# C

## C HORIZON

See Horizon, Profile.

# CALCAREOUS SOILS

Calcareous soils as defined here are the soils that fall between the near neutral soils and the alkaline soils (Figure C1) in redox-pH space. They straddle the calcite fence of the pedo-genic grid [\(Figure C2\)](#page-1-0). The fence itself marks the pH zone below which calcite dissolves and above which it precipitates, by the reaction

 $CaCO<sub>3</sub> + H<sup>+</sup> = Ca<sup>2+</sup> + HCO<sub>3</sub><sup>-</sup>$ 

The deposition of calcium carbonate in soil takes place when the product of the activities of  $Ca^{2+}$  and  $CO_3^{2-}$  in the soil solution is  $10^{-8.48}$  (Berner, [1976\)](#page-2-0), and is commonly considered to be an inorganic process. However, evidence for the involvement of organisms (biomineralization) in the soil, especially bacteria, is accumulating (e.g., Goudie, [1996](#page-2-0); Parraga et al., [2004\)](#page-2-0).

[Figure C3](#page-1-0) shows a detail of [Figure C2](#page-1-0) with typical calcareous soils added: Calcic Luvisols, Calcaric Phaeozems, Chernozems and Kastanozems. Calcisols (considered also amongst the alkaline soils) have carbonates extending throughout the profile, though even in these soils, the surface pH may be too low to allow solid calcium carbonate to persist.

Calcrete (which is also sometimes termed caliche or calcareous duricrust when indurated) is in essence a variety of Calcisol. It has been defined as 'a near surface, terrestrial, accumulation of predominantly calcium carbonate, which occurs in a variety of forms from powdery to nodular to highly indurated. It results from the cementation and displacive and replacive introduction of calcium carbonate into soil profiles, bedrock and sediments, in areas where vadose and shallow phreatic ground-water become saturated with respect to calcium carbonate' (Wright and Tucker, [1991](#page-2-0), p. 1). Calcretes may cover as much as 13% of the total land surface, being a prominent surface feature in arid and semi-arid climatic zones.

The pH range 5.5 to 7.0 in A horizons, covers a set of conditions too alkaline for notable amounts of  $Al^{3+}$  to be in solution,



Figure C1 Approximate field of calcareous soil as defined in this article. The dashed envelope encloses the field of the common mineral soils.

<span id="page-1-0"></span>

Figure C2 The calcite geochemical fence in relation to the common mineral soils.

and too acid for  $Ca^{2+}$  (or  $Mg^{2+}$ ) to reach saturation values with respect to carbonate phases. Clay can disperse under these conditions and be transported to the B horizon (illuviation), where a higher concentration of divalent cations in the soil solution will cause the clay to flocculate to form an argic horizon. Amongst the calcareous soils of Table C1, this is seen predominantly in the Luvisols (and Albeluvisols) and in luvic units of the other calcareous soils.

At the high end of the precipitation range of Table C1, the presence of calcite in soil is a benefit agriculturally as a pH buffer. Natural rainwater has a pH around 5.7, and a net addition of such precipitation to the soil system inevitably leads to acidification over the long term (more quickly if the rain is acidified by industrial and automobile emissions – as in the case of acid rain) As precipitation and consequent throughflow



Figure C3 Detail of Figure C2 showing characteristics of the soils of Table C1 with respect to the presence or absence of calcite in their various horizons.

diminishes, the concentration of  $Ca^{2+}$  in the soil solution will increase to the level of calcite saturation [\(Figure C4](#page-2-0)). This is higher than the level for saturation with respect to the phosphate mineral apatite so that there will be a tendency for soil P to be fixed as apatite  $Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, F, Cl)$ , or as one of its precursors such as brushite  $CaHPO<sub>4</sub> \cdot 2H<sub>2</sub>O$  (Tunesi et al., [1999](#page-2-0)).

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Table C1 Spectrum of soils that traverse the calcite fence of the pedogenic grid as climatic conditions change from cool to temperate humid. The pH indicated, is for the A horizon. In each of the soils referred to, pH also increases with depth (adapted from FAO, 2001)

Temp.	Precipitation (mm)	Vegetation	Soil group/Unit	pH
Increases	>550 500 500 450 $200 - 400$ ${<}200$	Deciduous forest Prairie and forest Tall grass prairie Tall grass prairie Short grass prairie Open vegetation	Luvisols, Albeluvisols Phaeozems Luvic Chernozem Haplic Chernozem Calcic Chernozem, Kastanozem Calcisols	$6.5 - 7$ Increases $7.5 - 8$

<span id="page-2-0"></span>

**Figure C4** Calcite and apatite saturation in aqueous solution under a partial pressure of CO<sub>2</sub> of 10<sup>-3.5</sup> bars (the normal atmospheric value) (adapted from Chesworth et al., 1987).

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## Cross-references

Biomes and their Soils Calcisols Chernozems Classification of Soils: World Reference Base (WRB) for Soil Resources Classification of Soils: World Reference Base (WRB) Soil Profiles Duricrusts and Induration Kastanozems Luvisols

## CALCISOLS

Calcisols are soils with a significant secondary accumulation of calcium carbonate resulting from precipitation from solution brought about by evaporation under arid or semi-arid conditions. The following summary is taken from FAO ([2001\)](#page-3-0).

- Connotation. Soils with substantial secondary accumulation of lime; from L. calcarius, calcareous
- Synonyms. Desert soil is a common international term. Definition. Defined by FAO [\(2001](#page-3-0)) as soils having
- 1. a calcic or petrocalcic horizon within 100 cm of the surface; and
- 2. no diagnostic horizons other than an ochric or cambic horizon, an argic horizon which is calcareous, a vertic horizon, or a gypsic horizon.



Figure C5 Distribution of Calcisols.

<span id="page-3-0"></span>Parent material. Mostly alluvial, colluvial and aeolian deposits of base-rich, commonly calcareous, weathering material.

Environment. Level to hilly land in arid and semi-arid regions (see [Figure C5](#page-2-0)). The natural vegetation is sparse and dominated by xerophytic shrubs and trees and/or ephemeral grasses.

Profile development. 'Typical' Calcisols have ABC or AB(t) C-profiles with a pale brown ochric surface horizon over a cambic or argic subsurface horizon. Finely textured subsurface horizons may develop some or all of the characteristics of a vertic horizon. Substantial secondary accumulation of lime occurs within 100 cm from the surface.

*Origin*. Solution and precipitation of calcite  $(CaCO<sub>3</sub>)$  is the characteristic genetic process in Calcisols. The chemistry of this process is dealt with in the article on Carbonates. Commonly the surface horizon is wholly or partly de-calcified with calcite re-precipitated in a horizon of accumulation in the subsoil. Erosion, or the activities of burrowing animals, may lead to homogenization within the profile so that calcite may be re-introduced to the surface.

Use. Dryness, and in places also stoniness and/or the presence of a shallow petrocalcic horizon, limit the suitability of Calcisols for agriculture. If irrigated, drained (to prevent salinization) and fertilized, Calcisols can be highly productive under a wide variety of crops. Hilly areas with Calcisols are predominantly used for low volume grazing of cattle, sheep and goats.

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## Cross-references

Alkaline Soils Biomes and their Soils Calcareous Soils Classification of Soils: World Reference Base (WRB) for Soil Resources Classification of Soils: World Reference Base (WRB) Soil Profiles

## CAMBISOLS

Cambisols are soils at an early (incipient) stage of soil formation. There is generally a brownish discoloration below the surface horizon, to mark the beginning of pedogenesis. The subsoil has a soil rather than a geological structure. This article is based on FAO [\(2001](#page-4-0)).

Connotation. Soils with beginning horizon differentiation evident from changes in color, structure or carbonate content; from L. cambiare, to change.

Synonyms. The name was first used in the legend to the FAO World Soil Map. The equivalent term in Soil Taxonomy is inceptisols. Other classifications use terms connoting brown soil e.g., 'Braunerde' (Germany), 'Sols bruns' (France), 'Brown soils'/'Brown Forest soils' (USA pre-Soil Taxonomy), and 'Brunizems' (Russia).

Definition. Cambisols are defined by FAO [\(2001](#page-4-0)) as soils having

- 1. a cambic horizon; or
- 2. a mollic horizon overlying subsoil with low base saturation within 100 cm depth; or
- 3. one of the following:



Flat polar quantic projection

Figure C6 Distribution of Cambisols.

FAO-GIS, February 1998

- <span id="page-4-0"></span>4. an andic, vertic or vitric horizon starting between 25 and 100 cm below the surface; or
- 5. a plinthic, petroplinthic or salic or sulfuric horizon starting between 50 and 100 cm below the soil surface, in the absence of loamy sand or coarser material above these horizons.

Soils at an incipient stage in their formation with a cambic horizon (in practice a section of the soil profile between an A horizon and a relatively unaltered C horizon, that has soil rather than a rock structure and that differs in color from that the C horizon).

Parent material. Medium and fine-textured materials derived from a wide range of rocks, mostly in colluvial, alluvial or aeolian deposits.

Profile development. ABC profiles. Cambisols are characterized by slight or moderate weathering of parent material and by absence of appreciable quantities of illuviated clay, organic matter, aluminum and/or iron compounds.

Origin. Weathering by hydrolysis is the characteristic process though it is not advanced and consequently appreciable quantities of weatherable minerals (feldspars and ferromagnesians for example) persist in the soil. Signs of incipient weathering will normally be present only in the case of primary ferromagnesian minerals, which may release iron and allow the formation of ferric hydroxides to color and coat other grains in the soil. Minor amounts of clay and gibbsite may also form, accompanied by minimal leaching of alkalies and alkine earths. Migration of Fe, Al, organic matter or clay will not be evident.

Environment. Level to mountainous terrain in all climates and under a wide range of vegetation types (see [Figure C6\)](#page-3-0).

Use. Used in arable farming, grazing and forestry. Cambisols are subject to the usual restrictions due to climate and topography, as well as to characteristics associated with early stages of soil formation such as shallowness, stoniness, or low base status.

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- Zech, W., and Hintermaier-Erhard, G., 2007. Soils of the World. Heidelberg, Berlin: Springer-Verlag, 130 pp.

### Cross-references

Classification of Soils: World Reference Base (WRB) for Soil Resources Classification of Soils: World Reference Base (WRB) Soil Profiles

# **CAPABILITY**

The possibilities inherent in a soil or land in general, of being capable of conversion to a particular use. Many classifications of the capability of land for particular uses exist, and a large number are 'pedocentric' (Rossiter,

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# CAPILLARY PRESSURE

Two fluids are *immiscible* if they retain a distinct phase identity when they are mixed. As a consequence of the different degrees of attraction between molecules of a different nature a tension exists at the interface, which is called surface tension. The surface tension  $\sigma$  has the dimension of a force per unit length of the interface edge (Figure C7).

If the interface between two fluids, e.g., water and air, in equilibrium is flat, the pressures (in the water and in the air) are equal. In contrast, if the interface is curved, as shown in Figure C8, there exists a pressure difference between the two phases. At equilibrium for a spherical bubble of air in water, it can be shown (e.g., Morel-Seytoux, [1969](#page-14-0), p. 472 and Sumner, [2000](#page-14-0), p. A69) from a consideration of balance of forces on a small element of interface (Figure C8) that

$$
p_{\rm a} - p_{\rm w} = \frac{2\sigma}{R} \tag{1}
$$



Figure C7 Surface-tension forces at fluid–fluid or fluid–solid interfaces.



Figure C8 Capillary force equilibrium at an interface between two immiscible fluids.

<span id="page-5-0"></span>where  $p_a$  is air pressure,  $p_w$  is water pressure, and R is the radius of the bubble. The difference in pressure between the fluid at the higher pressure and the fluid at the lower pressure is called the *capillary pressure* and is usually denoted by the symbol  $p_c$ . If the interface is not spherical in shape (see [Figure C8](#page-4-0)), Equation  $(1)$ generalizes to a form, known as Laplace's or Plateau's Equation:

$$
p_{\rm c} = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \tag{2}
$$

where  $(1/R_1) + (1/R_2)$  is the total curvature of the interface at point m, and  $R_1$  and  $R_2$  are the radii of the curvature of interface lines in any two mutually orthogonal normal planes at M (see [Figure C8](#page-4-0)). The radii of curvatures  $R_1$  and/or  $R_2$  are algebraic quantities, which are positive if the center of the curvature lies within the phase at higher pressure and negative otherwise.

By definition, the capillary pressure is always a *positive* (or zero) quantity. The capillary pressure is often expressed as an equivalent water height, denoted  $h_c$  and called *capillary*pressure head. The term "capillary pressure" is misleading because the definition of capillary pressure assumes in no way the presence of a solid wall, as introduced by a capillary. It does, however, assume the presence of two immiscible fluids. However, the presence of a solid wall may have a bearing on the shape of the interface and consequently a bearing on the *magni*tude of the capillary pressure.

## **Wettability**

Just as there exists a surface tension between immiscible fluids, there exists a surface tension between a fluid and a solid. The surface tension between water and air,  $\sigma_{wa}$ , differs from that between water and solid material,  $\sigma_{\text{ws}}$ . A water drop on a glass plate tends to spread as shown in [Figure C7](#page-4-0). The contact angle  $\alpha$  between the water–air interface with the solid at equilibrium fulfills the requirement of zero resultant force at the contact of the three phases, and consequently,

$$
\cos \alpha = \frac{\sigma_{\text{as}} - \sigma_{\text{wa}}}{\sigma_{\text{wa}}}
$$
 (3)

Equation (3) is known as Dupré or Young's formula.

As  $\alpha$  is less than  $\pi/2$ , water is said to be the *wetting* fluid while air is the *nonwetting* fluid. In contrast, the contact angle of the air–mercury interface is greater than  $\pi/2$ , (Figure C9), in which case air is the wetting fluid.

## Capillary rise in a tube

Consider a cylindrical capillary tube with radius  $R$  vertically located in a water container in which the water level is at elevation  $z = z_0$  (Figure C10). Because water wets the capillary, at equilibrium the air–water interface has the shape of a spherical





Figure C10 Capillary rise.

meniscus concave toward the air, of total curvature  $2(\cos \alpha/R)$ , where  $\alpha$  is the contact angle. According to [Equation \(1\)](#page-4-0) since air pressure is atmospheric, the water pressure is

$$
p_{\rm w}=p_{\rm A}-\frac{2\sigma\cos\alpha}{R}
$$

where  $p_A$  is atmospheric pressure. If atmospheric pressure is used as a reference pressure, then the water (gauge) pressure at the interface is negative, i.e., less than atmospheric; in other words, the water is under suction. As a result of this imbalance, the water rises in the capillary tube up to an equilibrium level  $h_c + z_0$ . At hydrostatic equilibrium the total head of water must be constant; thus

$$
\phi = \frac{p_{\rm w}}{\rho_{\rm w} \, \mathsf{g}} + z
$$

where  $\rho_w$  is specific mass of water, and g is the acceleration of gravity. As the water (gauge) pressure is zero at  $z = z_0$ , it follows that  $\phi = z_0$  everywhere in the water phase. Consequently, at the meniscus level, one must have:

$$
\frac{p_{\rm w}}{\rho_{\rm w}g} + z = -\frac{p_{\rm c}}{\rho_{\rm w}g} + h_{\rm c} + z_0 = z_0
$$

or

$$
h_{\rm c} = \frac{p_{\rm c}}{\rho_{\rm w} g} = \frac{2\sigma \cos \alpha}{R\gamma_{\rm w}}\tag{4}
$$

where  $\gamma_w = \rho_w g$  is the specific weight of water. Equation (4) is usually referred to as the capillary rise equation.

#### Capillary head in unsaturated porous media

It is customary to view an unsaturated soil as consisting of capillary "pores" in which menisci separate the two phases. This viewpoint is usually valid in granular soils at sufficiently large moisture contents where forces in the water body other than those due to individual fluid pressure, surface tension, and Figure C9 Contact angle of air–mercury interface. gravity can be neglected. At equilibrium it is assumed that for

a given (macroscopically uniform) water content, the air–water interfaces have the same constant total curvature throughout the porous medium. Soil scientists traditionally define this state by the *capillary head*,  $\psi = -P_c/\gamma_w$  which is the *negative* of the capillary pressure head defined previously. The total (hydraulic) head is thus

$$
\Phi = \psi + z \tag{5}
$$

Clearly at low water contents and with soils of fine texture such as clays, the major fraction of the water content in the medium is distributed in thin films covering the solid matrix. In such cases the interaction between the water–air interface and the water–solid interface must be considered, and the simple mechanical model for capillary pressure is no longer valid. This latter conclusion can be understood visually from a description of the microscopic and macroscopic geometry (Figures C11 and C12). Consider two wetted soil particles covered with thin, yet observable, films of water (Figure C11). So-called pendular (Stallman, 1964) water exists between the two soils particles. In one region (point  $a$  of Figure C11), the total curvature is positive; hence  $p_c$  is positive. In another region (point b), the overall curvature is negative, yielding a negative value of  $p_c$ . At equilibrium the air pressure is constant, and based on the



Enlarged view of air - water interface surrounding grain contact; shows curvature of interface.  $R_1$  and  $R_2$  are radii of curvature, taken at right angles to each other. Plateau's equation for the capillary pressure of this system is:



Figure C11 Geometry of capillary equilibrium.



Figure C12 Capillary pressure versus water content.

capillary geometrical mechanical model, the water pressure would be of different signs around each soil particle. As the water phase is continuous and in equilibrium, it is clear that *other* forces must compensate for this pressure difference in the water and maintain the equilibrium.

Figure C12 displays a profile of water content  $\theta$  above a water-saturated medium at rest. Above the water table (*phreatic* surface) at  $z = z_0$ , the water content gradually decreases with elevation. Immediately above the water table the rate of change of water content with elevation,  $d\theta/dz$ , is negligible. As elevation rises,  $d\theta/dz$  gradually decreases to an inflection point and then increases again toward zero as the water content approaches  $\theta_{r}$ , the *residual* water content. This low residual value of water content may be observed at more than several hundred meters above the phreatic surface. As water is in equilibrium throughout the soil, the total head  $\Phi$  is also constant and equal to  $z_0$ . If [Equation \(2\)](#page-5-0) were generally valid, then the pressure of water at the low water contents would be less than 10 atm. Actually, suction in water cannot exceed 0.7 atm, which shows that the mechanical model of capillary pressure is not generally valid. It is possible, however, to apply Equation (5) for the saturated–unsaturated soil profile with  $\psi$  representing the cumulative effect of pressure and other *unspecified* (though effective) factors. The value of  $\psi$  for a given equilibrium water content is determined from the total head equation, for  $\Phi$  equals constant, yielding

$$
\psi = -(z - z_0) \tag{6}
$$

where  $z$  is the elevation of the given water content. For convenience, soil scientists continue to refer to  $\psi$  as the "capillary" head."

The dependence of  $\psi$  on the water content – sometimes called the *water-retention* curve  $-$  is an important soil characteristic because it indicates physical properties of the soil such as texture and structure and determines the water availability for plants under various boundary conditions. [Figures C13](#page-7-0) and [C14](#page-7-0) show  $\psi(\theta)$  curves for sands and silt loam and for heavy soils. The difference between the two extreme types is considerable: (1) the porosity generally increases as the soil texture gets finer. While sand particles function as independent units, fine-texture soils tend to develop structure with different

<span id="page-7-0"></span>

Figure C13 Water-retention curve for sand, fine sand, and silt loam (after Brooks and Corey, 1966).



