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Chemical Forms of Mercury, Cadmium, and Zinc in Natural Waters

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Published information on the chemical forms of mercury, cadmium, and zinc in natural wet environments (water, suspended or colloidal particles, deposits, biota) and on their toxicity and biological interconversions is generalised and critically discussed, and the mechanisms for the absorption and expulsion of these materials through the appropriate phase separation surfaces are considered. The chemical forms of these and other trace metals are shown to be the controlling factor in their geochemical cycles and their anthropogenic effects on ecological equilibria in the natural environment. 224 references.

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I. INTRODUCTION

In the natural wet environment metals are found in waters, suspended or colloidal particles, the biota†, and in sludge deposits. Their distribution between these phases is controlled by complex and little understood mechanisms, involving a variety of chemical, physicochemical, biological, and physical processes which can be mutually exclusive or complementary. Existing chemical information and phenomenological models cannot adequately predict the distribution of metals between the various phases in aqueous media, which are usually very complex systems of variable composition. Though the metals are conveyed to the aqueous medium by wind erosion of dry land and by volcanic activity, a significant proportion (at least in some areas) is now contributed by man. Undesirable ecological effects can be expected as soon as the rate of supply of metals to the aqueous medium begins to exceed the rate of supply through the natural cycle: such effects have been noted in inland and coastal waters of industrially developed countries as a result of effluent disposal, of fuel combustion, and of the manufacture of cement. The atmosphere plays an important role in the transport of metals[1].

Large-scale poisoning by mercury and cadmium in Japan[2] dramatically showed that the ability of the natural environment to free itself from chemical substances of anthropogenic origin is limited, and that the chemical form of the metals (rather than, as previously assumed, their concentration) may be the controlling factor in determining the unfavourable ecological consequences. This incident also showed the need for improved methods of analysis of trace metals (TM) in natural media. A surprising trend has been recently reported in trace metal analysis: as the sensitivity and the selectivity of the analytical methods improve, the concentration of TM in the natural medium appears to decrease (by several orders of magnitude in some cases) in spite of the concurrent increase in industrial effluent levels. This observation has cast serious doubts on the validity of analytical results. Only very recently have truly reliable analytical data been obtained: these are quoted below in the appropriate sections.

The aim of this review is to generalise published information on the chemical forms of mercury, cadmium, and zinc in natural aqueous media: water (data for sea water are discussed, in part, in Refs.3 and 4), suspended and colloidal particles, sludge deposits, and the biota. Data on the toxicity and on biological conversions of trace metals are also discussed. With very few exceptions, existing analytical techniques are inadequate for the determination of the distribution of chemical forms of the TM in natural media, because the concentrations involved are exceedingly small. We shall therefore devote a special section of this review to a discussion of the chemical properties of mercury, cadmium, and zinc in aqueous solutions, in order to explain the chemical behaviour of these trace elements in nature. Many models have been proposed to account for the distribution of dissolved TMs in natural waters, but they have not been confirmed experimentally. Difficulties in interpretation arise from uncertainties in the stability constants of the complexes between the TM and some ligands, and also from the lack of reliable activity data for the reacting forms. Therefore we shall only mention the most recent models, with the most accurate values of these parameters.

To keep the length of the review within bounds the discussion of some topics (geochemistry, bio-inorganic chemistry, and hydrology) is short, or even fragmentary. For the same reason we have failed to mention many publications in spite of their direct relevance to our topic; the list of references would otherwise have been at least twice as long. Only the most recent research papers and review articles have been included.

† A historically as opposed to biologically related group of plants and animals sharing a common environment.

II. SOME CHEMICAL PROPERTIES OF MERCURY, CADMIUM, AND ZINC IN AQUEOUS SOLUTIONS

Mercury, cadmium, and zinc are typical ("non-transition") metals, because they do not show variable valency and they do not form compounds with an unfilled *d*-shell. They do not form carbonyl or olefin complexes (which are characteristic of transition metals), and they do not show the ligand field stabilisation effect. The failure to oxidise these metals to the tervalent state arises from the very high value of their third ionisation potential, and also from the high solvation energies or lattice formation energies needed to stabilise this state.

Although these metals are classified together in subgroup IIb, the chemical and physical properties of mercury (both in the elementary state and in its compounds) are markedly different from those of cadmium and zinc. Whereas the latter are electropositive metals, mercury has a high ionisation potential and a high oxidation potential, and it is chemically rather inert. The chemical properties of Hg, Cd, and Zn are discussed in detail in Refs.5 and 6. All three metals (especially, mercury) are low-melting and fairly volatile. Mercury has a vapour pressure of 1.3×10^{-3} mmHg at 20 °C, and its solubility in water is 58.8–63.9 μg litre^{-1} at 25 °C, increasing from 19.2 to 368 μg litre^{-1} between 5 and 60 °C in accordance with Henry's law (with a heat of dissolution of 5.3 kcal mole^{-1}).[7] In hydrocarbons and in ethers the solubility of mercury is over an order of magnitude greater than in water[8].

In dry air at ordinary temperature all three metals are practically unaffected (mercury reacting exceedingly slowly), but on being heated they form oxides, though at temperatures above 400 °C mercuric oxide dissociates into its elements. Cadmium and zinc do not liberate hydrogen from water, and in moist air they are quickly covered by an oxide film which protects them from further oxidation. Cadmium plating offers better corrosion protection than zinc plating or nickel plating. All these metals react with sulphur, halogens, etc.: the metallic properties become less marked on going from Zn to Hg, the heats of formation of all the compounds decreasing in that sequence[6]. Mercury reacts with many transition metals and some typical metals to form amalgams, which can have a definite composition (for example, Hg_2Na). The most typical coordination numbers of Hg, Zn, and Cd are 4, 4, and 6 respectively.

Cadmium and zinc cannot exist in aqueous solutions in the univalent state, whereas mercury forms the Hg_2^{2+} ion in which the two atoms are bivalent though the pair is electrochemically univalent and does not undergo electrolytic dissociation. The Hg_2^{2+} ion is related to other oxidation forms of mercury by the reversible disproportionation reaction $Hg_2^{2+} \rightleftharpoons Hg^0(l) + Hg^{2+}$, for which $E^0 = -1.31$ V and $K = [Hg^{2+}]/[Hg_2^{2+}] = 6.0 \times 10^{-3}$, and in which the equilibrium is strongly shifted towards the left. However, in the presence of strong complexing agents (forming strong covalent bonds), of strong oxidising agents, or in alkaline solutions, the equilibrium is shifted almost irreversibly towards the right. The Hg_2^{2+} ion has a low complexing power and it does not form covalent bonds with other elements: as a result, it cannot form metal–organic derivatives[5].

The high stability of the M^{2+} ions in aqueous solution is due to two effects. The first is their tendency to form covalent rather than ionic bonds, especially mercury, many of whose compounds are low-boiling and soluble in organic solvents more readily than in water, and differ from true salts in this respect. The second important property of these ions is their tendency to form complexes with many ligands, the Hg complexes being significantly more stable than those of Cd and Zn.[5,9] The hexa-solvates $M(H_2O)_6^{2+}$, with an octahedral structure, are formed in solution according to an X-ray diffraction study[10] of Hg^{2+}; their heats of solvation lie in the sequence Zn ≫ Cd > Hg. The enthalpy of solvation is much greater for ZnX_2 and CdX_2 (where X is a halogen) than for HgX_2, in keeping with the much stronger interaction between the water molecules and the ion in the case of cadmium and zinc. As a result, the Zn and Cd salts have a tetrahedral or octahedral structure in solution, with water molecules coordinated like those of other ligands, whereas the mercury salts have a linear structure and are very weakly solvated[11]. It is assumed that HgX_3^- ions (where X = Br, I) form a flattened pyramid in solution, whereas HgX_4^{2-} ions form a regular pyramid and CdX_4^{2-} form a regular tetrahedron (as shown by X-ray diffraction results in the case of CdI_4^{2-}).[10,12]

In aqueous solution the degree of dissociation of MX_2 (where X = halogen) falls in the series Zn > Cd ≫ Hg, the mercury halides being ~99% in the form of molecules. The form of the metal is very sensitive to concentration. Thus, $ZnCl_2$ can exist as $Zn(H_2O)_6^{2+}$, $ZnCl^+(aq)$, $ZnCl_2(aq)$, and $ZnCl_4(H_2O)^{2-}$ ions, with out any $ZnCl_3^-$ or $ZnCl_4^{2-}$ ions on the evidence of Raman spectral data[5], whereas CdX_2 exists as Cd^{2+}, CdX^+, CdX_2, CdX_3^-, and CdX_4^{2-}.[5,6] In concentrated solutions of $HgCl_2$ (with $c_{Hg} \geq 1$ *M*) containing a large excess of Cl^- corresponding to a molar ratio Cl/Hg ≥ 4.5 the predominant ion is $HgCl_4^{2-}$, but at $c_{Hg} \geq 0.5$ *M* and a molar ratio Cl/Hg ≅ 3 we find poly-nuclear complexes of the type of Hg_2Cl_4, $Hg_3Cl_{8,3}$, etc.[12] At molar ratios X/Hg < 4 (X = Br, I) HgX_3^- complexes are formed, whereas dilute solutions of HgX_2 contain HgX^+, HgX_2, HgX_3^-, and HgX_4^{2-}, but no poly-nuclear complexes (according to X-ray diffraction and Raman spectral data)[13].

It is believed that the great variety of cadmium forms (and, to some extent, of zinc and mercury forms) is due to self-complexing, for example by the reaction $3CdI_2 \rightleftharpoons Cd(CdI_3)_2$, which drastically lowers the concentration of Cd^{2+}. We note that these reactions take place even in very dilute solutions. At a 0.01 *M* concentration the relative amount of the various cadmium halide forms decreases in the series[6] $CdX^+ > Cd^{2+} \gg CdX_2 \gg CdX_3^- \gg CdX_4^{2-}$.

The ratio of the various forms depends also on pH and concentration. At pH 5 only Cd^{2+} ions are present, but at higher pH values colloidal forms are present together with their ionic and molecular hydrolysis products. In solutions of concentration $\leq 5 \times 10^{-7}$ *M* many pseudo-colloids are formed by the adsorption of $CdOH^+$ and $Cd(OH)_2$ on colloidal impurities, but at pH ≤ 7 and Cd^{2+} ion is predominant whereas at pH 8–10 the predominant species is $CdOH^+$. In solutions of 5×10^{-6} *M* concentration the hydrolysis products polymerise with formation of colloidal $Cd(OH)_2$ or of basic salts[14].

Mercury forms metal-organic compounds of the R_2Hg and RHgX type (where R is an organic radical and X is an inorganic or organic acid residue). The reactivity of these compounds is strongly dependent on the nature of R and X: they are very stable towards water and air (differing in this respect from the corresponding cadmium and zinc compounds[5,15]) because of the very low affinity of mercury for oxygen rather than because of the strength of the Hg–C bonds, which are rather weak (13–52 kcal mole^{-1}, depending on R).[5] Thus, Me^2Hg is stable for about one day in a saturated acid solution or in a 1 M solution of KOH at 85 °C, and it is resistant to photolysis with λ > 290 nm even in the presence of photosensitisers (acetone and singlet oxygen). At 10^{-4} *M* concentration MeHgX (X = Cl, OH) and $MeHg^+$ are photochemically stable for 17 h, but for X = Br, I the compounds are degraded by 10 and 90% respectively in 3.7 h (according to u.v. spectral data); at pH 5 the acidolysis half-life of Me_2Hg is 33 h.[16] Phenyl-mercury compounds decompose under irradiation with a quantum yield of 0.2–0.3, which is independent of pH. The

decomposition is accelerated by adding photosensitisers with a triplet state energy ≥80 kcal mole^{-1}. The photolysis half-life of these compounds and of Ph_2Hg is 17 and 8.5 h respectively[17]. Me_2Hg evaporates from aqueous solution 2.3 times more slowly than mercury vapour[16], probably because of its higher solubility (3.0 g litre^{-1} at 20 °C).[18]

After lengthy exposure to air, light, and heat the mercury-organic compounds undergo abiotic degradation, with oxygen attack by a free-radical mechanism to give both addition and degradation products[19]: $R_2Hg + O_2 \rightarrow RHgOR$ and $(C_nH_{2n+1})_2Hg + O_2 \rightarrow C_nH_{2n+1}OH + C_nH_{2n}O + Hg^0$. In u.v. light they are decomposed by the same mechanism but to free radicals and mercury: $R_2Hg \rightarrow R^{\cdot} + RHg^{\cdot} \rightarrow R^{\cdot} + Hg^0$.

