
INTRODUCTION

No one regards what is at his feet; we all gaze at the stars.

—Quintus Ennius (239–169 BC)

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 quotations illustrate how differently humans see the soil that gives them life and feeds them. Those opinions have been held for a long time. Most people are still at the knowledge level of Quintus Ennius who lived more than 2000 years ago. They take for granted the food that the soil produces, the clean water and air that the soil provides. Thoreau's and Cowper's wonder and fascination of soils is rarely expressed or felt. Yet the soil is wondrous if one looks closely. The soil—the solid but porous surface of the earth to about one meter depth, the depth that roots penetrate—has many mysteries. The soil is as mysterious and exciting as any other science and any other part of the universe.

Soil is a mixture of inorganic and organic solids, air, water, microorganisms, and plant roots. All these phases influence each other: Weathering and adsorption by the soil affect air and water quality, air and water weather the soil, microorganisms catalyze many of the reactions, and plant roots absorb and exude inorganic and organic substances. Soil chemistry considers all these reactions but emphasizes the reactions of the *soil solution*, the thin film of water and its solutes (dissolved substances) on the surfaces of soil particles.

1.1 THE SOIL SOLUTION

The soil solution is the interface between soil and the other three active environmental compartments—atmosphere, biosphere, and hydrosphere (Fig. 1.1). The boundaries are dashed lines to indicate that matter and energy move actively from one compartment to another; the environmental compartments are closely interactive rather than isolated. The interface between marine sediments and seawater, and between groundwater and subsoils, is chemically much the same as the interface between surface soils and the soil solution. Sediments remove and release ions from the bodies of water they contact by the same processes as the interface between the soil and the soil solution.

The soil solution is the source of mineral nutrients for all terrestrial organisms. As the soil solution percolates below the root zone, it becomes groundwater or drains to streams, lakes, and the oceans, and strongly affects their chemistry. The amounts of matter transferred are much greater and the rates of these reactions are much faster in the soil than in the other environmental compartments. The soil solution is the most important transfer medium for the chemical elements that are essential to life.

The soil solution differs from other aqueous solutions in that it is not electrically neutral and usually contains more cations than anions. The net negative charge of soil clay particles in most soils extends electrically out into the soil solution, and the charge is balanced by an excess of cations in the soil solution. These cations belong to the solid but are present in the soil solution. Soils in old and heavily weathered soils, as in parts of Australia, Africa, and South America, or in soils of volcanic origin, as in Japan and New Zealand, may have a net positive charge. There the soil solution has an excess of anions.

The interactions of ions and electrical charge at the soil particle–soil solution interface happens at all particle interfaces. In cases outside of the soil, this interaction

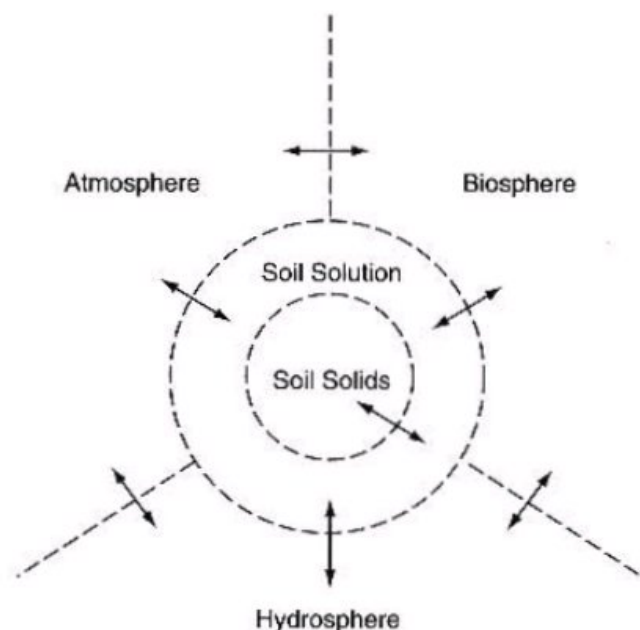


FIGURE 1.1. The soil and the soil solution are the heart of the environment.

is generally negligibly small. The soil is unique because the soil's surface area is so large that this interaction becomes so extensive. Because of this interaction, 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 to the soil solids.

The diffuse layer extends out as much as 50 nm into the aqueous solution from the particle surface. For clay (colloidal)-size ($<2 \mu\text{m}$) particles with their large surface area, this interaction is great enough to significantly affect the composition of the soil solution next to the colloidal particles. Because soils contain considerable clay, a large part of the soil solution is affected by colloids. At the so-called field capacity water content, most of the soil solution is in the $< 10 \mu\text{m}$ contacts and pores between sand (50–2000 μm) and silt (2–50 μm) particles. Clay particles and microbes congregate at these contacts so the soil solution interacts closely with these reactive bodies in these contact zones. The soil solution on open sand and silt surfaces is only 10–100 nm thick, so much of this water is also affected by the particle's charge. The portion of soil solution affected by soil colloids increases as the soil dries.

Most soil reactions occur at the soil solution/soil interface. Ions in water can move and react fast enough to measure easily. Slower but still measurable reactions occur in the weathered surfaces of soil particles. These poorly understood surfaces contain considerable water. Reaction rates in the truly solid phase at soil temperatures, however, are too slow to be measured in our lifetimes.

Because the mass and reactivity of soils are great, the chemistry of the atmosphere and fresh water are largely controlled by the chemistry of the soil solution. Reactions that require days and years in air, and hours in water, require only seconds and minutes in soils. The compositions of the air, water, and biomass compartments in the environment evolved from, and still respond to, the chemistry of the soil. The soil came first and as it changed, it changed the others. The change in the others also changed the soil, but to a lesser extent because of the soil's mass.

The soil solution contains a wide variety of solutes, including probably every element in the periodic table. This book discusses those solutes that are active in the environment—the solutes that affect plant and animal life, or have been of concern in pollution.

Figure 2.1 shows the chemical elements that are essential to living organisms, those that are reactive, and those that are in significant amounts in each environmental compartment. Chapter 2 discusses the life-essential and other important elements in more detail. All of the major and minor essential elements are stored and available for transfer in soils; the amounts in the other compartments, although important, are generally much, much smaller. Major and minor refer only to the amounts needed by organisms; all are essential and all are needed in their proper amounts. Too little is deficiency, too much is toxicity. The essential elements are also called essential nutrients, but elements is a better term because nutrients implies energy content, such as in the carbohydrates and fats of food.

With few exceptions, the soil supplies these elements to living organisms in about the right amounts. Although not perfect, the soil's supplying power is remarkably effective. This is not simply a happy coincidence; life evolved in response to the availability of these elements in soils.

