

# **ISSUE PAPER ON THE ENVIRONMENTAL CHEMISTRY OF METALS**

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Submitted to:

U.S. Environmental Protection Agency  
Risk Assessment Forum  
1200 Pennsylvania Avenue, NW  
Washington, DC 20460  
Contract #68-C-02-060

Submitted by:

ERG  
110 Hartwell Avenue  
Lexington, MA 02421

August 19, 2004  
(corrected reference on January 25, 2005)

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# ENVIRONMENTAL CHEMISTRY

## 1. INTRODUCTION

Metals in the environment are of concern to almost all EPA programs. The Safe Drinking Water Act mandates maximum contaminant levels and maximum contaminant level goals for a variety of metals; the Clean Water Act mandates the development of ambient water quality criteria for the protection of human health and aquatic life against the potential toxic effects of metals; CERCLA requires that hazardous metals released into the environment be remediated to levels which do not pose an unacceptable risk to human health or the environment; and RCRA regulates the management of waste containing metals and metal compounds. To varying degrees, each of these programs relies on scientific information regarding the metals. For example, toxicity, bioavailability, bioaccumulation, and environmental fate and transport are all significant characteristics of metals that should be considered by EPA risk managers.

Over time, EPA has developed a paradigm for the assessment of the behavior and effects of organic compounds in the environment. Key elements of this framework are the fundamental principle of lipophilicity as a driving force for many environmental and exposure events, the significance of Henry's law for intermedia transfers, the degradability and potential for chemical transformation of a hazardous material, and the fact that most organics in the environment typically exist in one form.<sup>1</sup> With few exceptions (mainly for strongly covalent inorganic compounds or organo-metallics), metals do not exhibit these behaviors. In particular, although metals can undergo a variety of intermedia transfers and chemical reactions, they are indefinitely persistent and conservative in the environment. Possibly most important, the speciation, or chemical form, of a metal has a profound impact on its environmental behavior and effects.

The term "speciation" as used by many environmental chemists is poorly defined. Forstner (1995) refers to speciation as those aspects of metal chemistry including precipitation-dissolution, adsorption-desorption, and complex formation in relation to pH; redox conditions; and the content of soluble chelating agents. Bodek et al. (1988) identify a group of properties or processes that are important for the environmental behavior of metals, including volatilization, photolysis, sorption, atmospheric deposition, acid/base equilibria, polymerization, complexation, electron-transfer reaction, solubility and precipitation equilibria, microbial transformation, and diffusivity. For regulatory purposes, the recommended IUPAC definition might be more useful (Templeton et al., 2000). In that definition, "speciation" refers to the distribution of an element among defined chemical species, which are the specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.

The oxidation state of a metal is often a significant feature of its speciation due to its impact on other processes. The well-known example of the high mobility of Cr(VI) compared to

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<sup>1</sup> There are a few exceptions to this rule. Organic acids and bases can exist in ionized or neutral forms, and some organics exist as structural isomers (e.g., the hexachlorocyclohexanes).



Cr(III) demonstrates the significance of oxidation state. Toxicity depends both on the oxidation state and form of a metal (as cation or anion) and its tendency to form complexes with ligands. For example, the toxicity of As(III) to aquatic life is significantly different from the toxicity of As(V). Cr(VI) is considered a known human inhalation carcinogen, whereas Cr(III) is generally considered to have low human toxicity. Cupric ion is more toxic to fish than is the cupric carbonate complex. Dimethyl mercury is generally thought to be more toxic and to have a greater bioaccumulation potential than mercuric chloride.

Mobility is affected by a variety of factors. The ability of a metal to sorb to a substrate is usually the determining factor in its mobility. Physical adsorption—which is important for molecular organic compounds—is largely inapplicable to the sorption of the trace metals, which are usually adsorbed as ionic species. Ion exchange, too, rarely applies, in part because of the relatively low concentrations of trace metals compared to those of major ions. In fact toxic metal adsorption is often relatively independent of the concentrations of the major ions (Langmuir, 1997a). Metal sorption is usually strongly pH-dependent and a function of metal complex formation and ionic strength. The most accurate and mechanistic approach to modeling and predicting metal adsorption is surface complexation modeling, which ideally can take into account all of these variables (cf. Stumm and Morgan, 1996; Langmuir, 1997a). Factors that are important to metal sorption in soils, aquifers, and sediments include:

Soil Solids	Soil Solution	Solutes
Soil mineral composition	pH	Chemical identity
Specific surface areas	Eh	Complexation chemistry
of metal sorbing solids	Dissolved oxygen	Solubility
Surface site density or	Solute composition	Precipitation chemistry
cation exchange capacity	and concentrations	Redox behavior
of metal sorbing solids	(activities)	Vapor pressure
Aeration status	Dissolved organic carbon	
Microbial type, activity, and	Ionic strength	
population	Temperature	
Organic matter content		
and character		
Temperature		

The degree of mobility of organic contaminants is often expressed by means of a single partition coefficient that describes the extent of equilibrium between sorbed and dissolved forms of a compound (U.S. EPA, 1995). Mobility is then calculated from the partition coefficient. Such an approach is only applicable to metal adsorption when the conditions listed above are practically constant, which is rarely the case. In fact when metal adsorption is described using partition coefficients, the value of such coefficients typically needs to be varied by two or more orders of magnitude to reproduce metal adsorption behavior.

The bioavailable fraction of metals includes metal species that are environmentally available and are absorbed or adsorbed by an organism (see the issue paper on bioavailability

and bioaccumulation of metals for a detailed definition of metal bioavailability). “Bioavailability” refers to a specific route of exposure—oral, inhalation, or dermal in the case of a human; oral, gill, or dermal in the case of a fish. Oral bioavailability varies with oxidation state, chemical form, and mineralogy. Inhalation bioavailability is strongly dependent on solubility and particle size. Uptake of metals by biota or bioaccumulation is important for determining concentrations and species of metals to which organisms can be exposed. EPA is typically interested in the biouptake of metals by aquatic life (including aquatic vegetation), terrestrial vegetation, terrestrial and avian wildlife, and farm animals. The concentration of a chemical in an organism is usually calculated by application of a bioconcentration factor or a transfer coefficient (U.S. EPA, 1998) that relates the concentration of a chemical in an organism to the concentration in its food. Sorption, solubility, oxidation state, chemical form, complexation, and competing chemical species are all important to the biouptake of metals.

In a few cases, metabolism may impact the speciation and subsequent fate and effects of a chemical at a given location in a food chain. For example, fish are capable of metabolizing carcinogenic inorganic arsenic to non-carcinogenic forms (Nriagu, 1994). Various microorganisms are capable of creating organic forms of mercury (e.g., methyl-, ethyl-) from inorganic mercury. The organic mercury forms are more toxic and better absorbed by animals than the inorganic forms (U.S. EPA, 1997).

Some regulatory programs rely heavily on chemical characterization. In SARA/CERCLA, the characterization of a material as a hazardous substance and the reportable quantity depend on metal speciation. For example, reportable quantities for nickel range from 0.454 kg for nickel carbonyl, to 454 kg for nickel hydroxide, to 227 kg for nickel chloride. The RCRA characteristic of toxicity is based on performance in a leaching test that is used to predict the mobility of a metal under specified laboratory conditions.

Thus, at least in theory, EPA needs to have methods, either analytical or mathematical, for evaluating and/or predicting dissolved vs. sorbed metals, oxidation states, solubility, complexation, and chemical form for a group of elements with widely diverse physicochemical and chemical properties.

EPA has identified three types of regulatory risk assessments where information regarding speciation of metals is useful and desirable: national hazard/risk ranking and characterization, site-specific assessments, and National Regulatory Assessments. National hazard or risk ranking assessments are typically used by EPA for broad priority setting. An example of this type of assessment is the Hazard Ranking System (HRS) used to determine the eligibility of a contaminated site for inclusion on the National Priorities List. Site-specific assessments are performed to determine if a site requires remediation and, if so, what the type and extent of remediation should be. A Superfund risk assessment is an example of this type of assessment. The third type, the National Regulatory Assessment, is typically used for standard setting. Development of ambient water quality criteria is an example of this type of assessment. These three examples will be used to illustrate the concepts of metal chemistry developed in this paper.

## **2. METALS OF CONCERN**

Because of their abundance at contaminated sites and potential toxicity to plants or animals, the elements of concern are aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, thallium, vanadium, and zinc. Phillips and Williams (1965) consider all of these elements to be metals, with the exception of arsenic and selenium, which are nonmetals. Webster's New World Dictionary (1970) defines a metal as an element that acts as a cation in chemical reactions, forms a base with the hydroxyl radical, and can replace the hydrogen of an acid to form a salt. Unlike the other elements listed, antimony, arsenic, molybdenum, selenium, and vanadium generally occur as oxyanions in waters and soils, and not as cations. These elements are sometimes described as metalloids. For simplicity, though, the following discussion describes all the elements listed above as metals.

## **3. NATURAL OCCURRENCE OF METALS IN THE ENVIRONMENT**

For reasons that may be unrelated to human activity, many surface and ground waters contain natural concentrations of metals that exceed the EPA drinking water standards (cf. Runnells et al., 1992). Soils can also contain naturally elevated levels of metals (cf. McBride, 1994; Salminen and Tarvainen, 1997). When a regulatory decision is made to restore affected waters or soils to a presumed earlier state, it is obviously unrealistic to assign clean-up goals that are below preexistent metal levels. It is critically important therefore, to attempt to distinguish between metal amounts that were naturally present and amounts added as a result of human activities.

### **3.1 Baseline and Background Metal Concentrations**

It is useful to introduce two concepts at this point. The first is that of geochemical baseline (cf. Salminen and Tarvainen, 1997; Salminen and Gregorauskiene, 2000), which may also be described as ambient concentration. This is the regional metal concentration in a medium, a concentration that has not been further increased by a local source of contamination. Baseline values may have been elevated by regional contamination. For example, arsenic concentrations in soils exceed 9 parts per million (ppm) in a 100-kilometer-wide, 1,000-kilometer-long belt that extends southwest from New York state across Pennsylvania, Ohio, and Kentucky (Gustavsson et al., 2001). There is evidence that these high arsenic values are chiefly derived from the burning of coal (Smith, 2003). An assessment of arsenic contamination of soils by a local source in this area would need to account for the high regional baseline values.

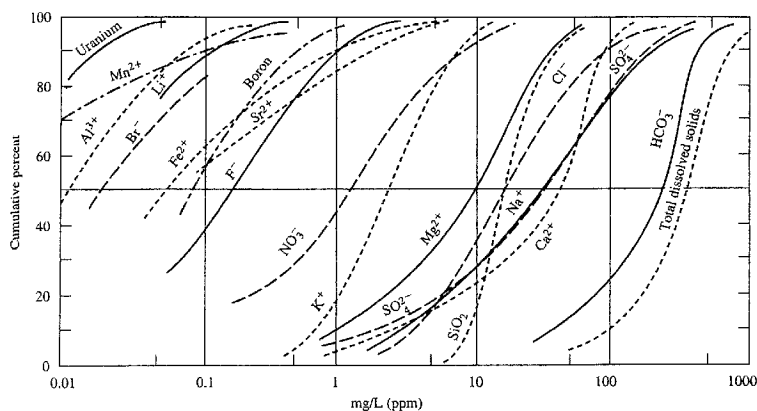
The second concept is that of background, which is the concentration of a metal in a medium as it existed before being affected by human activity. Background concentrations are a function of regional geology and local soil and sediment conditions. The metal background in soils also depends on the depth of the sampling (i.e., location within the soil profile) and whether the analysis is of the total soil or of a specific size fraction (cf. Salminen and Tarvainen, 1997). Metal concentrations are generally higher in the fine-grained fraction of soils than in the coarse

fraction (sand fractions and medium/coarse silt fraction). It is important to note that baseline and background metal concentrations are not single values, but a distribution of values that can range over orders of magnitude over distances of a few centimeters in porous media and meters in surface waters (cf. Gustavsson et al., 2001). It is also important to recognize that background metal concentrations can exceed environmental quality criteria at some sites.

### 3.2 Mean and Median Metal Concentrations

Though metal concentrations in the environment can range widely, it is still useful to consider their mean and median values in waters and soils and the Earth's crust (Table 1). Values for iron and sulfur are included in Table 1 for purposes of comparison and later reference. Data on typical baseline levels of several metals in every state have recently been compiled (Table 2). It is often assumed that species present in water at less than 1 milligram per liter (mg/L) but more than 1 microgram per liter ( $\mu\text{g/L}$ ) are minor species, while those present at below 1  $\mu\text{g/L}$  are termed trace species (Langmuir, 1997a). Based on these definitions, most of the metals of concern are minor species and some are trace species, particularly in surface waters which are in general more dilute than soil or ground waters.

Median groundwater concentrations of metals and major species that exceed 1 mg/L, as per Table 3, do not differ much from the median metal values for ground waters in Table 1, or the averages for major species in Table 4. However, given the wide variability of metal concentrations in waters, soils, and rocks, average and median values can be deceiving. Figure 1 shows a plot of the cumulative percentages of some major, minor, and trace constituents in mostly surface and some ground waters. The data for trace metals, which are most complete for ground waters (see Table 3), show that their concentrations range over 2 to 6–7 orders of magnitude in the case of As, Cd, Cu, and Zn.



**Figure 1. Cumulative percentages showing the frequency distribution of various constituents in potable (chiefly surface) waters. From Davis and DeWiest, 1966.**

Although the data are limited for metals, their concentrations in soils are generally higher than in surface or ground waters, presumably because of concentration in soils by evapotranspiration and because of the relatively high solid to water ratio of soils. In recent years, methods of chemical analysis such as ICP-ES and ICP-MS have been adapted for the determination of metals in soils and soil moisture. These methods have vastly lowered metal detection limits and improved the accuracy of analysis of trace metals at low concentrations. Shown in Table 5 is a chemical analysis of the metals of concern and some major elements in a Swedish Cambisol (Tyler and Olsson, 2001a). The soil has 8% organic matter, 10% clay, and a pH of 5.2. Metal concentrations were determined either by ICP-ES or ICP-MS.

**Table 1. Median or Mean Concentrations of Some Metals and Related Elements in Natural Waters, Soils, and the Earth's Crust**

<b>Metal</b>	<b>Symbol</b>	<b>Ground Waters (mean detects) (U.S. EPA, 2002a)</b>	<b>Ground Waters (mean) (Newcomb and Rimstidt, 2002)</b>	<b>Soils (mean) (Shacklette and Boerngen, 1984)</b>	<b>Earth's Crust (mean) (Fortescue, 1992)</b>
		(µg/L)	(µg/L)	(mg/kg)	(mg/kg)
Aluminum	Al			72,000	83,600
Antimony	Sb	5		0.66	0.2
Arsenic	As	8	13.9	7.2	1.8
Barium	Ba	140	77	580	390
Beryllium	Be	2		0.92	2.0
Cadmium	Cd	1		0.35	0.16
Chromium	Cr	7	4.4	54	122
Cobalt	Co		4.3	9.1	29
Copper	Cu		70.6	25	68
Iron	Fe			26,000	62,200
Lead	Pb		2.6	19	13
Manganese	Mn			550	1,060
Mercury	Hg	2		0.09	0.086
Molybdenum	Mo			0.97	1.2
Nickel	Ni		11.5	19	99
Selenium	Se	5	2.5	0.39	0.050
Silver	Ag		0.5	0.05	0.08
Strontium	Sr			240	384
Sulfur	S				340
Thallium	Tl	6		0.2 <sup>b</sup>	0.72
Vanadium	V		12.5	80	136
Zinc	Zn		265	60	76

<sup>a</sup>U.S. EPA (2002a), occurring as sulfate.

<sup>b</sup>Bowen, 1979.

**Table 2. Mean Baseline Metal Concentrations in Soils (µg/g-dry) by State (from U.S. EPA, 2003a)**

State	Al	As	Ba	Be	Cd	Co	Cr	Cu	Mn	Ni	Pb	Se	V	Zn
Alabama	23100.0	4.7	200.0	0.6		4.4	30.6	9.6	420.0	11.0	9.3	0.3	38.0	26.0
Arkansas	33429.0	9.7	336.0	0.9		12.0	53.1	17.0	731.0	18.0	21.0	0.7	52.0	39.0
Arizona	32933.0	9.6	364.0	1.0	0.4	9.9	37.3	23.0	447.0	23.0	16.0	0.4	42.0	51.0
California	75633.0	5.1	598.0	1.1	0.4	14.0	119.9	39.0	640.0	48.0	26.0	0.2	118.0	113.0
Colorado	61557.0	6.7	662.0	1.4		6.8	41.7	21.0	343.0	13.0	31.0	0.4	74.0	87.0
Connecticut	85000.0	4.1	400.0	0.5		7.5	40.0	15.0	450.0	13.0	5.0	0.8	60.0	40.0
Deleware	22500.0	1.4	400.0	0.5		3.3	30.0	5.0	85.0	6.0	15.0	0.3	20.0	23.0
Florida	9944.0	3.0	48.0	0.6	0.1	1.6	15.4	5.6	86.0	8.5	12.0	0.3	11.0	12.0
Georgia	38250.0	5.0	232.0	0.6		6.9	32.4	21.0	252.0	17.0	19.0	0.4	43.0	47.0
Iowa	64667.0	7.3	617.0	1.3		11.0	64.7	31.0	603.0	26.0	19.0	0.4	97.0	57.0
Idaho	58500.0	6.4	757.0	1.1		12.0	52.1	28.0	580.0	22.0	22.0	0.3	90.0	83.0
Illinois	48714.0	7.1	551.0	0.7		9.8	48.4	24.0	646.0	19.0	39.0	0.5	62.0	67.0
Indiana	50000.0	7.5	500.0	0.7		10.0	46.8	27.0	518.0	18.0	18.0	0.4	74.0	56.0
Kansas	61818.0	6.8	694.0	1.0		8.9	49.0	25.0	452.0	17.0	32.0	0.4	77.0	67.0
Kentucky	54123.0	7.8	349.0	1.1		11.0	79.8	17.0	483.0	23.0	16.0	0.5	66.0	35.0
Louisiana	42188.0	7.6	441.0	0.6		8.6	60.8	33.0	470.0	33.0	16.0	0.7	76.0	55.0
Massachusetts	34083.0	8.6	203.0	1.3	0.2	7.8	39.5	16.0	439.0	13.0	13.0	1.9	87.0	54.0
Maryland	39167.0	3.8	393.0	1.3		7.5	47.9	20.0	291.0	13.0	22.0	0.2	63.0	39.0
Maine	65385.0	9.4	319.0	1.6		10.0	71.2	28.0	581.0	30.0	19.0	0.7	98.0	80.0
Michigan	10964.0	4.2	127.0	0.7	0.9	4.6	13.8	12.0	230.0	12.0	9.2	0.3	44.0	33.0
Minnesota	49457.0	5.5	571.0	0.7	0.3	7.2	25.4	20.0	583.0	14.0	9.9	0.3	72.0	38.0
Missouri	42094.0	10.0	499.0	1.0		12.0	50.0	19.0	940.0	20.0	23.0	0.5	72.0	53.0
Mississippi	45368.0	8.8	390.0	0.9		12.0	53.2	20.0	471.0	21.0	18.0	0.5	68.0	45.0
Montana	70938.0	8.8	739.0	1.1		7.5	63.3	29.0	366.0	20.0	14.0	0.4	101.0	69.0
Nebraska	59474.0	5.5	711.0	1.1		5.9	32.5	15.0	306.0	15.0	16.0	0.4	62.0	54.0
North Carolina	60105.0	4.8	356.0	0.6		15.0	64.8	34.0	563.0	24.0	17.0	0.4	107.0	56.0
North Dakota	62857.0	7.0	682.0	0.9		6.9	53.2	23.0	530.0	20.0	13.0	0.4	83.0	64.0
New Hampshire	66667.0	4.4	500.0	2.3	0.6	5.3	18.4	12.0	633.0	10.0	28.0	0.3	57.0	23.0
New Jersey	10075.0	7.0	54.0	0.3	0.3	1.7	13.9	14.0	221.0	3.8	35.0	0.9	30.0	22.0
New Mexico	54423.0	5.9	727.0	1.0		8.8	55.5	21.0	367.0	28.0	18.0	0.3	72.0	44.0
Nevada	66078.0	9.0	822.0	1.3		8.4	36.8	25.0	481.0	15.0	25.0	0.3	78.0	69.0
New York	58800.0	6.4	666.0	1.4	0.2	9.1	66.9	36.0	418.0	21.0	20.0	0.3	132.0	82.0
Ohio	54615.0	12.0	469.0	1.0		13.0	55.0	28.0	550.0	25.0	23.0	0.6	88.0	69.0
Oklahoma	39200.0	7.0	430.0	1.1		7.1	46.0	16.0	465.0	15.0	18.0	0.3	50.0	50.0
Oregon	94412.0	5.1	682.0	0.9		16.0	121.6	53.0	725.0	23.0	15.0	0.3	168.0	70.0
Pennsylvania	63438.0	13.0	366.0	1.4		15.0	52.8	37.0	609.0	24.0	23.0	0.5	80.0	81.0
Rhode Island	100000	3.5	500.0	0.5		10.0	50.0	15.0	500.0	15.0	15.0	0.9	70.0	30.0
South Carolina	39143.0	3.9	151.0	1.4		3.5	21.4	16.0	87.1	7.8	5.0	0.3	45.0	25.0
South Dakota	74333.0	8.5	1043.0	1.4		7.7	58.7	29.0	1013.0	28.0	16.0	0.5	108.0	75.0
Tennessee	31894.0	16.0	193.0	0.8	0.2	14.0	40.3	17.0	1112.0	18.0	23.0	0.6	49.0	57.0
Texas	41958.0	6.4	404.0	0.9		5.3	39.6	15.0	303.0	12.0	14.0	0.3	52.0	39.0
Utah	45638.0	8.0	493.0	0.9		6.6	45.6	26.0	371.0	13.0	35.0	0.3	70.0	96.0
Virginia	60438.0	5.1	436.0	0.9		9.7	54.3	33.0	441.0	17.0	36.0	0.4	77.0	233.0
Vermont	56667.0	3.6	333.0	1.7		12.0	66.7	18.0	800.0	25.0	20.0	0.4	70.0	43.0
Washington	66834.0	4.5	606.0	0.9	0.8	18.0	49.9	31.0	760.0	23.0	14.0	0.3	160.0	78.0
Wisconsin	48000.0	4.4	543.0	2.0		7.7	40.3	12.0	365.0	14.0	12.0	0.3	48.0	44.0
West Virginia	67000.0	8.6	360.0	1.0		14.0	46.0	22.0	770.0	23.0	17.0	0.5	65.0	60.0
Wyoming	56125.0	6.5	756.0	0.7		8.3	47.9	21.0	416.0	16.0	17.0	0.5	84.0	57.0

**Table 3. Sample Population Distribution Parameter Estimates for Trace Elements Dissolved in Ground Water.** Trace element sample populations are censored at multiple reporting limits.

<b>Element</b>	<b>No. of Records</b>	<b>% Censored</b>	<b>Min.</b>	<b>Max.</b>	<b>Mean</b>	<b>Median</b>
Antimony	1893	94	0.2	44	-	-
Arsenic	7199	53	0.03	42,600	13.9	1.4
Barium	9957	6	1.0	5,000	77	35
Beryllium	5550	94	0.03	10	-	-
Cadmium	7088	90	0.02	19,200	-	-
Chromium	9097	76	0.5	3,800	4.4	1.0
Copper	9582	70	0.1	74,000	70.6	1.1
Lead	9061	76	0.1	2,020	2.6	0.3
Mercury	2031	91	0.02	7.3	-	-
Nickel	8460	70	1.0	10,300	11.5	2.0
Selenium	4674	81	1.0	186	2.5	0.2
Silver	9528	87	0.04	139	0.5	0.2
Thallium	670	90	0.02	60	-	-
Vanadium	4498	80	0.4	19,000	12.5	1.1
Zinc	9464	40	0.09	633,000	265	5.7

This table is based on 104,280 dissolved-fraction ground water concentration records for samples obtained in 1996–1998 from the STORET database (U.S. EPA, 2000). Concentrations are in µg/L.

From Newcomb and Rimstidt, 2002. Robust data analysis techniques (Helsel, 1990; Helsel and Hirsch, 1992) were used to determine central value estimates and variables in sample populations with <90% censored (below detection) data. See discussion in Newcomb and Rimstidt, 2002.



**Table 4. Fe, Al, and Major Constituents (>1 mg/L) or Parameters in Some Surface and Ground Waters**

<b>Constituent or Parameter</b>	<b>Average River, World<sup>a</sup></b>	<b>Average River, N. America<sup>a</sup></b>	<b>Average Ground Water, World<sup>b</sup></b>
Na <sup>+</sup>	6.3	9	30
K <sup>+</sup>	2.3	1.4	3
Mg <sup>2+</sup>	4.1	5	7
Ca <sup>2+</sup>	15	21	50
Fe	0.67	0.16	
Al	0.07		
Cl <sup>-</sup>	7.8	8	20
NO <sub>3</sub> <sup>-</sup>	1	1	
HCO <sub>3</sub> <sup>-</sup>	58.4	68	200
SO <sub>4</sub> <sup>2-</sup>	11.2	20	30
SiO <sub>2</sub> (aq)	13.1	9	16
pH			7.4
TDS	120	142	350

<sup>a</sup>Livingstone, 1963.

<sup>b</sup>Turekian, 1977.

**Table 5. Metals in an Acid Cambisol (10% Clay) Formed on a Mixed Shale-Gneiss Moraine in Southern Sweden: Metal Concentrations in Dried Soil and in Soil Solution (pH = 5.2)**

	<b>Dried Soil (µg/kg)</b>	<b>Soil Solution (µg/L)</b>
<b>Ag</b>	0.88	0.1
<b>Al</b>	75,500	297
<b>As</b>	65.9	3.2
<b>Ba</b>	646	132
<b>Be</b>	3	0.025
<b>Cd</b>	0.72	0.36
<b>Co</b>	7.72	0.4
<b>Cr</b>	66	1.3
<b>Cu</b>	142	59
<b>Hg</b>	0.16	0.13
<b>Mn</b>	231	66
<b>Mo</b>	93.1	5.7
<b>Ni</b>	11.4	11
<b>Pb</b>	43.9	2.4
<b>Sb</b>	0.4	0.86

	<b>Dried Soil (µg/kg)</b>	<b>Soil Solution</b>	
		<b>µg/L</b>	<b>mg/L</b>
<b>Se</b>	1.74	1.7	
<b>Sr</b>	73.6	77	
<b>Tl</b>	3.9	0.15	
<b>V</b>	815	7.2	
<b>Zn</b>	63	90	
<b>Ca</b>	1,620	27,300	27
<b>Fe</b>	50,800	280	0.28
<b>K</b>	25,000	6,800	6.8
<b>Mg</b>	2,750	2,170	2.2
<b>Na</b>	170	4,550	4.6
<b>P</b>	527	119	0.12
<b>S</b>	4,938	23,900	23.9
<b>C (org)</b>	80,000		45

From Tyler and Olsson, 2001b.

**Table 6. U.S. Environmental Protection Agency (2002b) Drinking Water Standards for Select Inorganic Species in Community Water Supplies**

Contaminant	MCL(µg/L)	Note	Contaminant	SMCL ( µg/L)	Note
Antimony	6	a	Aluminum	50 to 200	a
Arsenic	10	a	Iron	300	a
Barium	2,000	a	Manganese	50	a
Beryllium	4	a	Silver	100	a
Cadmium	5	a	Copper	1,000	a
Copper	1,300	b	Uranium	30	a
Chromium	100	a	Zinc	5,000	a
Lead	15	b			
Mercury	2	a			
Nickel	100	a			
Selenium	50	a			
Thallium	2	a			

Maximum contaminant levels (MCLs) are enforceable standards for substances that may constitute a health hazard at higher concentrations. Secondary maximum contaminant levels (SMCLs) are not enforceable, but are set for aesthetic reasons, to avoid tastes, odors, and staining of plumbing fixtures.

<sup>a</sup>Current standard.

<sup>b</sup>Treatment triggered at 1.3 mg/L Cu and 0.015 mg/L Pb.

It is instructive to compare EPA drinking water standards for inorganic species in water supplies (Table 6) to the average concentrations of the same species in ground waters (Table 3). The comparison shows that the median concentration of As is 14 percent of the standard. This suggests that a large percentage of background waters will have natural concentrations of As that exceed drinking water standards.

### 3.3 General Sources of Metals Data and Maps

The U.S. Environmental Protection Agency, the U.S. Geological Survey of the Department of Interior, and the Department of Energy have all compiled extensive databases of chemical analyses of various environmental media that are readily available on CD-ROM or for downloading from the World Wide Web. EPA's STORET (STOrage and RETrieval) data

system, which can be accessed at <http://www.epa.gov/storet/>, contains 200 million water sample observations from about 700,000 sampling sites for both surface and ground waters. Reported data include stream flow information and measured concentrations for most of the metals of concern. There is no requirement that the data in STORET be evaluated using quality assurance procedures, however. For the data from STORET, or from the other sources listed below, it is important that prospective users be aware that such data may or may not have been screened for accuracy. Because of the potential for sample contamination and sampling/analysis artifact, trace metal concentration data could be unreliable—in particular those data collected before the late 1980s, since the necessity for using “trace metal clean techniques” had not been recognized by that time.

The U.S. Geological Survey Water Web site (<http://waterdata.usgs.gov/nwis>) provides access to chemical and physical records for 1.5 million sampling sites in all 50 states, the District of Columbia, and Puerto Rico as part of the National Water Quality Assessment Program (NAWQA). A stated goal of NAWQA is “to describe the status and trends in the quality of a large representative part of the Nation’s surface and ground-water resources and to identify the natural and human factors that affect their quality.” Available through the Web site are chemical analyses and physical data for streams, stream sediments, lakes, springs, and wells that include their metals concentrations. A map of arsenic in 31,350 samples of ground water in the contiguous United States based on Welch et al. (2000) is featured on the Web site. As part of the NAWQA program, Rice (1999) reported on the concentrations of As, Cd, Cr, Cu, Pb, Hg, Ni, Se, and Zn in 541 streambed samples obtained from across the conterminous United States. In the analysis she takes into account background and baseline metal concentrations.

The USGS also maintains the National Geochemical Data Base (NGDB), which contains more than 2 million data records for samples of stream sediment, soil, rocks, water, and vegetation. This database is also accessible via the Web. The NGDB includes approximately 260,000 sediment and soil samples collected by the U.S. DOE in the 1970s and 1980s as part of the National Uranium Resource Evaluation (NURE) program. Most of the soil, sediment, and rock samples from which the NGDB was generated are held in archival storage and are available for further study. Data in the NGDB are available on CD-ROM, and can be used to generate metal concentration maps, so as to help determine metal baseline and background concentrations and contamination levels. The Geological Survey also maintains the PLUTO.RASS database, which lists geochemical data for about 500,000 samples—chiefly rocks, but also stream sediments, soils, heavy-mineral concentrates, waters, and vegetation.

A number of national surveys of metals concentrations in soils have been published. The most famous and still useful was that of Boerngen and Shacklette (1981) and Shacklette and Boerngen (1984), which involved collecting soil and other regolith samples from 1,323 sites in the conterminous United States. Samples were obtained at a depth of 20 centimeters from untilled, naturally vegetated soils away from roads in the period 1961–1975. The results of Shacklette and Boerngen have been reviewed and statistically assessed by Gustavsson et al. (2001), who present colored national maps for Al, As, Ba, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, V, and Zn among other metals. Metals in soils results from the U.S. study of Shacklette and

Boerngen (1984) are included in an assessment of metals and other elements in soils worldwide in a report by Darnley et al. (1995).

Detailed soil survey maps are available from the offices of the USDA/ARS Natural Resources Conservation Service (formerly the U.S. Soil Conservation Service). These generally include areal maps that show soil types and classifications by county, along with the pH and organic matter contents of typical soil types. The soil surveys also describe soil associations and soil-forming processes for the soils within specific areas.

### **3.4 National and Regional Metals Problem Areas**

The previous section cites a number of published and Web-accessible sources of metals data for streams, ground waters, and soils. Of particular value to anyone identifying and prioritizing metal problems regionally or nationally are maps on which metals data for soils, sediments, and waters have been plotted and the metals concentrations contoured. Such maps have been published for soils, although they are based on limited data (see Gustavsson et al., 2001), but are less available for surface and ground waters. Welch et al. (2000) have published a map of arsenic in U.S. ground waters, and discuss geologic and climatic (e.g., evapotranspiration) controls on elevated arsenic values. David B. Smith of the U.S. Geological Survey maintains a national database of metals data for stream sediments and has colored regional maps of such data for Al, As, Ba, Be, Co, Cr, Cu, Mn, Hg, Ni, Pb, Se, Sr, V, and Zn for a large part of the U.S. (See <http://water.usgs.gov/osw/techniques/workshop/smith.html>.)

Dissolved metals in lower order streams, which are often fed by ground water, can be expected to correlate with local geology. The chemical compositions of river waters are the results of rainfall, rock-weathering reactions, and evaporation-crystallization (cf. Langmuir, 1997a). The relative contribution of climate-related factors will be more important for major rivers.

A comparison of maps for the metals with a geologic map of the United States often shows a correlation between local or regional geologic formations and metal levels in soils and ground waters. The correlations are most obvious in areas away from major urban and industrial centers, which have contributed important metal amounts to the environment through their waste disposal and land use practices. Colored national and state geological maps are available in digital form on the Web at <http://pubs.usgs.gov/dds/dds11/> and <http://nationalatlas.gov/geologym.html>.

Broad-scale soil survey data for the contiguous United States are available in the State Soil Geographic (STATSGO) database (cf. Schwarz and Alexander, 1995). Shirazi et al. (2001) developed mathematical models relating the soil characteristics of soil map units from the STATSGO to predict water quality parameters. They found that with statistical information on soil particle size distribution, they could estimate soil, lake, and stream water quality parameters including acid neutralizing capacity, pH, dissolved organic carbon, nitrate, and turbidity.

Because such water quality parameters importantly influence the concentrations and mobility of the metals of concern, such soil information can be used to predict metal behavior.

