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ENVIRONMENTAL CHEMISTRY OF SOILS

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The solution reached predicts that phosphate should move no deeper than 1 meter after ten years, and the shallow well is at no immediate risk from phosphate contamination.[1] Nitrate contamination of the well would, however, be likely because NO_3^- is a very mobile anion.

9.3. PROPERTIES OF INDIVIDUAL ELEMENTS IMPORTANT IN SOIL

A description of the most important properties of elements of interest, because they are essential for (or toxic to) life, is given in this section. A preliminary outline of biological function and level of toxicity is provided in Table 9.1. Those elements listed in the table that are more toxic to animals than to plants present the most insidious hazard to human health because the elements may accumulate in apparently healthy plants to levels that are poisonous to humans and animals. That is, for such elements the plant fails to play the role of a biological alarm that would warn of toxicity. The rating of elemental phytotoxicity in Table 9.1 should not be confused with the actual likelihood or frequency of toxicity in the field. For example, manganese is rated to have a fairly low intrinsic toxicity to plants, yet its toxicity is commonly seen because very high Mn^{2+} concentrations can develop in wet soils. In contrast, chromium and lead are rated as more phytotoxic, but they are generally so insoluble in soils that toxicity from these metals is rarely seen.

The chemistry of the elements listed in Table 9.1 is now discussed in more detail, excluding Fe and Al, which have been dealt with in some detail throughout the text. The parts per million (ppm) unit is used to report total elemental content by weight in the dry soil, and is equivalent to micrograms of the element per gram of soil ($\mu g/g$). These reported contents are averages given by Kabata-Pendias and Pendias (1984) for soils that were selected to try to avoid polluted sites. Being averages, they indicate typical contents but do not reveal the actual wide variation of elemental concentrations that can be encountered in some regions of the world. The following approximations may be useful in converting the reported contents to practical units:

$$1 \text{ ppm} \approx 2 \text{ pounds of element per acre of soil (6 inches deep)}$$
$$\approx 2 \text{ kilograms of element per hectare (15 cm deep)}$$

9.3a. Silver

The only stable oxidation state of Ag in aerated solutions is +1. The Ag^+ cation, having a very large radius, does not hydrolyze to AgOH until quite high pH. Ag_2O precipitates at high pH, reaching minimum solubility near pH 12. The important soluble form of Ag in the pH range of most soils is, therefore, the Ag^+ cation. At very low pH, the element has medium mobility in soils, sorbing selectively on clay exchange sites, humus, and oxides. At neutral or alkaline pH, Ag has very low mobility because chemisorption on minerals and organic matter is favored at higher pH.

1. Possible complicating factors in this analysis include the regeneration phenomenon, which would restrict P movement even further than predicted, and channel flow of water, which might allow some P to reach the well before all of the soil volume above had encountered P.

Table 9.1. Biological Function and Toxicity[a] of Important Trace Elements

Element	Biological Function	Phytotoxicity[b]	Mammalian Toxicity
Ag Silver	None known	H (5–10)	H
Al Aluminum	May activate succinic dehydrogenase	M (50–200)	L
As Arsenic	None known in animals. Constituent of phospholipid in algae and fungi	MH (5–20)	H
B Boron	Essential to plants. Phosphogluconate constituent	M (50–200)	L
Ba Barium	None known	L (500)	H (soluble forms)
Be Beryllium	None known	MH (10–50)	H
Cd Cadmium	None known	MH (5–30)	H Cumulative poison
Co Cobalt	Essential for mammals. Cofactor in numerous enzymes. Role in symbiotic N_2 fixation	MH (15–50)	M
Cr Chromium	May be involved in sugar metabolism in mammals	MH (5–30)	H(Cr^{6+}) M(Cr^{3+})
Cu Copper	Essential to all organisms. Cofactor in redox enzymes, O_2-transport pigments	MH (20–100)	M
F Fluorine	Strengthens teeth in mammals	LM (50–500)	M
Fe Iron	Essential to all organisms. Cofactor in many enzymes, heme proteins	L (>1000)	L
Hg Mercury	None known	H (1–3)	H (soluble or volatile forms). Cumulative poison.
Mn Manganese	Essential to all organisms. Cofactor in numerous enzymes. Involved in H_2O-splitting reaction of photosynthesis.	LM (300–500)	M
Mo Molybdenum	Essential to almost all organisms. Enzyme cofactor in N_2 fixation and NO_3^- reduction	M (10–50)	M
Ni Nickel	None known in mammals. May be essential to plants. Found in urease enzyme	MH (10–100)	M
Pb Lead	None known	M (30–300)	H Cumulative poison
Sb Antimony	None known	M (150)	H
Se Selenium	Essential to mammals and some plants	MH (5–30)	H
Tl Thallium	None known	MH (20)	H
V	Required by green algae; may be involved	H	H

Table 9.1. (continued)

Element	Biological Function	Phytotoxicity[b]	Mammalian Toxicity
Vanadium	in N_2 fixation. Porphyrin and heme constituent	(5–10)	
Zn Zinc	Essential to all organisms. Cofactor in numerous enzymes	LM (100–400)	LM

[a]Letters rate the elemental toxicity as low (L), moderate (M), and high (H).

[b]Numbers in parentheses denote the concentration of element in leaf tissue (μg/g dry weight or ppm) that shows toxicity in plants that are neither highly sensitive or tolerant (data from Kabata-Pendias and Pendias, 1984).

Source: Adapted from J. E. Huheey. 1972. *Inorganic Chemistry*. New York: Harper & Row.

The Ag^+ ion is a "soft" acid, displaying an extremely high affinity for "soft" bases, particularly S-containing ligands such as sulfhydryl and sulfide. To the extent that soil organic matter contains sulfhydryl groups, Ag^+ should associate strongly with the organic fraction of soils. In anaerobic soil environments, sulfide precipitates Ag^+ into highly insoluble solids, and Ag mobility is very low.

