SOILS AND NUTRIENT CYCLING

What is soil: - The unconsolidated mineral or organic matter on the surface of the earth that has been subjected to and shows effects of genetic and environmental factors of: climate (including water and temperature effects), and macro- and microorganisms, conditioned by relief, acting on parent material over a period of time. A product-soil differs from the material from which it is derived in many physical, chemical, biological, and morphological properties and characteristics. (From the Soil Science Society of America, 2003)


The chemical elements that function in ecosystems occur as neutral atoms, molecules, and electrically charged ions. The biotic portion of ecosystems (plants, animals, insects and other critters) are made up primarily of C, N, H, O held tightly together.

Soil is filled mostly with inorganic ions; a kin to billiard balls of various sizes with different amounts of charge. Silicate sand grains, for example, are “large” atoms of negatively charged oxygen and small strongly positively charges silicon ions. Less than 1% by weight of the ions in the soil are mobile; these include the nutrient ions: Ca, Mg, K, P, N, S, Fe, Zn, Mn, B. There are also other important ions in the soil that affect plants such as Al, Pb, As, Hg, and H. Most of these elements are accessed primarily through root systems from the soil; so we are interested in how these elements move from soils to plants and back to soils. To do this, we have to understand the electrical and chemical properties of soils.

Nutrient Cycling: Behavior of Ions in Soils

Soils are dominated by aluminosilicate crystals since these are some of the most stable, hard, and chemically resistant crystals which make up rocks and are subsequently weathered into soils. These crystals form various crystal lattice structures, which impart different properties to soil. From a nutrient cycling perspective, what is important to know is that the interior platy crystal and the exposed planar surfaces are electrically neutral (balanced); the electrical stray forces reside at exposed unsatisfied ions on the corners, edges, and verticals faces. These spots attract other ions, water molecules, and organic substances. The degree of weathering of a soil determines in part the numbers and ionic strength of these edges available for free ions to grab on to. The arrangements of the crystals are also important because they form interstitial spaces which can be where certain elements can get locked away from plant roots, like K or P in many ultisols and oxisols. When these crystals dissolve (weather) the freed ions go into solution and become highly reactive; many become fully hydrated (surrounded by water molecules). Many reassociate to form neutral pairs (NaCl);
In soils most ions are intimately associated with solid particles like clay and humus, limiting their mobility. They move through ion exchange. Most ion exchange goes on at the edges, corners and broken spots on tetrahedral or octahedral clays. Charge properties develop as the clay platelet is synthesized when a charge imbalance arises from the substitution of ions with different valence (for example Al$^{3+}$ for Si$^{4+}$). The oxygen plane then gains an extra unsatisfied negative charge; nature balances this by placing a cation on the exposed negative charge, but these bonds are relatively weak and the new cation is pulled back and forth from the surrounding water to the particle surface; the amount of cations held in this loose fashion is characterized as Cation Exchange Capacity (CEC).


Colloidal particles are clay (inorganic) and humus (organic), and are the small sized particles in soils where most of the chemical, physical, and biological processes occur. These are tiny particles (<2 micrometers in diameter). Because they are very small, they expose a large external surface area per unit mass (1 g clay has +1000 times more surface area than 1 g sand). Some have lots of internal surface area on plate-like crystals; clays can have as much as 10m$^2$/g with no internal surfaces to +800m$^2$/g with internal surfaces.

These surfaces, interior and exterior, carry positive and negative charges. For most soils colloids, electronegative charges predominate; the presence and activity of the charge influences the attraction or repulsion of particle towards each other, as well as the chemical and physical properties of the soil.

This charge sitting out there in space creates an attraction for ions of opposite charge to the colloidal surface; the colloidal particles are called micelles (for micro cells) attract cations (positively charged ions) such as K$^+$, Mg$^{2+}$, Al$^{3+}$, H$^+$. A negatively charged surface with a swarm of loosely attached (adsorbed) cations is called an ionic double layer. Water molecules also congregate near the negatively charged soil colloids both through attractions to the hydrated cations and also in the inner layer of the colloids.

There are 4 major types of colloids in soils: layer silicate clays, iron and aluminum oxide clays, allophane and other amorphous clays, and humus.

