fact that slow chemical reactions and diffusion processes in the soil tend to gradually increase the measured value of Q_M as time goes on, a phenomenon referred to as "regeneration" of sorption capacity. That is, sorption capacity is not so well determined and fixed as the model would suggest. Regeneration has practical consequences for the mobility of chemicals in soil. For phosphate, it means that the tipping bucket model overestimates mobility, especially in cases where phosphate movement in the soil is measured over a long time. In fact, phosphate migration through mineral soils and into groundwater has not been detected very often, even when phosphate loadings have exceeded the short-term sorption capacity of the soil (Q_M) by a wide margin.

It is perhaps worthwhile to use a simple problem to illustrate the application of the tipping bucket model.

Example Problem: Suppose that a deep and fairly homogeneous soil is going to be used to dispose of septic tank waste water that contains 10 mg/liter of soluble phosphorus in the form of phosphate. A sorption isotherm is measured for the soil, from which the sorption capacity of the soil is estimated at $Q_M = 200$ mg P/kg soil. The 600 liters of waste water that is generated each day is evenly disposed of over a 70 square meter area. Estimate the depth of phosphate movement in the soil after ten years, and make a decision whether a shallow well (10 meters deep) at the edge of the disposal area could become contaminated by phosphate.

Solution: This problem is approached by first calculating the total "P load" on the disposal area from the information given. A discharge of 600 liters per day containing 10 mg P/liter amounts to:

$$600 \text{ liters/day} \times 10 \text{ mg/liter} = 6000 \text{ mg P/day}$$

which, over ten years, accumulates a "P load" of

$$6000 \text{ mg P/day} \times 365 \text{ days} \times 10 = 21.9 \times 10^6 \text{ mg P}$$

Because the soil's average sorption capacity is 200 mg P/kg, the weight of soil that can sorb the entire P load is

$$\frac{(21.9 \times 10^6 \text{ mg P})}{(200 \text{ mg P/kg soil})} = 1.10 \times 10^5 \text{ kg soil}$$

This weight has to be converted to a volume using the soil's bulk density. A reasonable estimate is 1.5 g/cm³ (1.5 kg/liter), so that the soil volume needed to retain all of the phosphate is

$$\frac{(1.10 \times 10^5 \text{ kg soil})}{(1.5 \text{ kg/liter})} = 7.3 \times 10^4 \text{ liters} = 73 \text{ m}^3$$

Since the waste water is spread over a 70 m² area, the depth of phosphate penetration below the surface is determined by dividing the "phosphate-saturated" volume of soil by the disposal area:

$$\frac{73 \text{ m}^3}{70 \text{ m}^2} \approx 1 \text{ meter}$$

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 (μg/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 ($\mu g/g$ 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.

Soil Ag (range of means, worldwide) = 0.03 to 8 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:

$$As(OH)_3 + H_2O = As(OH)_4^- + H^+ \qquad \log K = -9.29$$
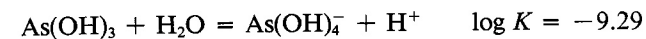
The weak acidity of $As(OH)_3$ causes adsorption of arsenite on oxides and soils to be weaker than that of arsenate, at least when the pH is below 7. Like borate, arsenate appears to adsorb most effectively in the pH 7 to 9 range.

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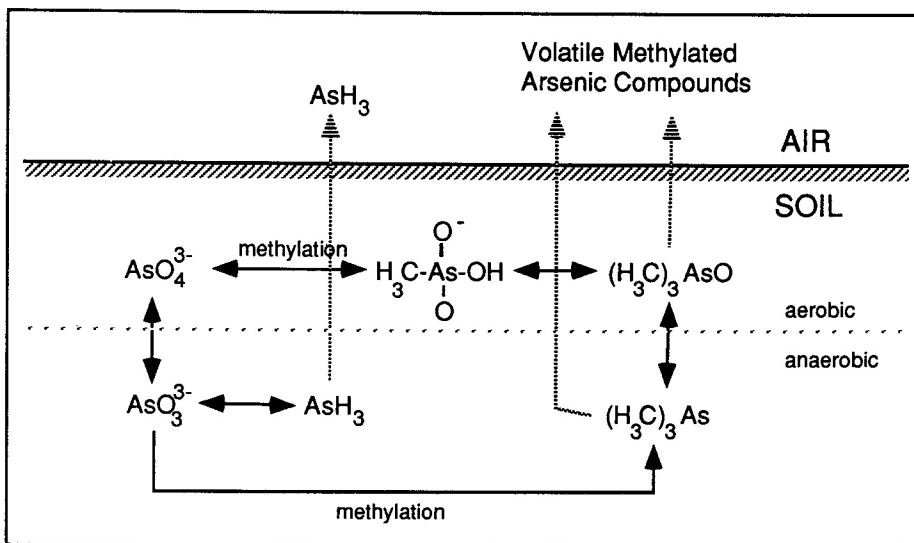Soil As (range of means, U.S.) = 3.6 to 8.8 ppm

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:

$$B(OH)_3 + OH^- = B(OH)_4^- \qquad K = 10^{-9.0}$$
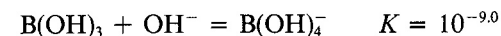
Thus, $B(OH)_3$ is a Lewis acid rather than a Brønsted acid (see Chapter 1). Because boron adsorbs most effectively in the pH 8 to 9 range on Al and Fe oxides and silicate minerals, its availability is generally low in coarse-textured, acid-leached soils and in calcareous soils. Deficiency in acid soils 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

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.

$$\text{Soil Be (range of means, U.S.)} = 1.2 \text{ to } 2.1 \text{ ppm}$$

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 $\mu g/g$ 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.

$$\text{Soil Cd (range of means, worldwide)} = 0.06 \text{ to } 1.1 \text{ ppm}$$

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.

$$\text{Soil Co (range of means, worldwide)} = 1.6 \text{ to } 21.5 \text{ ppm}$$
$$\text{Soil Co (range of means, U.S.)} = 1 \text{ to } 17 \text{ ppm}$$

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.

$$\text{Soil Cr (range of means, worldwide)} = 7 \text{ to } 221 \text{ ppm}$$
$$\text{Soil Cr (range of means, U.S.)} = 20 \text{ to } 85 \text{ ppm}$$

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-

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.
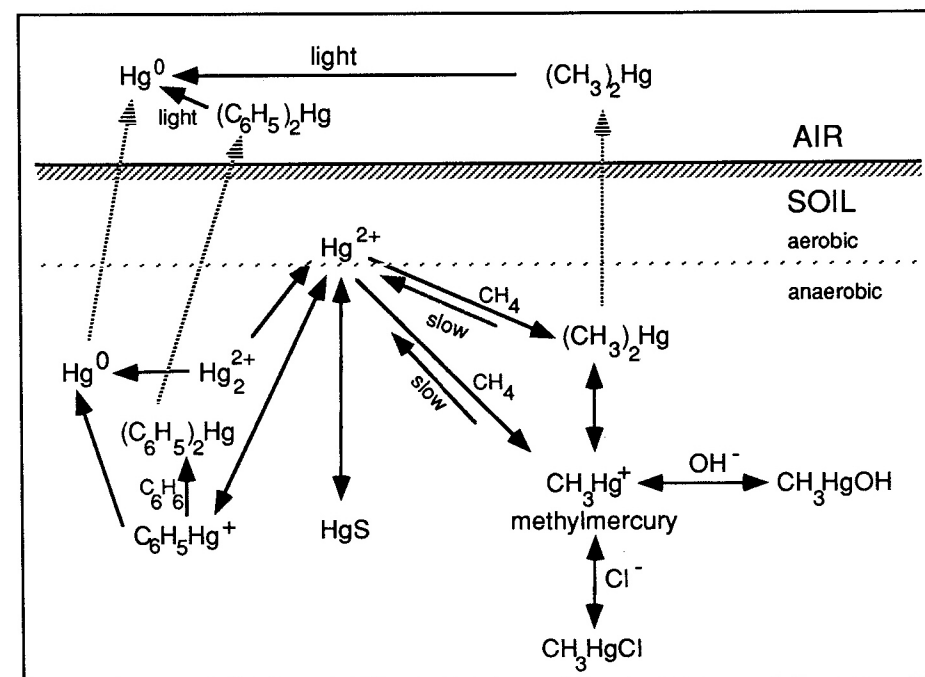

