EFFECT OF CALCIUM ON THE MINERALIZATION OF ORGANIC CARBON AND STABILITY OF SOIL AGGREGATES

by

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SUMMARY

A general review of literature on the agents responsible for the formation and stability of soil aggregates is presented in this thesis, including the role of calcium in the decomposition of organic matter. Aggregate formation and stability is the result of the combined actions of soil physical, chemical and biological agents operating in the soil. Slaking of aggregates and dispersion of clay were identified as the two most important processes involved in the deterioration of soil structure. It is suggested that the stability of soil aggregates is dependent on organic matter, polyvalent cations, or complexes of clay–polyvalent cations—organic matter. Clay-metal-organic matter complexes may also inhibit the loss of organic matter by mineralization.

Calcareous soils are generally well aggregated because of the presence of soluble calcium in the exchange complex, which keeps clay flocculated. The beneficial effect of $CaCO_3$ is reduced when $CaCO_3$ is present as coarse particles. It is suggested that the size of the carbonate particles is more important than the amount of $CaCO_3$ present in the soil.

The physical, chemical, and micromorphological characteristics of eight calcareous soils were studied to identify the agents involved in the stability of soil aggregates. No simple correlation existed between the dispersible clay and $CaCO_3$ content of the soils. Stability of aggregates (1000-2000 μm diameter), water holding capacity, hydraulic conductivity and soil density were primarily related to the organic matter content of the soils. The higher the organic matter content, the better the physical condition of the soils. In soils poor in organic matter most of the particles existed in aggregates 50-250 μm range.

The results of the investigation indicated that the distribution of $CaCO_3$ in the soil profile, and presence of $CaCO_3$ as nodules is primarily dependent on the rainfall of the areas, although other factors (e.g. porosity, parent material, topography and biota) can influence the process.

The effect of calcium on the decomposition of organic matter was assessed by incubating soil with ^{14}C-glucose, with or without addition of $CaCO_3$ and $CaSO_4$, for up to

120 days. $CaSO_4$ decreased the release of $^{14}CO_2$ during the entire incubation period, compared to soils treated with ^{14}C-glucose+$CaCO_3$ and ^{14}C-glucose only. $CaCO_3$ stimulated the release of labelled CO_2 in the early stages of incubation, compared with the other treatments. However subsequent release of $^{14}CO_2$ was inhibited. The stimulating effect of $CaCO_3$ on ^{14}C-glucose decomposition was thus transient and the long term effect was one of stabilization. Both $CaCO_3$ and $CaSO_4$ increased the residual ^{14}C in the soil. Soluble Ca^{2+} inhibited the release of $^{14}CO_2$ by protecting residual ^{14}C from decomposition, presumably due to the interaction of Ca^{2+} with humic substances.

A field experiment was conducted to observe the effect of calcium on the decomposition of ^{14}C-labelled wheat straw in a Red brown earth (Rhodoxeralf). Soil, 0-8 cm depth, was mixed with ^{14}C-labelled wheat straw with or without addition of $CaCO_3$ and $CaSO_4$. Measurement of residual ^{14}C was determined at intervals over 32 weeks. Both $CaCO_3$ and $CaSO_4$ increased the amounts of residual ^{14}C in the soil. $CaSO_4$, because of its higher solubility, was more effective than $CaCO_3$ in increasing the residual ^{14}C.

The biomass contents of the soil during the decomposition of ^{14}C-labelled wheat straw were measured by a chloroform fumigation technique. The amount of biomass was greatest after one week of incorporation of the plant material, and then declined gradually with time of decomposition. The amount of ^{14}C in the biomass was significantly reduced in the soil treated with ^{14}C-wheat straw+$CaSO_4$, compared to soil treated with ^{14}C-wheat straw only. The treatment comprising ^{14}C-wheat straw+$CaCO_3$ did not significantly reduce the level of ^{14}C in the biomass until the thirty second week of decomposition.

The electrical conductivity of soils was reduced after the addition of glucose+calcium, when compared to soils where only calcium was added. This indicates that some of the soluble calcium became insoluble by complexing with decomposition products of glucose. The above findings were confirmed by determining water soluble, exchangeable and EDTA extractable calcium. The results show that the water soluble, exchangeable, and EDTA extractable calcium were lower in soils treated with glucose+calcium compared to soils treated with calcium only.

The presence of Ca reduced the efficiency of extraction of humic acid by NaOH. However, leaching of the soil with 1M HCl, which removed $Ca^{2+}$and other polyvalent cations, increased the efficiency of extraction of organic matter with NaOH by 55%.

The influence of calcium and organic matter on soil structure was assessed by wet sieving to determine the size distribution of water stable aggregates and, a measure of dispersible clay. Slaking refers to the macroscopic fracturing of dry aggregates on rapid wetting, and usually results in the breakdown of large aggregates into smaller fragments. The subsequent slow release of clay sized particles from slaked fragments or the unslaked aggregates is known as dispersion. Addition of $CaCO_3$ and $CaSO_4$ decreased the dispersible clay, and increased the percentage of aggregates 50-250 µm diameter. $CaSO_4$ was more effective than $CaCO_3$, because of its higher solubility and electrical conductivity in solution. An increase in clay dispersion was observed due to organic matter addition to the soil, presumably due to organic anions which formed complexes with metal ions favouring the dispersion of clays. However, treatment of soils with calcium and organic matter together reduced the dispersible clay. Organic matter was the main agent responsible for binding particles <250 µm diameter to particles >250 µm diameter. It was also observed that soil aggregates formed in the presence of calcium and organic matter were stable for a longer time than aggregates formed in the presence of organic matter only. The stability of soil aggregates in the presence of calcium and organic matter was presumably due to interaction of clay, calcium and decomposed products of organic matter.

Water stability of soil aggregates was determined after treatments with 0.02M NaCl, 0.1M $Na_4P_2O_7$, 0.02M HCl and 0.1M HCl. Pyrophosphate solution, which is supposed to disrupt complexes of clay-polyvalent metals-organic matter, had little effect on the stability of aggregates > 2000 µm diameter. Similarly, the aggregates were insensitive to treatment with 0.02M HCl. These results indicate that the complexes involved in the stabilization of aggregates were very resistant to both pyrophosphate and dilute hydrochloric acid treatment. However, when the concentration of HCl was increased from 0.02M HCl to 0.1M HCl,

significant breakdown of soil aggregates (>2000 μm diameter) occurred. This disruption of aggregates was probably due to the partial removal of cation bridges, due to Ca^{2+} bridging the soil clays and organic polymers. It seems that the cation bridges involved in the stability of aggregates were very stable, and severe chemical treatments were necessary to disrupt the aggregates. From the results, a model of the stabilization of aggregates in soil containing calcium and organic matter is proposed.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university. To the best of the author's knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

I consent to this thesis being made available for photocopying and loan.

January, 1987

Muhammad Muneer

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CHAPTER 1

LITERATURE REVIEW

1.1 SOIL STRUCTURE

The arrangement of the individual soil particles of sand, silt and clay with respect to each other into a pattern is called soil structure. Since in a soil the pore spaces are as important as the solid particles, Marshall (1962) defined soil structure as "the arrangement of particles and of the pore space between them". It includes the size, shape and arrangement of the aggregates formed when primary particles are clustered together into larger, separable units. According to this definition, a soil has structure even if no aggregates are present. For the purposes of agriculture, soil structure should be defined in terms of pores for the storage of water available to plants, pores for the transmission of water and air, and pores in which roots can grow (Oades, 1984). The importance of these factors have been recognized by various authors.

Hillel (1980) has described an optimum soil structure for plant growth as one containing a loose, friable, and porous assemblage of aggregates which permits the free movement of water and air, easy cultivation and planting, and unobstructed germination and root growth. An important factor omitted from this definition is the ability of the soil to store plant available water. Good soil structure for crop growth depends on the presence of aggregates of soil particles 1 to 10 mm diameter which remain stable when wetted (Edwards and Bremner, 1967; Kritz, 1976). Such water stable aggregates should be porous (pores >75 μm diameter) so that they remain aerobic, and yet possess sufficient numbers of pores 0.2-30 μm diameter to retain water for the growth of plants. The pores between the aggregates should be large enough to allow rapid infiltration and drainage. Oades (1984) suggested that a desirable range of pore size for a tilled layer occurs when most of the clay fraction is flocculated into microaggregates, defined as < 250 μm diameter, and when these microaggregates and other particles are bound together into macroaggregates >250 μm diameter.

Soil structure should be stable under normal agricultural practices, and should be resistant to soil physical and chemical changes which could swell and disperse the soil aggregates. Rengasamy et al. (1984) presented different units of structural organization, their size and the average pore size within each unit, their significant agricultural function and the major mechanisms responsible for the instability of these units in water (Table 1).

The structure of the surface soil is complex, and subjected to more change than subsoil structure. Wetting and drying, mechanical manipulation, plant roots, exposure to action of wind and water at the surface are all stresses which rearrange, break down and reform aggregates. The effect of each of these processes decreases with depth, but at different rates (Warkentin 1982). As a result, alterations in the structure of aggregates in surface soil proceeds at a much faster rate than that of peds in subsoils. Warkentin (1982) suggested that surface soil aggregates show measurable change over several years; subsoil ped units may be stable for hundreds of years.

1.2 AGGREGATE STABILITY

The ability of soil aggregates to withstand the stresses caused by immersion in water is known as aggregate stability. The binding of soil particles into stable aggregates is essential for the production of optimum soil tilth. Well aggregated soils provide stable traction for farm implements, adequate physical conditions for the penetration, growth, and anchorage of plant roots, and free drainage with moderate retention of rainfall. These conditions facilitate the existence of an air-moisture regime, favourable for plant growth and microbiological activity. Furthermore, well aggregated soils are more resistant to erosion than primary particles of sand, silt, and clay.

Aggregates result primarily from the action of natural agencies, or any process by which parts of the soil are caused to clump together and separate from adjacent masses of soil. If soils are initially dispersed (as in alkaline soils), flocculation is essential for aggregate formation; if they are partially puddled or solid, fragmentation into smaller units is essential. There are two types of process involved. The first is concerned with the building up of aggregates from dispersed materials; the second involves the breaking down of larger coherent masses into

Table 1. Soil structural organisation involving clay particles, and the mechanisms causing aggregate instability in water (Rengasamy et al., 1984).

Structural units	Average size (µm)	Average pore-size (µm)	Pore function	Mechanisms causing aggregate instability
Platelets (unit layer)	0.002	<0.002 (inter-layer)	Bound water (inter-layer)	Swelling (adsorption of water)
Clay crystals and quasi-crystals	0.05	0.005 (inter-crystalline)	Bound water	Crystalline swelling (limited) Dispersion of platelets
Domains	1-2	0.1 (inter-domain)	Bound water Available water Micro-organisms Aeration (limited)	Very limited swelling Dispersion of clay crystals and quasi-crystals
Micro-aggregates	2-250	50 (inter-aggregate)	Available water Aeration Root growth Slow drainage Micro-organisms	Slaking-due to (i) breaking of organic bonding in loamy soils (ii) differential swelling pressure Dispersion of domains
Macro-aggregates	250-2000	1000 (inter-aggregate)	Fast drainage Earth worms Root growth	
Clods	>2000	Cracks and fissure (undefined)	Fast drainage	Swelling and shrinking Dispersion within clod matrix

favorably sized aggregates. Since most soils become more dense and compacted due to clay dispersion and the loss of organic matter with continued farming, the first case is of greatest interest.

Because soils are subjected to intermittent wetting and drying throughout the year, aggregate stability in water is fundamental for the maintenance of proper tilth. The extent of the disruption of soil aggregates on wetting depends on the relative importance of two processes, slaking and dispersion (Rengasamy et al., 1984b), which may occur independently or simultaneously. Slaking refers to the macroscopic fracturing of dry aggregates on rapid wetting, and usually results in the breakdown of large aggregates into smaller fragments, which may themselves be aggregates or single grains. The subsequent slow release of clay sized particles from slaked fragments or the unslaked aggregates is known as dispersion. Slaking alone is a problem and when dispersible clay is also present; soil porosity is decreased, soil density increased and generally unfavourable physical conditions prevail.

