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The retention of organic matter in soils

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Key words: organic matter, turnover, organomineral interactions, clay, base status, cation bridges, oxide surfaces

Abstract. The turnover of C in soils is controlled mainly by water regimes and temperature, but is modified by factors such as size and physicochemical properties of C additions in litter or root systems, distribution of C throughout the soil as root systems, or addition as litter, distribution of C within the soil matrix and its interaction with clay surfaces.

Soil factors which retard mineralization of C in soils are identified from correlations of C contents of soils with other properties such as clay content and base status. The rate and extent of C mineralization depends on the chemistry of the added organic matter and interaction with clays of the microbial biomass and metabolites.

The organomineral interactions are shown to depend on cation bridges involving mainly Ca in neutral to alkaline soils, Al in acid soils and adsorption of organic materials on iron oxide surfaces. The various organomineral interactions lead to aggregations of clay particles and organic materials, which stabilizes both soil structure and the carbon compounds within the aggregates.

Introduction

Soils represent a major pool (172×10^{10} t) in the cycling of C from the atmosphere to the biosphere and are the habitat for terrestrial photosynthetic organisms which fix some $11 \times 10^{10}\,\mathrm{t\,C\,y^{-1}}$, about one half of which eventually finds it way into soils. About the same amount of C is returned to the atmosphere annually as the fauna and flora utilize plants as a source of energy and nutrients. Organic matter in soils is thus represented by plant debris or litter in various stages of decomposition through to humus, and includes the living organisms in soils. Above ground phytomass is generally excluded from soils, but roots may be included. It is necessary to establish a consistent terminology and the following definitions will be used:

- *Organic matter*: natural-C-containing-organic materials living or dead, but excluding charcoal.
- *Phytomass*: materials of plant origin usually living but also includes standing plants which are dead, e.g. trees.

- *Microbial biomass*: the living population of soil microorganisms.
- *Litter*: dead plant (and animal) debris on the soil surface.
- *Macroorganic matter*: organic fragments in soils from any source which are $> 250\,\mu m$.
- *Light fractions*: organic fragments obtained from soils by flotation on heavy liquids of densities 1.6–2.0 $Mg\,m^{-3}$. This fraction may be equated with macroorganic matter. Both fractions are readily obtained by combinations of sieving, flotation and centrifuging after appropriate disruption of soils.
- *Humus*: material remaining in soils after removal of macroorganic matter. It should be noted that in some texts humus is synonymous with organic matter, and that biomass may or may not be included in humus.

The relative proportions of humus and macroorganic matter vary widely in different soils. Generally cold, acid, arid and sandy soils contain higher proportions of organic matter as plant debris than as humus because low temperature, low pH, or lack of water limit comminution of litter by fauna. Low base and nitrogen contents and high lignin contents of litter are also involved.

Humus may be further characterised chemically, physically and biologically. Chemical description is often based on extraction of organic matter by alkali to give the procedurally defined fractions known as humic acid, fulvic acid and insoluble humin. Descriptions of the development and details of this chemical approach and studies of 'non-humic' materials such as carbohydrates, proteins, lipids and other groups of biological chemicals with well defined subunits, such as sugars, amino acids, and fatty acids can be found in a range of textbooks (e.g. Stevenson 1982; Soil Biochemistry Vols 1–5; Aiken et al. 1985).

Studies of soil organic matter using isotopes have shown clearly that the classical fractionation scheme is not well aligned with biological and biochemical processes operating during decomposition of plant materials and the formation of humus (Oades & Ladd 1977). The chemical fractions all contain recent C and other elements from both plants and microorganisms and the processes of decomposition of even simple substrates such as glucose cannot be usefully followed using this classical chemical scheme. Thus, other approaches to studies of dynamics of organic matter in soils have developed over the last two decades. The first approach is biological and has concentrated on the microbial biomass. Techniques are now available for detecting and measuring the biomass in toto using specific constituents of living organisms such as ATP. More significantly, fumigation techniques have been developed which not only allow a measure of the biomass, but in conjunction with the use of isotopic tracers enable studies of the sizes of 'pools' and fluxes of C, N, P and S between them (Jenkinson & Ladd 1981).

The second approach has been to consider the soils as a physical and biological system. Soils have been fractionated using physical methods in attempts to separate plant debris from microorganisms, microorganisms from metabolic products, and all these materials from clay. Proliferation of microorganisms in the presence of clay leads to a currently ill-defined organo-clay complex involving both living organisms and and metabolic products. This involvement of the biological cycle with inorganic components in soil results in protection of organic materials from degradation and increases the residence time of C in soils. This short review examines factors responsible for retention of C in soils based on:

— turnover of C in soils,
— C contents of soils,
— the chemical composition of organic materials,
— interactions of organic matter with clay, and
— the role of cation bridges and oxides.

Turnover of organic C in soils

The C cycle, in which soils represent one station, is driven by solar energy. The maximum capture of energy by photosynthetic reactions is 6% of incoming radiation, but this is rarely achieved, and in agroecosystems the efficiency of capture is about 1%. Gross photosynthetic production is controlled primarily by latitude, modified by topography, as these factors control solar radiation, mean annual temperature, precipitation and evaporation, i.e. the water regime. Maximum photosynthetic fixation of C occurs in forests (2–4 kg C $m^{-2} y^{-1}$). Almost as much is fixed in some savannas, with production in temperate grasslands being about 1 kg C $m^{-2} y^{-1}$. In general about one half of the photosynthate reaches the soil, and thus mean inputs to soils in a given biome can be derived. "Turnover times" for organic C in soils can be derived by dividing the organic matter content of the soil by the annual input, expressing the answer in years. The turnover time for global C is 30 to 40 years, but varies by orders of magnitude in different ecosystems. The values obtained are subject to many errors and are "average" values calculated assuming the soil is in a steady state. Even so, they serve as a guide to the speed with which C moves through the soil and can direct us to the factors involved in retention of C in soils. Turnover times will be used in this review rather than half lives or rate loss constants. The rate loss constant (k y^{-1}) is the reciprocal of the turnover time. Half lives, usually designated $T_{1/2}$, are obtained by dividing 0.693 by k. Thus a turnover time of 30 years represents a rate loss of 0.033 y^{-1} and $T_{1/2} = 21$ y.

Using inputs and contents of C quoted for different ecosystems by Bolin et al (1970) and Bolin (1983), we can calculate turnover times for C in different systems.

Two conditions which lead to organic matter accumulation in soils are low temperatures and waterlogging. Either, or both, can lead to the formation of peats with turnover times exceeding 2000 years, or soils in the tundra with turnover times exceeding 100 years. Conversely, the shortest turnover times, 4 years, apply to equatorial forests where there is maximum net primary production. Presumably rapid decomposition does not allow accumulation of organic matter in the soils under equatorial rain forests.

Interesting comparisons can be made between forests and grasslands. For example a soil under savanna has twice the turnover time of that under tropical seasonal forests and even wider differences occur between forests and grasslands in temperate regions. Thus, although the forests produce more organic matter and perhaps twice as much debris reaches the soil surface, mineralization is rapid and organic matter contents are lower in forest soils than in grassland soils. These trends are valid within the same climatic zone, and one major factor involved is the distribution of organic matter. Most organic matter in forest soils is added as litter to the soils surface and is mineralized before it is incorporated in the soil. In grasslands, most of the organic matter is added to the soils as root systems and is well distributed in the top metre. It is thus thoroughly mixed with soil before mineralization. This undoubtedly slows the flow of C through soils. Material on the surface is readily accessible to organisms and is mineralized rapidly. This does not apply to standing dead trees, in which lack of surface area and unfavourable temperature and water regimes limit the rate of decomposition so that turnover times are measured in decades.

The rapid mineralization of surface litter compared with root systems in the soil is a major factor involved in the differences in retention of C under grasses and forests. Similarly organic matter in B horizons, or at depth in the soil is not easily accessible to organisms and is protected from rapid oxidation. This point is well illustrated by the linear relations showing increased mean residence times, based on determination of ^{14}C, with depth in many soils (Scharpenseel 1971). In Mollisols and also Alfisols, C is substantially older with increasing depth so that turnover times increase with depth in the profile.

Thus, the amounts and distribution of C inputs are important with respect to subsequent mineralization. The proportion of photosynthate transferred below ground via root systems is greatest for grasses compared with dicotyledonous plants and trees. For example, in natural temperate grasslands the mean ratios of underground biomass to green shoot biomass ranged from 2 to 13 (Sims & Coupland 1979). It was the lowest in desert grasslands, 3 to

6 in mixed prairie, 6 in mountain grassland and 13 in short grass prairie. Both low temperature and aridity favour production of below ground biomass. For tropical grasslands the ratios were much lower (Singh & Joshi 1979) and ranged from 2 to 0.5.

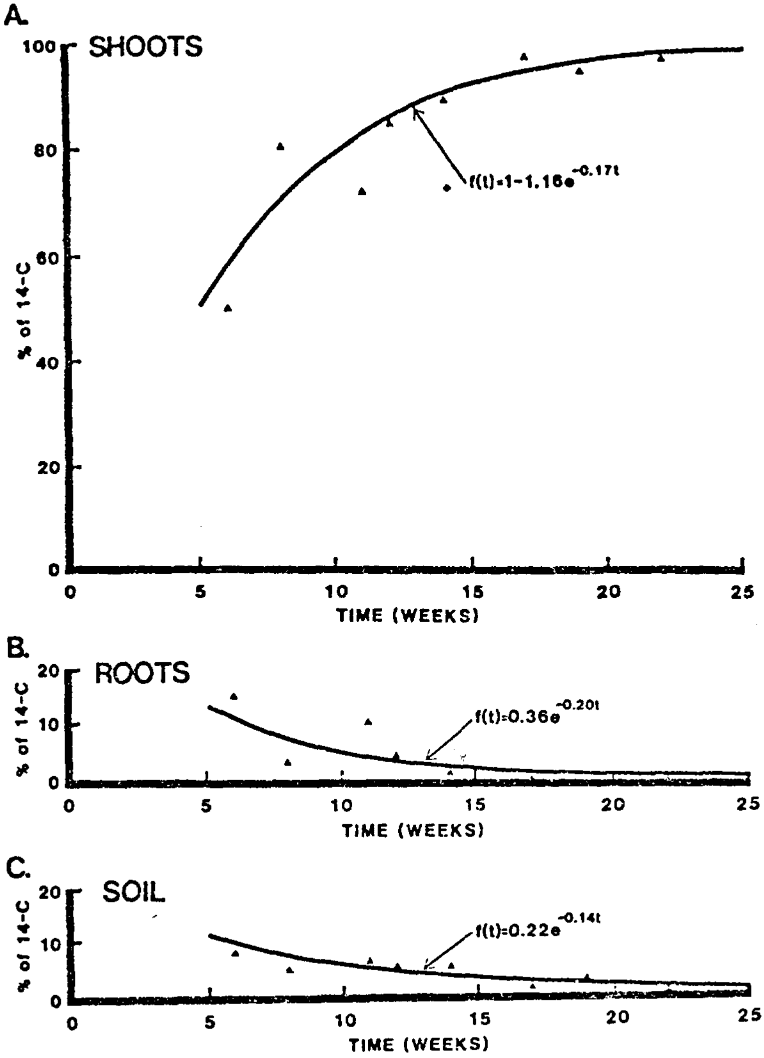
Data for forests indicates that the ratio of net primary production which goes below ground to that above ground (root:shoot ratios) is often about 2 (Harris et al. 1973). However ratios range from 4 for boreal coniferous forests to < 0.25 for forests in Mediterranean climates (Cole & Rap 1980). Studies on Douglas firs have shown that root:shoot ratios were greatest in older trees and on impoverished sites (Grier et al. 1981; Keyes & Grier 1981). While the more recent work recognises a greater underground component for forests the proportion of production below ground does not match that in grasslands such as prairies.

