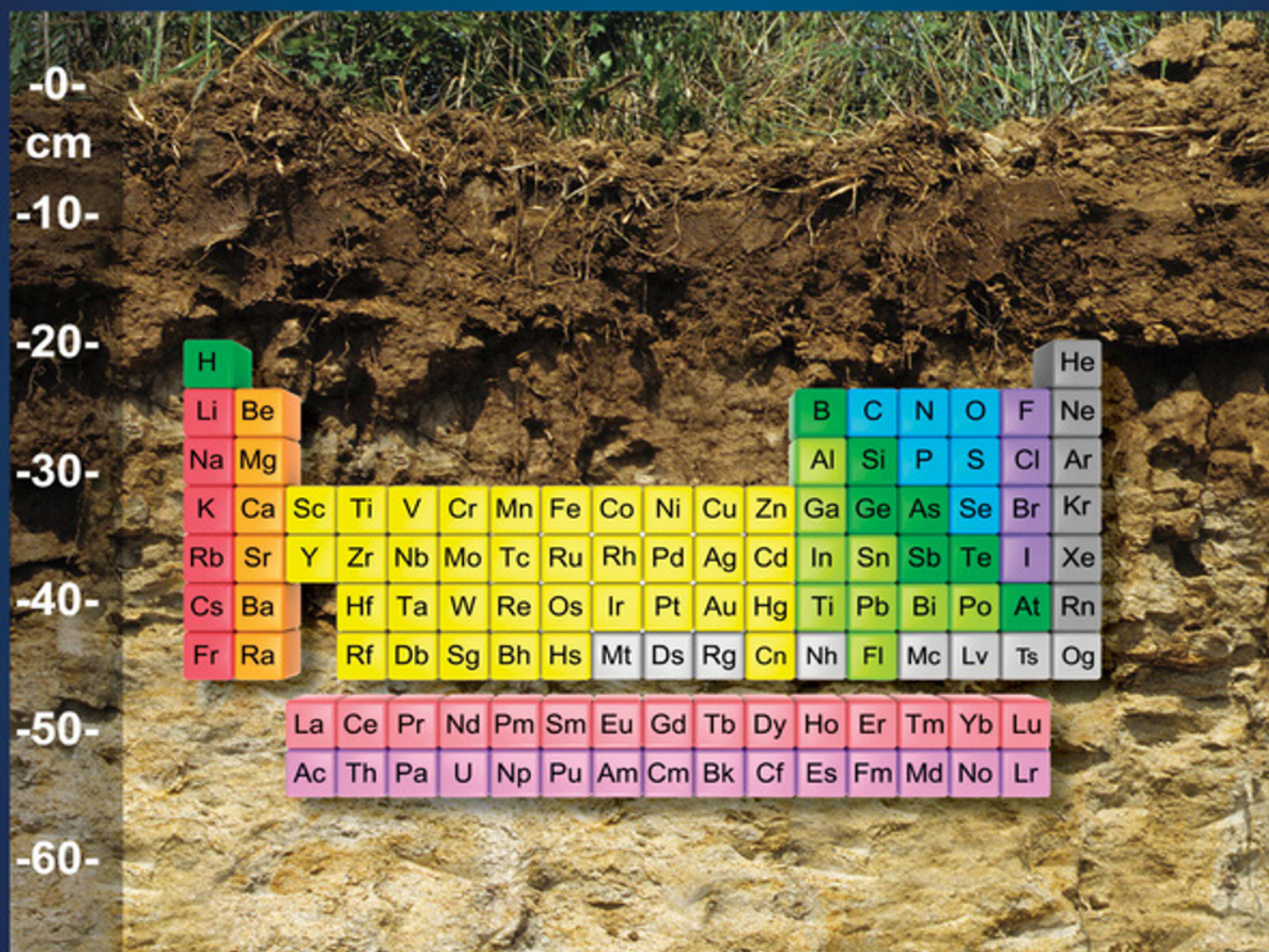


SOIL CHEMISTRY

FIFTH EDITION



DANIEL G. STRAWN

HINRICH L. BOHN

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WILEY Blackwell

Soil Chemistry

Soil Chemistry

5th Edition

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WILEY Blackwell

This edition first published 2020
© 2020 John Wiley & Sons Ltd

Edition History

Wiley (1e, 1979); Wiley-Interscience (2e, 1985); Wiley (3e, 2001); Wiley-Blackwell (4e, 2015)

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Registered Office(s)

John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

Editorial Office

9600 Garsington Road, Oxford, OX4 2DQ, UK

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Library of Congress Cataloging-in-Publication Data

Names: Strawn, Daniel, author. | Bohn, Hinrich L., 1934– author. |

O'Connor, George A., 1944– author.