Peaty soils can have Ag contents exceeding 1 ppm. Much higher levels of Ag (> 10 ppm) are generally an indication that the soil has been polluted by human activities such as mining.

$$\text{Soil Ag (range of means, worldwide)} = 0.03 \text{ to } 8 \text{ ppm}$$

9.3b. Arsenic

The most probable oxidation states of As in soil environments are +3 and +5, although the −3 and 0 oxidation states are at least possible in strongly reduced soils and sediments. Arsenite (+3), which takes various forms such as $As(OH)_3$, $As(OH)_4^-$, $AsO_2(OH)^{2-}$, and AsO_3^{3-}, is the reduced state of As that is most likely to be found in anaerobic soils. Arsenate (+5), AsO_4^{3-}, the oxidized state, is stable in aerobic soils.

Arsenate has chemical behavior similar to that of phosphate in soils; it is chemisorbed by Fe and Al oxides, noncrystalline aluminosilicates, and, to a smaller extent, layer silicate clays. Being the anion of the strong acid, H_3AsO_4, with pK_a values (2.24, 6.94, and 11.5) similar to those of phosphoric acid, arsenate adsorbs most effectively at low pH. Consequently, its mobility is fairly low in acid soils with high clay or oxide content. In neutral to alkaline soils, especially those that are sodic, As may be mobile in the soluble Na arsenate form. Soil microbes and Mn oxides are able to promote the oxidation of arsenite to arsenate under aerobic conditions.

Based on chemical arguments, arsenite might be expected to adsorb more strongly on clays and oxides than arsenate (see Chapter 4). However, $As(OH)_3$ behaves like boric acid, forming the anion only at high pH:

$$As(OH)_3 + H_2O = As(OH)_4^- + H^+ \qquad \log K = -9.29$$

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The weak acidity of $As(OH)_3$ causes adsorption of arsenite on oxides and soils to be weaker than that of arsenate, at least when the pH is below 7. Like borate, arsenate appears to adsorb most effectively in the pH 7 to 9 range.

In soils that are poorly drained, once anaerobic conditions are established, both arsenate and arsenite can be released into solution by the dissolution of Fe and Mn oxides. Subsequently the desorbed arsenate is reduced to arsenite, which eventually is converted to insoluble forms (McGeehan and Naylor, 1992). Thus, As solubility may first increase and then decrease if anaerobic conditions are maintained. This reaction sequence explains the fact that the flooding of soils has been reported to *increase* As solubility, whereas increasing the redox potential of flooded soils has generally *reduced* As availability to plants.

Several competing processes are evidently involved when soils remain anaerobic for extended periods. Sulfides formed under anaerobic conditions may co-precipitate As in its lower oxidation state, a consequence of the chalcophilic tendencies of this element. However, volatile alkylarsene compounds may also form under strongly reducing conditions, causing loss of some As from the soil. The various biological and chemical transformations that interact to control solubility, mobility, and availability are diagrammed in Figure 9.8.

Amendments of ferrous salts, which oxidize to $Fe(OH)_3$ in soils, and calcite (lime), which sorbs arsenate and supplies Ca^{2+} to form Ca arsenate precipitates, seem to diminish the level of toxicity of As in soils.

Soil As (range of means, worldwide) = 2.2 to 25 ppm
Soil As (range of means, U.S.) = 3.6 to 8.8 ppm

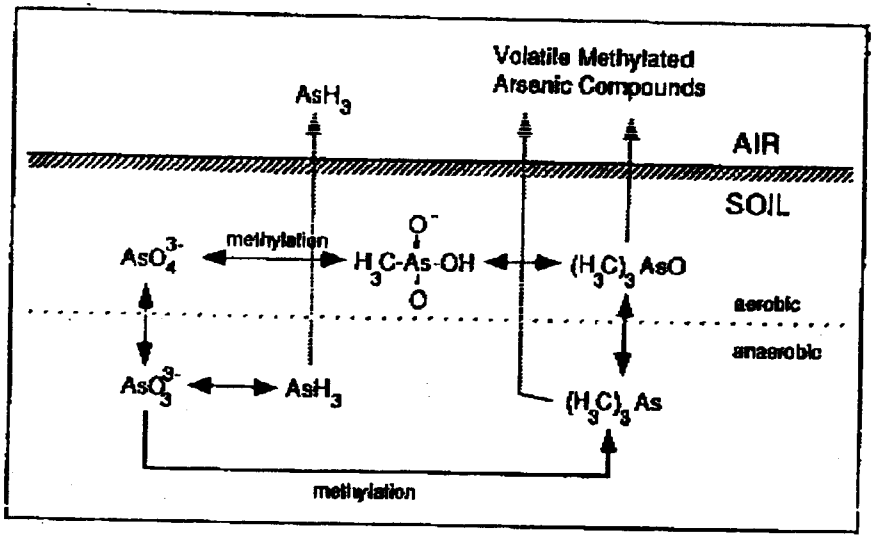

Figure 9.8. Biological and chemical transformations of arsenic in the soil. Broken arrows denote the loss of volatile forms of As to the atmosphere or the air-filled pores of the soil. (Modified from B. E. Davies. 1980. Trace element pollution. In B. E. Davies (ed.), *Applied Soil Trace Elements*. New York: Wiley.)

9.3c. Boron

Boron occurs in solution as boric acid, $B(OH)_3$, which is a very weak acid, but instead of donating a H^+ like most acids, it accepts an OH^- to convert to borate at high pH:

$$B(OH)_3 + OH^- = B(OH)_4^- \qquad K = 10^{-9.0}$$

Thus, $B(OH)_3$ is a Lewis acid rather than a Brønsted acid (see Chapter 1). Because boron adsorbs most effectively in the pH 8 to 9 range on Al and Fe oxides and silicate minerals, its availability is generally low in coarse-textured, acid-leached soils and in calcareous soils. Deficiency in acid soils is the result of boron depletion by leaching, while deficiency in calcareous soils is caused by strong adsorption and precipitation as relatively insoluble Ca borate salts. In contrast, B toxicity is most commonly found in alkaline soils of arid regions; these soils often contain high levels of Na^+ which forms quite soluble borate salts. A lack of rainfall allows soluble borate to accumulate to phytotoxic levels.

