1

Introduction to Soil Chemistry

No one regards what is at his feet; we all gaze at the stars.   Quintus Ennius (239 … 169bc)

Heaven is beneath our feet as well as above our heads.   Henry David Thoreau (1817 … 1862)

The earth was made so various that the mind of desultory man, studious of change and pleased with novelty, might be indulged.   William Cowper (The Task, 1780)

The Nation that destroys its soil destroys itself.   Franklin Delano Roosevelt (1937)

The quotations illustrate how differently humans see the soil that gives them life and feeds them. In recent decades, great strides in understanding the importance of soils for healthy ecosystems and food production have been made, but the need for preservation and improved utilization of soil resources remains one of society's greatest challenges. This requires a better understanding of soil processes.

Soil is a complex mixture of inorganic and organic solids, air, water, solutes, microorganisms, plant roots, and other types of biota (**Figure 1.1**). All of these soil components influence each other, and as a result, soil processes are complex and dynamic. For example, air and water weather rocks to form soil minerals and release ions; microorganisms catalyze many soil weathering reactions; and plant roots absorb and exude inorganic and organic chemicals that change the distribution and solubility of ions. Although it is difficult to separate soil processes, for the purpose of study, soil scientists have organized themselves into sub-disciplines that study physical, biological, and chemical processes, soil formation and distribution, and specialists that study applied soil science topics such as soil fertility.

The discipline of soil chemistry has traditionally focused on abiotic transformations of soil constituents, such as changes in oxidation state of elements and association of ions with surfaces. Chemical reactions in soils often lead to changes between solid, liquid, and gas states that dramatically influence the availability of chemicals for plant uptake and leaching out of the soil, which are important aspects of fate and transport of nutrients and contaminants in the environment. With the ever-increasing pressures humans are placing on soil resources, detailed knowledge and understanding of soil processes is imperative. Modern soil chemistry strives to understand interactions between different soil processes, such as interactions of soil microbes and soil minerals.

The focus of soil chemistry is chemical reactions and processes occurring in soils. A chemical reaction defines the transformation of reactants to products. For example, potassium availability for plant uptake in soils is often controlled by cation exchange reactions such as:

$$K^+ + Na\text{-clay} = Na^+ + K\text{-clay} \tag{1.1}$$

where Na^+ adsorbed on a clay mineral (Na-clay) and aqueous K^+ are reactants, and aqueous Na^+ and K^+ adsorbed on a clay mineral (K-clay) are products. The reaction occurs between aqueous solution in
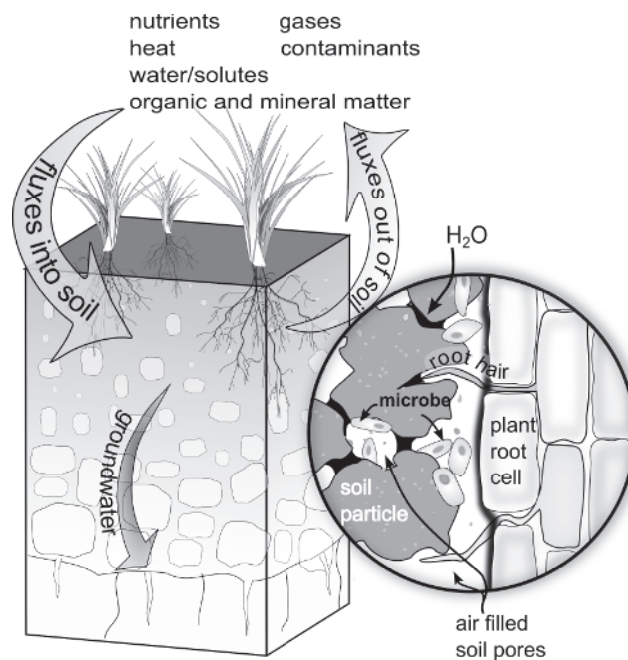
Figure 1.1   Soils are composed of air, water, solids, ions, organic compounds, and biota. The soil in the microscopic view shows soil particles (e.g., aggregates of minerals and organic matter), air and water in pore spaces, microbes, and a plant root. Fluxes of material or energy into and out of the soil drive biogeochemical reactions, making soils dynamic. Fluxes can be to the atmosphere, eroded or leached offsite into surface water, or percolated to groundwater.

the soil pore and clay minerals, and is thus a solid-solution interface reaction. Cation exchange reactions are a hallmark of soil chemistry.

One goal of soil chemistry is predicting whether a reaction will proceed or not, which can be done using thermodynamics of the reactants and products. Soils are complex, however, and predicting the fate of chemicals in the environment requires including multiple competing reaction pathways occurring simultaneously. In addition, many reactions are slow, and thus are time-dependent. The complexity and dynamic aspect of soils make understanding chemical reactions in nature a challenging problem. In the past 150 years, great advances have been made in understanding chemical processes in soils. The goal of this book is to present the fundamentals of soil chemical processes so that students can include them in understanding the environmental fate of chemicals.

1.1   Historical background

The senate of ancient Athens debated soil productivity 2500 years ago, and voiced the same worries about sustaining and increasing soil productivity that are heard today: *Can this productivity continue, or is soil productivity being exhausted?*

In 1790, Malthus noticed that the human population was increasing exponentially, whereas food production was increasing arithmetically. He predicted that by 1850 food demands would overtake food production, and people would be starving and fighting like rats for morsels of food. Although such

predictions have not come to fruition, there are real challenges to feeding the world's increasing population, especially in light of predicted changes in climate that will have significant impacts to food production systems and regional populations.

It is encouraging that food productivity has increased faster than Malthus predicted. The earth now feeds the largest human population ever, and a larger fraction of that population is better fed than ever before. Whether this can continue, and at what price to the environment, is an open question. One part of the answer lies in wisely managing soil resources so that food production can continue to increase and ecosystem functions be maintained. Sustainable management requires careful use of soil, and knowledge of soil processes. Soil chemistry is an important sub-discipline required for understanding soil processes.

Agricultural practices that increase crop growth, such as planting legumes, application of animal manure and forest litter, crop rotation, and liming were known to the Chinese 3000 years ago. These practices were also learned by the Greeks and Romans, and appeared in the writings of Varro, Cato, Columella, and Pliny, but were unexplained. Little progress on technology to increase and maintain soil productivity was made thereafter for almost 1500 years because of lack of understanding of plant-soil processes, and because of undue dependence on deductive reasoning. Deduction is applying preconceived ideas, broad generalities, and accepted truths to particular problems, without testing if the preconceived ideas and accepted truths are valid. One truth accepted for many centuries and derived from the Greeks was that all matter was composed of earth, air, fire, and water; a weak basis, as we later learned, on which to increase knowledge.

In the early 1500s, Sir Francis Bacon promoted the idea that the scientific method is a much more productive approach to gaining new knowledge: observe, hypothesize, test and measure, derive ideas from data, test these ideas again, and report findings. The scientific method brought progress in understanding our world, but the progress in understanding soil's role in plant productivity was minimal in the ensuing three centuries.

Palissy (1563) proposed that plant ash came from the soil, and when added back to the soil could be reabsorbed by plants. Plat (1590) proposed that salts from decomposing organic matter dissolved in water and were absorbed by plants to facilitate growth. Glauber (1650) thought that saltpeter (Na, K nitrates) was the key to plant nutrition by the soil. Kuelbel (ca. 1700) believed that humus was the principle of vegetation. Boerhoeve (ca. 1700) believed that plants absorbed the "juices of the earth." While these early theorists proposed reasonable relationships between plants and soils, accurate experimental design and proof was lacking, and their proposals were incomplete and inaccurate.

Van Helmont, a sixteenth-century scientist, tried to test the ideas of plant-soil nutrient relationships. He planted a willow shoot in a pail of soil and covered the pail so that dust could not enter. He carefully measured the amount of water added. After five years, the tree had gained 75.4 kilograms. The weight of soil in the pot was still the same as the starting weight, less about two ounces (56 g). Van Helmont disregarded the 56 grams as what we would today call experimental error. He concluded that the soil contributed nothing to the nutrition of the plant because there was no loss of mass, and that plants needed only water for their sustenance. Although he followed the scientific method as best he could, he came to a wrong conclusion. Many experiments in nature still go afoul because of incomplete experimental design and inadequate measurement of all the experimental variables.

John Woodruff's (1699) experimental design was much better than Van Helmont's. He grew plants in rainwater, river water, sewage water, and in sewage water plus garden *mold*. The more solutes and solids in the growth medium – the "dirtier" the water – the better the plants grew, implying that something in soil improved plant growth. The idea developed that the organic fraction of the soil supplied the plant's needs.

In 1840 Justus von Liebig persuasively advanced the idea that inorganic chemicals were key to plant nutrition and that an input-output chemical budget should be maintained in the soil. Liebig's theory was most probably based on Carl Sprengel's work in 1820–1830 that showed that mineral salts, rather

than humus or soil organic matter, were the source of plant growth. Liebig's influence was so strong that subsequent findings by Boussingault (1865) that more nitrogen existed in plants than was applied to the soil, implying nitrogen fixation, was disregarded for many years. Microbial nitrogen fixation did not fit into the Sprengel-Liebig model.

Soil chemistry was first recognized as distinct from soil fertility in 1850 when Way and Lawes, at Rothamsted, England, reported on the ability of soils to exchange cations (**Figure 1.2**). Their work suggested that soils could be studied apart from plants to discover important aspects for soil fertility. Van Bemmelen followed with studies on the nature of clay minerals in soils, and popularized the theory of adsorption (published in 1863). These founding fathers of soil chemistry stimulated the beginning of much scientific inquiry into the nature and properties of soils, which continues to this day.

Despite the significant advances in understanding soils and environmental processes, environmental complexity is too great for any single discipline to fully understand. Scientific training necessarily tends to specialize, learning more and more about less and less. Nature, however, is complex, and scientists of various disciplines apply their background to the whole environment with mixed results. Among other things, they bring along biases, one of which is that their background field is the most important. Atmospheric scientists, for example, naturally believe that the atmosphere is the most important part of the environment. The authors of this book are no different. We argue, without apology, that the soil plays the central and dominant role in the environment.

XXI.—*On the Power of Soils to absorb Manure.* By J. Thomas Way, Consulting Chemist to the Society.

In the paper which is now placed before the members of the Society, an attempt has been made to develope, in part at least, a newly observed property of soils, which will, in all probability, prove of great importance in modifying the theory and in confirming or improving the practice of many agricultural operations. The investigation, which has now occupied many months of my personal attention, took its rise in observations made to me fully two years ago by Mr. Huxtable and Mr. H. S. Thompson. The former of these gentlemen stated that he had made an experiment in the filtration of the liquid manure in his tanks through a bed of an ordinary loamy soil; and that after its passage through the filter-bed, the urine was found to be deprived of colour and smell—in fact, that it went in manure and came out water. This, of itself, was a singular and interesting observation, implying, as it did, the power of the soil to separate from solution those organic substances which give colour and offensive smell to putrid animal liquids.

