Metals and Semi-Metals in the Hydrosphere

Environmental Chemistry, vanLoon & Duffy – Chapter 13

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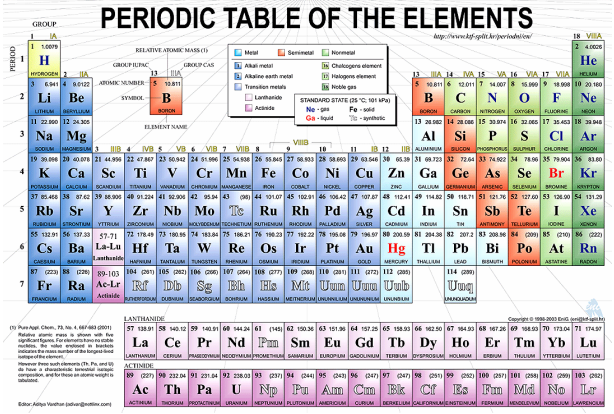
Metals in the Aqueous Environment

Metals and semi-metals make up 75% of all elements on the periodic table, and they are found as ions and complex compounds throughout the hydrosphere.

The concentration of metal species in various types of water covers a wide range (Na is abundant in sea-water, other elements in the ultratrace range).



Metals in the Aqueous Environment

The environmental chemistry of metals is of interest and importance for several reasons:

❖Besides being dissolved I water, metals are present in the solid components of the Earth and there are ongoing interactions between the soluble forms and the solid phase materials.

❖Some metals (K, Ca) are important nutrients required in substantial amounts by plants, animals, and microorganisms.

❖Other metals (Cu, Zn) are also nutrients, but their amounts required are very small.

❖These micronutrients, if present in excessive amounts, can be toxic.

❖Other metals (Cd, Hg) are not essential nutrients for most organisms, and even at very small amounts they can be toxic to many living organisms.

Metals in Drinking Water

Maximum permissible levels for metals in drinking water (USEPA standards)

Metal	Max. Level (ppb)	Metal	Max. Level (ppb)
Antimony (Sb)	6	Lead	50
Arsenic	50	Mercury	2
Barium	2000	Nickel	100
Beryllium	4	Selenium	50
Cadmium	5	Thallium	2
Chromium	100		

Classification of Metals

1. Type A metals ions:

Their stability is correlated to the charge squared to radius (Z^2/r) ratio for both the metal ion and the ligand species. Thus, highly charges small ions form stronger complexes as shown by the realtive stability of most complexes with the alkaline earth metals Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}. They form stable complexes with small ligands (preference for O or F over S and higher halides).

2. Type B metals ions:

Have nd^{10} and $nd^{10}(n+1)s^2$ electronic configurations. They exhibit high polarizability. As they have high electronegativity, they form stable complexes with ligands exhibiting low electronegativities. In general, they form more stable complexes than do the type A cations. Their complexes with sulphide and organosulphides are common and stable. Their complexes with carbon are observed (ex. $(CH_3)_2Hg$).

3. Transition metals ions:

Those with nd^x ($0 < x < 10$) electronic configurations. This category exhibits properties that are intermediate between those of the type A and B classes.

Metal Speciation in the Hydrosphere

Aquo Complexes

This is the simplest form in which a metal ion exist in water. Where no other ligand is available to form complexes with a metal in aqueous solution, it exists as an aquo complex.

As noted in the classification, type A metal ions favour coordination with oxygen-containing ligands and so aquo complexes are particular compounds with these elements.

Depending on circumstances, coordinated water molecules may lose a proton. The degree to which deprotonation occurs is, to a large extent, a property of the metal ion under consideration.

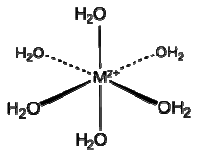
The pH of the solution is also important in determining whether protons are lost. This type of reaction is an acid-base reaction and the general equation is:

$$M(H_2O)_a^{b+} + H_2O \Leftrightarrow M(H_2O)_{a-1}(OH)^{(b-1)+} + H_3O^+$$

An alternative simplified description of the reaction omits the waters of hydration in the formulae

$$M^{b+} + 2\,H_2O \Leftrightarrow MOH^{(b-1)+} + H_3O^+$$

Further deprotonation steps may also occur.



