0.027	0.007	0.108	306
Southern Calif. Bight (13 m)	1.17	0.043	0.002	0.112	306
Southern Calif. Bight (1 m)	0.160	0.870	0.020	0.236	306
Southern Calif. Bight (17 m)	1.27	0.061	<0.008	0.132	306

by Batley and Florence.[140] Anodic-stripping voltammetry at a hanging-mercury-drop electrode in 1 *M* HCl produces stripping peaks for Sb(III) and not Sb(V), but in 5 *M* HCl, both Sb(III) and Sb(V) are codeposited. Alternatively, use of a thin-film electrode in 2 to 5 *M* HCl will produce a peak due to Sb(III) only, with no response from Sb(V). The method offers potentially greater sensitivity than the solvent-extraction method described earlier, but to date, it has not been applied to the analysis of seawater.

N. Selenium

Selenium is erratically dispersed in geologic materials in concentrations up to 1 $\mu g\ g^{-1}$, with an average crustal abundance of 0.05 $\mu g\ g^{-1}$. It is an essential element at concentrations below 40 $\mu g\ g^{-1}$, but is toxic above 4000 $\mu g\ g^{-1}$.[311] Very little data are available for selenium speciation in natural waters. The metal is transported to rivers and oceans as a result of weathering of minerals. Typical river concentrations average 0.2 $\mu g\ l^{-1}$, although in some surface waters concentrations exceeding 200 $\mu g\ l^{-1}$ have been reported.[311] The selenium content of seawater has an average value of 0.1 $\mu g\ l^{-1}$.[311]

Selenium exists in two common oxidation states as either Se(VI) or Se(IV). Calculations by Sillen[308] suggest that the equilibrium form of selenium in seawater should be SeO_4^{2-}. Chau and Riley,[312] however, stated that selenium(IV) is thermodynamically the most probable form of selenium in oxygenated waters, and that the element is dissolved from rocks in this form. They measured 0.34 $\mu g\ l^{-1}$ and 0.50 $\mu g\ l^{-1}$ in samples from the Irish Sea and English Channel, respectively. These concentrations were almost entirely attributable to Se(IV), since the iron(III) hydroxide coprecipitation technique used removed less than 2% of an added Se(VI) spike.

Shimoishi[313] reported a similar dominance of selenium(IV) in the concentration range 0.04 to 0.08 $\mu g\ l^{-1}$ for Japanese coastal waters. Attempts to reduce any Se(VI) to Se(IV) resulted in no detectable increases in Se(IV) concentrations. The latter were measured by extraction as the piazselenol derivatives, formed by reaction with 4-nitro-*o*-phenylenediamine, followed by gas chromatographic analysis. Sugimura et al.[314] separated selenium(IV) as the diethyldithiocarbamate complex on Amberlite XAD-2 resin. Total selenium was determined by a fluorimetric method using the 2,3 diaminona-

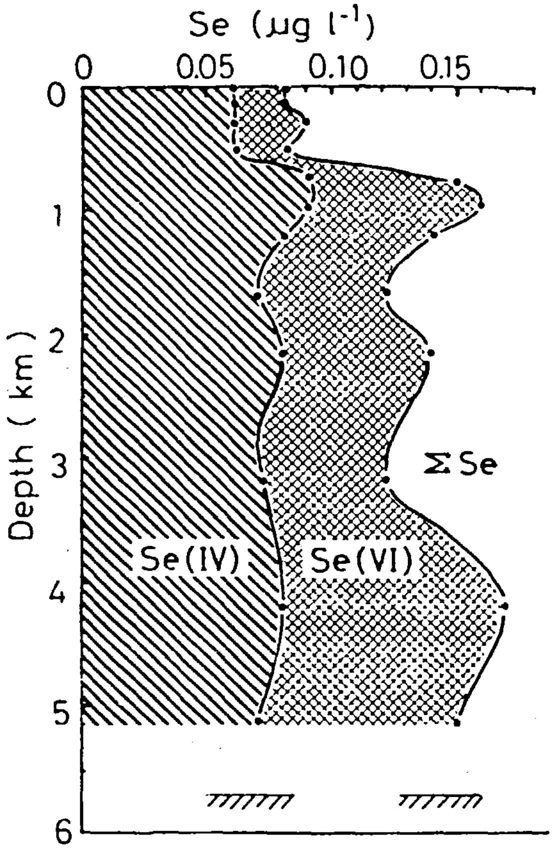


FIGURE 24. Vertical distribution of selenium(IV) and selenium(VI) in the western North Pacific. (From Sugimura, Y., Suzuki, Y., and Miyake, Y., *J. Oceanogr. Soc. Jpn.*, 32, 235 (1976). With permission.)

