



## Introduction

If you consider all the ways in which soils influence element cycling, hydrologic cycling, species diversity, biotic growth, productivity, and global carbon storage, it is clear that soils have a profound effect on ecological relationships. Soils are a primary determinant of **site quality** and environmental conditions in terrestrial ecosystems, providing water, nutrients, acid neutralizing capacity, shelter, and anchorage for terrestrial life forms. Beyond these essential functions in terrestrial ecosystems, soils also exert a strong influence on aquatic systems through effects on the chemistry and hydrologic routing of drainage water inputs to lakes and streams. Depending upon (i) the hydrologic flow path of water movement into aquatic systems, (ii) the characteristics of soils and **surficial materials** contacted by drainage water, and (iii) the degree of chemical reaction between aqueous and solid phases, soils in a watershed may serve as a source or sink for acidity, alkalinity, nutrients, dissolved organic matter, or toxic pollutants in waters draining to nearby aquatic receptor systems.

## Soil Formation and Pedogenesis

Soils and their life support characteristics vary across the biosphere, with examples ranging from deeply weathered tropical Oxisols of the Amazon Basin, to fertile prairie

Mollisols of the U.S. Midwest, and extending to acidic forest Spodosols of New England. Major differences among soils originate through variations in one or more of the following five soil forming factors described by soil scientist Hans Jenny: (i) nature of the **parent material**; (ii) climatic conditions; (iii) age of the **soil profile**; (iv) soil topographic position and drainage conditions; and (v) influence of biological soil-forming agents.

In comparing soils, it is clear that one of the primary reasons for distinct differences among soils is the strong influence of geologic conditions and soil parent materials on **pedogenesis** or soil formation. At a given location, soil parent material may consist of a coarse textured sandy glacial deposit versus a volcanic ash deposit, or fertile alluvial floodplain sediments versus an ancient weathered granite bedrock **saprolite** or residuum. Each initial substrate may give rise to differing physical and chemical characteristics over the time course of soil formation. Examples of major types of soil parent materials are shown in Table 2.1.

A second major influence on soil characteristics is the climatic regime in which soil development occurs. Is the climate seasonal, wetter, drier, cooler, or warmer? How would you expect soil formation to compare in the cool humid climate of New England versus the warm humid climate of North Carolina or the warm arid conditions of Arizona and New Mexico? In general, we would expect greater soil development in warmer and wetter climates where favorable drainage conditions have permitted long-term leaching by large amounts of infiltrating precipitation.

Because soil formation is a relatively slow process, soil age is also a strong determinant of soil conditions. In glaciated regions, soils may have experienced less than 10,000–12,000 yr. of pedogenesis since the last glacial retreat; as a result, the soil profile may extend <1 m below the surface. In contrast, many sub-tropical and tropical soils are much older (i.e., > > 10,000 years old); consequently, profile development may extend tens of meters below the soil surface at these sites (Richter and Markewitz 1995).

**Table 2.1** Examples of different parent materials that act as substrates for soil formation

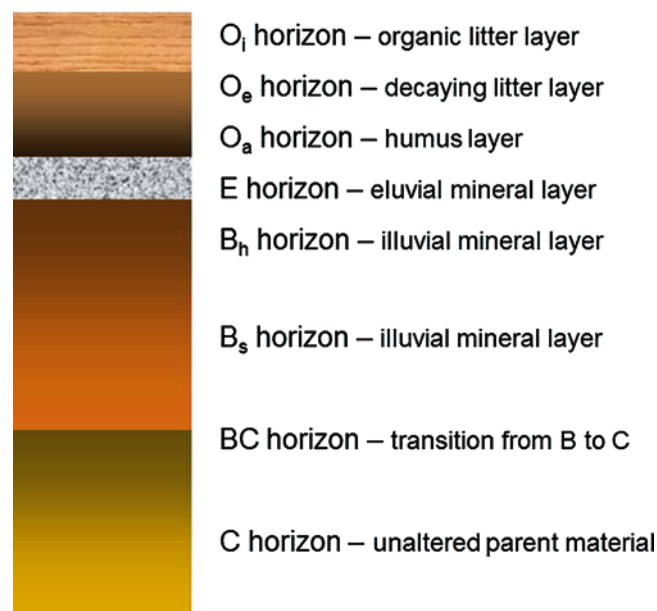
Surficial geologic deposits	Bedrock geology
Alluvial floodplain sediments	Granitic saprolite or residuum
Glacial till or outwash	Limestone or dolomitic residuum
Aeolian (wind-blown) silt	Sandstone residuum
Volcanic ash	Metamorphic schist residuum
Lacustrine (lake) sediments	Volcanic lava
Marine sediments	Basalt

Yet a fourth factor affecting pedogenesis is the topographic location of a soil. If a soil is well-drained, it will have a very different profile development compared to a lowland soil that is waterlogged or poorly-drained. In a soil with high permeability, a deeper water-table, and a mesic climate with adequate annual precipitation, the cumulative effects of water infiltration through the soil parent material promote gradual development of distinctive soil horizons. However, when water infiltration and drainage are impeded by topographic position or physical barriers in the parent material, pedogenesis is inhibited and soil horizon differentiation occurs only very slowly.

The fifth and final major influence on soil development is biological activity in the form of soil invertebrates, plants, burrowing mammals, and microbes. Respiration and metabolic activities by these organisms generate the carbonic and organic acids that promote mineral weathering and soil leaching. In addition, the life processes and organic matter derived from living organisms help to build up the structure, exchange capacity, porosity, and soil moisture storage capacity of the soil.

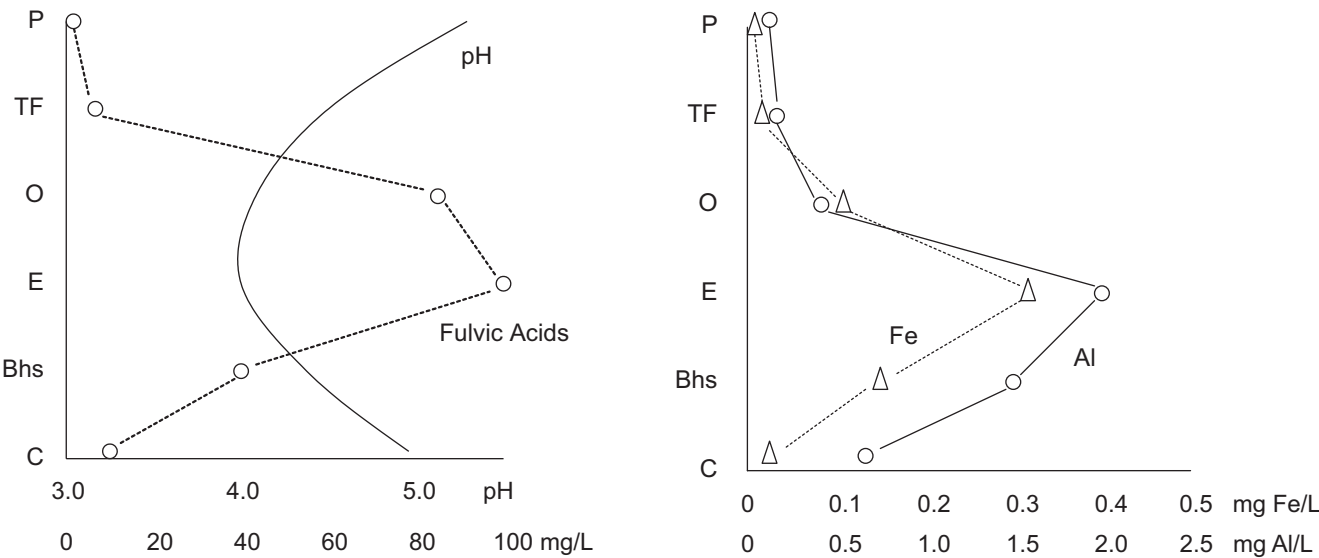
During pedogenesis, soils gradually develop a vertical zonation composed of various layers or **soil horizons**, each with particular properties. Soil formation is largely driven by (i) the percolation of water and acids through the soil profile, (ii) subsequent **weathering** and **leaching** of soil minerals exposed to acid attack, and (iii) differential mobilization, transport, and deposition of soluble organic matter and metals in the soil profile. Over time, forest soil development generally leads to the formation of a surficial O horizon composed of the detrital organic remains of plants and other organisms; beneath that uppermost organic horizon, soils typically contain several distinctive **mineral soil** layers such as the A, E, B, and C horizons.

In the example shown in Fig. 2.1, the soil horizons of this well-drained, cool temperate forest **Spodosol** have developed under the influence of a process termed **podzolization**. This process begins when precipitation moisture infiltrates the O horizon and leaches organic acids from the decaying litter and **humus**. As the drainage water percolates through the underlying mineral soil, the acidic water attacks the mineral soil particles through acid weathering, ion exchange, and organic complexation. This **cheluviation** process strips

**Fig. 2.1** Idealized soil profile showing vertical zonation of a northern well-drained forest soil. The combined O horizon layers are often referred to as the forest floor, and the uppermost mineral horizon is usually either an A or E horizon

cations from the A or E horizon, leaching them to the underlying B horizon. One of the key features of this process is the mobilization or **eluviation** of iron (Fe) and aluminum (Al) from the A or E horizon as soluble organic complexes, followed by vertical transport of the metal-organic complexes to the B horizon. In the mineral B horizon, the dissolved Fe, Al, and organic carbon are removed from solution through precipitation and/or adsorption reactions. This soil **illuviation** process leads to the accumulation of iron and aluminum oxides and **humic** coatings in the soil matrix of the upper B horizon. It should be noted that if we examined soil formation under different environmental conditions than this, a number of other possible pedogenetic processes and outcomes could be expected (Brady 1984).

Evidence of the dynamic processes of podzolization in cool temperate forest soils can be observed with examples of soil and solution chemistry data from two different field investigations. Figure 2.2 shows a vertical gradient of water samples collected as precipitation inputs, **throughfall** solutions sampled beneath the tree canopy, and soil moisture in the upper and lower soil horizons of a forest ecosystem in the Cascade Mountains of Washington. As expected, solutions in the upper mineral soil profile (E horizon) contain the highest concentrations of acidity, organic acids (**fulvic acids**), and soluble Fe and Al. This pattern occurs because the O horizon is the location where organic acids are being released by decomposition processes, causing intense weathering and metal cheluviation in the adjacent uppermost mineral soil horizon. Moving downward in the soil through the B horizons, concentrations of acidity, organic acids, and soluble Fe and



**Fig. 2.2** Vertical gradients of water chemistry in a western conifer forest at Findley Lake, WA sampled as precipitation, throughfall (TF), and soil solutions in the O, E, B, and C horizons (Data used by permission from Ugolini and Dahlgren 1987)

**Table 2.2** Concentrations of extractable soil aluminum fractions in the vertical profile of a northern forest Spodosol in New York (Cronan et al. 1990)

Soil horizon	Organic Al <sup>a</sup>	Amorphous hydroxy Al <sup>a</sup>
O	3.0	11.0
E	2.4	9.1
Bhs	11.7	42.7
Bs2	24.1	153.4
C	2.7	72.1

<sup>a</sup>Units in cmol<sub>c</sub> kg<sup>-1</sup>. Organic Al was estimated by extraction with copper acetate, while amorphous hydroxy Al was extracted with ammonium oxalate

Al all decline as a result of further weathering, ion exchange, and illuviation processes (Fig. 2.2).