An important reaction of this type of compound is the reversible symmetrisation reaction $2RHgX \leftrightharpoons R_2Hg + HgX_2$. The equilibrium is shifted towards the right by adding symmetrising agents (iodides, amides, cyanides, aluminium or magnesium oxide, etc.): this effectively removes the inorganic mercury by complex formation, precipitation, or reduction[19]. However, we should note that in aqueous solutions precipitants and sulphur compounds do not act as symmetrising agents[20]. Nevertheless organic mercury has a much lower coordinating power than inorganic mercury. Only the following complexes with simple ligands have been described: $MeHgX_2$ (where X = Br, I, Cn)[21,22], and $RHgX_3^{2-}$ (where X = I and SCN, but not Cl and Br). The $MeHg(SCN)_3^{2-}$ molecule forms a distorted tetrahedron, with two very weak Hg–SCN bonds[23]; $MeHg^+$ exists in water in the forms MeHgOH, $MeHgOH_2^+$, $(MeHg)_2OH^+$, and $(MeHg)_3O^+$, which are mutually related by reversible acid–base and self-association reactions. The last of the above forms has a low stability constant: $K = 0.3–0.7$ (according to titration curves and to PMR and Raman spectra)[21,23,24].

Alkylmercury, like inorganic mercury, forms a much stronger bond with sulphur atoms than with nitrogen, oxygen, or halogens. This effect is clearly shown by the values of log[MeHgX] in water (21.2, 9.37, 7.25, and 5.25 for X = S^{2-}, OH^-, NH_3, and Cl^- respectively[23]), and also by the shift of electron density from the ligands towards the mercury in complexes of the $HgY_2.XCH_2CH_2X$ type (Y = Cl, Br, I; X = OMe, SMe, NMe_2) indicated by NMR measurements on the halogen nuclei, which show a decrease in complex forming power in the series S >N >O.[25]

The very insoluble compounds HgS and $(MeHg)_2S$ give rise to the soluble species HgS_2^{2-}, $HgSH^-$, and $(MeHg)_3S^+$ in the presence of an excess or deficit of sulphide ions[26]. The latter dissociates in water by the scheme

$$(MeHg)_3S^+ \rightleftharpoons MeHg^+ + (MeHg)_2S \rightleftharpoons MeHg^+ + MeHgS^- \rightleftharpoons MeHg^+ + S^{2-}.$$

The K_{diss} values for the above steps are given[21] as 10^{-7}, 10^{-16}, and 10^{-21} respectively. In spite of the high affinity of mercury for sulphur, methylmercury is not decomposed by active thiols in water, unlike phenylmercury which undergoes the reaction[20] $Me(Ph)HgCl + RSH \rightarrow MeHgSR$ or RSHgCl: however, it is volatilised in the presence of H_2S, probably with formation of Me_2Hg.[27]

It has been shown that Hg_2^{2+} can form complexes in water with aniline (of composition Hg_2A^{2+}, where A is a monodentate ligand),[28] with organic acids (Hg_2A^+ and Hg_2A_2),[29] and with polyphosphates and dibasic acids ($Hg_2L_2^{-2q+2}$ and $Hg_2L(OH)^{-q+1}$, where L^{-q} is an anion)[30]; some of these complexes are unstable towards disproportionation. Complexes of Hg^{2+} with amines[28] (of composition HgA_2^{2+}) and with organic acids[29] (of composition HgA^+ and HgA_2) have been described, but the formation of 5-, 6-, or 7-membered chelate rings with *O*-substituted carboxylic acids could not be detected.

PMR spectra have been used to demonstrate the formation in aqueous solution of compounds of methylmercury with amines ($MeHgA^+$) and with organic acids (MeHgOCOR), stable at pH 7.5–9.5 and 0.5–13.0 respectively. A detailed description of the interaction of $MeHg^+$ with various ligands is given in Ref. 23. The existence of $[(MeHg)_2OCOMe]^+$ is also suggested[31].

Hg^{2+} is readily alkylated by organic compounds undergoing photolysis. Thus, mixtures of mercuric chloride with small amounts of acetic acid, methanol, or ethanol give MeHgCl (mixed with EtHgCl in the case of propionic acid). The same product is obtained from α-aminoacids of the alanine and leucine type, but not from RHgCl, which suggests that $Me^{\cdot}$ radicals are formed from the acids and methylate the mercury[32]. The yield of methylmercury chloride is very high during the photolysis of mercury acetate, which is reduced as far as the Hg_2^{2+} state in the presence of Cl^-.[33]

Mercury can be easily methylated also by exchange reactions with silicon-, tin-, and lead-organic compounds[34]. These reactions, described by the equation $Me_3E^+ + Hg^{2+} \rightarrow MeHg^+ + Me_2E^{2+}$, go to completion. For E = Sn, Pb the reaction rate can vary by 4–5 orders of magnitude depending on the salinity and the ionic strength of the solution. On the other hand, the arsenic analogue forms metallic mercury[35]: $Me_3As + Hg^{2+} \rightarrow Me_3As^{2+} + Hg^0$.

In the presence of the Hg^{2+} ion many aromatic compounds are easily mercurated by the reaction $Hg^{2+} + C_6H_5X \rightarrow XC_6H_4Hg^+$, accompanied by the formation of labile complexes between the reaction products and Hg^{2+}.[36]

III. CHEMICAL FORMS OF MERCURY, CADMIUM, AND ZINC IN NATURAL WATERS

Natural waters (NW) are complex solutions of different substances. Their chemical composition is extremely varied: they are conventionally classified according to mineral content into fresh waters, brackish waters, sea waters, and brines, with total ion concentrations of < 1.0, 1–25, 25–50, and >50 g kg^{-1} respectively.[37] However, this classification ignores all compositional differences.

The main types of NW are atmospheric precipitation, subterranean waters, and the waters of rivers, lakes, reservoirs, seas, and oceans. The mineralisation of atmospheric precipitation over dry land is usually 10–20 mg litre^{-1} (< 5 mg litre^{-1} for water in clouds), whereas in subterranean and in lake waters it varies from a few tens of mg litre^{-1} to 650 and 350 g kg^{-1} [mg kg^{-1}? (Ed.of Translation)]. According to chemical composition, NW can be classified into five groups: 1) the ion present at the highest concentration (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}); 2) dissolved gases (O_2, N_2, CO_2, H_2S, etc.); 3) biogenic materials (nitrogen, phosphorus, and silicon compounds); 4) trace elements (compounds of all the other elements); 5) organic compounds[37]. The arbitrariness of this classification is evident. For example, Na, Ca, and Fe can be assimilated by living organisms as well as the biogenic elements; also, the concentrations of the biogenic elements are often lower than those of the trace elements.

Most of the Earth's rivers show a low (< 200) or an intermediate (200–500 mg litre^{-1}) degree of mineralisation. High (500–1000) or very high (>1000 mg litre^{-1}) mineralisation of river water is seldom found. However, the chemical composition of river waters is far from uniform, especially along the length of the river (with a smaller non-uniformity across the width of the river and a negligible non-uniformity in the depth), arising from the inflow of tributaries, seepage of subsurface waters, and the uncontrolled timing of the various water flows along the length of the river[37].

Sea (and ocean) waters have a time-independent composition, uniform in different parts of the ocean as well as in depth. In the open ocean the quantitative relationship between the concentrations of the main ions is always constant, irrespective of absolute concentration. This is a fundamental rule in the chemistry of ocean waters. The constancy of the composition of oceanic waters can be perturbed only in the coastal regions, where decreasing salinity is found, and in land-locked seas, where the salinity (S) is usually low and the exchange of water with the ocean is hindered. Sea water shows another distinguishing feature as a chemical environment: a high hydrostatic pressure.

Mercury, cadmium, and zinc are present in NW at concentrations below 1 mg kg^{-1} (1 ppm), and therefore they can be classified as trace metals (TM). However, the true concentrations of TM in NW have only recently been determined[38,39], and found to be at least an order of magnitude lower than previously reported. Precise measurements of [TM] concentrations require careful attention to purity in all stages of the analysis, from sampling to end-determination, and the analytical conditions are very strict. For example, specially air-conditioned premises from which all metal surfaces are excluded are recommended[38]. Water samples for the determination of TM in hydrochemistry are usually filtered through a membrane with a pore diameter of 0.45 μm: this is done in order to compare NW having different concentrations of suspended particles (on which the TM are adsorbed, or chemically bound). These analyses yield the concentration of dissolved TM, whereas unfiltered samples give the total concentrations.

In fresh waters (Alaska snow) the concentration of Zn, Cd, and Hg was found[40] to be 1.07–1.67, 0.08–0.22, and ≤ 0.005–0.026 μg $litre^{-1}$ respectively. The concentration of Hg in ice cores was ~0.01 μg kg^{-1}, varying between 0.002 and 0.019 μg kg^{-1} in the period 1727–1971.[41] In subsurface waters the concentration of TM is strongly dependent on the location and on the sampling time within a particular month, variations as high as 10–100-fold being reported[42]. In the Mississippi estuary# the concentration of Hg was found[43] to be 0.05 μg $litre^{-1}$, and in the fresh river water 0.01–0.039 μg $litre^{-1}$.[44–46] Of the various forms of mercury, only $MeHg^+$ was determined, though it accounts for only a small part of the dissolved mercury. In the Great Lakes < 2.4×10^{-4} μg $litre^{-1}$ was found; in some other lakes of Canada 5–7×10^{-4} μg $litre^{-1}$; in the Mississippi estuary and in the Everglades less than 2 and 1% respectively[43]. The concentration of Cd in two rivers of Australia[47] was 0.02–0.30 μg $litre^{-1}$, and at the mouth of the Amazon[48] 0.067 μg kg^{-1}.

The mercury content of the surface water in the Atlantic and the Indian Ocean is 0.008–0.0335 and 0.0112–0.0201 μg $litre^{-1}$ respectively, in the China Sea 0.016–0.0284 μg $litre^{-1}$, and near the shores of Great Britain 0.0061–0.028 μg $litre^{-1}$.[49–51] The concentration in unfiltered water in the Atlantic Ocean increases with depth (0–4030 m) from 0.03–0.04 to 0.142 μg $litre^{-1}$.[52] In the Arctic Sea the concentration of Cd is 0.11 μg $litre^{-1}$,[53] in the Atlantic Ocean 0.04 μg $litre^{-1}$ [54] and 0.060 μg kg^{-1},[55] and in coastal waters < 0.05–0.8 μg $litre^{-1}$.[54] In the Pacific Ocean the concentration of Zn and Cd increases with depth (0.2–2950 and 0.3–5500 m respectively) from 0.01 to 0.6 μg $litre^{-1}$ [41] and from 0.1 to 1.1×10^{-9} mole kg^{-1},[48] indicating absorption of these metals by living organisms near the surface and regeneration at great depth from biological deposits under pressure[39,48]. The same explanation applies to the distribution of Cd (< 0.01–0.025 μg $litre^{-1}$) in the Sargasso Sea[56]. The rate of vertical transfer of Zn by biologicial means from pelagic organisms to those of the benthos§ is calculated to be much lower than the rate of transfer through excreta, and is approximately two years[57]. On the whole there is no evidence of contamination of the waters of the open oceans by Hg, Cd, and Zn.