For most people the major reason to study soil chemistry is to insure and to increase production of food and fiber crops. The soil is and will be the main source of human nutrition. The oceans supplement our food supply but their productivity is limited by the osmotic potential of the water, the limited availability of essential elements, the low temperature of ocean water, and the long food chain between photosynthetic organisms and those large enough to harvest. The oceans can provide only a small amount of society's needs and wants. The soil's productivity per unit area is many times that of the oceans. Terrestrial plants remain the cheapest and best means of converting solar energy into life support for this planet. The growth of plants on soils is the basis of most of the world's economy and of a nation's well being.

Soil chemistry is only one of many factors that affect plant growth. In contrast to climate and other uncontrollable factors, however, agriculturalists can influence and modify soil chemistry to considerable extent. The amounts of essential elements needed by plants over a season are small enough that supplementing the soil supply is feasible. Increasing the efficiency of that fertilization is a continuing soil chemistry challenge. The toxicity of materials that harm plant growth can also be controlled by soil chemistry.

People are now learning to appreciate the soil's large role in the biogeochemical cycling of the elements. Soils can mitigate many undesirable human-caused changes (pollution) of the environment. Safe removal of wastes from the environment has been recognized to be as important for continued civilization as food production. The retention, exchange, oxidation, and precipitation of waste in soils make them unequaled as recycling media.

In earlier times when the population was less dense and industries were few and small, wastes were distributed widely on and in the soil and could readily return to their natural biogeochemical cycles. By concentrating wastes in urban areas, industrial facilities, landfills, feedlots, and sewer outfalls—releasing wastes to the air and water rather than allowing them to react in soils—by fertilization, and by creating synthetic chemicals that react slowly, humanity has occasionally and in local areas exceeded the rate at which these materials can return to their biogeochemical cycles. "Advanced" societies sometimes overlook the degradative functions of soil and look instead for expensive, and only partially satisfactory, technological methods of waste disposal. Humanity creates pollution, which has awakened a new awareness of the importance of soil chemistry.

Soil chemistry is closely related to colloid (surface) chemistry, geochemistry, soil fertility, soil mineralogy, and soil microbiology or biochemistry. Soil fertility considers soil as a medium for plant growth. Soil mineralogy examines the structural chemistry of the solid phase. Soil microbiology studies soil biochemical reactions. Such subdivision is necessary to study the soil thoroughly, but these subdivisions sometimes obscure the interaction between soil components, and this interaction is often as important as the properties of the components alone.

Soil chemistry traditionally has had two branches: inorganic and organic, but strict separation of the two fields is difficult and pointless in many cases. The direction of biochemical soil reactions is largely based on the inorganic phase. Soil organic

processes affect primarily the rate of soil chemical reactions. Biochemical reactions are carried out by soil microorganisms, whose vast numbers in soils influence many reactions. For several elements, notably carbon, nitrogen, and sulfur, the microbial role almost totally determines soil reaction rates. Biochemical and microbial reactions are primarily catalytic processes affected by the independent variables of soil mineral composition, climate, gas exchange with the atmosphere, and energy from photosynthesis. Despite the importance of biochemical reactions, research in soil chemistry historically has been more oriented toward inorganic processes.

1.2 BACKGROUND

Food and fiber production were already important before agriculture began. After fear, food is the dominant concern of every animal. 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 and that food production was increasing arithmetically. He predicted that by 1850 the demand for food due to population growth would overtake food production, and people would be starving and fighting like rats for morsels of food. Similar apocalyptic predictions continue to crop up and cannot be disregarded. It is encouraging, however, that productivity has increased since the Greek senate debates and faster than Malthus predicted. In recent history food productivity has been increasing faster than ever. 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 and other organisms is an open question. One encouraging part of the answer is the rapidly declining human birth rate on most continents in recent decades, thus putting less stress on the soil's resources in the future. Another part of the answer lies in soil chemistry, and much progress is still to be made in our understanding of the soil and its potential.

Agricultural practices that increase crop growth—planting legumes, manuring with animal dung and with litter from forests, rotating crops, and liming—were known to the Chinese 3000 years ago. These practices had also been learned by the Greeks and Romans and appeared in the writings of Varro, Cato, Columella, and Pliny. The reasons for their effectiveness, however, were unknown. Little or no further progress was made in the Western world for almost 1500 years because of ignorance and *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 accepted truth, derived from the Greeks, was that 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 pointed that *inductive reasoning*, the *scientific method*, is a much more productive approach to gaining new knowledge—

observe and measure, derive broader ideas from the data, and test these ideas again. The scientific method brought progress, but the progress in soil chemistry was slow.

Palissy (1563) thought that plant ash came from the soil and when added back to the soil could be reabsorbed by plants. Plat (1590) thought that salts from decomposing organic matter dissolved in water and absorbed by plants were responsible for plant 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.” Others have found this idea in Pliny’s writings. None of them, however, had experimental proof.

Van Helmont (1592) tried to test these ideas. 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 “200 lb (90.8 kg) 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 and that plants needed only water for their sustenance. Although he followed Bacon’s suggestions and the scientific method as well as he could, he unfortunately came to a wrong conclusion. Many experiments in nature still go afoul because of incomplete control and measurement of all the experimental variables.

John Woodruff’s (1699) experimental design was much better. He grew plants in rainwater, river water, sewage water, and in sewage water plus garden mould. 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, but without further testing, that the organic fraction of the soil supplied the plant’s needs. That idea persists to this day. Organic substances absorbed by plants from the soil may affect plant growth, but this has been difficult to prove.

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 when Boussingault (1865) measured more nitrogen appearing in plants than he put into the soil, his work 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, discovered cation exchange. Their work suggested that soils could be studied apart from plants; yet the results would still have implications for soil fertility.

The Information Age is upon us and the information is both accurate and inaccurate. From the information available about nutrition and health, for example, one might deduce that life is becoming riskier. In reality we are living longer and healthier lives than ever before. To make sense of what we hear and read, we sometimes still resort to deductive reasoning. Science no longer has the certainty that it once seemed to have and can be very complicated. People look for answers and ideas

they can understand. Many current ideas about health, nutrition, and organic farming and gardening, for example, are popular not because they have been tested, but because their simplicity is easily understandable and because not-always-sound logic makes them look good. Although science cannot provide all the answers, our lives are healthier and longer because we have broken away from deductive reasoning. The spurious logic, oversimplification, and rejection of careful testing that can be part of deductive reasoning are steps backward rather than forward.

1.3 SOIL-ION INTERACTIONS

Solutes, electrolytes, and nonelectrolytes in the soil solution are the immediate sources of the elements required by plants for growth. This supply can be continuously renewed by the many mechanisms of ion-soil interaction that remove and add ions in the soil solution: (1) mineral weathering, (2) organic matter decay, (3) rain, (4) irrigation waters containing salts, (5) fertilization, and (6) release of ions retained by the colloid or clay fraction of soils.

