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Soil organic matter accumulation and humification during pedogenesis

Akumulace organické hmoty a tvorba humusu v půdách během pedogenese

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Disclaimer:

I declare that I prepared this bachelor thesis independently and I declare all the information sources and literature. BT submitted paper version is identical to the electronic version embedded in the SIS.

Prague, 02.05.2013

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Malika Inogamova

Thank **Doc. Ing. Mgr. Frouz Jan, CSc.** for his time, boundless willingness and patience, without which this work couldn’t be possible. Thank also my family, whose support is really appreciated.

Abstract

Soil is comprised of minerals, SOM , water, and air. Soil development is caused by climate and living matter acting upon parent material (weathered mineral or organic matter from which the soil develops), as conditioned by topography, over time. SOM is a dynamic component of the soils system. Plant productivity is effected by the SOM. SOM provide nutrients and habitat to the organisms living in the soil, including plants, roots and SOM also binds soil particles into aggregates and improves the water holding capacity of soil. SOM is a product of biological decomposition that affects the chemical and physical properties of the soil and its overall fertility. Humus is only partly metabolized by soil organisms but improves the physical and chemical properties of soil. It consists of different humic substances: fulvic acid, humic acid, and humin. Soil is a solid material that results from the interaction of weathering and biological activity on the parent material or underlying hard rock. The fundamental pedogenic processes, used also as a criterion for classifying soils, is associated with SOM accumulation. We discuss the nature and interrelations of the SOM humification and accumulation processes during pedogenesis and the environmental factors on pedogenic processes influencing the rate of SOM accumulation such as climate, organisms, parent material, topography, and time.

Keywords: soil organic matter, humus, soil, pedogenesis, humification, and SOM accumulation

Abstrakt

Půda se skládá z minerálů, organické hmoty, vody a vzduchu. Vývoj půdy je ovlivňuje klima a živé organismy, které působí na geologický substrát, dále je ovlivněn topografií a stářím půd. Organická hmota (OH) je dynamická složka půdního systému a oráží svými vlastnostmi charakter organické hmoty vstupující do půdy a průběh půdotvorného procesu.

Produktivita půd je ovlivněna množstvím a kvalitou půdní organické hmoty, OH poskytuje živiny pro růst rostlin a stanoviště organismů žijících v půdě včetně kořenů rostlin. OH se také váže na půdní minerální částice a zlepšuje zadržování vody v půdě. OH ovlivňuje i další chemické a fyzikální vlastnosti půdy, sorpční schopnost, teplotní režim, pufrování pH atp., a její celkovou úrodnost. Humus se mikrobiálně rozkládá jen nepatrně, ale zlepšuje fyzikální a chemické vlastnosti půdy. Skládá se z různých huminových látek: fulvokyselin, huminových kyselin a huminu. Základní půdotvorné procesy, jsou spojeny s akumulací OH a jsou významným kritériem pro klasifikaci půd. Práce dále diskutuje vzájemné vztahy dekomposice OH, humifikace a akumulace OH v půdě během pedogeneze a jejich vztah k dalším faktorům prostředí ovlivňujícím půdotvorný proces.

Klíčová slova*: Půdní organická hmota, humus, půdy, pedogeneze, humifikace a akumulace OH*

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ABBREVIATION

AEC - Anion exchange capacity

CEC - Cation Exchange Capacity

DOM - Dissolved organic matter

EC - Electrical conductivity

HA - Humic acids

HS - Humic substances

LF - Light fraction (of SOM)

NHS - Non-humic substances

OM - Organic matter

PAW - Plant available water

POM - Particulate organic matter

PWP - Permanent wilting point

SOM - Soil organic matter

WHC - Water holding capacity

INTRODUCTION

The healthy and productive soils are the foundation of the agriculture, and therefore of the food system as it is produces crops that are nourishing people. Plant productivity is based on the organic matter (Bauer and Black, 1994) as plants obtain nutrients from two natural sources such as SOM and minerals. SOM includes any plant or animal material that returns to the soil and goes through the decomposition process. Moreover, while providing nutrients and habitat to the organisms living in the soil, SOM also binds soil particles into aggregates and improves the water holding capacity of soil (Brady and Weil, 1999).

The SOM is a product of biological decomposition that affects the chemical and physical properties of the soil and its overall fertility. SOM content is a function of SOM inputs (litter and roots) and its decomposition. It relates to moisture, temperature and aeration, physical and chemical properties of the soils as well as bioturbation (mixing by soil macrofauna), leaching by water and humus stabilization (organomineral complexes and aggregates) (Bot et al., 2005).

The humus absorbs the ions namely cations and makes them available as a nutrient for the plant in exchange for H^+. Humus controls and regulates many soil functions, the better the humus in the soil the healthier and more productive soil is, and the better the crop grown yield. Humus in soil holds soil moisture longer, thus less water is required for crop production, and also good humus count reduces the wind erosion of soil (Stevenson, 1994 a).

Crop production worldwide is affected by a decline in SOM levels and, consequent, decline of soil fertility. Where the soil is exploited for crop production without restoring the SOM and nutrient contents and maintaining a good structure, the nutrient cycles are broken, soil fertility declines and the balance in the agro-ecosystem is destroyed (Bot et al. 2005). Maintaining SOM content requires a balance between addition and decomposition rates, and is essential to the sustained productivity of agricultural systems. A key to soil restoration is to maximize the retention and recycling of SOM and plant nutrients, and to minimize the losses of these soil components caused by leaching, runoff and erosion (Bot et al. 2005).

The aim of this contribution is to consider the chemical nature of SOM role in formation of the soil properties, SOM turnover and transformation into humus, and indentify how the fundamental pedogenic processes are associated with organic matter accumulation and humification as well as how this process is influenced by the environmental factors.

1. Soil Organic Matter

1.1 Definition and Role of Organic Matter in Soils

Organic matter is the material originating from living organisms. Material may be alive or dead, and may be found in the atmosphere, in organisms, or in the water and soil (Daniels and Galbraith, 2007). OM is considered as a vital component of a healthy soil. It is an important part of soil physical, chemical and biological processes and fertility (Table 1).

Table 1 Functions of organic matter in soil

Physical functions	Chemical functions	Biological functions
• Bind soil particles together in stable aggregates • Influence water holding and aeration • Influence soil temperature	• Major source of cation exchange capacity • Source of pH buffering • Binding site for heavy metals and pesticides	• Food source for microbes and small animals • Major reservoir of plant nutrients

Source: Sparrow et al. (1999); Cotching et al., (2001, 2002)

OM may be from plant or animal tissues that contain C. There are many types of organic matter, and the C content varies widely (Daniels and Galbraith, 2007). C:N ratio is also used to indicate the type of material and ease of decomposition; hard woody materials with a high C:N ratio being more resilient than soft leafy materials with a low C:N ratio (Bot et al. 2005).

SOM is determined as a complex of plant and animal resides at various stages of decomposition ranging from cells and tissues of soil organisms to well-decomposed substances (Brady and Weil, 1999). SOM includes all OM of the soil surface, or already incorporated into the soil.

Since the 1940s, SOM has been further recognized as an integrated part of the complex bio-organo-mineral system, and as a pivotal indicator for soil quality and agro-ecosystems fertility. This has resulted to: (a) methodological and conceptual breakthroughs in its study, leading to significant scientific developments in characterizing the role of humus as an ecosystem component; (b) a growing demand of society for the assessment of the environmental cost of intensification in modern agricultural practices, which has led to growing interest in organic farming, agroforestry, conservation tillage, and the use of plant cover; (c) investigation of the potential of SOM as a sink for greenhouse gas carbon in response to concerns about global climate change (Manlay et al. 2007).

SOM is now recognized by soil scientists as a major factor (Figure 1) controlling the capacity of soil resources to deliver agricultural and environmental services and sustain human societies at both local (e.g. fertility maintenance) and global (e.g. mitigation of atmospheric carbon emissions) scales (Tiessen et al., 1994; Syers and Craswell, 1995).

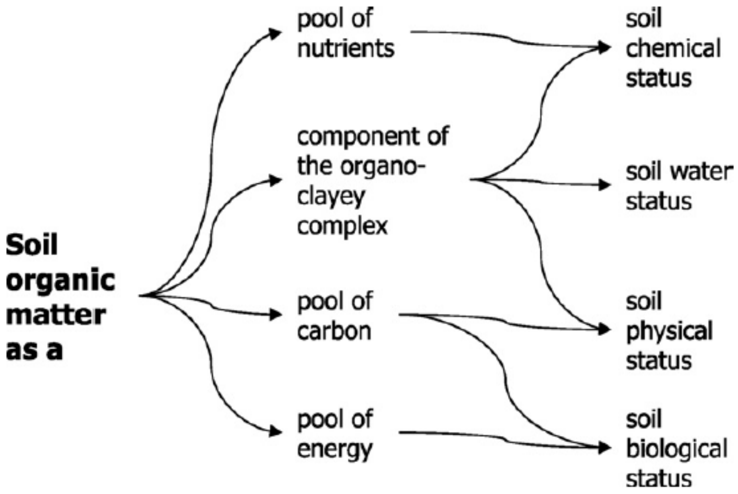

Figure 1 **Relationships between soil organic matter and soil properties**

Source: Manlay et al., 2007

1.2 Composition of Soil Organic Matter

The forms and classification of soil organic matter have been described by Tate (1987) and Theng (1987). Distribution SOM can be considered as follows (Figure 2):

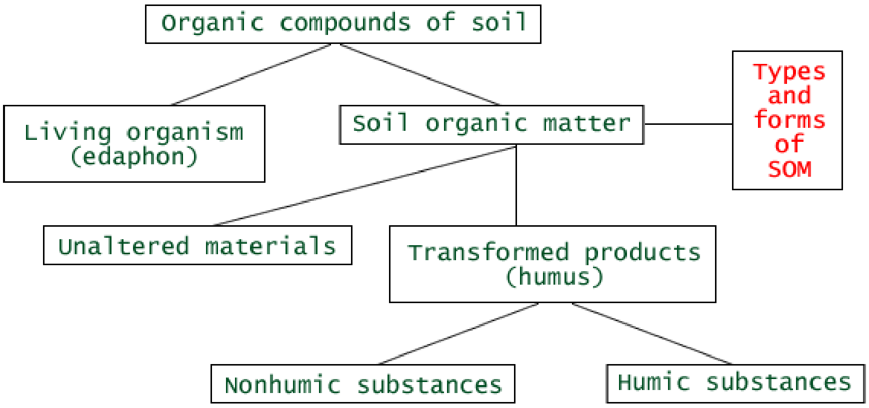

Figure 2 **Basic categories of Soil Organic Matter**

Source: Weber, http://www.bionorden.dk

SOM "pool" can be also divided into four categories (Figure 3) (Moravec et al., 2011):

- living organisms and roots, making up less than 5% of the total pool;
- residues from dead plants, animals and soil organisms that have not yet begun to decompose (<10%);

- portion undergoing rapid decomposition (20-45%); and
- stabilized organic matter (humus) remaining after further decomposition by soil microorganisms (50-80%) (Moravec et al., 2011).

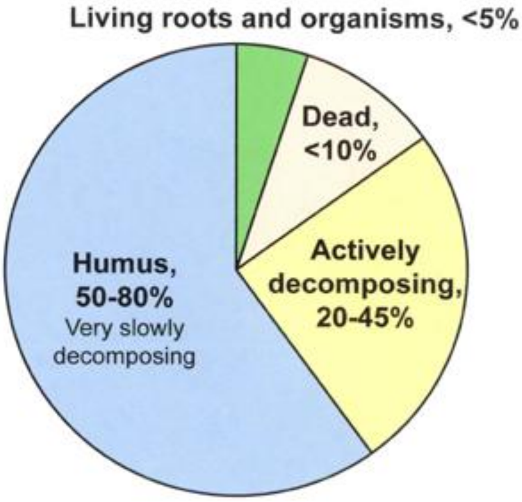

Figure 3 **Composition of Soil Organic Matter (%)**

Source: Moravec et al., 2011

Plant residues contain 60-90% of water. The remaining dry matter consists of carbon (C), oxygen (O), hydrogen (H) – 95%, and small amounts of sulphur (S), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg). Although present in small amounts, these nutrients are very important from the viewpoint of soil fertility management (Bot et al., 2005).

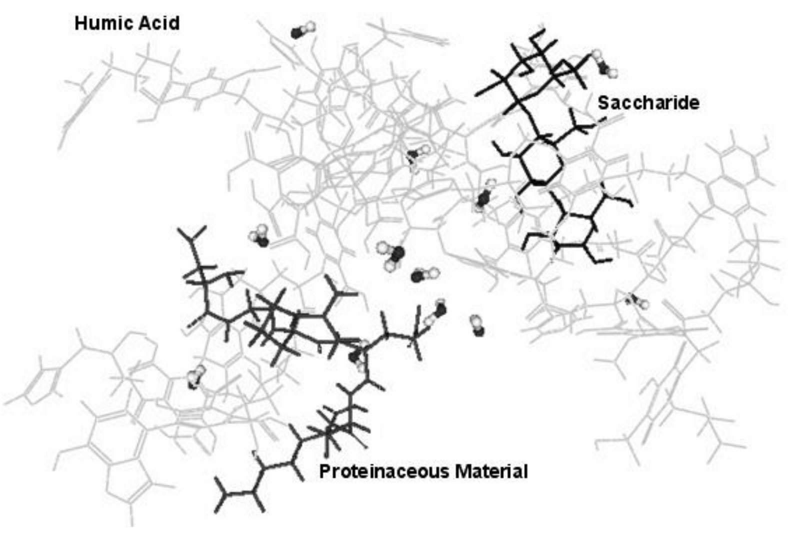

Figure 4 **Schulten and Schnitzer's model of soil organic matter**

Source: Schulten et al., 1998.