Measuring either annual inputs or losses is difficult. The two major problems are root respiration and root turnover. Annual rates of turnover for grass roots range from 20 to 80% in temperate regions and up to about 100% in the tropics (Singh & Yadava 1974; Sims & Coupland 1979; Dickinson 1982).

Surprisingly little information is available for partitioning assimilate above and below ground for agricultural crops such as cereals, in spite of the fact that most soils used for regular cereal production are losing organic C, especially in semi-arid regions. Earlier data for wheat plants obtained from glasshouse studies were extremely variable due in part to the different age of the plants (Keith et al. 1986). The distribution of assimilate in wheat plants growing in the field has been determined by successive pulse labelling with ^{14}C. The graphs in Fig. 1 show that during the first 6 weeks of growth half the photosynthate goes below ground, but one half of this is respired as CO_2, either directly from the roots, or through the microbial biomass. After 12 weeks growth more than 80% of the photosynthate remained in the tops. Total C fixed by the wheat crop amounted to 4403 $kg\,ha^{-1}$ of which 1305 $kg\,ha^{-1}$ (30%) was translocated below ground. This 30% includes all C lost from the root system by various means such as respiration and root exudates, and is thus higher than the 20% C in roots of cereals at the flowering stage or harvest obtained by other workers (Schultz 1974; Wojick 1979). From the growth data obtained through the season it is clear that root mass determined at harvest for cereals represents about two thirds of the total annual input of C to the root system (Hansson & Steen 1984).

For most agricultural soils turnover times are usually between 20 and 40 years and rarely exceed 160 years except in soils cultivated regularly for more than several decades (Jenkinson & Rayner 1977; Campbell 1978). The high turnover time in soils cultivated for a long time is assumed to be due to loss of the more readily available C as soil structure deteriorates. Thus another "spatial" factor emerges, i.e. the distribution of organic matter within the soil fabric.

Two other approaches to measuring annual inputs of C have been developed. One involves using the pulse of ^{14}C put into the atmosphere by atomic bombs between 1954 and 1963. The requirements for this approach are soil samples taken before and after the "bomb effect" from a soil under steady state conditions. The specific activity of C entering the soil each year must be known, and the amount of C remaining in the soil from additions



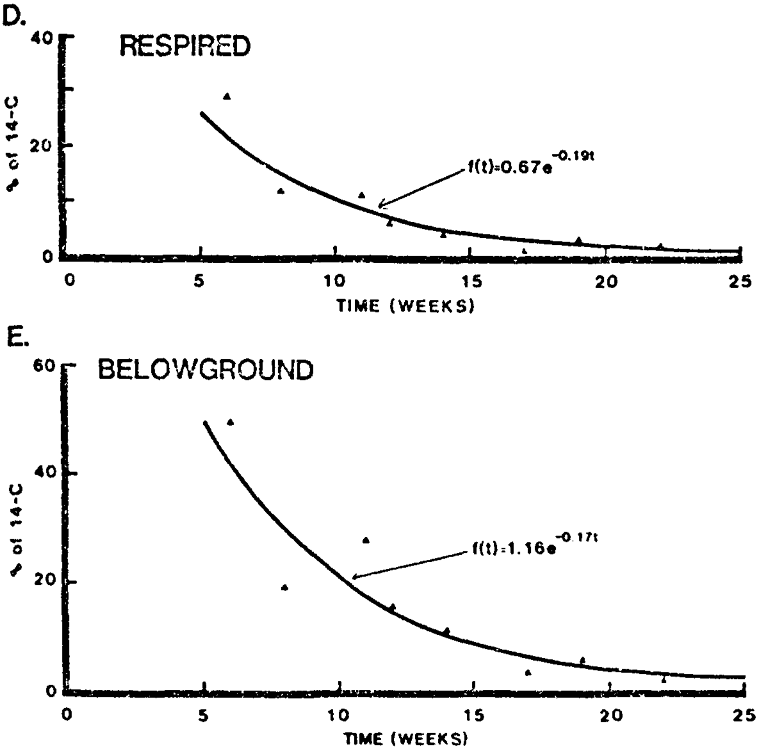


Fig. 1 (A, B, C, D, E). The proportion of ^{14}C components of the plant-soil system during growth of wheat plants. Reproduced from Keith et al. (1986) with permission from Pergamon Press.

of plant materials made in previous years must also be known. Jenkinson & Rayner (1977) obtained turnover times of 16 and 22 years for soils at Rothamsted from such information, indicating an annual input of 5 to 6% of the organic matter content. The problems and possibilities of this approach have been discussed by O'Brien (1984). A second isotopic approach uses the different ^{12}C to ^{13}C ratios in photosynthate fixed by C3 and C4 plants (Balesdent et al. 1986). The natural abundance of ^{13}C in C3 plants is -26% and for C4 plants -12%. Thus a change from C3 to C4 vegetation will slowly change the natural abundance of ^{13}C in soil organic matter. Measurement of the change of ^{13}C natural abundance with time allows annual inputs of C from the C4 vegetation to be calculated.

From this section we can conclude that there are a number of important spatial factors related to C additions to soil which will influence the time of retention of C in the soil. These can be listed as:

— the size and pysicochemical properties of the litter and root systems (Schlesinger 1977);

- whether the C is added to the soil surface as detritus, or distributed throughout the soil in root systems;
- the distribution of organic matter within the soil matrix, i.e. within aggregates;
- the distribution of C at the molecular level, i.e. its interaction with clay surfaces, to be discussed below.

Amounts of organic C in soils

Another approach to recognising factors involved in retaining organic matter in soils is to determine which factors are positively correlated with high organic matter contents and then to assess whether or not the factors are responsible for the high organic matter contents. There are problems if amounts of organic matter are expressed as per cent carbon. To what depth in the soil does the carbon content apply and has it been corrected for bulk density? If so, what recovery factor was used and how was C converted to organic matter? It is difficult to obtain sets of data for which organic matter contents are expressed in a consistent manner. Such data have been compiled for Australian soils (Fig. 2) and when soils are arranged in order of gravimentric organic matter content some interesting factors emerge. Fourteen out of 29 of the Great Soil Groups contained more than 2% organic C in the 0–10 cm layer. Five of these Soil Groups were calcareous soils, 3 dominated by Al and Fe, and 3 others were waterlogged to some extent; the rest were Ultisols. Of the other 15 Soil Groups with $<2\%$ C, only the Aridisols and Vertisols were calcareous and they existed in areas where low rainfalls limited annual inputs from vegetation. Thus, excluding soils subject to waterlogging, there is a positive correlation between organic carbon contents and either high base status or the presence of substantial contents of Al and Fe oxides. Andosols would also fit into this category (Jackman 1964; Zunino et al. 1982). These are the classical intrazonal soils which are often quoted in the older texts as being richer in organic matter than soils on other parent materials in the same climate. Note also the comparison between calcareous and siliceous sands. These sands contain little or no clay and indicate an influence of calcium without complications from clay.

There is also a positive correlation between clay and organic C contents because clay content and base status are usually related. Thus both base status and clay content are positively correlated with organic C content. The original causative agent in these cases is probably the parent rock as there is ample evidence to show that soils formed on base rich parent materials contain more clay and organic matter than soils formed under similar

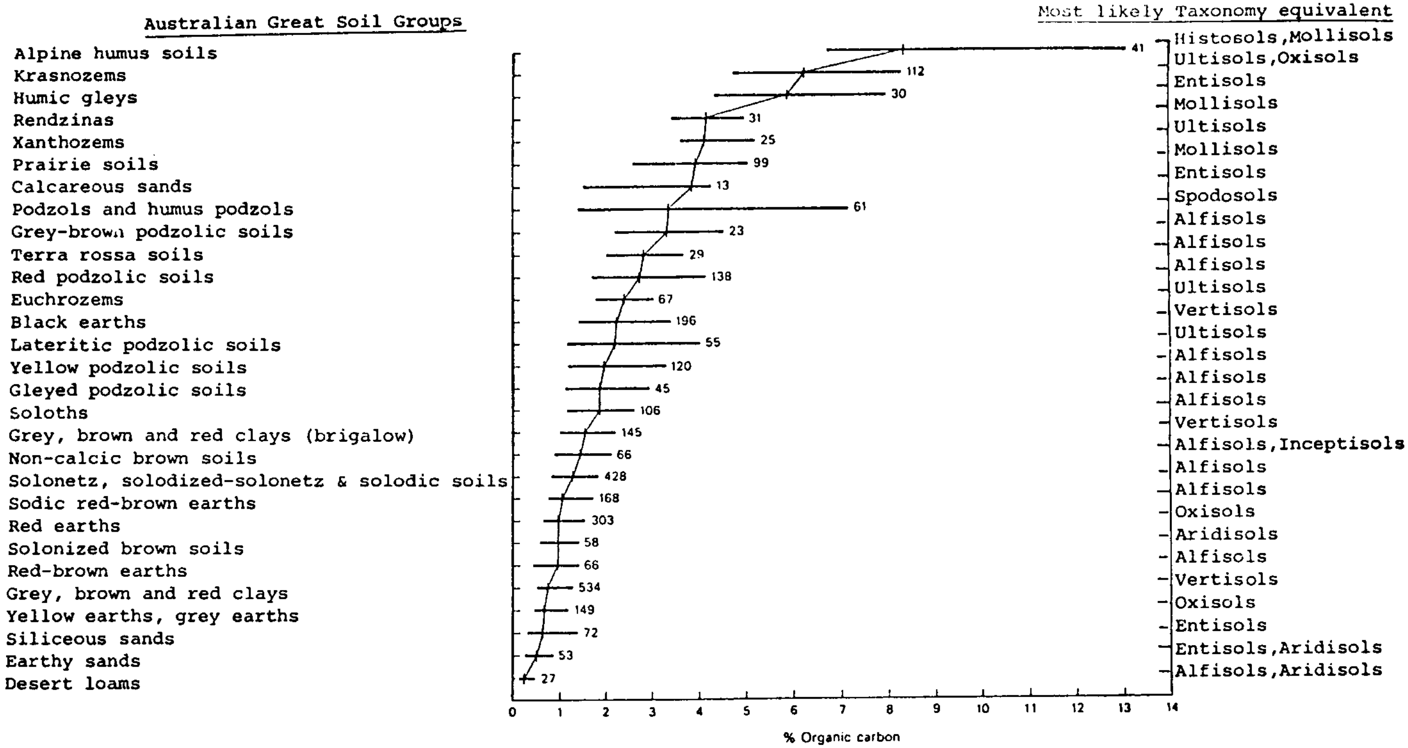


Fig. 2. Organic matter content of Australian soils (0–10 cm). Modified from Spain et al. (1983) with permission from CSIRO Editorial and Publication Service.