1.2.1 Slaking

When the disruptive forces encountered by a dry aggregate on rapid wetting are stronger than the forces of aggregate stabilization, slaking results (Collis-George and Lal, 1971; Emerson, 1977). The strength of soil aggregates decreases with water content, because of reduced cohesion and the softening of cements. If microscopic swelling occurs during absorption of water, this will cause uneven strains throughout an aggregate, so that its structure will be distorted and weakened.

Aggregation is ultimately determined by the forces acting between the soil particles, and of these the swelling forces between clay particles are of prime importance, especially in soils containing large amounts of clay. The swelling behaviour of clay is largely dependent on the nature of the clay minerals and particularly on their surface properties.

The susceptibility of soil aggregates to slaking can be reduced by the presence of cements or soil binding agents (Russell, 1971). Cements or binding agents (iron oxides, aluminium oxides, calcium carbonate and organic materials) may prevent aggregates from slaking either by strengthening bonds within the aggregates (Quirk and Panabokke, 1962) or by water-proofing the aggregates (Emerson, 1977). In the field, slaking occurs mainly in aggregates in the surface layer, since those below the surface may never become air-dry, and are usually wetted slowly during irrigation or rainfall (Marshall, 1956). When slaking is severe, a crust of low permeability forms, which when full of water leads to poor aeration (McIntyre, 1955; Millington, 1959) and when dry becomes hard (Arndt, 1965): such a crust may prevent emergence of seedlings.

1.2.2 Dispersion

Dispersion is a physicochemical feature of the clay fraction (<2 μm diameter particles) of soil, and exerts a profound influence on many agriculturally significant properties (Rengasamy et al. 1984b). Under field conditions, dispersion of clay particles from the external surfaces of aggregates and the swelling of clays within the aggregate matrix may induce severe soil physical problems (Emerson, 1977; Frenkel et al., 1978; Rengasamy et al., 1984b). The factors controlling swelling and dispersion are essentially identical, with the only distinction between the two processes being the distance to which adjacent clay particles separate (Rengasamy et al., 1984b). If the separation of the clay particles is restricted by either a deficiency of free water (eg. unsaturated soil conditions), an external pressure (eg. overburden pressure), or the cementation of adjacent particles by organic or inorganic compounds (eg. organic matter or sesquioxides), clay particles may not be able to separate sufficiently to disperse. However, where the separation of adjacent clay particles is not restricted, the extent of dispersion of aggregates when exposed to water is controlled largely by the balance of the attractive and repulsive forces existing between the clay particles.

1.2.2.1 *Factors Responsible for Clay Dispersion*

When aggregates are immersed in water, spontaneous dispersion occurs if the clay swells to such an extent that attractive forces between the particles are no longer strong enough to keep them together (Emerson, 1977). The breakdown of microaggregates into clay size particles due to dispersion is largely controlled by the physico-chemical properties of the clay fraction eg., type of clay mineral, the size of the particles, the type and quantity of exchangeable ions occurring on the surface of the clay mineral and the type and concentration of ions in the water. It has been observed that if a fine-grained clay mineral with sodium as its exchangeable cation is shaken up in distilled water , it will usually disperse into individual particles. In this state the clay mineral is said to be deflocculated. If sufficient electrolyte is added to such a suspension, the individual particles will begin to stick to one another and form a loose aggregate or floc. The clay mineral is then said to be flocculated. This change in the behaviour of the clay particles is explained in terms of a shift in the balance between forces of repulsion and attraction, consequent upon addition of the electrolyte. The cations associated with a clay surface immersed in water are subjected to an electrostatic force of attraction towards the clay surface, as well as a tendency to diffuse into the bulk. The net result of this competition is to establish a dynamic equlibrium in which the concentration of cations diminishes exponentially as a function of distance from the clay surface. This partition of cations between surface adsorption (the Stern or Helmholtz layer) and solution (the Gouy layer) is the electrical double layer and leads to the mutual osmotic repulsion of opposing surfaces in dilute electrolyte solutions (Quirk, 1986).

1.2.2.2 *Diffuse double-layer forces between clay particles*

Clay minerals carry a net negative charge on their basal surfaces due to isomorphous substitutions within their lattices, mainly in the octahedral layer. In addition to the isomorphic charge, at the edges of the clay particles pH dependent charges exist where chemical bonds have been broken. Under acidic to neutral pH conditions these edge charges are positive, and as the pH increases above neutrality, the positive charges are replaced with negative charges. In most soils the net charge (i.e. the sum of the isomorphic and edge charges) associated with the clay fraction is negative; however in highly weathered acidic soils with high contents of iron and aluminium oxyhydroxides the net charge may be positive.

This negative charge is balanced by the adsorption of cations on the basal surfaces. When a clay particle is placed in distilled water, there will be a tendency for these cations to move away from the particle surface into the water, in order to reduce the concentration gradient between the two. The majority however, do not move very far away from the particle surface and there is a diffuse clustering of ions about the clay particles. The clay surface with its negative charge is regarded as one layer, while the surrounding cluster of cations is regarded as another; together they are referred to as a diffuse double layer. Particles in this state repel one another because the outer parts of the double layers have the same net electrical charge. The range and effectiveness of the repulsive force is controlled by the thickness of the double layer, which is thought to vary from 50Å to 300Å (Paton, 1978).

The distance to which the electrical double layer extends into the bulk solution is a function of the valence of the compensating cations and the electrolyte concentration of the solution. The extension of the double layer in the solution decreases with increasing electrolyte concentration (Fig.1). At very low electrolyte concentration, the counter-ion concentration which decreases asymptotically with increasing distance from the surface is still appreciable at a distance which is comparable with the diameter of the particle. However, with increasing electrolyte concentration a considerable compression of the diffuse atmosphere towards the surface occurs.

The thickness of the diffuse double layer is also dependent on the type of cation occurring in the exchangeable positon. Sodium and potassium are responsible for forming diffuse double layers of the greatest thickness, while those formed by calcium and magnesium are less thick and those formed by aluminium are the least thick. This of course is related to the ease with which cations will dissociate from the clay surface. Sodium seems to dissociate to the greatest extent and will thus form the thickest double layer. Calcium is much less active than sodium. At equivalent concentrations of electrolyte, divalent cations decrease the thickness of the double layer more strongly than monovalent, and trivalent more strongly than divalent.

1.2.2.3 *Limitations of double layer theory in predicting the dispersive behaviour of clay in soil aggregates*

The application of the diffuse double layer theory explains the dispersion and flocculation of clay quantitatively only when the surfaces of the particles are sufficiently separated to permit formation of complete diffuse layers. However, if the proximity of adjacent surfaces restricts diffuse layer formation, as in the case at the internal surface of clay

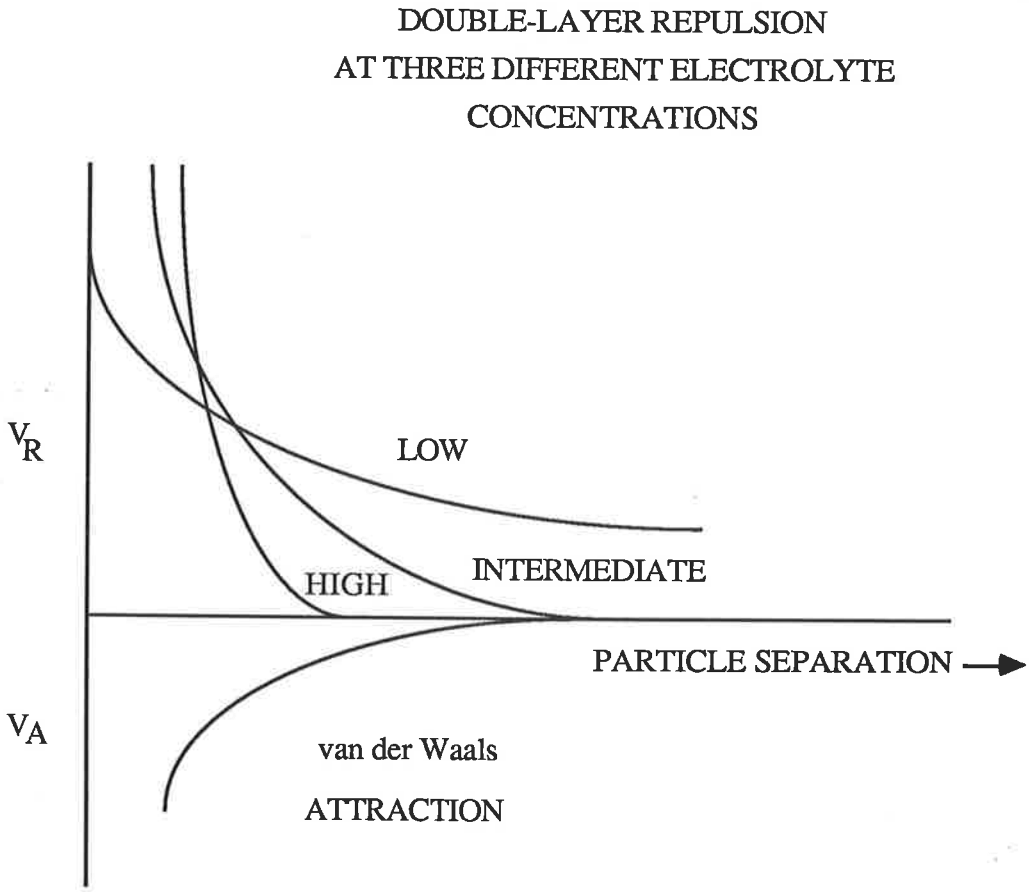


Fig. 1. Repulsive and attractive forces as a function of particle separation at three electrolyte concentrations indicated by "low," "intermediate," and "high,". V_R is the repulsive potential and V_A is the attractive energy, (van Olphen, 1977).

aggregates stacked face-to-face (eg. quasi-crystal), the theory is no longer satisfactory (Rengasamy et al., 1984b). The failure of this theory can be caused by factors such as partial blocking of negative surfaces by adjacent particles, incomplete double layer formation on some or all surfaces, and ion-pair formation between the counterions and the negative sites of the clay (Swartzen-Allen and Matijevic, 1974). Thus, the organisation of the particles in clay systems plays a vital role in dispersion and flocculation phenomena.

1.2.2.4 *Soil factors controlling dispersion*

The dispersion of clay from aggregates is controlled by many factors, including the composition of the cation exchange complex, the concentration and composition of electrolyte in the soil solution, the particle size and mineralogy of the clay fraction, soil pH, the nature and strength of any interparticle bonding, and organic anions (Bloomfield, 1963; Gillman, 1974; Emerson 1977; Shanmuganathan and Oades, 1983; Durgin and Chaney, 1984; Gupta et al., 1984; Rengasamy et al., 1984b; Oades, 1984).

The effect of electrolyte composition and concentration on clay dispersion has been discussed in detail in section 1.2.2. The effects of exchangeable cations and electrolytes in controlling swelling and dispersion in aggregates are largely dependent on the dominant type of clay mineral present in a soil. At low levels and in weak electrolyte solutions, smectitic and micaceous soils disperse more than kaolinitic soil (Velasco-Molina et al., 1971). In the absence of electrolytes, the dispersion of a soil is related to the dominant clay minerals in the order: smectite> kaolinite>mica.

Variations in pH have been found to affect dispersion in many clay systems (Schofield and Samson, 1954; Arora and Coleman, 1979; Suarez et al., 1984). Changes in pH affect edge charge on clays and the surface charge of minerals such as iron and aluminium oxides. At low pH values the positive charge on edge surfaces leads to an edge to face association which inhibits dispersion. In acid soils, kaolinite is dominated by exchangeable aluminium and its hydrolysis products can decrease the dispersive behaviour of soils (Emerson, 1977).