phthalene complex extracted into cyclohexane after an initial separation by reduction and coprecipitation. Selenium(VI) was determined using the above method after separation of Se(IV).[315] It is conceivable that the measured Se(VI) could contain colloidal Se(IV) species not retained by the resin. Adsorption of ^{75}Se from both seawater and river water onto colloidal ferric hydroxide and a range of clays has been demonstrated by Kharkar et al.[278]

Fractions of the adsorbed selenium(IV) species in the above studies could also originate from selenium organic species. Ridley et al.[302] have discussed the formation of compounds such as dimethylselenide by biomethylation reactions. These products are volatile and are slowly oxidized by molecular oxygen to stable, water-soluble species. Their presence in natural waters has yet to be demonstrated, although methods for their detection have been developed.

For seawater samples from the western North Pacific Ocean, total selenium was in the range of 0.06 to 0.12 µg l^{-1} for surface waters, and increased to 0.20 µg l^{-1} in deeper layers. Selenium(IV) showed rather uniform distribution with depth, but Se(VI) increased to about three times the surface value. The ratio of Se(IV) to Se(VI) ranged from 1 to 4 for surface samples, to 0.7 to 1.5 for deep samples (Figure 24). It was noted that the total selenium content of coastal river waters was considerably lower (0.04 µg l^{-1}) than open sea values.[314]

Results so far published[312, 314, 316, 317] indicate significant differences between the speciation of selenium in river water compared to seawater. Whereas the latter appears to have significant selenium(IV) concentrations, this oxidation state contributes less than 8% of the total selenium in riverwater. Measures and Burton[316] suggested that the remainder was most probably selenium(VI) as the selenate ion, but the presence of organically associated species, or more importantly selenium adsorbed on colloidal matter, could contribute significantly. These species would need to be slowly dissociated at pH 1 when selenium(IV) was separated as the complex with 4-nitro-*o*-phenylenediamine. The method used by these authors is essentially that of Shimoishi,[313] although the detection limit of 2 ng ℓ^{-1} is significantly lower than the 30 ng ℓ^{-1} calculated on the basis of the standard deviation of Shimoishi's results. These latest results appear to be supported by recent Japanese studies showing Se(IV) to be 2 to 16% of the total selenium in river samples[317] and up to 25% in a further river sample.[318] No reasonable explanation of the marine dominance of Se(IV) has yet been proposed.

O. Mercury

The burning of fossil fuels, the smelting of sulfide ores, cement manufacture, and the heating of other materials containing mercury, release about 10^4 t of mercury into the global atmosphere each year.[319] This amount is similar to the total equilibrium atmospheric loading of mercury. Many other industrial operations add huge amounts of mercury to the oceans and other natural waters.[320]

World attention was focused on the toxicity of mercury in the 1950s when many fatalities occurred among people living near Minamata Bay, Japan, as a result of eating fish and shellfish from the bay. The poisonings were eventually traced to methylmercuric chloride, which had been discharged into the bay from a vinyl chloride plant and had been accumulated by the marine life.[320] A most important aspect of the environmental chemistry of mercury is that aquatic sediments can oxidize metallic mercury to Hg^{2+}, and that certain organisms are capable of rapidly methylating Hg^{2+} to mono- and dimethylmercury. The methylated forms of mercury are much more toxic than inorganic forms and can be concentrated from water or through the food chain by virtue of their much higher solubility in lipids than in water. Bioaccumulation factors of 10^3 to 10^4 have been reported for mercury in fish and freshwater invertebrates, with 85 to 95% of the total mercury in contaminated fish being in the methylmercury form.[320, 321] For these reasons, most of the research carried out on the speciation of mercury in natural waters has been aimed at developing methods for the separation and determination of alkyl and other organo derivatives of mercury in the presence of inorganic mercury.