Figure 9.9. Biological and chemical transformations of mercury in the soil. Broken arrows denote the loss of volatile forms of Hg to the atmosphere or the air-filled pores of the soil. (Modified from B. E. Davies. 1980. Trace element pollution. In B. E. Davies (ed.), *Applied Soil Trace Elements.* New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

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:

$$2Mn^{3+} + H_2O = 2Mn^{2+} + 2H^+ + \tfrac{1}{2}O_2$$
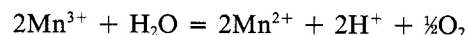
Needless to say, Mn^{3+} has a very short life in solution, but it can be detected in some cases if complexing anions such as pyrophosphate, oxalate, or sulfate are present to stabilize it for a time.

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:

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

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

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

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 ($VO_3(OH)^{2-}$, $VO_2(OH)_2^-$, $VO(OH)_3^0$, 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

References

Davies, B. E. 1980. Trace element pollution. In B. E. Davies (ed.), *Applied Soil Trace Elements*. New York: Wiley, pp. 287–351.

Huheey, J. E. 1972. *Inorganic Chemistry.* New York: Harper & Row.

Kabata-Pendias, A. and H. Pendias. 1984, 2nd ed. 1992. *Trace Elements in Soils and Plants.* Boca Raton, Fl.: CRC Press.

McGeehan, S. L. and D. V. Naylor. 1992. In *Agronomy Abstracts.* Madison, Wis.: Soil Science Society of America. p. 242.

Millot, G. 1970. *Geology of Clays.* New York: Springer-Verlag.

Suggested Additional Reading

Alloway, B. 1990. *Heavy Metals in Soils.* Halsted Press, New York.

Davies, B. E. (ed.). 1980. *Applied Soil Trace Elements.* New York: Wiley.

Swift, R. S. and R. G. McLaren. 1991. Micronutrient adsorption by soils and soil colloids. In G. H. Bolt, M. F. DeBoodt, M.H.B. Hayes, and M. B. McBride (eds.), *Interactions at the Soil Colloid-Soil Solution Interface.* Dordrecht, Netherlands: Kluwer, pp. 257–292.

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:

$$Ca_3(AsO_4)_2 \quad K_{SO} = 6.8 \times 10^{-19}$$
$$FeAsO_4 \quad K_{SO} = 5.7 \times 10^{-21}$$
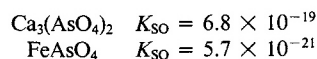
Assuming that the soils have been contaminated by the use of arsenate pesticides, calculate the upper limit of solubility of AsO_4^{3-} in:

(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.)

3. Ferrous chloride, $FeCl_2$, is known to be an effective soil amendment for lowering soluble levels of selenium in alkaline soils. Propose a reaction sequence that would explain this.

4. Explain the phenomenon of bioaccumulation, that is, the gradual buildup over time of certain trace metals in the humus fraction of the soil surface.

5. Given that Al^{3+} is not intrinsically a highly phytotoxic element (see Table 9.1), how can the widespread and common toxicity of Al to crops, especially in soils of the humid tropics, be explained?

6. A calcareous soil, contaminated with a high level of copper, was found to contain the Cu hydroxycarbonate mineral, malachite. The solubility of malachite is defined by the dissolution reaction:

$$Cu_2(OH)_2CO_3(s) + 4H^+ = 2Cu^{2+} + 3H_2O + CO_2(g) \quad \log K = 14.16$$
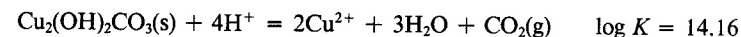
(a) If the pH of this soil is 7.4, and the gas pressure of CO_2 in the soil air is assumed to be $P_{CO_2} = 10^{-2}$ atmospheres, calculate the activity of the Cu^{2+} ion in soil solution. (Ignore activity corrections for solution concentrations in this problem.)

(b) Severe symptoms of Cu toxicity were observed in a corn crop grown in this soil. Does the answer in (a) provide a reliable indication that toxicity is likely to develop over a growing season?

(c) How can the rhizosphere manipulate the activity of Cu^{2+}?

7. The fallout from nuclear tests in the 1950s resulted in widespread deposition of the radioactive metal, ^{90}Sr, in trace amounts on soils. This metal takes the form of the exchangeable cation, Sr^{2+}, in soils. Consider the question of the downward migration of Sr^{2+} by saturated flow (leaching) through a well-drained nonacid clayey soil with exchange sites occupied largely by Ca^{2+}. The soil has a porosity of 0.42 and a bulk density of 1.5 g/cm³.

(a) Calculate the value of the distribution coefficient, K_d, to be used in equation 9.5 if the soil has a CEC of 150 mmoles/kg and a solution Ca^{2+} concentration of 10^{-3} *M*. (Sr^{2+} shows some preference for exchange sites over Ca^{2+}, so that $K_S \approx 2$ is a reasonable estimate for the cation exchange selectivity coefficient.)

(b) Use equation 9.5 to determine how many years it would take for the radioactivity to leach out of the reach of the root systems of most annual crops (about 1 meter). Assume a humid climate with about 40 cm of rainfall that actually leaches through the soil.

8. In Chapter 7, Table 7.1, the reduction potentials of MnO_2 and $MnOOH$ are listed. Use the Nernst equation to determine if either of these Mn oxides in a soil solution at pH 7 would be able to generate chromate from precipitated $Cr(OH)_3$. Assume that ion exchange limits Mn^{2+} solubility to 10^{-5} M. What would be the significance of this reaction to the environment?

(Note: The relevant chromate-chromic half-cell reaction is:

$$CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3(s) + 5OH^- \quad E_h^\circ = -0.13V$$

9
Trace and Toxic Elements in Soils

Fertile soils supply plants with all of the trace elements essential for growth, believed at the present time to be Fe, Mn, Zn, B, Cu, Mo, and Cl.[1] These seven elements are called the *micronutrients,* a term that indicates the small quantities needed by plants but not necessarily the concentrations found in soils. Deficiencies can occur in soils either because they contain extremely low concentrations of these elements or because the elements are present in very unavailable (insoluble) forms. Conversely, many trace elements, including all of the micronutrients, can reach concentrations in soils that are toxic to plants and microorganisms. Some of the most toxic are mercury (Hg), lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), and cobalt (Co). The first three are particularly toxic to higher animals. The last three are more toxic to plants than animals and are termed *phytotoxic.* From the standpoint of potential hazard to human health, an extended list of "priority metals" has been established. This list presently consists of:

As	Hg
Be	Ni
Sb	Se
Cd	Ag
Cr	Tl
Cu	Zn
Pb	

It is no exaggeration to state that modern analytical methods can detect most of the natural elements in soils at some level of concentration. The specific elemental composition of each particular soil reflects, to a degree modified over time by weathering, the chemical composition of the parent material from which the soil formed. However, knowledge of a soil's composition in terms of *total elemental content* is usually not very useful when it comes to understanding the processes and dynamics of element availability and cycling. Nevertheless, if elemental concentrations are

1. Some plant species need Na and Si, legumes require Co to fix nitrogen, and there is evidence that Ni is a plant micronutrient as well. Essential elements for humans and animals are not the same as those for plants.

greatly in excess of those expected for a particular soil type, this may be a sign of pollution from human activity or accumulation from natural biogeochemical processes.