AUB
Metal Speciation in the Hydrosphere
Aquo Complexes

Since these reactions ultimately involve a separation of two positive charges, they are favored in the case of more highly charged metal ions and smaller ions, usually expressed in combination as the Z^2/r ratio, where Z is the numerical value of the charge and r is the ionic radius in nm.

The inverse relation between pK_{a1} and Z^2/r holds up well for the type A elements, but other factors are more important in the case of transition metal ions (especially heavy ones).

Metal Speciation in the Hydrosphere

Aquo Complexes

Table 13.1 Values of Z^2/r and pK_{a1} for aquo complexes of selected metal ions[a].

Metal ion	Z^2r^{-1} / nm^{-1}	pK_{a1}	Metal ion	Z^2r^{-1} / nm^{-1}	pK_{a1}
Na^+	8.6	14.48	Ni^{2+}	48	9.40
K^+	6.6	>14	Cu^{2+}	46	7.53
Be^{2+}	68	6.50	Zn^{2+}	46	9.60
Mg^{2+}	47	11.42	Cd^{2+}	37	11.70
Mn^{2+}	48	10.70	Hg^{2+}	34	3.70
Fe^{2+}	43	10.1	Al^{3+}	133	5.14
Co^{2+}	45.2	9.6	Fe^{3+}	115	2.19

[a] In each case, the radius, r, used is for the 6-coordinate high spin metal aquo complex. pK_a values are taken from Yatsimirksii, K.B. and V.P. Vasil'ev, *Instability constants of complex compounds*, Pergamon, Elmsford, New York; 1960.

Metal Speciation in the Hydrosphere

Aquo Complexes

For pH < pKa1, the metal ion is coordinated largely with by water molecules.

For pH > pKa1, a hydroxy (OH) group replaces a water molecule.

The waters of hydration surrounding metal ions with a single positive charge exist exclusively in protonated form throughout the entire pH range.

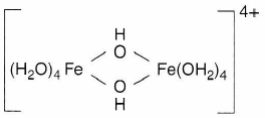
Of the +2 ions, deprotonation occurs more readily for smaller species (due to the larger value of Z^2/r).

Deprotonated species begin to assume significance in environmentally common situations for +3 ions including Fe^{3+} and Al^{3+}.

One consequence of this is that such ions can lose several protons, eventually becoming neutral and insoluble in water.

Iron(III) exists in pure water as an aquo complex, $Fe(H_2O)_6^{3+}$ (Fe^{3+}) and being a +3 ion, there is considerable tendency for deprotonation to occur, $Fe(H_2O)_5(OH)^{2+}$ or simply $Fe(OH)^{2+}$ is the product and in the second step, $Fe(H_2O)_4(OH)^{2+}$ i.e. $Fe(OH)^{2+}$ is formed.

As well as the two deprotonated products, a bridged dimer can also be formed from two of the second deprotonated iron species. This *polynuclear* species of iron has the following structure but can be written as $Fe_2(OH_{)2}^{4+}$.



$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^- \qquad K_{sp} = 1.6 \times 10^{-39} \qquad (13.3)$$

$$Fe^{3+} + 2H_2O \rightleftharpoons FeOH^{2+} + H_3O^+ \qquad K_{a1} = 6.3 \times 10^{-3} \qquad (13.4)$$

$$FeOH^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + H_3O^+ \qquad K_{a2} = 3.2 \times 10^{-4} \qquad (13.5)$$

$$2Fe^{3+} + 4H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H_3O^+ \qquad K_{ad} = 1.3 \times 10^{-3} \qquad (13.6)$$

AUB
Metal Speciation in the Hydrosphere
Aquo Complexes

Example 13.1 **Concentrations of iron species in pure water**

Using reaction 13.3,

$$[Fe^{3+}][OH^-]^3 = K_{sp}$$

$$[Fe^{3+}][10^{-7.00}]^3 = 1.6 \times 10^{-39}$$

$$[Fe^{3+}] = 1.6 \times 10^{-18}\ \text{mol L}^{-1}$$

Using reaction 13.4,

$$\frac{[FeOH^{2+}][H_3O^+]}{[Fe^{3+}]} = 6.3 \times 10^{-3}\ \text{mol L}^{-1}$$

Now substitute in the value of $[Fe^{3+}]$ calculated above

$$[FeOH^{2+}] = \frac{6.3 \times 10^{-3} \times 1.6 \times 10^{-18}}{1.0 \times 10^{-7}}$$

$$= 1.0 \times 10^{-13}\ \text{mol L}^{-1}$$

Similarly, calculations are done to determine the equilibrium concentrations of the two additional species.