### **3.5 Local Sources of Metals Data**

In studies of localized environmental contamination by metals (e.g., as associated with a Superfund Site cleanup), it is especially important to define background and baseline metals concentrations, which will in some cases exceed health standards for aquatic life and drinking water. If data and maps describing metal concentrations at a site prior to its contamination are not available, the preferred approach is to take water, soil, sediment, rock, or plant samples from a nearby area with similar characteristics, but that is unaffected by contamination as a measure of background (cf. Banks et al., 1995; Lahermo et al., 1995; Miller and McHugh, 1999). In populated and urbanized or extensively mined areas, however, it may be difficult to locate a sample that has not been contaminated. All that may be available are baseline values. A second approach to determine background for waters is to assume that background water quality is the same as that measured in similar streams or well waters in similar topographic, climatic, and geological settings. Lacking this information for ground waters, White et al. (1963) have summarized typical ground water compositions from different rock types that may be useful.

Perhaps the most defensible way to distinguish background or baseline concentrations and more elevated metal values in the waters of a given area is to use statistical analysis. Cumulative probability plots can be drawn onto which all of the concentration data for a metal are plotted (Levinson et al., 1987; Fleischhauer and Korte, 1990). Such plots may allow the classification of samples into a background or baseline group and one or more contaminated groups, with an estimate of the median and standard deviation for each group. Such a plot for Cd in ground waters of Front Range of Colorado is shown in Figure 2 (Langmuir and Klusman, 1997).

## **4. METAL SPECIATION: METAL COMPLEXES**

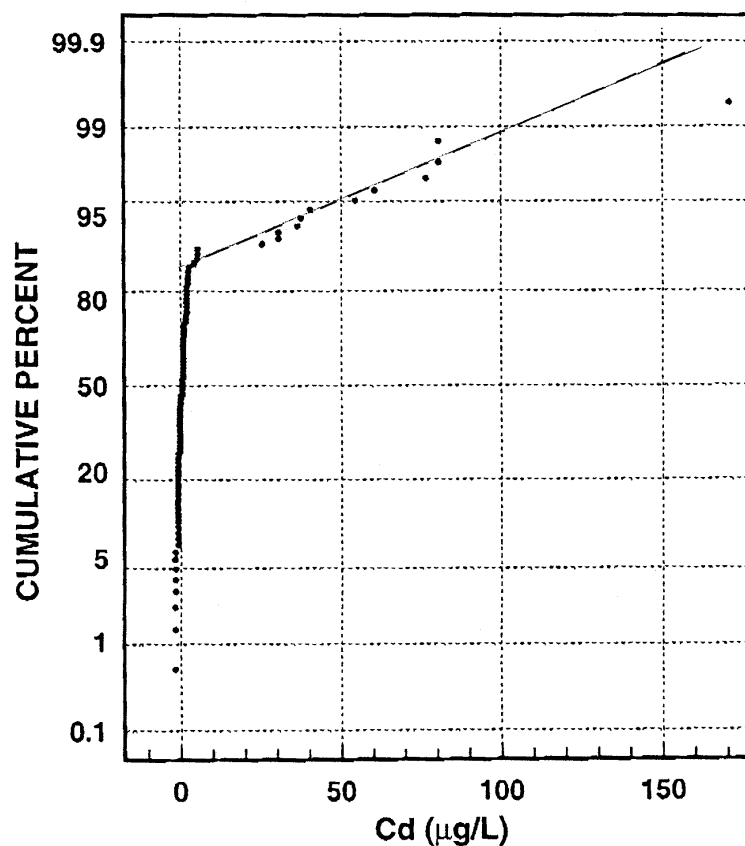
Chemical analytical laboratories generally determine and report total metal concentrations. However, in recent years it has become increasingly apparent that metal toxicity is a function of the concentrations of specific metal species, not of the total metal (cf. Stumm and Morgan, 1996; Langmuir, 1997a). In fact, toxicity was often found to be best predicted by the free metal ion activity (Morel and Herring, 1993). In natural waters, its concentration, or those of other metal species, can sometimes be measured directly, although often with difficulty. Alternatively, given the appropriate solution analysis and thermodynamic database, the concentrations of individual species can be computed using a geochemical equilibrium modeling program such as MINTEQA2 (U.S. EPA, 1991) or PHREEQC (Parkhurst and Appelo, 1999). Errors in the thermodynamic database of the earlier versions of MINTEQA2 (Serkiz et al., 1996) have been corrected in version 4.0 (1999). Unfortunately, MINTEQA2 is a DOS-based program and cannot be used on computers with Windows operating systems more recent than Windows 98. However, a Windows version of MINTEQA2 version 4.0 (1999), a program called Visual

MINTEQ (VMINTEQ, version 2.30; Gustafson, 2004), is available and may be downloaded free of charge from the Web.

However, PHREEQ and MINTEQA2 are not suitable for predicting metal complexation by natural organic matter. The presence of several potential complexation sites with different affinities and electrostatic interactions will affect metal complexation by humic substances, which are the main components of natural organic matter. The PHREEQC model approximates complexation by natural organic matter by using two generalized complexation constants for fulvate and humate. MINTEQA2, version 4.0, allows the use of a competitive Gaussian model to estimate the complexation of metals by natural organic matter, but the database provided is not adequate (Allison and Perdue, 1994).

More elaborate databases and models have also been developed to account for multiple binding sites on humic substances and electrostatic interactions. For example, the Windermere Humic Aqueous model (WHAM) is based on an extensive literature review and applies the humic ion-binding model VI (Tipping, 1994, 1998), in which discrete sites with a range of affinities as well as bidentate complexation sites are considered. Another example of such models is the non-ideal competitive adsorption (NICA)–Donnan model (Kinniburgh et al., 1996), which is included in the chemical speciation and transport program ECOSAT (Keizer and van Riemsdijk, 1994). The model uses the NICA to model specific binding to humic substances and the Donnan electrostatic model to consider non-specific binding.

In all cases, the capacity of geochemical equilibrium models to predict metal speciation in waters containing natural organic matter is limited and has not yet been validated in the field. The development and calibration of both models are based on laboratory titrations of isolated natural organic matter; very few studies are available to validate their use for natural waters. Even with more elaborated models, only the humic substances fraction of natural organic matter is considered in terms of complexation. In fact, input parameters for these models are the humic and fulvic acid concentrations, while the dissolved organic carbon pool is generally not characterized. For some natural waters, however, other organic ligands with higher affinities might be more important ligands than humic substances (Xue and Sigg, 1999).



**Figure 2. Cumulative percent plot of cadmium concentrations in Colorado Front Range ground waters.** Cd concentrations in the  $10^1$ – $10^2$  µg/L range are anomalously elevated. Concentrations below 10 µg/L are presumably background values. The linear trend of higher values can be derived from contamination. From Langmuir and Klusman, 1997.

#### 4.1 Metal Complexes: Concepts and Importance

Dissolved species in water can be described as free ions or aquo-complexes, or simply complexes. A complex is a dissolved species that exists because of the association of a cation with an anion or neutral molecule (Langmuir, 1997a). A ligand is an anion or neutral molecule that can combine with a cation to form a complex. The total analytical concentration of a given metal in water is the sum of the concentrations of its free ion and complexes and any metal associated with suspended solids, whether organic or mineral. For example, the total molal concentration of lead,  $\Sigma\text{Pb}$ , in a natural water might equal:

$$\Sigma\text{Pb} = m\text{Pb}^{2+} + m\text{PbOH}^+ + m\text{PbCO}_3^0 + m\text{PbHCO}_3^+ + m\text{PbSO}_4^0 + m\text{Pb}(\text{suspended solids}) \quad (1)$$

In most natural waters the concentration of free lead ion,  $m\text{Pb}^{2+}$ , is less than the sum of the concentrations of its complexes, which in this case are lead complexes with hydroxyl,



carbonate, bicarbonate, and sulfate ions. Other metals that are found in natural waters most often as complexes and not as free ions include  $\text{Al}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Hg}^{2+}$ . As, Se, Cr, Mo, Sb, and V occur most often in aerobic waters and soils not as cations but covalently bonded to oxygen in oxyanions that under oxidizing conditions include arsenate, selenate, chromate, molybdate, and vanadate, which themselves are complexes. Important chemical species (including metal complexes common in soils and waters at intermediate pH values) are listed in Table 7.

Complexes that incorporate metals play a major role in controlling the availability and fate of metals in the environment. Increasing the fraction of a metal that is complexed increases the solubility of minerals of that metal (Langmuir, 1997a). For example, the solubility of lead sulfate is related to the molal concentrations of free lead and sulfate ions, through the expression:

$$K_{\text{sp}} = [(\gamma_{\text{Pb}} \cdot m_{\text{Pb}^{2+}})(\gamma_{\text{SO}_4} \cdot m_{\text{SO}_4^{2-}})] \quad (2)$$

where the terms  $\gamma_{\text{Pb}}$  and  $\gamma_{\text{SO}_4}$  are the activity coefficients of the ions.<sup>2</sup> The product of the ion activity coefficient and molal concentration of each species equals the activity of the ion. Equation 2 shows that the activity of free lead ion controls the solubility of lead sulfate. For a given total lead concentration (Equation 1), the more of the lead that is complexed, the lower will be the concentration of free lead ion. This means that as the extent of lead complexing increases, the total lead concentration must also increase in order to reach saturation with lead sulfate. In other words, metal complexing increases total metal solubility.

Metal complexing also has a direct influence on metal adsorption to organic matter or mineral surfaces. For example, metal carbonate, sulfate, and fluoride complexes are usually poorly adsorbed, whereas metal hydroxide complexes are strongly adsorbed (Langmuir, 1997a). In summary, metal complexing generally increases the solubility and mobility of metals in surface and ground waters.

#### 4.2 Hard and Soft Acids and Bases: The Stability of Complexes and Metal Toxicity

Complexes are formed between metals (acids) and ligands (bases) both in solution and at the surfaces of minerals and of organisms. Toxic reaction of organisms to metals can be directly related to the nature of the metal complexes formed in solution and at the surface of the organism.

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<sup>2</sup> By definition, the product of the activity coefficient and the molal (or molar) concentration for an ion,  $i$ , is equal to the activity ( $a_i$ ) of that ion. That is:  $a_i = \gamma_i \cdot m_i$ . Activity coefficients of ions are generally less than one in fresh waters, and decrease with increasing salinity or ionic strength (cf. Stumm and Morgan, 1996; Langmuir, 1997a). The activity of an ion can be considered its effective concentration in water.

**Table 7. Dominant Chemical Species of Metals in Soils and Natural Waters, Not Considering Most (Especially Weak) Metal Complexing**

Metal	Soils	Waters	Best Predictor of Metal Toxicity
Ag	$\text{Ag}^+$	$\text{Ag}^+$ , $\text{AgCl}$	$\text{Ag}^+$
As	$\text{AsO}_4^{3-}$	$\text{AsO}_4^{3-}$ , $\text{AsO}_3^{3-}$	$\text{AsO}_3^{3-}$
Ba	$\text{Ba}^{2+}$	$\text{Ba}^{2+}$	$\text{Ba}^{2+}$
Be	$\text{Be}^{2+}$ , $\text{Be}_x\text{O}_y^{2x-2y}$	$\text{Be}^{2+}$	$\text{Be}^{2+}$
Cd	$\text{Cd}^{2+}$	$\text{Cd}^{2+}$	$\text{Cd}^{2+}$
Co	$\text{Co}^{2+}$	$\text{Co}^{2+}$	$\text{Co}^{2+}$
Cr	$\text{Cr}^{3+}$	$\text{CrO}_4^{2-}$ , $\text{Cr}^{3+}$	$\text{CrO}_4^{2-}$
Cu <sup>a</sup>	$\text{Cu}^{2+}$ , $\text{Cu-OM}^b$	$\text{Cu}^{2+}$ , -fulvate	$\text{Cu}^{2+}$
Hg	$\text{Hg}^{2+}$ , $\text{CH}_3\text{Hg}$	$\text{Hg}(\text{OH})_2^0$ , $\text{HgCl}_2^0$	$\text{CH}_3\text{Hg}$
Mn	$\text{Mn}^{4+}$ , $\text{Mn}^{2+}$	$\text{Mn}^{2+}$	$\text{Mn}^{2+}$
Mo	$\text{MoO}_4^{2-}$	$\text{MoO}_4^{2-}$	$\text{MoO}_4^{2-}$
Ni	$\text{Ni}^{2+}$	$\text{Ni}^{2+}$	$\text{Ni}^{2+}$
Pb	$\text{Pb}^{2+}$	$\text{Pb}(\text{OH})^+$	$\text{Pb}^{2+}$
Sb	$\text{Sb}_{\text{III}}\text{O}_x?$	$\text{Sb}(\text{OH})_6^-$	?
Se	$\text{SeO}_4^{2-}$ , $\text{HSeO}_3$	$\text{SeO}_4^{2-}$	$\text{SeO}_4^{2-}$
V	$\text{V}_{\text{IV}}\text{O}_x?$	$\text{HVO}_4^{2-}$	?
Zn	$\text{Zn}^{2+}$	$\text{Zn}^{2+}$	$\text{Zn}^{2+}$

Modified after Logan and Traina, 1993.

<sup>a</sup>Typically, much or most of Cu in soils is complexed with organic matter.

<sup>b</sup>Cu-OM denotes copper complexed with organic matter.

A useful definition that helps to explain the strength of metal complexing and metal toxicity is that of hard and soft acids and bases (Pearson, 1973). In this definition, cations are Lewis acids and ligands Lewis bases, with the metal cation and ligand in a complex acting as electron acceptor and donor, respectively. Soft implies that the species' electron cloud is deformable or polarizable with the electrons mobile and easily moved. Such species prefer to participate in covalent bonding. Hard species are comparatively rigid and nondeformable, have low polarizability, hold their electrons firmly, and prefer to participate in ionic bonds in complex formation (Langmuir, 1997a). Hard acids form strong, chiefly ionic bonds with hard bases, whereas soft acids and soft bases form strong, chiefly covalent bonds when they form complexes. In contrast, the bonds formed between hard-soft or soft-hard acids and bases are weak, such that their complexes tend to be rare. Table 8 summarizes hard and soft acid and base relationships for the metals of concern. Its footnotes summarize the applicability of hard and soft concepts to the formation of metal complexes.

**Table 8. Hard and Soft Acids (Cations) and Bases (Ligands)**

Hard acids	$\text{Al}^{3+}$ , $\text{Ba}^{2+}$ , $\text{Be}^{2+}$ , $\text{Co}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Mn}^{2+}$ , $\text{Sr}^{2+}$ , $\text{U}^{4+}$ , $\text{UO}_2^{2+}$ , $\text{VO}^{2+}$
Borderline acids (between hard and soft)	$\text{Co}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Fe}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Zn}^{2+}$
Soft acids	$\text{Ag}^+$ , $\text{Cd}^{2+}$ , $\text{Cu}^+$ , $\text{Hg}^{2+}$ , $\text{Hg}^+$ , $\text{CH}_3\text{Hg}^+$ , $\text{Ti}^{3+}$ , $\text{Ti}^+$
Hard bases	$\text{F}^-$ , $\text{H}_2\text{O}$ , oxyanions: $\text{OH}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ , $\text{HCO}_3^-$ , $\text{C}_2\text{O}_4^{2-}$ , $\text{CrO}_4^{2-}$ , $\text{MoO}_4^{2-}$ , $\text{H}_2\text{PO}_4^{n-3}$ , $\text{H}_2\text{AsO}_4^{n-3}$ , $\text{SeO}_4^{2-}$ , $\text{H}_2\text{VO}_4^-$ , $\text{NH}_3$ , $\text{RNH}_2$ , $\text{N}_2\text{H}_4$ , $\text{ROH}$ , $\text{RO}^-$ , $\text{R}_2\text{O}$ , $\text{CH}_3\text{COO}^-$ , etc.
Borderline bases (between hard and soft)	$\text{Cl}^-$ , $\text{Br}^-$ , $\text{NO}_2^-$ , $\text{SO}_3^{2-}$ , $\text{H}_2\text{AsO}_3^{n-3}$ , $\text{C}_6\text{H}_5\text{NH}_2$ , $\text{C}_5\text{H}_5\text{N}$ , $\text{N}_3^-$ , $\text{N}_2$
Soft bases	$\text{I}^-$ , $\text{HS}^-$ , $\text{S}^{2-}$ , $\text{CN}^-$ , $\text{SCN}^-$ , $\text{Se}^{2-}$ , $\text{S}_2\text{O}_3^{2-}$ , $-\text{SH}$ , $-\text{SCH}_3$ , $-\text{NH}_2$ , $\text{R}^-$ , $\text{C}_2\text{H}_4$ , $\text{C}_6\text{H}_6$ , $\text{RNC}$ , $\text{CO}$ , $\text{R}_3\text{P}$ , $(\text{RO})_3\text{P}$ , $\text{R}_3\text{As}$ , $\text{R}_2\text{S}$ , $\text{RSH}$ , $\text{RS}^-$

Modified after Huheey et al., 1993, and Langmuir, 1997a. "R" refers to an organic molecule.

**Hard acids and hard bases.** Complexes formed between divalent hard acid cations and monovalent or divalent hard bases are ionic and relatively weak, and are often termed "ion pairs." Complexes formed between  $\text{Be}^{2+}$  or trivalent hard acids, and hard bases tend to be ionic and relatively strong.

**Soft acids and soft bases.** Strong, relatively covalent bonds are formed in complexes between soft and borderline soft acid cations and soft bases. Ligand binding sites on the external or internal surfaces of organisms are often of soft base character, and so bond strongly with soft and borderline soft acid cations.

The Lewis acids in natural waters include  $H^+$  and metabolically essential metal cations such as  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ , and the toxic metal species  $Hg^{2+}$ ,  $CH_3Hg^+$ ,  $Pb^{2+}$ , and  $Cd^{2+}$ , which are soft acids. These species, along with the soft acid thallium (Tl) and the essential protein and enzyme metals  $Fe^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$  and  $Zn^{2+}$ , which are borderline soft, form strong bonds with soft base sulfur species. The ligands at the surfaces of biota are chiefly sulfur, nitrogen and oxygen electron donor groups, and also include the solute bases  $HCO_3^-$ ,  $HPO_4^{2-}$ , and  $OH^-$  (Stumm and Morgan, 1996).

Although the hard acid metals Ca, Mg, and Na bond weakly with soft base sites on the surfaces of biota, their concentrations in most waters are typically  $10^3$  times greater than those of the trace metals, so that they often effectively compete with trace metals such as  $Zn^{2+}$  and  $Cd^{2+}$  for surface bonding sites. However, when metal adsorption is by organic matter, metals such as  $Cu^{2+}$  in particular may be strongly adsorbed, practically independent of concentrations of the major metals (cf. Lu and Allen, 2002).

The proton is the most effective competitor of all with adsorbed metals. The proton can displace essential and trace metals from surface sites at pH values as high as 6. The role of pH as a fundamental control on metal concentrations and metal transport is discussed extensively below.

Mechanisms by which toxic metals poison plants and animals relate to their tendency to form strong complexes with the generally soft functional groups on biomolecules (cf. Sposito, 1989; Morel and Herring, 1993). Sposito (1989) proposes several processes by which soft-metal cations cause phytotoxicity. First, a soft metal such as Cd can displace an essential metal such as Ca bound to a bioligand. Also, complexation of a bioligand by a soft-metal cation can block that ligand from reacting normally or modify it structurally and thus interfere with its intended activity. Enzymes have active or catalytic sites with which they bind to biological substrates and that facilitate enzyme function. These sites are especially vulnerable to damage by soft-metal cations. The amino acids cysteine and methionine present at the active sites in some enzymes contain  $-SH$  and  $SCH_3$  groups (Manahan, 1994). These sulfur-containing groups are soft ligands and form strong covalent bonds with soft-metal cations such as Hg, Ag, Cd, Cu, and Pb. Such bond formation can result in the breakdown of normal enzyme function and a toxic reaction by the affected organism.

#### **4.3 Predominant Inorganic Species in Fresh Waters**

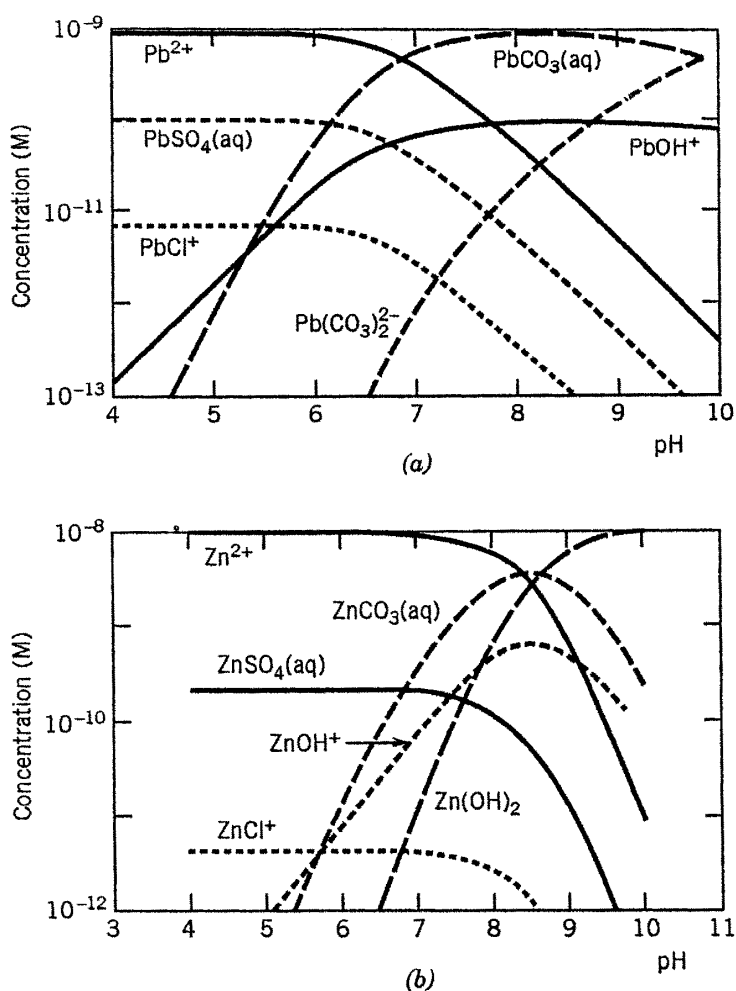
It is instructive to compute the distribution of dissolved metal species including their complexes in a typical natural water. Such computations are readily accomplished using a geochemical computer code such as MINTEQA2 (U.S. EPA, 1991). Stumm and Morgan (1996) discuss such a calculation for an oxygenated fresh water with a pH of 8.0 that has the following total concentrations:  $Na = 5.7$  mg/L,  $Mg = 73$  mg/L,  $Ca = 40$  mg/L,  $Cl = 8.9$  mg/L,  $SO_4 = 29$  mg/L, and  $HCO_3^- = 122$  mg/L. Aqueous speciation for the metals of concern is given in Table 9. Also shown is the percentage of the metal present as the free ion, which in most cases is the

percentage of the total metal present in toxic form. Note that at pH 8, Al, Be, Cu, Fe(III), Hg, Ni, Pb, Tl, and Zn are chiefly present as complexes. In contrast, it was recently suggested that metal-sulfide complexes could dominate the speciation of some soft acid metals such as Ag and Cu, given that such inorganic complexes are stable in oxic waters (e.g., Rozan et al., 2000).

The anionic species of As, Cr, Mo, Se, and V generally form weak complexes with monovalent or divalent cations, but may be precipitated as minerals by high concentrations of dissolved Fe(III) and Al(III), which are generally present only in acid systems.

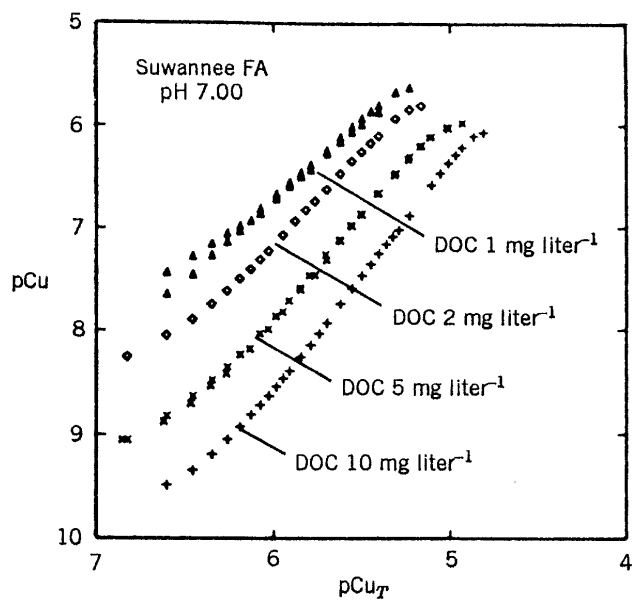
#### **4.4 Effect of pH on Metal Complexing**

In natural waters, sulfate, phosphate, and fluoride tend to be important in acid waters (c.f. Langmuir, 1997a), whereas carbonate and hydroxide complexes become increasingly important at pH values above 6–8. This is evident from Figure 3, which shows the concentrations of species of Pb and Zn as a function of pH, as computed with a geochemical model for the same concentrations used to derive Table 9. Total lead and zinc concentrations assumed for these figures are  $10^{-9}$  M (0.2  $\mu\text{g/L}$ ) for lead and  $10^{-8}$  M (0.65  $\mu\text{g/L}$ ) for zinc. As the salinity and thus chloride content of water increases, the borderline soft chloride ion forms important complexes with the soft and borderline soft metal cations  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ .

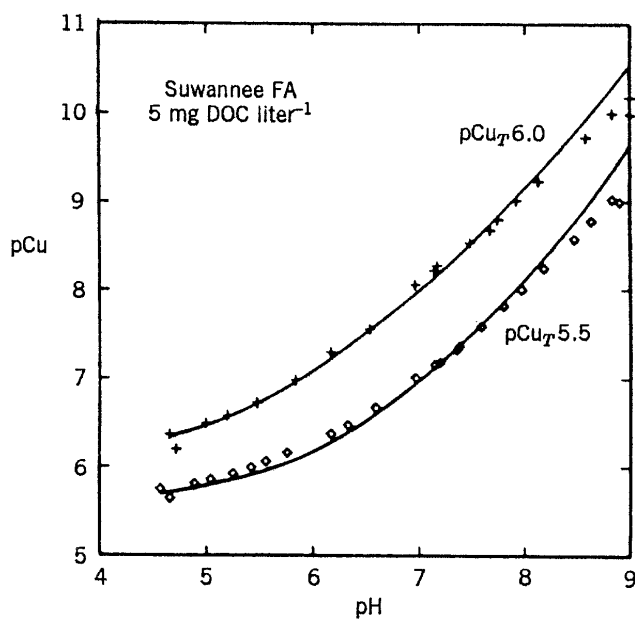


**Figure 3. Speciation of Pb(II) ( $10^{-9}$  M) and Zn(II) ( $10^{-8}$  M) under freshwater conditions.** Total carbonate equals  $2 \times 10^{-3}$  M. Figure is computed. From Stumm and Morgan, 1996.

Several milligrams of dissolved organic carbon (DOC) per liter of soil solution is common in humid climate soils. The DOC is composed of humic substances, which include humic and fulvic acids. These acids form metal complexes under the same pH conditions that favor metal carbonate and hydroxide complexes (Stumm and Morgan, 1996). Metal bonding is with carboxylic and phenolic hydroxyl groups of the acid anions. Recent work has also highlighted the importance of sulfide-thiolate groups as high-affinity binding sites for soft acid metals (e.g., Smith et al. 2002). Shown in Figure 4 is the effect of increasing pH and total copper on the extent of copper-fulvic complexing. Free  $Cu^{2+}$  ion concentrations can be seen to decrease with increasing DOC and increasing pH in the presence of Suwannee River fulvic acid. Increasing DOC should thus reduce the toxicity of a given concentration of dissolved  $Cu^{2+}$  or other toxic metal that forms fulvic acid complexes.



(a)



(b)

**Figure 4. Titrations of fulvic acid (FA) and copper.** (a) shows dissolved  $Cu^{2+}$  ion concentration as  $pCu$  ( $-\log Cu$  [mol/L]), plotted as a function of total copper ( $[Cu]_T$ ) for different fulvic concentrations at pH 7. (b) shows  $pCu$  as a function of pH for two total copper concentrations. From Cabaniss and Shuman, 1988.

**Table 9. Major Inorganic Species in a Hypothetical Natural Water (see text)**

Condition	Metal/Element	Major Species	Percent as Free Metal Cation
Oxyanions	As(V)	$\text{HAsO}_4^{2-}$	
	Cr(VI)	$\text{CrO}_4^{2-}$	
	Mo(VI)	$\text{MoO}_4^{2-}$	
	Se(VI)	$\text{SeO}_4^{2-}$	
	V(V)	$\text{HVO}_4^{2-}, \text{H}_2\text{VO}_4^-$	
Predominantly free aquo-ions	Na <sup>+</sup>	Na <sup>+</sup>	100
	K <sup>+</sup>	K <sup>+</sup>	100
	Mg <sup>2+</sup>	Mg <sup>2+</sup>	94
	Ca <sup>2+</sup>	Ca <sup>2+</sup>	94
	Sr <sup>2+</sup>	Sr <sup>2+</sup>	94
	Ba <sup>2+</sup>	Ba <sup>2+</sup>	95
Complexed with OH <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup>	Ag(I)	Ag <sup>+</sup> , AgCl <sup>0</sup>	60
	Al(III)	Al(OH) <sub>3</sub> (s), Al(OH) <sub>2</sub> <sup>+</sup> , Al(OH) <sub>4</sub> <sup>-</sup>	1 x 10 <sup>-7</sup>
	Be(II)	BeOH <sup>+</sup> , Be(OH) <sub>2</sub> <sup>0</sup>	0.15
	Cd(II)	Cd <sup>2+</sup> , CdCO <sub>3</sub> <sup>0</sup>	50
	Co(II)	Co <sup>2+</sup> , CoCO <sub>3</sub> <sup>0</sup>	50
	Cu(II)	CuCO <sub>3</sub> <sup>0</sup> , Cu(OH) <sub>2</sub> <sup>0</sup>	2
	Fe(III)	Fe(OH) <sub>3</sub> (s), Fe(OH) <sub>2</sub> <sup>+</sup> , Fe(OH) <sub>4</sub> <sup>-</sup>	2 x 10 <sup>-9</sup>
	Hg(II)	Hg(OH) <sub>2</sub> <sup>0</sup>	1 x 10 <sup>-8</sup>
	Mn(IV)	MnO <sub>2</sub> (s)	
	Ni(II)	Ni <sup>2+</sup> , NiCO <sub>3</sub> <sup>0</sup>	40
	Pb(II)	PbCO <sub>3</sub> <sup>0</sup>	5
	Tl(I), Tl(III) <sup>a</sup>	Tl <sup>+</sup> , Tl(OH) <sub>3</sub> , Tl(OH) <sub>4</sub> <sup>-</sup>	2 x 10 <sup>-19</sup>
	Zn(II)	Zn <sup>2+</sup> , ZnCO <sub>3</sub> <sup>0</sup>	40

The right-hand column is the percent of the total metal concentration present as the free metal cation. Based on Stumm and Morgan (1996).

<sup>a</sup>Redox state of Tl(I) under natural conditions is uncertain; ratio is for Tl(III).



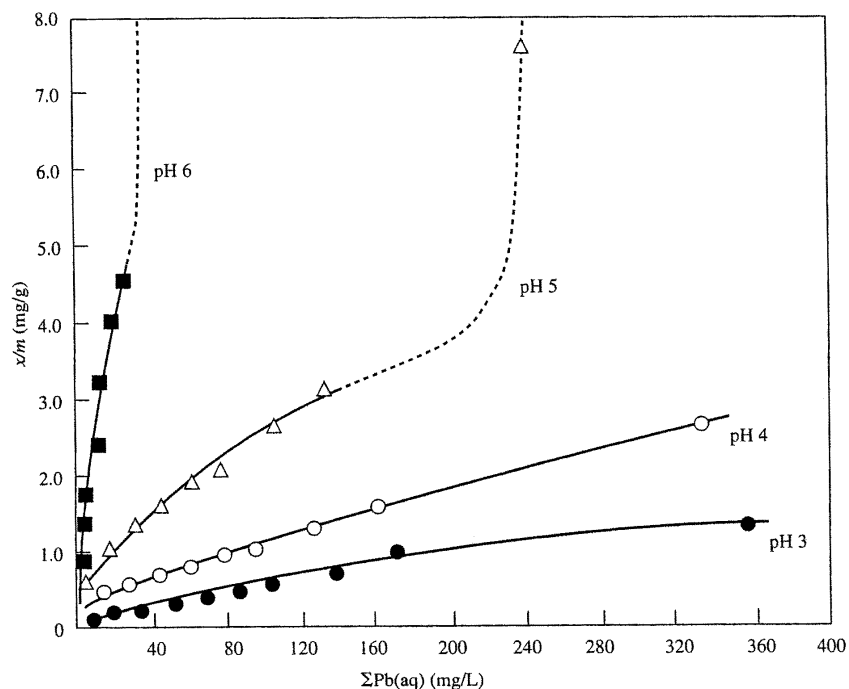
## 5. ADSORPTION CONTROLS ON METAL CONCENTRATIONS AND MOBILITIES

### 5.1 Introduction

Except for Al and sometimes Mn, concentrations of trace metals in the environment are generally too low for those metals to exceed the solubility products of their pure metal solids and thus to precipitate. Instead, toxic metal concentrations are generally limited by sorption onto the surfaces of minerals, and onto organic matter including microbial cell wall surfaces. For aluminosilicate-rich soils, however, surface precipitation of Zn, Ni, and Co as layered double hydroxides was reported (e.g., Ford and Sparks, 2000). As metal concentrations further increase and fill available sorption sites, most metals tend to be incorporated in the structures of major mineral precipitates as “coprecipitates” in which they substitute for major metal cations, forming so-called solid solutions (Langmuir, 1997a). At higher metal concentrations, the metals may be precipitated in pure metal phases, limiting further increases in metal concentration. For a hypothetical metal, M, the general trend of such reactions with increasing metal concentrations in soil pore waters or surface or ground water might be:

- Adsorption control of M  
( $M < 100 \mu\text{g/L}$ )
- Coprecipitation of M in a major metal hydroxide, carbonate, sulfate or silicate mineral (etc.)  
( $M > 100 \mu\text{g/L}$  and  $< 10 \text{ mg/L}$ )
- Precipitation of M in a “pure” metal phase  
( $M = 10 \text{ mg/L}$ )

Practically, it is difficult to distinguish adsorption and coprecipitation reactions. These concepts are illustrated in Figure 5, which shows adsorption of lead from a landfill leachate by kaolinite clay as a function of pH. In the figure the adsorbed lead in mg/g of clay is plotted against the total lead in the leachate. The plot indicates that lead adsorption increases with increasing pH. Geochemical modeling of the leachate solution at pH 5 and 6 shows that at about 240 and 40 mg/L lead, respectively, (as indicated by the vertical dotted lines) further increases in dissolved lead are limited by precipitation of solid lead hydroxy-carbonate ( $\text{Pb}_3[\text{OH}]_2[\text{CO}_3]_2$ ).