The concentration of metals in NW is highest in a microscopic surface layer (or film) in which micro-organisms, plankton, organic compounds, and biogenic elements are also concentrated. In comparison with the underlying layers the concentration factor of the micro-layer can be as high as 100 or 1000. In these circumstances correct sampling becomes a fundamental (and so far unsolved) problem. A film 100 μm thick is usually taken, but this is too thick in comparison with a monolayer of organic and inorganic molecules (5–30 × 10^{-3} μm). Therefore the concentration factor in reality is very much greater than the measured factor. It is important to note that in surface layers from sea water the metals are bound exclusively to organic substances, the concentration of inorganic forms being the same as in the underlying layers of surface waters[58]. Since these layers can form an easily collected foam in the wind, the concentration factor for foams should be very much higher than for layers collected by submerged metal gauzes. Factors of 408 and 300 for Zn and Cd respectively were obtained for the foam from a lake in the USA.[59]

The total metal content of the ocean is believed to be held constant by the balance between the rates of addition and of removal. The mean residence time of metals in the ocean is determined from the rate of precipitation into the bottom deposits or from the rate of supply from the rivers to the ocean. These times, which are an indication of the relative reactivity of Hg, Cd, and Zn, are 26000 and 42000 years[60], 7700 and 92000 years, and 7800 and 18000 years[61] respectively.

Table 1. Estimated average concentrations of the main inorganic components dissolved in river and sea waters[62].

Component	River water		Sea water (S=35‰)	
	concn, mg $litre^{-1}$	proportion of total dissolved solids, %	concn. mg $litre^{-1}$	contribution to S, %
Na^+	6.3	5	10 770	31
K^+	2.3	2	399	1
Mg^{2+}	4.1	3.5	1 294	4
Ca^{2+}	15	12.5	412	1
Fe	0.7	<1	<0.01	—
Cl^-	7.8	6.5	19 340	55
SO_4^{2-}	11.2	9	2 712	8
HCO_3^-	58.4	49	140*	0.4
Silicon	13.1**	11	<0.1—>10***	—

* Inorganic carbon as HCO_3^-.
** As SiO_2.
*** Value depends on location and depth.

The dissolved forms of TM in NW are largely determined by the nature of the main ions and of the organic substances present. Estimates of the average concentrations of the main inorganic components of river and sea waters[62] are given in Table 1. Among the main ions of sea water, making a significant contribution to the salinity with concentrations

Funnel-shaped mouth of a river, widening out towards the sea.

§ From organisms swimming or passively drifting in the sea to those living on (or in) the bottom deposits, or moving along the sea bottom.

greater than 1 mg kg^{-1}, should be included boron compounds, Sr^{2+}, Br^-, and F^-: their concentrations are given[63] as 4.5, 7.9, 67.3, and 1.3 mg kg^{-1} at a salinity of $S = 35‰$.

Depending on the analytical method and separation technique used, several schemes have been proposed for classifying the chemical forms of metals in NW (see, for example, Ref.64). It is convenient to subdivide the forms of metals into: simple hydrated ions (M^{2+}.aq), simple compounds and complexes with inorganic (MCl_4^{2-}, MCO_3) and with organic ligands (aminoacids and citrates), stable compounds and complexes with inorganic (MS, $MSiO_3$) and with organic ligands (M-humates), and metals adsorbed by inorganic colloidal particles (M^{2+}–$Fe_2O_3.nH_2O$, M^{2+}–$MnO_2.nH_2O$, M^{2+}–clay) and by organic colloidal particles (M^{2+}–humic acids, M^{2+}–organic detritus).[65] Because of the specific chemical properties of mercury, to these forms of M^{2+} we should add $MeHg^+$ and Hg_2^{2+}, and also Hg^0 (the solubility of mercury in sea water at 30 °C obeys Henry's law and increases from 17.2 to 69.7 μg $litre^{-1}$ between 5 and 30 °C)[7] and Me_2Hg (whose solubility in sea water decreases from 2.84 to 1.88 g kg^{-1} between 0 and 26 °C).[18] The methods used to determine the forms of metals in NW are discussed in Ref.65. In particular, it is shown that Cd and Zn are present as M^{2+}.aq, as well as hydroxyl and chloride complexes (in the case of sea water).[53] We note that $^{65}Zn^{2+}$ is not transferred to the organic fraction even one year after being added to sea water[53]. No isotope exchange takes place between Hg^{2+} and MeHgCl in fresh waters[67].

NW always contain very small amounts of soluble organic compounds (SOC) consisting mainly (up to 80%) of highly oxidised and biologically stable polymeric compounds similar to the humus materials (HM) extracted from soils. The concentration of SOC in fresh waters is usually 1–10 mg $litre^{-1}$,[68] but in sea waters it is only 0.5–1.0 mg C $litre^{-1}$,[69] because of the dilution and flocculation which occurs at the boundary between fresh water and sea water[70]. The rest of the SOC consists of a mixture of polypeptides, polysaccharides, amino-acids, fatty acids, hydrocarbons, vitamins, and many other compounds. The low concentration of these materials (0.008–0.5 mg $litre^{-1}$ in the case of amino-acids[71]) is the result of bio-degradation. It makes identification very difficult: for example, in the case of sea water only ~10% of the compounds have been identified, since only a few compounds are present at a concentration $>10^{-6}$ M.[69] The problem of SOC in sea water is specially discussed in Ref.72. In polluted rivers, on the other hand, ~100 different compounds have been identified, including organic solvents and poly(ethylene glycols).[73]

Humus materials are transferred to NW through the fractional extraction of organic compounds from soils by atmospheric precipitation. They are subdivided into three components: humic acids (HA), which are soluble in basic solutions, fulvic acids (FA), which are soluble in both basic and acid solutions (and produce a yellow colour in fresh waters and subsurface waters[68]), and insoluble humus material. The distinction between these three classes is not always clear, and differences may arise from variations in elemental composition, acidity, degree of polymerisation, and molecular weight (MW).[74] In fresh waters FA and HA have MW of 300–2000 and 5000–100000 respectively[68]. The average MW of unfractioned humus from water is ~1000.[70]

The structure of humus materials is unknown. They are high-molecular poly-electrolytes of indeterminate composition. However, it is usually assumed that HA molecules consist of benzene and heterocyclic rings (probably condensed), with di- and trioxy groups, connected by CH_2–, O–, NH–, –N–, and S-groups to which are attached side chains with various functional groups. FA are believed to differ from HA by having a much greater proportion of functional (especially carboxylic acid) groups and aliphatic carbon, and a smaller proportion of aromatic carbon[68,74]. HA from soils have been shown by the NMR method (^1H and ^{13}C) to contain up to 65% of aromatic and carboxylate carbon and a large number of aliphatic OH groups: their structure is quite different from that of coal and lignin[75]. The chemical characteristics of humus from water and of sea-water FA are discussed in Refs.76 and 77.

Humus materials combine with metal ions, take part in cation exchange, contain free radicals, and adsorb metal hydroxides, proteins, insecticides, alkanes, etc. They can adsorb metal ions (up to 1–17% by weight).[68] Being stable organic free radicals[68], HA can reduce Hg^{2+} to Hg^0 in aqueous solution at pH 6.5–8.2 by a first-order reaction ($k = 0.009$ h^{-1}).[78]

The chemical nature of the combination of metal ions with HA and FA is not understood at present. It has been suggested that binding occurs through all the ion-forming functional groups, and that chelation plays an important role, as in the case of salicylic acid and pyrocatechol.[74,79] However, the analogy is not clear: for example, in HA at least 1/3 of the phenol groups has been shown not to be in the *ortho*-position with respect to the carboxyl groups[80], and the nature of the remaining phenol groups is uncertain. The metals may be combined in a tetrahedral or an octahedral coordination, in which they are fairly stable towards complex formation and reduction (as demonstrated by ESR and Raman spectra in the case of Fe^{3+}).[81] Two complex formation centres have been found in HA, with K values differing by an order of magnitude[82].

Because of the difficulty of identifying and quantitatively determining all the organic ligands dissolved in NW, the concept of the complex-forming power of the NW itself has been proposed. This quantity is a measure of the ability of the NW to form complexes with (or mask) a given metal ion. Methods of determining it are discussed in Ref.79. Values of $1–7 \times 10^{-7}$ M have been reported[83] for Cu^{2+} in fresh waters, whereas in sea water the values for Cu^{2+} and Pb^{2+} are 10^{-8}–3×10^{-7} M[53,65] and 3.2×10^{-7} M[53] respectively. Biological methods of determining complex-forming power have also been proposed[84]. These results include only a small fraction of the real complex-forming ability of the NW, since most of the reactive centres in the organic ligands are already occupied by strongly bound metals such as Fe^{3+} and Al^{3+}. For example, 7 mg $litre^{-1}$ of FA contain ~20 μmole $litre^{-1}$ of potentially reactive sites, but typical values of the measured complex-forming power[83] lie in the range 0–2 μmole $litre^{-1}$.

In NW the extent to which trace metals are combined with SOC depends on the concentration of the TM, on competition from other ions present in higher concentrations, and on pH. However, the results of the measurements can be strongly influenced by the chosen method. Thus, several workers find that most of the Zn,[85] Cd,[86,87] and Hg[44,85,87] in fresh waters is combined with SOC, whereas Florence[88] reaches the opposite conclusion for the first two of these metals. In coastal sea waters Hg[43,44,50] and Zn[53] (but not Cd) will also be found preponderantly in the organic fraction, though the effect is not observed in the open ocean[51]. FA combine with metals very strongly[43,87,89], but the complex-forming power of HA depends on their origin[90], on the pH, and on the presence of Ca^{2+} and Mg^{2+}.[91] The stability of the Zn^{2+} and Cd^{2+} complexes decreases in the sequence HA > OH^-, HCO_3^-, CO_3^{2-} > glycine[91]. FA from soils, with an average MW of 2775, forms Cd complexes of 1 : 1, 2 : 1, and 3 : 1 composition having stability constants $K = 10^{6.0}$, $10^{10.7}$, and $10^{15.4}$ respectively[79] at pH 7.7.

