

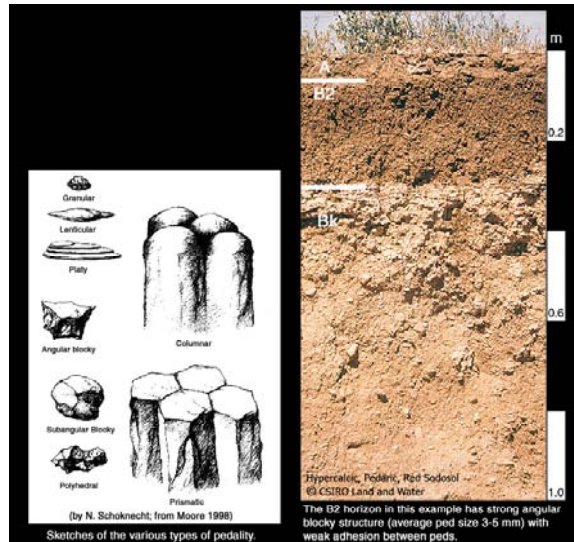
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Residue Management, Soil Organic Carbon and Crop Performance

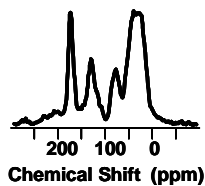
# Functions of Soil Organic Matter and the Effect on Soil Properties

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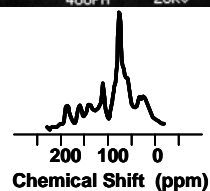
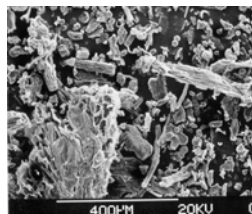
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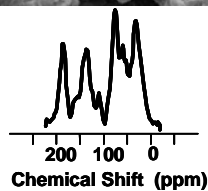
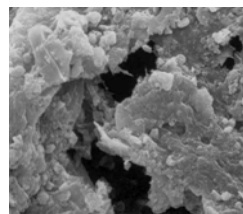
**Dissolved material**



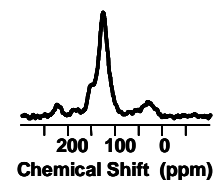
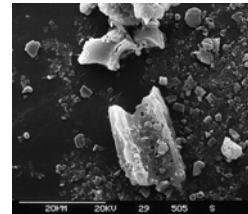
**Particulate material**



**Humus**



**Charcoal**



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## **SUMMARY**

Soil organic matter (SOM) and specifically soil organic carbon (SOC) are known to play important roles in the maintenance as well as improvement of many soil properties. While agriculture is the area most concerned with key functions and critical levels of SOC, forestry and grazing as well as groundwater contamination and C sequestration are areas where knowledge about the functions of SOC is vital.

This literature review aims to provide a comprehensive assessment of the current state of knowledge of the functions of SOC and its effect on the physical, chemical and biological properties of soil. Particular emphasis of this report, in context with the GRDC project, is placed on the effect of SOC on soil structure (aggregate stability), on cation exchange capacity (CEC) and buffer capacity (BC) of soils and on the soil's water holding capacity (WHC). Although these properties are discussed separately, it is important to emphasise the dynamic and interactive nature of the soil system and that changes in one property will likely affect other soil properties as well. Thus, functions of SOC almost always affect several different properties and engage in multiple reactions.

While this review primarily focuses on the effect of SOC on physical, chemical and biological soil properties, it was vital to include a brief discussion on soil methodology to provide a summary of methods currently used and their respective advantages and shortcomings. Furthermore, the rationale for separating SOM into discrete organic pools by particle size separation is discussed. Specifically, we highlight that total SOC is often not a good indicator for assessing soil properties. Frequently, such properties are affected by specific pools with particular properties. Only by studying these pools separately and in conjunction with a specific function is it possible to understand what the key impacts of a SOC pool are.

The last part of the review examines the value of SOC in an ecological sense and reviews the cost and effectiveness of the carbon trading scheme, particularly with respect to mitigation of greenhouse gases.

## **INTRODUCTION**

### **What is soil organic matter?**

The term “Soil organic matter” (SOM) has been used in different ways to describe the organic constituents of soil. In this report, SOM will be used as defined by Baldock and Skjemstad (1999) as “all organic materials found in soils irrespective of origin or state of decomposition”. Since SOM consists of C, H, O, N, P and S, it is difficult to actually measure the SOM content and most analytical methods determine the soil organic carbon (SOC) content and estimate SOM through a conversion factor.

The amount of SOC that exists in any given soil is determined by the balance between the rates of organic carbon input (vegetation, roots) and output (CO<sub>2</sub> from microbial decomposition). However, soil type, climate, management, mineral composition, topography, soil biota (the so-called soil forming factors) and the interactions between each of these are modifying factors that will affect the total amount of SOC in a profile as well as the distribution of SOC contents with depth. It is important to note that any changes made to the natural status of the soil systems (e.g. conversion to agriculture, deforestation, plantation) will result in different conditions under which SOC enters and exits the system. Therefore, perturbed systems may still be in the process of attaining a new equilibrium C content and any measurements of SOC have to take into account that the soil is in the process of re-establishing equilibrium, which could take >50 years (Baldock and Skjemstad, 1999).

### **Soil quality and the role of SOC**

It is now widely recognised that SOC plays an important role in soil biological (provision of substrate and nutrients for microbes), chemical (buffering and pH changes) and physical (stabilisation of soil structure) properties. In fact, these properties, along with SOC, N and P, are considered critical indicators for the health and quality of the soil. Since Lal’s (1993) initial definition of soil quality as the capacity of soil to produce economic goods and services and to regulate the environment, the term “soil quality” has been refined and expanded by scientists and policy makers to include its importance as an environmental buffer, in protecting watersheds and groundwater from agricultural chemicals and municipal wastes and sequestering carbon that

would otherwise contribute to a rise in greenhouse gases and global climate change (Reeves, 1997). Doran and Parkin (1994) and Doran and Safley (1997) initially distinguished between “soil quality” and “soil health” before inclusively using the term “soil health” and defining it as “the continued capacity of soil to function as a vital living system, within ecosystem and land-use boundaries, to sustain biological productivity, promote the quality of air and water environments, and maintain plant, animal and human health”. However, the general perception of a healthy or high-quality soil is one that adequately performs functions, which are important to humans, such as providing a medium for plant growth and biological activity, regulating and partitioning water flow and storage in the environment and serving as an environmental buffer in the formation and destruction of environmentally hazardous compounds. Considering this wide variety of performance indicators, Karlen et al. (2003) and Norfleet et al. (2003) pointed out that soil quality needs to be assessed with regard to what the soil is used for, as a particular soil may be of high quality for one function and may perform poorly for another.

In particular, the suitability of soil for sustaining plant growth and biological activity is a function of physical (porosity, water holding capacity, structure and tilth) and chemical properties (nutrient supply capability, pH, salt content), many of which are a function of SOM content (Doran and Safley, 1997). Similarly, Elliott (1997) indicated that SOM was a key indicator of soil health but further suggested that particulate organic matter (POM) could be used as an indirect measure of soil health because of its short turnover time. Swift and Woomer (1993) regarded POM as the “organic fertiliser” property of SOM. In general, increases in SOM are seen as desirable by many farmers as higher levels are viewed as being directly related to better plant nutrition, ease of cultivation, penetration and seedbed preparation, greater aggregate stability, reduced bulk density, improved water holding capacity, enhanced porosity and earlier warming in spring (Carter and Stewart, 1996; Lal, 2002). Reeves (1997) noted that “SOC is the most often reported attribute from long-term agricultural studies and is chosen as the most important indicator of soil quality and agronomic sustainability because of its impact on other physical, chemical and biological indicators of soil quality”. However, Janzen et al. (1992) pointed out that the relationship between soil quality indicators (e.g. SOC) and soil functions does not always comply to a simple relationship increasing linearly with magnitude of the indicator and that therefore “bigger is not necessarily better”.

## Do generic critical threshold values exist for SOC?

SOM concentrations are often cited as major indicators of soil quality. However, only few studies attempt to discuss minimum or maximum threshold values of soil carbon, above or below which the beneficial effect of SOC is diminished. For example, Janzen et al. (1992) showed from the relationship between SOC in the uppermost 15cm and soil productivity, an upper threshold of SOC existed, beyond which no further increases in productivity were achieved (Fig. 1). The threshold value for SOC for these dryland sites in Alberta, Canada, was at 2% SOC, which is in accordance with the observations by Howard and Howard (1990), who estimated that the threshold value for most soils was at 2% SOC (equivalent to 3.4% SOM), below which most soils are prone to structural destabilisation and crop yields are reduced.

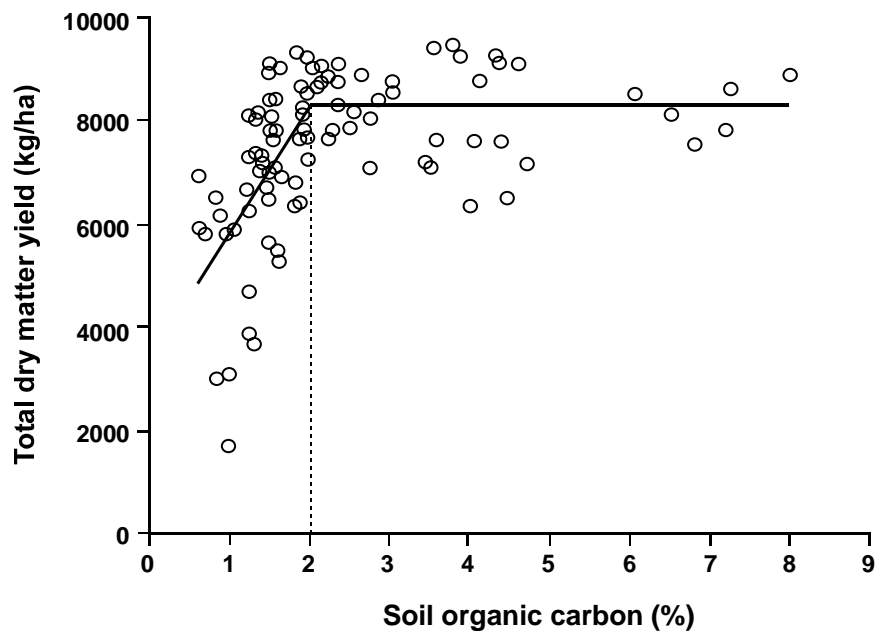


Figure 1: Relationship between organic C concentration in the surface 0-15cm of soil and soil productivity as determined by total dry matter yield at dryland sites in Alberta, Canada (redrawn from Janzen et al., 1992).

Kay and Angers (1999) and Greenland et al. (1975) observed similar relationships between SOC content and aggregate stability. Using the Emerson crumb test, Greenland et al. (1975) found that at SOC <2%, soil aggregates were considered unstable, moderately stable at 2-2.5% and very stable at SOC contents >2.5%. Carter (1992) also found that maximum structural stability was obtained at 4.5% SOC. However, Doran and Safley (1997) argued that different soil types are

likely to have different threshold values. For example, threshold values established for highly weathered Ultisols in the southeastern US indicate that surface SOC levels of 1.2% are sufficient to attain maximum productivity. By comparison, the same value for Mollisols under grasslands in the Great Plains would be regarded as an indicator for degraded conditions, limiting soil productivity. Baldock and Skjemstad (1999) showed that different soil types not only have different total SOC contents but that the distribution of SOC with depth varies according to soil type. Similarly, Körschens et al. (1998) found that soils with different clay contents reach different SOC equilibria. In a 90 year field trial, they found that sandy soils containing 3% clay equilibrated at 0.7% SOC and soils with 21% clay reached 2.0% SOC; however, the mineralisable carbon content for both soil types was 0.4-0.5%. Based on their data, the authors proposed lower and upper limits for total SOC for soils with different clay contents to maintain optimum crop production. For soils with 4% clay, the lower and upper limit was proposed to be at 1% and 1.5% and for soils with 38% the respective limits were 3.5 and 4.4%.

Baldock and Skjemstad (1999) proposed contents of SOC which are considered to be low, medium and high for various climatic and management combinations and soil types. The influence of climate and management on SOC levels was evident and demonstrated that attributes such as “low” or “high” can only be used in a relative sense. They further pointed out that the amount of C required to perform a specific function is likely to be different as, for example, the amount required to ensure an adequate nutrient supply is likely to differ from the amount required to ensure structural stability. In conclusion, it is apparent from the studies discussed here, that soil type and climatic setting can affect the individual SOC threshold values. However, irrespective of soil type it appears that if SOC contents are below 1%, it may not be possible to obtain potential yields (Kay and Angers, 1999).

To effectively increase SOC, the rate of input must exceed the rate of loss from decomposition and leaching processes. In most agricultural cases, this is achieved by stubble retention, rotating crops with pasture, or the addition of organic residues such as animal manure, litter or sewage sludge. For example, Johnston (1991) showed that SOC of a sandy soil could be increased from 0.7 to 0.9% over 6 years by return of crop residues, which was associated with a consistent increase in arable crop and sugar beet yields. Subsequent annual applications of farmyard manure (FYM) increased SOC from 1% to 3.4% whereas long-term application of fertiliser N had no measurable effect on SOC levels. Similarly, Paustian et al. (1992) showed in a 30-year-long Swedish field trial that biannual additions of various organic carbon residues (straw, sawdust,



green manure, and FYM) had positive effects on soil C levels (Fig. 2). The highest accumulations occurred with sawdust plus N and manure amendments. It was suggested that the quality of the amendments was related to these trends as lignin contents were high for sawdust and FYM (30%) and low for straw (15%). This is in accordance with a study by Grace et al. (1995) at the Waite Permanent Rotation Trial, showing that residues high in lignin and with high C/N ratios were more resistant to decomposition than low lignin residues. However, Paustian et al.'s (1992) study also showed that green manure had only 6% lignin but had higher C accumulation compared with straw. In turn, this was related to higher crop productivity and returned inputs due to the higher N content supplied by green manure.

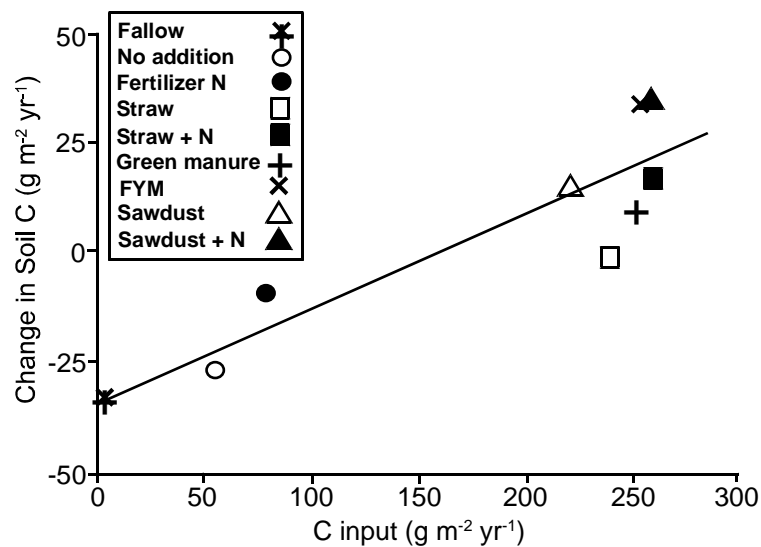


Figure 2: Effect of amendment carbon input rate and type on soil C accumulation (0-20cm) in a 30 year old Swedish field experiment (redrawn from Paustian et al., 1992).

The positive effect of FYM addition on SOC content, its effect after discontinued application and the comparative effect with NPK fertilisation was summarised by Haynes and Naidu (1998). A long-term field trial at the Hoosfield continuous barley experiment showed that plots that had received annual NPK fertilisation had a 15% higher SOC content than unfertilised plots. FYM application resulted in an exponential increase over the 140-year period, at which time the soil approached a new SOC equilibrium level, which was three times that of the unfertilised plot (Fig. 3). When FYM additions ceased, SOC content immediately started to decline; however, even 104 years after the last addition, the plot contained more SOC than the control plot. The rapid decline together with the levelling off at levels higher than the control plot was attributed to the initial

rapid loss of labile carbohydrate material and the increased level of long-term stabilised humic material.

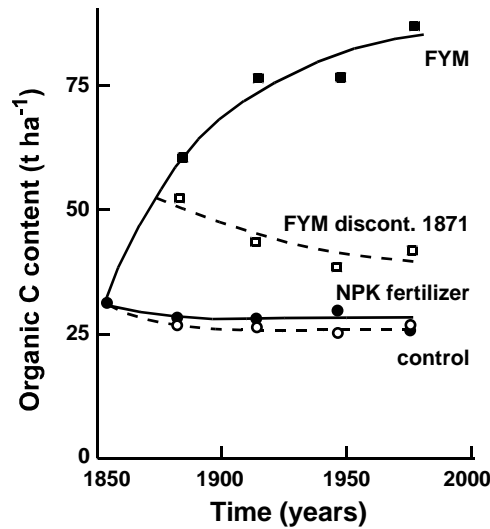


Figure 3: Changes in SOC content on the Hoosefield continuous barley experiment with no fertiliser applied (control), annual application of NPK fertiliser, annual application of FYM (35 t ha<sup>-1</sup>) and FYM applied from 1852-1871 (modified from Haynes and Naidu, 1998).

The importance of examining threshold values at which organic carbon becomes effective and asserts a positive influence on soil properties should not be underestimated, as detrimental effects can occur if too much carbon is added to the soil. Therefore, although carbon increase is usually helpful to improve soil functions (especially in Australian soils, which are poor in carbon), more is not always better. For example, too much carbon can result in surface crusting, increased detachment by raindrops and decreased hydraulic conductivity (Haynes and Naidu, 1998). One reason for structural breakdown is a high content of monovalent cations, which can occur if too much animal waste is added. Similarly, high additions of NH<sub>4</sub><sup>+</sup> fertiliser may accumulate and both high organic and N additions could cause not only environmental problems but would contribute to increased dispersive effects (summarised in Haynes and Naidu, 1998). As a rule of thumb, waste applications of over 100 t ha<sup>-1</sup> are considered a possible hazard (Haynes and Naidu, 1998). Water-repellency is another possible consequence of too much organic matter application (Olsen et al., 1970). It is important to note, however, that alkyl carbon is a major contributor to water-repellent attributes and it is therefore possible that water repellent soils do not contain particularly high amounts of organic matter but are rather dominated by alkyl carbon (Shepherd et al., 2001).

## Overview of principal functions of SOM in soils

The functions of SOM can be broadly classified into three groups: biological, physical and chemical (Fig. 4). These groups are not static entities and dynamic interactions occur between these three major components.

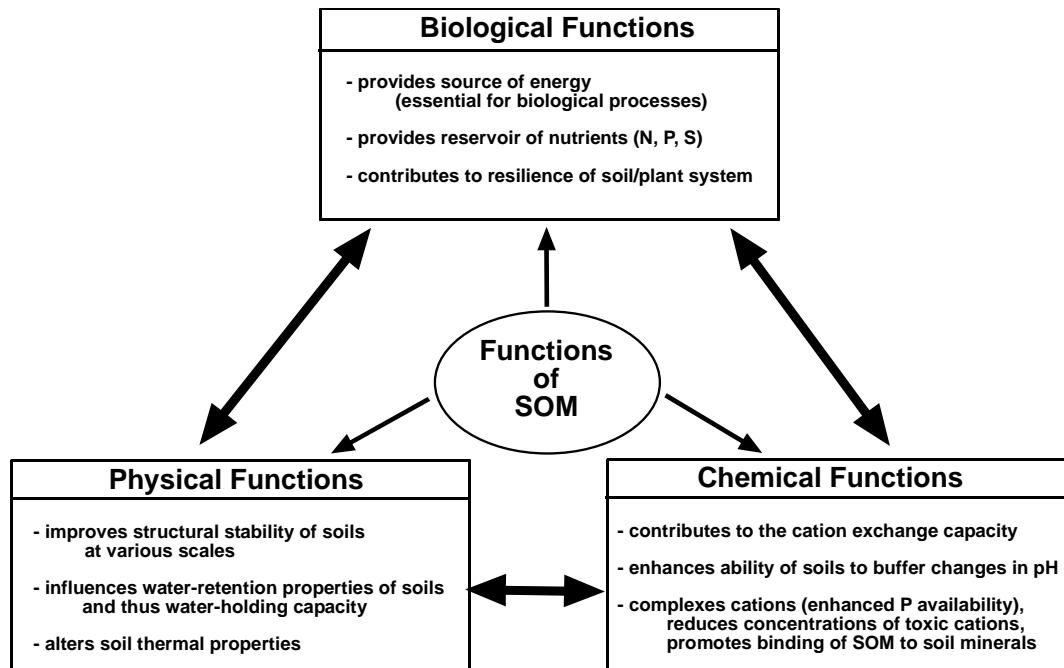


Figure 4: Functions ascribed to SOM. Note that interactions occur between the different soil functions modified from Baldock and Skjemstad, 1999).

It is these interactions among the soil functions, the different requirements for optimal SOM levels for each function and the individual soil mineralogical characteristics that preclude a generic number for optimal SOM levels. Furthermore, SOM is a highly heterogenous substance and varies in its chemical and physical properties, depending on the soil forming factors listed previously.

SOC requirements are likely to differ according to function and soil type. Figure 5 illustrates how soil type (represented by clay content) relates to requirements of SOC to perform specific functions. For example, for CEC SOC is of greater importance in sandy compared with clayey soils. SOC is required in larger amounts in sandy soils because most clayey soils can provide a substantial proportion of CEC through charge derived from clay minerals. For biological (energy

for biological processes and provision of nutrients) and thermal properties, SOC is required irrespective of clay content. Baldock and Skjemstad (1999) and Skjemstad (2002) noted that total SOC may not be a good indicator for assessing how well a particular soil function is likely to perform; mainly because the different pools, which make up the bulk SOC, vary considerably in their physical and chemical properties. Figure 5 illustrates the selective importance of SOC pools in performing specific functions. For example, the humic fraction is considered the principal pool in contributing to the soil's CEC, whereas soil structure is provided and maintained by both the humic and particulate organic carbon (POC) fractions. Here, the POC fraction plays a greater role in sandy soils as a means of physically binding particles together. For soils with a higher clay content, both humic materials and POC are required to develop optimal structural support as both chemical and physical binding play critical roles. By comparison, POC is most important in providing energy for biological processes and humus is an important source of essential soil nutrients. Soil thermal properties (i.e. the ability to warm up quickly in cold climates) are a function of colour, and the inert carbon pool, which consists of highly aromatic structures such as charcoal, plays the most important role here.

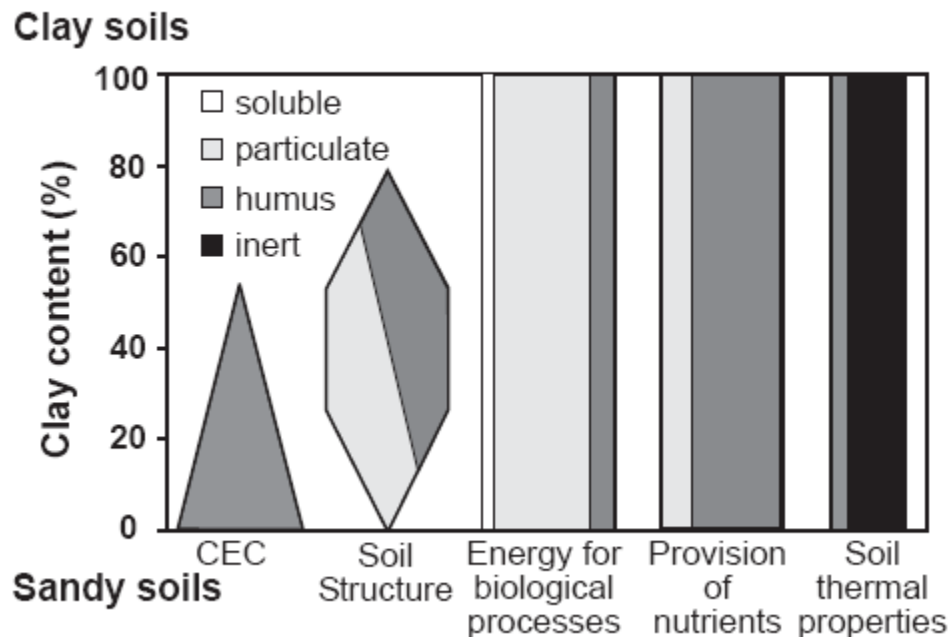


Figure 5: The optimal expression of each SOM function requires different proportions of soil organic carbon pools (soluble, particulate, humus and inert). To which degree SOM can influence a particular function may also vary by soil type (represented by clay content).

## **Soil carbon fractions and SOC analytical methods**

Due to the difficulties in measuring SOM directly, it is substituted by measurement of SOC (Baldock and Skjemstad, 1999). A convenient way to calculate SOM is by multiplying the percentage of organic carbon by a factor; however, conversion factors vary between 1.4 and 3.3 (Kuntze, 1988, Rasmussen and Collins, 1991) and this large range is due to the inherent differences between soils. Most commonly, a conversion factor of 1.72 is used (Baldock and Skjemstad, 1999). Therefore, to ensure consistency and allow reliable comparison of data, it is advantageous to report results as SOC rather than as SOM.

SOM studies have included 1) detailed study of humus chemistry to elucidate the chemical structure of SOM via fractionation schemes, 2) empirical methods to quantify effects of SOM by evaluating field experiments, and 3) simulation by soil models (Körschens et al., 1998). Determination of SOC can be made by various methods and a comprehensive review can be found in Nelson and Sommers (1996). Determination of SOC by wet oxidation is typically made by acid dichromate oxidation (Kalembasa and Jenkinson, 1973), also known as the Walkley-Black method (no heating) or Heanes method (externally heated and addition of concentrated sulphuric acid). However, several workers have found that the Walkley-Black method does not determine organic C quantitatively and depending on soil type, recoveries can vary from 56% to 100% (summarised in Skjemstad and Taylor, 1999). Determination of SOC by dry combustion converts all carbon in the presence of oxygen to CO<sub>2</sub> during a heating process. The most commonly used dry oxidation method is done by a LECO Carbon Analyzer (Merry and Spouncer, 1988). Kalembasa and Jenkinson (1973) reviewed both dry and wet oxidation methods and concluded that dry oxidation methods were more accurate. Similarly, Baldock and Skjemstad (1999) recommended analysis of SOC by dry combustion and measurement of CO<sub>2</sub> with an infrared detector.

An important, but often overlooked, issue in SOC studies is the question of to what depth should soil profiles be sampled and at what intervals. Because there is no agreed standardised sampling protocol across disciplines, sampling intervals commonly vary from 5, 10, 15, 20 to 30 cm. More importantly, while many studies refer to “surface samples” as the uppermost 10 cm, some studies use the uppermost 15 or 20 cm. Unger (1995), on the other hand, suggested that sampling of the surface soil should be confined to the uppermost 4 cm, as the most significant changes in SOC content are apparent in this interval and deeper sampling would obscure these effects.

Wilhem (2001) pointed out that while high organic matter levels in soils are vital to productivity and sustainability, the current estimates (commercial soil tests, e.g. Walkley-Black organic carbon test) are not sensitive to subtle changes in composition, as they measure total organic carbon levels. Franzluebbers (2002) further concluded that SOM was an unreliable predictor of soil and crop performance because SOM includes several different pools of organic carbon, and specific pools are relevant to structural stability, nutrient provision and cation exchange capacity. Thus, analysis of total organic carbon dilutes vital information with regard to organic pools that are sensitive to management practices and makes it difficult to quantitatively assess the effects of SOM constituents.

Current characterisation of SOM has largely moved away from definitions based solely on chemical extraction procedures, such as humic and fulvic acids (Reeves, 1997). Instead, definitions based on physical fractionations are preferred as physical separation of SOM relates better to the role that organic matter plays in soil structure and soil function (Christensen, 1992; Hassink, 1995 and reviewed by Collins et al., 1997).

A systematic categorisation of SOM is necessary to divide SOM into discrete, measurable and biologically significant entities, so-called “pools”. Separation of SOM into biologically significant pools is commonly done by size and/or density fractionation. However, it is important to note that separation of soil into different size fractions is not just a mere separation into sand, silt and clay categories, but aims to partition SOM into components that differ in their life time (“turnover time”), chemistry (size of molecules, types of functional groups), and origin (plant-derived versus microbially-derived). The separation of SOC by a standard scheme into biologically significant pools is important to provide scientists from different geographic regions with a tool that allows their measurements to be comparable. It may also provide data that can be applied in soil carbon models.

Typically, SOC is divided into fractions having different properties and rates of turnover. For example, a commonly used separation scheme is to fractionate SOM into four pools: dissolved organic matter (DOM), particulate organic matter (POM), humus and inert organic matter (Fig. 6).

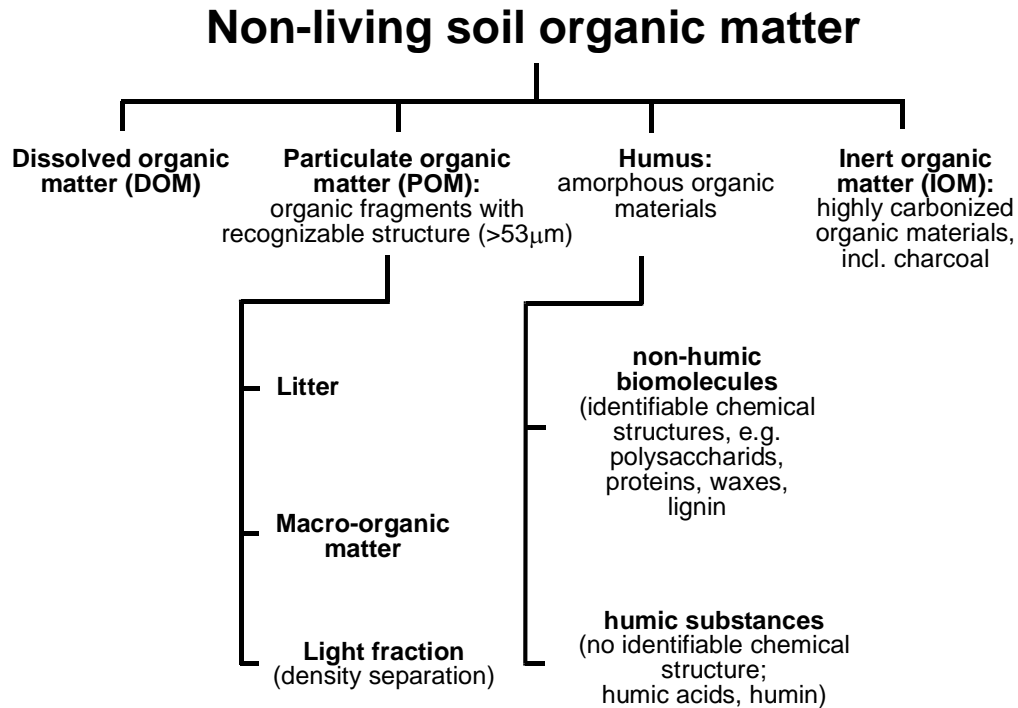


Figure 6: Composition of soil organic matter (modified from Baldock and Skjemstad, 1999).

DOM constitutes the <0.45µm diameter organic materials in solution. POM includes any organic fragments with a recognizable structure >53µm as well as the light fraction, which in turn can be separated by floatation or density separation. Humus constitutes usually the largest pool of SOM and includes non-humic and humic substances. Finally, inert organic matter (IOM) is mainly comprised of highly aromatic materials, such as charcoal or geologic forms of carbon. Figure 7 illustrates a fractionation scheme as devised by Skjemstad et al. (1996).

The light fraction and POC pool are often considered the active pool and have a relatively fast turnover time of <10 years, whereas the humified pool is estimated to have a turnover time of 10's of years (summarised in Krull et al., 2003). This latter pool not only differs from the POC pool in size and turnover time but also in its chemistry (e.g. less carbohydrate material, lower C/N ratios) and in the fact that it includes a fraction termed "protected organic matter". Protected SOM may or may not be as decomposed as the unprotected fraction; importantly, this association with the mineral matrix, which prevents rapid decomposition, extends the turnover time of that carbon fraction beyond that dictated by its chemistry (summarised in Skjemstad et al., 1998; Baldock and Skjemstad, 2000; Dalal and Chan, 2001; Krull et al. 2003). Finally, the highly recalcitrant IOM pool may reside for 100's to 1000's of years.

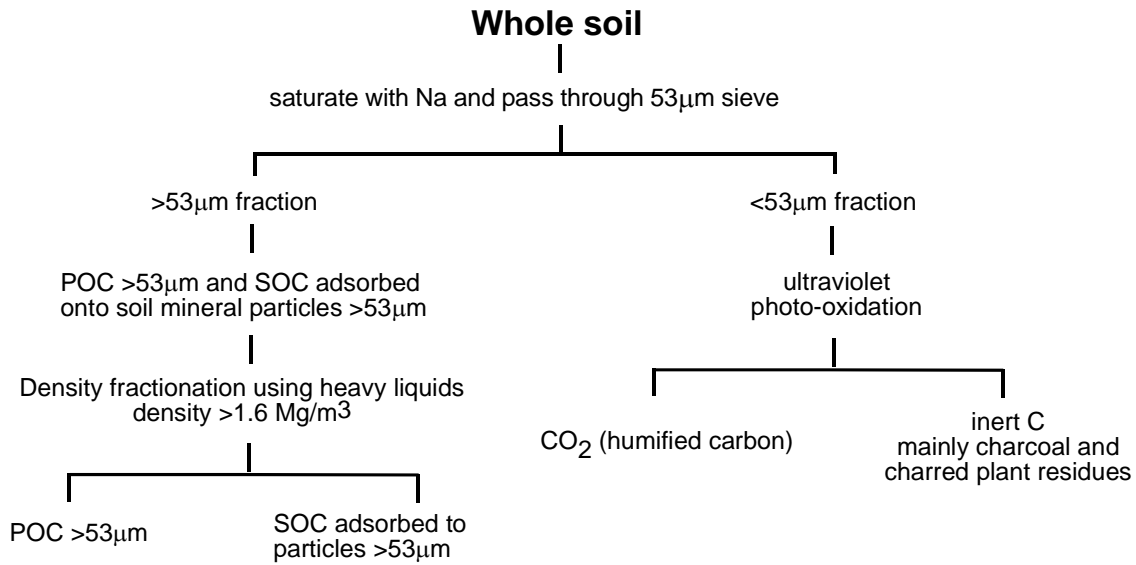


Figure 7: Modification of the fractionation scheme used by Skjemstad et al. (1996) to quantify the contents of POC, humus and inert organic carbon content of soils (redrawn from Baldock and Skjemstad, 1999).