As a result of these processes, we would expect that concentrations of extractable Fe and Al oxides and metal-organic complexes in the soil profile would be highest in the B horizons where these metals are accumulating through illuviation processes. Indeed, the data in Table 2.2 from a northern temperate forest ecosystem illustrate that concentrations of extractable organic Al and extractable amorphous Al oxides are five to ten-fold higher for soil particles within illuvial B horizons compared to other horizons. In summary, soluble Al leaches from the upper mineral horizons and accumulates as solid phase Al oxides in B horizons.

### Soil Classification

There are many different types of soils besides the forest Spodosol depicted in Fig. 2.1. In Table 2.3, world soils are listed taxonomically by major **soil orders** that reflect the degree of vertical stratification and the nature of soil forming

processes and factors at a given site or regional location (Fig. 2.3). Where time and climatic conditions have allowed long-term leaching of the mineral soil profile, one generally finds a strongly developed soil profile such as a northern **Spodosol**, a warm temperate or subtropical **Ultisol**, or a tropical **Oxisol**. A Spodosol is characterized by an intensely leached whitish or gray E horizon and a dark brown to chestnut brown B<sub>s</sub> or B<sub>2</sub> horizon that is enriched with Fe, Al, and organic C. In contrast, older more highly weathered Ultisols and Oxisols typically exhibit a deep B horizon with abundant accumulation of red iron oxide. Sites with younger parent material, a drier or colder climate, or waterlogged conditions may have soils such as **Inceptisols**, **Aridisols**, or **Histosols** that lack obvious mineral soil horizons.

It should be noted that when soils are classified and their horizons are described, soil scientists use various subordinate horizon abbreviations to convey information about the characteristics of each horizon. These abbreviations, which are placed beside the master horizon designation as a subscript letter (e.g., B<sub>s</sub>), include the following designators: (a) highly decomposed organic matter; (c) concretions; (e) partially decomposed organic matter; (g) gleyed and saturated; (h) accumulation of illuvial organic matter; (i) slightly decomposed organic matter; (m) cementation; (p) plowed; (r) soft or weathered rock; (s) accumulation of metal sesquioxides; (t) accumulation of silicate clay; and (x) **fragipan** character.

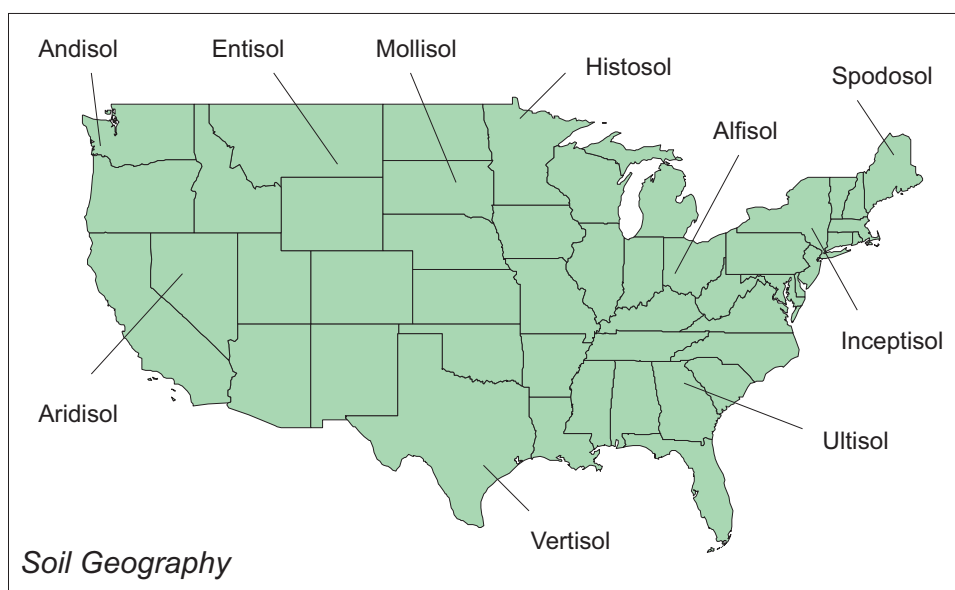
### Soil Texture and Coarse Fragments

**Soil texture** is an important soil physical property defined in terms of the relative proportions of three size classes of soil particles: **sand** (diameter = 0.05–2.0 mm), **silt** (0.002–0.05 mm),

**Table 2.3** Major soil orders defined in the taxonomy of the Soil Conservation Service (USDA Soil Conservation Service 1975; Singer and Munns 1996)

Order name	Distinctive features
Alfisol	Soils have accumulations of illuviated clay in subsoil, moderate to high base saturation, and low organic matter in upper soil
Andisol	Soils are formed on volcanic parent materials, have a low bulk density, and the clay fraction is poorly crystallized or amorphous
Aridisol	Soils are found in arid regions where moisture is limiting; upper horizons may be enriched in sodium, carbonates, or gypsum
Entisol	Soils generally lack distinctive pedogenetic horizons as a result of inadequate time for soil formation, inert parent material, steep slopes, a weatherable parent material that leaves no residue, or profile mixing
Histosol	Soils are primarily composed of organic matter (e.g., peaty soil)
Inceptisol	Soils tend to form in fine-textured parent material where annual rainfall is moderate, but leaching and translocation are insufficient to create distinctive subsurface horizons and strong profile differentiation.
Mollisol	Soils form under grassland conditions and have a thick dark brown to black surface horizon that is high in organic matter and base cations.
Oxisol	Soils develop in humid tropical and subtropical regions where leaching and weathering are intense, creating a thick subsurface accumulation of iron and aluminum oxides.
Spodosol	Soils tend to form in cool humid climates on coarser parent materials and exhibit a diagnostic subsurface “spodic” B horizon containing translocated metal oxides and humic substances; the spodic B horizon is often found beneath an “albic” E horizon that is white to light grey.
Ultisol	Soils form in warm humid climates, have a subsurface accumulation of translocated clays, have a lower base saturation than Alfisols, and often exhibit more of a red iron oxide appearance than do Alfisols.
Vertisol	Soils form in clay-textured parent material in dry or seasonally dry climates; the clays swell with moisture and shrink upon drying, causing the formation of cracks in the soil surface.

**Fig. 2.3** Examples of geographic locations where specific soil orders are common in North America



and **clay** ( $< 0.002$  mm or  $< 2.0$   $\mu\text{m}$ ). These primary soil particles typically aggregate into larger structural units resembling plates, blocks, or crumbs that may be bound together by **soil organic matter**. In many soils, coarse particles or fragments larger than sand also occur in the form of pebbles, cobbles, and boulders.

Soil textural classes based on particles  $\leq 2$  mm in size are commonly described using the soil textural triangle shown in Fig. 2.4. This conceptual model allows us to describe the texture of a soil as a function of the percent sand, silt, and clay. For a soil developed from silty **lacustrine** or lake sediments, the textural class would likely fall near the silt loam category at the lower right corner of the triangle in Fig. 2.4. In contrast,

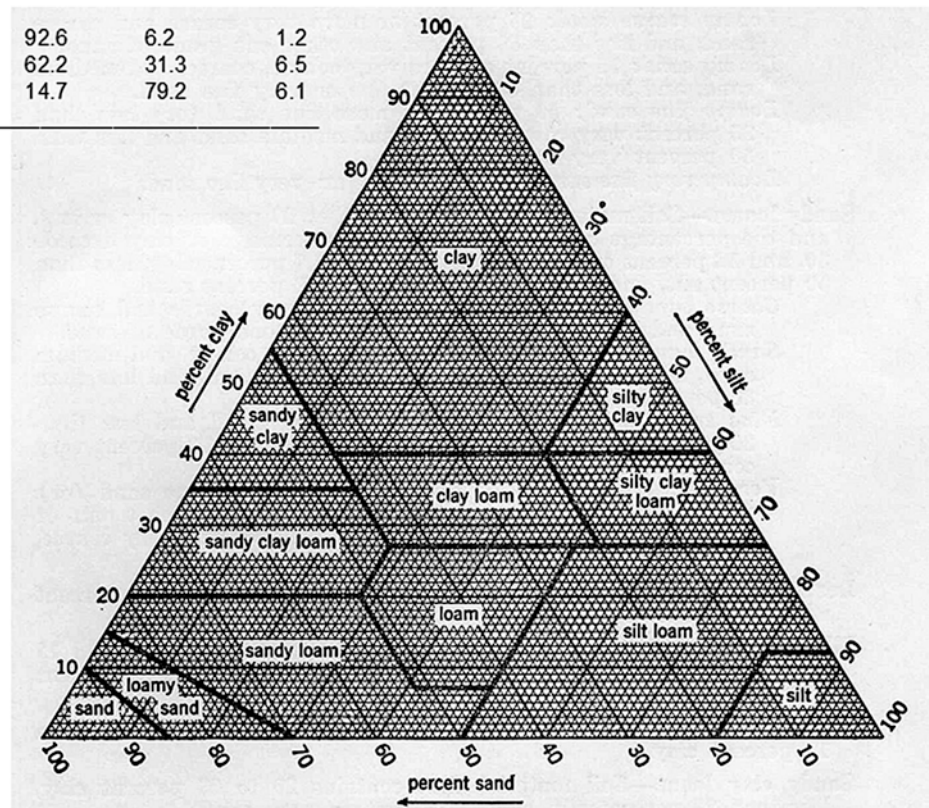
a soil developed from coarse glacial outwash material might plot in the lower left corner as a sand or loamy sand.

The illustration in Fig. 2.5 provides a comparison of texture for two contrasting mineral soil profiles in North America – a forest Ultisol in central Tennessee versus a forest Spodosol in the Adirondack Mountains of New York State. For the southern Ultisol, the upper mineral soil profile is dominated by sand and silt, with a small percentage of clay. Yet, with increasing depth, the soil texture shifts to a finer texture, reaching 60% silt and 30% clay at a depth of 60 cm. In contrast, the northern soil (formed in glacial till) is virtually uniform from 0 to 60 cm depth, with  $> 60\%$  sand,  $> 25\%$  silt, and  $< 5\%$  clay (Cronan et al. 1990).

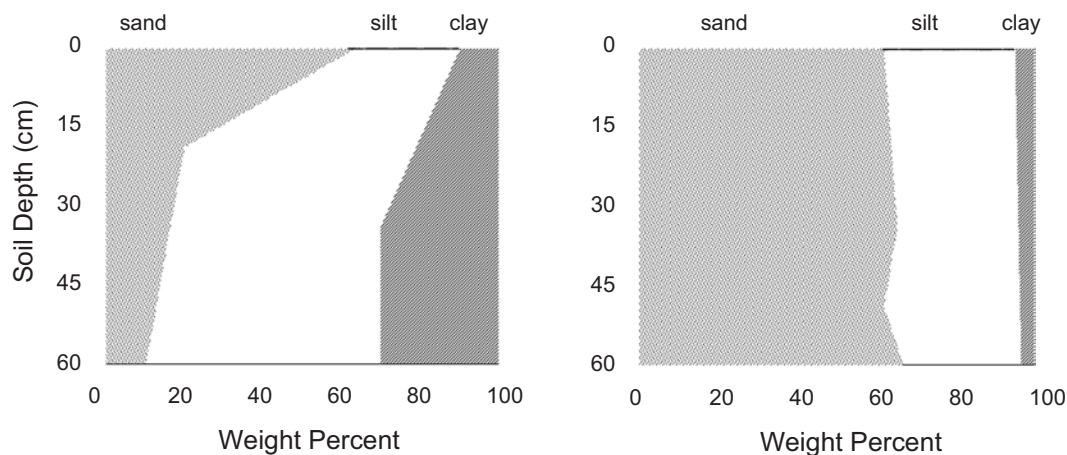


Comparison of soil textures for three northern soils

Soil Series	Parent Material	Sand (%)	Silt (%)	Clay (%)
Adams	Outwash	92.6	6.2	1.2
Becket	Till	62.2	31.3	6.5
Unadilla	Lacustrine	14.7	79.2	6.1



**Fig. 2.4** Soil texture classes delineated as a function of the percent sand, silt, and clay. Use the insert data table to place the Adams, Becket, and Unadilla soils in the triangle (Source: USDA 1951)



**Fig. 2.5** Comparison of soil textural changes through a vertical soil profile in a contrasting southern Ultisol (*left*) and northern Spodosol (*right*)

## Soil Moisture

The water infiltration and moisture retention characteristics of a soil are largely controlled by the combined influence of soil texture, aggregate structure, and organic matter content.