**Figure 5. Adsorption of Pb from DuPage landfill leachate by kaolinite at 25°C, as a function of pH.** Dashed vertical lines show the Pb concentration at saturation with Pb-hydroxycarbonate solid. From Griffin and Shimp, 1976.

## 5.2 Metal Adsorption and Desorption

Distribution Coefficients, Isotherm Equations and Ion Exchange:  
They Don't Generally Apply to Adsorption of the Metals of Concern

The distribution coefficient ( $K_d$ ) for lead adsorption by kaolinite is defined as  $K_d = (x/m)/\Sigma\text{Pb(aq)}$ , where  $x/m$  is the weight of lead adsorbed,  $x$ , divided by the weight of sorbent,  $m$ , at a specific concentration of total dissolved lead,  $\Sigma\text{Pb(aq)}$ . Based on this definition, every tangent to a curve in Figure 5 has a different value of  $K_d$ . The solid curves in Figure 5 are termed sorption isotherms, and can be model-fit with Langmuir or Freundlich isotherm equations (cf. Stumm and Morgan, 1996; Langmuir, 1997a). Clearly, a single distribution coefficient or isotherm equation cannot predict lead adsorption for all of the conditions described in Figure 5. This is because the extent of lead adsorption depends on the total lead concentration and the pH. Further analysis shows that adsorption also varies with the amount of lead complexed by carbonate, sulfate, chloride, and organic ligands, and by the nature and amounts of one or more sorbent phases present. Given all of these variables,  $K_d$  values for metal adsorption can vary by two to three orders of magnitude for a single soil or sediment. In other words, adsorption of

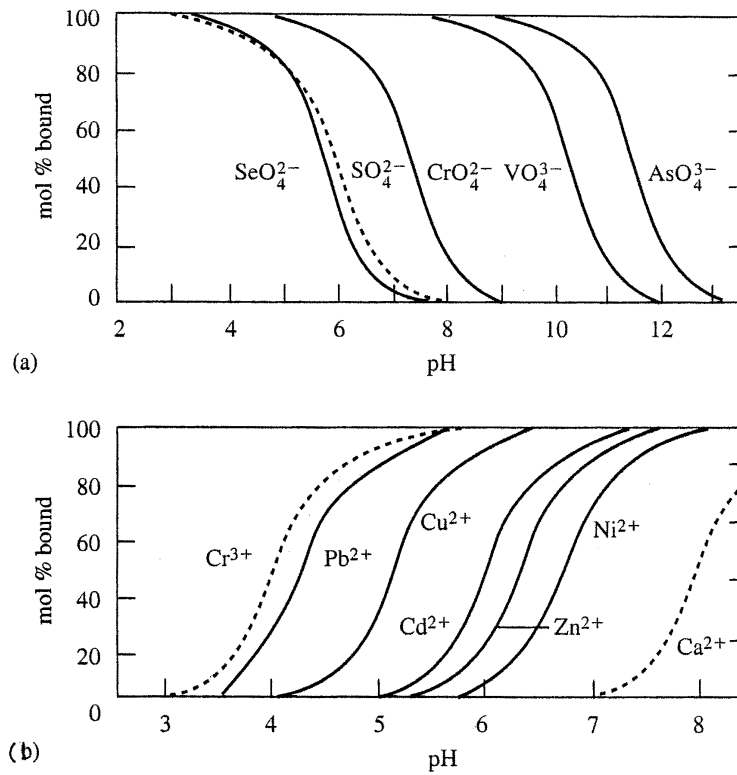
metals is far more complicated than adsorption of organics, which can often be adequately modeled using a distribution coefficient or isotherm approach.

Ion exchange models are also generally inappropriate to explain and model adsorption of trace metals. Simple ion exchange models best apply when concentrations of competing ions are at comparable values, which is not the case for most trace metals most of the time. Except in highly metal-contaminated waters and sediments, concentrations of toxic metal cations are typically  $10^2$  to  $10^3$  times lower than concentrations of the major cations  $\text{Na}^+$  and  $\text{Ca}^{2+}$  which are competing for sorption sites on clays, for example. Concentrations of the anionic trace metals are also in most cases less than 1% of the concentrations of major anions such as sulfate. (See Tables 1 and 3.) At trace concentrations, metals are preferentially adsorbed relative to major metal ions, but not according to the principles of simple ion exchange (Langmuir, 1997a).

### 5.3 Adsorption Behavior of the Metals of Concern

In porous media the most important sorbent solids for metals are clay minerals, organic matter, and oxyhydroxides of Fe and Mn. Their important surface properties are given in Table 10. For a given weight of sorbent, metal sorption capacity is proportional to surface area and surface site density. The greatest surface site densities (positively or negatively charged sites) and cation exchange capacities (negatively charged sites only) are those of organic material and the oxyhydroxides. These phases are the strongest and most important sorbents of trace metals. The clays, except for kaolinite, have a surface charge that is largely independent of pH, whereas the surface charge of organic matter and the oxyhydroxides is strongly pH dependent. The pH at which a solid surface changes sign is referred to as the zero point of charge (ZPC). The ZPCs of organic matter and kaolinite are below the range of natural pHs and, while their surface charge will decrease with decreasing pH, their surfaces will remain negatively charged at low natural pH. In contrast, some oxyhydroxides (such as goethite,  $\alpha\text{-FeOOH}$ ) have ZPCs within the range of natural pHs and will have positive surface charges at low pH and negative surface charge at high pH. Thus, the negative surface charge of the oxyhydroxides increases with increasing pH, which means their sorptive capacity for metals increases with increasing pH. Conversely, the positive surface charge of the oxyhydroxides increases as the pH drops, making these phases more effective sorbents for anions under low pH conditions.

These effects are shown in Figure 6, which is a plot of percent sorbed versus pH for metal adsorption by ferrihydrite, or hydrous ferric oxide (HFO). The curves are called *sorption edges* for each metal. The diagram shows that the oxyanions are strongly adsorbed by HFO under acid conditions, but are desorbed (become mobile) with increasing pH. Based on Figure 6, combined with adsorption data assembled by Dzombak and Morel (1990), the order of desorption from HFO with increasing pH is, selenate, antimonate, molybdate, chromate, vanadate, arsenate, and phosphate. Selenate desorbs between pH 3 and 8, whereas arsenate is strongly held at lower pH values and desorbed between pH 9 and 11. Also based on Figure 6 and Dzombak and Morel (1990), with increasing pH, HFO preferentially adsorbs metals in the order  $\text{Hg}^{2+} > \text{Be}^{2+} > \text{Ba}^{2+} > \text{Cr}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} \approx \text{Zn}^{2+} > \text{Ni}^{2+}$ .



**Figure 6. Adsorption of various metal cations and oxyanions, each at  $5 \times 10^{-7}$  M, by ferrihydrite ( $\Sigma\text{Fe[III]} = 10^{-3}$  M) as a function of pH at an ionic strength of 0.1 mol/kg. There are  $2 \times 10^{-4}$  M of reactive sites on the oxyhydroxide. The dashed curves are calculated. After Stumm, 1992.**

**Table 10. Surface Areas, Surface Site Densities, and Cation Exchange Capacities (CECs) of Some Important Sorbent Phases and the pH Dependence of Metal Sorption**

<b>Sorbent Mineral/Phase</b>	<b>Surface Area (m<sup>2</sup>/g)</b>	<b>Site Density (sites/nm<sup>2</sup>)</b>	<b>Site Density (mmol sites/g)</b>	<b>CEC (meq/100g)</b>	<b>pH Dependence</b>
Kaolinite	10 to 38	1.3 to 3.4	0.022 to 0.21	3 to 15	Strong
Illite and chlorite	65 to 100	0.4 to 5.6	0.043 to 0.93	10 to 40	Slight
Smectite-montmorillonite	600 to 800	0.4 to 1.6	0.4 to 2.1	80 to 150	Absent or negligible
Organics in soils, humic materials <sup>a</sup>	260 to 1300	2.31	1.0 to 5.0	110 to 500	Strong
Mn oxyhydroxides	143 to 290	2 to 18	0.48 to 8.7	100 to 740	Strong
Fe(III) oxyhydroxides (ferrihydrite)	250 to 600	20	8.3 to 20	100 to 740	Strong

Modified after Langmuir (1997a).

<sup>a</sup>Paulson and Balistrieri (1999) suggest 1 mmol of sites per gram of organic carbon.

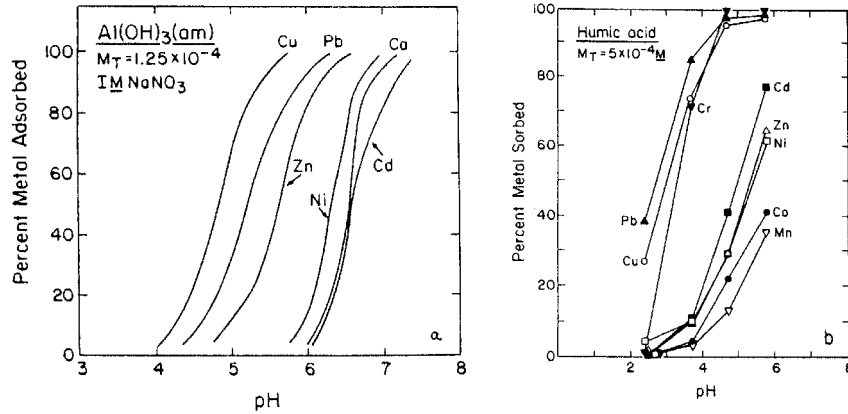
Metal adsorption onto soils and sediments is probably more dependent on changes in pH than on any other solution variable. For a divalent metal cation,  $M^{2+}$ , the general sorption reaction can be written:



where SOH and SOM<sup>+</sup> are surface sites with an adsorbed proton and a metal ion. For adsorption of a divalent metal anion,  $L^{2-}$ , we can similarly write:



Sorption edges for metal adsorption, by amorphous  $Al(OH)_3$  and by soil humus material, are given in Figure 7. The plots show a strong pH dependence of metal adsorption on both substrates. Metal selectivity with increasing pH is similar to what was observed for adsorption by HFO.



**Figure 7. Percent metal adsorbed: (a) by  $\text{Al}(\text{OH})_3(\text{am})$  at total metal concentrations of  $1.25 \times 10^{-4} \text{ M}$  in  $1 \text{ M NaNO}_3$  solutions, and (b) by humic acid at total metal concentrations of  $5 \times 10^{-4} \text{ M}$ . From Sposito, 1984.**

#### 5.4 Surface Complexation Adsorption Models

The most useful and mechanistic sorption models for predicting and modeling toxic metal adsorption in surface and ground waters are probably the *electrostatic or surface complexation (SC) adsorption models* (cf. Westall and Hohl, 1980; Davis and Kent, 1990; Langmuir, 1997a). These include the constant capacitance (CC), diffuse layer (DL), and triple layer (TL) models, all of which are available in the EPA geochemical program MINTEQA2 (U.S. EPA, 1991). The DL model is also included in the U.S. Geological Survey program PHREEQC (Parkhurst and Appelo, 1999).

The SC models employ the electrical double layer (EDL) theory, according to which the sorbent surface charge results in an electrostatic potential gradient between the solid surface and the bulk solution. The layer close to the surface has a fixed charge equal to the surface charge. This layer is associated with specific adsorption, which is not influenced by ions in the bulk solution. In all SC models,  $\text{H}^+$  and  $\text{OH}^-$  are specifically adsorbed within the first layer. In the second layer, however, the accumulation of counter ions results in a charge with a sign opposite to the surface charge and in an absolute charge that decreases toward the bulk solution. According to EDL, it is assumed that the concentration of a sorbed ion ( $X_s^z$ ), which is not measurable, is related to the ion's concentration in the bulk solution ( $X^z$ ) by an exponential Boltzmann expression:

$$(X_s^z) = (X^z)[e^{-\psi F/RT}]^z \quad (5)$$

in which  $z$  is the charge of the ion,  $e^{-\psi F/RT}$  is the Boltzmann factor (unitless),  $\psi$  is the potential in volts at the plane of adsorption, and  $F$ ,  $R$ , and  $T$  are the Faraday constant (96,480 C/mol), the ideal gas constant (8.314 J/mol), and the absolute temperature, respectively.

The SC models consider and compute activity coefficients of ions and ion activities, as well as the concentrations of free and complexed metals in solution. The models treat metal adsorption onto surface sorption sites as a complexation reaction. Required model inputs include the specific surface area of sorbent phases ( $\text{m}^2/\text{g}$ ), the site density (moles of sites/moles of sorbent), and intrinsic surface complexation constants for adsorption of each metal by each sorbent phase. These constants are analogous to the equilibrium constants that describe the formation of metal complexes in solution. Because the SC models are relatively atomistic and mechanistic in the way they treat adsorption, they are far better at predicting metal adsorption behavior for conditions beyond those used to determine model parameters than are models based on adsorption isotherms or ion exchange. In fact, even if the SC models have been developed in the laboratory, they have been used with success to predict adsorption on natural particles (e.g., Tessier et al., 1996).

The diffuse layer (DL) model is the simplest of the SC models (U.S. EPA, 1991; Langmuir, 1997a). In the DL model, adsorption is considered to occur specifically at the surface, and the effect of adsorbed electrolyte ions on the potential away from the surface is neglected. Both MINTEQA2 and PHREEQC contain a database of sorption parameters (intrinsic constants) for the adsorption of metals by HFO from Dzombak and Morel (1990). Sorption parameters for all of the toxic metal cations and anions of concern, except for Al and Tl, are included in the database. Diffuse layer model parameters for adsorption of  $\text{H}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  by  $\delta\text{-MnO}_2$  have recently been published by Pretorius and Linder (2001), but are not yet included in MINTEQA2 or PHREEQC.

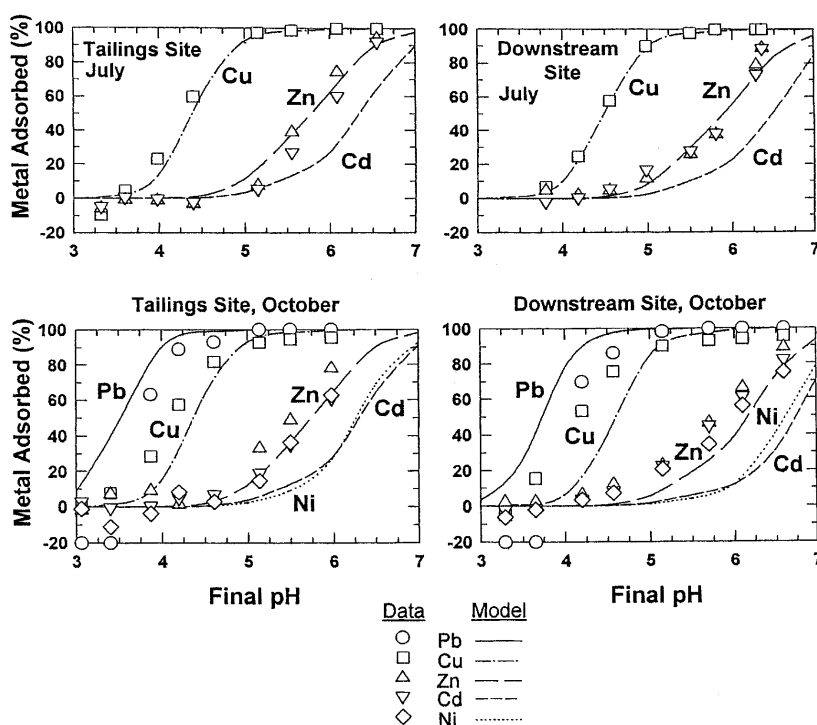
## 5.5 Applications of the Diffuse Layer Model to Natural Systems

It has been observed that in many soils and sediments low in organic matter, HFO is the most important metal sorbent, and the only sorbent that needs to be considered in predictions of toxic metal sorption behavior (cf. Benjamin and Leckie, 1981). The diffuse layer model (also called the generalized two-layer model, or GTLM) in MINTEQA2 has been extensively applied in aquatic environmental studies of metal transport and attenuation. Loux et al. (1990) used the DL model and MINTEQA2 to predict the adsorption and precipitation behavior of eight metals in an oxidized, sandy aquifer as a function of pH. Assuming that HFO was the only sorbent, DL model adsorption adequately described changes in the concentrations of Ni, Pb, and Zn. Cadmium behavior was better understood, assuming its precipitation in  $\text{CdCO}_3$  (otavite). Changes in Cu, Ba, Be, and Tl were not simply explained. Copper may have been adsorbed by organic matter, which was not considered in the modeling.

More recently, adsorption of metals by organic matter and aluminum oxyhydroxides, as well as HFO, has been included in DL modeling with MINTEQA2 (Paulson and Balistrieri, 1999). These authors studied neutralization of acidic ground waters by ambient surface and ground waters using a mixing model approach. Particulate organic matter (POC) and HFO were the chief metal sorbents. In pristine systems, Cu is usually the chief metal associated with POC;

however, in their study, Zn and Cd were mostly adsorbed by POC and Cu was mostly absorbed by HFO.

In another study of metals in acid mine waters, Smith et al. (1998) measured and modeled the adsorption of Cd, Cu, Ni, Pb, and Zn by streambed sediments as a function of pH using MINTEQA2 and the DL (GLTM) model. Figure 8 shows their measured adsorption results, obtained in batch experiments, assuming 2.9 g/L of HFO as the only sorbent. The plot shows fair to excellent agreement between measured and predicted metal adsorption values. These authors also measured and predicted metal concentrations in three mine drainage waters, assuming that metal adsorption was by suspended HFO. The results, listed in Table 11, show good general agreement between measured and predicted metal concentrations.



**Figure 8.** Comparison of experimental data (symbols) for Pb, Cu, Zn, Ni, and Cd sorption onto streambed sediment from St. Kevin Gulch, Colorado, with computer-model simulations (curves) for sorption onto hydrous ferric oxide, at a streambed concentration of 2.9 g/L. From Smith et al., 1998.



**Table 11. Comparison of Model Predictions and Measured Values of Percent Metals Associated with the Suspended Particulate Fraction of Mine-Drainage Waters from Selected Sites**

	Argo-3 (pH 5.6, HFO = 0.007 g/L)		Rawley-3 (pH 6.2, HFO = 0.11 g/L)		Leadville Drain (pH 7.2, HFO = 0.001 g/L)	
	Predicted (%)	Measured (%)	Predicted (%)	Measured (%)	Predicted (%)	Measured (%)
<b>As</b>	--	--	98	<78 <sup>a</sup>	--	--
<b>Pb</b>	82	<71 <sup>a</sup>	80	<93 <sup>a</sup>	86	<71 <sup>a</sup>
<b>Cu</b>	18	27	60	63	–	--
<b>Zn</b>	<1	0 to 8	<1	0 to 9	2	3
<b>Ni</b>	<1	<1	<1	1	–	--
<b>Cd</b>	<1	<1	<1	6	<1	<1

Model predictions made with the DL model and MINTEQA2. From Smith et al., 1998.

<sup>a</sup>Dissolved concentration was below the detection limit. Value computed using the limit of detection for the dissolved concentration.

Cederberg et al. (1985) and Yeh and Tripathi (1991) considered surface complexation modeling of metal adsorption and metal transport in ground water. Parkhurst (2002) has developed a computer model called PHAST,<sup>3</sup> which is a 3D reactive transport model that combines PHREEQC, which has the DL metal adsorption model, with HST3D, a ground-water flow and transport model.

Several recent studies have measured and modeled trace metal adsorption and metal transport in streams using a surface complexation approach to adsorption. U.S. Geological Survey researchers of the Toxic Substances Hydrology Program have published a number of papers using the OTEQ and OTIS models. OTEQ is a one-dimensional model for studying the fate and transport of metals in streams and rivers. The model couples the OTIS transient storage model with MINTEQ, which includes DL model adsorption of metals by HFO (cf. Ball et al., 1999; Runkel et al., 1999). In their study, Runkel et al. (1999) considered in-stream metal transport, metal oxide precipitation-dissolution, and pH-dependent sorption of copper and zinc.

<sup>3</sup> See [http://wwwbrr.cr.usgs.gov/projects/GWC\\_coupled](http://wwwbrr.cr.usgs.gov/projects/GWC_coupled).

## 5.6 WHAM and Related Models for Predicting Metal Activities in Soil Pore Waters

MINTEQA2 (U.S. EPA, 1991) and VMINTEQ (Gustafson, 2003) both contain subroutines that allow estimates of the importance of metal-organic complexing if the concentration of dissolved organic carbon (DOC) is known. Perhaps more useful in studies of metals in soil pore waters are programs such as WHAM (Tipping, 1994, 1998), and NICA (Goody et al., 1995) (see Section 4 for more information). Application of the chemical speciation model WHAM has been discussed by Tye et al. (2003), who successfully predicted  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  activities in soil pore water assuming the metals were adsorbed by soil humus according to a pH-dependent Freundlich isotherm model. Competitive adsorption between  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  could be ignored because it did not improve model fits.

## 6. SOLUBILITY CONTROLS ON METAL CONCENTRATIONS AND MOBILITIES

### 6.1 The Importance of pH

The solubility of most metals that occur as cations is strongly pH dependent. Their greatest solubilities are usually measured in acid systems, with solubilities that decrease as the pH rises. For a few metals (e.g., Be[II], Zn[II], Al[III], and Fe[III]), metal solubility increases again at alkaline pH values, a property which is termed amphoteric behavior (Figures 12 and 16). In the following discussions of solubility, we will focus on the pH range between 4 and 9, which includes that of most natural waters and soils.

Tyler and Olsson (2001a, 2001b) mixed calcium carbonate with an acid Swedish Cambisol to vary the soil pH from 5.2 to 7.8. They then studied the effect of the pH change in the oxidized soil on concentrations of 60 elements in soil pore waters. With increasing pH, concentrations of As, Mo, S, Sb, and to a lesser degree Co, Cr, Hg, and Sr increased, whereas Al, Ba, Fe, Mn, and Tl concentrations decreased. The pH effect on Be and Cu concentrations was poorly defined. Metal concentration changes with increasing pH may have been caused by increasing desorption of anionic elements (As, Mo, S, Sb, and Cr), increasing adsorption of cationic species, the precipitation of oxyhydroxide solids (Al, Fe, Mn) and, at least for Ba, the precipitation of sulfate or carbonate. The ill-defined behavior of Cu with rising pH may reflect its participation in competing reactions: (1) complexation by increasing amounts of dissolved humic substances with increasing pH, which tend to solubilize  $\text{Cu}^{2+}$ ; and (2) increased  $\text{Cu}^{2+}$  adsorption by solid organic matter and metal oxyhydroxides.

### 6.2 Oxidation Potential and pH

Shown in Table 12<sup>4</sup> are the possible oxidation states and speciation of the trace metals in natural systems. Also indicated are their hard or soft acid or base characters, which depend on the oxidation state, their forms in oxidized and reduced systems, and whether they can

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<sup>4</sup> Information for Table 12 was obtained from the following sources: Baes and Mesmer, 1976; Bodek et al., 1988; Brookins, 1988; Langmuir, 1978, 1997a; Pourbaix, 1966; and Rai and Zachara, 1984.

precipitate in sulfide minerals. This distinction is important because the metal sulfides are extremely insoluble, and if precipitated tend to reduce metal concentrations to below the microgram per liter range.

The table shows that all metals forming sulfide phases (sulfide is a soft ligand) are either soft or borderline soft.

The Eh-pH diagrams allow a graphical representation of the simultaneous influence of pH and redox conditions on metal speciation. In the following discussion, the figures describe the oxidation state in terms of Eh and/or pe or pE. At 25° C and 1 bar pressure, the two are related through the expression:

$$pe \text{ or } pE = Eh(\text{volts})/(0.0592) \quad (6)$$

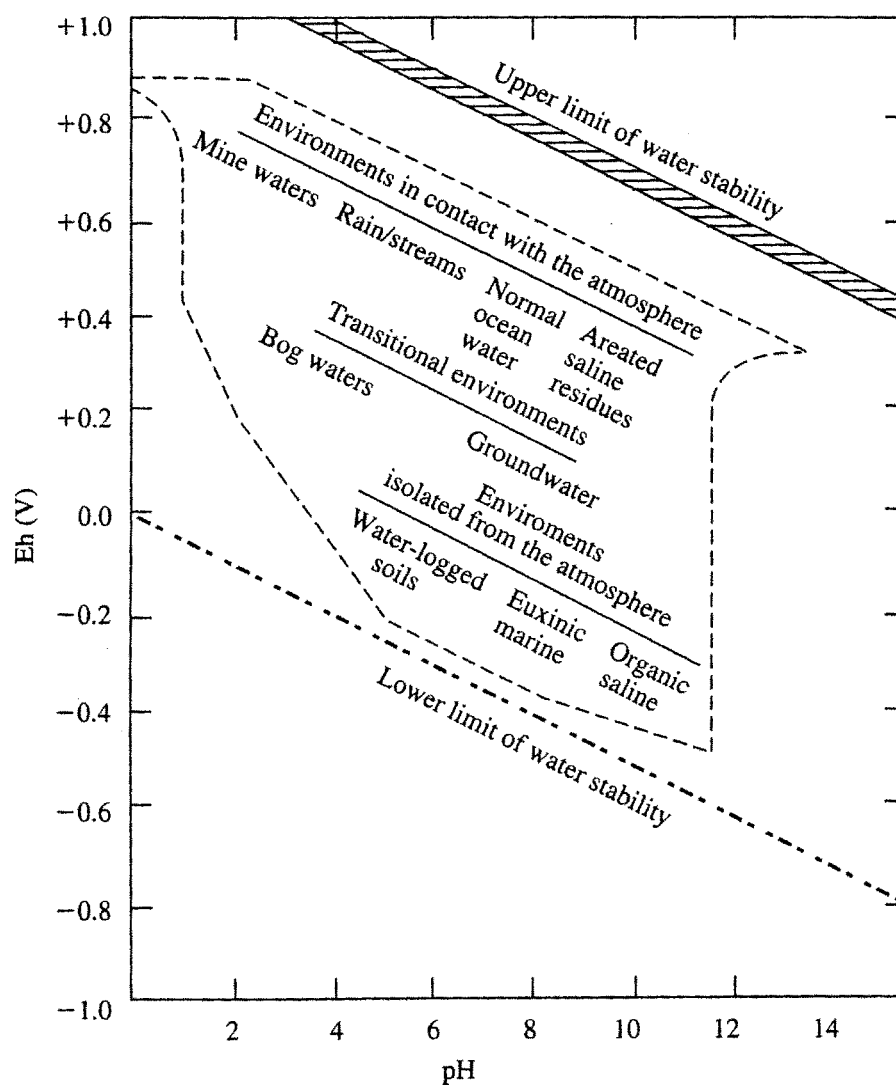
Figure 9 describes the locus of measured pH and Eh values in natural waters, and the types of waters in which the measurements have been made.<sup>5</sup> Oxygenated surface and near surface environments have Eh values that plot near the area titled “Environments in contact with the atmosphere.” Ground waters, because they are out of direct contact with the atmosphere, tend to be more reducing. Waterlogged soils and sediments are among the most reduced aqueous systems. Differences in the oxidation potential or Eh of these environments are usually related to the abundance of organic matter and their isolation from air. Oxygen is relatively insoluble in water, with a solubility of 8.25 mg/L at 25° C. In principle, it takes only 2–3 mg/L of labile DOC in water to deplete this oxygen content (Langmuir, 1997a). Leenheer et al. (1974) reported a median DOC of 0.7 mg/L for U.S. ground waters. In temperate and tropic regions, soils have a mean organic matter content of about 2–4% (Bohn et al., 1985). Langmuir (1997a) has observed that 4 mg/L of DOC in ground water is sufficient to make the water anaerobic.

An Eh-pH diagram for carbon is shown in Figure 10. The stability field of organic matter, generally, if it could be plotted, would overlay the stability fields of methane and native C (graphite) in the low Eh part of the diagram. When organic matter is in excess, and oxygen not replenished fast enough, microbial activity can generate reducing conditions. The sequence of reductions that result is shown in Figure 11. In waters and sediments where oxygen or other oxidants are in excess, the sequence of oxidations shown in Figure 11 may proceed.

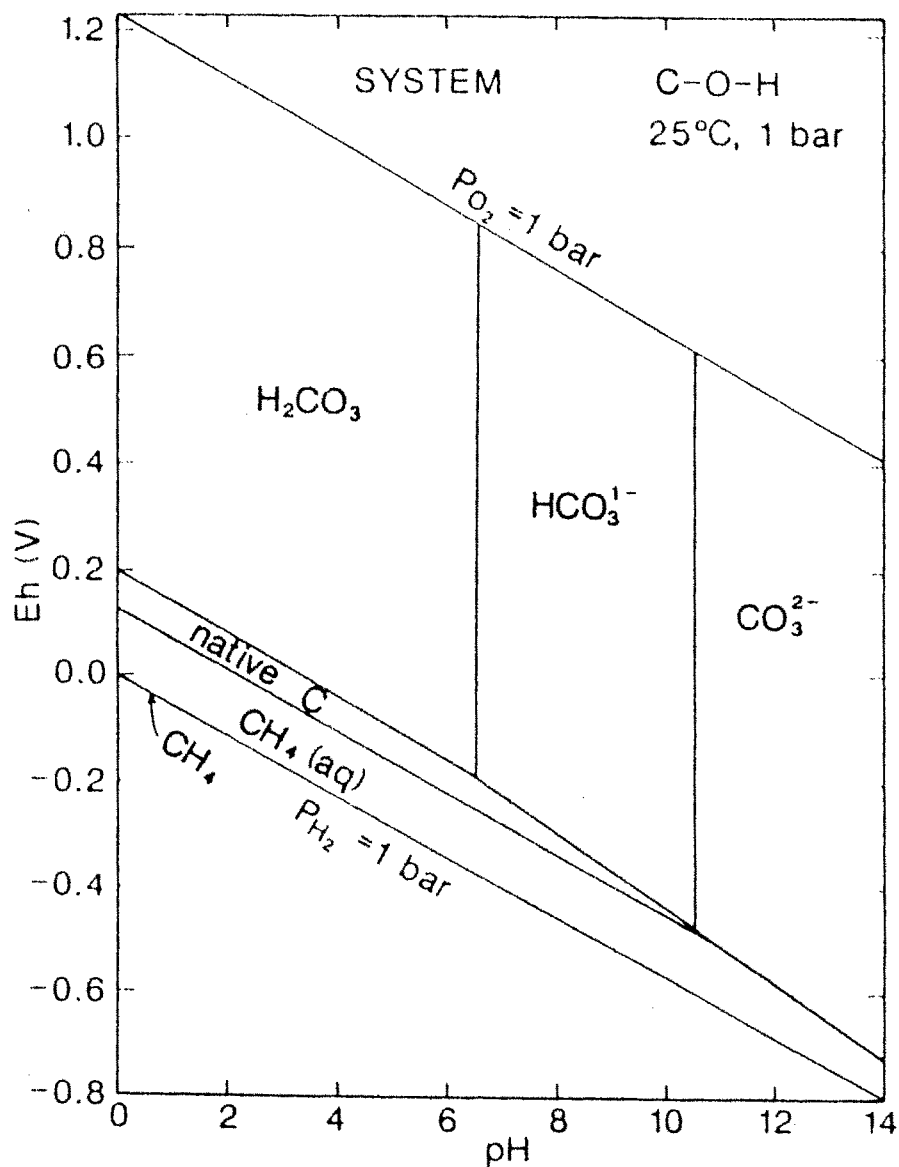
Oxidation of the organic matter in an isolated aquatic environment can deplete the oxygen and provide conditions suitable for sulfate reduction. Precipitation of metal sulfides is preceded by reduction of more abundant soil Fe(III) oxyhydroxides to dissolved Fe(II) (Figure 11). This is then followed by precipitation of Fe(II) sulfides in association with the less abundant sulfides of Cd, Zn, Co, Ni, Pb, Ag, Cu, Hg, and Mo.

