



Water-Quality Principles

QW1022–TEL

Lesson 6—Trace Elements

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Heavy Metals and Metalloids

The term *heavy metals* is used generally to mean metallic elements with atomic numbers greater than about 20, the atomic number of calcium. Metalloids are elements such as arsenic and selenium that have both metallic and non-metallic properties. The term *heavy metals* will be used loosely to include metalloids. By and large, the concentrations of heavy metals in unpolluted natural waters are quite low. The main question we are trying to answer is: Why does a particular element have the concentration we observe in a particular water? Once we understand the answer to that question, we shall be in a position to predict the consequences of specific human interventions such as waste disposal and mining. Many elements—for example, selenium and molybdenum—are essential in trace amounts for biological systems. Understanding the circumstances that make such elements unavailable is sometimes as important as understanding the causes of toxic concentrations. Some economic ore deposits, such as those of uranium, are formed when elements present in trace concentrations in solution are extracted from solution at a particular location. To understand (and hence locate) such deposits, we need to understand the factors controlling the dissolution, transport, and precipitation of specific elements.

SOURCES OF HEAVY METALS

Heavy metals may be derived from the weathering of rocks or, increasingly, they may be introduced into the atmosphere and hydrosphere by human activities. Average concentrations of some trace elements in rocks and in waters are shown in Table 9-1. For some elements, there are few reliable measurements, so the numbers should be taken as qualitative indicators only.

Whether a particular metal goes into solution during weathering depends on the mineral in which the element occurs and on the intensity of chemical weathering. Many of the metals do not substitute readily in feldspars or the common ferromagnesian minerals. They may be present in chemically resistant accessory minerals such as zircon, apatite, or monazite, or as sulfides, which generally weather rapidly in oxygenated water. The resistant minerals generally remain unaltered unless weathering is very intense (gibbsite formation, see Chapter 12),

TABLE 9-1 Typical Concentrations of Selected Elements in Rocks [mg/kg (ppm)] and in Streams and the Ocean [µg/kg (ppb)]
 [from Turekian, 1971; Martin and Meybeck, 1979; and other sources]

	<i>Granite</i>	<i>Basalt</i>	<i>Shale</i>	<i>Sandstone</i>	<i>Limestone</i>	<i>Streams</i>	<i>Ocean</i>
Lithium	30	17	66	15	5	10	170
Beryllium	3	1	3				0.006
Boron	10	5	100	35	20	20	4,450
Fluorine	800	400	740	270	330	100	1,300
Aluminum	Major	Major	Major	Major	4,200	50	1
Scandium	10	30	13	1	1	0.004	0.0004
Titanium	Major	Major	Major	Major	400	10	1
Vanadium	50	250	130	20	20	1	2
Chromium	10	170	90	35	11	1	0.2
Manganese	450	1,500	850	50	1,100	8	0.2
Iron	Major	Major	Major	Major	Major	40	2
Cobalt	4	48	19	0.3	0.1	0.2	0.05
Nickel	10	130	68	2	20	2	0.5
Copper	20	87	45	2	4	7	0.5
Zinc	50	105	95	16	20	30	2
Gallium	17	17	19	12	4	0.1	0.03
Germanium	1	1	2	1	0.2		0.06
Arsenic	2	2	13	1	1	2	3
Selenium	0.05	0.05	0.6	0.05	0.9	0.2	0.1
Bromine	4	4	4	1	6	20	67,300
Rubidium	150	130	140	60	3	1	120
Strontium	250	465	300	20	600	60	8,100
Yttrium	40	25	35	10	4	0.07	0.001
Zirconium	150	140	160	220	20		0.03
Molybdenum	1	1.5	2.6	0.2	0.4	0.5	10
Silver	0.04	0.1	0.07			0.3	0.04
Cadmium	0.13	0.2	0.3		0.03		0.05
Antimony	0.2	0.1	1	0.4	0.3	1	0.3
Iodine	0.5	0.5	2	1	1	7	64
Cesium	3	1	6	6	6	0.03	0.3
Barium	600	330	580		10	50	10
Rare earths	0.5-70	1-80	1-80	0.05-15	0.05-8	0.001-0.1	0.001
Tungsten	1.7	0.7	1.8	1.6	0.6	0.03	<0.001
Gold	0.002	0.002	0.005	0.006	0.006	0.002	0.004
Mercury	0.03	0.01	0.4	0.03	0.04	0.07	0.03
Thallium	1.5	0.2	1.4	0.8			<0.01
Lead	17	6	20	7	9	1	0.03
Thorium	14	2.7	12	5.5	2	0.1	<0.0005
Uranium	3	1	4	2	2	0.1	3.3