These master variables determine whether water drains rapidly through the soil profile, puddles up on the soil surface, or is absorbed and retained by sponge-like **soil colloids**. In a soil with favorable texture, structure, and organic matter content, water drains from larger pores and is retained in the smaller pores, giving a proper balance of water availability and aeration.

The moisture supply characteristics of different soils can be compared if we know the amount of water held by the soils at **field capacity** and at the **wilting point** (Fig. 2.6). The difference between these two measurements is the quantity of **available water** that can potentially be used by plants and other organisms during drying intervals between precipitation events. As shown in Fig. 2.7, the retention and availability of moisture can vary considerably among soils with different textures. For example, sandy soils tend to exhibit low field capacities and limited amounts of available water, producing droughty conditions and more frequent **water stress** in plants. In contrast, silty loams have much more optimal soil moisture conditions, with higher field capacities and reservoirs of available water. Clay soils generally have a high water holding capacity, but exhibit lower permeability for water infiltration and gaseous diffusion.

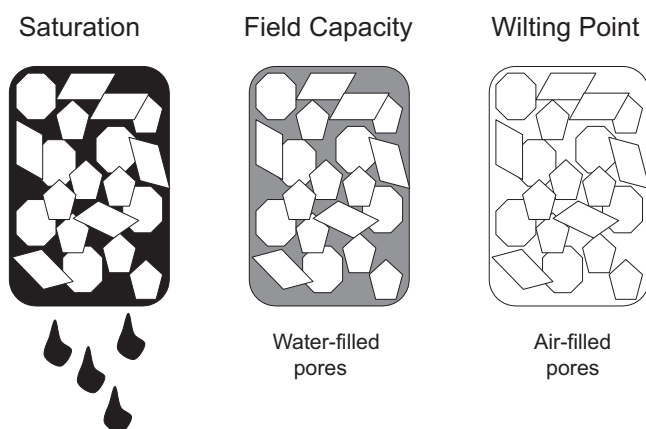
Another important physical feature of soils is water-table depth and its influence on soil moisture conditions. In low-land and wetland habitats, a high water-table can produce

seasonal or chronic water-logging or **gleying** of the soil profile. The resulting saturated conditions can decrease aeration of the soil, inhibit aerobic processes in plants and microbes, and affect nutrient uptake and leaching processes. In soils that experience seasonal waterlogging, one can often detect rusty iron oxide mottles in the soil matrix near the uppermost extent of the seasonal water-table.

## Mineralogy

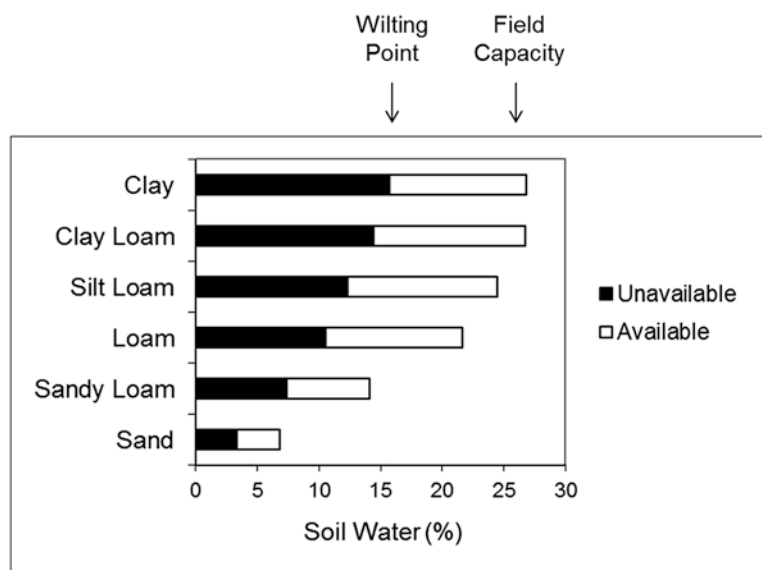
Differences in soil mineralogy are important in determining the kinds of weathering reactions that occur in the soil, release rates for various elements, patterns of alkalinity and acidity generation in the soil profile, and the nature and extent of **secondary mineral** formation in soils. If one soil is predominantly glacial outwash sand composed of  $\text{SiO}_2$ , whereas another soil contains fluvial sediments composed of multiple minerals, these mineralogical differences can translate into marked contrasts in soil fertility and chemistry.

The potential influence of mineralogical differences on soil conditions can be illustrated by looking at an example from the field. In their analysis of soil mineralogy in a forested watershed located in the Adirondack Mountains of New York, April and Newton (1985) reported that soil parent material in the C horizon at a depth of 60–90 cm was composed of 38% quartz, 50% feldspars, 2% hornblende, and various minor minerals. Further analysis of mineral chemistry indicated substantial differences in the elemental composition of these soil particles (Table 2.4). For example, hornblende was identified as a potentially rich source of calcium, magnesium, and iron, whereas plagioclase was an important source of sodium and calcium. K-feldspar was an important source of potassium, but otherwise contained negligible amounts of other nutrients besides small amounts of sodium.



**Fig. 2.6** Amounts of soil moisture at saturation, field capacity, and wilting point

**Fig. 2.7** Comparative availability of water in soils with different textures. Water held at soil tensions greater than the wilting point (*black bars - left side*) is not readily available to plants



# Physical-Chemical Features of Clays and Other Soil Colloids

The chemical behavior of soils is intimately linked with the physical-chemistry of soil colloids and ion exchange processes in the soil matrix. Soil **colloids**, consisting of clay-sized mineral particles  $<2\ \mu\text{m}$  in diameter and microscopic **humic colloids**, are crucial in storing and controlling the availability of many elements in soils. Mineral colloids include metal oxides such as  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , as well as different layer silicate clays, including kaolinite and vermiculite (Table 2.5). Both types of mineral colloids are termed **secondary minerals**, because they result from the breakdown of **primary minerals** such as feldspars, micas, and pyroxenes. As a general rule, soil colloids are characterized by enormous surface areas and often exhibit large ion exchange capacities (Table 2.5).

**Table 2.4** Comparative chemical composition of different minerals sampled in the C horizon of Panther Lake Watershed, Old Forge, NY (Data from April and Newton 1985)

Weight % oxide	Quartz	Plagioclase	K-feldspar	Hornblende
$\text{SiO}_2$	>99	64	64	40
$\text{MgO}$	0	0	0	6
$\text{CaO}$	0	3	0	11
$\text{Na}_2\text{O}$	0	10	1	2
$\text{K}_2\text{O}$	0	0.1	15	2
$\text{FeO}$	0	0	0	24

**Table 2.5** Comparison of properties of clay minerals and organic soil colloids

Colloid	Mineral type	Surface area ( $\text{m}^2\ \text{g}^{-1}$ )	Cation exchange capacity* ( $\text{cmol (+)}\ \text{kg}^{-1}$ )
Kaolinite	1:1 aluminosilicate	10–20	1–10
Montmorillonite	2:1 aluminosilicate	600–800	80–120
Vermiculite	2:1 aluminosilicate	600–800	120–150
Mica	2:1 aluminosilicate	70–120	20–40
Chlorite	2:1:1 aluminosilicate	70–150	20–40
Humic acid	Aromatic polycarboxylic organic colloid	800–900	100–300

\*cmol represents a centimole or 0.01 mole

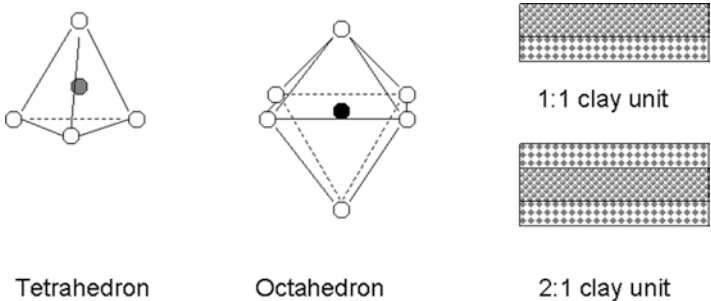
**Fig. 2.8** Structure of 1:1 layer silicate and 2:1 layer silicate clays, along with enlarged views of the tetrahedral and octahedral crystal units

# Clay Colloids

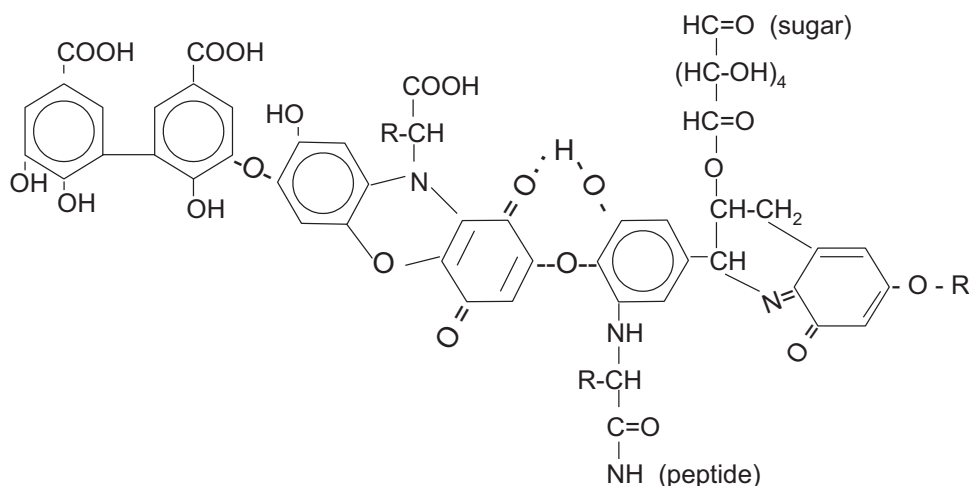
A typical layer silicate clay is a combination of two structural units: (i) sheets of silicon-oxygen (Si-O) tetrahedra and (ii) octahedral sheets containing a central atom of aluminum (Al), magnesium (Mg), or iron (Fe) surrounded by oxygen atoms (Fig. 2.8). In **1:1 clays** such as kaolinite, the basic clay structural unit contains one tetrahedral Si-O sheet plus one Al-O octahedral sheet, giving a stoichiometric formula of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . By comparison, **2:1 clays** such as vermiculite and montmorillonite exhibit a colloidal clay structural unit composed of two tetrahedral Si-O sheets plus one octahedral sheet containing a mixture of Al-O and Mg-O octahedra (Fig. 2.8). In the case of vermiculite, the clay composition can be represented by the following formula:  $\text{Na}_x[(\text{Mg}_3)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2]$ .