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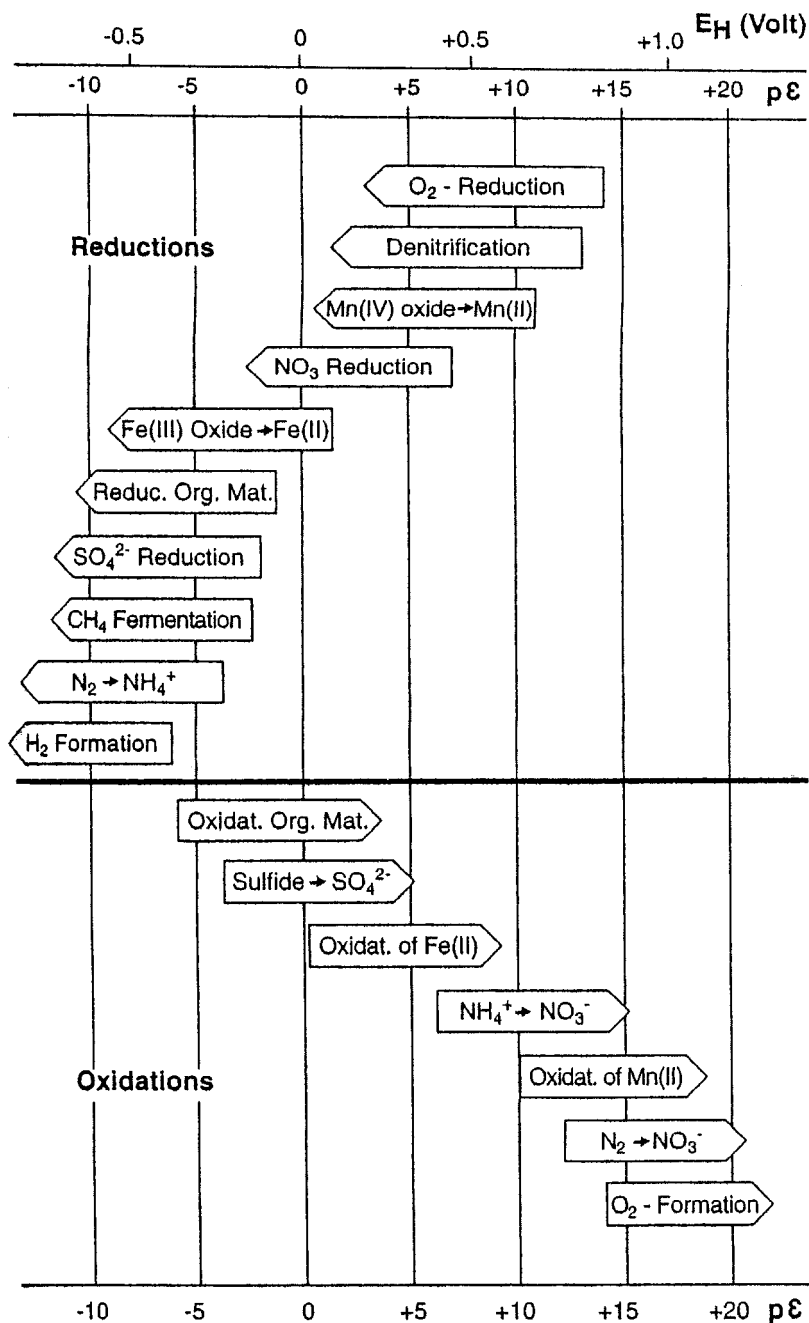
<sup>5</sup> Problems with measuring Eh and the difference between measured and theoretical Eh values are discussed at length elsewhere (cf. Langmuir, 1997a).



**Figure 9. Approximate positions of some natural environments in terms of Eh and pH.** The dashed line represents the limits of measurements in natural environments, as reported by Baas-Becking et al. (1960).



**Figure 10. Eh-pH diagram for the system C-O<sub>2</sub>-H<sub>2</sub> at a total carbonate concentration of 10<sup>-3</sup> M.** Native C is graphite. If shown, the upper boundary of the stability field for carbohydrates would be at slightly higher Eh values than the methane/carbonate boundary. After Brookins, 1988.



**Figure 11. Sequence of microbially mediated oxidation-reduction reactions.** This sequence is often observed in natural systems and represents the thermodynamic order of the reactions. Modified from Stumm and Morgan, 1996.

**Table 12. Oxidation States of Trace Metals as They Occur in Natural Waters and Mineral Systems, Their Redox Sensitivity, and Their Tendency to Form Sulfides at Low Eh**

Metal	Symbol	Hard or Soft	Oxidation States	Oxidized Forms	Reduced Forms <sup>a</sup>	Can Form Sulfides at Low Eh
Aluminum	Al	H	3+	Al <sup>3+</sup>	Al <sup>3+</sup>	no
Beryllium	Be	H	2+	Be <sup>2+</sup>	Be <sup>2+</sup>	no
Barium	Ba	H	2+	Ba <sup>2+</sup>	Ba <sup>2+</sup>	no
Strontium	Sr	H	2+	Sr <sup>2+</sup>	Sr <sup>2+</sup>	no
Cadmium	Cd	S	2+	Cd <sup>2+</sup>	Cd <sup>2+</sup>	yes
Zinc	Zn	B	2+	Zn <sup>2+</sup>	Zn <sup>2+</sup>	yes
Cobalt	Co	B	(3+), 2+	(Co <sup>3+</sup> ), Co <sup>2+</sup>	Co <sup>2+</sup>	yes
Nickel	Ni	B	(3+), 2+	(Ni <sup>3+</sup> ), Ni <sup>2+</sup>	Ni <sup>2+</sup>	yes
Manganese	Mn	H	(4+), (3+), 2+	(4+), 2+	(3+), 2+	no <sup>b</sup>
Lead	Pb	B	(4+), 2+	Pb <sup>2+</sup>	Pb <sup>2+</sup>	yes
Silver	Ag	S	1+, (0)	Ag <sup>+</sup>	Ag <sup>+</sup> /Ag(s)	yes
Copper	<sup>a</sup> Cu	<sup>b</sup> B/S	2+, 1+, 0	Cu <sup>2+</sup>	Cu <sup>+</sup> /Cu(s)	yes
Mercury	Hg	S	2+, 1+, 0	Hg <sup>2+</sup>	Hg <sup>+</sup> /Hg(l)	yes
Thallium	Tl	S	(4+), (3+), 1+	(Tl <sup>4+</sup> ), (Tl <sup>3+</sup> )	Tl <sub>2</sub> O(s)/Tl <sup>+</sup>	yes
Arsenic	As	<sup>b</sup> H/S	5+, 3+, 0	HAsO <sub>4</sub> <sup>2-</sup>	H <sub>3</sub> AsO <sub>3</sub> <sup>0</sup> /As(s)	yes
Antimony	Sb	H/S	5+, 3+, 0	Sb(OH) <sub>6</sub> <sup>-</sup>	Sb(OH) <sub>3</sub> <sup>0</sup> /Sb(s)	yes
Chromium	Cr	H	6+, 3+	CrO <sub>4</sub> <sup>2-</sup>	Cr <sup>3+</sup> , Cr(OH) <sub>3</sub> (s)	no
Molybdenum	Mo	H/S	6+, (5.33+), 5+, (4+)	HMoO <sub>4</sub> <sup>-</sup>	MoO <sub>2</sub> <sup>+</sup> /Mo <sub>3</sub> O <sub>8</sub> (s)/ MoS <sub>2</sub> (s)	yes
Selenium	Se	H/S	6+, 4+, (0), 2-	SeO <sub>4</sub> <sup>2-</sup>	SeO <sub>3</sub> <sup>2-</sup> /Se(s)/ HSe <sup>-</sup>	no
Vanadium	V	H	5+, 4+, 3+	H <sub>2</sub> VO <sub>4</sub> <sup>-</sup>	VO <sup>2+</sup> , V(OH) <sub>3</sub> <sup>0</sup>	no

Oxidation states in parentheses are found in mineral systems only. Hard (H), soft (S), and borderline soft (B) metals are indicated.

<sup>a</sup>Cu<sup>2+</sup> is borderline soft, and Cu<sup>+</sup> is a soft cation.

<sup>b</sup>B/S or H/S denotes whether the oxidized species is borderline hard or hard, and the reduced species is soft.

Other ligands that can limit maximum metal concentrations include oxygen and hydroxide, which react with the hard acid cations Al(III), Mn(III, IV), and Cr(III) to produce insoluble oxyhydroxides. Phosphate, sulfate, and carbonate also form relatively insoluble mineral precipitates when they react with divalent and trivalent metal cations. These are noted on a case by case basis below.

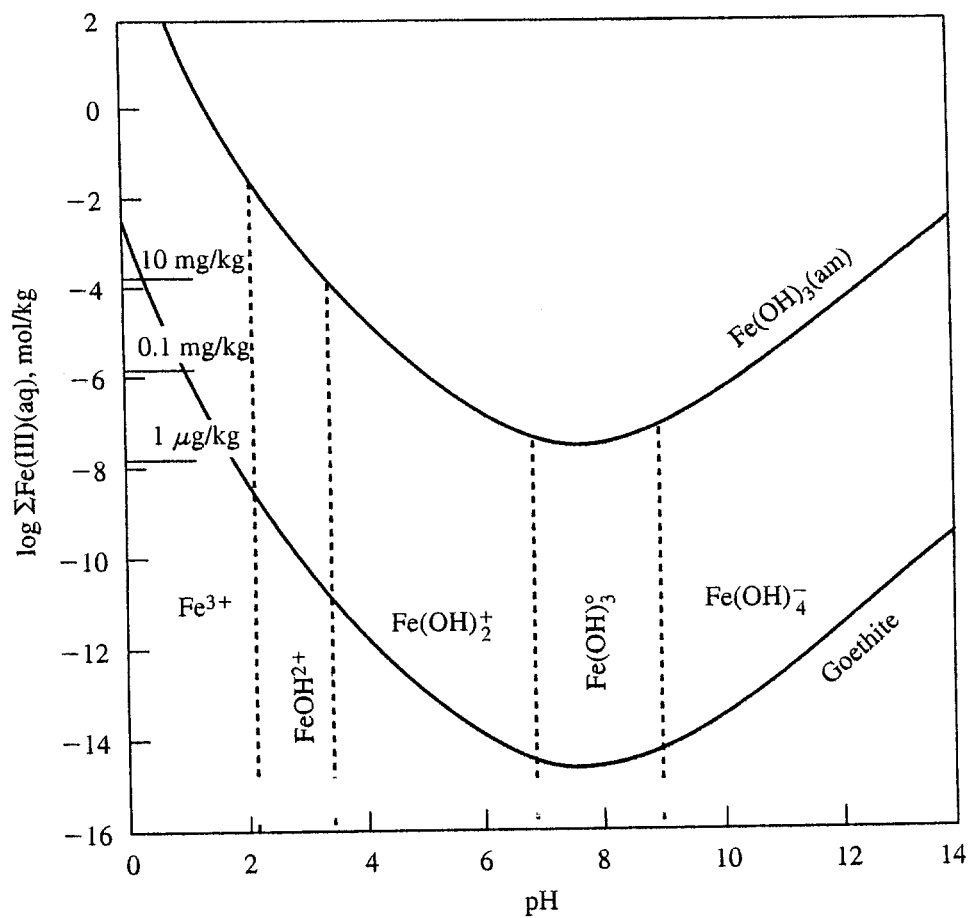
### **6.2.1 Iron and Sulfur**

Although iron and sulfur are not elements of concern, their behavior needs to be discussed because it has a pivotal impact on the fate and transport of the trace metals. Shown in Figure 12 is a solubility diagram for the Fe(III) oxyhydroxides as a function of pH. Plotted are curves showing the solubility of  $\text{Fe}(\text{OH})_3(\text{am})$ , which is also termed ferrihydrite or HFO, and a solubility curve for the crystalline mineral goethite. Initial precipitates of Fe(III) oxyhydroxide tend to be relatively amorphous, with a strong capacity to adsorb or coprecipitate trace metals. As they crystallize with time towards goethite, they lose surface area and adsorption capacity and tend to desorb trace metals. Figure 12 also shows that as the pH is reduced below 7, HFO tends to dissolve, becoming quite soluble below pH 3–4. Thus, soils and sediments at low pH typically have little capacity to retain the metals of concern, whereas soils at higher pH values that contain ferric oxyhydroxides may limit the release of the trace metals to the environment.

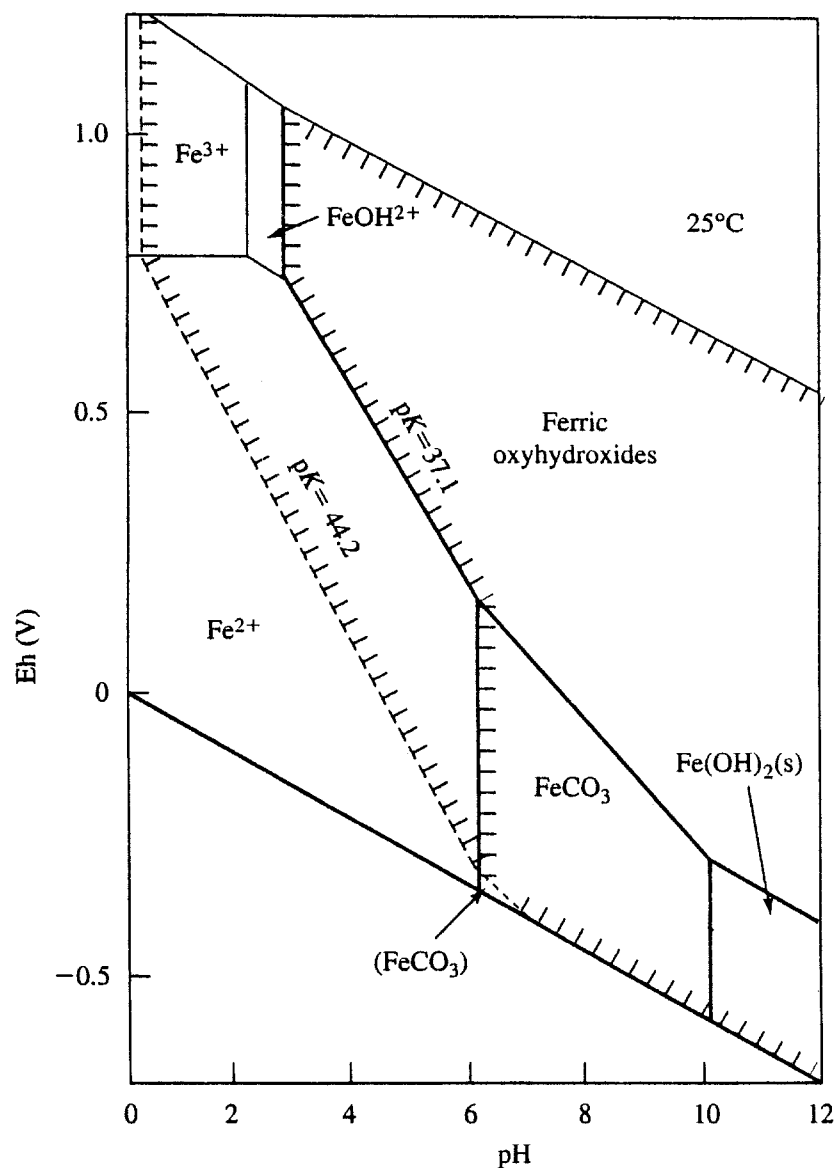
An Eh-pH diagram for iron in the presence of carbonate is shown in Figure 13. The ferric oxyhydroxides occupy most of the diagram for oxidizing conditions, which reflects their great stability and insolubility. The figure shows that the stability field of amorphous  $\text{Fe}(\text{OH})_3$  ( $\text{pK}_{\text{sp}} = 37.1$ ) is much smaller than that of the crystalline phase, goethite ( $\text{pK}_{\text{sp}} = 44.2$ ), and that under strongly reducing conditions the ferric oxyhydroxides are unstable relative to dissolved ferrous iron and the mineral siderite ( $\text{FeCO}_3$ ).

A sulfur Eh-pH diagram is given in Figure 14. The large size of the sulfate field is consistent with the fact that sulfate is the dominant form of sulfur in most environments. The position of the stability fields for native sulfur ( $\text{S}^0$ ), hydrogen sulfide, and bisulfide ion indicate that these forms are stable only under highly reducing conditions. When we add sulfur to the iron Eh-pH diagram as shown in Figure 15, a large stability field for pyrite ( $\text{FeS}_2$ ) appears at low Eh values. Acid mine drainage is produced when pyrite is exposed to atmospheric oxygen. Oxidation of the iron and sulfur in pyrite generates strong acidities and pH values as low as 1–2. This tends to dissolve any nearby HFO as well as trace metals that were present as sulfides or adsorbed to the HFO.

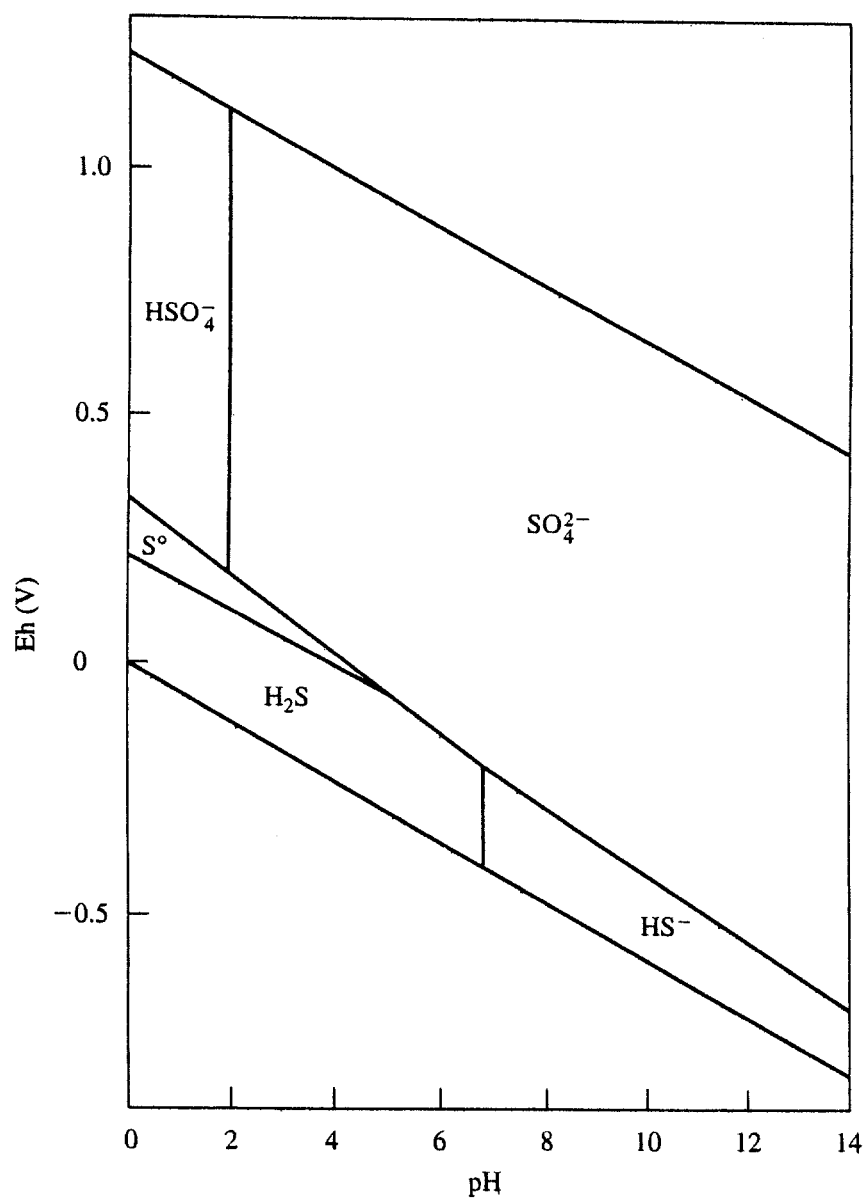




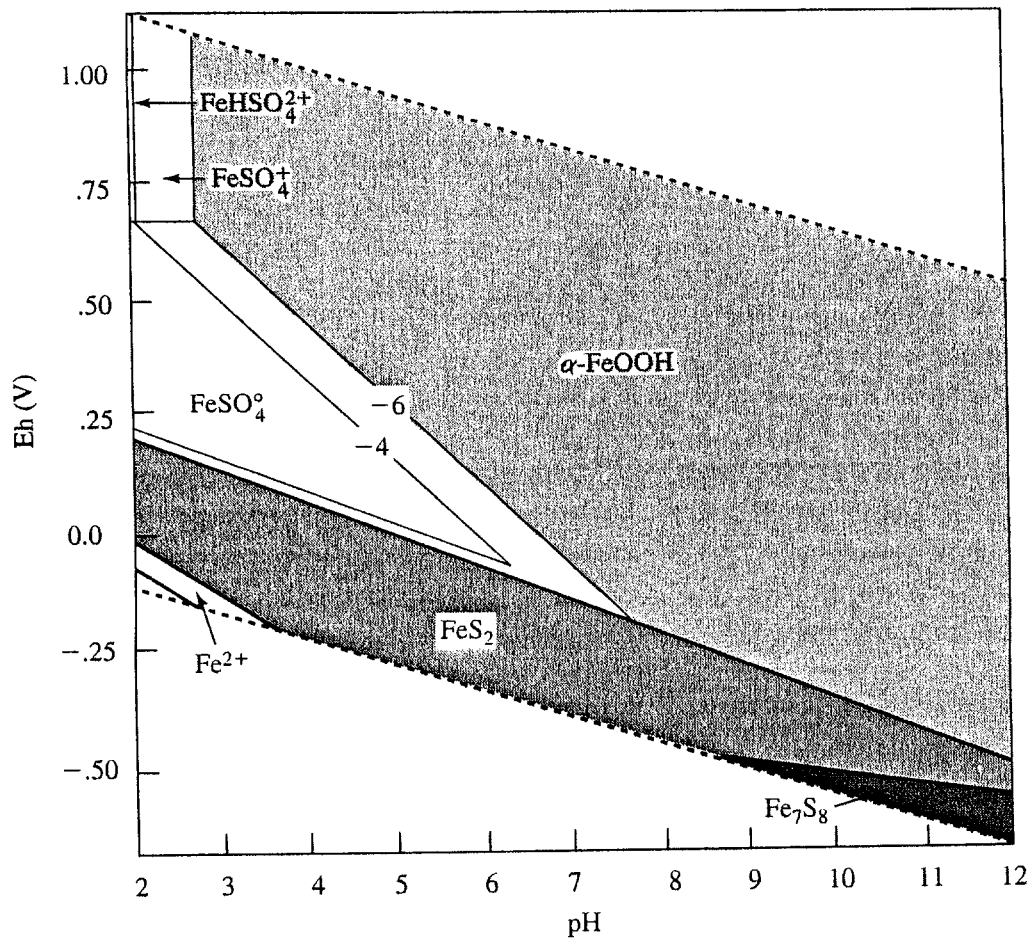
**Figure 12.** Solubility of amorphous  $\text{Fe(OH)}_3$ ,  $\text{pK}_{\text{sp}} = 37.1$  (top curve), and goethite [ $\alpha\text{-FeOOH}$ ],  $\text{pK}_{\text{sp}} = 44.2$  (bottom curve) as a function of  $\text{pH}$  at  $25^\circ \text{C}$ . Also shown are fields of dominance of  $\text{Fe}^{3+}$  ion and  $\text{Fe}^{3+}$ -OH complexes. After Langmuir, 1997a.



**Figure 13. Eh-pH diagram for the system Fe-O<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O, assuming that total dissolved carbonate equals 10<sup>-3</sup> mol/kg and total dissolved iron is 10<sup>-3</sup> mol/kg at aqueous solid boundaries.** Also shown is the position of the aqueous/solid boundaries for amorphous Fe(OH)<sub>3</sub> with  $pK_{sp} = 37.1$  and goethite with  $pK_{sp} = 44.2$ . The figure shows that siderite (FeCO<sub>3</sub>) is metastable in the presence of goethite. After Whittemore and Langmuir, 1975.



**Figure 14. Eh-pH diagram for the system S-O<sub>2</sub>-H<sub>2</sub>O at 25° C, showing the fields of predominance of the aqueous species and of elemental sulfur (S<sup>°</sup>) for  $\Sigma S(aq) = 10^{-3}$  mol/kg at aqueous/S<sup>°</sup> boundaries. After Langmuir, 1997a.**



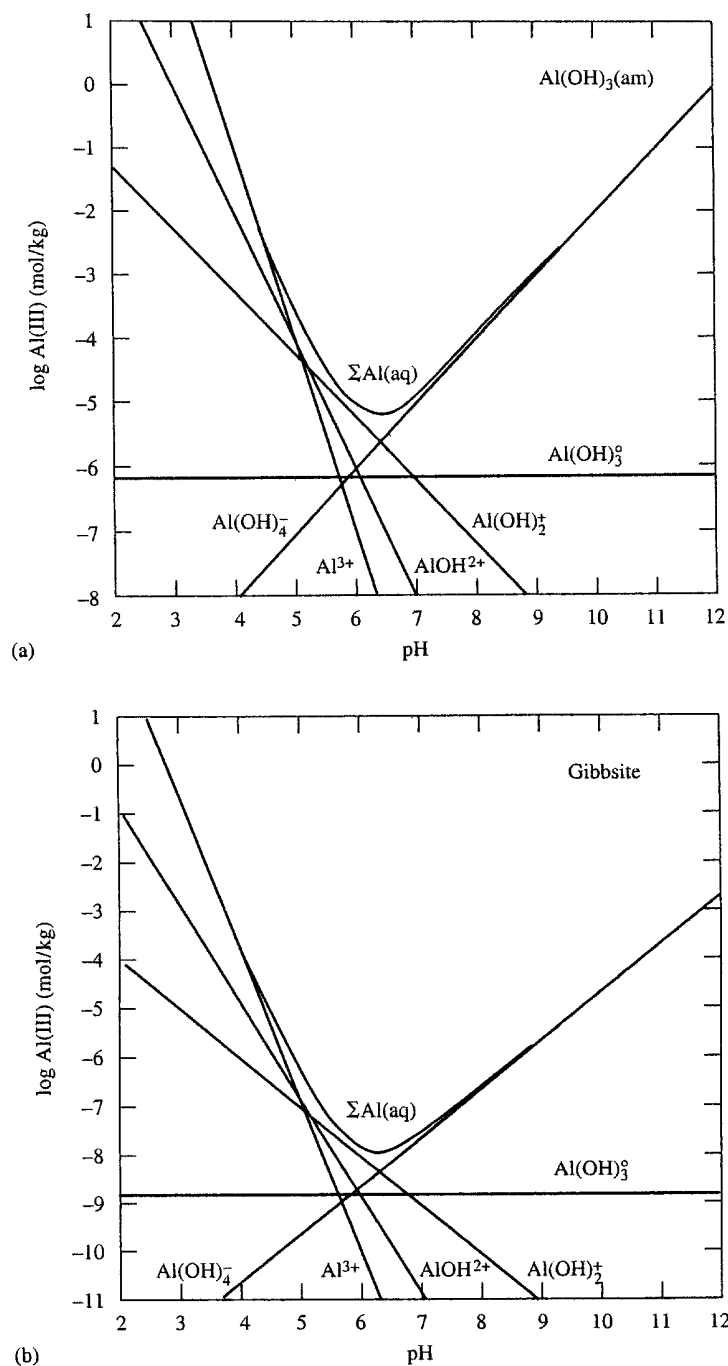
**Figure 15. Eh-pH diagram for the system Fe-O<sub>2</sub>-S-H<sub>2</sub>O at 25° C, showing stability fields of goethite ( $\alpha$ -FeOOH), pyrite (FeS<sub>2</sub>), and monoclinic pyrrhotite (Fe<sub>7</sub>S<sub>8</sub>) for  $\Sigma S(aq) = 10^{-2}$  mol/kg, and total carbonate  $10^{-4}$  mol/kg.  $\Sigma Fe(aq) = 10^{-6}$  and  $10^{-4}$  mol/kg at aqueous/solid boundaries. The diagram shows that dissolved iron occurs chiefly in sulfate complexes. From Barnes and Langmuir, 1979.**

### 6.2.2 Aluminum, Beryllium, Strontium, and Barium

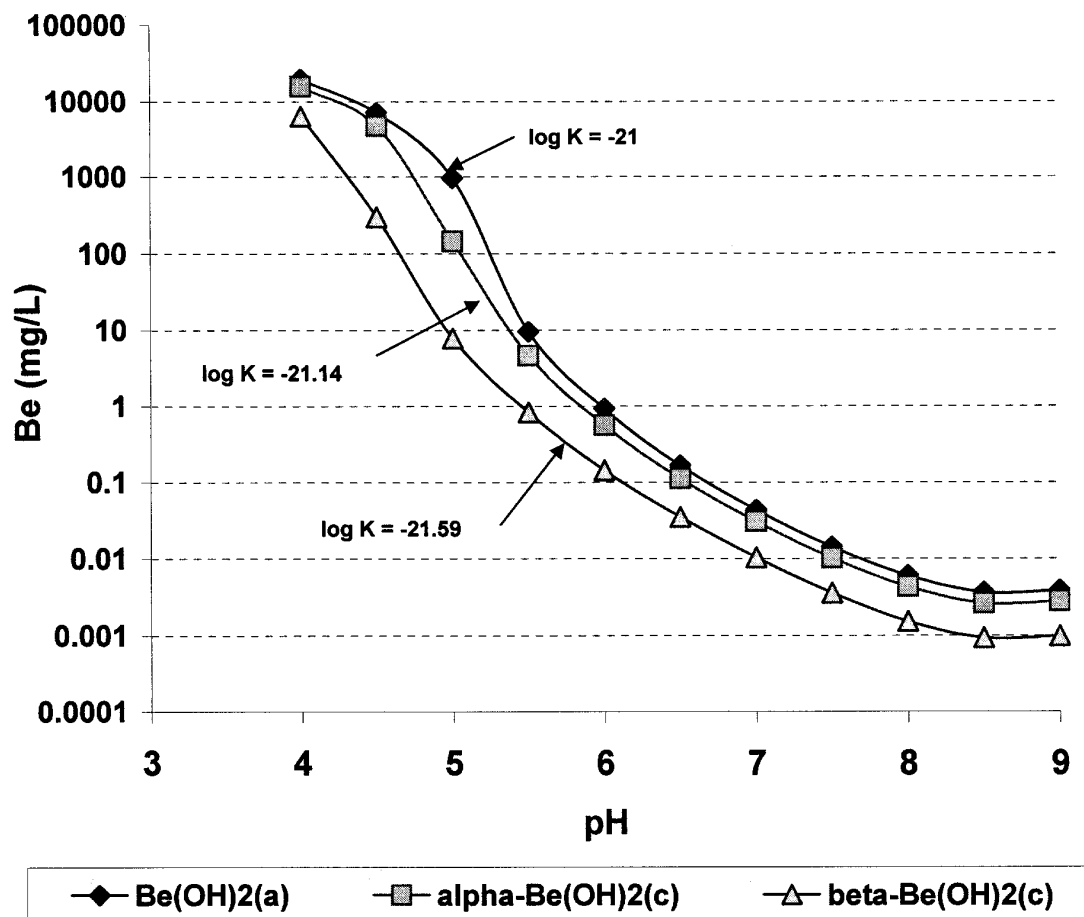
As shown in Table 12, the hard acid cations, Al, Be, Sr, and Ba occur in only one oxidation state. Their least soluble solids (strongest bonds) are formed with hard bases such as  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ . Maximum Al(III) concentrations are generally limited by the solubility of aluminum oxyhydroxide solids. Depending on the degree of crystallinity of  $\text{Al}(\text{OH})_3$ , the maximum dissolved Al concentrations will range between the solubility of gibbsite, the least soluble form, and the solubility of amorphous  $\text{Al}(\text{OH})_3$ , the most soluble form (Figure 16). The solubility of amorphous aluminum hydroxide is about 0.17 mg/L at pH 6.5, and 6 mg/L at pH 5. If the aluminum in soils or water is derived from the leaching of the crystalline gibbsite, its equilibrium concentration is 0.34  $\mu\text{g/L}$  at pH 6.5 and 12  $\mu\text{g/L}$  at pH 5. These calculations suggest that the Al concentration of 0.07 mg/L in average world rivers (Table 4) that have a pH near 7 must be largely in suspension, probably in the colloidal size range (particles less than  $\sim 10^{-5}$  m). Figure 16 also suggests that high Al concentrations in soils—concentrations toxic to many plants—will generally not be found except in acid soils.

It is unclear what solid or solids control maximum beryllium concentrations, but the least soluble Be phases for which there are such data are  $\beta\text{-Be}(\text{OH})_2$  and beryllium silicate ( $\text{Be}_2\text{SiO}_4$ ) (Bodek et al., 1988). The computed solubility of  $\beta\text{-Be}(\text{OH})_2$  decreases from about 7.8 mg/L Be at pH 5 to 1.0  $\mu\text{g/L}$  at pH 9 (Figure 17). The silicate is considerably less soluble, with a solubility of about 7.2  $\mu\text{g/L}$  at pH 5, decreasing to 0.006  $\mu\text{g/L}$  at pH 8–9. These values may be compared to the median Be concentration in surface and ground waters, which is 5  $\mu\text{g/L}$  (Table 1).

The least soluble minerals of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  are strontianite ( $\text{SrCO}_3$ ), celestite ( $\text{SrSO}_4$ ), and barite ( $\text{BaSO}_4$ ). The solubility product of strontianite is  $10^{-9.27}$ , that of celestite is  $10^{-6.63}$ , and for barite  $K_{\text{sp}} = 10^{-9.96}$  (Nordstrom et al., 1990). At a sulfate concentration of 96 mg/L, PHREEQC modeling calculations give a barite solubility of 32  $\mu\text{g/L}$  Ba. This value is not far from the median Ba concentration of 20  $\mu\text{g/L}$  in surface and ground waters (Table 1), suggesting that barite solubility must often limit maximum Ba concentrations in soils and natural waters. Modeling calculations indicate that celestite and strontianite are too soluble to limit Sr concentrations in general, so that strontium is most often limited by coprecipitation with the Ca carbonates or adsorption by clays.



**Figure 16.** Solubility of (a) amorphous  $\text{Al(OH)}_3$ ,  $K_{\text{sp}} = 10^{-31.2}$  and (b) gibbsite ( $\text{Al[OH]}_3$ ),  $K_{\text{sp}} = 10^{-33.9}$ , as a function of pH at 25°C. Also shown are lines indicating the solubility contributions of  $\text{Al}^{3+}$  and individual Al-hydroxy complexes. From Langmuir, 1997a.



**Figure 17. Solubility of three forms of  $\text{Be}(\text{OH})_2$  as a function of pH.** Diagram computed using the geochemical model PHREEQC (Parkhurst and Appelo, 1999).

### **6.2.3 Cadmium, Zinc, Cobalt, Nickel, and Lead**

These metals are classified as either soft or borderline soft. Their metal sulfides are quite insoluble at low Eh, even at low metal and sulfide concentrations (Figures 18 through 23). For example, CdS (greenockite) precipitates and has a large stability field even for Cd = 11  $\mu\text{g/L}$  ( $10^{-7}$  mol/kg) and total sulfur at 0.3 mg/L. The insolubility of the sulfides of Zn, Co, Ni, and Pb is similar. Other important Cd and Zn minerals include their carbonates, although the carbonates are relatively soluble at pH values below 8. Pure metal-containing mineral phases generally do not control the dissolved concentrations of Cd, Ni, or Zn in aerobic soils. These metals are more often controlled through adsorption or coprecipitation by oxyhydroxides of iron, manganese, and aluminum.