and so their alteration never causes high trace-metal concentrations in waters (where weathering is intense, dilution prevents high concentrations). Many metals (e.g., copper, zinc, molybdenum, silver, mercury, and lead), occur in high concentrations in sulfide deposits and these sulfides often contain selenium, arsenic, and cadmium. Since sulfides weather rapidly, such ore deposits can give rise to locally high concentrations of dissolved trace elements (e.g., Alpers and Blowes, 1994). One aspect of *geochemical prospecting* is to use the concentrations of trace elements in water as a means of locating ore deposits.

Human activities introduce heavy metals to the hydrosphere in many ways. Burning of fossil fuels and smelting of ores put metals into the atmosphere, where they are washed out by rain and dry deposition into surface waters. Municipal sewage and industrial effluent introduce metals directly. Mining activities can result in release of metals, both because previously impermeable rocks are broken up and exposed to water, and because sulfide containing rocks are exposed to oxygen, resulting in rapid alteration and dissolution. Landfills and underground toxic waste disposal, including radioactive wastes, have the potential to release a variety of substances to groundwater, and hence to surface waters. In many rivers and lakes, the human input of trace elements is many times greater than the natural input (Nriagu et al., 1979; Stumm and Baccini, 1978), and even in the oceans the human input is significant (Galloway, 1979).

High concentrations of heavy metals, regardless of their source, generally do not persist as the metals are transported through aquatic systems. The purpose of this chapter is to discuss some of the processes regulating trace element concentrations in natural waters.

SPECIATION

For any calculations involving chemical equilibria, adsorption, or, indeed, toxicity, it is necessary to know the chemical form in which the element is present. For example, in Chapter 7 we discuss the solubility of $\text{Fe}(\text{OH})_3$ in terms of the species Fe^{3+} , Fe^{2+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}(\text{OH})_4^-$. If we had simply assumed that all dissolved iron was Fe^{3+} , we would have very little understanding of the processes regulating dissolved iron concentrations.

BEHAVIOR OF SPECIFIC ELEMENTS

Several specific elements are discussed here to provide an overview of their behavior and to illustrate patterns of behavior that are common to many other elements.

Copper, Zinc, Cadmium, and Lead

These elements have several features in common. The dominant species in solution is a divalent cation (free or complexed). Under oxidizing conditions, they are soluble under acid conditions and their solubilities at higher pH are limited by the solubility of a carbonate or oxide/hydroxide (Figs. 9-12 to 9-16; these and subsequent figures have been simplified by omission of some possible complexes in solution involving sulfate, sulfide species, carbonate species, and OH^- . These omissions do not significantly change the diagrams for the conditions commonly encountered in fresh waters). Under reducing conditions, in the presence of sulfur all form relatively insoluble sulfides. In the absence of sulfur, copper is insoluble as the native metal (Fig. 9-16). The others behave as they do in oxidizing environments: they are relatively soluble at low pH and insoluble as carbonates/oxides/hydroxides at high pH. Copper, zinc, and cadmium form anionic species at high pH. It is rare, however, for pH values in nature to be sufficiently high for such species to be important. The response of these elements to a change in redox conditions is determined less by redox reactions involving the elements themselves than by changes occurring in sulfur species, and in Fe and Mn oxyhydroxides, which are important substrates for adsorption.

All members of the group are complexed by natural organic matter. Some binding constants for complexing of the M^{2+} ion with humic substances are shown in Table 9-2. These constants give a general indication of the strength of interaction between the metal and dissolved organic matter. The constant for calcium is included for comparison. In general, copper is the most strongly complexed member of the group and is very commonly influenced by organic complexation. Lead is next, followed by zinc and cadmium. Complexing of zinc and cadmium by organic solutes is, generally speaking, important only where concentrations of dissolved organic carbon are relatively high.

FIGURE 9-12 Simplified pe - pH diagram for the system $Cu-S-O-H_2O$ at $25^\circ C$ and 1 atm. Solubility is defined as a dissolved Cu activity of 10^{-6} . Total activity of sulfur species = 10^{-2} . Malachite ($Cu_2(OH)_2CO_3$) becomes stable at a P_{CO_2} of about 0.6 atm; its stability field replaces that of CuO (Fig. 9-16). Data are consistent with Appendix III.