$$[Fe(OH)_2^+] = 3.2 \times 10^{-10}\ \text{mol L}^{-1}$$

$$[Fe_2(OH)_2^{4+}] = 3.3 \times 10^{-25}\ \text{mol L}^{-1}$$

Therefore, the total concentration of the various aquo species of Fe^{3+} in water at pH = 7.00 is 3.2×10^{-10} mol L^{-1} ($= 1.8 \times 10^{-8}$ g $L^{-1} = 0.018$ ppb), and the most significant species is $Fe(OH)_2^+$.

Metal Speciation in the Hydrosphere

Aquo Complexes

Table 13.2 Principal inorganic aqueous species of environmentally important metal ions[a] (only inorganic species are considered and coordinated water molecules are not included in the formulae).

	pH = 4		pH = 7[b]		pH = 10	
	Oxidizing environment	Reducing environment	Oxidizing environment	Reducing environment	Oxidizing environment	Reducing environment
Sodium	Na^+	Na^+	Na^+	Na^+	Na^+	Na^+
Potassium	K^+	K^+	K^+	K^+	K^+	K^+
Magnesium	Mg^{2+}	Mg^{2+}	Mg^{2+}, $MgSO_4^0$(sw)	Mg^{2+}, $MgSO_4^0$(sw)	Mg^{2+}	Mg^{2+}
Calcium	Ca^{2+}	Ca^{2+}	Ca^{2+}, $CaSO_4^0$(sw)	Ca^{2+}, $CaSO_4^0$(sw)	Ca^{2+}	Ca^{2+}
Aluminium	Al^{3+}, $AlOH^{2+}$	Al^{3+}, $AlOH^{2+}$	$Al(OH)_2^+$, $Al(OH)_3^0$ $Al(OH)_4^-$ (sw)	$Al(OH)_2^+$, $Al(OH)_3^0$ $Al(OH)_4^-$(sw)	$Al(OH)_4^-$	$Al(OH)_4^-$
Vanadium	$H_2VO_4^-$, VO_2^+	VO^{2+}	$H_2VO_4^-$, HVO_4^{2-} $V_{10}O_{28}^{6-}$	VO^{2+}	VO_4^{3-}	
Chromium	$HCrO_4^-$	$CrOH^{2+}$	$HCrO_4^-$, CrO_4^{2-}	$CrOH^{2+}$, $Cr(OH)_2^+$	CrO_4^{2-}	$Cr(OH)_4^-$
Manganese	Mn^{2+}	Mn^{2+}	MnO_2^0, $MnCl^+$(sw)	Mn^{2+}, $MnCl^+$(sw) $MnSO_4$(sw)	MnO_2^0	$MnCO_3^0$
Iron	$FeOH^{2+}$ $Fe(OH)_2^+$	Fe^{2+}	$Fe(OH)_3^0$	Fe^{2+}, $FeCO_3^0$	$Fe(OH)_4^-$	$FeOH^+$, $Fe(OH)_2^0$
Cobalt	Co^{2+}	Co^{2+}	Co^{2+}, $CoCO_3$	$CoCO_3$	Co_3O_4	$CoCO_3$
Nickel	Ni^{2+}, $NiSO_4^0$	Ni^{2+}	Ni^{2+}, $NiHCO_3^+$ $NiCl^+$(sw)	Ni^{2+}, $NiHCO_3^+$ $NiCl^+$(sw)	$NiOH^+$ $Ni(OH)_2^0$, $NiCO_3$	$NiOH^+$ $Ni(OH)_2^0$, $NiCO_3$
Copper	Cu^{2+}	Cu^{2+}	Cu^{2+}, $CuOH^+$, $CuHCO_3^-$ $CuCl^+$(sw)	Cu^{2+}, $CuOH^+$ $CuHCO_3^+$, $CuCl^+$(sw)	$Cu(OH)_2^0$ $Cu(CO_3)_2^{2-}$	$Cu(OH)_2^0$ $Cu(CO_3)_2^{2-}$
Zinc	Zn^{2+}	Zn^{2+}	Zn^{2+}, $Zn(OH)_2^0$, $ZnCl^+$(sw)	Zn^{2+}, $Zn(OH)_2^0$, $ZnCl^+$(sw)	$Zn(OH)_2^0$	$Zn(OH)_2^0$
Molybdenum	$HMoO_4^-$		$HMoO_4^-$		$HMoO_4^-$, MoO_4^{2-}	
Lead	Pb^{2+}, $PbSO_4^0$	Pb^{2+}	Pb^{2+}, $PbOH^+$, $PbHCO_3^+$ $PbCl^+$(sw), $PbSO_4^0$(sw)	Pb^{2+}, $PbOH^+$, $PbHCO_3^+$ $PbCl^+$(sw), $PbSO_4^0$(sw)	$Pb(OH)_2$ $PbCO_3$, $Pb(CO_3)_2^{2-}$	$Pb(OH)_2$ $PbCO_3$, $Pb(CO_3)_2^{2-}$
Mercury	$HgOH^+$ $Hg(OH)_2^0$ $HgCl_2^0$	Hg^0	$Hg(OH)_2^0$, $HgCl_2^0$ $HgCl_4^{2-}$ (sw), $HgCl_3^-$(sw)	Hg^0	$Hg(OH)_2^0$	Hg^0