The functional importance of clays as chemical storehouses and regulators of nutrients in the soil environment results from two special features of these colloids: (i) their tremendous surface area (up to  $600\text{--}800\ \text{m}^2\ \text{g}^{-1}$ ) and (ii) the unsatisfied electrical charges in clay lattices that attract oppositely charged ions. The enigmatic electrical charges in clays arise from three key processes – **isomorphic substitution**, ionization, and edge breakage – that can be explained as follows. In 2:1 layer silicates (e.g., vermiculite), a relatively large **permanent charge** originates during clay formation or weathering as a result of isomorphic substitution of lower valence cations for higher valence cations in the tetrahedral and octahedral sheets. For example,  $\text{Mg}^{2+}$  ions may replace some of the  $\text{Al}^{3+}$  ions in an Al-O octahedral sheet or  $\text{Al}^{3+}$  may replace or substitute for some of the  $\text{Si}^{4+}$  ions in a Si-O tetrahedral sheet. In each case, the substitution results in unsatisfied negative charges in the clay lattice, because of the introduction of a cation with lower valence.

Ionization and edge breakage are the major sources of negative charge in 1:1 clays such as kaolinite and are a secondary source of charge in 2:1 clays. Above a certain pH defined as the **isoelectric point**, some OH groups in the clay structure ionize, releasing an  $\text{H}^+$  ion and exposing a negatively charged oxygen atom. The resulting charge is **pH-dependent** and increases as the soil pH rises above roughly 4.5. There is also evidence that clays develop negative charges through physical



**Fig. 2.9** Theoretical partial structure of a humic acid colloid found in soils (Republished with permission of John Wiley and Sons Inc. from Stevenson, F.J. 1982. Humus chemistry: genesis, composition, reactions. Permission conveyed through Copyright Clearance Center Inc.)



edge breakage that exposes electronegative oxygen atoms at the perimeter of a clay lattice.

It is important to note here that soil mineral colloids can acquire a positive charge under acidic soil conditions. As soil pH declines below the isoelectric point of a mineral colloid, the increasing  $H^+$  ion activity in the soil solution shifts thermodynamic conditions toward protonation of pH-dependent oxygen groups, creating a net positive charge on parts of the clay or oxide surface. This process will be more fully developed later in this chapter.

## Humic Colloids

Humic colloids occur in soils as a mixture of aromatic and aliphatic organic molecules enriched with carboxylic acid and phenolic hydroxyl functional groups (Fig. 2.9). Because of their low density in  $g\ cm^{-3}$  and complex physical structure, soil humic substances have a tremendous surface area per unit mass. Likewise, humic colloids have an enormous pH-dependent negative charge that results from ionization of oxygen-containing COOH and OH functional groups. With increasing pH above  $\sim 4.0$ , the negative charge or **cation exchange capacity** of soil humus increases significantly as these groups progressively ionize.

Soil chemists often focus on two major classes of soil humic substances – **humic acid** and **fulvic acid** – that are defined operationally by accepted laboratory extraction procedures. Both of these are poorly characterized mixtures of aromatic polycarboxylic organic acids. By definition, humic acids (HA) are soluble in dilute NaOH, are insoluble at  $pH < 1$ , and have average molecular weights greater than  $\sim 2000$  daltons. Fulvic acids (FA), on the other hand, are soluble in acid and base, and typically have molecular weights  $< 2000$  daltons.

## Chemical Processes in Soils

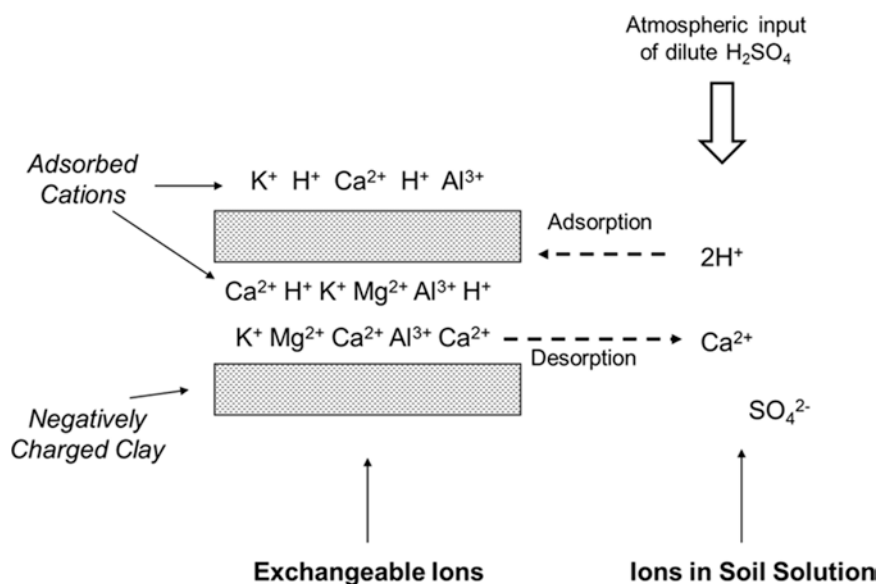
### Ion Exchange and Adsorption in Soils

Cations (e.g.,  $Ca^{2+}$ ) and anions (e.g.,  $SO_4^{2-}$ ) are retained and conserved to varying degrees in the soil environment through the processes of **cation** and **anion adsorption** on soil colloids. The mechanism of retention generally involves a dynamic electrostatic attraction between a charged ion and a colloid surface with an opposite electrical charge. After adsorption, ions may subsequently be subject to reversible **ion exchange**, a competitive process that acts to buffer soil solution chemistry through exchanges of ions in soil solution for adsorbed ions at the colloid surface (Fig. 2.10). As one example, when acidic precipitation containing dilute sulfuric acid leaches through a mineral soil horizon, cation exchange processes occur, resulting in adsorption and retention of exchangeable  $H^+$  ions on soil colloids and a corresponding release of previously adsorbed or exchangeable cations such as  $Ca^{2+}$  and  $Mg^{2+}$  (Fig. 2.10). This process helps to neutralize the  $H^+$  ions entering the soil solution from atmospheric inputs of acidic precipitation.

Cation exchange in soils can be described in terms of a general chemical equilibrium expression of the following form:  $Ca \cdot X + 2NH_4^+ \leftrightarrow (NH_4)_2 \cdot X + Ca^{2+}$ , where X is the soil colloid exchanger,  $Ca \cdot X$  is the adsorbed calcium, and  $NH_4^+$  is ammonium ion in solution. This reaction can be rearranged to provide an equilibrium constant, K, as follows:  $K_{eq} = [(NH_4)_2 \cdot X][Ca^{2+}] / [Ca \cdot X][NH_4^+]^2$ , which can be estimated with laboratory measurements of the amounts of adsorbed calcium, adsorbed ammonium, free calcium, and free ammonium ion at equilibrium. The implication of the reaction illustrated above is that ion exchange processes can potentially control the concentration of an ion in solution.



**Fig. 2.10** Conceptual representation of ion exchange in the soil environment. In this example, cation leaching through the soil occurs in response to acidic precipitation inputs containing dilute  $\text{H}_2\text{SO}_4$

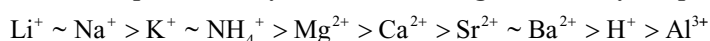


It should be noted, however, that there are innumerable possible exchange reactions involving different soil colloids and cations that may help to determine the chemistry of the soil solution (Reuss 1983; Reuss and Walthall 1990).

Cation exchange processes in soils are characterized by a number of important chemical features. The rate of cation exchange is rapid, so that equilibrium is reached in a matter of seconds after the addition or removal of a cation from the system. The exchange process is also influenced by mass action, so that when the concentration of a cation in solution increases, the exchange reaction is pushed to the right, and there is an increase in the amount of the added cation that is

adsorbed. Another aspect of cation exchange is that soil colloids exhibit differential selectivity toward cations, largely as a result of cation differences in **charge density** (the ratio of ionic charge to ionic radius). Thus, a highly charged ion that is relatively small will be more strongly attracted to an exchange surface than one that has a low charge density. Selectivity for exchangeable cation adsorption to clay minerals is described by the Lyotropic series shown below, and ranges from the weaker binding of some monovalent cations to the stronger binding of cations such as  $\text{H}^+$  and  $\text{Al}^{3+}$ . It should be noted that cation selectivities may differ between clay minerals versus humic colloids.

#### Likelihood of replacement by another cation higher on the Lyotropic series



Lower charge density ----->> Higher charge density

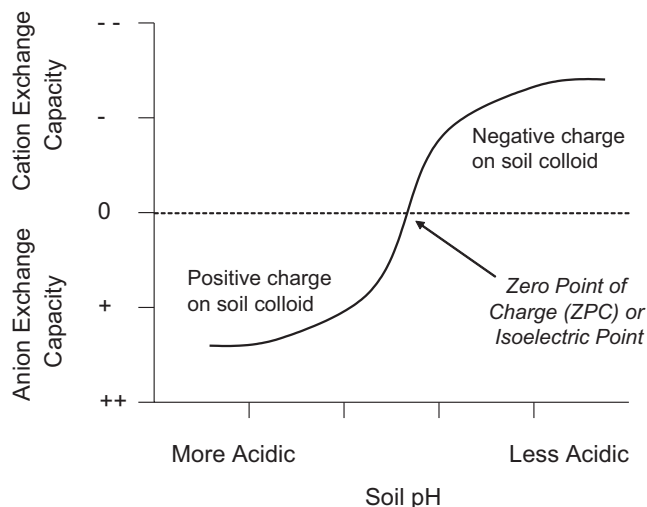
Least affinity for exchanger

Greatest affinity for exchanger

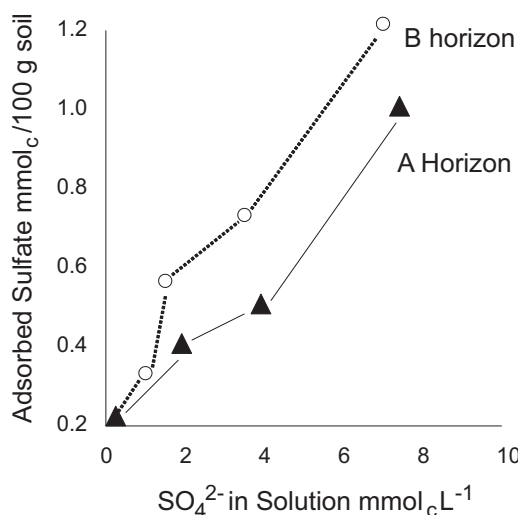
**Anion adsorption** commonly occurs in soils containing net positive surface charges on metal hydroxides, oxides, and **sesquioxides** such as  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$ . The charge on these soil colloids originates when soil pH drops below the **zero point of charge** (ZPC) or isoelectric point for the metal colloid (Fig. 2.11); as a result, the surfaces become protonated. The impact of anion adsorption can be very dramatic – in one of our soil column leaching experiments, sulfate inputs of  $>300 \mu\text{mol}_\text{c} \text{ L}^{-1}$  were depleted by sulfate adsorption to less than  $20 \mu\text{mol}_\text{c} \text{ L}^{-1}$  during infiltration through 50 cm of a sandy Adams soil from New Hampshire (Cronan 1985b).

The affinity of anions for positively charged soil surfaces varies, with stronger adsorption by phosphate and humic ligands, intermediate adsorption by sulfate and chloride, and lower adsorption affinity for nitrate and bicarbonate. In northern soils, much of the potential anion adsorption capacity may be masked by organic matter coatings originating from pedogenetic leaching of dissolved organic matter from the forest floor, followed by accumulation of **organo-metallic complexes** in the mineral soil. The presence of organic matter coatings can markedly diminish the effective anion adsorption capacity of a soil.