Figure C14 Water-retention curves for heavy soils: Grenville silt loam (Staple, 1965); Silt mont cenis (Vachaud, [1966](#page-14-0)); Clay loam (Bruce, [1972\)](#page-14-0) and Chino clay (Gardner, [1959](#page-14-0)).

degrees of stability. Small particles adhere together with the aid of colloidal material to create greater particles, called aggregates, with greater pore space between them. Hence the observed water content at  $\psi = 0$  in heavy soils is greater than in sandy soils. (2) Sands usually have a minimum critical value of  $\psi$  (in absolute value), which must be exceeded before a reduction in water content can be observed. Thus for  $\psi_{\rm cr} \leq \psi \leq 0$ ,  $\theta$  remains essentially constant at the saturated value,  $\theta_s$ . At this value of  $\psi = \psi_{\rm cr}$ , air starts to penetrate into the soil, and for this reason it is also called the air-entry value. Soils of very fine texture have no clear air-entry value because reduction of the water content occurs first as a result of compression of the soil while it is still saturated with water. (3) The  $\psi(\theta)$  curve of granular soils displays an abrupt drop in water content within a small range of decrease in  $\psi$ . It occurs at a relatively high value of  $\psi$  ( $\psi$  > –100 cm of water). From the mechanical capillary perspective, the implication is that sands have a narrow *pore*-size distribution  $(q, v)$ . On the other hand, for soils of fine texture the capillary pores represent only a small portion of the total void volume. Even at relatively high water contents, most of the water lies in thin films covering the solid particles. Strong forces hold this film water to the soil, and high energy is required to extract it. The rate of change of water content with  $\psi$  is very small, and the effective range of values of  $\psi$  may be as low or even lower than  $-150$  m of water. The residual water content (also called the irreducible water content) at low values of  $\psi$ , where  $d\theta/d\psi$  tends to zero, is much greater in heavy soils (as high as 20%) than in sands (usually less than 6%).

The shape of the  $\psi(\theta)$  curve is affected by both soil and fluid properties. Beside the factors previously mentioned – namely, soil texture, structure, and interface contact angle – other factors play a significant role. These are: the type of soil minerals, the composition and amount of the organic fraction, the chemical components of the fluids considered, the temperature, and the history of the process. The process history is very important and is thus discussed thoroughly in a succeeding section headed "capillary hysteresis."

The water-retention curves  $\theta(\psi)$  are determined experimentally. No theory has yet been developed that is accurate or simple enough to derive analytically the  $\theta(\psi)$  curve. There is, however, value in fitting the observed data by analytical expressions. Such analytical yet empirical expressions serve two purposes: (1) They permit solutions to unsaturated-flow problems in closed form, and (2) they eliminate the truncation errors introduced in the estimation of  $\psi$  and  $d\psi/d\theta$  in numerical solutions. A variety of expressions have been proposed in the literature. The simplest one is the power function:

$$
\psi = a \, \theta^{-n} \tag{7}
$$

where *a* and *n* are adjustable parameters. Equation (7) can be modified to account for air-entry value and residual water content in the form

$$
\theta(\psi) = \theta_{\rm s} \qquad \text{for} \quad \psi > \psi_{\rm cr} \n\psi = S_{\rm e}^{-n} \quad \text{for} \quad \psi < \psi_{\rm cr}
$$
\n(8)

where

$$
S_{\rm e} = \frac{\theta - \theta_{\rm r}}{\theta_{\rm s} - \theta_{\rm r}}
$$

is called the *effective saturation*. For  $\theta(\psi)$  curves with monotonically decreasing slope, a similar expression is used:

<span id="page-8-0"></span>
$$
S_e = \frac{a}{a + \psi^n} \tag{9}
$$

Two other expressions are respectively of exponential nature, namely

$$
\theta = \theta_{\rm s} \qquad \psi \ge \psi_{\rm cr}
$$
  

$$
S_{\rm e} = e^{\alpha(\psi - \psi_{\rm cr})} \qquad \psi < \psi_{\rm cr}
$$
 (10)

or logarithmic, namely

$$
\theta = \theta_{\rm s} \qquad \psi \ge \psi_{\rm cr}
$$
  

$$
S_{\rm e} = 1 - \frac{\ln(\psi - \psi_{\rm cr} + 1)}{\ln(\psi_{15} - \psi_{\rm cr} + 1)} \qquad \psi < \psi_{\rm cr}
$$
 (11)

Equation (11) mixes dimensional and dimensionless terms and as a result can be used only if  $\psi$  is expressed in centimeters of water.

None of these analytical curves except that defined by Equation (9) has an inflection point and can be accurately adjusted only to the experimental curves for a limited range of  $\psi$  or  $\theta$ values. More flexible and realistic expressions can be derived such as

$$
\psi = a \theta^n (\theta_s - \theta)^m \tag{12}
$$

$$
S_{\rm e} = a \frac{\cos h \left[ \left( \frac{\psi}{\psi_0} \right)^n + b \right] - c}{\cos h \left[ \left( \frac{\psi}{\psi_0} \right)^n + b \right] + c} \tag{13}
$$

where a, b, c, n, and  $\psi_0$  are adjustable parameters (King, [1964\)](#page-14-0), or any combination of the more elementary functions mentioned previously. These latter expressions are of limited value, however, as the amount of work required for adjustment is considerable, and they are too complicated to be used in the derivation of closed analytical solutions. The most commonly used soil water retention model was developed by van Genuchten (1980). For a detailed review and references, see Mualem and Dagan ([1976](#page-14-0)) and Kosugi et al. (2002).

## Experimental determination of capillary head

There are a variety of ways to measure the capillary head in a soil. One method determines directly the pressure difference between air and water and the corresponding water content in the soil. Suppose a rock (or soil) sample, completely saturated with water at atmospheric pressure, is placed in contact along a fraction of its surface with air. Pressure in the air phase is increased and remains constant. A certain volume of air penetrates the core and expels a corresponding amount of water, which is measured.

The air is retained in the porous medium by a semipermeable membrane that transmits the displaced water but not the air. Ultimately a no-flow condition is established. Due to the expulsion of a certain volume of water, the remaining water fills up only a fraction of the total pore space. (The fraction of the total pore volume occupied by water is called the water saturation.) Pressure in the air is increased again. When equilibrium is reached, a new and lower equilibrium water saturation prevails in the core. Ultimately, repeating the operation successively (and patiently), a curve of capillary head versus water saturation or water content is obtained (Figure C15). Because water was drained from the core in the procedure, the curve so obtained is labeled "drainage" or "drying curve." Because



Figure C15 Nomenclature of capillary hysteresis.

the core was initially *fully* saturated (no air present at all), the curve is labeled "first draining curve."

It is found experimentally that a point is reached when even a tremendous increase in capillary pressure no longer induces a saturation change. The water saturation is said to have reached its irreducible, or residual, value. The concept of irreducibility is relative to the process. For example, the residual water saturation could be reduced further by placing the core in an oven at an elevated temperature.

#### Capillary hysteresis

Once residual water content has been established in the core by displacement by air, the *imbibition*, or *wetting*, curve can be obtained by letting the pressure drop stepwise and water imbibe back. *Imbibition*  $(q, v)$ , or wetting, are the terms used if the water content increases with time. However, a different curve is obtained (Figure C15), which implies that given a water content, several equilibrium states are possible depending on previous history. The capillary-pressure curve is said to display hysteresis. By the time the capillary pressure has returned to the zero value, all the air has not been expelled. A fraction of it has been trapped, the residual air content. This imbibition curve is referred to as the "main wetting curve." If the soil is drained again, the main drying curve is described. If the process is reversed before the capillary head has reached the value  $\psi_{\min}$ (point a on Figure C15), a primary wetting curve is described. But if the process is reversed only after the value  $\psi_{\min}$  has been reached, then the main wetting curve is described again. The main drying and main wetting curves form the main hysteresis loop. Depending on the location of the reversal point in the process of successive wetting and drying, the described curves are referred to as "primary," "secondary," "tertiary," etc.

The observed capillary hysteresis results from the cumulative effects of several factors. Probably the most important one is the geometry of the porous system. Let us adopt the mechanical capillary-pressure model discussed earlier. Under these conditions it is possible to depict different porous-matrix geometries that lead to hysteresis. They have in common the existence of cavities with converging and diverging walls. The isolated pores so constructed are connected by narrow channels, which permit different configurations of the interface at equilibrium for the *same* value of  $\psi$ . Figure C16 displays a pore with two degrees of filling, yet with the same curvature radius for the interface and consequently the same capillary head. Figure C<sub>17</sub> displays another type of geometry that causes hysteresis (the "ink-bottle" effect), as the same curvature can exist with various degrees of filling of the void space.

A second effect is the hysteresis of the contact angle  $\alpha$ . As stated previously in the discussion of the capillary rise in a capillary tube, the capillary pressure depends on the contact angle according to the formula

$$
p_{\rm c} = \frac{2\sigma}{r} \cos \alpha \tag{14}
$$



Figure C16 Different degrees of saturation for the same capillary pressure.

In general, the wetting angle is not constant. It reaches its maximum value when water (or more general a liquid) moves toward a dry surface and takes it's minimum value when it recedes. This phenomenon can be observed visually in the process of filling and emptying a capillary tube (Figure C18). As a result of this wetting angle hysteresis, a row consisting alternately of air bubbles and of water drops can maintain rest against a significant pressure drop between the two ends of a tube (Figure C19).

Entrapment of air during the imbibition (or wetting) process is another important factor. The appreciable difference between



Figure C18 Hysteresis of wetting angle.







Figure C17 The "ink-bottle" effect.

Figure C19 Equilibrium induced by a series of wetting-angle hysteresis.

the first drainage (or drying) curve (abbreviated F.D. curve) and the main drying (M.D.) curve displayed on [Figure C15](#page-8-0) is the direct result of this air entrapment. This entrapment may be explained in a simple way by the closing of narrow entrances of pores or groups of pores by the wetting fluid in a slow wetting process. The air content in the sample varies with time as air dissolves in water and moves away by diffusion. It is a known fact that if  $\psi$  is kept constant for a long time, the water content increases as air disappears from the soil (Bloomsburg and Corey, [1964](#page-14-0)).

Comparisons of numerical studies of water redistribution in soils, including or excluding the hysteretic effects, have shown that the profiles differ substantially. In the presence of hysteresis higher water contents prevail in the upper part of the soil, and wetting of the lower part is delayed. This delay in the drainage rate enhances the evaporation from the soil surface. For a detailed review and references, see Mualem and Dagan ([1972\)](#page-14-0).

## Theory of capillary hysteresis

The fundamental theory of hysteresis based on the "independent domains" concept was initiated by Preisach [\(1935](#page-14-0)) and Néel (1942–1943) and thoroughly analyzed by Everett and his coworkers (1952–[1955](#page-14-0)) and Enderby (1955). According



to this theory a porous medium is viewed as a system consisting of independent elementary pore domains. Each domain is characterized by two length scales,  $\rho$  and r, which can be interpreted geometrically as the radius of the pore and the radius of its constricted connection with other pores, respectively. Using the capillary law  $(\psi \sim a/R)$ , the variables  $\rho$  and r can be uniquely related to the wetting and drying capillary head  $\psi_w$ and  $\psi_d$ , respectively. The pore domain has therefore only two stable states, either empty or full (Figure C20). In a wetting process, the pore is empty until  $\psi$  reaches the value  $\psi_w$  at which time it flips over to a filled state. There is no change in water content of the pore when  $\psi$  is increased further. In drainage the pore remains water filled until  $\psi$  takes to value of  $\psi_d$ . At this point the pore is totally drained. The elementary pore domain displays hysteresis. It is assumed that these properties are independent of the states of the neighboring pores. Denoting  $\Delta V$  as the pore volume and taking  $\psi_w$  and  $\psi_d$  as independent variables continuously distributed between  $\psi_{\min}$  and  $\psi_{\text{max}}$ , it is possible to define a pore-water density distribution function

$$
f(\psi_{\rm d}, \psi_{\rm w}) = \frac{\Delta V(\psi_{\rm d}, \psi_{\rm w})}{V} \tag{15}
$$

where V is the total volume of the sample. Now  $f(\psi_w, \psi_d)d\psi_w d\psi_d$ represents the relative pore volume which is filled at  $\psi_w$  and drained at  $\psi_d$  due to differential changes  $d\psi_w d\psi_d$ . Essentially,  $f(\psi_w, \psi_d)$  is positive with  $\psi_w \ge \psi_d$ . Figure C21b and C21c show the diagram of the filled-pore domains, "Néel diagrams," at a given  $\theta$  for the main wetting and the main drying processes.

Assuming that the independent-domains theory applies conceptually, it is possible to relate the measurements of  $\psi$  and  $\theta$  to the pore-water density function  $f$ . It is customary to operate with finite differences and to define approximately the integral function  $F(\psi_{\rm wi}, \psi_{\rm di}) = f(\psi_{\rm wi}, \psi_{\rm di})\Delta \bar{\psi}_{\rm w}\Delta \psi_{\rm d}$ , which permits calibration of the model on the basis of a family of either primary wetting or primary drying scanning curves.

This model has been experimentally tested for a wide variety of soils and glass-beads samples. While the theory held for some samples, in most cases discrepancies between the measured and the predicted  $\theta(\psi)$  curves were observed. Poulovassilis [\(1962](#page-14-0), [1970a](#page-14-0)) found a good agreement between the predicted and the measured scanning curves for glass beads and sand. Other investigators reported considerable discrepancies between the theory and observations; Topp and Miller [\(1966\)](#page-14-0), Figure C20 Hysteretical behavior of the isolated pore domain. Morrow and Harris ([1965](#page-14-0)), and Bomba and Miller [\(1967\)](#page-14-0)



Figure C21 (a) Schematic representation of capillary hysteresis. (b) Filled-pore diagram (shadowed region) for the main wetting process. (c) Filledpore diagram for the main drying process (after Mualem, [1973](#page-14-0)).

<span id="page-11-0"></span>observed discrepancies for glass-beads medium; Vachaud and Thony ([1971](#page-14-0)), Talsma [\(1970\)](#page-14-0), and Poulovassilis and Childs [\(1971](#page-14-0)) observed them for sand; Topp [\(1969,](#page-14-0) [1971a\)](#page-14-0) observed them for various loam soils. It seems that the measured discrepancies are due partly to the method of measurement because the poorest agreement between theory and measurements has been observed for unsteady-flow experiments. The main problem, however, stems from the fact that the computed pore-water distribution function derived in this method becomes negative in part of the  $(\psi_w, \psi_d)$  domain, in contradiction to its basic definition. As a result, part of the predicted scanning curves are depicted outside the main loop and sometimes indicate a process opposite to the actual one, namely, drainage instead of wetting

and vice versa. This phenomenon is intensified when a considerable region of the hysteretical domain is observed within the range (0,  $\psi_{cr}$ ) and when the sample is dried to a lower water content  $\theta_{\min}$ , close to  $\theta_{\rm r}$ .

Mualem [\(1973](#page-14-0)), following Philip's [\(1964](#page-14-0)) approach, suggested a modified variant of the independent-domain theory. This model used a similarity hypothesis, according to which the pore-water distribution function  $f(\psi_w, \psi_d)$  is represented as a product of two independent distribution functions,  $h(\psi_w) \ell(\psi_d)$ . This hypothesis considerably simplifies the computational procedures. Only the measured boundary curves are required for the calibration of the model, and the scanning curves are expressed analytically. Moreover, the modified model is better adapted to



Figure C22 Scanning curves predicted by the usual Néel-Everett model (dashed line), by model I (solid line), and the measured data for Caribou silt loam (points) (after Mualem, [1973](#page-14-0)).



Figure C23 (a) Schematic representation of capillary hysteresis and the filled-pore diagrams in the (unknown)  $r\rho$  plane (the shaded domains) for (b) the main wetting process, (c) the main drying process, (d) the primary drying process, and (e) the primary wetting process (after Mualem, [1974](#page-14-0)).

<span id="page-12-0"></span>

Figure C24 The function  $C(S_e)$  for three soils measured after several cycles of imbibition and drying. The hollow symbols denote results in the wetting process, and the solid symbols denote measurements in the drying process (after Mualem, [1974](#page-14-0)).

the independent-domain principles [\(Figure C22\)](#page-11-0) as the computed poredistribution function is always positive. As a result, the predicted  $\theta(\psi)$  curves are in better agreement with observations than those derived by using the original Néel-Everett model.

A more flexible independent-domain theory, which accounts also for a reversible contribution of the pore domains to the wetting and drying processes, has been suggested by Mualem ([1974\)](#page-14-0). This model is underlain by three basic assumptions:

• The two parameters r and  $\rho$ , characterizing a pore volume of the porous medium, vary in the whole range between  $R_{\text{min}}$  and  $R_{\text{max}}$  (which correspond to  $\psi_{\text{min}}$  and  $\psi_{\text{max}}$ , respectively, by the capillary law  $\overline{R} \sim 1/|\psi|$ ). After the normalization, that is,

$$
\bar{r} = \frac{r - R_{\min}}{R_{\max} - R_{\min}} \quad \bar{\rho} = \frac{\rho - R_{\min}}{R_{\max} - R_{\min}} \tag{16}
$$

the pore-volume distribution function  $f(\bar{r}, \bar{\rho})$  is defined in the square *OABC* of [Figure C23.](#page-11-0)

- In a wetting process under a change from  $\psi(\bar{R})$  to  $\psi(\bar{R} + d\bar{R})$ pores characterized by  $\bar{R} \leq \bar{p} \leq \bar{R} + d\bar{R}$  are filled, while in drainage when  $\psi$  diminishes from  $\psi(\overline{R})$  to  $\psi(\overline{R}-d\overline{R})$ , only the pores characterized by  $\bar{R} - d\bar{R} \leq \bar{p} \leq \bar{R}$  and  $\bar{R} \leq \bar{r} \leq 1$ are drained. Diagrams of the filled-pore domains in the  $\bar{r}, \bar{\rho}$ plane (corresponding to four different processes) are given in [Figure C23](#page-11-0).
- The simplifying similarity hypothesis

$$
f(\bar{r}, \bar{\rho}) = h(\bar{r})\ell(\bar{\rho})\tag{17}
$$

is adopted.

The effective water content  $\theta$  is subsequently defined as

$$
\theta = \Theta - \Theta_{\min} \tag{18}
$$

where  $\Theta$  and  $\Theta_{\min}$  are the actual and the residual water content. Two integral distribution functions are defined as

$$
L(\bar{R}) = \int_0^{\bar{R}} \ell(\bar{p}) d\bar{p} \quad H(\bar{R}) = \int_0^{\bar{R}} h(\bar{r}) d\bar{r}
$$
 (19)



Figure C25 Measured hysteretic curves outside and inside the main loop (solid lines) and the predicted curves using model II (dashed lines) for glass-beads sample (after Mualem, [1974\)](#page-14-0).

The effective water content in the main wetting process  $\theta_w(\overline{R})$  is determined by the integration of  $f(\overline{r}, \overline{\rho})$  over the corresponding region of the filled pores [\(Figure C23b](#page-11-0)):

$$
\theta_{\rm w}(R) = L(\bar{R})H(1) \tag{20}
$$

and similarly, in the main drying process ([Figure C23](#page-11-0))

$$
\theta_{\mathbf{d}}(\bar{R}) = L(\bar{R}) + [L(1) - L(\bar{R})]H(\bar{R})
$$
\n(21)



Figure C26 Two families of secondary drying scanning curves predicted with model III (solid lines), computed with model II (dashed lines), and measured (dotted lines) for the glass bead sample (after Mualem and Dagan, [1975](#page-14-0)).

Choosing  $H(1) = 1$  and realizing that there is a unique relationship between  $(\overline{R})$  and  $\psi$ , we may express H and L as functions depending directly on  $\psi$  by

$$
L(\psi) = \theta_{\rm w}(\psi) \tag{22}
$$

$$
H(\psi) = \frac{\theta_{\rm d}(\psi) - \theta_{\rm w}(\psi)}{\theta_{\rm u} - \theta_{\rm w}(\psi)}
$$
(23)

Once  $L(\psi)$  and  $H(\psi)$  are determined from the two measured boundary curves of a given soil, any hysteretic path is described afterwards in a simple way with the aid of these two basic functions. For instance, the water content along a primary drying scanning curve (obtained by integrating  $f(\bar{r}, \bar{\rho})$ over the region of filled pores of [Figure C23d](#page-11-0) is given by

$$
\theta \begin{pmatrix} \psi_1 \\ \psi_{\min} \psi \end{pmatrix} = \theta_{\rm w}(\psi) + H(\psi)[L(\psi_1) - L(\psi)] \tag{24}
$$

while the primary wetting scanning curve ([Figure C23e\)](#page-11-0) is given by

$$
\theta \left( \frac{\psi_{\max} \psi}{\psi_1} \right) = \theta_{\rm w}(\psi) + [\theta_{\rm u} - L(\psi)] H(\psi_1)
$$
\n(25)

This new model considerably facilitates the computational work as  $H(\psi)$  and  $L(\psi)$  are very simply related to  $\theta(\psi)$  on the main boundary curve. Theory has been extended further to account for the entrapment of air. Using Cary's ([1967\)](#page-14-0) experiments, it was found that the entrapped air content constitutes a constant fraction of the water content. [Figure C24](#page-12-0) shows that the factor  $c = \theta_w/(\theta_w + \theta_a)$ , where  $\theta_a$  is entrapped air content, is approximately 0.9. On this basis it was assumed that by rewetting a sample that was previously drained starting from saturation, a well-defined quantity of air is trapped. Moreover, it is assumed that subsequent drying and wetting cycles do not cause additional entrapment. This hypothesis permits predicting the first drying curve and any other scanning curves branching from it [\(Figure C25\)](#page-12-0). The agreement between the forecast  $\theta(\psi)$  relationships and observations is quite satisfactory. It should be noted that this theory permits using the first drying curve and the main wetting curve, solely, for calibration of the model. This way, less experimental work is required while theory applies to the whole hysteretical domain.

