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How Deep Is Soil?

Soil, the zone of the earth's crust that is biologically active, is much deeper than has been thought by many ecologists

Daniel D. Richter and Daniel Markewitz

Earth is a most remarkable planet but not only because of its prodigious life, vast oceans, and oxygen-enriched atmosphere. Earth is remarkable because of its soil.

Soil is the biologically excited layer of the earth's crust. It is an organized mixture of organic and mineral matter. Soil is created by and responsive to organisms, climate, geologic processes, and the chemistry of the aboveground atmosphere. Soil is the rooting zone for terrestrial plants and the filtration medium that influences the quality and quantity of Earth's waters. Soil supports the nearly unexplored communities of microorganisms that decompose organic matter and recirculate many of the biosphere's chemical elements. Ecologists consider soil to be the central processing unit of the earth's environment (Sanchez 1994).

One of the most significant outcomes of biological evolution has been the coevolution of soil and terrestrial ecosystems. This coevolution was initiated during the Devonian era, approximately 350 million years ago. Plants spread across upland continental regions during the explosion of life that led directly

Once soils were considered only as deep as a plow could cultivate, but analysis of biogenic processes illustrates that many soils are tens of meters deep

to today's soils (Algeo et al. 1995, Retallack 1992). During the Devonian, the early forest ecosystems became complex, containing large, seed-bearing trees that were deeply rooted. As ecosystems affected and were affected by an increasing depth and volume of soil, respiration from roots and microbes increased the concentration of carbon dioxide in soil atmospheres, weathering underground rocks via carbonic acid dissolution and releasing nutrients for subsequent root and microbial uptake. Although there are various perspectives on the coevolution of soil and ecosystems (Beerbauer 1985, Berner 1992, Holland 1984, Keller and Wood 1993, Schwartzman and Volk 1991), soil changes and developments such as these are called soil genesis, or pedogenesis. Some typical soils that form during soil genesis are illustrated in Figure 1.

Scientific understanding about soil developed rapidly during the

nineteenth and early twentieth centuries in Russia, western Europe, and North America. The developments of soil science were propelled by both the practical need to increase crop-plant production and the basic scientific desire to understand soil as a natural component of ecosystems (i.e., to understand soil genesis). Soil science began as the study of temperate zones, often motivated by agricultural application. Now, soil science is more global and its applications are environmental as well as agricultural. Recent decades have brought enhanced agricultural yields and a better understanding of the depth of the biota's influence zone (Creemans et al. 1994, Holland and Zbinden 1988, Nepsted et al. 1994, Sinclair and Ghiorse 1989, Stone and Kalisz 1991); widely used systems of quantitative soil classification (Buol et al. 1989, Richter and Babbar 1991, Soil Survey Staff 1992); the first soil surveys and maps of enormous regions of the tropics (Richter and Babbar 1991); and increased application of soil sciences to environmental problems such as soil and water pollution, ecosystem sustainability, and soil-atmospheric issues that involve carbon dioxide, nitrous oxide, and methane (Sanchez 1994).

Throughout the development of soil science, the concept of soil as a component of ecosystems has included increasingly deeper layers of the earth's crust. Chizhikov (1968) traced this pattern, starting in late nineteenth-century Russia when only surface accumulations of soil or-

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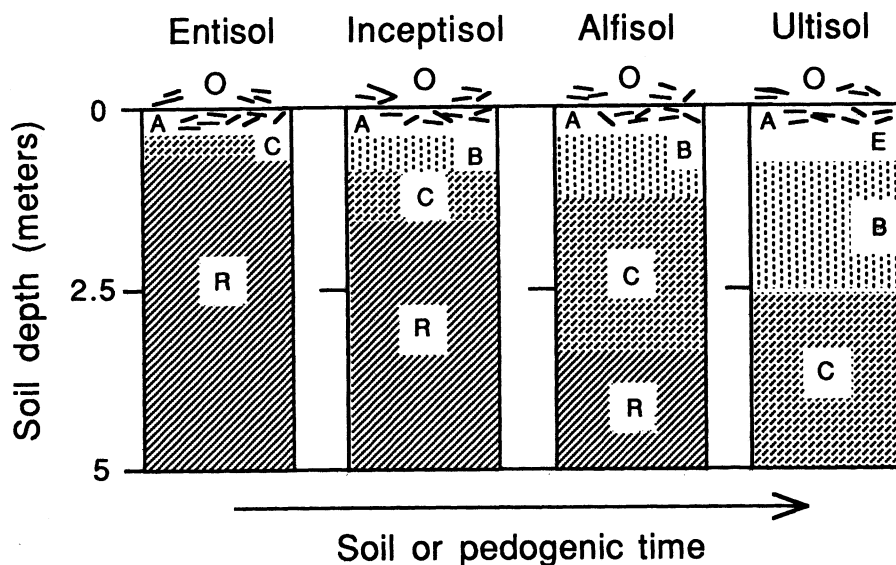


Figure 1. Some common soil orders and soil horizons that result from the ecosystem process we called soil genesis. The illustrated soils from left to right constitute a general age sequence of soil development (i.e., a chronosequence). Soil horizons such as the O, A, E, B, and C horizons and the underlying unweathered rock (R) are shown. The soil chronosequence illustrates the gradual formation of the B and C horizons and the deepening of the soil profile through time. When organic matter initially accumulates in O and A horizons, an Entisol is formed, and soil formation is initiated. Entisols exhibit a simple soil profile with A and C horizons. Once a B horizon develops, the soil is classified as an Inceptisol. Both Entisols and Inceptisols are often youthful soils, not strongly weathered. Alfisols form following more intensive weathering and as clays accumulate within the B horizons. Generally, Alfisols are not strongly acidified and are often nutrient-rich. The products of Alfisol acidification are often Ultisols. Like Alfisols, Ultisols have high clay contents in their B horizons, but in Ultisols these clayey B horizons are strongly acidic and are highly weathered.