Investigators have found that the mobility of sulfate ion derived from acidic precipitation can be limited in forest soil solutions by pH-dependent sulfate adsorption processes. In soils where this occurs, leaching export of sulfate ions below the rooting zone is generally less than sulfate inputs from atmospheric deposition. An example of a sulfate adsorption isotherm is illustrated in Fig. 2.12 for a soil supporting mature Douglas-fir forest in Washington. The graph illustrates that as the soil is exposed to increasing concentrations of sulfate ion in solution, there is increased adsorption of sulfate by soil solid phase colloids such as Fe and Al



**Fig. 2.11** Influence of pH and isoelectric point (zero point of charge) on cation and anion adsorption by soil colloids. Above the isoelectric point pH, the colloid becomes negatively charged and contributes to CEC



**Fig. 2.12** Sulfate adsorption by an Everett soil in Washington as a function of equilibrium sulfate concentration (Reproduced with permission of Springer with data from Johnson DW, Cole DW (1977) Sulfate mobility in an outwash soil in western Washington. *Water Air Soil Pollut* 7:489–495. © 1977 by D. Reidel Publishing Company)

oxides. It is also apparent that the B horizon in this soil profile adsorbs more sulfate than the A horizon, presumably because of illuvial accumulation of metal sesquioxides in this horizon.

It is important to note that cation and anion adsorption processes are not mutually exclusive in the soil environment. In soils containing suitable mineral colloids where the pH is below about 5.0–5.5, anion adsorption sites can co-exist with cation adsorption sites. Generally, the pH-dependent anion adsorption capacity will increase as a soil becomes more acidic; conversely, pH-dependent cation adsorption capacity increases as soil acidity decreases through liming or base addition.

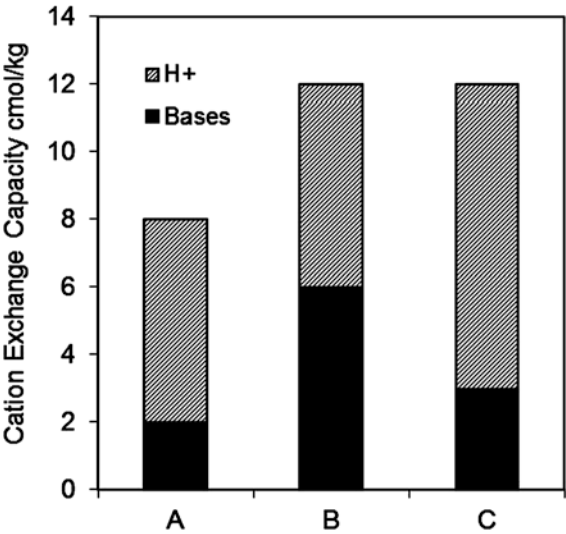
### Soil Ion Exchange Chemistry and Base Saturation

In evaluating a soil, it is important to determine the size of the cation or anion exchange capacities (CEC or AEC) and the composition of adsorbed ions on soil exchange sites. Soil CEC values are typically larger in neutral or slightly acidic soils with abundant clay or humus, whereas AEC values are generally higher in acidic soils with abundant Fe and Al oxides and limited organic matter coatings.

Soil CEC can be viewed as a “serving table” filled with a mixture of desirable nutrient cations and less desirable acidic cations. The percentage of CEC filled with nutrient **base cations** (Ca + Mg + K + Na) is referred to as the **base saturation** (% B.S.). Better soils are usually characterized by larger CEC values and higher percent base saturation levels (Fig. 2.13). Because base saturation is expressed as the ratio of the sum of base cations (in **charge equivalents**) divided by the CEC, it is important to specify whether the CEC term represents the ideal CEC estimated at pH 7.0 or the **effective CEC** estimated as the sum of total extractable cations at field pH. As implied in Fig. 2.13 and shown in Fig. 2.14, soil % B.S. exhibits a positive relationship with soil pH, although the relationships for organic O horizons and mineral horizons are offset considerably from each other. At the same base saturation, O horizons generally exhibit a much lower pH than mineral soil horizons from the same profile.

Figure 2.15 illustrates that cation exchange capacity (CEC) and base saturation (% B.S.) can change markedly moving vertically through a soil profile. In this example from a northern Spodosol, the highest CEC occurs in the organic O horizon, and this horizon also exhibits the highest concentrations of exchangeable nutrient cations. The next highest CEC occurs in the illuvial zone of the Bh horizon where metals, organic matter, and clays have accumulated. This subsoil horizon is dominated by exchangeable acidity ( $H^+$  and  $Al^{3+}$ ), and contains very low concentrations of

exchangeable base cations. The other horizons illustrated in the figure – E, Bs1, Bs2, and C – all have much lower CEC values, are dominated by exchangeable acidity, and contain extremely low stores of exchangeable base cations.



Soil	pH	CEC	% B.S.
A	4.8	8.0	25
B	5.8	12.0	50
C	5.0	12.0	25

**Fig. 2.13** Comparison of soil pH, cation exchange capacity (CEC), and base saturation (% B.S.) for three contrasting theoretical soil samples. For any given CEC, soil pH tends to rise with increasing base saturation

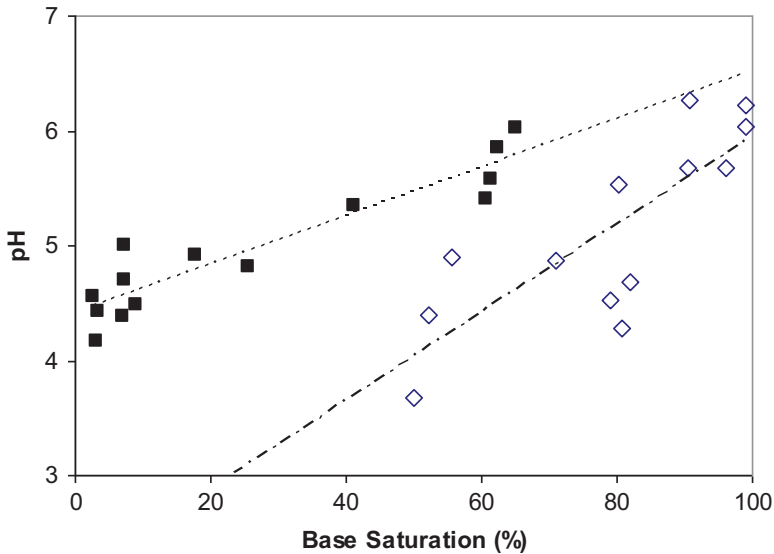
# Acidification

Soil acidification is an ongoing process that results from the acid attack of natural carbonic and organic acids released by plant and microbial metabolism, from hydrogen ions produced by plant roots, and from **strong acids** derived from either atmospheric pollution (acidic deposition) or microbial oxidative breakdown of reduced sulfur and nitrogen compounds in decaying organic matter. As soils acidify, exchangeable nutrient base cations (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^{+}$ ) are lost from the soil and are replaced by **exchangeable acidity** (measured as  $\text{H}^{+}$  and  $\text{Al}^{3+}$  ions extracted with 1 M KCl). The decline in soil base saturation over time makes it increasingly difficult for plants to acquire essential nutrients. Acidification processes may be counterbalanced to varying degrees by neutralization from rock weathering processes, by plant cycling of nutrients from less acidic to more acidic soil horizons, by atmospheric inputs of base cations, and by human applications of lime to a soil.

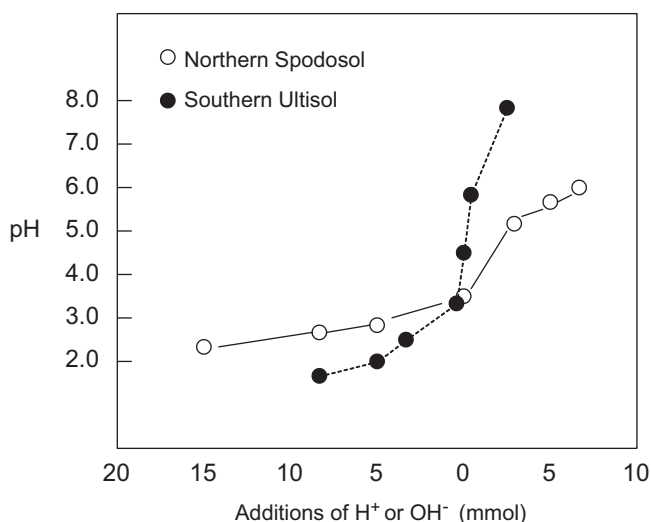
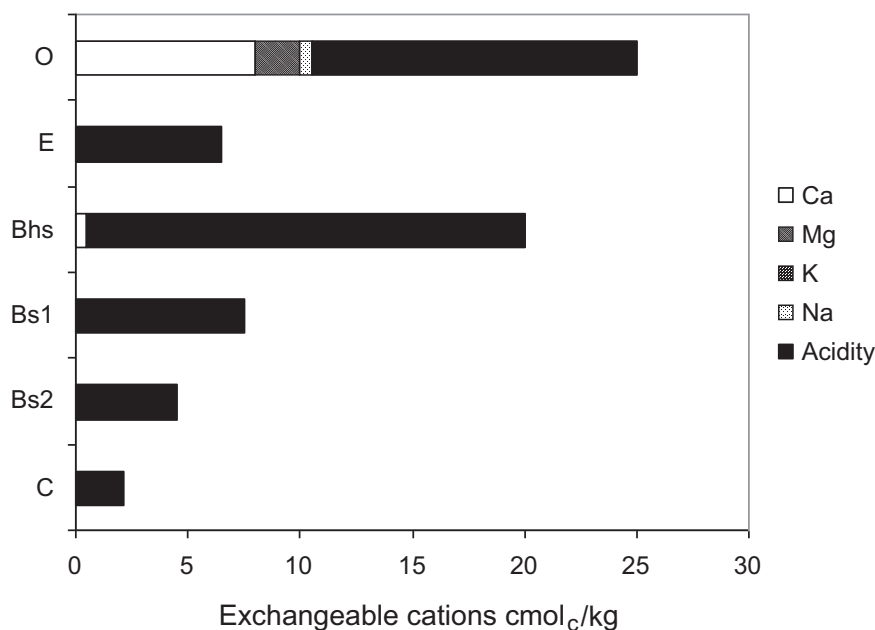
In a study of biogeochemical changes associated with stand development of loblolly pine on an old-field site in North Carolina, Richter et al. (1994) provided a striking example of rapid soil acidification and base depletion within a successional time frame. During the first three decades of pine growth, KCl-exchangeable acidity increased by  $37 \text{ kmol}_e \text{ ha}^{-1}$  in the upper 0.6 m of soil and exchangeable Ca and Mg decreased by 35 and  $9 \text{ kmol}_e \text{ ha}^{-1}$ , respectively. In the uppermost 7.5 cm of soil, percent base saturation declined from ~70% to ~10% over the 30 yr time period.

Acidic deposition and intensive forest harvesting are two important anthropogenic processes that contribute to biotic stress in forest ecosystems by promoting soil acidification, depleting soil nutrients, and increasing the concentration of ionic aluminum in the soil solution. The resulting decline in

**Fig. 2.14** Comparison of base saturation versus soil pH for O horizons (open boxes) and B horizons (black boxes) in a range of forest ecosystems. Note that O and B horizons both exhibit increasing pH as base saturation increases (Data from Cronan 1994)



**Fig. 2.15** Vertical soil profile showing CEC and relative proportions of exchangeable acidity and base cations for an Adirondack forest Spodosol (Cronan 1985a)



**Fig. 2.16** Buffer capacity curves for mineral B horizons in a northern Spodosol from Big Moose, NY and a southern Ultisol from Camp Branch, TN (Data from Cronan et al. 1990)

the Ca/Al and Mg/Al ion ratios in the soil rhizosphere can impair plant community productivity through aluminum toxicity or as a result of calcium and magnesium deficiencies (Cronan and Grigal 1995).

**Soil buffer capacity** curves can be used to compare the resistance of different soils or horizons to pH changes or acidification. In Fig. 2.16, the much flatter response of the northern Spodosol B horizon to additions of strong acid or strong base indicates that it has a greater buffer capacity than the southern Ultisol B horizon. In other words, as a result of

inherent organic and mineral proton buffering systems, the northern soil horizon exhibits much less change in pH in response to acidic or basic inputs.