Lead is relatively immobile in soils, sediments, and ground waters. This reflects its strong tendency to be adsorbed by Fe and Mn oxides, but also the insolubility of a number of lead minerals including lead hydroxycarbonate (Figure 22), which limits lead concentrations in some public water systems, and pyromorphite (Figure 23), which controls lead concentrations in some soils adjacent to highways affected by road salt and leaded gasoline exhaust.

### **6.2.4 Manganese**

Unlike the other metals of concern, in most cases except aluminum, manganese is often precipitated in soils and sediments as manganese minerals. Environmentally, the most important of these minerals are the Mn(III/IV) oxides. Figure 24 shows that these phases are stable and relatively insoluble in oxidized systems above pH 6–7. The Mn oxides are often stronger sorbents of trace metals than is HFO. Suarez and Langmuir (1975) found that most of the Co, Ni, Cu, Zn, Pb, Ag, and Cd in a Pennsylvania soil were associated with Mn and Fe oxides. The Mn oxides held the highest metal amounts relative to their abundance. Rhodochrosite is an important Mn mineral, but only under reducing conditions. Manganese does form a sulfide, but it has a small stability field and is a rare mineral.

### **6.2.5 Silver, Copper, and Mercury**

Eh-pH diagrams for these metals are shown in Figures 25 through 27. As soft metals, silver and mercury form strong complexes with borderline soft Cl ion, which may dominate the solution chemistry of these metals. Silver and mercury form even stronger complexes with the soft halogens bromide and iodide. Silver, copper, and mercury are highly insoluble in reduced environments, where they precipitate as metals or as sulfides. In the absence of ligands other than OH<sup>-</sup> and depending on the copper concentration, the solubility of copper above pH 7–8 can be very low, due to the precipitation of tenorite (CuO). Moreover, in the presence of abundant carbonate, relatively insoluble Cu<sup>2+</sup> carbonate minerals can precipitate.

Bodek et al. (1988) offer a useful summary of the behavior of mercury. Hg(II) is usually complexed—in pure water as Hg(OH)<sub>2</sub><sup>0</sup>, and at chloride concentrations typical of fresh waters



(<10<sup>-2</sup> mol/kg) as HgCl<sub>2</sub><sup>o</sup>. Both Hg(II) and Cu(II) form strong humate complexes, so that in soils >99.9% of the metals may be complexed.

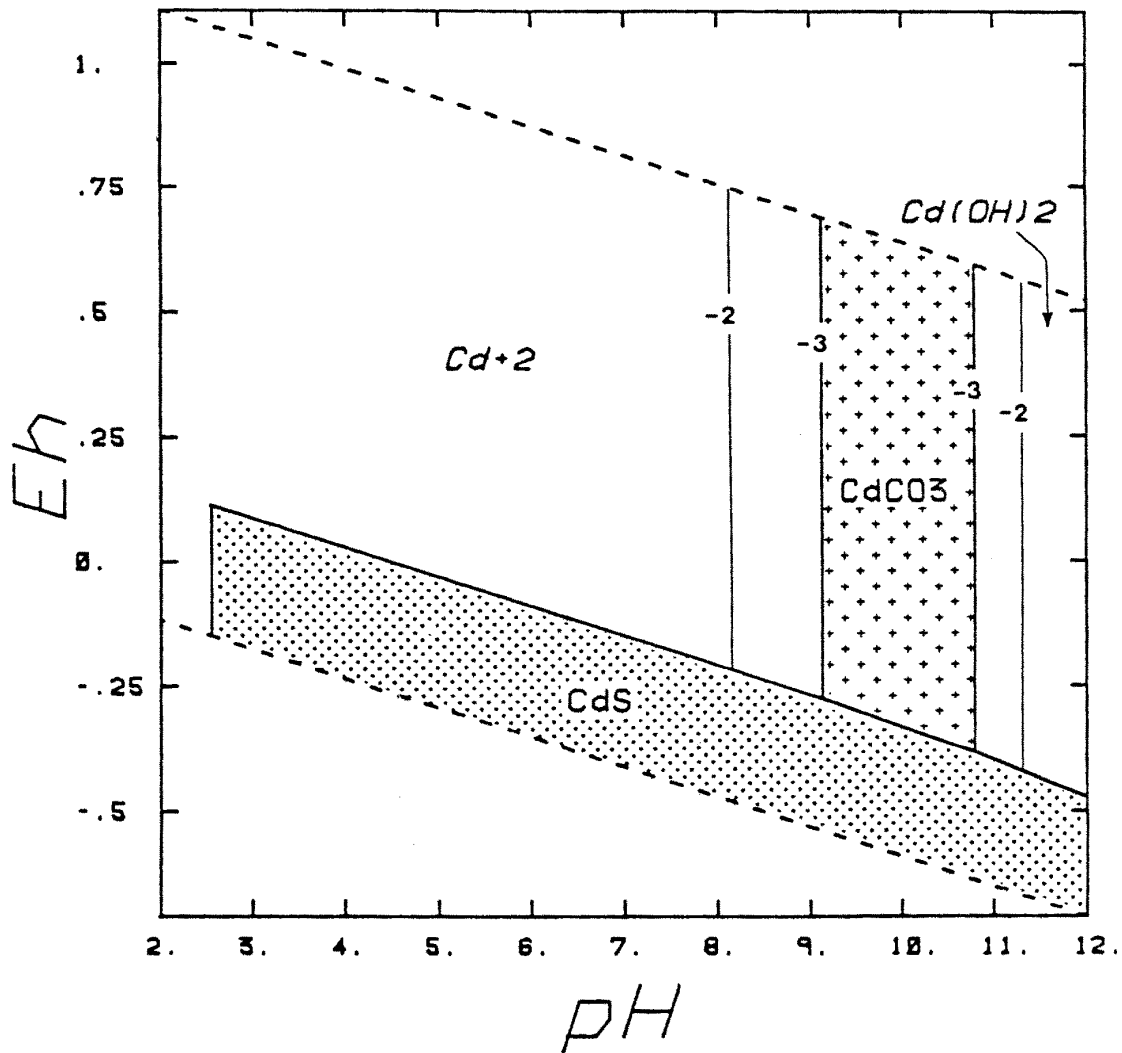


Figure 18. Eh-pH diagram for the system Cd-O<sub>2</sub>-CO<sub>2</sub>-S-H<sub>2</sub>O for  $\Sigma\text{Cd} = 10^{-7}$  mol/kg,  $\Sigma\text{S} = 10^{-5}$  mol/kg, and total carbonate  $10^{-2}$  and  $10^{-3}$  mol/kg. From Barnes and Langmuir, 1978.

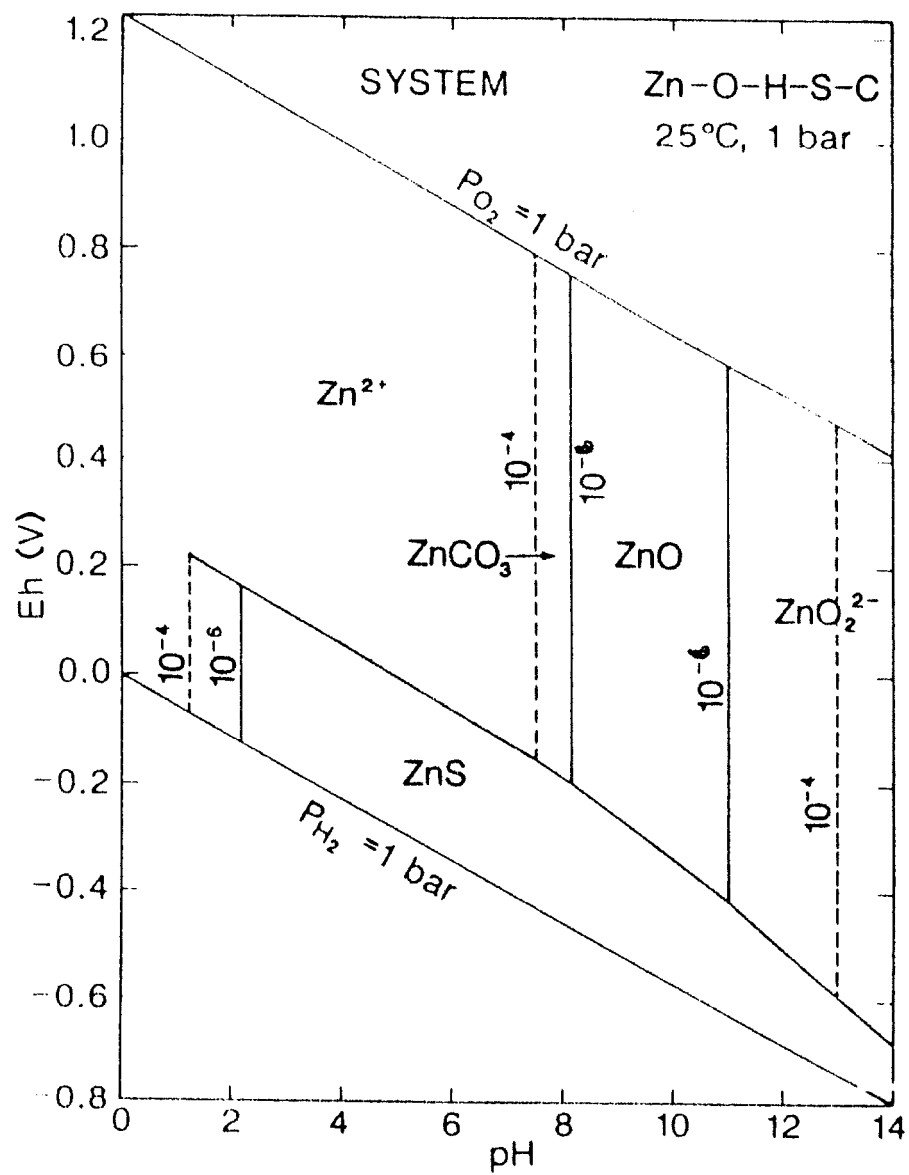


Figure 19. Eh-pH diagram for the system Zn-O<sub>2</sub>-CO<sub>2</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma Zn = 10^{-6}$  and  $10^{-4}$  mol/kg,  $\Sigma C = 10^{-3}$  mol/kg, and  $\Sigma S = 10^{-3}$  mol/kg. After Brookins, 1988.

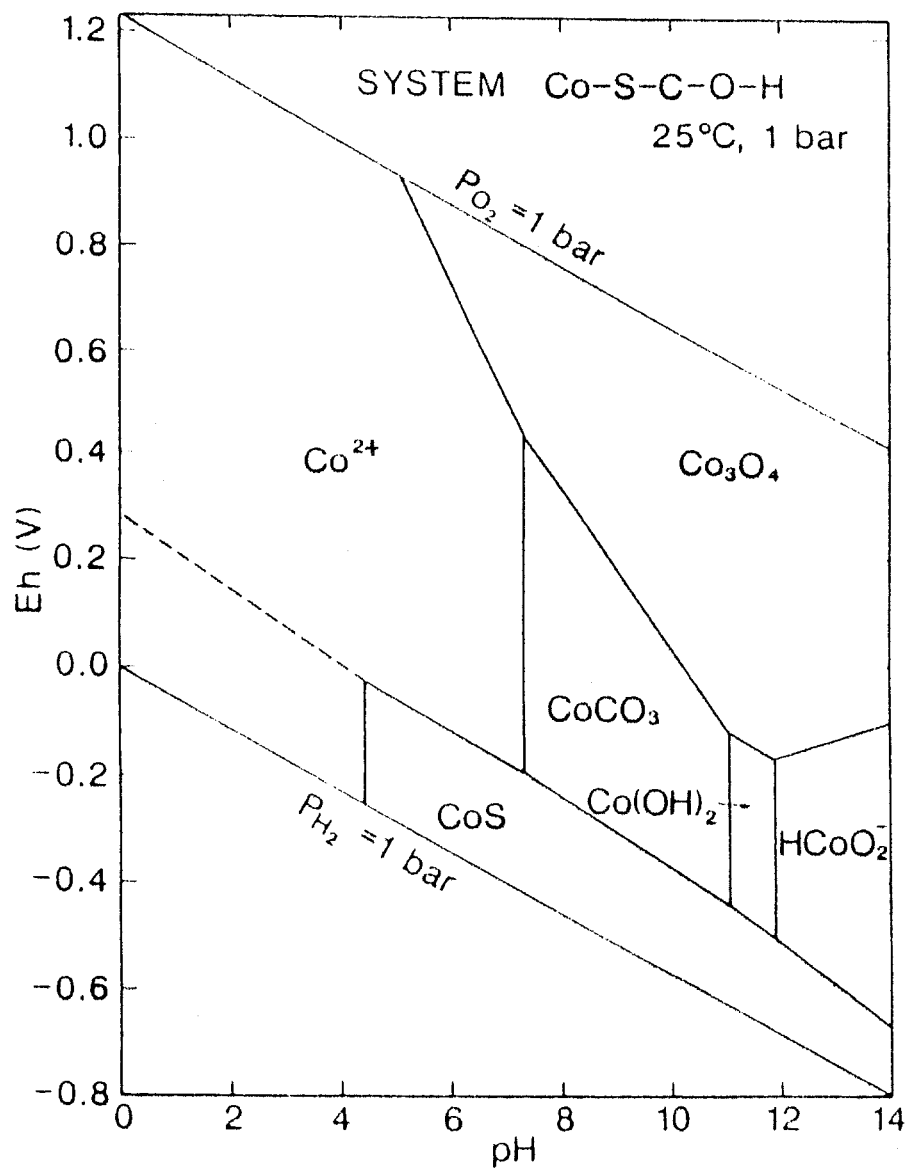


Figure 20. Eh-pH diagram for the system Co-O<sub>2</sub>-CO<sub>2</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma Co = 10^{-6}$  mol/kg,  $\Sigma C = 10^{-3}$  mol/kg, and  $\Sigma S = 10^{-3}$  mol/kg. After Brookins, 1988.

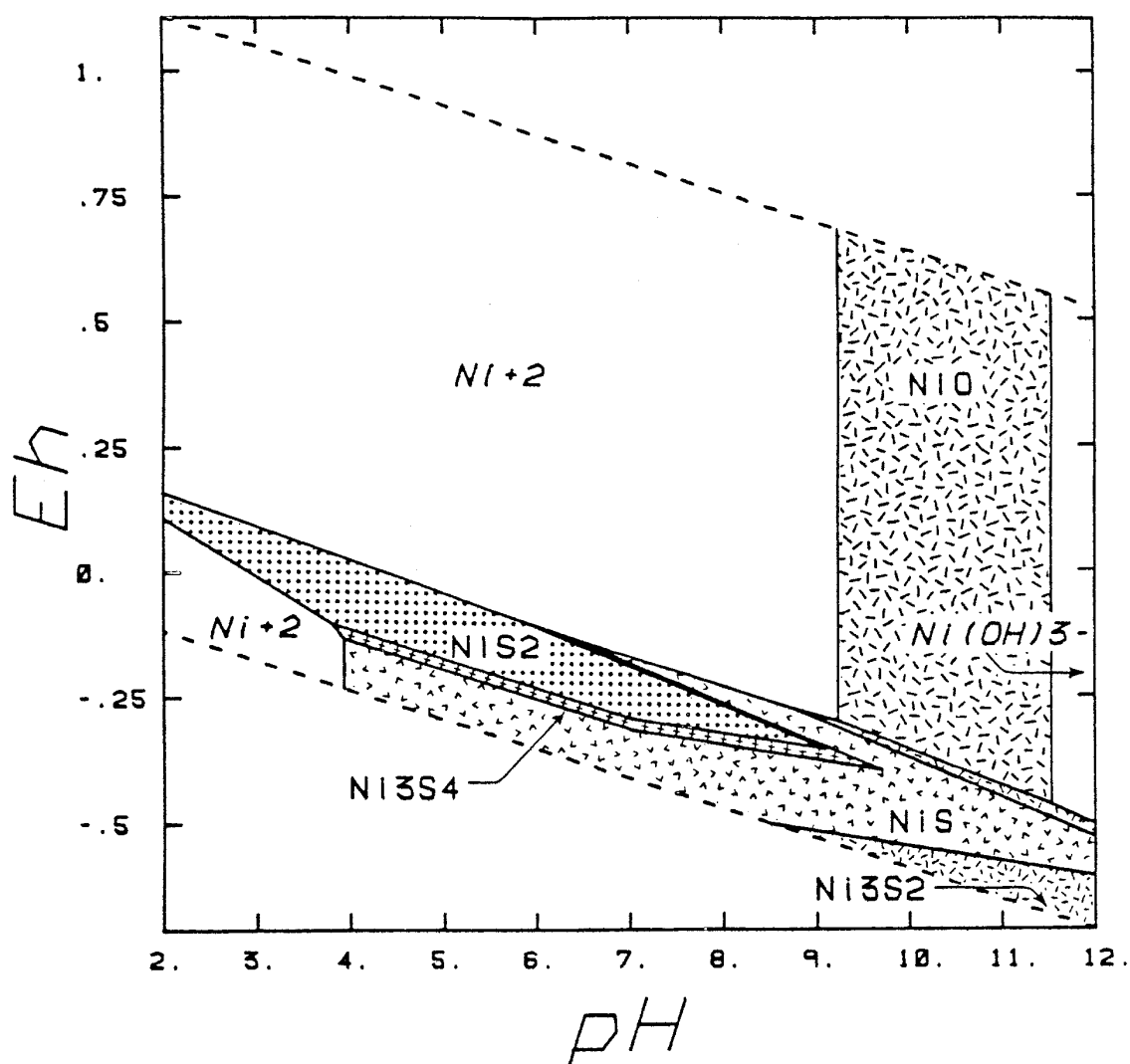


Figure 21. Eh-pH diagram for the system Ni-O<sub>2</sub>-CO<sub>2</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma\text{Ni} = 10^{-6}$  mol/kg and  $\Sigma\text{S} = 10^{-5}$  mol/kg. After Barnes and Langmuir, 1978.

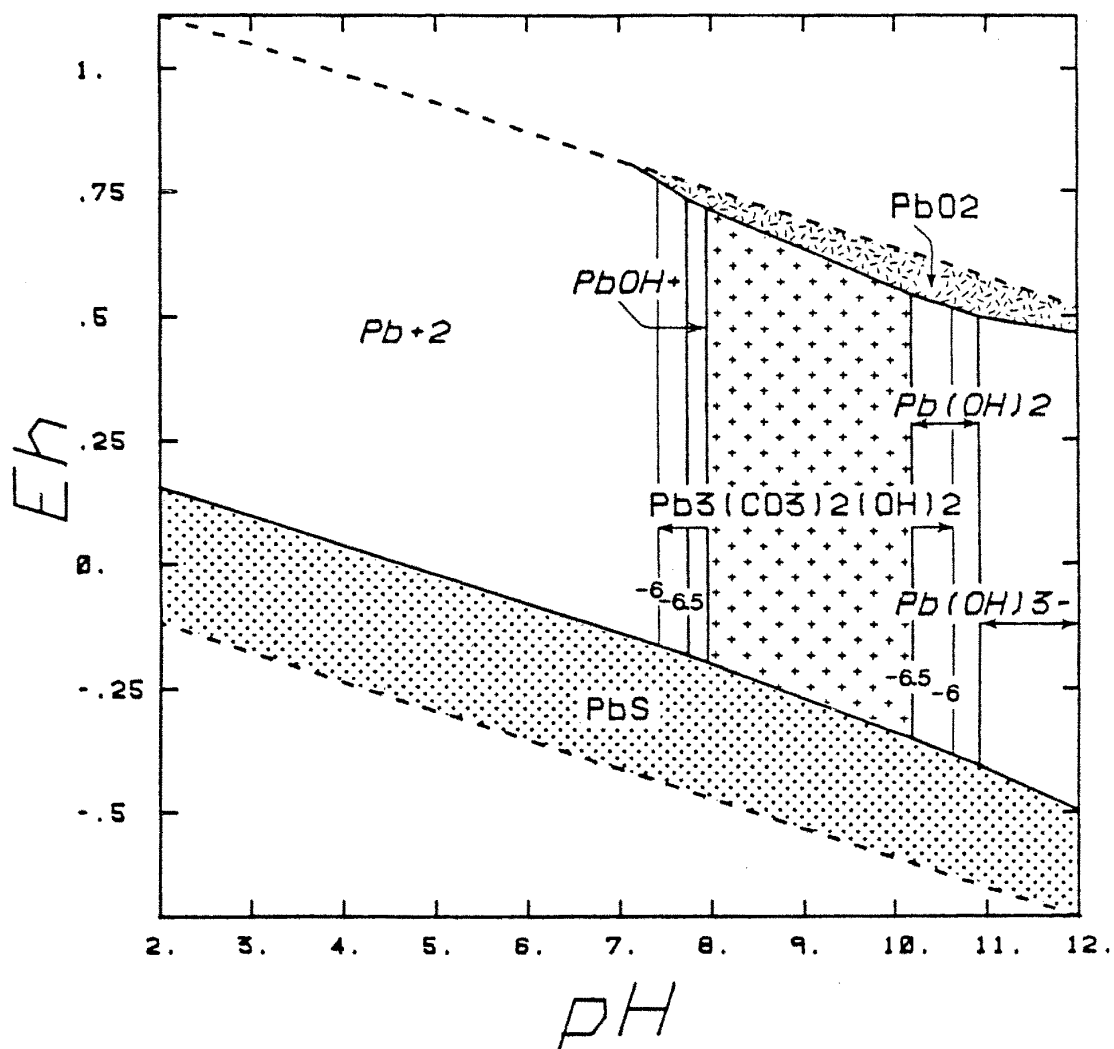


Figure 22. Eh-pH diagram for the system  $\text{Pb-O}_2\text{-CO}_2\text{-S-H}_2\text{O}$ , assuming that  $\Sigma\text{Pb} = 10^{-6}$  and  $10^{-6.5}$  mol/kg,  $\Sigma\text{C} = 10^{-4}$  mol/kg, and  $\Sigma\text{S} = 10^{-5}$  mol/kg. Diagram shows the stability fields of lead hydroxycarbonate and galena (PbS). After Barnes and Langmuir, 1978.

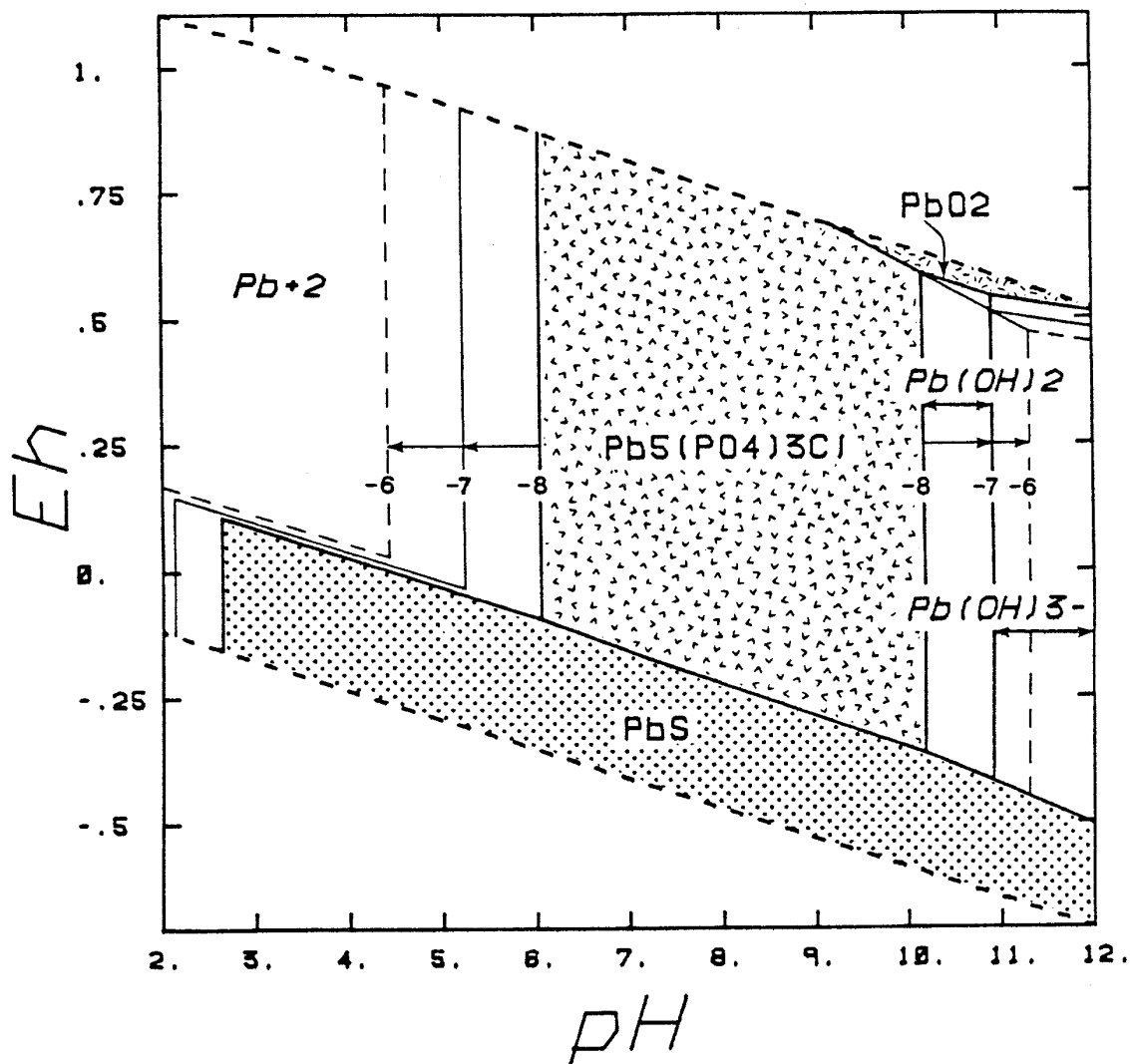


Figure 23. Eh-pH diagram for the system Pb-O<sub>2</sub>-PO<sub>4</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma\text{Pb} = 10^{-8}$ ,  $10^{-7}$ , and  $10^{-6}$  mol/kg at solid/liquid boundaries;  $\Sigma\text{S} = 10^{-5}$  mol/kg; and  $\Sigma\text{PO}_4 = 10^{-6}$  mol/kg. Diagram shows the stability fields of the lead phosphate, pyromorphite, and galena (PbS). After Barnes and Langmuir, 1978.

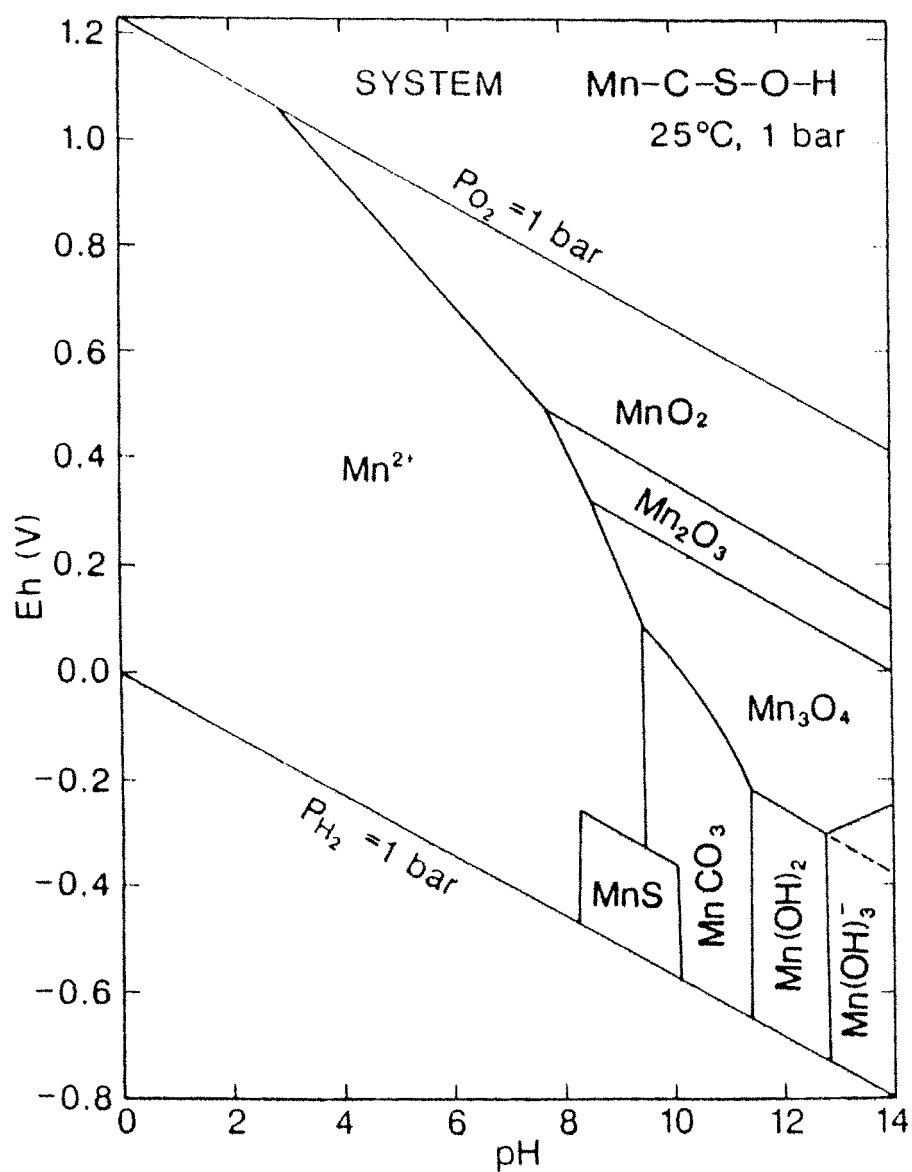


Figure 24. Eh-pH diagram for the system Mn-O<sub>2</sub>-CO<sub>2</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma Mn = 10^{-6}$  mol/kg,  $\Sigma C = 10^{-3}$  mol/kg, and  $\Sigma S = 10^{-3}$  mol/kg. MnS is the very rare mineral alabandite. After Brookins, 1988.

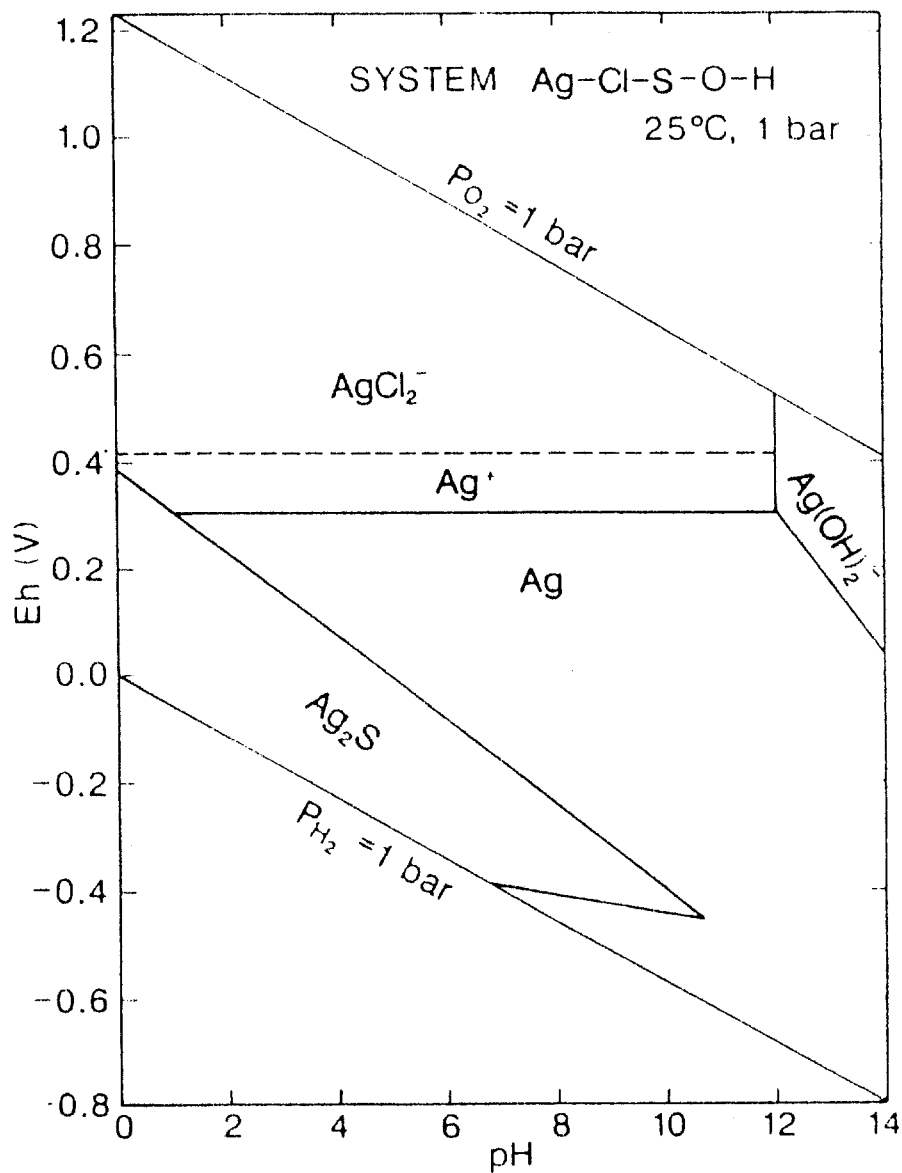
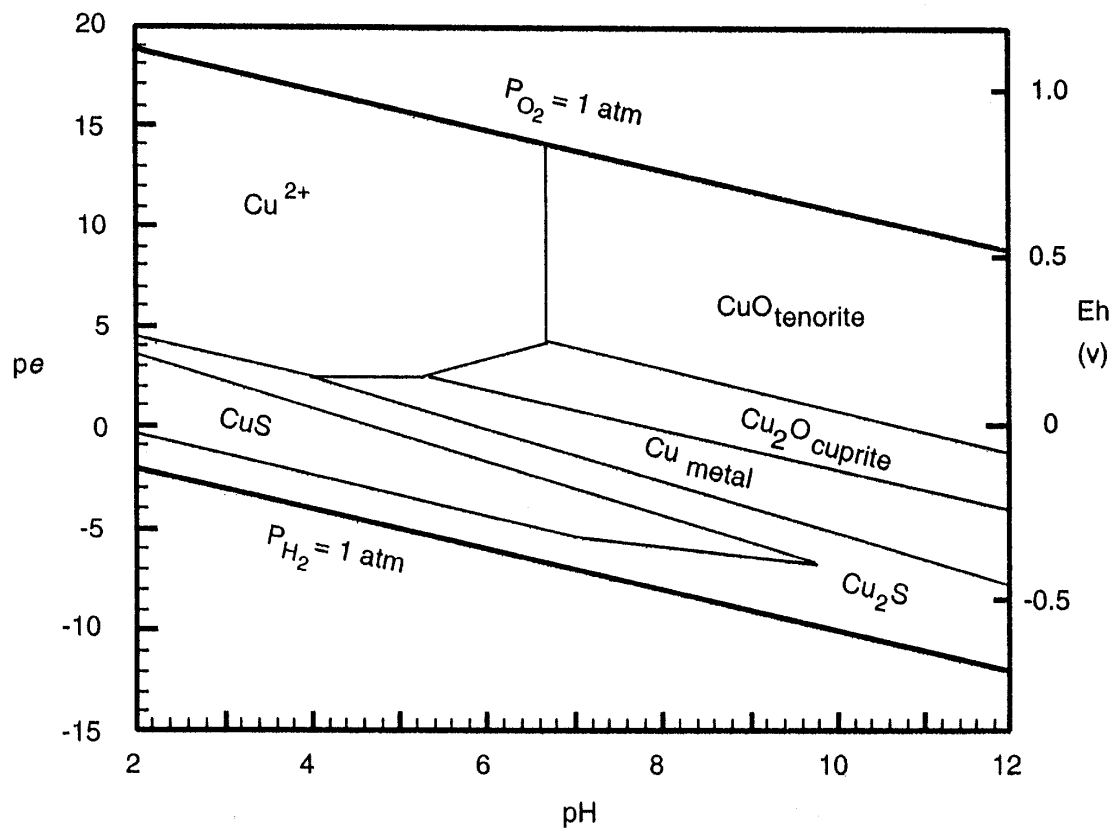


Figure 25. Eh-pH diagram for the system Ag-O<sub>2</sub>-Cl-S-H<sub>2</sub>O, assuming that  $\Sigma Ag = 10^{-8}$  mol/kg,  $\Sigma Cl = 10^{-3.5}$  mol/kg, and  $\Sigma S = 10^{-3}$  mol/kg. Diagram shows the importance of Ag chloride complexing and the large stability field for metallic silver. After Brookins, 1988.