Results from chemical modeling calculations on the inorganic speciation of mercury in seawater and freshwater are shown in Table 20.[83] Because of the very strong complexes formed between Hg^{2+} and chloride, it has been computed that all the mercury in seawater exists as chloro complexes, whereas in freshwater most of the Hg^{2+} is complexed by OH^- and adsorbed on inorganic particles, with minor concentrations as chloro complexes.

The concentration of mercury in seawater has been determined by molecular spectrophotometry,[322] atomic absorption spectrophotometry,[322] and neutron activation analysis.[323] Flameless atomic absorption spectrophotometry is simple, reliable, and the most popular technique. Gardner[324] found mean values of 11 ng ℓ^{-1} and 34 ng ℓ^{-1} for total mercury in filtered waters from the southern and northern hemispheres, respectively. The higher concentrations found in northern hemisphere water were explained by industrial pollution. Fitzgerald and Lyons[325] reported 45 to 78 ng ℓ^{-1} (total) in unfiltered waters of Long Island Sound. These workers used UV irradiation to distinguish

Table 20
COMPUTER MODELING RESULTS FOR THE SPECIATION OF MERCURY IN SEAWATER AND FRESHWATER

Mercury species	Species (%) Seawater	Freshwater[a]
Hg^{2+}	—	—
Hg-chloro	100	4.8
$HgSO_4^0$	—	—
$HgOH^+$	—	39.9
$Hg(OH)_2^0$	—	39.9[b]
$HgHCO_3^+$	—	—
$HgCO_3^0$	—	—

[a] pH 8.0

[b] Inorganic particulates adsorbed 55.3%.

From Sibley, T. M. and Morgan, J. J., *Proc. Int. Conf. Heavy Metals Environ.*, Vol. 1, Hutchinson, T., Ed., University of Toronto, Ontario, 1975, 319. With permission.

between organic and inorganic mercury. They found that some samples contained as much as 63% organic mercury. Their results, however, are difficult to interpret because particulate matter in the unfiltered samples could have contributed to the organic mercury figure. Mercury is often strongly associated with particulate matter,[326] especially humic material.[327, 328] Williams et al.[323] found 12 to 30 ng kg^{-1} of mercury in the northeastern Pacific, and little variation with depth down to 6 km. Much higher concentrations (50 to 150 ng kg^{-1}) were present in polar waters. Surface ocean film contained 16 to 90 ng kg^{-1}, and pack ice and snow about 20 ng kg^{-1}. Williams et al.[323] believed that the higher mercury concentrations found in polar regions could be caused by submarine volcanism.

The mercury content of riverwater varies considerably,[320, 325] but unpolluted streams often contain about 10 ng l^{-1}, which is very similar to the unpolluted seawater value.[324, 325, 329, 330] There is little doubt that many of the early results for mercury in natural waters were seriously in error, usually high because of contamination,[331] but sometimes low as a result of adsorptive losses on the sampling bottle. It has recently been shown that the presence of hydrogen sulfide can lead to the formation of a very volatile compound, *bis*(methylmercuric) sulfide,[332]

$$2MeHgCl + H_2S \rightleftharpoons (MeHg)_2S + 2HCl \qquad (4)$$

This reaction could provide an unexpected route for losses of mercury.

A gas-liquid chromatograph coupled to a flameless atomic absorption detection system provides a very powerful tool for the separation and determination of mercury species.[96, 333] Gonzalez and Ross[334] and Longbottom[335] described simple, specific GLC techniques for the identification and measurement of subnanogram amounts of mercury alkyls in fish and sediments (Figure 25). Battisberger and Knudson[336] used ion exchange chromatography to separate Hg^{2+}, Hg_2^{2+}, and CH_3Hg^+ before determination by flameless atomic absorption spectrophotometry. The ion-exchange column consisted of cation exchange resin loaded with isothiocyanatochromium(III) ($CrCNS^{2+}$) and provided a method for the differentiation of the three mercury forms at the 1 to 100 ppb level.