[a] Sulphate, chloride, and carbonate in concentrations that approximate those found in average river water are assumed to be present in the water. The metal concentrations are also assumed to be in the range of those found in 'normal' water. Some neutral species such as $Fe(OH)_3$ and MnO_2 are highly insoluble and will be present as colloids even when the metal concentration is very small.

[b] The notation (sw) indicates that this additional species is present in sea water. Note that sea water pH is approximately 8.

Biogeochemical cycle of metal species

All metals cycle naturally through the environment.

Sources: weathering of rocks

Transportation: uptake and processing by plants and microorganisms.

- Plants living in soils rich in metal species have evolved protective mechanisms.
- These plants can be used in remediation of soils contaminated with metals.

Human intervention have greatly perturbed the natural biological cycles of the metals.

- Mining and metallurgy
- Coal burning

Metals can not be broken down into simpler, less toxic forms. As a result, they persist in the environment and bioaccumulate through food chain.

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Biogeochemical cycle of metal species

Calcium

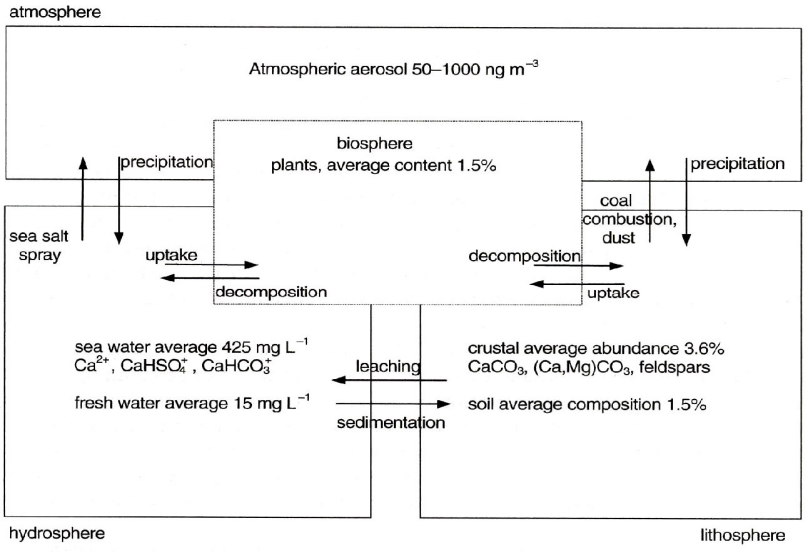


Fig. 13.4 Major components of the calcium environmental cycle.