ganic matter were considered to be the soil. These upper layers are now called the O and A horizons. Occasionally, below the A is an E horizon, which is notable for its low organic matter, clay, and iron. The concept of soil deepened, as repeatable characteristics of roughly horizontal layers, now referred to as the B horizons, were recognized below the A, O, and E horizons. The B horizons differed from the other horizons in being enriched with clay, iron, aluminum, and sometimes salts. The B horizons are also distinguished by their typically lower concentration of organic matter. Eventually, a C horizon, or the so-called parent material, was recognized to lie beneath the B horizons.

There is disagreement whether the C horizon is less integral a part of the soil than are the A, O, E, and B horizons (Brady 1990, Buol et al. 1989, Fanning and Fanning 1989, Harpstead et al. 1988, Jenny 1941, 1980, Plaster 1992, Ramaan 1928,

Richter et al. 1994b, Troeh and Thompson 1993, Ugolini et al. 1977). For example, the C horizon is often considered to be a part of the geologic domain and thus "little influenced by soil-forming processes" (Soil Survey Staff 1975, 1992). The C horizon's most critical role for the soil may be to provide the material from which the more superficial horizons are formed. Some widely used textbooks describe the C to be the regolith, loose, unconsolidated rock that often lies above bedrock (Brady 1990), and others use the term *true soil* to describe the A, O, E, and B horizons (Plaster 1992). These perspectives diminish the C horizon as an important component of the soil system.

On the other hand, the C horizon is classified as an integral part of the soil by many scientists throughout the history of soil science. Ramaan (1928) conceived of soil as simply being "the entire upper weathering layer of the earth's crust," a layer

that includes the C horizon. Glinka (1931) stated that soil was not only the entire weathering zone of the earth's crust but that many soils were tens of meters deep. Hunt (1986) referred to the thin, upper A and B horizons of the full weathering crust as "agriculturists' soil," at least partly in an effort to develop a broader perspective about the soil and weathering processes of the earth's crust.

The C horizon is currently of great scientific interest, whether or not it is viewed as an integral component of the soil (Brady 1990, Brimhall et al. 1991, Chapelle 1993, Graham et al. 1994, Holland 1984, Nepstedt et al. 1994, Pavich 1986, Richter et al. 1994b, Schlesinger 1991, Soil Survey Staff 1992, Stolt et al. 1992, Stone and Kalisz 1991). It is far more voluminous than the horizons above. The C horizon has been the topic of recent investigation by water resource scientists interested in control of water chemistry, runoff, and the fate of chemical pollutants; plant-soil scientists interested in deep rooting and subsoil fertility; and soil scientists (i.e., pedologists) interested in a wide range of issues from global biogeochemistry to watershed and ecosystem management. Due to the burgeoning interest in C horizons, Buol (1994) recently led a large group of soil scientists, engineers, and geologists that developed the first taxonomy of C horizons.

Although there are many perspectives on the lower boundary of the soil, many ecology, soil, and geology texts use the dichotomous concept of soil and parent material to describe the earth's weathered zone. In other words, soil is the relatively thin O, A, E, and B horizons that are positioned above the C-horizon parent material, which is highly variable in depth (Brady 1990, Plaster 1992, Troeh and Thompson 1993). The lower boundary of soil is difficult to determine precisely, so the Soil Survey Staff (1992) recommended that, for convenience, the lower limit of soil be considered to be at a depth of 2 meters.

Like other Russian ecological soil scientists beginning in the nineteenth century with V. V. Dokuschaev (Chizhikov 1968, Sibertzev 1914), Hans Jenny (1941, 1980) and in the

United States E. W. Hilgard (Jenny 1961) conceived of soil as being the material that resulted from the interaction of biota, climate, geologic substrate, topography, and time. We share these classical views of soil and present data to argue that if soil is conceived with the perspective of Jenny (1941, 1980), we must explicitly include the C horizon within the concept of soil. The C horizon is formed or affected by soil-forming processes, often being highly influenced by soil biological processes (Calvert et al. 1980). Because the C horizon is often the thickest and most voluminous of all soil horizons, its omission from what we conceive to be the biological influence zone of the earth's crust would be a serious shortcoming.

Characterizing soil's lower boundary

Our objective in this article is to examine several biologic processes that can help characterize the lower boundary of soil. We contend that depth of many soils is much greater than that described in many textbooks. The intense biogenic and chemical influences of many C horizons is inconsistent with the idea that the C horizon is little influenced by soil-forming processes. We examine deep spatial and temporal patterns of three reaction products of biologic activity: carbon dioxide in soil atmosphere, carbonic acid in soil solution, and soil-exchangeable acidity (Binkley and Richter 1987).