The importance of analysing soil carbon fractions, particularly with respect to monitoring changes in land use management, is illustrated in a review by van Noordwijk et al. (1997) (Fig. 8). Deforestation was followed by long-term sugarcane cultivation and the data show that the decline in forest-derived SOM continued during the 50 years of the study and that the apparent equilibrium value of the total SOC content of the soil is based on the balance between gradual build-up of sugarcane SOM and decay of forest-derived SOM. By comparison, when forest was converted to pasture, the decline of labile forest-derived SOM was much faster; however, the accumulation of labile pasture-derived C returned the total SOC content to its original level 7 years after conversion.



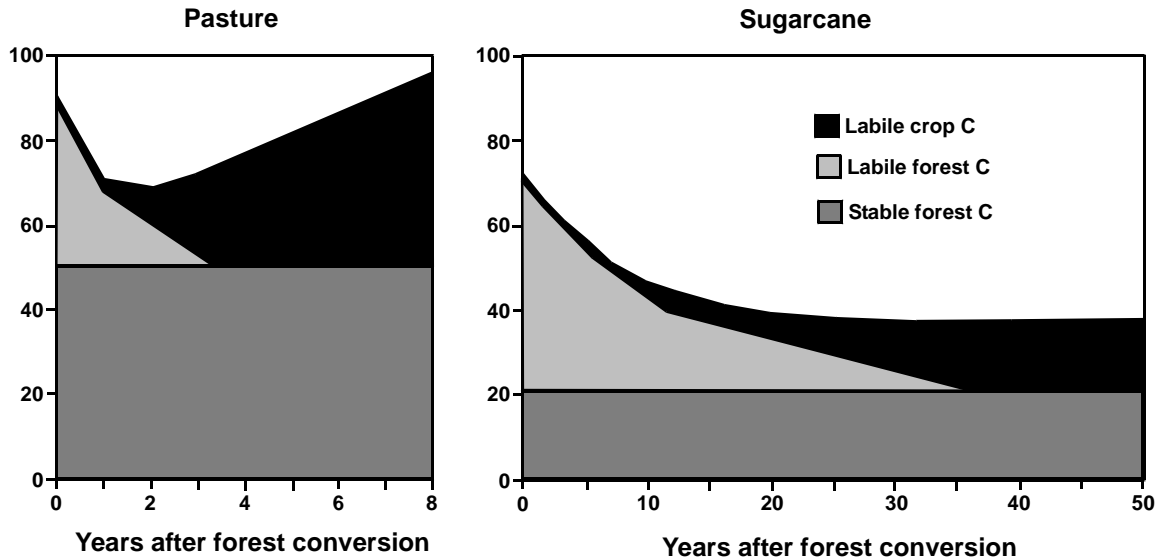


Figure 8: Time course of total soil carbon stocks and its components, stable and labile forest C and labile crop C after conversion of forest to pasture (left) and sugarcane (right) (redrawn from van Noordwijk et al., 1997).

Measurement of the degree of structural stability of a soil is often reported as being related to SOC content and a high degree of structural stability is desirable for adequate plant growth. However, there is no single standardised method that is universally used to determine aggregate stability, which makes it problematic if one wants to compare results from the literature obtained by different analytical processes. In particular, the energy applied (to determine stable from unstable particles) and the particle size class used to determine macro- from micro-aggregates need to be standardised in order to quantitatively compare results from different studies with each other (Feller et al., 1996). Three main approaches are used to study soil aggregates (Feller et al., 1996):

- 1) Single or multiple sieve techniques (wet and dry sieving): Most workers consider the 250 $\mu$ m fraction as the defining boundary between macro- and micro-aggregates; the process of disaggregation is problematic: slaking or dispersion?
- 2) Measurement of the 'dispersed' fraction (0-2 or 0-20 $\mu$ m; for soils rich in swelling clays)
- 3) Whole aggregate analysis from the macro-aggregates to dispersed 0-2 $\mu$ m fraction of the same sample and taking into account energy input level (used by Oades and Waters, 1991)

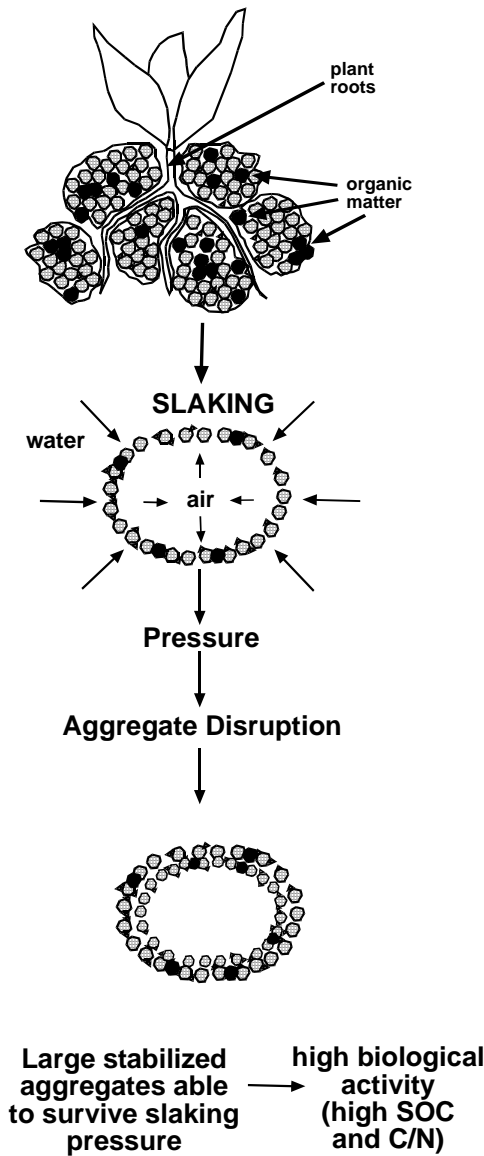
Using the wet sieving method, Haynes and Swift (1990) observed that air-drying aggregates before wet sieving increased the aggregate stability of pasture samples but decreased aggregate stability of arable samples. Wet sieving without air-drying first showed the same trend (greater aggregate stability of pasture compared with arable samples) but less pronounced, which suggests that air-drying accentuated the differences in stability. Boix-Fayos et al. (2001) stressed that the use of aggregate size distribution to assess the soil condition or degree of degradation, must be used with caution. For example, large aggregates (>10, 10-5, 5-2mm) were found in the most arid areas of their study due to presence of earthworm casts. They termed these “untruthful” aggregates as they did not improve soil structure but increased bulk density ( $D_b$ ) and decreased water retention capacity. This implies that the structure of a soil is not necessarily improved by the presence of large aggregates. By comparison, small aggregates (1-0.105 and <0.105mm) were shown to improve soil water retention and served as a good indicator of soil condition.

Ashman et al. (2003) reviewed two of the most commonly used aggregate fractionation methods: The slaking method is commonly used to simulate wetting stresses in the field and the shaking method to simulate mechanical disruption followed by wet sieving. Slaking refers to the disintegration of large aggregates (2-5mm diameter) into finer aggregates when placed in water. Rapid disintegration is believed to be due to a lack of organic bonding between particles. They found that slaking resulted in macro-aggregates being enriched in SOC and, after incubation to measure microbiologically-available carbon, showed a faster respiration rate than in shaken treatments. Here, micro-aggregates (<250 $\mu$ m) had more soil SOC and faster respiration rate. While the general concept of aggregate hierarchy (depending on the size of aggregates, different organic binding agents are active in aggregate stabilisation) (Oades, 1993) is generally accepted, when reviewing the literature there are often different and conflicting results, depending on the kind of fractionation scheme used (Ashman et al., 2003).

Overall, results from the slaking treatment agreed with the aggregate hierarchy model and can be regarded as a process that preferably selects macro-aggregates, characterised by greater concentrations of stabilizing organic matter. Weaker macro-aggregates tend to fall apart in this method and are often recovered as micro-aggregates, characterised by low organic matter concentrations. Results from shaking treatments disagreed with the aggregate hierarchy model as the highest concentration of organic matter was found in the micro-aggregates and aggregate size was inversely proportional to C/N. These results might be explained by the fact that aggregates which line pore walls are enriched in carbon, which in turn results in small and stable micro-

aggregates with relatively undecomposed organic matter. The different results suggest that chemical and biological properties of aggregates depend on the fractionation scheme used. Accordingly, observed relationships can only be interpreted with respect to the specific disruptive mechanism used and aggregate size can only be related to ‘energy inputs’. The results from fractionation schemes therefore provide information with regard to the resistance of soil to disruption, which is different from information about the “true” structure of the soil (Fig. 9).

### Slaking (aggregate hierarchy)



### Shaking (crack hypothesis)

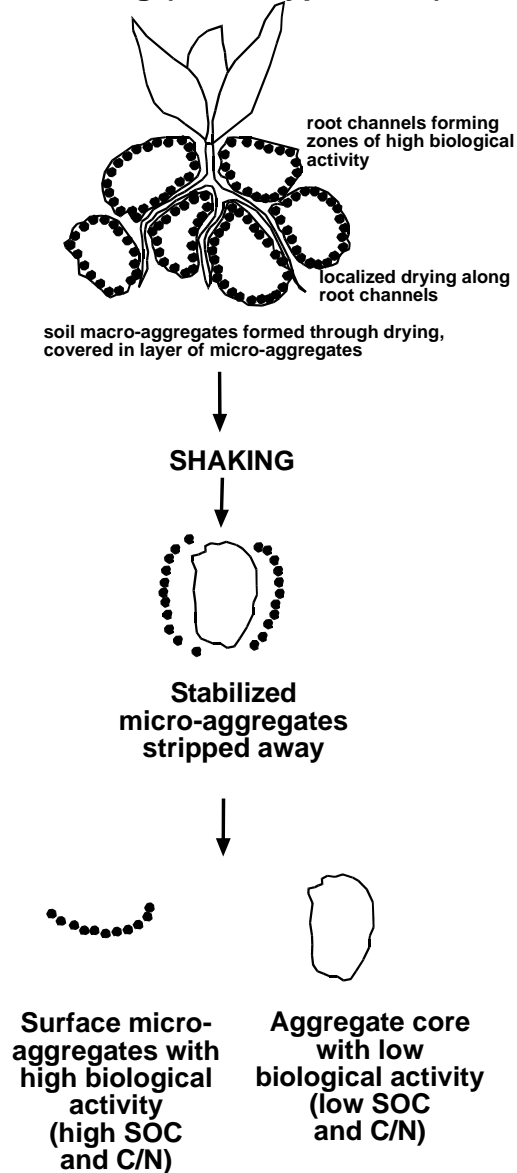


Figure 9: Influence of fractionation procedures on biological and chemical properties of different aggregate sizes (redrawn from Ashman et al., 2003).

Several different chemical extraction schemes exist to separate chemically significant pools. Traditionally, SOM was separated according to its degree of acid solubility and divided into humic and fulvic acids as well as into insoluble humin (summarised in Tsutuski, 1993).

The use of hot-water extractable C or water-soluble carbon has been used in several studies to calculate the readily decomposable carbon pool and to link it to the microbial pool. A close relationship between the hot-water extractable fraction and the soil microbiological pool has been inferred from the significant correlation between the hot-water extractable fraction and soil respiration ( $r^2 = 0.97$ ) and with the nitrate release during incubation ( $r^2 = 0.91$ ) (Schulz, 1997). For example, Körschens et al. (1998) found a good correlation between hot-water extractable C (decomposable carbon), clay content and rate of farmyard manure application (Fig. 10). They stressed that while this fraction was not well-defined, it contained parts of the microbial biomass, simple organic compounds, hydrolysable compounds and was therefore considered the 'active' part of SOM with strong correlations to the microbial biomass pool. This was also supported in studies by Haynes (2000), who noted that water-soluble carbon was an important fraction as it was considered the main energy source for microbes, the primary source for soil nutrients (N, P, S) and reacted quickly to changes in the soil quality status. Further examples of studies utilizing hot-water extractable carbon are provided in the subsequent chapters.

Another commonly used method is oxidation of SOM by  $\text{KMnO}_4$  at various strengths, to separate the most resistant fraction from the more labile pools (e.g. Conteh et al., 1997; Blair et al., 1998; Graham et al., 2002). However, this method is not without contention as it is not well established exactly which chemical fraction is oxidised and which one is retained (Skjemstad, unpublished data).

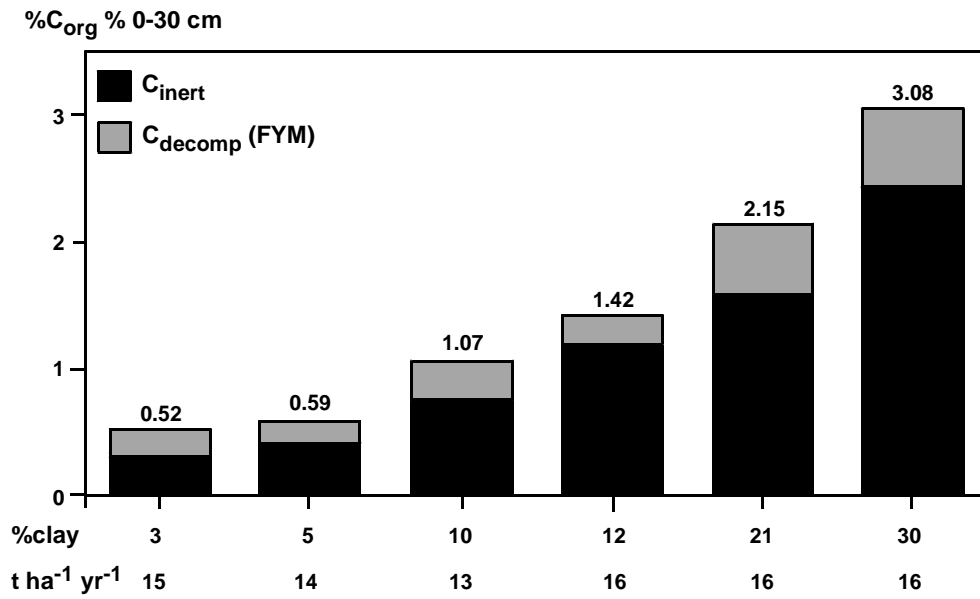


Figure 10: Influence of clay content and farmyard manure application on the inert and decomposable organic carbon content in selected long-term field experiments (from Körschens et al., 1998).

## ROLE OF SOM ON SOIL FUNCTIONS

### Physical Functions

#### Soil structure and aggregate stability

Soil structural stability refers to the resistance of soil to structural rearrangement of pores and particles when exposed to different stresses (e.g. cultivation, trampling/compaction, and irrigation). The interrelationship between SOC and soil structure and other physical properties has been extensively studied, and excellent reviews can be found in Tisdall and Oades (1982), Oades (1984), and Carter and Stewart (1996). It is well established that addition of SOM can not only reduce bulk density ( $D_b$ ) and increase water holding capacity, but also effectively increase soil aggregate stability. Angers and Carter (1996) noted that the amount of water-stable aggregates (WSA) was often associated with SOC content, and that particularly labile carbon was often positively related to macro-aggregate stability. Kay and Angers (1999) reported that a minimum of 2% SOC was necessary to maintain structural stability and observed that if SOC content was between 1.2-1.5%, stability declined rapidly. Boix-Fayos et al. (2003) showed that a threshold of 3-3.5% SOC had to be attained to achieve increases in aggregate stability; no effects on aggregate stability were observed in soils below this threshold. Haynes (2000) found that the mean weight diameter (MWD) of aggregates exhibited a curvilinear increase with carbon content, suggesting an upper limit of influence of SOC (Fig. 11).

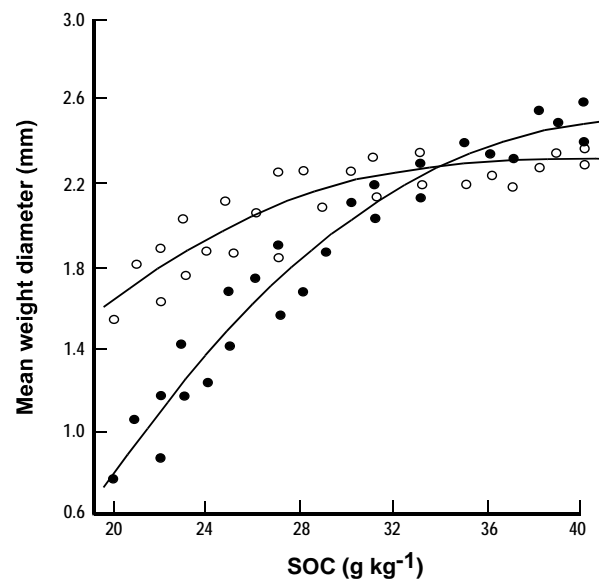


Figure 11: Effect of increasing SOC content on aggregate stability, measured by wet-sieving (MWD, mm), using air-dried (●) and field moist (○) samples ( $R = 0.98^{***}$ ) (modified after Haynes, 2000).

Carter (1992) found that maximum levels for an agronomically designed aggregation index (AI) were obtained at SOC contents of > 2.5% and at microbial biomass carbon contents of 250 $\mu\text{g C/g}$  soil, whereas maximum soil structural stability (determined by MWD) was found at SOC levels of 4.5%. Carter (1992) suggested that 2.5% could serve as a critical limit to define minimum concentrations of SOC required to provide optimum structural stability in fine sandy loams.

Several algorithms have been proposed that relate the percent of WSA, an indicator for good structural stability, to SOM. For example, Chaney and Swift (1984) investigated aggregate stability of 26 soils from agricultural areas and found a highly significant linear correlation between aggregate stability and organic matter content (Fig. 12).

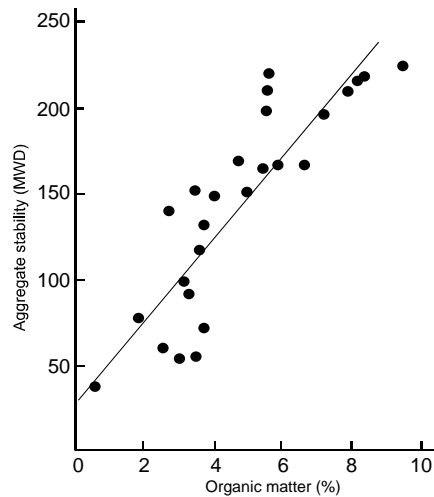


Figure 12: Relationship between aggregate stability and organic matter content for 26 soils (redrawn from Chaney and Swift, 1984).

In fact, most studies report a linear increase of aggregate stability and aggregate size with increasing levels of SOM or SOC. While many studies agree on a positive relationship between aggregate stability and SOM, there is no agreement whether a defined threshold value exists for organic carbon levels, and Loveland and Webb (2003) concluded, after a review of several studies, that no universal threshold levels of SOC contents could be established. Table 1 summarises some of the algorithms reported in the literature as well as studies where no significant relationship was found. Unfortunately, there is often inconsistent and interchangeable usage of the terms “SOM” and “SOC”, and while the term “SOC” is often applied to algorithms, the term “SOM” is sometimes utilised in the discussion of the algorithm.

Study	Algorithm	Measured property	Additional information
Carter (1992)	$127 \text{ SOC}\% - 63.4 (R^2 = 0.94, P < 0.01)$	MWD of WSA	Canadian soils under tillage
Carter et al. (1994)	No relationship		
Chaney and Swift (1984)	$(\text{SOM} + 24) \times 31 (P < 0.01)$	MWD	Different soil types
Ekwue (1990)	$3.32 \text{ SOC}\% - 1.44 (R^2 = 0.87, P < 0.001)$	WSA>0.5mm	Sandy soils under grass
Gerzabek et al. (1995)	$-62.41 + 82.84 \text{ SOC}\% - 16.6 \text{ SOC}\%^2$	% soil aggregate stability	Response of soil aggregate stability to amendments
Haynes et al. (1991)	$0.60 \text{ SOC}\% + 0.65$ $1.09 \text{ SOC}\% - 0.86$ $0.62 \text{ SOC}\% + 0.27$	MWD of air-dried aggregates	sandy loam silt loam clay loam
Haynes et al. (2000)	$-4 + 0.32 \text{ OC}(\text{g kg}^{-1}) - 0.004 \text{ OC}(\text{g kg}^{-1})^2 (R^2 = 0.98, P < 0.001)$ $-0.89 + 0.17 \text{ OC}(\text{g kg}^{-1}) - 0.002 \text{ OC}(\text{g kg}^{-1})^2 (R^2 = 0.93, P < 0.001)$	MWD of air-dried samples (wet sieving)  MWD of field moist samples (wet sieving)	Silty loam (Udic Dystrochrept)
Jastrow (1996)	$96.6 (1 - 0.637^{-0.012 \text{ year since cultivation}})$	SOC% in aggregates	Conversion to grass
Macrae and Mehuys (1987)	No relationship		Clover intercropped with maize in clay and sandy soils
Perfect and Kay (1990)	No relationship		Canadian silty loam under different land uses
Stengel et al. (1984)	$11.57 \text{ SOC}\% + 12.75 (R^2 = 0.61, P < 0.001)$	WSA	Different soil types
Tyagi et al. (1982)	$158.9 \text{ SOC}\% - 9.5$	% aggregates>0.25mm	Black soils under agriculture

Table 1: Synopsis of studies that defined algorithms to relate aggregate stability to SOM content. Included are also studies that failed to find a significant correlation between aggregate stability and SOM content.

Thus, the lack of a consistent analytical scheme and a standard way of reporting result in limited usability of some published data, as it might only be applicable to the particular study from which they were derived.

The concept of aggregation as a process involving different organic binding agents at different scales was pioneered by Tisdall and Oades (1982) and based on their work, Oades and Waters (1991) introduced the concept of aggregate hierarchy. Large aggregates (>2000µm) were hypothesised to be held together by a fine network of roots and hyphae in soils with high SOC content (>2%), while 20-250µm aggregates consist of 2-20µm particles, bonded together by various organic and inorganic cements. Water stable aggregates of 2-20µm size, in turn, consist of <2µm particles, which are an association of living and dead bacterial cells and clay particles. The concept of aggregate hierarchy suggests that organic matter controls aggregate stability, and



degradation of large (relatively unstable) aggregates creates smaller, more stable aggregates. Stabilisation of macro-aggregates occurs mainly via binding by fungal hyphae and roots. Particulate organic matter, on the other hand, serves as a substrate for microbial activity, resulting in the production of microbial bonding materials for micro-aggregates and for the encrustation of plant fragments by mineral particles. In this model, three principal organic binding agents are involved in the aggregate formation and stabilisation: transient, temporary and persistent organic matter. Transient organic binding agents are rapidly decomposed by micro-organisms and are thought to be mostly composed of glucose-like components (mono and polysaccharides), effectively lasting only for a period of a few weeks, after which their effect diminishes. Temporary organic binding agents are thought to consist of roots and hyphae and may persist for months and years. Persistent organic binding agents are composed of degraded humic materials mixed with amorphous forms of Fe and Al and Al-silicates. Tisdall and Oades (1982) proposed that the 'fresh' or 'active' part of SOM (consisting of mono- and polysaccharides, exudates from roots and fungal hyphae) was largely responsible for stabilisation of aggregates. They attributed the key aspect of aggregate formation by polysaccharides to the presence of functional groups, which upon deprotonation, become negatively charged and interact with positively charged oxides, producing stable organic-inorganic microstructures (Oades et al., 1989). However, they found that due to the variability of organic matter, the strength and time for formation of aggregates varied. For example, glucose-like components acted strongly in aggregate formation for the first 2-3 weeks of the experiment after which the effect declined. By comparison, cellulose showed the maximum effect after 6-9 months but was never as effective as glucose. Ryegrass residues were most effective after 3 months and maintained the effect for another 4-6 months, after which the effect declined (Oades et al., 1989).

Based on these data, it is apparent that a specific group or groups of organic matter are key agents for aggregate formation and maintenance of structural stability in soils and Puget et al. (1995) stated that the type of organic matter was more critical to structural stability than the net amount of organic matter. This was further substantiated by observations from Haynes and Swift (1990), Haynes et al. (1991) and Angers and Carter (1996) who observed that after conversion from arable crops to pasture, stability of aggregates changed more rapidly than overall soil organic matter content (Fig. 13).

However, there is no general agreement as to the type of organic matter essential for aggregation. This is most likely due to the fact that different types of organic matter perform different

functions at different times during the aggregate formation and conservation process. In fact, Kay and Angers (1999) suggested that most or all SOC fractions were involved to different degrees in aggregate formation and stabilisation. The following studies illustrate different phases of aggregate formation and types of organic components involved.

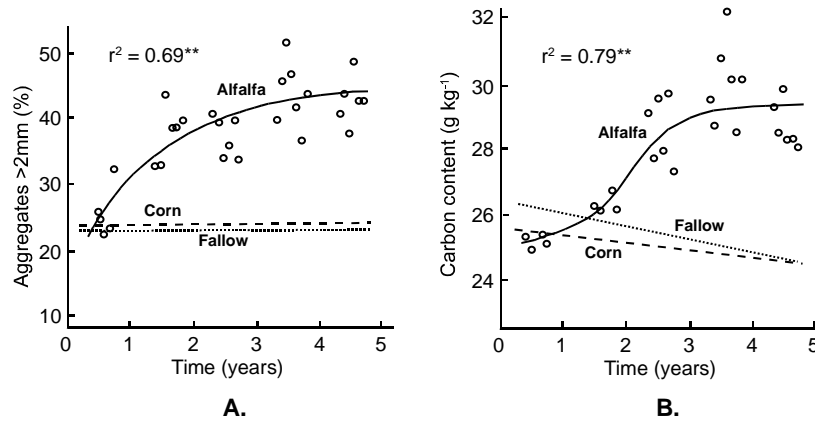


Figure 13: Changes in a) water-stable macroaggregation and b) organic carbon content under alfalfa, corn and fallow soil in a Humic Gleysol (modified from Angers and Carter, 1996).

The importance of polysaccharides and readily extractable carbohydrates in aggregate formation has been indicated in several studies (Chaney and Swift, 1984; Haynes and Swift, 1990; Robertson et al., 1991). Martens and Frankenberger (1992) showed that for an irrigated clay loam, receiving 25 t ha<sup>-1</sup> per year of organic amendments (barley straw, poultry manure, sewage sludge and alfalfa) the total saccharide content was the most important factor in improvement of aggregate stability, compared with total SOC and  $D_b$ .

Other studies stress the particular importance of microbially produced polysaccharides: Friedel et al. (1996) found that the ‘microbially active’ part of SOM was closely related to the amount of WSA, and Rogers et al. (1991) noted that inoculation of sterilised soil with unicellular algae led to an increase in soil aggregate stability, accompanied by an increase in soil polysaccharide content. Similarly, Lynch (1984) showed that some organic residues are only effective in producing aggregates when microbes are active and abundant, and Oades (1984) and Degens (1997) stated that microbially-derived carbohydrates were mainly responsible for soil stabilisation. Gerzabek (1995) explained the greater aggregate stability after addition of FYM as a result of greater production of soil microbial biomass due to readily available carbon sources, and Carter (1992) found that among soils of similar mineralogy and particle size, a linear relationship

existed between MWD and both SOC and microbial biomass carbon but that the relationship between MWD and microbial biomass was better than for total SOC. He suggested that the portion of SOM, which reflects biological activity, is a better indicator of structural stability as it would contribute directly to bonding mechanisms.

From these studies it is evident that the labile carbon fraction, consisting mainly of carbohydrates, is instrumental in aggregate formation (see summary in Kay and Angers, 1999). Several studies have tried to further distinguish the specific components of the labile carbohydrate fraction, which might act as key drivers in aggregate formation. Shepherd et al. (2001) extracted hot-water soluble (HWC) and acid hydrolysable carbohydrates (AHC) of arable soils to study their influence on aggregate stability. Under cropping, total SOC, HWC and AHC declined but conversion back to pasture returned HWC and AHC to previous levels, but not total SOC (remained at 60-70% of original SOM after 10 years). Aggregate stability was found to be strongly correlated to SOC, HWC and AHC ( $p < 0.001$ ); however, the HWC and AHC fractions were considered to be more informative in determining aggregate stability as a decline in this fraction was consistent with decline in soil structure. They also noted that fine textured soil contained more WSC than coarse-textured soils but that the decline in HWC was faster in fine-textured soil as was the structural deterioration. Soils with the highest aggregate stability also had the highest amount of AHC, which suggests that the more complex sugars of the AHC might play a greater role than the simple sugars of the HWC. This is supported by the fact that HWC does not extract microbially synthesised carbohydrates. A study by Haynes et al. (1991) showed that HWC (80°C) showed greater correlation coefficients with aggregate stability than cold water extractable polysaccharides or total SOC. Baldock et al. (1987) and Haynes and Swift (1990) reported similar findings in that aggregate stability was more closely correlated with HWC than with SOC or hydrolysable carbohydrates and suggested that HWC represented a crucial pool of carbohydrates involved in aggregate formation. However, Haynes and Swift (1990) stress that at least two significant stages are involved in aggregate formation: an initial aggregation phase (driven by microbial polysaccharides) and a stabilizing phase (driven by humic materials). Ghani et al. (2003) also advocated the use of HWC as a sensitive indicator for determining subtle changes in soil quality as HWC includes microbial biomass, soluble carbohydrates, amines and labile nutrients. They found that HWC was composed of about 40-50% carbohydrates and the glucose/mannose ratios suggested that they were mostly derived from extracellular microbial polysaccharides. The sensitivity of HWC to land management changes was illustrated by the

findings that P fertiliser application did not affect SOC contents but increased HWC contents and that cropping and cultivation had greater effect on HWC than on total SOC (Ghani et al., 2003).

The effects of different cropping sequences on the respective carbohydrate fractions and the related aggregate stability were investigated by Angers et al. (1999). They evaluated aggregate stability and SOM properties in the 0-15 cm layer of a fine sandy loam under eight potato cropping sequences (rotations with barley, clover, ryegrass and red clover) by measuring total SOC, C in the light fraction (LF-C:  $<1.7\text{g/cm}^3$ ), microbial biomass C (MBC), alkaline phosphatase activity (APA) and carbohydrate content (dilute acid hydrolysable carbohydrates AHC). Samples were taken in the 6<sup>th</sup> and 10<sup>th</sup> year of the trial. They found that total SOC and N contents as well as aggregate stability were greater in sequences that included a high frequency of clover. Importantly, the response of MBC, LF-C and APA was greater than in total SOC, suggesting that these parameters may be more sensitive to variations in management. However, while there was a 33% improvement in WSA in clover rotations compared with the control in the 6<sup>th</sup> year, no difference was found in the 10<sup>th</sup> year, indicating that temporal variability (due to climatic conditions) may be large enough to mask management-induced changes.

However, the relevance of carbohydrate extractions to WSA is not without contention. Carter et al. (1994) found that water-extractable carbohydrate content did not prove useful to assess aggregate stability in a 4 year study of different grass species on soil aggregate stability. Instead, they found that rooting habit and root architecture can significantly influence mycorrhizal symbiosis, in turn influencing C/N and total N values. Similarly, Degens (1997) questioned the usefulness of the contribution of carbohydrate carbon (both acid and water extractable fractions) to aggregate stabilisation. In an incubation experiment, where clover tops were added to soil, they found no difference in carbohydrate content in  $>1\text{mm}$  aggregates and bulk soil and the carbohydrate fraction did not increase in stable compared with weaker aggregates. An explanation of these discrepancies for water and acid extractable carbohydrates on aggregate stability was offered by Degens and Sparling (1996). They noted that specifically the macro-aggregation of sandy soils (9.8% clay) did not relate to microbial biomass or carbohydrate content. By comparison, studies that had reported positive effects of carbohydrate extracts on aggregate stability were all carried out on loam or clay soils (e.g. Haynes et al., 1991; Carter, 1992). This suggests that aggregation in sandy soils might be more dependent on fungal than bacterial growth and here different organic fractions are required for structural stabilisation.

While polysaccharides have long been implicated in the importance of aggregate formation, humic substances, particularly those with a high aromatic content, are often thought to be of lesser importance in aggregate formation (Shepherd et al., 2001). However, several studies have found the opposite, namely that aromatic, humic components can play a critical role in aggregate formation and stabilisation. For example, Chaney and Swift (1984) showed that correlation coefficients for aggregate stability were better for humic materials extracted by sodium hydroxide, following a pyrophosphate extraction, than those for pyrophosphate extracts themselves, suggesting that high-molecular weight humic materials are more important than low-molecular weight humic substances; however, they also found that carbohydrate content was also highly correlated with aggregate stability, indicating that both, carbohydrate and humic substances, are important for aggregate stability. In a subsequent study, Chaney and Swift (1986) investigated the effects of adsorbed humic materials on aggregation, using mono-ionic soils (Na or Ca saturated). Physical addition of humic acid alone had no effect while subsequent incubation with glucose produced low stability aggregates. However, if humic acids were adsorbed on soil minerals and incubated, aggregate stability was high and persisted with time, and stability increased even further after incubation with glucose. Similar results were observed for both surface (3.6% SOC) and subsurface soils (0.5% SOC). Therefore, the adsorption of humic acid (opposed to physical addition) seemed essential to stabilise aggregates. In a later study, Swift (1991) specifically studied the effects of microbially produced polysaccharides (xanthan gum and alginate), glucose and humic substances on aggregation. Crushed soils were incubated with glucose, xanthan gum and alginate to study the production of stabilised aggregates. He found that the stabilising effects from xanthan gum and alginate were due to the binding action of these compounds whereas the effects from the glucose treatment were not due to the action of glucose *per se* but due to the production of exocellular polysaccharides by micro-organisms as a result of metabolising the glucose. All treatments produced stable aggregates in the first four weeks of the incubation and declined over the total of 12 weeks incubation. Addition of glucose produced more stable aggregates, which persisted longer than xanthan gum and alginate, suggesting that *in-situ* produced microbial polysaccharides were more effective than externally added ones. However, when incubating mono-ionic soils, where the original aggregate structure was destroyed by ion-washing, all carbohydrate treatments were ineffective in producing aggregates. Only after incubation with adsorbed humic acid were new aggregates produced and glucose addition further enhanced the production of new aggregates.