Table 1. Some properties of soils developed on acidic and basic rocks (Jenny et al. 1968).

Soil property	Soils formed on	
(%)	Acidic rocks	Basic rocks
Clay	12	21
Silt	21	33
Sand	58	35
C	1.7	2.8
N	0.07	0.12
Bases me/100 g	5.3	10.9

conditions from acidic materials. Data in Table 1 illustrates this point (see also Jones 1973; Kadeba 1978). Clay soils of high base status are usually more fertile and have greater annual inputs of organic matter than their acidic counterparts. Thus one cannot assume that correlations between organic matter contents and high base status and clay contents are causative. However, some mechanistic evidence suggesting that clay and Ca play a role in retaining C in soils will be discussed later.

It is interesting to plot the same Groups of soils against C/N ratios (Fig. 3). All the calcareous soils have C/N ratios < 15: they are neutral to alkaline and have mull type humus and low proportions of organic matter present as plant debris (macroorganic matter or light fractions). Conversely acid soils with mor type humus have C/N ratios from 15 to 30 and high proportions of C present as litter and plant debris. The general interpretation is that the basic environment accelerates the *initial* stages in the decomposition of plant debris, but the intimate mixing with soil components retards the *later* stages of organic matter decomposition increasing bulk retention time and organic carbon content. In acidic environments, the initial breakdown of litter is retarded but subsequent oxidation of C proceeds relatively quickly to CO_2 because of a lack of stabilizing mechanisms. We would thus predict shorter turnover times for C in acidic soils compared with calcareous soils. This statement apparently conflicts with the old concept that liming stimulates organic matter decomposition, but not if we consider the time scale for the stimulation which is relatively short and probably involves the decomposition of plant debris. The resulting biomass and its products are stabilized, and this stabilization eventually becomes the dominant factor.

The Australian data have also been examined using regional subsets and, as expected, precipitation is positively correlated and temperature negatively correlated with both C and N content of soils. the overall correlations are summarized in Table 2. The correlations are dominated by precipitation but the relative importance of the two soil factors, pH and clay content, are different for C, and N and between tropical and temperate regions.

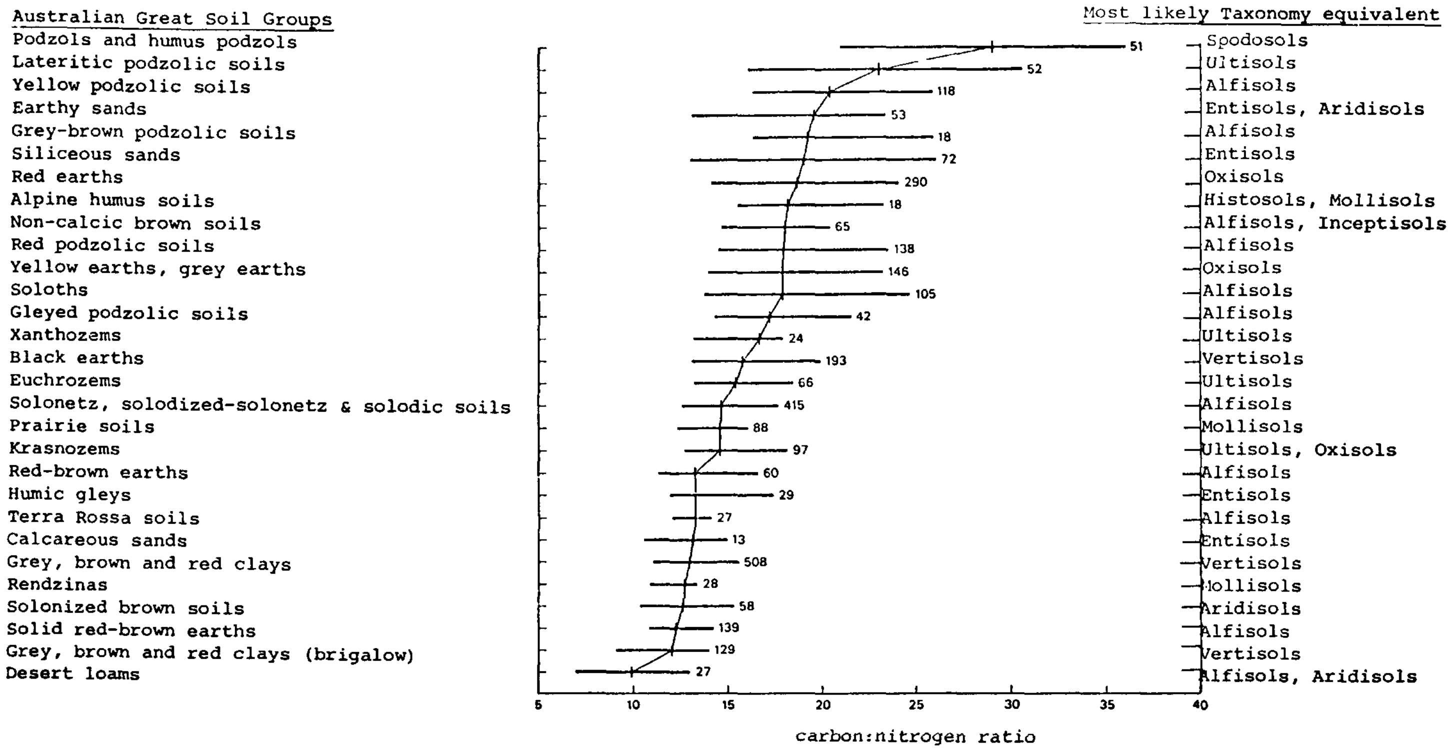


Fig. 3. C/N ratios of Australian soils (0–10 cm). Modified from Spain et al. (1983) with ermission from CSIRO Editorial and Publication Service.

Table 2. Overall correlations between C and N contents and other parameters. (For details of statistics see Spain et al. 1983.)

	Precipitation (P)	+C	+N
	Temperature (T)	−C	−N
	pH	−C	−N
	Base status	+C	+N
Temperate regions			
For C	P > pH > T > clay content		
For N	P > T > clay content > pH		
Troical regions			
For C	P > pH > clay content > T		
For N	P > clay content > T		

From data in this section we can conclude that high base status and clay content may be involved in retention of C in soils and need to be considered, along with the distribution of organic matter in the profile, and within the soil fabric.

Chemical composition of organic materials

In the first instance, it would seem that the nature of organic materials added to soil would have a major influence on the time they are retained in the soil. This is certainly true over short periods measured in terms of weeks or months but does not seem to be an important factor over periods of years, in aerobic soils at least. The mineralization rates of different organic materials are different but still rapid compared with the relatively slow mineralization of the microbial biomass and its metabolic products. It is the interaction of the biomass and recently-formed organic products with the soil matrix that inhibits the rapid mineralization which occurs when the restraints imposed by the soil matrix are removed. This has been demonstrated by extraction of specific chemicals from soils, e.g. lignin and polysaccharides, which were rapidly mineralized when added back to soils.

The rates of decomposition of a wide range of organic substances labelled with ^{14}C or ^{15}N have been reviewed (Oades & Ladd 1977; Paul & van Veen 1978). The rates of decomposition, even for simple substrates such as glucose, vary widely due to differences in water content, temperature, pH, and the availability of nutrients such as P and N for the microbial biomass. However, we can generalise and state that natural monomers from carbohydrates, proteins and many polyphenolic materials are decomposed in soils within weeks. Polymers are decomposed more slowly and resistance to decomposition increases with complexity. These principles are well illustrated in Fig. 4 which shows residual ^{14}C in soils after addition of a range

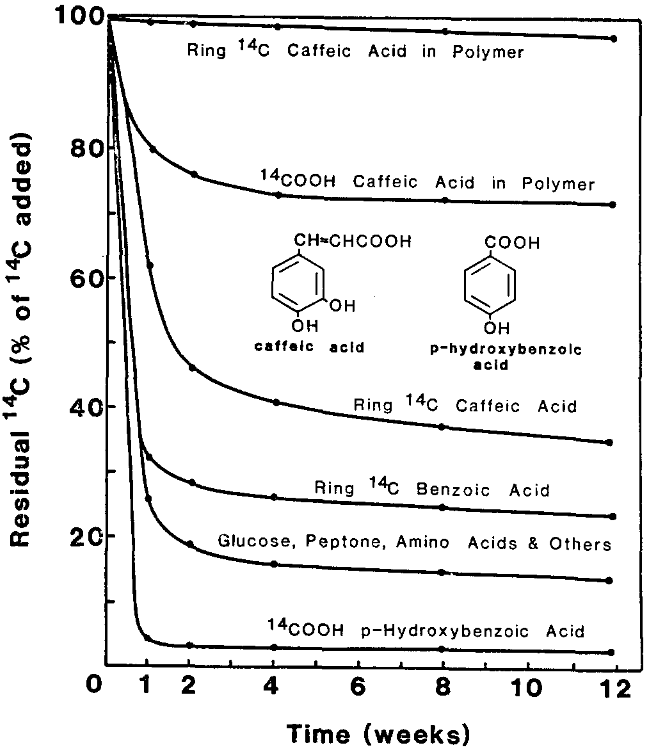


Fig. 4. Decomposition of ring compounds in soils. Redrawn from Haider & Martin (1975) with permission from the American Society of Soil Science.

of ^{14}C labelled materials. These comparisons were made during incubation periods of months and no attempt has been made to correct for residual ^{14}C present in biomass. Correction for ^{14}C in the biomass would reduce the content of residual ^{14}C in all cases, and to zero in the case of amino acids and sugars. Some natural polymers may persist in soils for years, e.g.:

— cellulose because it is crystalline and often encrusted with lignin and is not readily accessible to enzymes;

— polyphenols, particularly in random polymers such as humic materials, because they inhibit a range of organisms and are naturally recalcitrant; and

— proteins by interaction with polyphenols by a tanning reaction.