In some cases, for soils having a narrow pore size distribution with a major portion of the hysteretic loop in the range of airentry value or when the soil is drained to a very low water content, the independent-domain models are not really satisfactory. In these cases the pore interaction effects are significant. Everett [\(1967](#page-14-0)) and Topp ([1971b](#page-14-0)) suggested a dependent-domain theory, which accounts for pore blockage against air entry near saturation and air blockage against water entry at low water content. While this theory leads to better agreement with observations, Topp's procedure is laborious and requires a large amount of measured data, comprising sets of both drying and wetting families of scanning curves. Poulovassilis and Childs ([1971\)](#page-14-0) suggested another dependent-domain model. This model, however, requires even more experimental data.

Mualem [\(1974](#page-14-0), [1976](#page-14-0)) and Mualem and Dagan ([1975\)](#page-14-0) generalized Mualem's model previously discussed to incorporate the fundamental ideas of Everett and Topp. The computational procedure requires one primary drying scanning curve and one primary wetting scanning curve in addition to the boundary loop to determine the two functions corresponding to water and air blockage. They concluded that in most cases pore blockage against air entry is of lesser significance and can be disregarded to simplify computation. The generalized theory, however, significantly improves the prediction when the effect of the pore blockage against air entry is considerable (Figure C26). Thus the new models attain a high degree of generality and capability of representing observed phenomena more accurately.

Hysteretical phenomenon is observed also in the  $K(\theta)$  and the  $K(\psi)$  relationship. The subject is discussed under the title Permeability.

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## Cross-references

Conductivity, Hydraulic Imbibition Infiltration Percolation **Permeability** Soil Pores Water Budget in Soil Water Content and Retention Water Movement Wetting Front

# CARBON CYCLING AND FORMATION OF SOIL ORGANIC MATTER

Carbon (C) can form potentially endless hybridized atomic orbitals resulting in the potential to create a vast array of complex organic compounds. The diversity of C compounds no doubt influenced the evolution of life and the diversity of organisms. Carbon was not found on the primordial earth and only after the continuous bombardment by carbonaceous comets and asteroids did appreciable amounts of C accumulate (Anders, [1989](#page-20-0)). The extraterrestrial C was complex containing a vast array of hydrocarbons and important biological compounds such as amino acids and carboxylic acids, constituents required to assemble primitive life. Early Earth's atmosphere was thought to contain primarily simple hydrocarbons that were continuously

altered through ultraviolet photolysis. In addition, the atmosphere contained appreciable amounts of carbon dioxide  $(CO<sub>2</sub>)$ as a result of meteor and asteroid impacts and volcanic activity. The  $CO<sub>2</sub>$  dissolved in water to form carbonic acid and may have been instrumental in mineral weathering and soil development. The respiratory activities of early microorganisms added to the increasing levels of  $CO<sub>2</sub>$  and methane (CH<sub>4</sub>) in the atmosphere. Early Earth contained atmospheric  $CO<sub>2</sub>$  levels in excess of 100 times of what they are today. The high concentrations of  $CO<sub>2</sub>$  lead to the emergence of biological C fixation (photosynthesis), which began to reduce the atmospheric  $CO<sub>2</sub>$  level and increase the oxygen level. The evolution of primary producers resulted in the accumulation of complex organic compounds. The production of organic material immobilized essential nutrients, such as nitrogen (N) and phosphorus (P) that had to be recycled by the decomposing activity of heterotrophs to maintain primary production. The biological processes of photosynthesis and decomposition are two fundamental processes that sustain ecosystem productivity and are an integral part of the global C cycle.

## The global  $CO<sub>2</sub>$  cycle today

Increasing fossil fuel use, forest clearing, and the conversion of land to agriculture have led to a net transfer of terrestrial C to the atmosphere. Today's atmosphere contains approximately 370 ppmV compared to about 260 ppmV  $CO<sub>2</sub>$  during the middle of the 19th century. Atmospheric  $CO<sub>2</sub>$  continues to increase because of the reliance on fossil fuels and as developing countries embrace a higher standard of living afforded through industrial development. The increasing atmospheric  $CO<sub>2</sub>$  level has been partially offset by the net uptake of C into the oceans, which contain the largest reservoir of inorganic C at 38 000 Pg C (Figure C27).

In the terrestrial environment, soils contain about 1 500 Pg C. The atmosphere contains approximately 790 Pg C and land vegetation 650 Pg C. Both soils and vegetation have been impacted greatly by anthropogenic activity and thus the C cycle can be considered one of the more sensitive biological cycles subject to human influence. Increased atmospheric  $CO<sub>2</sub>$  may lead to higher photosynthetic rates, although elevated  $CO<sub>2</sub>$  research has produced little corroborating evidence to suggest plants are C limited. Plant water use efficiency will increase for plant species that rely on the photosynthetic enzyme Ribulose bisphosphate carboxylase to produce a  $3C(C_3)$  sugar during photosynthesis.  $C_3$  plants can loose up to 50% of fixed C to photorespiration and would benefit greatly under higher partial pressures of  $CO<sub>2</sub>$ that reduce transpired water loss during photosynthesis. In comparison, plants fixing  $CO<sub>2</sub>$  to 4C sugar  $(C<sub>4</sub>)$  or those using Crassulacean acid metabolism (CAM) are more efficient at fixing  $CO<sub>2</sub>$ and show little if any change under elevated  $CO<sub>2</sub>$ .

The global C cycle is dependent on numerous processes that operate at different spatial or temporal scales. The cycling of the vast majority of  $\overline{C}$  found on Earth is on the order of millions of years as  $CO<sub>2</sub>$  from the atmosphere and biological activity is adsorbed by oceans and sequestered into carbonates that eventually form sedimentary rocks such as limestone and dolomite. Over time these rocks release their C back to the atmosphere, either through subduction into the Earth's mantle followed by expulsion of  $CO<sub>2</sub>$  through volcanic processes, or as a result of tectonic plate upheaval where they are exposed to weathering processes leading to the release of  $CO<sub>2</sub>$  through mineral dissolution and soil development. On a smaller time scale, measured from hours to thousands of years, biological processes dominate the C cycle. The biological cycling of C is dependent on the ability of primary producers such as



Figure C27 Pool sizes and annual fluxes (Pg C) of major reservoirs (solid lines) and fluxes (Pg C/year) (dashed lines) in the global C cycle (adapted from Houghton et al., 2001).

plants and cyanobacteria to fix atmospheric  $CO<sub>2</sub>$  into organic substances.

The biological fixation of  $CO<sub>2</sub>$  or photosynthesis to produce organic compounds is termed gross primary production (GPP). Following losses to respiration, growth and maintenance the newly formed biomass is termed net primary production (NPP). Net secondary production (NSP) occurs when consumers such as herbivores or decomposers of NPP produce new biomass. The decomposition of NPP leads to the selective preservation of some resistant plant constituents, such as lignin. In addition, the turnover of microorganisms produce compounds, which are precursors to soil organic matter (SOM). These precursors or humic substances are resistant to decay and can persist for thousands of years.

## Composition and decomposition of soil C inputs

The quantity and quality of NPP and subsequent NSP determines the outcome of decomposition processes and regulates the accumulation of SOM. The various constituents of NPP and NSP consist of a range of materials from simple lipids and organic acids to complex polymers found in plant and microbial cell walls. The constituents of cytoplasm and cell walls require a complex scheme of enzymes to degrade into substrates suitable to be used to produce NSP, indicating that microbial diversity and production are significant controlling factors of decomposition processes. The cell walls of plants and microorganisms are resistant to decomposition and are thought to contribute significantly to the maintenance of SOM. A small yet nutrient rich component of plant litter found within the cytoplasm contains sugars, amino compounds and organic acids and comprises up to 10% of plant residue dry weight (Table C2). The labile cytoplasm components are readily leached from plant residues and provide the initial energy and nutrients to start the decomposition process. The protein content of plant litter and exudates ranges from about 1% in roots to up to 4 or 5% in foliar tissue. Biological N fixers tend to have greater overall tissue N concentrations. The meristimatic regions of plants can have N contents in excess of 20% by weight. The secondary cell walls of higher plants generally have less than 1% N. The majority of secondary cell wall is comprised of hemicellulose and cellulose, comprising up to 70% of total plant residue. Plant lignin ranges from 5 to 30% and is a unique compound of terrestrial plants providing a rigid exoskeleton to counter the effects of gravity and provide a physical defense against pathogens. Extractable phenols and tannins are often a significant component of some plants, especially in forest and shrub systems, and comprise up to 30% of the dry weight.

Table C2 Percentage of cytoplasm and cell wall components in plants. (adapted from Horwath 2002)

Plant component	$%$ of total	
Waxes and pigment		
Amino acids, sugars, nucleotides etc.	5	
Starch	$2 - 20$	
Protein	$5 - 7$	
Hemicellulose	$15 - 20$	
Cellulose	$4 - 50$	
Lignin	$8 - 20$	
Secondary compounds	$2 - 30$	

The various components of plant, microbial and faunal soil inputs undergo decomposition at different rates. Ecologists often relate the decomposability or quality of plant litter inputs to C to N ratio, total N or lignin content, which have been shown to influence decomposition and the long-term fate of soil C. Other plant constituents such as polyphenols and tannins (secondary plant metabolites) may impact decomposition through phytotoxic interactions and chemical interactions with both organic and inorganic N sources. The availability of exogenous nutrients is a major determinant of decomposition processes through its regulation of the growth potential of decomposers. Above all, the major factors controlling both NPP and NSP are temperature and moisture. Temperature controls metabolic activity while sufficient moisture is required to maintain metabolic function. Following is a description of plant and microbial components and the factors controlling their fate during decomposition.

#### Cytoplasm and storage components

Lipids represent a diverse class of compounds ranging from simple fatty acids to complex sterols, phospholipids, chlorophyll, waxes and resins (cutins and suberins). As a class of compounds, the decomposability of lipids depends on their chemical complexity. Long chain aliphatic fatty acids and phospholipids, components of membranes, are degraded relatively quickly depending on the degree of saturation or double bond content. More complex waxes and resins are resistant to decomposition and form some of the most resistant substances in soil. The hydrophobic character of these substances allows them to sorb into hydrophobic domains of SOM, shielding them from enzymatic attack. In addition to plant lipids, the accumulation of polyaromatic hydrocarbons (PAH) from fossil fuel combustion in soils is gaining attention. Enzymes and degradative processes of the more recalcitrant lipid substances and PAH are not well understood.

Starch is a polymer of glucose synthesized and stored in plastids, such as amyloplasts of roots and tubers. Starch consists of two glucose polymers, amylose and amylpectin. Amylose contains long unbranched chains of  $\alpha(1-4)$ -glucose units. For most plants, amylose can account for up to 30% of the total starch. Amylopectin has a similar structure linked every 20 to 30 glucose residues by  $\alpha(1-6)$ -glucose bonds. A class of enzymes known as amylases readily degrades starch into glucose. Starch represents a significant energy source but requires a supply of exogenous nutrients to complete microbial growth and other NSP.

#### Hemicelluloses, pectins and cellulose

The majority of plant carbohydrates are found as the polysaccharides, cellulose hemicellulose and pectin in the secondary cell wall. All of the monsaccharides that form cell wall polysaccharides are derived from glucose, which upon alteration form a variety of 5C (pentoses) and 6C (hexoses) sugars. Hemicelluloses contain xylans (xylose polymer), an uronic acids (i.e., sugar acid), and arabinose (another 5C sugar). Pectin is composed of three main polysaccharide types: polygalacturonan (repeating galacturonic acid monosaccharide subunits), rhamnogalacturonan I (alternating rhamnose and galacturonic acid subunits) and rhamnogalacturonan II (highly branched polysaccharide). Hemicellulose/pectin because of their sugar content are a rich energy source, but require an extensive suite of enzymes and exogenous nutrients to complete its decomposition.

Cellulose consists of glucose units linked by  $\beta(1-4)$  bonds to form long glucose chains. The chains are cross-linked by hydrogen bonds to form paracrystalline assemblages called microfibrils. The cellulose microfibrils are cross-linked into a network or scaffold with hemicellulose. Cellulose microfibrils are decomposed by the enzyme system cellulase composed of endoglucanase, exoglucanase and  $\beta$ -glucosidase (also known as cellobiases). Cellulose degradation begins with the disruption of the crystalline structure of the microfibrils followed by the depolymerization into short glucose chains. A wide range of organisms degrade the energy rich cellulose, but only a few have demonstrated the complete depolymerization and hydrolysis of the crystalline microfibril structure in vitro. The conversion of plant polysaccharides into sugars and fuel such as ethanol has received much attention as a source of energy to replace or substitute for fossil fuels.

#### Lignin

Lignin is a complex and dense amorphous secondary cell wall polymer typically found in the trachea elements and sclerenchyma of terrestrial plants. The dense hydrophobic nature of lignin makes it difficult for enzymes to penetrate. The precursors of lignin come from the shikimic and phenylpropanoid pathway that converts the amino acids phenylalanine and tyrosine to hydroxycinnamyl alcohol and then to monlignols –p-coumaryl, coniferyl and synapyl alcohols. The monolignols are assembled randomly on a protein template. The lignin polymer provides structural rigidity and a mechanical barrier against pest and pathogens.

The decomposition of lignin is primarily attributed to fungi, actinomycetes, and bacteria under aerobic conditions. Fungi are the most efficient lignin degraders in nature and for this reason play a key role in C cycling. Fungal species that degrade lignin are often grouped into soft rot, brown rot and white rot fungi based on the color of the decayed substrate. The majority of wood decay is done by brown and white rot fungi from the Basidiomycetes. White rot fungi are the most active lignin degraders. Several thousand species of white rots are known. White rot fungi are often inhibited by high N levels, suggesting that lignin degradation is a secondary metabolic response. The interaction of cellulose and lignin to form lignocellulose produces a difficult to degrade structure compared to its' individual components. The recalcitrance of the plant cell wall requires that numerous microorganisms and enzyme systems work together to free substrates to complete growth.

## Plant secondary compounds

Plants produce an array of secondary compounds or metabolites that are not essential for growth and development. There are three major groups of secondary compounds including terpenoids, alkaloids and phenylpropanoids. Many of these compounds are thought to play a role in defending against herbivory and microbial infection, as attractants for pollinators and seed dispersers and as allelopathic agents. These compounds affect the quality of plant litter residues and exudates by negatively affecting organisms and/or processes controlling decomposition processes. These compounds range in molecular weight from 500 to 3 000 Daltons and commonly precipitate proteins through tannin reactions (Kraus et al., [2003\)](#page-20-0). The tanning of leather is an example where a natural product is protected from microbial attack. The ability to precipitate proteins can have profound effects on N availability and microbial succession during decomposition processes.

#### Microbial constituents

Microbial biomass represents NSP derived from photosynthetically fixed C. Net secondary production may be recycled to produce more generations of microbial decomposer biomass. The turnover of the soil microbial biomass represents a significant source of labile and resistant C and potential substrate for SOM formation. Bacteria have many C compounds that are similar to plants. Protein makes up 55% of the cell dry weight of common bacteria. Fungi have less protein than bacteria, concentrating their metabolic constituents at the tips of growing hyphae. For this reason, bacteria have narrow C to N ratios that range from 5 to 8 while fungi often have C to N ratios in excess of 8. Differences in C to N ratio and cell wall components are often related to the decomposability of soil organisms, as was mentioned earlier for plant residues.

The complexity of the microbial cell walls makes them resistant to decay, similar to that of plants, but the building blocks are vastly different. Microbial cell walls contain constituents such as amino sugars and the D-form of certain amino acids that are resistant to decay. Most amino sugars in soil are of microbial origin. Bacterial cell walls are composed of a rigid layer of N-acetylglucosamine and N-acetylmuramic acid chains. They are linked into a rigid layer called petidoglycan by peptide bonds. The cross-linked peptidoglycan called murein is composed repeating units of L-alanine, D-alanine, D-glutamic acid, and either lysine or diaminopimelic acid. Bacterial cell walls contain anywhere from 10 to 90% peptidoglycan with grampositive bacteria containing the most. A major component of the fungal cell wall is chitin, which is composed of repeating units of N-acetylglucosamine. Fungi also contain dark-colored pigments called melanins that are resistant to decay and are thought to contribute directly to SOM formation. The decomposition of plant litter and microbial products normally occurs through a succession of different organisms capable of degrading and utilizing specific chemicals, structures and substrates.

## Turnover of soil inputs

 $\ddot{\phantom{a}}$ 

The turnover of C inputs to soil is often substrate dependent and therefore follows first order reaction kinetics. Proteins and sugars are degraded rapidly and exhibit high turnover rates. The turnover of polymers such as cellulose, lignin and peptidoglycan that require extensive enzyme suites and microbial succession have longer turnover rates. The rate of turnover of a soil C input or substrate  $(A)$  with time  $(t)$  is defined as

$$
\frac{dA}{dt} = -kA\tag{1}
$$

where the product of the decomposition rate constant  $k$  and  $A$ describes the change in A with time. The time required to transform or turnover substrate  $A$  is

$$
turnover time = \frac{1}{k}
$$
 (2)

The turnover time is often referred to as the mean residence time (MRT). Upon integration Equation (1) becomes

$$
A_t = A e^{-kt} \tag{3}
$$

where  $A_t$  is the substrate remaining at any time during the decomposition processes. The decomposition rate constant  $k$  is expressed as per unit of time (e.g., min<sup>-1</sup>, h<sup>-1</sup>, d<sup>-1</sup>, yr<sup>-1</sup>, etc.). The time required to turnover one half of substrate  $A$  is expressed as the logarithmic function

$$
\ln\left[\frac{A\frac{1}{2}}{A}\right] = -k t_{1/2} \tag{4}
$$

where  $t_{1/2}$  is the time required to turn over one half of substrate A (half life). Equation  $(4)$  is integrated to

$$
t_{1/2} = \frac{0.693}{k} \tag{5}
$$

Figure C28 shows both a normal and log plot of a typical turnover response of a substrate that follows first order kinetics. Plotting turnover on a log scale yields a straight line. Table C3 shows typical turnover times of various plant and microbial inputs to soil. The turnover times reflects the decomposability of the soil inputs.

## Soil organic matter formation

Soil decomposers act as the "Waste Management" crew of an ecosystem. The decomposition of plant and microbial inputs to soil plays an important role in maintaining the global C budget by cycling most of the  $CO<sub>2</sub>$  fixed through NPP back to the atmosphere. The C fixed as NPP and converted to NSP is decomposed at a rate very similar to the amount produced on an annual basis. A small fraction of NPP and NSP is persevered as stable soil C in the form of SOM through a process called humus formation.

Humus formation is an essential process that determines NPP and NSP by controlling the availability of essential nutrients. The most efficient procedure to remove humic substances from soil is an alkali extraction. The extraction yields fulvic and humic acids. Fulvic acids are characterized as having low molecular weight (1 000 to 30 000), soluble in water and are commonly found in soil solution and aquatic environments. Humic acids have higher molecular weight (10 000 to 100 000 and more), are insoluble in water and generally are the larger fraction of the two acids. The higher molecular weight of humic acids is presumably due to the condensation of smaller compounds. The alkali unextractable portion of SOM is termed humin and represents up to 30 to 50% of total SOM. Humin is thought to be strongly attached to soil minerals and according to <sup>14</sup>C-dating studies is often 1 000 or more years in age. During the formation of SOM, nutrients such as N, P and S are incorporated into its structure. The structure of SOM consists of approximately 50–55% C, 5% H, 33% O, 4.5% N, and 1% S and P. In addition, other metals and micronutrients, such as Ca, Zn and Cu are present in much smaller amounts. Besides being a reservoir of essential plant nutrients, SOM has qualities that contribute directly to plant and microbial growth through its effect on the physical, chemical, and biological properties of soil. The association of SOM with secondary minerals such as clay and amorphous oxides create soil structure through the formation of aggregates. Aggregate formation enhances soil physical structure by ordering soil mineral grains, promoting aeration and water infiltration and storage.