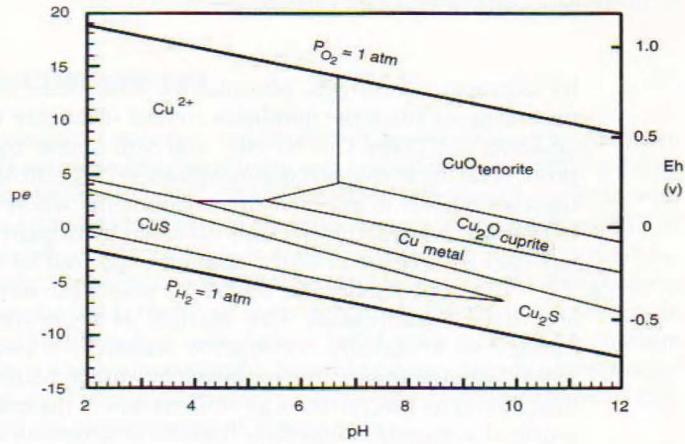


FIGURE 9-13 Simplified pe - pH diagram for the system $Zn-CO_2-S-O-H_2O$ at $25^\circ C$ and 1 atm. Solubility is defined as a dissolved Zn activity of 10^{-6} . Total activity of sulfur species = 10^{-2} , $P_{CO_2} = 10^{-2}$ atm. Dashed lines are the solubility of ZnO (zincite) in the absence of CO_2 , and short dashes are the solubility of the carbonate in the absence of S species. Data are consistent with Appendix III.

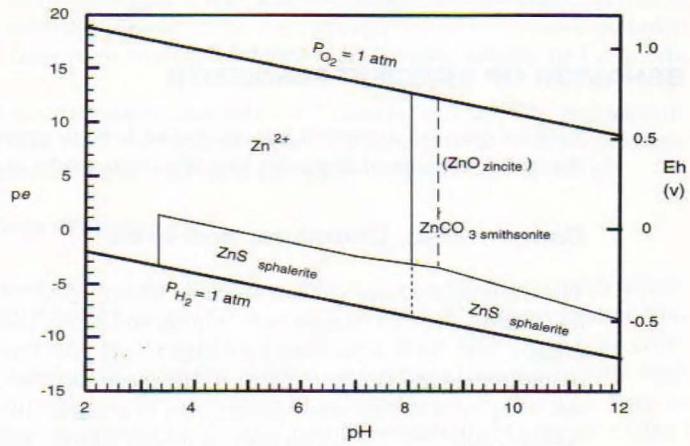


FIGURE 9-14 Simplified pe - pH diagram for the system $Cd-CO_2-S-O-H_2O$ at $25^\circ C$ and 1 atm. The P_{CO_2} has to be very low for the oxide, CdO (monteponite) to be stable relative to the carbonate. Solubility is defined as a dissolved Cd activity of 10^{-6} . Total activity of sulfur species = 10^{-2} , $P_{CO_2} = 10^{-2}$ atm. Solid lines are solubility in the presence of S species, and dashed line is solubility of the carbonate in the absence of S species. Data are consistent with Appendix III.

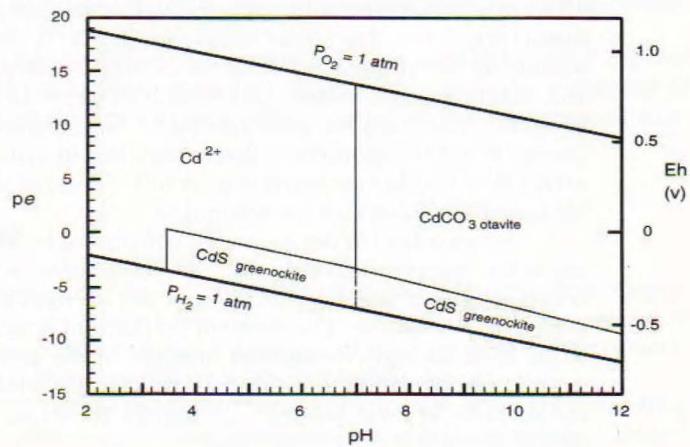


FIGURE 9-15 Simplified pe - pH diagram for the system $Pb-CO_2-S-O-H_2O$ at $25^\circ C$ and 1 atm. Solubility is defined as a dissolved Pb activity of 10^{-6} . Total activity of sulfur species = 10^{-2} , $P_{CO_2} = 10^{-2}$ atm. The P_{CO_2} has to be very low for the oxide, PbO (litharge) to be stable relative to the carbonate. Solid lines are solubility in the presence of S species, and the dashed line is solubility of the carbonate in the absence of S species. Data are consistent with Appendix III.