**Figure 26. Eh-pH diagram for the system Cu-O<sub>2</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma\text{Cu} = 10^{-6}$  mol/kg and  $\Sigma\text{S} = 10^{-2}$  mol/kg. After Drever, 1997.**

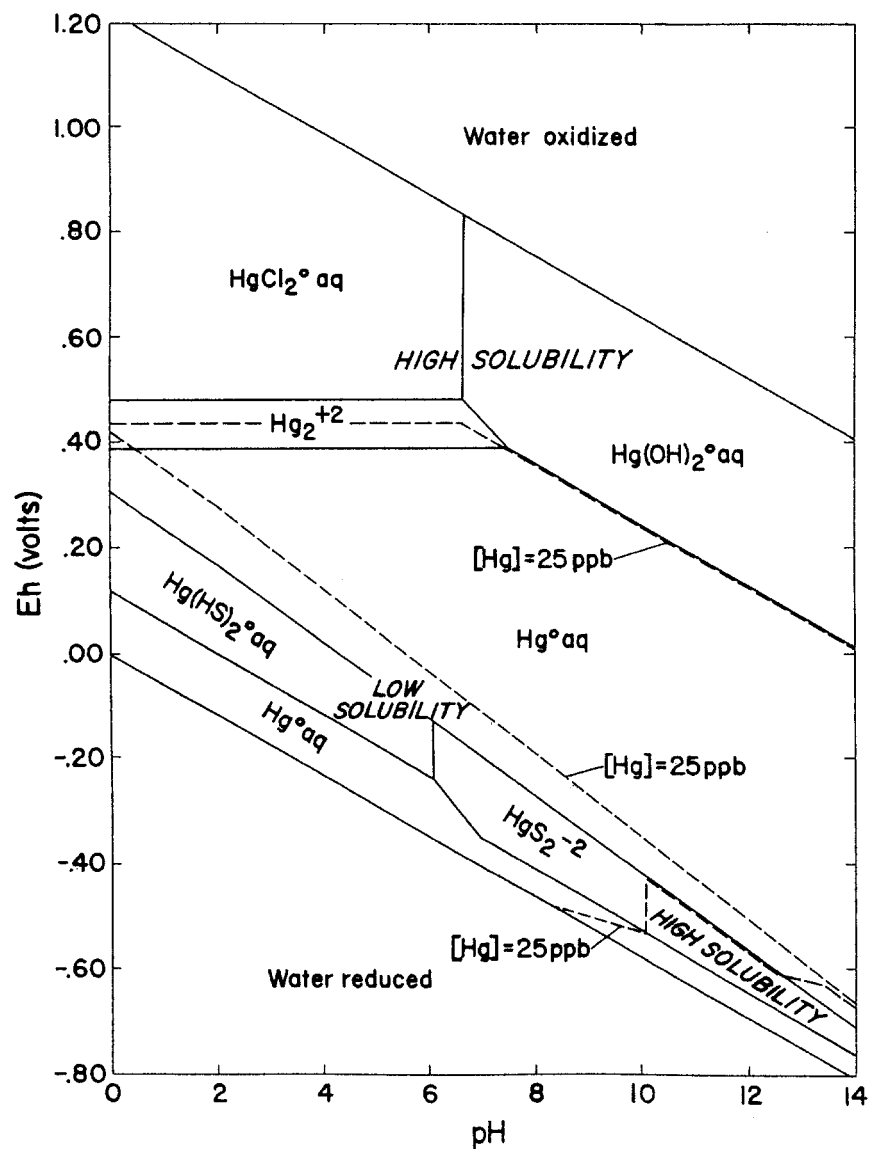


Figure 27. Eh-pH diagram for the system Hg-O<sub>2</sub>-Cl-S-H<sub>2</sub>O, assuming that  $\Sigma\text{Hg} = 10^{-6.9}$  mol/kg,  $\Sigma\text{Cl} = 10^{-3}$  mol/kg, and  $\Sigma\text{S} = 10^{-3}$  mol/kg. Diagram shows the importance of Hg-Cl complexing. After Bodek et al., 1988.

Mercury is biologically methylated only in environments low in sulfide. The observed decreases in biological methylation at high sulfide concentrations are generally attributed to the precipitation of  $\text{HgS(s)}$ . Alternatively, Benoit et al. (1999, 2001) have suggested that the reduction of biological methylation at high sulfide concentrations is associated with a decrease in Hg uptake by sulfide-reducing bacteria, due to decreases in the concentrations of the neutral complex  $\text{HgS}^0$ . The stable methyl mercury species in fresh waters is  $\text{CH}_3\text{HgOH}$ . The methyl mercury cation,  $\text{CH}_3\text{Hg}^+$ , complexes with ligands containing C, P, O, N, and the halogens, and forms very stable complexes with sulfur-containing ligands. In oxidized fresh waters, the  $\text{Hg(II)}$  methyl hydroxo and methyl chloro complexes predominate.

Mercury and copper are strongly adsorbed by organic matter. All three metals are also strongly adsorbed by  $\text{Fe(III)}$  and Mn oxides, and secondarily by clays. Sorption of mercury is very fast and practically irreversible (Bodek et al., 1988). By inhibiting mercury sorption,  $\text{Hg-Cl}$  complexing helps to mobilize the metal. Dimethyl mercury is very insoluble in water and tends to be volatilized from soils.

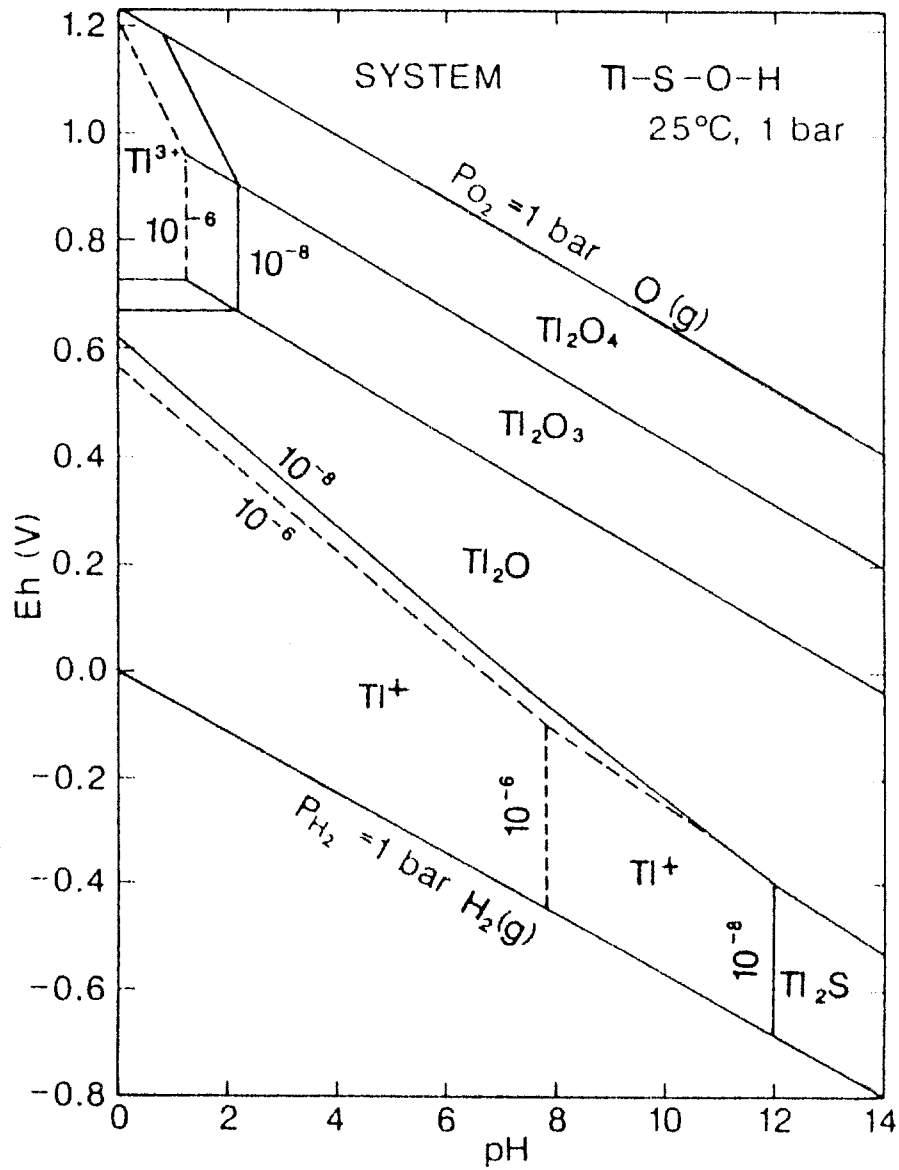
### 6.2.6 *Thallium*

In oxidizing environments, dissolved thallium is limited to concentrations of less than  $2\text{ }\mu\text{g/L}$  ( $10^{-8}\text{ mol/L}$ ) by the low solubilities of the thallium 4+, 3+ and 2+ oxides (Fig. 29). The solubility product of  $\text{Tl(OH)}_3$ , which should be more soluble than  $\text{Tl}_2\text{O}_3$  in Figure 28, is  $10^{-45.2}$ , which makes this phase highly insoluble between pH 4 and 10. Only in highly reducing systems as  $\text{Tl}^+$  is the metal soluble.  $\text{Tl}^+$  is a weak complex former. The sulfide of  $\text{Tl}^+$  is stable only above pH 12. Limited data indicate that Tl is strongly adsorbed by montmorillonite clays and manganese oxides (Bodek et al., 1988).

### 6.2.7 *Arsenic, Antimony, Chromium, Molybdenum, Selenium, and Vanadium*

These six elements occur chiefly as oxyanions in oxidizing environments. As such they are relatively mobile, although they are adsorbed by ferrihydrite under acid to neutral conditions. Consistent with Figure 6, on a number of different sorbent phases, the decreasing order of adsorption is usually  $\text{As} > \text{Cr} \geq \text{Mo} \geq \text{Se} \approx \text{S}$  (Bodek et al., 1988). Arsenic and phosphorus chemistry are similar under oxidizing but not reducing conditions. Figure 29 shows the stability fields of dissolved  $\text{As(V)}$  and  $\text{As(III)}$  species in pure water. With the addition of sulfur, insoluble As sulfide minerals are precipitated at low Eh (Figure 30) in the field otherwise occupied by arsenious acid species.

As suggested by the absence of a solid phase field in Figure 31, antimony may be too soluble for its concentration to be limited by mineral precipitation. The least soluble Sb phase is probably  $\text{Sb(OH)}_3$ , which does not precipitate until  $\Sigma\text{Sb}$  concentrations exceed about  $10^{-6.67}\text{ mol/kg}$ , or  $26\text{ }\mu\text{g/L}$  (Barnes and Langmuir, 1978). Antimony is a weak complex former, except for its reaction with sulfur at low Eh to form sulfide complexes.



**Figure 28. Eh-pH diagram for the system  $\text{Tl-O}_2\text{-S-H}_2\text{O}$ , assuming that  $\Sigma\text{Tl} = 10^{-8}$  and  $10^{-6}$  mol/kg and  $\Sigma\text{S} = 10^{-3}$  mol/kg.** The diagram shows the insolubility of the higher-valent Tl oxides under oxidizing conditions. After Brookins, 1988.

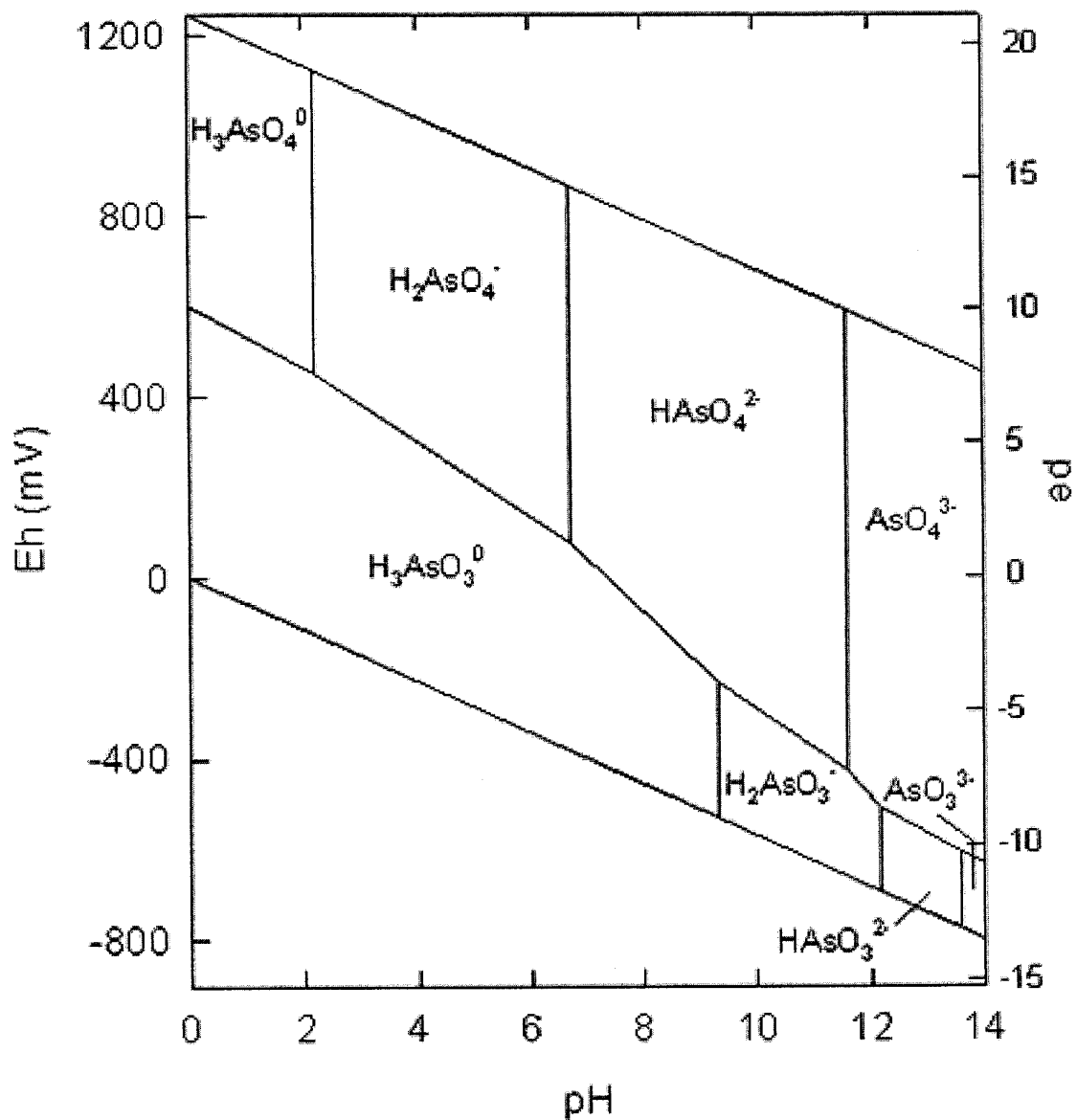
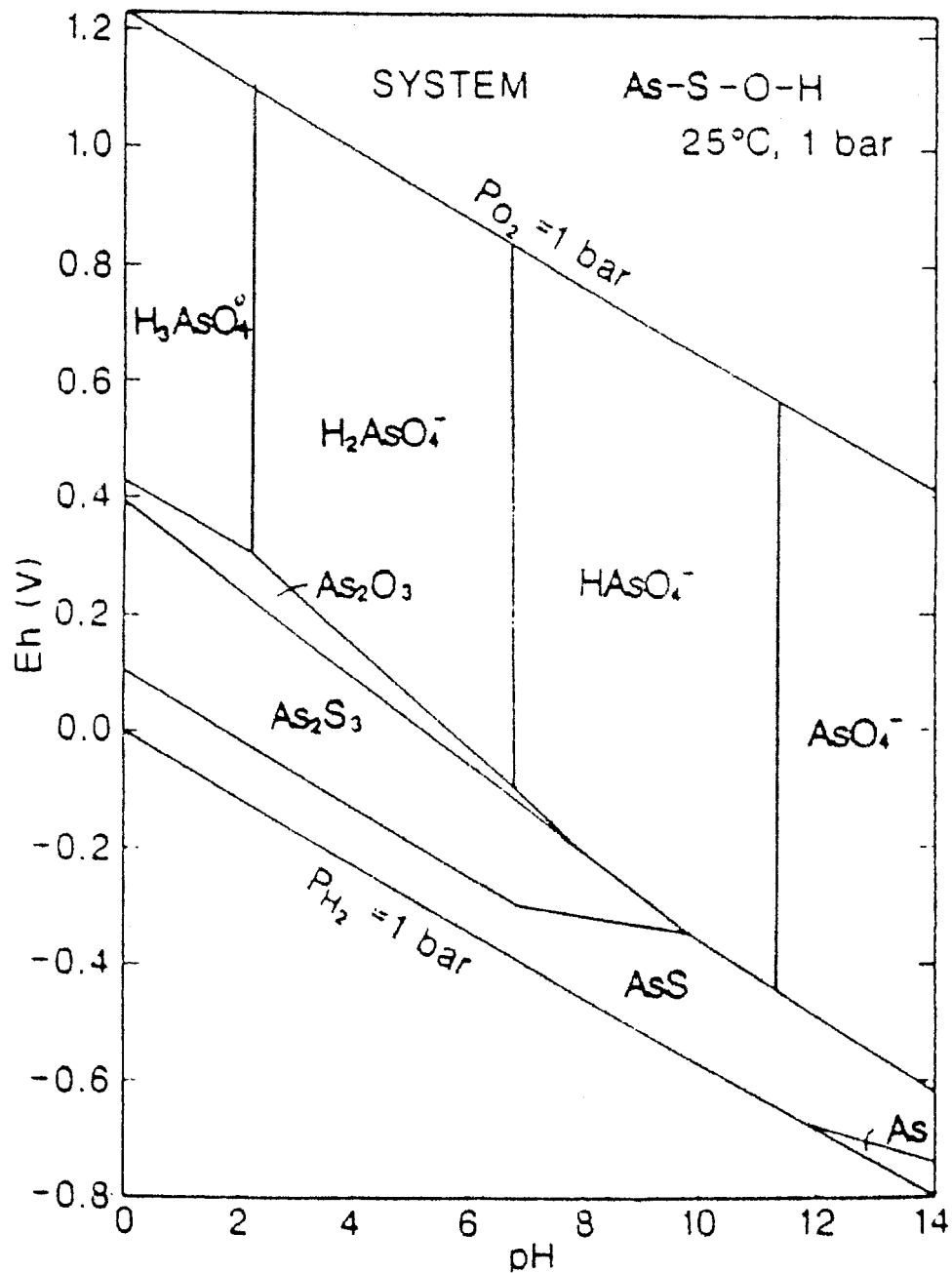


Figure 29. Eh-pH diagram for the system  $\text{As-O}_2\text{-H}_2\text{O}$  showing the relative stabilities of arsenate (arsenic acid, As[V]) and arsenite (arsenious acid, As[III]) species under oxidizing and reducing conditions.



**Figure 30. Eh-pH diagram for the system As-O<sub>2</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma As = 10^{-6}$  mol/kg and  $\Sigma S = 10^{-3}$  mol/kg.** The diagram shows that in the presence of reduced S, the As sulfides control As solubility and take over the stability field of dissolved As(III) species in Figure 25. After Brookins, 1988.

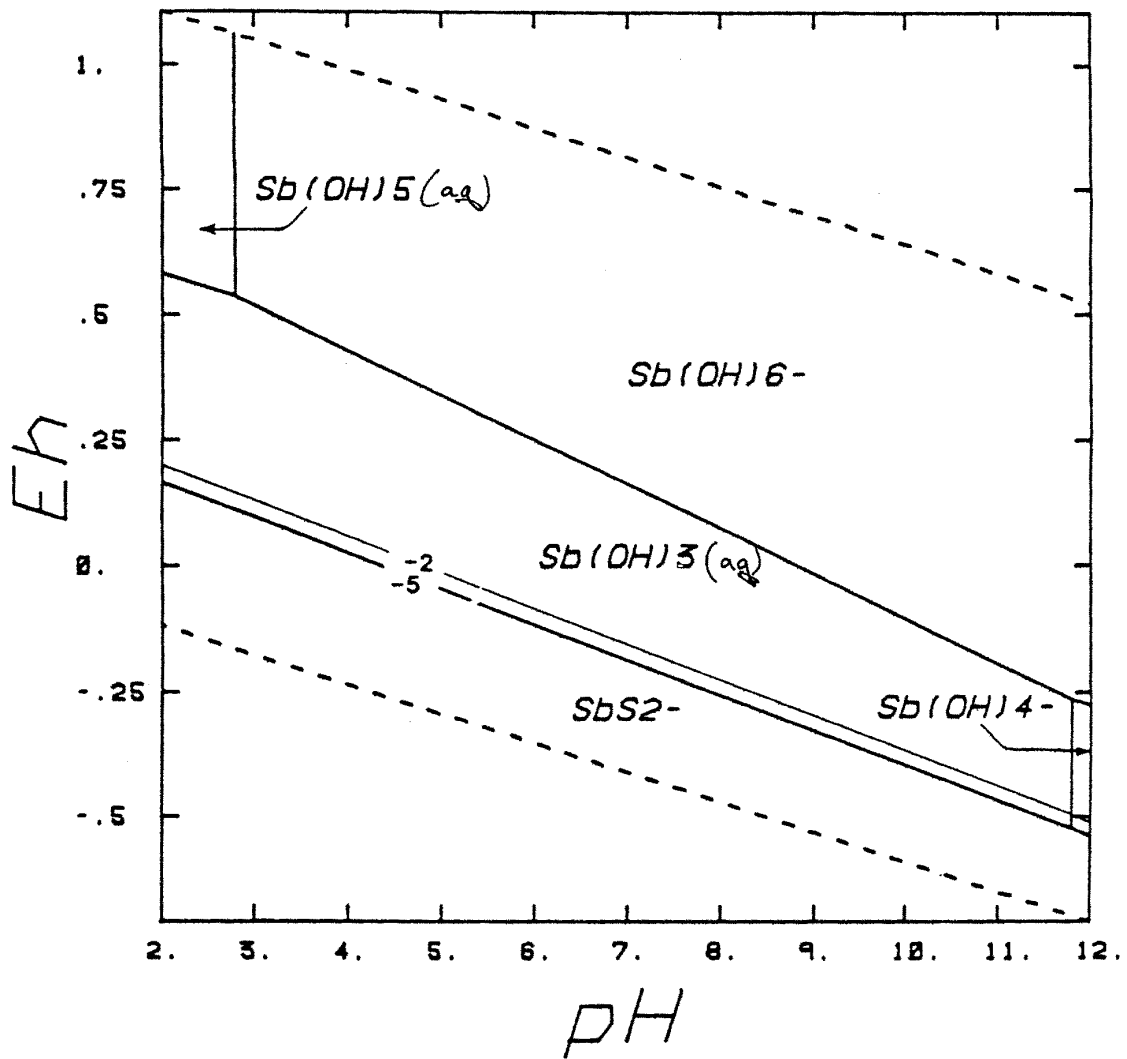


Figure 31. Eh-pH diagram for the system Sb-O<sub>2</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma\text{Sb} = 10^{-8}$  mol/kg and  $\Sigma\text{S} = 10^{-2}$  and  $10^{-5}$  mol/kg. After Barnes and Langmuir, 1978.

Chromate (Cr[VI]) species (Figure 32) predominate and are highly mobile in oxidized systems, except for their tendency to be adsorbed, particularly by Fe(III) and Mn oxides below pH 8. Chromate is in general weakly complexed. In contrast, Cr(III), which dominates in reducing environments, is a strong, hard-acid substance that readily forms complexes. Cr(III) complexes with hydroxyl, sulfate, organic ligands, and other species, which increases its stability and thus raises the Cr(III)/Cr<sub>2</sub>O<sub>3</sub> boundary to higher pH values. This increases the solubility of Cr<sub>2</sub>O<sub>3</sub>. Organic matter, Fe<sup>2+</sup>, and H<sub>2</sub>S can reduce Cr(VI) to Cr(III). Manganese oxides in soil can adsorb Cr(III) and oxidize it to Cr(VI). As shown in Figure 6, adsorption of chromate by HFO decreases with increasing pH, whereas Cr(III) adsorption increases as the pH rises.

Molybdate is highly mobile in oxidized environments (Figure 33), except for its tendency to be adsorbed by Fe(III) oxides below pH 7. Also under acid conditions, in soils and waters high in Fe(III), molybdate may precipitate as ferrimolybdite (Fe<sub>2</sub>[MoO<sub>4</sub>]<sub>3</sub>[s]), which is stable up to pH 5 for  $\Sigma\text{Fe(III)} = \Sigma\text{Mo} = 10^{-6}$  mol/kg (Barnes and Langmuir, 1978). Under reducing conditions, Mo is immobilized by the low solubility of the Mo oxides and MoS<sub>2</sub>.

The redox behavior of selenium (Figure 34) is similar to that of sulfur (Figure 14) in that (1) Se(VI) oxyanions predominate under oxidizing conditions, (2) the element has a stability field under reducing conditions, and (3) metal cations react with Se(2-) to form insoluble selenides. Selenate is highly stable and not readily reduced by H<sub>2</sub>S or Fe<sup>2+</sup>. The very low solubility of native Se indicates that it is an important sink for dissolved Se in reducing environments. Se(2-) forms very insoluble metal selenides with the following -log K<sub>sp</sub> values: 26.0 (FeSe), 60.8 (Cu<sub>2</sub>Se), 48.1 (CuSe), 29.4 (ZnSe), 35.2 (CdSe), 64.5 (HgSe), and 42.1 (PbSe) (Bodek et al., 1988).

Selenite salts are less soluble than selenate salts. Selenite and selenate are both strongly adsorbed by the Fe and Al oxyhydroxides. Phosphate and sulfate effectively compete with selenite and selenate for sorption sites on Fe oxides.

Like chromium, vanadium occurs as an oxyanion at high Eh values and in cationic form under reducing conditions (Figure 35). Vanadate probably forms an insoluble precipitate with Fe(III) below pH 7, although the evidence is limited. The V(III) and Fe(III) oxides are isostructural, suggesting that V(III) may substitute for Fe(III) in the iron oxides (Rai and Zachara, 1984). A problem with this idea is the low Eh stability of V(III) versus the higher Eh stability of the Fe(III) oxides. In soils, the distribution of V closely follows that of secondary Fe(III) oxides, probably because of V adsorption by the oxides. Vanadium is readily reduced and mobilized by soil organic matter, even under oxidizing conditions.



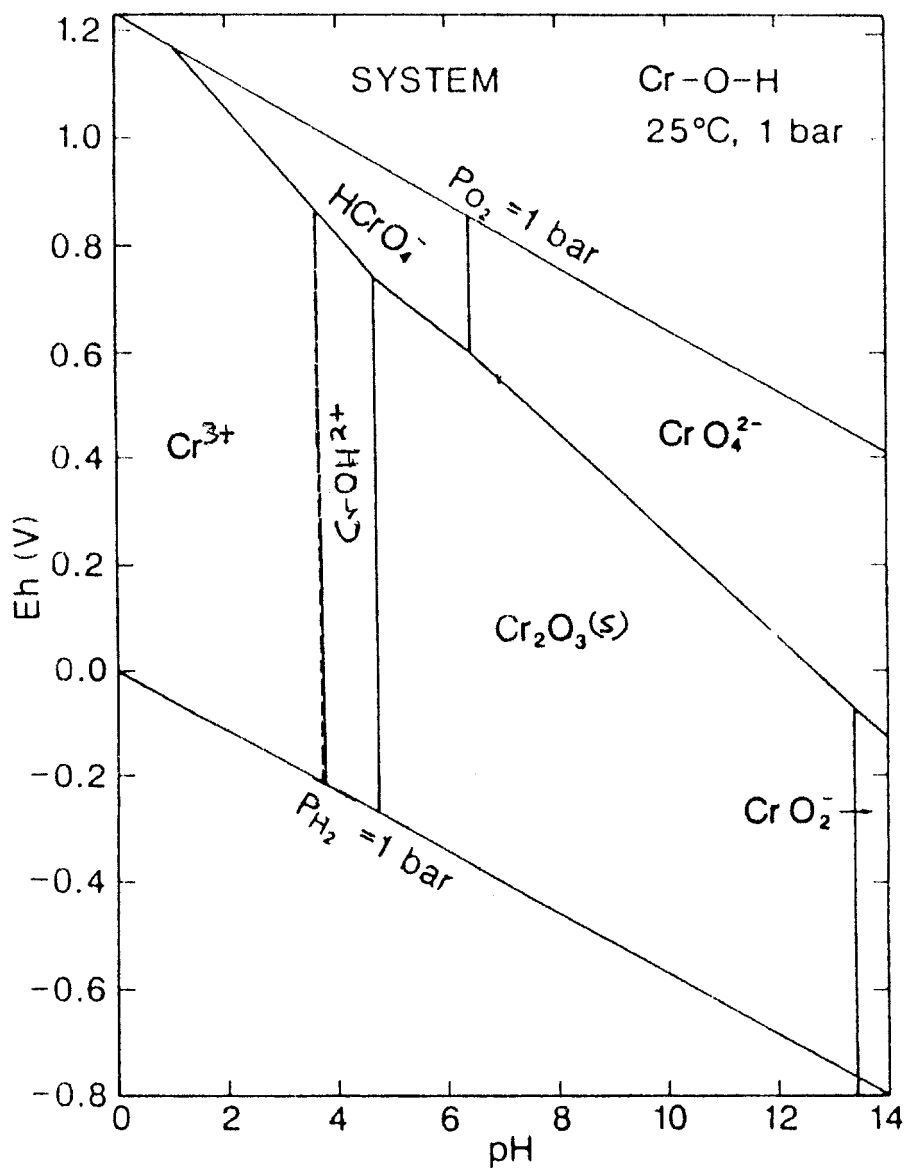


Figure 32. Eh-pH diagram for the system Cr-O<sub>2</sub>-H<sub>2</sub>O, assuming that the concentration of  $\Sigma\text{Cr} = 10^{-6} \text{ mol/kg}$  at solid/liquid boundaries. After Brookins, 1988.