Biogeochemical cycle of metal species

Copper

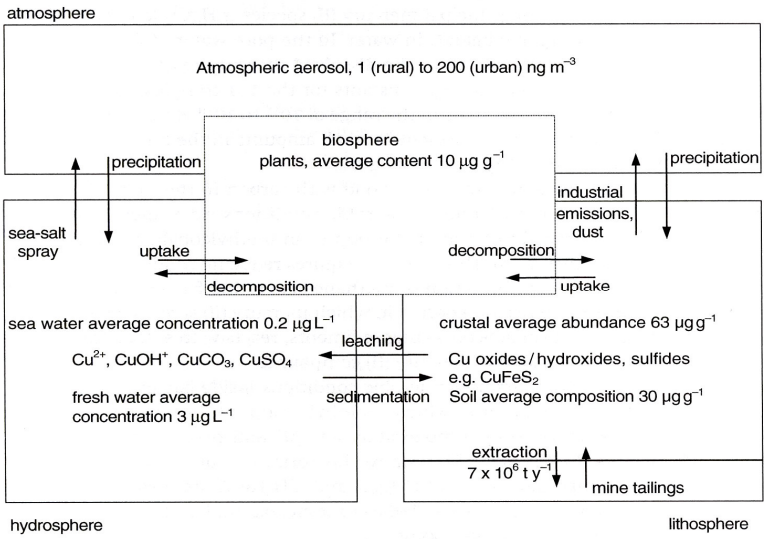
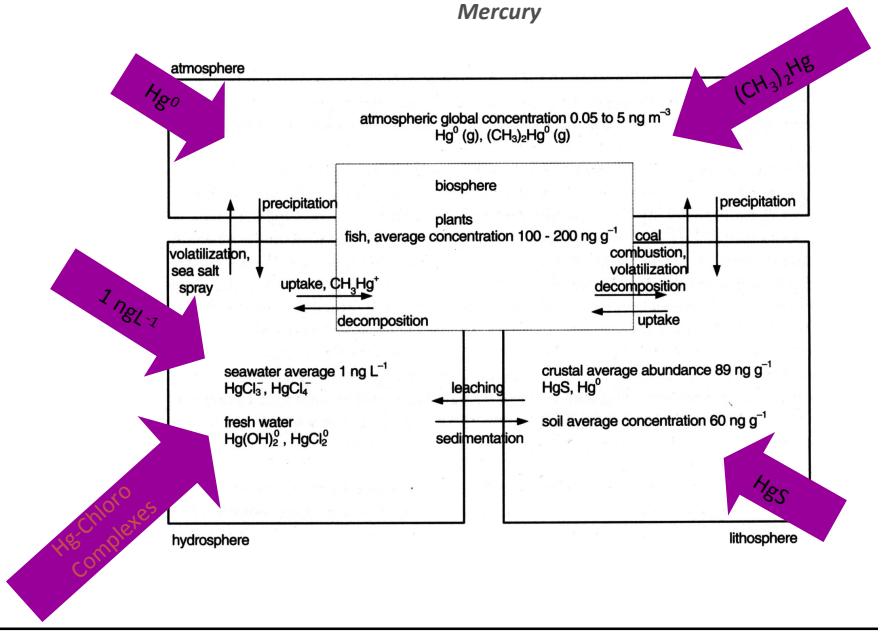


Fig. 13.5 The principal features of the environmental cycle for copper.