By using the gel filtration method at pH 8.0 it was found[92] that the stability of the complexes formed by HM with particular trace metals depends on the origin of the HM: $\log K = 4.83$–5.87 for Zn, 4.57–4.95 for Cd, and 18.0–21.3 for Hg. On the

whole the stability of metal–HM complexes follows the Irving–Williams stability series for metal chelates: Mg < Ca < Cd ≅ Mn < Co < Zn ≅ Ni < Cu < Hg.[92]

Because of the exceedingly low concentration of TM in NW their chemical form cannot be established by existing analytical techniques, but the effect of various equilibria on the chemical form is discussed in Refs.69 and 93. Therefore, equilibrium concentrations are calculated by using models relying on arbitrary values of the stability constants (β) of the complexes formed with inorganic ligands in conjunction with the analytically determined concentrations of the TM. However, very different β values may be used for a given complex by different workers, leading to large differences in composition and relative abundance of the various forms. For example, by inserting into the model more accurate values of β for $Zn(OH)_2$ and $ZnCO_3$ the calculated distribution of the main forms of zinc in sea water ($S = 35‰$, pH 8.1) changed from 60% $Zn(OH)_2$, 17% Zn^{2+}, 7% $ZnCl^+$, and 5% $ZnCO_3$ to 47% Zn^{2+}, 20% $ZnCl^+$, 10% $ZnCl_2$, and 10% $ZnSO_4$.[92] Other calculations suggest that in fresh waters at pH 5–9 the main forms of $MeHg^+$ are $MeHgS^-$, $(MeHg)_2S$, and MeHgSR, or (in the absence of sulphur compounds) MeHgOH and MeHgCl.[94] Sea water of salinity $S \cong 10‰$ and pH 8.2 contains 11.8% $HgCl_2$, 22.8% $HgCl_3^-$, and 64.5% $HgCl_4^{2-}$,[95,96] but under reducing conditions the main forms of zinc are $Zn(SH)_3^-$ and $Zn(SH)_2$.[97] In estuarine waters at pH 6.5–9.5 zinc and cadmium are found predominantly in the M^{2+}, MCl^+, and $M(OH)_2$ forms[98], but in fresh waters, allowing for adsorption[99], the predominant form is M^{2+}.

Table 2. Arbitrary stability constants of some inorganic forms of Hg, Cd, and Zn.[92]

Ligand	lg β₁			lg β₂			lg β₃			lg β₄		
	Zn	Cd	Hg	Zn	Cd	Hg	Zn	Cd	Hg	Zn	Cd	Hg
Cl^-	0.40	2.0	7.28	0.61	2.7	14.01	0 53	2.1	14.98	0.20	—	15.76
SO_4^{2-}	2.3	2.3	2.42	—	3.5	3.52	—	—	—	—	—	—
HCO_3^-	1.9	1.8	2.5	—	—	—	—	—	—	—	—	—
CO_3^{2-}	4.8	4.4	6.3	—	—	—	—	—	—	—	—	—
OH^-	4.40	5	10.86	10.0	10.6	12.24	14	10	—	15	10	—

Table 3. Calculated concentrations of the chemical forms of metals in lake waters, mole %.[92]

Component	Free ion	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	OH^-	HM
Mg	98.2	—	0.5	0.5	—	—	0.8
Ca	97 8	—	0.6	0.9	—	—	0.7
Cu	—	—	—	—	—	—	99.97
Zn	88.8	—	0.5	3.1	0.6	—	7.0
Cd	92.8	0.7	0.5	3.0	0.2	0.1	2.7
Mn	90.6	—	0.5	2.9	0.9	—	5.1
Hg	—	—	—	—	—	—	100.0
Ni	69.6	—	0.4	11.1	11.2	—	7.7
Co	76.0	—	0.5	9.6	9.8	—	4.0

HM	free	Mg	Ca	Cu	Zn	Mn	Ni
	75.2	6.4	15.0	0.8	1.0	1.5	0.1

Using improved values of β for the complexes of metals with inorganic ligands (Table 2) in conjunction with experimental values of the stability constants of the complexes with humus materials and of the concentrations of main ions, TM, and HM, and of the total inorganic carbon and carbonate alkalinity and pH, the forms of the metals in lake waters have been calculated (Table 3). We note that >99% of the Hg and Cu is combined in the HM, whereas in the case of the other metals 70% or more is in the form of free cations. On the other hand in sea water >99% of the HM is combined with Ca and Mg, which are present at relatively high concentration, and among the TM only Cu is combined to a significant extent (~10%). The equilibrium forms of the TM have been calculated also as a function of salinity (Figs.1–3).[92] All these calculations ignore the formation of mixed or poly-nuclear complexes, and interfacial reactions.

We should stress that the formation of dissolved chemical forms of TM in NW is determined by several parameters: the pH, the redox potential, the nature and concentration of the TM, of inorganic and of organic ligands, and of colloidal particles (and the accessibility of their surface), and the possibility of interfacial reactions (precipitation, dissolution and sorption, biological and physical processes, etc.). The qualitative and quantitative effects of most of these factors on the chemical forms of dissolved metals are unknown. Therefore we cannot determine the extent to which the calculated forms of metals in NW approach the real distribution, even when very correct models are used in the calculation.

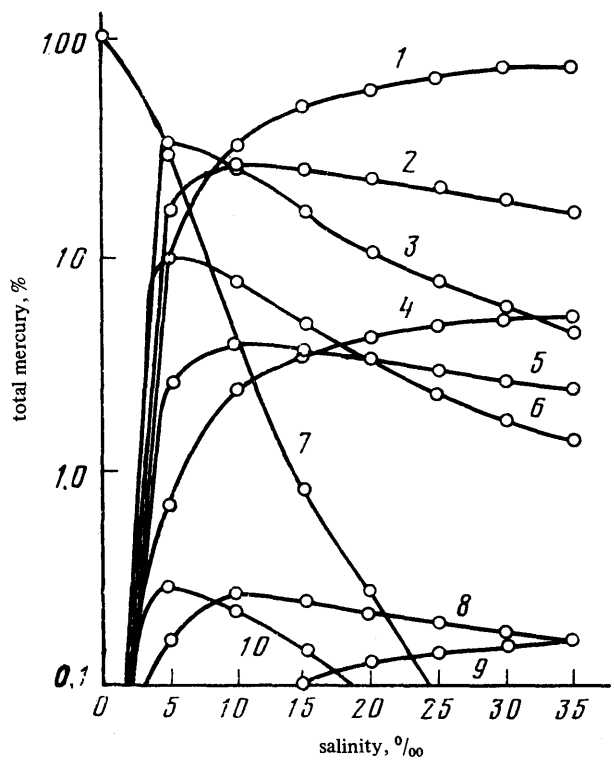


Figure 1. Equilibrium chemical forms of Hg^{2+} in the water of a model estuary[92]: *1*) $HgCl_4^{2-}$, *2*) $HgCl_3^-$, *3*) $HgCl_2$, *4*) $HgCl_3Br^{2-}$, *5*) $HgCl_2Br^-$, *6*) HgClBr, *7*) mercury combined with humus materials, *8*) $HgClBr_2^-$, *9*) $HgCl_2Br_2^{2-}$, *10*) $HgBr_2$.

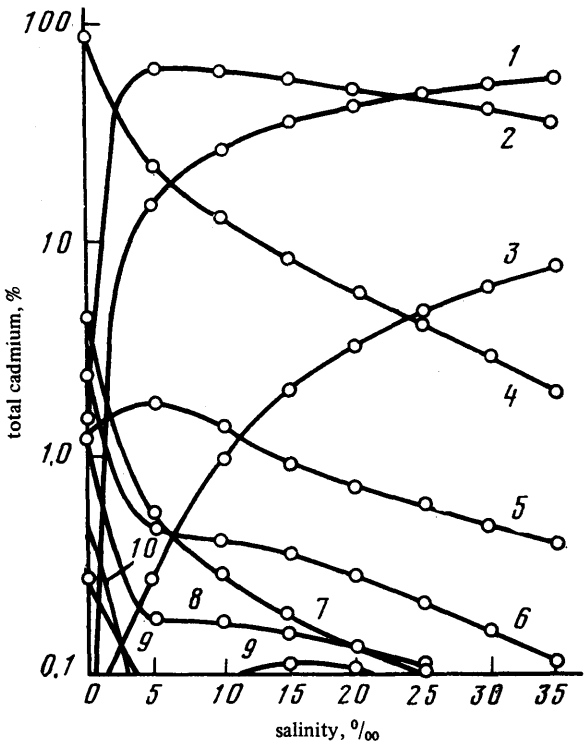


Figure 2. Equilibrium chemical forms of Cd^{2+} in the water of a model estuary[92]: *1)* $CdCl_2$, *2)* $CdCl^+$, *3)* $CdCl_3^-$, *4)* Cd^{2+}, *5)* $CdSO_4$, *6)* $CdHCO_3^+$, *7)* $CdOH^+$, *8)* $CdCO_3$, *9)* $Cd(OH)_2$, *10)* cadmium combined with humus materials.

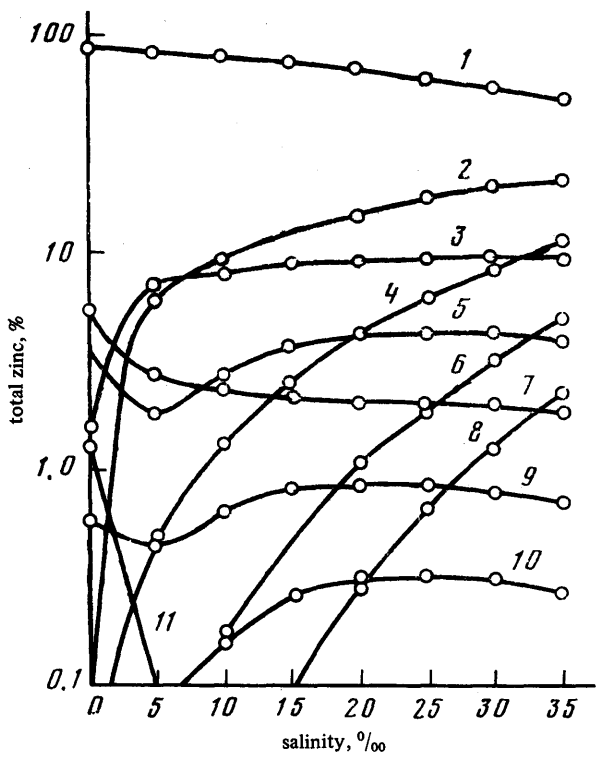


Figure 3. Equilibrium chemical forms of Zn^{2+} in the water of a model estuary[92]: *1)* Zn^{2+}, *2)* $ZnCl^+$, *3)* $ZnSO_4$, *4)* $ZnCl_2$, *5)* $ZnCO_3$, *6)* $ZnCl^+$, *7)* $ZnHCO_3^+$, *8)* $ZnCl_4^{2-}$, *9)* $ZnOH^+$, *10)* $Zn(OH)_2$, *11)* zinc combined with humus materials.

IV. FORMS IN SUSPENDED AND COLLOIDAL PARTICLES

Filtration of any NW through a membrane filter of 0.45 μm pore size produces a small residue of suspended particles (SP). The concentration of SP in the oceans is very much smaller than was previously thought: only 10 μg kg^{-1} at depths >200 m, though in surface waters the concentration varies with the season and can reach several hundred μg kg^{-1}. Most of the particles are 1–10 μm in diameter, a few are >10 μm, and the biological particles can be as large as 1 mm. The size distribution of the SP is usually independent of depth[100].

The majority of SP are particles of biological origin, found near the surface of the ocean[101]; their concentration is often greatest in regions where plankton is most abundant[102,103]. However, detritus forms are the predominant type of biological particle. In surface waters (at depths < 100 m) solid skeletal phases of marine organisms ($CaCO_3$ and SiO_2) account for 25–50% of the mass of SP, and organic substances for 30–70%.[100] The distribution and recycling of SP is particularly influenced by the presence of zooplankton[100,102]. Some of the biological particles are transferred to the sea bottom as fecal pellets[100,101], which account for 99% of the vertical transport of SP at depths >380 m (as compared with only 4% near the surface).[101]

Suspended particles are subdivided into two main groups: biogenic and non-biogenic, each of which consists of two or more subgroups. The first group includes both organic and inorganic materials ($CaCO_3$, $SrSO_4$, opal SiO_2), and the second consists mainly of alumino-silicate particles including clay and anhydrous minerals, but it includes other minerals (quartz, pyrites, dolomite, barytes, titanite, and iron and titanium oxides[103,104]). As the SP sink their inorganic content increases, mainly by the addition of sea salts in proportion to their concentration in sea water[105]. Near the sea bottom large amounts of SP are formed by the re-suspension of silt under the influence of various flows[106]. For example, a sample of SP taken at a depth >5000 m in the Sargasso Sea and consisting of 50% clay, 20% $CaCO_3$, 20% SiO_2, and 5% organic matter had originated mainly from the sea bottom[107].