Title: Soil chemistry.

Description: Fifth edition / Daniel G. Strawn (University of Idaho),
Hinrich L Bohn, George A O'Connor. | Hoboken, NJ : John Wiley & Sons,
[2020] | Includes index.

Identifiers: LCCN 2019035987 (print) | LCCN 2019035988 (ebook) | ISBN

9781119515180 (hardback) | ISBN 9781119515159 (adobe pdf) | ISBN

9781119515258 (epub)

Subjects: LCSH: Soil chemistry.

Classification: LCC S592.5 .B63 2020 (print) | LCC S592.5 (ebook) | DDC

631.4/1–dc23

LC record available at <https://lcn.loc.gov/2019035987>

LC ebook record available at <https://lcn.loc.gov/2019035988>

Cover image: Periodic table: © ALFRED PASIEKA/SCIENCE PHOTO LIBRARY/Getty Images

Soil image: Lithochrome_color by The John Kelly Collection / Soil Science downloaded via Flickr is licensed under CC BY

Cover design by Wiley

Set in 10/13pt Palatino by SPi Global, Pondicherry, India

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PREFACE TO FIFTH EDITION

This new edition of *Soil Chemistry* contains more examples, more illustrations, more details of calculations, and reorganized material within the chapters, including nearly 100 new equations and 51 new figures. Our goal remains to provide an introductory text for senior-level soil chemistry students. This requires compromise on depth of explanation of the topics so that the main points are not lost on students, while providing sufficient information for explanation. We strive to achieve this balance throughout. Students wanting more details can review the more than 200 references provided in figure and table captions and at the end of the chapters. Additional details can also be found in textbooks in chemistry, geology, pedology,

geochemistry, colloid science, soil chemistry, and soil fertility.

The textbook's focus is on species and reaction processes of chemicals in soils, with applications to environmental and agricultural issues. Topics in the 13 chapters range from discussion of fundamental chemical processes to review of properties and reactions of chemicals in the environment.

In producing this new edition, we have corrected a few errors from the previous edition. However, with the addition of new material, introduction of new errors is inevitable. Please send notifications of errors to lead author Dan Strawn at the University of Idaho. An erratum will be made available on Dr. Strawn's website.

PREFACE TO FOURTH EDITION

The goal of the First Edition of *Soil Chemistry* published in 1976 was to provide a textbook for soil science students to learn about chemical processes occurring in soils. The First Edition, and subsequent Second Edition (1985) and Third Edition (2003), focused on explaining the principles of chemical reactions in soils and the nature of soil solids. Intricacies and advanced details of theories were omitted for clarity. In the Fourth Edition, Dr. Dan Strawn, a professor at University of Idaho for 15 years, has led a revision of the classic text, working closely with original authors Dr. Hank Bohn (Professor Emeritus, University of Arizona) and Dr. George O'Connor (Professor, University of Florida). The collaboration has resulted in a new version for this classic text.

The Fourth Edition of *Soil Chemistry* is a major revision, including updated figures, tables, examples, and explanations; but it maintains the goal of the early editions in that it is written at a level to teach chemical properties and processes to undergraduate students. Graduate students and professionals, however, will also find the textbook useful as a resource to understand and review concepts, as well a good source to look up soil chemical properties listed in the many tables. To improve readability for undergraduates, citations have been omitted from the discussions.

Many of the ideas covered, however, are emphasized in graphs and tables from the literature, for which citations are included.

The topics covered in *Soil Chemistry*, Fourth Edition, are presented in the same order as previous versions. We have added a chapter on surface charge properties (Chapter 9), and the adsorption chapters of the previous editions have been completely reorganized—explanation of cation, anion, and organic chemical adsorption processes are presented in Chapter 10, and quantitative modeling of adsorption processes is presented in Chapter 11. New to this version are special topics boxes that provide highlights of topics, historical information, and examples. Enhanced discussion of carbon cycling, new theories of SOM formation and structure, details of soil redox properties, and information on chemicals of emerging concern have been added. In each chapter, key words are bolded; students should use key words as study aides to ensure they understand main concepts.

We have made every effort to minimize errors. It is said that *with each edit, only half the errors are found*, and thus, 100% accuracy is fleeting. Please forward errors or questions to Dr. Dan Strawn at the University of Idaho. We will make an erratum available.

ACKNOWLEDGMENTS

We are like dwarves perched on the shoulders of giants, and thus we are able to see more and farther than the latter. And this is not at all because of the acuteness of our sight or the stature of our body, but because we are carried aloft and elevated by the magnitude of the giants.