Iron and aluminium compounds effectively flocculate clays by bridging the particles. They may also, under certain pH conditions, neutralise the negative charge in clay particles by the formation of positively charged species (Rengasamy and Oades, 1977). Adsorption of these compounds on clay surfaces can also lead to an increase in the point of zero charge (PZC). PZC is defined as the pH at which the net surface charge of the system reduces to zero (Parks and de Bruyn, 1962). This may result in the development of a net positive charge (charge reversal) which will increase clay dispersion. When the pH exceeds the PZC, the increase in negative charge results in increased dispersion.

There is some evidence that organic anions promote dispersion by blocking positive sites on colloid surfaces, and by complexing polyvalent cations in solution (Bloomfield, 1963; Gillman, 1974). Adsorption of various anions can increase the net negative charge in the clay system and thus aid dispersion (Shanmuganathan and Oades,1983). Emerson (1977) has reported the peptizing effect of organic matter: if this occurs, the organic polymers do not bind the soil particles and hence clay dispersion is increased. Gupta et al. (1984) showed that the presence of humic substances in alkaline soils (high pH), or the addition of organic matter to such soils, increased clay dispersion. Durgin and Chaney (1984) also showed that dissolved organic matter from Douglas-fir roots caused increased dispersion.

Oades (1984) suggested that organic anions which form complexes with metal ions, favour the dispersion of clays in a manner similar to that of calgon and other phosphates. It was suggested that at least two factors are involved in clay dispersion; (i) the complexing of trivalent and divalent metal ions which reduces concentrations in solution, and a reaction with any positive sites associated with trivalent metals situated on the edges of clay lattices or on oxide surfaces, and (ii) the sorbed organic anions increase the negative charge on colloid surfaces, thus increasing the diffuse layer of cations associated with the surfaces. This favours the dispersion of clay particles and mobilization of fine clay down the profile.

In spite of the dispersing action of organic anions, many long-chain organic polyanions are excellent flocculators of clays (Ruehrwein and Ward, 1952; Hagin and Bodman, 1954; Packter, 1957; Holmes and Toth, 1957; Warkentin and Miller, 1958). Flocculation is due to formation of interparticle bonds. Negatively charged polymers which are extended in solution and do not collapse to negatively charged surfaces, are particularly effective flocculants

(Greenland, 1965). Uncharged compounds are generally less effective, unless they are very large. They will however form interparticle bonds if they are added to clay systems where the particles are already in close proximity (Greenland, 1963). Thus poor flocculators such as polyvinyl alcohol and some carboxymethylcelluloses are very effective in the stabilization of soil aggregates (Emerson, 1956; Davis and Heald, 1964).

The mode of action of charged and uncharged polymers in stabilizing soil aggregates is different (Greenland, 1965). Polyanions become attached to several particles, but only a few segments of the polymer are bonded to each particle; flexible uncharged polymers spread over the surfaces with which they come into contact, and if such surfaces are already adjacent, they form many bonds to each surface. The action of negatively charged polymers may be likened to the formation of "strings of beads" and of uncharged polymers to the spreading of "coats of paint" around groups of particles already in proximity (Greenland, 1963).

It has been suggested that the blockage of pores, as a result of clay dispersion and movement, is the mechanism which controls the structure and permeability of the soil (Shainberg et al., 1971; Felhandler et al., 1974; Frenkel et al., 1978; Oster and Schroer, 1979).

1.3 THEORIES OF SOIL AGGREGATION

In soils with an appreciable clay content, the primary particles tend under favorable circumstances to group themselves into structural units known as secondary particles, or aggregates. Such aggregates are not characterized by any universally fixed size, nor are they necessarily stable. The visible aggregates which are generally of the order of several millimeters to several centimeters in diameter are often called peds or macroaggregates. These are usually assemblages of smaller groupings or microaggregates, which themselves are associations of the ultimate structural units, being the flocs, clusters, or packets of clay particles. Bundles of these latter units attach themselves to, and sometimes engulf the much larger primary particles of sand and silt.

A prerequisite for aggregation is that the clay should be flocculated, however flocculation alone is not a sufficient condition for aggregation. Aggregates result from the cementation of flocculated particles.

1.3.1 Clay Domain Theory

Emerson (1959) proposed that crumbs are formed from units of colloidal clay, or domains, and coarser particles of silt and sand (quartz) cemented together by humus. A domain was defined as "a group of clay crystals having suitable exchangeable cations which are oriented and sufficiently close together for the group to behave in water as a single unit" (Aylmore and Quirk, 1960).

Quirk and Aylmore (1971) used the term quasi-crystals to describe the regions of parallel alignment of individual lamellae of aluminosilicates in montmorillonite, which exhibit intra-crystalline swelling; and the term domain to describe the regions of parallel alignment of crystals for illite and other clays with fixed lattices, which exhibit inter-crystalline swelling only. The concept of domains gives a more realistic way of thinking about the organization of clay particles in soils than a card-house type structure. This concept is particularly useful when considering the reactions of stabilizing agents with soils.

Emerson (1959) proposed a model for soil crumbs, consisting of four possible types of bonds. These are (i) quartz-organic matter-quartz, (ii) quartz-organic matter-domain, (iii) domain-organic matter-domain, and (iv) domain-domain edge-face (Fig. 2).

The theory may explain many of the properties of soil crumbs, but it fails to take into account the extensive occurrence of clay-organic complexes. In soils that are well supplied with organic matter, and which are often well-aggregated, most of the clay will be coated with organic matter. The "clay" domains of Emerson may in reality exist partly as "clay-humus" domains.

1.3.2 Microaggregate Theory

Several models have been proposed to describe the way in which individual mineral particles are held together to form water-stable aggregates in soil. Misono and Sudo (1958) and Sudo (1962) suggested that particles < 20 μm diameter are bound into water-stable secondary particles 20-60 μm diameter, and these secondary particles in turn form larger soil aggregates. Edwards and Bremner (1967) proposed a mechanism of soil aggregation based on

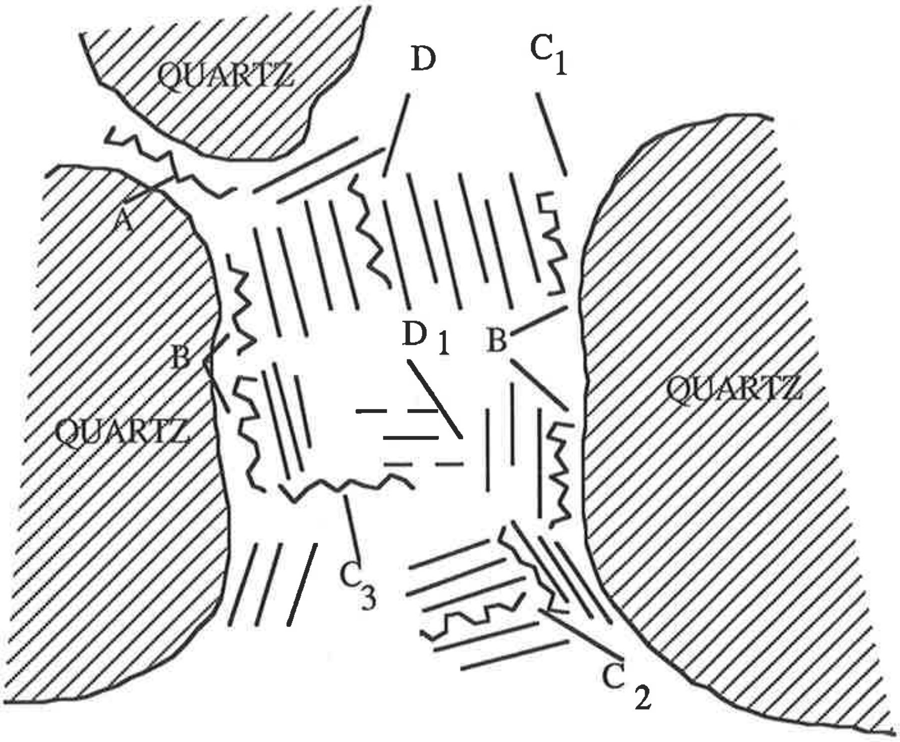


Fig. 2. Possible arrangements of organic matter, clay domains, and quartz to form a soil crumb: A. Quartz-organic matter-quartz. B. Quartz-organic matter-clay domain. C. Clay domain-organic matter-clay domain (C_1=face-face, C_2=edge-face, C_3= edge-edge). D. Clay domain-clay domain, edge-face, (Emerson, 1959).

the dispersion of soil particles by ultrasonic vibrations. The concepts that have evolved from these studies are as follows:

1. In soils well-supplied with exchangeable cations, the fine sand and silt-size microaggregates are mostly <250 µm in diameter, and consist largely of clay and organic colloids linked together through polyvalent cations. These microaggregates can be represented as

$$[(\text{C—P—OM})_x]_y$$

where C indicates clay, P the polyvalent metal ion (Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, etc.), OM the humified organic matter, and C—P—OM the clay-size particles (<2µm); x and y are finite whole numbers dictated by the size of the primary clay particle.

2. The bonds linking the C—P—OM particles into the larger $(\text{C—P—OM})_x$ and $[(\text{C—P—OM})_x]_y$ units can be disrupted by mild shaking if the inter-particle bonds are weakened, such as by substitution of Na^+ for the polyvalent metals.

3. Stable microaggregates are formed by a mechanism that is a reversal of what occurs when soil particles are dispersed by shaking in water.

4. The formation of microaggregates renders organic material inside the aggregates physically inaccessible to micro-organisms.

Thus the size, shape , and stability of the microaggregates are determined to a great extent by such factors as the absolute and relative amounts of clay and humified organic matter.

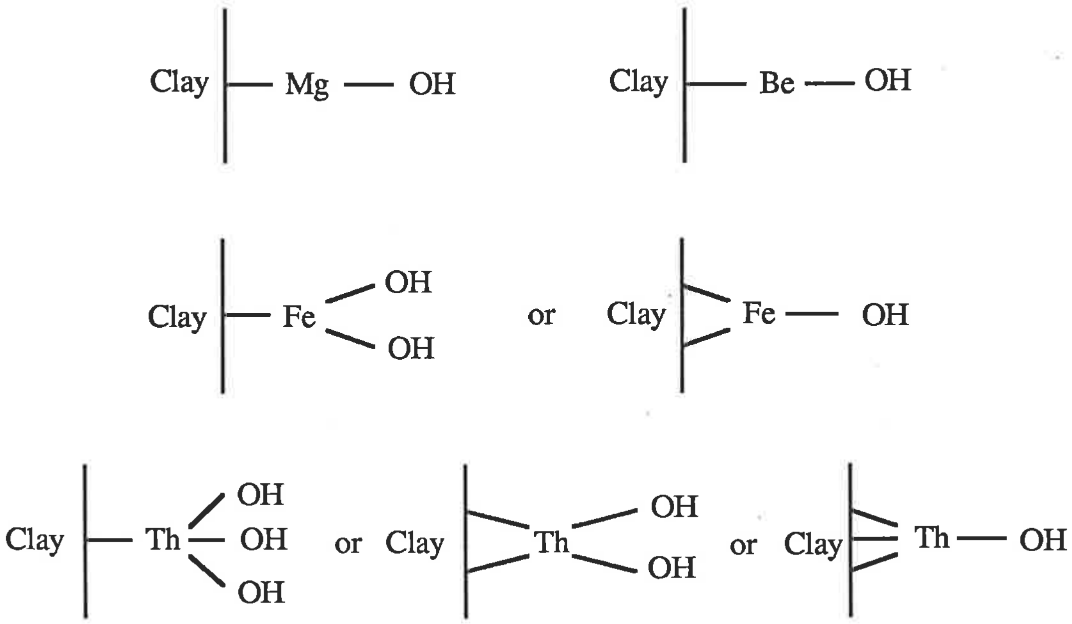
1.3.3. Macroaggregate Theory

The beneficial influence of organic matter on soil structure has been known for a long time. Rost and Rowles (1941) and Kemper and Koch (1966) suggested that the stability of soil aggregates >250 µm diameter is dependent on the soil organic matter, whereas Eagle (1975) and Clement (1975) found no relationship between the percentage of water-stable aggregates and soil organic matter levels.This suggests that total organic matter levels alone may not be sufficient to explain variations in aggregate stability, but certain fractions within the soil organic matter may be particularly active. Tisdall and Oades (1982) suggested that the correlation between water-stable aggregates and organic matter is not always good for any one or all of the following reasons: (i) only part of the organic matter is responsible for water-stable aggregation, (ii) there is a content of organic carbon above which there is no further increase in water-stable aggregation, (iii) it is the disposition rather than the type or amount of organic matter which is important, and (iv) some of the water-stability in virgin soils is related to physical factors in such a way that the particle reorganization associated with the first disturbance of virgin soil reduces water stability (Heinonen, 1955; Malik et al., 1965; Greenland, 1971b; Low, 1972; Tisdall and Oades, 1980). It was suggested that the water-stability of soil aggregates is sometimes related to free organic materials in a better way than to total organic matter, because this fraction acts as a substrate for microbial production of organic glues (Oades, 1967) and/ or because this fraction is a measure of roots and hyphae.