Mr. Thompson, about the same time, mentioned to me that he had found that soils have the faculty of separating ammonia from its solution: a fact appearing still more extraordinary, inasmuch as there is no ordinary form of combination by which we could conceive ammonia to become combined in a state of insolubility in the soil. At the time I was not aware, as I have

Figure 1.2 Snippet of paper authored by J. Thomas Way in the 1850 *Journal of the Royal Agriculture Society of England* describing the discovery of the ability of soil to _absorb_ ammonia from manure. It is now known that ammonium exchanges for other cations on the soil clay particles, which is an _adsorption_ reaction. (Source: Way 1850. Reproduced with permission of Royal Agricultural Society of England.)

1.2   The soil environment

Soils are the *skin of the earth*, and interface with the atmosphere, hydrosphere, lithosphere, and biosphere (**Figure 1.3**). The interaction of Earth's spheres within soil results in a mixture of solid, liquid, gas, and biota, called the **pedosphere**. A fifth Earth component is the anthrosphere, which describes human's interaction and influence on the environment. The **critical zone** is a concept that encompasses all of the life-supporting parts of the earth, including soils, groundwater, and vegetation. Regardless of how the environment is compartmentalized for study, chemical processes occurring in the soil are important aspects affecting healthy and sustainable environments.

In this section, we discuss the relationships between soil chemicals, the biosphere, soil solid phases, the hydrosphere, and the soil atmosphere. A typical soil is composed of ~50% solid, and ~50% pore space; the exact amount varies as a function of the soil properties, such as aggregation, particle size distribution, and so on (**Figure 1.4**). Throughout this text, the term *soil chemical* is used as a general term that refers to all of the different types of chemicals in a soil, including ions, liquids, gases, minerals, soil organic matter, and salts.
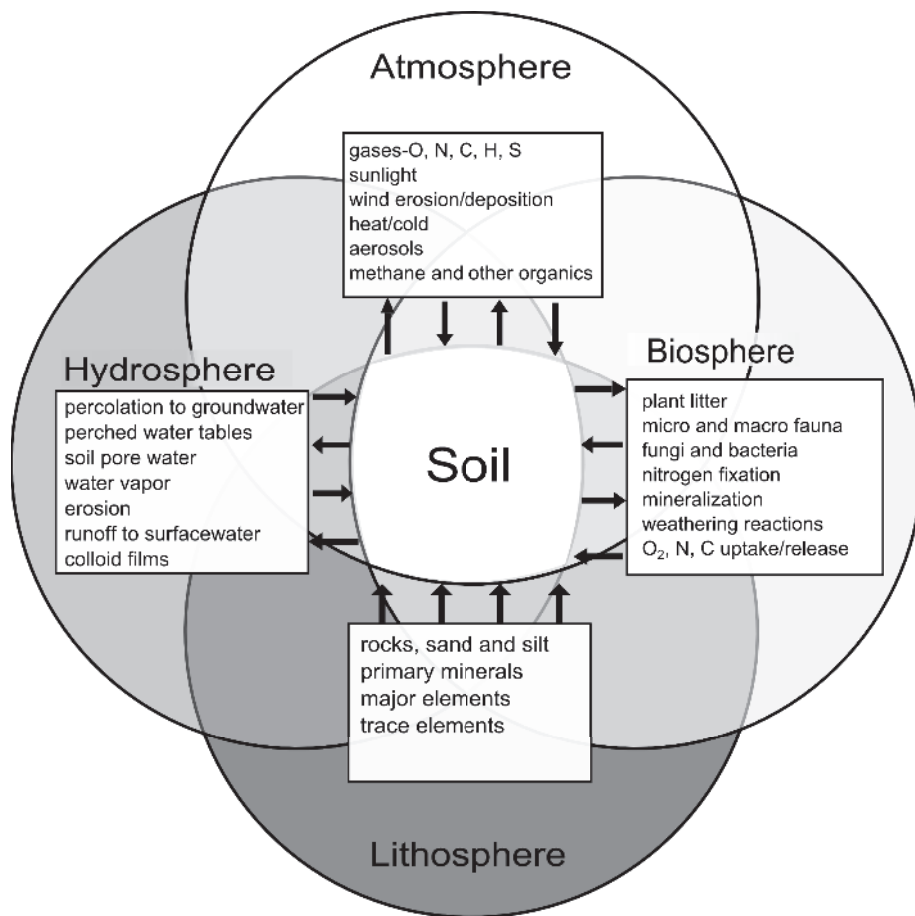

Figure 1.3   Soils interface with Earth's other spheres. Biogeochemical cycling within the soil influences flows of chemicals and energy into the hydrosphere, biosphere, and atmosphere. Arrows between the different spheres and the soil indicate important transformations.
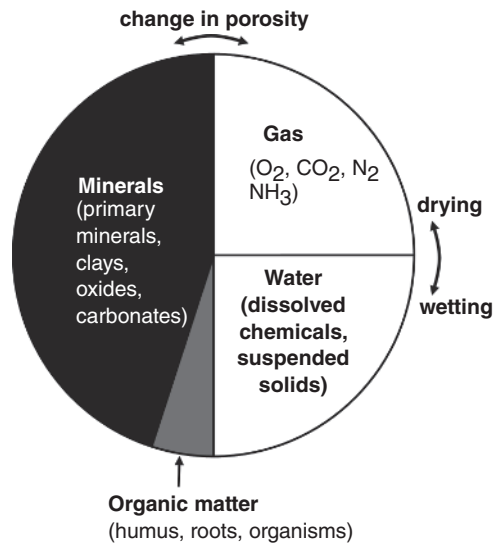
Figure 1.4   Typical volumetric composition of soils. Soil gases and solution fill the pore spaces at different ratios, depending on soil moisture content. The ratio of solid to pore spaces is controlled by the soil porosity.

1.2.1   Soil chemical and biological interfaces

A basic tenet of biology is that life evolves and changes to adapt to the environment, driven by reproductive success. Because soils have a significant impact on environmental conditions, there is a direct link between evolutionary processes and soils. Some even theorize that the first forms of life evolved from interactions of carbon and nitrogen with clay minerals of the type commonly observed in soils. It is hypothesized that clays catalyzed the first organic prebiotic polymers. While such a theory is controversial, one cannot deny the role of soils in maintaining life and the environment. Even marine life is affected by chemicals and minerals that are transferred from the land to the sea by water flow or air-borne dust particles. Thus, chemical processes in soils are critical for maintenance and growth of all life forms, and soils are locked in a partnership with the biosphere, hydrosphere, lithosphere, and atmosphere in providing critical ecosystem services.

The atmosphere, biosphere, and hydrosphere are weakly buffered against change in chemical composition and fluctuate when perturbed. Soils, in contrast, resist chemical changes, and are a steadying influence on the other three environmental compartments. Detrimental changes in the hydrosphere, atmosphere, and biosphere due to human activities often occur because the soil is bypassed, causing imbalances in important ecosystem processes that would otherwise occur in soil, and would therefore be better buffered. High nutrient concentrations entering surface waters for example, bypass soil's nutrient cycles, and cause algal blooms that deteriorate water quality.

Ion exchange on mineral and organic matter surfaces, and mineral dissolution and precipitation reactions that occur in soils are soil reactions that buffer elemental availability to organisms. Soils act as sources and sinks of most of the essential nutrients required by organisms. Plants, for example, derive almost all their essential nutrients from the soil; with the exception of carbon, hydrogen, oxygen, and minor amounts of nitrogen and sulfur gases (NO_x, NH_3, and SO_2) directly absorbed from the atmosphere by leaves, plus a small amount of ions absorbed from dust and foliar sprays on the leaves.

Plants depend on soil's ability to buffer essential nutrients, and otherwise retard nutrient leaching out of the plant-root zone. Thus, the entire terrestrial ecosystem depends on the **biogeochemical cycling** of

nutrients such as potassium, calcium, magnesium, phosphorus, nitrogen, and micronutrients within soils. Under natural conditions, the major factors affecting ion availability to plants are: 1) ion concentration in the soil solution; 2) the degree of ion interaction with, and rate of release from, soil solid phases; 3) the activity of soil microorganisms; and 4) discrimination by the plant root during ion uptake. This book is concerned primarily with the first two factors: the soil solution and ion interaction with the solid phase.

Soil is an O-Si-Al-Fe matrix containing relatively small amounts of the essential elements. But the small amounts of ions held by that matrix are vital to plant growth. **Table 1.1** shows representative contents of important elements in soils and plants. Concentrations of elements in plants depend on plant species, and soil concentrations. Soil concentrations depend on the **soil formation factors**, especially parent material and biologically driven fluxes of elements. As a result of the many factors that influence plant uptake and soil concentration, average values in **Table 1.1** are instructive only; actual concentrations vary widely.

Figure 1.5 shows typical elemental concentrations in plants as a function of typical soil concentrations. The data points represent *approximate* indices of the relative availability of elements in soil to plants. Thus, trends should be interpreted with caution because individual plant species and soil properties greatly influence element bioavailability. The general trend in **Figure 1.5** is that plant concentration of elements increases as soil concentration increases. Elements that deviate from this relationship suggest that a process in the soil is affecting availability of the element for plant uptake. Nitrogen, sulfur, chlorine, and boron concentrations in plants are above the 1:1 trend line, suggesting these elements are readily available for uptake by plants. The plant concentrations of potassium, calcium, magnesium, molybdenum, zinc, and copper occur on the 1:1 line, suggesting uptake of these ions is correlated to soil concentration. Concentrations of iron, nickel, and cobalt in plants are below the 1:1 line, suggesting relatively low availability of these elements for plant uptake. Mercury is a contaminant, and appears to be readily taken up in plants compared to typical soil concentrations. Other contaminants, such as arsenic, lead, cadmium, and aluminum appear to have relatively low concentrations in plants compared to soil concentrations. One goal of soil chemistry is to explain why soil chemicals have such variability for plant availability.

In natural systems, the biosphere is at equilibrium with respect to nutrient cycling in soils, and in properly managed agricultural systems, soils are integral to supplying adequate nutrients for sustainable crop production. The Exhaustion Plot at Rothamsted Experiment Station in England, for example, has operated continuously since 1845 and revealed that even extreme management practices such as removing all plant material at harvest from the soil each year and no fertilization, reduced crop yields, but did not stop plant growth. While such fertility management demonstrates soil's natural resilience, the decreased yields are clear indicators that this type of management of agronomic systems is not desirable for food production.

Immediate sources of the elements required for plant growth are solutes and electrolytes in the soil solution. Nearly all of the plant-essential nutrients exist in soils as ions. Some elements can have several different **oxidation states** and **valences**. Oxidation state is the difference in electrons and protons in an atom, while valence is the net charge on an ion or molecule. For example, nitrogen has several oxidation states that occur as different types of moelcules in soils; such as nitrate (NO_3^-), ammonium (NH_4^+), nitrite (NO_2^-), amino N (R-NH_2), and nitrogen gas (N_2). The valence of the different nitrogen forms ranges from negative, to zero, to positive, which has an important effect on the reactivity and availability of the various nitrogen species. Many elements exist in soils as ions with a single oxidation state, such as magnesium (Mg^{2+}) and calcium (Ca^{2+}), but their valence depends on the molecular species in the soil solution or solid.