Layer Silicate Clays: these are crystalline clays with layered sheets of Si, Al, Mg, and/or Fe surrounded and help together by O and OH. These layers are made up of tetrahedral and octahedral sheets depending upon the composition of the primary mineral (Mg, Al or Si). As layered silicates weather, ions of similar size can replace the primary minerals in these sheets without changing the basic structure of the clay. Although these ions are of similar size, they are generally of different ion strength (Al$^{3+}$ for Si$^{4+}$) so this process, called isomorphous substitution, can change the charge properties of the clay and results in the wide variety of clays that exist in nature. The charge imbalances created through isomorphous substitution result in the net charge on the clay surface. Generally the negative charges predominate.
**Iron and Al oxides**: These are common in the southern US and in the tropics. These are often the classic red clays. They are predominantly gibbsite ($\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$) and goethite ($\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$), also written $\text{Al(OH)}_3$ and $\text{FeOOH}$. These clays vary between crystalline and amorphous, and are not as sticky or plastic as layer silicates. At high pH values, the micells carry a small negative charge; in very acid soils, these clays can carry a net positive charge that attracts anions instead of cations.

**Allophane and Other Amorphous Materials**: amorphous material or crystalline material that is not sufficiently structured to be detected with X-ray diffraction; allophane is derived from volcanic ash; has high cation and anion absorption capacity.

**Organic soil colloids**: organic matter dominantly C, O, and H; amorphous; generally negatively charged, but charge is pH dependent similar to Fe and Al oxides. When the organic matter is very acid the negative charge is low. In basic soils, the $\text{H}^+$ are replaced by adsorbed $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and other cations.

These colloids are where all the action is for nutrient availability in soils. The charged surfaces hold ions; ions are held preferentially depending upon their relative abundance; if all things were equal they would vary such that: $\text{Al}^{3+}>\text{Ca}^{2+}>\text{Mg}^{2+}>\text{K}^+=\text{NH}_4^+>\text{Na}^+$; these ions can be displaced relatively easily through cation exchange.

**Permanent Charge**: as weathering occurs (over very long time spans) isomorphous substitution takes place. When a smaller cation substitutes for a larger one (a $\text{Mg}^{2+}$ for an $\text{Al}^{3+}$) a negative charge goes unsatisfied resulting in a net negative charge. It is also possible for a cation of larger charge to substitute for one of lesser charge $\text{Al}^{3+}$ for $\text{Mg}^{2+}$. This results in a net positive charge. The net negative producing type substitutions are far more common than the net positive ones for layer silicate clays so that these are dominantly negatively charged. The rate at which these substitutions take place are so slow and they are so stable that we call these soils permanent or constant charge soils.

**pH dependent charge**: Kalonite which are 1:1 layer silicates, humus, allophane, and Fe and Al oxides have a different source of charges. The charges on these colloids is affected by pH since OH groups on the edges and surfaces of organic and inorganic colloids can dissociate as the pH changes. As the pH goes up, the H dissociates and produces a net negative charge. As the pH drops, there is less and less negative charge. In Al and Fe oxides, as well as some silicate clays, exposed OH groups in moderate to acid conditions experience protonation. This occurs as an $\text{H}^+$ attaches to the OH group forming $\text{OH}_2^-$. In theory changes in pH at one spot could make a soil go from a net negative charge (high pH) to no charge (intermediate pH) to positively charged (low pH). Since organic matter is generally negatively charged and it is usually present to some degree in most soils, there is a mix of positive and negative charges. In some tropical soils, anion exchange capacity can exceed cation exchange capacity.

**Cation Exchange**: soil colloids comprise a mix of positive and negative charges, even though most often the negative charges predominate. The ability of the soil to supply cations to plants is called cation exchange capacity (CEC). It is expressed as the moles of positive charge per unit of soil mass; to make the number more convenient we convert it to cmol$^+$/kg; for example if a
soil has a CEC of 10 cmol\(^+\)/kg it can adsorb 10 cmol\(^+\) of H\(^+\) per 1 kg soil and can replace those 10 cmol\(^+\) with 10 cmol\(^+\) of another monovalent cation like K\(^+\) or Na\(^+\); or it can be replaced by 5 cmol\(^+\) of a divalent cation such as Ca\(^{2+}\) or Mg\(^{2+}\); regardless the soil is attracting 10 cmol\(^+\) of positive charge; chemical equivalency must be maintained. In other words you can have a one for one exchange between H\(^+\) and K\(^+\), but 1 for ½ exchange with H\(^+\) for Ca\(^{2+}\); and 1 for 1/3 for Al\(^{3+}\).