The three products of respiration activity have been examined in deep soils at the Calhoun Experimental Forest in the southern Piedmont of South Carolina. We hypothesize the generalities drawn about the lower boundary of the Calhoun soil can be applied, with minor modification, to many soils and ecosystems. In this article, we first describe the Calhoun Experimental Forest, highlighting the extreme acidity and weathering of soil studied to a depth of more than 8 m. We then examine the biogeochemistry of gas, liquid, and solid phases of these deep Calhoun soils, specifically:

- respiration-derived carbon dioxide in pores of the upper 6

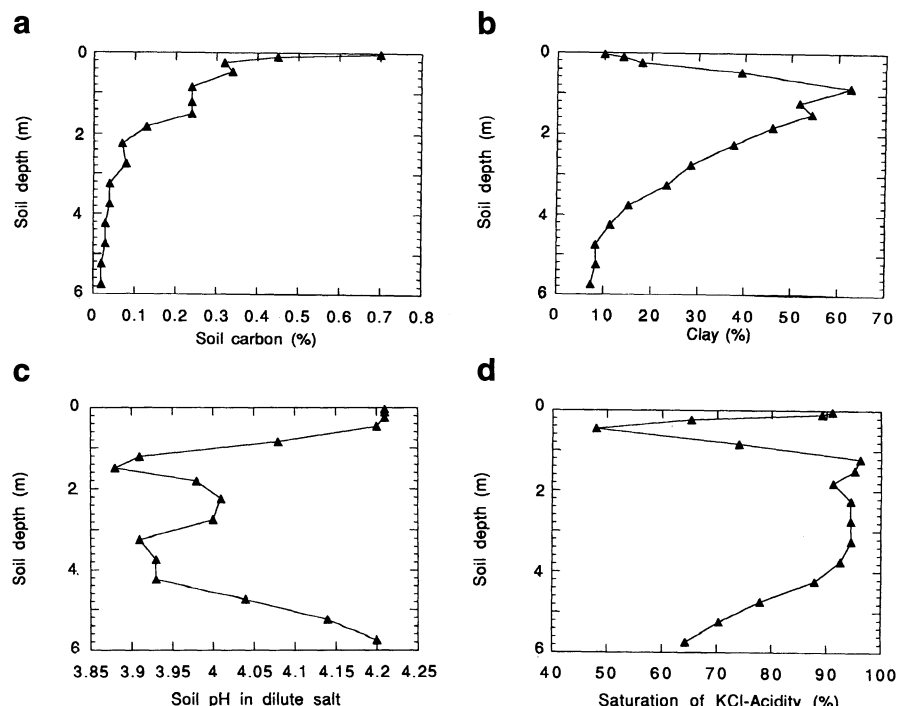


Figure 2. Soil properties often vary in regular patterns with depth. The illustrated example is the Ultisol soil of the South Carolina Piedmont at the Calhoun Experimental Forest. The Ultisol soil is old and highly weathered. (a) Soil organic carbon has a steep gradient with depth, decreasing from 0.7% in the upper 7.5 centimeters of the A horizon down to approximately 0.03% in the C horizon at more than 4-meter depth. With increasing depth, the soil carbon is increasingly old; the soil carbon at more than 2 m has an equivalent ^{14}C -age of 4500 to 8000 years since photosynthetic fixation. (b) Percentage of clay has a maximum (63%) in the B horizon and is much lower above and below this depth. Clay moves from the A and E horizons to accumulate in the B horizon. In this Ultisol soil, the clay is predominantly a crystalline mineral known as kaolinite and is highly acidic with iron-oxide coatings. These iron-oxide-rich clays are common to many of the world's most weathered soils and are resistant to further weathering and decomposition. (c) The Calhoun soil is low in pH (less than 4.2) throughout the entire 6-meter profile. In contrast, the granite-gneiss bedrock from which these soils are derived has a pH of 7.9. (d) Soils have large amounts of exchangeable acidity. Soil clays and organic matter have a primarily negative charge, known as cation exchange capacity (CEC), which attracts and adsorbs nutrient and acidic cations (positive ions). In low-fertility Ultisols, few of these adsorbed cations are nutrients, most are acids. In the extremely acidic Appling soil, much of the profile has more than 90% of its negative charge balanced by acids.

m of soil;

- sources of acidity in these forested soils including not only the carbonic acid system but also organic, nitric, and sulfuric acids;
- extreme acidity and thus of weathering of an entire 8-meter depth of soil.

These chemical data emphasize the intensity with which respiration-derived carbonic acid can acidify soil and weather enormous volumes of the earth's crust. Temporal patterns of soil carbon diox-

ide and dissolved carbonic acid are used along with soil acidity to emphasize that soil must be considered to include not only O, A, E, and B horizons but also the C horizons. Because the C horizon is probably most often the soil layer with highest carbon dioxide concentration (Amundson and Davidson 1990), it is apt to be acidifying in humid climates and may be intensively weathered. We agree with Glinka (1931) and other environmentally and ecologically oriented soil scientists that soil can be many tens of meters thick.