It has also been suggested that a similar reaction may be involved in stabilizing polysaccharides (Griffiths & Burns 1972). These mechanisms of chemical stabilization are probably common to all soils and it is difficult to see how they can be used to explain differences in turnover times for different soils.

The lowest rate constants for classes of organic materials listed by Paul & van Veen (1978) were for phenols and waxes. We are familiar with the retention of phenols in soils as integral components of humic substances. The stability of waxes has not been given much attention and may be far more important than is currently realised. For example, it is often stated that waxes, sometimes termed "bitumens" represent only 1 to 5% of the C in aerobic soils and it is assumed that maintenance of such low equilibrium contents indicated ready decomposition of plant waxes. However, there are several recent indications that soil organic matter contains a greater proportion of alkane materials than has been considered likely during the last few decades. The application of both liquid and solid state ^{13}C nuclear magnetic resonance (NMR) to soil organic materials has shown repeatedly that soil organic matter is more aliphatic than degradative chemical studies described in the text books would have us believe (Hatcher et al. 1981; Farmer & Pisaniello 1985).

Isopropanol-ammonia is a better extractant for waxes than the conventional petroleum ether or methanol-benzene lipid extractants (Ma'shum et al. 1987). Isopropanol-ammonia removed all the materials responsible for hydrophobic properties of a range of "problem" sands in Australia and in some cases the waxes extracted represented more than a quarter of the C

Table 3. Plant waxes extracted from soils with isopropanol-ammonia (Ma'shum et al. 1987).

% C	% of soil C extracted with isopropanol-ammonia
Sandy soils — South Australia	
1.34	14
0.32	25
1.03	17
0.60	15
0.47	23
0.36	47
0.67	27
0.67	27
0.24	21
0.33	21
0.49	31
Sandy soil — Western Australia	
1.18	23
3.41	13
2.22	11
Loams	
7.14	37
2.74	7

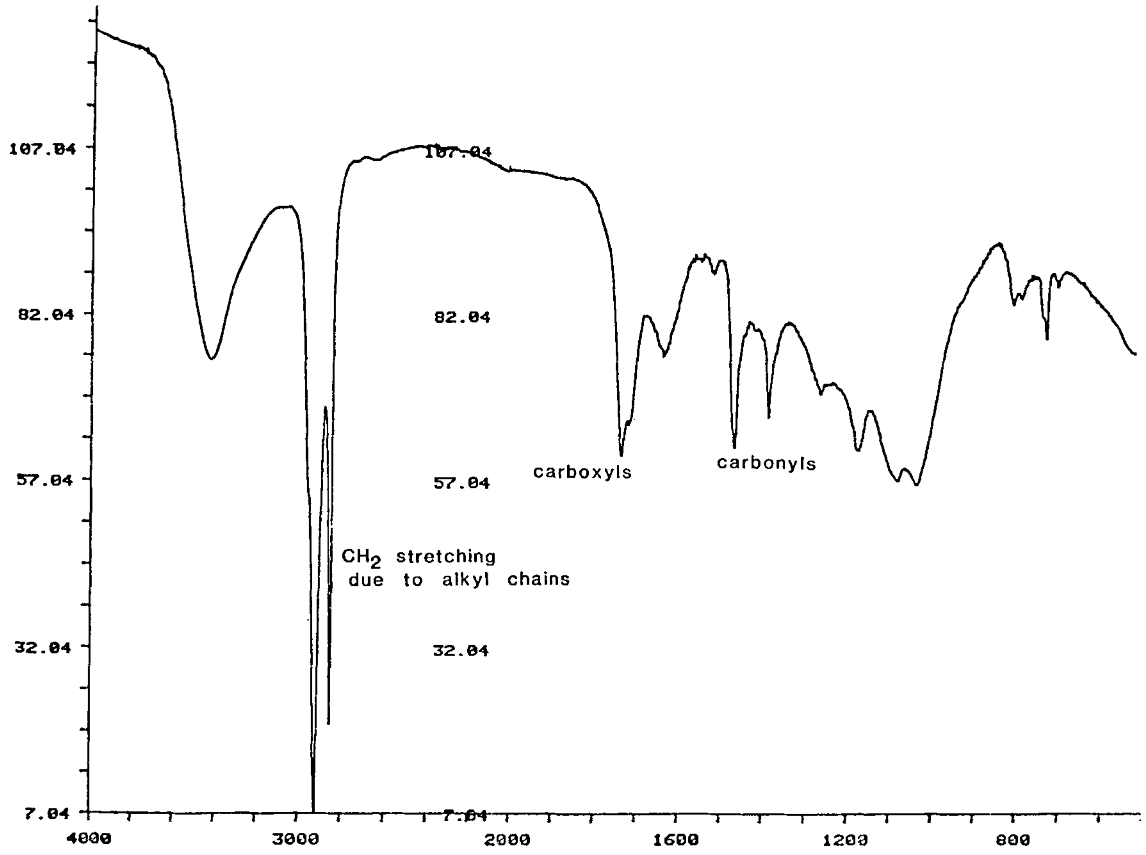


Fig. 5. Infra-red spectrum of waxes extracted from a non-wetting sand (Ma'shum et al. (1987).

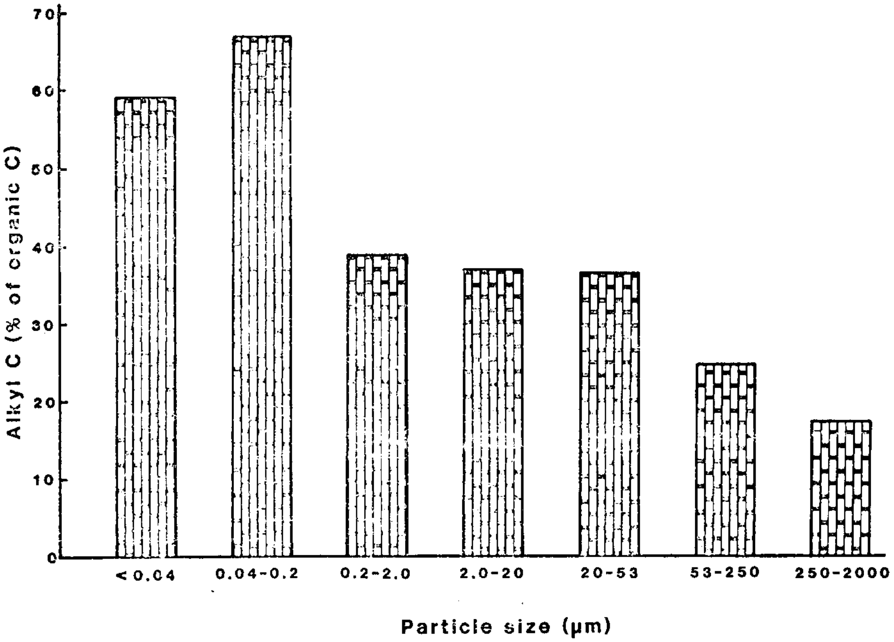


Fig. 6. Proportion of aliphatic C in particle size fractions of a Rhodoxeralf (Oades et al. 1987).

present (Table 3). The selectivity of the extractant for long chain materials is shown in the infra-red spectrum in Fig. 5. It has been confirmed by gas chromatography-mass spectrometry and other techniques that substantial proportions of the waxes are long chain acids, alcohols and resistant esters. The overall composition of the waxes is similar to that of plant waxes.

In a Rhodoxeralf which does not exhibit non-wetting phenomena, we have shown by NMR techniques that the alkane peak is completely dominant in fine clay fractions. Computer integration of the various peaks in the NMR spectra showed increasing contents of aliphatic materials in the smaller particle sizes (Fig. 6). Up to one half of the organic matter in clay fractions appeared to be aliphatic. While there are still problems in interpretating solid state NMR spectra, particularly in the presence of paramagnetic ions such as iron, it is clear that long chain hydrocarbons are present in large amounts. Considering the stability of carotene chains in materials such as sporopollenin, and biogenic sources of hydrocarbons in both coals and oils, perhaps we should be looking carefully at the alkanes as a source of the elusive "inert" pool of C in soils. This inert pool is used to explain the linear depth-mean residence time functions which apply to many soils and is included in more recent models of the C cycle in soils. There are other recalcitrant chemicals which are retained in soils and sediments for a long

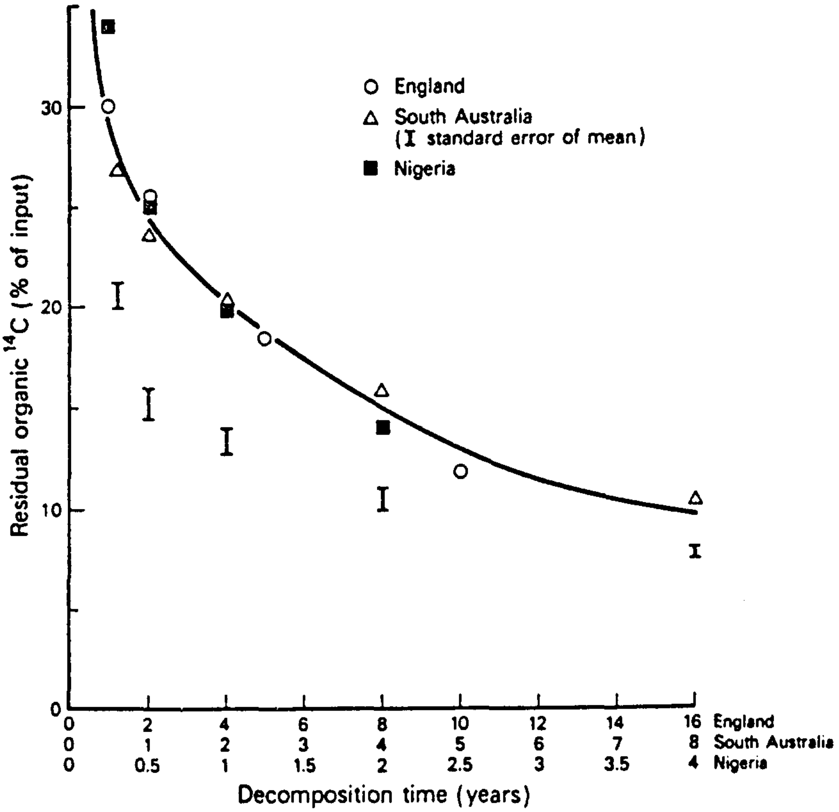


Fig. 7. Decomposition of plant materials in different climates. Reproduced from Ladd et al. (1985) with permission from the Australian Journal of Soil Research.

time, e.g. porphyrins which are stabilized as metal porphyrin complexes, and inositol polyphosphates which are stabilized by interaction with aluminium and iron species. Generally, the amounts of C involved are small and provide interesting interactions rather than major mechanisms to explain turnover times of C in different soils.