CEC is determined by the relative amounts of colloids in the soils and the CEC of each type of colloid. Thus sandy soils have a lower CEC than clay soils or an organic soil; similarly a 1:1 clay like kaolinite or an iron and al oxide will have lower CEC than a 2:1 silicate clay with similar amounts of humus.

**Methods for determining CEC:** There are many methods to measure CEC. Soil scientists determined that we can estimate the number of available exchange sites on soil colloids by flushing a soil with a concentrated salt solution, usually NH\(_4\)Cl, KCl, or BaCl. The salt solution is concentrated with lots of monovalent ions and through laws of diffusion and mass flow we flood the exchange sites and knock off all the loosely held cations. These can then be analyzed separately; then we flood the system again, this time with a different monovalent cation and measure the NH\(_4\)^+ . We then measure the NH\(_4\)^+.

**Soil Taxonomy and Soil Orders**

Soil Profiles are like road cuts where a fresh face of soil is exposed showing the changes in color and texture with depth and showing the depth to which the plant roots grow. We can tell a lot from soil profiles since soil forming processes result in the color and texture variation we can observe. Profiles are described by the Soil Horizons: which are differentiated by colorations, plasticity, texture, and moisture and reflect the impacts of climate, vegetation patterns, and landuse. For example, At the Harvard Forest in Petersham, MA, you can dig a hole and see the various deposits of old farming eras buried within the soil, followed by succession to forest and then replacement by pastures or agriculture. Dark bands of smooth material is organic matter from farming. You may also see earthworm casts. At this site, whitish layers represent eluviated zones where all the iron and most of the other primary mineral have been leached out (due to the highly acid leachate from leaf litter decomposition). Below that is a layer of reds and browns called the layer of illuviation where material leached from above is deposited and accumulating. Some soils have grayish zones where the oxygen is decreased and the iron is in a reduced state, or reddish layers where the iron is oxidized. Iron is a good indicator of these processes because it commonly abundant and changes color in relation to the oxidation/reduction (or redox) of a soil.

**Soil classification systems** have been developed to describe soil profiles and there has been considerable efforts made to standardize techniques so that soils will be comparable. (Somewhat like the fact that tree diameters are measured at 1.3 meters above the ground, and the use of a particular taxonomic system like Cronquist for describing vegetation). The US soil conservation service has guidelines that are followed in the US, and the FAO has a different, but related system. In the US, we call the organic layer that generally resides on or very near the surface the O (for organic) horizon. This can be followed by the AO and the A horizon. The zone where the organic acids leach the primary minerals from the soil particles and leave a whitish layer,
sometimes called an E for elluviated layer. The A and AO horizons are layers that are definitely affected by the O layer, but not an O and not a B horizon. The B layer is the zone of accumulation of the stuff lost from above and the mineral soil from below. This can be divided into the B1-2, B22-23, the Bh, the Bs, Bir, etc., all referring to the chemical and physical characteristics of the soil, but distinguished by visual or tactical characteristics. Other layers: p (plow) which is a buried OA or A, a CA (carbonate or caliche layer), CN layer with concretions like Fe or Mn which form hard rock-like little balls of minerals, h (humic), g or m (mottling), m (hardpan or impermeable layer). Hans Jenny called soil classification using this type of system a fine art; as a first approximation it definitely has value.

Soil Color: Color is determined using a Munsell color chart: 175 color swatches are given numbers for hue (related to the wavelength of light), value (relative lightness), and chroma (relative purity diluted by grayness). For example, 2.5YR4/6 is a certain red; there are 8 blacks, although if you have a brown black or a black brown the opportunities are many more. Certain colors are generally associated with particular soil properties. Red is common in iron rich well aerated, well drained soil (rust); yellow is high iron, but less well drained or wetter. Black is often humus, but can be charcoal or other substances. Light gray and white is the absence of iron (elluviated horizons in spodosols or podzols). Mottling is when a soil has a mix of browns, oranges, and grays in irregular splotches indicating mixed drainage or poor drainage as the iron becomes reduced. All of these factors affect plants and soil organisms.