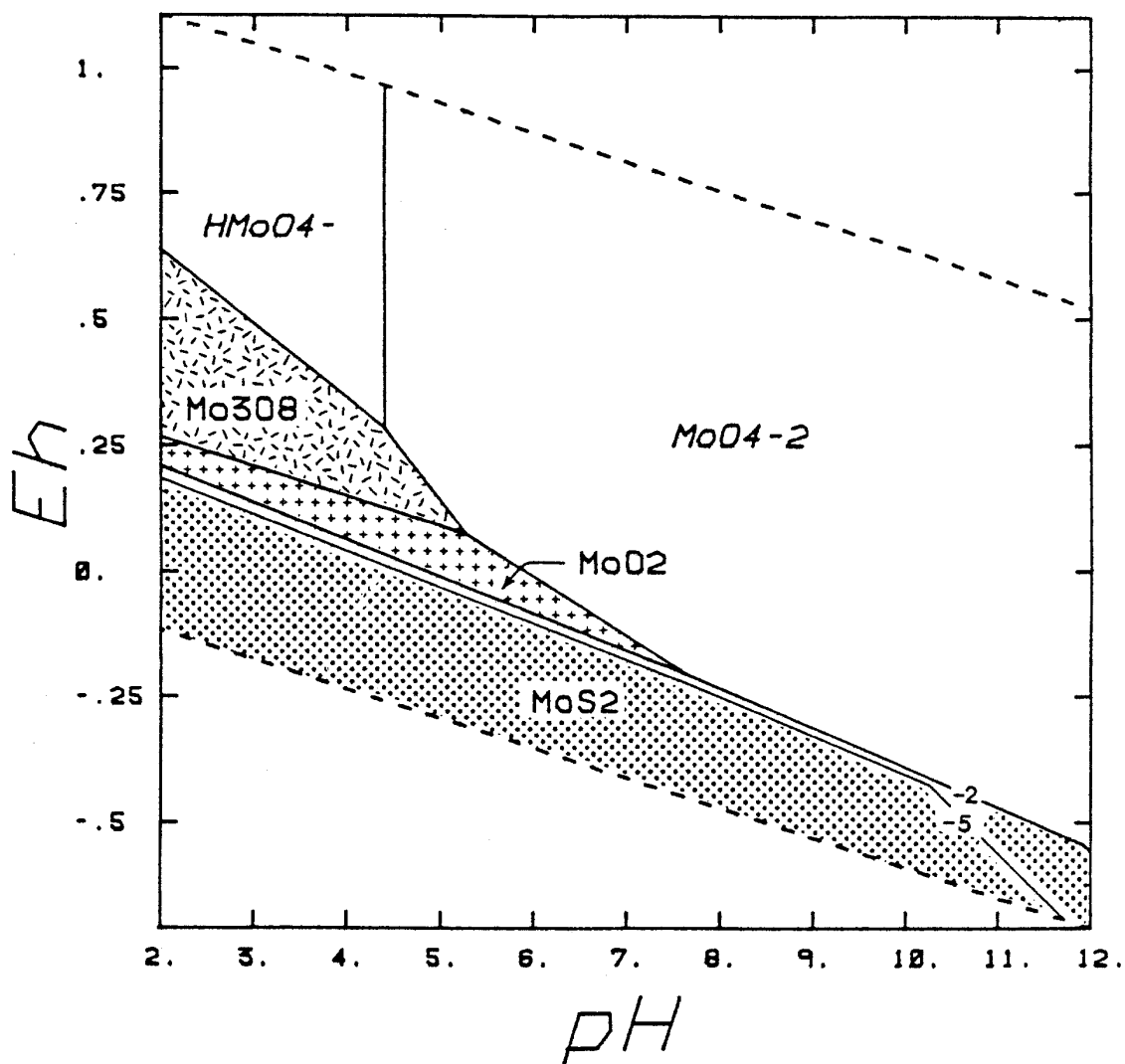
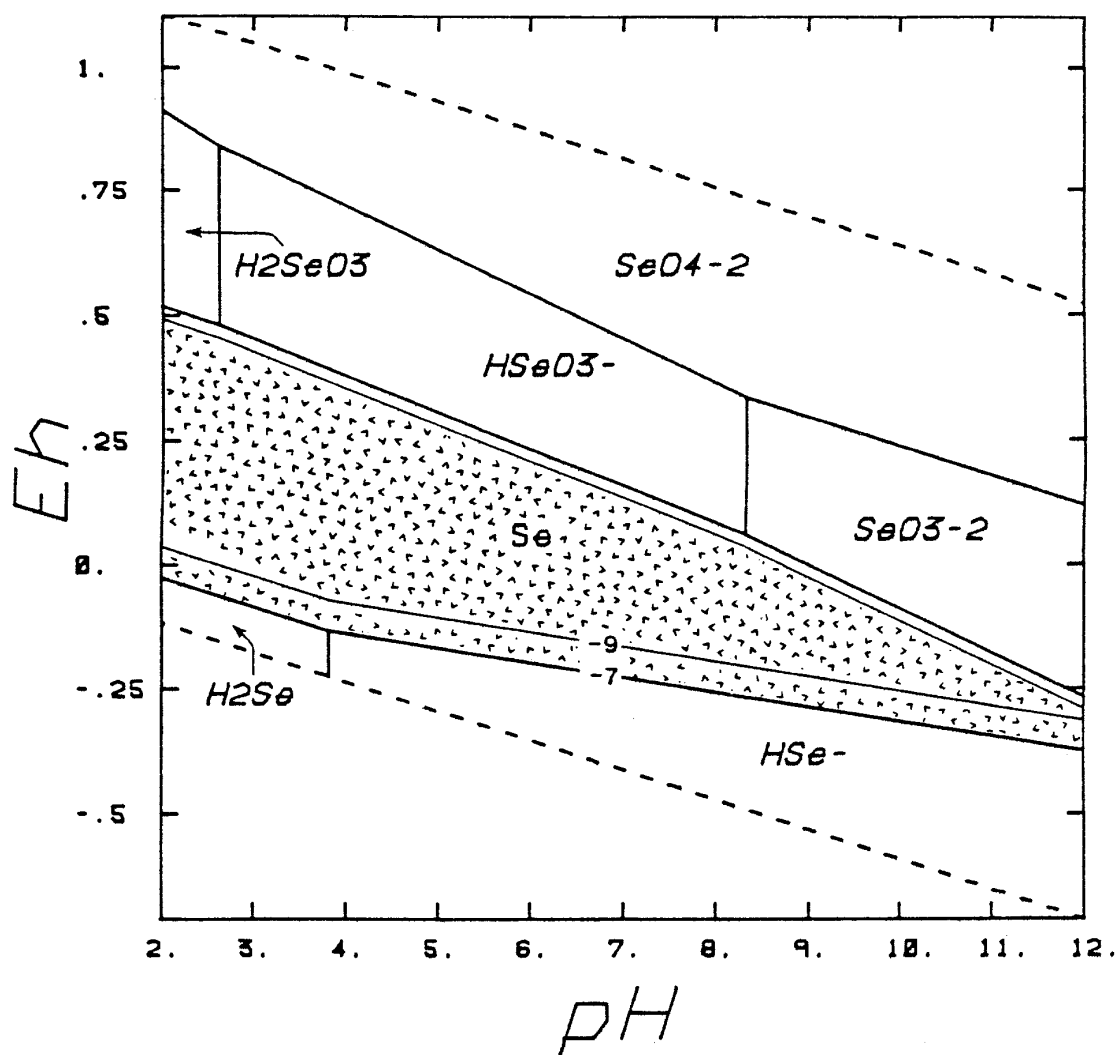


Figure 33. Eh-pH diagram for the system Mo-O<sub>2</sub>-S-H<sub>2</sub>O, assuming that  $\Sigma\text{Mo} = 10^{-6}$  mol/kg and  $\Sigma\text{S} = 10^{-2}$  and  $10^{-5}$  mol/kg. After Barnes and Langmuir, 1978.



**Figure 34. Eh-pH diagram for the system Se-O<sub>2</sub>-H<sub>2</sub>O.** Solid/liquid boundaries drawn for  $\Sigma\text{Se} = 10^{-7}$  and  $10^{-9}$  mol/kg. After Barnes and Langmuir, 1978.

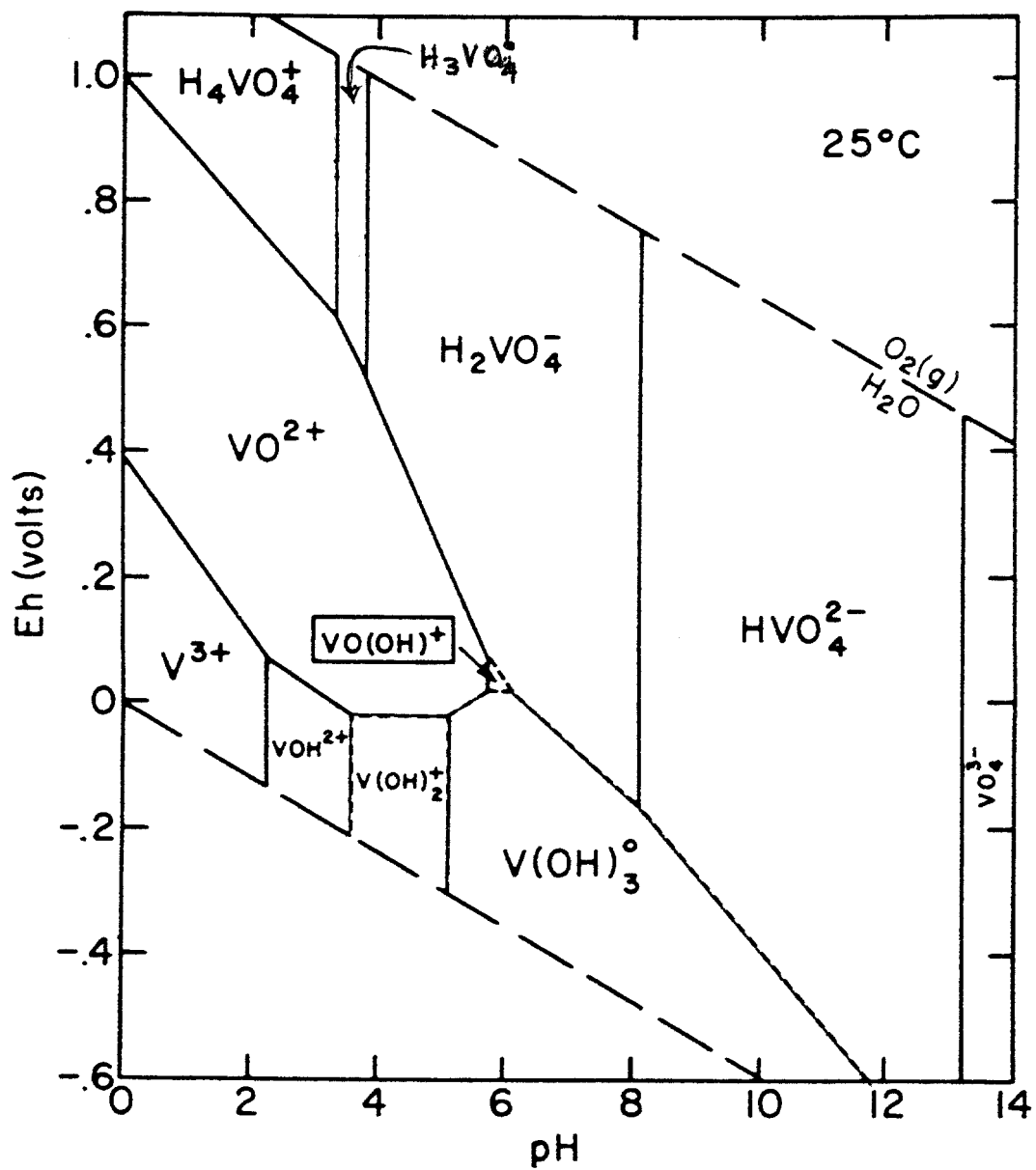


Figure 35. Eh-pH diagram for the system V-O<sub>2</sub>-H<sub>2</sub>O, for dissolved  $\Sigma V < 10^{-4}$  mol/kg (11.5 mg/L as VO<sub>4</sub>). After Langmuir, 1978.

## 7. SOIL TRACE METAL TRANSFER TO PLANTS AND THE BIOAVAILABILITY OF SOIL-METALS

The potential risk that trace elements in soils pose to the feed- and food-chain has been intensively examined during the last 35 years. One purpose of that investigation has been to understand the risk from application of biosolids (municipal sewage sludge) and other metal contamination sources to soil.

During this period, the “soil-plant barrier” concept was introduced to communicate how metal addition, soil chemistry, and plant chemistry affected the risk to animals from metals mixed in soil (Chaney, 1980). Reactions and processes that take place at the soil-plant barrier are influenced by the following: (1) solid metal sources (e.g., Fe, Al, and Mn oxyhydroxides and organic matter) may have adsorptive surfaces that influence soil chemistry; (2) adsorption or precipitation of metals in soils or in roots limits uptake-translocation of most elements to shoots; (3) the phytotoxicity of Zn, Cu, Ni, Mn, As, B, Al, F, etc., limits residues of these elements in plant shoots to levels chronically tolerated by livestock and humans; and (4) food-chain transfer of an element may not constitute a risk, but the direct ingestion of the contaminated soil may.

A summary of metal tolerances by plants and livestock is presented in Table 13. It should be noted that the NRC (1980) committee which identified the maximum levels of metals tolerated by domestic livestock based its conclusions on data from toxicological-type feeding studies in which soluble metal salts had been mixed with practical or purified diets to examine animal response to the dietary metals. If soil is incorporated into diets, metal solubility and bioavailability will probably be much more limited than in the tests relied on by NRC (1980). For example, it has been noted that until soil exceeds about 300 mg Pb kg<sup>-1</sup>, animals show no increased body burden from ingesting the soil (Chaney and Ryan, 1993). Other metals in equilibrium with poorly soluble minerals or strongly adsorbed in soils are often much less bioavailable than they would be if they occurred in more soluble salts.

The chemistry of metals in soils is affected by the presence of ions which can cause precipitation of the metal, organic matter and sesquioxides which can adsorb metals, redox changes which affect the chemical species of the metal present, and similar factors discussed in the section about water chemistry. Soils are usually in a relatively restricted pH range of 5.5 to 8 for high-producing soils, and as wide as 4 to 9 in nearly all soils in the general environment. Industrial contamination with acids or bases can cause lower and higher pH than this practical natural pH range: as low as pH 2 and as high as pH 11. Usually, such contaminated soils are barren due to infertility or phytotoxicity of soil elements affected by extreme pH.

Many elements (e.g., Si, Ti, Fe, Pb, Hg, Al, Cr<sup>3+</sup>, Ag, Au, Sn, Zr, and other elements that serve as a label for soil contamination of plants and diets) are so insoluble in oxidized soils between pH 5.5 and 8 that they are not a risk even when soils with relatively high concentrations are ingested by livestock. When present at very high concentrations, elements that may pose a

risk because of absorption in the intestine when contaminated soils are ingested include F, Pb, As, and Zn. This process is also important for animals that consume soil biota such as earthworms. The earthworm is consumed without depuration on internal soil, giving exposure to high levels of dietary soil—perhaps 35% of dry weight.

**Table 13. Maximum Tolerable Levels of Dietary Minerals for Domestic Livestock in Comparison with Levels in Forages**

Element	“Soil-Plant Barrier”	Level in Plant Foliage <sup>a</sup>		Maximum Levels Chronically Tolerated <sup>b</sup>			
		Normal	Phytotoxic	Cattle	Sheep	Swine	Chicken
		mg/kg <sup>-1</sup> dry foliage		mg/kg <sup>-1</sup> dry diet			
As, inorg.	Yes	0.01–1.0	3–10	50	50	50	50
B	Yes	7–75	75	150	(150)	(150)	(150)
Cd <sup>c</sup>	Fails	0.1–1	5–700	0.5	0.5	0.5	0.5
Cr <sup>3+</sup>	Yes	0.1–1	20	(3,000)	(3,000)	(3,000)	3,000
Co	Fail?	0.01–0.3	25–100	10	10	10	10
Cu	Yes	3–20	25–40	100	25	250	300
F	Yes?	1–5	-	40	60	150	200
Fe	Yes	30–300	-	1,000	500	3,000	1,000
Mn	?	15–150	400–2,000	1,000	1,000	400	2,000
Mo	Fails	0.1–3.0	100	10	10	20	100
Ni	Yes	0.1–5	50–100	50	(50)	(100)	(300)
Pb <sup>c</sup>	Yes	2–5	-	30	30	30	30
Se	Fails	0.1–2	100	(2)	(2)	2	2
V	Yes?	0.1–1	10	50	50	(10)	10
Zn	Yes	15–150	500–1,500	500	300	1,000	10,00

<sup>a</sup>Based on literature summarized in Chaney et al., 1983.

<sup>b</sup>Based on NRC, 1980. Continuous long-term feeding of minerals at the maximum tolerable levels may cause adverse effects. NRC estimated the levels in parentheses by extrapolating between animal species when data were not available for an animal.

<sup>c</sup>NRC based the maximum levels tolerated of Cd or Pb in liver, kidney, and bone in foods for humans rather than simple tolerance by the animals. Because of the simultaneous presence of Zn, Cd in animal tissues is less bioavailable than Cd salts added to diets.

Freshly applied metal salts are not in equilibrium with soil and have a greater phytoavailability than they would exhibit upon equilibrating with the soil over time. The phytoavailability and bioavailability of metals may also be reduced if the metals are adsorbed, chelated, or precipitated before ingestion by children or grazing livestock.

An example of the interaction phenomenon is the toxicity of biosolids or manure-applied Cu or Zn to animals. Cu-deficiency-stressed animals are more sensitive to dietary Zn than animals fed Cu-adequate diets, but biosolids-fertilized crops are not low in Cu, so ordinarily Zn phytotoxicity protects all livestock, including the most sensitive ruminants. Similarly, Cu toxicity to sensitive ruminant animals is substantially reduced by increased dietary levels of Zn, Cd, Fe, Mo, and  $\text{SO}_4$  or sorbents such as soil organic matter. In contrast with the predicted toxicity from Cu in ingested swine manure or biosolids, reduced Cu absorption has been observed unless ingested biosolids exceed about 1,000 milligrams Cu  $\text{kg}^{-1}$  or manure is fed at 50% of diet.

An important interaction which reduces risk from Cd is the normal 1 Cd:100 Zn ratio of geogenic Cd. Although culture of crops in strongly acidic soils allows uptake of increased levels of Cd and Zn, the presence of Zn in the crops inhibits uptake of Cd. Because Cd and Zn are taken up from acidic soils at about the ratio of the total metals in the soil, Zn phytotoxicity (at 500 mg Zn  $\text{kg}^{-1}$ ) serves as a natural maximal limit on crop Cd, and plant (intrinsic) Zn inhibits absorption of plant Cd in animals. These factors very significantly reduce soil Cd risk compared to risks observed in toxicological studies that tested risks from Cd salts.

The potential for plant uptake to allow metals to be transferred to feed- and food-chains has been extensively studied. Uptake slopes measured in pot studies are much higher than those found in the field, so greenhouse or growth chamber studies cannot be used to estimate environmentally relevant uptake slopes. Unfortunately, the majority of the valid field studies were conducted under poor management conditions rather than recommended “Best Management Practices” for managing mobile nutrients and minimizing threats to the environment. It is very clear that strongly acidic soils increase plant uptake of Zn, Cd, Ni, Mn, and Co, and increase the potential for phytotoxicity from Cu, Zn, and Ni. Alkaline soil pH increases uptake of Mo and Se, while Pb and Cr are not absorbed to any significant extent at any pH (Chaney and Ryan, 1993).

For strongly adsorbed metal cations and in the absence of artifacts due to the research methodology used, plant metal uptake does not increase linearly with biosolids-applied metal concentrations, but instead saturates at elevated metal concentrations. First, comparison of application rates is only valid after the system has equilibrated for a given period, for example, because of the rapid biodegradation of biosolids-applied organic matter. When biosolids are applied at high rates, uptake can be increased for several years due to the formation of biodegradation by-products which increase metal diffusion and convection to the roots. The effect is more significant for *Poaceae* than other species, perhaps due to the role of phytosiderophores in metal uptake. Second, soil pH levels should be equal across rates studied;

co-variance of soil pH should be used to correct for unequal soil pH. Studies by Bell et al. (1988) found a strong plateau response when pH co-variance was incorporated in the data assessment. Third, the metal concentration in the source applied affects the slope of metal uptake (or the increase above the background plant metals when the plateau is reached). Higher metal concentration in the source means higher phytoavailability at equal metal applications (Jing and Logan, 1992). The presence of metal-adsorbing sesquioxides in many biosolids decreases the slope or increment at the plateau. The natural limitations on metal uptake and bioavailability, including the plateau response, prevent toxic levels of most metals being reached in plants used as food or feed.

Protection of wildlife is similar to that of livestock; wildlife's diet can consist entirely of plants grown on a contaminated site. In cases involving wildlife in unmanaged ecosystems, maximal plant residues may exceed those allowed on managed farmland—wildlife may eat sick plants which would not be harvested by a commercial grower. Evaluation of a rich literature on wildlife exposure to metal-contaminated soils indicates that animals which consume earthworms are the highly exposed individuals (Brown et al., 2002): 35% of an earthworm is soil, on a dry matter basis. But the soil in the earthworm can adsorb metals, reducing their bioavailability. Of the metals, only mercury in the methyl-mercury form is actually biomagnified, and very little of the mercury in soils is in that form. Se can be incorporated into proteins and also be biomagnified. Other metals are instead “biominified,” according to many studies (Beyer and Stafford, 1993). Nearly all of the metals ingested in forage materials or earthworms—in some cases, >99.9%—are excreted. Thus, the increase in risk with increasing trophic level seen with chlorinated hydrocarbons has not been seen with metals in soils .

Each element must be considered separately because of its unique chemistry. For example, arsenate is more strongly adsorbed than arsenite; when a soil is flooded to grow rice, soil microbes can reduce arsenate to arsenite and the higher concentration of dissolved arsenite can be phytotoxic to rice in more highly contaminated soils. Generally, for As, the most sensitive crop is rice because soils are reduced for rice production. Most elements have little potential for redox change with change in the redox status of soils. Besides forming arsenite, reduced soils also form less soluble forms of U. Reduced soils can form sulfide, and sulfide forms low-solubility compounds with most of the metals of concern in soils, including Pb, Zn, Cd, Cu, and Ni (Table 12). These low-solubility species can become deficient for rice. Upon oxidation of the soil, sulfide is quickly oxidized and the metals are returned to more normal equilibrium reactions of aerobic soils.

Much research has been conducted using multi-element analysis of plants and animals exposed to soil metals. One group of studies used neutron activation analysis of biosolids, soils, crops, and animals (e.g., Chaney et al., 1978). More recently, ICP-MS and other very sensitive analytical methods have been used to examine soil solution and soil-plant transfer of 60 elements as a function of soil pH (Tyler and Olsson, 2001a, 2001b). These studies provide evidence which further supports the concept of the soil-plant barrier. A few elements may require further evaluation in connection with industrial sources that can—despite the fact that they are normally



poorly absorbed from soils—introduce them into soils at very high concentrations. When a high metal concentration source reaches soil, the soil processes that limit risk may be overwhelmed, at least for elements that are weakly accumulated by plants (e.g., Tl, Be).

## **8. LINKING METAL SPECIATION AND METAL TOXICITY: THE BIOTIC LIGAND MODEL APPROACH**

### **8.1 Overview of Biotic Ligand Model Development**

The biotic ligand model (BLM) approach is used to predict metal toxicity by linking chemical equilibrium models (which estimate metal speciation in solution) to metal complexation at the biological surface. The framework of the BLM approach synthesizes over 30 years of research on the geochemistry and toxicity of trace metals (Paquin et al., 2002). The first general descriptions of the approach were provided by Pagenkopf (1983), with his gill surface interaction model, and by Morel (1983), who formulated a free ion activity model. About 10 years later, Playle et al. (1992, 1993a, 1993b) provided additional information on the effect of anionic complexation and competition with other cations on trace metals binding to fish gills. These data were later integrated with toxicity data by Di Toro et al. (2001), who developed a version of the BLM model to predict the acute toxicity of copper and silver to several freshwater species.

### **8.2 Metal Speciation Estimation**

A key component of the BLM approach is the estimation of trace metal complexation by inorganic and organic ligands in solution. While the use of chemical equilibrium models for complexation by inorganic and synthetic ligands is relatively straightforward, predicting complexation by dissolved natural organic matter is more challenging, given such matter's heterogeneous character. Basically, two different estimation approaches have been used in the BLM. The first (e.g., Di Toro et al., 2001), uses a modified CHESS speciation code (Santore and Driscoll, 1995) that includes the WHAM V (Tipping, 1994) approach to model complexation by organic matter. WHAM V is based on an extensive dataset for natural organic matter and considers mono- and bidentate complexation and the influence of electrostatic interactions on binding. Proton binding and competitive metal binding are described for two types of acid groups. Each group is assigned a range of intrinsic pKs that are given median and range values. The second approach uses the MINEQL+ (Schecher and McAvoy, 1994) speciation code, and a single binding constant measured for a natural organic matter sample (e.g., McGeer et al., 2000).

The other key component of metal speciation by BLM models is the complexation by the biotic ligand, for example by the gills of fish in the original models. Two approaches are currently used to estimate the amount of metal associated with a biological surface. The first, which is more mechanistically based, relies on measured conditional binding constants of the metals to the biological surface (e.g., MacRae et al., 1999). The second BLM approach is more empirical and uses complexing by a hypothetical biologically active surface ligand as a fitting

parameter to relate metal speciation to the observed metal toxicity (e.g., De Schamphelaere and Janssen, 2002). In the later approach, in addition to the free metal ion, binding of metal complexes such as  $\text{CuOH}^+$  (De Schamphelaere and Janssen, 2002) and  $\text{AgCl}^0$  (Paquin et al., 1999) may also be considered.

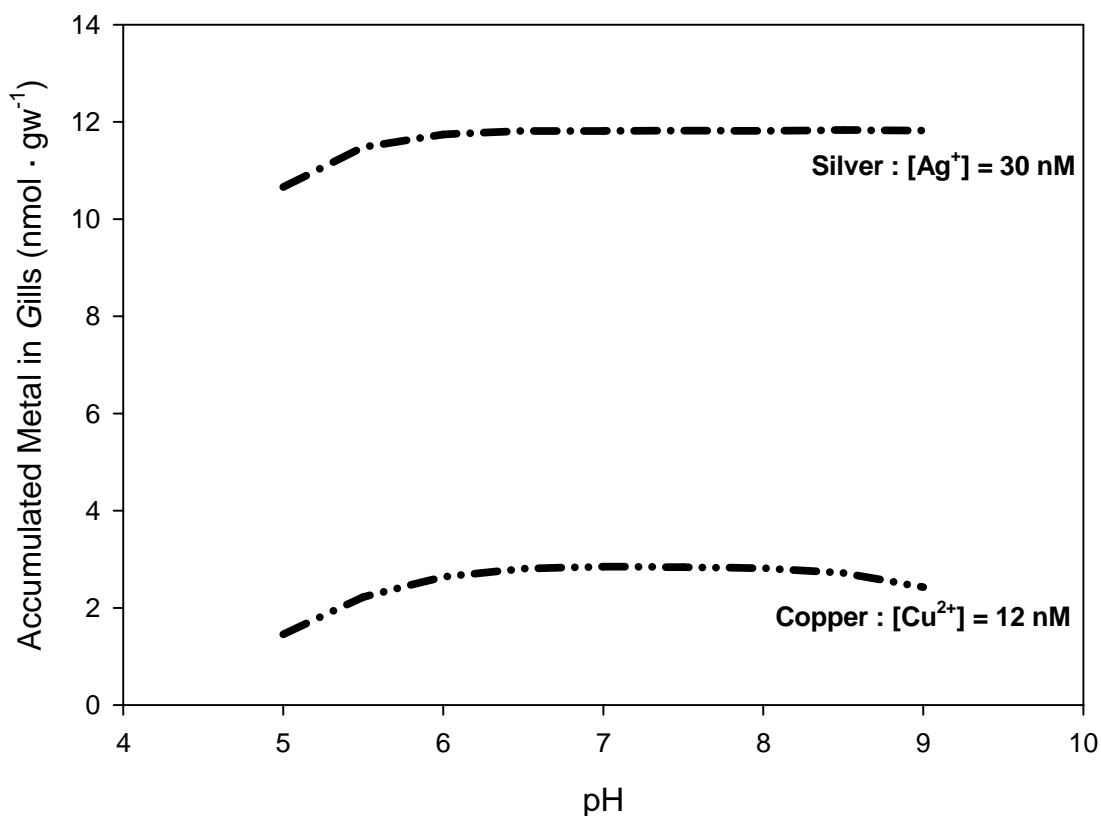
In toxicity testing at relatively high metal concentrations, the measured or estimated binding constants are often roughly constant for different biological ligands. This is presumably because surface complexation is associated with similar low-affinity chemical moieties in each case. For example, Heijerick et al. (2002a) noted the similarity of published binding constants for zinc: experimentally derived  $\log K_{\text{ZnBL}}$  values of 5.3 to 5.6 (Alsop and Wood, 2000) and 5.1 (Galvez et al., 1998) for rainbow trout, and estimated values of 5.4 for steelhead trout (Cusimano et al., 1986) and 5.3 for *Daphnia magna* (Heijerick et al., 2002b). Conditional stability constants for copper are also almost constant for fish gills, with experimentally derived  $\log K_{\text{CuBL}}$  values of 7.5 for rainbow trout and 7.3 for brook trout (MacRae et al., 1999) and 7.4 for fathead minnows (Playle et al., 1993a). But the binding constants are different for other organisms, with an estimated  $\log K_{\text{CuBL}}$  of 8.0 for *Daphnia magna* (De Schamphelaere et al., 2002) and expected differences for non-chitinous invertebrates such as *Lumbriculus variegatus* (Meyer et al., 2002). Some of these differences may also be due to differences in experimental and model design, as there are no standardized methodologies and procedures for deriving data for conditional stability constants.

The effects of pH on metal toxicity can be illustrated with the BLM model, which can consider changes in aqueous metal speciation and competition of  $\text{H}^+$  with metals for binding sites at the biological surface. For example, using the BLM approach (Di Toro et al., 2001), we estimated the competitive effect of  $\text{H}^+$  from pH 5 to pH 9 on copper and silver binding to the gills of fathead minnows in Lake Superior water (Figure 36). The effect shown in the figure only relates to competition for binding to the gill surface, not to changes in copper or silver speciation in solution. This is because total dissolved metal concentrations were increased with pH so that free metal concentrations remained constant. In a toxicologically relevant metal concentration range and pH, the direct competition of protons for binding to the gill surface is weak due to the higher affinity of  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  ions for binding sites. Neither copper nor silver is completely displaced from the surface even at pH 5. Copper associated with the gills almost doubles from pH 5 to pH 7, and competition between  $\text{Cu}^{2+}$  and  $\text{CuOH}^+$  becomes significant at pH 8 and above. In contrast to copper, there is almost no predicted competition of  $\text{H}^+$  with silver. In fact, no experimental data support competition of  $\text{H}^+$  with silver; the small reduction of  $\text{Ag}^+$  bound to the gill at pH below 6 is presumably an artifact related to the use of an empirically derived lower proton binding constant for the silver BLM (Paquin et al., 1999).

### 8.3 Validation Studies

While the toxicity of trace metals can vary by several orders of magnitude, studies that have validated the BLM approach with independent datasets indicate that BLM-predicted toxicity is generally within 2 times the observed toxicity. De Schamphelaere et al. (2002)

validated their BLM model for predicting acute copper toxicity to *Daphnia magna* using independent toxicity test data conducted with 25 reconstituted media representative of European natural waters and with 19 spiked European natural waters. Heijerick et al. (2002b) conducted a similar validation using 17 reconstituted media to predict zinc acute toxicity to *Daphnia magna*. Santore *et al.* (2001) have also tested their BLM model for acute copper toxicity to fathead minnows by comparing their prediction to the toxicity test results for two effluent-impacted streams in the United States. Finally, the model developed by McGeer et al. (2000) to predict acute silver toxicity to rainbow trout also accurately predicted the toxicity measured in 31 toxicity test results obtained from 10 different independent studies. The BLM approach has thus been validated and shown to be mechanistically based for the prediction of trace metal acute toxicity to certain indicator species.



**Figure 36. Effect of pH on the BLM-predicted (HydroQual, 2002)  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  accumulation in the gills of *Pimephales promelas*.** Lake Superior average composition (Erickson et al., 1996) and freshwater criteria maximum total dissolved concentrations (U.S. EPA, 2002b) of 205 nM for copper and 32 nM for silver assumed at pH 5. Total dissolved concentrations were increased with increasing pH so that free copper and free silver concentrations would remain constant,  $[\text{Cu}^{2+}] = 12 \text{ nM}$  and  $[\text{Ag}^+] = 30 \text{ nM}$ . Silver BLM:  $\text{Log } K_{\text{H}^+-\text{gills}} = 4.3$  and  $\text{Log } K_{\text{Ag}^+-\text{gills}} = 7.3$ . Copper BLM:  $\text{Log } K_{\text{H}^+-\text{gills}} = 5.4$  and  $\text{Log } K_{\text{Cu}^{2+}-\text{gills}} = 7.4$ .

## 8.4 Current Limitations and Future Research

The BLM approach's limits are mostly related to its inherent assumption that (1) trace metal speciation and metal uptake are in chemical equilibrium and (2) the biotic ligand remains unmodified through exposure. The model also assumes that metal uptake or expression of the biological response is the rate-limiting step. Trace metals in surface waters and exposure media are not always in chemical equilibria, especially with natural organic matter. Campbell (1995) reviewed other exceptions to the BLM's assumptions, such as direct uptake through passive diffusion of lipophilic complexes or kinetically controlled uptake of some trace metals because of their fast uptake. The assumption that the affinity of the biotic ligand is constant has also been challenged. There are physiological responses to metal exposures that might affect metal uptake. In addition, prior sublethal exposures to metal or the quality of the diet have been shown to affect the binding of metal to fish gills (e.g., Alsop and Wood, 2000; Szebedinszky et al., 2001). Variation in the affinity of the biotic ligand for metals will be especially important for the prediction of chronic toxicity.

Extensive current research is focused on predicting chronic toxicity and metal mixture toxicity. Applying the BLM model to chronic toxicity is not straightforward, since the physiological mechanisms involved are likely to be much different. Similarly, predicting the toxicity of metal mixtures that have different modes of action is difficult. For example, Cu and Ag affect ionoregulation, whereas metals such as Ni have respiratory effects. Accounting for such differences will require further refinement of the BLM model. However, it can be expected that the toxicity of metal mixtures in which the metals have the same mode of action can be predicted using the current BLM framework.

## 9. ATMOSPHERIC CHEMISTRY OF THE METALS

Metals are ubiquitous components of particulate matter in ambient air and are emitted by numerous natural and anthropogenic sources. Richardson (2002) included volcanic eruptions and emissions, entrainment of soil and dust, entrainment of sea salt spray, and natural forest fires as significant metals emission sources. Most metals are removed from the atmosphere by deposition and have relatively short atmospheric half-lives. Table 14, abstracted from Seinfeld and Pandis (1998), presents average atmospheric residence time and airborne concentrations for some metals in California.