Boron is rated as a quite mobile element, leaching out of soils in humid climates and concentrating in the surface soil in arid and semiarid climates. In some soils, a large fraction of the total B is extractable by water.

Soil B (range of means, worldwide) = 9 to 85 ppm
Soil B (range of means, U.S.) = 20 to 55 ppm

9.3d. Barium

Barium occurs only in the +2 oxidation state, associating geochemically with feldspars and biotite micas in soils. It substitutes readily for K^+ in these structures because of the similar ionic radii of the large Ba^{2+} cation and K^+. As soils weather, the released Ba^{2+} can be immobilized by precipitation with sulfate or carbonate, or by "fixation" on high-charge layer silicate clays such as vermiculites. Clay exchange sites and humus show a high cation exchange selectivity for Ba^{2+} over more strongly hydrating cations such as Ca^{2+} and Mg^{2+}. Consequently, barium is rated as a rather immobile element in soils. Its average concentration in soils is higher than that of most of the trace elements.

Soil Ba (range of means, worldwide) = 84 to 838 ppm
Soil Ba (range of means, U.S.) = 265 to 835 ppm

9.3e. Beryllium

Beryllium in soils exists in the +2 oxidation state only. Its chemistry in soil solution parallels that of Al^{3+}. The free cation, Be^{2+}, is predominant below pH 6, but as the pH is raised, soluble Be-hydroxy species form (e.g., $BeOH^+$, $Be(OH)_2^0$, $Be_3(OH)_3^{3+}$) as $Be(OH)_2$ begins to precipitate. $Be(OH)_2$ reaches its minimum solubility near pH 9, because at higher pH the soluble anions, $Be(OH)_3^-$ and $Be(OH)_4^{2-}$, raise the solubility of total Be.

In soils of low pH, Be chemisorbs on surfaces as the cation, and is known to complex particularly strongly with organic matter. Since Be^{2+} is the smallest of all metal cations, it has the potential to form a very strong ionic bond with the abundant

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negatively charged functional groups in organic matter. In soils of neutral to slightly alkaline pH, hydrolysis reactions of Be^{2+} form hydroxy cations and solid $Be(OH)_2$, further reducing Be solubility. Mobility of Be in neutral to alkaline soils is consequently low. In very alkaline soils, soluble anionic Be-hydroxy and Be-carbonate complexes form, and the element may be mobilized to some degree.

Soil Be (range of means, U.S.) = 1.2 to 2.1 ppm

9.3f. Cadmium

Cadmium is a chalcophile, associating geochemically with Zn in the sulfide minerals of rocks. The oxidizing conditions of weathering in soils release Cd as the soluble and mobile Cd^{2+} ion. This cation is even more soluble than Zn^{2+} in acidic oxidizing solutions, and is rated as having medium to high mobility in well-drained acid soils. The high mobility is attributable to the fact that Cd^{2+} adsorbs rather weakly on organic matter, silicate clays, and oxides unless the pH is higher than 6. Above pH 7, Cd^{2+} can co-precipitate with $CaCO_3$ or precipitate as $CdCO_3$, and Cd phosphates may limit solubility as well. Therefore, mobility and bioavailability of Cd in neutral to alkaline soils is low. Liming acid soils is an effective means of limiting uptake of Cd by plants.

In continuously waterlogged soils, the low solubility of CdS results in low mobility. This fact can be used to advantage in severely contaminated soils to limit bioavailability. Well-drained soils polluted with Cd often allow hazardous levels of Cd uptake by crops; the same soils flooded for rice production allow much less uptake by that crop.

Generally, Cd concentrations in soils exceeding 0.5 μg/g are considered to be evidence of soil pollution from one of a number of possible sources: industry (mining, metallurgy, etc.), proximity to highways, high-Cd phosphate fertilizers, or sewage sludge application. Nevertheless, natural geochemical processes have been known to concentrate Cd in surface soils. Like Hg, Cd tends to accumulate in peaty soils by precipitation in sulfide minerals, and Cd levels may also be high in poorly drained soils or soils of arid and semiarid climates. This has created a problem in some irrigated farming regions where the climate is too dry for leaching to deplete naturally high levels of Cd in the soil. The combination of generally high bioavailability in soils and very high toxicity to animals and humans has made Cd the element of greatest concern in considering the value of sewage sludge as a soil amendment.

Soil Cd (range of means, worldwide) = 0.06 to 1.1 ppm

9.3g. Cobalt

Cobalt occurs in two oxidation states in soil, +2 and +3, but Co^{2+} is the dominant form in soil solution. This metal associates preferentially with Fe and Mn oxides because of chemisorption and co-precipitation. There is evidence that, on Mn oxides, Co^{2+} is oxidized and strongly bound as Co^{3+}. Consequently, strongly oxidizing conditions in the soil are likely to favor the adsorption of cobalt. As the soil pH is raised, Co solubility decreases because of increased chemisorption on oxides and silicate clays, complexation by organic matter, and possibly precipitation of $Co(OH)_2$. Organic matter complexes with Co^{2+} are fairly labile, so that organically bound Co^{2+}

is bioavailable. Cobalt is considered to be somewhat mobile in acid soils, but less so as the pH approaches neutrality. Under strongly reducing conditions, the formation of Co sulfides can restrict mobility.

Cobalt toxicity is occasionally found in high-Co soils formed from serpentinite and other ultrabasic rocks. Deficiency is most likely in coarse-textured, acid-leached soils; alkaline or calcareous soils; and humus-rich soils. Extractability by strong acids can range from very little (<1%) to a large fraction (>30%) of the total Co, depending on the forms of Co in the soil.