Similar results were observed by Haynes and Naidu (1998), who noted that after addition of easily decomposable organic matter, there was a flush of microbial activity, fungal growth and production of extracellular polysaccharides, resulting in a rapid rise in aggregate stability. However, this effect was only temporary and only addition of well-decomposed material achieved a slow and steady increase in aggregate stability, suggested to result from the presence of humic substances. These data support Guckert's (1975) proposition that microbially-produced polysaccharides are of importance in the initial production of stable aggregates and that humic substances are essential for ensuring longer term aggregate stability. Piccolo and Mbagwu (1990) investigated the specific role of humic acids in aggregate formation by applying hydrophilic polysaccharide gum and hydrophobic stearic acid to soil with organic matter (OM) retained and with SOM removed by H<sub>2</sub>O<sub>2</sub> and with and without addition of humic acid. They found that aggregate stability was greatest for polysaccharide gum when SOM was removed whereas aggregate stability was better for stearic acid when SOM was retained. Addition of humic acid (at 0.2g kg<sup>-1</sup> = 400 kg ha<sup>-1</sup> as lignite) further increased and prolonged the aggregate stability effect of stearic acid, suggesting a synergistic effect of humic acids and stearic acid and showing that aggregate stability of soil was improved and maintained with time better by hydrophobic than hydrophilic components. In a later study, Piccolo et al. (1997) investigated the effects of cyclic wetting and drying and pre-treatment of soils with coal-derived humic substances on aggregate stability. They found that clay mineralogy and organic chemistry both affected aggregate stability. Under wetting and drying cycles, smectitic-illitic soils lost aggregate stability but kaolinitic soils showed improved aggregate stability after a few cycles. Low rates (0.10g kg<sup>-1</sup> = 100kg ha<sup>-1</sup>) of humic substances with over 70% aromatic carbon improved aggregate stability in all soils and reduced the disaggregating effect of wetting and drying cycles. The reason for the beneficial effect of humic substances to aggregate stability was thought to be due to the formation of clay-humic complexes (through bridging of polyvalent cations adsorbed onto clay surfaces), which would orient the chelating acidic functional groups of the humic materials (carboxyl and phenols) towards the interior of the aggregates, leaving aliphatic and aromatic hydrophobic components to face outward. This would lead to the formation of a water-repellent coating with high surface tension, effectively reducing water infiltration into aggregates.

The positive effect of hydrophobic materials on aggregate stability has been shown by Capriel et al. (1990), who found a high correlation coefficient between aggregate stability and the aliphatic (hydrophobic) fraction (extracted with supercritical hexane) and soil microbial biomass ( $r^2=0.91$ ). It appeared that the hydrophobic fraction formed a water-repellent lattice around the aggregates,

enhancing the water stability of the aggregates. They found that of two soils with similar chemical properties (SOC, TN, polysaccharide content and amino N), the one with twice the amount of hydrophobic components had also twice as high MWD values. Similarly, Shepherd et al. (2001) attributed the high aggregate stability of a humic pasture soil to the presence of long-chain polymethylene compounds, thought to form a water-repellent lattice around soil aggregates. They further noted that the observed high aggregate stability of an allophanic soil under long-term cropping was related to the high alkyl carbon content in the  $<2\mu\text{m}$  fraction and the physical occlusion of alkyl carbon in micropores (Shepherd et al., 2001).

The studies by Piccolo et al. (1997) and Piccolo and Mbagwu (1990) and other studies (Chaney and Swift, 1986; Fortun et al., 1989) suggest that application of humic substances (lignite or oxidised coal) would be an economically viable source for rehabilitation of degraded soils as humic substances are relatively inexpensive (US\$ 0.5-1.0) and only small amounts (100-300 kg  $\text{ha}^{-1}$ , depending on substance) are required compared with much larger amounts for farmyard manure applications (50-200 t  $\text{ha}^{-1}$ ). However, Piccolo et al. (1997) also found that there was an upper limit beyond which the beneficial effects of humic substances failed. Beyond 0.1 g/kg of humic substances, MWD of the aggregates decreased, suggesting that high rates of humic substances can penetrate the clay domain (Theng, 1982), effectively displacing less strongly bonded clay particles. This in turn would cause clay dispersion, leading to lower stability. Visser and Caillier (1988) investigated the dispersive effect of humic substances (humic acid extracted from soil sample of a humic gleysol at pH 6.7) at concentrations of 40 mg/l (0.004%). When compared to hexametaphosphate at the same concentration, humic acids were 140 times more effective in dispersing fine clay ( $<0.6\mu\text{m}$ ) fraction and 1.2 times more effective for dispersing coarse clay (0.6-20 $\mu\text{m}$ ) (Fig. 14).

Similarly, Durgin and Chaney (1984) found that high molecular weight aromatic and aliphatic polycarboxylic acids were able to disperse kaolinite by offsetting the positive charge on the edges of clay particles and promoting clay dispersion. Visser and Caillier (1988) suggested that the dispersive power of humic substances might affect soil processes such as podzolisation where humic acid concentrations of up to 60 mg/l occur and where the dispersive power could contribute to the formation of clay-leached A horizons.

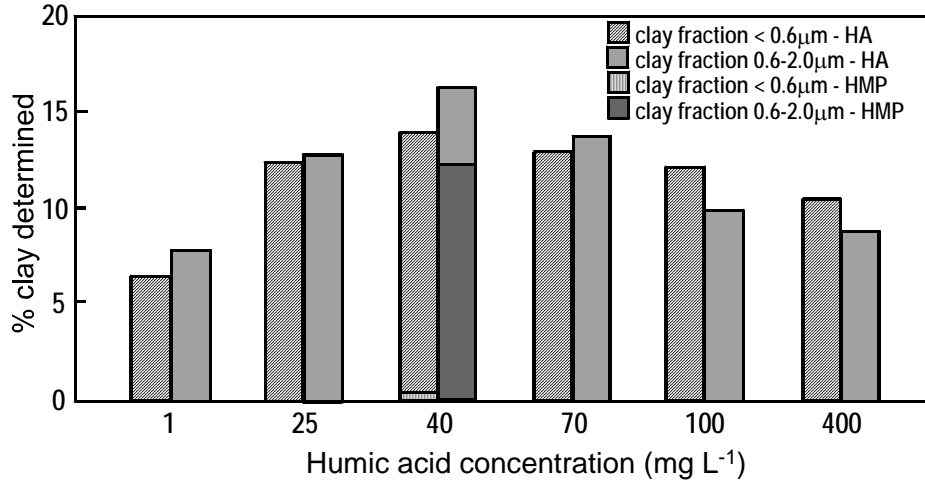


Figure 14: Distribution of clay fractions from humic gleysol obtained by using humic acid (HA) at different concentrations as dispersant. For comparison, the effect of hexametaphosphate (HMP) at 40mg L<sup>-1</sup> is also shown (modified from Visser and Caillier, 1988).

Angers and Carter (1996) noted that agricultural management practices such as perennial forages, organic amendments and no, or reduced, tillage can significantly improve soil macro-aggregation and carbon storage. Similarly positive effects can be achieved by cover crops and short-term forage based rotations if net carbon input to soil is increased. Several studies observed greater aggregation in pasture compared with arable soils. Douglas and Goss (1982) and Tisdall and Oades (1982) noted that aggregate stability is greatest under grass (continuous production) and decreases under arable production and Oades (1984) suggested that the more efficient production of stable aggregates under grass might be due to the high (50%) below-ground production of photosynthate. Haynes et al. (1991) stated that in soils with different clay content in New Zealand, the best predictor of MWD of aggregates was the length of time under grass and the type of land use influenced aggregate stability more than total SOC or polysaccharide content. In a subsequent study by Haynes (2000), they noted that after 3 years of converting arable land to pasture, aggregate stability increased. While organic carbon content did not change significantly, the amount of labile carbon (light fraction and HWC) increased along with aggregate stability, suggesting (as stated previously) that these fractions are more suitable in tracking short term changes compared with total carbon. Haynes and Swift (1990) observed that aggregate stability at a re-grassed site (13 years arable + 2 years pasture) was higher than at the corresponding long-term cropped site, and pasture aggregates were found to have overall greater carbon contents. Jastrow (1996) observed a similar relationship in a chronosequence of prairie restorations, having



converted from arable land to prairie 1, 4, 7 and 10 years ago: the rate constant in aggregation (formation of stable macro-aggregates >212 $\mu\text{m}$ ) was 35 times the rate constant of total SOC and the time to reach 99% equilibrium was 10.5 years for macro-aggregates and 384 years for total SOC (Fig. 15). This suggests that a phased relationship exists between macroaggregate formation and SOC accrual, with macroaggregate formation occurring earlier and proceeding at an exponential rate compared with a linear increase in SOC.

With regard to the source of the accumulating organic matter, Jastrow (1996) found an increase in macroaggregate-associated C/N ratios and suggested that accumulating organic matter was relatively fresh but that less than 20% of the accumulated carbon occurred in the form of POC. Instead, most of the accrued carbon was found in the mineral-associated fraction of macro-aggregates, suggesting that fresh organic matter inputs were transformed relatively rapidly into particles that were associated with mineral matter. In turn, this would lead to more physically protected organic matter, slowing decomposition and promoting development of stable microaggregates. Data shown in Figure 15 also suggest the existence of a threshold of organic carbon for aggregate formation. Furthermore, Jastrow and Miller (1998) showed that there are positive feedback cycles between accruing SOC, its accumulation in macro-aggregates and enhanced aggregate stability.

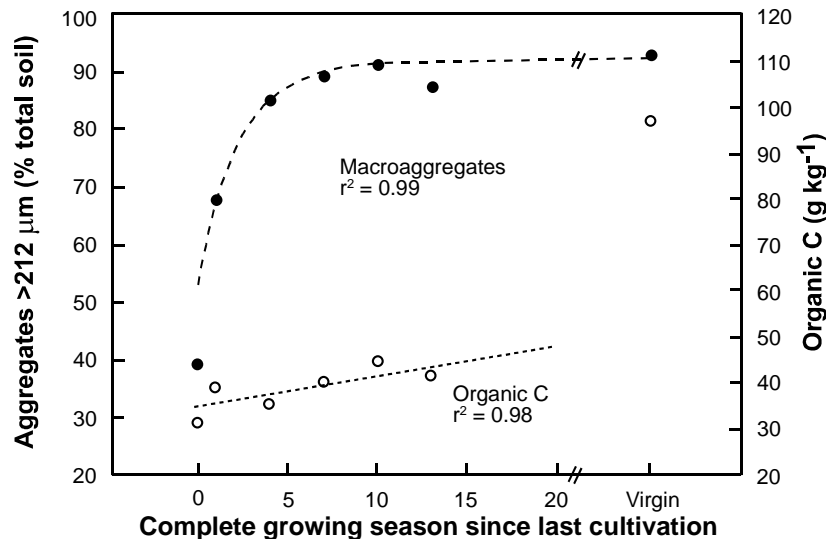


Figure 15: Changes in percentage of macroaggregates and accumulation of whole-soil organic C with time since cultivation (modified from Jastrow, 1996).

The effect of different crop species (barley, wheat, prairie grass, ryegrass, white clover, lupin) on aggregate stability was studied by Haynes and Beare (1997). They discovered that leguminous versus non-leguminous plants vary in the way they contribute to aggregate stabilisation. For non-leguminous crops, higher root mass (greatest in ryegrass, least in barley) translated into greater aggregate stability, as rhizodeposition of carbon contents was enhanced, in turn favouring increased microbial activity. This was supported by the galactose+mannose/arabinose+xylose ratio of 2.1, indicating primarily microbial origin. By comparison, legumes had higher aggregate stability than non-leguminous species, but had comparably less root mass and microbial biomass. Subsequent studies showed that the fungal hyphae length in lupin was four times that of wheat, suggesting that leguminous plants favour fungal growth, which appears to be a critical factor for aggregate formation.

Diaz et al. (1994) conducted a study to investigate the effects of two organic amendments (peat and urban refuse) on soil structure over a period of two years. They found that average percentage of stable aggregates increased with amount of urban refuse applied compared with the control site. By comparison, no improvement in stable aggregate formation was found in peat applications. For the urban refuse application, no significant correlation was found between total and extractable organic carbon and percentage of stable aggregates; however, the amount of fungal and bacterial populations correlated well with the level of aggregation. They attributed the enhanced aggregation in urban refuse treatment to the high polysaccharide content (13%), compared with the low polysaccharide content of peat (3%), and its combined action as cementing agent, food source and stimulant for microbial activity. The observed improvement in structure remained for the two years of the experiment and the authors concluded that only one application of urban refuse was sufficient to regenerate degraded soils. It needs to be noted, however, that the urban refuse application resulted in increased vegetation cover compared with the control and peat treatment, which is likely to have also contributed to the long-term stabilisation of aggregates.

A study by Ekwue (1990), which compared the effect of a peat amended soil to pasture soils, found similar results. Under grass, the percentage of WSA increased from 2.2 to 21.6% and the individual aggregate energy (IAE, measured by single drop method) increased from 4 to 33 mJ with increasing organic matter content. By comparison, the peat amended soils showed a decrease in WSA from 2.5 to 0.9 and a small reduction in IAE from 3.9 to 3.5 mJ. Ekwue (1990) interpreted these findings as a result of the low quality and degradability of the peat. However, it

must be noted that the application rates of peat were very high (at rates of 4, 11 and 17%, air-dry weights), possibly causing dispersion of clay minerals. Furthermore, the connection between “high” quality carbon and enhanced aggregation and “low” quality carbon and detrimental effects, should be viewed with caution. Bossuyt et al. (2001) characterised high quality carbon as containing a high proportion of N (relatively low C/N) values but Elliott and Lynch (1984) indicated that such high quality carbon is not inevitably better for long-term aggregate stability. They argued that high quality organic matter tends to encourage microbial biomass synthesis with only very little by-product production, which is thought to be the responsible aggregating agent. By comparison, low quality SOM discourages fast microbial reproduction but stimulates greater by-product production, suggesting that low quality SOM is more advantageous in stabilisation. These findings were supported by studies by Acton et al. (1963) and Harris et al. (1964, 1966), showing that addition of N to high carbon amendments decreased the long-term aggregation effectiveness. Bossuyt et al. (2001) reported that fungi dominated low quality residue and bacteria dominated high quality residues, and Amezketa (1999) showed that addition of N decreased aggregation and fungal biomass but that it had no effect on bacteria, suggesting that fungi appear to be of greater importance in aggregation process than bacteria.

Manure as well as fertiliser (Nitrogen-Phosphorus-Potassium = NPK) applications are often used to maintain or even enhance the ability of soil to produce arable crops. In the long-term, increased crop yields and SOM returns with regular application result in higher SOM content and biological activity (Haynes and Naidu, 1998). The effects of different SOM and fertiliser treatments on soil structure and organic matter content have been investigated in various studies. Aoyama et al. (1999) followed the effects of long-term (18years) application of manure and NPK fertiliser on organic matter fractions and water stable aggregates in the 0-10 cm of a humic gleysol. Manure application ( $20\text{Mg ha}^{-1} \text{ yr}^{-1}$ ) led to an increase in carbon content in most fractions and increased the pools of protected carbon (x3) and nitrogen (x4), located in small macro-aggregates (250-1000 $\mu\text{m}$ ). In contrast, NPK fertiliser only increased the pool of macro-aggregate protected nitrogen (x2.5) but not that of carbon. They concluded that manure application, compared with sole application of NPK, contributed to the accumulation of macro-aggregate protected carbon and nitrogen and provided a mechanism for protection of labile soil organic matter in annually tilled cropping systems.

In order to investigate whether different types of organic amendments differ in their effects on soil physical parameters, Martens and Frankenberger (1992) amended an irrigated coarse loamy

Alfisol with three loadings of poultry manure, sewage sludge, barley straw and alfalfa. Compared with the control, organic amendments increased soil respiration rates (139-290%), soil aggregate stability (22-59%), SOC content (13-84%), soil polysaccharide content (25-41%), soil moisture content (3-25%) and decreased  $D_b$  (7-11%). While sewage sludge and poultry manure resulted in higher SOC contents, barley straw improved aggregate stability more than the other amendments (increase by 59% compared with 23% for sludge and manure) and had the greatest effect on total polysaccharide content, infiltration rate and respiration rate. Multiple linear regression analyses indicated that initial stimulation of microbial activity led to increased aggregate stability, which was shown by the presence of glucose and mannose after the first addition. After the second addition, aggregate stability correlated with extractable polysaccharides (galactose and glucose) but no significant correlation was found after the third treatment. This implies that polysaccharides initially contribute to stabilisation of soil aggregates but that other soil organic fractions (humic materials) may be responsible for the long-term stabilisation of aggregates. Interestingly, even the unamended plots (in fallow state) increased in aggregation, which could have been due to the weekly irrigation schedule and the resulting positive influence of wetting and drying cycles (Fig. 16).

As the previous studies have shown, organic amendments generally result in an increase in soil structural stability. Adediran et al. (2003) specifically investigated the effect of different organic amendments on crop yield. They used poultry litter with organic wastes, maize residues, leaf litter, urban waste, weed biomass, and soybean residue and applied these to amaranthus and tomato crops. They found that for optimal crop yield different amendments were required for different crops: while urban waste was best and soybean residue worst for amaranthus production, maize and soybean residues proved to be best for tomato production.

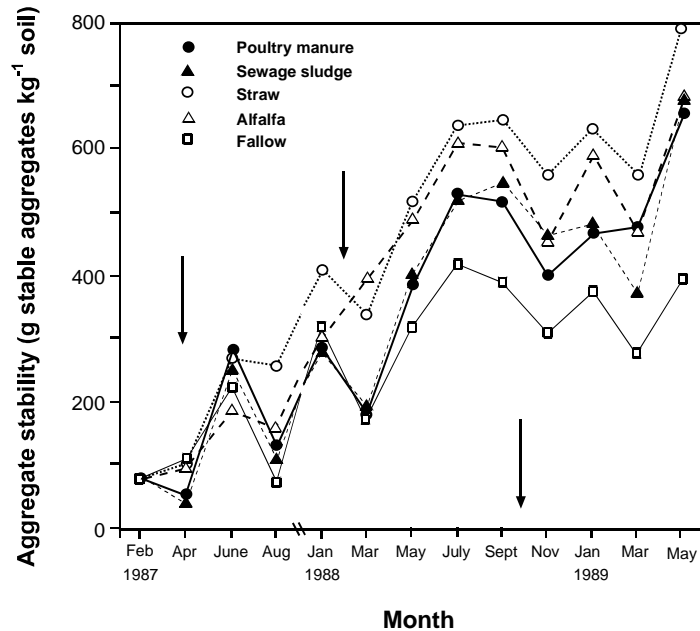


Figure 16: Influence of organic amendments on soil aggregate stability. Arrows indicate addition of organic amendments (modified from Martens and Frankenberger, 1992).

While some of these results might be due to greater nutrient content, there was not a consistent trend and it is more likely that the specific requirements from the different crops need to be matched by specific amendments. Whalen et al. (2003) found that corn residues were better than soybean residues for improvement in aggregation under corn-soybean rotations. They attributed this to a lower phenolic content in soybean residues. They also found that only 2 years of compost application together with no tillage was required to obtain a dramatic improvement of aggregate stability in these arable soils.

The effect of rate of mulch addition on SOC levels and aggregation was investigated by Saroa and Lal (2003). Mulch treatments of 0, 8, 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> were added to soil and samples were taken at 0-5 cm and 5-10 cm depth at 4 and 11 years after trial start. They found that a higher mulch rate increased SOC and TN concentrations only in the 0-5 cm and that mulch rate explained 41% of the variations in SOC after 4 and 52% after 11 years. Water stable aggregation increased with mulch rate but only in the 0-5cm layer after 4 years and no increase was observed after 11 years. Similarly, SOC concentrations significantly correlated with %WSA after 4 but not after 11 years. Based on their data, it appears that mulching rate has to be increased over time in order to retain a similar increase as seen for the first 4 years.

Many studies on the effect of organic amendments cover only relatively short intervals, ranging from several weeks (incubations) to a couple of years (field trials). Gerzabek et al. (1995) investigated the long-term effects of bare fallow and organic amendments on soil aggregate stability (macro-aggregates >0.25 mm) from a plot trial in Sweden, which had been running for 38 years. Treatments had started in 1956 and additions were made in 1960, 1963 and continuing every other year. There was a clear response of aggregate stability to type of management and organic amendment and aggregate stability increased in the order bare fallow < no N < green manure < peat < FYM. While there was generally a good correlation between increasing aggregate stability and increasing SOC contents, this relationship did not hold true for the C-rich peat amendments (Fig. 17).

Gerzabek et al. (1995) related this to the high C/N ratio of peat (63 compared with 21 for FYM), which would discourage microbial biomass production. This was supported by the observation that the size of the microbial biomass was 7.4 times greater in FYM, 9.3 times higher in green manure and about 6 times higher in bare fallow compared with peat. Furthermore, pH decreased under peat from 6.4 to 5.9 (compared with an increase to 6.6 under FYM), which could have had an additional negative effect on aggregate stabilisation (decrease in negative charge of SOM).

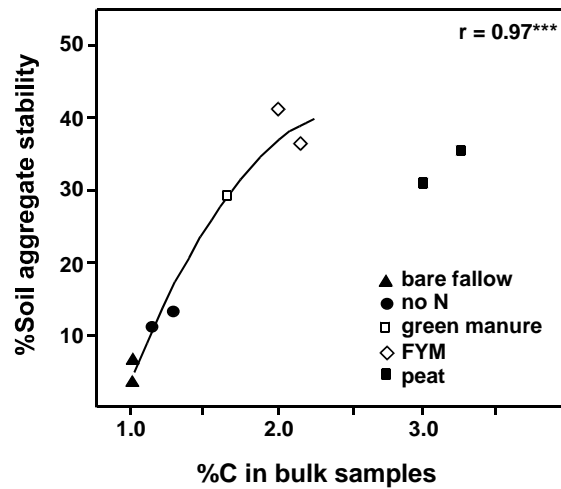


Figure 17: Response of soil aggregate stability to increasing carbon contents in Ap horizons of Eutric Cambisols from the Ultuna long-term organic matter experiment (modified from Gerzabek et al., 1995).

However, if the peat treatment is disregarded, there was a clear positive influence of organic carbon on aggregate stability, which increased at a rate of 10% up to 1.5% SOC and levelled off at >2% SOC content

The importance of tillage on aggregate stability has been studied by Six et al. (1989, 1999, 2000) and is summarised in Krull et al. (2003) and the following studies were chosen to highlight some of the recent findings in this field. Franzluebbers and Arshad (1996) determined the distribution and SOC content of 5 water-stable aggregate classes at depths of 0-5, 5-12.5 and 12.5-20 cm in loam, silt-loam, clay loam and clay soil managed for 4-16 years under conventional tillage (CT) and zero tillage (ZT) in Alberta, BC. While macro-aggregates (>0.25 mm) and MWD were greater under ZT than CT in coarse-textured soils to a depth of 12.5 cm, macro-aggregation and MWD increased with increasing clay content under CT. Thus, the potential of ZT to improve macro-aggregation in soils with high clay content was reduced. SOC was greater in macro-aggregates of coarse-textured soils but lower in micro-aggregates under ZT compared with CT, while clay-rich soils did not show a significant difference between aggregate classes. This suggests that the potential of ZT to increase SOC was found to be greatest (in cold semiarid climates) for coarse-textured soils.

Carter (1992) used two indices to determine changes in SOM and microbial biomass carbon in comparison with structural stability for several different soils (0-5cm) under different management types and tillage practices: mean weight diameter (MWD) and aggregation index (AI). AI assigns a weight factor to aggregate size ranges based on a value for plant germination and root growth, which is an agronomic value in providing optimum air-water conditions. He found that direct drilling and reduced tillage resulted in greater SOC contents (10-17%) compared with mouldboard ploughing and that under these less invasive practices, organic carbon content was greater in the 1-2 and 4.75-9 mm aggregates compared with the whole soil. This suggests that direct drilling or reduced tillage, opposed to mouldboard ploughing, can aid in the improvement of soil structure and SOC content.

Douglas and Goss (1982) investigated the effects of different tillage treatments (direct drilling, shallow tine cultivation, mouldboard ploughing) on aggregate stability and organic matter content on soils with different clay contents. Soil organic carbon content was greater in soils with higher clay content but the effects of different tillage techniques on aggregate stability followed the same trend: greatest loss in aggregate stability occurred under mouldboard ploughing whereas direct

drilling had the least detrimental effects. Similarly, Shukla et al. (2003) found that no tillage (NT), compared with mouldboard ploughing and chisel ploughing, had more SOC and N in 0-10 cm and had a greater amount of WSA in 0-10 and 10-20 cm. Importantly, they noted that mouldboard and chisel ploughing had lasting effects on soil physical properties: 20 months after the last tillage, the NT plot still had greater amounts of WSA, MWD and N compared with mouldboard and chisel ploughed fields.

Many studies that investigated the effect of SOC on aggregate stability overlook the fact that increased aggregate stability is most likely driven by several factors, often synergistically enhancing one another. For example, Rose (1991) stressed that the application of FYM increased not only aggregate stability by up to 20% but also increased the soil's water holding capacity. Accordingly, they attributed the change in aggregate stability to changed flow rates and a reduction in intra and inter-aggregate porosity. Idowu (2003) examined 72 surface (0-10cm) soil samples from Alfisols under different cultivation practices in Nigeria for their aggregate stability. In order to relate soil functions to aggregate stability, he devised an aggregate stability index (ASI) by calculating the total kinetic energy required to shatter a given mass of soil:

$$\text{ASI (J/kg)} = (n \times K_e)/m,$$

where  $K_e$  = kinetic energy per drop ( $7.4 \times 10^{-4}\text{J}$ ) and  $m$  = mass of aggregates (kg).

He found that SOM, pH,  $D_b$ , silt, coarse and fine sand, and gravimetric moisture content were linearly correlated with ASI. Surprisingly, relationships between ASI and clay content were not significant. This could have been due to the relatively low clay content of the soils, ranging from 3.1-11%, since previous studies had shown that a clay content of about 15% was required before it could contribute significantly to soil aggregation. The fact that moisture content gave a positive relationship with ASI could be explained by the fact that the air-dried moisture content of soil is strongly dependent on SOM content and thus the response of moisture content to ASI may be an indirect reflection of the influence of SOM rather than being a direct causal factor. This was confirmed by a positive correlation between SOM and moisture content. ASI was also found to be related to pH and decreased with increasing pH (pH ranging from 4.5-7). The greater stability at lower pH values could be related to the presence of Al and Fe in soil solution, which contribute to the formation of organic matter complexes. A stepwise multiple regression was used to determine four variables (SOM,  $D_b$ , pH and moisture content) which were significant in predicting ASI, and



SOM was the variable contributing most as additional variables improved the predictions by only 8%. Principal component analysis with subsequent multiple regression was performed with ASI as the dependent variable. Results indicated that pH and SOM were most influential in determining ASI, represented by the following equation:

$$\text{ASI} = 2.234 + 0.602 \text{ SOC} + 0.213 \text{ pH},$$

with SOC having a partial correlation coefficient of 0.76 while pH had  $-0.3$ . Idowu (2003) concluded that SOM was the property most closely related to aggregate stability.

The influence of water potential and organic carbon on the sensitivity of soil to mechanical disturbance was shown by Watts and Dexter (1997) (Fig. 18). Their study showed that soils become more sensitive to mechanical damage when wetter and the most dramatic effect is observed for soils with  $<1.5\text{g}/100\text{g}$  organic carbon. Ketterings et al. (1997) performed a multiple regression analysis of WSA, total SOC content of dry-sieved aggregates, antecedent soil moisture content and total clay content of bulk soil. The relationship for the 4-10 mm size class is illustrated in Figure 19. They showed that SOC explained 61% of variability in WSA, and clay and SOC together explained 67% of variability. While a higher SOC content contributed to enhanced stability, independent of clay content, the model shows that the optimum concentration in WSA and C content was dependent on clay content (levelling off at 10-17% clay content).

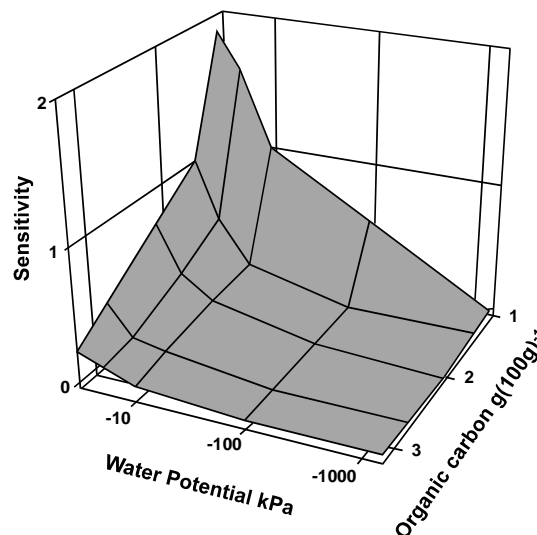


Figure 18: Sensitivity of soil to mechanical damage during simulated tillage as influenced by SOC and water potential. Sensitivity is relative clay dispersion per  $\text{J kg}^{-1}$  energy input  $\times 10^{-3}$  (redrawn from Watts and Dexter, 1997).

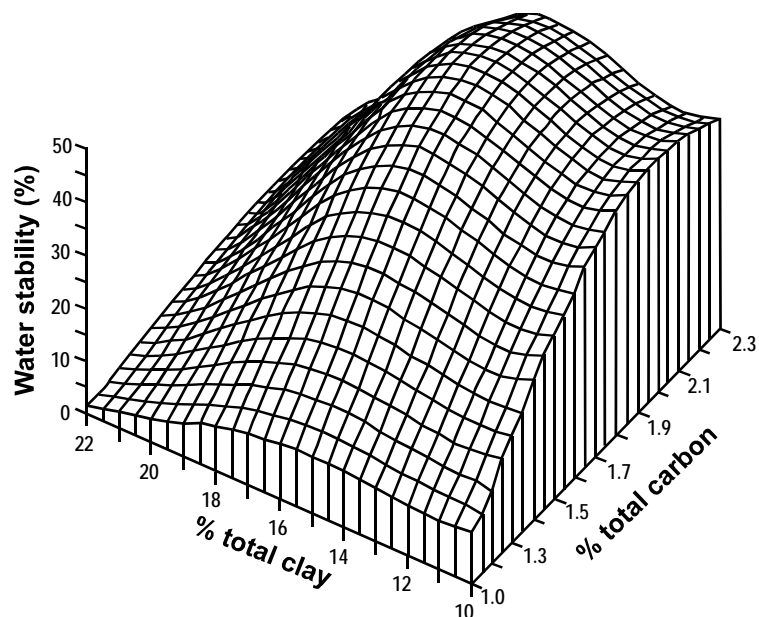


Figure 19: Graphical presentation of model by Ketterings et al. (1997), representing the relationship between percentage total carbon in dry sieved aggregates, percentage total clay of bulk soil, and water stability of 4-10 mm aggregates. The model explained 67% of the total variability in water-stability of aggregates of this size class (redrawn from Ketterings et al., 1997).

As shown by the summary of the previous studies, the difference in analytical techniques to determine aggregate stability and the possibility of generating artefacts due to certain laboratory procedures makes a quantitative comparison of data difficult. While a standardised analytical scheme would be preferable, the usage of an independent and relatively simple measure to assess structural stability could improve the consistency and ability for comparison of data. The amount of water-dispersible clay as a means to measure the structural stability of soil has been used in several studies, which also found a good correlation with SOM. For example, Dong et al. (1983) reported a correlation between the degree of dispersion of clay and the amount of organic matter adsorbed. Clays rich in organic matter (3.4-4.4 %C) showed a greater degree of aggregation and less dispersion compared with clays with low organic matter content (0.5-2.5 %C). Jastrow and Miller (1998) showed that amounts of dispersed clays decreased and aggregate stability increased after return of arable land to pasture and that these improvements were directly associated with increasing SOC. Skjemstad (2002) showed in GRDC project CSO 195 that water dispersible clay (WDC) can be successfully used as a measure of structure and that it was sensitive to POC levels in a red-brown earth at the Waite Long-Term Trial. They found that for a rotation trial of four years of pasture followed by two years of wheat (PPPPWW), TOC and POC increased under

pasture and showed decreasing trend under wheat. WDC declined rapidly (equivalent to greater structural stability) once a threshold of 5 t/ha for >200 $\mu\text{m}$  POC fraction was reached, suggesting that this could be a critical threshold value and that an increase in POC content through return of crop residues could reduce clay dispersion. Figure 20 shows averaged data for SOC content over each year, illustrating an increase in SOC under pasture and decrease under wheat with a larger effect for the >200 $\mu\text{m}$  than the 53-200 $\mu\text{m}$  fraction. WDC showed a similar trend of declining values under pasture and increasing values under wheat, suggesting that upon pasture establishment, SOM increases, soil structure improves and clay dispersibility decreases.

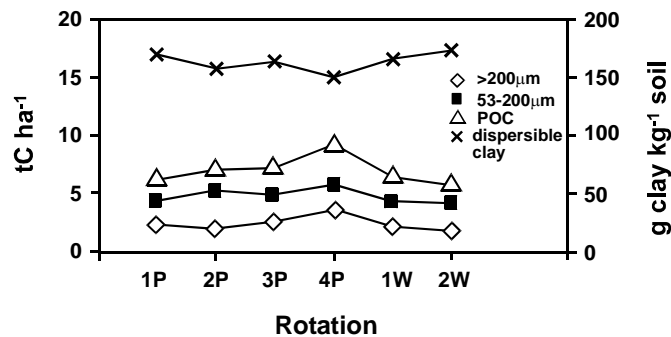


Figure 20: Changes in annual averages in >200 $\mu\text{m}$  and 53-200 $\mu\text{m}$  fractions and total POC and dispersible clay (modified from Skjemstad, 2002).