Application of new techniques in organic chemistry (chromatography, analytical pyrolysis, nuclear magnetic resonance and the use of isotopes) confirmed that SOM is one of the most complex of natural materials contained a mix of molecules (Figure 4) of varying polymericity and aromaticity (Skjemstad et al., 1997; Stevenson and Cole, 1999). Nonetheless the elucidation of the nature, synthesis and decomposition of SOM at a detailed process level remains a major scientific challenge (Manlay et al. 2007).

1.3. Soil Organic Matter Turnover

SOM turnover (Figure 5) consists of four main processes carried out by soil microorganisms (Brady and Weil, 1999):

1) decomposition of organic residues;
2) nutrient mineralization;
3) transfer of organic carbon and nutrients from one SOM pool to another;
4) continuous release of carbon dioxide (CO_2) through microbial respiration and chemical oxidation.

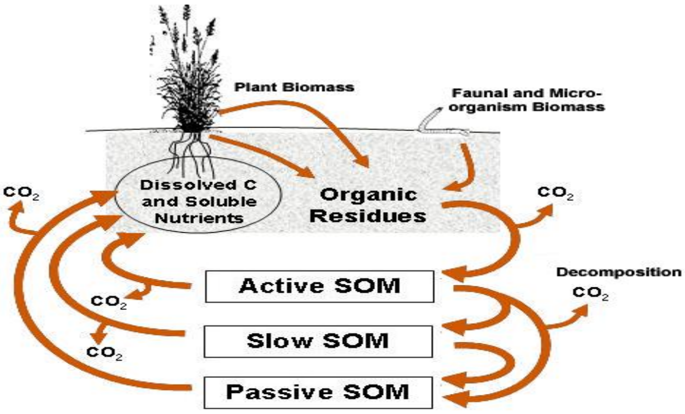

Figure 5 Organic matter sources and transformation in soils

Source: Brady and Weil, 1999

Decomposition is the breakdown of plant derived material into its simpler organic constituents. There are three main pools of SOM determined by their time for complete decomposition, are active (1-2 years), slow (15-100 years) and passive (500-5000 years) (Brady and Weil, 1999).

Both active and slow SOM are biologically active, and they are continually being decomposed by microorganisms. Active SOM is primarily composed of fresh plant and animal residues and decomposes rapidly. SOM that is not completely decomposed then moves into slow or passive SOM pools (McCauley et al., 2009).

Slow SOM consists primarily of detritus (cells and tissues of decomposed material), and is partially resistant to microbial decomposition and will remain in the soil longer than active SOM. An intermediate SOM fraction falling within both active and slow pools is a particulate organic matter (POM) (Brady and Weil, 1999). POM is more stable than other active SOM forms (yet less than passive SOM) and serves as a long-term supply of nutrients (Wander et al., 1994). POM can ranging from a few percent up to 25% of the total SOM, and as the most easily decomposable fraction of non-living SOM after microbial biomass, POM fulfills many soil functions mediated by OM. It is a source of food/energy for microorganisms and soil animals as well as nutrients for plant growth. POM enhances aggregate stability, water infiltration and soil aeration; it increases cation exchange capacity and buffering pH. It also binds environmental pollutants such as heavy metals and pesticides (Carter et al., 2003).

As soil organisms decompose OM, they transform nutrients (N, P and S) into mineral forms that plants can use and this process is called *mineralization*. Without soil microorganisms, insects, and worms feeding on organic matter, nutrients in OM would remain bound in complex organic molecules that plants can’t utilize. Waste products produced by micro-organisms are also SOM. This waste material is less decomposable than the original plant and animal material, but it can be used by a large number of organisms (Bot et al., 2005).

The rate of decomposition affects by C/N ratio. Since the organisms that decompose residues need N (and other essential elements) as well as C, if there is little N in the residue, and decomposition is slow. Also, if there is little N in the residue, microorganisms will utilized inorganic N in the soil to satisfy their N requirement, thereby competing with plants for N and reducing the amount of soil N available for plant growth. The C/N ratio in soil is relatively constant and = 12 (Weber, http://www.bionorden.dk).

By breaking down carbon structures and rebuilding new ones or storing the C into their own biomass, soil biota plays the most important role in nutrient cycling processes and, thus, in the ability of a soil to provide the crop with sufficient nutrients to harvest a healthy product (Bot et al., 2005). Carbon cycling is the continuous transformation of organic and inorganic carbon compounds by plants and micro- and macro-organisms between the soil, plants and the atmosphere (Figure 6) (Bot et al., 2005).

Carbon dioxide is a by-product of a complex chain of processes (as microbes breathe out CO_2), and over half of the carbon added to soil is lost as CO_2 during breakdown. The organic matter that does not degrade completely to carbon dioxide forms humic substances through secondary synthesis reactions (Stevenson, 1994 a; Lichtfouse et al., 1998). During microbial degradation process not all of the carbon is released as CO_2 but humic substances also liberate carbon dioxide (CO_2) from calcium carbonates present within the soil. The released CO_2 may be taken up by the plant or it may form carbonic acids. The carbonic acids act on soil minerals to release plant nutrients (Pettit, 2010).

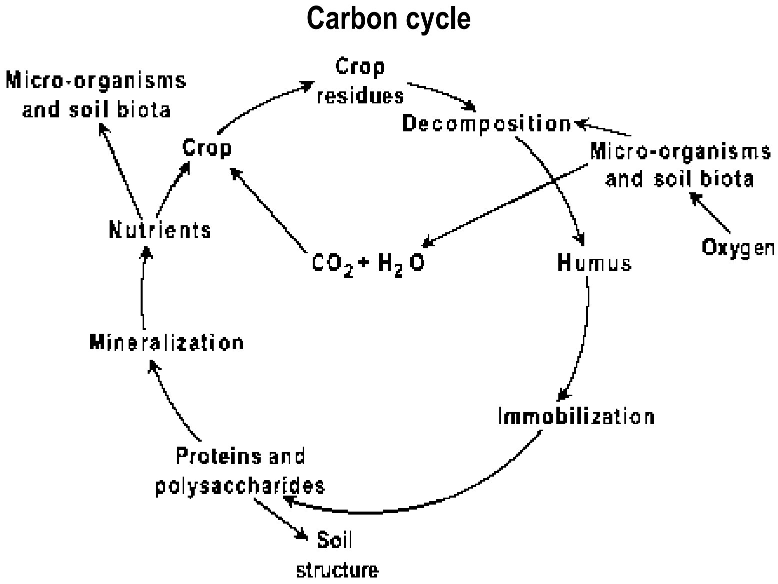

Figure 6 Carbon cycle to plant and soil processes

Source: Bot et al., 2005

Crop residues contain mainly complex carbon compounds originating from cell walls (cellulose, hemicellulose, etc.). Chains of carbon, with each carbon atom linked to other carbons, form the “backbone” of organic molecules. These carbon chains, with varying amounts of attached oxygen, H, N, P and S, are the basis for both simple sugars and amino acids and more complicated molecules of long carbon chains or rings. Depending on their chemical structure, decomposition is rapid (sugars, starches and proteins), slow (cellulose, fats, waxes and resins) or very slow (lignin) (Bot et al., 2005).

Carbohydrates occur in the soil in three main forms: free sugars in the soil solution, cellulose and hemicellulose; complex polysaccharides; and polymeric molecules of various sizes and shapes that are attached strongly to clay colloids and humic substances (Stevenson, 1994 a). The simple sugars, cellulose and hemicellulose, may constitute 5-25% of the OM in most soils, but are easily broken down by micro-organisms (Bot et al. 2005). Cellulose (Figure 7) is a carbohydrate and is the single most abundant organic molecule in the biosphere, and about 70% of plant structural material is made of cellulose (Daniels and Galbraith, 2007).

Cellulose

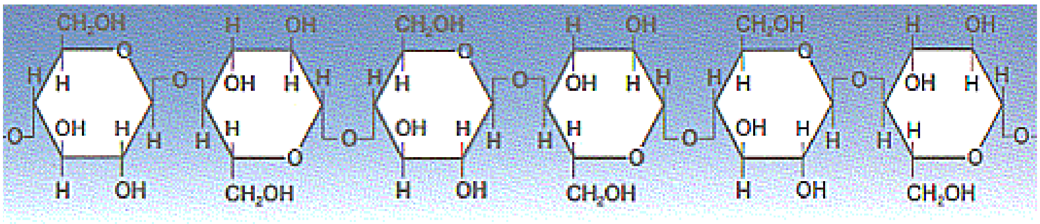

Figure 7 **Chemical structure of Cellulose**
Source: Daniels and Galbraith, 2007

Polysaccharides (repeating units of sugar-type molecules connected in longer chains) promote better soil structure through their ability to bind inorganic soil particles into stable aggregates (Elliot and Lynch, 1984). The soil lipids form a very diverse group of materials, of which fats, waxes and resins make up 2-6% of SOM. (Bot et al., 2005). Within the non-humic (organic) substances (NHS) (Table 2), there are large differences in decomposition rates (Daniels and Galbraith, 2007).

Table 2 **Rates of NHS decomposition**

Substance	Decomposition rate
Sugars, starch, proteins	rapid
Hemicellulose	↓
Cellulose	
Fats, waxes	
Lignin and phenols	very slow

Source: Daniels and Galbraith, 2007

Lignin (Figure 8) is found in plant structural material and provides high strength to cell walls (Daniels and Galbraith, 2007). Lignin is particularly difficult to degrade, and reduces the availability of other attached cell wall constituents. Only a few microbes can break the bonds in lignin (mainly white rot fungi). Decomposition is very slow at first until these aerobic microbes synthesize the lignin into secondary compounds that bacteria can decompose (Daniels and Galbraith, 2007).

Lignin

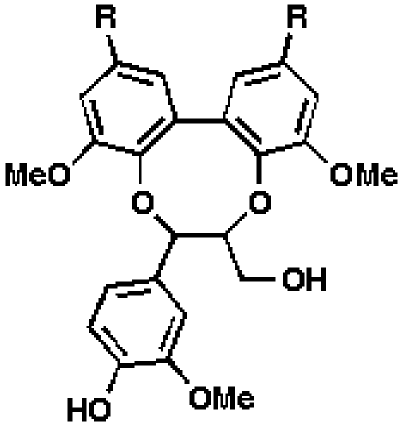

Figure 8 Chemical structure of Lignin

Source: Daniels and Galbraith, 2007

Decomposition is closely related to humification, mineralization, DOM dynamics, and SOM stabilization. SOM pools and SOM dynamics with special reference to litter decomposition and humification (including microbial resynthesis, selective preservation, and direct transformation), mineralization, leaching of DOM, and stabilization by interactions within organic compounds presented at the (Figure 9) below. These processes are controlled by different factors: (A) control of the quality and quantity of the primary resources; (B) control of the microbial activities; (C) possible catalytic effects on direct transformation; and (D) control by stabilization with inorganic compound. During the first phase of decomposition, rapid mineralization of labile components is the dominant process. In the second phase of decomposition, mineralization still occurs but is slowed down due to the accumulation of refractory molecules (Zech et al., 1997).