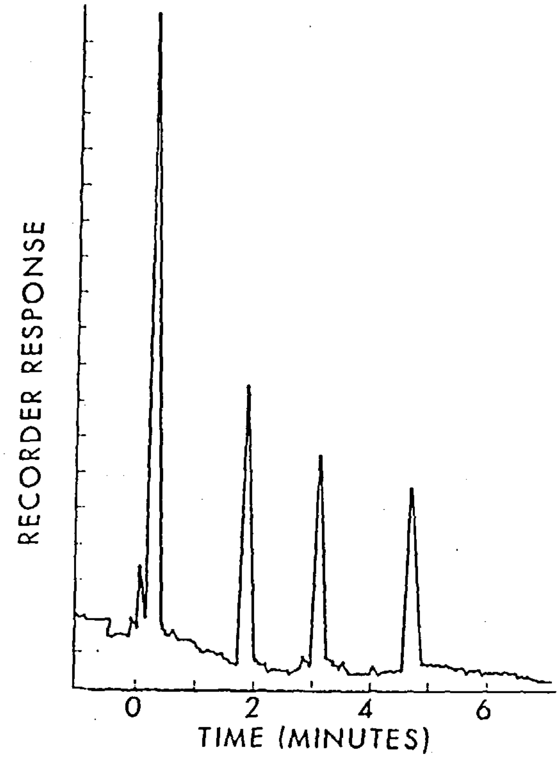


FIGURE 25. Gas chromatogram for a mixture of 1.0 ng each of dimethylmercury, diethylmercury, dipropylmercury, and dibutylmercury. (From Longbottom, J. E., *Anal. Chem.*, 44, 1111 (1972). With permission.)

Benes[326] used dialysis, ultrafiltration, centrifugation, and electromigration to study the forms of ^{203}Hg in solution (3×10^{-8} to 1×10^{-6} *M*). At pH values above 1 to 2, significant amounts of mercury(II) can be separated by ultrafiltration and centrifugation. Most of this removal was shown to be the result of adsorption of neutral HgOHCl species on colloidal impurity particles. Hahne and Kroontje[337] also showed that hydrolysis of Hg(II) becomes important at pH values above 1.0.

Inorganic mercury reacts strongly with humic material and other terrestrial and marine organic matter. Millward and Burton[338] found that a sample of terrestrial humic acid (1 mg l^{-1}) reacted with radiotracer Hg(II) forming a product which could be extracted into chloroform at pH 8. Under similar conditions, fulvic acid showed no reaction with Hg(II), and methylmercury did not react with humic acid. Lindberg and Harriss[327] showed that in sediment from the Florida Everglades, sediment mercury was strongly associated with sediment organic matter. In the pore water, dissolved mercury was combined with organic matter, mainly in the <500 mol wt fraction. Interstitial dissolved mercury was 3 to 36 times higher than the mercury content of the overlying surface water. Organic-mercury association is also evident from the high concentration of dissolved mercury in some sulfide-rich pore waters, concentrations which far exceed that calculated from the solubility of HgS.[327]

P. Other Elements

Some isolated attempts have been made to study the speciation of less-common elements in natural waters. Considering the high toxicity of silver to fish (96-hr LC_{50} of

6.5 μg l^{-1} for rainbow trout in soft water),[339] and the likelihood of silver release from mining operations, it is surprising that no experimental investigations have been reported on silver speciation. Jenne et al.,[340] using chemical modeling techniques, calculated that Ag^+ should be the dominant form of silver in freshwaters, but the chloro complexes should predominate in marine waters. However, these calculations assumed the absence of sulfide, and Jenne et al.[340] showed that in the presence of free HS^- concentrations as low as 0.01 μg l^{-1}, $AgHS^0$ is the major species in both freshwater and seawater. Because of the very low total concentration of silver in natural waters (0.4 to 20 ng l^{-1} in seawater[340]), and the extreme sensitivity of its speciation to free sulfide (and possibly organic matter), experimental determination of the chemical forms would not be an easy task.

Some investigators have studied the speciation of iodine in seawater, mainly with the aim of measuring iodate/total iodine ratios. Truesdale,[341] using electrometric and catalytic methods, found about 30 μg l^{-1} of iodate-iodine, and 49 μg l^{-1} of total iodine in Menai Straits water, with only a small annual variation. These reults are similar to those reported for many surface ocean waters.[341] At depths below 200 m, ocean water contains about 60 μg l^{-1} of iodine, nearly all of which is iodate.[341] The lower concentrations of iodate in surface waters may be the result of reduction by algae or other organic matter. Truesdale[342] found that a fraction of the iodine in seawater (1 to 6 μg l^{-1}) was unreactive to the catalytic spectrophotometric method used and was measured only after UV irradiation of the sample. He suggested that this unreactive fraction is organically bound iodine.