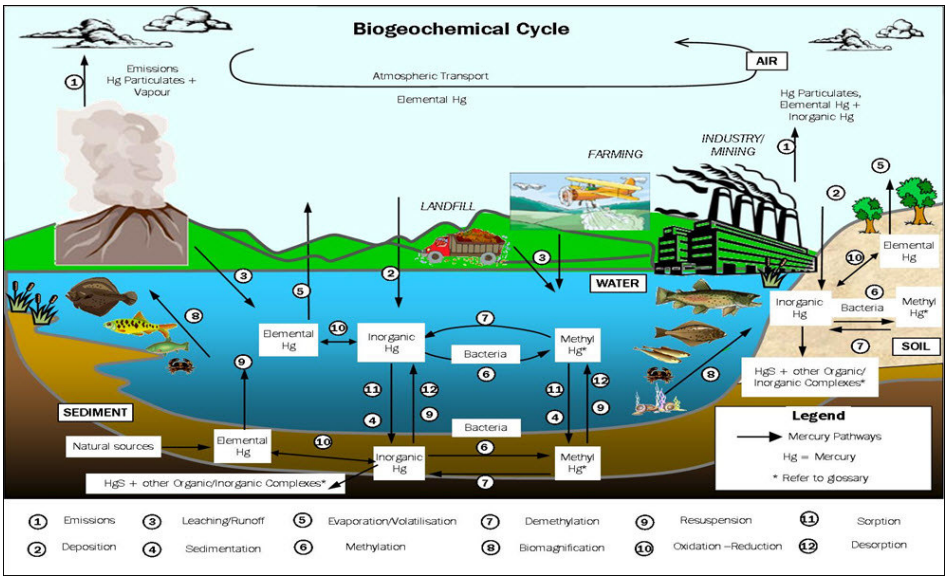
Biogeochemical cycle of metal species

Mercury



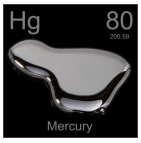
Biogeochemical cycle of metal species

Mercury



Biogeochemical cycle of metal species

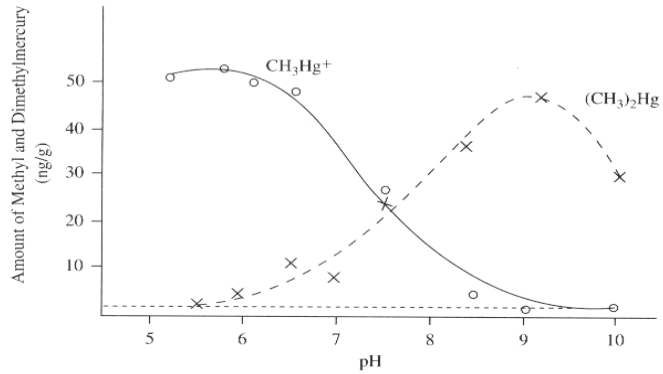
Mercury



- When ingested, Hg^0, Hg_2^{2+}, and Hg^{2+} are not toxic.
- Harmful forms: methylmercury ion $(CH_3)Hg^+$ regardless of the route of exposure, Hg vapor when inhaled.
- $(CH_3)Hg^+$ is produced from mercury ions by methanogens living in sediments.
- $(CH_3)Hg^+$ is soluble in water and bioaccumulates in the aquatic ecosystem food chain (in protein-laden tissues).
- $(CH_3)Hg^+$ binds with protein and peptide sulfhydryl groups.
- It is dangerous to eat large quantities of very big ocean fish such as tuna and swordfish!

Biogeochemical cycle of metal species

Mercury Methylation



Methylation of 100 ppm of Hg^{2+} in sediments over two weeks. *Source:* I. G. Sherbin (1979). *Mercury in the Canadian Environment,* Report EPS-3-EC-79-6 (Ottawa: Environmental Protection Service Canada).

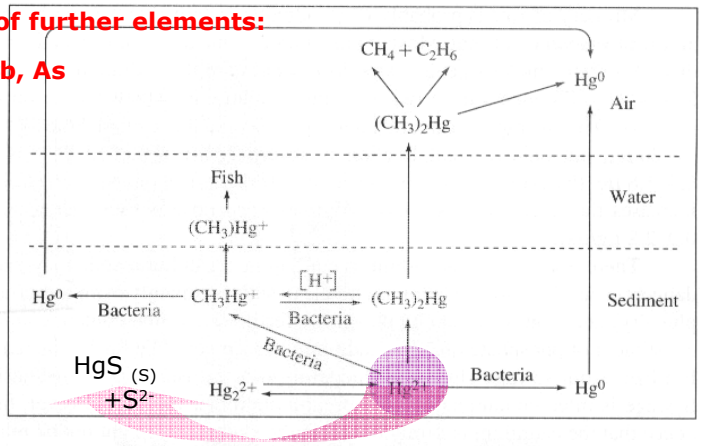
Lake acidification would increase mercury toxification

Biogeochemical cycle of metal species

Mercury Methylation

Biomethylation is known for a number of further elements:

Pb, Se, Sb, As



The biogeochemical cycle of bacterial methylation and demethylation of mercury in sediments. *Source:* National Research Council (1978). *An Assessment of Mercury in the Environment* (Washington, DC: National Academy Press).

Biogeochemical cycle of metal species

Mercury - Sources

- Coal-burning (Hg^0, Hg^{2+}, Hg bound to particulate).
- Chlor-alkali plants:
  Hg used as cathode for collecting metallic Na.
- Use in electrical devices and equipment, such as batteries, switches, lamps.

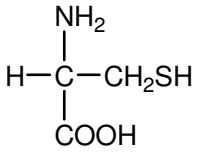
- Use in extracting gold or silver from ores.
- Dental amalgam fillings.
- Use of complexes of phenylmercury as paint preservatives.
- Organomercurials used as fungicides for seed treatment.