Soil Co (range of means, worldwide) = 1.6 to 21.5 ppm
Soil Co (range of means, U.S.) = 1 to 17 ppm

9.3h. Chromium

Chromium in soils potentially occurs in the +3 (chromic) oxidation state as the Cr^{3+} cation, and in the +6 oxidation state as chromate, CrO_4^{2-}. However, soil conditions generally favor the Cr^{3+} form, a very immobile cation that complexes strongly with organic matter and chemisorbs on oxides and silicate clays, even at quite low pH. Furthermore, Cr^{3+} readily substitutes for Fe^{3+} in mineral structures, and precipitates as insoluble $Cr(OH)_3$ at higher pH. The chromic form is, therefore, very immobile in most soils and generally unavailable to plants, at least if the soil is not exceedingly acid.

At higher pH, a small fraction of the Cr^{3+} in soils can be oxidized to chromate, CrO_4^{2-}, a very toxic form of chromium. This oxidation is promoted by Mn oxides. Chromate adsorbs less strongly than Cr^{3+}, and the mobility and bioavailability of this anion is consequently higher. Generally, however, if pollutants containing chromate are applied to soils, most or all of the chromate is spontaneously reduced to Cr^{3+}, especially under acid conditions and with organic matter present. Organic matter supplies reducing agents and complexing groups, stabilizing the chromic form. The soil therefore has the ability to detoxify chromate and immobilize the element.

Chromium is rated as an immobile element, most of which is difficult to extract from soils even by aggressive chemical agents. Toxicity of Cr to plants is occasionally seen in unusually Cr-rich soils formed from the parent rock, serpentinite, or under high pH conditions favorable to Cr^{3+} oxidation.

Soil Cr (range of means, worldwide) = 7 to 221 ppm
Soil Cr (range of means, U.S.) = 20 to 85 ppm

9.3i. Copper

Copper occurs in soil solids and solutions almost exclusively as the divalent cation Cu^{2+}. However, reduction of Cu^{2+} (cupric) to Cu^{+} (cuprous) and Cu^{0} (metallic copper) is possible under reducing conditions, especially if halide or sulfide ions ("soft" bases) are present to stabilize Cu^{+} (a "soft" acid). Copper is classified as a chalcophile, owing to its tendency to associate with sulfide in the very insoluble minerals, Cu_2S and CuS. In reduced soils, then, copper has very low mobility. Most of the colloidal material of soils (oxides of Mn, Al, and Fe, silicate clays, and humus) adsorb Cu^{2+} strongly, and increasingly so as the pH is raised. For soils with high Cu accumula-

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tions, precipitation as cupric hydroxide, oxide, or hydroxy-carbonates (malachite and azurite) is possible above pH 6. The trace quantities of Cu found naturally in most soils are probably widely dispersed on sorption sites and within structural (octahedral) sites of oxides and silicates. Organically complexed Cu^{2+} is bound more tightly than any other divalent transition metal; this fact is most evident at low metal loadings in humus when very selective complexing groups (amines or polyphenols) are involved. Lability of these complexes is rather low, limiting bioavailability. For this reason, farmers have been able to apply large amounts of Cu salts to organic soils over time without causing toxicity to crops.

Because of the high affinity of Cu^{2+} for soil colloids, copper is rated a low-mobility element in near-neutral soils. It builds up in the surface of contaminated soils, showing virtually no downward migration. In more alkaline soils, while free Cu^{2+} solubility is exceedingly low, soluble complexes of Cu^{2+} (most importantly hydroxy, carbonate, and organic matter complexes) form and increase the total copper solubility. Consequently, mobility may be significant under high pH conditions. Most of the total dissolved copper in surface soils over a fairly wide range of pH, and particularly at higher pH, is in the form of Cu^{2+}-organic complexes.

Copper deficiencies are most common in soils that are peaty, acid-leached, coarse-textured, or calcareous. Soils with less than 8 ppm total Cu may be deficient for crops.

Toxicity of natural origin is found in soils formed from Cu sulfide-rich parent rocks, especially when the soil is acid. Bioaccumulation of Cu in humus followed by episodes of reduction can concentrate the element in sulfide form in natural wetlands. Because copper is not only phytotoxic but also a commonly abundant metal pollutant in waste materials, Cu in wastes such as sewage sludges is often the first element to limit land application.

Soil Cu (range of means, worldwide) = 6 to 80 ppm
Soil Cu (range of means, U.S.) = 14 to 29 ppm

9.3j. Fluorine

Fluorine occurs exclusively as the fluoride anion, F^-, in soils, where it complexes strongly with metals such as Al^{3+} and Fe^{3+}. It is found in structures of hydrous minerals, isomorphously substituting for structural OH^-. Thus, F^- can be found in micas, amphiboles, layer silicate clays, apatite (rock phosphate), and numerous other minerals. Because it is associated with clay structures, the natural concentrations of fluorine in fine-textured mineral soils and sedimentary rocks can be high.

The fluoride ion chemisorbs on clays and oxides by ligand exchange of surface OH^-, a reaction favored at low pH and on oxide and silicate minerals of low crystallinity. Fluoride, a "hard" base, has a particular affinity for Al^{3+}, a "hard" acid. Soluble Al^{3+}-fluoride cationic and anionic complexes are quite stable, and can dominate the speciation of dissolved aluminum in low-humus soils. The mobility of Al can be increased by the presence of F^-; soluble complex formation with Al may explain the rather high solubility and mobility of F^- in acid soils.

In calcareous soils, F^- mobility is low. Perhaps its solubility is limited by incorporation into insoluble Ca minerals such as hydroxyapatite. In sodic soils, F^- mobility is enhanced by the fact that NaF is a very soluble salt.