Decomposition of plant materials yields curves similar to those obtained for individual compounds except that the time scale is now in years (Fig. 7). The initial portion of the curve represents the decomposition of soluble materials and macromolecules before the constraints of the soil matrix become important. Subsequently we are looking at the results of successions of organisms utilizing more resistant plant components, dead organisms and metabolic products as sources of energy and nutrients.

Recently added C and N turnover at a considerably faster rate for a number of years than the indigenous C and N. This is illustrated in Fig. 8

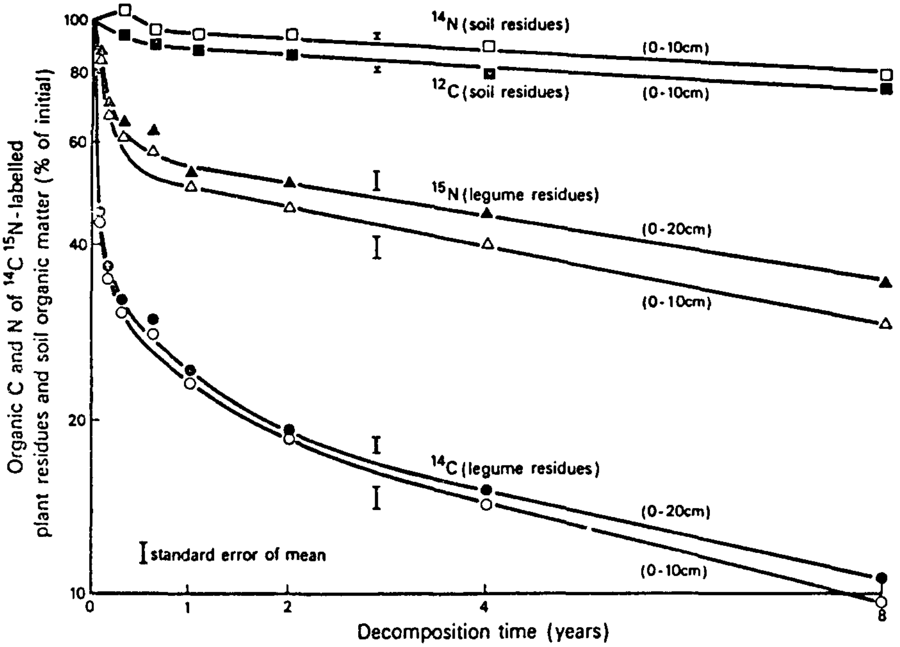


Fig. 8. Decomposition of ^{14}C, ^{15}N labelled legume material and soil organic matter. Reproduced from Ladd et al. (1985) with permission of the Australian Journal of Soil Research.

which shows the decomposition of ^{14}C-, ^{15}N-labelled legume material in the field. The residual C and N became increasingly less available or more stable. Part of the residual C and N was in the soil biomass which, after the first year of decomposition consistently had a turnover time of several years. The biomass declined at a faster rate than non-biomass (Fig. 9), so the proportion of residual ^{14}C and ^{15}N in the soil present in the biomass decreased with time. This occurs to a smaller extent in clays and loams than in sands, as we shall see later.

Interactions of organic matter with clay

While many workers agree that clay plays a role in stabilizing organic matter in soils it is difficult to find unequivocal evidence to support such a statement (e.g. Theng 1972; Paul 1984; Oades 1986). This is because:

— clay content is usually correlated with other factors and it is not clear which factors are causative,

— clay content is often correlated with greater plant growth for chemical

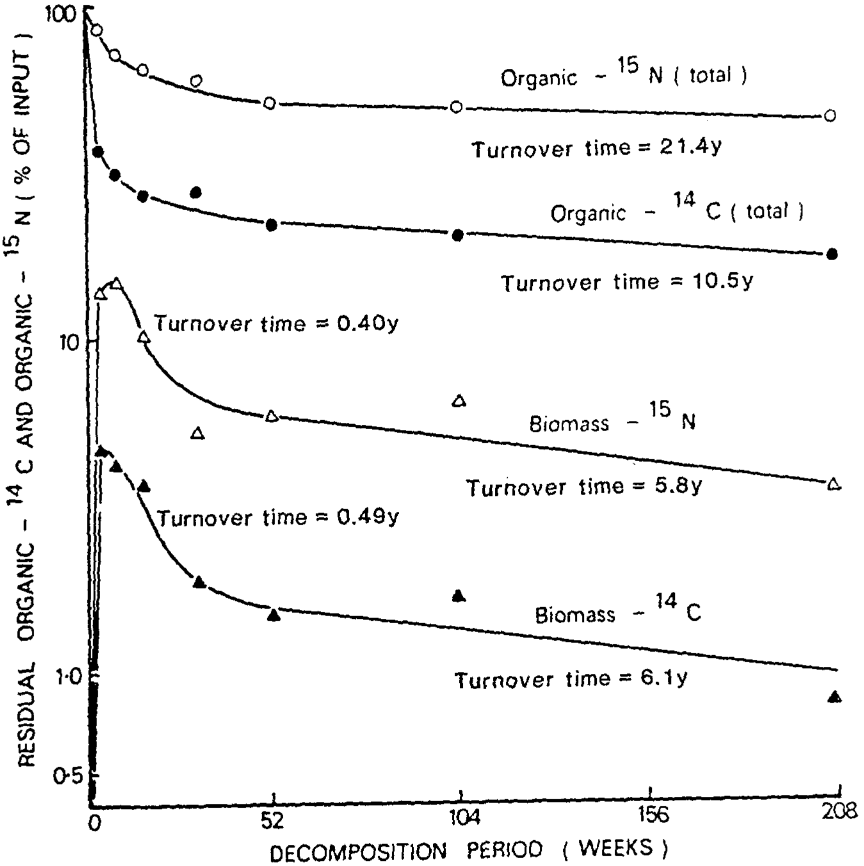


Fig. 9. Formation and decay of isotopically labelled microbial biomass during decomposition of ^{14}C, ^{15}N-labelled medic in soil. Modified from Ladd et al. (1981) with permission from Pergamon Press.

(plant nutrients) and physical (water regime) reasons and results in a greater annual input of C.

In the various comparisons made in the literature of organic matter contents and clay contents, base status is not usually considered but it may well be that the important mechanism for stabilizing organic matter in clay soils is cation bridging by Ca, and that the clay along with sparingly soluble Ca compounds acts as a source of Ca in equilibrium with soil solution.

The influence of clay content on stabilization of organic matter is exemplified in Fig. 10. The data were obtained from field plots which formed part of a long term decomposition experiment described by Ladd et al. (1985). There were no inputs for 8 years. The four soils were calcareous and it could be assumed that loss of C is directly related to clay content. All sites are in

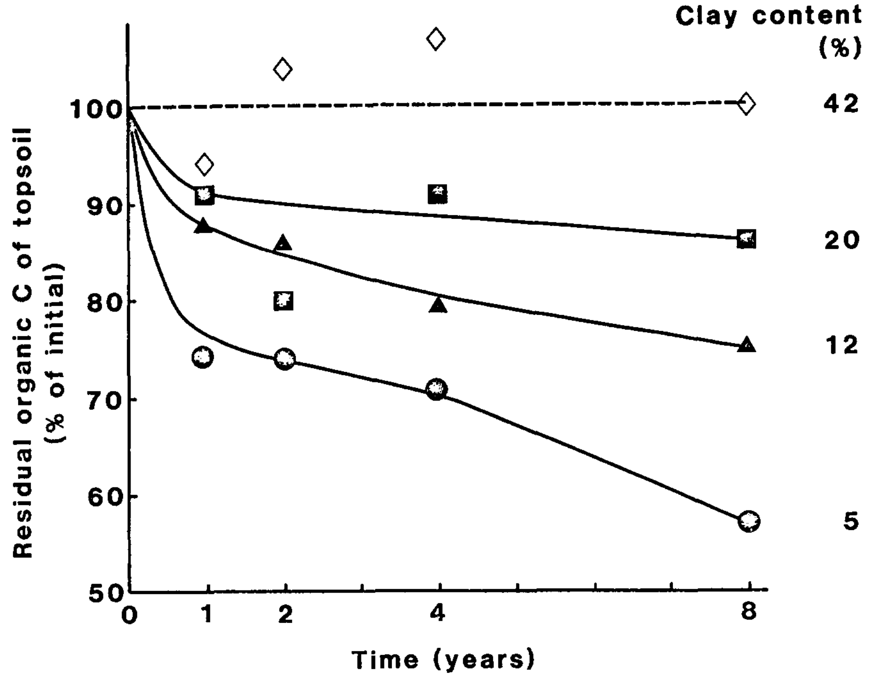


Fig. 10. Losses of organic C from calcareous soils with different clay contents.

southern Australia with similar Mediterranean climates so the results are not confounded by major differences in temperature and rainfall. Lower losses of C from cultivated soils with higher clay contents have also been obtained for a range of Vertisols in Queensland, a tropical environment (Dalal & Mayer 1986a) and for a range of Mollisols and Alfisols in the Great Plains of USA (Cole et al. unpublished).