Solutes in the soil solution and ions retained on soil particle surfaces are generally the largest fraction of the elements available to plants. Weathering of ions from soil particles is slow compared to plant needs. Organic decay releases ions much faster than weathering, but most of the ions released react with the soil's solid phase before they can be absorbed by plants or microorganisms. When retaining ions, soils strike a delicate balance between preventing losses by leaching and supplying plants and microorganisms. Ion retention by soils does not completely prevent leaching losses but is sufficiently strong that ions can recycle many times through soils, plants, and animals before they are finally lost to groundwaters, rivers, and the sea.

Ions and molecules are retained in soils by cation and anion exchange, precipitation, weak electrostatic attraction, reactions with soil organic matter (SOM), and retention within microbial cells. If each ion were retained by only one such mechanism and by only one soil component, soil chemistry would be relatively simple. Instead, each ion reacts by several mechanisms, and to varying degrees, with many different solid phases. For simplification, soil chemists generally either measure a single parameter that reflects most soil interactions with a given ion (e.g., its overall availability to plants), or fractionate the soil and measure the ion's interactions with each soil component separately. Neither approach has proved totally satisfactory. Single-parameter measurements fail to account for variations from one soil to the next. Fractionation procedures may neglect the important interactions between soil components.

1.4 COLLOIDS AND THE SOIL SOLUTION

The complexity of ion interactions with the soil's solid phase is greatly increased by the colloidal properties of the soil's clay and organic fractions. *Colloids* are substances of about 1- to 1000-nm particle size that form unique mixtures when sus-

pended in air or water. The components in colloidal mixtures tend to lose their individual identities so that the mixtures are like new substances. Colloidal mixtures are so ubiquitous and so distinctive that they have their own names: fog, smoke, smog, aerosol, foam, emulsion, gel, soil, and clay. All are small particles suspended in a liquid or gaseous fluid. Other colloidal mixtures include metal alloys, pearls, butter, and fine-grained rocks. The particles do not settle out of the suspending fluids, but also do not mix homogeneously with them. The physical properties of many colloidal mixtures tend to be similar regardless of the chemical composition of the colloid, because the size and the interaction are so important. Colloidal suspensions of starch, soap, salad dressing, and clay in water, for example, look the same, are similarly viscous, similarly colored, opaque, and stable (do not separate into separate phases).

Solutions are also mixtures but, in contrast to colloidal mixtures, solutions retain many properties of the major component—the solvent—while the minor component—the solute—loses its identity. Salts disappear when they dissolve in water. Aqueous solutions containing the same amounts of matter are as fluid and transparent as water. A mixture of 5% Na bentonite in water is a thick white gel; a solution of 5% NaCl is quite fluid and is transparent. When particles larger than ca. $2\ \mu\text{m}$ are suspended in air or water, they settle out of suspension into separate phases. The properties of such mixtures are the sum of the properties of the separate components.

Colloidal particles interact strongly with the fluid, but the individual particles have some structural integrity, so they cannot be said to dissolve homogeneously. The colloidal mixture behaves so distinctively because of the large surface area of interaction between the particles and water or air. The ions at the boundary interact with the ions and molecules of both phases. This is true at any surface or phase boundary, but the interaction of colloidal phases is large because their surface areas are so large. A 1-mm sand particle has a surface area/mass ratio of about $0.002\ \text{m}^2\text{g}^{-1}$; a $1\text{-}\mu\text{m}$ clay particle, $2\ \text{m}^2\text{g}^{-1}$; and a 1-nm particle, $2000\ \text{m}^2\text{g}^{-1}$.

The important colloidal properties that clays impart to soils include ion and molecular retention and exchange and water and gas adsorption. The colloidal properties of clay create the intimate mixture of solids, liquids, and gases in the soil that is essential to life.

1.5 COMPOSITIONS OF SOILS AND PLANTS

Except for carbon as CO_2 , H as H_2O , and oxygen as O_2 , plants derive their essential elements from the soil. The minor exceptions are nitrogen and sulfur gases (NO_x , NH_3 , and SO_2) absorbed directly from the atmosphere by leaves, plus ions absorbed from dust and foliar sprays on the leaves. Foliar absorption can be significant in polluted atmospheres or where agricultural sprays are purposely applied. Under natural conditions, the major factors affecting ion availability to plants are (1) the ion's concentration in the soil solution; (2) the degree of ion interaction with, and rate of release from, the soil's solid phases; (3) the activity of soil microorganisms; and (4) discrimination by the plant root during ion uptake. This book is concerned pri-

marily with the first two factors: the soil solution and ion interaction with the solid phase.

Table 1.1 shows representative contents of important elements in soils. Soil contents vary and the values in Table 1.1 are averages. The composition of plants is less variable, partly because soil development tends to narrow the range of element availability compared to the range of the elemental composition of rocks. The soil is an O–Si–Al–Fe matrix containing relatively small amounts of the essential elements. The matrix is virtually inert in terms of plant nutrition, but the small amounts of ions held by that matrix are vital.

Table 1.1. Typical concentrations of essential elements in soils, ratios of plant ash to soil content, annual plant uptake, and the ratios of soil content (to 1-meter depth) compared to annual plant uptake

Element	Soil Content (Weight%)	Plant Ash Content/Soil Content	Annual Plant Uptake (kg ha ⁻¹ yr ⁻¹)	Soil Content/ Annual Plant Uptake (yrs)
Oxygen	49	—	—	—
Hydrogen	—	—	—	—
Silicon	33	0.3	20	21 000
Aluminum	7	0.03	0.5	180 000
Iron	4	0.1	0.4	100 000
Carbon	1	—	—	—
Calcium	1	25	50	260
Potassium	1	15	30	430
Sodium	0.7	1	2	4 600
Magnesium	0.6	3	4	2 000
Titanium	0.5	0.08	0.08	62 000
Nitrogen	0.1	15	30	40
Phosphorus	0.08	4	7	150
Manganese	0.08	0.6	0.4	3 000
Sulfur	0.05	70	2	320
Fluorine	0.02	1	0.01	26 000
Chlorine	0.01	10	0.06	200
Zinc	0.005	5	0.3	2 000
Copper	0.002	5	0.1	1 000
Boron	0.001	50	0.003	400
Tin	0.001	2	0.001	~ 10 000
Iodine	0.0005	0.1	0.00003	22 000
Molybdenum	0.0003	~ 2	0.003	1 000
Cobalt	0.0008	1	0.0006	17 000
Selenium	0.000001	~ 500	0.003	40

From Vinogradov's data in N. F. Ermolenko, 1972. *Trace Elements and Colloids in Soils*. Israel Program for Scientific Translations, Jerusalem.

Column 2 of Table 1.1 shows the ratio of plant content to soil content of important ions. The hydrogen, carbon, and oxygen ratios are omitted because these ions are not derived directly from soils. The ratios are crude indices of the relative availability of soil components to plants. Calcium, sulfur, nitrogen, and potassium in soils are more available than iron and manganese. One goal of soil chemistry is to explain why ions in soils vary widely in their degree of plant availability.