Large numbers of SP are found in the surface micro-layer and in the foam of NW, producing an enhanced concentration of suspended TM.[59,108,109] For example, enrichment factors of 235 and 800 have been reported for Zn and Cd in lake foams[59]. TM are assumed to be concentrated at the water–air interface by atmospheric precipitation, and by adsorption and transport from the surface layer by air bubbles[108,109] formed by the waves, which are also the main source of aerosol particles containing sea salts[108].

Little is known about the content of TM in suspended particles. In the surface layer of the Pacific Ocean the average concentration of Zn in SP is 220 μg g^{-1};[110] in the Baltic Sea values of 0.006 and 0.99 μg $litre^{-1}$ were obtained for Cd and Zn respectively[111]. Relatively high TM concentrations are found in the fecal pellets of zooplankton, even in comparison with the amounts found in zooplankton itself: Cd (9.6 and 0.74), Zn (950 and 62), and Hg (0.34 and 0.35 μg g^{-1} respectively).[112] When the SP sink to a relatively small depth the metal content does not change significantly[111], but at greater depths there is a marked decrease (to 1.7 and 3.3% of the total concentration for Cd and Zn respectively[113]), the concentration in the case of Cd being lower by a factor of 4 at depths <400 nm.[55]

The concentration of suspended trace metals (especially Zn and Cd) in the ocean is determined by the amount of suspended organic matter[114] with which the TM are combined[103]. The composition and concentration of suspended organic matter have not been adequately studied, but proteins always appear to be present (up to 270 and 32 μg litre^{-1} have been reported for coastal and open waters respectively of the Pacific Ocean[115]). In rivers and lakes the concentration of suspended organic compounds is substantially (6–10-fold) lower than the concentration of SOC.[70] The chemistry, biology, and vertical distribution of SP in the ocean are discussed in Refs. 100–102 and 116, and their role in the detection of TM in Ref. 117.

By far the greater part of the TM transferred to the ocean from rivers is on suspended particles[118]: the proportion can be as high as ~80% (for Zn and Cu)[119] and even 90% (including Zn and Cd) in the Mississippi river[120]. The only exception is mercury, ~80% of which is transported in a soluble form while only 15–19% is found on SP.[121,122] Where fresh waters mix with sea water in estuaries, i.e. where a decrease in the flow rate is accompanied by an increase in salinity and (sometimes) in pH, two opposing processes take place[60,118,123]: 1) settling of the SP, and rapid formation and precipitation of flakes of colloidal particles containing Fe, Mn, Al, P, organic carbon, and HM,[124] accompanied by the coprecipitation of TM; 2) the release of the TM from the SP to the water. The relative importance of these two processes has not yet been determined. In some rivers of Europe[118] and of America the TM content (including Hg and Zn) of the SP decreases as the salinity increases: for example, from 403 to 240 for Zn and from 1.8 to 0.9 μg g^{-1} for Cd.[123] The influence of SP on the distribution of TM in estuaries is discussed also in Refs. 125 and 126.

Because of their rapid initial release, followed by a much slower release, the TM can be in an ionic or a complex form: this happens mainly as a result of breakdown (by oxidation) of the supporting particle[118,127], but it may be due also to desorption caused by dilution[127], stoichiometric exchange of Ca and Mg,[60] or complex formation with organic or inorganic ligands[127].

Trace metals are taken up by SP by adsorption on oxide surfaces[128]: Cd is combined only with Mn, and Zn mainly with Fe.[129] Alternatively, the TM are incorporated into the SP by complex formation, by ion exchange with clay minerals, or by reaction with humus materials[118] or with colloidal organic particles. The degree of combination is very sensitive to pH,[60,130] and can be controlled by chemical reactions at the interface through (for example) redox processes involving the substrate ($Fe^{3+} \rightarrow Fe^{2+}$) or the metal ions[131]. Humus materials can adsorb TM as well as reacting chemically with them: the adsorbed TM are held octahedrally (relatively weakly), they easily form complexes, and they are easily reduced[81].

Colloidal particles of inorganic (hydrated Fe, Mn, and Si oxides, clays, sulphides) or organic origin (HM, residues from living organisms) play an important role in controlling the degree of combination of TM in NW.[65] Inorganic colloidal particles can sorb (or chemically combine with) organic colloidal particles, and therefore they have hydrophilic properties and they oppose agglomeration.[69] It has been suggested[65] that most of the SOC in NW are in a colloidal state. Colloidal particles can combine with Cd, Pb, and Cu to the extent of 15–30, 45–70, and 40–60% respectively of their total content in sea water, but Cd and Pb are found mainly in inorganic forms, and Cu is found also in organic forms.[132] Although the colloidal fraction of TM is classified with the soluble forms the mechanisms by which the metals are combined with colloidal and with suspended particles must be similar.

V. FORMS IN SLUDGE DEPOSITS

Depending on their origin, sludge deposits consist of: 1) a lithogenous fraction (clay minerals, quartz, etc.) formed by soil erosion and usually carried by rivers into the sea; 2) particles of the hydrated Fe_2O_3 type, formed in water by inorganic reactions; 3) a biogenic fraction consisting of inorganic particles of the $CaCO_3$ type, of biological origin, and organic materials including residues from dead biota[60]. They usually have a redox potential of 100–(−400) mV, or 300–600 mV in surface waters, and pH 6.5–7.5.[133]

The upper few centimetres of bottom sludges in estuaries and coastal waters are usually in an oxidised state and are often brown, whereas the deeper layers tend to be in a reduced state, black in colour, and smelling of H_2S. Organic matter, which can account for up to 10% of the bottom sludge (or more), is decomposed by micro-organisms under both aerobic and anaerobic conditions[60]. The resulting humus material has a MW ranging from < 500 to >300000: for most of the HA the MW is >300000, but for the FA the MW is < 500 or > 100000–300000 (see Ref. 74).

Sludge deposits showing different levels of contamination may contain the following metal concentrations (expressed as μg g^{-1} of dry weight): Hg from 0.01 to 14.3, Cd from 0.05 to 60, Zn from 3 to 2500.[135] In rivers the concentrations of Cd and Hg are 1.0–9.8[136] and 0.03–1.28[122] respectively, and in the Atlantic the concentrations of Cd and Zn are 0.13–0.21 and 17–134[55] respectively (μg g^{-1} of dry weight). In rivers the biota contains only 0.02% of the total mercury, and the bottom sludge contains ~97%.[122] The fractional amount of $MeHg^+$ in the bottom deposits varies from 0.1 to 2.1%, and is 100 times greater than in the biomass of the river[67]. It is important to note that only a small proportion of the metal content of the bottom sludge can be transferred to the sea by the flow of the river. In the case of mercury, for example, the proportion is ~1% of the total amount of mercury carried by the river[121,122]. However, the concentration of TM in bottom sludges is not uniform. It is highest (by a fairly large factor) in the fractions with the smallest particles[122,137] and in the fractions richest in organic matter[74,122,136,138,139]. The latter fractions are usually found downstream from regions with a highly developed heavy industry, and they are composed of settled SP.[139]

The main components of the organic fraction of free sea sludges are HM, amounting to 40% of the sludge and formed in the marine environment. Marine HA have a very high sulphur and nitrogen content.[140] They combine with TM by cation exchange and complex formation through oxy-, amino-, and thio-groups, and also by surface adsorption[140,141]. The HA are usually formed in the sludge by diagenesis¶, and they leach the TM out of the solid mineral phases[74,140] (a reaction of great importance in geochemical processes). However, the form in which the metal exists in the bottom sludge is determined by various allochthonous interactions and autochthonous processes[142]. Thus, in some sludges the Cu, Zn, and most of the Mo are combined with organic substances, and the Ni and Co with sulphides[140], whereas in others the Mn and Zn are found predominantly in the carbonate phase, the Pb in the hydroxide phase, and most of the Cd can be readily exchanged[142]: in some samples the Cd is found in the carbonate, sulphide, and organic form (80, 10, and < 5% respectively), and >90% of the Zn is in the carbonate and the organic phase in comparable amounts[143], but in other samples the Hg is accumulated in the sulphide phase[144].

¶ The totality of the natural processes by which loose deposits at the bottom of water basins are converted into sedimentary rocks.

The MS sulphides (M = Hg, Zn, etc.) are stable under anaerobic conditions, but under aerobic conditions they are oxidised in proportion to their solubility in water[145]; also, Hg^0 can be oxidised to Hg^{2+} in soils (2–27%) and it can combine with organic substances[146]. The affinity for Hg^{2+} adsorption decreases in the series RSH ≫illite >montmorillonite >RNH_2 >kaolinite >RCOOH >fine sand >medium sand > coarse sand[147]. In contaminated sludge the concentration of the Zn forms decreases in the series organically bound >carbonate >sulphide >adsorbed >exchangeable, and that of Cd in the series carbonate >sulphide >organically bound >adsorbed > exchangeable.[148]

The TM transferred to the ocean by different routes (by the rivers and from the atmosphere, through effluent waters and ship discharges, etc.) always accumulate in the bottom sludges of the coastal areas of seas and lakes. Therefore a core sample of the sludge taken without disturbing the stratification can describe the accretion of TM in a given basin over any period of time up to several centuries. The geochronology of the deposits is determined from the distribution of the radioactive isotopes ^{210}Pb, $^{239+240}Pu$, and ^{137}Cs. In the surface layers of sea and lake deposits near large industrial, mining, and urban regions the concentrations of Cd, Zn, Hg, Pb, Cu, and other TM can be 5–10 times greater than in the layers laid down 50–100 years ago, thus reflecting their anthropogenic origin.[149–153] A historical plot of the vertical Zn and Cd profiles in one of the lakes of the USA[151] is reproduced in Fig.4: we note that the anthropogenic supply of these metals began in ~1910.

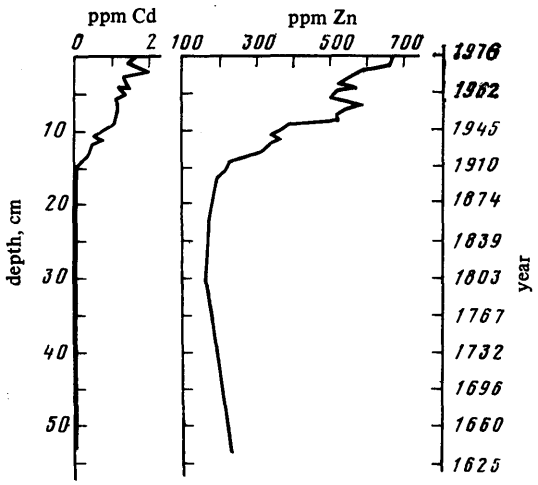


Figure 4. Concentrations of Cd and Zn as a function of depth in the bottom sludge of a lake in the USA.[151]

The sludge waters in contact with the bottom deposits always differ from the water in higher levels because of slow reactions in the sludge, which change the chemical composition of the water[154]. The composition of the sludge waters also depends on the depth of the deposits[155]; their organic content is high (30–800 mg C $litre^{-1}$ in marine sludges[69]), and in fresh water sludges the MW is >300.[74] Sulphide ions and oxygen are the most important components, because they determine the concentration of TM in sludge waters: under reducing or oxidising conditions [TM] can be 1–2 orders of magnitude lower or higher than in sea water.[154,156,157] This effect is ascribed to the formation of complexes with SOC[140] and of insoluble sulphides[60,156,157]. However, we should note that the concentrations of TM under reducing conditions are very much higher than the thermodynamic solubilities of their sulphides. This is due to the enhanced solubility of the sulphides in the presence of organic compounds, or to the formation of the more soluble polysulphides[60,158]. Under oxidising conditions most of the dissolved Hg is present as complexes with organic compounds of MW < 500 or >100000.[158] The most important dissolved forms of Zn, Cd, and Hg in marine sludge waters, calculated by combining experimental results with an equilibrium model[156], are listed in Table 4. However, the model ignores complexes formed by metals with HM, which are very important in the case of mercury.