However, Martins et al. (1991) showed that increased clay dispersion occurred after 5 years of clearing native rainforest, followed by crop establishment. The increase in dispersibility of clay minerals was 38% and coincided with a decrease of 35% in carbon in the A horizon. Most of the loss in carbon (88%) was from litter and from the 50-2000 $\mu\text{m}$  fraction (64%).

The relationship between SOM and dispersible clay and the processes that govern this relationship was investigated by Nelson et al. (1998, 1999). They found that dispersibility of clay was positively correlated with Na and negatively correlated with SOM and it was a function of amount and type of SOM, CEC, selectivity for cations and particle size. In fact, an interrelationship between decomposition of organic matter, electrolyte concentration and dispersibility of clay was observed by Nelson et al (1998) as an increase in stability of easily dispersible clay (EDC) during a wetting and drying experiment could be attributed to a change in electrolyte concentration in the soil due to mineralisation of SOM and release of divalent cations. Furthermore, EDC tends to have a lower organic carbon content and a higher proportion of amino acids and proteins than difficult to disperse clay (DDC). These substances could aid in dispersion

of clays as amino acids would form complexes with Ca and increase the negative charge of clays (by decreasing the Ca concentration in solution). DDC on the other hand, contained high proportions of aliphatic C in topsoil and carbohydrate C in subsoil, which are known to form complexes with clay minerals via cation bridging. Another possibility to explain the degree of dispersibility could lie in the relationship between size fraction and type of organic matter. Dispersion might be controlled by particle size and surface charge characteristics and certain types of organic matter might become preferentially adsorbed by larger particles with lower surface charge and vice versa. Another synergistic relationship was observed by Muneer and Oades (1989a,b), who noted that both Ca and organic matter were instrumental in improving soil aggregation (increase in WSA), increasing the resistance of organic matter to decomposition and decreasing the amount of dispersible clay.

The effect of organic amendments on SOM and clay dispersibility was investigated by Debosz et al. (2002). Sandy loam was amended with anaerobically digested sewage sludge and household compost and incubated for 11 months at constant temperature (10°C). They found that clay dispersibility of the unamended soil increased, indicating progressive destabilisation of soil structure, whereas waste-amended soil remained at initial levels. Biomass C increased by only 0.2% (sludge) and 1% (compost), suggesting that the effects of organic matter on soil properties are more likely to be related to quality not quantity. However, polysaccharide content did not show significant changes, and they argued that this fraction is probably not instrumental in reducing the dispersibility of clay. What was somewhat surprising was the fact that the % wet stable aggregates (>0.25mm) of soil showed an almost immediate increase (25 to 50%) under sludge and a delayed increase in both compost and unamended soils, all of which levelled out thereafter and obtained similar final percentages of WSA. Debosz et al. (2002) suggested that the lack of differentiation of %WSA compared with the trends in dispersible clay might be due to the fact that incubation for 11 weeks might not be long enough for structural changes to manifest in a way that they can be distinguished among treatments. If this is the case, then dispersible clay might be a more sensitive measure of short-term structural changes than WSA.

The effect of vegetation change on clay dispersibility was investigated by Koutika et al. (1997). They sampled the clayey Oxisols of a pasture chronosequence (at 7, 12 and 17 years) and the original virgin forest soil from Amazonia. They observed an increase in negative surface charges and clay dispersibility with increasing age in the pasture soils. Accordingly, WSA were more stable in the youngest pasture soil (7 years since clearing) and decreased with increasing pasture

age. To evaluate what caused these trends, they used the difference in pH values ( $\Delta\text{pH}$ ) determined in water and in 1M KCl as this value was assumed to be proportional to negative surface charges.  $\Delta\text{pH}$  values were higher in pasture soils compared with those from the virgin forest soil, which was consistent with higher CEC values in the pasture soils. They interpreted this increase in  $\Delta\text{pH}$  to be due to a greater amount of organic acid functional groups after vegetation change. Similarly, Martins et al. (1991) showed a significant co-variation between CEC, fulvic acids and dispersible clays as a consequence of forest clearing. Furthermore, Koutika et al. (1997) illustrated that a relationship existed between WDC/clay and  $\Delta\text{pH}$  (Fig. 21). They suggested that although structural stability, as indicated by increased WDC/clay values, was declining in the older pasture soils, the increased CEC was able to compensate for the degradation in the physical function of soil. Similar to the study by Debosz et al. (2002), they did not find a statistically significant difference between WSA in pasture and forest soils compared with the apparent increase in clay dispersibility with pasture age; however, they noted that there was a clay dispersion threshold at 1%SOC and the fact that SOC contents did not change significantly between pasture and forest soils might have contributed to the lack of change in WSA.

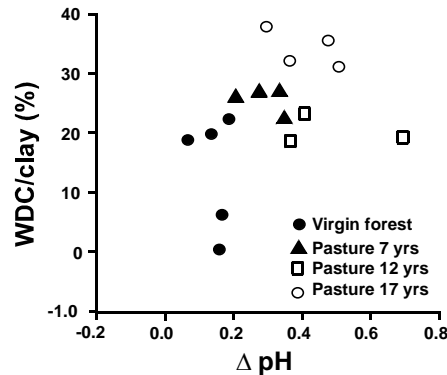


Figure 21: Relationship between water-dispersed clay/total clay ratios (WDC/clay) and  $\Delta\text{pH}$  ( $\text{pH}_{\text{water}} - \text{pH}_{\text{KCl}}$ ) values (modified from Koutika et al., 1997).

## Summary

- A good correlation exists between SOC content and structural stability.
- There is no effect on structural stability below a threshold value of 2% SOC content.
- Carbohydrates (HWC as well as AHC) are important in improving aggregate stability; however, the efficiency might vary by soil type (greater effect in clay soils).
- In addition to relatively short-lived effects from carbohydrates, humic materials are necessary to ensure long-term stability of aggregates.
- Hydrophobic components (lipid material) might also aid in improving aggregate stability; however, a large amount of hydrophobic material can contribute to water-repellency.
- In agricultural soils, aggregate stability can be improved by reduced tillage, rotations of crops with pasture, and organic amendments; however, peat amendments were not as effective as other organic amendments.
- Aggregate stability can be assessed by measuring clay dispersibility, which would provide a more consistent methodology compared with the various techniques to directly measure aggregate stability.

## Water-Holding Capacity

An important indicator of soil physical fertility is the capacity of soil to store and supply water and air for plant growth. The ability of soil to retain water is termed water holding capacity (WHC). In particular, the amount of plant-available water in relation to air-filled porosity at field capacity is often used to assess soil physical fertility (Pevehill et al, 1999). Total plant available water (PAW) is the amount of water held between the wettest drained condition (field capacity FC, at matric suction of -10 kPa) and the water content at which plants are unable to extract water (permanent wilting point PWP, at matric suction of -1500 kPa). However, some studies use -10 kPa for coarse textured soils only and use -33 kPa for fine-textured soils (Bauer and Black, 1992). WHC of soils is controlled primarily by the number of pores and pore-size distribution of soils, and by the specific surface area of soils. In turn, this means that with an increase in SOC content, there is increased aggregation and decreased  $D_b$ , which tend to increase the total pore space as well as the number of small pore sizes (e.g. Khaleel et al., 1981; Haynes and Naidu, 1998). These relationships highlight the interconnectivity between soil structure,  $D_b$  and WHC. The effect of organic carbon on the WHC of soil is generally assumed to be positive but the types of carbon responsible for this effect and synergistic behaviour with other soil properties is not well understood.

For example, de Jong (1983) and Haynes and Naidu (1998) found an increase in water content with increasing SOC content and Wolf and Snyder (2003) stated that an increase of 1% SOM can add 1.5% additional moisture by volume at FC. Emerson and McGary (2003) showed that per gram of additional carbon at -10 kPa suction, a 50% increase in water content was achieved (Fig. 22). They suggest that the organic carbon from exudates ('gel') from ectotrophic mycorrhiza would bond soil particles, which would result in a change in the size of the pores and a change in water retention at -10 kPa.

Calhoun et al. (1973) found that if "organic matter" was added to pedotransfer functions (PTFs) a significant improvement of the PTF for -33 kPa was noted; however, results for -1500 kPa were ambiguous. Notably, PTFs have been used by Kay et al. (1997) to assess the sensitivity of structural characteristics of coarse and medium textured soils to changes in SOC and PAW. These PTFs are based on fitting empirical equations to soil water retention (SWR) characteristics data.

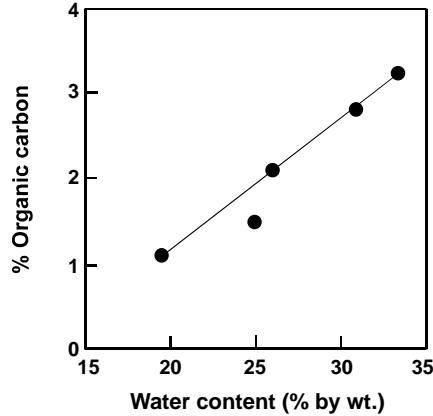


Figure 22: The increase with %C in water retention at 10 kPa suction of silty aggregates (redrawn from Emerson and McGary, 2003).

The empirical equations, in turn, are used to model the SWR characteristics data from a range of soils and multiple linear and non-linear regression analyses are used to develop predictive functions. Their analysis predicted that an increase in SOC content of  $0.01 \text{ kg kg}^{-1}$  would increase PAW from  $0.02$  to  $0.04 \text{ m}^3 \text{ m}^{-3}$ , with the largest increase occurring in coarse-textured soils. Their predictions further showed that an increase in SOC increased WHC at FC and PWP across a range of clay contents. However, the increase at FC tended to be greater than at PWP and the effect of increasing SOC on PAW diminished as clay content increased. These findings are very similar to results obtained from actual measurements, substantiating the value of PTFs in providing sensible results for large data sets. Baldock (unpublished data) used Kay et al.'s (1997) continuous PTFs to assess the effect of an increase in SOC on the WHC for Red Brown Earths from Australia by utilizing the following equation:

$$\theta_v = a \Psi_m^b, \text{ where}$$

$\theta_v$  = volumetric water content  $\text{cm}^3 \text{ cm}^{-3}$

$\Psi_m$  = matric potential

$$a = \exp(-41518 + 0.6851 \ln \text{clay} (\%) + 0.4025 \ln \text{SOC} (\%) + 0.2731 \ln \text{BD}) \quad r^2 = 0.94$$

$$b = -5456 + 0.1127 \ln \text{clay} (\%) + 0.0223 \ln \text{SOC} (\%) + 0.1013 \ln \text{BD} \quad r^2 = 0.94$$

BD = bulk density

His results showed that if organic carbon in soil is increased by  $0.01 \text{ g}$  organic carbon per gram of soil, WHC can be increased by up to 30%, depending on clay content (Fig. 23).



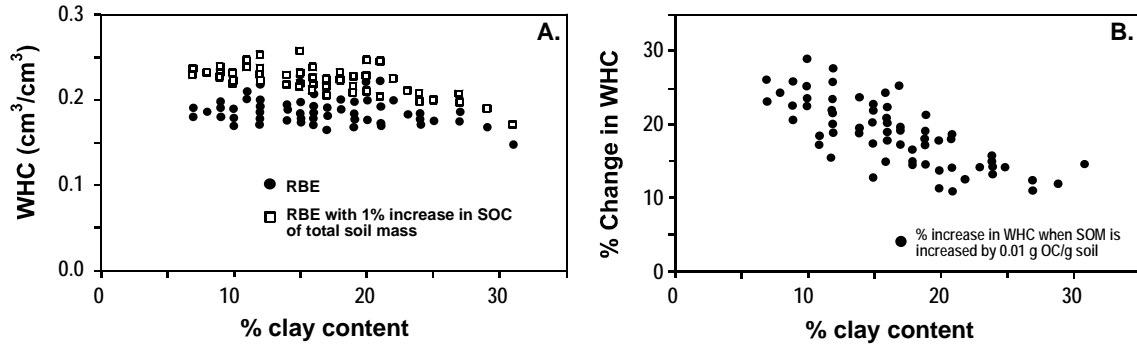


Figure 23: WHC (volume basis) of Red Brown Earths as a function of clay content and SOC, using PTFs of Kay (1993) (a) and % change in WHC of Red Brown Earths derived by PTFs of Kay (1993) when SOC is increased by 0.01g organic C g<sup>-1</sup> soil (b) (Baldock, unpublished data).

However, reports about relationships between SWR and SOC content can be contradictory. Thomasson and Carter (1989) found that for agricultural top soils, SOC contributed no more than 15% to the variance in soil water content and there was no apparent threshold value with SOC content. Similarly, Loveland and Webb (2003) reported that SOC contributed <13% to the variance in soil water content, and Lal (1979) and Danalatos et al. (1994) did not find any effects of SOM on water retention. Furthermore, experiments at different matric potentials are likely to influence the effect of SOC as McBride and MacIntosh (1984) reported that SOC affected water retention at -1500 kPa only if the SOC content was >5%.

Rawls et al. (2003) attributed the conflicting results between SOC and WHC to the synergistic effects of textural components and SOC. To assess the influence of texture, they used 1200 samples from the Soil Survey Staff, where texture, SOC content, water retention at -33 and -1500 kPa,  $D_b$  at -33 kPa and taxonomic characterisation were known. These data were analysed using regression trees and group method of data handling (GMDH), which have been recently used to develop PTFs. Based on these GMDH equations, isolines of water content at -33 kPa and -1500 kPa for 1, 2 and 3% SOM and proportions of clay and sand were generated (Fig. 24). These data show that at -33 kPa, SWR tended to increase with increasing SOC and the largest increment in water contents occurred in coarse textured soils. However, a decrease in SWR with SOC increase was observed for fine textured soils with high clay content. The analyses further showed that clay or sand content alone were not good predictors for the effect of SOC on SWR at -33 kPa because the 35% isoline, for example, with 2% SOC was applicable to three combinations: 20% sand/5% clay, 10% sand/20% clay and 20% sand/35% clay (Fig. 24).

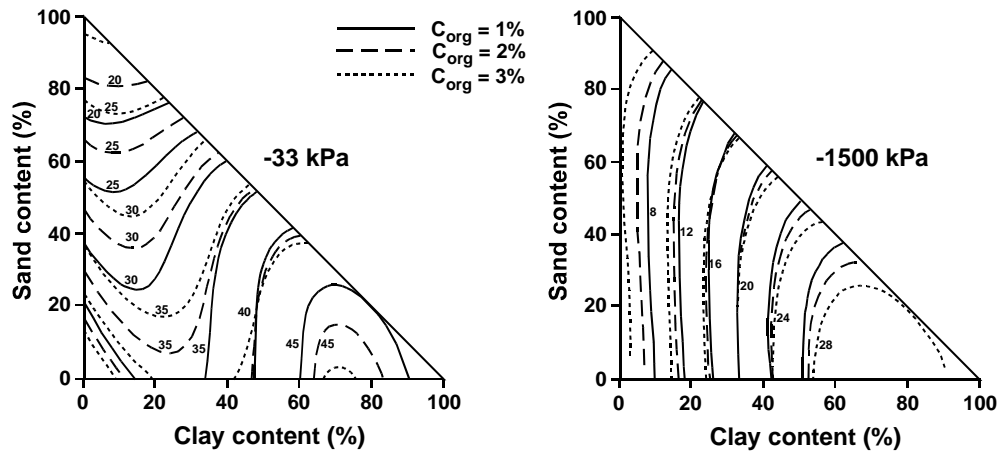


Figure 24: Isolines of water content at -33 kPa and -1500 kPa in a textural triangle at different organic carbon contents (redrawn from Rawls et al., 2003).

Analyses for the -1500 kPa matric potential showed that soils with low clay content showed the largest increase in SWR with increasing SOC content (Fig. 24). Based on the results from the analyses at -33 kPa, Rawls et al. (2003) assessed the sensitivity of SWR to changes in SOC for different levels of initial SOC content and texture and found that sensitivity decreases as initial SOC content increases (Fig. 25). At low SOC contents (1%), the sensitivity of SWR to changes in SOC is highest and SWR increases with low clay but decreases with high (>50%) clay content. Similar but less sensitive results were achieved at 3% SOC, whereas at 5% SOC there was a small but consistent increase in SWR in all textures.

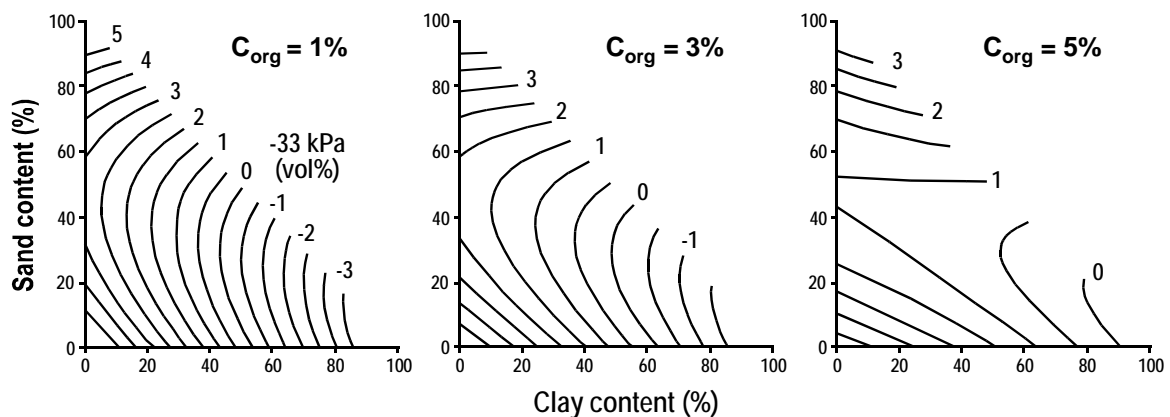


Figure 25: Changes in soil water content at -33 kPa (vol.%) per 1% change in organic carbon content with various initial carbon contents ( $C_{org}$ ) shown in the graph.

Based on the predictions from Rawls et al.'s (2003) GMDH data, it appears that a) SOC was an important soil property to improve estimation of SWR, b) SWR of coarse textured soils were more sensitive to changes in SOC than fine textured soils and that c) SWR in heavy clay soils decreased with increasing SOC content.

The effect of texture on soil water content and SOC was investigated by Bauer and Black (1992), using actual field trials. They compared coarse- and fine-textured soils from two cropland management systems (conventionally cultivated and stubble-mulched) and two grassland systems (grazed and relict virgin). Similar to Rawls et al.'s (2003) predictions, they found that the greatest changes in SWR were observed in sandy soils, where the change accounted for 75% of the change in water concentration by weight ( $P_w$ ) at both FC and PWP. A unit change in SOC content in sandy soils caused a greater change in  $P_w$  at FC than at the PWP, but in medium and fine-textured soils, the change in  $P_w$  at FC was parallel with the change at PWP (Fig. 26).

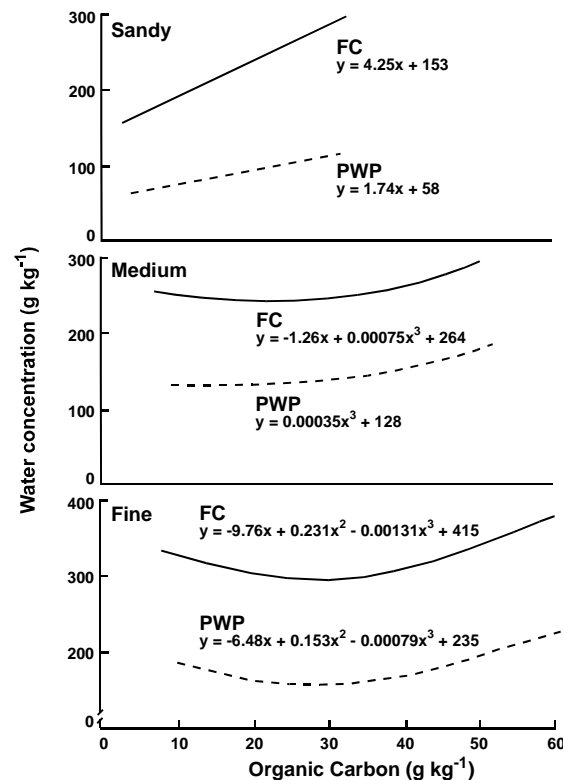


Figure 26: Water concentration at field capacity (FC) and the permanent wilting point (PWP) in relation to organic carbon concentrations in three textural soil groups (n = 256) (redrawn from Bauer and Black, 1992).

In the medium-textured soils, there was essentially no change in FC and PWP when SOC was  $< 30\text{g kg}^{-1}$ . In the fine-textured soils, however, the  $P_w$  at both FC and PWP was lowest at SOC contents of around  $30\text{g kg}^{-1}$  and the largest change occurred between  $40\text{-}60\text{ g kg}^{-1}$ . This means that PAW remained constant in sandy and increased in fine-textured soils because the differences in increases between FC and PWP were offset by a concurrent decrease in  $D_b$ .

Increases in SOC can be achieved by adding organic matter (as manure, plant residues or sewage sludge) to the soil and positive effects of organic amendments on WHC have been reported by Khaleel et al. (1981) and Haynes and Naidu (1998). Similar to the results obtained from Rawls et al. (2003), Khaleel et al. (1981) found that the relative increase in WHC became smaller as the amount of organic matter from amendments increased. WHC increased at both FC and PWP with organic waste amendments, but the relative increases varied with soil texture. Fine-textured soils showed a greater increase in WHC at FC than at PWP, whereas for coarse-textured soils, a larger increase in WHC was observed at PWP. Importantly, if an increase in SOC causes an increase in moisture content at both FC and PWP, the net result on PAW may not be greatly affected since PAW is defined as the difference between moisture content at FC and PWP. Furthermore, the decrease in  $D_b$  in the waste-incorporated soil tended to counterbalance any increase in PAW on a weight basis. The observations by Khaleel et al. (1981) agree with the findings by Haynes and Naidu (1998), who noted that since WHC of soils is generally increased by additions of organic waste at both FC and PWP, PAW is often not greatly affected. However, they differentiated between different processes affecting WHC after SOC amendments at high (PWP) versus low (FC) tensions. An increase in WHC due to SOC amendments at FC was attributed to an increased number of small pores. At PWP, on the other hand, the soil moisture content is determined by surface area and thickness of water films and addition of SOC would increase the specific surface area, resulting in increased WHC at higher tensions. However, the positive effect of organic amendments on WHC is not without contention as, for example, Gupta (1977) reported no significant changes in PAW after application of sewage sludge to a sandy soil. By comparison, large and positive effects of organic amendments on PAW were reported by de Silva et al. (2003), who found that after 16 months of repeated incorporations of both FYM and municipal waste compost (MWC) at  $50\text{t ha}^{-1}$ , PAW doubled compared to an unamended soil. MWC proved to be better in conserving soil water than FYM for sandy soils; however, over the 16 months of the experiments, they observed a high variability in SOC contents due to the dynamics between addition of amendments, breakdown of organic matter and translocation to deeper depths and accordingly, the positive results on PAW became apparent only after 12 months.

Mapa and de Silva (1994) achieved comparable results: They investigated the effects of adding FYM, rice straw or green manure on soil water content of sandy soils. After the first month, the highest increase in PAW was observed with FYM (10,000 kg ha<sup>-1</sup>) and the lowest increase occurred under straw. However, after three months, straw and green manure showed increases in PAW whereas the effect of FYM treatments declined (Fig. 27). This was attributed to the low C/N ratio of FYM (10.5), resulting in a faster decomposition rate compared with green manure (intermediate C/N ratio: 13.4) and straw (highest C/N ratio: 15.3). However, the range of C/N ratios is rather narrow and it is uncertain whether the small changes in the ratios or a difference in organic composition (e.g. greater lignin concentration) were responsible for the observed trends. SOC increased after one month for all treatments but showed greatest decline for FYM and least for straw after three months. Thus, positive relationships between SOC and available water could only be established for the first month but were not maintained for three months. Based on the data from these experiments, the authors concluded that it was not possible to verify a consistently positive relationship.

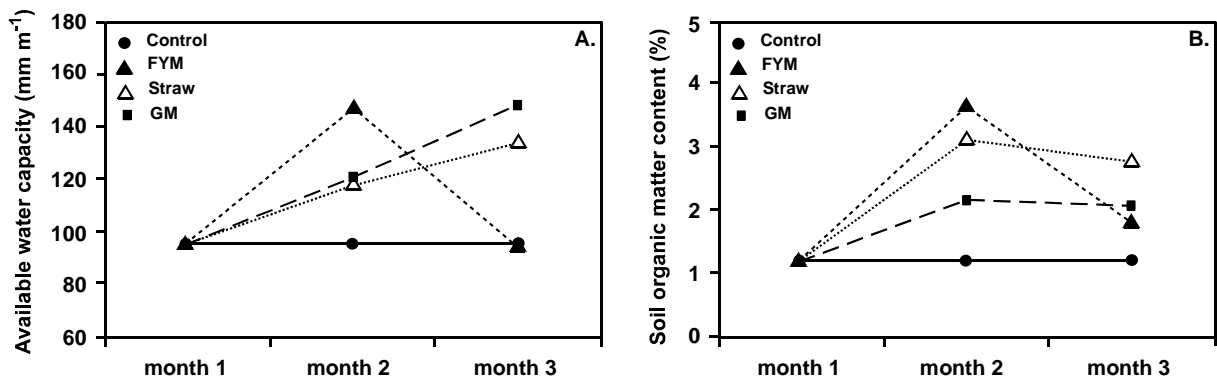


Figure 27: Changes in available water capacity (A.) and SOM (B.) after organic amendments with farmyard manure (FYM), straw and green manure (GM) over a three month period (data from Mapa and de Silva, 1994).

### Summary

- Most studies show a positive relationship between increase in WHC and increase in SOC; however, the fact that some studies show little or no effect suggests that SOC threshold values and/or specific SOC components are required for WHC to be increased.
- The effect of SOC on SWR tended to be greater in coarse textured compared with fine textured soils; in fact, SWR in heavy clay soils decreased with increasing SOC content.
- There is a strong relationship between clay content, SOC content and WHC and it is likely that these factors influence each other synergistically.
- Low initial SOC content resulted in decreased effects on WHC capacity compared with higher initial SOC contents, suggesting that a lower threshold value exists for SOC content.
- It is important to note that if an increase in SOC causes an increase in moisture content at both FC and PWP, the net result on PAW may not be greatly affected since PAW is defined as the difference between moisture content at FC and PWP.

## Soil Colour

Soil colour is often used as the highest categorical level in many soil classification systems, e.g. the concept of the Russian chernozem was centered around the thick dark soils of the Russian steppe and the Mollisol order of the US soil taxonomy is specifically defined to include most soils with relatively thick, dark surface horizons (Schulze et al., 1993). Generally good soil conditions are associated with dark brown colours near the soil surface, which is associated with relatively high organic matter levels, good soil aggregation and high nutrient levels (Peveerill et al. 1999). Schulze et al. (1993) found that within similar landscapes and soil texture classes, there was a good linear correlation between Munsell soil colour and SOM for Ap horizons from Indiana and Illinois (Fig. 28).

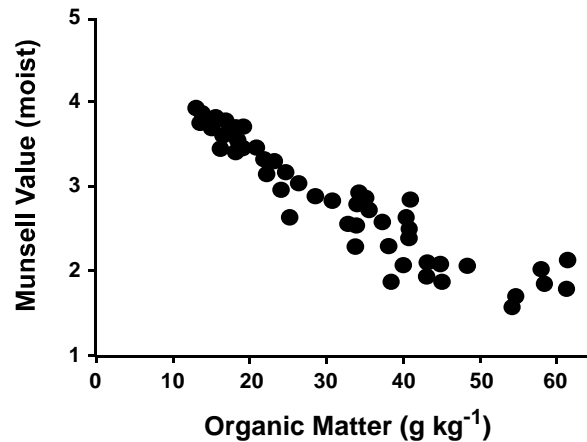


Figure 28: Relationship between Munsell value (moist) and soil organic matter content for Ap horizons from different landscapes from similar parent materials (loess) (modified from Schulze et al., 1993).

The effect of usually dark brown or black SOM on soil colour is important not only for soil classification purposes, but also for ensuring good thermal properties, which in turn contribute to soil warming and promote biological processes (Baldock and Nelson, 1999). Only about 10% of the solar energy reaching the earth's surface is actually absorbed by the soil, which can be in turn used to warm the soil. Naturally, dark-coloured soils absorb more energy than light-coloured ones. However, this does not imply that dark-coloured soils are always warmer: since dark-coloured soils usually have a higher amount of organic matter, which holds comparatively larger amounts of water, a greater amount of energy is required to warm darker soils than lighter-coloured ones (Brady, 1990). Thus, the thermal property of soil is to a large degree influenced by

water content,  $D_b$ , soil texture (fine versus coarse) and soil colour. In addition, the surface cover of soil affects the heat transfer in and out of a soil, as bare soils warm up and cool off more quickly than those with a vegetation or mulch cover. For example, Sharratt and Flerchinger (1995) investigated the effect of straw colour treatments (black, white and natural colour) on surface temperature, thaw depth and latent, sensible and soil heat flux over a two-year-period. They found that with the black straw cover daily soil temperatures at 0.05 m, soil surface heat flux and thaw depth were 0.5°C, 0.5MJ m<sup>-2</sup>, and 10 mm greater compared with the other treatments. Simulations from an atmosphere-snow-straw-soil system model showed that straw colour did not influence the proportion of absorbed radiation utilised in latent heat flux, but black straw treatment had the greatest percentage of net radiation allocated to sensible heat flux. The additional energy absorbed by the soil-black straw surface, however, was largely dissipated through sensible heat loss. Thus, Sharratt and Flerchinger (1995) concluded that only a small gain in soil heat was achieved by the black straw treatment. The results from these studies can be likened to the effect of burning and the generation of charcoal on soil colour. Ketterings and Bigham (2000) proposed a correlation between fire severity, burned soil colour and soil fertility and investigated the effect of fires of different severity (temperature and duration) on soil colour. They found that Munsell colour and chroma decreased with increasing heat severity and that at temperatures >600°C, much of the surface carbon was depleted and the soil was reddened. By comparison, lightly burned areas (short exposure at 100-250°C) were characterised by incompletely combusted material and blackened soil. In laboratory experiments, Ketterings and Bigham (2000) studied the effects of duration of exposure at different temperatures on soil colour and found that samples rapidly darkened (lower Munsell value) with heating time at 300°C but became lighter at 600°C (Fig. 29). The results from this study highlight the importance of soil chemistry on soil colour: Soils with similar SOC contents may have very different colours (specifically hues) if their respective proportion of charcoal differs.

Konen et al. (2003) investigated 130 Ap horizons to quantify the relationship between soil colour SOC content and particle sizes. As already reported in several other studies (e.g. Hassink, 1997; Hassink et al., 1997) they found good linear relationships between % clay and % sand and SOC contents. Significant relationships were also observed for SOC concentrations and the percentage of reflectance, Munsell value and soil chroma (Fig. 30). However, as observed by Schulze et al. (1993), it was found that unique relationships exist for different soil landscapes as differences in mineralogy, texture and organic carbon composition are likely to cause differences in soil



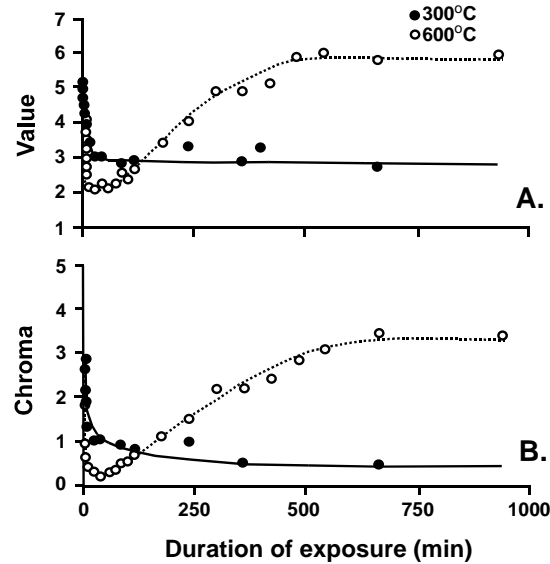


Figure 29: Effect of static heat exposure over time of soil samples (Hapludox, under secondary forest) on Munsell value (a) and Munsell chroma (b) (modified from Ketterings and Bigham, 2000).

colour parameters. Despite these differences between soil types and position in the landscapes, the studies by Konen et al. (2003) and Schulze et al. (1993) confirm that a consistent relationship exists between SOC content and soil colour. Thus, the influence of organic matter on thermal properties of soils may not only be affected by its colour but by other soil organic properties as well (e.g. bulk density, structure). For example, Abu-Hamdeh and Reeder (2000) investigated thermal conductivity as a function of texture, moisture content, salt concentration and organic matter.

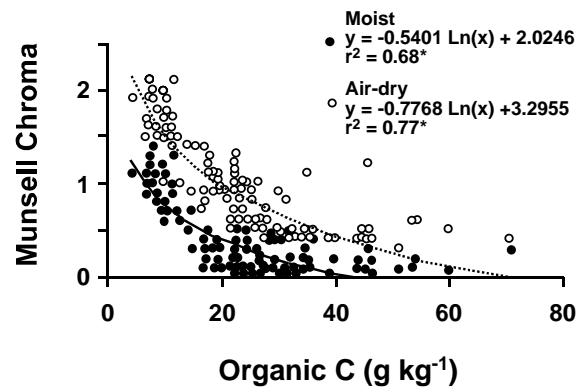


Figure 30: Organic carbon and Munsell chroma meter relationships for moist and air-dry soil samples of different soil types from Iowa (redrawn from Konen et al., 2003).

Laboratory experiments were carried out on sieved and repacked soils of different textures (sand, sandy loam, loam, clay loam). Thermal conductivity was generally greater in sandy compared with clayey soils and the addition of salts (at a given moisture content) decreased thermal conductivity. Interestingly, when organic matter was increased by the addition of peat moss, thermal conductivity decreased notably (Fig. 31).