The formation of humic substances has been studied for more than 200 years because of their influence on soil properties and soil fertility. Since the 17th century, scientists have debated whether plant materials were directly incorporated into these humic substances or altered through microbial activity. Modern analytical techniques have shown that SOM consists of partially decayed plant residues, soil microorganisms, soil fauna, and the byproducts of decomposition. Decomposition of plant and animal residues leads to the formation of byproducts that are highly reactive. The humification process is both biological and nonbiological or abiotic where decomposition byproducts condense randomly to form larger molecules or aggregates of molecules that closely associate with soil minerals. One of the most popular theories of SOM formation is the polyphenol theory. Amino acids are thought to react with a

Table C3 Decomposition rates and turnover of various plant and microbial soil inputs

Soil input	Decomposition rate constant $\text{(day}^{-1})$	Half life (days)	Turnover (days)
Sugar, amino acid	0.2	3.5	5.0
Cellulose	0.08	8.7	12.5
Lignin	0.01	69.0	100.0
Fungal cell wall	0.02	34.7	50.0



Figure C28 The normal and log plots show the half life ( $t_{1/2}$ ) of substrate A is 0.5 h. Using Equation (5), the decomposition rate constant is  $(t_{1/2} = 0.693/k$  or 0.5 = 0.693/k or k = 1.36) 1.36 units of A per hour. The MRT or turnover is calculated using from Equation (2) (1/k = 1/1.36 = 0.74 h).





 $^{a}$  Adapted from Houghton et al. (2001).<br> $^{b}$  Adapted from Raich and Schelsinger (1992) and Paul and Clark (1996).

phenol (catechol) derived either from the alteration of lignin or from microbial products such as pigments (melanins) to produce humic substances. The aminoquinone intermediates condense to form brown, high-molecular-weight nitrogenous humates. Though no two humic substances are presumably alike in structure they behave similarly in function. For example, the sorption of pollutant and pesticides is best explained by total soil C content and generally does not correlate to SOM formed in different ecosystems or environments. Aliphatic long chain C compounds also react with the nitrogenous/aromatic matrix and can comprise the majority of SOM. More details on humification are available in the publications by Aiken et al. ([1985\)](#page-20-0), Haider ([1992](#page-20-0)), Stevenson ([1994\)](#page-20-0) and Piccolo [\(1996](#page-20-0)).

#### Quantity and distribution of organic matter in soils

The importance of SOM in regulating nutrient cycling and impacting physical properties plays a major role in sustaining ecosystem productivity. The quantity of SOM is dependent on the balance between NPP and the rate of decomposition as previously described. The presence of silt and clay generally preserves more C through organomineral interactions while anaerobic soil (e.g., peat soils) tends to preserve C because of the lack of oxygen to complete decomposition. The highest accumulation of C is found in swamps and marshes (723 t ha<sup>-1</sup>) (Table C4). Decomposition also is inhibited by cold in tundra soils and C tends to accumulate primarily as partially decomposed litter. Tropical lowland forests and boreal and temperate forests and temperate grasslands all accumulate up to approximately  $200 \text{ t} \text{ ha}^{-1}$  with turnover times that range from 29 to 91 years. In contrast to temperate grassland, where C accumulates with an overall turnover time of about 60 years, the low levels of SOM in tropical grassland have turnover rates of about 10 years.

## Role of methane in the C cycle

Methane comprises less than 1% of the global C budget. Methane is found as natural gas in fossil fuel deposits, as hydrates or clathrates compounds in ice (e.g., permafrost), deep ocean, and in the atmosphere. Soil microorganisms both produce (methanogens) and consume (methanotrophs) CH<sub>4</sub>. Microbial production of methane results from the decomposition of organic materials in the absence of oxygen. Carbon dioxide is used as an electron acceptor and a reduced organic compound as the donor. The reduction of  $CO<sub>2</sub>$  will occur in soil under





Adapted from Paul and Clark (1996) and Houghton et al. (2003).

extended reduced conditions such as in flooded environments or where oxygen diffusion is limited such as within soil aggregates. Waterlogged soils such as rice paddies, wetlands, waste disposal sites and the enteric fermentation are typical examples (Table C5). The production and distribution of fossil fuels contributes significantly to  $CH_4$  emissions. Most of the annual flux of methane reacts with atmospheric hydroxyl radicals (OH<sup>o</sup>) to form water and  $CO<sub>2</sub>$ . Soil organisms consume about 10 to 30 Tg CH<sub>4</sub> yr<sup>-1</sup>, far below that required to mitigate emissions from anthropogenic sources. The difference between production and consumption of  $CH<sub>4</sub>$  results in an increase in atmospheric CH<sub>4</sub> of approximately 28 to 32 Tg CH<sub>4</sub> yr<sup>-1</sup>. Methane is a more potent greenhouse gas compared to  $CO<sub>2</sub>$  and its production and release has garnered much interest from the scientific community.

## Future considerations

The close link between NPP, NSP, and SOM and their influence on the sources and sinks for greenhouse gases indicates the importance of the global C cycle in regulating ecosystem productivity and climate. The major production and turnover of the components of the C cycle are fairly well characterized at the process level and microscale, for example in a gram of soil. However, on a global scale the interaction of organismal and metabolic diversity, sources and sinks for C, and anthropogenic influences have yet to be fully appreciated. These interactions <span id="page-20-0"></span>must be better understood to adequately predict ecosystem response to perturbations such as climate change. Continued research on the biology and physical factors affecting the global C cycle is required to fully comprehend the global C cycle.

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# Cross-references

Biogeochemical Cycles Carbon Sequestration in Soil Earth Cycles Humic Substances

## CARBON SEQUESTRATION IN SOIL

Carbon sequestration is the result of a series of processes through which carbon dioxide in the atmosphere is removed from biogeochemical circulation and accumulated in soil and biomass. The present article emphasizes the soil-dependent factors that have bearing on the effectiveness of C sequestration regardless of the general climatic constraints.

In a first stage, atmospheric carbon is incorporated by photosynthetic plants, which synthesize complex biomacromolecules. When organic remains in addition to microbial bodies decay in soil, a portion of the C stabilizes into the soil (soil C sequestration or humification), the remainder being released mainly as  $CO<sub>2</sub>$  and  $H<sub>2</sub>O$  (mineralization). In environmental situations where the above balance shifts to humification, a progressive increase in soil C concentration will be produced through time. This contributes to alleviating the greenhouse effect, global warming and hence climatic change (Batjes, [1998](#page-22-0)).

Rough estimations point to the fact that the principal C reservoir in the Earth's surface is not terrestrial or marine biomass, but soil organic matter, the latter amounting about 1 500 to 2 000 Pg  $(1 \text{Pg} = \text{petagram} = 1 \text{ billion})$  soil organic C (Batjes, [1996;](#page-22-0) Post et al., [1982\)](#page-22-0). Assuming that soil organic matter pool represents more than twice the C in living vegetation (around 560 Pg) or in the atmosphere (750 Pg), it is clear that changes in soil C sequestration rates in local sinks could have a noticeable bearing on the global C balance (Buringh, [1984;](#page-22-0) Eswaran et al., [1995](#page-22-0)).

Despite their importance on a global scale, the major formation mechanisms of biodegradation-resistant humic substances are understood only in very broad terms. It is clear that the effectiveness of the whole C sequestration process varies from one soil type to another, as well as in the different ecosystem compartments. It is more intense when several abiotic (climatic, geologic and so on) and biotic (vegetation type, microbial community) factors work together to strengthen the effect. For this reason, studies of the potential of the soil as a reservoir of C, as reported for different bioclimatic regions and in soils developed on different geological substrates, provide a wide range of results so that the topic remains controversial.

#### Side-effects of soil C sequestration

The sequestration of C in soils has both positive and negative side-effects. Apart from alleviating the greenhouse effect, soil C sequestration leads to additional benefits regarding soil quality defined in terms of sustainable productivity. These indirect benefits are mostly reflected in the improvement of soil structural stability, water holding capacity, continuous release of available nutrients, biological activity, and others. In addition, the stabilized organo-mineral matrix also enhances the potential of the soil to act as an environmental filter regulating leachability and bioavailability of organic and mineral pollutants in the soil solution such could be some agrochemicals and heavy metals (Almendros, [1995](#page-22-0); Wershaw, [1977\)](#page-22-0).

On the negative side, the stabilization and sequestration of atmospheric C into soil is connected with the fact that, in addition to C, other bioelements such as N, P and S, are also sequestered in slowly bioavailable forms. Therefore (and this is mainly in forest ecosystems) effective plant and soil C sequestration may often be associated with the accumulation of raw humus types (moder, mor), low-performance biogeochemical cycles, limited primary productivity and (though this is not necessarily causally related) a low biodiversity. In such soil systems the organic matter is weakly associated to the mineral fraction compared to systems with active (mull) humus, and most of the pedogenic processes do not end in the formation of stable organo-mineral complexes. This causes the vertical redistribution of the organic matter down the soil profile on a macroscopic scale. It is also connected with the generation of leachates and the exportation of plant nutrients out of the soil. In some cases, this may have undesirable effects on water quality.

In other words, in a global soil management policy, it will perhaps be more important to monitor the *quality* rather than the total quantity of the organic matter sequestered in the soil. Certain forest or brushwood sites in the semi-arid Mediterranean region provide an illustration. Here, deeply transformed soil organic matter is commonly in low concentration (e.g., less than 20 g  $kg^{-1}$ ). However, it is of high resilience as regards any possible future climatic change. This is in marked contrast with soil formations in the boreal forest for example, where there are greater amounts of slightly transformed organic matter. With the possible rise in ambient temperature occasioned by future global warming, these areas could turn into active  $CO<sub>2</sub>$  sources, because the thick layers of organic matter they contain, are of a low degree of humification with a weak association between the organic and mineral fraction. Peat and bog soils in temperate zones (often



Figure C29 Hypothetical soil-dependent processes responsible for the formation of humic substances and soil C sequestration.

sapric in type, with low C/N ratio) are also at risk. Global temperature rise would likely have a drying effect, and it is well known that a drop in the phreatic level of a few centimeters is enough to turn these local C sinks into self-burning sources of CO2 after an intense episode of microbial thermophilic activity.

Basic research on soil C sequestration – Experimental approaches to monitor soil C stabilization mechanisms The scientific reappraisal of humification mechanisms has acquired renewed interest in the light of the global change scenario. Progress over the last few years has taken advantage from the development of new analytical and instrumental tools.

Clearly, different processes are involved in soil C sequestration (Figure C29): such as selective preservation of biomass, diagenetic alteration of biomacromolecules and humification by neoformation sensu stricto (microbial, enzymatic or abiotic). All these mechanisms occur simultaneously and are closely interrelated. In the most favorable cases, the assessment of their variable extent, in space and time, can be carried out by using specific techniques of isolation and analysis of free biomarker – or signature – compounds occurring in the lipid fractions. This is often complemented by the molecular characterization of humic substances by chemical and thermal degradation followed by mass spectrometry. Alternatively, non-destructive methods such as visible, infrared or nuclear magnetic resonance spectroscopies are available. In some cases, there is no valid experimental approach to identify the substances formed by each of the above processes. Commonly, different humification pathways lead to substances with common structures and properties.

These and future techniques will be necessary to quantify the processes involved in soil C sequestration, and will enable a better assessment than was formerly possible of the potential of soil as a repository of C in ameliorating the effects of a global increase in temperature.

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## Cross-references

Carbon Cycling Histosols Humic Substances Peat

## **CARBONATES**

The essential structural unit of the carbonates is the  $(CO_3)^{2-}$  group. Deer et al. ([1992](#page-24-0)) state that there are about 60 known carbonates in nature though only one, calcite, commonly forms in soil. Dolomite is the second most common in soils, though it is always inherited rather than neoformed. The only other carbonate likely to be encountered in the soil environment is siderite, which forms in hydromorphic environments. Basic properties of these three carbonates are shown in Table C6. All three carbonates have high birefringence, and show the phenomenon of twinkling in thin section. This is strongest in the case of calcite.

## **Calcite**

 $CaCO<sub>3</sub>$  exists in several polymorphous forms. Calcite is the only common one in soil, with aragonite occurring in highpressure metamorphic rocks, or in a low-pressure modification in the tests of some invertebrate organisms. The structure of calcite is analogous to a distorted halite, in which Ca and  $(CO)$ <sub>3</sub> ions replace Na and Cl ions respectively in the structure. The cube of the halite structure is imagined as being compressed along one of its axes of three-fold symmetry to produce a face-centered rhomb. The distortion makes it possible to accommodate the large planar  $(CO_3)$  groups into the structure. Most calcites in nature are close to the ideal composition, though substitution of Mg, Fe and other metal-cations for Ca occurs. For calcites formed in low temperature environments, the substitutions are negligible.

In calcareous soils calcite is invariably accompanied by silicates, and in humid climates is the most reactive common mineral there. Consequently, if calcite is present in a soil, it has the effect of generating an alkaline pH (usually between 7 and 8). The relevant reactions may be considered within the framework of the system  $CaO-H<sub>2</sub>O-CO<sub>2</sub>$ .

## The system  $CaO-H<sub>2</sub>O-CO<sub>2</sub>$

An isobaric, isothermal cross section of this system is shown schematically in Figure C30. There are two stable two-phase assemblages and two stable three-phase assemblages. The two-phase assemblages are:

- a. calcite  $+$  aqueous solution (at higher partial pressures of CO<sub>2</sub>). b. portlandite  $+$  aqueous solution (at lower partial pressures
- of  $CO<sub>2</sub>$ ).

The three phase assemblages are:

- a. calcite + aqueous solution +  $CO<sub>2</sub>$
- b. calcite  $+$  portlandite  $+$  aqueous solution
- c. calcite  $\phi$  portlandite  $\phi$  lime (in the absence of aqueous solution).

Clearly, lime will not be stable in soil since the partial pressure of water is never going to be close enough to zero. Neither will portlandite be stable, since the partial pressure of  $CO<sub>2</sub>$  for the three-phase assemblage c, is approximately  $10^{-13}$  atmospheres (point x in Figure C30). Calcite will be stable as the three phase assemblage c with point y lying between  $P_{CO2}$  values of  $10^{-3.5}$  atmospheres (the average value in the Earth's



Figure C30 The system CaO-H<sub>2</sub>O-CO<sub>2</sub> at 1 atmosphere (100 kPa) total pressure and 25 °C (see text for explanation). The positions of x and y are schematic in the interests of clarity. All natural conditions in terrestrial soils will be on the  $CO<sub>2</sub>$  side of the Calcite-x tie line.

Table C6 The commonest carbonates in soil

Name	Formula	Crystal system	Effervescence with dilute HCl	Stain color
Calcite	CaCO3	Trigonal	Vigorous	Pink to red-brown with Alizarin Red S
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	Trigonal	Slow in the cold	Very pale blue with K ferricyanide
Siderite	FeCO <sub>3</sub>	Trigonal	Unreactive in the cold	Deep blue with K ferricyanide

<span id="page-23-0"></span>atmosphere) to  $10^{-1.5}$  atmospheres (the possible maximum in the solum – this being due to the respiration of roots, and the microbial breakdown of organic matter).

[Figure C30](#page-22-0) does not give the complete picture since it contains no direct information on the conditions of pH under which calcite is stable at the surface of the Earth.

Table C7 presents the data for answering this question. The calculation is in three steps:

$$
[H_2CO_3*] = KHP_{CO2} = 10^{-5}
$$
\n(1)  
\n[H\_2CO\_3] = (H\_2CO\_3\*(H\_1H\_1)H\_2 + 10^{-11.35}H\_1H\_2 + (2))

$$
[\text{HCO}_3^-] = ([\text{H}_2\text{CO}_3^*]/[\text{H}^+])K_a = 10^{-11.35}/[\text{H}^+]
$$
(2)  
\n
$$
[\text{Ca}^{2+}] = ([\text{H}^+]K_S)/[\text{HCO}_3^-]
$$
  
\n
$$
= ([\text{H}^+]/10^{1.91})/(10^{-11.35}/[\text{H}^+])
$$
  
\n
$$
= [\text{H}^+]^2 \times 10^{13.26}
$$
(3)

The last relationship can be written in the form:

$$
\log[\text{Ca}^{2+}] = 2\log[\text{H}^+] + 13.26
$$

or

$$
-\log[\text{Ca}^{2+}] = -2\log[\text{H}^+] - 13.26
$$

or

$$
pC_{Ca2+} = 2\,\text{pH} - 13.26
$$

This is plotted as a pC-pH diagram for the system  $H_2O$ – $CO_2$ (Figure C31). The point of charge balance in the presence of calcite is achieved where the concentration of  $HCO_3^-$  is twice the concentration of  $Ca^{2+}$ . The point of charge balance is calculated in the following way:

$$
[Ca^{2+}] = [HCO_3^-]/2
$$
 (4)

which is substituted into Equation (3) to give

 $[HCO_3^-]^2 = 2[H^+]K_S$  (5)

which is substituted into Equation (2) to give

$$
[HCO_3^-]^2 = 10^{-22.7} / [H^+]^2
$$
 (6)

Equating  $(5)$  and  $(6)$ :

$$
2[H^+]K_S = 10^{-22.7}/[H^+]^2
$$
  
\n
$$
[H^+]^3 = 10^{-22.7}/2 \times 10^{1.91}
$$
  
\n
$$
= 10^{-24.61}/2
$$
  
\n
$$
[H^+] = 0.5 \times 10^{-8.2} = 10^{-8.5}
$$
\n(7)

In other words at the partial pressure of  $CO<sub>2</sub> (10<sup>-3.5</sup>$  atmospheres) in the atmosphere, at 25  $\degree$ C, and 100 kPa (1 atmosphere) total pressure, calcite becomes stable at pH 8.5. This means that rainwater falling on a limestone-dominated landscape would rise in pH from 5.7 to 8.5. For this reason limestone terrain is almost always considered to be at low risk from acid rain. Under a humid climate this high value is not likely to be reached in a calcite-bearing soil, since  $P_{CO2}$  may be as high as  $10^{-1.5}$  atmospheres. In the latter case a pH of 7.6 will prevail in the presence of calcite and provided there is a Table C7 Values for the partial pressure of  $CO<sub>2</sub>$  and for equilibrium constants of significant reactions, used in the calculations. It is difficult to distinguish  $H_2CO_3$  and  $CO_2$  in solution.  $H_2CO_3^*$  is a hypothetical species that represents them both





**Figure C31** pC–pH diagram for the system CaO–H<sub>2</sub>O–CO<sub>2</sub> for  $[H_2^{\prime}CO_3^{\dagger}]=10^{-5}$ . Temperature is 25 °C and pressure 100 kPa. The point of charge balance (and pH of the system) is 8.5.

continuous supply of rain, this will be the pH (water) of the soil. In semi-arid or arid climates however, where atmospheric precipitations are infrequent, the pH may rise to higher values because there is no tendency for calcite to dissolve to give the isobaric, isothermal value of the equilibrium pH.

## Dolomite

The structure of dolomite is similar to that of calcite and can be thought of as comprising alternating layers of calcite with magnesite ( $MgCO<sub>3</sub>$ ). In the field it is distinguishable from calcite in only reacting notably with dilute HCl, when the acid is heated. In thin section it takes on a pale blue tinge with potassium ferricyanide, which is also true for a low Fe ferroan calcite. However, unlike the latter, it does not react with the stain alizarin red S.

Dolomite does not appear to form in weathering systems but is inherited from soil parent materials. It weathers more slowly than calcite in humid climatic zones, though in a mature soil will eventually be removed from the solum, as will calcite. Calcite may reprecipitate in the C horizon (of a Luvisol, for example), whereas dolomite will not. A small fraction of the released Mg however may be incorporated into the secondary calcite.