Table 4. Main dissolved forms of mercury, cadmium, and zinc in the sludge waters of marine deposits at pH 7.5[156] (as % of total concentration).

Oxidising condition		Reducing conditions	
component	content	component	content
$HgCl_4^{2-}$	80.4	HgS_2^{2-}	98.5
$HgCl_3^-$	15.4	Hg (cysteine)	1.2
$HgCl_2$	4.1	$HgS(HS)_2^{2-}$	0.2
$Hg(OH)_2$	<0.1	$Hg(HS)_3^-$	<0.1
HgClBr	<0.1	$HgS(H_2S)_2$	<0.1
$CdCl^+$	56.5	$Cd(HS)_2$	97.2
$CdCl_2$	15.2	$Cd(HS)_3^-$	2.2
$CdCl_4^{2-}$	10.0	$Cd(HS)_4^{2-}$	0.1
$CdCl_6^{4-}$	9.1	$Cd(HS)^+$	<0.1
$CdCl_3^-$	9.0	$CdCl^+$	<0.1
Zn^{2+}	38.1	$Zn(HS)_3^-$	99.2
$Zn(OH)_2$	29.6	Zn^{2+}	0.2
$ZnCl^+$	18.0	$Zn(OH)_2$	0.1
$ZnCl_2$	6.6	$ZnCl^+$	<0.1
$ZnSO_4$	4.3	$ZnCl_2$	<0.1

The direction of the migration of TM in the water–sludge system is determined by the redox potential and by the pH,[156,159] and also by the chemical composition of the sludge waters and of the water in the higher levels[156]. Two opposite points of view on the effect of the redox potential can be defended[159]: 1) the presence of sulphides under reducing conditions will cause precipitation of the TM, but oxidation to SO_4^{2-} will make the TM mobile and transfer them to the supernatant waters; 2) the TM will be solubilised under reducing conditions because of the reduction of the Fe and Mn hydroxides on which the TM are sorbed or coprecipitated under oxidising conditions. It is experimentally found that the extent to which the Fe and Mn become mobile increases as the redox potential is displaced towards reducing conditions, and the mobility of Zn, Cd, Cu, Pb, and Ni increases in the oxidising region, whereas in the case of Hg and Cr the redox conditions appear to be irrelevant. Mobility can be produced by redox reactions, complex formation, dissolution, diffusion, desorption, biological effects, and dynamic processes[156]. For example, TM become mobile when river sludges are mixed with sea water.[160]

VI. FORMS IN THE BIOTA

Only about 20 elements of the Periodic Table contribute significantly to the maintenance of life on Earth, though up to 60 have been detected in living tissues, and all the elements found in the surrounding environment must be present in trace amounts in living tissues. In cells the elements exist as compounds and complexes of various kinds. About one-third of the enzymes known in biochemistry are active only in the presence of metal ions. Of the metals discussed in this review zinc is biologically the most important[161].

Pelagic organisms can store TM from their surroundings and adapt to changes in their natural concentrations in water and in their nutrients. Geometric mean concentrations of Hg, Cd, and Zn in different types of marine organism (excluding data from heavily polluted regions[60]) are listed in Table 5 together with their ranges (including pollution effects).[162] The TM content is not the same in different tissues of the organism: in heavily contaminated environments the concentration of TM is highest in liver and kidney tissues[60]. The take-up of TM is usually proportional to the growth and final size of the living organism.[163,164] In general the TM content is controlled by many factors which are difficult to consider jointly. For example, in fishes the concentration of mercury depends on the availability of food and on its mercury content, on the chemical form and concentration of mercury in the dissolved state, on the type of fish and its position in the food chain, and on the age, sex, and size of the fish. It is important to note that the concentrations of TM in fishes recently netted from one particular region and in fishes netted several decades ago (museum specimens) are almost identical[165]. However, concentrations can fluctuate, seasonally as well as annually[166]; a marked decrease in TM concentration has been noted[167] in starving invertebrates. The dynamics of the biological accessibility of mercury in a small estuary are discussed in Ref. 168.

Table 5. Geometric mean concentrations of mercury, cadmium, and zinc in different groups of marine organisms (over the whole organism, except shell molluscs)[60] and concentration ranges[162] in μg g^{-1} of dry weight.

Dry weight, %	Organism	Hg		Cd		Zn	
		Ref.60	Ref.162	Ref.60	Ref.162	Ref.60	Ref.162
~20	Marine algae (all types)	0.15	0,002—0.008	0.5	0.86—2.41	90	11—666
—	Phytoplankton	0.17	—	2	1.5—1.8	38	7.1—136
~11	Zooplankton (Copepoda)	0.1	—	4	1.2—2.6	113	9.9—625
~5	Tunicata (mainly Ascidia)	0.1	—	1	0.02—0.2*	200	10—14*
~20	Bivalve molluscs	0.4	—	2	—	100	—
~20	Oysters	0.4	—	10	—	1700	—
~20	Gastropoda	0.2	0.03—0.33	6	0.25—46	200	2.6—2354
22—54	Echinoderms	0.3	—	2	—	100	—
~30	Crustaceans (Decapoda)	0.4	<0.02—0.44	1	0.1—5	80	20—121
3—19	Coelenterata	0.1	—	1	—	50	—
~25	Cephalopoda	0.3	—	5		250	—
~25	Fishes	0.4	0.026—2.6	0.2	0.01—200	80	0.5—396

* per 1 g of live weight.

Organisms can accumulate relatively large amounts of metal: for example, in fishes the concentration factor (from water to fish) is 2.9×10^3 and 10.6×10^3 for open and coastal sea waters respectively[169]. Species such as swordfish and tunny, being at the apex of the food chain, usually contain large concentrations of TM (for example, mercury[170]), which are normal for these species. Some organisms (such as large sea-weeds and mussels) can accumulate TM selectively in some tissues only, and have therefore been selected as indicators of the level of contamination of the water medium.[171] The metal content of organisms can reflect fairly accurately the concentration in the water: for example, mussels have been used to determine mercury in water to a sensitivity of 0.005—0.010 μg $litre^{-1}$.[172]

Metals are absorbed by the tissues of living organisms as a result of adsorption on body surfaces, breathing organs, and alimentary canals (in the case of metals ingested with the food); adsorption is followed by diffusion through cell membranes and combination with organic ligands contained in the cells.[60] The extent of absorption depends on many factors: the chemical and physical forms of the metals, their concentration, the temperature, the presence of various organic or inorganic compounds, the state of the body surface of the organism, etc. For example, organic mercury is absorbed much more easily than inorganic mercury by fishes, crustaceans, and molluscs because of its solubility in the mucilaginous surface layer of their bodies and gills, which assists its penetration through the cell membranes[60,173]. The rate of absorption of $MeHg^+$ by fishes increases (but not in direct proportion) with concentration and temperature, is independent of the presence of organic compounds (for biochemical oxygen demand values of 8—800 mg $litre^{-1}$), and is a maximum for a Cl^- concentration of ~200 mg $litre^{-1}$.[96] The influence of natural factors on the absorption of mercury and cadmium by mussels is discussed in Refs. 174 and 175. However, great care is needed in predicting *in situ* absorption of metals by marine fauna from laboratory data[173].

After the metal has been absorbed by the organism its distribution in the various tissues can vary markedly with time. Thus, a trout exposed for one day to a solution of MeHgCl containing 10.7 μg Hg $litre^{-1}$ was found to contain ~10 times more methylmercury in its gills than in its other organs, the concentration of MeHgCl being lowest in the brain and in the skeletal muscles. However, the relative amounts changed with time, and after 6 weeks the MeHgCl level of the fish was highest in the brain, skeletal muscles, and gonads[176]. On the other hand the absorption of Cd^{2+} from sea water involves a time lag, but is then linearly related to time and to the concentration of Cd^{2+} (if not too high). The maximum concentration factor is 165 at a concentration of 0.7 μg Cd ml^{-1}. However, the complexes of cadmium with EDTA, humic and alginic acids, and even pectin are absorbed without time lag, and both the rate of accumulation and the final concentration in the tissues increase by a factor of two in the series kidneys ≫ viscera > gills ≫ mantle > muscle. Cadmium is excreted 18 times more slowly than it is absorbed (mainly through the kidneys).[176]

The tendency to accumulate different chemical forms of the metals in different tissues has been demonstrated in the case of mercury. Hg^{2+} accumulates mainly in the kidneys, and its concentration in the brain tends to be low. Inhaled mercury vapour enters the blood (in small amounts) as Hg^0, which rapidly diffuses through the hematoencephalitic barrier and is oxidised to Hg^{2+} in the brain. Over 90% of the mercury in blood is found in the erythrocytes, combined with haemoglobin, the remainder being combined with proteins in the plasma. Most of the mercury found in the bile is combined with di- and tri-peptides containing cysteine. On the whole, the distribution of mercury after inhalation of mercury vapour or ingestion of phenylmercury or mercuric diuretics is similar (except for the brain) to the distribution of Hg^{2+}, because of the rapid biotransformation of these forms of mercury into Hg^{2+}. On the other hand in $MeHg^+$ and its alkyl derivatives the Hg—C bond is relatively stable in biological systems, and

therefore these compounds show a different distribution and different biological effects. The high lipid solubility of $MeHg^+$ allows it to pass through the hematoencephalitic barrier and to accumulate in the brain, where it produces irreversible poisoning of the central nervous system.[178] It has been shown that $MeHg^+$ can catalyse the hydration and hydrolysis of vinyl ether bonds in plasmogens (the main constituents of the phospholipids in the cell membrane).[179]

The relative toxicity of these metals towards many forms of marine and estuary life decreases in the sequence[60,180] Hg ≫ Cd > Zn, and the mercury compounds lie in the sequence[181] $RHg^+ > ArHg^+ > Hg^{2+}$. However, these sequences are arbitrary, since the toxicity of the metals depends on their chemical and physical forms, on the dose, on the path by which the metal enters the organism, etc.[180,181] For example, the toxicity is proportional to the concentration of free Cd^{2+} ions in water[182], and decreases in the presence of factors which tend to lower this concentration by changes in form or by complex formation (increased water hardness[183] and salinity[182], presence of organic[182] and humus substances[86]). In general, chelate formation lowers the toxicity of the metals[182], which can be correlated with parameters defining the "hardness" or "softness" of the metals[184]. Surprisingly, $MeHg^+$ and Cd^{2+} inhibit the regeneration of tail-fins in fish, but the effect disappears when these forms are mixed with Hg^{2+}.[185] A toxicological comparison of the effect of Cd, Hg, and Cu on natural and on culture populations of Copepoda has been reported[186]. The toxicology of mercury compounds has been studied in great detail, and widely reported, including biological effects[178,181,187].

Direct electron microscopic evidence has been obtained that oysters can store Cu and Zn in the form of different compounds within bubbles surrounded by membranes in the amebocytes which are present in all the soft tissues, and that these metals are combined with S and P respectively. It is suggested that this mechanism of storage and de-toxification of TM in biological systems may be wide-spread. However, there are important differences between the different metals and the different organisms. Whereas Cu and Zn are stored in amebocytes, and they accumulate mainly in the gills and in the mantle, Fe and Pb are found in bubbles of epithelium cells of the kidneys[188], and Cd becomes concentrated in the kidneys and viscera[177].