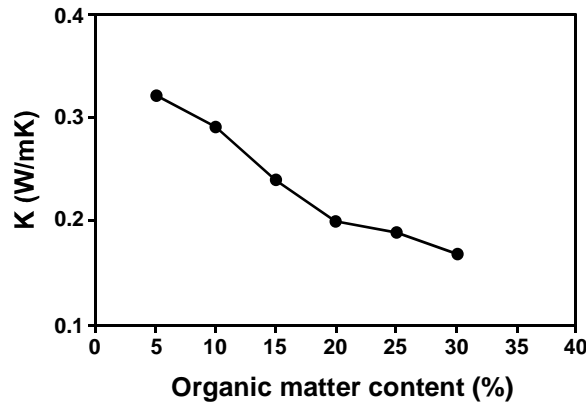


Figure 31: Soil thermal conductivity of clay loam as a function of organic matter content (as peat moss addition) (redrawn from Abu-Hamdeh and Reeder, 2000).

Finally, soil colour is used as a parameter for Landsat studies and to predict soil properties (e.g. Post et al., 1994; Bishop and McBratney, 2001). Post et al. (1994), in fact, noted that colour characteristics of sparsely vegetated landscapes were more strongly correlated with Landsat digital numbers compared to particle size, slope and vegetation.

#### Summary

- A good linear correlation exists between soil colour and SOC content
- While dark-coloured soils absorb more energy than light-coloured soils, dark-coloured soils are not always warmer.
- Dark-coloured soils with a higher amount of organic matter hold comparatively larger amounts of water, which require a greater amount of energy for heating.
- The thermal property of soil is largely influenced by a combination of water content,  $D_b$ , soil texture (fine versus coarse) and soil colour.

## Chemical Functions

### Cation Exchange Capacity

Cation exchange capacity (CEC) is defined as the measure of the total capacity of a soil to hold exchangeable cations and indicates the negative charge present per unit mass of soil (Peeverill et al., 1999). A high CEC is regarded as favourable as it contributes to the capacity of soils to retain plant nutrient cations. CEC is most commonly expressed as centimols of positive charge per kilogram of soil ( $\text{cmol}_c/\text{kg}$ ), which provides values that are numerically equivalent to the previous conventional unit of  $\text{mequiv.}/100\text{g}$ . Soils can have permanent and variable charge. Permanent charge is derived from certain clay minerals (e.g. smectite) when Mg is replaced by Al or Si is replaced by Al. The strength of variable charge (provided by clay minerals and organic matter) depends on ionic strength and pH and is therefore influenced by the chemical environment of the soil (Fig. 32).

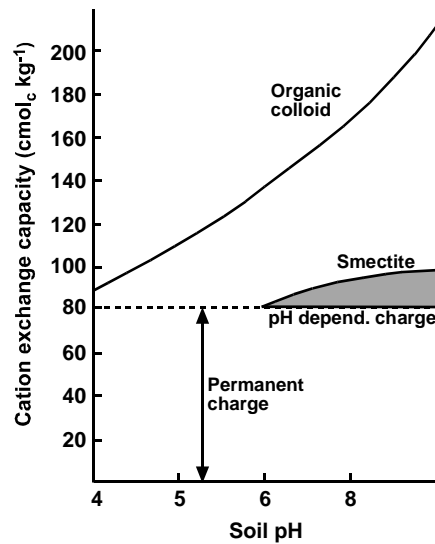


Figure 32: Influence of pH on CEC of smectite and SOM. Below pH 6 the charge for clay minerals is relatively constant (permanent CEC charge); above pH 6, contribution of the variable charge from clay minerals is evident (ionisation of  $\text{H}^+$  from hydroxy groups). By comparison, almost all of the charges on the organic colloid are considered to be pH dependent, i.e. variable charge (modified from Brady 1990).

Several different methods exist to measure CEC and it is important to bear in mind the factors influencing CEC (e.g. pH and ionic strength) and degree of variable and permanent charge when choosing a particular method together with the pre-treatment required. For example, if soluble

salts are not removed during pre-treatment, the cations obtained are extractable rather than exchangeable cations, which is likely to exceed the actual CEC value (Peveerill et al., 1999).

Table 2 provides a summary of common methods used for measuring cation exchange capacity (modified from Peveerill et al. (1999)).

	Method	Reference
Non-calcareous soils, permanent charge	Exchange with 1M NH <sub>4</sub> Cl, pH 7	Rayment and Higginson (1992)
Calcareous soils, permanent charge	Exchange with 1M NH <sub>4</sub> COOCH <sub>3</sub> , pH 7	Blakemore et al. (1987)
	Exchange with 1M NH <sub>4</sub> Cl, pH 8.5	Rayment and Higginson (1992)
	Exchange with 1M (OHC <sub>2</sub> H <sub>4</sub> )(CH <sub>3</sub> ) <sub>3</sub> NCl	Tucker (1985)
Variable charge soils	Compulsive exchange with BaCl <sub>2</sub> /NH <sub>4</sub> Cl	Gillman and Sumpter (1986); Rayment and Higginson (1992)
	Exchange with 0.01M silver thiourea	Blakemore et al. (1987); Rayment and Higginson (1992); Oorts et al. (2003)
Exchange acidity determination	Exchange with 0.01M KCl	Rayment and Higginson (1992)
	Exchange with BaCl <sub>2</sub> in triethanolamine at pH 8.2 and acid titration of excess triethanolamine	Blakemore et al. (1987); Rayment and Higginson (1992)
Removal of soluble salts	Pre-treatment with a solvent	Tucker (1985); Rayment and Higginson (1992)

Table 2: Common methods used for measuring CEC (modified from Peveerill et al., 1999).

As pointed out by Tan and Dowling (1984) it is important to distinguish between permanent (CEC<sub>p</sub>) and a pH-dependent variable charge (CEC<sub>v</sub>), as it illustrates the contribution of SOM and minerals to soil CEC. Most soils carry both types of charges, which can be seen by the common observation that soil CEC tends to increase with increasing pH, and what is considered the total CEC (CEC<sub>t</sub>) is the one measured at pH 8.2. CEC<sub>p</sub> is considered to be derived from the clay fraction and other mineralogical components (e.g. amorphous oxides) while CEC<sub>v</sub> is regarded to be derived from soil humus and accordingly, the presence of organic matter generally causes the CEC in variable-charge clay soils to be greater. However, some components of SOM are known to be of greater importance in contributing to CEC<sub>v</sub> than others.

Functional groups of SOM have been associated with an increase in CEC<sub>v</sub> (Oades et al., 1989). The importance of the contribution of soil organic matter components to CEC<sub>v</sub> as well as CEC<sub>t</sub> has been highlighted by several studies. For example, Oades et al. (1989) observed a decline of CEC with soil depth along with a decline in SOM but unchanged clay content and composition. Based on further studies, they described the relationship between CEC<sub>v</sub> and organic carbon:

$$CEC_v = 1.32 + 1.09 \text{ SOC } (r^2 = 0.76),$$

which means that a 1% increase in SOC leads to 1 unit ( $\text{cmol}_c \text{ kg}^{-1}$ ) of increase in CEC in variable charge soils. The effect of SOM on the point-of-zero charge ( $\text{pH}_0$ ) of the soil variable-charge component is considered the most important aspect in increasing  $\text{CEC}_v$  (Fig. 33).

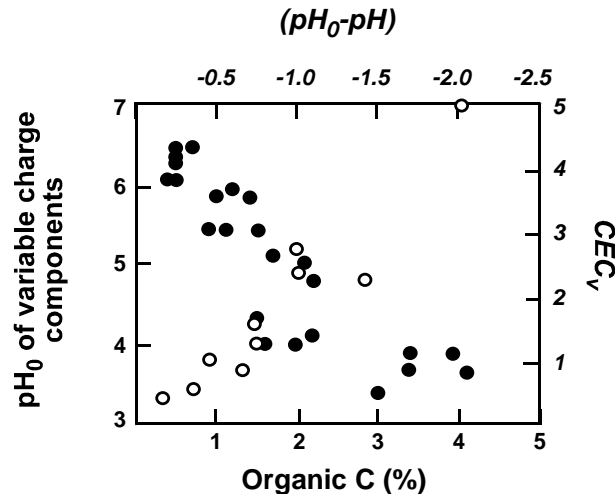


Figure 33: Relationship between  $\text{pH}_0$  and SOC content (filled circles) and increase in CEC of variable charge components ( $\text{CEC}_v$ ) with increasing negativity ( $\text{pH}_0 - \text{pH}$ ) (open circles) in Oxisols under virgin rainforest from northern Queensland (modified from McBride, 1994).

The point-of-zero charge is defined as the pH value where the number of protonated and deprotonated sites is equal, and higher levels of SOM result in a lowering of the zero point. Therefore, the greater the difference between soil pH and  $\text{pH}_0$ , the greater the net surface charge will be on variable charge components, and if  $\text{pH}_0 - \text{pH}$  is  $< 0$  the net charge is negative.

Organic matter itself generally has a low  $\text{pH}_0$ , which is due to the presence of carboxyl groups (Oades et al., 1989) and here the high molecular weight (HMW) fraction contributes less to CEC ( $c. 170 \text{ cmol}_c \text{ kg}^{-1}$ ) compared with the low molecular weight (LMW) fraction ( $c. 500 \text{ cmol}_c \text{ kg}^{-1}$ ) (Wolf and Snyder, 2003). Because permanent charge is generally only 1-2  $\text{cmol}_c \text{ kg}^{-1}$ , Oades et al. (1989) recommended that it is important to maximise the variable charge by maintaining the highest possible SOC contents. The effect of SOM on the point-of-zero charge was also noted by Gillman (1985), who found that  $\text{pH}_0$  decreased by 1 pH unit for each 1% increase in organic C, which would equate to 17  $\text{t ha}^{-1}$  of SOM in the 0-10 cm (assuming  $\text{SOM} = 1.7 \times \text{organic carbon}$ ). Furthermore, the importance of SOM to CEC increases as soils weather and change from 2:1

aluminosilicates (CEC = 15-30  $\text{cmol}_c \text{ kg}^{-1}$  soil) to kaolinite and amorphous oxides of Fe and Al (CEC =  $<5 \text{ cmol}_c \text{ kg}^{-1}$  soil). In fact, most of the CEC in kaolinitic soils is associated with SOM and maintaining high SOM levels is especially important in tropical and sandy soils (Duxbury et al., 1989). Based on statistical analyses, Parfitt et al. (1995) estimated CECs for a variety of components, which illustrates the dependence of SOM to CEC in highly weathered soils: 221  $\text{cmol}_c \text{ kg}^{-1}$  for OC, 70-110  $\text{cmol}_c \text{ kg}^{-1}$  for smectite, 50  $\text{cmol}_c \text{ kg}^{-1}$  for allophane, 25  $\text{cmol}_c \text{ kg}^{-1}$  for chlorite, illite and vermiculite and 10  $\text{cmol}_c \text{ kg}^{-1}$  for kaolinite. The relationship between effective CEC (ECEC = CEC at field pH) and SOM in krasnozems (Oxisols) was investigated by Moody (1994). He found that in these soils, which were characterised by relatively low ECEC values (2-20  $\text{cmol}_c \text{ kg}^{-1}$ ), SOM accounted for as much as 70% of the ECEC in the 0-10 cm soil.

It is apparent from the cited studies that organic matter is usually associated with a variable charge while clay minerals are assumed to have both constant and variable charges. Emerson and McGary (2003) aimed to further distinguish the charge carried by organic matter. They found that organic matter in a sodic Hydrosol under native trees consisted of a proportion of uncharged organic matter ( $\%C_o$ ), which did not change with depth, and a negatively charged proportion, which linearly decreased with depth (30 cm) and SOC content. In the top 5 cm,  $\%C_o$  accounted for 40% of the SOC present. Emerson and McGary (2003) hypothesised that the main portion of negatively charged SOC was derived from the lignified portion of feeder roots and that  $\%C_o$  is from highly lignified portions of main roots. By comparison, the negatively charged SOC under a cane field remained constant with depth (30 cm), which was attributed to aryl carboxylic groups from incompletely burnt cane residues.

While charge development in SOM is predominantly negative, as it is provided by functional groups (mainly carboxylic and phenolic acids), positive charge can occur through the protonation of amino groups but this is considered to be relatively small (Duxbury et al., 1989). The contribution of SOM to CEC can vary between 25-90% (Stevenson, 1994), depending on soil type, but most studies observed a contribution between 30-60% (Tsutsuki, 1993; Loveland and Webb, 2003), 40-50%, respectively (Thompson et al., 1989; Haynes and Naidu, 1998). Accordingly, there is generally a good correlation between SOC and CEC and McGrath et al. (1988) noted that the CEC of a sandy soil increased from 75 to 158  $\text{cmol}_c \text{ kg}^{-1}$  as SOC increased from 0.46 to 1.39%. Eshetu et al. (2004) also noted that in forest soils of the Philippines, there was a strong linear correlation between total CEC, SOC content and exchangeable and total Ca and that SOC content accounted for most of the variability:

$$\text{CEC} = 144 + 18.3 \times \text{SOC} \quad (R^2 = 0.93^{**}).$$

They further noted that SOC concentrations > 2% increased the CEC of surface soils by up to 4 times compared with mineral soil with SOC concentrations < 2%. Furthermore, at SOC contents < 2%, there was no measurable effect on CEC and they suggest that 2% could indicate a minimum threshold value. Parfitt et al. (1995) found in their studies that most of the soil CEC was due to organic matter (carboxyl groups) and, furthermore, that the presence of SOC reduced the CEC of smectite: 1% of SOC reduced the CEC of smectite by about 5.5 cmol<sub>c</sub>/kg. Loveland and Webb (2003) reported that CEC values for agricultural soils can range from 2-50 cmol<sub>c</sub> kg<sup>-1</sup>, and values of around <4 cmol<sub>c</sub> kg<sup>-1</sup> are common in sandy soils. By comparison, the amount of CEC from SOM components is commonly around 150-250 cmol<sub>c</sub>kg<sup>-1</sup> (Wolf and Snyder, 2003) and Addiscott (1970) found that for arable, calcareous soils with SOC contents between 0.8-2.3%, the CEC from SOM was 230±47 cmol<sub>c</sub> kg<sup>-1</sup>. Similarly, Helling et al. (1964) found that SOM contributed 180 cmol<sub>c</sub> kg<sup>-1</sup> organic matter at pH 5 and 350 cmol<sub>c</sub> kg<sup>-1</sup> organic matter at pH 8.2 and that one pH unit change altered CEC by 30 cmol<sub>c</sub> kg<sup>-1</sup> organic matter. However, the CEC of organic matter itself is much higher as reported by Duxbury et al. (1989), who found that average values for total acidity of extracted humic substances were between 700-1000 cmol<sub>c</sub> kg<sup>-1</sup> organic matter and Bloom (1999) obtained a mean CEC value for SOM of 2000 cmol<sub>c</sub> kg<sup>-1</sup> (n=60, pH 8). The reason that such high values are usually not expressed in soils is due to the partial blocking of negatively charged sites by Al and Fe (particularly in Oxisols). However, the significant contribution of SOM to CEC is not without contention as Martel et al. (1978) reported that in 11 clay soils with an average SOC content of 3.1%, organic carbon contributed only 10-15% to the total CEC.

A commonly used technique to assess the effect of organic matter on CEC<sub>p</sub> and CEC<sub>v</sub> is by the destruction of SOC by H<sub>2</sub>O<sub>2</sub> oxidation. Clark and Nichols (1968) showed that removal of organic matter by H<sub>2</sub>O<sub>2</sub> oxidation could be used in estimating the amount of organic (pH dependent) CEC in soils with spodic and non-spodic horizons. While it was considered possible that oxalates were produced during the oxidation procedure, only negligible amounts of oxalates were detected. The CEC (at pH 7) after H<sub>2</sub>O<sub>2</sub> oxidation decreased in all samples and the difference in CEC (ΔCEC) before and after removal of organic matter was well correlated with organic matter content (Fig. 34).

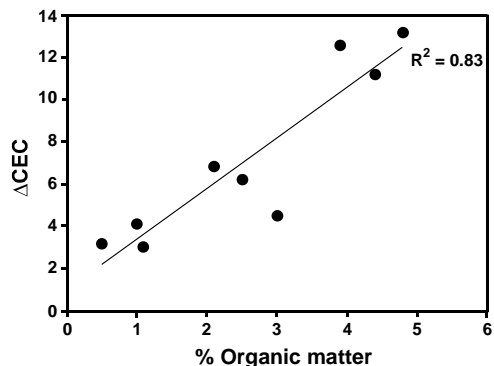


Figure 34: Relationship between  $\Delta\text{CEC}$  and SOM (data from Clark and Nichols (1968)).

They equated  $\Delta\text{CEC}$  with the organic, pH-dependent CEC and noted that soils with a  $\text{pH} < 5.4$  showed a better correlation between SOM content and  $\Delta\text{CEC}$  compared with the total CEC at  $\text{pH} 7$ . Clark and Nichols (1968) explained that, due to the relatively high clay content of the studied soils, a large proportion of the pH-dependent CEC may have been derived from clay exchange sites that were blocked by hydrous oxides of Al. The effect of  $\text{H}_2\text{O}_2$  oxidation on CEC values as a function of organic matter and type of soil horizon (spodic versus non-spodic) is summarised in Figure 35.

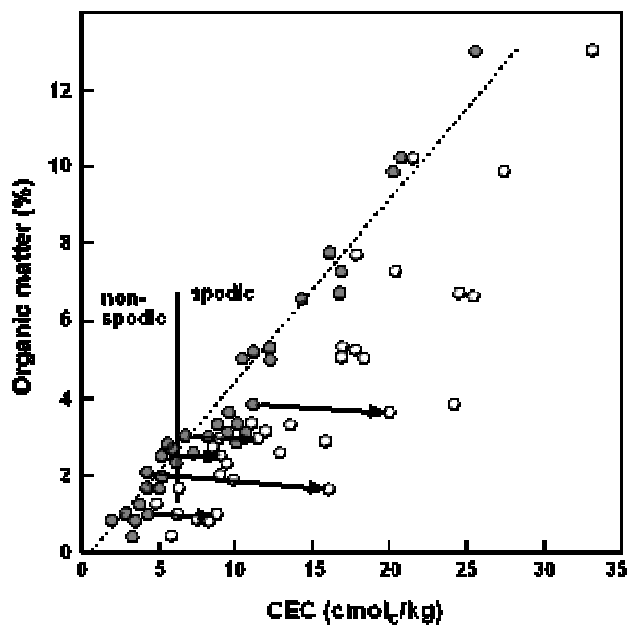


Figure 35: Relationship between total  $\text{pH} 7$  and organic pH-dependent CEC and the organic matter content of B horizon samples. Closed symbols represent organic pH-dependent CEC and open symbols represent total  $\text{pH} 7$  CEC values. Arrow indicate the effect of oxidation on CEC values of selected samples (modified from Clark and Nichols, 1968).



Tan and Dowling (1984) studied five soils with very different clay content (46.4 to 4.8%), SOC content (1.7 to 0.12%), pH (5.3 to 7.95) and mineralogy (kaolinite, vermiculite, illite, montmorillonite). Their results showed that the lowest  $CEC_p$  values were in kaolinitic soils with low SOC contents (Ultisols) and the highest  $CEC_p$  values were from soils dominated by montmorillonite clay (Houston black Vertisol). This is in accord with other studies that show that montmorillonitic clay has a higher permanent charge compared with soils with a mixed mineralogy. Interestingly, after the removal of SOC by  $H_2O_2$ ,  $CEC_p$  values increased in the Vertisol, suggesting that the permanent charges of the clay had been partially blocked by SOM. Thus, in montmorillonitic soils SOM and clay tend to be in competition for available exchange sites. On the other hand, SOC removal from soils with a mixed mineralogy, decreased  $CEC_p$ , which suggests that SOC and clay had a synergistic effect as reflected by the higher  $CEC_p$  values when SOM was present. In kaolinitic soils, there was no observable effect of SOM or OM-clay interactions on  $CEC_p$ . The overall contribution of  $CEC_v$  to  $CEC_t$  was high (40-50% in almost all soils) and was 70% in Ultisols and 68% in Vertisols. However, not all of the  $CEC_v$  could be attributed to OM, and Tan and Dowling (1984) suggested that of greater importance than SOM alone was the interaction between organic and inorganic components, which provided sites for both  $CEC_{p\text{ and }v}$  and was controlled by soil mineralogy.

Interpretation and comparison of data of variable charge CECs from different studies is difficult, because of its dependence on pH, especially if the field pH is far removed from the measurement pH. For example, Lopes and Cox (1977) investigated the effect of pH and SOM content on the ECEC values of Oxisols from Brazil. They reported that if the soil pH was  $<5.5$ , there was no significant relation between ECEC and SOM content but at  $pH >5.5$ , ECEC increased markedly with increasing SOM (Fig. 36). This pH dependence, particularly in Oxisols, is most likely related to blockage of exchange sites by Fe and Al at more acidic pH values or due to protons being strongly held at low pH.

While this study emphasised the effect of pH in achieving a greater number of negative sites due to dissociation of carboxyl and phenolic groups, it also highlights the importance of liming to increase CEC. In fact, Oades et al. (1989) noted that too much addition of organic residues could result in acidification due to increased nitrification of N and addition of lime would be required to maintain a steady-state saturated CEC.

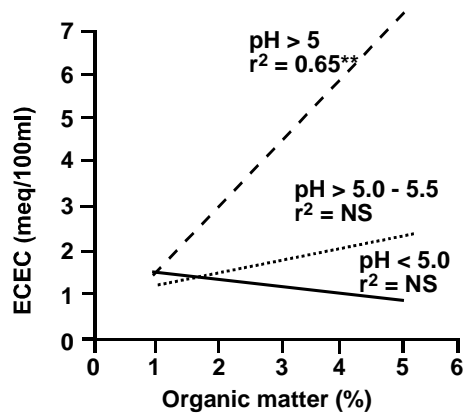


Figure 36: ECEC as a function of organic matter at various ranges of pH values. Relationships were not significant at pH <5; at pH>5, the influence of organic matter was significant (modified from Lopes and Cox, 1977).

To form functional relationships between different measures of CEC, it is important to understand how CEC of organic and mineral components change with pH. Furthermore, the pH dependence of CEC is also important to assess the buffer capacity of soils as within a pH range of 5-8, the pH buffering in non-calcareous soils is mainly due to CEC reactions (functional groups acting as sinks for  $H^+$  and  $OH^-$ ) (Curtin et al., 1996). Therefore, a differentiation of CEC into organic and mineral fractions is necessary because organic and mineral sites differ in their affinity for cations, as SOM shows a strong selectivity for divalent cations over Na and for Ca over Mg compared with clay (Curtin et al., 1998). Curtin and Rostad (1997) suggested that a mathematical expression was needed to describe the relationship between CEC and ECEC. They analysed a large ( $n = 1622$ ) dataset, from which they developed a relationship to estimate CEC as a function of pH. A regression equation with SOC and clay as independent variables explained 86% of the variability in CEC at pH 8.2 (BaCl<sub>2</sub> as buffer) and estimated the CEC of organic matter (assumed to be 58% C) and clay at 213  $cmol_c kg^{-1}$  and 51  $cmol_c kg^{-1}$ , respectively (at pH 8.2):

$$\text{buffered CEC (} cmol_c kg^{-1} \text{)} = 23 + 368 \text{ SOC } kg^{-kg} + 51 \text{ clay } kg^{-kg} \text{ (} R^2 = 0.861 \text{)}.$$

The intercept (23  $cmol_c kg^{-1}$ ) is the value of CEC if clay and organic matter were equal to zero. Curtin and Rostad (1997) noted that the buffered CEC could not be fully accounted for by clay and SOM alone (large intercept at 23) and they attributed the difference to the presence of layer silicates in the silt fraction. They concluded that contribution to the buffered CEC from clay was 60%, 25% from SOM and 15% from silt:

$$\text{buffered CEC (} cmol_c kg^{-1} \text{)} = 18 + 362 \text{ SOC} + 51 \text{ clay} + 3 \text{ silt (} R^2 = 0.863 \text{)}.$$

They further established a function to describe ECEC, based on the assumption that ECEC of SOM and clay increase linearly as pH increases to 8.2, when SOM and clay reach the respective values of 213 cmol<sub>c</sub> kg<sup>-1</sup> and 51 cmol<sub>c</sub> kg<sup>-1</sup> (R<sup>2</sup> = 0.86\*\*\*):

$$\text{ECEC} = a + [b_1 - (8.2 - \text{pH})b_2]\text{OC} + [b_3 - (8.2 - \text{pH})b_4]\text{clay},$$

where *a* is the intercept and *b*<sub>1</sub> and *b*<sub>3</sub> are buffered CECs (pH 8.2) of SOM and clay and *b*<sub>2</sub> and *b*<sub>4</sub> are amounts by which ECEC of SOM and clay change for a unit change in pH. Further analyses showed that the pH-dependency of the organic ECEC was higher than that of the mineral ECEC, which in turn is a measure of the buffer strength of SOM and clay.

The contribution of silt to CEC or ECEC was also noted by Asadu et al. (1997). They conducted a survey of several different soil types from sub-Saharan Africa and found that SOM content accounted for *c.* 60% of the mean ECEC, and clay, silt and SOM content together accounted for up to 72% of variability. However, there were differences in terms of topographic and climatic zones. In soils of non-humid, lowland humidic and mid-altitude zones, the contribution of silt to ECEC was greater than in subhumid, highland humidic and low altitude zones. Asadu et al. (1997) attributed the greater influence of silt to the formation of clay-OM complexes (OM bonding to smectite or kaolinite via cation bridging) which would reduce exchange sites for both the clay- and organic-associated CEC. They suggest that these processes would be partly influenced by climate and landscape position.

While several studies use clay content as a measure to assess CEC, the use of specific surface area (SSA) is often advocated as a better estimate of CEC and to study the effects of SOM on CEC. For example, Curtin and Smilie (1976) found that for a set of 51 soils with variable SOC contents (0.1-8.9%), clay contents (0.4-56%) and pH values (3.8-8.3), CEC was well correlated with SOC and specific surface area (SSA), accounting for 97% of variation in CEC. In comparison, clay content accounted for only 58% of variation and Curtin and Smilie (1976) suggested that SSA measurements were able to account for the presence of phyllosilicates in both the sand, and more importantly, the silt fraction of the soil. Accordingly, they advocate the use of SSA instead of clay content to estimate the inorganic component of soil CEC. In a more detailed study, Thompson et al. (1989) used particle size separation (20-50, 2-20, 0.2-2 and <0.2µm) to investigate the soil CEC, OC, SSA and SSA of peroxidised (PSSA) soil from paired sites that had undergone land use change (cultivation of native prairie and woodland). Multiple regression

analysis to evaluate the contribution of organic matter to soil CEC showed that of all fractions and horizons, 91% of variability in CEC and fractionated material could be explained by SOC content and PSSA. However, it was mainly the fine fraction that showed greatest dependence on PSSA and when excluded, 99% of the variability was explained by SOC content while PSSA and SOC alone accounted for 94% of variability, and the total contribution of SOC of all size fractions to CEC was  $559 \text{ cmol}_c \text{ kg}^{-1}$ .

$$\text{CEC} = 4.95 + 0.559 \text{ OC}^{***} + 0.259 \text{ PSSA}^{***},$$

where \*\*\* indicates significant at the 0.01 level.

Similarly, the non-peroxidised SSA was well correlated with organic carbon content and size fractions, except for the finest fraction, which was not well correlated with SOC. Excluding the data of the fine fraction resulted in a regression analysis of 99% (compared with 86% when fine fraction data were included):

$$\text{SSA} = -9.84 + 0.722 \text{ OC}^{**} + 1.371 \text{ PSSA}^{***},$$

where \*\*\* and \*\* indicate significant at the 0.01 and 0.05 level, respectively.

Overall, soil CEC and SOC content was greatest in the 0.2 and 0.2-2 $\mu\text{m}$  fraction, indicating that size, and probably type, of SOM influenced CEC. An estimate of the net contribution of SOC from the size separated material (<50 $\mu\text{m}$  fraction) to the soil CEC was greater (estimate of 49% from Least Squares Analysis (LSQ) and 54% from principal component analysis (PCA)) than the estimate for the whole soil (28% of total CEC). The authors suggested that organic colloids may coat the inorganic surfaces, resulting in the net CEC and SSA to be lower than what would be predicted if the organic and inorganic contributions were additive. With respect to the effect of land use and land use changes, the CECs of the cultivated and native forest site were more affected by SOM removal by peroxide treatment compared with the tall prairie site and the CECs of the 0.2-2 and 2-20 $\mu\text{m}$  fractions of the forest site were more affected by cultivation than the tall prairie sites (Fig. 37). The overall SSA was lower in the forest than in the prairie soils. These findings support the view that the source and chemistry of SOM influences its net contribution to CEC.

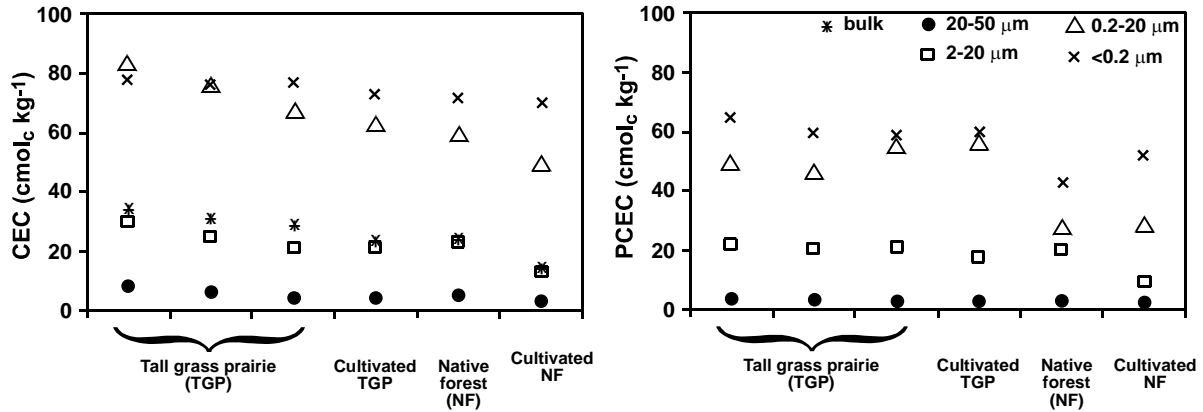


Fig. 37: Changes in CEC after peroxide treatment (PCEC) in native tall grass prairie, cultivated tall grass prairie, native deciduous forest and cultivated deciduous forest (data from Thompson et al., 1989).

However, it is important to consider the methodology used here before generalizing the results obtained from this study. Particle size separation was done by ultrasonic dispersion and sonification for 15 min at 140 W, separation at 50 μm was done by wet-sieving, separation at 20 and 2 μm was done by repeated sedimentation and siphoning, and separation at 0.2 μm was done by centrifugation and coagulation. As summarised in Krull et al. (2003), sonification may lead to breakdown and redistribution of particulate organic matter into silt and clay size fractions; therefore, the production of artefacts may be a possibility. Furthermore, CEC measurements were made at pH 7 but since CEC and to a certain degree SSA are pH dependent and sensitive to ionic strength variations, measurement of ECEC might have been more informative.

Leinweber et al. (1993) compared not only the effect of different size fractions on soil CEC but investigated also the type of organic material. They noted that CEC of different clay fractions (organo-mineral clay fraction <0.63 μm, coarse clay 0.63-2 μm, total clay <0.2 μm) were closely correlated with SOC concentrations in fertilised soil treatments and that all of these fractions, compared with whole soil samples, were enriched in n-alkanes/alkenes and N compounds as well as mono- and polysaccharides. Similar to the study by Thompson et al. (1989), they found that the largest CECs were associated with the organo-mineral clay fraction, which the authors attributed to the type of SOM associated with minerals. Regression equations showed that an increase in the C concentration by 1% resulted in an enhancement of the CEC by 3 cmol<sub>c</sub> kg<sup>-1</sup> (organo-mineral clay) and 6 cmol<sub>c</sub> kg<sup>-1</sup> (coarse clay). However, the correlation between SOC and the CEC of the fine clay fraction was lower ( $R^2 = 0.537^*$ ), compared with that of coarse clay ( $R^2 = 0.789^{***}$ ). They estimated that the contribution of organic carbon from the organo-mineral clay

fraction to CEC of the whole soil was 12-48% (organo-mineral clay:  $R^2 = 0.91^{***}$ ), 17-24% (coarse clay:  $R^2 = 0.601^{**}$ ) and 29-66% (total clay:  $R^2 = 0.803$ ). They concluded that the higher CEC values of the clay fraction were due to a) higher CEC of clay minerals, b) higher SOM conc, c) higher CEC of organic substances. Importantly, they showed that CECs increased over time with fertiliser application (NPK and FYM) in the organo-mineral clay fraction and that compost had the greatest effect on CEC over 34 years.

Kahle et al. (2002) took a different approach in that they investigated how good the prediction was for SOC with SSA and CEC as variables. They found that SSA and CEC of bulk soils after C removal by peroxide oxidation were better predictors for SOC than clay content as SSA explained 55% and CEC 54% of variation in C content. Carbon content was positively correlated with the increase in SSA after SOC removal ( $\Delta$ SSA) and Kahle et al. (2002) suggested that the part of the surface area that became accessible to  $N_2$  after SOC removal was the important part of SOC storage. This would imply that SOM tended to accumulate in fractions of smallest size and highest SSA. The fact that  $\Delta$ SSA and CEC of the C-free soil explained 90% of variability in C content was viewed as an indicator that C storage is controlled by the amount of cations adhering to mineral surfaces.

Caravaca et al. (1999) placed particular emphasis on the effect of the fine fractions (<2 and 2-20 $\mu$ m) on CEC. They studied cultivated and forest sites (top 20cm) in a semi-arid climate (250-300mm/yr MAP) in southeastern Spain. As observed in other studies, they found that the CEC of whole soil and fine fractions was closely correlated with the respective C contents and correlation coefficients between fractions and SOC content were highly significant ( $R^2 = 0.82^{***}$  for <2 $\mu$ m and  $R^2 = 0.97^{***}$  for 2-20 $\mu$ m). While around 11 cmol<sub>c</sub> kg<sup>-1</sup> of the total CEC was estimated to be derived from SOM and 9 cmol<sub>c</sub> kg<sup>-1</sup> were from mineral particles, it was the clay-sized fraction that had the highest CEC (27.1 cmol<sub>c</sub> kg<sup>-1</sup>, four times greater than that of the silt sized fraction), and both organic and inorganic sources contributed to this high CEC value. By comparison, the CEC of the silt fraction, which accounted for 2-65% of the total CEC, was almost exclusively due to SOM. Caravaca et al.'s (1999) data further showed that the contribution of the silt fraction to soil CEC was greater in calcareous soils compared with acidic soils, where the CEC of the clay fraction tended to be higher.