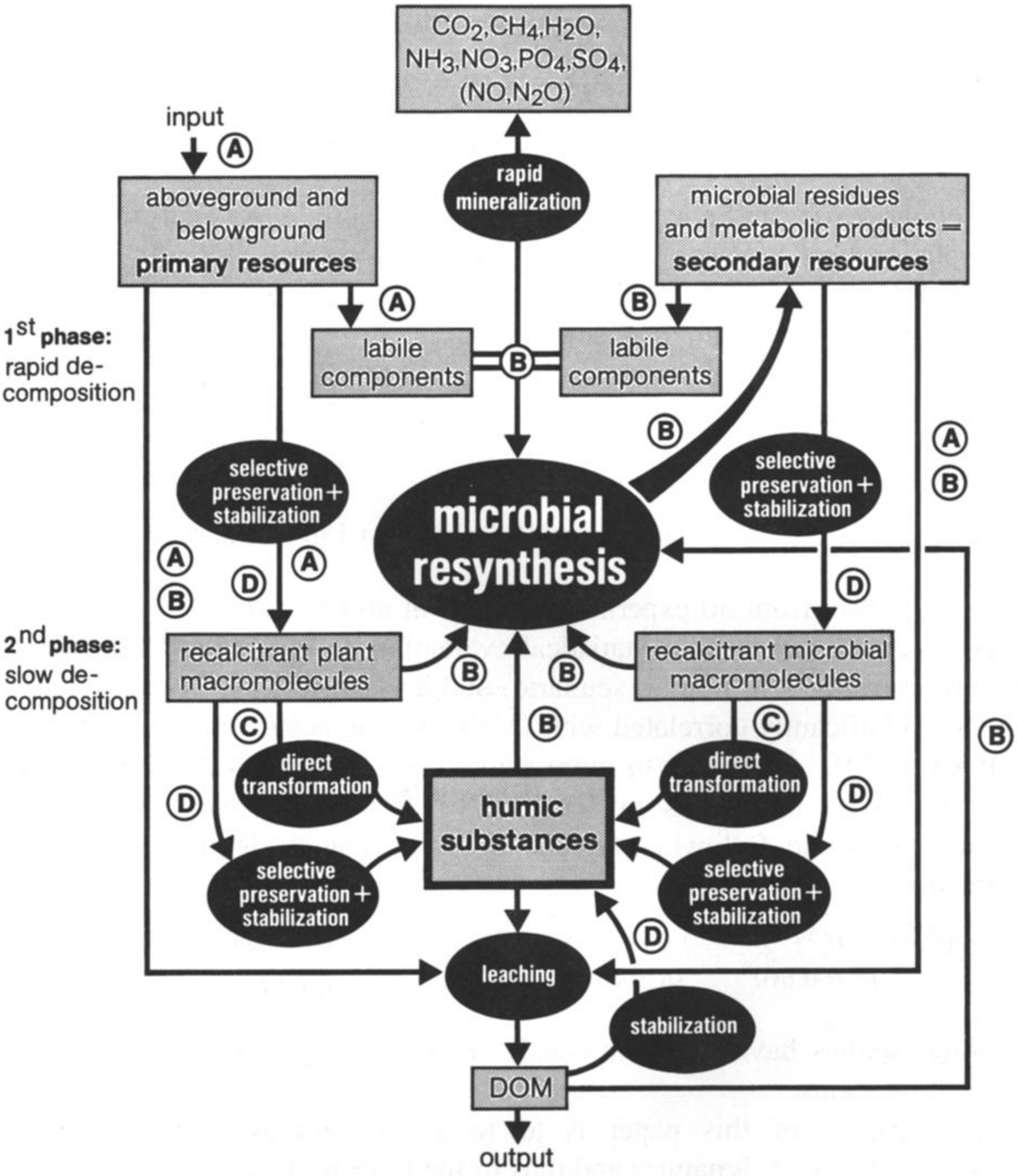

Figure 9 **Soil organic matter pools and dynamics**

Source: Zech et al., 1997

2. Humus

2.1 Definition and Importance of Humus

In soil science, humus (Dictionary.com Unabridged (v 1.1), 2008) refers to any OM that has reached a point of stability, where it will break down no further and might, if conditions do not change, remain as it is for centuries, if not millennia (Whitehead et al., 2006). It is a highly complex substance, the full nature of which is still not fully understood (Manlay et al., 2007). In the conclusion ‘‘Humus as an organic system” of the masterwork ‘‘Humus. Origin, chemical composition and importance in nature’’ (Waksman, 1938) the following definition is provided: “*The importance of humus inhuman economy seldom receives sufficient emphasis. Suffice to say that it probably represents the most important source of human wealth on this planet. Nature has stored in and up on the earth, in the form of humus, the source of a vast amount of readily available energy, a large part of the carbon needed for life processes, and most of the combined nitrogen, so much needed for plant growth*”. In most literature, humus is considered as an integral part of soil organic matter.

In contrast to active and slow SOM, passive SOM (i.e. humus) is not biologically active and is the pool responsible for many of the soil chemical and physical properties associated with SOM and soil quality such as:

- sorption
- ability of soil to hold water (water holding capacity), or
- pH buffering (McCauley, 2009).

<u>Soil sorption</u> describes the transition of molecules from the solution phase to any phased fixed (possibly temporarily) to any of the solid components of soil. SOM is not a single and homogeneous material but a mixture of materials with different sorption properties. It is not only SOM can exert influence on soil sorption properties. Minerals namely clays posses sorption capacity as well (usually lover than HS), moreover the presence of soil minerals can also influence the soil sorption properties by reducing soil sorption affinity through blocking OM sorption sites or by causing conformational changes in its structure (Ahangar, 2011).

The amount of capillary water available to plants is the soil’s ‘<u>water holding capacity</u>’ (WHC) or ‘plant available water’ (PAW). This water is available for plant uptake until the ‘permanent wilting point’ (PWP) is reached, a point at which water is held too tightly by the soil for plants to extract it (McCauley et al., 2005). SOM is able to hold and retain large quantities of water and SOM aggregates have been shown to increase WHC, infiltration, and porosity, and reduce compatibility (Carter, 2002).

Representing approximately 50-80% (Moravec et al., 2011) of total SOM, humus is a dark, complex mixture of organic substances modified from original organic tissue, synthesized by various soil organisms, and resistant to further microbial decomposition (Prasad and Power, 1997). Humus or humified organic matter is the remaining part of organic matter that has been used and transformed by many different soil organisms. It is a relatively stable component formed by humic substances, including humic acids, fulvic acids, hymatomelanic acids and humins (Tan, 1994). It is probably the most widely distributed organic carbon-containing material in terrestrial and aquatic environments. Humus cannot be decomposed readily because of its intimate interactions with soil mineral phases and is chemically too complex to be used by most organisms (Bot et al., 2005).

Humus improves the physical and chemical properties of soil. As it slowly decomposes, it colors the soil darker; increases soil aggregation and aggregate stability; increases the CEC (the ability to attract and retain nutrients); and contributes N, P and other nutrients. Humus increases the capacity to store water and store (sequester) C from the atmosphere (Bot et al., 2005).

2.1.1 Decomposition and Humification

Soil organic matter is understood today as the non-living product of the decomposition of plant and animal substances (Manlay et al., 2007). When plant residues are returned to the soil, various organic compounds undergo decomposition. Decomposition is a biological process that includes the physical breakdown and biochemical transformation of complex organic molecules of dead material into simpler organic and inorganic molecules (Juma, 1998).

Successive decomposition of dead material and modified organic matter results in the formation of a more complex organic matter called humus (Juma, 1998). This process is called humification. Humification process includes enrichment of C and loss of H and O content in the by-products of OM decomposition (Daniels and Galbraith, 2007).

The humification process, whereby plant and microbial remains are transformed into more recalcitrant humic substances (HS) through biochemical and abiotic pathways, is one of the least understood and most intriguing aspects of humus chemistry (Stevenson, 1994a). Understanding the evolution of OM residues into HS is of key importance in elucidating C biogeochemistry, especially in waterlogged areas such as peatlands. In fact, because the rate of biomass production is greater than the rate of decomposition in these environments, they represent one of the largest global reservoirs of refractory organic C (Clymo, 1983).

2.1.2 Chemical Composition of Humus

About 50-80% of the non-living part of SOM is humus (Moravec et al., 2011). It is an important buffer, reducing fluctuations in soil acidity and nutrient availability. Compared with simple organic molecules, humic substances are very complex and large, with high molecular weights. The characteristics of the well-decomposed part of the organic matter, the humus, are very different from those of simple organic molecules (Bot et al., 2005).

Humus consists of different humic substances (Hayes, 1998):

- **Humic acids**: the fraction of humus that is soluble in water, except for conditions more acid than pH 2. Common colors are dark brown to black. Humic substances are extracted by dilute bases, but are insoluble in dilute acids like those found in the soil solution (thus they are stable in acid wetland soils). Humic acids are the dominant HS in the fine roots of grasses and grass-like plants;
- **Fulvic acids**: the fraction of humus that is soluble in water under all pH conditions. Their color is commonly light yellow to yellow-brown. The fulvic substances are soluble in both acids and bases like those found in the soil solution (thus they are the most easily decomposed HS in wetland soils). Fulvic acids are the dominant HS in tree leaves, leachates, and exudates;
- **Humin**: the fraction of humus that is not soluble in water at any pH and that cannot be extracted with a strong base, such as sodium hydroxide (NaOH). Commonly black in colour. Humin is insoluble in alkaline solutions (thus it is stable in alkaline wetland soils).

These fractions (Figure 10) increase in molecular weight and get darker in color in the order fulvic acid, humic acid, and humin (Stevenson, 1994 a; Tan, 2003).

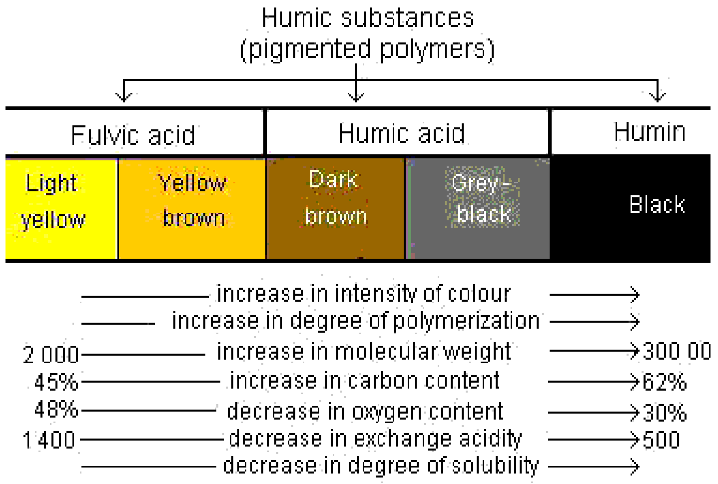

Figure 10 Chemical properties of humic substances

Source: Stevenson, 1982

Humic acids are formed during the decomposition and further transformation of dead organic matter (Frouz et al., 2011). Recently experiments were performed (Frouz et al., 2011) for determination of the role of soil invertebrates to favor formation of humic substances during the interaction of proteins and phenols, and role of clay minerals in the reaction between them (Frouz et al., 2011). When these substrates passed through the digestive tracts of the invertebrates, the polymerization of organic substances and the inclusion of proteins and phenols into humic acids occurred (Frouz et al., 2011).

The amount of organic carbon in the soil in the form of humic substances exceeds that which makes up living organisms (Engel and Macko, 1993). Approximately 80% of the total carbon in terrestrial media and 60% of the carbon dissolved in aquatic media are made up of humic substances (Peña-Méndez et al., 2005).

The elemental composition of different FAs and HAs shows that the major elements in their composition are C, H, O, N, and S (Peña-Méndez et al., 2005). Moreover, group composition is also used to characterize HS as it gives information about the chemistry and structural properties of HS (Purdue 1988). Fulvic acids contain more functional groups of an acidic nature, particularly -COOH. The total acidities of fulvic acids (900-1400mmol/100g) are considerably higher than for humic acids (400-870mmol/100g) (Peña-Méndez et al., 2005). An important difference is that while the oxygen in fulvic acids is largely in known functional groups (-COOH, -OH, -C=O), with a high oxygen content, the acidity and degree of polymerization all change systematically with increasing molecular weight (Peña-Méndez et al., 2005). All the humic substances can be divided into components according to their solubility in different media:

- HAs and FAs represent alkali-soluble humus fragments (Peña-Méndez et al., 2005);
- HAs are commonly extracted using diluted alkali and precipitated with an acid, and so are separated from the soluble FAs (Peña-Méndez et al., 2005).
- Humin represents the insoluble residue (Thorn et al., 1996).

Humic acids (Figure 11) are larger than fulvic acids (Figure 12) (Stevenson, 1982).

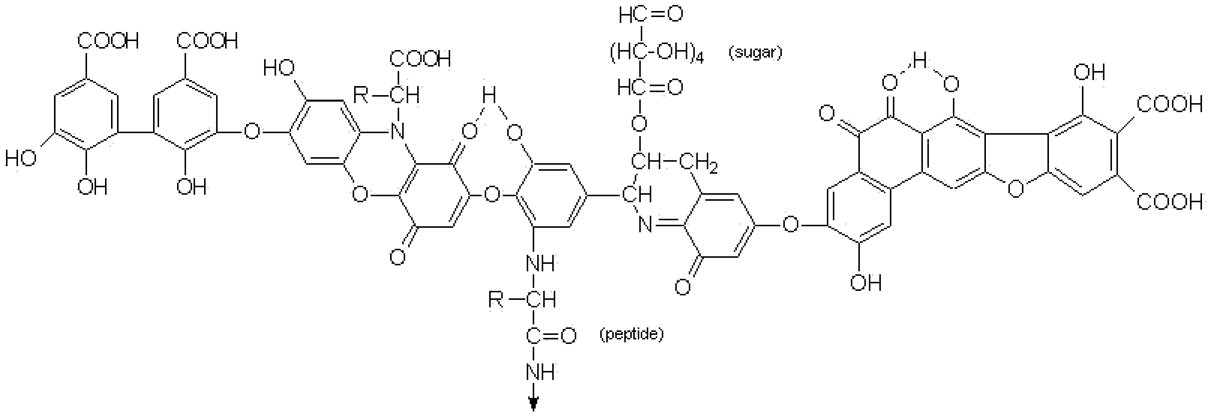

Figure 11 Model structure of humic acid

Source: Stevenson, 1982

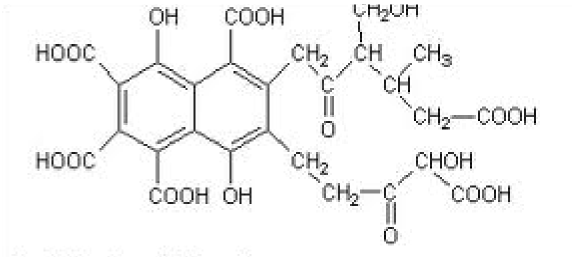

Figure 12 Model structure of fulvic acid
Source: Baffle, 1977

Humin comprises 20% to 50% of SOM and is its most recalcitrant fraction (Stevenson, 1994; Rice, 2001). It is a significant contributor to the stable carbon pool in soils (Song et al., 2011). The recalcitrant humin materials extracted in DMSO+H_2SO_4 are largely biological molecules that are protected from degradation by their hydrophobic moieties and by sorption on the soil clays (Song et al., 2011).