## The system  $MgO$ –CaO–H<sub>2</sub>O–CO<sub>2</sub>

Dolomite is common in calcareous soils derived from dolomitic limestones or from sediments such as tills derived from rocks of this kind. It is invariably accompanied by calcite and the <span id="page-24-0"></span>two carbonates together determine the pH of soils in which they both occur. This is supported by the measurements of soil water composition in the C horizons of Luvisols in the Blue Springs watershed in Southern Ontario, about 100 km west of Toronto (Figure C32; Shulman and Chesworth, 1985).



Figure C32 The system MgO-CaO-H<sub>2</sub>O-CO<sub>2</sub> at 1 atmosphere (100 Pa) total pressure and 25  $\degree$ C. Water compositions were monitored in the Blue Springs watershed of Southern Ontario. The soil water and groundwater compositions fall within the uncertainty zone for the three-phase equilibrium calcite  $+$  dolomite  $+$  aqueous solution. This is consistent with the soil water and groundwater having compositions in part controlled by this equilibrium (Shulman and Chesworth, 1985).



Figure C33 Redox-pH relationships among minerals and an aqueous phase for the system Fe–Ca–K–S–C–H–O. Conditions: 1 atmosphere<br>total pressure, 25 °C,  $P_{CO2} = 10^{-3.5}$  atmospheres, activities of Fe and  $Ca = 10^{-5}$ , S activity unspecified, the sulfide field is shown at its maximum possible extent.

## Siderite

In structure siderite is similar to calcite, though unlike calcite, the composition may depart substantially from the ideal formula of [Table C7,](#page-23-0) with Mg and Mn as common substitutes for Fe. Iron is present in ferrous form, so that siderite is a product only of reducing environments. Its usual occurrence in soils is in  $CO<sub>2</sub>$ -rich hydromorphic environments such as peatlands.

## Redox-pH conditions for siderite

Figure C33 shows the predominance field for siderite in terms of Eh (pe) and pH. Clearly the conditions required are highly reducing and might be expected to prevail in a hydric environment. In the absence of substantial concentrations of  $HS^-$  in solution, so that pyrite does not form, siderite will be produced provided that the requisite partial pressure of  $CO<sub>2</sub>$  develops. In a peatland this may come about from the respiration or decay of water plants such as sphagnum species.

Ward Chesworth

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Deer, W.A., Howie, R.A., and Zussman, J., 1992. An introduction to the Rock Forming Minerals. Harlow, UK: Longmans. 696 pp.

Shulman, D., and Chesworth, W., 1985. Calcium carbonate solubility in the C horizon of a Southern Ontario, Canada, luvisol. Chem. Geol., 51: 115–122.

#### Cross-references

Acidity Biomes and their Soils Bog Calcareous Soils Calcisols Duricrusts and Induration Hydric Soils Luvisols Micromorphology Mire Peat

## CATCHMENT

Term applied to a natural drainage area or basin, wherein the rainfall is caught and collected to supply the local rivers, streams, lakes and subsurface waters. Also catchment basin.

## CATENA

A chain, string, or connected series of soils, related by their sequence in a landscape. Synonymous in part with toposequence chronosequence. The variability of soils in a topographic sequence is a function of gradient and position on the slope (Birkeland, 1999, p 235).

#### Bibliography

Birkeland, P.W., 1999. Soils and Geomorphology, 3rd edn. New York: Oxford University Press, 430 pp.

# CATION EXCHANGE

Ion exchange involving cations. In soils the exchange takes place on the surfaces of clay minerals, amorphous inorganic phases and organic matter. The cation exchange capacity (CEC) is the quantity of cations reversibly adsorbed per unit weight of the solid (McBride, 1994, chapter 3). The conventional unit for CEC is cmoles/kg.

## Bibliography

McBride, M.B., 1994. Environmental Chemistry of Soils. New York: Oxford University Press, 406 pp.

# Cross-reference

Sorption Phenomena

## CEMENT

Any substance, which binds together the discrete particles in a soil or sediment. See Consistence and *Pan*.

## CHELUVIATION

The downward movement of chemical species in a soil in chelated form. A combination of chelation and eluviation. Organic constituents are integral to the process in providing acid to attack the mineralogical components of a soil, and complexants capable of holding released elements such as Al in solution, in which form they are capable of being transported downwards in the profile. See Table 1 in van Ranst and de Coninck (2002).

#### Bibliography

Van Ranst, E., and De Coninck, F., 2002. Evaluation of ferrolysis in soil formation. Eur. J. Soil Sci., 53(4): 513-520.

## CHEMICAL ANALYSES

## Introduction

Chemical analyses of soils are important in assessing the nutrient status of soils for agricultural production, and in determining the environmental hazards imposed on soils by industrial, municipal, and agricultural wastes. Traditionally, the emphasis of soil chemical analyses has been on evaluating soils in regard to their agricultural productivity. Specifically, to measure plant nutrient levels and other chemical factors (pH, organic matter content, cation exchange capacity, etc.) which determine a soil's suitability as a plant growth medium. More recently, the scope of soil chemical analyses has expanded to evaluation of a soil in regard to environmental quality. Worldwide, concerns have been expressed about numerous soil and water contaminants. These include nitrates and phosphates, metalloids and metals such as arsenic, cadmium, chromium, copper, lead, mercury, and nickel; radionuclides, pesticides, and contaminants from municipal and animal wastes.

Soil chemical analyses range from simple routine tests that can be conducted with hand kits in the field or in soil testing laboratories, to costly sophisticated analyses involving stateof-the-art equipment. Chemicals, both inorganic and organic, undergo sorption reactions in soil systems that often render them insoluble. It is therefore necessary to use appropriate reagent solutions to extract chemicals of interest prior to conducting the actual analysis. After the pertinent extraction is complete, chemical analysis is generally accomplished using either spectroscopic, chromatographic, potentiometric, gravimetric, or titrimetric techniques. These techniques utilize instruments such as: colorimeters, atomic absorption and inductively coupled plasma spectrometers and gas, high-performance liquid, and ion chromatographs. A routine chemical characterization of a soil should include a determination of pH, organic matter content, cation exchange capacity, and extractable bases such as Ca, Mg, K, and Na. These measurements provide general information concerning the chemical nature of a soil.

#### Soil chemical extractions

Chemical components (defined as any of the minimum number of substances required to completely specify the composition of all phases of a chemical system) can precipitate from the soil solution, and can be electrostatically or chemically adsorbed to the surfaces of soil minerals. Furthermore, the soil organic fraction can bind inorganic and organic ions, as well as partition non-polar organic molecules. These retention processes render chemical components insoluble; therefore, it is often necessary to treat the soil with reagent solutions to extract the particular chemical component of interest (Peck and Soltanpour, [1990](#page-30-0)). However, prior to conducting any chemical analysis, soils are usually air-dried, pulverized, sieved (generally through a 2 mm sieve), and mixed to obtain a homogeneous composite sample.

Several extracting solutions, along with their functions, are listed in [Table C8.](#page-26-0) Each of these extractants was designed to remove a distinct category of chemical constituent from a soil. For example, the total sorbed metals procedure used by the U.S. Environmental Protection Agency would be the recommended extractant to evaluate heavy metals in soils. This extrac $t$ ant is comprised of concentrated  $HNO<sub>3</sub>$  and  $HCl$  acids, and hydrogen peroxide (30%). It provides a measure of total metal concentrations that are exchangeable or adsorbed by soil components (Risser and Baker, [1990](#page-30-0)). To determine plant available micronutrients, an extractant containing the chelate diethylenetriaminepentaacetic acid (0.005 M DTPA) along with 0.01 M  $CaCl<sub>2</sub>$  and 0.1 M triethanolamine (TEA) may be employed. This extractant, developed by Lindsay and Norvell ([1978\)](#page-30-0), removes labile pools of metals that correlate well with plant nutrient concentrations. Other trace metal extractants that are in common use globally include 1 M or 0.1 M HCl or  $HNO<sub>3</sub>$ , 0.5 M CH<sub>3</sub>COOH, 1 M CH3COONH4, 0.05 M Na2-EDTA or (NH4)-EDTA, 0.01 M CaCl<sub>2</sub>, and boiling water (Hamilton, [1980\)](#page-30-0).

Extraction schemes have also been developed that fractionate a soil element into different pools. Kuo ([1996\)](#page-30-0) cites a fractionation method for inorganic P pools, which are based on the ability of specific extractants to solubilize P present in <span id="page-26-0"></span>Table C8 Common soil chemical extractants



\* Mehlich, A. [1984](#page-30-0).

References for all other extractants are given in the texts: Page et al. [\(1982](#page-30-0)) and Westerman ([1990\)](#page-31-0).

Al-, Fe- and Ca phosphates, and accounts for P that is occluded and nonoccluded within Fe- and Al oxides. The procedure consists of the following extractions: (i) 0.1 M NaOH to remove nonoccluded Al- and Fe- bound P, (ii) 1 M NaCl and citratebicarbonate (CB) to remove P sorbed by carbonates during the preceding NaOH extraction, (iii) citrate-dithionite-bicarbonate (CDB) to remove P occluded within Fe- and hydrous oxides, and  $(iv)$  1 M HCl to remove Ca- bound P. Similar extraction schemes are also used for fractionation of heavy metals in soils, such as nickel, cadmium and lead (Amacher, [1996\)](#page-30-0) and organic S (Tabatabai, [1996](#page-31-0)).

Solutions used to extract a particular element may vary regionally due to inherent differences in the chemical, physical, and biological properties of soils. For example, an extractant comprised of dilute acid (0.025 M HCl) and dilute ammonium fluoride (0.03 M  $NH_4F$ ) is frequently used as an index of available P in the Eastern and Midwestern states of the USA. This extractant is appropriate for slightly acid to neutral soils. The NH4F complexes with Fe and Al in the acidic solution, hence, dissolving Fe- and Al-phosphates (Kuo, [1996](#page-30-0)). In contrast, a solution consisting of  $0.5$  M NaHCO<sub>3</sub> at pH 8.5 is more regularly used to extract available P from soils in the Western region of the USA that are often alkaline and calcareous and contain Ca-phosphates. This extractant prompts precipitation of Ca as  $CaCO<sub>3</sub>$ , decreasing the Ca concentration and consequently, increasing the P concentration in the soil solution (Olsen and Sommers, [1982](#page-30-0)).

Many laboratories have adopted the use of "universal extractants" that can extract several elements simultaneously. Two of these are the Mehlich-III (0.2 M CH<sub>3</sub>COOH  $+$  0.25 M  $NH_4NO_3 + 0.15 M NH_4F + 0.013 M HNO_3 + 0.001 M$ EDTA, adjusted to pH 2.5) developed to extract plant available P, K, Na, Ca, Mg, Mn, Zn and Cu (Mehlich, [1984\)](#page-30-0) and the ammonium bicarbonate (AB)-DTPA extractant (AB-DTPA: 1 M NH<sub>4</sub>HCO<sub>3</sub> + 0.005 M DTPA, adjusted to pH 7.6), which removes available P,  $NO<sub>3</sub>$ , K, Zn, Fe, Cu, and Mn (Soltanpour and Schwab, [1977;](#page-31-0) Kuo, [1996\)](#page-30-0). The versatility of these "universal" extractants can be illustrated using the AB-DTPA mixture as an example. The DTPA is used to chelate micronutrients, the  $NH<sub>4</sub><sup>+</sup>$  extracts K, and the  $HCO<sub>3</sub><sup>-</sup>$  extracts P (Kuo, [1996](#page-30-0)). The use of the universal extracts also varies regionally. For instance, the Mehlich-III extractant is generally preferred in the Eastern region of the U.S., while the AB-DTPA extractant is favored in the Western states.

Soil chemists, pedologists, as well as soil microbiologists are often interested in determining the total elemental composition of soils and/or soil constituents. A total elemental analysis of soils and rocks, however, initially requires that these materials be solubilized by acid digestion or fusion with various fluxes. The usual dissolution procedure for total elemental analysis is the use of hydrofluoric acid (HF) with perchloric acid ( $\text{HClO}_4$ ) for decomposition of both the inorganic and organic soil fraction. Hydrofluoric acid dissolves silicates by the reaction of F with Si to form SiF, which is volatile when heated with strong acids. Perchloric acid becomes a strong oxidizer of organic matter when heated and also effectively removes excess HF from the sample. Variations of the HF digestion technique are reported in Hossner ([1996\)](#page-30-0).

The sodium carbonate fusion technique is used for determination of total soil Si, Al, Fe, Ti, Ca, Mg, Mn, and trace metals and was originally designed for elemental analysis of silicate rocks and minerals. Fusion of silicates with sodium carbonate renders them soluble in hydrochloric acid. However, the presence of Fe- and Mn-oxides should be considered because they form alloys with the platinum crucibles during fusion, which can damage them. Therefore, it is recommended that samples containing  $>40\%$  Fe and  $>1\%$  Mn oxides be pretreated with aqua regia to dissolve the majority of oxides.

In summary, extracting solutions are used to solubilize chemical components that are "fixed" or rendered insoluble by soil systems. They are designed to extract a particular soil fraction, for example, the plant available fraction or perhaps all sorbed species (electrostatically and chemically adsorbed species). The type of extractant used depends upon the inherent nature of a soil and therefore, extracting solutions used for a specific element may vary regionally. Many laboratories are employing "universal" extractants that can simultaneously remove several elements, and efforts are now being made to standardize procedures. To determine the total elemental composition of soils, HF acid digests as well as fusion techniques are employed which decompose the soil matrix, solubilizing soil chemical elements.

## Soil chemical characterization

There are a number of routine soil chemical analyses that provide the investigator with general information regarding the chemical nature of a soil ([Table C9\)](#page-27-0). Examples of these include: soil pH, organic matter content, and cation exchange capacity. A brief discussion of these three important analyses will be given.

## Soil pH

Soil pH is one of the most common soil chemical measurements. It provides the investigator with information about the solubility of various soil compounds, the adsorption behavior of ions to soil surfaces, and the microbial activity of soil systems. Most soil

<span id="page-27-0"></span>



<sup>a</sup> References for these analyses are given in the texts: Page et al. [\(1982\)](#page-30-0) and Westerman ([1990\)](#page-31-0).

laboratories measure soil pH using a combination glass indicator electrode coupled with a calomel reference electrode connected to a pH meter. A potentiometrically measured soil pH is essentially an index of the  $H^+$  ion activity in a solution that is in equilibrium with soil particles (van Lierop, [1990\)](#page-30-0).

Detailed reviews on soil pH are provided by McLean [\(1982\)](#page-30-0) and Thomas [\(1996](#page-31-0)). Both suggest using a soil to solution ratio (weight of air- or oven-dried soil: volume of water) of 1 : 1 when water is used as the suspension medium. However, factors such as salt or electrolyte content and liquid junction potential can influence soil pH measurements. Cations of salts (e.g.,  $K^+$  in KCl) can displace  $H^+$  and  $Al^{3+}$  ions, decreasing soil solution pH. Furthermore, a liquid junction potential can arise at the interface where two dissimilar electrolyte concentrations are in contact (e.g., soil suspensions) and is a basic limitation in accurately making direct potentiometric measurements (Harris, [2002](#page-30-0)). When a pH electrode is placed in a soil suspension, the mobilities of  $K^+$  and  $Cl^-$  ions from the salt bridge are no longer similar, as they would be in aqueous solution, and a liquid junction potential develops. The differential mobilities are a result of the attraction of  $K^+$  ions to negatively charged soil particles. Therefore, soil pH is often measured in a 0.01  $\rm{M\,CaCl_{2}}$ solution (soil: solution ratio equal to  $1:2$ ) to mask the influence of variable salt content and minimize the liquid junction potential (McLean, [1982;](#page-30-0) Thomas, [1996](#page-31-0)). Junction potential can also be minimized by placing the KCl salt bridge in the clear supernatant and the glass indicator electrode in the settled soil suspension.

## Soil organic matter

Soil organic matter is defined by Brady and Weil [\(2004](#page-30-0)) as the organic fraction of the soil that includes plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the soil population. The active colloidal behavior of the organic fraction has a significant influence on the chemical and physical properties of soils. It can account for one third or more of the cation exchange capacity (CEC) of surface soils and is the most significant factor responsible for the stability of soil aggregates.

Soil organic matter (SOM) is usually measured by determining the organic C content of a soil, and multiplying this value by a constant based on the percentage of organic C (48 to 58% by weight) in organic matter – published values for this constant range from 1.7 to 2 (Nelson and Sommers, [1996\)](#page-30-0). Nelson and Sommers [\(1996](#page-30-0)) provide a detailed review of procedures and instrumentation used for SOM determination. They recommend that the actual organic C content be reported rather than the percent organic matter due to the difficulties in accurately determining SOM.

Soil organic carbon (SOC) content is measured using dry or wet combustion techniques. Dry combustion utilizes either medium-temperature resistance or high-temperature induction furnaces that provide the heat necessary for the combustion of organic C to  $CO<sub>2</sub>$ . The  $CO<sub>2</sub>$  liberated is then quantified using gravimetric, titrimetric, volumetric, infrared, or thermal conductimetric methods. Resistance furnaces heat samples by radiation, conduction, and convection in a sample holder surrounded by high-resistance materials. Accelerators such as CuO are often mixed with a soil sample to promote the combustion of SOC. Induction furnaces use high frequency electromagnetic radiation as the heat source. Since soils cannot be heated by induction, it is necessary to add susceptors (Fe or Sn) that indirectly heat the sample by radiation, conduction, and convection.

Wet combustion usually involves digesting a sample with a  $60:40 \text{ H}_2\text{SO}_4: \text{H}_3\text{PO}_4$  mixture containing  $\text{K}_2\text{Cr}_2\text{O}_7$  and boiling the sample at  $210\text{ °C}$ . The SOC content is determined from the  $CO<sub>2</sub>$  evolved, which is adsorbed by a suitable adsorbent and weighed, or it is absorbed by a standard base and titrated. Since dry and wet combustion techniques are a measure of total soil C content (organic plus inorganic C), it is necessary to correct for the inorganic C contribution. This is accomplished by predigesting the sample to remove inorganic C present as carbonates, or measuring inorganic C and subtracting it from the total C content.

Alternately, soil organic matter content is frequently determined using the Walkley-Black method, described in detail by Allison ([1965\)](#page-30-0). This method, which involves oxidation of soil organic C by  $Cr_2O_7^{2-}$ , can be described by the following reaction:

$$
2Cr_2O_7^{2-} + 3C + 16H^+ = 4Cr^{3+} + 3CO_2 + 8H_2O \qquad (1)
$$

where organic C is assumed to have an average valence of zero. The excess dichromate is then titrimetrically measured with a standard  $FeSO<sub>4</sub>$  solution and the amount of organic C oxidized is calculated from the amount of dichromate reduced. A colorimetric determination of the amount of  $Cr^{3+}$  produced can also be used to quantify organic C.

#### Cation exchange capacity

The cation exchange capacity (CEC) of a soil is defined as the sum total of exchangeable cations that a soil can adsorb, expressed in moles of positive charge adsorbed per unit mass  $(\text{cmol}_c \text{ kg}^{-1})$  (Brady and Weil, [2004\)](#page-30-0). It is the quantity of readily exchangeable cations required to neutralize negative charge in soils (Sumner and Miller, [1996\)](#page-31-0). The negative charge of soil colloids is derived from isomorphous substitution within the structure of layer silicate minerals, broken bonds at mineral edges and external surfaces, dissociation of organic acid functional groups, and preferential adsorption of specific ions on particle surfaces. Thus, CEC is a soil property that is often dependent upon the conditions under which it is measured. For instance, in soils containing variable charge minerals such as kaolinite, metal oxides, and OM, CEC increases with an increase in pH.

There are numerous methods used for CEC analyses that can be categorized as: summation, direct displacement, displacement after washing, and radioactive tracer methods (Rhoades, [1982](#page-30-0); Sumner and Miller, [1996\)](#page-31-0). The summation method involves displacing the exchangeable cations on a soil with a saturating salt

solution such as ammonium acetate. The CEC is equivalent to the sum of exchangeable cations present in the leachate. The direct displacement method consists of saturating the exchange sites with an index cation. Then the adsorbed index cation, and the small amount of entrained solution left in the soil after centrifugation, is directly displaced with another salt solution. The saturating index cation and anion concentrations are measured and the CEC is calculated from these values. In the displacement after washing method, exchange sites are saturated with an index cation. The soil is then washed free of excess saturating salt; the index cation is displaced and then quantitatively measured. The *radioactive tracer* method involves using a radioactive isotope of the saturating cation. The CEC is then calculated by measuring the distribution of the tracer between the soil and soil solution.