As shown previously, pH affects variable charge CEC and while most studies investigate only the effect on the whole soil fraction, Oorts et al. (2003) investigated the CEC in plots of different tree

species after 20 years to determine the contribution of different particle size fractions to CEC of soil, assess the CEC-pH relationship of SOM in different particle size fractions and to test the effect of biochemical composition of SOM inputs on CEC of SOM. They used the silver thiourea (AgTU) method to measure CEC, which allows CEC measurements at low ionic strength (0.01M) and at any desired pH. CEC was measured at 6 pH levels (3-7) and soil was fractionated into four size fractions (POC (250-53 $\mu$ m), coarse silt (53-20 $\mu$ m), fine silt (20-2 $\mu$ m) and clay (<2 $\mu$ m)). They found that the CEC of size fractions increased with decreasing particle size and that the clay and fine silt fractions were responsible for 76-90% of the soil CEC at pH 5.8 with fine silt being the most important fraction (at pH 5.8: 35-50% contribution). Differences in CEC between treatments for whole soil and fractions could be mostly explained by C derived pH-dependent charge. The contribution of CEC from these different fractions at pH 5.8 varied between 283  $\text{cmol}_c \text{ kg}^{-1} \text{ C}$  for POC and 563  $\text{cmol}_c \text{ kg}^{-1} \text{ C}$  for fine silt fraction and CEC of SOM at pH 5.8 was around 400  $\text{cmol}_c \text{ kg}^{-1} \text{ C}$ :

Based on these relationships, CEC could be estimated from SOC content alone

$$\text{CEC} = 0.15 + 0.43\text{C} \text{ (g/kg)} \text{ (r}^2\text{=0.77)},$$

or from SOC and pH together:

$$\text{CEC} = -6.97 + 1.25 \text{ pH} + 0.41\text{C} \text{ (g/kg)} \text{ (r}^2\text{=0.87)}.$$

However, clay content failed to explain any additional significant variation. The silt fraction was seen as the most important fraction as it determined the differences between whole soil samples (Fig. 38), whereas the clay fraction was the only fraction where the mineral component seemed to have significant input to CEC, and SOM explained only 8% of the variation. By comparison, in the fine silt fraction, pH explained only 24% and C and pH together accounted for 95% of the variability.

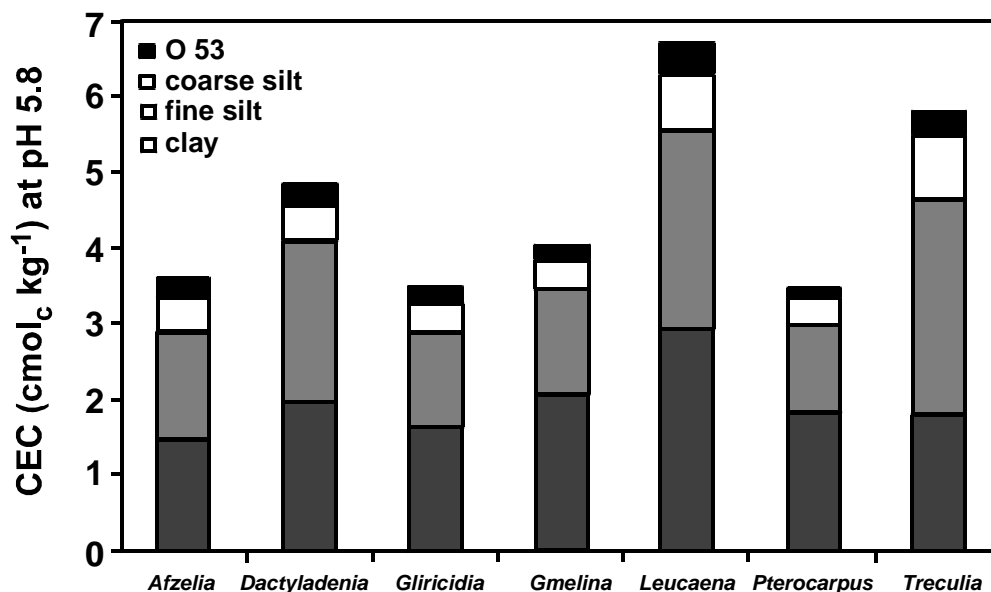


Figure 38: Contribution of the different fractions to the soil CEC at pH 5.8 for different tree species. O 53 indicates the POC fraction (modified from Oorts et al., 2003).

Although no effect of SOM composition to organic inputs to CEC was observed, Oorts et al. (2003) found that the carbon content of the whole soil and fractions was positively correlated with concentrations of polyphenolics and negatively correlated with cellulose.

The effect of different organic amendments on soil CEC was investigated by Haynes and Naidu (1998). They noted that after 90 years, the plots that received annual applications of NPK fertilisers had an 11% higher SOC content, and FYM amendments caused a 30% increase, compared with control plots. As a result of the higher SOC content, the plots also had a greater CEC compared with the control site, with SOM derived from NPK application having a CEC of 560 cmol<sub>c</sub>kg<sup>-1</sup> and SOM derived from FYM having a CEC of 381 cmol<sub>c</sub>kg<sup>-1</sup>. The reason for the increased CEC of SOM derived from NPK fertilisation was proposed to be due to a greater proportion of aromatic compounds from the SOM returned by crops compared with the FYM treatment.

The effect of two different management systems for sugar cane production, 6-9 years after their implementation, on CEC and ECEC was investigated by Noble et al. (2003). The two management systems included a long-term green trash blanketed (GCTB)/burn trial and a rotation experiment including long-term continuous GCTB, grass ley and bare fallow. They found that



SOC levels increased under GCTB compared with the burnt trial by 4 t ha<sup>-1</sup>, but the greatest increase was under grass ley with 9 t ha<sup>-1</sup> compared with continuous cane. Accordingly, CEC at pH 5.5 increased under GCTB by 0.67 cmol<sub>c</sub>kg<sup>-1</sup> and by 0.75 cmol<sub>c</sub>kg<sup>-1</sup> under grass ley, compared with the burnt trial and continuous cane (0-10cm). Furthermore, they noted a positive relationship between both CEC at pH 5.5 and pH buffer capacity and SOC content (Fig. 39).

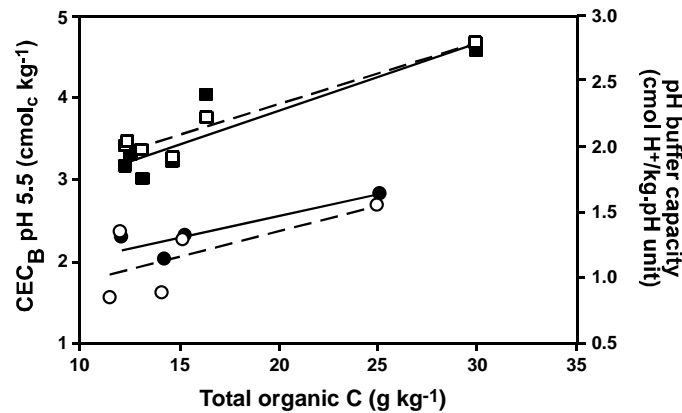


Fig. 39: Relationship between pH buffer capacity (filled symbols) and CEC<sub>B</sub> (base cation exchange capacity) at pH 5 (open symbols) and SOC content; squares = GCTB/burnt trial, circles = rotation trial (modified from Noble et al., 2003).

When ECEC was compared with CEC, Noble et al. (2003) noted that 9-31% of the cations measured were not associated with the exchange complex (ECEC was sometimes larger than the CEC), indicating that greater amounts of cations were extracted than accounted for by the CEC, which in turn would be subject to loss by leaching (Fig. 40).

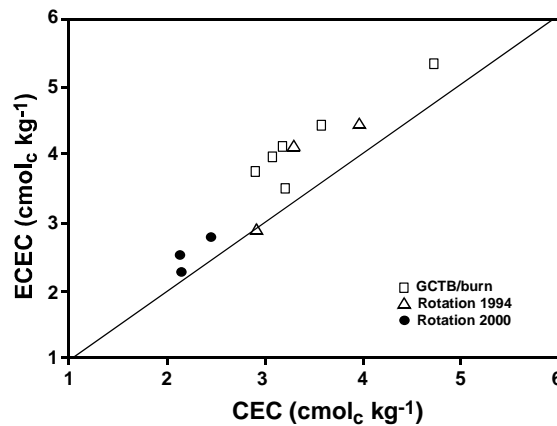


Figure 40: Relationship between ECEC and CEC for the GCTB/burnt trial and two rotation trials (modified from Noble et al., 2003).

This study showed that increased SOC under certain management systems can affect a variety of soil properties as it is associated with the generation of increased surface charge, which aids in retaining and supplying nutrients (CEC), and enhanced water holding capacity. Similarly, Moody (1994) aimed to both decrease P adsorption and increase CEC in highly weathered Oxisols. He suggested that inclusion of green manure would be more advantageous with regard to both P sorption and increase in CEC than retention of crop residues because of the greater availability of carboxylic acids in green manure compared with crop residues.

These amendment studies clearly illustrate that type of SOM plays an important role in determining soil CEC. In fact, Moody (1994) suggested that in order to understand the effect of SOM on CEC, SOM should be distinguished into labile and recalcitrant forms as it would be the labile fraction, which was most likely to influence soil chemical properties. Important in this regard would be the production of carboxylic acids from easily decomposable OM, which would contribute important exchange sites. Moody et al. (1997) aimed to assess how the different degrees of oxidisability of SOM would affect the CEC, ECEC and CEC at pH 6.5 of different soil types. They used different strengths of  $\text{KMnO}_4$  to distinguish between carbon fractions of various degrees of oxidisability:

C1 = amount of C oxidised by 33mM  $\text{KMnO}_4$

C2 = difference between C1 and amount oxidised by 167mM  $\text{KMnO}_4$

C3 = difference between total carbon and (C1+C2)

However, they found it difficult to detect significant differences between the different carbon fractions as all of them contributed to ECEC and CEC at pH 6.5. While the combination C3 (most difficult to oxidise) and clay explained 80.9% of the variation in some soils, this relationship was not significant for Ferrosols. C3 was also shown to make a significant contribution to  $\text{CEC}_{\text{pH } 6.5}$  when combined with clay; again, this relationship could not be applied to Ferrosols where C1 showed the best correlation. These results illustrate the importance of distinguishing between different soil types and that chemical relationships may be soil type specific.

As pointed out in previous studies, carboxyl groups are considered to be one of the most influential organic matter functional groups in contributing to CEC and Parfitt et al. (1995) noted that most of the CEC from organic matter was due to carboxyl groups. Furthermore, they noted that the CEC of SOC was less in the A than in the B horizon. This is consistent with the presence

of more highly charged, low molecular weight molecules and the presence of more humified organic matter in the B horizon. Interestingly, the CEC of B horizons containing allophane was lower than for samples with no allophane, which suggest that allophane was blocking or complexing carboxyl groups of OM, making them unavailable for cation exchange reaction. However, the CEC of the A horizon was higher when allophane was present, which Parfitt et al. (1995) attributed to the stabilisation and retention of otherwise labile OM, which then was able to contribute to the CEC.

However, other organic fractions besides carboxyl group might be of importance with respect to their contribution to soil CEC. Glaser et al. (2002) observed that higher nutrient retention and nutrient availability were found after charcoal addition, which they related to higher CEC and surface area. Furthermore, most cations in ash contained in charcoal were not bound by electrostatic forces but present as dissolvable salts, and are therefore readily available for plant uptake. This means that charcoal may not only act as a conditioner (CEC increase) but also as a fertiliser. They further found that higher charring temperatures improved exchange properties and increased the surface area of charcoal. Surface area of charcoal is high and the inner surface areas were estimated to be 200-400 m<sup>2</sup> g<sup>-1</sup> of charcoal formed between 400-1000°C. In addition, application of charcoal has been shown to increase pH by up to 1.2 units and decrease Al saturation of soils (Mbagwu and Piccolo, 1997). Hardwood charcoal proved to be more effective in reducing soil acidity and increasing CEC compared with softwood charcoal. They hypothesised that charcoal may form organo-mineral complexes, probably due to slow (biotic or abiotic) oxidation of the edges of the aromatic backbone of charcoal and the subsequent formation of carboxyl groups. They further found that addition of N compounds during charring enhanced charcoal properties by aiding oxidation processes and forming carboxyl and phenol groups.

## Summary

- Most studies show a linear correlation between SOC and CEC; however, below a threshold value of 2% SOC content, there appears to be little or no effect on CEC.
- SOM contributes mostly to an increase in the variable-charge CEC ( $CEC_v$ ) and can account for up to 70% of the ECEC in highly weathered soils.
- Functional groups (e.g. carboxylic acids) of SOM are believed to be one of the main contributors to  $CEC_v$  as they provide negatively charged sites.
- pH contributes to CEC as dissociation of functional groups at  $pH > 5$  increases the number of negatively charged sites; in addition a decrease in CEC at low pH might be related to blockage of exchange sites by Fe and Al.
- Apart from functional groups, smaller particle size fractions (especially the organo-mineral clay fraction) had a greater influence on CEC than coarser fractions.
- Fertiliser and manure application can both increase the CEC of the soil.
- Charcoal (especially high temp char) has been shown to be a potentially important contributor to increasing CEC.

## Buffer Capacity and pH

From the previous chapter it is evident that there is a close relationship between soil CEC, pH and buffer capacity (BC) and that all of these parameters are influenced to certain degrees by SOC content. However, since BC of soils and acidity are often dealt with independently in the literature, a separate chapter is committed to the relationship of BC, pH and SOM.

The close relationship between CEC, pH and BC is illustrated by the observation that with increased CEC, there is a concomitant increase in BC. This is due to the fact that more acidity is neutralised to affect a given increase in the percentage of base saturation (base saturation = sum of exchangeable bases/buffered CEC).

Soil buffering is considered to be an important aspect of soil health, as it assures reasonable stability in soil pH (preventing large fluctuations) and influences the amount of chemicals (lime or sulfur) needed to change the soil pH. The BC of a soil is defined as its resistance to changes in pH when an acid or base is added. Buffering at intermediate pH values (5-7.5) is mainly governed by exchange reactions where clays and functional groups of SOM act as sinks for  $H^+$  and  $OH^-$ . The relationship of pH to percent base saturation varies from substance to substance. For example, different types of clay will affect the pH-base saturation to different degrees, and Al and Fe compounds are known to affect the BC of soils. At low pH values,  $Al^{3+}$  and hydroxy aluminium tend to block exchange sites in silicate clays and humus, thereby reducing the CEC of the colloids. As a consequence, liming is required to raise the pH and increase the CEC (Brady, 1990).

The availability of different functional groups (e.g. carboxylic, phenolic, acidic alcoholic, amine, amide and others) allows SOM to act as a buffer over a wide range of soil pH values. BCs are usually greater in the organic rich surface soil compared with the mineral horizons, and James and Riha (1986) reported BCs for forest soils of 18-36  $cmol_c kg^{-1}$  (surface soil) and 1.5-3.5  $cmol_c kg^{-1}$  (mineral soil). However, in a summary provided by Bloom (1999), buffering capacities of SOM can easily approach 200  $cmol_c kg^{-1}$ , and Aitken et al. (1990) estimated that SOC may have a BC >300 times compared with that of kaolinite. Table 3 provides a summary of BCs of different materials, which shows that with the exception of  $CaCO_3$ , the pH BC of SOM is equal to or greater than that of other soil components. It is apparent that because of the weak BC of the clay

minerals illite and kaolinite, highly weathered soils that are low in SOM would be highly susceptible to acidification.

Material	Capacity (cmol <sub>c</sub> kg <sup>-1</sup> )
smectite	80-150
vermiculite	150-200
illite	20-40
kaolinite	1-5
SOM	200
Allophane/imogolite	20-50
Fe and Al oxides and hydroxides	5-40
carbonate	2000

Table 3: Approximate maximum proton donation or adsorption capacity of soil materials in the pH range 3.5 to 8 (modified from Bloom (1999)).

The tight dynamics between SOC content, clay content, ECEC, change in CEC with pH (= ΔCEC) and BC were investigated by Aitken et al. (1990). They found that the major factor affecting ΔCEC was SOC content and ΔCEC could be best estimated by:

$$\Delta\text{CEC} = \text{OC} + \text{clay} + \text{ECEC} \quad (R^2 = 0.77^{**}).$$

Importantly, even for soils with an SOC content <2.5%, ΔCEC still proved to be a major determinant for BC. In fact, multiple regression analysis of SOC content, clay content, and exchange acidity (or exchangeable Al) accounted for 85% of the variability in BC with SOC content being the most important parameter. Similar to the study by Magdoff and Bartlett (1985), they found that the relationship between CEC and pH was linear over a pH range of 4-6.5. At a pH>6.5, the relationship became curvilinear with a marked increase in CEC with relatively small increases in pH, which illustrates the importance of ΔCEC in determining BC. The increase in negative charge of SOM with increasing pH is well documented and the added positive effect of clay content on ΔCEC was suggested to be due to variable charge minerals.

Poudel and West (1999) investigated the relationships between ECEC, base saturation (BS) and pH and the potential buffer capacity for potassium (PBC<sup>K</sup> = measures the ability of soils to maintain the labile K against depletion) in volcanic soils of the Philippines. They found that PBC<sup>K</sup> was lower for Inceptisols than for Oxisols and was higher in alluvial terraces than mountain soils. They attributed the lower PBC<sup>K</sup> in mountain soils to the presence of a thin recent capping of ash, which would represent a rather young, base-depleted parent material. There was a

positive correlation between  $PBC^K$ , soil pH and BS, suggesting that acidification and base cation depletion resulted in lower  $PBC^K$  values. Soil pH was the property most highly correlated with  $PBC^K$  (Fig. 41). Because of the correlation between ECEC, BS and pH, they concluded that acidification will not only lower  $PBC^K$  but will also lower the ECEC and BS percentage.

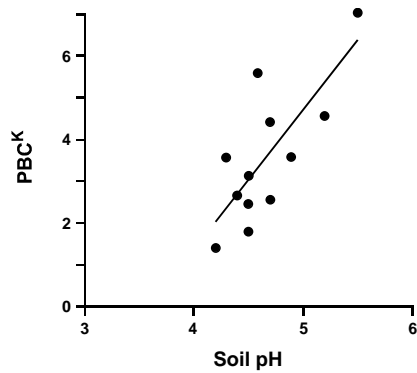


Figure 41: Relationship between potential buffer capacity for K and soil pH (redrawn from Poudel and West, 1999).

A good correlation between BC and organic matter content has been documented in several studies (e.g. Starr et al., 1996; Curtin et al., 1996) and the importance of SOM to maintain fairly stable pH values, despite acidifying factors, was documented by Cayely et al. (2002). In a long-term experiment that involved fertiliser application (superphosphate) and stocking rates, they showed that while pH in the topsoil decreased at a rate of  $0.005 \text{ pH}_{Ca} \text{ units year}^{-1}$  or  $0.008 \text{ pH}_W \text{ units year}^{-1}$ , there was little effect due to fertiliser or stocking rate. The relatively slow rate of change in pH, despite the acidifying measures of fertiliser application and high stocking rates, was attributed to the high BC of the soil ( $41 \text{ kmol H}^+/\text{ha.pH unit}$  in 0-10cm), which in turn was hypothesised to be due to the high soil SOC content (4.6% in 0-10cm), which had not changed over the 20 years of the experiment. Magdoff et al. (1987) took a different approach and estimated the degree of buffering on a soil volume basis (VBC), as specific BC and  $D_b$  are both correlated with SOM. Their analyses showed that at low SOM levels (E, B and C horizons) a small change in SOM resulted in a large change in the calculated VBC whereas at large SOM levels, the change in VBC was rather small (Fig. 42). They found that BC of SOM was close to or greater than the change in CEC with pH, and Kalisz and Stone (1980) estimated that the pH-dependent CEC was about  $0.3 \text{ mol kg OM}^{-1} \text{ pH}^{-1}$ .

However, Ngatunga et al. (2001) found only a weak correlation between BC and SOC content and a far better correlation between clay content, base saturation and the CEC of the clay fraction.

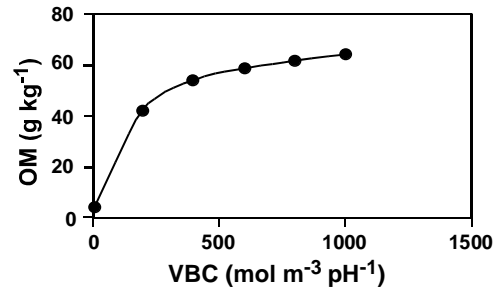


Figure 42: Change of calculated volumetric buffer capacity (VBC) with SOM (data from Magdoff et al.1987).

They further showed that a high correlation existed between BC and the initial pH value of the subsurface horizon. That is, more acidic soils were better buffered than less acidic ones. Interestingly, soils tended to be poorly buffered between pH 4.5 and 6.5, considered to be the optimum pH range, and well buffered below 4 and above 7. Similar results with respect to the pH range, were obtained by a study from Magdoff and Bartlett (1985), where changes in BC were investigated by adding an acid or a base to several different soils. They found that soils were well buffered at pH >7 and <4 (Fig. 43A). When the amendment (acid or base) added was expressed on an SOM basis, all soils appeared to follow a similar relationship (described by a unified buffer curve) and pH buffering was approximately linear in the pH range 4.5-6.5 (Fig. 43B).

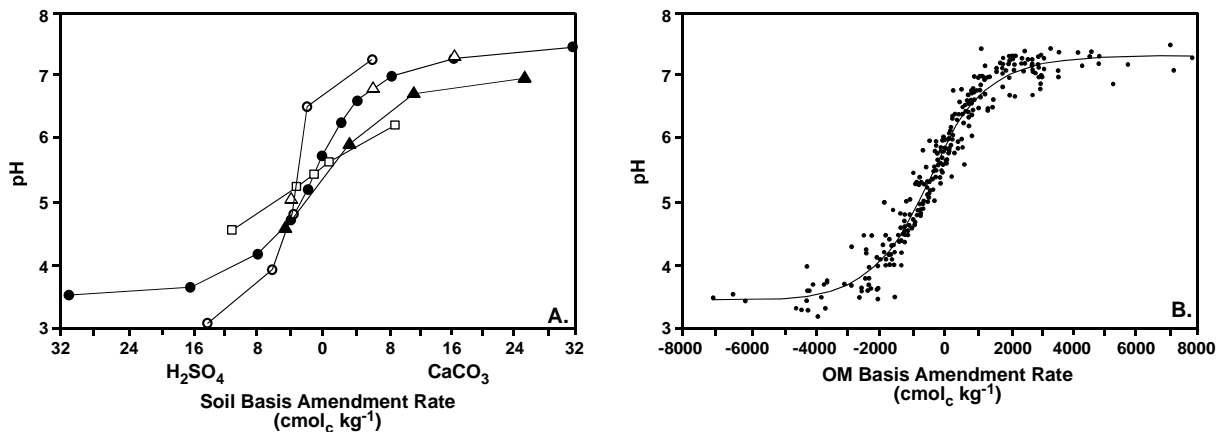


Figure 43.: Titration curves with zero amendment transposed to soil (●) and (A) and plot of all titration curves (amendment added per g OM) with zero amendment transposed to curve for soil (●) (B). Other symbols represent different sets of soils (modified from Magdoff and Bartlett, 1985).



The change in slope indicated that soils were least well buffered between 5-5.6, which they suggested was due to the low increase in CEC. They further advocated that care should be taken when assuming that the much used pH versus % base saturation relationship was essentially the same as the pH versus lime addition titration curve; because in soils without appreciable exchangeable Al, the %BC is essentially the CEC of the soil at its current pH. Unlike Ngatunga et al. (2001), Magdoff and Bartlett (1985) found that pH buffering was related to SOM content as shown in Figure 43A.

The effect of different organic materials on soil pH was investigated by Wong et al. (2000). They incubated an Oxisol and an Ultisol with prunings of young tree shoots and observed an increase in pH and decreased exchangeable Al content during the first 14 days. This trend continued, albeit at a slower rate, over the next 42 days and then decreased slightly over the last 56 days. The BC of the Oxisol was  $48 \text{ mmol OH}^- \text{ pH}^{-1} \text{ kg}^{-1}$  and  $45 \text{ mmol OH}^- \text{ pH}^{-1} \text{ kg}^{-1}$  for the Ultisol and soil pH increased from 4.1 to 6.8 in the Ultisol and from 4.8 to 5.8 in the Oxisol. Both soils had similar clay contents but the Oxisol had a higher C content (4.5% compared with 2.6%). While total base cation content of the prunings was a better predictor of pH changes in the Ultisol, it did not apply to the Oxisol and differences in SOC content appeared to have little effect on BC. Wong et al. (2000) proposed that acid neutralisation was due to complexation of protons and Al by organic anions. Adsorption of Al would result in undersaturation which would in turn result in 3 mol of protons consumed for each mol of Al dissolved. Therefore, dissolution of Al-bearing minerals due to Al complexation by organic anions would result in proton consumption and pH increase. In fact, Haynes and Mokolobate (2001) pointed out that pH increase might not be the primary cause for the decrease in exchangeable and soluble Al, but that it is the increased adsorption onto humic substances that reduces the concentration. For example, Thomas (1975) found that with soil depth there was a negative correlation between SOM content and exchangeable Al and that the effect of SOM was greater at lower pH values. Therefore, Wong et al. (2000) argued that the maximum amount of base cation complexes or salts of organic anions produced would depend on the total base cation content of the decomposing material. While the relationship between increase in soil pH during this decomposition and base cation content of the added material was also reported by Bessho and Bell (1992) and Wong et al. (1998), Wong et al. (2000) did not offer an explanation why this relationship could only be verified for the Ultisol and not for the Oxisol.

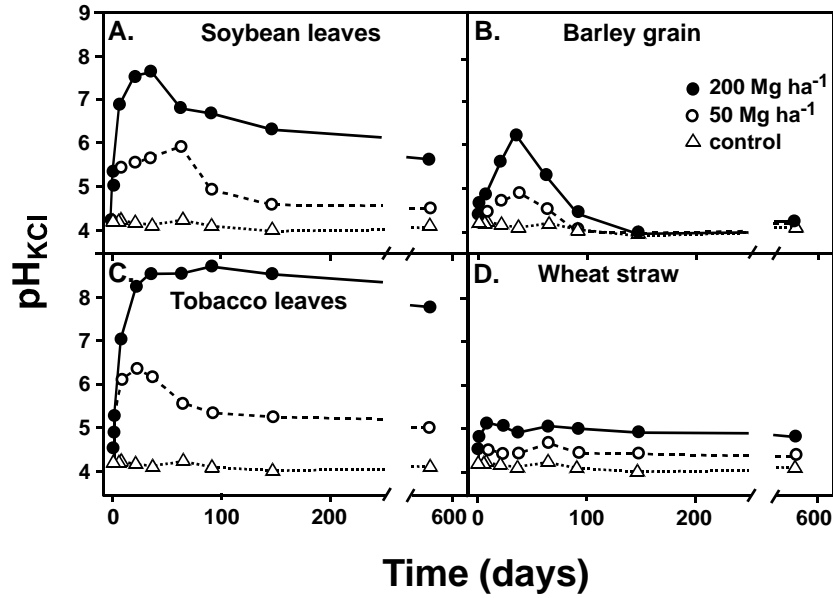


Figure 44: Effect of addition of different organic matter types and rates on soil pH (modified from Pocknee and Sumner, 1997).

Pocknee and Sumner (1997) incubated an acid topsoil (Hapludult: 13% clay, CEC 2.8 cmol<sub>c</sub> kg<sup>-1</sup>, SOC 8 g kg<sup>-1</sup>, pH<sub>KCl</sub> 4.01) with different types of plant materials to study the effect of type of SOM and rate of amendment on soil pH (Fig. 44). While all treatments increased pH<sub>KCl</sub> within a matter of days or weeks, the magnitude of change and the duration of the effect (declining or stable) varied with SOM type and rate of application (50 and 200 Mg ha<sup>-1</sup>), as greater application always resulted in greater pH shifts. They suggested that the long-term pH shift could be attributed to mineralisation of basic-cation containing compounds and initial N content. This was evident from the responses of the plant amendments. Barley had a relatively high N content relative to its basic cation content and the pH response was only short-lived. Soybean and tobacco, on the other hand, were intermediate in N content and intermediate and high in cations respectively, and the pH response curves showed two distinct phases. Wheat straw was both low in N and base cation content and the effect on pH was small (Fig. 44). Pocknee and Sumner (1997) reproduced these effects with the addition of pure substances ( $\beta$ -alanine and calcium gluconate) and obtained similar results as with the plant amendments. Addition of Ca alone was similar to the response of wheat straw, N only amendments (alanine) were similar to the response curve of barley and N and Ca together produced a similar response compared with that observed in soybean and tobacco amendments. Interestingly, alanine additions alone increased pH first as NH<sub>4</sub><sup>+</sup> was produced with degradation of alanine. Upon conversion to NO<sub>3</sub><sup>-</sup> the pH declined. At

greater rates, however, the pH remained high, and the authors suggested that the build-up of  $\text{NH}_3$  inhibited nitrification. Thus, Pocknee and Sumner (1997) concluded that the major factors of organic amendments that influenced soil pH were basic cation and N contents. Similar results were obtained by Nkhalamba et al. (2003), who noted greater pH increases when acidic soils were incubated with soya bean residues compared with maize residues. However, the application rates were very large ( $150$  and  $56 \text{ t ha}^{-1}$ ) compared with applications normally applied in the field ( $1 \text{ t ha}^{-1} = 0.08\%$ ).

The two-phase pH response, reported by Pocknee and Sumner (1997) was also noted in a review by Haynes and Mokolobate (2001). Based on several studies, they deduced that an initial pH increase commonly occurred after addition of organic materials, which lasted for approximately 1-2 months, followed by a pH decline. The magnitude of the initial pH rise was dependent on the type of residue, application rate and BC. For example, for amendments of  $20 \text{ t ha}^{-1}$ , pH increases of 0.2-0.6 pH units were reported compared with increases of 0.8-1.5 pH units at  $40\text{-}50 \text{ t ha}^{-1}$  rates. However, there did not appear to be one single explanation for the initial rise in pH, and Haynes and Mokolobate (2001) suggested that several different mechanisms exist that may produce the initial increase in pH:

1) Oxidation of organic-acid anions of decomposing residues

Organic anions (e.g. oxalate, citrate, malate) balance the plant-derived cations and accordingly, oxidation of anions would release  $\text{OH}^-$  and consume  $\text{H}^+$  ions. When stable or highly decomposed material is added, a rise in pH might occur due to complexation of protons by organic anions, whereas with the addition of undecomposed plant material, most of the rise in soil pH was attributed to the decarboxylation of organic anions during microbial decomposition.

2) Ammonification of residue organic N

Transformation of organic N during decomposition to ammonia results in a release of  $\text{OH}^-$ . However, as subsequent nitrification causes the release of  $\text{H}^+$ , the overall transformation of organic N to nitrate is acidifying with one  $\text{H}^+$  produced per mole of N transformed. In fact, nitrification was often the reason why soil pH declined after the initial increase.

3) Specific adsorption of organic molecules

Specific adsorption of humic materials and/or organic acids onto Al and Fe hydrous oxides results in release of  $\text{OH}^-$  ions. This process is similar to the self-liming effect when gypsum is added to

soil and  $\text{OH}^-$  ions are released due to adsorption of  $\text{SO}_4^{2-}$ . Figure 45 illustrates the adsorption of oxalate onto a metal (M) surface with subsequent release of  $\text{OH}^-$ .

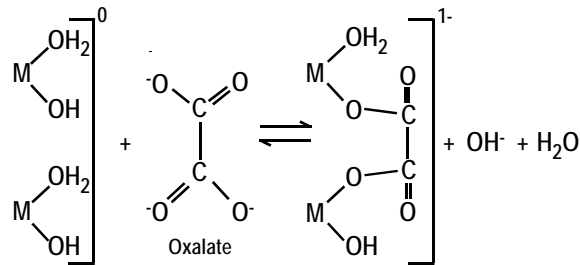


Figure 45: Specific adsorption of oxalate to an Al or Fe (M) hydrous oxide surface (redrawn from Haynes and Mokolobate, 2001).

It needs to be considered, that although addition of organic residues may increase soil pH for some time (depending on the type of material), it is really only a transfer of alkalinity from one place to another as organic residues do not independently synthesise alkalinity (Haynes and Mokolobate, 2001). Finally, long-term addition of organic residues ultimately results in accumulation of humic material, which is able to complex Al, increase the CEC and decrease the amount of monomeric Al in the soil solution. Furthermore, humic materials may coat surfaces of Al-containing minerals and decrease their solubility. In such cases, SOM reactions with Al and Al-bearing minerals could be considered as a way to “protect” soil from reaching toxic soluble metal concentrations. It further highlights the dynamic interactions between SOM, pH, CEC and adsorption processes.

#### Summary

- There is generally a good correlation between BC and organic matter content.
- A close relationship exists between CEC, pH and BC and an increase in CEC is often associated with an increase in BC.
- Functional groups are believed to be responsible for SOM to act as a buffer over a wide range of soil pH values.
- Soils tend to be well buffered at  $\text{pH} > 7$  and  $< 4$  whereas pH buffering was approximately linear in the pH range 4.5-6.5.

## Adsorption and Complexation

Adsorption reactions involving SOM are highly dependent on pH as well as CEC. This is mainly due to the fact, that similar types of organic carbon species are involved in adsorption reactions as are in the control of CEC and buffer capacity. Accordingly, the presence of functional groups (-OH, NH<sub>2</sub>, -NHR, -CONH<sub>2</sub>, and -COOR) is a critical factor for adsorption of ions on humus particles and the formation of complexes with SOM.