1.3.4. Cation bridges

Clay interacts with many organic compounds to form complexes of varying stabilities and properties. Similarly complexes of calcium and organic anions have also been reported, especially in biological systems (Henglein, 1943; Johnston, 1956). Because clays and organic materials are polyanions, they can be bridged by polyvalent cations, and are probably responsible for the stability of soil aggregates in a number of soils.

Results of studies by Lutz (1934), Joffe and Levine (1940), and Bower and Truog (1941) have shown that where polyvalent cations are used to saturate clays, higher saturations are obtained than when monovalent cations are used. Bower and Truog (1941) also noted that the results with monovalent cations were in good agreement, whereas those with polyvalent cations were increasingly higher, with a decrease in the strength of the base formed by the respective cations. This observation led them to suggest that clay acids, like other weak acids, formed basic salts when neutralized with weak bases of polyvalent cations. They pictured the mechanism as follows:



According to this diagram not all the charges of the adsorbed polyvalent cations are used by a single clay particle. The surplus charges are available for attracting some other negative ion, such as the hydroxyl groups as shown on other clay particles and organic ions. On the basis of the idea that Ca^{2+} acts as a bridge between carboxyl groups or uronide particles, and existence of surplus charges on some of the Ca cations adsorbed by clay, Peterson (1947) proposed calcium linkage as a mechanism in the cementing of water-stable granules in soils. The calcium linkage may be viewed as follows:

Clay ---Ca ---OOC ---R ---COO --- Ca ---OOC ---R ---COO ---Ca ---Clay

Stevenson (1982) suggested that organic anions are normally repelled from negatively charged clay surfaces, and adsorption of humic and fulvic acids by clay minerals such as montmorillonite occurs only when polyvalent cations are present on the exchange complex. Unlike Na^+ and K^+, polyvalent cations are able to maintain neutrality at the surface by neutralizing both the charge on the clay and the acidic functional group of the organic matter (e.g., COO^-).

The main polyvalent cations responsible for the binding of humic and fulvic acids to soil clays are Ca^{2+}, Fe^{3+}, and Al^{3+}. The trivalent cations are more effective than divalent cations because they may form coordination complexes with organic molecules.

Stevenson (1982) suggested that two major types of interactions may be involved in the adsorption of organic polyanions by mica-type clay minerals. In the first type the polyvalent cation acts as a bridge between two charged sites. In this case hydration water of the exchange cation is not displaced, but forms a H-bond with the organic matter. In the second type, the organic anion becomes coordinated to the cation, with displacement of a water molecule from the hydration shell. For a long chain organic molecule , several points of attachment to the clay particle are possible.

Stevenson also suggested that other bonding forces may also operate between polar groups of the organic molecule and adsorbed water molecules or oxygen of the silicate surface. The strength of an individual bond is small, but they are additive; thus total adsorption energy can be appreciable.

Hamblin and Greenland (1977) suggested the role of cation bridges on soil aggregation based on increased disaggregation after treatments of the soil with complexing agents or after treatments with acids. The complexing agents most commonly used have been pyrophosphate and acetylacetone, which was aimed particularly at Al and Fe. It has been shown consistently that pyrophosphate aids disruption of aggregates beyond that due to saturation of the system with Na. Pyrophosphate extracted more oxidised, aromatic components of the humic-fulvic system which have the most functional groups in close proximity, and therefore likely to complex with metal cations (Turchenek and Oades, 1979; Oades, 1981). It also extracts some polysaccharides. The extraction of organic polyanions is considered to be due to dispersion of the system and sequestering of polycations which have bridged clay and organic matter.

The complex interrelationship of physical, biological, and chemical reactions involved in the formation and degradation of soil aggregates was reviewed by Harris et al. (1966). An outline of possible mechanisms is given in Table. 2.

Table 2. Possible Bonding Mechanisms in the Formation of Stable Aggregates in Soil (Harris et al., 1966).

Clay Domain-Clay Domain[a]
Domain face-Domain face
Cation[b] bridge between negative faces. Mechanism similar to that for orientation of clay platelets into domains

$\text{Face}^{-}\text{----}M^{n+}\text{----}^{-}\text{Face}$

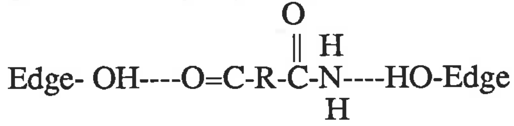
Domain edge-Domain face
Positive edge site to negative face

$\text{Edge Al-OH}_2^{+}\text{----}^{-}\text{Face}$

Clay Domain-Organic Polymer[c]-Clay Domain
Domain edge-Organic polymer- (Domain)
Anion exchange: Positive edge site to polymer carboxyl

$\text{Edge Al- OH}_2^{+}\text{----}^{-}\text{OOC-R-COO}^{-}\text{----}$

Hydrogen bonding between edge hydroxyl and polymer carbonyl or amide



$\text{Edge- OH----O=C-R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-}\underset{\text{H}}{\overset{\text{H}}{\text{N}}}\text{----HO-Edge}$

Cation bridge between negative edge site and polymer carboxyl

$\text{Edge-O}^{-}\text{----}M^{n+}\text{----}^{-}\text{OOC-R-COO}^{-}\text{----}$

Van der Waals attraction between edge and polymer
Domain face-Organic polymer-(Domain)
Hydrogen bonding between polymer hydroxyl and external or internal (expanding lattice minerals) face silicate oxygens

Face Si-O-----HO-R-OH----

Cation bridge between domain external face and polymer carboxyl or other polarizable group
$\text{External Face}^{-}\text{----}M^{n+}\text{----}^{-}\text{OOC-R-COO}^{-}\text{----}$

Van der Waals attraction between face and polymer (Greenland, 1965).
Quartz-(Silt, Inorganic and Organic Colloids)-Quartz
Chemical bonds established between quartz surface gels of hydrated aluminum silicates and active groups of other aggregate constituents
Quartz grains held in a matrix of silt and clay stabilized primarily by:
Oriented clay particles
Irreversibly dehydrated silicates, sesquioxides, or humic sesquioxide complexes
Irreversibly dehydrated humic materials
Silt-size microaggregates stabilized by iron humates
Organic colloids and clay domains bonded by mechanisms cited above

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[a] Clay domain defined as a group of clay crystals oriented sufficiently close together by cations or hydrogen bonds between the crystal faces to behave as a single unit.
[b] M^{n+} = Free cation or positively charged metal oxide or hydroxide.
[c] R = Organic polymer with axis horizontal or perpendicular to clay domain.

1.4 FACTORS INFLUENCING AGGREGATION

Physical, biological and chemical agents are involved in micro- and macro-aggregation of soil. However, the relative contribution of these agents to the formation of water stable aggregates depends on the local conditions at the site.

1.4.1.Physical Agents

1.4.1.1 *Freezing and Thawing:*

The effects of freezing and thawing on aggregation are inversely related to each other, and depends on the manner in which soil water crystallizes (Jung, 1931). Slow freezing results in the formation of few large ice crystals and large aggregates of soil particles. Since there is about a 9% increase in volume when water changes to ice, the pores are enlarged, which loosens the soil. Water is drawn from around the clay particles to the ice crystals during this process. The resulting dehydration promotes aggregation. On the other hand large numbers of small crystals are formed if the cooling is rapid, and the integrated effect of many expansions is the breakdown of soil aggregates. Richardson (1976) showed that the freezing and thawing cycles on a sandy loam that had been puddled severely resulted in better aggregation than that of untreated soil.

1.4.1.2 *Wetting and drying*

The effect of wetting and drying on aggregation is a function of the type of soil and the moisture content of aggregates at the time of the wetting treatment. The dehydration of a soil mass cannot be uniform, especially if the drying process is rapid. Consequently, unequal strains arise throughout the mass that tend to form clods. At least two processes operate to cause disruption of the clod into smaller units when the dry clod is wetted. The rapid intake of water causes unequal swelling throughout the clod, which produces fracturing and fragmentation along the cleavage planes. Moreover, the absorption of water into the capillaries results first in a compression of the occluded air and finally in virtual explosion within the clod, as the pressure of the entrapped air exceeds the cohesion of the particles. Since soil wetting and drying in the field are usually from one side only, the formation of cracks in larger aggregates occurs much more readily than in smaller aggregates. As a consequence, the decrease in the strength in larger aggregates occurs much more rapidly than that in the smaller aggregates (Woodburn, 1944; Utomo, 1980).

Wetting and drying cycles can also contribute to the degradation of soil aggregates by increasing oxidation of soil organic matter (Broadbent et al. 1964; Adu and Oades,1978a; Tisdall et al., 1978). It was suggested that differential swelling and shrinking, which occurs within aggregates during the wetting and drying process, results in the formation of microcracks. These microcracks effectively open up the soil, thereby weakening existing aggregates and exposing organic matter which was previously physically inaccessible to microbial attack.

1.4.1.3 *Mechanical stress*

Mechanical stress can cause closer packing or breakdown of soil particles. In most agricultural soils the major mechanical stresses are caused by plant roots, surface loads including the action of agricultural implements, and stresses imposed through the activity of soil animals.

Plant roots exert pressures which compress aggregates and separate adjacent ones. Water uptake by roots causes differential dehydration, shrinkage, and the opening of numerous small cracks as roots force their way through the soil.

Intensive mechanical cultivation has a great impact on soil structure. Cultivation of excessively wet soil causes puddling (plastic remolding), whereas cultivation of excessively dry soil is likely to result in grinding or pulverizing the soil into dust.

Soil animals also influence the soil structure by their burrowing activity.

1.4.2 Organic Binding Agents

Organic matter is considered to be of immense importance in forming stable aggregates in a wide range of soil types, particularly those representative of the Mollisols, Alfisols, Ultisols, and Inceptisols (Clement, 1975; Eagle, 1975; Hamblin and Davies, 1977; Douglas and Goss, 1982; Chaney and Swift, 1984). Organic matter is somewhat less important in the Oxisols, where hydrous oxides may play a predominant role. Stevenson (1982) illustrated these relationships, which are presented in Fig. 3.