Ion availability in solution is continuously renewed by soil reactions that add ions back to the soil solution after they are depleted. Main sources of ions to soil solution are: 1) mineral weathering; 2) organic matter decay; 3) rain; 4) irrigation waters; 5) fertilization; and 6) release of ions retained by clays in soils. With respect to ion availability for plant uptake, soils play an integral role in the delicate balance between preventing losses by leaching and supplying nutrients to plants and microorganisms. In other words, ion retention by soils does not completely prevent leaching losses, but is sufficient to maintain ions within the soil so that they can recycle between soils and plants before they are finally lost

Table 1.1   Concentration ranges (mg kg^{-1} dry weight) of elements in plants and soils. *Reference Plant* (column 3) is a concept proposed to represent a *typical* non-accumulator plant species; soil median represents the median for *typical* soil samples. Data compiled from (Bowen, H.J.M. 1979. *Environmental Chemistry of the Elements*, Academic Press, London; New York. Markert, B. 1992, Presence and significance of naturally occurring chemical-elements of the periodic system in the plant organism and consequences for future investigations on inorganic environmental chemistry in ecosystems. *Vegetatio* 103: 1–30. Markert, B. 1992, Establishing of reference plant for inorganic characterization of different plant-species by chemical fingerprinting, *Water Air Soil Pollution* 64: 533–538. Marschner, H. 1995, *Mineral Nutrition of Higher Plants*. 2nd ed., Academic Press, London. Adriano, D.C. 2001, *Trace Elements in Terrestrial Environments: Biochemistry, Bioavailability, and Risks of Metals*, 2nd ed. Springer).

Element	Plant Range	Reference Plant	Soil Range	Soil Median
		----(mg kg^{-1})----		
Major Elements				
Calcium	1000–50 000	10 000	700–500 000	15 000
Carbon	–	445 000	7000–500 000	20 000
Hydrogen	41 000–72 000	65 000	–	
Magnesium	1000–9000	2000	400–9000	5000
Nitrogen	12 000–75 000	25 000	200–5000	2000
Oxygen	400 000–440 000	425 000	–	490 000
Phosphorus	120–30 000	2000	35–53 000	800
Potassium	5000–34 000	19 000	80–37 000	14 000
Sulfur	600–10 000	3000	30–1 600	700
Micro-nutrients				
Boron	30–75	40	2–270	20
Chlorine	2000–20 000	20 000	8–1 800	100
Cobalt	0.02–0.5	0.2	0.05–65	8
Copper	2–20	10	2–250	30
Iron	5–200	150	2000–550 000	40 000
Manganese	1–700	200	20–10 000	1000
Molybdenum	0.03–5	0.5	0.1–40	1.2
Nickel	0.4–4	1.5	2–750	50
Silicon	200–8000	10 000	250 000–410 000	330 000
Zinc	15–150	50	1–900	90
Other				
Aluminum	90–530	80	10 000–300 000	71 000
Arsenic	0.01–1.5	0.10	0.1–40	6
Barium	10–100	40	100–3000	500
Cadmium	0.03–0.5	0.05	0.01–2	0.40
Chromium	0.2–1	1.5	5–1 500	70
Iodine	0.07–10	3	0.1–25	5
Lead	0.1–5	1	2–300	35
Mercury	0.005–0.2	0.1	0.01–0.5	0.06
Selenium	0.01–2	0.02	0.1–2	0.4
Strontium	3–400	5	4–2000	250
Vanadium	0.001–10	0.5	3–500	90

to groundwater, rivers, and the sea. Details of the different soil reactions that control ion availability for plant uptake are discussed later in this and other chapters.

1.2.2   Soil solids

Soils contain both organic and inorganic solids. Inorganic solids in soils comprise mixtures of various types of minerals existing as rocks, sand, silt, and clays (**Figure 1.6**). Organic solids, such as soil organic
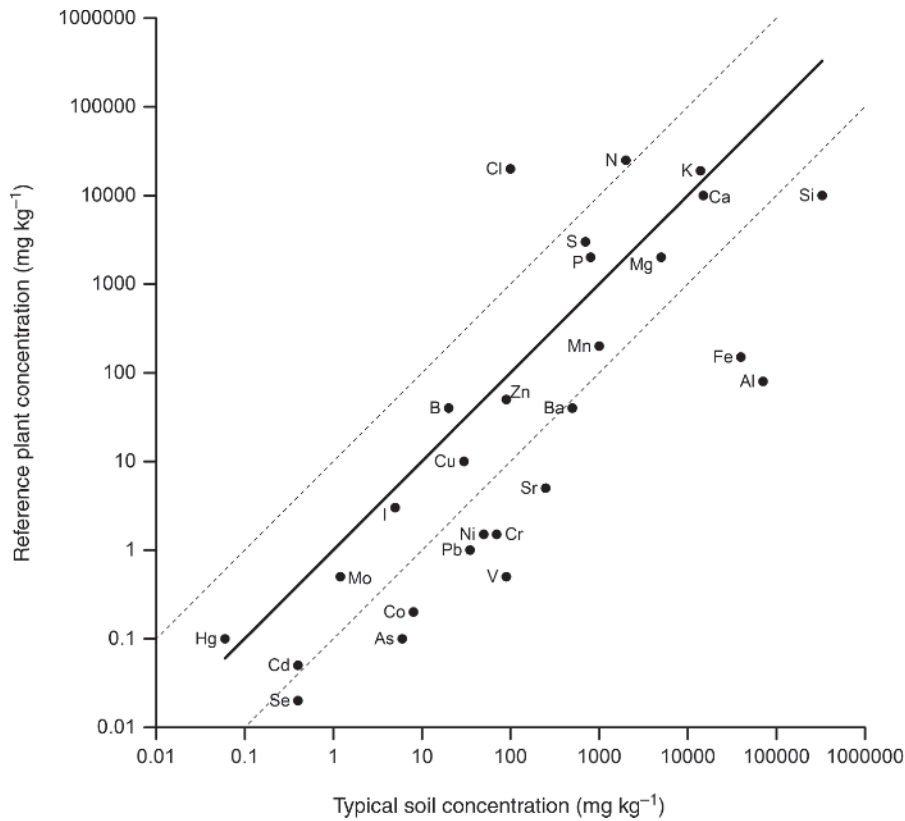
Figure 1.5   Log-log plot of elemental concentration of a typical plant as a function of total elemental concentration of a typical soil (See Table 1.1). Solid line is the 1:1 relationship indicating that plant concentrations are directly proportional to soil concentrations. Dashed lines represent one tenth and ten times the 1:1 relationship. Elements above the 1:1 line are more readily absorbed by plants than elements below the line.

matter, are equally important solid phases in soils, particularly in the O and A horizons of soils. Soil chemical processes are greatly influenced by interactions with soil solids, thus, the study of solid-phase properties (soil mineralogy) is a sub-discipline of soil science that is of great importance for soil chemistry.

The interface between solids and solution is called the **solid-solution interface**. The greater the **surface area** of the solid in a given volume or mass, the greater the area of the solid-solution interface, which means more reactive surfaces. Smaller particles have greater solid-solution interface (specific surface), and are more reactive than larger particles. For example, a 1-mm spherical sand particle has a surface area/mass ratio of about $0.002\,m^2\,g^{-1}$; a 1-μm clay particle, $2\,m^2\,g^{-1}$; and a 1-nm particle, $2000\,m^2\,g^{-1}$. **Figure 1.7** shows the change in surface area if a hypothetical rock of volume $1\,m^3$ were crushed into different particle sizes.

In soils, the smallest particles are termed **colloids**, which are particles that are 1 to 1000 nm in size. Colloids form unique mixtures when suspended in air or water. The components in colloidal mixtures tend to lose their individual identities so that the mixtures can be considered unique substances. Other examples of colloidal mixtures are fog, smoke, smog, aerosol, foam, emulsion, and gel. All are small particles suspended in a liquid or gaseous fluid. Colloidal particles interact strongly with fluid, but the individual particles have some structural integrity, so they cannot be said to be homogenously dissolved.
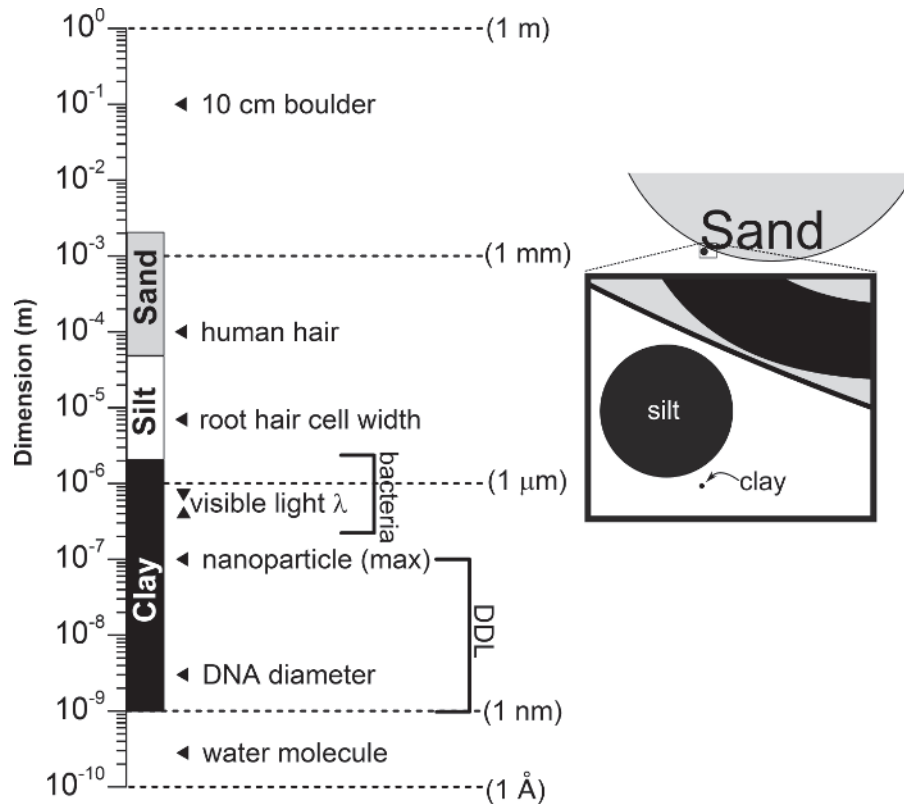
Figure 1.6   Diameter of sand, silt, and clay particles compared to other common objects. Drawing shows relative sizes of sand, silt, and clay (in blown up section the lower curve from the *S* from *Sand* is shown to emphasize relative size). DDL is the size of a typical diffuse double layer.

A colloidal mixture behaves so distinctively because of the large surface area of interaction between the particles and water or air. Thus, colloids in soils are important solid phases that greatly influence soil reactions.

The important colloidal properties that clays impart to soils include adsorption and exchange of ions, and absorption of water and gasses. The colloidal properties of clay facilitate the soil chemical reaction processes essential to life. The surface properties of colloids are dictated by the type of colloid, which are typically either degraded plant materials, termed humus, or clay-sized mineral particles (soil clays) such as phyllosilicates and iron and aluminum oxides.