There has been considerable interest in determining the speciation of radionuclides of elements such as cerium, ruthenium, plutonium, and other actinides in seawater, from the point of view of their uptake by marine organisms and incorporation in the food chain.[343, 344] The concentrations, however, are usually too low for detailed measurement of chemical forms, and speciation is confined to the distinction between particulate and dissolved forms. Schell et al.[345] determined plutonium and americium in fresh and saline waters using an alumina-column sorption technique which allowed separation into dissolved, particulate, and possibly colloidal forms. In samples of seawater taken near Bikini Atoll, most of the ^{241}Am was found to be associated with the particulate fraction, but plutonium (^{239}Pu and ^{240}Pu) speciation varied considerably, some samples having high fractions of dissolved plutonium.

VI. HEAVY METALS IN INTERSTITIAL WATERS

There has been an increased interest recently in the measurement of heavy metals in sediment interstitial water since the important role that these waters play in the exchange of metals between the sediment and overlying waters has been realized. The deposition and release of metals in the sediment reservoir will be controlled by chemical and biological processes occurring in the interstitial water whose chemical composition may differ significantly from the overlying water. The former may be considered to be in equilibrium with the sediment of which it is part. Rapid exchange of dissolved species occurs across the sediment-interstitial water interface, while within the sediment column, concentration gradients are established as a result of transport between the sediment and overlying water.

The problem of sampling and storage of interstitial waters has received considerable attention. The most common separation procedures involve low-pressure squeezing[346] or centrifugation.[347] Recently, Batley and Giles[348] described an improved centrifugation technique in which a dense, inert, fluorocarbon solvent was added to the sediment. During centrifugation, water separated above the solvent layer and could be readily removed. The authors investigated the possibility of extraction of heavy metal species in the solvent layer and found this to be insignificant, although a fraction of the total dissolved organic carbon content was extractable.

There have been surprisingly few studies of heavy metal speciation in interstitial waters. Of particular interest are metals such as iron and manganese, known to be reduced and solubilized in the low Eh conditions generally established some distance below the sediment-water interface as a result of microbial degradation of organic matter.

Studies of manganese distribution in lake and deep-sea sediment pore waters indicate a decrease in dissolved manganese towards the top of the cores.[349, 350] In oxidizing sediments, dissolved manganese is generally one to two orders of magnitude lower than in reducing sediments. It is generally agreed that the reason for this behavior is that sedimentary manganese, consisting of manganese(II) adsorbed by hydrated ferric and manganese oxide coatings on sedimentary particles, is mobilized under anoxic conditions. This process involves (1) a decrease in pH due to heterotrophic activity which shifts the exchange-adsorption equilibrium to desorb Mn(II), (2) reduction of ferric oxides releasing sorbed iron(II), and (3) reduction of manganese oxides to soluble Mn(II) by iron(II) and organic matter. A model to predict dissolved manganese distribution in anoxic pore waters has been developed by Holdren et al.[351] They assumed solubility to be controlled by carbonate equilibria and neglected possible organic complexation.

A number of studies have examined total dissolved metal concentrations in interstitial waters as a function of sediment depth.[352-354] Enrichment of cobalt, zinc, cadmium, and copper was found in surface sediments, attributable to biological release.[352] Iron and nickel were greater in reducing sediments. Hoshika et al.[355] applied anodic stripping voltammetry to measure labile cadmium, lead, and copper in interstitial waters of Hiro Bay sediment (Japan). Unfortunately, no comparisons were made with total dissolved metals.

Lu and Chen[356] studied the migration of trace metals in the seawater-sediment interface. They obtained data particularly relevant to interstitial-water speciation studies. An equilibrium model was developed to predict major species in both oxidizing and reducing conditions, and the predictions were confirmed by long-term incubation experiments.[356] Calculations included both inorganic and organic ligands. For reducing conditions, sulfide complexes were calculated as the most important soluble species for cadmium, lead, and mercury. Chloro complexes were most important for manganese. Hydroxy complexes were most important for chromium. Organic complexes were most important for iron and nickel. Results agreed well with predictions except in the cases of zinc, copper, and iron, where humic complexes, not included in the model, could be important. Under oxidizing conditions, most trace metals, with the exception of chromium and mercury, were released from sediments. However, analyzed concentrations were generally not in agreement with calculated equilibrium concentrations, unlike those for reducing conditions. Metal migration was shown to be regulated mainly by the chemistry of both the immediate overlying water and that of the interstitial water. To fully understand this process, it is clear that many more practical measurements of metal speciation in these systems need to be done.