Stabilization of microbial biomass by clay

The biomass plays a central role in the decomposition of organic matter and therefore we would expect differences in rates of organic matter mineralization to be reflected in the biomass at an early stage during decomposition. There is information which illustrates the presence and stabilization of more biomass in soils containing more clay. Ahmed (1981) incubated ^{14}C-glucose in a sandy loam (18% clay) and a clay (42% clay) and obtained the data illustrated in Fig. 11. Van Veen et al. (1985) incubated ^{14}C-glucose and ^{15}N-$(NH_4)_2)SO_4$ in two calcareous soils with 12% and 42% clay respectively. Their results showed a slower turnover of ^{14}C in the clay soil. The clay soil contained more biomass early in the incubation period which turned

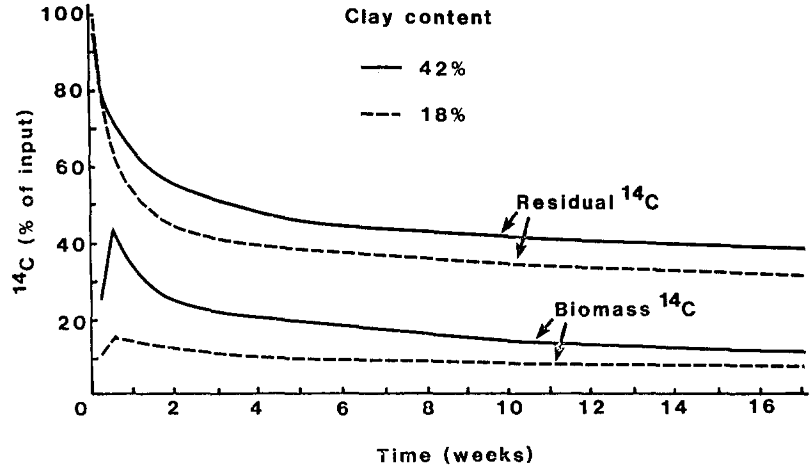


Fig. 11. The influence of clay content on biomass and residual ^{14}C in soils.

over more slowly than in the sandy loam for the rest of the incubation period. Similar trends were also evident for biomass ^{15}N.

Slower rates of decomposition, N immobilization and mineralization of nitrogen and more biomass in residues have been found in finer textured soils in other field and laboratory experiments (Ladd et al. 1977; Ladd et al. 1981, 1985) in which both simple ^{14}C-labelled compounds and plant materials were used (Sorensen 1975, 1981; Zunino et al. 1982).

Mechanisms of stabilization

It is important to realize that the clay fraction includes many minerals, both aluminosilicates and oxides, with very different surface areas and surface properties and, moreover, very different arrangements of individual particles. These arrangements are also controlled by the Ca status of the exchange complex and soil solution. For example, clay minerals with platy morphology such as montmorillonites exist in soils in the form of packets of quasi-crystals in which individual clay plates are aligned more or less parallel. Each quasi-crystal consists of at least several aligned plates and may be up to several microns across. The major ion between the plates is Ca, which prevents the plates from moving apart beyond three layers of water molecules even in conditions of excess water and low electrolyte concentrations. There is little convincing evidence that under natural conditions organic materials intercalate the plates or sheets which would certainly offer considerable protection against attack by enzymes. However in mont-

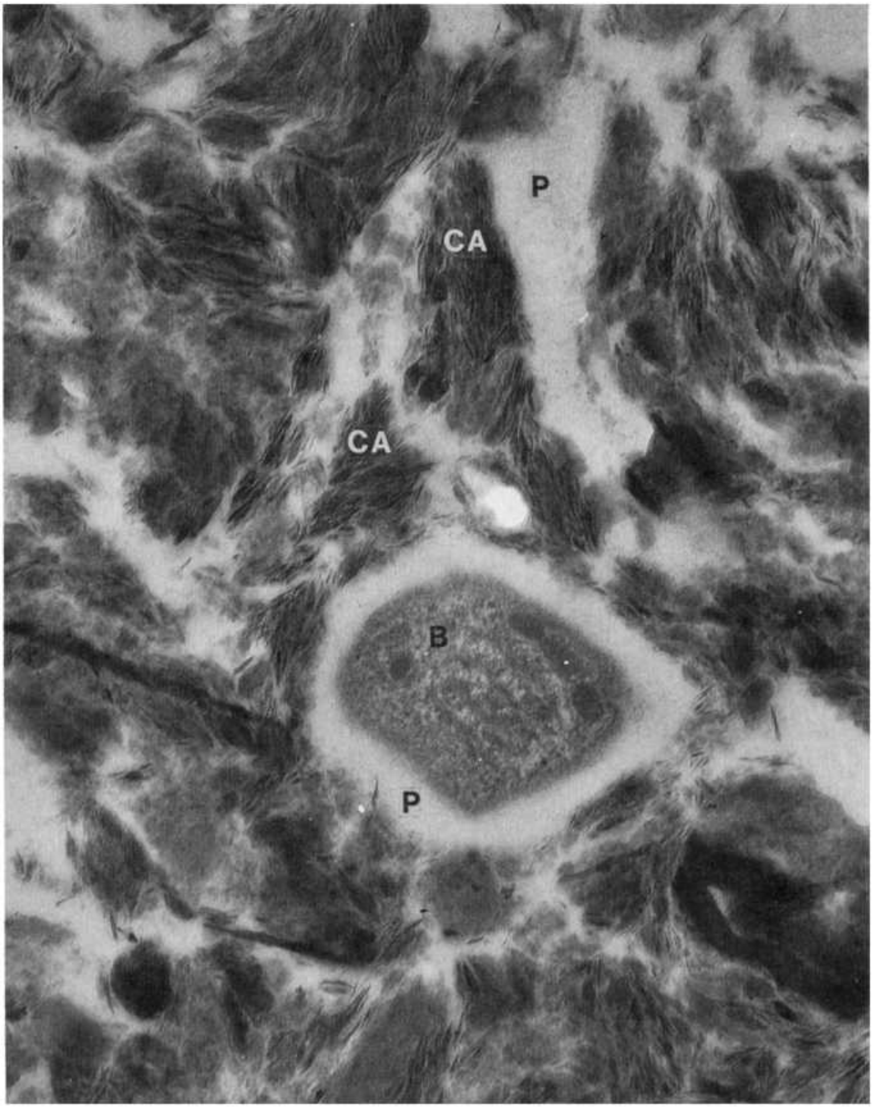


Fig. 12. Transmission electron micrograph of bacterium (B) surrounded by clay aggregates (CA) a clay with polysaccharide (P) between aggregates. Diameter of bacterium 1–2 μm. Reprinted with permission from R.C. Foster "Ultramicromorphology of some South Australian Soils". Plate 4 in Modification of Soil Structure, W.W. Emerson, R.D. Bond & A.R. Dexter (Eds)(1987). J. Wiley: New York.

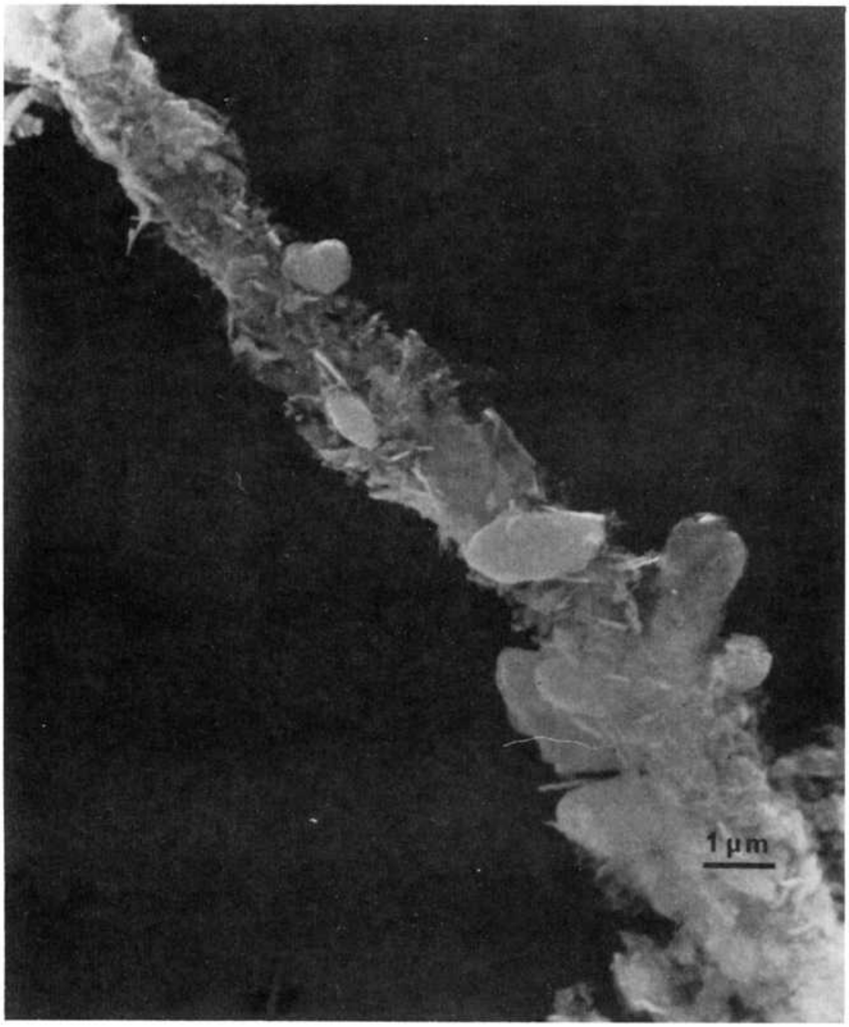


Fig. 13. Scanning electron micrograph of fungal hyphae coated with clay particles. Reproduced from Tisdall & Oades (1979) with permission from the Australian Journal of Soil Research.

morillonitic clays the organic matter may penetrate the pores between quasi-crystals, which are still generally less than one micron in diameter, and become inaccessible to most organisms.

The view in Fig. 12 of the detailed arrangement of clay and organic matter, including a bacterium, shows clearly how some organic matter is stabilized because neither other organisms nor their enzymes could move in such a system. Unless the system is stressed by drying and wetting or sheared by mechanical stress, e.g. by cultivation, root growth or soil animals, the organic matter will remain. Autolysis within the cell has been seen to have occurred as in micrographs the cell contents are missing leaving a ghost cell. Fungal hyphae may also become "crusted" with clay particles (fig. 13).

According to Kilbertus (1980), bacteria within soil aggregates exist only in pores at least three times their own diameter. Thus bacteria are excluded from more than 90% of the pore space in soils. The greater the clay content, the greater is the proportion of the pore space inaccessible to bacteria. About two-thirds of bacteria are associated with organic fragments and their distribution in soil is clumped (Gray et al. 1968). Bearing in mind that much of the organic matter in soil is particulate and not evenly spread through the soil it is easy to visualize how substrate and organisms are generally separated by physical barriers.