Column 3 shows the approximate annual plant uptake per hectare (ha) of the elements, assuming an annual dry matter production of 10 000 kg ha⁻¹. The amounts of calcium, potassium, and nitrogen absorbed greatly exceed plant absorption of the other elements.

Column 5 is the annual plant uptake of the elements divided by their total amounts in the soil. The result is the length of time the soil could supply that element to plants, if the plants were totally removed at harvest and nothing were added to the soil. The weakness of this assumption is that only a small fraction of plant matter is removed from soils during harvesting; most of the plant dies and decays where it grew. The assumption also ignores atmospheric and fertilizer inputs. Nonetheless, the ratios in column 5 roughly illustrate the relative size of the soil's store of essential elements. The soil's reserves of nitrogen, chlorine, and sulfur are low but are continually replenished by microbial nitrogen fixation, gas absorption, and rain. Despite this replenishment, nitrogen and sulfur concentrations are often less than optimal for plant growth. Nitrogen is the element that most commonly limits crop productivity. The low selenium ratio may be questionable because of limited data. The soil's supplies of potassium and calcium are also relatively low but are not cause for alarm. Calcium and potassium are constantly replenished by weathering of lower soil horizons and by decay of plant material, and they are easily replenished by liming or fertilization. The soil/plant conditions indicated in column 5 have existed for several thousand million years and are unlikely to change very much in the near future.

The data in Table 1.1 are illustrative rather than quantitative. Soil has supplied the essential elements to living organisms since terrestrial life began. The Exhaustion Plot at Rothamsted Experiment Station in England, for example, has operated continuously since 1845 and has shown that the worst agricultural practice—removing all plant material at harvest from the soil each year and no fertilization to make up the losses—reduces but does not stop plant growth or crop yields.

1.6 NONAGRICULTURAL SOIL CHEMISTRY

Soil chemistry is also important to the nonagricultural uses of soil. Soil is a building material for earthfill dams and roads and is being rediscovered in industrial nations as a building material for homes. Brick and cement are, after all, only baked soil material. Lesser-developed nations have always recognized the livability of mud huts and adobe houses. The physical stability of soil structures depends in part on their soil chemical status. The longevity of mud and wattle construction in medieval European homes and of the adobe buildings of Southwestern Native Americans depends on high calcium and low salt concentrations of the soils used to build those walls.

The persistence through many centuries of the temples at Angkor Wat in Southeast Asia depends on the high concentrations of iron and aluminium oxides in the soils used to form the building blocks. Such *laterite* (now more properly called *plinthite*) materials from soil can dry irreversibly and thus resist slaking and weathering even in a humid tropical climate.

The use of clay suspensions as drilling muds for lubrication and for clay liners for sealing landfills and lakes depends on the ability of Na^+ on colloidal surfaces to keep the clay from settling out and aggregating. The strong interaction of clay colloids and water is also useful in overcoming diarrhea, as a diluent for drugs, and as a drying agent.

Many iron and aluminium ore deposits are the end result of long and extreme soil chemical weathering at the end of the plinthite stage. The time scale puts their formation into the category of geochemistry, but the mode of formation involves the same chemical reactions as soil formation.

At the opposite end of the reaction time scale, soil clays are being investigated as catalysts to speed industrial chemical reactions. The “cracking” of petroleum into gasoline and other organic reactions is catalyzed by certain clays. Adsorption to clay surfaces imparts catalysis by holding reactive molecules in positions that encourage reaction and polymerization of organic chemicals. The Cu^{2+} , Al^{3+} , $\text{N}(\text{CH}_3)_4^+$, and rhenium phosphine and rhenium phospho-organic complex ions adsorbed on clays have such catalytic properties. The large surface area of the clays produces such an intimate reactant–catalyst mixture as to be almost a homogeneous single phase. At the end of the reaction, the clay catalyst is easily removed by filtration.

1.7 BIOGEOCHEMICAL CYCLES AND POLLUTION

The soil is a major part of the cycling of elements at the earth’s surface. The elements that humans release as wastes are derived from the soil and the earth. Ions that are weathered at the earth’s surface and released to the atmosphere or leached to the seas eventually circulate back to the land. They return to soils as gases absorbed from the atmosphere, as wastes removed from waste water, as solids buried in soils, as solutes in rain, as uplifted marine sediments, and as igneous rock uplifted to the land surface. Carbon, nitrogen, and sulfur cycle rapidly among the atmosphere, oceans, and soils. Other elements cycle more slowly between rocks, soils, and oceans but their movement is still rapid on a geologic time scale. The removal rate of elements from soils is slowed significantly by adsorption, precipitation, pH buffering, and plant uptake.

Chemical pollution is the diversion of chemical elements from the natural biogeochemical cycles. The carbon, nitrogen, and phosphate in municipal wastes released to streams and lakes are removed from the soil–plant cycle, which is the source of the nitrogen and much of the phosphate. If those substances were instead put back directly into the soils from whence they came, much less pollution would result. Air and water only slowly convert their wastes back into their natural sites in plants and soils. Soil, on the other hand, has enormous surface area and microbial catalytic activity plus oxygen and water with which to deactivate pollutants. Soil degrades most

wastes quickly and returns the components to their natural cycles, thereby minimizing environmental disturbance.

If one considers pollution to be the rendering of soils to be unfit for plant growth, then the greatest contribution to pollution is the salinization and urbanization of soils. Careless irrigation slowly adds increasing amounts of salts to soil, which can reduce and stop plant growth. Covering soils with asphalt and concrete also renders soil unfit for plant production.

Human consumption of food, water, wood, metals, and fuel diverts substances from their natural cycles, if one assumes that humans are unnatural. Humans are trying to take care of themselves, just as other species do. The difference is that we concentrate wastes on a much larger scale and are better at using water and wind to carry them away. Humans, however, presumably have the capacity to analyze and improve their activities. This is hopeful and seems superior to ants, for example, which denude their environment and leave behind a totally barren land before moving to a new location. Even the worst of too-frequent shifting cultivation, monoculture cropping, clearcutting of forests, industrial pollution, and suburban sprawl are no worse than what ants do, and we have the ability to change and improve the situation.

Consumption is the transformation of matter and energy into less useful forms, including dilution to concentrations less than those recoverable by our current technology. Fertilizers, for example, are made from concentrated sources and diluted by spreading on agricultural lands. Over the short term, only a fraction is recovered by plants. The remainder is consumed by the soil when the fertilizer is converted into slowly recoverable or nonrecoverable forms. Not one atom is lost by this consumption, but the availability, chemical states, concentrations, and locations of the atoms change.

Consumption of water includes discarding wastewater to the sea, where marine salts contaminate the water. It is usually much easier and cheaper to remove the small amounts of pollutants in wastewater than to remove the large amount of salt added to the water when it is dumped into the sea. Artificial desalination of seawater is costly because of the energy required. Water is recovered naturally from the sea by solar evaporation. The resulting rain is unevenly distributed over the land so one-time use of water, in arid regions particularly, seems very wasteful. Water can often be used consecutively in the home, industry, and agriculture, thus decreasing water consumption. Wastewater spread on land can be agriculturally beneficial and simultaneously renovated for reuse.