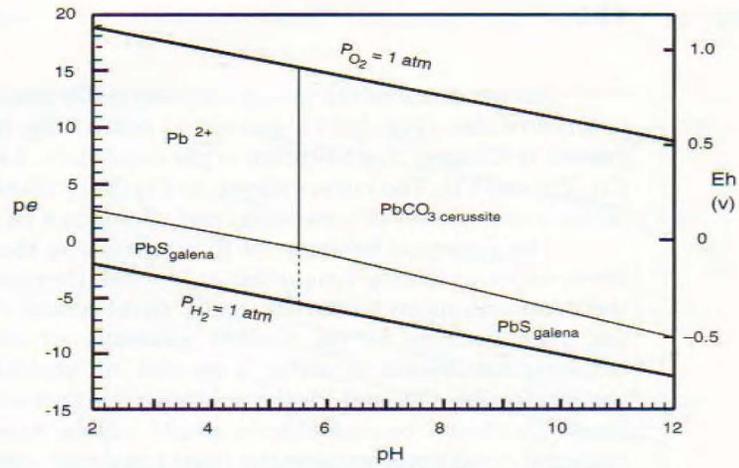


FIGURE 9-16 Simplified pe - pH diagram for the system $Cu-CO_2-O-H_2O$ at $25^\circ C$ and 1 atm. Solubility is defined as a dissolved Cu activity of 10^{-6} . No sulfur species present. The stability of malachite ($Cu_2(OH)_2CO_3$) is shown for a P_{CO_2} of 1 atm. At P_{CO_2} values below about 0.6 atm, malachite becomes unstable, and tenorite (CuO) becomes the stable phase. Dashed lines are the stability field of CuO in the absence of CO_2 . Data are consistent with Appendix III.

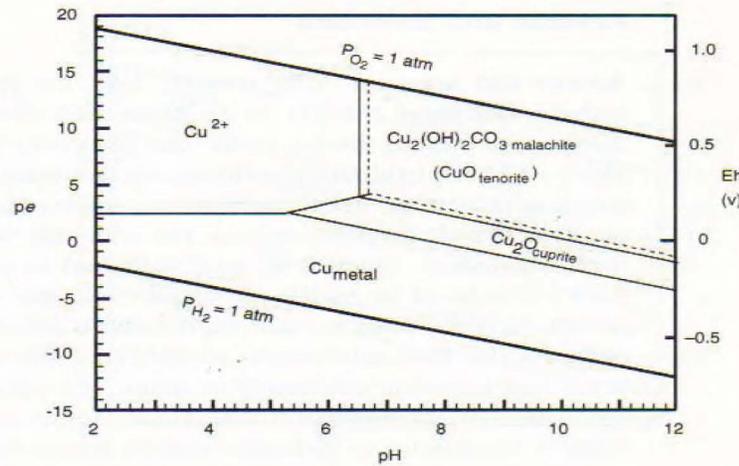


TABLE 9-2 Logarithms of Intrinsic Binding Constants^a for Complexes Between Metals and Dissolved Humic Substances (from Tipping and Hurley, 1992)

	<i>log binding constant</i>
Cu^{2+}	-0.72
Pb^{2+}	-0.81
Zn^{2+}	-1.04
Cd^{2+}	-1.63
Ca^{2+}	-2.67

^aThe exact definition of intrinsic binding constant is rather complex; readers should consult the original reference before attempting to use the numbers. The numbers are a good indication of the relative extent of complexing to be expected between the individual metals and natural dissolved organic matter. A smaller number (larger negative logarithm) means weaker binding.

All members of the group are potentially affected by adsorption on iron and manganese oxyhydroxides (Fig. 9-17), and Cd is potentially affected by adsorption on calcite. As discussed in Chapter 5, adsorption is pH dependent. Lead adsorbs at the lowest pH, followed by Cu, Zn, and Cd. The curves shown in Fig. 9-17 illustrate the results of experiments conducted under a specific set of conditions and should not be overgeneralized.