One of the most striking characteristics of humic substances is their ability to interact with metal ions, oxides, hydroxides, mineral and organic compounds, including toxic pollutants, to form water-soluble and water-insoluble complexes. Through the formation of these complexes, humic substances can dissolve, mobilize and transport metals and organics in soils and waters, or accumulate in certain soil horizons. This influences nutrient availability, especially those nutrients present at micro concentrations only (Schnitzer, 1986).

The percentage of the humus which occurs in the various humic fractions varies considerably from one soil type to another. The humus of forest soils is characterized by a high content of fulvic acids while the humus of peat and grassland soils is high in humic acids. The humic acid/fulvic acid ratio usually, but not always, decreases with increasing depth (Weber, http://www.bionorden.dk).

2.1.3 Humus Forms and Types

Humus form is defined as the group of organic and organic enriched mineral horizons at the soil surface, hence humus form reflect rather morphology then chemistry of soil, however as will be shown latter certain soil morphology correspond with specific soil chemistry (Green et al., 1993). Humus forms may be the first tool to assess qualitatively OM turnover in soils; as such they should be related to the stocks of organic C a soil can store, to the characteristics of OM that affect its stability and, more generally, to the factors of soil formation (Bonifacio et al., 2011). The variability of humus forms reflects the varying degradation rates of OM in different environments (Duchaufour, 1997).

Classification of the humus form profile is based on characteristics of the first 40 cm below surface (Figure 13). The soil profile describes the first 120 cm below surface. Humus form profile describes all layers that contain OM while only the first 40 cm below surface are taken into account for the humus form type classification (http://www.humusvormen.wur.nl).

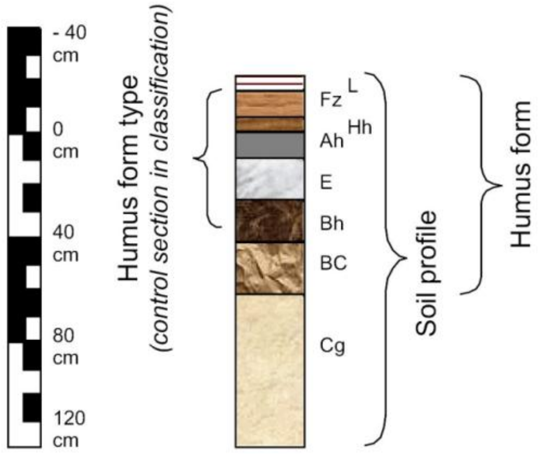

Figure 13 **Humus form in relation to other soil profiles**

Source: http://www.humusvormen.wur.nl

Humus occurs in soils in many types, differs in regard to morphology and fractional composition. A type of humus is it a morphological form of naturals of HS accumulation in the profile or on the surface of soil, conditioned by general direction of soil-forming process and humification of OM. The types of humus in terrestrial environment are as follows (Weber, http://www.bionorden.dk):

- **Mor** is humus usually develops beneath coniferous woodland or heather moorland, under cool, wet climatic conditions. Breakdown is slow due to the absence of soil biota, FA typically prevail in this humus form, they are typically saturated by H^+ Al^{3+} Fe^{3+};
- **Moder** is humus that is intermediate between mor and mull
- **Mull** is humus that is developed under deciduous woodland, where base-rich plant remains are actively broken down by a prolific soil biota, HA and humin dominate in this humus form, typically saturated by Ca^{2+}

The quality of OM in litterfall is only one of the factors influencing its degradation, basically, the development of one humus form or another should depend on the same factors that affect soil formation such as climate, topography, vegetation, parent material and time (Jenny, 1941). All these factors interact and drive the processes of accumulation and degradation of organic matter.

2.1.4 Factors Influencing Humus formation

The transformation and movement of materials within soil organic matter pools is a dynamic process influenced by:

- vegetation
- soil organisms
- climate
- soil type

All these factors operate within a hierarchical spatial scale. Soil organisms are responsible for the decay and cycling of both macronutrients and micronutrients, and their activity affects the structure, tilth and productivity of the soil (Bot et al., 2005).

Vegetation

The humus content of soil depends on quantity of plant material and rate of its decomposition. Many factors influence the type and quantity of vegetation (Allison, 1973). Under tropical conditions, applications of readily degradable materials with low C:N ratios, such as green manure and leguminous cover crops, favour decomposition and a short-term increase in the labile nitrogen pool during the growing season. On the other hand, applications of plant materials with both large C:N ratios and lignin contents such as cereal straw and grasses generally favour nutrient immobilization, organic matter accumulation and humus formation (Bot et al., 2005).

Root turnover also constitutes an important addition of humus into the soil, and consequently it is important for carbon sequestration. In forests, most organic matter is added as superficial litter. However, in grassland ecosystems, up to two-thirds of organic matter is added through the decay of roots (Quideau, 2002). Grassland soils have higher OM content than forest soils due to larger amount of raw material for humus synthesis is produced under grass; humus forms in the rhizosphere that is more extensive under grass than under forest vegetation, and more severe climate conditions at which grasslands are formed result in preservation of OM (Stevenson, 1994 a).

Soil organisms

Soil fauna and microflora are the living organisms that are mostly responsible for plant material decomposition. Although the animal population, especially the earthworms, is often are of the most importance in incorporation of plant restudies into the soil, it is bacteria and fungi that play the major role in transformation process (Allison, 1973). Decomposition of plant and animal debris can proceed in absence of all soil animals bur humus formation in the absence of microflora does not occur (Allison, 1973). However (Frouz et al., 2011) show faster formation of HA in gut of soil animals then in surrounding soil. Plant residues are major source of material for humus formation but soil microbes and soil animals contribute to the secondary resources, however are of less quantitative importance (Swift et al., 1979). Microbial standing biomass contributes 1-4% of the soil organic carbon, and the total edaphon about 10% (Kassim et al., 1981). The chemical composition of the secondary resources is even more complex than that of the primary resources. For instance, fungal cell walls contain chitin, chitosan, cellulose, and different non-crystal line polysaccharides, and lipids, lipopolysaccharides, peptidoglycan, and non-crystallinepolysaccharides were found in bacterial cell walls (Rogers et al., 1980).

Climate

Climatic conditions influence soil biota populations, dynamics and activity, and a low degradation of otherwise easily decomposable organic substrates is visible upon changes in temperature (Wetterstedt et al., 2010) or in the presence of water stress (Andresen et al., 2010). Field studies have shown that temperature is a key factor controlling the rate of decomposition of plant residues. Decomposition normally occurs more rapidly in the tropics than in temperate areas (Bot et al., 2005).

Increase of rainfall that is a moisture component of climate influences the SOM content as it is promotes plant growth and therefore greater production of raw material required for humus synthesis. Amount of plant tissue produced and then returned into the soil varies in arid and arctic zones (just a trace) and in warm climate areas (several tons), and both roots and tops are serving as a source for humus formation (Stevenson, 1994 a).

Soil type

Percentage of the humus in the various humic fractions varies considerably from one soil type to another. Humus of forest soils is characterized by a high content of fulvic acids while the humus of peat and grassland soils is high in humic acids (Figure 14) (Stevenson, 1982)

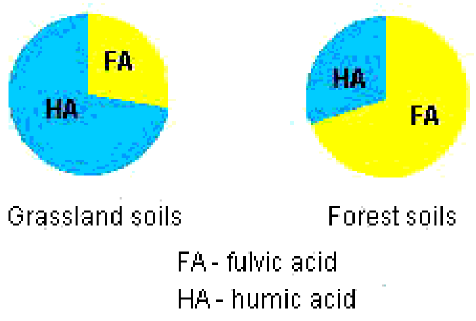

Figure 14 **Distribution of humus forms in grassland and forest soils**

Source: Stevenson, 1982

Soil texture is very important factor for the humus content of the soil. OM level is usually higher in undisturbed soils as all native vegetation remains in the soil, erosion and oxidation are minimal (Allison, 1973). Soil organic matter tends to increase as the clay content increases. This increase depends on two mechanisms. First, bonds between the surface of clay particles and organic matter retard the decomposition process. Second, soils with higher clay content increase the potential for aggregate formation. Macroaggregates physically protect organic matter molecules from further mineralization caused by microbial attack (Rice, 2002). Under similar climate conditions, the organic matter content in fine textured (clayey) soils is two to four times that of coarse textured (sandy) soils (Prasad and Power, 1997).

Parent material influences organic matter accumulation not only through its effect on soil texture. Soils developed from inherently rich material, such as basalt, are more fertile than soils formed from granitic material, which contains less mineral nutrients. Moreover, the former experience more organic matter accumulation because of abundant vegetative growth (Bot et al., 2005).

Salinity, toxicity and extremes in soil pH (acid or alkaline) result in poor biomass production and, thus in reduced additions of organic matter to the soil. The pH affects humus formation in two ways: decomposition, and biomass production. In strongly acid or highly alkaline soils, the growing conditions for micro-organisms are poor, resulting in low levels of biological oxidation of organic matter (Primavesi, 1984). Soil acidity also influences the availability of plant nutrients and thus regulates indirectly biomass production and the available food for soil biota. Fungi are less sensitive than bacteria to acid soil conditions.

2.1.5 Extraction of humus from soil

Humic substances have been extracted from soils for many purposes including the study of their molecular structure (Piccolo et al., 1998; Spaccini et al., 2000), thermal analysis (Rosa et al., 2005; Francioso et al., 2005; Baglieri et al., 2007), isotopic analysis (Webb et al., 2004; Piccolo et al., 2005; Francioso et al., 2005; Spaccini et al., 2006), and spectroscopic analysis (Fründ and Lüdemann, 1991; Piccolo et al., 2005; Shirshova et al., 2006).

A variety of techniques (Table 3) have been employed, depending upon the nature of the material to be examined, and many of which involve the separation of soil organic matter into its various humic fractions based on the solubility of humic and fulvic acid in base solutions.

Table 3 Reagents used for extraction of organic constituents from soil

Extractant	Organic matter extracted %
NaOH	to: 80%
$Na_4P_2O_7$ and other	to: 30%
Organic chelates: acetyloacetone, cupferron, hydroxyquinoline	to: 30%
Formic acid (HCOOH)	to: 55%

Source: Stevenson, 1982

Although the International Humic Substances Society (IHSS) provides a standardized protocol for humic extractions (Figure 15), this method is intended to preserve the chemical characteristics of each humic fraction but does not consider potential fractionation of carbon isotopes (Prentice et al.,2010).

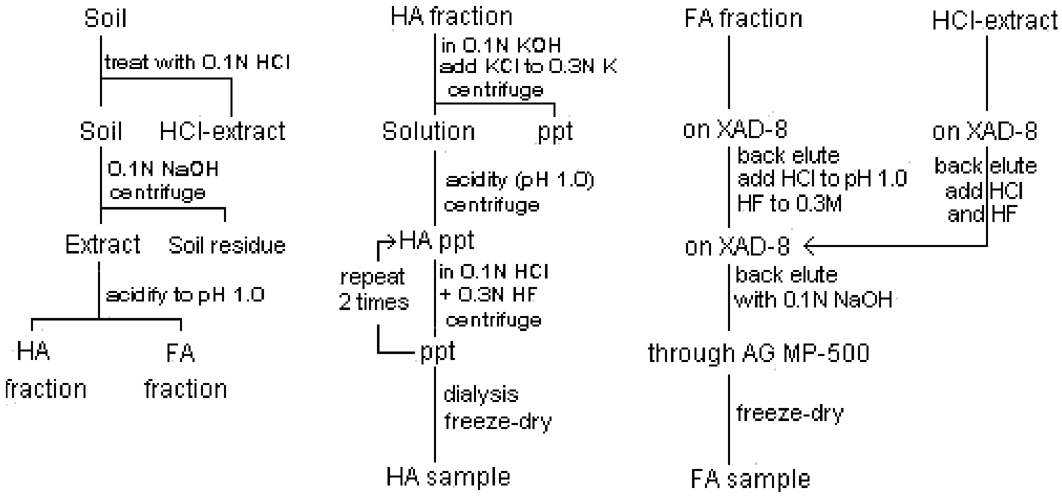

Figure 15 Preparation of humic acid and fulvic acid samples (IHSS method)
Source: Weber, http://www.bionorden.dk

2.1.6 Humus Fractionation

Typically, soil fractions belonging to the labile pool present turnover rates of days to a few years, while for fractions in intermediate and passive pools turnover rates range from a few years to centuries (Stevenson, 1994a; Wander, 2004). Soil fractions consisting largely of labile SOM are recognized as potential indicators of soil quality changes in the short-term due to variation in management practices (e.g. tillage, fertilizer and manure applications, and crop rotation) (Sequeira et al., 2011). Particulate organic matter (POM) and light fraction (LF) are important soil fractions that, depending on the system evaluated (e.g. soil type and quality of residue input), to a large extent consist of labile or active SOM, and are potentially sensitive indicators to changes in soil management practices (Marriott and Wander, 2006; Sharifi et al., 2008; Yoo and Wander, 2008). Assuming that sorption is an important mechanism in SOM stabilization (formation of organo-mineral complexes), soil fractions within the sand fraction are allocated to the labile pool and soil fractions in silt and clay fractions to the intermediate and passive pools (Sequeira et al., 2011). These fractions consist mainly of partially decomposed plant residues, microbial residues, seeds, and spores forming organo-mineral complexes with soil mineral particles (Baisden et al., 2002; Gregorich et al., 2006).