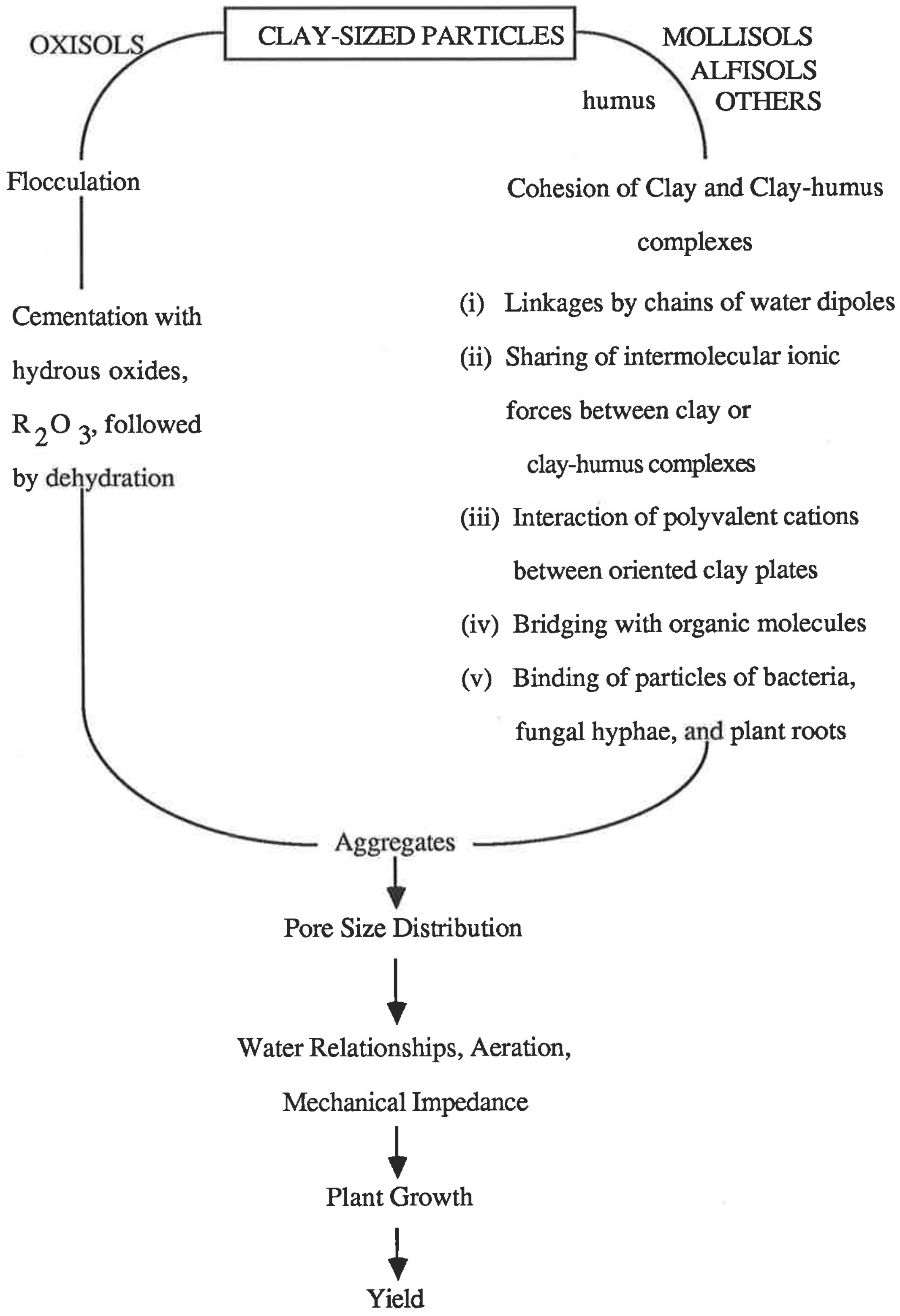


Fig. 3. Relationships between organic matter and the formation of soil aggregates.

(Stevenson, 1982)

A range of organic materials can increase the stability of soil aggregates. Tisdall and Oades (1982) demonstrated that the water-stability of macroaggregates depends largely on roots and hyphae, and thus on growing root systems. However, the amount of roots and hyphae present in the soil account for only a small amount of the total soil. According to Rasmussen et al. (1980) and Hooker et al. (1982), incorporation of straw increases both soil organic matter and microbial polysaccharide levels. Several authors (e.g. Swincer et al., 1968; Cheshire, 1979; Martin, 1971) have suggested that polysaccharides produced by the decomposition of organic materials act as glues in soil aggregation. Most of the aggregation is in the top layers of soil, because organic residues accumulate at the surface (Clement and Williams, 1958).

The organic colloidal material, produced largely through microbial activity, together with clay is responsible for the major portion of soil aggregation. Moreover, it is more effective than clay in causing the formation of stable aggregates with sand. The beneficial effects of organic matter on soil aggregation originate from the integrated activity of microorganisms, fauna, and vegetation. Changes in aggregation following the addition of organic material to soil indicate that aggregating effectiveness relates to microbial decomposition. Various sterilized substrates possessing no binding ability have been added to sterilized soil without the presence of microorganisms, and no increase in aggregation was observed (Waksman and Martin, 1939; Peele, 1940; Hubble and Chapman, 1946).

It was observed that where soil is cultivated frequently, aggregates are exposed repeatedly to physical disruption by rapid wetting and raindrop impact as well as to shearing by implements. The net effect is to expose inaccessible organic matter to micro-organisms and to stimulate oxidation and loss of organic matter (Low, 1954; Rovira and Greacen, 1957; Clement and Williams, 1958; McCalla, 1959; Martel and Paul, 1974; Adu and Oades, 1978). Materials which are decomposed slowly tend to exert their binding effect over a longer period of time (Meredith and Kohnke, 1965; Tisdall and Oades, 1982). The balance between aggregation and disaggregation is related to the resistance and availability of the aggregating agents to microbial decomposition.

Organic constituents may influence soil aggregation in at least three different ways (Stevenson, 1982). First, organic substances serve as binding agents for the cohesion of clay particles, such as through H-bonding and coordination with polyvalent cations. Flocculation of clay is considered to be an obligate prerequisite for aggregation. A wide variety of organic compounds may be involved in the cementation of clay or clay particles, including humic and fulvic acids, which are probably linked to clay as a clay-metal-humus complex.

Second, gelatinous organic materials surround soil particles and hold them together through a cementing or encapsulation action. Whereas a variety of compounds may be responsible, several workers (e.g. Swincer et al., 1968; Martin, 1971; Cheshire, 1979) indicated that the major role is played by the polysaccharides. For the most part, polysaccharides are readily attacked by microorganisms; thus their effect on aggregation would be expected to be shortlived. This explains why fresh organic matter in the form of plant or animal residues needs to be returned periodically to the soil in order to provide energy for resynthesis through the activities of microorganisms.

Third, soil particles are held together through physical entanglement by fungal hyphae and microscopic plant roots. The mycelia of fungi are often extended throughout the soil and particles are entrapped and tied together. Aggregation through this mechanism is transient and dependent on maintaining a high content of fungal hyphae. The fibrous root systems of the grasses not only ramify and open up the soil, but they encompass individual crumbs in a netlike web to form clusters resistant to the slaking action of water.

Tisdall and Oades (1982) suggested that three main groups of organic binding agents are involved in stabilizing aggregates based on the age and degradation of the organic matter, and not on the proportions of chemically defined compounds. The various binding agents determine the age, size and stability of aggregates. The three groups of organic binding agents considered are (i) transient; composed of microbial and plant-derived polysaccharides, which are rapidly decomposed by microbes, (ii) temporary; including roots and hyphae, especially mycorrhizal, and (iii) persistent; aromatic humic material in association with amorphous Fe and Al compounds and polyvalent metal cations. The metals act as clay-organic matter and organic matter-organic matter bridges (Edwards and Bremner, 1967). Persistent binding agents are thought to be mainly responsible for the integrity of the microaggregates, which range in size from 50-250 µm . Microaggregates which are generally <250 µm in diameter are the building blocks of soil structure because they can become united to form macroaggregates, through the action of temporary and transient binding agents.

1.4.3 Inorganic Binding Agents

The major inorganic soil components which may act as soil binding agents consist of hydroxides and oxides of iron and aluminium, gypsum and soil carbonate.

1.4.3.1 *Iron and aluminium oxides and hydrous oxides*

Oxides or hydrated oxides of iron and aluminium may serve as cementing or binding agents in many soils (Oades, 1963; Taylor and Schwertmann, 1974; Nvaka and Voronova, 1980). These investigators stressed the probability that sesquioxides act as cementing agents in the formation of aggregates in prairie soils as well as in lateritic soils. Hydrous oxides of aluminium and iron cement particles together in water-stable aggregates with diameters greater than 100 µm, especially in soils which contain more than 10 per cent sesquioxides. The full extent of cementation by oxides is evident in bauxite and ferricrete (Kroth and Page, 1946; Chester et al., 1957; Kuznetsova, 1966; Krishna Murti et al., 1977).

Deshpande et al. (1964, 1968) found that complete removal of free iron oxides by treatment with Na-dithionite and citrate, or Na-dithionite and 0.05N HCl had little effect on the aggregation or structural stability of a number of soils (e.g. Laterite, Krasnozem, Rendzinas, Terra Rossas and Red Brown Earths). It was concluded that stability of soil aggregates in these soils was dependent on the organic materials, and iron oxides were present as discrete crystals and do not cement the soil particles. These findings were supported by Greenland et al. (1968). By using electron microscopy in conjunction with selective extraction methods, it was observed that certain iron oxides occur as discrete particles or clusters. On the other hand, chemical removal of iron oxides and sub-plastic materials caused decreasing aggregate stability and complete dispersion (McIntyre, 1976). The decline in aggregate stability after selective removal of inorganic and organic complexes from soil aggregates by aqueous solutions of inorganic salts was also reported (Greenland et al., 1962; Clapp and Emerson, 1965).

In the study of clay minerals, iron has not been shown to be so effective in aggregation, probably because above pH values of about 3, iron is precipitated as a separate phase from the clay minerals as shown by electron microscopy (Follet, 1965; Greenland and Oades, 1968). However, ferrihydrite freshly precipitated in the presence of clay was shown to be effective in aggregating clay fractions (Blackmore, 1973).

Shanmuganathan and Oades (1982a,b) demonstrated that the addition of iron in the form of polycations flocculated clay to give water-stable aggregates 50-250 μm diameter and also created pores 40-100 μm in diameter. The treated soil had greater water holding capacity , hydraulic conductivity and lower bulk density, modulus of rupture and was more friable. These changes in physical properties increased plant growth and yield.

1.4.3.2 *Gypsum* ($CaSO_4 \cdot 2H_2O$)

Gypsum, because of its general availability and low cost, is the most used source of calcium for amelioration of soil structure. Addition of gypsum has been shown to improve various physical properties of soil such as porosity, hydraulic conductivity and plant available water (Davidson and Quirk, 1961; Loveday, 1974,1976; Keren et al., 1980; Shanmuganathan and Oades, 1983).

Gypsum is used to reclaim sodic soils and to improve soil water infiltration when it has been decreased by low electrolyte concentration. In a review Oster (1982) suggested that the electrolyte concentration of the soil water and exchangeable sodium fraction (E_{Na}), are the two predominant chemical factors that influence soil hydraulic properties. It was also indicated that for the reclamation of sodic soil with gypsum, the maximum electrolyte concentration needed to maintain stability increases with increasing E_{Na}: for soil solutions in eqilibrium with both gypsum and an E_{Na} of 0 and 0.4, the concentrations are 15 and 133 mol m^{-3}. These concentrations are generally adequate to maintain the existing hydraulic conductivity. Higher concentrations can increase the soil hydraulic conductivity and the rate of reclamation. Sims and Rooney (1965) demonstrated that surface applications of gypsum reduced soil crusting, increased water infiltration and in turn, crop yield.

Quirk (1977) suggested that a threshold concentration of electrolyte is required to maintain hydraulic conductivity which is dependent on exchangeable sodium percentage (ESP). The electrolyte effect produced by gypsum is perhaps the dominant factor, and both ESP and electrolyte must be considered. Non-sodic clays will disperse on shaking when the electrolyte concentration is low (Shanmuganathan and Oades 1982a). Even in the absence of electrolytes, calcium-saturated]Red Brown Earth disperse due to weak mechanical forces (Rengasamy, 1983). Addition of a small amount of gypsum (0.2% W/W) in a sandy loam soil coagulated most of the clay by lowering the ESP and raising the electrolyte concentration (Shanmuganathan and Oades 1983). However the clay gradually dispersed as the soil was subjected to wetting and drying cycles and the electrolyte concentration was decreased. It was suggested that the most efficient use of gypsum would appear to be as small annual additions.