The expected behavior of these metals in the environment can be summarized as follows: under oxidizing conditions at low pH, they are all soluble and mobile. As the pH rises, their concentrations tend to decrease, first because of adsorption (particularly for Pb and Cu), and then because of the limited solubility of carbonates and oxides/hydroxides. Under reducing conditions, if sulfur is present, all should be immobilized as sulfides. If sulfur is absent, for Zn, Cd, and Pb the solubility control will be the same as under oxidizing conditions; Cu should be insoluble at all pH values. Adsorption is generally less important under reducing conditions because the most important substrates for adsorption, Fe and Mn oxyhydroxides, tend themselves to dissolve.

Arsenic and Selenium

Arsenic and selenium differ strongly from the previous examples in that both elements undergo important changes in oxidation state themselves, and both occur in solution as anions or as neutral species rather than as cations. *pe*-pH diagrams are shown in Figs. 9-18 and 9-19. Under oxidizing conditions, the dominant form of arsenic is the +V oxidation state, which is present as arsenic acid and its anions (arsenate), corresponding closely to phosphoric acid and phosphate species. For selenium, the dominant form under oxidizing conditions is selenate, which is closely analogous to sulfate. As conditions become reducing, As(V) is reduced to As(III)—arsenious acid and arsenite anions. When sulfate reduction occurs, As precipitates as a sulfide; if sulfur is absent, it remains in solution as arsenious acid or an arsenite. Elemental arsenic should be a stable species under highly reducing conditions, but it does not occur commonly in nature. For selenium, selenite species (analogous to sulfite) occur at intermediate redox levels, followed by elemental selenium and hydrogen selenide (analogous to hydrogen sulfide) species under strongly reducing conditions. Both

FIGURE 9-17 Adsorption of Cu^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} , Cr^{3+} , and Ca^{2+} (for comparison) on hydrous ferric oxide as a function of pH. Each metal shows an adsorption "edge"; at pH values below the edge, the ion is not adsorbed or very weakly adsorbed. At pH values above the edge, the ion is strongly adsorbed. Conditions correspond to a high ratio of hydrous ferric oxide to adsorbing cation and an ionic strength of 0.1 m. The edges move towards higher pH as the ratio adsorbing cation:hydrous ferric oxide increases. From data in Dzombak and Morel (1990).

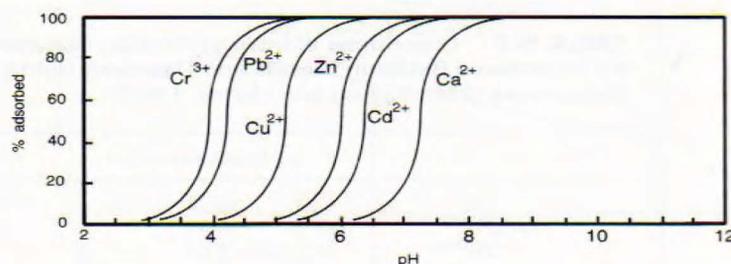


FIGURE 9-18 Simplified pe - pH diagram for the system As-O-H₂O at 25°C and one atm. Total activity of sulfur species = 10^{-2} . Light lines are boundaries involving dissolved species only. Dashed line is field of solid elemental arsenic in the absence of sulfur. Solubility is defined as a dissolved As species activity of 10^{-6} .

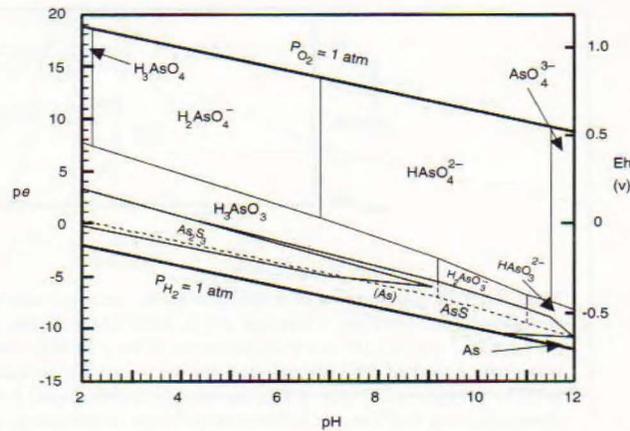
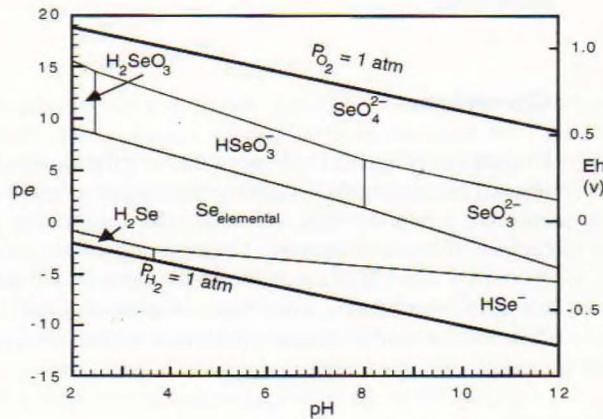