Whether an element is present naturally in the soil or has been introduced by pollution, a measure more useful than total elemental content for most purposes is an estimation of "availability" or "lability" of the element, since it is this property that can be related to mobility and uptake by plants and extractability by chemical treatments. Chemical soil tests are designed to extract a quantity of the element from the soil solids that correlates statistically to the size of the "available pool" in the soil, defined by the quantity of element taken up by plants. Thus, soil tests are empirical, giving little insight into the chemical mechanisms in the soil that control availability. They estimate the potential for toxicity (or deficiency) to plants and animals. However, the extractability of different elements depends on their properties, such as their tendency to:

1. Complex with organic matter
2. Chemisorb on minerals
3. Precipitate as insoluble sulfides, carbonates, phosphates or oxides
4. Co-precipitate in other minerals

Consequently, some elements are at least partially extracted from many soils with solvents such as water or salt solutions, whereas others may resist extraction even by chemically aggressive solutions such as concentrated acids or powerful chelating agents.

Generally speaking, neither the total quantity of an element in the soil nor the quantity extracted by aggressive reagents is closely correlated to the plant-available "pool" of the element. The concentration of the element at any one time in soil solution often seems a better measure of availability. However, concentrations of trace elements *in natural soil solutions* commonly fall in the range of 1 to 1000 μg/liter, with some elements falling below the 1 μg/liter level. Consequently, the solution concentration is often below the detection limit of standard analytical methods. Furthermore, the solution concentration reveals only part of the situation regarding availability, providing a "snapshot" of a very dynamic and complex equilibrium, represented in a much-simplified form by Figure 9.1. Since prediction of plant availability is such a critical (and elusive) goal in soil and environmental science, a more detailed discussion of the meaning of availability follows.

9.1. AVAILABILITY OF ELEMENTS

9.1a. Controlling Processes

There are five steps that must be considered in getting an element from soil solids to plant tops. These are depicted in Figure 9.2, and a brief description of each of them is given here.

1. **Desorption or dissolution.** This step can be fast or slow depending on the element (see Chapter 4), and may limit availability to plants if desorption is particularly difficult or if the dissolution of a very insoluble solid is involved.
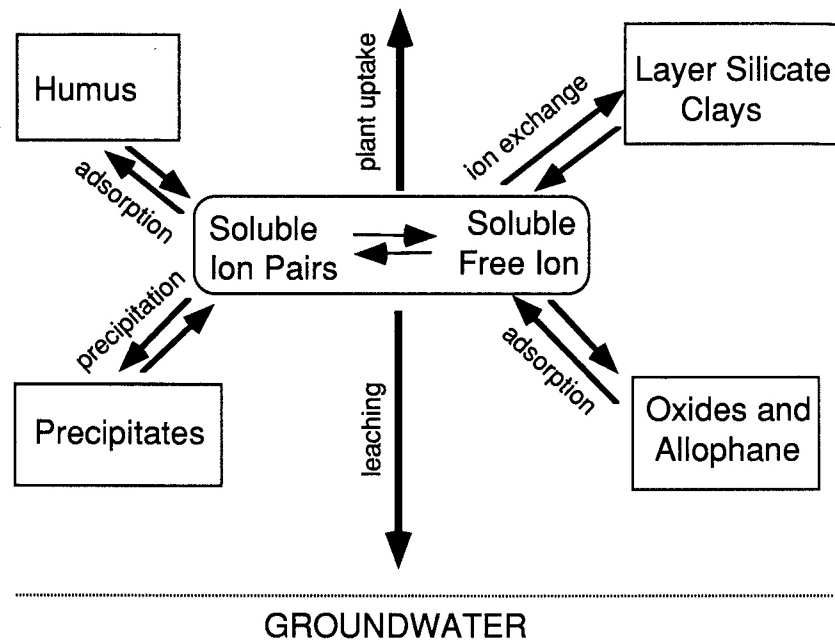
Figure 9.1. Dynamic interactive processes governing solubility, availability, and mobility of elements in soils.

2. **Diffusion and convection.** This step can be very slow for trace elements because extremely low solution concentrations of these elements are common, resulting in small quantities of ions moved by diffusion. Convection is important for non-trace elements, such as Ca^{2+}, that tend to be found at fairly high concentrations in soil solutions. Plants transpire water to create a flow of water in soil pores toward the roots, carrying amounts of these elements sufficient for plant growth.

3. **Sorption or precipitation at new sites.** After desorption, the element in question has some probability of resorbing before reaching the root. This can greatly limit movement of certain elemental forms in soils that have high levels of humus or clays. For example, phosphate ions move extremely slowly through oxidic soils because, even when these anions desorb from oxide surfaces, their probability of readsorbing on nearby sites is high. In contrast, Cd^{2+} can move fairly rapidly through the soil matrix because it tends to adsorb in exchangeable form.

4. **Absorption by roots.** Absorption of elements by roots may be passive or active, but in either case uptake depends on the concentration of the element in the soil solution near the root. The root may modify the solution chemistry of the root zone (creating the "rhizosphere effect"), locally changing soil properties such as pH or redox potential. This rhizosphere effect can be useful to plants by decreasing availability of toxic elements or increasing availability of deficient elements. However, some toxic metals (e.g., Pb) may become more soluble in the rhizosphere. One way the plant creates this effect is to exude protons and organic chelating agents that tend
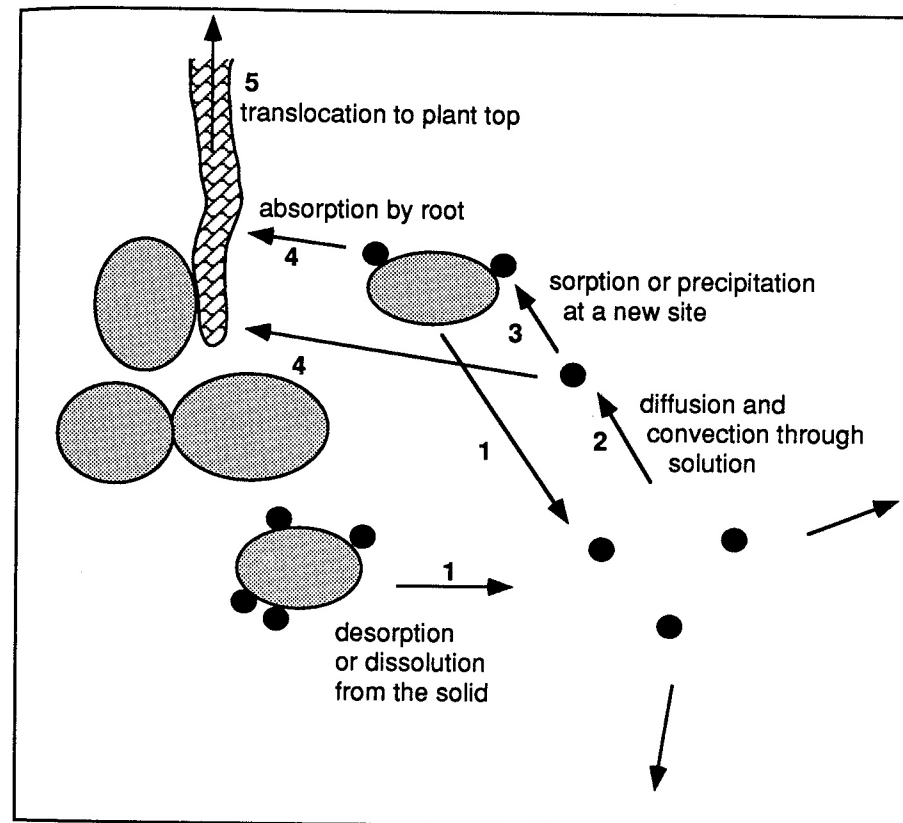
Figure 9.2. The five steps necessary for an element to move from soil solids to plants.