John of Salisbury (1159 AD)
after Bernard of Chartres, circa 1115 AD.

As this well-known quote elegantly illustrates, the ideas presented in this book are not my own, but are compiled from the years of research and teachings of soil scientists, chemists, and physicists. I drew from many resources to write this textbook, including other textbooks, review articles, and research articles. I acknowledge the *giants* who have benefited my understanding.

Every effort was made to present the work of others in a careful and meaningful way to illustrate and explain the discipline of soil chemistry. In several cases, authors provided clarification, as well as encouragement to use their data and figures. I am grateful for their generosity.

Hank Bohn was unavailable to assist in the Fifth Edition. He was instrumental in the Fourth Edition overhaul, and his spirit and contributions live on in the Fifth Edition.

I appreciate George O'Connor's collaboration in preparing the Fifth Edition. The content greatly benefited from his keen eye for relevance and attention to detail.

Writing a textbook is a labor of love. I gratefully acknowledge those who inspired my passion for soil science at University of California, Davis, where I was an undergraduate student, and Dr. Don Sparks at the University of Delaware, where I completed my PhD.

I am indebted to the students at the University of Idaho who inspired me to work hard to teach better; this text is for them. I am also grateful to my colleagues in the Department of Soil and Water Systems at the University of Idaho for providing me a home to practice my profession.

The thrill of writing a textbook is soon overshadowed by the seemingly infinite time sink. I am grateful to Kelly, Isabell, and Serena for their patience and support as I completed this project.

Dan Strawn, 2019
University of Idaho

Soil Chemistry

1

INTRODUCTION TO SOIL CHEMISTRY

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

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)

1.1 The soil chemistry discipline

The above quotations illustrate how differently humans see the soil that gives them life and sustenance. 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. Success 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 that influence each other, making soil processes complex and dynamic (**Figure 1.1**). 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, soil scientists have organized themselves into subdisciplines 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

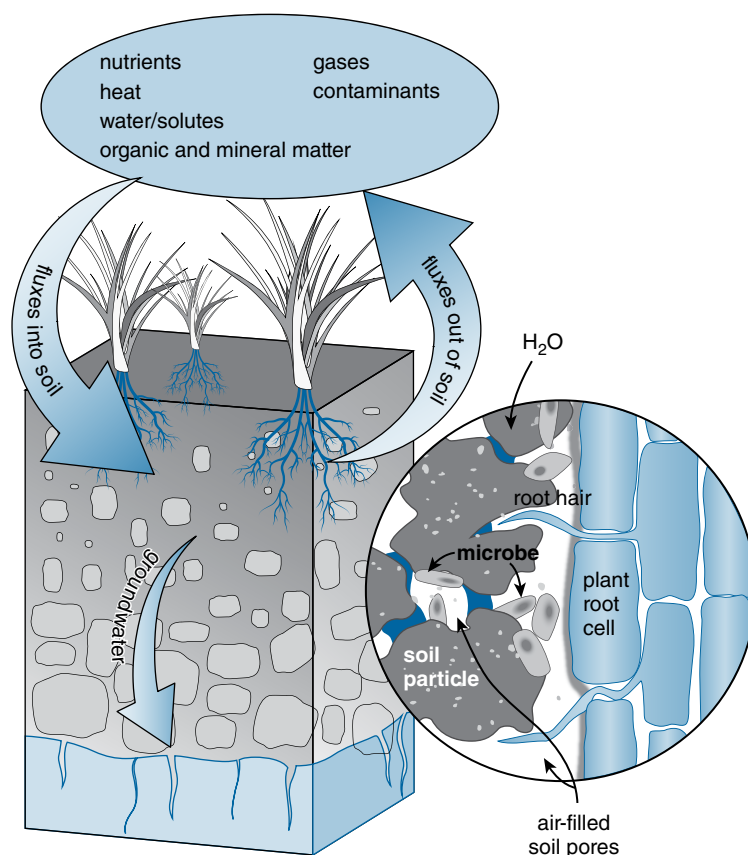
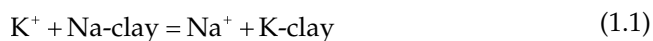


Figure 1.1 Soils are composed of air, water, solids, ions, organic compounds, and biota. The soil in the microscopic view shows soil particles (e.g., aggregates of minerals and organic matter), air and water in pore spaces, microbes, and a plant root. Fluxes of material or energy into and out of the soil drive biogeochemical reactions, making soils dynamic. Fluxes can be to the atmosphere, eroded or leached offsite into surface water, or percolated to groundwater.