1.8 SOIL AND THE HYDROSPHERE

The amount of water in soils is only a tiny fraction of the earth's total water supply. Table 1.2 shows two estimates of the distribution of water at the earth's surface. The two estimates differ widely but agree that the fraction present as soil moisture is small, 0.001 to 0.0005%. Either of these fractions of soil water seems perilously small to supply all terrestrial life and to help moderate climate. The periodic droughts around the world also emphasize that the amount of soil moisture is small. Assuming

Table 1.2. Two estimates of the distribution of the earth's water

Ocean Water	80% ^a	97% ^b
Ice	19	—
Groundwater	—	0.06
Pore water in rocks	1	2
Lakes and rivers	0.002	—
Fresh	—	0.007
Saline	—	0.007
Soil moisture	0.001	0.0005
	(2×10^{16} kg)	(7×10^{16} kg)
Atmospheric water	0.0006	0.0001
Biota	—	0.0001
Total	1.7×10^{21} kg	1.35×10^{21} kg

^aFrom R. M. Garrels, F. T. Mackenzie, and C. Hunt. 1975. *Chemical Cycles and the Global Environment*. W. Kaugman, Los Altos, CA.

^bFrom D. A. Speidel and A. F. Agnew. 1982. *The Natural Geochemistry of Our Environment*. Westview, Boulder, CO.

that the world's soils contain 10% water by volume, the 1.2×10^{14} m² of terrestrial soils contain 1.2×10^{13} m³ of water to a meter depth. This imposing amount is the water that supports plants, weathers rocks, forms soil, and is the medium in which most soil chemical reactions occur.

Terrestrial water receives most of its dissolved solutes from the soil, where rain first reaches the earth's surface and where weathering is strongest. The composition of water is less affected when it percolates to greater depths because the water already contains the salts obtained from the soil above. The composition and concentration of dissolved solutes can change at depths if the water contacts subsurface CaCO₃ or if it is stored for long periods in underground basins. In most cases, however, percolating waters retain the character of solute composition initially conferred on them by the surface soil.

Stream water is soil drainage plus surface runoff. Natural drainage waters contain relatively low concentrations of the essential ions. This slow and steady input from drainage waters supports what is generally regarded as a natural and desirable aquatic population in streams and lakes.

Runoff water is richer in sediments, nutrients, and organic matter. The fraction of surface runoff in temperate and humid regions is relatively small compared to drainage water under natural conditions. Dense plant cover prevents erosion and the soils are relatively permeable. Agriculture can increase the nitrate and phosphate concentrations, in runoff particularly, by removing the natural plant cover. Proper management can minimize runoff from agricultural lands, but some changes in water composition due to agriculture may be inevitable. Urbanization also increases runoff. The velocity of runoff increases as the overall permeability of the land surface is decreased, and runoff increased, by paving, compaction and destruction of natural contours.

In arid regions, surface runoff is a considerable fraction of the stream flow. The intense storms, sparse plant cover, and relatively low soil permeability create intermittent streams "too thick to drink and too thin to plow." The invisible solute concentration in such waters is also high and can be as important to the downstream ecology as the sediment.

1.9 SOIL AND THE ATMOSPHERE

The interaction of gases with soils is much less obvious than soil-water interaction, but is important to maintaining the low amounts of carbon, nitrogen and sulfur gases in the atmosphere. Gases that are foreign to the atmosphere are adsorbed by soils and plants and degraded to the natural and nongaseous forms of these elements. Soils also release gases, such as H_2O and CO_2 from organic decay and N_2 and N_2O from natural soil nitrogen compounds and from fertilizers. Soil has affected environmental chemistry since the earth began, and the soil in turn has been affected by other components of the environment.

Soil is a prominent part of the natural cycles of carbon, nitrogen, and sulfur. In the nitrogen cycle, nitrate and ammonium ions in rainwater are absorbed by soil, plant roots, and soil microorganisms and converted to amino acids or to gaseous N_2 and N_2O , which diffuse back to the atmosphere. Ammonia is also emitted and absorbed by soils. Under natural conditions the gaseous nitrogen loss is approximately balanced by N_2 uptake and conversion to amino acids by symbiotic and free-living soil microorganisms.

Soil absorbs sulfur dioxide, hydrogen sulfide, hydrocarbon, carbon monoxide, nitrogen oxide, and ozone gases from the air. The reactions are subtle and are often forgotten in considerations of the composition of the atmosphere. Direct soil absorption is perhaps most obvious in the case of the rapid disappearance of atmospheric sulfur dioxide in arid regions. The basicity of arid soils makes them an active sink for acidic compounds from the atmosphere. The relative 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.

The soil's role in the carbon cycle is very large. Table 1.2 shows the estimated amounts in the active carbon reservoirs at the earth's surface: the atmosphere, living biomass, freshwater, and ocean water above the thermocline (a temperature inversion that isolates the surface 50 m from the deeper ocean). The amount of soil carbon far exceeds the others. The emission of CO_2 by organic decay in soils is the largest CO_2 input to the atmosphere. The change in amount of organic soil carbon resulting from climate changes must have affected atmospheric CO_2 concentration. Varying organic decay rates in soils due to climate and atmospheric CO_2 changes have not been considered adequately in most discussions of the carbon cycle. A slower decay rate would have the same net effect on atmospheric CO_2 that direct soil absorption of CO_2 from the atmosphere would have. *Peat* (organic-rich soil) has been accumulating in Canada and elsewhere since the glaciers retreated at an average rate of about 1

mm yr⁻¹. Virgin soils, when cleared and cultivated, on the other hand, lose one-third to one-half of their original organic carbon content by oxidation to CO₂. This amount of CO₂ production over the last 100 years equals or exceeds the highly publicized amount released by fossil fuel combustion.

Great changes in soil organic carbon levels have occurred during geologic time. The enormous carbon accumulation by soils during the Carboniferous Era must have affected the CO₂ content of the atmosphere greatly. Carbonate accumulation and loss in soils is probably a smaller buffer of atmospheric CO₂ than is organic soil carbon. The mass of soil carbon as carbonate is less, and its turnover rate is slower.

The atmosphere, in turn, affects soil development by providing oxygen and by wind erosion and deposition. Sand dunes are only the most obvious example. Loess soils are deposits of silt-sized particles carried by winds from riverbeds and glacial outwash. A large fraction of the clay content of the soils along the eastern shores of the Mediterranean Sea has been carried by winds several thousand kilometers from the Sahara Desert and Atlas Mountains of North Africa. Trade winds carry Saharan clay particles several thousand kilometers out into the Atlantic Ocean.