to increase total metal cation solubility and uptake. This is in spite of the fact that chelating agents *decrease* the concentrations of *free* (uncomplexed) metal cations in solution; plant roots either absorb the chelated metals or extract the metals from the chelate. In the particular case of Fe uptake, for example, Fe^{3+} chelators exuded by roots dissolve Fe^{3+} from minerals, thereby increasing Fe availability, because plant roots are able to reduce the strongly complexed Fe^{3+} to Fe^{2+}. The Fe^{2+} chelate is much less stable than the Fe^{3+} chelate, so that metal extraction from the chelate is facilitated by chemical reduction at the root. It is worth noting that the addition of metal chelating agents to soils raises metal mobility by influencing steps 1, 2, and 3 in Figure 9.2.

5. **Translocation in plant.** The last step in elemental availability is translocation from roots to tops, a biological process that would seem outside the control of soil chemistry. A number of trace elements, especially those that take the form of cations in soils, do not readily translocate to plant tops. Therefore it is common for metals such as Cu, Pb, and Cd, after absorption from the soil, to accumulate in (or on) roots. Translocation behavior of plants is complex and not understood for many of the elements of environmental concern, but soil chemical factors (alkalinity, phosphate

level, base cation concentration, etc.) and environmental factors can influence movement into plant tops.

The first three of these five steps combine to describe the *mobility* of the element in the soil, a soil property that may be directly related to plant availability, at least as long as the plant root itself does not complicate the situation further by altering the chemistry in the rhizosphere. A well-designed soil test could be expected to measure mobility, and perhaps availability as well.

From this outline of the factors that determine availability, we see that the soil controls elemental availability to the extent that it limits mobility (steps 1–3). The soil may also influence absorption by roots (step 4) because it has some control over the chemical forms (speciation) that elements take in solution. The important effect of speciation is discussed in more detail in the next section. The soil may even affect translocation of elements *within the plant,* since there is evidence that mobility in plants is sensitive to the specific chemical form absorbed from soil solution. For example, it appears that iron absorbed from soil solution as a bicarbonate salt is immobile within the plant root and not translocated to the top. Another example is the immobility of zinc and lead in plant roots that are well supplied with phosphate. It may be that chemical precipitation reactions within (or possibly on) roots are limiting translocation. The questions raised here about the chemical forms of elements within plants fall into the realm of plant physiology and will not be pursued further.

9.1b. Speciation and Availability

Elements, both metallic and nonmetallic, may occur in one of several oxidation states and in soluble complexes with different organic or inorganic ligands. A description of the chemical form(s) that an element takes in solution is termed its *speciation.* Each element has unique speciation tendencies. Soil solutions provide great opportunity for variety in speciation, as they contain organic ligands (fulvic acid), HCO_3^-, CO_3^{2-}, OH^-, and numerous other anions that are capable of forming soluble complexes with metal cations. The organic ligands in particular increase the "carrying capacity" of soil solutions for strongly complexing metals such as Cu^{2+}, increasing total metal solubility. Soluble complexing ligands usually enhance metal mobility, as described in Figure 9.1, influencing at least the first four steps that ultimately lead to elemental accumulation in plant tissues.

Dissolved hydroxyl (OH^-), HCO_3^-, CO_3^{2-}, and organic matter all increase in concentration as the soil pH is raised. At the same time, metal cation adsorption at mineral and organic surfaces is favored at higher pH (see Chapter 4). Consequently, total metal solubility in soil solutions often displays a two-stage trend, decreasing up to pH 6 or 7, but increasing again at higher pH as soluble ligands bring the metals into solution. This trend, shown for copper in Figure 9.3, is typical behavior for metal cations that form stable and soluble complexes with hydroxyl, carbonate, or fulvic acid.

The speciation behavior of an element in soils profoundly affects its bioavailability. Sometimes this is not evident until a soil property is changed. For example, absorption of metal ions such as Cu^{2+} and Cd^{2+} by plant roots is correlated to the
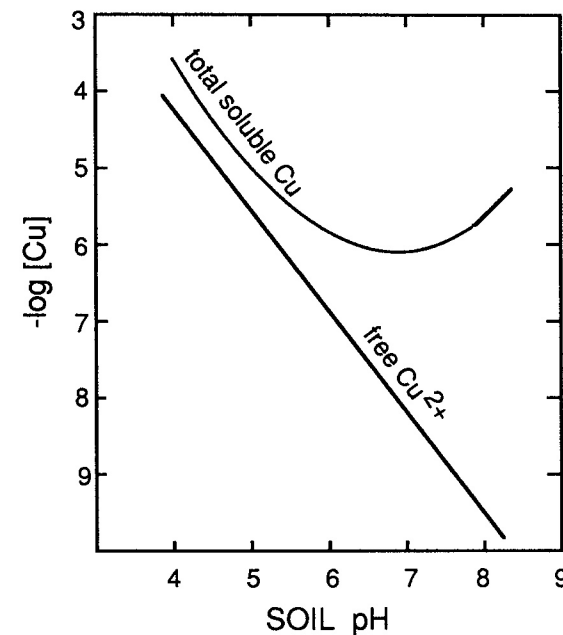
Figure 9.3. Dependence of solution concentration of total dissolved Cu and free (uncomplexed) Cu^{2+} on pH in a soil contaminated with 320 ppm of Cu.

free metal ion concentration in soil solution. Once high levels of organic matter are added to soils, however, a greater uptake of Cu^{2+} by roots occurs at any particular solution concentration of free (uncomplexed) Cu^{2+}. It is necessary to conclude that, at least for copper, soluble organic matter acts as a "cation carrier," facilitating metal diffusion from soil particles to roots. As Figure 9.3 illustrates, the carrier effect is readily explained by the much higher solution concentration of the Cu-organic complex compared with the free Cu^{2+} ion. As the roots take up copper, perhaps necessitating dissociation of the complex, the soluble complex replenishes the copper supply at the root surface at a much faster rate than diffusion of free Cu^{2+} ions could. For metals prone to forming soluble complexes with bicarbonate or carbonate, such as Cd^{2+}, the concentration of the "carrier" increases with both CO_2 level and pH in the soil. The latter effect arises from the greater total dissolved bicarbonate and carbonate in water at higher pH, so that even as free Cd^{2+} concentrations decrease at higher pH, total soluble cadmium may increase. Nevertheless, liming soils to raise the pH and enhance sorption or precipitation is generally found to be a successful practice for limiting cadmium uptake by plants.[1]

From these observations it appears that both free metal activity (or concentration), representing an *intensity* factor, and total sustained soluble metal concentration, representing a *capacity* (or buffering) factor, are important to biological systems.

1. It may be that part of the positive effect of lime is to increase competition from Ca^{2+} for plant uptake and translocation.