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 losses from soil that in turn are important aspects of fate and transport of nutrients and contaminants in the environment. With the ever-increasing pressures to produce more food and extract resources such as timber, oil, and water from the environment, pressures on soil resources are increasing. Addressing these pressures and challenges requires detailed knowledge and understanding of soil processes. Modern soil chemistry strives to understand interactions occurring within soils, such as interactions between 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 on clay minerals, such as:



where reactants are aqueous K^+ and Na^+ adsorbed on a clay mineral (Na-clay), and products are aqueous Na^+ and K^+ adsorbed on a clay mineral (K-clay). The adsorption reaction exchanges ions between aqueous solution in the soil pore and the soil solids (clay mineral in this case) and is thus a solid–solution interface reaction. Cation exchange reactions are a hallmark of soil chemistry.

A goal of soil chemistry is predicting whether a reaction will proceed, which can be done using thermodynamic calculations. Soils are complex, however, and predicting the fate of chemicals in the environment requires including multiple competing reaction

pathways occurring simultaneously. In addition, many soil reactions are slow and fail to reach equilibrium before the system undergoes a perturbation, making prediction of chemical species a moving target. The complexity and dynamic aspect of soils make understanding chemical reactions in nature a challenging problem, but, over the past 150 years, great advances have been made. The goal of this book is to present the current state of knowledge about soil chemical processes so that students can use them to understand the environmental fate of chemicals.

1.2 Historical background

About 2500 years ago, the senate of ancient Athens debated soil productivity and voiced the same worries about sustaining and increasing soil productivity 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 considering 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. 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 can be maintained. Sustainable management requires careful use of soil and knowledge of soil processes. Soil chemistry is an important subdiscipline 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 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 fifteenth century, Sir Francis Bacon promoted the idea that the scientific method is the best 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 essential experimental variables.

John Woodruff's (1699) experimental design was much better than Van Helmont's. He grew plants using rainwater, river water, and sewage water for irrigation, and added garden *mould* to the soils. 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) showing 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 J.T. Way, 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 that continues to this day.

Despite the significant advances in understanding soils and environmental processes, environmental complexity is too great for a single discipline to fully understand. Scientific training necessarily tends to

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 develop, 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).

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. Eighteenth-century naturalist Alexander von Humboldt popularized the concept that natural systems are interconnected, and proposed a link between soils, flora, and fauna in many essays and books published from 1800 to 1825. von Humboldt also proposed that human activity could have devastating effects on ecosystem functions – a radical idea for his time.

Specialists often try to compartmentalize natural systems, and bring along biases, one of which is that their area of study 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. However, the truth is more in line with von Humboldt's ideas proposed over two centuries ago: soils are an intricate part of the web of nature, and a soil's characteristics are intimately tied to the plants, microbes, atmosphere, geology, climate, and landscape surrounding it. The linkages and influences go both ways. The unique relationship between soils and plants and microbe communities associated with them is referred to as an *edaphic* quality.