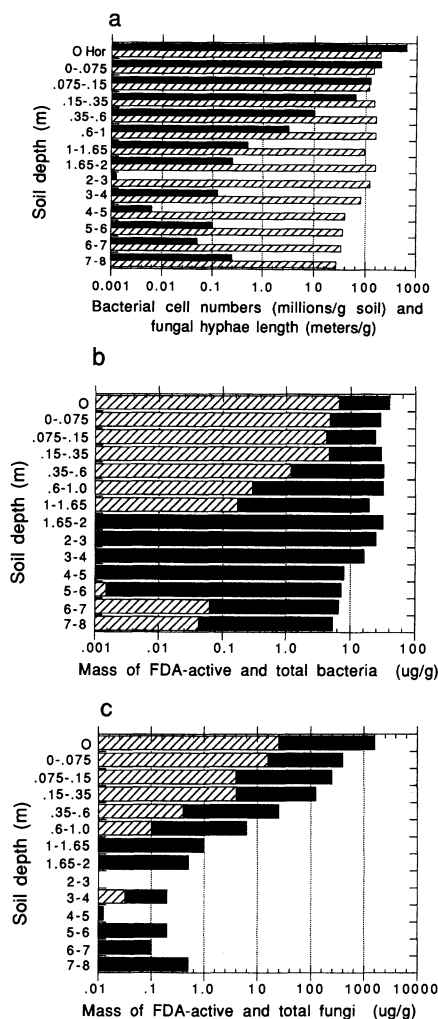


Figure 3. Microbes are prolific throughout the Calhoun soil profile, with bacterial cells present in high numbers throughout the 8-meter profile and fungi most prolific in the surficial horizons. (a) Bacterial cells number greater than 1.8×10^7 per gram of soil in all parts of the profile, whereas fungi have a total length of hyphae, living and dead, that reaches 0.59 km/g of soil in the O horizon but are less than 0.0001 km/g at the depths of 2 to 8 meters. (b and c) Total and active mass of bacteria and fungi are expressed in ug/g, with active fractions determined by fluorescein diacetate stain (FDA). ■ is total bacterial or fungal-hyphal counts, ▨ is FDA-active bacteria or fungi. Data courtesy of E. Ingham, Soil Microbial Biomass Service, Oregon State University, Corvallis, OR.

The Calhoun Experimental Forest

The research area at the Calhoun Experimental Forest is a loblolly pine forest whose forest-soil bio-

geochemistry has been studied for nearly four decades (Binkley et al. 1989, Richter et al. 1994a, b, Wells and Jorgensen 1975). Like much of the Carolina Piedmont, the research area supported row crops of cotton, corn, and wheat from the mid- to late-1700s through the first half of the twentieth century. Before the US Civil War in the 1860s, a shifting cultivation was typically practiced, whereas after the war, agricultural practices included more continuous cropping and increased use of lime, fertilizer, and soil conservation practices (Trimble 1974). In 1954, the last crop of cotton on the Calhoun research area was followed by a two-year fallow, after which loblolly pine (*Pinus taeda* L.) seedlings derived from seeds were planted in the winter of 1956–1957. Loblolly pines are native to the area.

The experimental site is located on two old cotton fields with less than 3% slopes that have soils classified as the Appling soil series. A soil series is a taxonomic category approximating that of a species for organisms. The Appling soil series is an acidic soil derived directly from the granite bedrock underneath, with relatively thick A and E horizons of sandy material that overlie approximately 2 m of acidic, clayey B horizons. The Appling's B horizons lie on top of more than 5 m of acidic, highly weathered C horizons, also called saprolite.

The Ultisol soil order. The Appling series belongs to the Ultisol soil order, one of 11 soil orders in the world. Ultisols (Figure 1) are best known for their clayey B horizons, which are acidic and low in fertility, and for their common occurrence on all continents having warm and humid regions. Ultisols dominate much of the landscape of the southeastern United States, where they support nearly 20 million ha of southern pine ecosystems (Richter and Markewitz 1995). Ultisols are also one of the most common soils in the tropics (Richter and Babbar 1991).

In the tropics, Ultisols cover more than 550 million ha, with large areas in the Brazilian Amazon (110 million ha) and in tropical Asia (250 million ha). Ultisols are concentrated

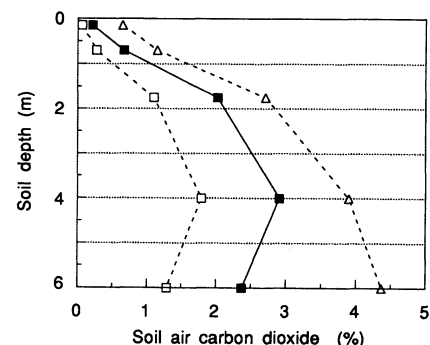


Figure 4. Carbon dioxide concentrations in soil atmospheres from 6-meter profiles at the Calhoun Experimental Forest. ■ is average concentrations in four or eight permanent plots over a three-year period (1992–1995). □ and Δ represent extreme values observed at a given soil depth. These data are replotted by date of measurement in Figure 5.

in warm, humid climates, which lead to intense weathering environments and soil leaching of silicon, calcium, magnesium, potassium, and sodium to drainage waters. Ultisols are some of the world's most highly weathered soils.

The Appling soil profile. At the Calhoun forest, aboveground air temperature averages approximately 16°C, annual precipitation averages approximately 1250 mm, annual evapotranspiration approximately 882 mm, and annual drainage loss approximately 368 mm (1973–1987). Surface soil temperature averages approximately the same as aboveground air temperature, but soil temperature has a much smaller range: In 1994–1995, soil temperature at 15 cm averaged 15°C and had approximately a 20°C range (from approximately 5° and 23°C); in contrast, temperature of aboveground air had at least 40°C range (from less than -5° to more than 35°C).

The Appling soil was cultivated with cotton for decades; it has now been under a forest stand of loblolly pine for nearly 40 years (1957–present) and has accumulated approximately 70 metric tons/ha of organic forest floor on the soil surface. This O horizon is composed mainly of pine needles and wood litter. It has many active fine roots and is extremely acidic (pH less than

4), due to its concentration of organic acids (Richter et al. 1994b). Under this organic layer is a sandy A horizon, the former plow layer, which now is intensively rooted by pine (Richter et al. 1994a). This 0.15-meter A horizon has only approximately 0.57% organic carbon (Figure 2a), a concentration that is slowly accumulating under the pine forest (Richter et al. 1994b). Before the current pine forest, soil carbon had been reduced due to cultivation-caused mixing, elevated soil temperature in the absence of shade, and reduced organic inputs. These sandy surface soils also have a relatively low potential to accumulate organic matter compared with soils that are more fine-textured and clayey.