## Complexation

Dissolution and aqueous transport of metals in soils can be enhanced through **complexation** processes involving binding of an electronegative **ligand** with a metallic cation (see Chap. 1). Formation of soluble complexes containing single **coordinate bonds** results when the proton of an acidic functional group such as a carboxylic group is replaced by a metal ion, forming an organo-metallic complex. Simple complexes can also be formed between metals and inorganic anions such as F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>; in fact, acidic streams often contain inorganic complexes of aluminum fluoride and aluminum sulfate (Al-F<sup>2+</sup> and AlSO<sub>4</sub><sup>+</sup>). Formation of a more stable **multi-dentate complex** or **chelate** is possible when an organic ligand provides two or more adjacent functional groups capable of bonding coordinately to a central metallic atom or ion (see Fig. 1.1). This can happen most readily when the organic ligand contains adjacent carboxyl groups (e.g., oxalic acid) or adjacent carboxyl and phenolic-OH groups (e.g., trihydroxybenzoic acid).

Complexation reactions are important in soil environments because they (i) increase the solubility and mobility of otherwise poorly soluble metals, and (ii) diminish the toxicity of metals such as aluminum and copper. Processes of eluviation and metal leaching in soils are often dominated by complexation reactions involving organic acids generated and released in the O horizon. Plants and microbes benefit



from complexation reactions, and are known to release organic ligands into the **rhizosphere** to improve availability of certain metals. Once formed, metal complexes may be subject to transport, transformation, and degradation.

## Leaching

**Soil leaching** is a key process for element transport through the soil profile and into groundwater and surface waters. Leaching occurs when soluble ions or other solutes are removed from a substrate or soil micro-zone under the influence of water. The amounts and kinds of nutrients and other elements that move through this cycling pathway are determined by the interaction of a number of geochemical, biological, physical, and hydrologic factors. For example, the **mobile anion** nitrate may easily leach through soils and into streams during April snowmelt. However, once plant nutrient uptake resumes in the spring, nitrate leaching may cease completely, because of the efficient removal of nitrate from the soil solution by plant absorption and microbial immobilization. In contrast, chloride that enters an ecosystem from atmospheric deposition or road salting may freely leach through soils and into stream water year-round with minimal biological retention. The diagram in Fig. 2.10 provides a visual example showing the leaching of  $\text{Ca}^{2+}$  ion that results when inputs of acidic deposition to a soil displace exchangeable calcium from clays and humus, promoting transport or leaching of the soluble cation out of the rooting zone. In that illustration, we would expect increased cation leaching in response to increased inputs of acidic deposition.

Investigators have described three major soil leaching paradigms that predominate under different environmental conditions in the biosphere: (i) **carbonic acid leaching**; (ii) **organic acid leaching**; and (iii) **strong acid leaching** (Cronan et al. 1978; Johnson and Cole 1980). Each of these major types of acids has different characteristics, sources, sinks, and potential consequences for soil formation and ion transport through the soil profile. Carbonic acid leaching occurs in soils with pH greater than about 4.5–5.0, and involves relatively weak acid conditions with little complexation of trace metals such as iron and aluminum. Organic acid leaching often predominates in cool temperate, boreal, and montane forest soils and peats containing large amounts of decaying organic matter. The high concentrations of organic acids in these soils enhance the leaching of iron and aluminum through complexation reactions. A third group of soils includes those that are affected by strong acid leaching by sulfuric and nitric acids derived from anthropogenic pollution or natural sources of strong acids. Strong acid leaching can accelerate the losses of nutrient cations and the mobilization of trace elements such as aluminum in soils.

For each of these leaching regimes, it is important to recognize that the principles of ionic charge balance mentioned in Chap. 1 are observed. Molecules of each acid contain equivalent charges of  $\text{H}^+$  and acid anions and as these acids react and interact with soil materials, cation and anion charge equivalents are maintained. Thus, adsorption of a mole of acid protons by soil colloids is balanced by a quantitative release of other cations from soil sources and/or a loss of anions to soil or biotic sinks.

## Dissolution and Precipitation Reactions

Solute concentrations in a soil profile are controlled to varying degrees by solubility relationships involving **dissolution** and **precipitation** reactions. As an example, aluminum occurs abundantly in many soils as an insoluble aluminosilicate framework in primary minerals and clays. Under favorable acidic conditions, particularly when complexing organic acids are present, dissolution and complexation reactions can release aluminum into solution as a free ion (e.g., trivalent  $\text{Al}^{3+}$ ) or complex. However, if the chemical activity of free aluminum increases enough or the solution pH rises and lowers the solubility of aluminum, then aluminum may precipitate from solution as a solid aluminum trihydroxide mineral such as gibbsite,  $\text{Al}(\text{OH})_3$ . Similarly, in an arid soil, calcium dissolution and transport may occur in surface soil horizons during moist seasons, but  $\text{Ca}^{2+}$  ions may be removed from soil solutions during dry periods through precipitation of calcium carbonate,  $\text{CaCO}_3$ . Soil chemists often express the potential for precipitation or dissolution of a mineral in a given soil environment using a **saturation index**, which is based on the ion activity product of the aqueous **counter ions** of interest divided by the solubility constant of the solid mineral formed from those ions.

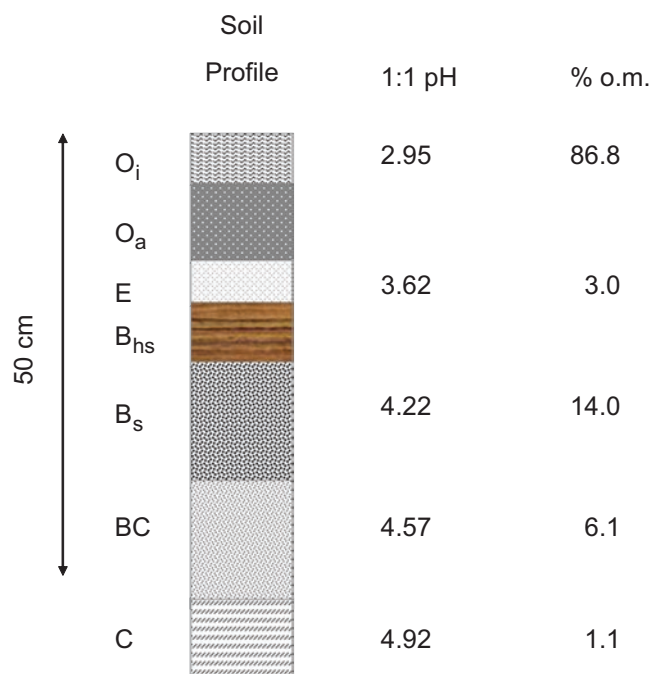
**Lithic elements** such as Ca, Mg, K, Na, Al, Si, Fe, and Mn that originate from primary minerals are strongly dependent on dissolution and weathering processes for their release into circulation within the biosphere. Each of these elements has a distinctive geochemical solubility that is differentially sensitive to changes in concentration, pH, and **redox** status. At one extreme, sodium ion is exceedingly soluble under a wide range of soil conditions. In contrast, iron solubility decreases as pH and  $\text{pO}_2$  (partial pressure of oxygen) increase (e.g., as solution acidity decreases and the micro-environment becomes more oxidizing). Aluminum is distinctive in other ways, because it exhibits a parabolic pattern of pH-dependent solubility, with minimum solubility around pH 7 and exponential increases in Al solubility above and below pH 7. Consider how these differences in aqueous solubility might affect the mobilization, immobilization, and distribution of metals in a soil profile!

Besides metals described above, several other elements are strongly influenced by solubility relationships in soil environments. Phosphorus (P), as an example, forms relatively insoluble solid-phase precipitates with iron and aluminum. There is evidence that microbes and plants release organic acids into the rhizosphere in an effort to solubilize iron and/or aluminum from these precipitates, thereby enhancing bioavailability of P. In some soils, aluminum sulfate minerals are found, suggesting that these precipitates help to control the solubility of aluminum and sulfate. Anaerobic wetland soils may contain insoluble iron sulfide (FeS) that forms through precipitation of ferrous iron with sulfide derived from microbial sulfate reduction. The insoluble sulfur can eventually be mobilized if the soil is aerated and becomes oxidized in the presence of water.

Carbon is also affected by dissolution-precipitation reactions in the soil environment. In soils containing calcite ( $\text{CaCO}_3$ ) or dolomite ( $\text{Ca/Mg}$  carbonate), dissolution processes can release inorganic carbonate species into solution. Likewise the precipitation of metal carbonate solid phases in the soil can remove inorganic carbon from solution. Soluble **humic substances** occur at high concentrations in surface horizons of many soils, but are stripped from solution in lower mineral soil horizons by both adsorption processes and precipitation reactions that generate insoluble metal-organic complexes and organo-mineral clay aggregates (Mayer and Xing 2001). Thus, both inorganic and organic carbon compounds can be influenced by precipitation reactions in soils.

## Comparative Analysis of Soil Chemical Properties

There are many lessons to be learned and insights to be gained by examining comparative soil data and trying to interpret the observed patterns and differences among contrasting soils and soil horizons. As an example, Fig. 2.17 illustrates the striking vertical profile development of a northern Spodosol, showing the distinctive changes in soil pH (1:1 in water) and soil organic matter content with depth. In this forest soil, pH rises two full units from the surface O horizon (at pH 2.95) to the subsurface C horizon (pH 4.92 at a depth of 50 cm below the surface). Presumably, this acidity gradient reflects the fact that acidic inputs to the O horizon are much greater than inputs of **acid neutralizing capacity** (ANC), whereas the C horizon is a zone with lower inputs of acidity relative to the generation of ANC. We also observe in this soil profile that organic matter concentration drops from 87% in the O horizon, to 3% in the eluvial E horizon, rises again to 14% in the upper B horizon, and declines to 1% in the parent material of the C horizon. How can we account for this pattern? In the O horizon, there are large annual inputs of organic detritus in the form of aboveground litter and fine roots that help to maintain a high concentration of organic



**Fig. 2.17** Soil profile patterns for pH (1:1 soil and water) and organic matter in a northern Spodosol. For reference, the E horizon is 4 cm thick. (Cronan 1985a)

matter. In the illuvial B horizon, organic matter enrichment results from two major processes: accumulation of soluble organic matter leached from the O horizon and death and turnover of fine roots within the B horizon.

## Soil Exchange Chemistry

How do soils and horizons compare in terms of concentrations of exchangeable cations and other chemical parameters? For perspective, let's examine the inter-horizon differences in soil chemistry for a northern forest Spodosol from New York versus a southern Ultisol from a forest in Tennessee (Table 2.6). In both soils, there are striking contrasts in exchangeable cation concentrations, CEC, and percent base saturation between the surface O horizon and the subsoil B horizons. For example, exchangeable Ca is two orders of magnitude higher in the O horizon compared to the B2 horizon. Whereas O horizons from both forest ecosystems have base saturation values ranging from 50% to 85%, the mineral B2 horizons have base saturation values <10%. There is also an interesting contrast in cation stoichiometries between the northern and southern soils. In the B2t horizon of the southern Ultisol, exchangeable Ca is roughly one fifth as large as exchangeable Mg; in contrast, exchangeable Ca in the Bs2 horizon of the northern Spodosol is ten times larger than exchangeable Mg. Can you detect other interesting patterns of soil properties in Table 2.6?