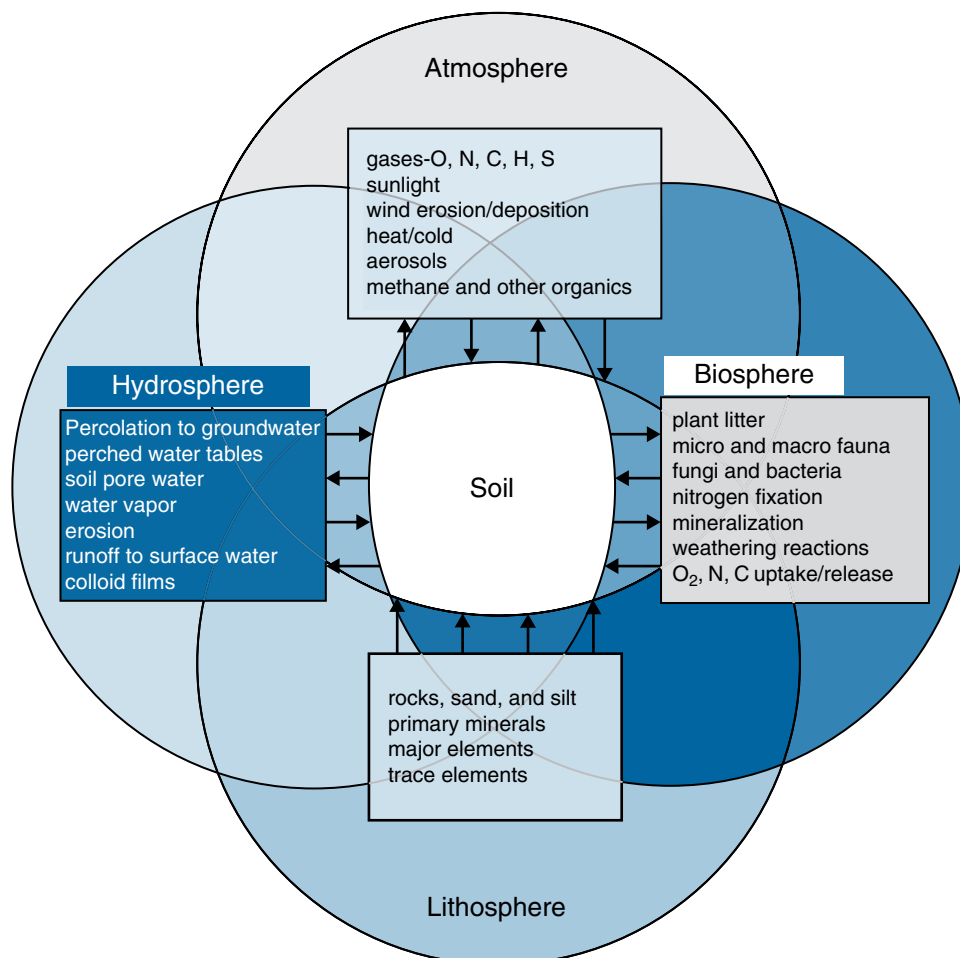


Figure 1.3 Soils interface with Earth's other spheres. Biogeochemical cycling within the soil influences flows of chemicals and energy into the hydrosphere, biosphere, and atmosphere. Arrows between the different spheres and the soil indicate important transformations.

1.3 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 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

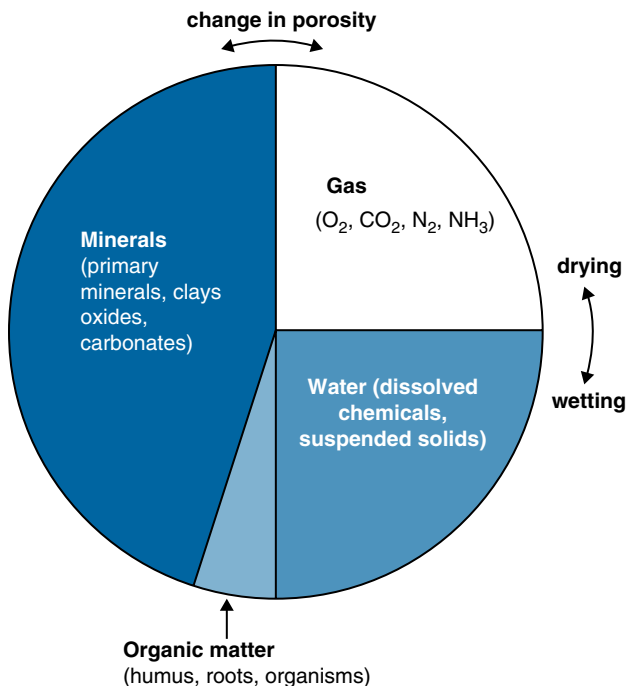


Figure 1.4 Typical volumetric composition of soils. Soil gases and solution fill the pore spaces at different ratios, depending on soil moisture content. The ratio of solid to pore spaces is controlled by the soil porosity.

the different types of chemicals occurring in soil, including ions, liquids, gases, minerals, soil organic matter, and salts.

1.3.1 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; where clays are hypothesized to have 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 airborne 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, better 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 regulate elemental availability to organisms (Figure 1.5), mediated by the root–soil interface called the **rhizosphere** (Figure 1.6). 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,

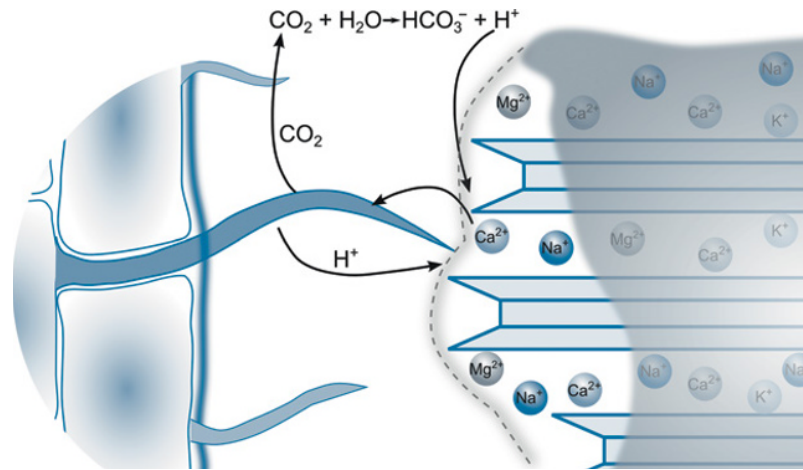


Figure 1.5 Plant root interaction with a soil aggregate composed of clay minerals. Carbon dioxide released by root respiration acidifies the rhizosphere. Cation exchange of protons and Ca^{2+} is depicted, where the Ca^{2+} is taken up by the plant root. Plant roots release protons to maintain charge balance when absorbing cationic nutrients. The protons released by the plant root and from CO_2 respiration cause weathering reactions that release additional cations from the soil minerals.