1.10 SOILS AND THE DEVELOPMENT OF LIFE

Soils have had a large role in the development of life and probably in the origin of life. Plants obviously have adapted to the physical and chemical characteristics of soils. These characteristics could also have aided the first steps of chemical organization that preceded life.

The earth's early atmosphere was rich in CH₄, H₂, CO₂, CO, NH₃, N₂, and H₂S, and contained no O₂. In the late 1940s Miller and Urey showed that lightning discharges in such a gas mixture could produce small amino acid-like and other organic molecules that could be the organic precursors needed for life. The next question is how do these molecules polymerize to larger molecules?

In the late 1920s a Soviet scientist noticed that hydrophobic substances in seawater cluster together, like the tar balls familiar to beachgoers. He suggested that this could have been a step in the organization of simple organic molecules into the more complex ones of living organisms. One problem with this hypothesis is that the molecules formed in lightning discharge are hydrophilic. They dissolve in water and disperse in the oceans rather than accumulate as do hydrophobic hydrocarbon globules.

In the 1930s the British biologist Haldane, inspired by this idea and rather ignorant of soils, thought that the initial polymerization of small molecules might have happened in an organic-rich ocean, which he called the "primordial (pre-life) soup." This phrase caught the public's attention even though the source of the simple organic molecules was then unknown. To make even a thin 1% soup in the approximately 1.4×10^{21} kg of ocean water requires about 1×10^{19} kg of organic carbon compounds. The total amount of organic carbon on earth is estimated to be 8×10^{18} kg, but these estimates were unavailable in Haldane's time. All of the carbon existing as methane and carbon dioxide in the atmosphere would have had to combine into small

organic molecules to create this primordial soup. The oceans would disperse these organic molecules rather than concentrate and orient them into structural polymers.

Bernal pointed out soon after that the adsorption by clays in soils and sediments would be important to concentrate and polymerize simple molecules. Although water neither concentrates nor catalyzes polymerization, his ideas were incorporated into the marine origin of life by marine workers' suggestions that the polymerization occurred in drying tidal pools. The drying also concentrates NaCl, which is inimicable to life. The marine biologists were eager to attribute as much importance to their discipline as possible. Evolution is opportunistic and would take advantage of the best chemical and physical conditions available for retaining, accumulating, and polymerizing organic compounds. These conditions are much more better realized in soils than in ocean water.

Clay particles formed before life began, so primordial soils had essentially the same chemical and physical characteristics as today's soils. Clays could adsorb and concentrate simple organic molecules as they fell in rain, or adsorb them directly from the atmosphere. Amino acids, for example, have been shown to polymerize when adsorbed on clay surfaces; benzene and phenol polymerize spontaneously on Fe(III)- and Cu(II)-coated clays. Whether such reactions actually led to the origin of life is speculation, but these reactions are much more likely in soils than in tidal pools.

In addition to concentrating organic molecules and catalyzing their polymerization, soils have several other properties that might be important in the origin and development of life: (1) protection of organic molecules from breakdown by ultraviolet light; (2) periodic drought, which encourages organic condensation (reactions that form water); (3) the relatively constant chemical composition of soil surfaces and the soil solution, much more so than that of the parent rocks; (4) higher availability of phosphate and microelements than in water; (5) the much lower osmotic potential of soil solution than marine water; and (6) a cation-rich solution. Living organisms produce mostly organic anions, which require cations for balancing and a great amount and variety of cations than anions. These factors suggest that life could have begun more easily in the soil than in the oceans.

Furthermore, the order of cation composition in plants and animals is $\text{Ca} > \text{K} > \text{Na} = \text{Mg}$ and is close to the order of availability in soils, $\text{Ca} > \text{Mg} > \text{K} = \text{Na}$. The order in living organisms is quite different from the composition of seawater, $\text{Na} > \text{Mg} > \text{Ca} = \text{K}$. The amounts of solutes in body fluids of plants and animals is also closer to that of soil solutions than of seawater. The osmotic potential of body fluids is lower than that of seawater. Terrestrial plants and animals therefore die by ingesting seawater; marine plants and animals survive by excluding NaCl at a considerable expense of energy. As a result, life is more active in and on terrestrial soils than in the sea. Indeed, the open sea is barren.

The concept of life originating in marine or tidal pools nonetheless persists and is supported by the rather complete fossil record in marine sediments. The fossil record on land is erratic, but this should be expected because of the rapid turnover of land surfaces compared to marine sediments. Soils have eroded, weathered, and dissolved into soluble salts into the sea many times since life began. A complete fossil record

under these circumstances would be highly unlikely. Much of the ocean bottom has remained intact, so fossils can accumulate readily and sequentially.

1.11 THE ROLE OF SOIL IN THE ENVIRONMENT AND THE MAINTENANCE OF LIFE

The role of soil in the origins of life is controversial. Its role in maintaining life and the environment is clear, but often unrecognized and taken for granted. Soil scientists are partly responsible because they have been too modest and too reticent about soil's control of the atmosphere and hydrosphere. The atmosphere, biosphere, and hydrosphere are weakly buffered against change and can fluctuate wildly when perturbed. Soils strongly resist chemical change and are a steadying influence on the other three environmental compartments. Changes in the hydrosphere, atmosphere, and biosphere due to human activities are often the result of bypassing the soil. The soil is the most robust environmental compartment. Treating solid, liquid, and gaseous wastes in soils before release to the hydrosphere or atmosphere can minimize environmental change. The soil is the source of most human wastes and ought to be site of their disposal.

The environment is large and very complex, too complex for anyone yet to understand fully. Scientific training necessarily tends to specialize—learning more and more about less and less. Scientists try to expand that myopic background to the whole environment, with mixed results. Among other things, they bring along biases, of which one is usually 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 (Fig. 1.1).

Table 1.3 shows which of the four environmental compartments store significant amounts of the essential elements. Table 1.4 shows the estimated quantities of the elements that circulate rapidly through the environment—C, fixed N, P, S, and water. The amounts shown for the oceans are those above the thermocline, a temperature inversion at about 50 m depth, which separates the surface water from the deeper water. The soil is the largest reservoir of almost all the essential elements and is the only reservoir for most of the essential elements.

The general chemical and related physical properties of the four active environmental compartments are summarized as follows:

Atmosphere. Poorly buffered against chemical changes; high amounts of readily available C as CO₂; high O₂; H₂O variable; otherwise chemically uniform worldwide; entrained dust is the only reactive surface; high mass transfer rates.

Biosphere. High C, N, and P concentrations; energy rich; high energy and mass transfer rates; high reactivity; ratio of biomass/soil is variable and climate dependent; complex and highly ordered structures.