**Table 14. Atmospheric Metals**

<b>Metal</b>	<b>Residence Time (days)</b>	<b>Average Concentration</b>
Arsenic	Unknown	2.4 ng/m <sup>3</sup>
Cadmium	7	1–2.5 ng/m <sup>3</sup>
Nickel	Unknown	7.3 ng/m <sup>3</sup>
Beryllium	10	0.11–0.22 ng/m <sup>3</sup>
Lead	7–30	270–820 ng/m <sup>3</sup>
Mercury	0.3–2 years	0.37–0.49 ppb

From Seinfeld and Pandis, 1998.

A substantial part of the atmospheric chemistry of metals takes place in the aqueous phase, where it is not significantly different from aqueous chemistry in other media. Constructs described elsewhere in this report (e.g., pH-Eh diagrams and geochemical computer models) may be used to determine metal speciation in atmospheric aquatic aerosols. However, the application of such diagrams and models, which assume that metal species are in chemical equilibrium, must be limited to describing metal speciation reactions that can equilibrate in seconds or less. These include many acid/base and metal complex formation reactions, but not most reactions involving adsorption, oxidation/ reduction, or mineral precipitation. Atmospheric metal reactions that take longer to equilibrate must be studied in terms of their reaction kinetics rather than equilibrium chemistry.

Seinfeld and Pandis (1998) present a detailed discussion of the acid-base chemistry of atmospheric water that may be useful in modeling metal speciation. In addition, sorption to particles, deposition, and gas phase redox chemistry may be important for some metals (Bodek et al., 1988). Deposition is largely a function of the properties of particulates, not the sorbed or incorporated metals. Redox chemistry takes place through oxidation with free radicals such as OH or through direct photolysis of metal complexes (Finlayson-Pitts and Pitts, 1986). Due to the oxidizing nature of the atmosphere, metals are often converted to their most oxidized stable forms.

Metals have not been a major component of EPA air programs. Lead is listed as a criteria pollutant under the Clean Air Act. A group of metals including antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium are listed as hazardous air pollutants under the Clean Air Act. Of these only a few have concerns related to speciation. Arsenic is listed for “inorganic” and arsine forms; the listing for chromium makes a distinction between Cr(III) and Cr(VI); mercury is listed for elemental, inorganic (apparently divalent), and methyl forms; and nickel is listed as salts, refinery dust or subsulfide, and carbonyl (U.S. EPA, 1994). Deposition of metals from the atmosphere is under consideration by the Office of Water (U.S. EPA, 2003b). This latter program is primarily concerned with deposition, speciation, and transformation after deposition of mercury, although lead and

cadmium are involved to a lesser extent. The State of California has a comprehensive program for monitoring airborne metals through its air toxics monitoring network.

With very few exceptions (e.g., hexavalent chromium, nickel refinery dust, mercury), EPA does not consider bioavailability or speciation in risk assessment of atmospheric metals; rather, risks are assessed on the basis of total or respirable airborne metal concentrations (U.S. EPA, 1998). EPA assesses risks for lead with a set of pharmacokinetic models known as the integrated uptake biokinetic (IEUBK) and Adult Lead models. Although these models explicitly consider oral bioavailability of lead, they do not consider inhalation bioavailability.

Most sampling and analytical techniques published by EPA for metals in air are oriented toward evaluation of particulate-phase total metals rather than metal species (U.S. EPA, 1999a). These methods involve collection of either total or respirable particulate fractions with subsequent analysis by X-ray fluorescence, atomic absorption, inductively coupled plasma, proton-induced x-ray emission, or neutron activation analysis gamma spectroscopy techniques. The one notable exception is a method for mercury (Method IO-5) that speciates vapor and particulate forms. To the extent that metals are sorbed to particulate phases, analysis of individual metal species can, at least theoretically, be accomplished by the same techniques used to analyze those species in other solid media.

Of all the metals of interest, mercury has the most complex and best understood atmospheric chemistry (Lindqvist, 1994; Munthe, 1994). In the gas phase, mercury is oxidized by  $O_3$  and  $NO_2$ ; aqueous-phase chemistry includes oxidation of elemental mercury by free radicals such as OH and  $HO_2$ . Both vapor phase and aqueous atmospheric chemistry may involve heterogeneous-phase components. EPA has made a substantial effort to evaluate the atmospheric fate of mercury due to the requirements of the Clean Air Act. The *Mercury Study Report to Congress* (RTC) (U.S. EPA, 1997) contains a complete qualitative and quantitative evaluation of mercury's atmospheric fate based on the state of knowledge when the report was written. EPA is also working with the University of Wisconsin to quantify mercury transformations in the atmosphere, including depositional behavior.<sup>6</sup>

## 9.1 Discussion and Recommendations About Atmospheric Metal Chemistry

Metal speciation and chemistry have not been significant components of EPA's evaluation and assessment of environmental metals. The impetus toward a more comprehensive evaluation of metals must start with qualitative and quantitative toxicology. If there is a significant difference among the various atmospheric metal species with respect to toxicology (as is the case with divalent and elemental mercury), then expenditure of resources on environmental fate models, development of analytical techniques, and monitoring may be warranted. To some extent, the Mercury RTC (U.S. EPA, 1997) is a paradigm for a complete multimedia exposure and risk assessment for metal species. The resources and management of

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<sup>6</sup> EPA Grant R829798. Project officer: Bill Stelz, NCER.

the development of the RTC may be used as a benchmark by EPA for the development of similar efforts for other metals.

## **10. DETERMINATION OF METAL SPECIATION IN WATERS AND SOILS**

### **10.1 Unfiltered Versus Filtered Water Samples**

The metals transported by surface and ground waters are present in true solution as ionic or molecular species, and in suspended particles (cf. Stumm and Morgan, 1996; Langmuir, 1997a). The suspended particles can be colloidal in size and as small as 10 to 100 Angstroms ( $10^{-9}$  to  $10^{-8}$  m). According to the widely used operational definition, metals that pass through a  $0.45\text{ }\mu\text{m}$  ( $4.5 \times 10^{-7}$  m) filter are dissolved. Because colloidal particles range in size from less than  $10^{-8}$  m to about  $10^{-5}$  m, a significant fraction of particulate metal concentrations can pass through a  $0.45\text{ }\mu\text{m}$  filter and be listed as dissolved. For example, Kennedy and Zellweger (1974) found that the concentration of colloidal-sized particles of Al, Fe, Mn, and Ti passing through a  $0.45\text{ }\mu\text{m}$  filter could exceed the dissolved concentration of these metals by an order of magnitude or more. (See also Bergseth, 1983; Puls and Barcelona, 1989; Pohlmann et al., 1994). Clark et al. (1992) reported that the type of pump used to sample ground waters had a major effect on total concentrations of Mn, Pb, and Zn, with higher turbidity and particulate metal concentrations collected from centrifugal pumps than from slower-flow-rate bladder pumps. Furthermore, the determination of dissolved metal concentrations is complicated by several potential sampling and filtration artifacts. For example, Horowitz et al. (1992, 1996) have demonstrated that several factors in addition to filter pore size can affect the dissolved metal measurements: the type of filters, the volume of water filtered, the amount of suspended matter, etc.

Usually the metals of concern are associated with the smallest particle size fractions (especially colloidal-sized) in soils and sediments which have the largest surface areas per weight, rather than with larger particle sizes on a weight basis. A variety of methods are available for separating dissolved and suspended metals. These include centrifugation, filtration, ultrafiltration, ion-exchange chromatography, and organic extraction. These methods are discussed in some detail by Salbu and Steinnes (1994).

The distinction between dissolved and particulate metal concentrations is important, because reactions such as adsorption, precipitation, oxidation/reduction, and complexation control metal amounts in true solution, but not the amounts in suspension. The latter are limited, if at all, by chemical coagulation and/or filtration in porous media, or, if the particles are large enough (larger than about  $10^{-5}$  m), by gravitational settling. Metals in suspension are usually adsorbed or coprecipitated with suspended Fe, Al, or Mn oxyhydroxides or adsorbed by suspended organic matter or clays. Only rarely, as in streams affected by acid rock drainage or at sources of metal contamination, do the metals of concern occur as pure metal oxyhydroxides or metal salts.

In public water supplies that are subject to pH control by lime addition, the addition of flocculants, and/or filtration, suspended metal concentrations may be largely eliminated. But the distribution systems that connect the utilities to their customers may contribute measurable amounts of dissolved and suspended metals to drinking water supplies (e.g., Singh and Mavinic, 1991).

## **10.2 Unstable Parameters or Species Including Metal Redox Pairs**

The reactions that control the mobility of the metals of concern in porous media are usually strong functions of pH, and—except for Al, Ba, Be and Sr—also depend on the oxygen content or Eh of the media (See Baedecker and Cozzarelli, 1992). An accurate assessment of metals mobility at a specific site requires that the values of these parameters used in any modeling calculation be the same as in the medium involved. Values of pH and Eh, temperature, and gas pressures (e.g., the partial pressures of O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>S) must be measured immediately upon collection, or when possible fixed in the field for later analysis. Otherwise their values will usually change rapidly due to temperature change, loss or gain of gases to or from the atmosphere, and the growth of organisms such as bacteria and algae. For such reasons, the pH of a water measured in the laboratory after a few weeks of sample storage at ambient temperature will usually differ from its value in the field by  $\pm 0.2$  to  $\pm 1$  pH units (Langmuir, 1971, 1997a).

Methods of field analysis of pH and Eh are discussed in detail by Langmuir (1971) and Wood (1976). (See also USGS, 1998.) Modern, battery-operated solid-state pH/millivolt meters for field use have greatly improved the ease of pH and Eh measurement. If pH meters and electrodes are properly calibrated using a double pH buffer check, field-measured values can be accurate to  $\pm 0.02$  to  $\pm 0.05$  pH units. Accurate and meaningful Eh measurements are usually far more difficult to obtain. In fact the U.S. Geological Survey (1998) states that Eh measurement “is not recommended in general because of the difficulties inherent in its theoretical concept and its practical measurement.” An accurate Eh measurement using a platinum (or other noble metal) or glassy carbon electrode depends upon the presence of significant concentrations (usually greater than  $10^{-5}$  M) of a pair of electroactive redox species that can attain rapid chemical equilibrium and greatly exceed the concentrations of the non-electroactive species also present. Most often the species that control an Eh measurement are species of iron, manganese, or sulfide and native sulfur (Langmuir, 1997a). This tends to limit thermodynamically meaningful Eh measurements to acid mine waters and iron-, manganese-, or sulfide-rich stagnant surface waters or ground waters. In other waters, which include most surface waters in contact with the atmosphere, Eh measurements are of qualitative value only. In such waters, a measurement of dissolved oxygen (DO) is the most reliable indication of the oxidation state. In fact field DO measurements should be performed any time redox sensitive metals of concern are of interest. DO is measurable in the field at concentrations as low as 0.03  $\mu\text{M}$  using modern analytical methods (cf. Kent et al., 1994).



Lovely et al. (1994) and others have suggested that instead of Eh, field measurements of dissolved  $H_2$  be performed to define the redox state of surface-water bottom sediments and ground waters. This reflects the fact that bacteria employ  $H_2$  in the reduction of nitrate Mn(IV), Fe(III), sulfate, and carbon dioxide.

Geochemical models such as MINTEQA2 (U.S. EPA, 1991) and PHREEQC (Parkhurst and Appelo, 1999) can compute the relative amounts of redox sensitive species of As, Se, Mo, Cr, N, C, and other metals of concern from the total metal concentration and measured Eh (at a given pH). This assumes of course that this Eh represents the overall oxidation state of the system (which is usually questionable), and that the redox pairs of these elements are electroactive and in equilibrium with the measured Eh, which they usually are not.

The only way to determine accurate relative amounts of redox pairs of As, Cr, N, C, or Se, for example, is to fix them upon collection and measure them directly (cf. Baedecker and Cozzarelli, 1992; Sule and Ingle, 1996). For example, Tretner et al. (2001) have shown that for non-sulfidic waters, the As(V)/As(III) ratio and As concentrations could be maintained for two weeks by first filtering samples, then acidifying them with HCl to pH 1.5–1.8 and refrigerating them to below 4°C. In general, the accurate measurement of concentrations of individual redox pairs is difficult and costly, and not recommended for routine studies.

### **10.3 Determination of Individual Species Concentrations in Water**

There are various methods for directly measuring the aqueous activity or concentration of individual metals, including specific ion electrodes and voltammetric techniques (cf. Salbu and Steinnes, 1994). Most of these methods, though, have interference problems and require the addition of reagents to the natural water, which may itself change the metal speciation. The simplest approach is to compute metal ion activities from a geochemical model calculation, based on a chemical analysis of concentrations of dissolved metal and related species in the water. However, prediction of metal speciation in systems containing natural organic matter is challenging (see Section 4).

## **11. SOILS**

### **11.1 Sampling of Soil Pore Waters**

A major challenge when sampling soil pore waters for chemical analysis is to avoid changing metal speciation in the sampling process. This means that methods involving the application of gas pressure should be avoided, in that they will change ambient gas pressures and so change the pH, for example. The most appropriate moisture sampling methods use either negative pressure as in suction lysimeters (cf. Knight et al., 1998; Davis et al., 1999; Tye et al., 2003), or positive pressure without contact between air or other foreign gases and the soil. The latter devices include gas pressure membrane extractors and pressure plate extractors (cf. SoilMoisture Equipment Corp., 1997).

## 11.2 Sequential Extractions To Determine the Nature of Metal/Soil Associations

The purpose of sequential extractions is to define the speciation of individual metals in the soil through a series of soil leaching steps. Using sequential extractions, Tessier et al. (1979) have categorized metals as exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, or residual. The extractions often involve (1) addition of a  $\text{MgCl}_2$  solution at pH 7 to define the exchangeable metals fraction; (2) addition of a pH 5 sodium acetate/acetic acid solution to selectively dissolve carbonates (the acid extractable fraction) and release their metals; (3) addition of an acidic hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) solution, which is a reductant, to dissolve the amorphous Fe-Mn oxyhydroxides and release their metals; (4) addition of a hydrogen peroxide extraction at pH 2 and  $85^\circ\text{C}$  to determine organic matter content and the metals associated with it; and (5) aqua regia destruction of remaining minerals to obtain the residual metal concentration. Typical extraction results show minor to below-detection concentrations of trace metals associated with the exchangeable fraction, and major metal concentrations released by both the acid extractable and reductant leaching steps (cf. Tack and Verloo, 1999). In another sequential extraction study, Tye et al. (2003) found that the behavior of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  in a variety of contaminated soils was best explained by assuming they were adsorbed by soil humus.

Tack and Verloo (1999) list some of the problems associated with sequential extractions, which include problems due to sample handling and preparation, the non-selectivity of the extractants, and the redistribution of trace metals among remaining solids during extraction. It has long been known that the five extraction steps do not cleanly distinguish the forms of metal association and speciation identified above (cf. Suarez and Langmuir, 1975). Tye et al. (2003) point out further that “single or sequential chemical soil extraction schemes provide a comparative classification system for soil metals but do not predict (metal) the bioavailability.”

The free metal ion activity in the soil solution phase has been shown to be a better indicator of bioavailability and toxic response than is the total soil metal content (cf. Tye et al., 2003). Most of the soil equilibrium models assume that the labile (bioavailable) metal content of a soil can be predicted from the total or extractable soil metal content (e.g., NICA, Goody et al., 1995; SCAMP, Lofts and Tipping, 1998; Tipping et al., 2000). Such an approach will generally overestimate the labile metal fraction. More directly, the soil pore waters may be sampled and chemically analyzed, and the solution speciation estimated from a model such as WHAM 6 (Tipping, 1998) to determine metal ion activities in the soil solution.

## 12. APPLICATION IN A REGULATORY CONTEXT

EPA needs to use the tools of environmental chemistry to determine metal speciation for use in risk assessments. In addition, EPA needs to be able to assess the mobility of metals in the environment, especially the subsurface. Each of these applications will be discussed in turn.

### 13. APPLICATIONS TO SPECIATION

Metal speciation may be required for risk assessment. If so, it is desirable to know the identity and form of a metal at the exposure point. If information regarding bioavailability, pharmacokinetics, and toxicology is also known, speciation information may be used in risk assessment. Note that to do so, risk assessors need to understand the dynamic nature of metal speciation, because of the chemical equilibrium among the different metal species. For example, even if metal toxicity is often best predicted from the free metal ion concentration, the free metal ion cannot be labeled “the toxic species,” since it is in equilibrium with all the metal species present. Even if there is biological uptake of the free metal ion, its concentration will be maintained through the dissociation of the other metal species present. EPA has developed bioavailability and toxicological data for very few metal species. A review of the Integrated Risk Information System (IRIS) shows that, disregarding organometallics and cyano complexes, EPA has developed toxicological information for the following metals:

- Arsenic—inorganic, arsine
- Chromium—Cr(III), Cr(VI)
- Mercury—elemental, mercuric chloride
- Thallium—oxide, acetate, carbonate, chloride, nitrate, selenite, sulfate
- Vanadium—pentoxide
- Uranium—soluble, natural
- Zinc—phosphide

EPA has not formalized toxicity reference values (TRVs) for ecological risk assessment, but there is little consideration currently given to metal speciation (with the possible exceptions of chromium oxidation state and organometallic forms of mercury) in contemporary ecological risk assessment. A limited number of Ambient Water Quality Criteria (Table 6) also exist for metal species.

It is useful to hypothesize a future condition, however, in which there are no limits on toxicological information and a real need exists to determine metal species. The exact information required and questions to be asked of the environmental chemist will depend on the nature of the assessment in the context of the framework:

- **Site-Specific Risk Assessment**—What are the existing metal species at the exposure points? Is there likely to be a change in speciation over the exposure duration? Can normal human behavior alter the speciation? If there is a strong likelihood of more than one species, should

different species be selected for risk assessment (i.e., a common, but possibly less toxic species for a central tendency risk and a rarer but possibly more toxic species for a high-end risk)?

- **National Regulatory Assessment**—What generalized information is available to determine the chemical species to which a receptor is exposed at any point in the United States? Is it possible to generalize speciation across the U.S. or is it necessary to develop regional (e.g., physiographic province) or water-body type (stream, lake, estuary) speciation? How do metals species change when traveling from a potentially regulated source to an exposure point?
- **National Hazard or Risk Ranking**—Is there a property of metals analogous to organic persistence that can be used to generalize across metals? How can chemical information be developed to perform the generalization? What degree of stability is required to determine if the property will persist?

Many of these questions need to be addressed by risk managers within their specific context. From a chemistry standpoint, there are several levels of information that can be used to answer these questions: regulatory defaults, literature information based on limited measurement, analytical chemistry, geochemical modeling, and chemical-specific modeling.

### 13.1 Regulatory Defaults

Current regulatory practice is to use total metal concentrations in risk assessments, with a few exceptions. The bioavailability of a metal is assumed to be the same as in the toxicological or epidemiological studies in which dose-response curves have been derived. This practice is conservative from an environmental health standpoint and is likely to continue as a default into the future. In a tiered risk assessment approach, the production of an unacceptable risk or exceedence of a standard or criterion by a total metal concentration could trigger a more refined approach to evaluate the speciation of the metal. A tiered risk assessment approach will also allow setting the level of details and the scope of the metal speciation information required based on a periodic review of the results of the completed tiers. An alternative approach to the use of total metal concentrations is to use the species that is the best predictor of toxicity from Table 7, for example. This is predicated on the availability of dose-response information for the particular species.

### 13.2 Literature/Limited Measurement

Obtaining speciation data at this level involves a combination of limited environmental measurements along with literature information. This technique is already in use for some metals to determine water quality criteria as a function of hardness. A more sophisticated use of combined analytical and literature information is the determination of metal speciation using look-up diagrams such as the pH-Eh diagrams presented in this paper. This requires reliable

measurements of pH and Eh for the system under evaluation. For example, Figure 18 presents an Eh-pH diagram for cadmium. At neutral pH in a mildly reducing environment, this diagram tells us, cadmium will exist as the slightly soluble cadmium sulfide, while under oxidizing conditions it will exist as the soluble divalent cadmium ion. This conclusion would, of course, depend on the availability of sufficient sulfide in the system. There are limitations to this approach which include the need to be aware of assumptions that were used in producing the diagrams and interactions from other chemicals. The analyst also needs to be aware of the fact that, especially in natural waters, pH and Eh are not static concepts. The values selected should be representative of both the current status of the system and reasonable future geochemical changes.

### 13.3 Analytical Chemistry

Most site-specific risk assessments, some ranking assessments (e.g., HRS), and many waste characterizations currently depend on analytical chemistry. With rare exceptions, the metals are treated as total metals or some subset of total metals such as total recoverable metals. EPA compendia of analytical methods such as SW-846 have traditionally focused on methods for total metal analyses such as atomic absorption or inductively coupled plasma. The primary exception is chromium. Several EPA methods currently exist to quantify Cr(III) and Cr(VI), including ion chromatography (0218.6), differential pulse polarography (7198) and speciated isotope dilution mass spectrometry (6800). EPA has also published methods for differentiating As(III) from As(V) by anodic stripping voltametry.

Analytical methods for identifying and quantifying chemical species have been discussed earlier in this paper. Most of these methods are used by academic or private research laboratories and are not currently amenable to routine use in a regulatory context. Before being used for site-specific risk assessment or waste characterization, for example, these methods require robust evaluations to determine if they are capable of meeting data quality objectives. This would include (but not be limited to) evaluations of accuracy, precision, and sensitivity when used on a routine basis by a contract laboratory.

Another class of analytical methods could be termed “adjunct” methods. These methods do not measure the metal of concern directly, but measure other aspects of environmental chemistry that are useful in determining metal speciation. DO, Eh, pH, and hardness are examples of adjunct measurements. If a metal species is to be determined by means of a look-up table, for example, system measurements of pH, Eh (or a surrogate), and DO are required. The quantification of major anions (chloride, bromide, nitrate, sulfate, carbonate) and cations (Na, K, Ca, and Mg) is necessary to compute metal speciation using a chemical equilibrium modeling approach. EPA has published methods for routine determination of these adjunct parameters.

### 13.4 Geochemical Modeling

Geochemical modeling probably has the most utility for regulatory application for metal chemistry of all the techniques discussed here. There are numerous geochemical models available in the literature. EPA (1999b) has reviewed many of these models and should be consulted for a more detailed discussion (see also Langmuir, 1997a). In general, geochemical models are classified as “speciation-solubility” or “reaction path” models. Speciation-solubility models may be used to calculate aqueous speciation/complexation and the degree of saturation with respect to the solids in the model’s database. Some specialization-solubility models also include limited mass transfer capabilities. Examples of refined speciation-solubility models include WATEQ, REDEQL, GEOCHEM, MINEQL, MINTEQ (see U.S. EPA, 1999b, for detailed references) and their subsequent versions. Reaction path models have more advanced mass transfer capabilities. At each step of a process (e.g., travel of an ion through an aquifer) reaction path models calculate masses of minerals precipitated or dissolved and the resulting composition of the solution. Reaction path models include PHREEQC, PATHCALC, and EQ3/EQ6.

MINTEQ2 (U.S. EPA, 1991; HydroGeologic, 1998; HydroGeologic and Allison, 1999a) has been widely used in a national regulatory context by EPA. Typically MINTEQ is used to calculate partition coefficients that are used in a subsequent national regulatory analysis (U.S. EPA, 1996; HydroGeologic and Allison, 1999b) or a site-specific risk assessment (U.S. EPA, 1998). This usage is discussed in more detail in previous sections of this paper. For systems with low concentrations of natural organic matter, for example deep aquifers, there is little technical reason why MINTEQ2 could not be used on a routine basis to determine chemical speciation for site-specific risk assessments. However, MINTEQ2 is inadequate for systems where metal speciation can be dominated by natural organic matter, such as shallow aquifers, soil pore waters, and surface waters.

### 13.5 Chemical-Specific Modeling

Chemical-specific modeling involves the construction of a mathematical model that is capable of predicting all of the significant fate and transport processes of a given chemical. It should be capable of tracing a chemical from a source to an exposure point and predicting both concentration and speciation at the exposure point with a sufficient degree of accuracy to reflect the objectives of the assessment.

The only model of this type for a metal is the modeling reflected in the *Mercury Study Report to Congress* (RTC) (U.S. EPA, 1997). In general, the RTC evaluates the behavior of three mercury species (divalent, elemental, and methyl). In the atmosphere, fate and transport in both particulate and vapor phases are assessed for long range and local behavior using established atmospheric transport models. Terrestrial and aquatic modeling is accomplished by application

of the IEM-2M model, which was specifically developed for the RTC.<sup>7</sup> This model simulates the behavior of mercury in watershed soils and water bodies using a mass balance approach. The RTC was a National Regulatory Assessment in the context of the framework. It generalized environments to the eastern and western United States and evaluated mercury behavior in these environments. The models may be applied on a site-specific basis (Foster et al., 2003) if sufficient environmental information is available. The IEM-2M model is data intensive. Each mercury species evaluated with the model requires input values for molecular weight, Henry's law constant, soil, bed sediment and suspended sediment partition coefficients, air diffusivity, chemical reaction rate constants for six processes in three media and biotransfer factors *f* or all biota of concern. Inputs of concentrations or emission rates of the various mercury species are also required, but in practice, default assumptions of speciation were used by EPA. The development and application of this type of model for other metals is limited by the amount of resources and scientific information required.

#### 14. APPLICATIONS TO MOBILITY

Quantification of the mobility of metals in the unsaturated zone or ground water is a significant regulatory application of speciation information. For example, metals criteria for the toxicity characteristic in RCRA depend on the development of a generic soil-to-groundwater dilution attenuation factor (DAF), as do the Soil Screening Levels (SSLs) for metals. Site-specific risk assessments for all programs need to be able to predict the rate of movement of metals through soils and subsequent movement and concentrations in groundwater. The primary processes governing the environmental fate and transport of metals in the subsurface are advection, dispersion, matrix diffusion, and retardation (U.S. EPA, 1994). Advection and dispersion are functions of the system rather than the contaminant. Matrix diffusion, which is a function of the contaminant, is relatively unimportant and omitted in most model transport algorithms. Retardation depends on a number of factors (U.S. EPA, 1994; Langmuir, 1997a) and may involve or be affected by the following:

- Sorption—the attachment of chemical species to mineral or other surfaces.
- Ion exchange—competitive adsorption of ionic species, including ionic contaminants and major ions, onto oppositely charged surfaces of geologic materials.
- Speciation—the distribution of a given constituent among its possible chemical forms, including metal complexes, which have differing tendencies to be adsorbed or desorbed.
- Precipitation—the process by which dissolved species exceed the solubility limits of their solids, so that some of the species precipitate from solution. When a metal species reaches mineral saturation, addition of further amounts of the species to solution are precipitated, not adsorbed.

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<sup>7</sup> The IEM-2M was also used by EPA to support development of mercury emissions limitations for hazardous waste combustors.

- Colloid formation—the process of forming colloids and the association of metal species with them. The metals may be sorbed or coprecipitated with colloidal-sized particles.
- Biofixation—the binding of metals to solid materials due to the interactions of microorganisms or plants.
- Natural organic matter interactions—sorption to natural organic matter particles and complexation of metals by natural organic matter in the dissolved/colloidal fraction.
- Anion exclusion—negatively charged mineral or other surfaces repelling anions and so preventing their sorption by those surfaces.
- Other importance processes—changes in pH, oxidation potential, salinity, concentrations of competing ions, the nature of sorbent phases and their surface areas, and surface site densities

Due to the complexity and multiplicity of the processes involved, recourse is often made to the use of a single partition or distribution coefficient that describes the degree to which the contaminant's transport is retarded relative to water. This approach starts with defining the retardation factor:

$$R_f = \frac{v_p}{v_c} \quad (7)$$

where  $R_f$  is the retardation factor,  $v_p$  the velocity of water through a control volume, and  $v_c$  the velocity of contaminant through a control volume. The retardation factor is related to the distribution coefficient through the expression:

$$R_f = 1 + \frac{\rho_b}{n_e} K_d \quad (8)$$

where  $\rho_b$  is the porous media bulk density and  $n_e$  is the effective porosity at saturation given as a volume fraction (cf. Langmuir, 1997a). This model only applies if fluid flow in the porous media is isotropic and adsorption is fast, reversible, and linear (cf. Freeze and Cherry, 1979). These assumptions are often not valid, particularly for metal adsorption. As discussed above, the distribution coefficient approach can provide accurate modeling results for organic contaminants, but is likely to be in serious error when applied to the transport of metals through



porous media at specific sites. This is because, as emphasized previously, the reactions and processes that control metal sorption are in general far greater in number than is the case for the adsorption of organic substances. Some transport models assume a constant partition coefficient, or assume linearity of the partition coefficient over all concentration ranges. To the extent that sorption is not constant and follows a non-linear isotherm—which is the usual case for metals—these models will be inaccurate and should be avoided. The best that can be hoped for when single partition coefficients are used to describe metal adsorption is that they represent bounding values in a given application.

Laboratory adsorption studies often find that, in simple systems, the value of  $\log K_d$  for metal adsorption increases linearly with pH. For example, for  $\text{Zn}^{2+}$  adsorption by HFO, Langmuir (1997a) noted that adsorption followed the equation  $\log K_d = -5.48 + 1.77 \text{ pH}$ . For natural assemblages of particles, such as lake sediments, reported  $\log K_d$  values for a given metal are highly variable, but  $\log K_d$  values also clearly tend to increase with pH (Tessier, 1992).

EPA (1999b) presents a comprehensive review of the properties and applications of partition or distribution coefficients for metals. These coefficients may be obtained from the literature, estimated using mathematical models, or measured. Partition coefficients tabulated as a function of pH by EPA (1998) are listed in Table 15 for several important elements of potential concern. EPA (1999b) has also presented non-pH-dependent values for lead (900), mercuric chloride (58,000) and elemental mercury (1,000), which for reasons just discussed should be used with considerable caution.

**Table 15. Partition Coefficients as a Function of pH for Several Important Elements of Potential Concern (U.S. EPA, 1998)**

Element	pH 4.9	pH 6.8	pH 8.0
Arsenic(V)	25	29	31
Barium	11	41	52
Beryllium	23	790	1E+5
Cadmium	15	73	4.3E+3
Chromium (III)	1.2E+3	1.8E+6	4.3E+6
Chromium (VI)	31	19	14
Nickel	16	65	1,900
Selenium (VI)	18	5.0	2.2
Silver	0.1	8.3	110
Thallium (I)	44	71	96
Zinc		62	

EPA (1999b) discusses the advantages and disadvantages of several methods for measuring partition coefficients, including laboratory batch testing, in situ field batch testing, flow-through testing, and field modeling. In many national assessments, EPA has used MINTEQ

and its subsequent versions to generate generic partition coefficients that may be applied to regional or national mobility evaluations.

The application of single partition coefficient values for individual metals should be limited to regional and national scale studies where accuracy is not required, and bounding or representative values are adequate. As noted previously in the discussion of adsorption, metal partition coefficients can vary by several orders of magnitude over short distances (meters or less) in porous media because of changes not only in pH, but also in metal complex formation, metal adsorption competition, the solid/solution ratio, the relative abundances, the surface areas, and the surface charge densities of the different metal-sorbing phases.

A number of papers have measured adsorption of radionuclide elements by a variety of minerals (including oxyhydroxides, clays, and other silicates), and have developed diffuse layer adsorption parameters which allow the prediction of radionuclide adsorption by these minerals (cf. Langmuir, 1997b). A similar effort has not been made for most of the metals of concern, for which diffuse layer modeling of adsorption is largely limited to their adsorption by Fe(III), Mn, and Al oxyhydroxides.

It may be possible to estimate metal adsorption with some accuracy without having to measure it, depending on the information available on a specific soil, surface water, or ground water system. What is needed minimally is the amounts of potentially sorbing materials (e.g., metal oxides, clays and organic matter) in a soil or sediment or in suspension in a stream. Literature information like that given in Table 10 can then be used to estimate the sorption properties of these materials for use in a sorption model. For example, as noted above in discussion of the diffuse layer adsorption model, where ferric oxyhydroxide (HFO) is the dominant sorbent, and the amount of it suspended in a stream is known, estimation of metal adsorption can be accurate to within 10–20%, as shown in Table 11 (Smith et al., 1998). As a general observation, other conditions being equal, it has been found that the surface charge density and thus the metal adsorption capacity of most minerals is largely a function of their surface areas exposed to water (cf. Pabalan et al., 1998). Thus, the adsorption of a given metal by Al and Fe(III) oxyhydroxides in a system at a given pH may be assumed to be the same if they have the same surface areas.

If greater accuracy or site-specificity is required, it may be necessary to measure metal adsorption in laboratory experiments. Such measurements can be performed on pure minerals or on whole (usually sieved) soils. The sorption results may be used to develop diffuse layer model parameters for metal adsorption (cf. Dzombak and Morel, 1990; Stumm, 1992). Model results may then be used to compute partition or distribution coefficients as a function of pH, for example.

Several chemical mass transport codes are available that can model metal transport through porous media using the more accurate diffuse layer adsorption model for metals. These models include PHREEQC (Parkhurst and Appelo, 1999) and CHMTRNS (Noorishad et al.,

1987), and—for transport by streams—OTIS/OTEQ (Runkel et al., 1999). Even if model parameters are estimated based on literature values, such models will generally predict metal adsorption and retardation more accurately than is possible when using single or linearly varying distribution coefficient values.

## **15. RESEARCH RECOMMENDATIONS**

In general, environmental chemistry of metals research could benefit from the development of more routine chemical-species-specific analytical methods, the development of extraction techniques that have general utility in assessing bioavailability and/or mobility, and the validation of geochemical and chemical-specific environmental fate and transport models. The quality of EPA's use of environmental chemistry could benefit from the training of risk managers and other decision-makers in inorganic environmental chemical science.

The environmental chemistry of metals occupies a key position in the regulatory understanding of mobility, exposure, toxicity, and waste characterization. However interesting in its own right, EPA-sponsored research into the environmental chemistry of metals should be structured to answer specific environmental problems. Typically, these problems are associated with particular instances in which mobility, bioavailability, bioaccumulation, or toxicity are important. Rather than environmental chemistry driving the research agenda, it is probably more important for risk assessment to drive the research agenda.

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