In fact, for metal cations in soils, the following general rules relate bioavailability to speciation:

> *Short term toxicity to plants and microorganisms is most closely related to* <u>free</u> *metal cation concentration in solution.*

> *Metal uptake over the long term depends to a large extent on the* <u>total</u> *metal concentration in solution and on the ability of the soil to maintain this concentration.*

9.1c. Soil Tests and Plant Availability

Soil tests attempt to predetermine, by a rapid procedure, the longer term availability of elements to crops. For some metals, such as Zn^{2+}, Co^{2+}, and Cd^{2+}, long-term uptake by plants may correlate fairly well with the slopes of measured sorption curves. That is, if the sorption curve of a soil, measured as the quantity of metal sorbed as a function of the concentration of the metal in solution, is steep, this indicates strong metal retention by soil particles and correspondingly low long-term plant uptake. This behavior arises from competition between roots and soil surfaces for metal ions. A soil test that is based on this correlation between uptake and sorption strength has the advantage that it automatically considers all the soil properties that influence metal sorption. Nevertheless, because the test requires that the element in question be added in increments to the soil to establish a sorption curve, it may fail in cases of elemental deficiency because it does not establish whether the soil initially contains the minimum level of the element to sustain growth. A soil test based on sorption curves may also fail because it does not measure the kinetics of desorption (dissolution) of the element, a necessary step for uptake. For example, the slopes of Cu sorption curves in soils do not generally correlate (negatively) with plant uptake, perhaps because desorption kinetics have not been accounted for.

For metal cations such as Cu^{2+} and Fe^{3+}, migration to the root is almost certainly in the form of organic complexes. As these forms of the metals are essentially non-adsorbing, factors (such as higher pH) that increase adsorption and decrease the solubility of the *free* metal cations may not markedly change metal uptake by plants. Thus it is not uncommon to observe little or no effect of raising the soil pH on Cu concentration in plants. For metal cations such as Zn^{2+} and Cd^{2+}, there is less tendency to form soluble organic complexes, and factors that promote adsorption and precipitation (notably, higher pH) inhibit uptake. Ideally, soil tests could be tailored to consider these differences in behavior among groups of elements.

Current soil-testing procedures for most trace elements bathe the soil in a solution of complexing, acidifying, or reducing chemicals. This alters soil properties that control the solubility of the element; redox potential, pH, mineral solubility, and organic matter solubility may all be modified. Information about elemental speciation and availability is lost in the process of attempting to extract part or all of the "bioavailable pool." Success in predicting availability has been limited with tests of this sort. More widely useful soil tests for trace elements, when they are developed, will probably measure activities or concentrations of the elements in undisturbed soil solutions (the intensity factor) and the capability of the soil solids to replenish the solution (the capacity factor). Ion exchange resins, when mixed with soils, act as a

sink for ionic forms of elements. They are known to be useful in predicting the capacity of soils to supply ionic forms of elements to plants.

9.2. MOBILITY OF ELEMENTS IN SOILS

9.2a. The Controlling Factors

As described earlier, movement of adsorbed elements in soils generally requires that a sequence of processes occurs, beginning with desorption or dissolution followed by diffusion and convection. Readsorption or precipitation can then immobilize the element at another location in the soil. Relative mobility of elements depends on several important factors, including:

1. **The chemical form and nature of the element.** Most trace metal cations have a low mobility in soils because they adsorb strongly on minerals and organic matter, or form insoluble precipitates (e.g., oxides, carbonates, sulfides). Some elements that take the form of anions in soils, such as boron, are relatively mobile. Other elements that form anions, like phosphorus, are considered to be immobile because they form insoluble precipitates and bond strongly with mineral surfaces. In Figure 9.4, many of the elements of interest in soils are classified on the basis of their ionic radii and valence. The elements tend to fall naturally into one of four groups:

> Group 1. Soluble weakly hydrating cations
> Group 2. Soluble, strongly hydrating cations
> Group 3. Easily precipitated amphoteric hydroxides
> Group 4. Soluble anions

The valence/radius ratio, or *ionic potential,* is a key parameter in determining which of these four chemical forms the element takes in water. Figure 9.4 can be used in a general way to predict chemical form for elements, but an assessment of elemental mobility requires knowledge of soil properties as well. In broad terms, the mobility of the four groups of elements in soils can be classified as follows:

> Group 1. Strongly held by clays and humus
> Group 2. Exchangeable and somewhat mobile, excepting strong chemisorbers such as Pb^{2+} and Cu^{2+}
> Group 3. Immobile as insoluble oxides
> Group 4. Mobile, excepting strong chemisorbers such as phosphate

2. **The chemical and mineralogical nature of the soil.** Elements are less mobile in those soils that provide a large quantity of sorption sites or a chemical environment favorable to precipitation of the element. Oxides of Fe, Al, and Mn provide chemisorption sites for both cation and anion forms of elements. Layer silicate minerals provide exchange sites for cations, and a few chemisorption sites (at edges, defects, etc.) for both cations and anions. Noncrystalline aluminosilicates (allophanes) possess large quantities of chemisorption sites for both cations and anions. Soil organic matter is principally involved in metal cation adsorption, although the borate anion (and perhaps several other anions) can bond covalently to organic mat-
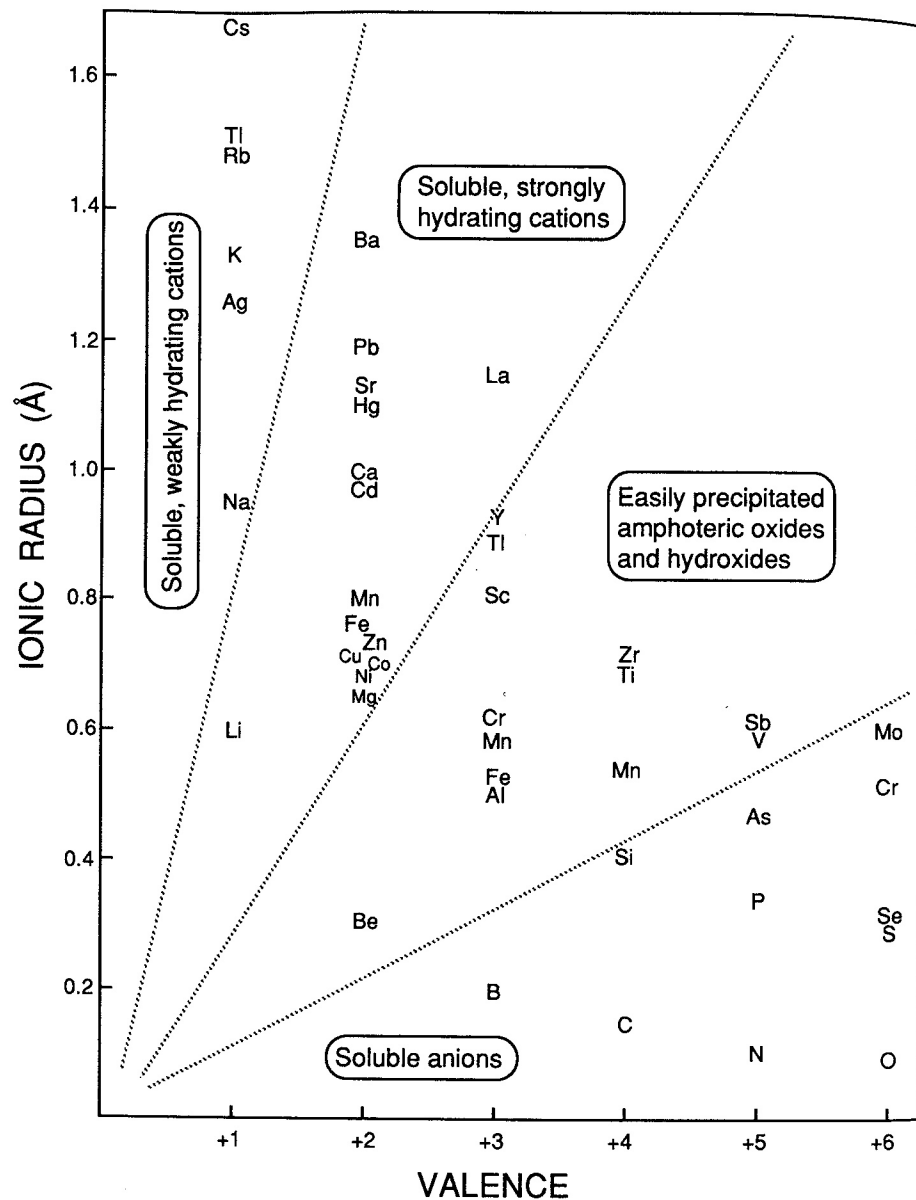
Figure 9.4. Classification of elements into four groups on the basis of ionic charge (valence) and radius. (Adapted from G. Millot. 1970. *Geology of Clays.* New York: Springer-Verlag.)