The action of many enzymes requires Zn and Cu in the ternary and quaternary protein structures. However, if these enzymes are exposed to excessive concentrations of the functional metals, or to other trace metals able to compete with them (like Hg and Cd), their normal functions may be impaired. This effect may be due to conformational changes, as a result of which the substrate molecules are unable for a long time to "adapt" themselves to the reactive centres of the enzymes. On the other hand, some toxic metals (including mercury) are able to split various enzymes into their regulating and catalytic sub-units, so that the normal regulatory function is lost. Therefore in order to ensure normal cell operation the excess of functional metals (or the toxic metals) must be removed from the biological sphere of action. This is accompanied by the formation of metal thionein (MT), which can combine with TM and biologically deactivate them.[189]

Metal thionein is the principal means of storing Zn and Cu in the liver and kidneys, where it is found in the cell walls of tissues, and it probably contributes to the control of metal adsorption in the mucous lining of the intestine. It is a protein with a MW of 10000–12000, containing an unusually high proportion of cystein (~30% of the total amino-acid residues). The presence of a large number of thiol groups gives the MT a high affinity for metals: 2–3 cystein residues are available to combine with each metal atom for a metal content of 7–10%.[190,191] In living organisms MT is always saturated with metals, and it contains Zn in approximately one-half of the reactive centres. Production of MT can be stimulated by adding Zn and Cu, and also Hg, Cd, and Ag.[190]

One of the modern theories of de-toxification is based on these properties of MT: it states that Hg and Cd are free from toxic effects as long as their concentration is insufficient to exceed the combining power of MT. Hence, when Hg and Cd are ingested into the organism they initially displace from the MT the Zn and Cu (which are much less strongly bound) and transfer them to high-MW proteins (metal-enzymes). Since the displaced metals are naturally occurring components of many of the proteins, they are relatively non-toxic. Only when the concentration of Hg and Cd exceeds the combining power of the MT are these metals transferred to the metal-enzymes, where they begin to display their toxic properties within the cell. However, this transfer depends also on the relative rates of supply of Hg (or Cd) and of MT synthesis (stimulated by the trace metal). Therefore it is suggested[191] that the critical factor determining the survival of the organism is not the concentration of Hg or Cd in the tissues (which can be quite high) but whether the trace metals are located in the MT or in the metal-enzymes.

As was stated above, some species of predatory salt-water fish may contain relatively large amounts of mercury (in some cases >2 mg g^{-1}) without any harm to themselves[170]. This was inexplicable until it was realised that in these cases the mercury is always accompanied by selenium in a 1 : 1 molar ratio (or by an excess of selenium): somehow, the selenium appears to moderate the toxicity of the mercury. It was recently shown that the selenium-containing enzyme glycinereductase is, in effect, a selenium cysteine, and the de-toxification of mercury by selenium was ascribed to combination of the mercury with selenium-containing peptides and proteins (as in the case of MT). This hypothesis is confirmed by the observation (from PMR spectra[192]) that the affinity towards $MeHg^+$ of the various groups decreases along the series SeH > SH ≫ Se–Se > NH_2 > S–S, SeMe, SMe. In the case of Cd^{2+} the detoxification effect of selenium and the distribution in different tissues were shown[193] to be similar to those of Hg^{2+} but different from those of $MeHg^+$.

At different concentration levels, Zn and Cd in tissues may compete for combination with proteins. Thus, in liver and kidney cytoplasms the inflow of Cd can combine with high-molecular proteins until the combining power of the MT is exceeded if these proteins are not already saturated with Zn. If they are, the excess of Zn and the Cd are taken up by the MT.[189] Even in poisoned molluscs the Zn, Cd, and Cu are combined with low-molecular proteins if the concentration factor is high but not if the concentration factor is low.[194] In water organisms Cd may be found also in the free state[195]. The degree to which Hg is combined with low-molecular proteins can differ in different organs (as was found in oysters)[196].

In spite of the important role of TM in the life processes of various organisms, very little was known until recently of their chemical behaviour in metabolism, their toxicology, and their bio-transformations. The earliest systematic studies concerned their interaction with sulphur-containing amino-acids. It was shown that all the ligand atoms of these amino-acids (sulphur, nitrogen, and oxygen) can combine with the metals, though the type of bond formed depends on the nature of the metal (even for metals from the same sub-group). In aqueous solutions the resulting compounds and complexes are very labile, and the interaction of a given metal ion with the ligand atoms is a function of pH. Therefore a given metal may be bound to different ligands in the crystalline and in the dissolved state. The same is true of the complexes formed with homologous amino-acids, due to differences in packing of the crystal lattice and to differences in conformational and configurational stability.

This effect is easily demonstrated by considering the interaction of M^{2+} with S-methylcysteine (mcyst) and methionine (met). Whereas in an acid solution Zn^{2+} and Cd^{2+} do not react, and Hg^{2+} forms 1 : 2 complexes with an Hg–S bond, in an alkaline solution the M^{2+} ions form chelates of 1 : 2 composition with M–N,O bonds, and in the case of mercury and mcyst with Hg–S,N bonds (according to the PMR spectra). Hence, in the case of mercury complexes in alkaline solutions the strength of individual bonds is less important than the very high stability of the 5-membered Hg–N,O ring as compared with the 6-membered Hg–S,N ring.[197] On the other hand, in the crystalline state the Zn and Cd in 1 : 2 complexes are combined with N and O atoms[198–200], but the Hg in the complexes with mcyst and met is combined with S[201] and with S and O[202] respectively. However, Cd forms 1 : 1 complexes with penicillamine (pen) containing Cd–S,N,O[203] and Cd–S,O[202] bonds, whereas mercury forms only Hg–S bonds[202] (according to X-ray diffraction analysis). In the complexes of Zn^{2+} and Cd^{2+} with histidine (1 : 2 composition) the metals are bound to N (both amino and imidazole) and to O.[204] Measurements of *K* have shown that the complex-forming power of M^{2+} towards five octadentate ligands containing sulphur and nitrogen atoms decreases in the series Hg > Zn > Cd > Mg > Ca.[205]

The change in the bonding centre with pH (due to competing reactions) has been studied most thoroughly for the $MeHg^+$ complexes of 1 : 1 composition. With simple amino-acids of the glycine type and at low pH the $MeHg^+$ is attached to the carboxylic acid group, and at high pH it is attached to the amino group[23]. With sulphur-containing amino-acids (for example, met) at pH 2 the $MeHg^+$ ion is combined with the thioether group, but as the pH is increased it begins to "float" along the met molecule and appears to form complexes with the carboxylic acid group (though this has not been proved), and at pH 8–9 it forms complexes with the amino group. As the pH is increased still further the complex begins to dissociate, and at pH 13.5 it is fully decomposed[206]. Bonding with cyst and met has been studied in a similar way[23], and the *K* values of the corresponding complexes have been determined. On the whole, the apparent stability of the complexes of methylmercury with various ligands depends on pH, and at pH 7–9 it decreases in the sequence thiol > amino > OH^- > carboxylic acid > thioether ligand.[206] The way in which $MeHg^+$ is combined in biologically important compounds is discussed in more detail in Ref. 23.

$MeHg^+$ and $PhHg^+$ have been shown[207] to form 1 : 1 complexes with ligands which coordinate through SNO and SSO (pen, cyst, 2,3-dimercaptopropan-1-ol), and 2 : 1 complexes when the ligands are in excess, with Hg–S, Hg–S,N, and Hg–S,S bonds, whereas with SO and NO ligands (N-acetylcysteine, glycine) only 1 : 1 complexes with Hg–S and Hg–N bonds respectively are formed. The *K* values for these complexes decrease in the series MeHgS > PhHgN ≳ PhHgS > MeHgN ≫ PhHgO, MeHgO and S > N > O (according to i.r. and PMR spectral data, and potentiometric titrations). The latter method also showed the formation of $MeHgL_2^-$ complexes[31] with simple amino-acids, but chelation in these compounds is still uncertain. The 1 : 1 compounds of $PhHg^+$ with cyst and pen are not very stable, and they undergo spontaneous symmetrisation[208]. Lastly, X-ray structural analysis has shown that Hg–S and Hg–S,N bonds are present in MeHg·pen and $(MeHg)_2$.pen complexes[209], Hg–S bonds in the MeHg.cyst complex[210], and Hg–N bonds in the MeHg.met complex[211], the mercury being also weakly coordinated to oxygen in the latter two complexes.

As in the amino-acids, the metal combination centres in peptides depend on pH. Thus, Zn^{2+} and Cd^{2+} in leucylglycine complexes of 1 : 1 composition at pH < 5 are combined with the carboxylic acid group of the glycine residue to form linear structures, whereas at pH > 5 they are combined with the amino and carbonyl groups of the leucine (according to the ^1H and ^{13}C NMR spectra)[212]. Under similar conditions di-, tri-. and pentapeptides form $[Zn_2L_2]^{2+}$ complexes whose *K* values have been determined by potentiometric titration[213]. In crystalline compounds, on the other hand, Cd and Zn combine with peptides through N (amino) and O (carboxylate and peptide) to give chelate compounds as a rule[199,204]. In the 2 : 1 complexes of $MeHg^+$ with glutathione at pH < 4 both cations are combined with thiol groups, but at pH 4–8 one of the cations is transferred to the amino group and at pH > 10 it dissociates to MeHgOH.[23]

However, the reactions of the metal ions with proteins differ from those with amino-acids and peptides, because in proteins the α-NH_2 and α-COOH groups of long polypeptide chains are separated by the covalent bonds of several residues. This interaction is affected also by the conformation of the peptide chain, which can block a potential attachment point while a remote side chain is in the correct position for the formation of a chelate ring. An example is provided by the metal-enzymes and metal-proteins, in which the strong interaction between the metal and the protein part plays a decisive and biologically specific role[204,214]. Depending on the type of protein, a given metal ion can fulfil various functions, determined by the limitations imposed by the protein environment. Hence the biologic specificity of the metal function probably has a stereochemical origin[161,204]. Information on the complexes of TM with proteins in the crystalline and the dissolved state is given in Ref. 215 with a statement of the amino-acid residue combined with the metal.

The chemical form of the metals undergoes substantial changes during absorption, transport, and storage in biological tissues and liquids. At physiological pH values they are usually combined with peptides, proteins, and other ligands, but in the acid regions of the digestive tract they can exist in uncomplexed forms[190]. The reactive centres of proteins and enzymes for the attachment of all forms of mercury[187] (and probably also of cadmium[216]) are almost exclusively thiol groups.