**Table 2.6** Comparison of soil chemical properties for a northern Spodosol at Big Moose, NY versus a southern Ultisol at Camp Branch, TN (Data from Cronan et al. 1990). Soil pH in water is abbreviated pH<sub>w</sub>; CEC refers to soil cation exchange capacity; and % BS is percent base saturation

				Exchangeable cations in cmol(+)/kg							
	pH <sub>w</sub>	%C	%N	Ca	Mg	K	Na	Al	H <sup>+</sup>	CEC	%BS
Southern											
Soil horizon											
Oa	4.68	36.9	1.27	13.13	2.35	1.96	0.05	2.44	2.94	22.87	76
A1	4.11	11.4	0.48	1.52	0.53	0.85	0.02	3.01	2.18	8.11	35
E	4.53	1.1	0.05	0.03	0.03	0.09	0.005	2.93	1.29	4.375	4
B21	4.51	0.5	0.03	0.03	0.07	0.1	0.005	6.76	0.78	7.745	3
B2t	4.71	0.4	0.04	0.09	0.46	0.13	0.01	7.29	2.31	10.29	7
C	4.71	0.2	0.04	0.02	0.31	0.08	0.01	7.22	3	10.64	4
Northern											
Soil horizon											
Oi	4.84	46.9	2.13	27.9	2.81	1.79	0.05	2.65	2.97	38.17	85
Oa	3.68	46.3	2.02	13.99	1.45	0.61	0.04	3.62	12.33	32.04	50
E	3.97	2.6	0.15	0.43	0.05	0.05	0.01	1.99	0.63	3.16	17
Bhs	3.79	6.9	0.32	0.92	0.08	0.06	0.03	7.14	1.08	9.31	12
Bs2	4.38	6.2	0.26	0.29	0.02	0.02	0.01	4.25	0.42	5.01	7
C	4.82	0.8	0.03	0.02	0.002	0.007	0.002	0.69	0.001	0.722	5

Additional insights emerge if we expand our comparison to a range of soils from different regions. Figure 2.18 presents an interregional survey of soil exchange chemistry in a mildly acidic forest Inceptisol in North Carolina, an acidic Ultisol in Tennessee, and two acidic Spodosols from New York and Germany. As shown by the data, O horizons tend to exhibit high concentrations of exchangeable base cations and large CEC values; yet, organic horizons in different soils can vary greatly in relative proportions of acidity and base cations. The data in Fig. 2.18 also suggest that CEC values in mineral B horizons tend to be much lower compared to O horizons, and are typically dominated by exchangeable acidity (mostly in the form of exchangeable Al).

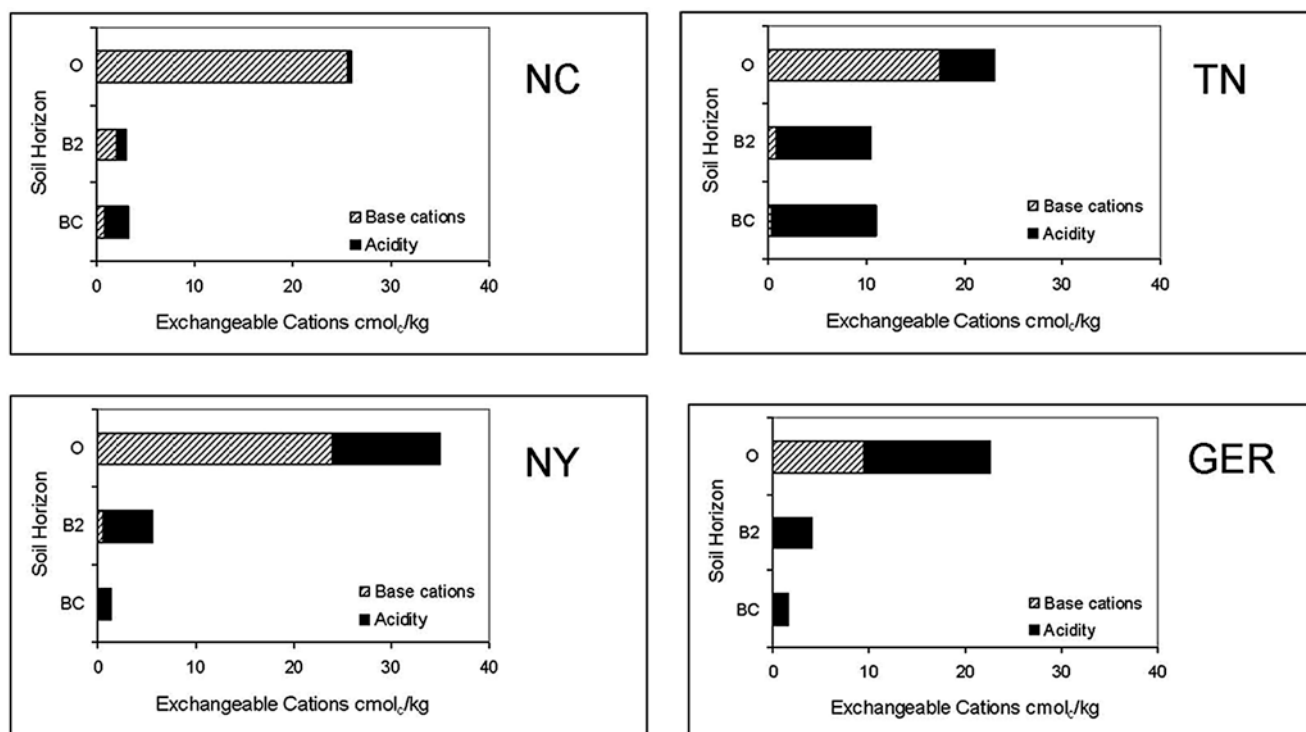
### Soil Distributions of Aluminum

Depending upon the focus of a given biogeochemical investigation, it is sometimes important to develop more detailed information about specific forms of elements distributed through a soil profile. For example, a study of soil aluminum biogeochemistry might require an analysis of extractable soil aluminum pools in each soil horizon. As shown in Fig. 2.19, pools of exchangeable Al, organically bound Al, and amorphous Al hydroxides differ greatly among soil horizons and different soil types. Exchangeable Al, the most reactive form of soil Al, tends to comprise a small portion of the total soil storehouse of Al, whereas amorphous forms of Al oxides and hydroxides tend to be the largest pool of soil Al. In forest soils such as the two Spodosols in Fig. 2.19, total Al concentrations tend to reach maximum values in the B2 horizons,

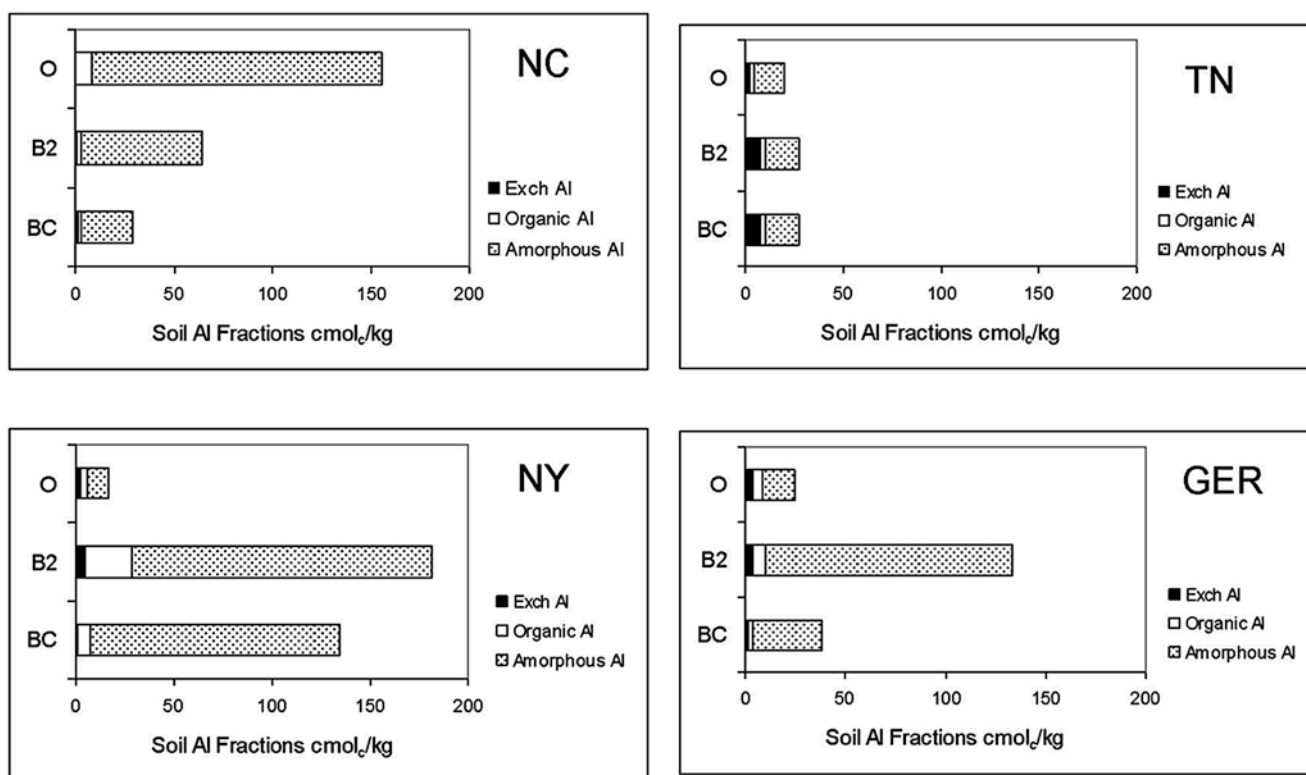
reflecting the influence of podzolization and illuviation processes on levels of soil Al in northern forest ecosystems. Given the contrasting patterns of soil Al distribution, we could explore a number of intriguing questions regarding Al biogeochemistry. How does the distribution of soil Al affect cycles of other elements and how stable are the distribution patterns? What are the residence times of the different Al fractions and are turnover rates for these forms of soil Al affected by environmental changes and disturbance?

### Vertical Distributions of Organic Carbon, Nitrogen, and Phosphorus in Soils

Many soils contain large amounts of detrital and adsorbed carbon, nitrogen, and phosphorus. In previous literature reviews, Jobbagy and Jackson (2000, 2001) analyzed a large interregional data base of soil chemical properties and prepared a broad synthesis of vertical distribution patterns of C, N, and P in the upper 1 m of soil. As illustrated in Fig. 2.20, the investigators found that roughly 50% of soil organic carbon (SOC) in the upper 1 m of forest soils was stored within the uppermost 0–20 cm, with the remaining SOC declining steeply below that depth. Total SOC content in the upper 1 m of forest soils ranged two-fold from 9.3 in boreal forests to 18.6 kg C m<sup>-2</sup> in tropical evergreen forests, and SOC values generally increased with precipitation amount and soil clay content (Jobbagy and Jackson 2000). Compared with that global data base, Huntington et al. (1988) estimated that total soil profile carbon content in the Becket soil at Hubbard Brook Experimental Forest, NH was approximately 16 kg C m<sup>-2</sup>.