To meet the higher demand of calcium for use in reclaiming sodic soils, Oster (1982) suggested that phosphogypsum would be a good alternative source. Phosphogypsum dissolves faster than mined gypsum, and hence it develops a higher electrolyte concentration during an infiltration event.

1.4.3.3 *Calcium carbonate* ($CaCO_3$)

The presence of fine calcium carbonate particles in soils is known to improve the physical condition of sodic soils (US Salinity Laboratory Staff, 1954). Because of the low solubility of $CaCO_3$ in soils having a pH greater than 7.5 , lime is not effective in the exchange mechanism by which exchangeable sodium is replaced by calcium, and thus sodic soils containing $CaCO_3$ are common in the semiarid and arid regions of the world. To explain the effect of $CaCO_3$, the US Salinity Laboratory Staff (1954) and Rimmer and Greenland (1976) suggested that lime in soil acts as a cementing agent which stabilizes soil aggregates and prevents clay dispersion. Another mechanism which explains the beneficial effect of $CaCO_3$ is its potential for dissolving, and maintaining the concentration of the soil solution at levels above the flocculation value of the soil clays, thus preventing their dispersion. According to the dissolution mechanism, exchange reclamation is still negligible because of the low concentration of Ca ions in the soil solution (Shainberg et al., 1981a). The mechanism by which $CaCO_3$ stabilizes soil structure is important in studies on infiltration rates and crust formation (from raindrop impact) in calcareous and noncalcareous soils (Agassi et al., 1981). If $CaCO_3$ acts as a cementing material, calcareous soils will not be as sensitive to crust formation as will noncalcareous soils. However, if the dissolution mechanism is dominant, the concentration of electrolytes at the soil surface exposed to rain will be insufficient, and both types of soil will be sensitive to crust formation.

The role of $CaCO_3$ dissolution in preventing losses in hydraulic conductivity of sodic soils was determined by Shainberg and Gal (1982) by mixing lime-free soils with low percentages of powdered lime (0.5 and 2.0 %). Although the hydraulic conductivity (HC) of the lime-free soils dropped sharply when 0.01 N solutions of sodium adsorption ratio 20 (SAR) were displaced with distilled water, mixing the soil with powdered lime prevented both losses in hydraulic conductivity and clay dispersion. The increase in electrolyte concentration in the soil solution due to $CaCO_3$ dissolution was suggested as the mechanism responsible for the beneficial effect of lime.

Shainberg and Gal (1982) found that powdered $CaCO_3$ (<44 μm diameter) prevented clay dispersion and increased the hydraulic conductivity of sodic soils. This investigation illustrates the importance of the size of the $CaCO_3$ particles on solubility, and hence the physical condition of the soil.

Shanmuganathan (1983) added calcium in the form of $CaCO_3$ and $CaSO_4$ to soils with a view to determining whether they have any effect on soil physical properties. Soil treated with $CaSO_4$ exhibited increased hydraulic conductivity and decreased clay dispersion; soil treated with $CaCO_3$ did not show any significant improvement of soil properties. It was suggested that the low efficiency of $CaCO_3$ was due to large particle size which inhibited its dissolution.

In a review, Harris et al. (1966) pointed out that $CaCO_3$ often stimulates microbial activity and that may have a beneficial effect on the aggregation of certain soils. Diamond and Kinter (1965) suggested that slower pozzolanic reactions are responsible for the increasing aggregate stability of $CaCO_3$ treated soils with time.

1.4.3.4 *Mixtures of gypsum and calcium carbonate*

The proposal to use $CaSO_4.2H_2O$ and $CaCO_3$ together to improve soil physical conditions was based on the idea; that (i) because of its higher solubility, $CaSO_4$. $2H_2O$ has an immediate effect on soil physical properties. However this effect is weakened as the Ca^{2+} is leached from the soil and (ii) due to the low solubility $CaCO_3$ which releases Ca^{2+} slowly, may help to maintain the physical conditions of soil.

Chemical models using CO_2, CO_3^{2-}, HCO_3^-, Ca^{2+} and pH interactions to calculate lime precipitation or dissolution (Langelier, 1936) and its effects on the sodium adsorption ratio and the exchangeable sodium percentage have been developed (Bower et al., 1968; Pratt and Bair, 1969). Gypsum models have also been developed to predict solution composition and concentration effects on $CaSO_4$ solubility (Dutt et al., 1972; Tanji et al., 1972). A detailed description for ($CaSO_4$-HCO_3^--CO_3^{2-} interactions in solution, given by Nakayama (1969) and Robbins et al. (1980) provides an invaluable overview of the combined lime and gypsum interaction in soil water systems. They demonstrated that $CaSO_4$-CO_3^{2-} equlibrium is pH dependent and at low pH's the $CaSO_4$-HCO_3 reaction is dominant, and at high pH's the $CaSO_4$-CO_3^{2-} reaction is dominant. In both reactions a greater fraction of the total dissolved Ca becomes complexed and is not in the Ca^{2+} form and consequently is unavailable for Na replacement. Kauschansky and Gat (1977) and Keren and Kauschansky (1981) showed that the rate of gypsum dissolution is reduced by a coating of precipitated $CaCO_3$. Thus it appears that the use of $CaSO_4.2H_2O$ and $CaCO_3$ together was not a good proposition.

1.5 CALCAREOUS SOILS

Calcareous soils are found in arid, semi-arid and humid regions of the world. Soils that develop from calcareous parent materials often have calcium carbonate somewhere in the profile. The physical condition of calcareous soils is usually satisfactory, because the exchange complex is usually saturated or nearly saturated with Ca^{2+}. There are calcareous soils which are poorly structured, although they appear to have sufficient calcium carbonate present to maintain the stability of soil aggregates. This indicates that some factors can operate in soils that reduce the efficiency of $CaCO_3$ by decreasing its solubility.

1.5.1 Factors influencing the distribution of $CaCO_3$ in the soil profile

Several factors can influence the distribution of $CaCO_3$ in the profile e.g. moisture, temperature, wind, parent material and biological activity. The relative importance of these factors on the distribution of $CaCO_3$ depends on the local conditions.

The depth of $CaCO_3$ horizons is strongly influenced by soil water flow, and increases with increasing mean annual precipitation (Arkley, 1963; Jenny, 1980). Marion et al. (1985) evaluated the depth of $CaCO_3$ horizon in southwestern deserts of the United States using the three Pleistocene climatic concepts: cold-dry, cool-wet (winter), and warm-wet (summer). It was observed that the cool-wet (winter) hypotheses caused a greater increase in the depth of $CaCO_3$ deposition than the cold-dry or cool-wet (summer) hypothesis, because all three factors changed in the cool-wet (winter) scenario, leading to an increased depth of $CaCO_3$ deposition. The factors are lower temperature, higher precipitation, and a concentration of the higher precipitation in the winter months. Low evapotranspiration was conducive to deeper leaching of $CaCO_3$ in the soil profile.

Temperature plays an important role in controlling water flow in the soil through its effect on evapotranspiration (Arkley, 1963). Wind also plays a critical role in the rate of formation of calcic horizons, because wind-borne dust and dissolved constituents in precipitation are considered the dominant sources of calcium for deposition of $CaCO_3$ in noncalcareous desert soils (Brown, 1956; Reeves, 1970; Gardner, 1972; Gile et al., 1981; Schlesinger, 1985).

Soils formed on calcareous parent materials accumulate pedogenic $CaCO_3$ at higher rates than soils formed from noncalcareous parent materials (Lattman,1973; Schlesinger, 1982,1985). Parent material also controls to a large extent, the water-holding capacity (WHC) of soils. The WHC in turn controls the depth of wetting and $CaCO_3$ deposition (Arkley ,1963; Stuart and Dixon, 1973; Gile et al., 1981).

The biotic factor can influence $CaCO_3$ deposition through its effects on (i) soil CO_2 concentrations, which largely control soil pH and $CaCO_3$ solubility, and (ii) evapotranspiration (Arkley, 1963; Gile et al., 1981).

1.5.2 Forms of carbonate present in the soil

Carbonate (most commonly calcite) usually occurs in three different forms in the horizon of carbonate accumulation (Brewer, 1972). In most soils they occur in the "fine earth" as crystallites (small intercalary crystals scattered through and embedded in the plasma of the s-matrix). This is a common form of occurrence in calcareous parent materials of aeolian or alluvial origin. Carbonates also occur as calcans and neocalcans. The third form of carbonates in soil horizons is the very common, dense, fine-grained nodules.

Churchward (1963) and Gile et al. (1966) suggested that there is a progression in the development of these three forms of carbonates with time. The crystallites in the s-matrix develop into larger intercalary crystals then to calcans and neocalcans and finally to nodules. This progression is continued into old soils which commonly have large dense sheets and/or columns of carbonates, often widely separated by carbonate-free soil material.

In most cases $CaCO_3$ exists in soils as nodules. Wieder and Yaalon (1974) distinguished three kinds of carbonate nodules according to their morphology and origin: (i) orthic nodules, which have skeleton grains similar to the surrounding soil and a gradual transition to the soil matrix; these are formed in situ, (ii) disorthic nodules, which on the basis of their sharp boundaries can be judged as having been subjected to some pedoturbation but have a fabric resembling the surrounding matrix; and (iii) allothic nodules, which have a fabric that differs in composition from the soil in which they are incorporated, and hence judged to have been transported into the soil.

To describe the distribution of carbonate nodules in a soil profile, Wieder and Yaalon (1974) suggested that orthic nodules are found in the main calcic horizon. They are therefore present at the depth of the seasonal moisture penetration below the major root zone, where active precipitation of carbonates takes place. In these horizons the nodules are compact, although if observed through a microscope they appear to be diffuse. The increase of compaction is presumably a function of age (Gile, 1970) or advanced stage of profile development (Sehgal and Stoops, 1972). The disorthic nodules are concentrated in the active root zone where they are subjected to repeated dissolution-precipitation cycles due to fluctuations in moisture content and CO_2 pressure. They are especially widespread in the upper horizons where bioturbation processes are most active. Near the main calcic horizon, the orthic nodules are common and the disorthic nodules decrease in frequency. The allothic types are especially frequent in the buried solum, and their origin is from the calcareous sandstone parent material. These nodules are similar to the parent material, and have microsparitic to sparitic cement pore filling with local recrystallization fractures. They also include biorelicts, pellets and glauconitic grains.

1.5.3 Mechanisms of carbonate nodule formation

Carbonate nodules and their formation in soils have been studied by several authors (Hawker 1927; Gile 1961; Gile et al. 1965, 1966; Ruellan ,1968), generally with the accent on macroscopic observations. Most authors agree that a gradual enrichment and precipitation of authigenetic carbonates takes place during nodule formation.

To describe the mechanism of carbonate nodule formation, Kubiena (1938) ascribes the interflorescence process to a precipitation of dissolved substances in the interiors of fabric bodies, following oversaturation produced by evaporation. Consequently, the dissolved lime precipitates in the form of small (1-1.5 µm), equant, calcite crystals. According to Brewer (1964) such interflorescences around pores (e.g. neocalcitans) may be formed by two processes, "by diffusion from within the body of the soil material towards the natural surfaces......or by movement of suspensions or solutions along the voids and penetration into the s-matrix of the soil material......"

An in-situ formation of hard, discrete glaebules in loesslike and sandy soils has been described by several authors (Durand, 1959; Gile, 1961; Tolchelnikov ,1962; Gile et al., 1966). It was suggested that hard nodules develop as a result of carbonate concentration around a privileged point (a pore, or meeting point of several pores), often due to the presence of large roots or the displacement of such roots. Wilbert (1962) found that such nodules can form in any cavity in the soil.

Wilbert also found that carbonate concentrations can easily change from one form into another. In many soils the accumulation of pedogenic carbonate starts with soft, powdery forms that can harden in a later stage due to dissolution and desiccation. Forms of pedogenic carbonate have been regarded representative of the stage in profile development from young to mature (Singh and Lal, 1946; Tolchelnikov, 1962; Suprychev, 1963; Gile et al., 1966).