Adsorption of SOM on clay particles is an important mechanism for the protection of SOM from decomposition. The significance of the adsorption of SOM onto clay mineral surfaces is illustrated by the well-documented positive relationship between SOC and clay content and soil surface area (e.g. Oades, 1989; Feller et al., 1991 and summarised in Krull et al., 2003). The SOM-clay interactions are mainly controlled by the chemical nature of the organic materials (presence of functional groups) and type of clay mineral (kaolinite, illite, smectite). As the protection of SOM by clay minerals covers an extensive area of research and is well summarised in Oades (1989) and Baldock and Skjemstad (2000), this report will place more emphasis on adsorption and complexation reactions where SOM acts as the sorbent of, and complexing agent for, various ions, metal and organic species.

The most common form of interaction between SOM and positively charged ions is via cation exchange reactions (e.g. between negatively charged carboxyl groups and positively charged cations) and is associated with proton replacement from acid functional groups (ligands). Complexation of inorganic materials by SOM may have important ramifications for soil fertility as it may increase the availability of P by blocking potential adsorption sites of Fe and Al as well as Ca. For example, Oades et al. (1989) found that the presence of SOM decreased the amount of P sorbed by Oxisols. Furthermore, they observed greater P sorption maxima for cultivated soils (800 mg P kg<sup>-1</sup>) compared with forest soils (560 mg P kg<sup>-1</sup>) and attributed this to the greater amounts of SOC in forest soils (6.8%) than in cultivated soils (3.8%).

McBride (1999) noted that with the exception of some non-crystalline minerals, SOM has the greatest capacity and strength of bonding with most metals of any soil component. This is illustrated by the commonly observed positive association between solubility of metals (for example Cu and Cd) and SOM content as well as the greater concentration of trace metals in

organic rich soils compared with organic-poor soils (McBride, 1999). A statistical relationship ( $p < 0.01$ ) between total Cd content and SOM was found for US soils:

$$\text{Cd} = 0.1 + 0.0094 \text{ SOM (g kg}^{-1}\text{)}.$$

In a study by McGrath et al. (1988) the effect of SOM was determined on concentrations of metals in solution and their extractability from the soil. They found that increased concentrations of SOM depressed the concentration of cupric ions in soil solution as well as the extractability into acetic acid and  $\text{CaCl}_2$  of both native and added Cu; effects on the extractability of Zn and Mn, on the other hand, were much smaller. Cu was observed to be more strongly adsorbed into acid-washed peat, peat and solid humic acids compared with clay minerals or iron oxides.

The effects of pH and SOM concentrations on extractable Al were shown by Thomas (1975). He observed that the amount of extractable Al from soils with varying SOM contents was lower in high SOM soils at any given pH level. However, extractable Al contents were greater in soils with strongly acidic pH (3.5) compared with less strongly acidic pH (4.75) (Fig. 46). The influence of SOM was greatest from 0.8% to 2.5% (almost linear relationship), showing that an increase of 1-2% SOM lowered exchangeable Al from 6 to 4.2 meq/100g. At SOM  $< 0.8\%$  and  $> 2.5\%$ , the positive influence of SOM appeared to diminish.

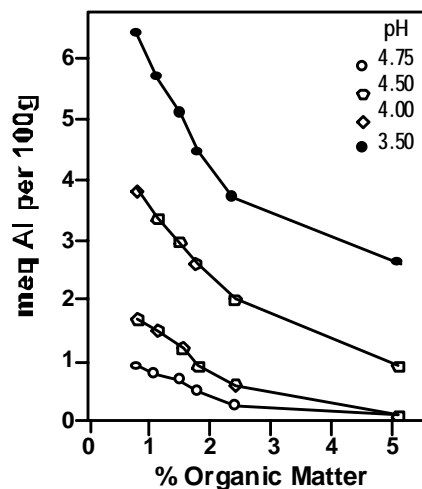


Figure 46: The relation between % organic matter and exchangeable Al at different pH levels (redrawn from Thomas, 1975).

Organic residues are often added to soil to reduce potential Al toxicity and increase P availability. Haynes and Mokolobate (2001) suggested that the most important organic carbon groups in complexation reactions were soluble humic molecules and low molecular weight (LMW) aliphatic organic acids. Both substances have been shown to complex monomeric Al (a phytotoxin) in soil solution and to adsorb to Al and Fe oxide surfaces, thereby blocking P adsorption sites. The presence of O-containing functional groups (carboxylic, phenolic, enolic, alcoholic) is critical in the formation of complexes between polyvalent metal ions (e.g. Al) and humic substances, and Grathwohl (1990) showed that sorption of chlorinated aliphatic hydrocarbons decreased with increasing proportions of O-containing functional groups. Furthermore, humic substances are able to confer a greater negative charge on mineral oxide surfaces which in turn decreases the effectiveness of P adsorption. Another positive effect of SOM is, as documented in the previous chapter, the transitory increase in pH during residue decomposition, which leads to the precipitation of Al as an insoluble hydroxyl Al compound. LMW organic acids (e.g. formic, acetic, propionic, butyric, lactic, oxalic, fumaric, citric, tartaric, etc), which are often derived from leaves and from microbial biomass, are known to form chelate complexes with  $Al^{3+}$ . Of these LMW acids hydroxy acids (e.g. citric acid) are able to form stronger complexes than carboxylic acids (Haynes and Mokolobate, 2001). However, many of these acids may only be present at sufficient concentrations for a short period of time, because of their susceptibility to microbial degradation and a regular supply would be needed for efficient Al detoxification.

Humic acids have also been shown to be important in inhibiting the formation of thermodynamically stable Ca-phosphates as documented by Alvarez et al. (2004), who studied the effect of humic materials on inorganic P availability in P-fertilised soils under conditions of high supersaturation and at pH values of 7.4 and 5.7. The different forms of P observed in this study were in the order of increasing stability: amorphous Ca-P (ACP), dicalcium phosphate dihydrate (DCDP, e.g. brushite), octacalcium phosphate (OCP) and hydroxyapatite  $Ca_5(PO_4)_3OH$  (HAP). They observed that at pH 7.4, humic acid delayed the transformation (by three times) of ACP to the more stable form of OCP, thus, stabilizing the normally unstable ACP. At 5.7 and in the presence of humic acid, ACP was precipitated whereas the more stable form of DCDP was precipitated in humic-free solution. Furthermore, ACP persisted longer than DCDP before being transformed to OCP. This implied that humic acids (as well as tannic, phytic, mellitic and citric acids) can act as effective inhibitors of Ca-P transformation and can modify the availability of P in soils by changing its crystallisation behaviour. The reason behind the change in crystallisation

behaviour was suggested to be due to the presence of carboxylate groups, providing ligands to bind with Ca to form Ca-humate complexes, which may precipitate at lower pH values. In addition, the carboxylate ligand was suggested to be in competition with the P ligand for complexing Ca ions. Alvarez et al. (2004) suggested that humic acids may be able to retard the natural crystallisation process by either chemically bonding or adsorbing to crystal growth sites.

However, several studies noted that the presence of functional groups might not be the only aspect that determines the sorption capacity of SOM and that synergistic effects involving hydrophobicity, aromaticity and polarity might be of similar if not greater importance. Kaiser (2003) investigated the interactions between synthetic goethite and 18 different forms of SOM on sorption to mineral surfaces. He found that hydrophobic fractions and fulvic and humic acids (rich in carboxyl and aromatic, lignin-derived C) sorbed more strongly to goethite than hydrophilic fractions (O, N-alkyl C and forms with a low abundance of aromatic C). He suggested that the degree of sorption was related to aromatic structures but that the strongest determinant was the presence of acidic groups, specifically the total content of carboxyl C. However, aromatic and aliphatic structures alone had only a small effect on sorption of SOM to mineral surfaces, and instead, sorption of the hydrophobic fraction was inversely related to the ratio of aromatic to carboxyl C (Fig. 47). Consequently, the number and position of acidic groups attached to aromatic molecules appeared to control the effectiveness of sorption.

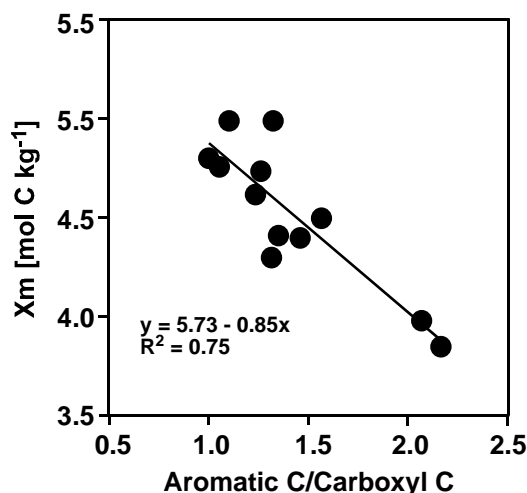


Figure 47: Relationship between sorption maximum ( $X_m$ ) according to Langmuir model and ratio of carboxyl C to aromatic C as revealed by liquid-state  $^{13}\text{C}$ -NMR of hydrophobic acids, and fulvic and humic acids (FA, HA).



Sorption reactions involving SOM are particularly important with respect to ameliorating the effect of organic pollutants (e.g. pesticides, herbicides) and metal contaminants. In fact, organic matter is considered the primary sorbent for non-ionic organic compounds, especially in soils and sedimentary environments with high SOM content. The sorption of hydrophobic organic compounds (HOC) is described by the Freundlich equation (Freundlich sorption coefficient  $K_f$ ), and the relationship between sorption capacity and hydrophobicity of HOC is described by

$$\log K_{OC} = a + b \log K_{OW},$$

where  $K_{OC}$  is organic carbon normalised sorption coefficient ( $\text{mL g}^{-1}$ ),  $K_{OW}$  is the octanol-water partition coefficient and  $a$  and  $b$  are empirical constants (Xing et al., 1994; Xing, 1997). This equation has been used in predictive models to assess the movement of organic pollutants in soil. However, Xing et al. (1994) and Xing (1997) cautioned that this relationship was only valid if the SOM was homogeneous and if octanol was an appropriate surrogate. In reality, however,  $K_{OC}$  is strongly affected by the quality and composition of SOM and Xing (1997) emphasised that  $K_{OC}$  of organic contaminants cannot be accurately predicted from their  $K_{OW}$  without consideration of the respective quality (aromaticity and polarity) of the SOM in question. These deviations from calculated versus predicted ( $K_{OC}$ ) values and the effect of aromaticity has also been documented by Chen et al. (1996).

To compensate for the inability of  $K_{OW}$  to predict  $K_{OC}$ , Xing et al. (1994) used a polarity index (expressed as the atomic mass ratio  $[(O+N)/C]$ ) to establish a relationship between  $K_{OC}$  and the sorption of  $\alpha$ -naphthol on various organic compounds. The compounds used in the study varied in aromaticity and polarity (two types of lignin (organosolv and alkali), cellulose, tannic acid, chitin and collagen). They showed that the  $K_{OC}$  of naphthol decreased with increasing polarity of organic sorbents and that  $K_{OC}$  values were either higher or lower than the  $K_{OC}$  value ( $340 \text{ mL g}^{-1}$ ) predicted from  $K_{OW}$  (Fig. 48A). For example, the  $K_{OC}$  of lignin was about 200 fold higher than that of cellulose and wetting energy was  $20 \text{ J g}^{-1}$  for chitin and cellulose but only  $5 \text{ J g}^{-1}$  for lignin, which shows that the polarity of organic sorbents influences their  $K_{OC}$  values. To test the validity and universality of the relationship between polarity index and  $K_{OC}$ , Xing et al. (1994) synthesised a collagen-tannic acid mixture (CTM) with a polarity index of 0.8. Figure 48A shows that the measured  $K_{OC}$  value of CTM was very similar to the one predicted from its polarity value. The importance of aromaticity and polarity was also investigated by Zhou et al. (1995), who demonstrated that sorptive capacity of organically-coated montmorillonite decreased with

polarity and increased with aromaticity, suggesting that hydrophobic bonding was associated with a sorptive mechanism.

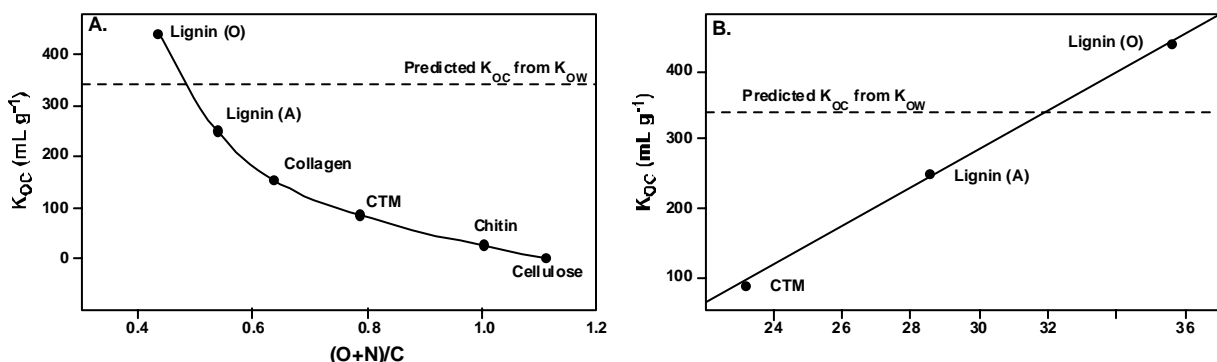


Figure 48: Relation between  $K_{OC}$  and polarity index of the sorbents (A) and relation between  $K_{OC}$  and aromaticity of the sorbents (B) (redrawn from Xing et al., 1994).

Xing et al. (1994) further proposed that SOM with a high percentage of aromaticity should adsorb more naphthol or other aromatic chemicals compared with those with low aromaticity. Based on the results in Figure 48B that show a linear relationship between  $K_{OC}$  values of naphthol with aromaticity of organic compounds, analogies can be drawn for other organic components. For example, the percentage of aliphatic contents of organic sorbents should be more important for sorption of nonpolar, saturated hydrocarbons and that young SOM (the POC fraction) with high contents of cellulose would adsorb less hydrophobic organic pollutants compared to well-humified SOM. Thus, the effectiveness of a particular sorbent is dependent on the characteristics of the material being sorbed.

In a subsequent study Xing (1997) investigated the sorption dynamics of HOC (naphthalene) in a number of different soils: coal with weathered shale (1), sedge peat (2), white clay (3), black chernozem (4) and brown chernozem (5). Figure 49 depicts the sorption isotherms for the five soils (determined by Freundlich equation), showing that  $K_{OC}$  values differed among soils. Figure 50A shows that  $K_{OC}$  increased with increasing aromaticity of SOM (determined by <sup>13</sup>C-NMR) in the order of shale > black chernozem > white clay > brown chernozem > sedge peat, indicating that the nature of SOM affects sorption capacity of HOC (naphthalene). These results are not limited to naphthalene but are consistent with earlier work on benzene, toluene, and o-xylene. Figure 50B also shows that the  $K_{OC}$  values, derived from the  $K_{OC}$  equation, were higher than soils

2 to 5 and lower than soil 1. Results show that  $K_{OC}$  varied inversely with effective polarity and directly with aromaticity and that young surface SOM had lower sorption capacity than old SOM.

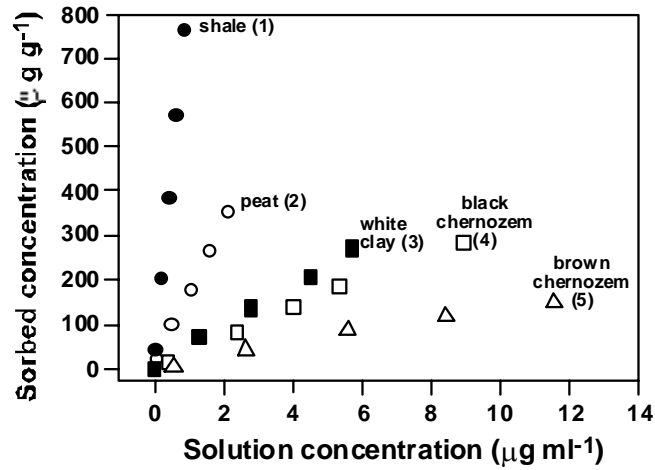


Figure 49: Sorption isotherms of naphthalene in the five soils (redrawn from Xing, 1997).

The relationship between sorption and degree of aromaticity was also reported in a study by Salloum et al. (2001), where 1-Naphthol (a metabolite of naphthalene) was used. While they observed that  $K_{OC}$  values were higher for humin than for humic acids, they did not find a good correlation between sorption and H/C values. Therefore, the authors suggested that the *accessibility* of SOC rather than the total SOC contents was the governing process that determined the extent of sorption.

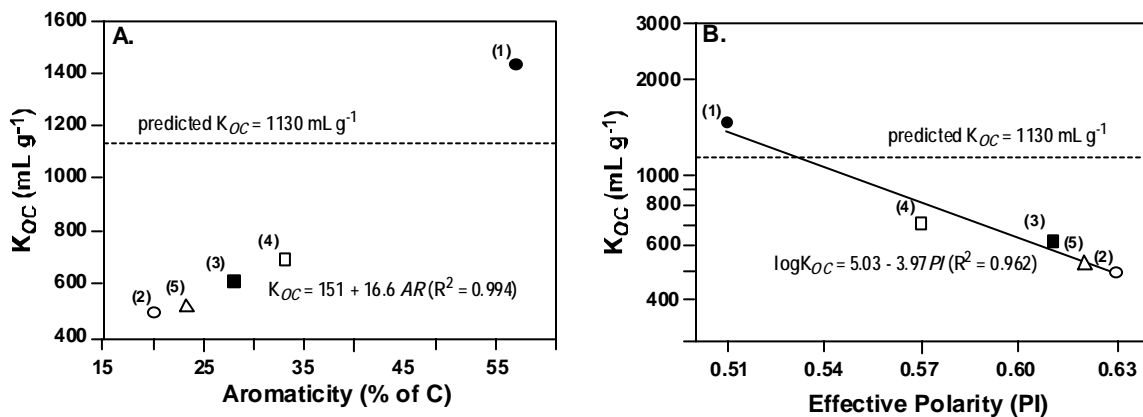


Figure 50: Relationship between  $K_{OC}$  of naphthalene and aromaticity (AR) of the five soils as compared with the predicted  $K_{OC}$  from  $K_{OW}$  (A). Relationship between  $K_{OC}$  of naphthalene and effective polarity (PI) of the five soils as compared with the predicted  $K_{OC}$  from  $K_{OW}$  (B). The dashed line represents the predicted Koc value (redrawn from Xing, 1997).

Beck and Jones (1996) investigated the linear sorption coefficients ( $K_d$ ) for atrazine and isoproturon in a clay soil with SOM present and removed by peroxide oxidation. With SOM removed, sorption was reduced for isoproturon and enhanced for atrazine, suggesting that the soil mineral component affected sorption of this herbicide more than SOM. Subsequent experiments on sorption by different size fractions (<2mm and <250 $\mu$ m) showed no significant differences in sorptive capacity.

The sorption characteristics of polycyclic aromatic hydrocarbons (PAH) on natural organic matter and black carbon were investigated by Accardi-Dey and Gschwend (2002). As documented in their review, several studies have found very high sorption affinities for PAHs, which were associated with the co-occurrence of soot, char and other carbonaceous particles, collectively referred to as black carbon. Gustaffson et al. (1997) suggested that the black carbon fraction in soils and sediments acted like activated carbon, thereby accounting for the high sorption coefficients. Further investigations by Accardi-Dey and Gschwend (2002) revealed that *absorption* into organic matter and *adsorption* onto black carbon act in parallel to bind PAH to sediments. Similarly, Cornelissen and Gustafsson (2004) noted that SOM in general is composed of two domains, one showing linear *absorption* and the other showing nonlinear *adsorption*. While the *absorption* domain is considered to be composed of amorphous SOM (humic/fulvic substances and lignin), more condensed moieties such as coal, kerogen and charcoal contribute to the *adsorption* domain with charcoal being one of the strongest sorbing forms of SOC. Finally, Kaiser et al. (2003) found that soils with a high content of black carbon showed increased sorption ability compared with plant- and microbial-derived SOM.

While the previous sorption studies emphasise the importance of aromatic and hydrophobic substances, Balabane and van Oort (2002) investigated the dynamics of POM in metal-contaminated soils. Several studies observed that the POM fraction of metal-contaminated soils is often particularly metal-enriched compared with other fractions. However, most studies investigated the effect of directly applied metal-enriched sewage sludge or other metal-enriched amendments. By comparison, Balabane and van Oort (2002) investigated whether metal-enrichment of POM can also be found in arable soils where the metal contamination is low and where organic inputs are not metal-enriched. The soils of their study were 1-3 km from former industrial plants and had overall low contamination levels of Zn, Pb, and Cd. However, the metal concentrations in the POM fractions were always higher (3-8 times for Zn, 1-7 times for Pb, 5-11 times for Cd) compared with the bulk soil and increased with decreasing particle size (>2, 2-0.2,

0.2-0.1, 0.1-0.05 mm). Since the metal enrichment in SOM could not be due to metal-enriched inputs from crop residues, they suggested that POM metal enrichment was linked to interactions between heavy metals in the soil and changes in the properties of POM throughout the biodegradation process. Decrease in size (higher specific surface area) and the biochemical transformation towards more humified components as a result of decomposition processes, increased metal sorption through increased intrinsic reactivity. Metal enrichment was not only related to the extent of POM decay but also to the respective residence time as the >2mm POM fraction (turnover time of a few years) was found to be less metal-enriched than the finer POM fractions with longer turnover time.

#### Summary

- There is generally a positive association between solubility of metals and SOM content.
- The influence of SOM on sorption of Al was greatest between 0.8 to 2.5% SOM, suggesting upper and lower threshold values.
- While the presence of functional groups is considered critical for adsorption of ions on humus particles and the formation of complexes with SOM, soluble humic molecules and LMW aliphatic organic acids have been also shown to be important for complexation and adsorption reactions.
- Humic acids may also be important in inhibiting the formation of stable Ca-phosphates, affecting P availability.
- $K_{OC}$  varied inversely with effective polarity and directly with aromaticity and sorptive capacity of organically-coated clays increased with aromaticity and decreased with polarity.
- While aromatic components had some effect on adsorption reaction, the number and position of acidic groups attached to aromatic molecules were shown to control the effectiveness of sorption.
- High sorption affinities have been demonstrated for PAHs, which are associated with soot, char and other carbonaceous particles; in fact, charcoal was found to be one of the strongest sorbing forms of SOC.

## Biological Function

The biological functions of SOM are primarily to provide a reservoir of metabolic energy that drives biological processes, to act as a supply of macro- and micro-nutrients and to ensure that both energy and nutrients are stored and released in a sustainable manner. Importantly, biological processes in turn influence both soil chemical and soil structural properties as they greatly affect soil structure and soil redox reactions.

### SOM as a Source of Energy

Baldock and Nelson (1999) stressed that one of the most fundamental functions of SOM was the provision of metabolic energy which drives soil biological processes. In essence, it is the transformation of carbon by plant, micro- and macro-biological processes that provides energy and results in the establishment of a cycle, that connects above- and belowground energy transformations (Fig. 51).

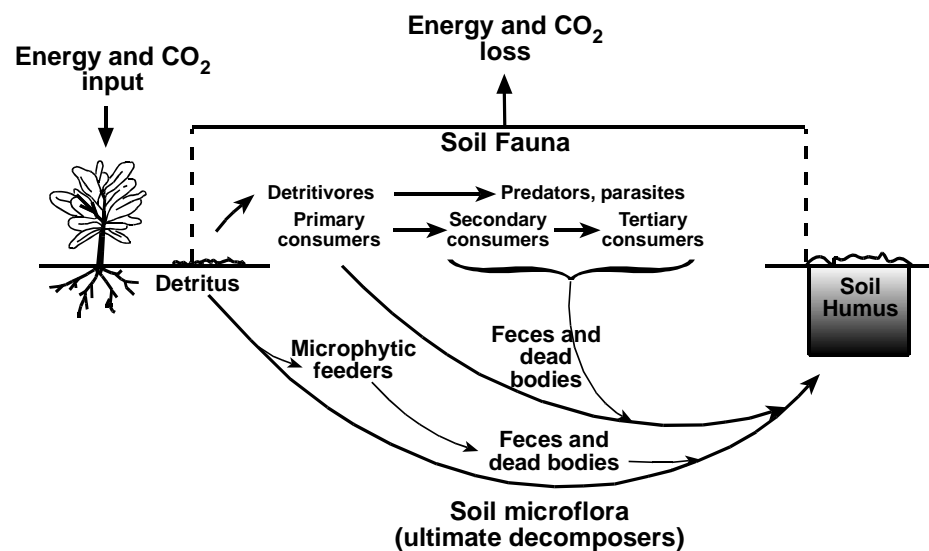


Figure 51: Diagram of the general pathway for the breakdown of higher plant tissue. Higher plants are considered primary producers as they capture energy and CO<sub>2</sub>. Debris from dead plants is degraded by the soil fauna and microflora, which are considered the primary, secondary and tertiary consumers. These organisms release energy and CO<sub>2</sub> and produce humus. About 80-90% of the total soil metabolism is carried out by the microflora (redrawn from Brady, 1990).

Plants assimilate carbon from the atmosphere into organic compounds (glucose) via photosynthesis (primary production). These simple carbon compounds are transformed into more complex plant biomolecules, which, upon plant senescence, enter the soil through litter, root material and root exudates. In turn, these materials provide energy for heterotrophic and, to a lesser degree, chemotrophic processes in the soil (including soil microbes, fungi and earthworms) which result in the formation of increasingly complex and increasingly recalcitrant organic matter as well as loss of CO<sub>2</sub> to the atmosphere via respiration (secondary production). Thus, the basic carbon and energy source for heterotrophic production is the carbon input from net primary production (NPP) and as long as NPP exceeds respiration, SOC will accumulate. Therefore, in a steady state, the amount of SOM stored in a soil reflects the balance between C produced (or added) in equilibrium with decomposition and leaching (or C lost). This balance is driven by the energy requirements of the biota and is externally influenced by environmental factors (temperature, moisture, clay content). Anderson (1995) suggested that the proposition “that natural systems have a tendency to self-organise in order to maximise useful power (i.e. store more energy that in turn can be fed back to catalyse the inflow of additional energy) (Veizer, 1988)” can be applied to soil ecosystems. Thus, the transformation from relatively labile SOM into increasingly complex, stabilised SOM can be viewed as a form of energy conservation as the largest pool of SOM consists of the humus pool which is recalcitrant enough to endure in an edaphic environment for longer periods of time but still allows for decomposition and nutrient release to take place. The energy released from decomposition processes in the soil is mainly in the form of heat and Russell and Russell (1950) calculated that the annual heat loss from a hectare of an untreated, low producing soil was equivalent to the heat value of nearly a metric ton of coal; by comparison, a hectare of a productive soil, receiving FYM, would release the equivalent of about 12 Mg of coal annually.

Microorganisms play a particularly important role in the transformation of organic matter and nutrients as 80-90% of the total soil metabolism is due to microbial processes (Brady, 1990), 1-5% of C and N in soil is stored in living microbial tissue (Duxbury et al., 1989) and microbial biomass in temperate grasslands is estimated to be 1-2 t ha<sup>-1</sup> (Nannipieri et al., 2003). In fact, a number of soil microbiological parameters (e.g. microbial biomass carbon, basal respiration rate) have been suggested as possible indicators of soil quality (summarised in Rees et al. 2001). The degree of microbial diversity, in particular, is thought to provide a measure of soil quality. Degens et al. (2000) introduced the concept of microbial catabolic evenness (CE) as a measure for soil microbial diversity, which is assessed by measuring short-term respiration responses of

soil to a range of organic compounds. In field studies, they found that differences in CE related to differences in SOC pools and that CE was higher under pasture and indigenous vegetation compared with arable soils. Figure 52 shows that depletion in SOC stocks may also cause a decline in catabolic diversity in soil microbial communities and losses of CE were greater where there was greater depletion of SOC.

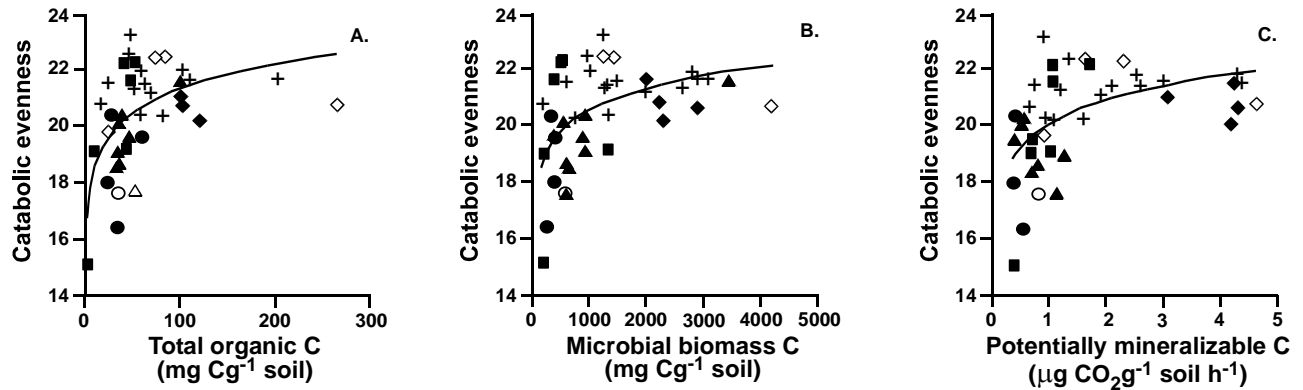


Figure 52: Catabolic evenness (Simpson-Yule index) of soil microbial communities in relation to (A) total organic carbon content, (B) microbial biomass carbon and (C) potentially mineralizable carbon cross a range of soils and land uses (redrawn from Degens et al., 2000).

Whether it is the reduced quantity or a reduction in quality that caused the decline in CE was not known; however, soils with high CE values contained a broader range of SOC pools. Loreau et al. (2001) summarised different aspects of microbial biodiversity and showed that the relationship between diversity and productivity is often described as a hump-shaped curve (Fig. 53), suggesting that there is an optimum level of biodiversity.



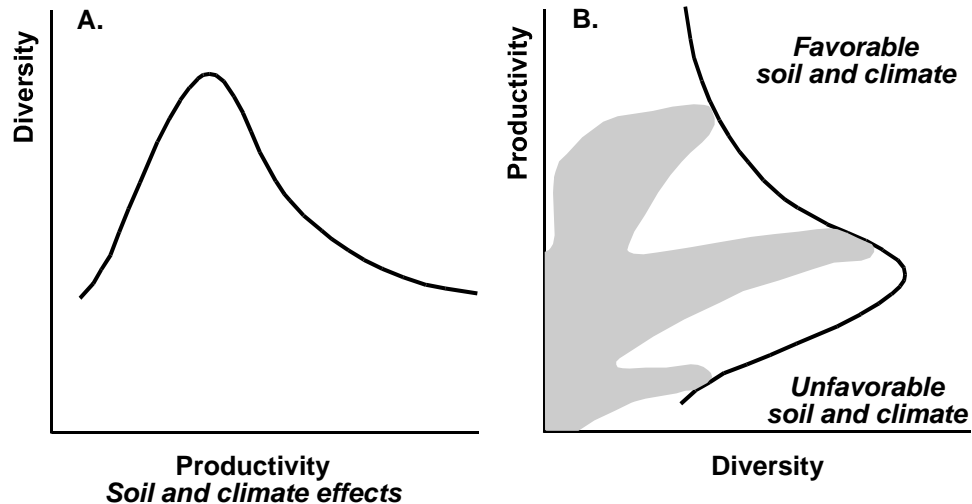


Figure 53: Hypothesised relationship between (A) diversity-productivity patterns driven by environmental conditions, and (B) the local effect of species diversity on productivity. Comparative data often show a uni-modal relationship between diversity and productivity, which is thought to be driven by changes in environmental conditions. Experimental variation in species richness under a specific set of environmental conditions produces a pattern of decreasing between-replicate variance and increasing mean response with increasing diversity, as indicated by the curved regression lines through the scatter of response values (shaded areas) (redrawn from Loreau et al., 2001).

#### Summary

- One of the biological functions of SOM is to provide a reservoir of metabolic energy that enables biological processes to be carried out.
- In a steady state, the amount of SOM stored in a soil reflects the balance between C produced (or added) in equilibrium with decomposition and leaching (or C lost).
- Microorganisms play an important role in the transformation of organic matter and nutrients as 80-90% of the total soil metabolism is due to microbial processes.
- Soil microbiological parameters (e.g. CE) have been suggested as possible indicators of soil quality.

## SOM as a Source of Nutrients

SOM is an important source of nutrients for plants in general and crops in particular. Nitrogen, phosphorus and sulphur are considered macronutrients, essential micronutrients are iron, manganese, zinc, copper, boron, molybdenum, and chlorine and beneficial but not essential elements are silicon, vanadium, cobalt and nickel. Particular emphasis will be placed here on the role of macronutrients.

Most of the nutrients in SOM are derived from the mineralisation of SOM and become available for plant uptake during decomposition and for this reason, the particulate organic matter fraction is often considered the most important proportion of SOM in providing nutrients to plants (Wolf and Snyder, 2003). Losses of nutrients might occur via leaching or conversion to gaseous forms or are the result of immobilisation. Due to the conversion of energy from primary sources to heterotrophic organisms, mineralisation of complex organic molecules by primarily microbial processes is possible. Some soil nutrients are used in the synthesis of new biomass, some are immobilised and another portion is mineralised and released as plant-available forms into the soil mineral nutrient pool. With the exception of fertilisers, SOM provides the largest pool of macronutrients with >95% of N and S and 20-75% of P found in SOM (Duxbury et al., 1989; Baldock and Nelson, 1999). A systematic review of the contents, chemical structures and transformations of N, P and S can be found in Baldock and Nelson (1999). Only about 40-50% of organic N is identifiable and quantifiable as amino acids and amino sugars and the remaining portion consists of unidentifiable structures. The principal form of organic S added to soil is amino acid S (methionine, cysteine, cystine), which accounts for up to 30% of the total organic S pool.