Naturally occurring F^- associated with hydrous minerals has low mobility because it is occluded in structures. Airborne fluoride pollutants (from smelters, rock phosphate fertilizer factories, etc.) are, in contrast, easily dissolved on contact with the soil. These forms of fluoride can be bioaccumulated by plants before leaching, sorption, or precipitation processes have a chance to lower solubility.

Soil F (range of means, worldwide) = 73 to 566 ppm
Soil F (range of means, U.S.) = 205 to 465 ppm

9.3k. Mercury

This element is a chalcophile, and in unweathered rocks is most commonly found as the mineral cinnabar (HgS). In soil environments, the cationic form, Hg^{2+}, is most common, as the reduced oxidation state (+1) has a limited stability range. Reduction to the metallic elemental form, Hg^0, is easily achieved in soils by both biological and chemical reactions. Elemental mercury is somewhat volatile, and the vapor is extremely toxic to organisms. Under anaerobic conditions at least, soil microbes methylate mercury, forming volatile organomercury compounds that are bioavailable and present a health hazard. At the same time, however, anaerobic conditions can convert Hg^{2+} into the exceedingly insoluble sulfide, HgS. Some of the more important transformations possible for mercury in soil are summarized in Figure 9.9.

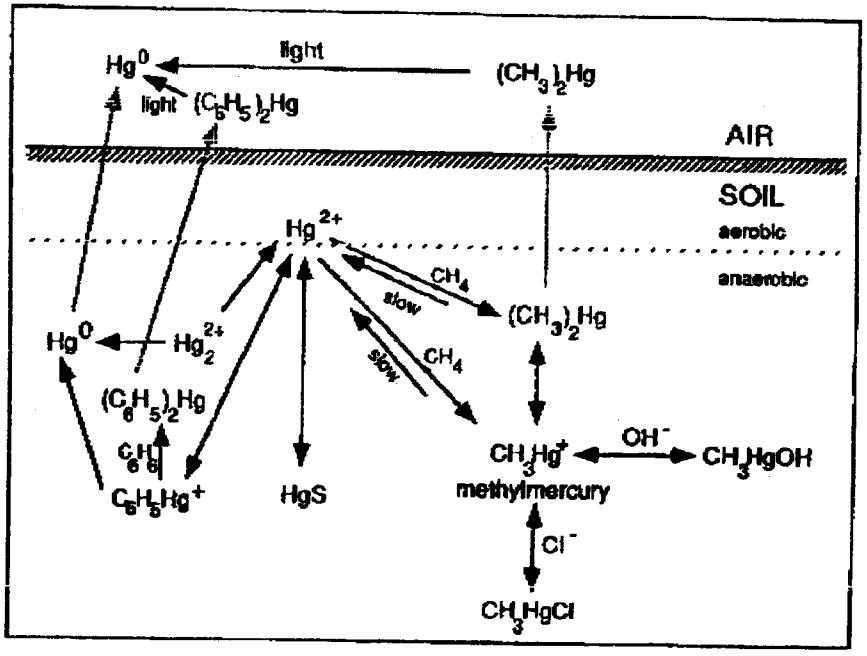

Figure 9.9. Biological and chemical transformations of mercury in the soil. Broken arrows denote the loss of volatile forms of Hg to the atmosphere or the air-filled pores of the soil. (Modified from B. E. Davies. 1980. Trace element pollution. In B. E. Davies (ed.), *Applied Soil Trace Elements*. New York: Wiley.)

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Because of the complex chemistry of Hg, general statements about mobility are difficult to make. Acidic oxidizing conditions in soils tend to stabilize the +2 oxidation state (Hg^{2+}), which complexes only moderately strongly with the predominant functional groups of organic matter, phenolic and carboxylate groups. However, the Hg^{2+} cation is a "soft acid," bonding very strongly with "soft" ligands such as sulfhydryl and sulfide. The sulfhydryl ligand (−SH) is a minor functional group in humus (which typically contains less than 1% total sulfur), and yet may bind chalcophilic metal cations such as Hg^{2+}, Cd^{2+}, and Pb^{2+}. Mobility of Hg^{2+}, then, is probably very sensitive to loading, with traces of Hg^{2+} being very immobile and higher levels having medium mobility.

Adsorption of Hg^{2+} on silicate clays and oxides is more favorable at higher pH, and hydrolysis of Hg^{2+} causes the dominant soluble form to be $Hg(OH)_2^0$ above pH 4. The solubility of this neutral molecule is high enough to prevent precipitation from lowering the solubility of mercury in Hg-contaminated soils to trace levels. Precipitation of $Hg(OH)_2$ does, however, limit the activity of the free Hg^{2+} cation to extremely low values in the neutral to alkaline pH range.

In reducing soil environments, the strong association of Hg with sulfide creates a situation of low mobility, although there is the danger that volatile forms of the element can lead to some mobilization.

Mercury accumulation in soils tends to correlate with the organic matter level. The highest natural Hg concentrations have been reported in peaty and waterlogged soils. Toxicity to organisms is usually attributable to soil conditions that favor the production of volatile forms of Hg; evidently, Hg^{2+} cations interact strongly enough with humus and clays to limit availability of this form to plants and animals.

Soil Hg (range of means, worldwide) = 0.02 to 0.41 ppm
Soil Hg (range of means, U.S.) = 0.04 to 0.28 ppm

9.3l. Manganese

Manganese has three possible oxidation states in soils, +2, +3, and +4. The most reduced form of Mn, the Mn^{2+} ion, is the only stable form in soil solution. The Mn^{3+} ion is a powerful oxidant that either disproportionates to Mn^{2+} and Mn^{4+} or oxidizes water to liberate O_2:

$$2Mn^{3+} + H_2O = 2Mn^{2+} + 2H^+ + \tfrac{1}{2}O_2$$

Needless to say, Mn^{3+} has a very short life in solution, but it can be detected in some cases if complexing anions such as pyrophosphate, oxalate, or sulfate are present to stabilize it for a time.