Silicate clay plays an active role in carbonate precipitation and also inhibits recrystallization. Wieder and Yaalon (1974) observed that during carbonate nodule formation part of the clay is expelled to the fringe of the nodule and into the matrix. The precipitation of carbonates and displacement of clay is not in any particular direction, but is random in response to local environments. By chemical analysis of calcareous concentrations in a loess-like clay-loam soil, Suprychev (1963) observed an increase of carbonate in the centre and an increase of Al_2O_3 and MgO at the periphery. Gillot (1969) also noted the coarseness of calcite in relation to the decrease of clay. Diagenetic alteration is also affected by the presence of clay minerals. It seems that the presence of more than 2% clay inhibits recrystallization (Bausch, 1968).

1.5.4 Solubility of calcium carbonate

Calcium carbonate in soil may be either detrital or pedogenic (Birkeland, 1974). Differentiation between these origins within a soil is not easy and has not been studied in detail. Determination of the solubility of $CaCO_3$ in the laboratory or in the field has not differentiated between the detrital and pedogenic carbonates, although it may be expected that they react differently in soil processes (Olsen and Watanabe, 1959; Plummer and Wigley, 1976; Suarez, 1977). For example, the rate of dissolution is known to be effected by the presence of minor elements like Mg (Berner, 1975), which is commonly found in the detrital carbonates, but only sometimes occurs in pedogenic carbonate (Arnaud, 1979; Magaritz and Kafri, 1979). Another reason that detrital and pedogenic carbonates may dissolve at different rates is that the latter is relatively more concentrated in the fine grained fraction. This higher specific surface of the pedogenic carbonate may lead to greater reactivity and a higher dissolution rate.

Abedi and Talibudeen (1974) measured the specific surface area of carbonate present in soil from Iran and Britain. For carbonate contents of <1% by weight, this was about 300 m^2g^{-1}, as compared with 15 m^2g^{-1} when 10-20% carbonate was present. It shows that small amounts of carbonate in a soil can be effective sources of calcium. This investigation illustrates the importance of the size of the $CaCO_3$ particles on solubility and hence the physical condition of the soil. A study of limestone soils in Southern England showed that the surface area of $CaCO_3$ was an inverse function of the $CaCO_3$ percentage (Holford and Mattingly, 1975).

Calcium carbonate in soil is generally assumed to behave like pure calcite. Equations relating calcium carbonate solubility to carbon dioxide pressure have been given , although their application to calcareous soils had not yet been tested thoroughly (Olsen and Watanabe, 1959; Yaalon 1958). Thus usually only the system $CaCO_3$-CO_2-H_2O is considered, neglecting a possible interaction between the carbonates and other soil components (Olsen and Watanabe, 1959). Studies by Suarez (1977) have indicated that ionic activity products for $CaCO_3$ in soils can vary , depending on the experimental conditions under which they were obtained. Lahav and Bolt (1963) observed that dissolution of carbonates on contact with clay is retarded due to the interaction between the surface of the calcium salts and dissolved compounds, presumably silicates, causing a surface coating of the carbonate particles with calcium silicate.

1.5.5 The role of calcium carbonate on organic matter decomposition

The prime source of soil organic matter is plant debris of all kinds such as dead leaves and branches, that fall onto the soil and are decomposed at a variable rate. The relationship between decomposition of organic matter and soil structure improvement has clearly been demonstrated by Harris et al. (1966). In general, easily decomposed material brings about a greater degree of aggregation due to the build-up of fungal mycelia and cementing agents, however the effect is short lived due to the loss of organic matter.

Several factors can affect the rate of decomposition of organic matter such as organic matter-metal ion complexing (Martin et al., 1966), nutrient availability (Coulson and Butterfield, 1978; Stotzky and Norman, 1961), clays (Marshall, 1975) and soil physical conditions (Adu and Oades, 1978; Martin et al., 1982; Zunino et al., 1982).

Microorganisms are responsible for the production of a variety of linear organic polymers; e.g. low molecular weight humic substances and various polysaccharides, or polyuronides. These are produced by many species of bacteria, fungi, actinomycetes and yeasts (Forsyth and Webley, 1949). It has been shown that the decomposition of microbial or plant polysaccharides was reduced by interaction with organic and inorganic constituents in the soil (Mattson, 1932; Martin et al., 1966; Martin, 1971; Cheshire et al., 1974), such as adsorption of polysaccharides onto clay surfaces, and the formation of polysaccharide-metal complexes (Swincer et al., 1969; Martin et al., 1974). These interactions either inhibit the activity of extracellular enzymes or increase the insolubility of the polysaccharides, restricting their availability to soil microorganisms (Cheshire, 1977). Mechanisms involved in the interaction are essentially the same as described in section 1.4.4. More complete description of the complexes of C—P—OM influencing the stability of organic matter are presented by Greenland (1971) and Theng (1979).

Gaiffe et al. (1984) demonstrated that by gradual removal of the exchangeable calcium held by the organo-mineral complexes of an organic soil resulted in the destabilization of the organo mineral complex by H^+, produced by the biodegradation of the most labile portion of the organic matter. The clay humus complex gradually dissociates. This process leads to the destruction of aggregates and organo-mineral complexes. The organic matter released becomes biodegradable because the protective effect of calcium has been removed.

Opposite effects of calcium carbonate on organic matter decomposition were also found by Shiel and Rimmer (1984). Shiel and Rimmer observed that addition of lime increased the decomposition of organic matter. It was postulated that increase in pH due to liming stimulated the microbial activity and hence resulted in the loss of organic matter. On the other hand Jenkinson (1977) demonstrated that changing the soil pH from 4.9 to 8.1 had little influence on the organic matter decomposition. Low pH (3.7) could initially slow down the decomposition, but the effect is temporary. It seems that the effect of pH on the decomposition of organic matter may have been overestimated, as other soil factors can also contribute to the process.

1.6 SUMMARY OF LITERATURE

Stable soil aggregates are essential to obtain a favourable soil physical condition for plant growth. Soil physical, chemical, and biological factors are involved in the formation and stability of aggregates. Evaluation of the part played by each constituent in creating water-stable aggregates is extremely complex and still unresolved, although it has been widely investigated.

Addition of organic materials to the soil increases the stability of soil aggregates, but the effect was found to be short lived, due to the loss of organic matter by decomposition. Therefore formation and degradation of soil structure is directly related to the availability and loss of the organic matter in the soil. It has been suggested that the loss of organic matter may be inhibited in the presence of metals, by forming organic matter-metal or clay—metal—organic matter complexes. Gypsum is the most widely used calcium compound for improvement of soil structure. Further study of the involvement of calcium on the decomposition of organic matter, and the formation and stability of soil aggregates is worthy of investigation.

CHAPTER 2

THE INFLUENCE OF CALCIUM CARBONATE ON SOIL PHYSICAL PROPERTIES

2.1 INTRODUCTION

A considerable portion of the agricultural land of South Australia is predominantly calcareous, covering a wide range of topographic forms, from undulating plains to hilly uplands. These soils all contain calcareous material in a number of different forms. The amount and type of carbonate may differ between profiles, and within the same profile, but is normally concentrated in the subsoil. The physical condition of calcareous soils is usually satisfactory for agricultural purposes, because the exchange complex is saturated, or nearly saturated with calcium, which keeps them well aggregated. The role of $CaCO_3$ in soil stabilization has not been clearly enunciated in available literature; however, several workers have proposed that $CaCO_3$ acts as a cementing agent which stabilizes soil aggregates (U.S. Salinity Staff, 1954; Rimmer and Greenland, 1976), and clay dispersion is prevented primarily because of the eletrolyte concentration effect (Shainberg et al., 1981a). However, there are calcareous soils which are not well aggregated, indicating the absence of a cementing or electrolyte effect.

From these observed differences in soil structure between calcareous soils, it was decided to investigate the role of $CaCO_3$ on the soil physical properties of eight calcareous soils with a range of $CaCO_3$ contents. The objectives of the study were to determine the following:

(i) the distribution of $CaCO_3$ in the soil profile,

(ii) the micromorphological characteristics of the soil surface horizons (0-10 cm depth) and carbonate nodules

and (iii) the role of $CaCO_3$ on soil aggregate stabilization , clay dispersion and other soil physical properties.

2.2 MATERIALS

2.2.1 Field sampling: Eight calcareous soils from the Adelaide plains and Mount Lofty ranges, located in South Australia, were collected (0-10 cm depth). The soils were selected on the basis of apparent $CaCO_3$ content (visually assessed in the field by the degree of effervescence with hydrochloric acid). Sampling of soils for profile description was carried out by auger borings, usually to a depth of 150 cm, but in some cases less, due to the presence of a hard pan. Macromorphological descriptions were made according to the Soil Survey Manual (Soil Survey Staff, 1951, see appendix A). The soils were also classified according to the Factual Key (Northcote,1974) and their approximate correlation between the great soil groups and world soil map are given in Table 3.

2.2.2 Analytical Methods

Soils were air dried in a glasshouse and then ground lightly with a mortar and pestle to pass through a 2 mm round-hole sieve. Undisturbed samples for bulk density and hydraulic conductivity measurements were also collected. The mechanical, mineralogical and chemical properties of the soils are listed in Tables 4, 5 and 6.

(a) Soil pH and electrical conductivity were measured in a 1:5 soil/distilled water suspension.

(b) Calcium carbonate was determined by a volumetric calcimeter method (Allison and Moodie, 1965).

(c) Hydraulic conductivity

Saturated hydraulic conductivity of undisturbed samples (7 cm d x 7.5 cm l) was determined by the constant head method of Klute (1965). The samples were saturated by placing the columns of soil one centimetre below the water level overnight, and then connected to a constant head of water. The outflow was collected for a known time when a constant rate was attained.

(d) Liquid limit, plastic limit and plasticity index were determined following the methods described by Kezdi (1974).

(e) The friability of field soils was determined using the method of Utomo and Dexter (1981), modified by Dexter and Kroesbergen (1985).

Table 3. Approximate correlations between: the great soil groups of 'A Handbook of Australian Soils' (Stace et al., 1968), the principal profile forms of 'A Factual Key' (Northcote, 1974), great groups of 'Soil Taxonomy' (Soil Survey Staff, 1975), and the soil units of 'FAO-Unesco World Soil Map' (FAO 1974).