ter. Overall, soils high in clays, oxides, or humus strongly retain most of the trace metals.

The chemical conditions in the soil can also be critical in element retention. For metal cations, high pH favors sorption and precipitation as oxides, hydroxides, and carbonates (see Chapter 4). For many anions, such as molybdate and selenite, low pH favors sorption and precipitation. Alkaline conditions in soils are generally associated with elevated Na^+ and K^+ levels relative to Ca^{2+} and Mg^{2+}. Because many anions form much more soluble compounds with Na^+ and K^+ than with Ca^{2+} or Mg^{2+}, soil alkalinity is usually accompanied by a high degree of anion mobility. For example, borate and molybdate are easily leached from alkaline soils of arid regions. Alkalinity may mobilize some metal cations (e.g., Cu) as well because it favors the formation of soluble metal complexes of organic matter and hydroxyl. Salinity in soils is associated with high levels of halide ions, particularly chloride, and this anion is able to mobilize certain heavy metals by forming soluble metal-chloride ion pairs. Mercury (Hg^{2+}) is especially prone to chloride-induced mobilization, but Cd^{2+} and Pb^{2+} are affected to some degree as well.

Soil redox potential is also critical in controlling elemental mobility. Some elements are much more soluble and mobile in one oxidation state than another (examples include Cr, Mn, Se, and others). The elements classified as *chalcophiles* (e.g., Hg, Cu, Pb, Cd, Zn, As, Se) form insoluble sulfide minerals in reducing environments where sulfide (S^{2-}) is generated from sulfate reduction (see Chapters 4 and 7). Mobility for chalcophiles is then extremely low unless oxidizing conditions are restored in the soil. Those elements that, in the sulfide form, have the very lowest solubility products (notably mercury, copper, lead, and cadmium) are the most likely to become highly immobile and unavailable in reduced soils.[1]

3. **The physical and biological environment of the soil.** High solubility of elements is not manifested as significant migration unless there is water movement through the soil. In arid climates, net water movement in the soil profile is upward, and the mobile elements that are carried to the surface become concentrated by evaporation. Conversely, in wet climates, mobile elements leach downward as long as there is free drainage. However, roots can intercept mobile elements and extract immobile elements, accumulating them in the plant. As the plant material decays to humus (which retains ions selectively), particular elements *bioaccumulate* in the surface soil. Some of these elements are not required nutrients and may even be phytotoxic.

Experience with many elements that have found their way into soils as pollutants from agriculture or industry suggests that mobility is so low that the presence of the undesired element is virtually permanent. This is certainly true for the strongly sorbing metals such as Pb and Cu. Agricultural sites that were subjected to the use of lead arsenate and copper sulfate as pesticides many decades ago still retain Pb and Cu in the soil surface today, although in some cases the arsenate has moved deeper in the soil profile. Even in wet climates where leaching is more or less continuous, removal of a large portion of these less mobile elements by natural processes could take thousands of years.

1. Unfortunately, mercury forms volatile organomercury compounds under reducing conditions, so that its bioavailability is not as low as the solubility of HgS would suggest.

Depending on the controlling factors for mobility, the elemental composition of soils may or may not reflect the composition of the soil's parent material. However, it is generally observed that, all other factors being equal:

a. Soils high in clay-sized minerals (particularly silicates and oxides) tend to have a higher concentration of most trace elements than coarse-textured soils such as sandy and gravelly soils.

b. Soils rich in humus tend to have higher concentrations of most trace elements than soils that are not. This observation applies to comparisons between sites as well as within a single soil profile, as many elements bioaccumulate in the organic-enriched surface horizon.

c. Soils of moderate to high pH tend to have higher concentrations of most trace elements than soils that have been acidified naturally (or otherwise) by acid water leaching.

9.2b. The Case of Mobile Elements

It may be instructive to analyze in some detail the situation of a reversibly adsorbed ion, whose mobility in the soil is relatively high. A case in point is Cd^{2+}, a toxic metal that adsorbs by cation exchange in acid and near-neutral soils, but may precipitate into carbonates and phosphates in calcareous and alkaline soils. The theory needed for the analysis of ion leaching through soils, in which the main retention mechanism is ion exchange, is developed in Chapter 3 (section 3.5) using Cs^+ as the example ion.

The problem posed is the following: Suppose a slightly acid clay soil, with a CEC of 50 mmoles/kg, has its exchange sites occupied largely by Ca^{2+}. A small amount of the soluble salt, $Cd(NO_3)_2$, is accidentally spilled on the surface of this soil in the field. An attempt is then made to leach the cadmium out of the soil surface using $0.01\ M\ Ca(NO_3)_2$, relying on the fact that Ca^{2+} and Cd^{2+} have nearly equal affinity for clay exchange sites. The practical question that arises is: What volume of $Ca(NO_3)_2$ solution must be surface applied to move the cadmium to 1 meter depth in the soil?

To address this question, we must first define K_S for $Ca^{2+}-Cd^{2+}$ exchange (see Chapter 3 for a description of K_S). The exchange equation that describes K_S is

$$K_S = \frac{N_{Cd}[Ca^{2+}]}{N_{Ca}[Cd^{2+}]} \approx 1 \tag{9.1}$$

The measured value of K_S is about 1 so long as the pH is relatively low and those anions most inclined to form soluble complexes with Cd^{2+} (e.g., chloride) are not present. A low pH inhibits both chemisorption and precipitation reactions of Cd^{2+}; otherwise the soil's apparent selectivity for Cd^{2+} would greatly exceed unity. Furthermore, only if the total soluble Cd can be approximated by the free Cd^{2+} concentration, $[Cd^{2+}]$, would equation 9.1 be expected to provide the basis for estimating cadmium retention and mobility in the soil. Soluble complexes of Cd, unless they happen to be cations, bypass cation exchange sites and are mobilized.