Biogeochemical cycle of metal species

Mercury Pollution: Long-Range Transportation

- It has been discovered that fish have elevated Hg levels even in lakes remote from any local sources. → evidence for the long-range transportation of Hg compounds.
- The two volatile forms of Hg, Hg^o and dimethyl mercury, are responsible via air transportation.
- Both Hg^o and dimethyl mercury are formed from other Hg species (Hg^{2+} and CH_3Hg^+) through bacteria actions.
- Acidic pH favors the formation of CH_3Hg^+ over $(CH_3)_2Hg$ → lake acidification would increase mercury toxification.

- All three are "soft" Lewis acids, i.e., with large polarizability.
- They have strong affinity for soft Lewis bases, such as the sulfhydryl side chain of cysteine residue.
- The heavy metals likely exert their toxic effects by tying up critical cysteine residues in proteins.



cysteine

Lewis acid is a species that can form a covalent bond by accepting an electron pair from another species.

Lewis base is a species that can form a covalent bond by donating an electron pair to another species

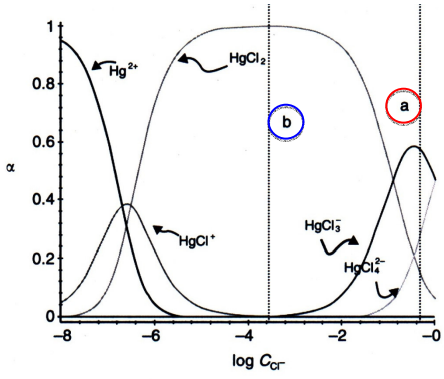


Fig. 1.3 Distribution of mercury chloro species in water as a function of chloride ion concentration, C_{Cl^-}(mol L^{-1}). The α value is the fraction of mercury in the form of a particular complex.

complex formation constants for Hg^{2+}

$\log K_1 = 7.30$
$\log K_2 = 6.70$
$\log K_3 = 1.00$
$\log K_4 = 0.60$

(a) Oceans:

$[Cl^-]$ =0.56 mol/L

(b) Well water

$[Cl^-]$ =9.5 ppm or 0.26 mmol/L

Biogeochemical cycle of metal species

Mercury Poisoning Tragedies

1. Minamata, Japan,1950s: A polyvinyl chloride plant released large quantities of Hg compounds (used as a catalyst) into Minamata Bay. Many residents who relied heavily on fish from the bay for their diet became sick. 52 people died and many suffered numbness, impaired vision, paralysis, and brain damage.

2. Iraq, 1972: Wheat grain treated with a methyl mercury fungicide was imported as seeds for planting. The warning label was in a language the Iraqis did not understand. The wheat was used to make bread. 500 people died from eating the bread.

Biogeochemical cycle of metal species

Chromium

Cr (VI) (know also as hexavalent chromium) is a carcinogenic.

Sources:

- Steel-making, cutting, grinding, and welding.
- Spills and residues of electroplating baths.
- Chromate emissions from cooling towers (used to inhibit corrosion).

Biogeochemical cycle of metal species

Cadmium

Cd is chemically similar to Zn.

- It is always found in association with Zn in Earth's crust, obtained as a side-product of Zn mining and extraction.
- It is always present as a contaminant in zinc products. (e.g. galvanized steel).
- It is actively taken by many plants since Zn is an essential nutrients.

Cd intake by human beings is mainly through food crops which take up Cd from Cd-laden soils.

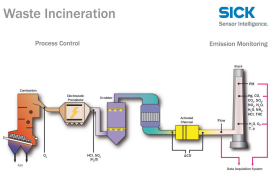
Jinzu vally, Japan Ouch-ouch disease, irrigation water from a river contaminated with waste water from a zinc mining and smelting plant

Biogeochemical cycle of metal species

Source of Cadmiun pollution

Airborne sources

- Coal burning
- Incineration
- Cement plants



Phosphate fertilizer: Cd is a natural constituent of phosphate ore.

Sources of Lead Pollution

- Pb-containing paints
  - $PbCrO_4$ provides the yellow striping on roads and for school buses.
  - Pb_3O_4 is the base for the corrosion-resistant red paints on metal structures.
  - $Pb_3(OH)_2(CO_3)_2$ is a white paint, which was widely used as the base of indoor paints.

- Leaded gasoline
  - Tetraethyl lead is used as gasoline additive to improve octane rating.