Ammonium acetate (pH 7.0) and sodium acetate (pH 8.2) are traditionally used as saturating solutions for CEC determinations in neutral and alkaline soils. However, with these solutions one must be concerned with dissolution of compounds such as  $CaCO<sub>3</sub>$  and  $CaSO<sub>4</sub>$ , and the interaction of  $NH<sub>4</sub><sup>+</sup>$  and  $Na<sup>+</sup>$  with layer silicates (Chapman, [1965](#page-30-0); Rhoades, [1982;](#page-30-0) Sumner and Miller, [1996](#page-31-0)). Modified procedures for CEC determination of arid and acid soils are presented by Rhoades ([1982\)](#page-30-0). With arid soils, a saturating solution of a 0.4 M sodium acetate/0.1 M NaCl in 60% ethanol, pH 8.2 mixture is used, while 0.1 M barium chloride dihydrate is recommended as the saturating solution with acid soils.

## Summary

Soil pH, organic matter content, and cation exchange capacity provide a general description of the chemical character of a soil. These determinations, along with physical and clay mineralogical data, provide the analyst with the necessary information to assess the general usefulness of a soil as a medium for plant growth or as a waste disposal site.

## Analytical techniques

Most quantitative soil chemical analyses are conducted using spectroscopic techniques. These primarily include molecular (ultraviolet (UV) – visible) absorption, atomic absorption, and inductively coupled plasma (ICP) spectrometry. Chromatographic techniques, which include gas, high-performance liquid, and ion chromatography, are also frequently utilized for the analyses of organic compounds and ions. Other important techniques that deserve mention include X-ray fluorescence spectrometry (Karathanasis and Hajek, [1996](#page-30-0)) and neutron activation (Helmke, [1996](#page-30-0)) for sensitive elemental analysis of soils, and the use of ion selective electrodes for potentiometric determination of ion activities (i.e.,  $K^+$ , Mg<sup>2+</sup>, Ca<sup>2+</sup>,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $Br^-$ , and  $F^-$ ) in soil solutions (Talibudeen, [1991\)](#page-31-0).

## Molecular absorption spectrometry

This technique utilizes a spectrophotometer (colorimeter) for the quantitative determination of compounds that absorb light. The spectrophotometer measures the transmission of light at a specific wavelength through a solution of a colored species that absorbs strongly at that wavelength (Smith and Scott, 1983). The basic components of a spectrophotometer are the radiation source, a monochromator, a sample cell, and a detector. Absorption of light is commonly measured by absorbance (A) or transmittance (T), which are defined as  $A = \log(I_0/I)$  and  $T = I/I_0$ , where  $I_0$  is the intensity of the incident light beam and I is the intensity of the transmitted light beam. The most common analytical application of spectrophotometry utilizes the relationship between absorbance and concentration. This relationship is described by Beer's law:  $A = abc$ , where absorbance  $(A)$  is proportional to the concentration  $(c)$  of the absorbing species,  $\bar{b}$  is the pathlength of the light through the solution, and  $a$  is the absorptivity, a proportionality coefficient. Beer's law works best for dilute solutions  $(<0.01$  M) of a light absorbing species. At higher concentrations, deviations from Beer's law occur that result in changes in the absorbing species or in the properties of the bulk solution (Harris, [2002](#page-30-0)).

A typical measurement using molecular absorption spectrometry would involve measuring the proportionality between the concentration and absorbance of a set of standards. Subsequently, an unknown quantity of the same species can be determined by directly comparing its absorbance to the standards. Orthophosphate concentrations in soil and aqueous solutions, for example, are commonly measured using colorimetry. Phosphate reacts with an acid molybdate solution to form a phosphomolybdate complex (Harwood et al., [1969;](#page-30-0) Kuo, [1996](#page-30-0)). This complex turns blue upon chemical reduction and the darkness of the color is an indicator of phosphate concentration.

#### Atomic absorption and emission spectrometry

Atomic absorption and emission spectrometry have become two of the principle analytical techniques for elemental analysis in agricultural and environmental laboratories. They are relatively easy to use and have detection limits sufficient for most elemental analyses. They routinely measure concentrations in the parts per million range, and in many cases concentrations in the parts per billion range. Atomic spectrometric methods require that a sample be atomized at high temperatures. The concentration of chosen atoms is then determined by measuring absorption or emission at characteristic wavelengths. The spectra of atoms consist of very sharp lines and are a result of transitions between electronic states of an atom. Because each element has its own distinct atomic spectrum, there is little overlap between spectra of elements in the same sample. For these techniques, standard curves are used to establish the relation between signal and concentration. For more detailed information readers are referred to Ure ([1991\)](#page-31-0) and Sharp ([1991](#page-30-0)), Wright and Stuczynski ([1996\)](#page-31-0), Soltanpour et al. ([1996\)](#page-31-0).

The basic components of an atomic absorption (AA) spectrometer are a hollow cathode discharge lamp, a burner/ nebulizer, a monochromator, a photomultiplier detector and an output device (Ure, [1991](#page-31-0)). The hollow cathode lamp is made from the element being analyzed and emits a spectrum characteristic of that element. The light generated by the hollow cathode lamp passes through the flame atomizer. A typical AA spectrometer uses a flame with a temperature of about 2 400–2 700 K produced from a fuel-oxidizer combination consisting of acetylene and air, respectively. The sample analyte is sprayed as a fine mist into the flame by a pneumatic nebulizer. Thermal processes in the flame atomize the spray mist and the analyte atoms absorb light from the hollow cathode lamp at the wavelength of the absorbing analyte line.

For greater sensitivity and smaller sample size, an atomic absorption spectrometer with an electrothermal furnace for sample atomization is used. Usually 1 to 2 ml of sample solution are consumed during flame analysis, however, only 1 µl is sufficient for use in a graphite furnace. Furthermore, since the graphite furnace temperature is 3 000  $^{\circ}$ C and the entire sample 106 CHEMICAL ANALYSES

is confined in the light path for a few seconds, atomization is more complete and the analytical sensitivity much higher. Instrument operation, however, requires greater skill. The light passing through the flame or furnace is received by a monochromator, which isolates the absorbing resonance line from other nonabsorbing lines. The photomultiplier detector produces an output current proportional to the incident light emitted by the monochromator. This current signal is amplified, electronically processed and finally exhibited by a readout device (printout or digital display).

With AA spectrometry one must be aware of spectral, chemical and ionization interferences. For example, spectral interferences are unwanted signals that overlap the analyte signal, while chemical interferences result from chemical reactions that decrease the concentration of the analyte atoms (formation of oxides as they rise through the outer core of the flame). Ionization interferences are caused by the ionization of analyte atoms decreasing the concentration of neutral analyte atoms in the flame.

Inductively Coupled Plasma (ICP) Atomic Emission spectrometry is a widely used technique for chemical analyses of soils. ICP utilizes a high temperature plasma resulting in more complete sample atomization and consequently, elimination of many interferences and sources of error encountered with conventional flames. It also offers the sensitivity and precision of an AA spectrometer and has simultaneous multielement capability. The plasma is generated in a quartz torch apparatus that is surrounded by a radio frequency induction coil. High purity argon gas is fed into the torch inlet and is ionized by a spark from a tesla coil. The  $Ar^+$  ions are immediately accelerated by the radio-frequency field oscillating around the load coil. The accelerated ions transfer energy to the entire gas by collisions between atoms. The temperature is maintained at 6 000 to 10 000 K in the flame and the quartz burner is protected from the high temperatures by argon coolant gas. Analyte is introduced into the plasma using a conventional nebulizer. The ICP requires no light source; atoms in the plasma are promoted to excited electronic states by collisions with other atoms. The excited atoms emit their characteristic radiation as they return to their ground state. A grating monochromator selects and isolates the specific wavelength of the analyte element. The emission intensity at a characteristic wavelength of an element is generally proportional to the concentration of the element in the sample being measured. A photomultiplier detector collects the emission light from an element, and converts it to an electric current signal. This signal is amplified, electronically processed, and displayed on a readout device. The coupling of ICP with mass spectrometry (ICP-MS) enables isotopic analyses to be made (e.g., Tyler and Olsson, [2001](#page-31-0)). An accessible description of the technique is given in Soltanpour et al. ([1996\)](#page-31-0) and Kennett et al. [\(2001](#page-30-0)).

## Chromatographic methods

Chromatography is a technique where molecules in a mobile phase are separated because of their different affinities for a stationary phase. The greater the affinity for the stationary phase, the longer the molecule is retained by that phase. The chromatographic methods most commonly used by soil science researchers are gas (GC), high performance liquid (HPLC), and ion chromatography (IC). Detailed reviews on chromatography are provided by Skoog ([1985](#page-30-0)), Harris ([2002](#page-30-0)), Smith and Arah [\(1991\)](#page-30-0), Eagle et al. ([1991](#page-30-0)), and Tabatabai and Frankenbuger [\(1996\)](#page-31-0).

In gas chromatography a volatile liquid or gaseous solute is carried by a gaseous mobile phase over a stationary liquid that is coated on a solid support. A compound is then identified by its retention time on different columns. Gas chromatography is used by soil scientists to measure gaseous constituents (permanent gases and volatile compounds) in soil atmospheres. The important features of gas chromatographs are: (1) a carrier gas system, (2) an apparatus that introduces the sample into the carrier gas stream, (3) a column that separates the components of the sample (commonly used adsorbents are synthetic zeolites, porous polymer beds, alumina, silica gel, activated charcoal, and graphitized carbon black materials), (4) a detector (usually measuring either thermal conductivity or flame ionization of sample analyte) signals the elution of each constituent and provides a quantitative measure of each component, and (5) a recording system (Smith and Arah, [1991](#page-30-0)).

High Performance Liquid Chromatography (HPLC) is similar to GC except that the solvent is a liquid, which is forced through a column using a high-pressure pump (Harris, [2002](#page-30-0)). It can separate and identify an extensive variety of volatile and nonvolatile organic compounds. The most common stationary phase usually contains nonpolar groups, which are covalently bound to 5 to 10 µm silica particles. High performance liquid chromatography employs isocratic elution (separation using a single solvent of constant composition) or separation efficiency can be enhanced using gradient elution (separation using two or more solvents that differ in polarity). Generally, HPLC detectors measure ultraviolet absorbance, refractive index, or polargraphic current of elution bands (Harris, [2002\)](#page-30-0).

Ion chromatography is very similar to HPLC, and the columns are comprised of ion exchange resins (Harris, [2002](#page-30-0)). An IC contains a combination of separator and suppressor columns. The former separates the analyte ions and the latter replaces the ionic eluent with a nonionic species. Thus, it is possible to measure analyte ions using a conductivity detector. Ion chromatography is especially useful for measuring the soil solution concentration of anionic species, such as nitrate, chloride, sulfate, phosphate, and bromine.

#### State-of-the-art research techniques

Many soil and environmental chemists are utilizing sophisticated spectroscopic and microscopic techniques to obtain information about interactions between soil surfaces and inorganic and organic molecules. Some of these techniques include Fourier transform infrared (FTIR), electron paramagnetic resonance (EPR), X-ray photoelectron (XPS), and X-ray absorption fine structure (XAFS) spectroscopies (Fendorf and Sparks, [1996](#page-31-0); Johnston and Aochi, [1996](#page-30-0); Senesi, 1996; and Vempati et al., [1996](#page-31-0)) along with scanning electron (SEM), transmission electron (TEM), and atomic force (AFM) microscopies.

For example, FTIR is often used to characterize the solid/ liquid interface at oxide and clay mineral surfaces, and can provide information regarding sorbed inorganic and organic pollutants at these inferfaces. XPS is another surface sensitive technique that has been used to provide information on the adsorption of species on mineral surfaces, leaching and weathering of mineral surfaces, atomic structure of minerals and glass, and the oxidation state of near surface atoms. Recently, there has been considerable interest in XAFS, a technique used

<span id="page-30-0"></span>for in-situ determination of the local chemical environment around a specific X-ray absorbing element (Fendorf and Sparks, [1996](#page-31-0); Brown et al., 1999). It can probe most elements at structural sites within crystals and glasses, as well as at mineral/water interfaces. XAFS has provided valuable information about the structural characteristics of heavy metals sorbed to the surfaces of iron and aluminum oxides.

Soil biochemists also routinely use spectroscopic techniques such as FTIR and <sup>13</sup>C-nuclear magnetic resonance (NMR) to characterize humic substances (Mao et al., 2000). Specifically, these methods are used to identify and to a certain extent quantify functional groups present in humic and fulvic acids. These structures include aliphatic and aromatic C and also phenolic, carboxyl, methoxy, and amino groups.

## Summary

Chemical analyses of soil systems are necessary to understand their highly variable and complex nature. Prior to conducting any chemical determination, soils are treated with solution reagents to extract the particular chemical component of interest. Extracts are designed to draw from a specific soil fraction. For example, some extracts will remove elements associated with the plant available fraction, while others will remove all elements sorbed to soil particles. After extraction, soil extracts are usually chemically analyzed (quantitatively) using colorimetric, atomic spectrometric, and chromatographic techniques. A routine chemical characterization of a soil should include determination of soil pH, soil organic matter, and cation exchange capacity.

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## Cross-references

Acidity Acids, Alkalis, Bases and pH Base Saturation **Carbonates** Humic Substances Soil Mineralogy Sorption Phenomena

## CHEMICAL COMPOSITION

See Chemical Analyses.

# **CHEMISORPTION**

Adsorption, usually irreversible, involving chemical action. Adsorbed ions or molecules are held to a surface by a strong chemical bond. The heat of adsorption is >20kcal/mole, as opposed to physical adsorption: <10kcal/mole (McBride, 1994, p 344).

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## Cross-reference

Sorption Phenomena

## CHERNOZEMS

Chernozems are soils with a thick black, organic-rich, surface layer. The name was coined by Dokuchaev in 1883 for the typical soils of the tall grass steppes in continental Russia. This article is based on FAO [\(2001](#page-32-0)).

Connotation. Black soils rich in organic matter; from R. chern, black, and zemlja, earth or land.

Synonyms. Equivalent to the chernozemic Soils in Canada, and to several sub-orders of the mollisols (Soil Taxonomy). Black Soils is a common term used internationally.

- Definition. Defined in FAO [\(2001](#page-32-0)) as soils having
- 1. a mollic horizon with a moist chroma of 2 or less if the texture is finer than sandy loam, or less than 3.5 if the texture is sandy loam or coarser, both to a depth of at least 20 cm, or having these chromas directly below any plow layer; and
- 2. concentrations of secondary carbonates starting within 200 cm from the soil surface; and
- 3. no petrocalcic horizon between 25 and 100 cm from the soil surface; and
- 4. no secondary gypsum; and
- 5. no uncoated silt and sand grains on structural ped faces.

Parent material. Mostly aeolian and aeolian sediments reworked by water (loess).

Environment. Regions with a continental climate with cold winters and hot summers; in flat to undulating plains with tall-grass vegetation (forest in the northern transitional zone) (see [Figure C34\)](#page-32-0).

Profile development. AhBC profiles with a dark brown to black mollic surface horizon over a cambic or argic subsurface horizon, commonly with redistribution of calcium carbonate to a *calcic* horizon or pockets of *secondary carbonates* in the subsurface soil.

Origin. The combination of inherently very fertile loess, and a sub-humid climate produces the typical flourishing grasslands (prairie, steppe, pampas) under which Chernozems develop. The important formative processes are the accumulation of humus, bioturbation and translocation of calcite. In tall grass prairie, the above ground biomass may be 1 to 1.5 t of dry matter per hectare, with 4 to 6 t ha<sup>-1</sup> of corresponding root mass below ground. The formation and accumulation of humus occurs principally in the upper 60 cm of soil where plant roots are mainly concentrated. An active mixing is generally brought about by earthworms, which produce the Vermic Chernozem. Larger, animals excavate burrows and may help to homogenize the soil by bioturbation. Calcite (ubiquitous in loess) tend to

<span id="page-32-0"></span>

Figure C34 Distribution of Chernozems.

be dissolved in the upper part of the profile in wet periods, to be precipitated at depth, while drier periods encourage the capillary uprise of soil solutions rich in  $\bar{C}a^{2+}$  and cause calcite to form higher in the profile.

Use. The high natural fertility of Chernozems and their favorable topography permit a wide range of agricultural uses including arable cropping (with supplemental irrigation in dry summers) and cattle ranging.

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## Cross-references

Biomes and their Soils Calcareous Soils Classification of Soils Classification of Soils: World Reference Base (WRB) for Soil Resources Classification of Soils: World Reference Base (WRB) Soil Profiles

## CHRONOLOGY OF SOILS

A timetable for an evolving soil on a geologic time scale, apart from recent anthropic (man-made) modification, depends on:

- a. Parent material (which may be the geological bed-rock, or wind-blown cover such as loess or sand dunes, or littoral accumulations such as beachridges, or alluvial deposits associated with flood plains).
- b. Zonal climate (which may be roughly stated as "latitude", but more precisely modified by oceanicity, or maritimicity, continentality, altitude and aspect, i.e., exposure to insolation, fetch, and prevailing wind).

c. Geomorphic history (which generally spans the period of time since the latest ice ages, thus in North America and Europe since about 12 000 years ago, but in South America, South Africa, India and Australia, about 265 Myr. ago. Even more for North Africa and much of Arabia, where it is 445 Myr).

Study of these three variables is integral to what constitutes "Soil Stratigraphy", a science that for understandable reasons found its birthplace in Australia, a continent relatively unscathed by the giant ice sheets that affected North America and northern Europe. A given paleosol in Australia can often be tracked down to a specific date in the stratigraphic timetable. Its basic composition may be cemented in place by the widespread silicification that commonly affects that continent's 15 to  $35^\circ$  S latitudes (see *Duricrusts and induration*). Because of these silicified paleosols, some quite remarkable examples of ancient soil stratigraphy are preserved, such as the "Kirup Conglomerate" found by Finkl on some hilltops in southwestern Australia. The paleosol in question contained glacially faceted boulders of the Permian glaciation and occupied former stream channels that must date from about 250 Myr (Fairbridge and Finkl, [1978\)](#page-34-0).

This sort of history is not unusual for the former soils associated with the landscapes of the ancient continent of Gondwanaland. For much of that history the landscapes in question were associated with the global distribution of the dinosaurs which required (in the case of the herbivores) a fertile soil and nearly universal spread of vegetation.

The plate-tectonic break-up of Gondwanaland was a progressive phenomenon, with one segment after another (Fairbridge, 1982). With each new rupture the isostatic response of the crust led to rapidly rising shoulders and a topography that changed from a flat plateau to a steep-sided escarpment such as marks the present-day Red Sea and typically developed in Yemen or northern Ethiopia.

With each fracture zone initiation ("taphrogenic triggering") with its Red-Sea-type sea-floor spreading, a new geomorphic cycle and soil-forming cycle is set in motion. The time clock is re-set. Lester King, in his magisterial "Morphology of the Earth" (1962), summarized cycles of this sort very well for Gondwanaland. For Eurasia and North America the problem was (and remains) a much more challenging one, because of Cenozoic glaciation and complex tectonics. The Gondwana cycles began soon after the end of the Permo–Carboniferous ice ages and could be followed across the southern continents in a succession of uplifted erosion surfaces mostly preserved today as "etchplains".

Each planation cycle corresponds to what Erhart [\(1956](#page-34-0)) called the "biostatic phase" in his "Theory of Biorhexistasy". And each taphrogenic break-up triggered his brief but violent "rhexistatic phase". The first, the biostatic condition, was one of adjustment of river networks to the new general base level and climatic stability. Fairbridge and Finkl (1980) called this a "cratonic regime", that is, corresponding to the continental interior plateaus, and in contrast to the continental margins (both cliffed and with coastal plains), which are subject to the new tectonic activity, maritime climates and multiple eustatic fluctuations.