As was already mentioned above, humic substances can be separated into fulvic acid, humic acid, and humin on the basis of their solubility. Fulvic acids are soluble in both alkali and acid, humic acids are soluble in alkali but precipitate in acid, and the humin fraction is both alkali and acid insoluble (Hayes, 1998). These fractions increase in molecular weight and get darker in color in the order fulvic acid, humic acid, and humin (Stevenson, 1994 a; Tan, 2003). Although the fractions are heterogeneous, differing both in molecular size and functional group contents, many researchers believe that humin, humic acid, and to some extent fulvic acid are structurally similar (Hayes and Clapp, 2001; Rice 2001). Their classification may represent arbitrary divisions within a spectrum of chemical properties among the larger group of humic substances (Schnitzer and Khan, 1972; Stevenson, 1982; Anderson and Paul, 1984; Fründ and Lüdemann, 1991; Hayes and Clapp, 2001). In any case, the humin fraction is more strongly associated with mineral material, often forming complexes with inorganic colloids, and contains more aliphatic components than the other humic fractions (Lichtfouse et al., 1998; Rice, 2001). These components are chemically and physically resistant to biodegradation and this contributes to the more resilient nature and longer turnover rate of humin relative to the other humic substances.

3. Accumulation of Organic Matters and Humus in Soil during Pedogenesis

3.1 Soil

Soil can be defined as the solid material on the Earth's surface that results from the interaction of weathering and biological activity on the parent material or underlying hard rock. Soil is comprised of minerals, soil organic matter, water, and air (Figure 16). Minerals and SOM make up the solid fraction, whereas air and water comprise the pore space fraction. A typical agricultural soil is usually around 50% solid particles and 50% pores. The composition and proportion of these components greatly influence soil physical properties, including texture, structure, and porosity, the fraction of pore space in a soil. In turn, these properties affect air and water movement in the soil, and thus the soil's ability to function (Brady and Weil, et al., 2002).

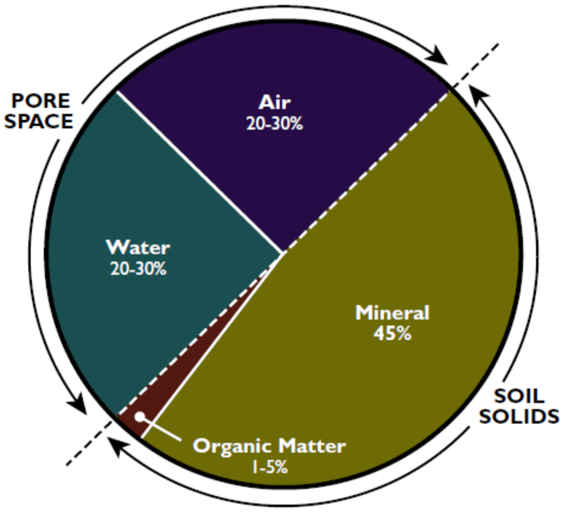

Figure 16 **Four components of soil**

Source: McCauley et al., 2005

3.1.1 Soil Development

The study of soils as naturally occurring phenomena is called pedology (from the Greek word *pedon*, meaning soil or earth). Soil development is caused by climate and living matter acting upon parent material (weathered mineral or organic matter from which the soil develops), as conditioned by topography, over time (Brady and Weil, 2002).

Parent material

This is the material from which the soil has developed and can vary from solid rock to deposits like alluvium and boulder clay. It has been defined as ‘the initial state of the soil system. Parent material can influence the soil in a number of ways: color, texture, structure, mineral composition, and permeability/drainage (Jenny, 1941).

Organisms

Organism, both plant and animal, play an important role in the development and composition of soil. Organisms add organic matter, aid decomposition, weathering and nutrient cycling (Jenny, 1941). Micro organisms such as bacteria and fungi assist in the decomposition of plant litter. The nature of the soil humus is determined by the vegetation cover and resultant litter inputs. Roots contribute dead roots to the soil, bind soil particles together and can redistribute and compress soil (Ritter, 2009). The richness and diversity of soil organisms and plant life that grows on the surface is also tied to climate.

Climate

Climate affects the rate and type of soil formation, and also both vegetative production and the activity of organisms. Soil climate has two major components such as moisture (precipitation) and temperature, influencing evaporation. When precipitation exceeds evaporation, leaching of the soil will occur. Temperature determines the rate of reactions; chemical and biological decay and so has an influence on weathering and humification (Ritter, 2009).

Topography

Topography has a significant impact on soil formation as it determines runoff of water, and its orientation affects microclimate which in turn affects vegetation. For soil to form, the parent material needs to lie relatively undisturbed so soil horizon processes can proceed. Water moving across the surface strips parent material away impeding soil development. Water erosion is more effective on steeper, unvegetated slopes (Marsh, 1984).

Time

Soils develop very slowly. Young soils retain many of the characteristics of the parent material. As time passes, the weathering processes continue to act on soil parent material to break it down and decompose it (Ritter, 2009). Over time they acquire other features resulting from the addition of organic matter and the activity of organisms. The estimation of relative age or degree of maturity of soils is universally based on horizon differentiation. In practice, it is generally maintained that the larger the number of horizons and the greater their thickness and intensity the more mature is the soil (Jenny, 1941)

3.1.2 Soil horizons

The soil forming factors resulted in a soil profile of varying layers, or ‘horizons,’ each with distinct texture, structure, color and other properties. According to the British systems, the most agricultural soils are grouped into four main ‘master’ horizons: O, A, B, and C (Figure 17).

Various subcategories may occur within these horizons and are designated by a lower case letter following the master horizon capital letter (e.g., Ap or Bt). The O horizon is an organic layer above the mineral soil that consists of fresh or partially decomposed organic material and is most common in forested soils. The A horizon is the mineral soil surface layer and is the horizon most impacted by biological and human activity. It usually has the highest percentage of SOM, which often results in it being darker in color than the rest of the profile (McCauley et al., 2005).

The OM content in the upper A horizon is directly related to different physical soil properties which are strongly related to soil quality viz. the percentage of aggregates and their stability (Tisdall and Oades, 1982; Chaney and Swift, 1984; Franzluebbers and Arshad, 1996), bulk density, porosity, water infiltration, and water holding capacity (Hudson, 1994; Moreno et al., 1997). The quality of the soil depends on these properties because they determine the ease of supply of nutrients, water and air, which are so important for the balance of the life in the soil (Mariscal et al., 2007).

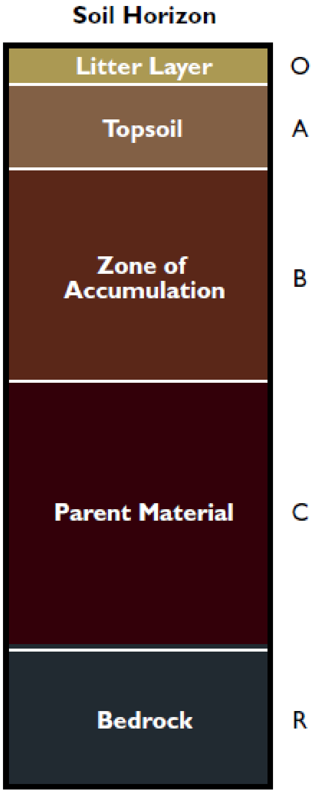

Figure 17 **General scheme of soil profile**

Source: McCauley, et al., 2005

Below the A horizon will be either an E horizon, usually not present in grassland/agricultural soils, or a B horizon, the horizon of accumulation. Material from the A (or E) horizon, such as clay and carbonates, leach downward and accumulate in the B horizon. The C horizon represents the weathered parent material. Bedrock (designated by R) or a deep accumulation of materials deposited by wind, water, glaciers or gravity often lies below the C horizon. Not all soils will have every horizon or sub-horizon present. For instance, a poorly developed soil may lack a strongly defined B horizon or highly eroded lands may have a thin, or nonexistent, A horizon (McCauley et al., 2005).

In the Czech Republic, basic taxonomic classification used for large-scale mapping of agricultural soils is based on the use of diagnostic soil horizons and features (Němeček et al., 1967), and nowadays a unified soil classification system (Figures 18 and 19) has been completed (Němeček et al., 2001).

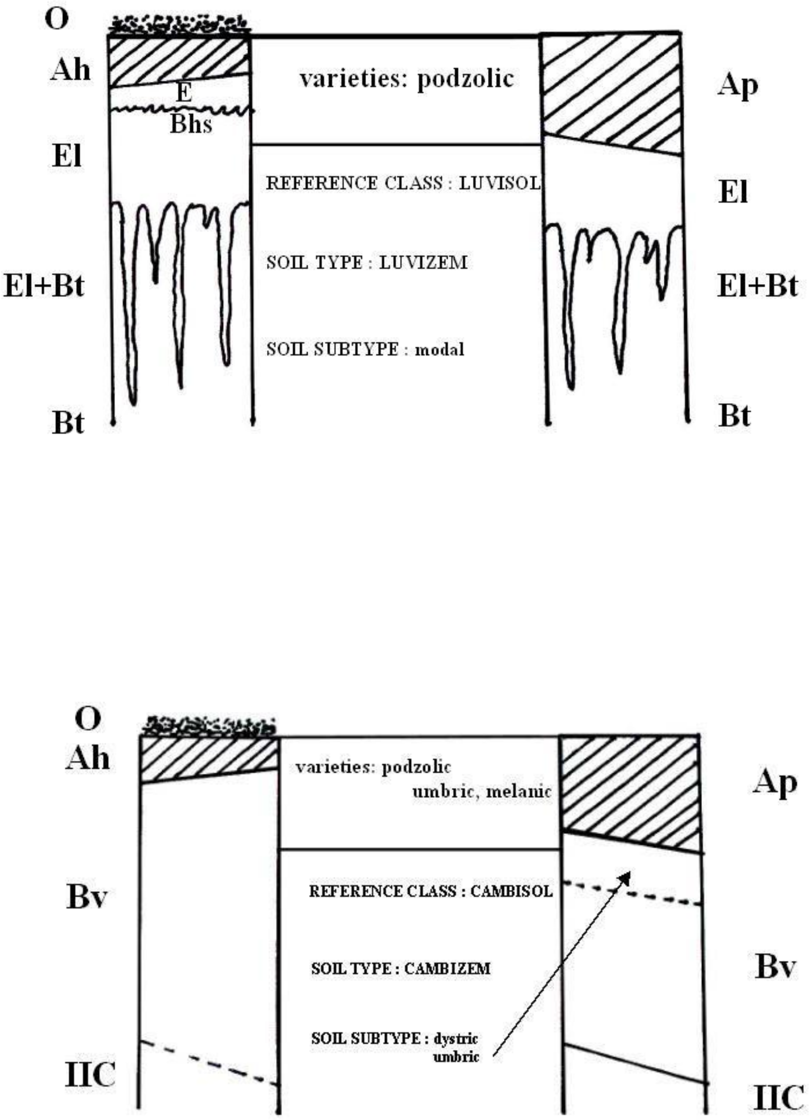

Figure 18 Soil horizons (Czech soil horizon classification system)

Source: Němeček et al., 2001

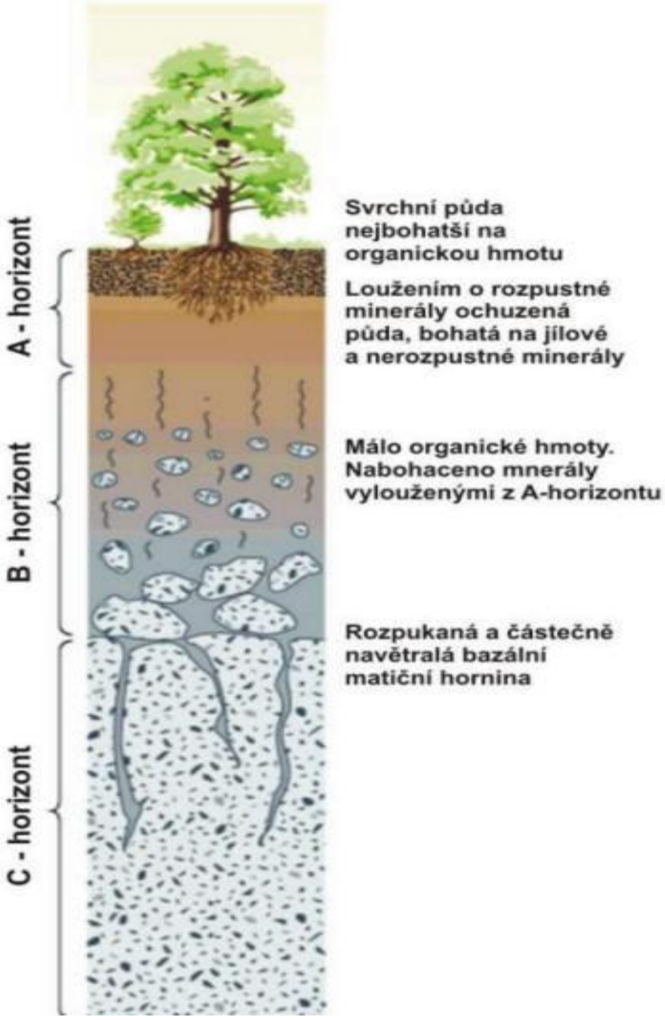

Figure 19 **Soil horizons (Czech soil horizon classification system)**

Source: http://geologie.vsb.cz

Diverse approaches to soil classification in Russia (Figure 20) contributed to the development of a new system, which embraced the ideas on soil genesis apparent in soil horizons and soil properties, on application profile formulas for classification purposes, and addressing to soil evolution and regimes. The new Russian system has common features with the International and American systems in methodology, in particular, in the attitude to soil horizons and features (Shishov et al., 2001).