About 30-80% of extractable organic P is in the form of monoesters, and phosphate esters of inositol are the most abundant identifiable P compound class (5-80%). Inositol may form insoluble precipitates with Fe, Al and C and adsorb onto Fe and Al oxide surfaces. At low soil pH (<4.5-5), precipitates of Al and Fe phosphates may form while at higher pH values (>6-6.5), Ca phosphates form; however, mostly, specific adsorption reactions control P concentrations in soil solution (Duxbury et al., 1989).

While C is required as a primary source of energy for the mineralisation of N and C-bonded S, biochemical mineralisation is necessary for the release of phosphate and sulfate via enzymatic hydrolysis. As a result, cycles of P and S are often decoupled from the C and N cycles, leading to

large variations in the ratios of the respective macro-nutrients. Furthermore, the type and amount of P is often a function of inorganic parameters such as parent material and degree of weathering.

Ratios of C/N/S in agricultural soils (130:10:1) differ from those under indigenous vegetation (200:10:1). These differences could either imply that there is preferential mineralisation of C in cultivated soils, or that differences exist with respect to retention of nutrients in the soil-plant systems, or that there is a higher nutrient concentration in arable soils due to fertiliser input (Duxbury et al., 1989). The N/S ratio usually varies between 6-8, and the C/N ratio of SOM, depending on the C/N ratio of the vegetation and degree of decomposition, can vary between 12-16 but may be much higher in plant litter or in environments where SOC decomposition is restricted (e.g. peats) (Baldock and Nelson, 1999; Baldock and Skjemstad, 2000). Table 3 presents a summary of C/N and lignin/N ratios for various forms of residues.

Residue quality	C/N	Lignin/N
Highly decomposable	<18	<54
Moderate	18-27	5-7
Slow	28-60	7.5-15
Least	>60	>15

Table 3: General categorisation of residue quality based on different quality index methods (modified from Praveen-Kumar et al., 2003).

While it is often suggested that wide C/P ratios are an indicator of P deficiency there are no defined values as the variability in C/P ratios is much greater (61-526, average of 115) compared with C/N ratios. This can be partly attributed to the fact that P mineralisation is largely uncoupled from C and N mineralisation. However, C/P ratios of <100 indicate a tendency for net P mineralisation whereas ratios of >300 indicate net immobilisation. Furthermore, P is mainly present in ester form (C-O-P) while N is covalently bonded to C. S can occur as C-S as well as C-O-S structures. Importantly, transformation and mineralisation of organic P can occur via extracellular hydrolysis (without C degradation) but it can also be assimilated and mineralised with the concomitant oxidation of C (Duxbury et al., 1989).

As summarised in Loveland and Webb (2003), while a decrease in total SOC content may not be in proportion to the decrease in release of nutrients, 1% SOC is considered a threshold value (in relation to N supply from plant residues), below which an effective N supply is reduced. Janzen (1987) and Matus and Rodriguez (1994) noted that particularly with respect to N, the ‘active’ or

POM pool of SOM was most important for providing N for crop growth and to increase the availability of micronutrients. As noted in Duxbury (1989), nutrients and SOM seemed to be most stable in the fine silt and coarse clay fraction, whereas nutrients associated with the fine clay fraction were easily mineralizable. These results are consistent with many other studies, where the 'active' fraction was implicated as being the most important component in providing nutrients and regulating nutrient supply (Loveland and Webb, 2003).

Aggregates, on the other hand, may provide an important, transient storage capacity for macronutrients and can influence nutrient availability, particularly in tropical soils. As summarised by Duxbury et al. (1989), the C, N, P, and S contents of aggregates and C/N ratios narrowed with decreasing aggregate size. Both S and P tended to be preferentially associated with the fine clay fraction. However, as pointed out in the previous discussion on aggregates, different methods of determining aggregates makes it difficult to compare the results from different studies. For example, while several studies found that SOM and nutrient mineralisation increased with decreasing aggregate size, Elliot (1986) found greater mineralisation of both C and N in macro-aggregates compared with micro-aggregates. He postulated that the mineralisation of inter-aggregate SOM was the main source of nutrient release.

Land management practices can affect the nutrient status and nutrient release of SOM. While reduction in tillage or no till usually increases the SOC content, it tends to reduce the availability of nutrients to crops and results in gradual accumulation of nutrient reserves in SOM (Duxbury et al., 1989). Table 4 summarises the effect of tillage on N contents in plant and soil.

Plant or soil component	Green panic, clay (kg N ha <sup>-1</sup> )			Buffelgrass, sandy clay loam (kg N ha <sup>-1</sup> )		
	No tillage	Chisel plough	difference	No tillage	Plough/resown	Difference
Plant tops	45	62	+17	28	41	+13
Plant roots	84	102	+18	116	94	-22
Soil NO <sub>3</sub> <sup>+</sup> and NH <sub>4</sub> <sup>-</sup>	4	10	+6	8	7	-1
Mineralizable N	945	882	-83	480	7	-1
Microbial biomass N	318	332	+14	153	116	-37
Total organic N	8143			3144		

Table 4: Effect of soil cultivation on N budgets for the 0-30 cm soil depth interval of grass pastures at two sites in Queensland, Australia (after Doran, 1987).

The data show that tillage can be effective in releasing nutrients and prevent increased immobilisation of N by microbial biomass; thus, periodic cultivation can have a beneficial effect on the nutrient dynamics of the soil system.

Similarly, while addition of organic amendments have been shown to increase yields by increasing the nutrient status of the soil, sustained nutrient availability may be compromised and crop yield can be depressed if immobilisation of nutrients occurs during decomposition of the organic residues.

As emphasised before, the cycling of P is largely decoupled from the C and N cycles; nonetheless, SOM can assert strong controls on the availability of P and it is therefore appropriate to review the P-SOM dynamics in more detail. Humic substances can have an important effect on P availability through specific adsorption reactions, as discussed in one of the previous chapters. As humic molecules become adsorbed onto oxide surfaces, they have a competitive effect on P adsorption and studies have found that treatment of soil with humic extracts caused surface charge to become more negative, resulting in decreased P adsorption (Haynes and Mokolobate, 2001). A study by Sibanda and Young (1986) showed that the presence of humic and fulvic acids on soil and oxide surfaces had an inhibitory effect on P adsorption. However, the competitive ability of humic molecules with P does not exclusively lie in the occupation of adsorption sites by humic functional groups, but can also be attributed to the unfavourable electrostatic field that is generated around the humic molecule (Haynes and Mokolobate, 2001). Saidou et al. (2003) investigated the effects of NPK and mulch additions on P-deficient soils. They found that the application of mulch alone had no effect on yields, which was attributed to P immobilisation, but combined applications of NPK and mulch as well as NPK alone increased yields. For the studied maize cultivar, NPK fertilisation resulted in efficient P uptake but not in an improved P utilisation efficiency, which was in fact lower than without NPK. Mulch on the other hand, increased P utilisation.

Similarly, Erich et al. (2002) investigated the role of SOM on P dynamics by amending soils (podzols) with compost and manure for 5-6 years. Plant available P and desorbable P were both higher in the amended soils compared with the control; however, both amended and unamended soils sorbed similar amounts of P. They observed that sorption of P was accompanied by release of C, suggesting that soluble C may influence P sorption. Erich et al. (2002) suggested that the release of C with increasing amounts of P sorbed was due to P displacing soluble organic ligands

from adsorption sites, which was supported by the observation that amended treatments had more C in solution than unamended treatments. However, given that the amended treatments received a greater net source of carbon, it is uncertain whether the C in solution is due to displacement or due to the amendments.

The linkage between P sorption and C desorption had been suggested previously for allophanic soils but not for podzols, suggesting that this process is not necessarily soil-type specific. In conclusion, if P sorption is reversible at higher levels of DOC, inputs of organic materials which increase levels of DOC may increase P solubility and availability to plants. However, a word of caution is warranted as increased levels of available P could also contribute to export of P to surface waters. The measured degree of P saturation (DPS) in the studied soils was 31-37%, and in the Netherlands, soils with >25% DPS are considered at risk for contributing P to groundwater. However, the P-OM relationship is not a simple one as some studies found no obvious relationship between P adsorption and SOM content and Boggard et al. (1990) found that the removal of SOM did not increase P adsorption.

With respect to the specific components of SOM, LMW organic acids (citrate, malate, oxalate) have been shown to compete with P for adsorption sites on Fe and Al hydrous oxide surfaces by ligand exchange reactions (refer to Figure 45). As adsorption of organic acids increases with decreasing pH, the competition with P is particularly enhanced at lower pH values. Citrate and oxalate appear to cause larger reduction in P adsorption than tartrate or acetate. The maximum reduction in P adsorption occurred when organic acids were added prior to P addition and the effectiveness in inhibition of P adsorption increased with decreasing pH (Haynes and Mokolobate, 2001). Consequently, addition of organic amendments can increase P availability to plants by decreasing the P adsorption capacity of soils. The often observed reduced P adsorption and increased P availability following application of organic amendments (e.g. animal manure) is thought to be a cumulative result of a) release of inorganic P from decaying residues, b) blockage of adsorption sites by organic acids and humic materials and c) rise in soil pH during decomposition (greater negative charge of adsorption sites) and complexation of soluble Al and Fe by organic molecules. Furthermore, when net P is released during the decomposition of organic residues, it is readily adsorbed and the proportion of adsorption sites occupied by P increases and the P adsorption capacity of soil is decreased with respect to subsequently applied P. Therefore, the greater the P content of the residue applied (e.g. lucerne, barley and grain opposed to sawdust, wheat straw and maize) the greater the decrease in P adsorption capacity of

soil (Haynes and Mokolobate, 2001). Finally, P deficiency in soils often occurs together with toxic levels of Al and low pH. Under these conditions P availability is in part controlled by precipitation reactions and precipitates in and around plant roots inhibit P translocation to stems and leaves. Thus, addition of SOM would result in complexation and precipitation of soluble Al, a reduction in activity of monomeric Al in soil solution and a rise in pH, which in turn would increase the availability of P to plants (summarised in Figure 54).

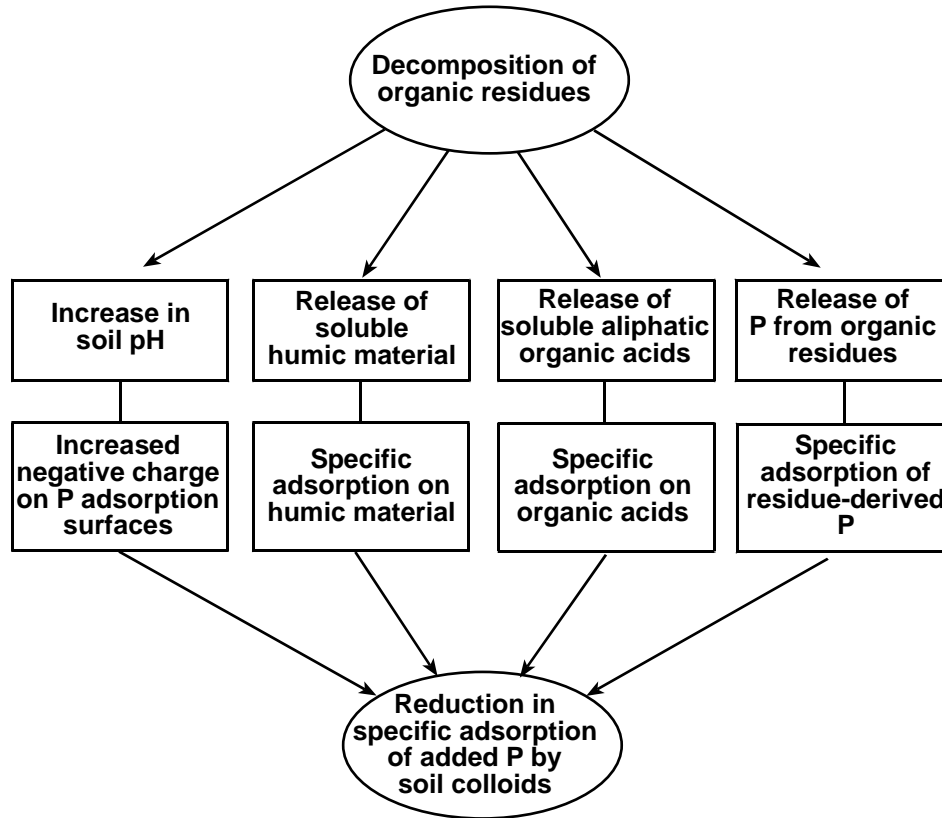


Figure 54: A conceptual model of the major processes that lead to a reduction in P adsorption and increased P availability when organic residues are applied to soils (redrawn from Haynes and Mokolobate, 2001).

The effect of inorganic fertiliser as well as FYM, compost and green manure on the soil fertility status in general was tested by Tolanur and Badanur (2003a,b). Their data confirmed the results from other studies (e.g. Agbenin and Goladi, 1997) that fertiliser (NPK) alone was not able to arrest the decline of C and N, and only a combination of NPK together with organic amendments increased and sustained soil productivity. The highest grain yield for sorghum and chickpea was

obtained with 50% each of green manure and fertiliser N. Organic manure specifically enhanced labile P content through complexation of cations.

While conversion of soils under native vegetation to agriculture usually results in a decline in nutrients and CNP levels, Zhang and He (2004) reported that the conversion of upland red soils to irrigated flooded rice fields in China increased C, N, P, K and POM contents and raised pH, ECEC and aggregate stability in the plough layer (0-15 cm). The study was conducted on 66 rice fields where conversion had taken place from 2 to 100 years ago. The increase in C and N levels was observed not only for the surface but also for the subsurface soil layers and lasted for 30-40 years after conversion and then stabilised (Fig. 55A and B), whereas total K and clay content decreased after that time period.

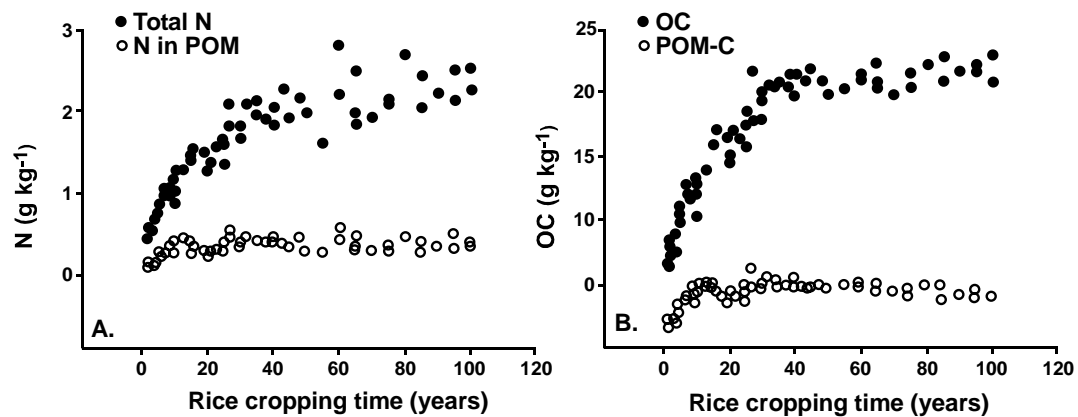


Figure 55: Concentrations of organic C and N in the surface layer (0-15 cm) as a function of rice cropping time: (A) total N and N in POM and (B) organic carbon (redrawn from Zhang and He, 2004).

POC content stabilised earlier than total SOC content and was related to the rate of increase in yield during the first 15 years and stabilisation after 40 years (Fig. 56). These changes were mainly attributed to the change from aerobic to anaerobic condition and C and N levels were increasing until a new input-output balance was reached.



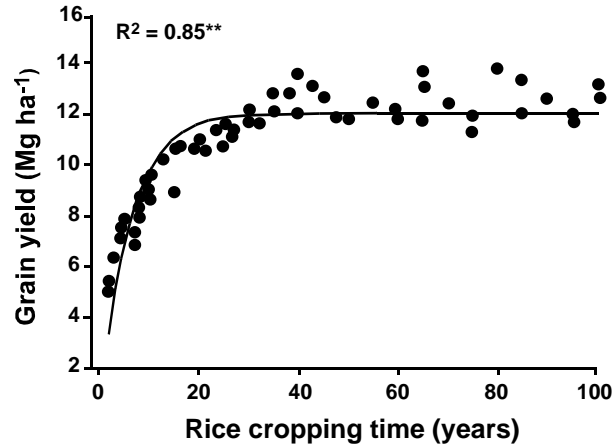


Figure 56: Relationship between grain yield in 1998 and rice cropping time (redrawn from Zhand and He, 2004).

#### Summary

- SOM ensures the supply and sustained release of macro-and micro-nutrients.
- With the exception of fertilisers, SOM provides the largest pool of macro-nutrients (C,N,P,S) for plant growth.
- 1% SOC content is considered a lower threshold value with regard to N supply from plant residues.
- the particulate organic carbon (or 'active') fraction is often considered the most important proportion of SOM in providing nutrients to plants.
- Ratios of C,N,P and S are often used to assess the nutrient status of SOM or plant residues.
- Soil aggregates are important in providing transient storage capacity for macronutrients.
- Periodic cultivation (tillage) releases nutrients to the soil system.
- Addition of organic amendments may improve the nutrient status of the soil, but nutrient availability may be depressed if immobilisation of nutrients occurs during decomposition.
- SOM (particularly LMW organic acids) can improve P availability through specific adsorption reactions as competition for adsorption sites decreases the amount of sorbed P.
- Fertiliser (NPK) addition alone cannot arrest the decline of C and N, and a combination of NPK together with organic amendments is necessary to sustain soil productivity.

### Soil resilience and organic matter

Resilience has been defined by Baldock and Nelson (1999) as the capacity of an ecosystem to return to its initial state after disturbance. In that respect, resilience is a soil property and an indicator of how well a system is able to recover. Together with soil resistance (the inherent capacity to withstand disturbance) it ultimately defines the stability of soil. Nannipieri et al. (2003) found that soils with a greater microbial diversity were more resistant and resilient to perturbations than soils with less diverse communities. Griffiths et al. (2000) found that soils fumigated with chloroform were more resistant and resilient to conditions such as heating or treatment with  $500 \mu\text{g Cu g}^{-1}$  soil if they had a high microbial diversity. Degens et al. (2001) noted that an arable soil was less resistant to microbial cell stresses and other disturbances, compared with a pasture soil. Since the SOC content, CEC, and microbial biomass were also greater in the pasture soil, these factors were suggested to have increased the resistance of soil microorganisms to stresses and disturbances.

These results indicate that the resilience of a soil is really a measure of the functionality of the whole ecosystem. Therefore it is governed by the adequate performance of physical, biological and chemical functions, which in turn is to a large extent determined by the SOM content and its chemical composition. In essence, resilience of a soil is a measure that provides a conclusive analysis as to how well the different functions of a soil are carried out and the ability of the ecosystem to maximise the utilisation of the SOM resource.

#### Summary

- The resilience of a soil is determined by a combination of SOC content, CEC and microbial biomass; in that sense, resilience of a soil is a measure of the functionality of the whole ecosystem.
- Soils with a greater microbial diversity were more resistant and resilient to perturbations than soils with less diverse communities.

## THE WORTH OF SOC

Soils play an important part in the global carbon cycle as they contain about 1550 Pg of organic carbon and 750 Pg of inorganic carbon (0-100 cm depth). Accordingly, the total soil carbon pool of 2300 Pg is three times that of the atmospheric and 3.8 times that of the biotic pool (Lal, 2002). However, historic loss of SOC due to inappropriate land use and mismanagement practices has caused a decline in soil quality and emission of C into the atmosphere. Agricultural practices have contributed to the depletion of the SOC pool through deforestation and biomass burning, drainage of wetlands, ploughing, removal of crop residues, summer fallowing and cultivation. The loss of SOC is attributed to three main processes: 1) oxidation and mineralisation due to the breakdown of aggregates leading to exposure of carbon, 2) leaching and translocation as DOC or POC and 3) accelerated erosion by runoff and wind (Lal, 2002). Soil degradation leads to the depletion of the SOC pool and emission of greenhouse gases from soil to the atmosphere. Physical, chemical and biological degradation lead to a reduction in biomass production and the amount returned to the soil, decline in soil quality and emission of trace gases to the atmosphere. However, strategies exist to sequester SOC and options are summarised in Figure 57.

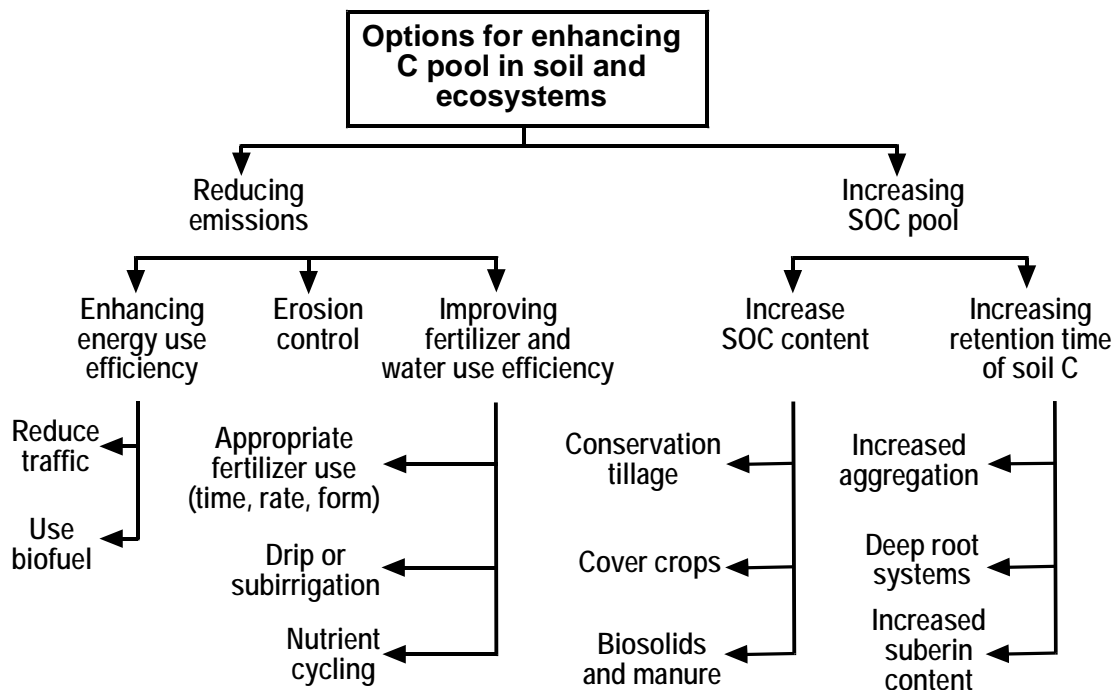


Figure 57: Technological options for enhancing C pool in soil and ecosystems (redrawn from Lal, 2002).

In fact, Lal (2002) advocated that 60-70% of the SOC loss can be re-sequestered through the adoption of sensible agricultural practices. He further advocates that while growing forests is an important measure to sequester greenhouse gases, C sequestration in agricultural soils does not only add to sequestration of greenhouse gas C, but also to an enhancement in soil quality and agronomic productivity. Over a short period (25-30 years), this is considered the most cost-effective option for sequestering greenhouse gases.

Thus, net soil carbon sequestration is of worth not only with regard to sequestration of greenhouse gases, for which accounting strategies are being developed, but also with respect to maintaining and possibly enhancing soil quality. Because SOC consists of several pools which act on different processes and over different time scales, the worth of soil carbon cannot be assessed by simply using the increase in crop yield as a measure. While the sequestration of greenhouse gases as SOC and the development of accounting schemes could provide an incentive for farmers to modify management practices, it only takes into account the net amount of C sequestered without its quality-defining attributes (e.g. functional groups, buffering capacity, nutrient storage). Stressing the beneficial effects of increased SOC as a system (i.e. a collective of several functions) rather than as a single quantity, may encourage landowners to adopt strategies that are promoted just for the benefit of greenhouse gas sequestration.

Antle et al. (2002) examined the implied costs of sequestering a tonne of C for dryland grain production areas in the northern plains of the U.S., and estimated that the marginal cost of soil C ranges from \$420 to \$100 per MT. Lal et al. (1998) calculated that approximately 49% of agricultural C sequestration can be achieved by adopting conservation tillage and residue management, 25% by changing cropping practices, 13% by land restoration and 7% through land use change and better water management. However, the important question is whether producers are willing to adopt practices that enhance soil C and if so, at what costs or at what benefits? Antle et al. (2002) estimated that agriculture is able to sequester C at a cost that is competitive with emissions reduction and afforestation. They advocate a per ha payment policy that should provide incentives to farmers to switch to a system which would increase soil C levels. Producers would enter into contracts with agencies to provide C sequestration services for a specified time period by adopting specific land use change or management practices. In such a scenario, the producer would only agree to such a contract if the profits per ha of the current (profit-maximizing) practices are less than the alternative practices in addition to the C contract payment.

Their analyses predicted that a policy that provides payments to adopt alternative practices to increase soil C ranged from \$12 to \$140/MT of C (avg \$50/MT).

Another study by Belcher et al. (2003) compared the impacts of carbon tax and carbon credit policies on the sustainability of agroecosystems and net emissions of CO<sub>2</sub>. Currently tax rates used to achieve CO<sub>2</sub> emissions reduction of 25% below 1990 levels for C vary between \$25-\$150 per t of C, and values of \$25, \$75 and \$125 per t of C were used in Belcher et al.'s (2003) study. They found that C tax had no significant effect on CO<sub>2</sub> emissions or environmental sustainability but decreased economic sustainability. Carbon credits, on the other hand, decreased emissions and increased environmental and economic sustainability. Carbon credits were thought to provide an effective incentive to farmers to increase soil C stocks.

Specifically, the benefits of the C credit scheme were related to the fact that C stocks in agricultural soils have a distinct economic value for landowners, which are incorporated into the farmer's profit, maximizing land management decisions. With regard to cropping practices, they found that wheat-wheat-fallow rotations had the greatest C sequestration potential (0.15t ha<sup>-1</sup> yr<sup>-1</sup>) and it also was the most economically attractive option (compared with wheat-fallow, wheat-canola-pea and wheat-fallow-pea). However, forage provided the greatest increase with 0.7t ha<sup>-1</sup> yr<sup>-1</sup>. Thus, at \$25 t<sup>-1</sup> credit, rates of C sequestration would increase revenues by \$3.75 and \$17.5 ha<sup>-1</sup>. Ideally, this would imply that there would be a shift from annual production towards increased forage. Belcher et al.'s (2003) simulations also indicated a positive feedback between yield and SOC content. Larger SOC stocks improved soil function (WHC) and nutrient availability (P and N), which in turn increased future yields. Accordingly, yield levels were maintained with lower requirements for N as soil N increased. Thus, greater SOC stocks translated into greater revenues directly through C credit payment and indirectly through the effect of increased soil function on crop yield and N fertiliser cost. However, their model did not explicitly incorporate feedback loops between the C storage capacity of soil and the C sequestration rate, as in reality the C sequestration rate will approach 0 as the C capacity is filled.

In conclusion, the benefits of increased SOC stocks by adopting sensible land management practices extend beyond the much-discussed greenhouse gas sequestration schemes. In fact, direct benefits of increased SOC content to the landowner include increased productivity, sustainability and, above all, improved soil quality.

## CONCLUSIONS

The previous chapters illustrate the importance of SOC by contributing to the adequate performance of various soil functions. However, it is also evident that the interactions between SOC and physical, chemical and biological soil functions are complex. Particularly, the use of total SOC content as a measure of, for example, soil quality, is not adequate. Instead, this review illustrates that discrete SOC pools can influence particular soil functions and that specific amounts are required to achieve optimal effects. Therefore, total SOC needs to be separated into biologically meaningful carbon pools to account for the value of each pool to overall soil quality. Only through such a separation will it be possible to a) determine which carbon pools (quality) contribute most to the performance of certain soil functions and b) how much (quantity) of the carbon pool is required for adequate performance.

Any fractionation scheme that divides SOC into pools is conceptual and it is important to bear in mind that SOC is not composed of distinct entities but exists as a continuum. In addition, most soil functions are not affected by only one particular carbon pool but are influenced by several carbon pools, often synergistically. The importance of interactions between SOC pools over time was exemplified in this review by the combined effect of labile and humified fractions, resulting in optimal and sustained structural stability.

In an earlier study, Baldock and Skjemstad (1999) demonstrated the potential consequences of land management changes on SOC pool structure over time by utilizing the Rothamsted soil carbon model (Skjemstad et al., 1998). The model was initialised by using data from the Waite Permanent Rotation Trial. Figure 58 shows the predicted changes in the contents of POC, humus and inert organic carbon after conversion of a wheat/fallow management system to permanent pasture.

The importance of changes in SOC pools relative to total carbon content is illustrated by examining the pool structure at two different times, before (at 15 years) and after (at 43 years) the conversion. At both times, the organic carbon content attained  $18 \text{ g C kg}^{-1}$  soil but the soil under the pasture had a much higher POC (+800%) and lower humus (-30%) content compared with the soil under the original wheat/fallow trial.

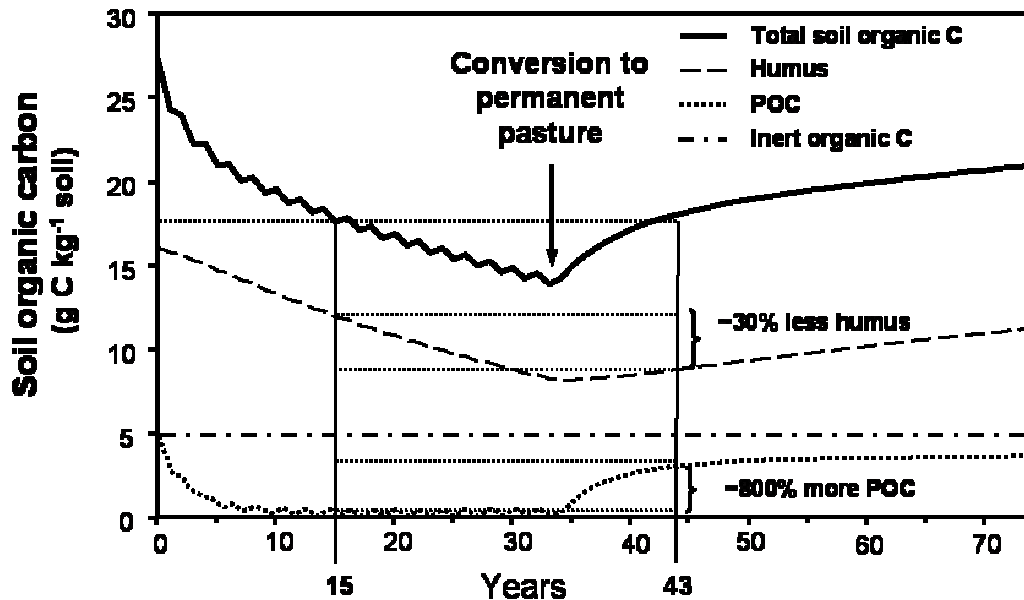


Figure 58: Predicted changes in the contents of POC, humus and inert organic carbon after conversion (33 years) from wheat/fallow to permanent pasture by using the Roth-C model. While SOC content at two different times (15 and 43 years) is the same, the composition of the SOC pool structure was quite different (modified from Baldock and Skjemstad, 1999).

Without the information from the SOC pools and relying only on total SOC content, it would appear that only eight years of permanent pasture were required to return the soil to the same level as it was after 15 years of wheat/fallow cultivation. Instead, the results from the model run indicate that the SOC pool structure at the two points in time was very different, which has an effect on the soil functions and the resilience of SOC to further management changes. Specifically, if the pasture system at 45 years changed back to a more intensive management, SOC losses would be greater as the stable humus pool had not reached the level at 15 years of cultivation.

Ultimately, the changes in the different carbon pools over time and the resulting effects on soil functions are the most important information with respect to land management and land use changes. Accordingly, the current GRDC project (CSO 00029) addresses this question by a) determining the effects of carbon pools on major soil functions and b) extending the concept given in Figure 58 by modelling changes of the SOC pool structure over time (e.g. due to soil degradation, land management changes, etc.).

## APPENDIX

### List of abbreviations

ACP = amorphous calcium phosphate  
AHC = acid-hydrolysable carbon  
AI = aggregate index  
Al = aluminium  
ASI = aggregate stability index  
BC = buffer capacity  
BS = base saturation  
C = carbon  
Ca = calcium  
CE = catabolic evenness  
CEC = cation exchange capacity  
CT = conventional tillage  
 $D_b$  = bulk density  
DCDP = dicalcium phosphate dihydrate  
DDC = difficult dispersible clay  
DOC = dissolved organic carbon  
DOM = dissolved organic matter  
DPS = degree of phosphorus saturation  
EDC = easily dispersible clay  
ECEC = effective cation exchange capacity  
FC = field capacity  
FYM = farmyard manure  
GMDH = group method of data handling  
HMW = high molecular weight  
HAP = hydroxyapatite  
HOC = hydrophobic organic compounds  
HWC = hot-water soluble carbon  
IAE = individual aggregate energy  
IOM = inert organic matter



$K_{OC}$  = organic carbon normalised sorption coefficient

$K_{OW}$  = octanol-water partition coefficient

LF = light fraction

LMW = low molecular weight

MWC = municipal waste compost

MWD = mean weight diameter

N = nitrogen

$NH_4^+$  = ammonium

NPK = nitrogen, phosphorus, potassium fertiliser

NPP = net primary production

NT = no tillage

O = oxygen

OCP = octa-calcium phosphate

OM = organic matter

P = phosphorus

$P_w$  = change in water concentration by weight

PAH = polycyclic aromatic hydrocarbons

PAW = plant available water

$PBC^K$  = potential buffer capacity for potassium

POC = particulate organic carbon

POM = particulate organic matter

PTF = pedotransfer function

PWP = permanent wilting point

S = sulfur

SOM = soil organic matter

SOC = soil organic carbon

SSA = specific surface area

SWR = soil water retention

TN = total nitrogen

VBC = buffering on a soil volume basis

WDC = water-dispersible clay

WSA = water stable aggregates

WHC = water holding capacity

ZT = zero tillage

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