It has been suggested that the whole of the $MeHg^+$ present in tissues is combined with cystein-containing peptides and proteins, containing thiol groups. However, in spite of the high thermodynamic stability of these compounds, they can easily exchange with other thiol groups as a result of bimolecular nucleophilic substitution by the reaction $MeHgSR + R'S^- \rightleftharpoons MeHgSR' + RS^-$. This fast exchange, which takes place at physiological pH values, is accompanied by redistribution of the $MeHg^+$ between these groups, which makes the identification of the initial compounds extremely difficult. Conversely, in the stomach (at pH 1.5–2.5 and high concentrations of Cl^-) exchange occurs by the reaction $MeHgSR + H^+ \rightleftharpoons MeHg^+ + RSH$, and most of the methylmercury is in the form of fat-soluble MeHgCl.[178,217]

Metal ions are necessary also for the biologic functions of nucleic acids, and they play an important part in many metabolic processes involving nucleotides as monomers. However, Hg^{2+} compounds can denature native DNA, sometimes reversibly, and $MeHg^+$ causes chromosome disturbance and therefore acts as a mutagen[181]. Furthermore, mercurated nucleotides hinder the synthesis of RNA in the nucleus (by 30–40%).[218] Hence, the interaction of Hg^{2+} (and especially of $MeHg^+$) with the components of nucleic acids has been studied in detail, whereas data for other metals tend to be fragmentary. In general metal ions can be combined with various reactive centres of purine and pyrimidine bases in nucleotides and nucleosides, with formation of both mono- and poly-nuclear complexes and compounds, depending on the base, the pH,

the metal, and the concentration. Thus, in solid complexes of Hg^{2+}, Cd^{2+}, and Zn^{2+} with ATP the metals are combined with N(7) of adenine and with phosphate[219], and Cd^{2+} with uridine (C=O(4)) and ribose, whereas with thymine only the deoxyribose group is involved (according to i.r. spectra).[220] The stereoselectivity of the attachment of the metals to the nucleic acid components is discussed in Ref. 221.

Hg^{2+} and $MeHg^+$ are usually attached to N(1) in purine nucleosides and to N(3) in pyrimidine nucleosides. With bases, $MeHg^+$ forms its strongest bonds with uracil and thymine. It is thought[181,222] that the denaturing of native DNA by Hg^{2+} and $MeHg^+$ involves initially the deprotonation of N(3) in thymidine, and then of N(1) in guanosine (according to Raman spectra). $MeHg^+$ may additionally be combined with ribose and (very weakly) with phosphate[181].

Relatively little is known about the action of TM on marine flora. The highest concentrations of individual TM (Hg, Cd, Zn, As, etc.) which are harmless to marine fauna are also non-toxic to fresh-water phytoplankton, but mixtures are extremely toxic, and can inhibit ~70% of the primary productivity. Cadmium can have both synergic (with Cu and Zn) and antagonistic effects (with Se).[223] At a cadmium concentration of 2 μg $litre^{-1}$ the growth rate of diatomaceous algae decreases by an order of magnitude[224], and at 5–10 μg $litre^{-1}$ the microbial colonisation and decomposition of foliated material is inhibited[225]. However, only a few of the 99 species of phytoplankton examined were found to absorb Hg^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} *in situ*, and these account for only a very small part of the bio-mass.[226] The effect of TM on the Laminariaceae is described in Ref. 227.

In an experiment lasting 72 days, carried out in a reservoir of 1300 m^3 capacity covered with a plastic sheet, the productivity of phytoplankton was found[228] to decrease after 12 days in the presence of 5 μg $litre^{-1}$ of mercury, and zooplankton could not be detected after 34 days. The concentration of dissolved mercury was less than 50% of the total mercury content, which fell by 3% per day. At the end of the experiment >90% of the mercury was found in the bottom sludge[228].

VII. BIOLOGICAL CONVERSION OF THE FORMS

Among the metals under discussion, only mercury can exist in nature in different states of oxidation and form stable mercury-organic compounds. Therefore, biological conversion of the forms (especially methylation and demethylation) has been studied mainly with mercury derivatives. In biological systems three coenzymes can act as methylating agents: S-adenosylmethionine, N^5-methyltetrahydrofolates (Me–N^5), and vitamin B_{12} derivatives (methyl corrinoids). All these substances can transfer a methyl group as the Me^+ cation, but only the methyl corrinoids can generate it also in the form of the Me^- anion and the Me· radical, which enables them to methylate Hg^{2+} salts and Hg^0 respectively. Methyl cobalamin Me–B_{12} (one of the methyl corrinoids) is found in microorganisms and in warm-blooded animals: it produces $MeHg^+$ and Me_2Hg by enzymic and non-enzymic paths in relative amounts depending on the concentration of mercury.

The mechanism of non-enzymic methylation of $Hg(OAc)_2$ by methyl cobalamin in aqueous solution is believed to involve heterolytic breaking of the Co–Me bond without change in valency of the Co^{3+}, followed by transfer of Me^- to the Hg to give $MeHg^+$ and aquocobalamin as the end-products. Being highly electrophilic, Hg^{2+} can also coordinate with the Me–B_{12} base through 5,6-dimethylbenzimidazole (DMBI) to give a mixture of Me–B_{12} complexes both with and without breaking of the Co–DMBI bond. The first complex reacts with Hg^{2+} at least 1000 times faster than the second, because of the greater electron density in the Co–C bond resulting from coordination to the DMBI. Me_2Hg is formed in a similar way, but only from $MeHg^+$, and at a rate 6000 times smaller[229].

However, the demethylation of Me–B_{12} induced by Hg^{2+} in chloride or acetate solutions was found[230] to occur in a single step, without breaking of the Co–DMBI bond, whereas Hg^{2+} in aqueous solutions can break this bond reversibly as a result of complex formation with DMBI by the reaction Me–B_{12} + $Hg^{2+} \rightleftharpoons$ Me–B_{12}–Hg^{2+}. In the latter case the methylation kinetics are complex, and depend on the concentration of Hg^{2+}.

The reaction rate is very sensitive to the degree of dissociation of the mercury salts, and for the synthesis of $MeHg^+$ it decreases in the sequence[231] $OAc^- > Cl^- > Br^-$ (the rate constant of the reaction for mercuric acetate and cyanide respectively being 260×10^{-4} and $< 0.01 \times 10^{-4}$ s^{-1}).[229] In the case of Me_2Hg the corresponding series is[187,229] $Cl^- > OH^-$. This reaction is inhibited by phosphates and thiols. Non-enzymic electrophilic methylation of mercury is found in aerobic organisms, which contain methyl corrinoids as metabolic intermediates.

The free radical mechanism for the methylation of mercury by Me–B_{12} has not been investigated, but in the case of other metals and metalloids (for example, for Cr^{2+}) it has been shown to involve homolytic breaking by these elements of the Co–C bond of methyl cobalamin to give Co^{2+}–cobalamin and the corresponding methyl derivative. The reaction takes place only in the presence of oxygen (which is needed to generate the radicals[229]).

It has been suggested that the mechanism of the methylation of elements by Me–B_{12} depends on the standard reduction potential E^0 of the element. For $E^0 > 0.8$ V an electrophilic mechanism is predicted for the most highly oxidised members of redox couples (for example, Pb^{4+}/Pb^{2+}, Pd^{2+}/Pd^0, and Hg^{2+}/Hg^0), and for $E^0 < 0.154$ V a radical mechanism for the least oxidised members of redox couples (for example, Sn^{4+}/Sn^{2+} and Cr^{3+}/Cr^{2+}). The range $0.154 \text{ V} < E^0 < 0.8$ V includes the elements for which both members of the couple can be methylated. It is important to note that for some elements (e.g. Se) the methylation mechanism can vary with pH.[229]

Methyl corrinoids also take part in the enzymic synthesis of $MeHg^+$ in the presence of the enzyme methionine synthetase, found in various aerobic and anaerobic micro-organisms and in the liver of mammals, which slowly catalyses the reaction. The suggested mechanism includes the transfer of Me^- from the Me–B_{12} co-enzyme to the enzyme in the presence of catalytically active amounts of S-adenosylmethionine. The enzyme–co-enzyme complex is re-methylated by Me^+ provided by Me–N^5. This complex can nucleophilically methylate Hg^{2+}, forming $MeHg^+$ and an aquocobalamin–enzyme complex which can be reconverted into the original complex by the action of flavin adenine dinucleotide (which reduces Co^{3+} to Co^+), followed by methylation of the complex by Me–N^5. In the presence of cysteine $MeHg^+$ forms methylmercury cysteine, which can give MeHgSMe in the presence of an excess of Me^+.[187]

The microbiological methylation of Hg^{2+} was first demonstrated *in vitro* with lake sludges[232], but it was subsequently found *in vivo* in marine[233] and river deposits[234]. With $PhHg^+$ the process occurs even more readily, and it seems likely that any form of mercury is converted (at least, partly) into $MeHg^+$ in a water environment. Bio-methylation by bacteria and molds is possible under both aerobic and anaerobic conditions[233,235,236]: in this case the main reaction product is $MeHg^+$ under aerobic conditions, and under anaerobic conditions (in the absence of S^{2-}) the main product is Me_2Hg [235] and methylation proceeds more easily[233]. The rate of the reaction is proportional to the metabolic activity of the microorganisms, to the total concentration of Hg^{2+} ions and their

availability, and to temperature[98,234-236]. Methylation is assisted by the presence of organic substances[96,233,234]; it depends on the salinity, and the process is most effective at a Cl^- concentration of ~200 mg litre^{-1}.[96] The optimum pH value for the synthesis of $MeHg^+$ is 4.5.[237] At pH 7 the rate of methylation is highest[96], and the main product is $MeHg^+$, but small amounts of Me_2Hg are also formed[236]. Early studies of methylation are reviewed in Refs. 235 and 238.

We should note that bio-methylation of mercury has not been observed in plants and soils[235]: in these systems $MeHg^+$ can be formed by a non-biological path. The methylating factor can be extracted by alkali, and is decomposed by radiation. It is thought to consist of fulvic rather than humic acids, since solutions of the latter do not methylate mercury[239].

Bio-methylation under natural conditions is always accompanied by bio-demethylation to inorganic mercury, leading to an equilibrium concentration of $MeHg^+$ (or, more exactly, an equilibrium ratio of $MeHg^+$ to total mercury). This conclusion was reached from studies of river[240] and marine[241] sludges *in vitro*. Bio-degradation is probably faster under aerobic than under anaerobic conditions[233], though similar rates have been reported[240].

Experiments with isotopically labelled mercury have shown that in river sludges the *in vitro* mineralisation of $MeHg^+$ and methylation of Hg^{2+} depends on the type of deposit, and that the two processes are favoured by low and by high concentrations of organic matter respectively. Equilibrium concentrations of $MeHg^+$ of 0.2 and 12% were obtained, the equilibration times being 3 and 6 months respectively[67].

Many organic derivatives of mercury are decomposed by bacteria to Hg^0.[187,238] The same end product can be obtained by reducing Hg^{2+} with an enzyme found in various bacteria, which requires reduced nicotinamide adenine dinucleotide as a co-enzyme (NADH):[237]

$$Hg^{2+} + NADH + H^+ \rightleftharpoons Hg^0 + 2H^+ + NAD^+ \ .$$

Aerobic micro-organisms bring Hg^{2+} into solution from HgS as a result of the oxidation of sulphide to sulphate ions.

Bacteria and their metabolites play an important role in the transport of Zn^{2+} and Cd^{2+} from sea water to the bottom deposits. Because of the large quantities of H_2S produced by bacteria it is assumed that the metals are precipitated as MS or coprecipitated with FeS, since only ~20% of the deposited Zn^{2+} and a negligible proportion of the Cd^{2+} are found within the bacterial cells.[242]

Very little work has been done on the biological conversions of mercury compounds in living marine organisms. Thus, $HgCl_2$ introduced in various ways into a rainbow trout is not methylated[243], whereas MeHgCl is partly decomposed after being absorbed by the trout[176] (*in vivo* experiments). However, these conclusions may be erroneous because of the inadequate experimental conditions. Published data on the ratio of $MeHg^+$ to total mercury in fishes tend to be inconsistent[244].

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We may conclude from this review that the penetration of chemical and physicochemical concepts and methods into our understanding of the role of the chemical forms of mercury, cadmium, and zinc in natural water environments is still inadequate. However, owing to the increasing impact of chemicals of anthropogenic origin on the ecological equilibrium, a more active participation in these studies from chemists of different specialisations is highly desirable.

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