Table 1.3. Distribution of carbon, nitrogen, sulfur, and oxygen at the earth's surface

Reservoir	Carbon ($\times 10^{12}$ kg)	Nitrogen ($\times 10^{12}$ kg)	Sulfur ($\times 10^{12}$ kg)	Oxygen ($\times 10^{12}$ kg)
Atmosphere	700 (CO ₂)	3 800 000 (N ₂)	4	1 000 000 (O ₂)
Surface ocean (above the thermocline at 50-m depth)	800	1 (organic)	0.1 (organic)	10 000 000 (H ₂ O)
Living biomass	500	14 (organic)	2 (organic)	500 (carbohydrate)
Soils, to 1-m depth	1 800 (organic)	180 (organic)	20 (organic)	20 000 (soil water)

Table 1.4. Estimated annual gains and losses from soils worldwide. ^a(rates before human influence, if significantly different, are in parentheses)

Process	Carbon (Tg yr ⁻¹)	Nitrogen (Tg yr ⁻¹)	Sulfur (Tg yr ⁻¹)
Soil organic matter decay	-35 000	—	—
Cultivation of virgin soils	-1000 to -2000	-100 to -200(0)	-10 to -20(0)
Peat accumulation	200	—	—
Soil nitrogen fixation	—	200	—
Atmospheric N ₂ fixation	—	4	—
NO _x (mostly N ₂ O), net	—	-8 to -25	—
Ammonia, net	—	-20 to -60	—
Nitrogen fertilization (1970)	—	30(0)	—
Sulfur emission from flooded soils, net	—	—	-3
Soluble or eroded to the sea	100 to 200	-0 to -20	-60
Sea spray and solutes	100 to 200	20 to 20	20
Weathering	—	—	40

^aLargely from B. H. Svensson and R. Soderlung, eds. 1976. *Nitrogen, Phosphorus and Sulphur—Global Cycles*. SCOPE Report 7, NFR, Stockholm.

^bFor comparison, the carbon released by fossil fuel combustion in 1975 was 3000 Tg yr⁻¹.

^cThe sulfur released by fossil fuel combustion in 1975 was 130 Tg yr⁻¹.

Hydrosphere. Poorly buffered against chemical changes; moderate O₂ availability; low water availability because of high osmotic potential of seawater; low ratios of biomass/unit area and photosynthesis/unit area (because of little light below the surface); low temperatures; low essential elements (especially P and Fe); high NaCl.

Soil. Chemically stable; strong buffering of elemental availability; variable H₂O availability; soil solution is cation-rich; active microbial and inorganic catalysis; source and sink of all the elements essential to living organisms; high P but low availability; ratios of biomass/unit area and photosynthesis/unit area vary widely; photosynthesis is seasonal; high mass and energy transfer rates.

1.12 CHEMICAL UNITS

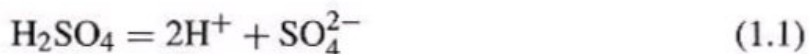
The number of atoms, not their mass or volume, determines the extent of a chemical reaction. The unit of numbers is the *mole*, Avogadro's number (6.02×10^{23}) of molecules, ions, electrons, and so on. The *atomic weight* and *molecular weight* are the mass in grams (g) of 1 mole of that substance. For example, one mole of H₂ has a mass of 2 g and contains 6.02×10^{23} H₂ molecules and 12.04×10^{23} hydrogen atoms. Ions have the same mass as their atoms, because the mass of electrons is insignificant. The numbers of moles of reactants and products can change during a chemical reaction, but the number of ions and the mass remain constant.

The *atomic weight* of a chemical element is usually not a whole number, because it is the weighted average of the natural isotopes of the elements. Hydrogen, for example, has three isotopes: normal hydrogen (${}^1_1\text{H}$), deuterium (${}^2_1\text{H}$), and tritium (${}^3_1\text{H}$). The superscript is the atomic weight of the isotope, the number of protons plus neutrons in the nucleus. The subscript is the *atomic number*, or number of protons, which chemically distinguishes each element. Deuterium and tritium are rare, so the distribution of isotopes in natural hydrogen yields an average atomic weight of 1.008 g. The atomic weights of the elements come closest to whole numbers when the natural mixture of carbon isotopes is assigned a mass of 12. The atomic weights and atomic numbers of the elements are shown in the periodic table (Table 1.5).

Gravimetry, measuring the mass of products and reactants, is the most accurate form of chemical measurement. Aqueous solutions are more conveniently measured by volume, as *molarity* (M), the number of moles per liter of the solution. Sometimes *molality*, moles per 1000 g of solvent, is preferred for concentrated solutions, such as seawater or when temperature is far from 25° C.

A 1 M (one molar) solution of CaCl_2 is 1 mole (147.03 g) of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in water and the mixture made up to 1 liter (L). The mixture is made up to volume after adding the solute, because salts and miscible liquids change the volume of water when added to it. Mixing 50 mL of ethanol with 50 mL of water, for example, yields about 80 mL of mixture. Salts also change the volume of water, but less dramatically.

The numbers of moles of products and reactants may be unequal, as in



The numbers of *moles of ion charge* (formerly *chemical equivalents*), however, are equal in the equation. Equation 1.1 means, "one mole of sulfuric acid yields two moles of hydrogen charge and two moles of sulfate charge." Moles of ion charge are the number of moles multiplied by (1) the number of moles of H^+ or OH^- that react with 1 mole of the substance, or (2) the number of "moles" or Faradays of electrons that 1 mole of the substance accepts or donates. The volumetric unit is *molarity of ion charge*, or moles of ion charge per liter.

Low concentrations are sometimes expressed as negative logarithms, the "p" scale. This is most familiar as "pH," the negative logarithm of the H^+ ion concentration:

$$\text{pH} = -\log(\text{H}^+) \quad (1.2)$$

The p scale is also used for other ions—pNa, pH_2PO_4 , and pCa—and for the negative logarithm of equilibrium constants (pK) and solubility products (pK_{sp}). The negative logarithm increases as the concentration or value decreases.

High concentrations of components in solid, liquid, or gaseous mixtures can be more conveniently expressed as *mole fractions*. The mole fraction is the ratio of moles of a substance to the total moles of all substances in the mixture.