Each of these rhexistatic cycles (e.g., mid-Mesozoic, terminal Cretaceous, mid-Cenozoic, etc.) is typically represented by paleosols with massive duricrusts (usually lateritized or silicified). In places these have often been buried by younger sedimentary strata, but may be re-exhumed, to be preserved today as monadnocks or plateaus. In the case of the Appalachian Mountains in the non-glaciated part of North America, the late Mesozoic was a biostatic phase that was progressively brought to an end by the plate-tectonic opening of the North Atlantic and catastrophically punctuated by the  $K/T$  asteroid event with its major drop in sea level. During the biostatic phase the porous sandstones of Paleozoic age became deeply silicified (10–20 m or more), but during the early Tertiary rhexistasy there was deep incision of major river valleys and progressive uplift, while progressive, differential erosion occurred in the soft-shale and calcareous sediments, leaving the silicified ridges behind. "Water gaps" mark the successful drainage systems. During the glacial advances, the entire region was subjected to periglacial erosion, still preserved today by patterned ground and boulder streams. The forest cover appears to be anchored in the "skeletal" or "fragmental" soils that survived the periglacial erosion (largely aeolian), but were supplemented by the small contributions from the wind-borne loess storms that swept across the Midwest.

Techniques for working out a soil chronology in a given region must vary with the materials available. Isotopic dating methods have some usefulness where a given horizon has been exposed to insolation or geochemical crusting. The role of dew may be significant when dust is trapped and forms a thin veneer or "desert varnish" over an exposed surface such as a pebble, boulder or rocky outcrop. Less precise, but nevertheless often very useful, are the stratigraphic "sandwich" methods, for example, an exhumed paleosol surface at some point is often found to plunge beneath a stratigraphic horizon that is datable from its fossils or isotopic aspects. This date then constitutes an upper limit of the paleosol. The archaeologists call this an "ante quem" date. Then a "post quem" date is one where a paleosol is found truncating that stratigraphic formation; the paleosol is then younger.

In the use of a sequence of paleosols, one over another, this is what Fairbridge and Finkl (1980) refer to as "stacked veneers". These are often to be found near the margins of cratonic units, where repeated uplift and successive climate changes can vary the characteristics of the individual veneers.

Climatic proxies can often serve as accurate pointers to the former climate associated with a given paleosol. Different types of duricrust reviewed in Fairbridge  $(1968)$ , and include: ferricrete, or lateritic duricrust, i.e., generally silicified latosols; or calcrete, i.e., calcified duricrust, "hardpan" or "caliche"; or silicrete, i.e., a silicified concretionary hardpan. They are all characteristic of different parent materials but have a commonality in the form of a semi-arid and strongly seasonal climate. Each is a distinctive indication of a specific climatic type:  $(a)$  the latosol speaks only of the tropical monsoon climate; (b) the calcrete is derived from a coastal belt fed by wave and wind action on comminuted shells and carbonate foraminifera, the carbonate dust being blown inland, but exceptionally the parent material consists of pre-existing limestones;  $(c)$  the silcrete is formed in swamps (with a distinctive pH range) which dry out seasonally.

"Stone lines" are a diagnostic feature of certain soils. They are most typical of tropical soils, in the rhexistatic belts. Clearly, they are relics of a colluvial nature, i.e., slope deposits, stone pavements or lag gravels. The stratification and transport may be the result of slope wash or even a mudflow, which can be tropical or even periglacial ("solifluction"), but certainly limited to heavy precipitation events or brief melt-seasons. The stones are angular to rounded, of resistant nature such as quartzite, granite and even fragments of termitaria (termite mounds). The pebbles may be concentrated by aeolian winnowing (a selection of photographs is provided in Fairbridge and Finkl, 1984).

Another aspect of paleoclimate indicators is the widespread development of white, podzolized sand plains and sandy deserts in the low latitudes (Paton et al., 1995). They are known as "siliciclastic", being dominated by quartz and other minerals of low solubility. It appears that they are the end products of either (a) tropical weathering, typically of granite or granitoid crystalline parent material under hydrologic processes, where the feldspars and micas revert to clays easily removed by running water. Or (b) recycled from glacial outwash where the sands have been mechanically generated and feldspatic components are well preserved; but when exposed to post-glacial humid weathering the insoluble components are eventually released.

The origin of the celebrated sands of the Sahara has long been debated. Three prominent source areas contribute: (a) Outwash from the Atlas Mts, Hoggar and other uplifts;  $(b)$ Recycled Ordovician glacial outwash in the western and central Sahara; (c) Recycled Nubian Sandstone in the east (a Cretaceous to Cenozoic product of former tropical rivers emanating from Central Africa. Eolian systems have changed throughout the Quaternary, so that the present dunes are representing a "wellstirred pot", predominantly quartz today, but Pleistocene dunes are often reddish in color, from the ferromagnesian minerals mobilized into solution during the long interglacial and monsoon-dominated intervals.

## Podzolization and laterization

These are two distinctive processes in the chronology of the paleosols. Both are essentially "end-members" in evolving histories.

According to Duchaufour ([1978\)](#page-34-0), podzolized soils are "characterized by the biochemical weathering of silicates by soluble and acid organic matter, with formation of more or less mobile organomineral complexes which accumulate in one or two

<span id="page-34-0"></span>'spodic' type horizons rich in amorphous material (dark  $B<sub>h</sub>$  horizon enriched with humic acids, and ocherous  $B_0$  horizon enriched with hydroxides)." The name "pod" comes from the Russian word for "ash", i.e., silica-enriched, with iron and aluminum complexes leached out. In temperate latitudes podzolization is only scattered but widespread in the boreal forests of northern Canada and Siberia. In the hydromorphic (acid) conditions of tropical coastal belts it is widespread, being derived from the polymictous beach and dune sands after extensive leaching of their carbonate content. From the paleoclimatic point of view they reflect extended intervals of intense pluviosity, which has led to their present status as "leached residuals" (Fairbridge and Finkl, 1984).

The other "end-member" state is here referred to as "laterization", a process recognized by geologists, but in the U.S. Soil Taxonomy represented by the OXISOLS, on the FAO-UNESCO World Map Legend as FERRALSOLS, or in Bridge's review (1978) as "ferrallitic soils". One of the problems associated with the varied terminologies is that the classic "laterite" is not found in North America or Europe. It stems from India, where it was described by Buchanan in a paper nearly two centuries ago. There the soft hydrous ferrallitic clay is commercially formed into brick-like shapes and laid out in the sun to dehydrate, the hydrous gel breaks down and the process is irreversible, so that an all-weather building material is created. The term latericius is Latin for "brick". The same process occurs in an environmentally catastrophic way when tropical rainforest is cleared as in the Amazon basin. Unless it is immediately replanted the soil becomes rock-hard and resistant to further tillage.

Both the economically sound and the disastrous activities serve to illustrate the term "laterization" (the Glossary of Geology places "lateritization" in synonymy). In the U.S. Soil Taxonomy it is called "plinthite", a product of ferrallitic desiccation, leading to a hardpan, durable crust or "carapace". It is a typical feature of the cratonic landscapes of India, Australia, Africa and Brazil. These landscapes have been repeatedly subjected to an alternation of intense rainfall and deforestation associated with ice-age desiccation that can be dated over about the last three million years. Isotopic dating of certain laterites in Australia disclose a Miocene date for their beginning. Others have been dated by igneous dikes of known age or overlapped by fossiliferous sedimentary formations.

In short, the process of "laterization" can hardly be regarded as a normal contemporary soil-forming process, but it should be borne in mind as a potential hazard in environmental review.

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#### Cross-references

Classification of Soils Crusts, Crusting Duricrusts and Induration Ferralsols Ice Erosion Iron Oxides Podzols Profile Weathering Systems in Soil Science

## **CHRONOSEQUENCE**

A sequence of soils in which the dominant variable accounting for any physical, chemical and biological differences has been the duration in time over which the sequence has developed. (Birkeland, 1999, p 178).

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## CLASSIFICATION OF SOILS: FAO

The FAO soil classification system is based on the Legend for the Soil Map of the world (FAO/UNESCO, [1974\)](#page-36-0).

The FAO legend was largely based on the diagnostic horizon approach developed under Soil Taxonomy (Soil Survey Staff, [1960](#page-36-0)) by the USDA during the 1950s and 1960s. Similar horizons were defined, and where definitions of the diagnostic horizons were slightly simplified, different names were used for comparable horizons such as the ferralic horizon equivalent to the oxic horizon, or the argic horizon equivalent to the argillic horizon in Soil Taxonomy. The grouping is based on measurable as well as observable soil properties.

Certain historical soil names were retained to accommodate some national sensitivities. Examples of these at the highest level were rendzinas, Solonetzes, Solonchaks, and Chernozems. Some of the names had a dubious scientific connotation (such as the podzoluvisols in which no podzolization takes place), while others were nearly identical to those developed in Soil Taxonomy, such as the Vertisols (Nachtergaele, [2003](#page-36-0)).

In contrast with Soil Taxonomy, climatic characteristics were not retained in the FAO Legend, although the xerosols and yermosols largely coincided with soils developed under an aridic moisture regime.

The FAO Legend of 1974 recognized 26 Great Soil Groups (world classes) subdivided in 106 Soil Units (world subclasses), which were the lowest category recognized on the world soil map. The units are designed primarily for the legends of the Soil Map of the World and do not correspond exactly to categories in other systems but they are generally comparable at the "Great Group" level. These map units are sufficiently broad to contain sufficient elements to reflect as precisely as possible the soil pattern of a large region.

In addition to the Great Soil Groups and Soil Units, twelve soil phases were recognized: This subdivision is based on characteristics, which are significant to use, or management. They are:

• stony phase: mechanized agricultural equipment impracticable.

- lithic phase: hard rock within 50 cm of surface.
- *petric phase*: a layer with  $>40\%$  oxidic concretions  $>25$  cm thick, the upper part occurring within 100 cm of the surface.
- petrocalcic phase: petrocalcic horizon within 100 cm of the surface.
- *petrogypsic phase*: petrogypsic horizon within 100 cm of the surface.
- petroferric phase: petroferric horizon within 100 cm of the surface.
- *phraetic phase*: ground-water table between 3 and 5 m from the surface.
- *fragipan phase*: fragipan within 100 cm of the surface.
- duripan phase: duripan within 100 cm of the surface.
- saline phase: electrical conductivity of  $>4$  mmho cm<sup>-</sup> within 100 cm of the surface.
- *sodic phase*: more than 6% exchangeable sodium saturation within 100 cm of the surface.
- cerado phase: areas with tall grass and low contorted trees.

Three general texture classes:

- *coarse textured*: sands, loamy sands and sandy loams with less than 18% clay and more than 65% sand.
- *medium textured*: sandy loams, loams, sandy clay loams, silt loams, silt, silty clay loams and clay loams with less than 35% clay and less than 65% sand; the sand fraction may be as high as 82% if a minimum of 18% clay is present.
- *fine textured:* clays, silty clays, sandy clays, clay loams and silty clay loams with more than 35% clay.

Three general slope classes:

- level to gently undulating: dominant slopes ranging between 0 and  $8\%$ .
- rolling and hilly: dominant slope ranging between 8 and 30%.
- steeply dissected to mountainous: dominant slopes are over 30%.

Most soil mapping units were in fact soil associations, the composition of which was indicated at the back of each paper map sheet (Nachtergaele, [2003](#page-36-0)). The dominant soil unit gave its name (and appropriate color) to the mapping unit, followed by a number unique to the associated soils and inclusions. Texture (1, 2, and 3) and slope symbols (a, b, and c) were included in the mapping unit symbol.

Although initially developed as a Legend for a specific map, not a soil classification system, the FAO Legend found quick acceptance as an international soil correlation system, and was used for several national soil classifications, as well as for soil inventories as in the soil map of the European Union. With the application as a soil classification, numerous comments and suggestions were received to improve the coherence of the system. The revision effort undertaken in the 1980s finally resulted in the publication of the Revised Legend of the FAO/UNESCO Soil Map of the World (FAO/UNESCO/ISRIC, [1988\)](#page-36-0) (see Table C10). This revised legend was applied to the World Soil Resources Map at 1 : 25 000 000 scale, accompanied by a report (FAO, [1993](#page-36-0)) and presented at the Kyoto ISSS Congress.

Table C10 The revised FAO World Classes (Great Soil Groups) of soils and their equivalents at the order, suborder and great group levels in the USDA Soil Classification System (adapted after Fitzpatrick, [1980,](#page-36-0) FAO, [1993](#page-36-0))



In the revised legend, the number of Great Soil Groups increased from 26 to 28: the rankers and rendzinas were grouped with the Leptosols, the "aridic" yermosols and xerosols disappeared, and new Great Soil groups of Calcisols and Gypsisols were created. The Luvisols (alfisols)–Acrisols (ultisols) division was further divided according to the activity of the clay fraction, resulting in four symmetric groups (Luvisols, high base saturation, high-activity clays; Acrisols, low base saturation, low-activity clays; Lixisols, high base saturation, low-activity clays; and Alisols with low base saturation and high-activity clays). The revised legend also created at the highest level the Anthrosols, grouping soils strongly influenced by human activities. The number of Soil Units increased from 106 to 152. Texture and slope classes remained unchanged, but were not represented on the map produced. A third hierarchical level of "Soil Subunits" was introduced to support soil inventory on larger scales. Soil subunits were not defined as such but guidelines for their identification and naming were given. This converted the map legend, with a finite number of entries, into an open-ended, globally applicable FAO-UNESCO Soil Classification System.

In a parallel development, a working group of the ISSS had been active in the development of an internationally acceptable soil classification system (first meeting in Sofia, 1982). In 1992, at a meeting of the Working Group RB (Reference Base), the strong recommendation was made that rather than developing a new soil classification system, the Working Group should consider the FAO Revised Legend as a base and give it more scientific depth and coherence. This principle was accepted, and the first draft of the World Reference Base (WRB) <span id="page-36-0"></span>appeared in 1994 (ISSS/ISRIC/FAO, 1994), still showing large similarities with the FAO revised legend.

In 1998, the International Union of Soil Sciences (IUSS) officially adopted the World Reference Base for Soil Resources (WRB) as the Union's system for soil correlation. The structure, concepts and definitions of the WRB are strongly influenced by the FAO-Unesco Soil Classification System. At the time of its inception, the WRB proposed 30 "Soil Reference Groups" accommodating more than 200 ("second level") Soil Units (FAO, 2001, World Soil Resources Reports, 94). Two new reference groups have since been added (FAO, 2006).

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#### Cross-references

Classification of Soils: Soil Taxonomy

Classification of Soils: World Reference Base (WRB) for Soil Resources Horizon Designations in the WRB

## CLASSIFICATION OF SOILS: SOIL TAXONOMY

## Introduction

Most countries of the world have some kind of soil survey program. Some programs assess soil resources at the farm level, while others are designed for county, state, or national levels. The United States began soil resource assessment around 1899, but it began an institutionalized, systematic detailed soil survey only in the nineteen thirties. By the end of the nineteen forties, about fifty million acres of land per year were being surveyed and more than one thousand soil scientists from the Soil Conservation Service (now called the Natural Resources Conservation Service – NRCS) and U.S. universities were involved. The then existing classification system did not serve the purpose of standardization, quality control, and communication between soil scientists. It was recognized that the national soil survey program needed a system of soil classification that could be applied uniformly by soil scientists, could be the basis of the soil survey program, serve the purpose of technical communication between soil scientists, and have the capability to predict the consequence of alternative uses. Soil surveys are useful because they have a scientific basis (which ensures their reproducibility) and because they can be employed for practical land use purposes. The role of soil classification is to act as a bridge to synthesize soil survey information and provide pragmatic groupings for the needed precise predictions. These were some of the motivating reasons for creating Soil Taxonomy, which was published in 1975 (Soil Survey Staff. [1975\)](#page-42-0) for the purpose of making and interpreting soil surveys. Several modifications have been made since its publication and in 1999 the second edition of the manual was published (Soil Survey Staff. [1999\)](#page-43-0) to commemorate the 100th anniversary of the national soil survey program.

The system of soil classification was developed over a period of 25 years, commencing in 1951, with Dr. Guy D. Smith coordinating the effort (Smith, [1983\)](#page-42-0). By 1960, a working draft was already available and was tested in the field over the next decade. Publication of the system took place in 1975. The system was developed by U.S. soil scientists with the collaboration of scientists from around the world. Major contributors to the nomenclature, for example, were Professors Rene Tavernier and Jacque Leeman of the University of Gent, Belgium. The system of soil classification was influenced by similar developments in other national classification systems, specifically those in Europe, Australia, and New Zealand and the FAO-UNESCO legend of the Soil Map of the World (FAO-UNESCO,  $1971-1981$  $1971-1981$  $1971-1981$ ). Many of these national systems have undergone modifications since their inception and a recent review (Eswaran et al., [2003](#page-42-0)) gives information on the current structures.

## Principles of the soil classification system

Classification of discrete objects such as plants or animals is in many ways easier than a continuum with no distinct boundaries such as soils. Every classification system attempts to group similar things together. Though this can be achieved by an analysis of soil properties, the additional dimension in soil classification is that 'similar soils' must have similar performance in most uses. In addition, because the system is designed to support a soil survey program, it must be able to differentiate between all soils on a landscape and the goal was also that every soil in the world would find a place in the system. Existing systems in the nineteen fifties were genetic in concept and based on soil processes, actual or perceived. To meet new requirements, a major shift in approach was necessary. This proved to be a major challenge and some compromises had to be made.

The guiding principles of Soil Taxonomy are enunciated by Cline [\(1949](#page-42-0)), Smith [\(1963](#page-42-0)), and Arnold and Eswaran ([2003](#page-42-0)). The major principle stresses that the classification is of soils and not of soil-forming processes or factors. This is a major distinction from the Russian school of classification. Soil genesis is employed to guide our thinking about soils but is not used as the basis for classification because if the genesis of a soil is not known the soil cannot be classified. Other principles employed to develop the system are as follows:

- Definitions are based on soil properties so that users can apply them systematically;
- The system is multi-categorical with the information content increasing in the lower categories; this enables ease of use of the system and the selection of categories based on the detail required by the purpose;
- The defined units must be of real bodies that are known to occur in the world;
- Although properties are precisely defined, to facilitate the field soil scientist an initial assessment could also be made in the field either through simple field tests or interpretation from landscape, vegetation, and/or geology;
- The system must be modular so that with new knowledge, changes may be made without disrupting the whole system;
- Properties selected are not markedly affected by normal management, so that the classification is not changed by plowing or fertilizing or other farming techniques;
- Finally the system should differentiate all soils in a landscape and provide a place for all known soils.

#### Diagnostic horizons and features

The use of diagnostic horizons and features probably distinguishes Soil Taxonomy from most other classification systems. Diagnostic horizons and features are the building blocks of the system and serve to define the different categories of the system. The significance of each horizon or feature is a function of the soil. Some diagnostic horizons or features are used to define the Order category, such as the mollic epipedon of mollisols. Within the mollisols, a diagnostic feature such as an ustic soil moisture regime (SMR) defines the Suborder, a diagnostic subsurface horizon defines the great group (argillic horizon for the argiustoll), and another diagnostic feature such as an aquic soil water regime is used for the subgroup (aquic argiustoll). The relative importance of the diagnostic horizons and features differs with soils, and selection is made based on the principles enunciated before.

#### Categories and nomenclature

The six categories in the classification system are Order, Suborder, Great Group, Subgroup, Family, and Series. There are twelve Orders, which are differentiated by the presence or absence of diagnostic features, or horizons which indicate differences in the intensity and kind of dominant soil forming processes, or their absence. These are:

- histosols organic soils resulting from accumulation of organic matter (histic materials) under very wet or cold environments;
- gelisols are soils that freeze sometime during the year and have a layer of frozen soils called permafrost at shallow depths;
- spodosols soils that have a spodic horizon that formed by the translocation and accumulation of iron, aluminum, and/or organic carbon;
- andisols soils that formed in volcanic materials (andic materials) in which weathering results in dominance of amorphous colloids;
- oxisols soils that have an oxic horizon characterized by low activity clays;
- vertisols soils that have vertic properties resulting from high amounts of clays such as montmorillionite that shrink when dry and swell when wet;
- aridisols soils that have an aridic soil moisture regime that can have in horizons of accumulated carbonates, gypsum, and soluble salts;
- ultisols soils that have an argillic horizon and low base saturation (low pH or acid) because of leaching;
- mollisols soils that have a mollic epipedon characterized by black colors and relatively high organic carbon content;
- alfisols soils that have an argillic horizon and high base saturation or high pH;
- inceptisols soils that have a cambic horizon or are at a youthful stage in soil formation;
- entisols soils that have no diagnostic horizon (except for an ochric epipedon) and formed in recent materials.