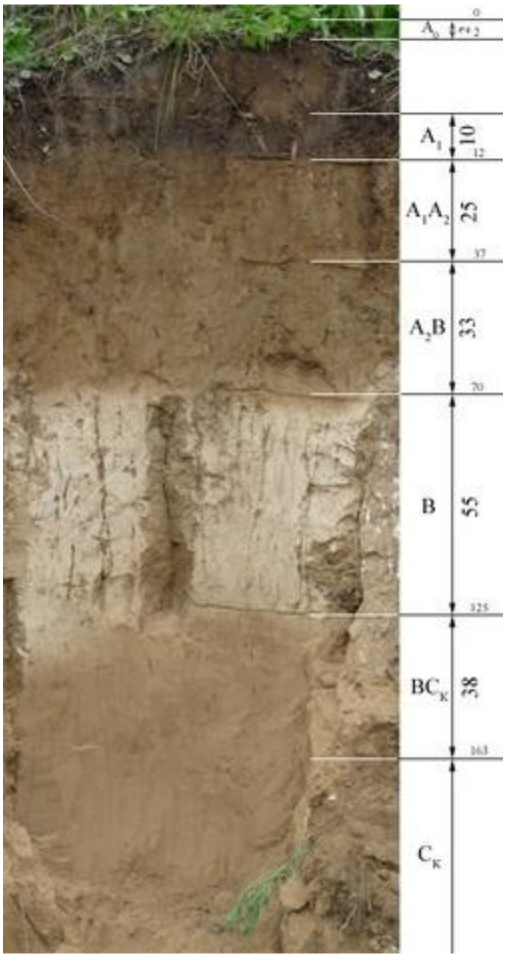

Figure 20 **Soil horizon STANDARDS 27593-88 (2005). (Russian soil horizon classification system)**
Source: Soils. Terms and Definitions. UDK 001.4:502.3:631.6.02:004.354; http://www.enci.ru

3.1.2 Soil Structure

Soil structure is the arrangement that is binding together of soil particles into larger clusters, called aggregates or ‘peds’. Aggregation is important for increasing stability against erosion, for maintaining porosity and soil water movement, and for improving fertility and carbon sequestration in the soil (Nichols et al., 2004). ‘Granular’ structure consists of loosely packed spheroidal peds that are glued together mostly by organic substances. Granular structure is characteristic of many A horizons, particularly those with high SOM content and biological activity. Larger peds, in the form of plates, blocks, or prisms, are commonly associated with the B horizon and are formed via shrink-swell processes and adhesive substances (Gardiner and Miller, 2004). As soil swells (wets or freezes) and then shrinks (dries or thaws), cracks form around soil masses, creating peds. Peds are held together and in place through the adhesion of organic substances, iron oxides, clays or carbonates. Cracks and channels between peds are important for water, air, and solute transport and deep water drainage. Finer soils usually have a stronger, more defined structure than coarser soils due to shrink/swell processes predominating in clay-rich soils and more cohesive strength between particles (McCauley et al., 2005).

3.1.3 Chemical Properties

Exchange Capacity

The soil's ability to absorb and exchange ions is its 'exchange capacity' (McCauley et al., 2005). Soil cation exchange capacity (CEC) is a vital predictor of soil quality and potential for pollutant sequestration in the environment (Tang et al., 2009). The soil CEC is mainly determined by the amount of clay and OM. Moreover, significant correlations between CEC and other soil properties, such as sand, silt, pH, bulk density, and electrical conductivity (EC), have also been observed (Manrique et al., 1991; Paz-González et al., 2000; Horn et al., 2005; Jung et al., 2006; Igwe and Nkemakosi, 2007).)

Soil pH

Soil pH is a measure of the soil solution's acidity and alkalinity. By definition, pH (Figure 21) is the 'negative logarithm of the hydrogen ion concentration [H^+]', i.e., pH = -log [H^+]. Soils are referred to as being acidic, neutral, or alkaline (or basic), depending on their pH values on a scale from approximately 0 to 14 (McCauley et al., 2009).

A pH of 7 is neutral (pure water), less than 7 is acidic, and greater than 7 is alkaline. Because pH is a logarithmic function, each unit on the pH scale is ten times less acidic (more alkaline) than the unit below it. Thus, a solution with a pH of 6 has a 10 times greater concentration of H+ ions than a solution with a pH of 7, and a 100 times higher concentration than a pH 8 solution. Soil pH is influenced by both acid and base-forming ions in the soil. Common acid-forming cations (positively charged dissolved ions) are hydrogen (H^+), aluminum (Al^{3+}), and iron (Fe^{2+} or Fe^{3+}), whereas common base-forming cations include calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+) (McCauley et al., 2009).

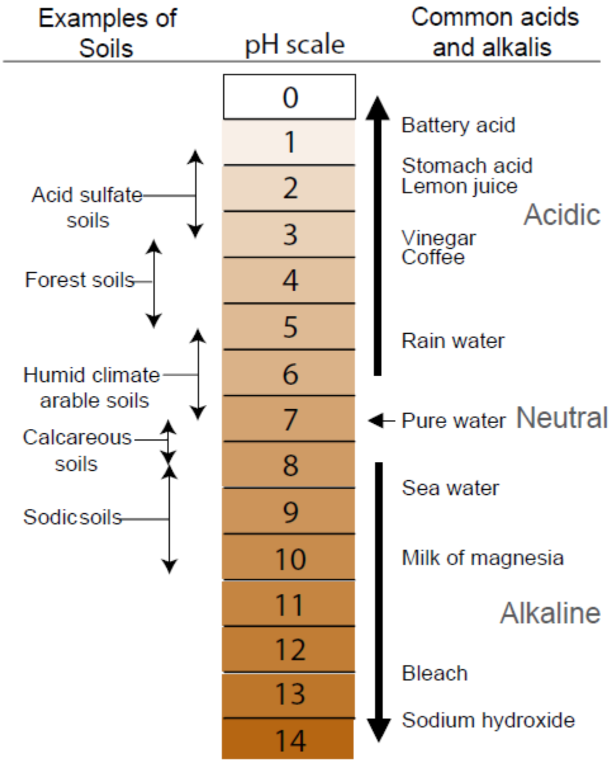

Figure 21 **pH scale**
Source: McCauley et al., 2009

Soil pH refers to a soil's acidity or alkalinity and is the measure of hydrogen ions (H^+) in the soil. A high amount of H^+ corresponds to a low pH value and vice versa. The pH scale ranges from approximately 0 to 14 with 7 being neutral, below 7 acidic, and above 7 alkaline (basic). Soil pH can affect cation exchange capacities (CEC) and anion exchange capacities (AEC) by altering the surface charge of colloids. A higher concentration of H^+ (lower pH) will neutralize the negative charge on colloids, thereby decreasing CEC and increasing AEC. The opposite occurs (Figure 22) when pH increases (McCauley et al., 2005).

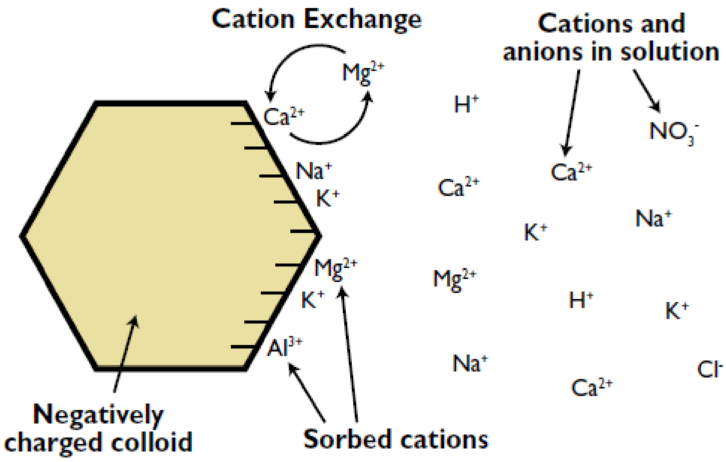

Figure 22 **Simplified representation of exchange capacity**
Source: McCauley, et al., 2005

3.1.4 Biological Properties

Soil Biota

The soil environment is teeming with biological life and is one of the most abundant and diverse ecosystems on earth. Soil biota, including flora (plants), fauna (animals) and microorganisms, perform functions that contribute to the soil's development, structure and productivity (McCauley et al., 2005). Different groups of organisms can be distinguished in the soil (Brussaard, 1995). Table 3 below classifies them by function.

Table 3 Essential functions performed by different members of soil organisms (biota)

Functions	**Organisms involved**
Maintenance of soil structure	Bioturbating invertebrates and plant roots, mycorrhizae and some other micro-organisms
Regulation of soil hydrological processes	Most bioturbating invertebrates and plant roots
Gas exchange and carbon sequestration (accumulation in soil)	Mostly micro-organisms and plant roots, some C protected in large compact biogenic invertebrate aggregates
Soil detoxification	Mostly micro-organisms
Nutrient cycling	Mostly micro-organisms and plant roots, some soil- and litter-feeding invertebrates
Decomposition of organic matter	Various saprophytic and litter-feeding invertebrates (detritivores), fungi, bacteria, actinomycetes and other micro-organisms
Suppression of pests, parasites and diseases	Plants, mycorrhizae and other fungi, nematodes, bacteria and various other micro-organisms, collembola, earthworms, various predators
Sources of food and medicines	Plant roots, various insects (crickets, beetle larvae, ants, termites), earthworms, vertebrates, micro-organisms and their by-products
Symbiotic and asymbiotic relationships with plants and their roots	Rhizobia, mycorrhizae, actinomycetes, diazotrophic bacteria and various other rhizosphere micro-organisms, ants
Plant growth control (positive and negative)	Direct effects: plant roots, rhizobia, mycorrhizae, actinomycetes, pathogens, phytoparasitic nematodes, rhizophagous insects, plant-growth promoting rhizosphere micro-organisms, biocontrol agents Indirect effects: most soil biota

Source: Bot et al. 2005

In particular, bacteria contribute to decomposition of organic mattes (HA), especially in the early stages of decomposition when moisture levels are high. In the later stages of decomposition (FA), fungi tend to dominate. *Bacillus subtilis* and *Pseudomonas fluorescens* are examples of decomposer bacteria, and ctinobacteria help to slowly break down humates and humic acids in soils. Actinobacteria prefer non-acidic soils with pH higher than 5 (Reid et al., 2005).

Soil flora

Plants act on the soil environment by aiding in structure and porosity, and in supplying SOM via shoot and root residue. Root channels can remain open for some time after the root decomposes, allowing an avenue for water and air movement. Roots also act to stabilize soil through aggregation and intact root systems can decrease soil loss. The ‘rhizosphere’, the narrow zone of soil directly surrounding plant roots, is the most biologically active region of the soil. It contains sloughed root cells and secreted chemicals (i.e., sugars, organic acids) that provide organisms with food (McCauley et al., 2005).

Soil fauna

Soil fauna work as soil engineers, initiating the breakdown of dead plant and animal material, ingesting and processing large amounts of soil, burrowing ‘biopores’ for water and air movement, mixing soil layers, and increasing aggregation. Important soil fauna include earthworms, insects, nematodes, arthropods and rodents. Earthworms are considered one of the most important soil fauna (McCauley et al., 2005). Through the process of burrowing, they provide channels that increase a soil’s porosity, water holding capacity (WHC), and water infiltration (Lee, 1985). They also increase further biotic activity by breaking down large amounts of SOM through digestion and supplying nutrient-rich secretions in their casts (Savin et al., 2004).

Soil microorganisms

Microorganisms represent the largest and most diverse biotic group in soil, with an estimated one million to one billion microorganisms per one gram of agricultural top soil (Tugel and Lewandowski, 1999). Microbes aid soil structure by physically surrounding particles and ‘gluing’ them together through the secretion of organic compounds, mainly sugars. This contributes to the formation of granular structure in the A horizon where microbial populations are greatest (McCauley et al., 2005).