VII. METAL COMPLEXING ABILITY OF NATURAL WATERS

The concentrations of dissolved organic carbon in seawater are typically below 2 mg C l^{-1}, but in freshwater the figures are generally higher. In organic-rich rivers, values as high as 20 mg C l^{-1} are not uncommon.[270, 357] Many of these organics are potential chelators and may, therefore, play an important role in the speciation of heavy metals in these waters. Attempts to study the chemical forms of dissolved organic matter have

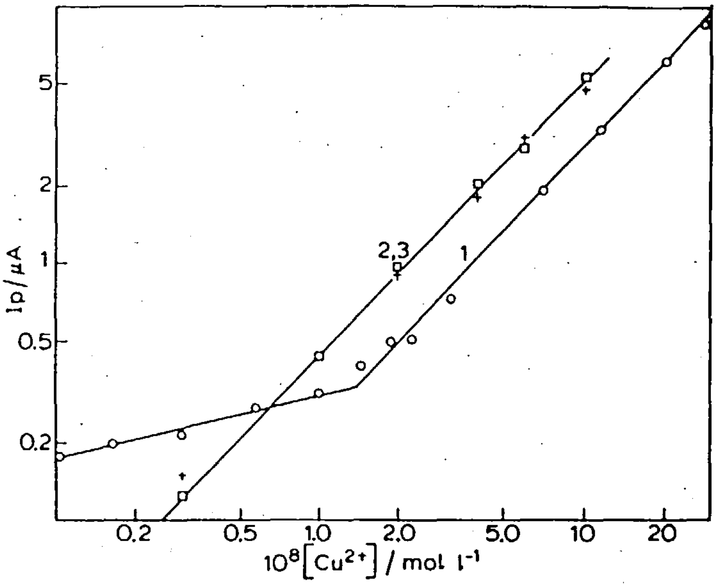


FIGURE 26. ASV peak-height concentration plots for copper added to (1) seawater, 0.016 *M* acetate buffer, pH 4.8, (2) seawater 0.016 *M* HNO_3, and (3) 0.5 *M* NaCl, pH 4.8. (From Florence, T. M. and Batley, G. E., *J. Electroanal. Chem.*, 75, 791 (1977). With permission.)

been reported.[358, 359] These exercises are quite demanding, but are of little value in providing information as to possible interactions of these species with inputs of heavy metals. In this respect, the concept of the complexing capacity of a natural water is extremely relevant. This defines the potential of an aquatic system to bind a metal, either through organic or inorganic molecules, by complexation and adsorption. In terms of both metal transport and toxicity, a knowledge of complexing capacity can be important in predicting how much of an added ionic metal component will remain in an available or labile form.

A number of techniques have been proposed for the measurement of complexing capacity, and the limitations of these methods should be carefully considered before applying them. Measurements should be quoted with respect to the particular metal titrant since the stability of complexes and possible metal exchange reactions are important. The copper complexing capacity of a given water would, for example, be expected to be greater than the zinc complexing capacity. To measure complexing capacity, a technique is required which is capable of discriminating between free and complexed metal ions. A titration or large standard addition of ionic metal is generally made, and the uncomplexed metal measured. Voltammetric methods can determine uncomplexed species, and the use of anodic stripping voltammetry to measure copper and lead complexing capacities has been reported.[360-362] Equilibration times must be adequate, and the effect of any buffer addition on the measured complexing capacities must be considered. The general adsorptive behavior of organic species at mercury electrodes could also affect their response to added metal. It is astute of Chau et al.[360] to refer to *apparent* complexing capacities. A typical titration graph is shown in Figure 26. The slope of the initial portion is related to the stability of the copper complex. The greater the stability constant, the lower the slope.[362] We have observed instances where two well-defined slopes were obtained,[363] possibly relating to distinctly different adsorbing or complexing species (Figure 27).