1.2.3   Soil interaction with the hydrosphere

The amount of water in soils is only a tiny fraction (0.001% to 0.0005%) of the earth's total water supply (**Figure 1.8**). Such a small amount of soil water seems perilously small to supply all terrestrial life. Yet, this miniscule portion is the water that supports plants, weathers rocks, forms soil, and is the medium in which most soil chemical reactions occur. The periodic droughts and resulting devastation around the world emphasize the importance of soil water for agriculture and ecosystem health.
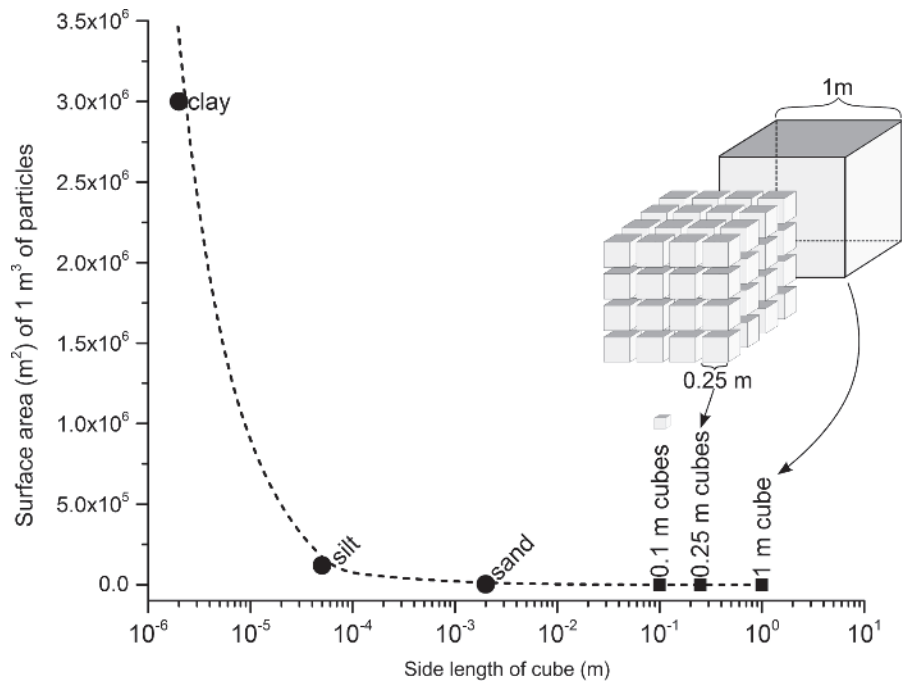
Figure 1.7 The effect of particle size on total surface area (SA) of 1 m^3 stacked particles (no space between sub-cubes). The edges of the different cubes are six different lengths: 1 m (total SA = 6 m^2), 0.25 m (total SA = 24 m^2), 0.1 m (total SA = 60 m^2), 0.02 m (sand size, total SA = 300 m^2), 0.00005 m (silt size, total SA = 120 000 m^2), 2 x 10^{-6} m (clay size, total SA = 3 000 000 m^2). The graph illustrates that the volume of 1 m^3 of clay-sized cube particles is 10 000 times greater than the surface area of the same volume of sand-sized cubic particles.
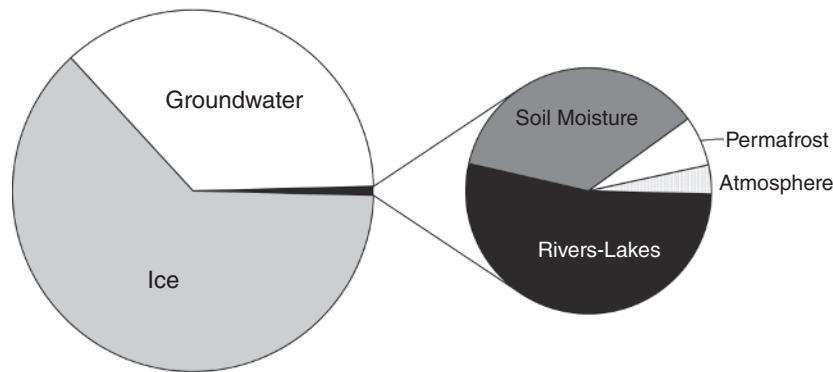

Figure 1.8 Estimate of distribution of non-ocean water on Earth. Ocean water volume (not shown) is 96.5% total water volume. Soil moisture (122 000 km^3) is only a small fraction (9×10^{-5} %) of the total water volume on Earth. Data from Trenberth, K.E., L. Smith, T.T. Qian, A. Dai, and J. Fasullo. 2007. Estimates of the global water budget and its annual cycle using observational and model data. *Journal Hydrometeorology* 8: 758–769.

Surface and ground waters receive most of their dissolved solutes from the soil, where rain first reaches the earth's surface and weathering is strongest. As water percolates to greater depths, the composition changes less dramatically because the water already contains the salts from the above soil. The composition and concentration of dissolved solutes can change at depths, however, if the water contacts soluble minerals in the subsurface (e.g., $CaCO_3$), or if it is stored for long periods in underground basins.

Stream water comes from soil and groundwater drainage, plus surface runoff. Natural drainage waters contain relatively low concentrations of the essential ions. The steady input of ions from drainage waters into surface water supports what is generally regarded as a natural and desirable aquatic population in streams and lakes. However, when concentrations of chemicals in runoff water increase above typical levels, such as in agriculturally modified watersheds, surface waters become contaminated.

Proper management can minimize runoff from agricultural lands, but some changes in water composition due to agriculture may be inevitable. Urbanization also increases runoff by creating less permeable surfaces such as rooftops and streets. The velocity of runoff increases as the overall permeability of the land surface decreases. In arid regions, surface runoff is a considerable fraction of stream flow when intense storms, sparse plant cover, and relatively low soil permeability create intermittent streams. The solute concentration in such waters is high, and is important to the downstream ecology.

The **soil solution** is a component of the hydrosphere. Soils exist at an interface between the hydrosphere, atmosphere, biosphere, and lithosphere, and soil solutions are greatly influenced by interactions with these other spheres. The soil solution is the direct source of mineral nutrients for all terrestrial plants, and is the most important transfer medium for chemical elements essential to life.

Soil solution includes the aqueous solution in soil pores and the film of water associated with mineral surfaces. Many soil clay particles have a net negative charge that extends into the soil solution, where the charge is balanced by an excess of solution cations. Thus, soil solution (including the film of water on negatively charged colloids) differs from other aqueous solutions in that it is not electrically neutral and usually contains more cations than anions. Old and heavily weathered soils in regions lying within the tropic and sub-tropic latitudes, or soils of volcanic origin, as in Japan, New Zealand, and the Pacific Northwest, USA, may have a net positive charge. In this case, the soil solution has an excess of anions.

At field capacity water content, most of the soil solution is in small ($<10\,\mu m$) contacts and pores between sand and silt particles (e.g., water-filled spaces illustrated in **Figure 1.1**). Clay particles and microbes congregate at the contacts, so the soil solution interacts closely with the reactive bodies in the contact zones. Because soil-particle charge extends into the film of water on the particle's surface, the boundary between soil solids and the soil solution is diffuse. The water and ions at the interface belong to both the aqueous phase and the soil solids. This solid-solution water layer makes up a **diffuse double layer** referring to the charge of the particle and the charge from the ions in the surface film of water (discussed in more detail in later chapters). In soils containing considerable clay, a large part of the soil solution is influenced by these colloids.

The soil solution contains a wide variety of solutes, including probably every element in the periodic table. The reactivity of soils greatly influences the composition of the soil solution. Aqueous reactions that require days and years in air, and hours in water, may require only seconds and minutes in soils. To understand processes controlling water quality, studying soil properties within the watershed as opposed to surface or groundwater properties provides valuable insight.

1.2.4   Interaction of soil and the atmosphere

Interactions of gases with soils are much less obvious than soil-water interaction, but soil-gas interactions are important aspects of carbon, nitrogen, and sulfur cycling. Soils absorb sulfur dioxide, hydrogen sulfide, hydrocarbons, carbon monoxide, nitrogen oxide, and ozone gases from the air. Soils release gases, such as H_2O, CO_2, and CH_4 that result from organic decay, and N_2 and N_2O from natural soil nitrogen compounds and fertilizers. Global cycles of carbon, nitrogen, and sulfur have prominent soil chemical processes that include soil-gas reactions (see Special Topic Box 1.1 for carbon cycle discussion).

Special Topic Box 1.1: Biogeochemical cycling of carbon in soils

Climate change and global biogeochemical cycling of carbon is a topic of great interest and research. Important aspects of the global carbon biogeochemical cycle are the magnitude of carbon pools and fluxes of carbon in soil, which are critical, and often neglected, parts of the earth's active carbon system. The active carbon system is the most relevant for immediate interests because fluxes are faster than changes in geologic carbon (carbon stored in deep rock or the deep sea). Understanding soil carbon biogeochemical cycling requires knowledge of soil chemical processes.

Active carbon in the earth exists in five main reservoirs: soil, biomass, ocean surface, atmospheric, and extracted fossil fuels (**Table 1.2**). The amount of carbon in the soil far exceeds the other pools, and the soil's role in the carbon cycle is very large. Soil carbon consists of organic and inorganic fractions (**Table 1.3**). Wetlands, peatlands, and permafrost soils are one of the largest reservoirs of organic carbon. In shrublands, grasslands, and arid lands, pedogenic inorganic carbon (caliche or calcium carbonates), may exceed organic carbon in the soil.

Table 1.2   Estimates of amount of carbon in the active reservoirs on earth (one petagram (Pg) = 1 gigaton (GT) = 10^{15} g).

Reservoir	Carbon (Pg)
Surface of Ocean	700-1000[1]
Atmosphere (2005 level)	805[1]
Fossil Fuel (recoverable)	5000-10000[1]
Vegetation	560[2]
Soil organic carbon (1 m)	1550[2]
Inorganic soil carbon (1 m)	950[2]
Northern circumpolar permafrost region[*]	1672[3]

[*]Total soil carbon mass in the 0-300 cm depth, **and** deep carbon in the permafrost (yedoma) and deltaic deposits

[1]Houghton, R.A. 2007. Balancing the global carbon budget. Annual Reviews in Earth Planetary Science 35:313–347.

[2]Lal, R. 2008. Sequestration of atmospheric CO_2 in global carbon pools. Energy & Environmental Science 1:86–100.

[3]Tarnocai, C., J.G. Canadell, E.A.G. Schuur, P. Kuhry, G. Mazhitova, and S. Zimov, 2009, Soil organic carbon pools in the northern circumpolar permafrost region, Global Biogeochemical Cycles 23.

Decay of organic matter in soils and vegetative respiration are the largest fluxes of CO_2 to the atmosphere. Thus, changing land management can significantly impact the global carbon cycle. For example, clearing and cultivation of virgin soils from 1850 to 1997 is estimated to have released 140 Pg (1 Pg = 10^{15} g) of carbon to the atmosphere, approximately 50% of the total carbon emitted by fossil fuel use in the same period (reported in Lal, R. 2008. Sequestration of atmospheric CO_2 in global carbon pools. *Energy & Environmental Science* 1: 86–100).