FIGURE 9-19 Simplified pe - pH diagram for the system Se-O-H₂O at 25°C and one atmosphere. Solubility is defined as a dissolved Se activity of 10^{-6} . Data are from Cowan (1988).



arsenic and selenium may be incorporated into iron sulfides under reducing conditions. The kinetics of redox transformations involving arsenic and selenium are slow, so disequilibrium is common (Kent et al., 1994; Runnells and Lindberg, 1990).

Arsenate species form inner-sphere complexes at the iron oxyhydroxide surface and are strongly adsorbed at near-neutral pH (Fig. 9-20). At high pH the strong negative charge on the oxide surface decreases adsorption of anions. As(III) apparently does not form inner-sphere complexes at the oxide surface. It is not strongly adsorbed at any pH value. For selenium, the adsorption picture is reversed. The oxidized form is only weakly adsorbed (similar to sulfate), whereas Se(IV) is strongly adsorbed under near-neutral conditions.

Organoarsenic compounds occur in nature but do not appear to be particularly important in the overall cycle of arsenic. Organic forms of selenium are more important, particularly in plants that accumulate selenium. Certain plants, notably vetches of the genus *Astragalus*, can accumulate high concentrations of selenium and may cause toxicity problems for livestock.

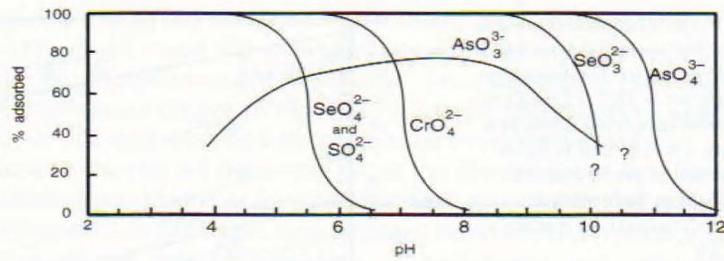


FIGURE 9-20 Adsorption of arsenate, arsenite, selenate, selenite, chromate, and sulfate (for comparison) on hydrous ferric oxide as a function of pH. Most of the anions show an adsorption “edge”: at pH values above the edge (for anions), the ion is not adsorbed or very weakly adsorbed. At pH values below the edge, the ion is strongly adsorbed. The anomalous behavior of arsenite is related to the fact that AsO_3^{3-} is fully protonated to H_3AsO_3 below pH 9 (Fig. 9-18); the symbol AsO_3^{3-} is used for all As in the +III oxidation state. Conditions correspond to a high ratio of hydrous ferric oxide to adsorbing cation and an ionic strength of 0.1 m. The edges move towards lower pH as the ratio adsorbing anion:hydrous ferric oxide increases. From data in Dzombak and Morel (1990).

Chromium

Chromium (Fig. 9-21) shows some similarities to both of the groups of elements discussed above. Under highly oxidizing conditions, the hexavalent form (chromate) is stable as an anion. It is not strongly adsorbed (adsorption edge at about pH 7, Fig. 9-20) and is therefore mobile in the environment. Under intermediate and reducing conditions, Cr(III) is the stable oxidation state. It is insoluble in the neutral and alkaline pH ranges. It is soluble (largely as $\text{Cr}(\text{OH})^{2+}$) under acid conditions. In general, Cr(III) species are strongly adsorbed (Fig. 9-17). Where dissolved chromium pollution occurs, the problem form is generally Cr(VI).

FIGURE 9-21 pe -pH diagram for the system Cr-O-H₂O at 25°C and one atm. Solubility is defined as a dissolved Cr activity of 10^{-6} . Data from Brookins (1988).