The ASV method will measure not only free metal ion, but all labile complexes. The

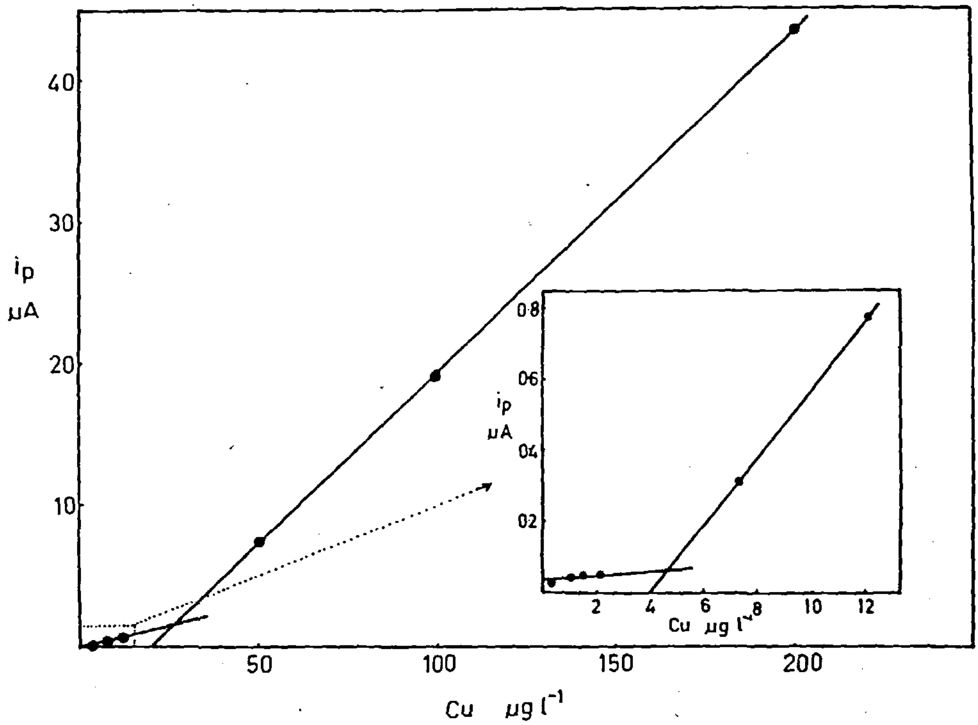


FIGURE 27. Copper-complexing capacity determination by anodic stripping voltammetry in 0.008 *M* acetate buffer, pH 4.8, on a freshwater sample from Coonjimba Billabong, N. T., Australia. (From Batley, G. E. and Farrar, Y. J., unpublished results, 1978.)

measured complexing capacity will, therefore, refer only to nonlabile, adsorbed, or complexed metal. To overcome this dissociation of weaker complexes at the electrode, Hanck and Dillard[364] measured the cobalt(III) complexing capacity by reaction of the sample with cobalt(II) and hydrogen peroxide. This method, however, most likely includes ligands from which other metals have been displaced.

Ion-selective-electrode measurements of complexing capacity are of questionable value. Such measurements will include all inorganic or organically complexed species except the hydrated metal ions.[357] By comparison with other methods, an overestimate of the complexing capacity may be obtained (Table 21). This is well illustrated by data of Ramamoorthy and Kushner,[357] who obtained values of 1.6 mg l^{-1} for copper, and 4 mg l^{-1} for lead complexing capacities of filtered waters in which the total organic carbon content was less than 6 mg l^{-1}. Values of 40 mg l^{-1} for copper were obtained for waters having less than 8.5 mg C l^{-1}.

Stolzberg and Rosin[365] used a chelating resin to separate excess ionic copper from copper complexed to or adsorbed on organic matter, the assumption being that only strong complexes will pass through the column. The method is, however, biased against the complete detection of polydentate ligands forming complexes with added indicator metal having a stability constant less than a certain critical value. The relationship between results using this method and the ASV method of Chau et al.[360] is best defined by reference to the speciation notation of Batley and Florence,[31] (Table 22). It is evident that the most useful measurements of complexing capacity are obtained by applying the indicator metal reaction to samples after a range of solution treatments such as used in the speciation scheme of Batley and Florence.[31]