The annual rate of net photosynthesis is roughly 50% terrestrial and 50% marine. Soils are typically at steady-state with respect to oxidation of organic matter, meaning that the degradation rate equals the photosynthetic CO_2 fixation rate. Agriculture and forestry practices can affect the decay of organic matter, and offer the possibility of carbon sequestration to mitigate atmospheric CO_2 concentration increases in the future.

Factors that affect soil biogeochemical cycling of carbon include temperature, microbial reactions, mineral composition, carbon inputs, soil permeability, and moisture content. Understanding details

of the soil biogeochemical carbon cycle requires knowledge of the different carbon species, reactions, and how they respond to fluxes. **Table 1.3** lists common carbon species and examples of their reactions in soils. Soil carbon reactions and species depend on various soil processes, such as microbial respiration and association of carbon with soil minerals, and the type of SOM molecules present. Because of the natural variability in processes and SOM inputs, developing reactions to quantify carbon release from SOM is challenging, and a topic of much research.

Table 1.3 Examples of carbon species and reaction in soils.

Types of Soil Carbon	Example Species	Example Reactions
Organic		
Biomolecules	Organic carbon in living or dead organisms and their metabolites (e.g., proteins, carbohydrates, methane)	1) Microbial oxidation of biomolecule to form CO_2 and SOM: $CH_2O - R + H_2O$ $= CO_2 + SOM + 4H^+ + 4e^-$ $CH_2O\text{-}R$ represents a carbohydrate moiety in a biomolecule; SOM is a partially degraded biomolecule
Anthropogenic chemicals	Pesticides and industrial chemicals (e.g., trichloroethylene, DDT)	
Soil organic matter (SOM)	Humic substances, humic and fulvic acids	2) Anaerobic methanogenesis (microbial production of methane): $CO_2(g) + 8H^+ + 8e^-$ $= CH_4(g) + 2H_2O$
Incomplete organic matter combustion products	Fire derived soil carbon, black carbon, biochar, soot, charcoal, graphite, tar	Biomass + heat = $C_xH_y + C_xH_yO_z$ $+ H_2O + CO_2 + CO + H_2 +$ etc. Heating of organic materials at high temperatures and limited oxygen presence produces gasification products C_xH_y and charcoal $C_xH_yO_z$, among other compounds
Inorganic		
Solid- carbonates	Calcite ($CaCO_3$), dolomite ($Ca_xMg_{1-x}(CO_3)$, siderite ($FeCO_3$)	Precipitation: $Ca^{2+}(aq) + CO_3^{2-}(aq) = CaCO_3(s)$
Gas- carbon dioxide	CO_2	Gas dissolution: $H_2O + CO_2(g) = H_2CO_3(aq)$
Liquid- carbonic acid	H_2CO_3, HCO_3^-, CO_3^{2-}, ion-carbonate complexes, e.g., $FeHCO_3^{2+}$ (aq)	Deprotonation: $H_2CO_3(aq) = HCO_3^-(aq) + H^+(aq)$ $HCO_3^-(aq) = CO_3^{2-}(aq) + H^+(aq)$ Complexation: $Ca^{2+}(aq) + CO_3^{2-}(aq) = CaCO_3(aq)$

   Organic carbon cycling reactions and inorganic cycling are inextricably linked by the production and consumption of CO_2. For example, aerobic microbial activity degrades organic carbon compounds and increases the partial pressure of CO_2 gas within the soil's pore space. The increased partial pressure increases carbon dioxide dissolution in soil water, which affects soil pH and precipitation of carbonate minerals. Increased accumulation of carbonate minerals in subsoil leads to a Bk soil horizon development (**Figure 1.9**). A Bk horizon significantly impacts the flow of water and gases, the plow-ability and chemical properties of soil.

   Because soil carbon can exist in solid, liquid, and gas phases, and involves both organic and inorganic chemical processes, understanding the complete soil biogeochemical carbon cycle requires all of

the disciplines of soil science. Soil chemistry predicts soil carbon fluxes in the soil, and therefore is integral to the study of carbon cycling within ecosystems and between the carbon pools (soil, ocean, atmosphere, and biosphere). Important aspects of the soil-carbon cycle studied in soil chemistry include dissolution of carbon dioxide into soil water, precipitation of carbon into carbonates, adsorption of dissolved carbon species such as bicarbonate onto mineral surfaces, formation and properties of soil organic matter, and oxidation of soil organic matter to CO_2. Soil organic matter is one of the most reactive components of soils, and imparts many of the soil's important physical and chemical properties.
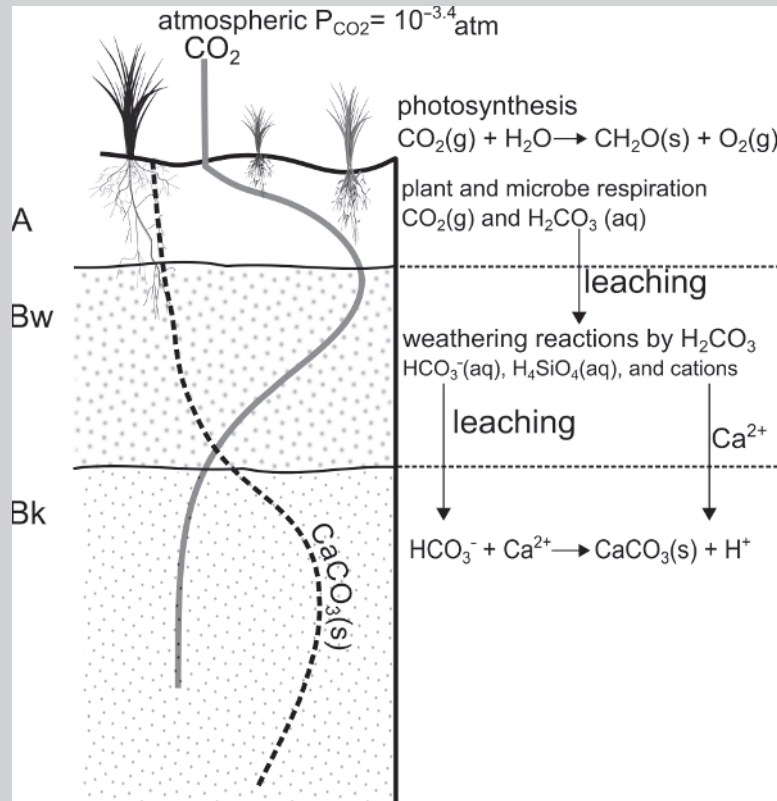

Figure 1.9   Soil profile showing carbon reactions that lead to calcite formation in the Bk horizon. Carbon dioxide concentrations (solid line in profile) are elevated above atmospheric concentrations in the A horizon where plants and microbes respire carbohydrates (CH_2O). Elevated carbon dioxide increases carbonic acid (H_2CO_3), which weathers rocks. Leaching of cations and carbonic acid into the lower profile creates local saturation of calcium carbonate minerals (dashed line in profile), and development of a Bk horizon, where the *k* is a subordinate descriptor indicating carbonate accumulation. The concentration of carbon dioxide then decreases in the profile as a result of precipitation of carbonates in Bk horizon. (Source: Adapted from Chadwick and Graham. Reproduced with permission of Taylor & Francis.)

The nitrogen cycle is an important example of soil-gas interactions. Nitrate (NO_3^-) and ammonium (NH_4^+) ions in rainwater interact with soils, plant roots, and microorganisms, and plants and microbes convert nitrogen to amino acids or to N_2 and N_2O gases that diffuse back to the atmosphere. Ammonia gas (NH_3) is also emitted and absorbed in soils. Under natural conditions, gaseous nitrogen loss is

approximately balanced by N_2 uptake and conversion to amino acids by symbiotic and free-living soil microorganisms.

Direct soil absorption of gases is perhaps most obvious in the case of the rapid disappearance of atmospheric sulfur dioxide in arid regions. The basicity of arid soils represents an active sink for acidic compounds from the atmosphere. The amount of direct soil absorption of atmospheric gases, inappropriately termed dry fallout by atmospheric scientists, is less in humid regions where plant absorption and rain washout of the gases are substantial.

Gas fluxes in soil are controlled by diffusion gradients and the permeability of the soil to the overlying atmosphere. Low permeability can result in gas concentrations within the soil that are several orders of magnitude greater or less than the overlying atmosphere. For example, root and soil microbial respiration consume oxygen and nitrogen, and produce CO_2, leading to increased carbonic acid concentrations in soil water. Increased carbonic acid promotes mineral weathering and increased concentrations of cations such as calcium in the soil solution. In arid regions, leaching of bicarbonate and calcium to lower horizons, as opposed to out of the soil profile such as occurs in soils in humid climates, leads to development of a cemented horizon called a Bk horizon (**Figure 1.9**) (*B* is the horizon designation and *k* designates the horizon as calcite cemented).

If a soil has low gas permeability due to small soil pores, high pore tortuosity, high clay content, or high water content, fluxes of gas to the atmosphere are hindered, and soil pore concentrations of gas are depleted or increased relative to the overlying atmosphere. Some wetland plants are able to transfer oxygen gas internally to the root zone. For example, in wetlands, fluxes of oxygen alter the availability of nutrients and contaminants, and the formation of iron and manganese solids.

1.3   Chemical reactions in soils

Chemistry is the study of chemical reactions and species, and factors that influence them. To study reactions, a **chemical *system*** is defined in which inputs and outputs can be controlled and monitored. For example NaCl dissolved in a beaker of water is a chemical system. Compared to a beaker used in laboratory chemistry, *soil systems* are much more complicated. Studying soil chemical processes require that system boundaries be defined so that fluxes of energy and matter can be accounted for and monitored (**Figure 1.1**). For example, a field plot has fluxes of heat, moisture, chemicals, organisms, and gases that impact soil chemical processes and are continuously changing. The multiple fluxes affecting field experiments makes measuring soil chemical processes challenging.

An alternative to monitoring soil processes at the field-scale is to impose constraints on the soil system. In the field, adding constraints on a system is difficult, but has been done by isolating a section of the soil by placing barriers around the edges of a section of the soil. Such **mesocosms** typically range in size from 10 cm to 2 m. An extreme case of attempting to isolate a system is the biosphere experiments conducted at the University of Arizona (*Biosphere 2*), where an entire ecosystem was sequestered in a controlled enclosure.

Given the difficulty of constraining natural systems for study of soil chemical reactions, an alternative is studying system properties ex-situ. There are two types of ex-situ experimental system approaches:

1.   Characterize the chemical properties on a soil sample taken from a field setting using various laboratory analyses, thus rendering a snapshot in time of the soil's conditions when sampled. For example, measuring total concentration of an element in a soil sample, or pH of a soil sample.
2.   Conduct experiments that monitor reactions and species in a **microcosm** that mimics field conditions. For example, a greenhouse experiment, or an anaerobic soil incubation in the laboratory.

Regardless of whether the system to be studied is in-situ in the field, or ex-situ in a laboratory, defining system boundaries and parameters is a requirement for conducting experiments and understanding chemical reaction processes occurring in soils.