Below the A horizon, the E horizon is sandy, well aerated, and low in iron, aluminum, and clay; the iron, aluminum, and clay have been mobilized and redeposited in the B horizon (Figure 2b). The B horizons are approximately 2 m in total thickness and are dominated by acidic kaolinite clay and iron oxides—two materials highly resistant to further weathering (Richter and Babbar 1991). Below the B horizon, the C horizon is many meters thick (more than 5 m) and is extensively rooted and acidic (Figure 2c and 2d). Only in the deepest part of the C horizon, directly adjacent to bedrock (Calvert et al. 1980), does the material appear to become much less acidic. The granite-gneiss rock that underlies the Appling soil is pH 7.9.

The full soil profile is deep by many measures. It is deeply rooted, with pine roots observed at 4-meter depths. The hydrologic rooting depth of the current pine ecosystem exceeds 3 m, based on pronounced seasonality of soil water depletion and recharge at this depth. The full soil profile is also heavily populated by microbes (Figure 3). Remarkably, bacterial mass, highest in surficial horizons, declines only slightly with depth. Bacterial numbers are more than 1.2×10^8 cells/g of soil in samples from the upper 1 m, and they decrease to approximately 1.8×10^7 cells/g in soil from the 8-meter depth (Figure 3). Total bacterial mass is exceeded by fungal mass only in the O horizon (the forest

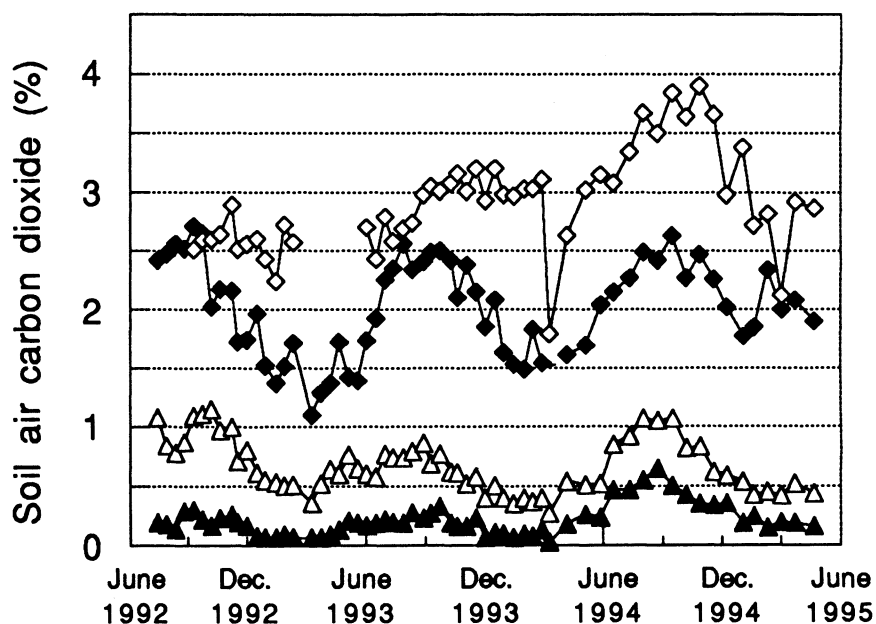


Figure 5. Seasonality of soil carbon dioxide illustrated by mean concentrations from four soil depths in four or eight permanent plots in the Calhoun soil profile. ▲ is carbon dioxide concentrations of soil at 0.15 m, Δ is concentrations at 0.6 m, ◆ is concentrations at 1.75 m, and ◇ is concentrations at 4.0 m.

floor) and in the thin layer of mineral soil between the surface and 0.35 m, the A and E horizons (Figure 3). Bacterial cells whose cell membranes are reactive with fluorescein diacetate stain are present throughout the 8 m of soil, whereas fungi reactive with that stain are observed only in surficial horizons. Respiring biomass is found throughout the 8-meter soil profile.

The gas phase: Belowground carbon dioxide

Soil respiration of plant roots and soil organisms greatly elevates carbon dioxide throughout the belowground atmosphere. Although carbon dioxide production is highest in surficial layers, carbon dioxide increases in concentration with increasing profile depth as a result of restricted diffusion of gases within soil pores. This phenomena is widely observed in soils of terrestrial ecosystems (Amundson and Davidson 1990).

Based on measurements made at the Calhoun Experimental Forest every two or three weeks between 1992 and 1994, carbon dioxide averaged approximately 0.035% aboveground but was higher below-

ground. It was measured at 0.13% to 0.21% in the A horizon, at 0.41% to 2.01% in the B horizon, and at 2.37% to 2.91% in the C horizon (Figure 4). The gradient of carbon dioxide concentration with soil depth is attributed to two main factors: carbon dioxide production and diffusion through the soil. Increasing concentrations of carbon dioxide with soil depth indicates prominent production of carbon dioxide via respiration of roots and microbes throughout at least the upper 4 m of soil. The concentration with depth also is affected by the upward molecular diffusion of the gas through the pores of the various horizons until it exchanges with the aboveground atmosphere. The coarse-textured A and E horizons allow rapid diffusion of gases in and out of the soil. The clayey B horizon retards carbon dioxide diffusion with its relatively low diffusivity. In B and C horizons carbon dioxide accumulates 83-fold higher than in concentrations of aboveground air.

Soil carbon-dioxide concentrations are strongly seasonal within the 6-meter profile; they correspond to the seasonality of biological activity (Figure 4). During the growing season, a wave of carbon diox-

ide penetrates the air-filled pore space of all subsoil horizons, especially late in the growing season (Figure 5). In contrast, by late winter, concentrations of carbon dioxide are lowest at all soil depths.