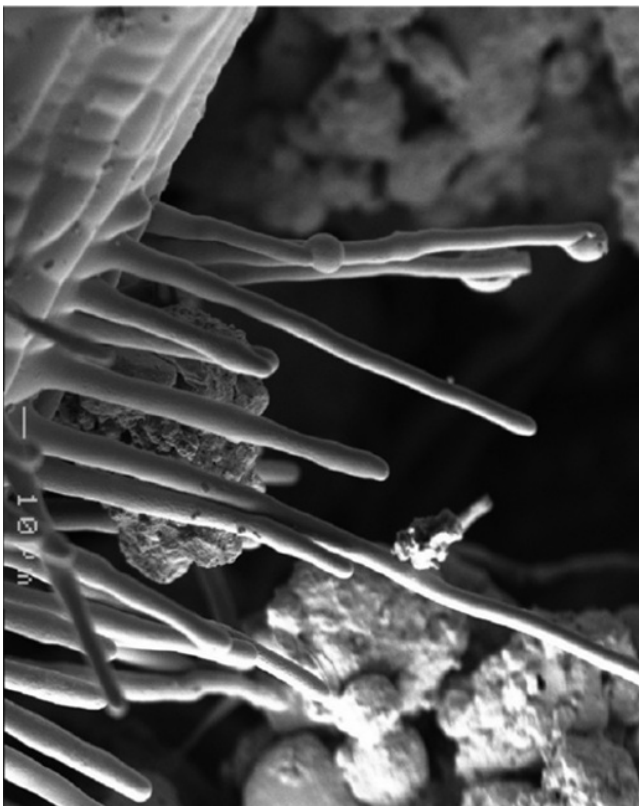


Figure 1.6 Cryo-SEM image of a plant root showing the root hairs interacting with the soil aggregates. ~10-micron diameter droplets of root exudate are seen on the tips of some of the root hairs. SEM image courtesy of Margret McCully, Australian National University.

oxygen, and minor amounts of nitrogen and sulfur gases (NO_x , NH_3 , and SO_2) directly absorbed from the atmosphere by leaves.

Plants depend on soil's ability to buffer essential nutrients, and otherwise retard nutrient losses, such as leaching out of the plant-root zone. Thus, the entire terrestrial ecosystem depends on the **biogeochemical cycling** of 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 oxygen-silicon-aluminum-iron 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. Concentrations of elements in soils depend on the **soil formation factors**, especially parent material, weathering processes, and biologically driven fluxes of elements. As a result of the many factors that influence

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* nonaccumulator plant species; soil median represents the median for *typical* soil samples. Data compiled from: Bowen (1979); Markert (1992); Marschner (1995).

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
Sodium	35–1000	150	150–25 000	5000
Sulfur	600–10 000	3000	30–1600	700
Micronutrients				
Boron	30–75	40	2–270	20
Chlorine	2000–20 000	20 000	8–1800	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	5–1500	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

plant uptake and soil concentration, average values in **Table 1.1** are instructive only; actual concentrations vary widely as shown by the ranges in **Table 1.1**.

Figure 1.7 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 compared to plant uptake. Thus, values should be interpreted with caution because individual plant species and soil properties greatly influence element bioavailability. The

general trend in **Figure 1.7** is that uptake of the elements by plants is directly proportional to the concentration of the element in soils. 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