1.3.1   Flow of chemical energy in soils

In soil, as in all the universe, energy flows towards the minimum (**Figure 1.10**). Science has put a theoretical framework on this axiom – the **Laws of Thermodynamics** – that allow predicting the state of a system and direction in which it will move. Thermodynamic treatment of relatively simple chemical reactions within a system is a well-developed science. However, as systems become more complex, as in soils and nature, implementing thermodynamics to predict reactions is more challenging. The difficulty in predicting thermodynamic processes of natural systems however, does not mean that the principles are not binding.

In natural systems, complexity of the reactants and products are not well defined, and fluxes into and out of the system are difficult to constrain and measure. In addition, many natural systems rarely reach their minimum energy before fluxes cause changes in the reactants, and thus the system equilibrium state changes. Examples of such fluxes in soils are changes in moisture, temperature, and vegetation. Fluxes change over time scales of minutes to years. Any input into a system, whether it is energy (heat), matter (chemicals), or pressure, causes the system to move toward a new equilibrium with a different distribution of chemical species. This requirement is referred to as **Le Chatelier's Principle**. To account for the fact that a system is undergoing change, but is not at equilibrium, scientists define system reactions as time-dependent or kinetically controlled.

The dynamic nature of natural systems causes some systems to never achieve a stable equilibrium. However, even in the absence of equilibrium, the total energy, whether it is chemical, pressure, or heat, always flows towards a minimum. In chemistry, theoretical energy of a system is quantified as a function of two thermodynamic factors: enthalpy (H) and entropy (S). Enthalpy is a measure of the heat of the system. Entropy is a measure of the tendency for energy to spontaneously go towards disorder. These factors embody the Laws of Thermodynamics. Enthalpy and entropy can be combined into a factor called Gibbs free energy (G):

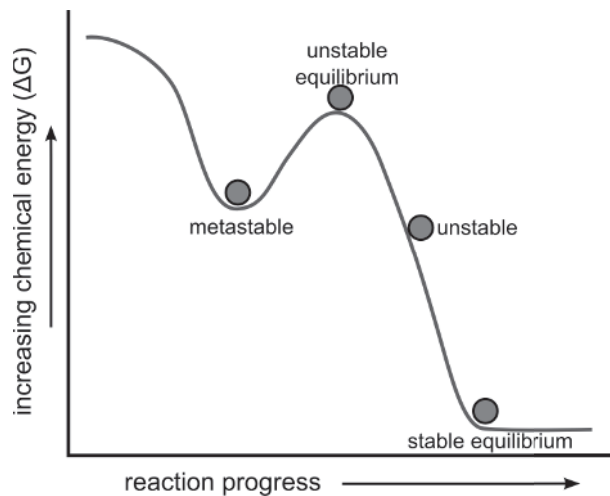$$\Delta G = \Delta H - T\Delta S \tag{1.2}$$

Figure 1.10   Chemical energy and reaction progress are analogous to a ball affected by gravity. Metastable and unstable positions are not the lowest energy, and will therefore react. The lowest energy position is equilibrium, where no net reaction occurs. Metastable and unstable equilibrium energy positions have some stability, and species may exist in these states for a fraction of seconds to very long periods; but, given time, the species will convert to the lower energy species. Typically, activation energy is needed for metastable species to overcome the higher energy (small bump). In nature, microbes, mineral catalysts, enzymes, moisture, sunlight, temperature, or pressure provide activation energy.

where ΔG is the change in free energy of the system and T is the temperature of the system. The delta symbols indicate a relative change from a known specified (standard) state.

Products and reactants have associated free energies, and their difference is the change in free energy of reaction (ΔG_{rxn}). Using the change in free energy to predict reaction status is useful for understanding which and how much of a chemical species should exist in a system. For example, one can predict the pH of a soil containing solid phase calcium carbonate using thermodynamic equations and system properties such as partial pressure of carbon dioxide (see Chapter 4).

A more detailed treatment of thermodynamic equations in soil chemistry will be given later. For now, the following points are emphasized:

1. All soil systems move toward the lowest energy state.
2. A system in which energy is at the lowest energy state is at equilibrium.
3. At Earth's surface, solar and geothermal (e.g., volcanic) energy continuously create new, unstable states of matter.
4. How fast chemicals go toward the lowest energy state is termed reaction kinetics.
5. Fluxes into and out of natural systems make them dynamic, and thus equilibrium state of soil chemical systems is constantly changing.

An example of the last point is the metastable iron oxide mineral ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) that exists in many soils (Color plate **Figure 1.11**). If the soil were static, that is, no input of energy or matter over time, the ferrihydrite would convert to more stable iron oxide minerals such as hematite (Fe_2O_3) or goethite (FeOOH), and ferrihydrite would cease to exist. Yet, ferrihydrite is found in many soils because it is continuously being created, at least as fast as it is disappearing. A system where a product is created as fast as it is disappearing is at **steady-state**.

1.3.2   Soil chemical speciation

Once a system of study has been defined, the next step in evaluating soil chemical processes is determining the species of the chemicals in the system. **Speciation** infers the phase (gas, liquid, solid), oxidation state, isotopic state, bonding environment, and structure of an element or molecule. For example, in soil, iron exists in two oxidation states (Fe^{2+} (ferrous) and Fe^{3+} (ferric)). Ferric iron has low solubility and commonly exists as solid iron oxide minerals such as goethite (FeOOH). Ferrous iron is more soluble and commonly exists in solution phase as aqueous ions, such as Fe^{2+} or $Fe(OH)^+$. Ferrous iron is a reduced phase that is common in soils that are wet and have limited oxygen, such as wetland soils.

A basic understanding of speciation for many chemicals in soils exists. However, there remain many unknowns about chemical species because soil environments are not fixed, and no two are alike. Speciation of a chemical in soil can be determined by either direct measurement or prediction. Prediction can be accurate, but should be supported with measurements. Measurements of soil chemical species are often difficult or time consuming. Advances in analytical technology, however, are allowing for better speciation determinations, and better ability to predict reactions and fate of chemicals in the environment.

1.3.3   Chemical reaction types in soils

Change in chemical speciation can be expressed as a **chemical reaction**. For example, reduction of ferric iron in the mineral goethite (FeOOH) to ferrous iron can be written as:

$$FeOOH(s) + 3H^+(aq) + e^- = Fe^{2+}(aq) + 2H_2O(l) \tag{1.3}$$
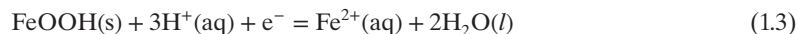
where e^- is an electron. The letters in the parentheses, s, aq, and *l* indicate *solid*, *aqueous*, and *liquid* states, respectively; the letter *g* in a written reaction indicates *gas* state. Symbols for states of matter are not always used in reactions, especially when the state is implied in the associated text. In the reaction in

Figure 1.11   Top section of soil showing Fe-enriched (red) and Fe-depleted (gray) zones in a wetland soil. Iron in this soil exists predominantly as the metastable mineral ferrihydrite, with lesser amounts of the thermodynamically stable minerals lepidocrocite and goethite. The dynamic redox conditions in wetland soils are responsible for the persistence of metastable ferrihydrite in the soil. (See **Figure 1.11** in color plate section for color version.)

Equation 1.3, oxidized ferric iron in goethite is a reactant that accepts an electron from an electron donor (biotic or abiotic, not shown in the reaction), and reduces to aqueous ferrous iron.

Writing soil chemical reactions is a straightforward exercise, but assigning the correct reaction to a complex soil system is more difficult. Thus, making species predictions using reactions and thermodynamic or kinetic constants is challenging. Fortunately, by constraining the system parameters, and making measurements of chemical species in the soil, relevant reaction processes can be identified, and predictions of soil chemical processes are possible.

A chemical reaction may go forward or backward. Reactions that go in both directions are called reversible. Some reactions are irreversible or unidirectional, depending on the system's properties and state of the chemicals. For example, weathering of the primary mineral muscovite in a soil to form the secondary clay mineral vermiculite is considered to be irreversible; meaning vermiculite will not reform to muscovite under soil conditions because heat and pressure are insufficient. Whether or not a reaction is irreversible is species and system dependent. Although some specific reactions may be irreversible in practice, reverse reactions can be written for all reaction types. The six basic reversible reaction processes that occur in soils are:

1. sorption/desorption
2. precipitation/dissolution
3. immobilization/mineralization

4.   oxidation/reduction
5.   complexation/dissociation
6.   gas dissolution/volatilization.

A chemical undergoing one of the above six reactions either changes its state of matter, its oxidation state, or its molecular composition or structure.

Sorption and desorption reactions describe association and release of a chemical from a particle surface, where the particles are minerals, soil organic matter (SOM), or perhaps a biological cell. Often sorption reactions are termed adsorption, which implies that the chemical resides on the solid surface, but is distinct from the solid or bulk solution, and is not forming a three-dimensional network of atoms on the surface (which is called surface precipitation). There are many different types of sorption, which will be covered in more detail in Chapter 10. One example is the adsorption of a sodium ion onto a clay mineral surface (Equation 1.1). The solid in this reaction, which could be the clay species montmorillonite, maintains its compositional integrity because the adsorbed ion is only associated with the surface of the mineral. The release of the potassium from the clay is a desorption reaction. Together, the adsorption and desorption reactions are termed **cation exchange**.

Precipitation and dissolution reactions describe the change in a chemical from solution to the solid state, where a new solid is formed from solution constituents. Dissolution is the reverse of precipitation, meaning ions from the solid are released to the solution. An example of a precipitation-dissolution reaction is the formation of the calcium carbonate mineral calcite in soils (see for example **Figure 1.9**).

Immobilization and mineralization reactions are generally biologically mediated. Immobilization refers to the uptake of chemical into the cellular structure of an organism, such as a microbe, fungi, or plant. The chemical within the organism is considered a biologically formed molecule (biomolecule). An example is the uptake of nitrate into a plant where it is utilized as a cellular metabolite. Mineralization implies degradation, release, or conversion of the chemical to a form that is no longer considered a biomolecule. Products of mineralization reactions are inorganic chemicals. Degradation of organic nitrogen to ammonium is an example of a mineralization reaction. Immobilization and mineralization reactions are important soil processes that determine the fate of chemicals in soils. Because immobilization and mineralization reactions require detailed discussion of microbiology and biochemistry, which is beyond the scope of fundamental soil chemistry, they are only broadly covered in this text.

Oxidation and reduction reactions refer to the gain and loss of electrons from an element, causing a change in oxidation state. Often times, redox reactions result in changes in the physical state or molecular structure, and thus may be combined with other reaction types. For example, the redox reaction shown for iron in Equation 1.3 describes both reduction and dissolution of iron, and is thus termed a reductive-dissolution reaction. Similarly, many mineralization and immobilization reactions are also redox reactions.