For this example of exchange between cations of equal charge, the fraction of exchange sites occupied by Cd^{2+} and Ca^{2+} are given by $N_{Cd} = m_{Cd}/CEC$ and $N_{Ca} = m_{Ca}/CEC$, where m_{Cd} and m_{Ca} are the equivalents (moles of charge) of these metals on the soil's exchange sites. Equation 9.1 then becomes

$$K_S = \frac{m_{Cd}[Ca^{2+}]}{m_{Ca}[Cd^{2+}]} = 1 \tag{9.2}$$

Since $[Ca^{2+}]$ is made nearly constant by the introduction of $0.01\ M\ CaCl_2$ into the soil, and $m_{Ca} \gg m_{Cd}$, then $[Ca^{2+}]$ and m_{Ca} can be replaced by N (solution normality) and the CEC, respectively. Equation 9.2 then becomes

$$m_{Cd} = CEC\left(\frac{K_S}{N}\right)[Cd^{2+}] \tag{9.3}$$

The specific values of variables in equation 9.3 for the present case, being careful to keep units consistent, are as follows:

$$CEC = 0.050 \text{ moles/kg}$$
$$K_S = 1.0 \text{ (unitless)}$$
$$N = 0.02 \text{ moles (of cation charge)/liter}$$

When these values are entered into equation 9.3, a simple relation is found:

$$m_{Cd} = 2.5[Cd^{2+}] \tag{9.4}$$

where 2.5 is now identified as the value of the distribution coefficient, K_d, for this particular system because it quantifies the relation between the concentration of Cd^{2+} in soil solution and the quantity of Cd^{2+} adsorbed on the soil exchange sites. K_d has units of liters per kilogram in this example as a result of the choice of units for the variables.

The K_d value determined in this way is then used in equation 3.102 from Chapter 3, which estimates the velocity of a chemical's movement under saturated flow, v_{Cd}, relative to the leaching velocity of water, v. For cadmium, that equation is

$$\frac{v_{Cd}}{v} = \frac{1}{[1 + (\rho_B/\wp)K_d]} \tag{9.5}$$

where ρ_B and $\wp$ are the bulk density and fractional porosity of the soil. Reasonable values for bulk density and porosity are $1.5\ g/cm^3$ and 0.42. These units remain consistent with those of equation 9.4 because $1.5\ g/cm^3$ equals 1.5 kg/liter. Equation 9.5 is then solved:

$$\frac{v_{Cd}}{v} = \frac{1}{[1 + (1.5/0.42)2.5]} = 0.10 \tag{9.6}$$

to reveal that the leaching velocity of the cadmium should be about 10 percent of the leaching velocity of water (or nitrate) when $0.01\ M\ Ca(NO_3)_2$ is applied to the surface.

From this result, the surface-applied $Ca(NO_3)_2$ solution must leach to a 10-meter depth to force the Cd^{2+} ions down 1 meter (on average). Because the soil's porosity is 0.42, a 10-meter depth of solution in the soil matrix is equivalent to a 4.2-meter depth of applied water. It would take a number of years of rainfall in a temperate humid climate to provide this extent of leaching, and since the concentration of exchanging cations in soil solutions (Ca^{2+}, Mg^{2+}, etc.) is typically well below the 0.01 $M\ Ca^{2+}$ concentration used in this calculation, cadmium movement out of the surface horizon of soils is likely to take several decades *even if no chemisorption of the*

metal occurs. Nevertheless, if the soil is somewhat acid, cadmium movement can be detected over time spans of years to decades, unlike more strongly bound metals for which movement can take centuries.

Accelerated leaching experiments using 0.01 *M* CaCl₂ to leach a column of acid mineral soil have produced some movement of trace metal ions initially applied to the column surface. Results are shown for Cd^{2+}, Zn^{2+}, Ni^{2+}, and Cu^{2+} in Figure 9.5a. Cd^{2+}, Zn^{2+}, and Ni^{2+} moved readily, so that most of these ions migrated below 30 cm depth after seven hours leaching. The mobility of Cu^{2+} was obviously lower than that of the other three metals, consistent with its strong chemisorption on clays, oxides, and humus. The same soil, after liming with $Ca(OH)_2$ to pH 6.5, retained all four metals more strongly (Figure 9.5b), so that even after seven hours of leaching, Cd^{2+}, Zn^{2+}, and Ni^{2+} remained within the soil column. Liming reduces both mobility and plant availability of many of the toxic heavy metals.
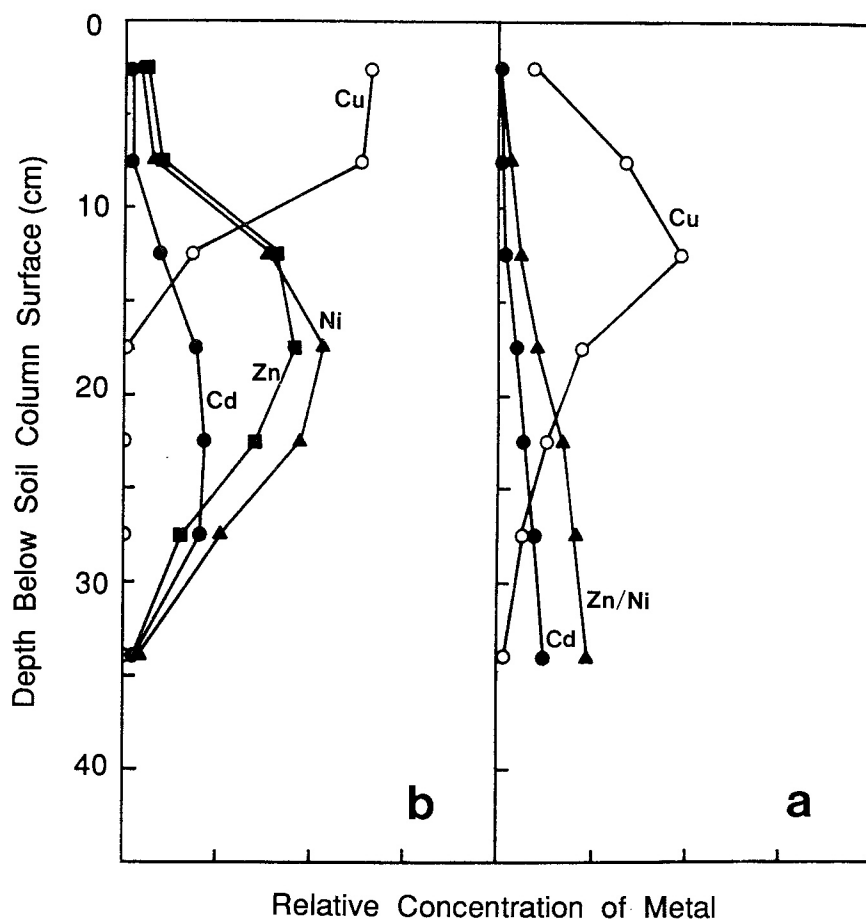

Figure 9.5. Profiles of adsorbed Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} concentrations in a soil column to which these metals were initially surface-applied and then leached with 0.01 *M* CaCl₂. The acid mineral soil was either left unlimed (a) or was limed to pH 6.5 (b).

While the attenuation of Cd^{2+}, Zn^{2+}, and Ni^{2+} migration is largely attributable to cation exchange in these columns, and could be modeled by equation 9.5, Cu^{2+} retention is by nonreversible chemisorption and is not subject to the same approach. A further danger in using such a simple model as that represented by equation 9.5, even for Cd^{2+}, is that it does not consider the importance of metal "load" in the soil. If a very small quantity of any of these heavy metals is applied to soil, selective retention processes such as chemisorption and chelation are likely to be active, and mobility will be much lower than that predicted from models based on fairly non-selective cation exchange reactions. For cases of strong and seemingly irreversible sorption of elements, a different approach is needed.

9.2c. The Case of Immobile (Fixed) Elements

Consider now adsorbed molecular or ionic species that are, practically speaking, immobilized in the soil. Unless the soil is extremely acid, metals such as Cu^{2+}, Cr^{3+}, and Pb^{2+} fall into this category. Also, certain anions such as phosphate bond so strongly on minerals that they too behave as immobile elements. The property that all of these ions have in common is that their sorption isotherms are not reversible within a time scale relevant to soil processes; the adsorption (forward) isotherm is usually approximated closely by a Langmuir function of the strong-affinity type,[1] but the desorption (backward) isotherm deviates markedly from the adsorption isotherm. This kind of nonequilibrium behavior, depicted in Figure 9.6, is sometimes referred to as *hysteresis.* Possible reasons for hysteresis in chemisorption are discussed in Chapter 4.