Several authors have measured complexing capacity on samples fractionated by ul-

Table 21
COPPER COMPLEXING CAPACITIES OF NATURAL WATERS

Sample	Complexing capacity (μg Cu l^{-1})	DOC[a] (mg l^{-1})	Method	Ref.
Ottawa River, Canada	1600	<6	Ion selective electrode	357
Rideau River, Canada	4000	<8.5	Ion selective electrode	357
Upper Three Runs, S. C., U.S.	152	5	Ion selective electrode	169
Skinface Pond, S.C., U.S.	952	20	Ion selective electrode	169
Boston Harbor, U.S.	38	nd[b]	Chelex-100 column	316
Hamilton Harbor, Ontario, Canada	44	nd[b]	A.S.V.	368
Sudbury Lakes, Ontario, Canada	9	nd[b]	A.S.V.	368
Coastal Pacific Ocean, Sydney, Australia	0.6	2	A.S.V.	369
Ogeechee River, Ga., U.S.	10	8	A.S.V.	105
Coonjimba Billabong, N.T., Australia	36	26	A.S.V.	363
Saanich Inlet, British Columbia, Canada	12	4	Bacterial bioassay	367
Vineyard Sound, Mass., U.S.	7	2	Bacterial bioassay	367
Sargasso Sea	3	0.5	Bacterial bioassay	367
Raleigh, N.C., U.S.	44	nd[b]	Cobalt (III) complexation	362

[a] DOC, dissolved organic carbon.
[b] nd, not determined.

trafiltration,[105, 169] and the results have been discussed earlier. These attempts come close to providing the desired breakdown of complexing species.

The use of bacterial bioassay methods can provide semiquantitative data on metal complexing capacity that are probably the most relevant, in terms of metal toxicity.[366, 367] Davey et al.[366] measured the effect of copper additions on the growth of *Thalassiosira pseudonona* to determine the complexing capacity of artificial seawater to which synthetic chelators such as EDTA were added. Gillespie and Vaccaro[367] used the ^{14}C-glucose assimilation of a copper-sensitive bacterium to measure copper complexing capacity. Typical data obtained by this and other methods are given in Table 21. This table shows clearly the 1 to 2 order of magnitude difference obtained using ion-selective electrodes.

VIII. SUMMARY

Knowledge of the chemical speciation of trace metals in natural waters is essential to an understanding of the toxicity and bioavailability of these metals, and of their role in metal transport. Measurement of the total concentration of a metal can be misleading, since only specific chemical forms of the metal may be biologically active. Two distinct approaches have been made to the problem of measuring chemical speciation — computer modeling and analytical determination. The computer modeling method suffers from a lack of information about the chemical species, particularly colloidal species, present in natural waters. Experimental techniques are plagued by

Table 22
METAL FORMS MEASURED IN TECHNIQUES FOR COMPLEXING CAPACITY DETERMINATION

Technique	Uncomplexed metal	Complexed metal	Ref.
Ion selective electrode	M	ML1, ML2, ML3, ML4, MA1, MA2, MA3, MA4	357
Anodic stripping voltammetry	M, ML1, ML2, MA1, MA2	ML3, ML4, MA3, MA4	360—363
Chelex-100	M, ML1, ML3, MA1, MA3	ML2, ML4, MA2, MA4	365

contamination and sensitivity problems. Because of these serious difficulties, some doubt must exist about the validity of all chemical speciation results so far published.

Despite these doubts, some broad generalizations can be made about trace-metal speciation in natural waters. For the fraction of dissolved metal existing as simple inorganic ions, free (hydrated) metal ion, hydroxy complexes, and carbonato complexes will often be the most important species present in freshwaters, while in seawater these same species, plus chloro complexes, are likely to predominate. In all natural waters, metal adsorbed on colloidal particles may be the major form of metal in the dissolved fraction. These colloidal particles, which are often ignored in speciation studies, include organic and inorganic substances, organically coated clays, and humic-acid-sheathed particles of hydrated ferric oxide. There is considerable doubt as to the existence of true molecular (i.e., nonpolymerized and noncolloidal) metal-organic complexes in most natural waters, although such species may be present in waste waters or some organic-rich freshwaters.

Perhaps the simplest and most useful speciation method at present available is the labile-bound metal discrimination using anodic stripping voltammetry. The result for labile metal may approximate metal which is toxic or otherwise bioavailable. Unfortunately, this method is only available for those metals which are amenable to the ASV technique. For natural waters, at least, the prospects of developing an analytical procedure which can measure the concentrations of all the individual chemical species present in a water are very bleak. Computer modeling techniques aim to perform this function, but until a great deal more reliable thermodynamic data become available, chemical modeling methods are unlikely to produce results which even approximate the true situation.

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