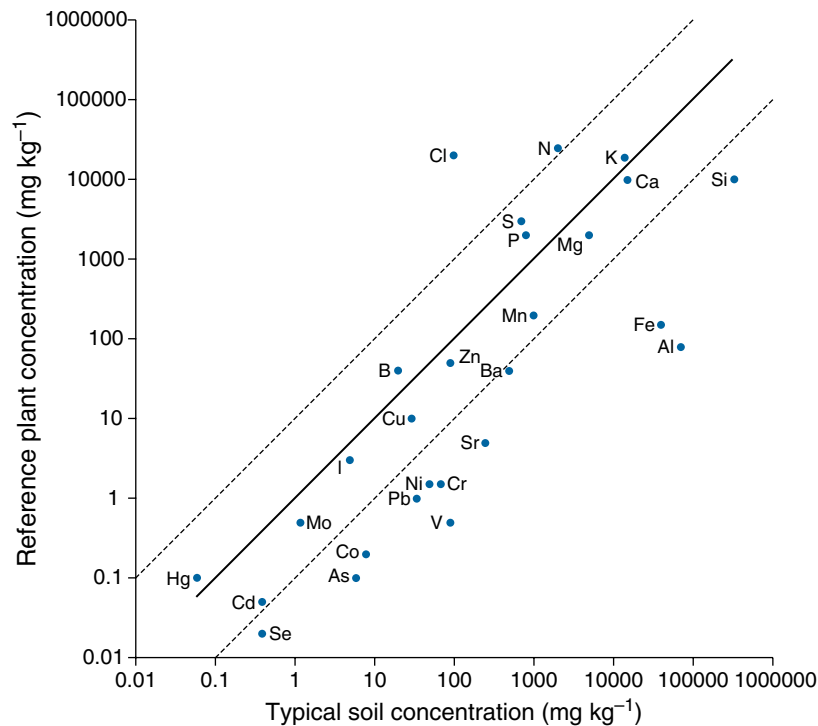


Figure 1.7 Log-log plot of elemental concentration of a typical plant as a function of total elemental concentration of a typical soil (See **Table 1.1**). Solid line is the 1:1 relationship indicating that plant concentrations are directly proportional to soil concentrations. Dashed lines represent 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.

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 with

no fertilization did not stop plant growth, although crop yields decreased. 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 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 molecules in soils; such as nitrate (NO_3^-), ammonium (NH_4^+), nitrite (NO_2^-), amino N ($R\text{-NH}_2$), and nitrogen gas (N_2). The valence of the different nitrogen forms ranges from negative, zero, to positive, which has an important effect on the reactivity and availability of the various nitrogen species. Many elements in soils have only 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. For example, some of the aqueous Ca^{2+} in soil solutions may be complexed to SO_4^{2-} , and present as the CaSO_4^0 aqueous complex, thus making it an uncharged species (denoted by the superscript zero).

Ion availability in solution is 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 adsorbed by clays and organic matter 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 (see **Figure 1.5**). 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 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.

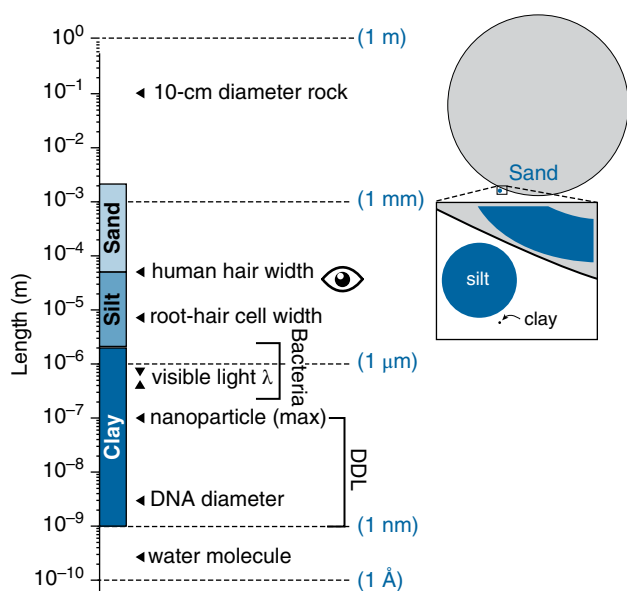


Figure 1.8 Diameter of sand, silt, and clay particles compared to other common objects. Drawing shows relative sizes of sand, silt, and clay (in blown up section the lower curve from the S from the Sand is shown to emphasize relative size). DDL is the size of a typical diffuse double layer thickness. Eye symbol indicates the approximate resolution of the human eye.

1.3.2 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 1.8**). Organic solids, such as soil organic matter, are equally important solid phases in soils, particularly in the O and A horizons. Soil chemical processes are greatly influenced by interactions with soil solids, thus, the study of solid-phase properties (soil mineralogy) 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 $0.002 \text{ m}^2 \text{ g}^{-1}$; a 1- μm clay particle, $2 \text{ m}^2 \text{ g}^{-1}$; and a 1-nm particle, $2000 \text{ m}^2 \text{ g}^{-1}$. **Figure 1.9** 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 solid–phase particles are still separate from the liquid, so they cannot be said to be homogeneously dissolved. 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 properties that colloidal clays impart to soils include adsorption and exchange of ions, and absorption of water and gasses; processes that are essential to life. The surface properties of colloids in soils 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.