There is a larger difference in carbon-dioxide concentration among the layers in the growing season than in the winter (Figure 4). Like respiration, diffusivity of carbon dioxide is also strongly seasonal. Upward diffusion during the growing season is higher not only due to increased soil respiration but also due to soil drying, which opens soil pores especially during late summer and fall months.

The solution phase: Three acid sources

In addition to physical processes of crustal weathering, it is biogenic acidification that transforms rocks into soil. Biogenic acidification solubilizes and releases rockbound elements in a process called mineral weathering. In weathering, nutrients are released from primary rock minerals in bioavailable forms. Nutrients liberated from rock are taken up by plant roots and microbes, recombined into secondary minerals, and lost to groundwater aquifers and rivers and eventually to the oceans. Although textbooks in many disciplines refer to this collection of weathering reactions as "chemical" or "geochemical," this chemistry is so biogenic in its origin that concepts of mineral weathering might better be described with terminology that explicitly recognizes the biogenic and biogeochemical nature of crustal weathering.

A soil's acidity is largely the integrated expression of many biological processes that circulate chemical elements in ecosystems (Table 1). At the Calhoun forest, contributions to soil acidity include organic acids, sulfuric acid, carbonic acid, and the ion-uptake dynamics of the growing pine stand. Nitrification—the microbial oxidation of ammonium to nitric acid—is a minor part of the current acid budget at Calhoun, though in some ecosystems it is more significant (Driscoll and Likens 1982, van Miegroet and Cole 1985). Although tree uptake of cations con-

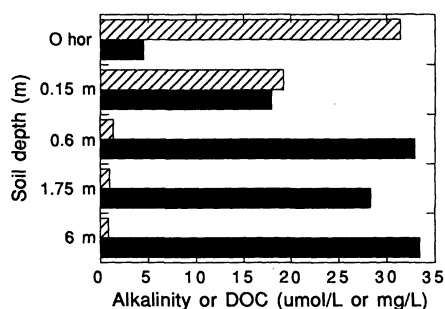


Figure 6. The carbon cycle affects soil acidity by contributing organic and inorganic carbon compounds to soil solution. This effect is illustrated at the Calhoun forest with concentrations of dissolved organic acid (DOC) and alkalinity in precipitation water as it infiltrates into the mineral soil profile (O horizon) and percolates through the A, B, and C horizons. ▨ is dissolved organic carbon (mg/L of DOC) and ■ is alkalinity (μmol/L). The organic carbon compounds are acidic and most concentrated in surficial soil horizons, whereas HCO_3^- alkalinity increases in concentration with soil depth. In fact, below 6 m, alkalinity continues to increase in concentration as a result of carbonic acid-driven mineral weathering, averaging 375 μmol/L in a nearby stream that drains these deep soils.

tributes acidity to soils (Richter 1986, Richter et al. 1994a), we lack data on its significance in deep horizons.

Organic acids. At the Calhoun forest, organic acids and atmospheric acids contribute mainly to the acidity of surficial horizons (Richter et al. 1994a, b). Based on chemical analysis of rainfall and soil solutions (Richter et al. 1994a, b) collected over a two-year period (1992–1994), organic acids that originate from the pine forest canopy and forest floor leached with rainwater through the upper mineral soil but practically disappeared from soil solutions when the rainwater reached the upper B horizons at 0.6-meter soil depth (Richter et al. 1994b).

Dissolved organic carbon averaged 31.4 mg/L (approximately 2.6 mmol/L) in solutions that leached from the O horizon and infiltrated into the upper mineral soil (into the A horizon). However, by the time that the rainwater reached 0.6-meter

soil depth, dissolved organic carbon had decreased 22-fold in concentration to only 1.4 mg/L of carbon (Figure 6). These sharp decreases in dissolved organic carbon with soil depth demonstrated that organic acids were effectively adsorbed and decomposed as they percolated into the clayey B horizons (Richter et al. 1994b).

Organic acids and their ligands (their anionic form) dominate the chemistry of soil solutions near the surface of the profile. Organic acids, derived from the leaching of the pine foliar canopy and the heavy forest floor, averaged 145 μmol/L of anionic charge in water that infiltrates into the A horizon (Cronan et al. 1978). At 0.15-meter depth, the average anionic charge of the organic acid ligands is 87 μmol/L. Significantly, this organic acid charge approached zero in soil solutions collected at 0.6 m and deeper (Figure 6).

Despite sharply decreasing concentrations of organic compounds with soil depth, organic acids do affect weathering reactions and acidification in the profile deeper than 0.6 m. These interactions are most concentrated in rhizospheres (i.e., localized preferential zones of rooting). At depths of 2–3 m, soil in intimate contact with roots had 2.5-fold more total bacteria per gram of soil than the bulk soil at this depth. The only fungi observed at this soil depth were found in rhizosphere soil. Organic acid weathering no doubt plays an important role in rhizospheres that are so biologically active.

Atmospheric deposition. Like organic acids, atmospheric acids also contribute to the acidity of surface layers. Sulfate, derived mainly from acid precipitation but also from microbial oxidation of organic sulfur, leaches through O and A horizons into upper B horizons at 0.6 m. Immediately below 0.6 m, however, sulfate is strongly adsorbed and retained by B horizons, presumably adsorbed to iron oxides and kaolin clay. For example, solution sulfate decreased from approximately 178 μmol/L at 0.6-meter soil depth to only 32 μmol/L at 1.75 m. Strong adsorption of sulfate to B horizons

has also been demonstrated in laboratory experiments.