Soil Texture: Soil particles are stones, cobbles, gravel, sand, silt, clay, molecules, ions and electrons and everything in between. Soil texture is determined by the particle size distribution, which is generally classified by groups of sand, silt and clay sizes. One way that this is done is to immerse soil in water and time the rate at which different size particles settle out. At 20°C the settling velocity in cm/sec is \( v = 36,700 \, r^2 \) where \( r \) is the effective particle radius in centimeters. It is most accurate for the intermediate size particles (fine sand to fine clay). Based on size and weight, clay is <2 microns (µm), but larger than small molecules regardless of chemical or mineralogical composition. Soils are classified with regard to the texture triangle, and the percent sand, silt, and clay. People who are good at texture classification can characterize a soil texture by feel in the field. Particles size distribution makes a difference to plants. Clays have high surface area, sands tend to be made of silica and thus hold few plant nutrients. Clays hold more water, but may hold it so tight that plants can not get at it. Sand doesn’t hold water well at all.

Soil colloidal material is submicroscopic particles that glue soil together. These particles can be both organic and inorganically derived and tend to stick together and bind to larger particles with weak chemical bonds. Colloidal material affects the way in which water and salts move through soil and the chemical and physical nature of the soil.

Soil Structure: soil structure is often used as a descriptive tool in soil classification and refers to the grouping or arrangements of soil particles called aggregates or peds. Structure affects soil aeration, drainage, penetrability by roots or soil fauna, and heat transfer. Different management practices can dramatically change soil structure, which feeds back on plants. The common groupings for structural classification are plate-like, prism-like, block-like, or spheroidal. Sub groupings include platy, leafy, flaky, columnar, blocky, angular to subangular, porous, or very
porous. Soil structure results from complex interactions with soil chemical and physical attributes, water movement, earthworm or other soil faunal activity, and root activity. Roots and microbes exude substances that bind soil to form soil aggregates.

**Soil Taxonomy**

The USDA (Soil Conservation Service) system for soil taxonomy was decided upon in 1975 to create a standardized system for describing soils (not an easy process I am sure). It was originally designed to facilitate research and extension primarily in agriculture. There are 12 basic groupings of soil orders that end in “sol” (meaning soil). The 12 soil orders are distinguished below:

**Entisols**: little if any profile development; most have ochric epipedons; shallow soils over rock like in the Rocky Mountain Region, sandy entisols (Psamments) are found in Florida, Alabama, and Georgia and the sand hill region of Nebraska, these are also found in the Amazon, Sahara and Saudi Arabia, southern Africa; Orthents are found in Quebec, Alaska, Siberia, and Tibet, and parts of the Andes

**Inceptisols**: generally a young soil relatively recently derived with few diagnostic features, can have ochric, umbric, or cambric horizons; middle eastern states have some ochrepts; tropets are inceptisols in warm regions and aquepts are found along the amazon river and ganges river

**Mollisols**: dark soils associated with grasslands, mollic epipedon, base rich; may have argillic, cambic, natric, or albic horizons but not spodic or oxic ones; great plains soils; occasionally found in low lying areas of forest; Udolls (humid-udus), and Ustolls dryer (ustus-burnt), and Xerolls (xeros-dry); tend to be very productive

**Alfisols**: argillic or natric horizon, medium high bases; no mollic, oxic or spodic horizon; commonly ochric, medium to high base status and have an illuvial horizon where silicate clays accumulate; an intermediate soil order;

**Ultisols**: argillic (clay) horizon, low bases; almost always formed in moderate to warm climates; common in the warm wet tropics (and Georgia); commonly orange and yellow in the subsurface profile due to the accumulation of iron oxides; highly weathered

**Oxisols**: oxic horizon, most highly weathered soil order; ochric or umbric epipedon, deep oxic horizon-mostly clay, dominantly hydrous oxides of iron and aluminum; weathering and intense leaching have removed most of the silica from silicate minerals; clay is non-sticky; common in the tropics (year round water, plant activity, human activity, high temperature).

**Vertisols**: dark, swelling clays; lots of sticky, swell-shrink clay (>1m deep) in warm regions with semi-humid to semiarid climates; drained wetlands

**Aridisols**: dry soils, ochric epipedon, low organic matter; can have calcic, gypsic, salic, or natric horizons; desert soils
**Spodosols:** spodic horizon, low bases; a subsurface horizon of organic matter and Al oxides (+/- Fe oxides) white eluviated horizon; moist to wet area in cold climates often under forests, very acid; conifers produce acid litter which leads to spodosols (podzolization)

**Histisols:** organic soils, 12% organic C (20 % organic matter); peat bog soils; any climate; when artificially drained they are good for agriculture

**Andisols:** new order, soils derived from recent volcanic ash; made of not highly weathered allophane and imogolite; amorphous material, poorly crystallize minerals, not much moves down

**Gelisols:** new order, boreal/arctic soils