Each Order has four to six suborders defined on the basis of properties that are major controls of soil formation or absence of such controls. Soil moisture and temperature regimes are considered as the controls and are employed at this level. The Great Groups are defined by the arrangement of diagnostic horizons in the soil and/or subordinate controls of soil-forming processes. The Subgroups are designed to show linkages to other categories in the system (intergrades) or to some special properties or even non-soil features (extra grades) such as a rock contact at shallow depth. Within each Subgroup, the Family is defined on similar physical and chemical properties that affect their response to management and manipulation for use. The lowest category, the Series, is defined almost essentially on field observable properties that are within the range of the Family. This is partly because; the Series category is used for detailed maps and for most farm level interpretations and recommendations. The definitions and functions of these categories are provided in Soil Taxonomy (Soil Survey Staff. [1975,](#page-42-0) [1999](#page-43-0)). Periodic refinements are made to the classification system and these are published in the monograph called "Keys to Soil Taxonomy"; the most recent is published by Soil Survey Staff ([2003\)](#page-43-0).

A number of classification systems already existed at the time of development of the U.S. system. In addition, many terms, such as laterite, have popular meanings, the original scientific definition being lost through popular use. A concerted effort was made to create new terms with each name being short, easy to pronounce, distinctive in meaning, and connotative. The name was also required to indicate the categorical level and thereby its position in the classification.

The names of the categories are recognized as follows:

- Order each Order name ends in 'sol': andisols, histosols;
- Suborder names are two syllables with the second syllable carrying the formative name of the Order: udox (oxisols), aquult (ultisols), orthent (entisols);
- $\bullet$  Great group carries the suborder name and a prefix: hapludox, kandiaquult, and torriorthent.
- Subgroup carries the great group name and an adjective: typic hapludox, aeric kandiaquult, vertic Torriorthent.
- Family names are polynomial and carry the subgroup name and adjectives that indicate one or more significant features (usually particle size class, mineralogy, and soil temperature regime): clayey, kaolinitic, isohyperthermic, typic hapludox.
- Series names are abstract and usually taken from place names where the soil was first recognized: Kluang series (a soil in Malaysia) is a member of the clayey, kaolinitic, isohyperthermic Family of typic hapludoxs.

## Determining the taxonomic class of a soil

The taxonomic class of a soil is determined by using the keys and definitions to the various categories in Soil Taxonomy. Prior to attempting to classify the soil, it is necessary to determine if the soil has diagnostic horizons and/or diagnostic features. The profile description, which is the field assessment of the soil, provides clues to possible diagnostic features. These are confirmed by testing the required criteria for the horizons. An estimate of the soil moisture regime (SMR) and soil temperature (STR) is also made from climatic records of the closest meteorological station if actual measurements at the site are not available.

Armed with this information of the soil, the Order placement is determined by using the 'Keys to Soil Orders' in the book (Soil Survey Staff. [2003\)](#page-43-0). The Keys are structured to systematically and sequentially test a class. If a soil does not meet criteria of the eleven Orders, it is placed in the last class, entisols. A soil must meet the class definition to qualify for the class. A page number directs the user to the appropriate Suborder key. This process of searching and elimination or fitness is done for each category until the Family category. For example, a soil in Malaysia (Kluang Series) has a SMR of udic and STR of isohyperthermic (continuously wet and continuously hot), an ochric epipedon (surface horizon) and an oxic subsurface horizon. It does not have any other features. In the "Keys to Soil Orders", the soil does not meet the definition of a gelisol, histosol, andisol, or spodosol, but meets the requirements of an oxisol. The soil is thus an oxisol. Following a similar procedure of testing of class membership, the soil is placed in the Suborder udox. The "Keys" for each category can then be followed systematically without short cuts, and the soil is finally determined to belong to the clayey, kaolinitic, isohyperthermic Family of the typic hapludoxs.

#### Evaluating soil properties from soil name

Apart from being mnemonic, soil names also are designed to provide information about the soils themselves. The Kluang Series described previously is used as an example.

- Oxisol the soil has low nutrient holding capacity; it has few weatherable minerals and thus has low potential to provide nutrient elements through weathering; it generally has a low water holding capacity; it has few rock fragments and thus has few restrictions to root growth.
- Udox the soil experiences little or no moisture stress.
- Hapludox the soil does not have high base saturation nor is it acid; it has no plinthite and has very little organic matter.
- Typic hapludox the soil is well drained and has few physical root-restricting layers.
- Clayey, kaolinitic, isohyperthermic typic hapludox soil temperature is not a constraint; nutrient fixation is not high though leaching losses may be high; tillage is easy.
- Kluang Series the soil has all the above properties. It is an ideal soil for growing rubber (*Hevea braziliensis*) and less suitable for oil-palm (Elais guinensis). Annual crops require good fertilizer management.

## Global distribution of soils

Many countries have classified their soils according to Soil Taxonomy, and it is possible to translate other classification systems to Soil Taxonomy. However, estimates of the distribution of the soils globally, are still not possible because many countries have yet to make detailed inventories. [Table C11](#page-39-0) provides some preliminary estimates made by the World Soil Resources section of the Natural Resources Conservation Service, U.S. Department of Agriculture and [Figure C35](#page-41-0) is a map showing the distribution.

In [Table C11](#page-39-0), the estimates of the soil Orders and Suborders occurring in the different climatic or major eco-regions are provided in addition to the global distribution; examples of each Order is shown in [Figure C36.](#page-42-0) Only the suborders that are extensive enough to be shown on the world map are listed. Soil patterns are distinct and show the role of soil moisture and temperature regimes interacting with parent materials. In Europe, the soil moisture regimes show a north-south trend and the consequent effect on soil formation is illustrated by horizontal patterns of the soils. In North America and particularly in the United States, the soil moisture regimes show an east-west trend and the soil patterns reflect this trend. On the eastern seaboard, the soils are ultisols, and as one proceeds westward, they give way to mollisols, alfisols, and aridisols. Finally, in the Rocky Mountains, the soils are inceptisols and some andisols. Farther north in North America, the soils are dominantly inceptisols and spodosols, which give way to histosols and gelisols in the northern tundra zone.

Gelisols, the most recent soil order introduced into the system of Soil Taxonomy, occupy about 9.1% of the ice-free land surface. Few detailed soil maps depict these soils, as previous classification systems did not differentiate the soils based on permafrost. The lower geographic limit of gelisols for this map is defined by a mean annual soil temperature of less than  $0^{\circ}$ C and by a mean summer soil temperature of less than  $10^{\circ}$ C. The northern part of the gelisol zone grades to ice. Areas of soils are indicated as a percent of the ice-free land surface.

Organic soils, or histosols, occupy about 1.2% of the land surface. This percentage does not include the 0.8% of histels, which are present in the gelisol region and which form the largest contiguous extent of organic soils. The next largest area of organic soils is adjacent to the tundra soils in the boreal belt. These organic soils are the "cryo" great groups of fibrists, hemists, and saprists. Tropical histosols are dominantly in Southeast Asia, mainly in Sumatra and Kalimantan. Many of the tropical histosols are on coastal plains and have very low pH because of the presence of acid sulfate materials. Unlike the temperate and boreal histosols, which formed in areas of moss and grassy vegetation, tropical histosols are woody and frequently contain large trunks of undecomposed trees. These woody materials make cultivation of such soils difficult.

Spodosols are dominantly in the colder regions of the world where STR is mesic or colder and SMR is udic or perudic. These boreal spodosols occupy about 2.2% of the land surface. Podzolization results from release of large quantities of organic acids in the organic-rich surface soil horizons. Characteristically, these soils form in sandy materials or in materials with only small amounts of weatherable minerals that have the potential to alter and release bases. In the Tropics, soils with similar morphology are in areas of coastal beach deposits. The largest contiguous extent of such soils is on the coastal plains of the Amazon Basin. The soils are described and classified as spodosols but frequently are not the result of the podzolization process that operates in the temperate or boreal climates. The sandy levee deposits or stranded beach deposits occur in association with aquepts and saprists. The dissolved organic colloids seep up the sands (capillary effect) and precipitate at the capillary fringe of the ground water table. The resulting morphology is that of a spodic horizon.

Andisols dominate the circum-Pacific belt, or the Ring of Fire. They are frequently associated with current or former volcanic activity. Depending on the intensity and periodicity of the volcanic activity, deposits of several ages may characterize a soil. In the colder and moister parts of the world, andisols are characterized by dark mollic-like or umbric-like epipedon. Buried horizons with similar organic-rich horizons may be typical. In the Tropics, organic accumulation is not so rapid. In addition, weathering and mineral alteration lead to the formation of a clay fraction dominated by halloysite and kaolinite. A normal toposequence in the Tropics is andisols on the upper slopes, in association with inceptisols, which give way to ultisols and oxisols on the gentler topography. In some andisols in which



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**Continued** 

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<span id="page-41-0"></span>

Figure C35 A generalized soil map of the world.

the content of organic matter is low and short-range-order minerals dominate the colloids, the soils may have a net positive charge. These andisols are counterparts of the suborder Anionic acrudox in terms of mineral-chemical composition.

Oxisols are confined to the intertropical regions, which by definition have an iso STR. Most of the oxisols occur between the Tropics of Cancer and Capricorn. The largest extent is in Brazil, followed by the Congo Basin in Central Africa. Characteristically, oxisols formed in pre-weathered and transported deposits. Weathering may continue in the post-depositional phase. Other pedogenic processes are slow unless there is a fluctuating water table. On the volcanic islands of the Pacific and in Southeast Asia, basic or ultrabasic rocks may weather to form oxisols. Although there is always the possibility of admixture with alluvial or colluvial products, these soils are generally thought to have formed directly on the rocks, unlike the oxisols of the Amazon or Congo Basins.

Vertisols occupy about 2.4% of the land surface and are about equally distributed in tropical and temperate areas. They are among the soils in which soil properties are a function of the mineralogical composition of the clay fraction. For the smectites to form and persist in the soils, one of the requirements is that the soil solution has a high pH, which results in high amounts of bases and soluble silica. Thus, most of the vertisols occur in semiarid or arid environments. The countries with large areas of vertisols are Sudan, India, Australia, and the United States. In semiarid southern Africa, large contiguous areas of vertisols are in Zambia, Zimbabwe, and South Africa. In other areas vertisols occur sporadically in basins adjoining andisols.

Although about a third of the landmass of the world is arid, aridisols occupy only about 12% of the land surface. By definition, aridisols must have a diagnostic horizon; the remaining soils in arid regions are entisols with associated unstabilized dunes and rocky land. About 75% of the aridisols are in the temperate parts of the world. The rest have tropical and boreal climates. Argids are the most extensive aridisols and are frequently in areas where the aridic SMR borders on the ustic or xeric SMR. Calcids, which occupy about 3.7% of the land area, are associated with the argids. Translocation and subsurface accumulation of carbonates, gypsum, and salts require some moisture. Formation of the horizons diagnostic for these suborders may be a current process or may have taken place in historic or geologic periods. Because of the current aridity of the sites where these soils occur, it is generally assumed that many of the diagnostic features may have a "paleo" origin.

Ultisols and alfisols occupy 8.5 and 9.7% of the land surface, respectively. Ultisols are more common in the intertropical areas, while alfisols are in the temperate areas. Also, there is greater proportion of alfisols than of ultisols in the semiarid parts of the world. The dominant feature of both ultisols and alfisols is the presence of an argillic horizon. Other diagnostic horizons or properties define the subclasses. A lighter textured surface soil, which makes tillage easy, and a heavier textured underlying argillic horizon, which enables greater storage of water and nutrients, favors crop production. Many of these soils occur on flat to gently undulating landscapes and have been used by farmers since the beginning of civilization.

Mollisols, which have a thick, organic-rich surface horizon, are among the most productive soils in the world. Some of the world's record yields have been obtained on these soils. Mollisols occupy about 7% of the land mass and are concentrated in the temperate and boreal regions of the world. They are important soils in the semiarid parts of the world, particularly in the

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Figure C36 Examples of the major soil orders.

regions with a Mediterranean climate. The cool climate permits a slow accumulation of the humified organic matter. Because of the excellent quality of the soils and the very favorable climate, these soils are very productive and make up the breadbasket of modern times. Large areas of such soils characterize the Midwest in the United States, the steppes of the former Soviet Union, the northern part of Argentina, and part of Uruguay.

Inceptisols and entisols together occupy about 33% of the land surface. Generally on young surfaces, they occur in association with rock outcrops and sand dunes. These soils formed in recent coastal and riverine deposits. They formed in marine alluvium under brackish water conditions. Entisols are potential acid sulfate soils, and inceptisols are actual acid sulfate soils. When drained, potential acid sulfate soils (sulfaquents) are converted to actual acid sulfate soils (sulfaquepts). The process results in release of a considerable amount of sulfuric acid, making these soils and the soils adjacent to them extremely acid.

## Concluding remarks

In the annals of Soil Science, Soil Taxonomy will remain as not only a major scientific and conceptual innovation but also the fact that it has withstood the test of time. In the last five decades it has demonstrated its value specifically in the United States; around the world, its technical merit has resulted in it being adopted for national use or major aspects being incorporated in the advancement of local systems. With the advent of advances in information technology, the future of Soil Taxonomy or any soil classification systems will be debated. With the ability to process large quantities of data and to generate any kind of use-related information from this data, soil classification systems must undergo marked modifications or remain as historical benchmarks.

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## Cross-references

Acid Soils Alkaline Soils Calcareous Soils Classification of Soils: World Reference Base (WRB) for Soil Resources **Horizon** Hydric Soils Near-Neutral Soils Soil

# CLASSIFICATION OF SOILS: WORLD REFERENCE BASE (WRB) FOR SOIL RESOURCES

In 1998, the International Union of Soil Sciences (IUSS) adopted the World Reference Base for Soil Resources (WRB) as the official system for international correlation of soils. In addition, the WRB is the accepted common scheme of soil databases and maps of the European Union (see Figure C37).

The structure, concepts and definitions of the WRB are strongly influenced by the revised legend of the FAO/ UNESCO Soil Map of the World (FAO/UNESCO-ISRIC, 1988), which in turn borrowed the diagnostic horizons and properties approach from USDA Soil Taxonomy.

The taxonomic units of the WRB are defined in terms of measurable and observable 'diagnostic horizons', the basic identifiers in soil classification. Diagnostic horizons are defined by (combinations of) characteristic 'soil properties' and/or 'soil materials'.

WRB comprises two levels:

- 1. the "Reference Base", which is limited to the first level only having 30 reference soil groups; and
- 2. the second level consists of combinations of qualifiers added to the reference soil groups providing more specific characterization and classification of soils.

## Short summary of the reference groups

Organic soils, such as peat, are brought together in one reference soil group called *Histosols* while all *man-made soils*, which vary widely in properties and appearance but have in common that their properties are strongly affected by human intervention are aggregated to the Anthrosols reference soil group. In some man altered environments non-natural materials, called 'technic materials' dominate the unit, therefore Technosols have now been added as a new Reference Group of the WRB.



Figure C37 World Soil Resources global map.

<span id="page-44-0"></span>Mineral soil whose formation is conditioned by the particular properties of their *parent material* are sub-divided into the Andosols of volcanic regions, the sandy Arenosols of desert areas, beach ridges, inland dunes or areas with highly weathered sandstone and the swelling / shrinking heavy clayey

Vertisols of back-swamps, river basins, lake bottoms and other areas with a high clay content.

Mineral soils whose formation was influenced by their topographic setting (for example, soils associated with recurrent floods or on steep terrain) range from the Fluvisols, which





show stratification or other evidence of recent alluvial sedimentation, non-stratified Gleysols in waterlogged areas and shallow Leptosols over hard rock or highly calcareous material, to the deeper Regosols, which occur in unconsolidated materials that have a minimal profile development because of low soil temperatures, prolonged dryness or erosion.

Soils that are only moderately developed on account of their young pedogenetic age or because of rejuvenation of the soil material are referred to as Cambisols.

The wet tropical and subtropical regions where high soil temperatures and ample moisture promotes rock weathering, rapid decay of soil organic matter, and a long history of dissolution and transport of weathering products have five types of deep and mature soil types. Plinthosols are marked by the presence of a mixture of clay and quartz ('plinthite') that hardens irreversibly upon exposure to the open air while deeply weathered Ferralsols have a very low cation exchange capacity and are virtually devoid of weatherable minerals. Alisols have high cation exchange capacity and much exchangeable aluminum, Nitisols have deep profiles in relatively rich parent material, Acrisols develop on acid parent rock with a clay accumulation horizon, low cation exchange capacity and low base saturation while Lixisols possess a low cation exchange capacity but high base saturation percentage.

Soil in arid and semi-arid regions are differentiated to Solonchaks with a high content of soluble salts, Solonetz with a high percentage of adsorbed sodium ions, Gypsisols with a horizon of secondary gypsum enrichment, Durisols with a layer or nodules of soil material that is cemented by silica and Calcisols with secondary carbonate enrichment.

Soils that occur in the steppe zone between dry and humid temperate climates where vegetation consists of ephemeral grasses and dry forest classify to three reference soil groups. Chernozems with deep, very dark surface soil and carbonate enrichment in the subsoil, Kastanozems with less deep, brownish surface soils and carbonate and/or gypsum accumulation at some depth and the Phaeozems, the dusky red soils of prairie regions with high base saturation but no visible signs of secondary carbonate accumulation.

The brownish and greyish soils of humid temperate regions show evidence of clay or organic matter redistribution. Eluviation and illuviation of metal-humus complexes produce the greyish (bleaching) and brown to black (coating) colors of soils. Five reference soil groups include the acid *Podzols* with a bleached eluviation horizon over an accumulation horizon of organic matter with aluminum and/or iron, Planosols with a bleached topsoil over dense, slowly permeable subsoil, base-poor Albeluvisols with a bleached eluviation horizon tonguing into a clay-enriched subsurface horizon, base-rich Luvisols with a distinct clay accumulation horizon and Umbrisols with a thick, dark, acid surface horizon that is high in organic matter.

All soils of permafrost regions that show signs of 'cryoturbation' (i.e., disturbance by freeze-thaw sequences and ice segregation) are assembled in one reference soil group, the Cryosols.

A simplified key to the 30 reference groups is given in [Table C12](#page-44-0). It is based on the presence, sequence or exclusion of diagnostic horizons and additional diagnostic features. Further characterization of soils is possible with the application of the qualifiers. Each qualifier has a unique meaning generally derived from the definitions of diagnostic features. The qualifiers are listed in table format in priority sequence for each Reference Groups. Two qualifiers may be used in soil unit names. If additional qualifiers are needed, they follow the reference soil group name between brackets. For example: Silti-Calcic Chernozem (Vermic).

Erika Micheli

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#### Cross-references

Classification of Soils: FAO

Classification of Soils: World Reference Base (WRB) Soil Profiles

Classification of Soils: Soil Taxonomy

Horizon Designations in the WRB: See also individual articles on each of the Reference groups

# CLASSIFICATION OF SOILS: WORLD REFERENCE BASE (WRB) SOIL PROFILES

[Figure C38](#page-46-0) displays profiles of all 32 reference groups in the WRB classification.

Otto Spaargaren

## CLASTIC

A geological term applied to rocks made up of fragments. The fragments are broken pieces of pre-existing rocks and minerals, and may themselves be referred to as clastic.

## CLAY MINERAL ALTERATION IN SOILS

Minerals, organic components, microbial organisms, soil fauna, plants, and aqueous solutions interact in the pedosphere in biogeochemical reactions collectively referred to as weathering. The full complexity of the interactions, especially important in the rhizosphere, and how the interactions relate to important aspects of soil science such as pedogenesis, mineral nutrition,

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**Acrisol from Madagascar** 



Albeluvisol from the Netherlands



Alisol from China



Andosol from Mexico



Anthrosol from the Netherlands



Arenosol from China



Calcisol from Italy

Figure C38 Continued



Cambisol from France



Chernozem from Germany



Cryosol from the Russian Federation



Durisol from South Africa



Ferralsol from Brazil



Fluvisol from the Netherlands



**Gleysol from Germany** 



Gypsisol from Israel



Histosol from Ireland Figure C38 Continued



Kastanozem from Kazakhstan



Leptosol from Israel



**Lixisol from Ghana** 



Luvisol from China





Phaeozem from South Africa



Planosol from the United States



Plinthosol from Ghana



Podzol from Germany Figure C38 Continued



Regosol from Ghana



Solonchak from China