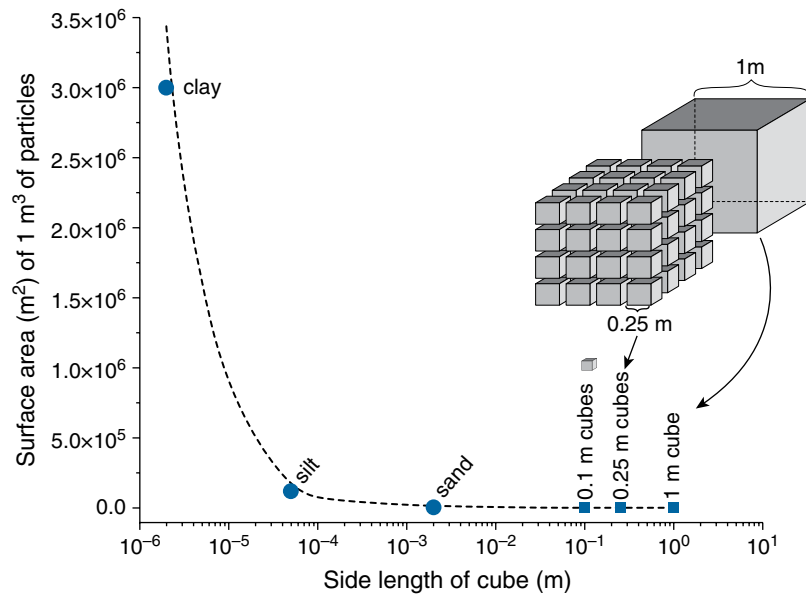


Figure 1.9 The effect of particle size on total surface area (SA) of 1 m^3 stacked particles (no space between sub-cubes). The edges of the different cubes are six different lengths: 1 m (total SA = 6 m^2), 0.25 m (total SA = 24 m^2), 0.1 m (total SA = 60 m^2), 0.002 m (sand size, total SA = 3000 m^2), 0.00005 m (silt size, total SA = 120000 m^2), 2×10^{-6} m (clay size, total SA = 3000000 m^2). The graph illustrates that the surface area of 1 m^3 of clay-sized cube particles is 10000 times greater than the surface area of the same volume of sand-sized cubic particles.

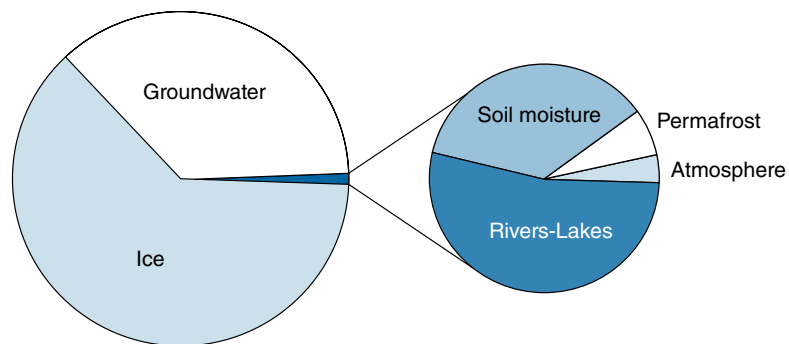


Figure 1.10 Estimate of distribution of non-ocean water on Earth. Ocean water volume (not shown) is 96.5% total water volume. Soil moisture (122000 km^3) is only a small fraction ($9 \times 10^{-5} \%$) of the total water volume on Earth. Data from Trenberth et al. (2007).

1.3.3 Soil interaction with the hydrosphere

The amount of water in soils is only a tiny fraction (0.001% to 0.0005%) of Earth's total water supply (**Figure 1.10**). 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.

Surface and ground waters receive most of their dissolved solutes from the soil because rain first reaches Earth's surface, causing the most intense weathering in soils. As water percolates to greater depths, the composition changes less dramatically because the water already contains the salts from the above soil. However, the composition and concentration of dissolved solutes can change at depths 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 subtropic 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 soil solution exists in small contacts and pores ($<10\ \mu\text{m}$) 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 are a distinct aqueous phase associated with the soil solids. This solid-solution water layer makes up a **diffuse double layer, which describes** the charge of the particle and the charge from the ions in the surface film of water. In soils containing considerable clay, a large part of the soil solution occurs in the diffuse double layer.

Soil solution contains a wide variety of solutes, including most natural occurring elements; albeit some at very low concentrations. 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. Because of the direct linkage between soil solution and surface water and groundwater, studying soil properties is an important aspect of water quality in rivers, lakes and aquifers.

1.3.4 Interaction of soil and the atmosphere

Interactions of gases with soils are less obvious than soil-water interactions, 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).

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