Complexation and dissociation reactions describe interactions of two or more chemicals in solution. Typically, the interactions are between aqueous ions. Protonation and deprotonation (gain and loss of H^+ ions) are specific types of complexation and dissociation involving acceptance and loss of a proton by an acidic ion or molecule. Hydrolysis is a dissociation reaction in which H^+ is released from a water molecule. Chelation is a type of complexation involving formation of chemical bonds between a molecule that has two or more bonding sites and a cation. Chelation increases nutrient availability for plants and microbes. Complexation reactions change the valence and molecular properties of chemicals in solutions, thereby changing the chemicals solubility, plant availability, and transport through the soil.

Dissolution and volatilization of gases in soils refers to reactions occurring between the soil atmosphere and the soil solution; specifically, transfer of gaseous chemicals into the aqueous phase, and the reverse. Since this reaction involves movement of gas into and out of liquid water, it is different than condensation and vaporization of a pure liquid to gas, and vice versa. Henry's gas law is used to predict equilibrium partitioning of gases into water (see Chapter 4). An example of gas dissolution in soil
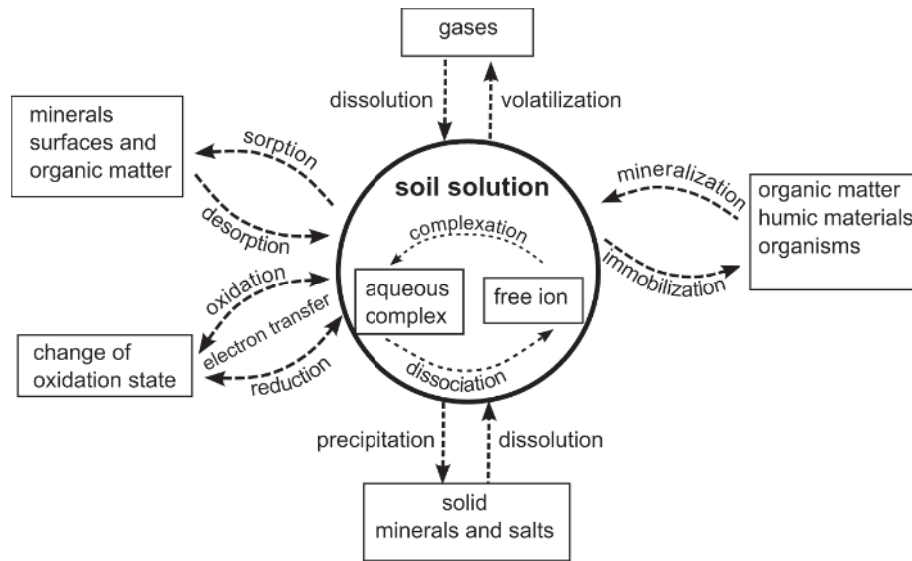
Figure 1.12   Chemical reactions in soil. Soil solution is in the center because most reactions occur between soil solution and either organisms, soil air, or solid phases.

solution is the reaction of carbon dioxide (gas) with water to form carbonic acid (aqueous), as shown in Special Topic Box 1.1. Oxygen, nitrogen, and sulfur also have important gas dissolution and volatilization reactions.

In soils, most reactions involve the soil solution. **Figure 1.12** is a comprehensive view of reactions that can occur in soils. Chemicals in soils exist in one of the states shown in the boxes, or soil solution. If the system is perturbed, the soil chemical may change via one of the six reactions to reestablish equilibrium. For a particular soil chemical, a detailed version of this diagram can be developed. For example, the nitrogen cycle is usually accompanied by a figure detailing biogeochemical cycling of nitrogen between solid, gas, organic, and solution phases, showing the different nitrogen oxidation states and molecular species.

1.4   Soil biogeochemical cycling

Because of the importance of interacting processes in soils, many soil chemists study soil **biogeochemical reactions**. Biogeochemistry implies that geochemical processes are coupled with biological processes, and includes cycling of energy and matter within a system. Two basic concepts of biogeochemical cycling are: 1) size of *pools* of chemicals; and 2) transfer of chemicals between the pools via fluxes of chemicals and energy. A biogeochemical pool, or reservoir, is a conceptual unit of the earth considered to represent a distinct part of Earth's systems; e.g., the plant biosphere, soils, groundwater, ocean, or atmosphere.

Biogeochemical cycles are studied at numerous scales – from the global scale to the soil-pore scale – depending on how one defines the system. Regardless of the scale of the system, fluxes must be considered, and are used as a way to understand the mass balance of the system pools. Elements readily involved in metabolic processes, such as carbon, oxygen, nitrogen, and sulfur, have active biogeochemical cycles, while elements such as titanium, aluminum, and cesium have less active biogeochemical cycles (less active does not necessarily imply simplicity).

An important example of the application of soil biogeochemistry is the carbon cycle. Soil carbon is the largest *active* carbon pool on earth, and thus soil reactions are an important component of global carbon cycling (**Figure 1.9** and Special Topics Box 1.1). For example, in the ∼10 000 years since the last ice age, massive amounts of carbon have moved from the equatorial regions of the earth to the newly un-glaciated polar regions. Accordingly, soil carbon stored in the soils and deep deposits in the northern circumpolar permafrost region represents a large deposit of Earth's terrestrial carbon. Ten thousand years is a very short geologic time, and active transfer of carbon between eco-regions illustrates how dynamic Earth's biogeochemical cycles are. Present day climate change may alter the rates of decomposition of the organic carbon in the northern circumpolar permafrost region. Thus a massive flux of carbon could potentially *be on the move* again, which may have significant impacts on the global climate.

1.5   Soil chemical influences on food production

Soil is the main source of human nutrition. The oceans supplement our food supply, but their productivity is limited. Terrestrial plants remain the cheapest and most efficient means of converting solar energy into life support for this planet. The growth of plants is a large fraction of the world's economy, and is fundamental to a nation's well-being.

Understanding soil processes, and developing best management practices is critical for sustainably growing plants needed for food and fiber. Early researchers designed experiments to better understand soil chemical processes so that crop growth could be maximized. Modern soil chemistry researchers continue to strive for new discoveries that will allow for more and healthier food production, while minimizing impacts on ecosystems.

Agriculturalists can influence and modify soil chemistry to a considerable extent. The amounts of essential elements needed by plants over a season are small enough that supplementing the soil supply is feasible. However, increasing the efficiency of that fertilization is a continuing challenge because producing fertilizers is expensive. For example, nitrogen fertilizer production is energy intensive, and phosphorus fertilizer sources are limited and therefore expensive to mine. Understanding soil chemical processes of amendments and fertilizers is important because they can change the availability of the applied nutrients. Application of pesticides or herbicides also increases the health of crops or grazing pasture. Soil chemical properties and processes affect the efficacies of such chemicals towards the pests, and control unintended side effects, such as damage to plants or other beneficial organisms, or leaching to surface and ground waters.

1.6   Soils and environmental health

In earlier times, when the population was less dense and industries were few and small, wastes were distributed widely on soil. Negative impacts were usually minor, and soils could readily assimilate insults (e.g., contaminants), and return to their natural biogeochemical cycles. Concentrating wastes in urban areas, industrial facilities, landfills, feedlots, and sewer treatment plants is causing contamination of the environment, and suggests that humanity has exceeded the rate at which these materials can be assimilated by the soil and return to their natural biogeochemical cycles. The need to deal with polluted environments is an important application of soil chemistry (**Figure 1.13**).

The elements that humans release as wastes are derived from the soil and the earth. Chemical contamination is the diversion of chemical elements from their *natural* biogeochemical cycles. For example, nitrogen and phosphate from waste-water treatment plants and agricultural operations that flow into streams and lakes are removed from the soil-plant cycle. Water bodies have a lower chemical buffering capacity than soils, and readily suffer nutrient overload effects that degrade water quality. If nitrogen and phosphorus were instead put back into the soils at levels that do not perturb natural processes too drastically, surface water quality would be much less degraded.
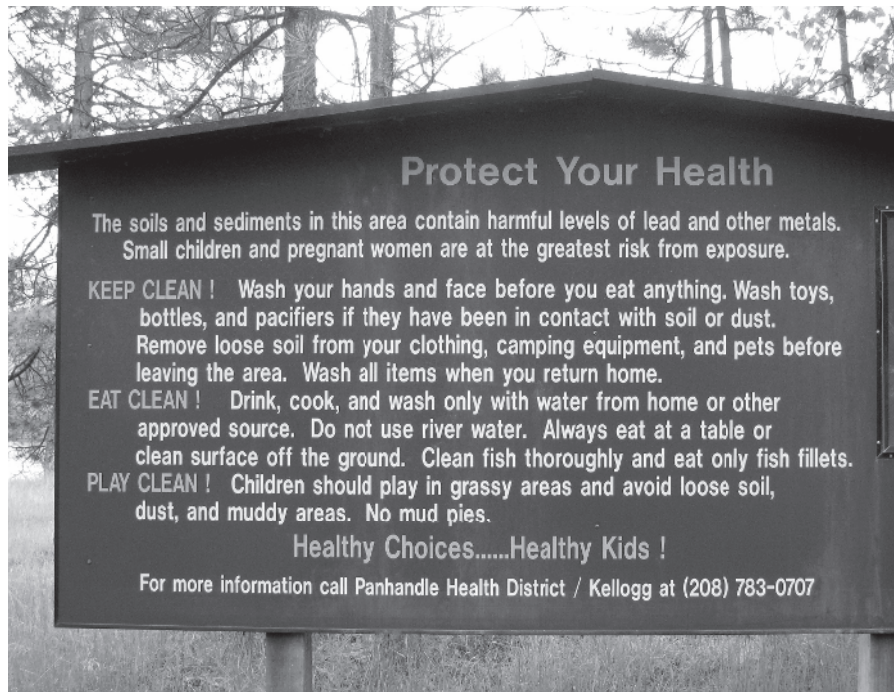
Figure 1.13   Sign from polluted site warning the public to avoid contact with the soil because of risk of lead poisoning.

Despite soil's natural ability to buffer or attenuate soil chemicals, soil degradation and environmental pollution are tremendous challenges for civilization. There are three general types of soil degradation:

1. Decrease in physical, chemical or biological properties such that the soil is less productive for plant growth. For example, depletion of nutrients or organic matter; increase in soil temperatures; compaction or surface crusting.
2. Reduction in soil depth by erosion.
3. Accumulation of chemicals to levels that detrimentally effect plant growth or ecosystem health. For example: salt accumulation, hydrogen ion accumulation (decreases pH), chemical contamination, excess nutrient buildup.

The most common soil degradation is desertification and salinization, either caused by overutilization of the soil for crop growth without regard to salt buildup, or overgrazing. Other issues that stem from environmental pollution occur when too much of a chemical exists in a soil, creating a potential toxicity issue for soil organisms, plants, or other organisms exposed to the chemical. Additionally, soil pollution creates off-site risks by leaching of the pollutant to ground or surface water.

Chemicals of concern can be either organic or inorganic. Most organic chemicals, such as pesticides and industrial chemicals degrade over time (although some take a relatively long time), and contaminated soil can eventually return to a non-polluted state. Other contaminants, such as inorganic chemicals or recalcitrant organic chemicals, do not degrade, and persist in soil until leached by water, volatilized and outgassed, or are sequestered by a plant. Common examples of inorganic pollutants are metals from industrial, mining, or agricultural sources. Even though inorganic chemicals do not degrade, their availability for uptake or leaching, and their hazard potential, is variable. Some chemicals are partially

removed from the soil by natural leaching, (e.g., zinc), while others are less soluble and more recalcitrant (e.g., lead), and thus remain in the soil solid phase. Many potentially toxic metals are sorbed so tightly onto soils that they are immobile and unavailable for plant uptake or leaching.