Soil microbes include bacteria, protozoa, algae, fungi and actinomycetes. Bacteria are the smallest and most diverse soil microbes. Bacteria are important in SOM decomposition, nutrient transformations and small clay aggregation. Some bacteria carry out very special roles in the soil, such as Rhizobia, the nitrogen-fixing bacteria associated with legume roots. Protozoa (e.g., amoebas, ciliates, flagellates) are mobile organisms that feed on other microbes and SOM. Algae, like plants, photosynthesize and are found near the soil surface. Fungi are a diverse group of microbes that are extremely important in the breakdown of SOM and large aggregate stability. Many fungi have long ‘hyphae’ or ‘mycelia’ (thin thread-like extensions) that can extend yards to miles underneath the soil surface and physically bind soil particles (McCauley et al., 2005). Actinomycetes are a microbial group that are classified as bacteria, but have hyphae similar to fungi. They are important for SOM breakdown, particularly the more resistant fractions, and give soil much of its ‘earthy’ odor. Bacteria dominate in agricultural and grassland soils, whereas fungi are more prevalent in forest and acid soils (Tugel and Lewandowski, 1999).

An important relationship found in almost all soils and plants, including many crop species, are mycorrhizae. Mycorrhizae are a plant-fungal symbiosis (a relationship between two interacting species) in which fungi infect and live in, or on, a plant root. The fungus depends on the plant for energy, and in return, the fungus and its hyphae can take up nutrients for the plant, and possibly improve plant growing conditions (McCauley et al., 2005). For instance, mycorrhizae associations have been shown to increase plant-water relations and reduce severity of some plant diseases (Smith and Read, 1997), as well as improve soil aggregate stability due to the binding actions of hyphae and glomalin, a mycorrhizal secreted chemical (Nichols et al., 2004). Table 4 below classifies the soil organisms by size and links them to humus.

Table 4 Classification of soil organisms

Micro-organisms	Microflora	<5 µm	Bacteria (HA) and Fungi (FA) play an important role in decomposition of OM (Reid at al., 2005)
	Microfauna	<100 µm	Protozoa and Nematodes Through repeated ingestion and excretion by microfauna OM are completely reduced to amorphous humic acids. This optimal humus type derived from earthworm excretes is known as mull or mild humus (Kubiena, 1953).
Macro-organisms	Meso-organisms	100 µm - 2 mm	Springtails and Mites are included into the “litter-transforming” system as they break vegetable matter down into humus (Suzuki, et al., 2004). They assist with decomposition by browsing on preferred fungi, thus preventing any one species from becoming dominant, and by transporting the spores through the soil. Springtails perform similar functions. Larger arthropods, slugs and snails burrow through the soil and feed on dead plant material.
	Macro-organisms	2 - 20 mm	Earthworms, Millipedes, Woodlice, Snails and slugs Macro-organisms perform the final task of humification, i.e. conversion of decomposed organic matter to stable humus colloids -- and mix the humus with material from the lower soil horizons. http://eap.mcgill.ca/MagRack/COG/COGHandbook/COGHandbook_1_3.htm
Plants	Algae	10 µm	Algae are considered as the primary stabilizers of bare eroded soils (Booth, 1941). They are autotrophic (i.e. have chlorophyll and are capable of performing photosynthesis) and eucariotic organisms. Some algae make symbiotic associations with fungi forming lichens. In addition to producing a substantial amount of organic matter in some fertile soils, certain algae excrete polysaccharides that have very favorable effects on soil aggregation (Round, 1981).
	Roots	> 10 µm	Roots are important contributors to C-cycling as root-released C in mull SOM is sufficient to relieve energy limitation to soil microbes and allow them to access appreciable amounts of soil-N (Bradley, 1996)

Source: adapted from Swift, Heal and Anderson, 1979

3.2 Pedogenesis

Pedogenesis is the science that studies processes that lead to the formation of soil and first explored by the Russian geologist Vasily Dokuchaev (1846 – 1903), who determined that soil formed over time as a consequence of climatic, mineral and biological processes. Since Dokuchaev's investigations in Russia, Chernozems were defined as steppe soils, with their pedogenesis dominated by the soil-forming factors of dry continental climate and steppe vegetation, with carbonaceous parent material, mainly loess, and bioturbation as other prerequisites (Dokuchaev, 1883; 1889). Dokuchaev's results for the Russian Chernozems were transmitted to Central European Chernozems (e.g. by Hohenstein, 1919) and his definition was assumed to be universally valid for Eastern and Central Europe.

Models of pedogenesis generally assume that the soil surface is static and that parent material is already in place so that soil-forming processes modify the parent material to progressively deeper levels with a downward-moving front (Schaetzl and Anderson, 2005), conceptually referred to as ‘topdown pedogenesis’. In contrast, ‘upbuilding pedogenesis’ (Almond and Tonkin, 1999) occurs when allochthonous minerals and organic matter are added to the soil surface whilst soil formation continues at a rate determined by the rate and thickness of the additions and by environmental conditions. If the additions are thin or infrequent topdown pedogenesis continues whilst the land surface gently rises (developmental upbuilding pedogenesis); if the additions are thick or the accumulation rates are rapid and frequent, then the antecedent soil becomes buried and isolated from the surface processes so that pedogenesis begins on the newly-deposited material (retardant upbuilding pedogenesis) (Lowe and Tonkin, 2010). Upbuilding is generally accomplished by, for example, aeolian deposition, the addition of organic materials from plants, and slopewash (in relevant landscape positions), as well as minor subsurface addition from plant roots or the immigration of fauna that die in situ (Schaetzl and Anderson, 2005). To help understand and quantify the process of upbuilding pedogenesis in soils of past landscapes, it is necessary to date the rates at which materials were added to the soil surfaces. Upbuilding pedogenesis is effectively a ”competition” between classical topdown soil forming processes and the addition of new materials to the profile via geological processes, such as tephra deposition or loess accumulation (McDaniel et al., 2011; Muhs et al., 2004).

Pedogenesis can be slow or fast depending on the internal chemical response to environmental forcing factors. Chemical reactions in soils and the probability that they will occur are determined by the thermodynamics of the soil system. Soils are open systems; pedogenic transformations are driven by a continuous flux of matter and energy acting on a progressively modified parent material (Figure 23) (Chadwick et al., 2001). Soil profiles are active mixing zones of living and dead organic matter, water, a trace gas laden atmosphere, decaying rock minerals and the residue of their interaction. The chemistry of pedogenesis is driven by solar energy both directly and through photosynthesis and gravitational energy through the movement of water through soil profiles. Water acts to mediate chemical reactions and to transport reactants and products through the profile. Mineral weathering acts as a sink for atmospherically and biospherically derived acids; the reaction products can accumulate within the profile or be lost through leaching. Reduced carbon compounds also provide ligands for complexing, reducing and leaching otherwise sparingly mobile cations. Chemical reaction rates are controlled both by the intensity of the extrinsic climatic factors and the intrinsic thermodynamic and kinetic properties of the soil system (Chadwick et al., 2001).

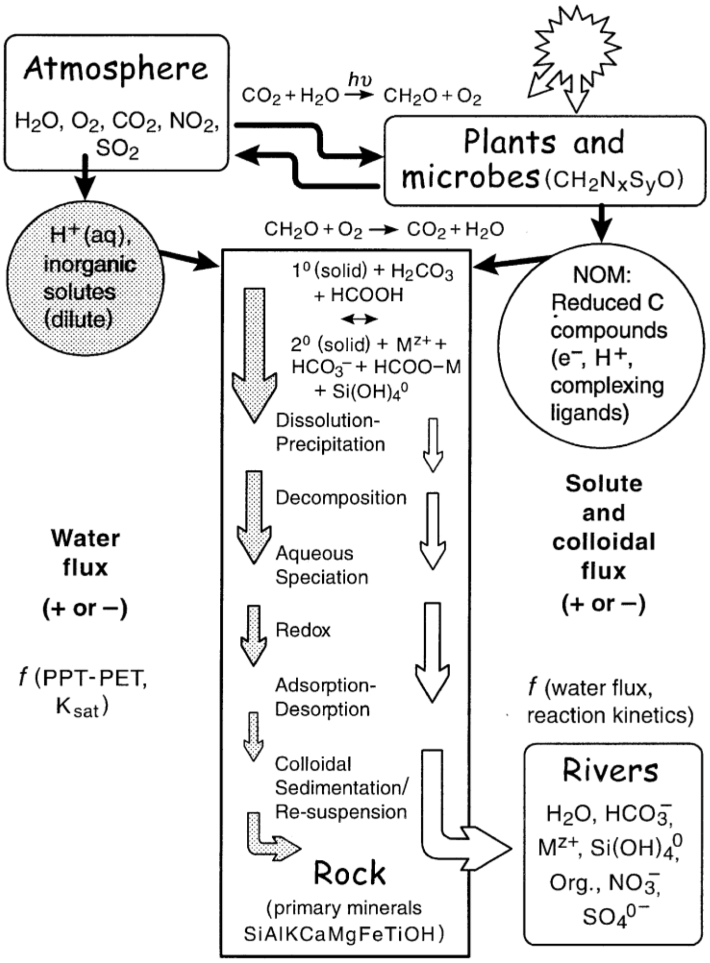

Figure 23 Chemistry of soil pedogenesis

Source: Chadwick et al., 2001

A primary suite of chemical reactions in soil involves the production of acids by biodecay and their consumption through weathering of minerals in parent material or added as mineral aerosol. Soil development can be characterized as a long-term acid–base reaction in which acids from the atmosphere (CO_2, NO_2, SO_2) and those generated by the biota react with bases in the form of rock minerals to form secondary minerals and soil solution alkalinity (Chadwick et al., 2001).

Along with soil solution pH, soil redox status (i.e., pe or Eh) is a master variable affecting the trajectory of pedogenesis. The capacity of the soil to buffer changes in redox status determines the rate and extent of soil morphological response to inputs of electrons (von der Kammer et al., 2000). Both biotic and abiotic soil processes result in electron transfer among soil constituents, with disequilibrium arising primarily from the incorporation of bioavailable, plant-derived reduced C compounds into soil. Since soils are open systems, the leaching of reaction products affects the degree to which dissolution products accumulate and secondary solids precipitate (Chadwick et al., 2001).

The amount and timing of water flux determines the rate and trajectory of soil evolution, since it carries reactants into the profile and contributes to down-gradient transport of solute and colloidal products. Extensive leaching promotes a deep penetration of freshwater that depletes the profile mass of water-soluble species (e.g., comprising Si, Ca, Mg, K and Na), whereas less soluble elements (e.g., Al, Fe, Ti) and biogenic C and N are enriched preferentially. Conversely, at low water flux even soluble constituents can accumulate in solid-phase weathering products (e.g., carbonates, opaline silica) close in proximity to the parent material source. Therefore, precipitation and potential evapotranspiration are critical determinants of pedogenesis (Chadwick et al., 2001).

The role of effective moisture (precipitation minus evapotranspiration) in developing soil properties has been studied intensively (Birkeland, 1999). Early soil classifications focused on zonal soils or the characteristic soil for a particular climate zone (Baldwin et al., 1938; Cline, 1949), and modern soil classifications use climate at several categorical levels (Soil Survey Staff, 1999).

Pedogenesis, therefore, is a biogeochemical process that is constrained by thermodynamics, but still maintains considerable flexibility as a result of parallel reaction kinetics, and a spatially heterogeneous matrix (Chadwick et al., 2001).

SOM is a dynamic component of the soils system, and there is evidence that portion of organic fraction retains features related to the soil forming process factors under which the humus formed (Wilding et al., 1983). Cultivation and application of minerals and organic fertilizers create substantial changes in the organic component of the soil. This resulted in intensification of new formation and decomposition of OM but humus preserves features characteristics of humus of a particular soil type (Kononova, 1975). For arable Chernozems in Russia, C:N ration is ranging from 10 to 12, and humus of Chernozems is characterized by a higher content of humic acid. Humic acid to fulvic acid ratios were 2 or higher in these soils (Kononova, 1975). In Canadian Chernozems distribution of soil carbon and nitrogen in humic fractions showed that about 84 kg of N per hectare were released from soil humus each year with 80% came from humic acid hydrolysate (Campbell, 1978).

3.3 Accumulation of soil organic matters

Environmental influences

The rate of OM accumulation varies greatly among soils, reflecting the influence of environmental factors on pedogenic processes (Jenny, 1941) such as climate, organisms, parent material, topography, and time (Quideau, 2002).

Climate

Climate influences organic matter accumulation by controlling the balance between litter production and decomposition rates. On a global basis, soil carbon content increases with increasing precipitation but decreases with increasing temperature (Post et al., 1982). High temperature and precipitation result in increased decomposition rates and a rapid release of nutrients to the soil. Some of the most rapid rates of SOM decomposition in the world occur in irrigated soils of hot desert regions (Brady and Weil, 1999). Conversely, decreases in temperature (below 25 ^{0}C) and precipitation (below 9%) cause decomposition rates to slow (Figure 24). This results in greater SOM accumulation and a less rapid release of nutrients. Generally, SOM decomposes at above 25 ^{0}C and accumulates at below 25 ^{0}C (Brady and Weil, 1999).