Both Mn^{3+} and Mn^{4+} are stable only in the solid phase of soils, where they form insoluble oxide and hydroxide minerals of variable structure and oxidation state (e.g., MnO_2, MnOOH, Mn_3O_4, $Na_4Mn_{14}O_{27}$). The Mn^{2+} ion is released from these solids by spontaneous dissolution or cation exchange, especially under acidic or reducing conditions. Release of Mn^{3+} can also be detected in the presence of pyrophosphate.

Manganese solubility is controlled by the redox potential and pH of the soil. The Mn^{2+} ion is a very soluble species in water, forming hydroxide and carbonate precipitates only at high pH (>7). However, as the pH is raised above 6 in soils,

Mn^{2+}, despite being the most weakly complexing transition metal, bonds with organic matter, oxides, and silicates and its solubility decreases. Small changes in the soil redox potential or pH can shift the Mn^{2+} − Mn oxide reaction. Low pH or low E_h (see Chapter 7) favors the reduction of insoluble Mn oxides and an increased solubility of Mn^{2+}. As a result, Mn solubility within any particular soil can fluctuate tremendously over time, sometimes ranging from deficient to toxic levels.

The mobility of Mn defies classification because it is extremely sensitive to soil conditions (acidity, wetness, biological activity, etc.). Toxicity to plants is most likely in waterlogged soils or acid soils with low humus content. Deficiency is most often found in soils that are saline and alkaline, calcareous, peaty, coarse textured, or acid leached.

Total Mn in soils is highly variable and not closely related to the Mn content of the parent material, probably because of the tendency for cyclical reduction-oxidation to rapidly mobilize, then reprecipitate Mn as oxides in nodules and other deposits. Mn tends to associate with ferric iron in these deposits.

Soil Mn (range of means, worldwide) = 80 to 1300 ppm
Soil Mn (range of means, U.S.) = 260 to 840 ppm

9.3m. Molybdenum

Molybdenum is primarily in the +6 oxidation state in soils, taking the form of the molybdate anion, MoO_4^{2-}. Protonation of this oxyanion, described by the reaction:

$$MoO_4^{2-} + H^+ = HMoO_4^- \qquad K = 10^{3.7}$$

occurs at low pH. Molybdate is chemisorbed in soils by oxides, noncrystalline aluminosilicates, and to a lesser extent, layer silicate clays, with sorption on all these minerals increasing at lower pH. Consequently, Mo is least soluble in acid soils, particularly those containing iron oxides. The availability of adsorbed molybdate diminishes with time. Phosphate additions to soil may release molybdate from bonding sites, increasing bioavailability of the element. Precipitation of Mo into pure phases is considered highly unlikely because of the very low concentration of the element in almost all soils.

Molybdenum has a high mobility in neutral or alkaline soils and medium mobility in acid soils. Liming soils is known to increase availability of the element. Factors controlling mobility in anaerobic soils are not understood. In one respect, the association of Mo in lower oxidation states with sulfide should reduce its solubility under poor drainage. However, poor soil drainage also leads to organic matter accumulation, and there is circumstantial evidence that molybdate bonds with organic matter by the same mechanism that borate does—via two adjacent OH groups such as would be found in the polyphenols of humus. Humus-rich soils then accumulate Mo as long as they remain poorly drained, because little leaching is occurring.

Molybdenum is most commonly deficient in coarse-textured acid soils and low-humus soils. Plant toxicity is associated with poor drainage and alkaline, calcareous, clayey, or peaty soils.

Soil Mo (range of means, worldwide) = 1 to 3 ppm
Soil Mo (range of means, U.S.) = 0.35 to 5.8 ppm

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9.3n. Nickel

The +2 oxidation state is the only stable form of nickel in soil environments. The Ni^{2+} cation is almost as electronegative as Cu^{2+}; this fact and its electronic structure favor the formation of complexes with organic matter that are comparable in stability to those of Cu^{2+}. Bioaccumulation of Ni in humus is pronounced, and like Cu^{2+}, Ni^{2+} favors bonding to "softer" organic ligands containing nitrogen and sulfur. As the smallest of the divalent transition metal cations, Ni^{2+} fits easily into octahedral sites, co-precipitating readily into Mn and Fe oxides in soils. Chemisorption on oxides, noncrystalline aluminosilicates, and layer silicate clays is favorable above pH 6, but lower pH favors exchangeable and soluble Ni^{2+}. Because solubility decreases markedly at higher pH, mobility of Ni, rated as medium in acid soils, becomes very low in neutral to alkaline soils. Under reducing conditions, Ni^{2+} is incorporated into sulfides that restrict mobility to very low levels.

Toxicity of Ni to plants is found in acid soils formed from serpentinite or other ultrabasic rocks. High organic matter levels in Ni-rich soils can solubilize Ni^{2+} as organic complexes, at least at higher pH. Nickel is a strongly phytotoxic element, being several times more toxic than copper. Like copper, it occurs commonly in industrial wastes and sewage sludges at appreciable levels, and may reach levels toxic to plants in waste-treated soils.

Soil Ni (range of means, worldwide) = 4 to 55 ppm
Soil Ni (range of means, U.S.) = 13 to 30 ppm

9.3o. Lead

Lead exists principally in the +2 oxidation state in soils. It is strongly chalcophilic, occurring primarily as PbS in rocks and becoming very insoluble in reduced soils because of its precipitation by sulfide generated from sulfate reduction. Sulfhydryl groups, if present in humus, strongly complex the Pb^{2+} cation. Under oxidizing conditions, the Pb^{2+} ion becomes less soluble as soil pH is raised. Complexation with organic matter, chemisorption on oxides and silicate clays, and precipitation as the carbonate, hydroxide, or phosphate are all favored at higher pH. In alkaline soils, solubility may increase by formation of soluble Pb-organic and Pb-hydroxy complexes. The Pb^{2+} ion has a particularly high affinity for Mn oxides, a fact perhaps explained by Mn oxidation of Pb^{2+} to Pb^{4+}, a very insoluble ion. Lead is the least mobile heavy metal in soils, especially under reducing or nonacid conditions.