The important consequence of the irreversibility illustrated by Figure 9.6 is that not many of the initially sorbed ions are able to desorb once the concentration of these ions is lowered in solution. This is behavior inconsistent with the ion exchange model of leaching described in the last section. That model would overpredict mobility of elements that are retained by chemisorption or precipitation reactions.

Taking phosphate for our example of an immobile ion, we know from equation 4.41 in Chapter 4 that this anion should adsorb according to the Langmuir function, having the form:

$$Q = \frac{Q_M[P]}{C + [P]} \tag{9.7}$$

where Q is the quantity of phosphate sorbed by the soil at equilibrium with the solution phosphate concentration, $[P]$. Q_M is the maximum quantity of phosphate sorbed, determined in principle by the number of available bonding sites in the soil. C, the bonding constant, is a function of pH and is described in more detail in Chapter 4.

In soils, phosphate sorption data usually take the shape of a high-affinity (H-type) isotherm, like that of Figure 9.6. Because of this and the nonreversible behavior of sorption, the downward movement of phosphate and other strongly bonded elements can be approximated by the "tipping bucket" model. This model visualizes the layers

---

1. See Chapter 10 for a description of this shape of adsorption isotherm, classified as L-type or H-type.
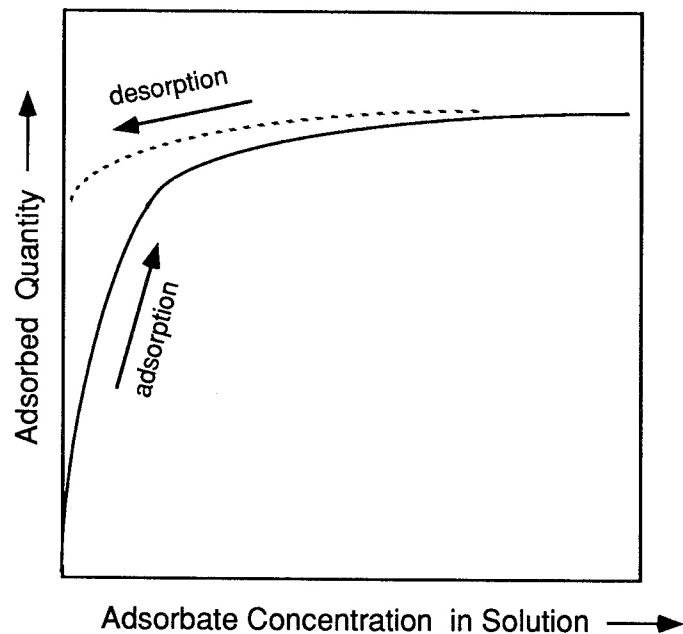
Figure 9.6. Typical adsorption-desorption hysteresis in isotherms for strongly bonding ions such as phosphate.

of a soil column as a stack of empty "buckets," each bucket symbolizing the sorption capacity of one soil layer. As phosphate is applied to the surface layer, the top bucket must be filled (the sorption capacity satisfied) before phosphate can "spill" into the soil layer immediately below. The changing status of the isotherms for each soil layer as phosphate moves deeper is shown schematically in Figure 9.7.

This model is most appropriate for adsorbates with high-affinity isotherms, because, as can be seen in Figure 9.7, very little of the adsorbate resides in soil solution until practically all of the sorption capacity in that layer has been satisfied. The opportunity for significant leaching into the next layer below arises only when sorption nears the sorption capacity ($Q \approx Q_M$), and a significant concentration of soluble adsorbate builds up. This is in contrast to the leaching model for mobile ions based on ion exchange, where mobility can be appreciable without saturating the exchange sites with the absorbate.

The tipping bucket model provides a straightfoward way to estimate at what soil loading level the chemical of concern is expected to "break through" a specific depth of soil into groundwater, drainage pipes, or surface waters. The only measurement needed for this estimate is a value for Q_M, the sorption capacity of the soil for that chemical. Because sorption of ions such as phosphate is a complex process in soils, involving both chemisorption and precipitation reactions, several mechanisms contribute to Q_M. Nevertheless, equation 9.7 is still useful as an empirical function describing overall sorption, even though use of this Langmuir function implies that a single chemisorption reaction is being described. The difficulty with this equation and the tipping bucket model, as they are applied to the sorption of chemicals, is the
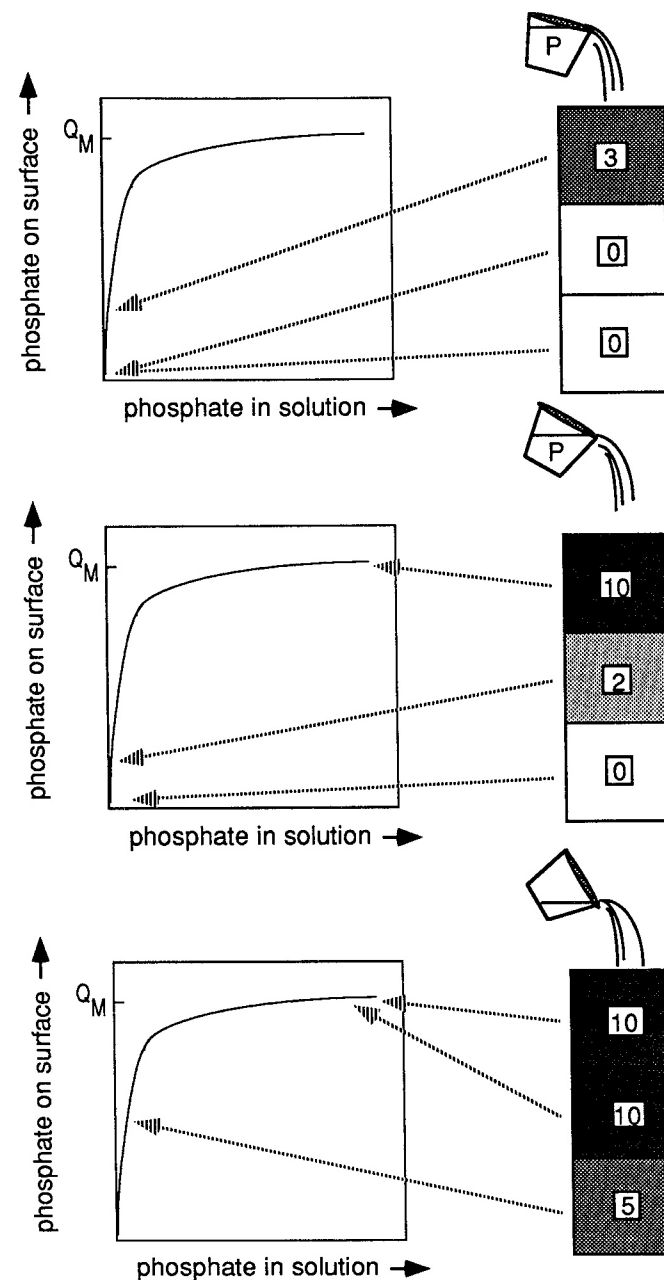

Figure 9.7. Progression of phosphate retention in a homogeneous soil column as increasing amounts of phosphate are applied to the surface. The position on the sorption isotherm, and the relative quantity of phosphate sorbed, is illustrated for each soil layer (Q_M, the sorption maximum, is 10 units).