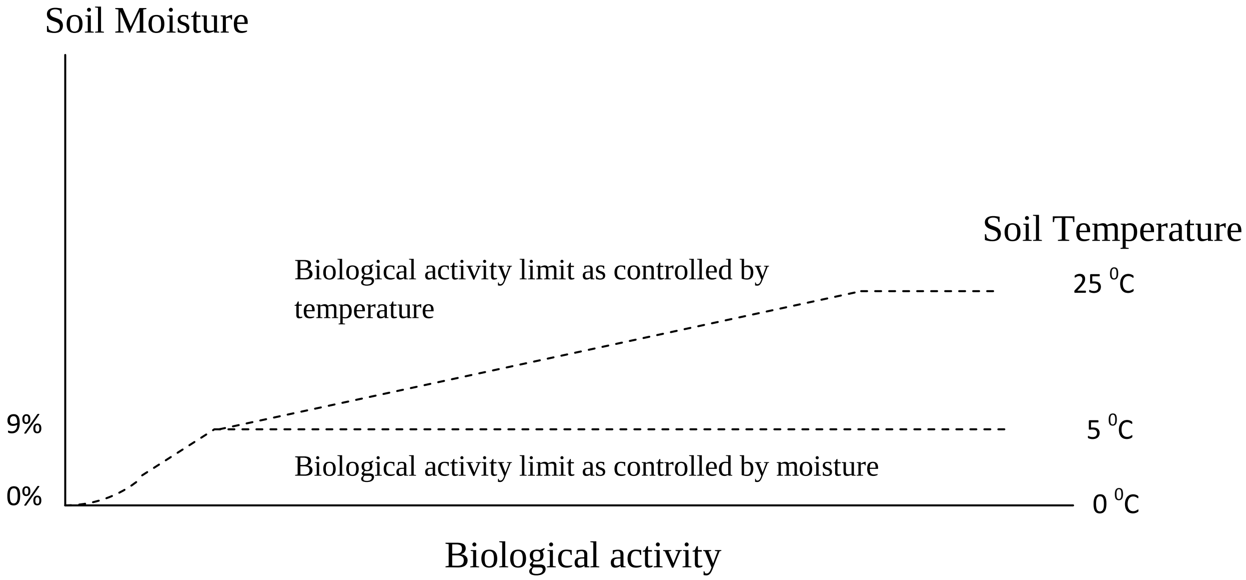

Figure 24 Temperature and moisture factors that affect SOM decomposition rate

Source: Daniels and Galbraith, 2007

Climate impacts decomposition and accumulation by affecting growth conditions for soil microorganisms.

Organisms

The amount, placement, and chemical composition of the organic residues of vegetation also affect OM accumulation (Quideau et al., 2000). Placement of organic residues affects the distribution of OM accumulation within the soil profile. In grassland soils, where belowground production is abundant, OM is more evenly distributed than it is in forest soils, where most accumulation occurs in the uppermost horizon. Chemical composition of litter also exerts a significant influence on the accumulation and turnover of SOM by determining the palatability of the plant material, which in turn can alter the distribution and activity of soil fauna. Soil animals, such as earthworms, may accelerate decomposition rates by contributing to the rapid mixing of fresh plant residues into the mineral soil (Quideau, 2002).

Parent material

Parent material may influence OM accumulation through its effect on soil fertility. Soils formed from base cation-rich volcanic rocks (e.g., basalt) are typically more fertile, and thus experience more OM accumulation than soils with lower inherent mineral-derived nutrients, such as those formed from granitic materials (Quideau, 2002). Parent material is also effective through its determination of soil texture. Soil clay content and OM accumulation are positively correlated. Soils high in clay and silt are generally higher in SOM content than sandy soils. This is attributed to restricted aeration in finer-textured soils, reducing the rate of OM oxidation, and the binding of humus to clay particles, further protecting it from decomposition (McCauley et al., 2009). Additionally, high clay content may induce OM accumulation by stabilizing humic substances formed during decomposition. Clay and OM form organomineral complexes that are resistant to further biodegradation (Quideau, 2002).

Topography

Topography interacts with microclimate to influence OM distribution in soils. OM accumulation is often favored at the bottom of hills where conditions are wetter than at mid- or upperslope positions (Quideau, 2002). Decomposition of OM occurs more slowly in poorly aerated soils, where oxygen is limiting or absent, compared with well-aerated soils. For this reason, OM accumulates in wet soil environments. Soil drainage is determined strongly by topography, e.g. soils in depressions at the bottom of hills tend to remain wet for extended periods of time because they receive water (and sediments) from upslope. Soils may also have a layer in the subsoil that inhibits drainage, again exacerbating waterlogging and reduction in OM decomposition. In a permanently waterlogged soil, one of the major structural parts of plants, lignin, does not decompose at all. The ultimate consequence of extremely wet or swampy conditions is the development of organic (peat or muck) soils, with OM contents of more than 30%. Where soils are drained artificially for agricultural or other uses, the soil OM decomposes rapidly (Bot et al., 2005).

Time

Long-term rates of OM accumulation in Holocene-aged soils vary from about 1 to 12 gCm_2 yr_1 (Chadwick et al., 1994). However, OM does not accumulate indefinitely in soils. Depending on other soil forming factors, an equilibrium level is reached over time. OM encompasses a series of pools with varying turnover rates. Amounts of the young, labile OM may level off in decades because plant biomass stabilizes, while amounts of the more recalcitrant fractions, composed of humic substances often complexed with clay minerals, may continue to increase for tens of thousands of years (Quideau, 2002).

Pedogenic processes

OM accumulation is used as a criterion for classifying soils into organic and mineral soil orders, and for identifying epipedons and diagnostic subsurface horizons (Quideau, 2002). The fundamental pedogenic processes associated with OM accumulation are classified in the Table 5 below (Quideau, 2002):

Table 5 Fundamental pedogenic processes associated with organic matter accumulation

Term	**Definition**	**Representative horizon (soil order)**
Littering	Accumulation of fresh organic detritus on the mineral soil surface to a depth of <30 cm	Oi horizon (all soil orders)
Decomposition	Breakdown of organic molecules into simpler compounds	Oe, Oa, and A horizons (all soil orders)
Mineralization	Release of inorganic constituents of organic matter	
Humification	Formation of humic substances from raw organic materials	
Synthesis	Formation of new organic molecules by combination of elements or constituents	
Paludization	Accumulation of thick (>30 cm deep) organic materials on the mineral soil surface	Histic epipedon (Histosols and Gelisols)
Ripening	Changes in organic soil promoted by entry of air into previously waterlogged material	Histic epipedon (Histosols)
Melanization	Darkening of light-colored initial mineral soil by addition of organic matter	Mollic epipedon (Mollisols) Melanic epipedon (Andisols)
Podzolization	Translocation of organic matter in the soil profile associated with Al and Fe migration	Spodic horizon (Spodosols)

Source: Buol et al., 1989

Littering is additions to soils and refers to the deposition of dead plant and decays, soluble organic products leach into the mineral soil. Alternatively, particulate litter can be incorporated into the soil by faunal *pedoturbation,* which is soil mixing by animals, including termites, earthworms, ants, rodents, and even humans (Quideau, 2002).

Decomposition represents OM transformation process and refers to the chemical and biochemical reactions occurring during the decay of plant and animal remains as soil microorganisms colonize them (Quideau, 2002). SOM content is equal to the net difference between the amount of SOM accumulated and the amount decomposed. Factors affecting SOM decomposition and accumulation rates include SOM form, soil texture and drainage, C:N ratios of organic materials, climate, and cropping practices. Varying SOM forms (i.e., active or passive) accumulate and decompose at different rates (McCauley et al., 2009). On the other hand, humus content is much more constant and fluctuates very little. Since SOM tests do not differentiate between SOM forms, changing particulate organic matter (POM) levels can cause fluctuations to occur in total SOM levels, even though humus content remains the same (McCauley et al., 2009).

Mineralization is also a part of OM transformation and releases soluble or gaseous inorganic constituents during decomposition processes (Quideau, 2002).

Humification is also a part of OM transformation process and is a multistage process (Stevenson, 1994, b). Source materials for humus synthesis include residual components from incomplete decomposition of organic litter and the products of microbial anabolic activities. Polyphenols derived from lignin degradation, together with those synthesized by microorganisms, are oxidized to quinones, which undergo self-polymerization or combine with amino compounds to form nitrogen (N)-containing polymers. Sugar-amine condensation reactions may also participate in the formation of humic substances (Quideau, 2002).

Paludization (accumulation in organic soils) can be considered a geogenic rather than pedogenic process because it involves deposition of initial parent material. It occurs when conditions impede decomposition, enabling the buildup of a thick mass of organic deposits. Decomposition is hampered by poorly drained conditions, as in Histosols, and by extreme cold, as in Gelisols (Quideau, 2002). Under anaerobic conditions, humic substances exhibit an accumulation of aromatic carbon (C) compounds arising from the absence of lignin-degrading fungi (Preston, 1996). Poorly drained soils typically accumulate higher levels of SOM than well-drained soils due to poor aeration causing a decline in soil oxygen concentrations. Many soil microorganisms involved in decomposition are aerobic (oxygen requiring) and will not function well under oxygen-limiting conditions. This anaerobic (absence of oxygen) effect is evident in wetland areas in which the ‘soil’ is often completely composed of organic material (McCauley et al., 2009). Aromaticity can also develop in organic horizons from sources without lignin, such as detritus from algae and mosses (Quideau, 2002).

In contrast to paludization, *ripening* refers to the decomposition processes occurring in the organic horizon under oxidizing conditions after exposure to the air (Quideau, 2002).

During the surface accumulation in mineral soils, *melanization* produces thick, dark-colored surface horizons characteristic of Mollisols. The formation of mollic epipedons is promoted by proliferation of grass roots that constitute a considerable input of plant residues (Oades, J.M., 1988). Another key factor in melanization is the active faunal community, which contributes to the rapid incorporation of the residues into the mineral soil and favors high initial mineralization rates. Subsequent decomposition and humification processes result in the formation of chemically stable, dark-colored humic substances, characterized by a high proportion of high-molecular weight, highly aromatic, acid-insoluble humic acids (Quideau, 2002).

Podzolization is the surface accumulation that results in the formation of subsurface horizons of organic matter accumulation characteristic of Spodosols. Subsurface organic matter accumulation occurs at the top of the spodic horizon due to the migration of water-soluble organic compounds from the mineral surface (Browne, 1995). Soluble organics are composed mainly of polyphenolics and lower molecular weight polymers (fulvic acids), originating from the decomposition processes of nutrient-poor, acidic organic residues, such as heath and coniferous litter (Quideau, 2002).

Various types of human activity decrease soil organic matter contents and biological activity. Tillage is one of the major practices, which reduces the organic matter level in the soil. Each time the soil is tilled, it is aerated. As the decomposition of organic matter and the liberation of C are aerobic processes, the oxygen stimulates or speeds up the action of soil microbes, which feed on organic matter (Bot et al., 2005).

Activities (Figure 25) that promote the accumulation and supply of organic matter, such as the use of cover crops and refraining from burning, and those that reduce decomposition rates, such as reduced and zero tillage, lead to an increase in the organic matter content in the soil (Sampson and Scholes, 2000).

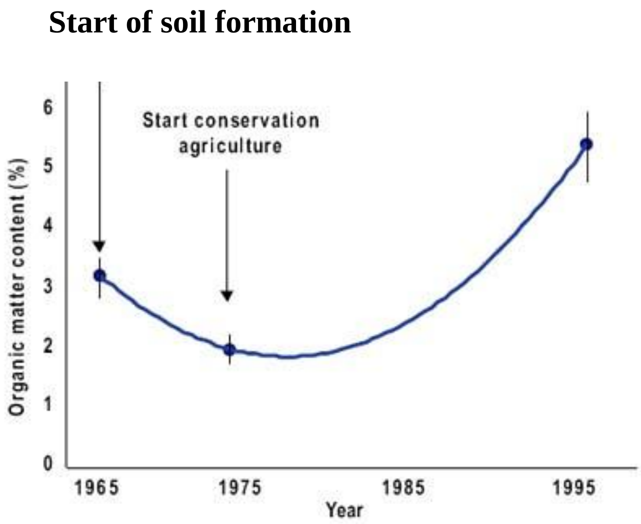

Figure 25 **Evaluation of the organic matter content of a soil in Paraná**

Source: Bot et al., 2005.

However, increasing the organic matter content of soils or even maintaining good levels requires a sustained effort that includes returning organic materials to soils and rotations with high-residue crops and deep- or dense-rooting crops (Bot et al., 2005).

4. CONCLUSION

Soil organic matter is important component of global carbon cycle and at the same time it affects many important soil properties such as pH, exchange capacity, water holding capacity, porosity and other. Soil organic matter is formed from dead plant material, which consists mainly from lignin and cellulose, by various decomposition and transformation processes. Consequently soil organic matter represents a wide variety of chemical compounds that vary greatly in their decomposability and persistence in soil. Humic substances belong to the most resistant component of soil organic matter. Humic substances can be divided by the type of accumulated humic acid closely correlated with soil formation and humus form. Soil organic matter content is a function of organic matter inputs (residues and roots) and litter decomposition. It is related to moisture, temperature and aeration, physical and chemical properties of the soils as well as bioturbation (mixing by soil macrofauna), leaching by water and humus stabilization. Accumulation of organic matter in soil is used as a criterion for classifying soils and identifying epipedons and diagnostic subsurface horizons, and the fundamental pedogenic processes are directly associated with organic matter accumulation. This process is controlled by balance between litter formation and decomposition rates through levels of precipitation and temperatures. Chemical composition of litter also substantively influences soil organic matter accumulation but parent material influences this process through its effect on the soil fertility. Rates of soil organic matter accumulation vary, however depending on other soil forming factors equilibrium is achieved over the time.

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