As expected from the strong complexation of Pb^{2+} by organic matter, lead bioaccumulates in the humus-rich surface layer of soils. Soils polluted at the surface with lead deposited from aerial contaminants show little indication of metal leaching over many years. Lead levels in sewage-sludge-treated soils are considerably higher than levels in most natural soils because of the generally high concentration of Pb in wastes contaminated by old plumbing and by various industries.

Most of the lead in soils appears to be unavailable to plant tops. Plant-absorbed Pb^{2+} concentrates in the roots, translocating very little from roots to tops as long as the plant is actively growing.[1] Toxic effects of lead on plants have not often been

1. There is some evidence that Pb translocates readily from roots to tops as plants senesce and die, perhaps due to breakdown of membrane barriers to ion transport.

observed, but a hazard to animals exists because of the inherently higher toxicity of this element to animals. The health concern with lead-polluted soils arises mostly from the contamination of plants by soil particles, and ingestion of soil by humans and grazing animals. The risk of lead movement from soils to edible plant parts is believed to be low.

Soil Pb (range of means, worldwide) = 10 to 84 ppm
Soil Pb (range of means, U.S.) = 17 to 26 ppm

9.3p. Antimony

Antimony has geochemical behavior similar to arsenic, as it occurs most commonly in the +3 (antimonite) and +5 (antimonate) oxidation states and also tends to associate with sulfides in rocks, sediments, and soils. In soil solutions, the Sb^{3+} and Sb^{5+} oxidation states are stable under reducing and oxidizing conditions, respectively.

In reducing soil solutions, Sb^{3+} is likely to have the form of the uncharged $Sb(OH)_3^0$ molecule, except at very acid and alkaline pH where $Sb(OH)_3^0$ converts into the $Sb(OH)_2^+$ cation and $Sb(OH)_4^-$ anion, respectively. The oxide of Sb^{3+}, Sb_2O_3, is too soluble to limit solubility of the element except in highly polluted soils. The oxide becomes more soluble below pH 3 and above pH 10.

In oxidizing soil solutions, Sb^{5+} is likely to form the anionic molecule $Sb(OH)_6^-$, above pH 4, and $Sb(OH)_5^0$ in more acid solution. As an anion, $Sb(OH)_6^-$ may adsorb by ligand exchange on oxides and silicate clays. Antimony associates with ferric hydroxide in soils, perhaps a result of chemisorption of the anion on this mineral.

Antimony is a common pollutant of soils in industrial and mining sites. Its mobility in soils is rated as medium, with reducing conditions associated with poor drainage probably lessening mobility.

Soil Sb (range of means, worldwide) = 0.19 to 1.77 ppm

9.3q. Selenium

Selenium, a chalcophile, tends to be associated with sulfide minerals in rocks. Weathering processes in the soil oxidize these very insoluble reduced forms, including elemental Se (Se^0), the selenides (Se^{2-}), and selenium sulfides, to the more soluble selenites (SeO_3^{2-}) and selenates (SeO_4^{2-}). With numerous oxidation states possible for Se in soils, redox potential is a critical factor in Se behavior.

In alkaline, oxidized soils, selenates are the dominant form. These oxyanions bond rather weakly to oxides and other minerals, so that Se mobility in neutral to alkaline soils is rated high. In slightly acid soils that are oxidized, selenites prevail, showing lower mobility than selenates because of the ability of SeO_3^{2-} to chemisorb strongly on oxides and aluminosilicates and to precipitate as the insoluble ferric selenite. In wet, acid, or humus-rich soils, the insoluble reduced forms of Se tend to predominate, so that Se mobility and bioavailability are very low. However, under reducing conditions, biological methylation of Se is possible, forming volatile compounds that may mobilize the element.

The solubility and total content of Se in many soils is quite low, so that crops often contain Se levels that could produce deficiencies in animals and humans. In contrast, Se often concentrates as the soluble and highly available selenate form in

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the surface soils of arid and semiarid regions. Plants can bioaccumulate this available Se, creating a potential toxicity hazard to foraging animals. The geographic distribution of Se in crop and forage plants of North America is, broadly speaking, low in the humid regions of the northwest, northeast, and southeast and moderate to high (sometimes toxic) in the arid and semiarid western plains. Irrigation of arid-region alkaline soils transports natural selenate into drainage water; this can contaminate bodies of water with levels of Se toxic to aquatic animals.

High Se levels are often associated with poorly drained sites, and yet, as described above, Se solubility is generally low under reducing conditions. Poor drainage allows dissolved Se salts to accumulate at the surface by evaporation of water.

A large fraction of Se in soils can be plant available and easily extractable. This is the case for nonacid soils, particularly calcareous ones, that often contain Se in the relatively soluble selenate form.

Soil Se (range of means, worldwide) = 0.05 to 1.27 ppm
Soil Se (range of means, U.S.) = 0.19 to 1.05 ppm

9.3r. Thallium

In soil solutions, both the +1 and +3 oxidation states of Tl are possible as Tl^{3+} is easily reduced to Tl^{+}. The Tl^{3+} cation behaves somewhat like Al^{3+} but hydrolyzes even more readily than Al^{3+}, and the insoluble oxide, Tl_2O_3, forms at lower pH (< 2) and remains insoluble to higher pH (>10) than Al_2O_3. Thus, mobility of the oxidized form of Tl (+3) should be very low due to precipitation and adsorption reactions. The reduced form of Tl (+1) has very different behavior, as the Tl^{+} ion acts more like an alkaline metal such as K^{+} or Rb^{+}. This reduced form should have higher mobility than Tl^{3+} under well-drained conditions, although fixation of Tl^{+} on clays may be possible. In poorly drained soils, the reducing conditions may limit solubility and mobility, since Tl^{+} is readily incorporated into sulfide minerals.