It is clear that we do not have quantitative information about the position of either organic substrates or the biomass and other larger organisms in the soil pore system. We require an understanding of soil fabrics viewed under the optical microscope and of the mechanisms involved in the formation of the fabrics. Similarly more ultra thin-section work is required using heavy metal stains for specific biological macromolecules including enzymes and specific functional groups so that they may be seen by transmission electron microscopy (Foster et al. 1983; Foster 1985). We need to know the characteristics of the major soil groups. Perhaps then it will be possible to quantify the importance of clay in retarding the decomposition of organic matter in different soils.

Cation bridges and retention of organic matter

Polyvalent cations in soil play a major role in the structure of both organic and inorganic colloids. The swelling of clays is limited by the presence of polyvalent cations. Similarly organic colloids which possess functional groups tend to be more condensed when saturated with polyvalent cations. For both types of colloids the system is flocculated rather than dispersed. Surfaces of both clays and organic materials will be least accessible in this flocculated stated. The cations thus bridge clay particles to each other and organic macromolecules to each other. In addition because both clays and organic matter are negatively charged the polyvalent cations bridge organic molecules to clay particles.

The cation bridging mechanism is thus crucial to the stability of soil microstructure and involves most colloidal particles including bacteria. Most workers are familiar with the dispersive effects of Na on colloids and the instability of sodic soils which become deficient in organic matter because the flocculated microstructure has been destroyed. Sodium causes both clays and organic colloids to swell and disperse which is partly why NaOH is such a good solvent for soil organic matter.

The major cations involved in the formation of bridges are Ca^{2+} and Mg^{2+} in neutral and alkaline soils and hydroxypolycations of Al^{3+} and Fe^{3+} in acid and ferrallitic soils. Dominance of these cations, particularly Ca and Fe, leads to insolubility of organic matter even in NaOH. Removal of the cations by an acid treatment almost always increases the extraction of organic matter, often by a factor of 2.

To understand the role of cation bridges we need to consider the architectural arrangements of particles in soils and to realise that we are dealing with particles which vary in size from a few nm to several mm, i.e. six orders of magnitude. It is helpful to consider the structure of a soil aggregate in stages. Tisdall & Oades (1982) proposed a model with four stages.

Stage 1		2	3	4
$< 0.2\,\mu$m	0.2–$2\,\mu$m	2–$20\,\mu$m	20–$250\,\mu$m	$> 2000\,\mu$m

The $< 0.2\,\mu$m particles are considered to be discrete crystals although this is an over-simplification. Some 0.2–$2\,\mu$m particles are discrete crystals but also present are aggregations of particles, sometimes with substantial alignment in quasi-crystals or domains, sometimes held together by organic materials such as polysaccharide mucilages or oxyhydroxides of Fe and/or short-range-order aluminosilicates. The second stage of aggregation leads to aggregates about 2–$20\,\mu$m. The binding mechanisms involve cation bridges between clay particles and negatively charged organic materials such as polyuronides and resistant cell wall debris from bacteria which are polycarboxylic and can be equated with humic materials. (Because most of these particles have densities $< 2\,\mathrm{Mg\,m^{-3}}$ their upper size limit is probably closer to $30\,\mu$m than the $20\,\mu$m calculated from Stokes law assuming a density of $2.6\,\mathrm{Mg\,m^{-3}}$.) The second stage aggregates are held together by various mechanisms into stage 3 aggregates with an upper size range set at $250\,\mu$m. When large dry aggregates are slaked by rapid addition of water the products are stage 3 aggregates. If dispersion occurs in addition to slaking then $< 2\,\mu$m particles are released and solutions become turbid or milky (Oades 1984). Slaking of large aggregates may be prevented by entanglement of particles within the aggregate by roots and associated hyphae. This has the effect of a "sticky string bag" and produces a stable and desirable structure in the top few centimetres of soils, particularly those which are cultivated. Tisdall & Oades (1982) referred to roots and hyphae as temporary binding agents because the stable aggregation of large aggregates

> 250 μm, termed macroaggregates, disappeared as roots and hyphae were decomposed. Thus stable macroaggregation is controlled by root growth and therefore by crop management, e.g. rotations. It is noteworthy that the decline in macroaggregation in a soil which has been under pasture for many years can be described by an exponential curve which is very similar to the decomposition curves for ^{14}C-labelled plant materials added to soils, e.g. Fig. 7. Thus stable macroaggregation disappears rapidly as soil is exploited and loses C because inputs from roots and hyphae are limited or cease (e.g. in a fallow system). However microaggregates (< 250 μm) which result from rapid wetting of a dry soil are considerably less sensitive to management because there are several persistent bonding mechanisms such as cation bridges, in which Ca has a dominant role.

After excessive cultivation there are no stage 4 aggregates and the soil with only microaggregation is very susceptible to crusting, surface runoff and erosion. The stage 3 aggregates also disintegrate, although far more slowly than the macroaggregates because the organic matter in them is persistent. Physical disruption of stage 3 aggregates shows that in clay soils with high base status a high proportion of the soil, and soil C, is in stage 2 aggregates, i.e. silt sized aggregates. In acidic, leached soils with low base status, which are usually sands to sandy loams, only small proportions of soil and C exist in stable silt sized particles.

The silt sized aggregates are richer in organic matter than coarser and

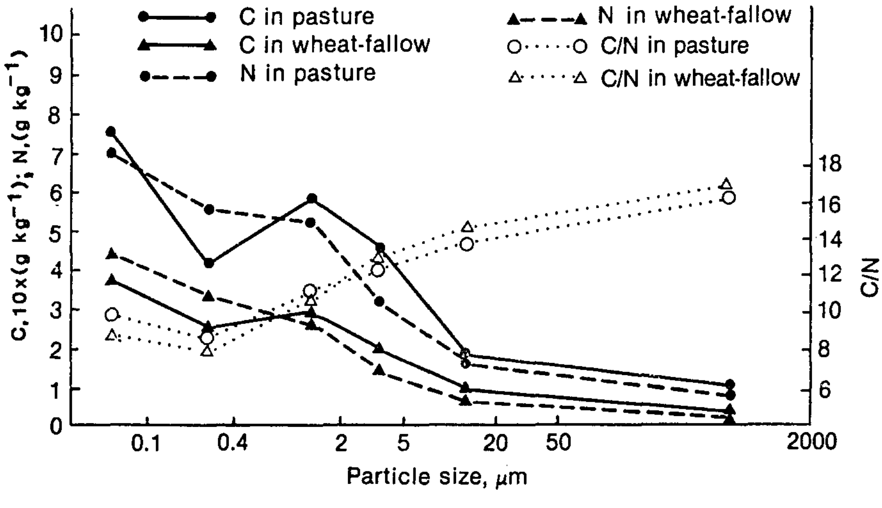


Fig. 14. C and N concentrations in particle size fractions from a Rhodoxeralf under pasture and cultivation. Redrawn from Turchenek and Oades (1979) with permission from Elsevier Science Publishers B.V.

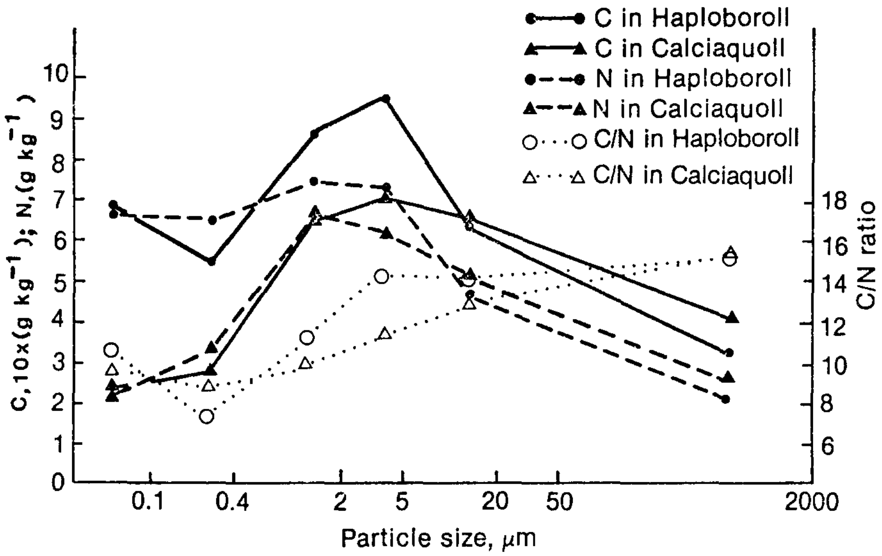


Fig. 15. C and N concentrations in particle size fractions from calcareous clay soils. Redrawn from Turchenek and Oades (1979) with permission from Elsevier Science Publishers B.V.

finer particles (Figs. 14, 15). They are rich in materials which would be classified as humic acids and represent the more resistant components derived from the biomass, perhaps debris from cell walls. The organic materials in these silt fractions can be concentrated to yield up to 30% C by flotation on heavy liquids of density 2.0 Mg m^{-3} because aggregates held together mainly by organic matter, disordered forms of Al and Fe oxides and Ca are less dense than mineral particles. Even in the Rhodoxeralf, which is not base saturated, the concentration of Ca in the inorganic residues of these fractions can exceed 10%. Removal of the Ca by acid treatment and Na saturation, or removal of "free" iron by dithionite caused substantial dispersion releasing clay particles and leading to large increases in surface area (Turchenek & Oades 1978, 1979 and unpublished data).