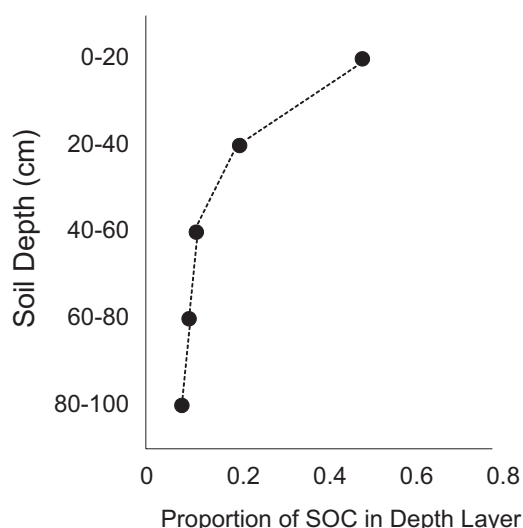
**Fig. 2.18** Total exchange capacity and proportions of exchangeable base cations and exchangeable acidity in O and B horizons for a forest Inceptisol in North Carolina, an Ultisol in Tennessee, and forest Spodosols in New York and western Germany (Data from Cronan 1994)



**Fig. 2.19** Comparison of soil aluminum fractions by depth for organic and mineral soil horizons in a southern Inceptisol (NC), a southern Ultisol (TN), and two northern forest Spodosols (NY and GER).

Stacked bars show concentrations of exchangeable Al, organically bound Al, and amorphous hydroxy Al in each horizon (From Cronan 1994)





**Fig. 2.20** Generalized vertical profile of soil organic carbon (SOC) content in the upper 1 m of a forest soil. Values are expressed as a fraction of the SOC pool in the entire 1 m depth (Data from Jobbagy and Jackson 2000)

In their examination of vertical depth profiles of other soil nutrients, Jobbagy and Jackson (2001) reported that roughly 40% of the N and P content of the top meter of soil was concentrated in the 0–20 cm depth for a wide range of soil series. A comparison of grassland Mollisols and warm temperate Ultisols indicated that extractable P in the upper 1 m of soil averaged 7.4 and 2.5 g m<sup>-2</sup> for the two respective soils, whereas mean total N content was 1227 and 542 g m<sup>-2</sup> in the two soils. For perspective, Huntington et al. (1988) estimated a total soil profile nitrogen content of 720 g N m<sup>-2</sup> at Hubbard Brook Experimental Forest, NH.

## Forms of Organic Nitrogen in Soils

There is broad research interest in the biogeochemical patterns of N distribution and turnover in soils. Unfortunately, many soil data sets in the literature include only estimates of total soil N concentration or total organic N concentration in a given soil horizon. How much soil N occurs in more versus less labile forms and how rapidly do these pools turnover? In their biogeochemical study of specific forms of organic N in the O<sub>a</sub> horizon of a Swedish forest Spodosol, Johnsson et al. (1999) found that roughly 40% of the N was associated with amino acids + amino sugars, whereas most of the remaining soil N pool consisted of uncharacterized non-amino forms of N (Table 2.7). A related study of soil amino acid abundance along a forest fertility gradient in Michigan by Rothstein (2009) indicated that free amino acid N represented 2–39% of the total potentially plant-available N.

**Table 2.7** Chemical characterization of O<sub>a</sub> horizon organic matter from a Norway spruce (*Picea abies*) stand in Sweden (Data from Johnsson et al. 1999)

Parameter	Concentration (mg kg <sup>-1</sup> )
Total C	344,000
Total N	9970 ± 1130
Extractable NH <sub>4</sub> <sup>+</sup>	113 ± 9
Extractable NO <sub>3</sub> <sup>-</sup>	0.45 ± 0.06
Total organic N	9860 ± 1124
Amino acid N	3540 ± 451
Amino sugar N	469 ± 77
Glucosamine	374 ± 61
Other forms of N	> 5137

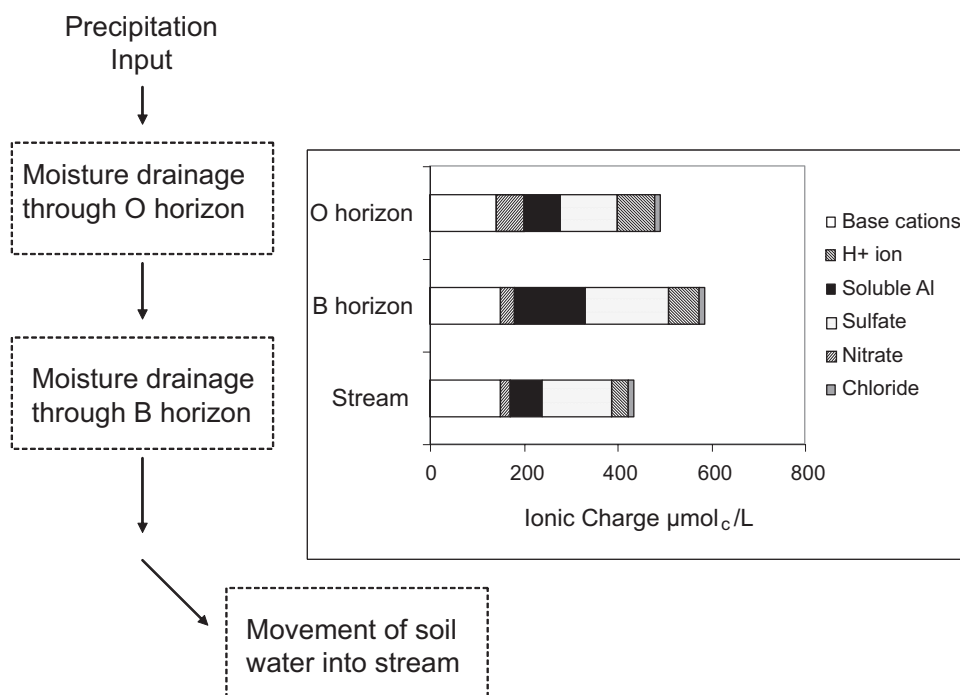
## Patterns of Soil Solution Chemistry

In addition to having variable patterns of solid phase chemistry, soil profiles also reveal striking differences in soil solution chemistry sampled with **lysimeters** or aqueous extraction. Figure 2.21 presents a comparison of solution chemistry sampled in the O and B horizons of the New York Spodosol shown in Fig. 2.18, along with stream water chemistry draining the same watershed. To the left of the figure, the flow diagram depicts the spatial sampling context for the three water samples. Each stacked bar provides a composite chemical description and proportions of ionic charge equivalents contributed by different soluble cations and anions in the O horizon, B horizon, and stream samples. It is clear that dynamic changes are observed moving through the vertical sampling gradient. For example, H<sup>+</sup> ion and nitrate concentrations decrease substantially from O horizon to stream runoff, whereas soluble Al peaks in the B horizon and declines in transit to the stream. What other changes do you see and how might you account for them?

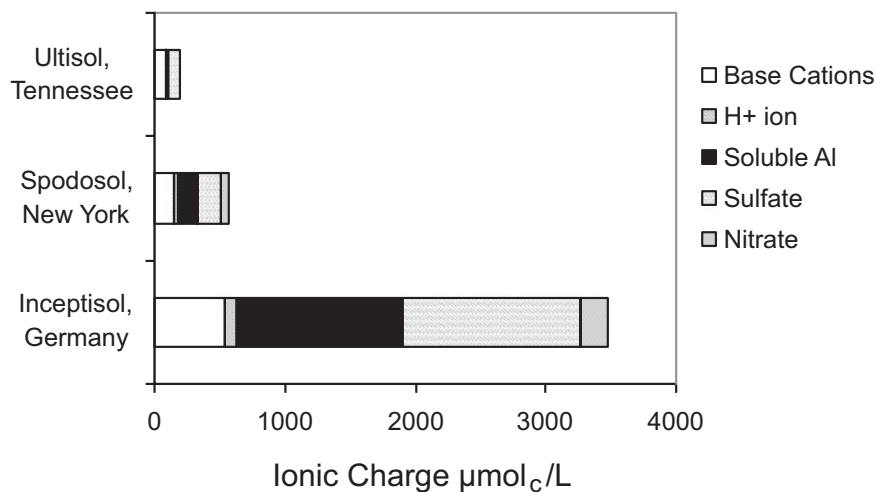
If we next compare the B horizon solution from Fig. 2.21 with two contrasting B horizons from other geographic locations, it is possible to glimpse the range of biogeochemical differences that can be observed among soils in different environmental settings. In Fig. 2.22, the three soil solutions from B horizons in New York, Tennessee, and Germany vary in ionic concentrations by a factor of ten and exhibit considerable variation in chemical composition. How can we account for these differences?

As it turns out, the contrasting chemistries for soil solutions at the three sites depicted in Fig. 2.22 are largely the result of differences in soil solid phase chemistry, atmospheric inputs of sulfuric and nitric acids, and ion exchange and adsorption processes in each soil. For example, there is relatively little ionic leaching at the Tennessee watershed, because of the strong influence of plant nitrate absorption and soil sulfate adsorption in this southern Ultisol. When nitrate and sulfate ions are removed from infiltrating

**Fig. 2.21** Charge balance relationships for major cations and anions in soil solutions and stream water at Big Moose watershed, NY (Data from Cronan et al. 1990)



**Fig. 2.22** Comparison of soil solution chemistries for acidic B horizons from a Tennessee Ultisol, a New York Spodosol, and a German Inceptisol exposed to respective sulfur deposition inputs of 20, 18, and 88 kg S ha<sup>-1</sup> yr<sup>-1</sup> (Data from Cronan 1994)



precipitation moisture, charge balance principles mandate a corresponding decrease in leaching of soluble cations derived from atmospheric deposition or soil cation exchange reactions. At the other extreme, the German site is a location with very large inputs of atmospheric sulfate (H<sub>2</sub>SO<sub>4</sub>) and nitrate (HNO<sub>3</sub>) and limited retention of those mobile

anions by soil adsorption and plant absorption processes. As a consequence, sulfuric and nitric acid inputs to the German forest soil generate substantial leaching of exchangeable soil cations released by H<sup>+</sup> exchange.

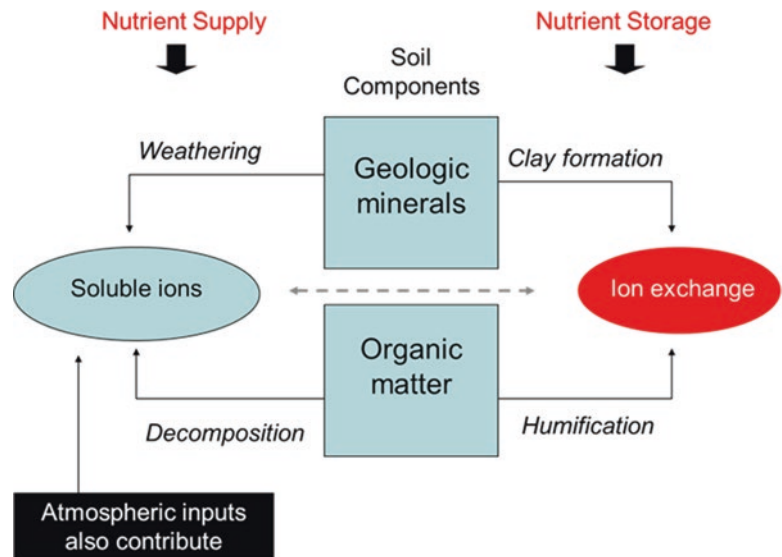
*Note: Concepts of soil solution chemistry introduced in this chapter will be examined in further detail in Chap. 9.*

## Integrated Processes of Nutrient Supply and Storage in Soils

In concluding this chapter, we can note that soils provide a remarkable system of nutrient supply and storage based on integrated contributions from geologic and organic source materials. As depicted in Fig. 2.23, geologic materials serve

both as a source of soluble nutrients and a substrate for the formation of clay minerals that contribute to ion exchange capacity. Likewise, detrital organic matter in the soil environment decomposes to release soluble nutrients, accompanied by the generation of soil humus that enriches the ion exchange capacity of the soil. As a whole, these processes and properties provide the basis for soil fertility and biological productivity.

**Fig. 2.23** A conceptual diagram illustrating how geologic and organic materials contribute to nutrient supply and nutrient storage in soils



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