Soil Tl (range of means, U.S.) = 0.02 to 2.8 ppm

9.3s. Vanadium

Vanadium in soil solutions exists predominantly in the +5 and +4 oxidation states, as the vanadate anionic forms ($VO_2(OH)^{2-}$, $VO_2(OH)_2^{-}$, $VO(OH)_3^{0}$, and more complex polymeric anions), and as the vanadyl cation, VO^{2+}. However, the V^{3+} ion, which is not stable in aerated solutions, may substitute readily for Fe^{3+} in minerals such as Fe oxides. The soil redox potential determines the oxidation state, and therefore solubility, with V having very high mobility and bioavailability in oxidized soils that are neutral to alkaline. It is likely that vanadate anions bond on oxides and silicates most effectively at low pH, following the pattern of phosphate and many other oxyanions. Consequently, V solubility should be quite high at high pH, but lower if the soil is more acid. Contributing to this trend is the fact that lower pH favors chemical reduction of vanadate to vanadyl, a cation that behaves much like Cu^{2+}, complexing tightly with organic matter and chemisorbing on oxides and aluminosilicates. As a result, the mobility of V under reducing or acid conditions is probably moderate to low. Since there is evidence that humus promotes the rather

easy reduction of vanadate to VO^{2+}, a low redox potential may not be necessary to immobilize V in organically bound form. In any event, it is observed that the element tends to associate with humus in soils.

Vanadium is found substituted into the structures of layer silicate clays as the VO^{2+} (V^{4+}) ion, a form that must have very low bioavailability. Its tendency to substitute into oxides and layer silicates as V^{4+} (and perhaps V^{3+}) may account for the correlation between clay content and total V content of soils.

Soil V (range of means, worldwide) = 5 to 190 ppm
Soil V (range of means, U.S.) = 38 to 136 ppm

9.3t. Zinc

As a chalcophile, zinc tends to occur as the sulfide mineral, sphalerite (ZnS) in rocks, but weathers to the soluble Zn^{2+} ion in the oxidizing environment of soils. The +2 oxidation state is the only one possible in the soil. In acid, aerobic soils, Zn has medium mobility, held in exchangeable forms on clays and organic matter. At higher pH, however, chemisorption on oxides and aluminosilicates and complexation with humus lower the solubility of Zn^{2+} markedly. Consequently, Zn mobility in neutral soils is very low. If soils are slightly alkaline, even though the activity of the free Zn^{2+} ion is extremely low, Zn-organic complexes can become soluble and raise mobility. In strongly alkaline soils, Zn-hydroxy anions may form to increase solubility.

In soils contaminated by high levels of Zn, precipitation of Zn oxide, hydroxide, or hydroxycarbonate may limit Zn^{2+} solubility at pH 6 or higher. Co-precipitation of Zn^{2+} into octahedral sites of oxides and silicates is theoretically possible, although the importance of this in soils is not known.

In the reducing environment of flooded soils, release of Zn^{2+} from dissolving Fe oxides may initially increase availability, but Zn mobility is ultimately restricted by the extreme insolubility of ZnS.

Under acidic, oxidizing conditions, Zn^{2+} is one of the most soluble and mobile of the trace metal cations. It does not complex tightly with organic matter at low pH. Acid-leached soils often have Zn deficiency because of depletion of this element in the surface layer. Calcareous and alkaline soils also commonly have Zn deficiency, but the cause is low solubility.

Toxicity of Zn to plants is most likely to appear in acid soils that have not been subjected to prolonged acid leaching. The rather high potential solubility of Zn^{2+} in acid soils, and the fact that Zn^{2+} is typically a high-concentration pollutant of industrial wastes and sewage sludges, combine to create a significant potential for phytotoxicity from land application of wastes. This is in spite of the fact that Zn toxicity to plants is inherently fairly low.

Soil Zn (range of means, worldwide) = 17 to 125 ppm
Soil Zn (range of means, U.S.) = 34 to 84 ppm

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Questions

1. The powerful metal chelator, EDTA (ethylenediaminetetraacetic acid), is an efficient extracting agent for organically bound trace metal cations in soils at pH 6 and higher. The formation constants, K_{ML}, for some metal-EDTA complexes in water are given below:

Metal	log K_{ML}
Cu^{2+}	19.7
Ni^{2+}	19.5
Zn^{2+}	17.2
Cd^{2+}	17.5
Ca^{2+}	11.5
Al^{3+}	17.6
Fe^{3+}	26.5

   (a) Why should EDTA be more efficient at extracting trace metals from neutral or alkaline soils than from acid soils?
   (b) The EDTA-extractable quantities of trace metals in soils amended with sewage sludges sometimes increase over a period of years. Can you propose a mechanism that would account for this change in the soil?
   (c) How would EDTA additions to a Ni-contaminated soil at pH 7 affect Ni^{2+} activity, total soluble Ni, and Ni availability to plants?

2. The availability of arsenic in soils could possibly be limited by the solubility product of Ca or Fe arsenate, given below:

$$Ca_3(AsO_4)_2 \quad K_{so} = 6.8 \times 10^{-19}$$
$$FeAsO_4 \quad K_{so} = 5.7 \times 10^{-21}$$

   Assuming that the soils have been contaminated by the use of arsenate pesticides, calculate the upper limit of solubility of AsO_4^{3-} in:
   (a) an acid mineral soil at pH 4.5, if the solution activity of Fe^{3+} is controlled by the solubility of $Fe(OH)_3$ ($K_{so} = 10^{-39}$).
   (b) a calcareous soil at pH 8, if the solution activity of Ca^{2+} is maintained at about 2×10^{-3} *M*.

   In which soil is arsenic likely to be more mobile and bioavailable? (Ignore activity corrections for solution concentrations in this problem.)

Note:

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