Some inorganic chemicals are nutrients, but at elevated levels are contaminants. This includes macro-nutrients for plants, such as nitrate, and micronutrients such as boron, zinc, and copper. The amount and speciation of chemicals are the most important factors for determining whether soils are contaminated. Chapter 3 discusses these factors for many of the more common chemicals that occur in soils.

1.6.1   Soil chemistry and environmental toxicology

Environmental toxicology is a discipline that specializes in the study of chemical risks or hazards in the environment. Because of the critical role of soil chemistry in chemical processes in the environment, there is an overlap with environmental toxicology. Thus, concepts and terms from environmental toxicology are frequently used when discussing soil chemistry topics. Definitions of toxicological terms commonly used in soil chemistry are:

Contaminant - A chemical of concern that is present at elevated concentrations. Does not necessarily imply an organism is at risk.

Pollutant - A contaminant judged to represent a hazard.

Toxicant or toxic chemical - A chemical present in an amount and form that may cause damage to an organism (animal, plant, or microbe). Does not imply exposure to an organism.

Toxin - A toxic chemical of *biological* origin, such as venoms and the active agents in poisonous plants. This term is often misused; soil chemistry does not typically deal with toxins.

Toxicity - The relative degree to which a chemical is poisonous.

Poison - A chemical that causes an adverse effect when an organism is exposed.

Bioavailability - The *measured* availability of a chemical for uptake into an organism. May consider only uptake into organism, or actual uptake into targeted organ (e.g., blood stream, or leaf tissue).

Bioaccessibility - The *potential* availability of a chemical to be taken up by an organism measured using an in-vitro method.

Often in soil chemistry, toxicity, bioavailability, or bioaccessibility are referred to in a more general sense using the term *availability* or *fate and transport*. Although not accurate for describing risks of chemicals, these broad terms are useful for generalizations or non-specific references to a chemical's environmental behavior.

To determine a chemical's potential toxicity, a risk-assessment screening model that categorizes risk based on four aspects is used:

1. **Sources** - Identify the chemical of concern and the environment in which it exists.
   Example: a mine-contaminated soil with elevated lead concentration.
2. **Pathways** - Identify the routes of exposure and factors that affect exposure from the chemical of concern to the *receptor*.
   Example: children have lead-laden soil particles stuck to their hands and put their hands in their mouth. The species of the Pb in the soil causes bioavailability to be variable.
3. **Receptors** - The organism(s) at risk from exposure to the chemical of concern.
   Example: humans (children) ingesting soil with elevated Pb.
4. **Controls** - Natural and engineered solutions to reduce risks. Site management decisions can be made to mitigate risk, or provide a management scenario that minimizes exposure of the risk to the receptors.
   Example: Pb-contaminated soil remediation options may entail removing the soil, amending the soil with a product that will decrease Pb bioavailability, or isolating the site so that children will not come into contact with the contaminated soil.

1.7   Units in soil chemistry

The International Union of Pure and Applied Chemistry (IUPAC) has developed recommendations of a common language to describe chemical concepts or processes, including nomenclature, symbols, and units used for describing quantities. Most of the information is published in "The Gold Book," which is available on the Internet. For the most part, soil chemistry adheres to IUPAC's convention of using SI units (Système International d'Unités). However, as with many disciplines, expression of some soil chemical properties deviates from SI units because of historical or convenience reasons.

Units of measurement are either extensive or intensive. **Extensive properties** measure the amount of a substance or energy. For example, mass of an object is an extensive unit because it describes *how much* something weighs, and changes depending on how much of the object is present. **Intensive properties** describe a property of an object or energy that does not change when the total amount increases or decreases. Density is an intensive unit, for example, because it describes the mass of a substance per volume – no matter how much of the substance is present, its density does not change. Concentration is another example of an intensive unit. **Table 1.4** provides a listing of some of the common units used in soil chemistry. Other units used in soil chemistry not listed in **Table 1.4** follow SI convention.

Table 1.4   Some specific units commonly used in soil chemistry.

Quantity	Unit	Symbol	Definition	Alternate unit
Land area	Hectare	Ha	10^4 m^2	1 Ha=2.471 acres
Mass of 1 Ha of soil to 15 cm	Hectare furrow slice	HFS	2200 Mg Ha^{-1} 15 cm^{-1}	assuming soil bulk density of 1300 kg m^{-3}
Volume	Cubic meter	m^3		
	Liter	L	10^{-3} m^3	
Conductance	Siemens per meter	S m^{-1}	ohm^{-1}	1 S m^{-1} = 10 mho cm^{-1}; 1 mho = 1 ohm^{-1}
Amount of ion charge	Moles charge	mol(+) or mol(-) or	mol ion times ion charge	equivalent = 1 mol charge; meq = 10^{-3} mol charge
Concentration	Moles per unit volume	M	mol L^{-1}	1 M = 10^3 mol m^{-3} 1 mol m^{-3} = 1 mmol L^{-1}
	Moles charge per unit volume (normality)	N	mol charge L^{-1}	
	Millimolar	mM	10^{-3} mol L^{-1}	
	Micromolar	μM	10^{-6} mol L^{-1}	
Cation exchange capacity	Millimoles charge per kg solid	CEC	mmol(+) kg^{-1}	10 mmol(+) kg^{-1} =1 cmol kg^{-1} = 1 milliequivalent 100 g^{-1}
Specific surface area	Square meters per kilogram	SA	m^2 kg^{-1}	
Interatomic spacing	Nanometer	nm	10^{-9} m	1 nm = 10 angstroms (Å)

1.7.1   Converting units

To describe chemical processes and quantities of chemicals, it is often necessary, or desirable, to convert units. **Dimensional analysis** is a mathematical treatment used to change units of intensive or extensive properties. Even practiced scientists should always do careful dimensional analysis, as this is often a source of error, sometimes leading to disastrous and costly effects. Below are examples of a few dimensional analysis problems commonly encountered in soil chemistry.

Example: Percent to parts per million.   One percent is equal to a part per hundred. Units of soil constituents that are present less than 1% are often listed as parts per million (ppm). Parts per million are not SI units, rather they are ratios of the amount of a part of one substance over one million parts of another substance. A solution 1 ppm in Ca^{2+} ions contains 1 g of Ca^{2+} ions in 1 million grams of solution. Care is needed when using the terms percent or ppm, or the similar unit part per billion (ppb), because they can be used to represent parts per whole on a volume, mass, or mixed basis. For example, the amount of chemical in soil can be represented as mg kg^{-1}, or a soil extraction can be represented by mg L^{-1}, both use the notation *ppm*; so, for example, stating a soil has 100 ppm Zn, for example, without appropriate context is ambiguous. Because of the ambiguity, scientists and regulators would do well to move away from using the abbreviation ppm altogether, and instead use the actual units, such as mg kg^{-1}, and so on.

One percent is equivalent to 10 000 ppm. For example, if a soil contains 1.8% organic carbon, then it is 18 000 mg kg^{-1} (ppm) of organic carbon. The dimensional analysis is:

$$1.8\% \times \frac{10000 \text{ mg kg}^{-1}}{\%} = 18000 \text{ mg kg}^{-1} \tag{1.4}$$

Note the percent units cancel.

Example: mg L^{-1} to mmol L^{-1}.   To convert a unit from mass basis to mole basis, such as mg L^{-1} to mmol L^{-1} requires using the atomic or molecular weight, which is the mass of a substance in 1 mole (6.022×10^{23} atoms or molecules) of substance. Units of atomic and molecular weights are g mol^{-1}. For convenience, because the unit mg L^{-1} is often used to describe concentrations in soil chemistry, the atomic mass unit of mg mmol^{-1} is often used instead of g mol^{-1} (note both units are equivalent), which saves from having to convert the milligram units to gram units. Example of conversion of mg L^{-1} to mmol L^{-1}: A soil is extracted and the solution has a Pb concentration of 8.06 mg L^{-1}, its molar concentration is 0.0389 mmol L^{-1} (0.0000389 mol L^{-1}). A mol L^{-1} is molar concentration (M). The dimensional analysis for this example is:

$$8.06 \frac{\text{mg Pb}}{\text{L}} \times \frac{1 \text{ mmol Pb}}{207.2 \text{ mg Pb}} = 0.0389 \text{ mmol Pb L}^{-1} \tag{1.5}$$

$$0.0389 \frac{\text{mmol Pb}}{\text{L}} \times \frac{1 \text{ mol Pb}}{1000 \text{ mmol Pb}} = 0.0000389 \text{ mol Pb L}^{-1} \tag{1.6}$$

IUPAC recommends not including the chemical identity in the units, for example, 0.0000389 mol L^{-1} instead of 0.0000389 mol *Pb* L^{-1}, however in dimensional analysis it is convenient to include this for clarity. Lines through the *mg* units are used to illustrate the cancelation of the units in the numerator and denominator. Note that the measurement with the *least* number of significant figures is used to dictate the number of significant figures in the answer.

Chapter 1 Questions

1. Starting with a cube 1 m on a side, calculate the change in surface area by subdividing it successively into sand, silt, and clay-size particles (assume perfectly stacking cubes). How many particles would be in each size group? Assuming that the particles are aluminosilicates, calculate the surface area/mass ratios of the above cubes (specific gravity of aluminosilicates is 2.65).
2. What is the difference between chemical species, an ion, and an element?
3. Discuss how LeChatelier's principle affects soil formation factors.
4. Provide examples of all possible reactions that can occur in soils.
5. Which of the following are not considered a soil chemical: Pb^{2+}, Fe^{3+}, plant root, ferrihydrite, soil organic matter, soil microbe, $NaHCO_3$ (s), $AlOH_2^+$, CO_2 (g)?

6. How is free energy used to understand biogeochemical cycling of chemicals in soils?
7. If phosphorus availability to a plant is measured using an extraction of the soil, does the measured value represent bioaccessibility or bioavailability?
8. What factors cause elements in soils to deviate from the 1:1 line in Figure 1.5?
9. A soil is analyzed for total iron content by dissolving 0.1 g of soil in 10 mL of acid and digesting in a pressure bomb. The digest is filtered, diluted to a final volume of 100 mL, and analyzed for Fe. The total Fe in solution is 40 mg L^{-1}. What is the total iron concentration in the soil in mg kg^{-1} (ppm) and mmol kg^{-1}? Assuming all the iron occurs as the mineral ferrihydrite with a hypothetical formula of Fe(OH)$_3$, what mass percentage of the soil is iron oxide? Note: 1% = 10 000 ppm.
10. Why are total soil concentrations poor indicators of the amounts of ions that may enter the food chain?
11. By what mechanisms are ions held by soils?
12. How is soil chemistry knowledge useful to agriculturalists, environmentalists, toxicologists, public health professionals, and concerned citizens?