The stability of microaggregates reflects the numerous bonding mechanisms involved between the clay and organic colloids. Not only is the cation bridge involved, but also the various interactions of charged and uncharged polymers with clay surfaces (Tiessen et al. 1984). The stability of the organic matter in these fractions has been shown in two ways. Firstly ^{14}C dating has shown that the coarse clay and silt fractions have less ^{14}C enrichments than finer and coarser fractions (Anderson & Paul 1984). In another study ^{13}C was determined in various particle size fractions of a soil on which maize (a C4 plant) was grown for 20 years after removal of natural vegetation (C3

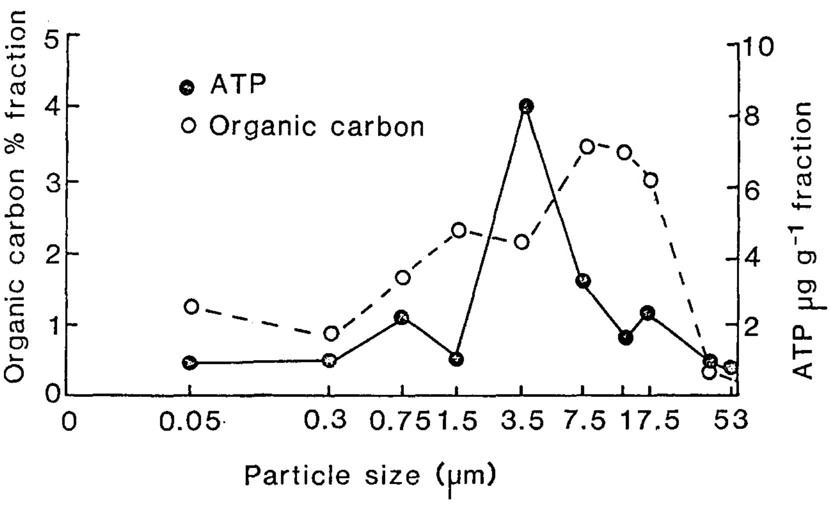


Fig. 16. Distribution of ATP in particle size fractions of a Vertisol after 120 days incubation with glucose (Ahmed, 1981).

plants)(Balesdent et al. 1986). Changes in ^{13}C enrichment indicated that the silt fraction was the most stable and least affected by a change in natural abundance of ^{13}C input caused by changing from C3 to C4 plants. A second approach has been to show that particle size fractions from about 1–2 μm have lost the least organic matter during decades of cultivation (Tiessen & Stewart 1983; Dalal & Mayer 1986b). Mechanistically, it appears that new biomass adheres mainly to clay fractions, and is separated with these fractions. However as substrate is exhausted and the organisms interact with clay surfaces, the biomass appears mainly in silt fractions. This has been demonstrated by incubating ^{14}C-labelled substrate and using ATP as a guide to biomass (Ahmed 1981). Initially ATP and ^{14}C were mainly in the fine clay fraction but as the incubation progressed they were found mainly in silt sized particles (Fig. 16).

Calcium and organic matter

The role of Ca in the stabilization of soil structure was described in earlier literature (e.g. Peterson 1947; Russell 1950). The higher organic matter contents of calcareous soils compared with adjacent non-calcareous soils was in part supposedly due to Ca-humates but the subject has been neglected until recently. It has been demonstrated that removal of Ca from a soil stimulates decomposition of organic matter and mineralization of nitrogen and, conversely, that addition of Ca inhibits release of CO_2 and stabilizes

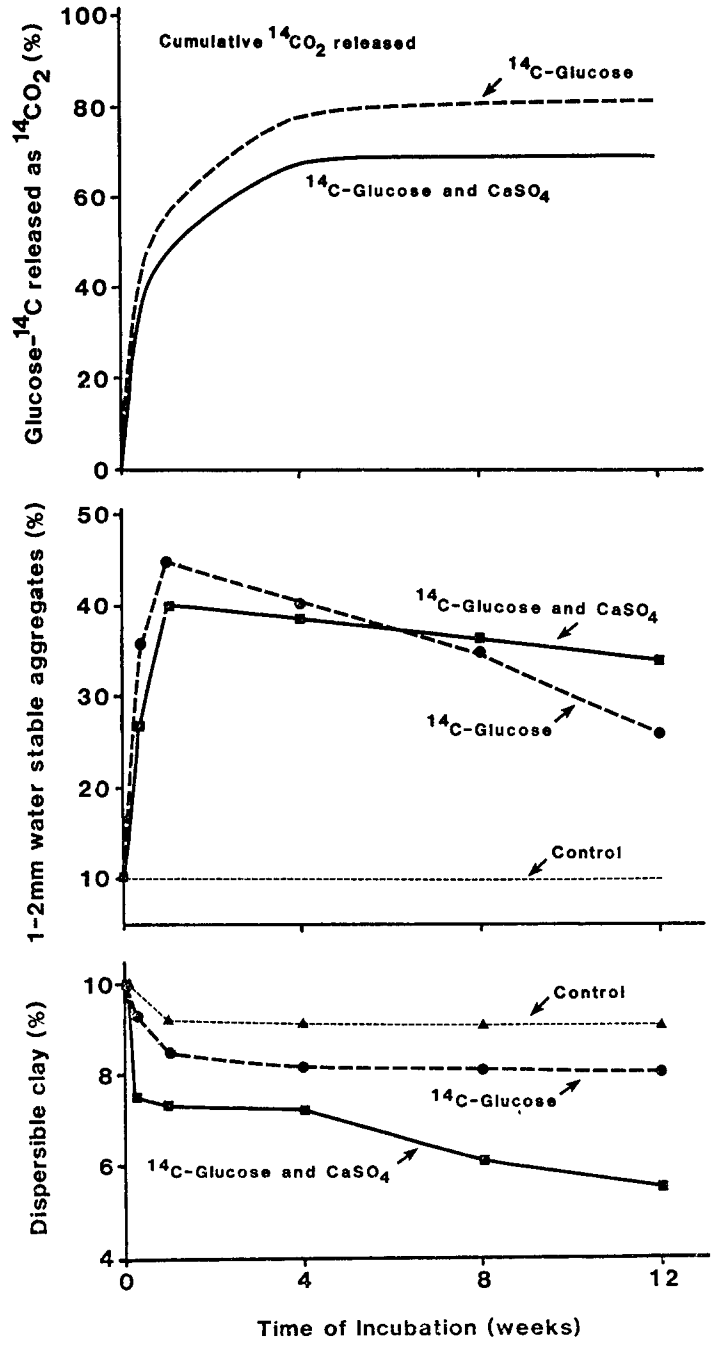


Fig. 17. Influence of Ca on decomposition of organic compounds and soil structure.

soil structure (Gaiffe et al. 1984; Muneer & Oades 1986, unpublished). A sample from 0–10 cm of a Rhodoxeralf was incubated with glucose with and without additions of Ca compounds. The results in Fig. 17 indicate that the presence of a continuous supply of Ca provided by $CaSO_4$ caused a greater retention of ^{14}C from labelled glucose than in the incubation involving only labelled glucose. Simultaneously the presence of Ca stabilized 1–2 mm aggregates for a longer time than occurred with glucose only. The presence of Ca also decreased the amount of dispersible clay.

The effect has been confirmed in field experiments involving $CaSO_4$ and $CaCO_3$ and ^{14}C-labelled wheat straw. The presence of Ca increased the residual ^{14}C in the soil for periods up to 6 months. $CaCO_3$ stimulated release of labelled CO_2 in the early stages compared with the control but subsequently a stabilizing effect was evident and the cumulative release curves for $^{14}CO_2$ crossed over and the $CaCO_3$ eventually showed inhibition of organic matter mineralization compared with the control. The stimulating effect of $CaCO_3$, e.g. liming, on organic matter decomposition is thus transient and the long term effect is one of stabilization.

The proposed mechanism is Ca bridging of cells and cell debris to clays to form aggregates which are physically, chemically and biologically stable. Thus a supply of Ca in leached and slightly leached soils is important for protecting perhaps both biomass and other organic materials from rapid mineralization.

Hydrous oxides and organic matter

While the work of Theng & Scharpenseel (1975) and Theng (1976) show clearly that Al^{3+} and Fe^{3+} should be very efficient cation bridges, the system is very complex because both Al and Fe hydrolyse at the pH values found in most soils. Trivalent Fe, in particular, is only sparingly soluble in most soils ($< 10^{-5}$ M in soil solution) and exists in a range of oxides with amphoteric surfaces on which organic anions are adsorbed (Oades & Tipping 1987). Where these oxide surfaces are extensive, as in the mineral ferrihydrite, large quantities of C are associated with the oxide and are involved in preventing its further crystallization. In most situations polycarboxylic materials are specifically adsorbed on the oxide surfaces which then have a net charge of 0 (point of zero charge or PZC) at a pH below that of the soil. In certain cases, such as rapidly weathering soils in the humid tropics or B horizons in some Spodosols, the surface characteristics of the oxides dominate and the PZC is higher than the measured pH of the soil. The PZC is controlled by the balance between the positive charge developed on the oxide surface and the negative charge developed on carboxylic groups of organic colloids.

The interaction of Al with organic materials is more likely to be an electrostatic interaction between a small, still unidentified Al species, and functional groups.

The role of Al and Fe in the organic cycle is not clear. Some soils, such as the surface horizons of Australian Krasnozems (mainly Oxisols & Ultisols) and Andosols (for examples see Martin et al. 1982; Zunino et al. 1982 & Theng 1980), are organic rich because of an oxide-organic interaction and there are indications that turnover times for allophanic soils are greater than for adjacent non-allophanic soils (Jackman 1964). The subject is complicated by the fact that Al is involved in acidity and that many acidic oxide-rich soils exhibit Al toxicity for vegetation, or low fertility due to specific adsorption of phosphate. Thus annual inputs of C are limited.

Factors which influence mineralization of C in soils

In conclusion we can list the various factors known to retard or accelerate the flow of C assimilated in plants through the soil before the C is fully oxidised and returned to the atmosphere as CO_2. Some measure of these various factors needs to be taken into account during the modelling of the mineralization phase of the C cycle.

Retarding factors	*Accelerating factors*
Assimilate distributed below ground	Assimilate added in litter
Assimilate deficient in nutrients	Assimilate rich in nutrients
Assimilate rich in lignin and waxes	Assimilate rich in carbohydrate
Waterlogging — anaerobiosis	Aeration in highly porous systems (but not arid)
Low temperatures	High temperatures
Clay textures	Sandy textures
High base status	Acidity
Aggregation	Apedality
Variable charge surfaces	Low charge surfaces

The retarding factors favour retention of C in soils leading to long turnover and mean residence times. The accelerating factors allow rapid mineralization of assimilate. There are no inferences here to amounts of C fixed by photosynthesis.

Certain combinations of the above factors may occur in a particular ecosystem and favour rapid mineralization or the opposite. Other ecosystems will have a mix of these factors and lie between the contrasting extremes of grasslands on Mollisols and other calcareous soils and forest systems on Spodosols and other acid sandy soils.

Grasslands on Mollisols	*Forests on Spodosols*
Assimilate	
Mainly underground	Mainly in litter
Fine pieces	Large pieces
Rich in organogenic elements	Poor in nutrients
	Rich in lignin
Incorporation	
Good distribution by fine root systems	Poor distribution in large roots and litter
Rapid comminution by soil fauna	Slow incorporation due to lack of fauna
Interactions with clay	
Many interactions	Interactions minimal
— sorption	— low clay content
— locking up in aggregates	— little aggregation
Aggregates often internally anaerobic	Soil well aerated
Consequences	
Retarded mineralization	Rapid mineralization
Accretion of insoluble "humin" and "humic acid" fractions	Results in small soluble "fulvic" materials and then CO_2
Long turnover and mean residence times	Short turnover and mean residence times

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