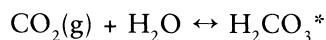
Overall, the annual acid deposition at the Calhoun forest is in the range of 0.5 to 0.75 kmol/ha. This deposition is minute compared to the exchangeable acidity in the deep soil profile (approximately 3000 kmol/ha in 8 m of soil).

The carbonic acid system. Our interest in biogenic acidification and the weathering of deep soil horizons has turned to soil respiration and carbon dioxide, the soil solution's carbonic acid system. Given enough time, warmth, and humidity, the carbonic acid system driven by high belowground carbon dioxide concentrations appears able to transform meters of granite into acidic kaolinite.

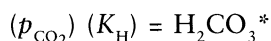
The acid biogeochemistry of the Calhoun forest demonstrates that the carbonic acid system can intensively acidify and weather enormous volumes of geologic material. Carbonic acid is the most important acidifying agent at more than 0.6 m within the Calhoun soils. Despite extreme soil acidity (Figures 2c and 2d), high concentrations of carbon dioxide in B and C horizons force approximately 30 $\mu\text{mol/L}$ of carbonic acid to deprotonate (Figure 6) and approximately 0.1 to 0.2 kmol/ha of bicarbonate salts to leach. The water that drains through the entire soil system emerges in a small stream that averages 375 $\mu\text{mol/L}$ alkalinity with pH more than 7.0. This pattern of carbon dioxide and alkalinity within the soil (Figure 6) indicates that weathering reactions consume acidity from carbonic acid and generate alkalinity at depths of more than 6 m directly as a result of biogenic soil respiration.

The high partial pressures of carbon dioxide from belowground respiration create a solution system with a great potential for acidification and weathering. Belowground carbon dioxide and carbonic acid strongly affect not only weathering reactions and acidity of the soil system but also influence the water chemistry of most of the world's ecosystems including streams, lakes, and oceans. For this reason, the carbonic acid system is worth summarizing for the soil's liquid phase

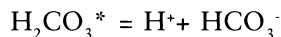
(Stumm and Morgan 1981):



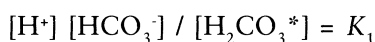
which is mathematically expressed:



where p_{CO_2} is the partial pressure of carbon dioxide, K_{H} is Henry's constant ($10^{-1.32}$ at 15°C and low ionic strength), and H_2CO_3^* is the sum of the carbon dioxide that is dissolved and hydrated ($\text{CO}_{2(\text{aq})}$ and H_2CO_3 , respectively). True carbonic acid, H_2CO_3^* , is typically a small fraction of H_2CO_3^* , thus hydration of $\text{CO}_{2(\text{aq})}$ to H_2CO_3 can be an important rate controlling process. In turn, H_2CO_3^* rapidly dissociates to H^+ and HCO_3^- :



which is mathematically stated:



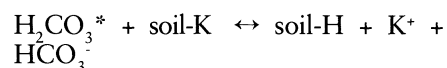
where K_1 is the first dissociation constant of carbonic acid, $10^{-6.419}$ at 15°C .

In the Calhoun soil, carbonic acid is currently the major source of pro-

tons to the soil solids from the 0.6-meter depth to bedrock, as illustrated by the soil-solution and stream chemistry. Given the relatively small magnitude of K_1 , it is remarkable that H_2CO_3^* continues to dissociate and acidify such an acidic soil.

The solid phase

The protons derived from soil respiration and carbonic acid participate in one of two reactions: one is proton exchange with the solid phase, displacing soil-adsorbed cations, summarized as:



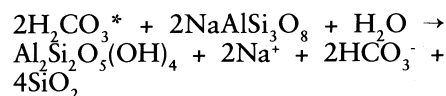
where products are acid-saturated soil (or Al-saturated soil; Thomas and Hargrove 1984) plus potassium-bicarbonate salt solution, which under humid conditions leaches and is lost from the soil profile. Similarly, exchangeable calcium, magnesium, and sodium may be displaced by H^+ from deprotonation of H_2CO_3^* and leached as bicarbonate salts.

The protons derived from soil respiration also react with soil min-

Table 1. The major sources of acidity that drive acid-induced weathering reactions in soils and rocks. Biologic processes are the most important generators of acidity in terrestrial ecosystems. Many of the details of this complex set of acidity reactions are well understood (Binkley and Richter 1987).

Acid source	Biotic process	References
Carbonic acid (H_2CO_3)	Plant and microbial respiration and accumulation of carbon dioxide belowground in soil pores; hydration of carbon dioxide, deprotonation of carbonic acid, and bicarbonate leaching	Johnson et al. 1977, Richter et al. 1994b
Organic acids	Complex products of plant detritus, microbial biomass, and decomposition reactions	Cronan et al. 1978
Nitric acid (HNO_3)	Microbial nitrification of ammonium; atmospherically deposited pollutants	van Breeman et al. 1982, van Miegroet and Cole 1985
Sulfuric acid (H_2SO_4)	Microbial oxidation of reduced forms of sulfur; atmospherically deposited pollutants	Driscoll and Likens 1982, van Breeman et al. 1982
Ion uptake by plants	The accumulation of tree biomass and forest floor, with a nutrient balance dominated by cations over anions, releases H^+ to rhizospheres to maintain ionic charge balance. Similarly, atmospheric NH_4^+ and NO_3^- deposition and uptake by roots or microbes releases H^+ or is a sink for H^+ in rhizospheres	Richter 1986, Richter et al. 1994a, Sollins et al. 1980

erals in a process known as mineral weathering. The mineral weathering of albite, a prominent primary mineral in granite, is summarized:



where reaction products are kaolinite plus sodium-bicarbonate salt and dissolved silica, which readily leach from the soil.