Gas concentrations are usually expressed as mole fractions or *partial pressures*. Partial pressure is a volume/volume ratio, and is equal to the mole fraction, at low

Table 1.6. Some SI units adopted by the Soil Science Society of America

Quantity	Unit	Symbol	Definition	Former or English Units
Length	Meter	m		= 3.281 feet, 39.87 inches, 10 ⁶ microns, 10 ¹⁰ angstroms
Area	Square meter	m ²		
	Hektar	ha	10 ⁴ m ²	= 2.471 acres
Volume	Cubic meter	m ³		
	Liter	L	10 ⁻³ m ³	= 1.057 U.S. quarts
Mass	Kilogram	kg		= 2.204 pounds
Time	Second	s		
Energy	Joule	J	kg m ² s ⁻²	= 0.2390 calories
Force	Newton	N	kg m s ⁻²	= 10 ⁵ dynes
Pressure	Pascal	Pa	N m ⁻²	= 10 ⁻⁵ bars, 9.87 × 10 ⁻⁶ atm
Power	Watt	W	J s ⁻¹	= 1.341 × 10 ⁻³ horsepower
Electric Current	Ampere	A		= coulombs/second
Potential difference	Volt	V	J A ⁻¹ s ⁻¹	
Resistance	Ohm	Ω	V A ⁻¹	
Conductance	Siemens	S	Ω	= 1 mho (1 mmho/cm = 1 dS m ⁻¹)
Charge	Coulomb	C	A s	= 1/(96 516) faradays
Amount of substance	Mole	mol	6.03 × 10 ²³ entities	Avogadro's number
	Moles of ion charge	mol ⁽⁺⁾ or mol ⁽⁻⁾	mol × ion charge	= equivalent
Temperature	Kelvin	K		
	Celsius	°C		0°C = 273.13 K
Radioactivity	Becquerel	Bq	s ⁻¹	= 2.7 × 10 ⁻¹¹ curies
Absorbed dose	Gray	Gy	J kg ⁻¹	= 100 rad
Concentration	Moles per unit volume	M	mol m ⁻³	
			mol L ⁻¹	= molarity
	Liquid		mol ⁽⁺⁾ L ⁻¹	= normality of cations
			mol ⁽⁻⁾ L ⁻¹	= normality of anions
Gas	molecular weight unknown	mol m ⁻³	kg ⁻³	= 1000 ppm
				= 10 ⁶ mg/m ³
			kg m ⁻³	= 10 ⁶ mg/m ³
	mole fraction, or volume per volume	mol m ³ m ³ or mol mol ⁻¹		= 10 ⁶ ppm (v/v)

pressures, where gases behave ideally. The volume of a gas is independent of other gases and is 22.4 L mol^{-1} at 25°C and 1 atmosphere pressure. The volume of each gas in a mixture is proportional to the number of molecules or moles in the gas. Low gas concentrations are often given as parts per million (ppmv), meaning the number of molecules of the gas per 1 million molecules of the gas mixture. Ppmv is a volume/volume and mole/mole unit for gases. (Ppm is a mass/mass unit for solids and liquids.) Ppmv in gases can be converted to mass/volume units by

$$\text{mg m}^{-3} = \frac{\text{molecular weight}}{24.06} \times \text{ppmv} \quad (1.3)$$

The metric system was modified as Systeme International (SI) units (Table 1.6) to prevent some confusion. The SI is based on seven fundamental units—including the mole, meter, kilogram, and second—from which the others are derived. The significant changes for soil chemistry are mole of ion charge for equivalent, siemens for mho, joule for calorie, and pascal for pressure. Table 1.4 summarizes the SI units most frequently encountered in soil chemistry. SI allows easier conversion and communication between disciplines, but unfortunately discards some useful and familiar units, such as angstrom and equivalent.

SI also recommends changes in the writing of numbers and units: avoiding the solidus (/), using the seven basic units in the denominator, using prefixes for large and small numbers (Table 1.7), and standardization of the decimal point. The solidus is removed by giving units in the denominator a negative exponent, so m/sec^2 becomes m sec^{-2} . Large numbers should be written without punctuation and with a space for each thousand—twenty five thousand is 25 000. Periods and commas in numbers are

Table 1.7. SI prefixes

Prefix	Multiple	Symbol
Exa	10^{18}	E
Peta	10^{15}	P
Tera	10^{12}	T
Giga	10^9	G
Mega	10^6	M
Kilo	10^3	k
Hekto	10^2	h
Deka	10^1	da
Deci	10^{-1}	d
Centi	10^{-2}	c
Milli	10^{-3}	m
Micro	10^{-6}	μ
Nano	10^{-9}	n
Pico	10^{-12}	p
Femto	10^{-15}	f
Atto	10^{-18}	a

confusing: the English and American 2,500 means $2\frac{1}{2}$ to Europeans. In SI the period and comma both denote the decimal point; 2.5 and 2,500 mean $2\frac{1}{2}$ in SI.

For soils in the field, soil area is usually more convenient and more meaningful than soil mass, but the square meter is too small and the square kilometer too large. The hektar or hectare ($\text{ha} = 10^4 \text{m}^2$) has been adopted as an area unit. To convert soil mass to area, the common factor for mineral soils is 2 million $\text{kg ha}^{-1} 15 \text{cm}^{-1}$ of soil, assuming a soil bulk density of 1300kg m^{-3} . Cultivated organic soils have bulk densities of about 300kg m^{-3} .

ADDITIONAL READING

- Bolt, G. H. (ed.). 1990. *Interaction at the Soil Colloid–Soil Solution Interface*. Kluwer, Dordrecht.
- Cresser, M. S., K. Killham, and T. Edwards. 1993. *Soil Chemistry and Its Applications*. Cambridge University Press, Cambridge, UK.
- Huang, P. M. (ed.). 1998. *Future Prospects for Soil Chemistry*. SSSA Spec. Pub. 55, American Society of Agronomy, Madison, WI.
- McBride, M. B. 1994. *Environmental Chemistry of Soils*. Oxford University Press, New York.
- Russell, E.W. 1987. *Soil Conditions and Plant Growth*, 11th ed. A. Wild, ed. Longman, London.
- Sposito, G. 1994. *Chemical Equilibria and Kinetics in Soils*. Oxford University Press, New York.
- Tan, K. H. 1998. *Principles of Soil Chemistry*, 2nd ed. Dekker, New York.

QUESTIONS AND PROBLEMS

- Starting with a cube 1 m on a side, calculate the change in surface area by subdividing it successively into cubes 1 mm, $20 \mu\text{m}$, or $1 \mu\text{m}$ on a side. How many particles would be in each size group?
- What is the mass of each of the above size particles? The specific gravity of aluminosilicates is 2.65. Calculate the surface area/mass ratios of the above cubes, assuming that they are aluminosilicates.
- What were the shortcomings of van Helmont's experiment and how could it have been improved?
- Compare the lists of macroelements for plants and for animals. Do the same for the microelements. Which are derived directly from the soil? What is the soil's role, if any, in providing the essential elements not directly supplied by the soil? Which elements are influenced significantly by the atmosphere and by humans?
- Which of the essential elements are metals? Nonmetals? Cations? Anions?
- Why was it necessary that the macroelements be of low atomic weight for life to evolve as we know it?

7. Early in the earth's lifetime, the atmosphere was apparently rich in methane and hydrogen and low in oxygen. Lightning can create simple amino acids in such a gas mixture. Describe the sequence of reactions and the soil properties that might aid polymerization of these amino acids in soils.
8. Discuss the differences between an element's extractability, "availability," and total content in soils.
9. Discuss why CO₂ exchanges between soils and the atmosphere.
10. Calculate the amount of water held in the world's soils if the average soil moisture content is 20% by mass (the land area is 1.2×10^8 km², the soil's specific gravity is 1.3, and the soil is 1 m deep). Compare this value with the soil water data in Table 1.2.