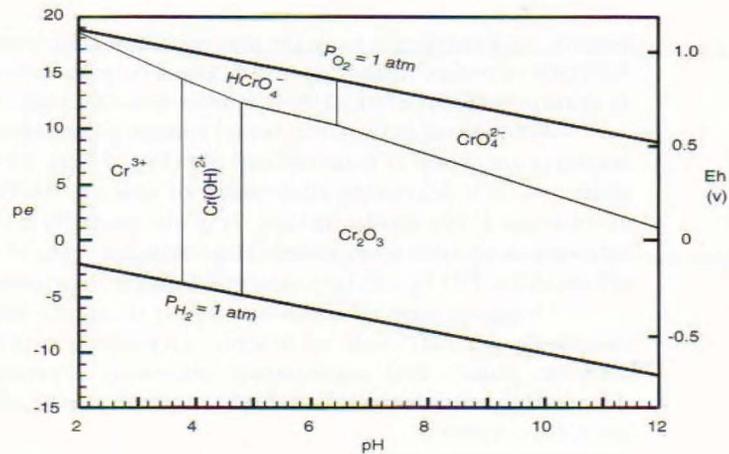
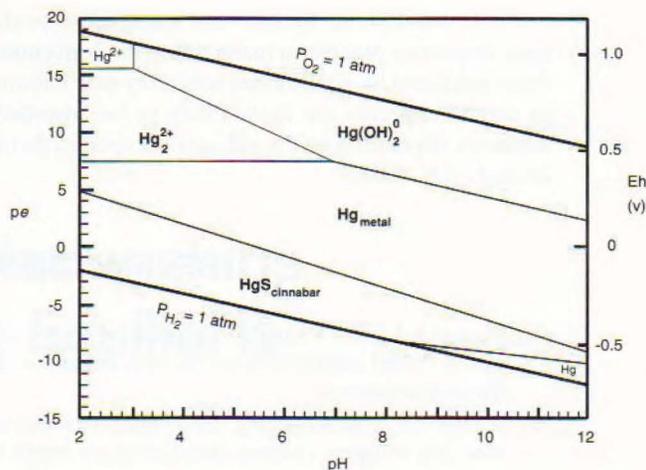


FIGURE 9-22 pe - pH diagram for the system $Hg-S-O-H_2O$ at $25^\circ C$ and one atm. Solubility is defined as a dissolved Hg activity of 10^{-6} . Total activity of sulfur species = 10^{-2} . The diagram is the same in the absence of S species, with the HgS (cinnabar) field replaced by Hg (metal). In the presence of chloride, the Hg_2^{2+} may be replaced by the insoluble mercurous chloride (calomel). Data are consistent with Allison et al. (1991).



Mercury

The chemistry of mercury in the environment is highly complex. The thermodynamically stable forms are shown in Fig. 9-22. The common soluble form is the oxidized (mercuric) Hg^{2+} ion and its hydrolysis product $Hg(OH)_2^0$, with the reduced (mercurous) Hg_2^{2+} ion being less important. Elemental mercury has a large stability field. The elemental form is volatile and slightly soluble in water. The global cycle of mercury is dominated by vapor-phase transport of Hg^0 through the atmosphere (Mason et al., 1994). Mercury is transformed by microorganisms into organic forms, notably monomethyl mercury (CH_3Hg) and dimethyl mercury [$(CH_3)_2Hg$]. These organic forms, in addition to being highly toxic, are volatile and tend to accumulate in the food chain. High concentrations of Hg in fish, which are common in polluted waters, generally result from accumulation of organomercury species. Pollutant Hg in sediments is partly transformed to organomercury species and partly to the sulfide.

Most of the metals discussed above—Cu, Zn, Cd, Pb, As, Hg, and, to a lesser extent, Se—are transformed to sulfides in anaerobic sediments. So long as conditions remain anaerobic and sulfur is available, they are relatively immobile. However, any disturbance, such as dredging, that brings the sediment into contact with oxygen will cause oxidation of the sulfides and release of the metals into solution. Cleaning up or moving contaminated sediments is a difficult problem because it may lead to oxidation and mobilization of these metals.

SUMMARY

1. To understand the behavior of any trace element in natural waters, it is essential to know the chemical form of the element in the water of interest. Anomalously high concentrations are often related to the presence of stable complexes in solution.
2. The solubility of phases containing the element as a major constituent (commonly an oxide/hydroxide, carbonate, or sulfide) provides a general upper limit to the concentration of a specific element.