Soil acidity is extreme throughout 8 m of the Calhoun soil and can be quantified in several ways. First, soil pH is 4.2 or less in all soil layers above 6 m—a marked depression from the granite bedrock's pH of 7.9, which is a pH value far above any soil sample from the site (Figure 2c). Second, the soil's negative electrical charge (its effective cation exchange capacity) is charge-balanced almost entirely by exchangeable acidity (H^+ and Al^{3+}) rather than exchangeable nutrient cations (Figure 2d). This exchangeable acidity totals approximately 3000 kmol/ha down to 8 m, an enormous capacity of acidity that would require more than 150,000 kg/ha of calcium carbonate limestone to neutralize.

Even more impressive, however, is the amount of acidity needed to transform the granite-gneiss bedrock into an Ultisol soil that has lost nearly all of its primary minerals due to acidification and weathering. On the order of 100,000 kmol/ha of acidity have been consumed by each meter of granite in the Calhoun soil as the primary minerals in the granite-gneiss have been weathered into kaolinite. This enormous and extreme acidification emphasizes the C horizon's profound alteration from the original chemistry and mineralogy of the granite-gneiss bedrock. It also raises questions about the long-term sources of acidity that have so thoroughly transformed these deep soils (Table 1).

Remarkably, despite extreme soil acidity, soil solutions that continue to leach from the B and C horizons are slightly acidic, bicarbonate-salt solutions. Annual hydrologic flux of HCO_3^- alkalinity from 0.6 to 6 m depth was estimated to range from 0.11 to 0.22 kmol/ha in a two-year field and modeling study (Richter et

al. 1994b). This flux is also the net rate of acidification of the 6-meter soil profile from the carbonic acid system (Johnson et al. 1991, Richter 1986, Richter et al. 1994a). Despite carbonic acid being a weak acid, elevated carbon dioxide not only lowers soil solution pH to 5.0 or less, but it also forces the deprotonation of H_2CO_3^* and contributes to continued acidification of the already acidic soil. In sum, bicarbonate salts continue to leach from this soil despite the fact that exchangeable acidity dominates the soil's cation exchange capacity (Figure 2d).

Carbonic acid is sometimes considered to be limited in its potential to acidify soils (Reuss and Johnson 1986). Like weak acids in general, carbonic acid is less able to deprotonate as the soil system acidifies. The carbonic acid system may not be capable of solubilizing and leaching much Al^{3+} (Reuss and Johnson 1986), but on the other hand, high carbon dioxide appears readily able to intensively acidify the soil's solid phase. In the Calhoun forest, for example, soil carbon dioxide below 1.75-meter depth ranged between approximately 1.0% to more than 4.0%, forcing total dissolved and hydrated carbon dioxide (H_2CO_3^*) to occasionally exceed 1.0 mmol/L in soil solutions. Even though carbon dioxide-enrichment of solutions in the acidic B and C horizons lowers solution pH to 5.0 or even less, the carbonic acid system continues to acidify the soil as evidenced by titratable alkalinity and by theoretical calculations based on the equations of Stumm and Morgan (1981). Indeed, the small stream that drains from deep soil horizons from a part of the research area averages 375 $\mu\text{mol/L}$ in alkalinity, approximately tenfold higher than soil solutions collected at 6 m (Figure 6). Low flow stream samples that probably represent a higher fraction of deep soil water exceed 500 $\mu\text{mol/L}$. Carbonic acid that is derived from biotic respiration has a great potential to acidify deep soil layers of forest ecosystems.

A full-profile concept of soil

The depth distributions of soil carbon dioxide, carbonic acid chemis-

try, and soil acidity lead us to consider the entire 8-meter profile to be soil, so that the C horizon is as much a soil horizon as are the A or B horizons. All three phases of the deep soil profile—gas, liquid, and solid—bear the strong imprint of biologic activity. The entire profile of more than 8 m has been transformed by intense biogeochemical processes of a distinctly pedogenic nature.

Explicit recognition that the C horizon is a fundamental soil horizon that may be strongly affected by soil genesis and biological activity has two important implications. First, the explicit recognition of the C horizon as a fundamental soil horizon emphasizes that the weathering of the earth's crust is a biogenic or biogeochemical process. In fact, the overall crustal weathering process might more precisely be called biogeochemical weathering rather than geochemical weathering, due to the intensity of biologic processes in weathering materials.

Second, soil is much more voluminous than it is often conceived. For example, in the southern Piedmont and Ridge and Valley Provinces of the eastern United States, the A plus B horizons may be only 0.5 to 2.5 m in depth, whereas the A through C horizons range up to 50 m in depth. In the humid tropics, 20 m of weathered and highly acidic saprolites are found on the Malaysian peninsula (Eswaran and Bin 1978). Similar profiles up to 100 m deep are found on the island of Hong Kong (Carroll 1970, Ruxton and Berry 1957). These enormous soil volumes and their occupation by plant roots and microbes need more detailed exploration by biologists, ecologists, and soil scientists. These volumes of weathered crustal material must be better integrated into concepts of soil and the biosphere.

Marlin Cline (1961), in a classic paper about the evolution of conceptual models of soil, pointed toward a future potential need for the concept of soil to be extended downward to greater depths to accommodate nonagricultural perspectives of soil. Excellent reasons to extend the concept of soil downward and fully embrace the C horizon include the growing understanding of deep root-

ing and deep microbial proliferation (Nepsted et al. 1994, Sinclare and Ghiorse 1989, Stone and Kalisz 1991), the great interest and importance of deep-soil environmental problems, and the intensity of biogenic effects on deep soil materials.

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