Location	Handbook of Australian soils	Factual Key	Soil Taxonomy	World Soil Map
Clarendon	Grey-brown and red calcareous soils	Um 5.16	Haploxeralf	Calcic Yermosol
Claremont	Black earth	Ug 5.11	Chromustert	Chromic Vertisol
Dublin	Solonized brown soils	Gc 1.12	Calciorthid	Calcic Luvisol
Grace (i)	Solonized brown soils	Gc 1.12	Calciorthid	Calcic Luvisol
Grace (ii)	Solonized brown soils	Gc 1.12	Calciorthid	Calcic Luvisol
Grace (iii)	Solonized brown soils	Gc 1.12	Calciorthid	Calcic Luvisol
Strathalbyn	Solonized brown soils	Gc 1.12	Calciorthid	Calcic Luvisol
Trott Park	Solonized brown soils	Gc 2.21	Palexeralf	Calcic Xerosol

Table 4. Soil Mechanical Analysis

Soils	% Sand	% Fine Sand	% Silt	% Clay	Texture
Clarendon	5.1	29.4	31.0	34.3	Clay loam
Claremont	6.2	9.1	55.7	28.8	Silty loam
Dublin	8.9	37.2	31.6	22.2	Loam
Grace (i)	3.3	48.6	29.0	19.9	Sandy loam
Grace (ii)	6.0	28.6	40.8	24.4	Loam
Grace (iii)	6.6	32.3	37.2	23.8	Loam
Strathalbyn	17.9	26.7	30.6	24.7	Loam
Trott Park	1.3	39.4	40.7	18.5	Loam

Table 5. Mineralogy of soil clays

Clay minerals (%)

Soils	IMS	Illite	Kaolinite	Chlorite
Clarendon	–	75	16	7
Claremont	36	40	23	–
Dublin	33	41	25	–
Grace (i)	50	29	20	–
Grace (ii)	38	38	24	–
Grace (iii)	45	34	20	–
Strathalbyn	29	50	20	–
Trott Park	52	34	13	–

(—) not present
IMS= Interstratified Mica-smectite

Table 6. Soil Chemical Properties

Soils	$CaCO_3$ (%)	Organic -C (%)	Total N (%)	C:N ratios	pH (1:5 soil/water)	EC (µS cm^{-1}) (1:5 soil/water)
Clarendon	+	3.3	0.28	12	8.0	145
Claremont	11.0	2.2	0.21	10	8.1	190
Dublin	19.5	1.4	0.10	14	8.1	190
Grace (i)	23.0	2.4	0.22	11	8.4	225
Grace (ii)	14.5	2.1	0.19	11	8.2	200
Grace (iii)	11.0	2.7	0.24	11	8.1	210
Strathalbyn	14.0	1.7	0.17	10	8.1	190
Trott Park	27.0	3.9	0.44	9	8.0	245

(+) trace

Exchangeable Cations (C g^{-1})

Soils	Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC (C g^{-1})	ESP
Clarendon	30.0	2.8	1.0	1.3	35.6	3.5
Claremont	25.3	6.3	0.7	3.8	33.7	2.1
Dublin	17.9	2.0	0.4	2.3	19.5	2.0
Grace (i)	18.3	2.6	0.7	3.6	23.4	3.1
Grace (ii)	27.0	2.6	0.7	4.0	28.4	2.4
Grace (iii)	26.1	4.1	0.9	3.6	29.4	3.1
Strathalbyn	21.8	1.5	0.6	1.8	23.7	2.8
Trott Park	28.0	3.0	1.0	1.0	30.0	3.4

C = Coulomb = 6.2×10^{18} electron charges
1 C g^{-1} = 1 meq 100 g^{-1} approx

(f) **Aggregate dispersion** was measured using a modification of Emerson's method (1967) by Loveday and Pyle (1973).

(g) **Water holding capacities** at different water potentials from -10 KPa to -1500 KPa were determined using sintered glass funnels and pressure plates (Richards, 1965).

(h) **Exchangeable cations and Cation Exchange Capacity** were determined following the methods described by Heanes (1981). Exchangeable cations were extracted with 1M NH_4Cl in 60% V/V ethanol and water at pH 8.5. Exchangeable sodium and potassium were determined by flame photometry and exchangeable calcium and magnesium by atomic absorption spectrometry.

Cation exchange capacity (CEC) was determined by dilution of the residual exchange cation extract with M/100 NH_4Cl, followed by extraction of the added forms of NH_4^+ and Cl^- with 1M KNO_3, 0.5 M $Ca(NO_3)_2$ and subsequent determination after steam distillation.

(i) Dispersible clay

Dispersible clay was determined following the methods described by Shanmuganathan and Oades (1982). Air-dried samples (25 g) were mechanically shaken end-over-end for 16 h in 200 cm^3 of distilled water , and the contents transferred to a 500 cm^3 measuring cylinder. After making up to volume, the amount of dispersible clay (<2 μm) was determined by measuring the optical density at 615 nm in 1 cm cells. The optical density at 615 nm was calibrated against the percentage clay, isolated from the soil and determined gravimetrically (Fig.4).

(j) Aggregate stability.

Air -dried soil (20 g) was wet sieved according to the method of Kemper (1965) in 4000 cm^3 distilled water in a cylinder (300 mm by 145 mm diameter) for 10 min. The material which had passed through the sieves was resuspended in the 4000 cm^3 of water by shaking the cylinder gently end-over-end four times, and the size distribution of water-stable particles (the term 'particles' is used for the fraction retained by the sieves which may include some single grain particles in addition to aggregates) was determined by sedimentation under gravity (equivalent spherical diameters < 50 μm, < 2 μm).

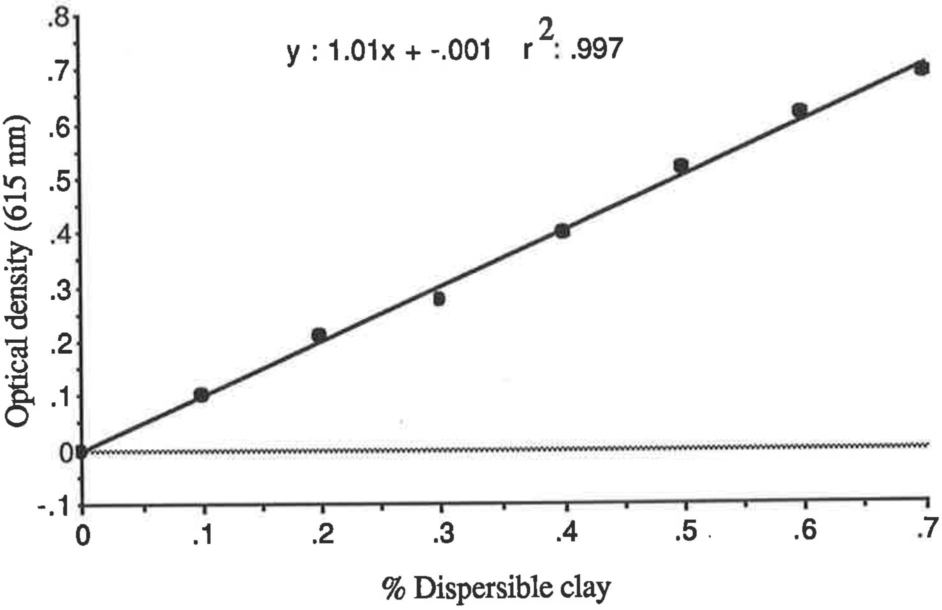


Fig. 4 Calibration of % dispersible clay and optical density

2.2.2.1 X-ray diffraction of soil clays

A suspension of 60 mg of clay in 5 cm^3 of H_2O was applied to a ceramic tile under vacuum. After removal of the free H_2O the following treatments were applied.

(1) Mg^{++} saturated and washed once with glycerol

(2) K^+ saturated and heated to 300°C

(3) heated to 550°C.

X-ray diffraction traces were run to identify the clay minerals present. Semi-quantitative measurement of the proportions of clay minerals present was carried out by the weighted peak area method of Avery and Bullock (1977). Relative to the area of the 10Å illite peak on the Mg^{++}/Glycerol trace:

(1) area of kaolinite 7Å peak on Mg^{++}/ Glycerol trace was divided by 3

(2) area of chlorite 14Å peak on K^+/300°C trace was divided by 2

(3) net area of interstratified mica-smectite band 15-17 Å on Mg^{++}/Glycerol trace was divided by 2.

2.2.2.2 Micromorphology

Undisturbed samples of soil for micromorphological analysis were taken from the sites on which the morphological descriptions were made. A column of soil (approximately 9 cm long x 5 cm wide x 15 cm deep) was carved with a knife from the top layer of the soil profile. The column was then removed from the soil mass and packed in a tin box. The soil was impregnated under vacuum with Escon- Ex 481 (75 % polyester resin and 25 % methyl methacrylate monomer as diluent, supplied by Daystar Chemicals Fyshwick, ACT, Australia). Catalyst used was cumene hydroperoxide, 0.5% by weight. Following polymerisation (approx. 6 weeks) polished thin sections 7 cm x 5 cm approximately 25 μm thick were prepared from the soil blocks.

2.2.2.3 Electron-microprobe analysis of polished thin sections

A Cambridge 'Geoscan' X-ray microanalyser was used to determine the Ca, Mg, Al, and Si on carbonate nodules and on the surrounding matrix for eight soils. The diameter of the probe was 10 μm, beam current 50 x 10^{-9} ampere and counting time was 10 sec. Corrections for mass absorption, fluorescence, and atomic number have been made.

2.2.2.4 Scanning electron microscopy

X-ray dot maps of Ca and Si in the carbonate nodules and the surrounding matrix were taken on SEM (Cambridge, S250 MK3) using an energy dispersive X-ray (EDS) system (Link AN 1000).

2.2.2.5 Chemical pre-treatment of aggregates

Sodium chloride, sodium pyrophosphate , hydrochloric acid

Air-dried soil (< 4mm; 20 g) was immersed for 6 h in 120 cm^3 of either 0.02 M NaCI or 0.1 M $Na_4P_2O_7$ at pH 10.00 (Stefanson 1971) , or for 1 h in 120 cm^3 of 0.1 M HCI or 0.02 M HCI (all solutions contained a crystal of thymol to inhibit biological activity). The soil was then drained for 2 h , and the size distribution of water-stable particles determined.

Hydrogen peroxide

Air-dried soil (<4 mm; 20 g) was moistened with distilled water, then small increments of 30% H_2O_2 were added until the suspension no longer effervesced.

2.3 RESULTS AND DISCUSSION

2.3.1 Distribution of $CaCO_3$ in the soil profile

Micromorphological characteristics of the soil matrix and carbonate nodules are given in appendix (B). Except for the Clarendon soil, carbonate nodules were common in all profiles, and the proportion increased with depth. Four sequences of calcite distribution were observed. These are:

Type 1. A uniform distribution of calcite throughout the profile which was indicated by a uniform response to HCl with depth. Samples contained hard and soft yellowish to brown accretions and concretions varying from 2 to 5 mm in diameter.

Type 2. The soil surface horizon has not been fully leached, and there was no accumulation of $CaCO_3$ in any particular horizon. Although the soils effervesced with hydrochloric acid from the surface downward, the strength of effervescence increased with depth. The carbonate nodules were 2 to 10 mm in diameter below the 20 cm depth mark.

Type 3. Moderate to high $CaCO_3$ concentration in the surface horizons, but the concentration of $CaCO_3$ increased with depth and 40 to 50 cm below the surface horizon a hard layer of carbonate was observed.

Type 4. The surface horizon was completely leached of excess carbonate. No effervescence with hydrochloric acid was observed. $CaCO_3$ accumulation increased with depth progressing to a thick, soft layer of almost pure $CaCO_3$. On the basis of above classification the eight soils fall into the following groups:

Type 1.	Dublin, Grace (ii)
Type 2.	Grace (i) , Grace (iii)
Type 3.	Trott Park, Claremont, and Strathalbyn
Type 4.	Clarendon

The uniform distribution of calcium carbonate throughout the soil profile in the Dublin, Grace (i), Grace (ii) and Grace (iii) profiles is attributed to long dry summers and low winter rainfall. Under such conditions the excess carbonate would not be leached down the profile.

Carbonate present in 0 to 10 cm depth at Trott Park generally occurred as fine grained particles distributed uniformly in the soil matrix. No excess carbonate occurred in the upper horizons at the Clarendon site. Leaching of excess calcium, or the presence of calcium as fine grained particles in the profile is probably the result of high rainfall (500-800 mm pa Trott Park and 550-1100 mm pa Clarendon). The presence of considerable quantities of organic carbon (3.9 % in Trott Park and 3.3 % in Clarendon) may also increase the carbonate dissolution process due to the production of soluble acids during the organic matter decomposition. Moisture retention capability is increased when organic matter is present, often preventing the soil from completely drying out during summer.

Calcic horizons, which are formed at or just below the depth of seasonal wetting, are enriched by calcium carbonate as the calcium saturated solution is slowly percolated downward to layers of higher moisture content. The moisture begins to evaporate during the summer, the solution becomes concentrated and calcium is precipitated as microcalcite, and gradually becomes more consolidated by repeated wetting and drying cycles.

The soils under examination receive varying rainfall (e.g. annual rainfall range of 400-450 mm at Dublin to 550-1100 mm at Clarendon). It seems that degree of carbonate leaching from these soils with attendant accumulation in a definite horizon appears to be largely affected by rainfall.

Although the depth of the $CaCO_3$ horizon is strongly dependent on soil water flow, and increases with increasing mean annual precipitation (Arkley, 1963; Jenny, 1980; Marion et al., 1985; Mann and Horwitz, 1979; Hutton and Dixon, 1981) other factors that can also influence the distribution of $CaCO_3$ and the formation of calcic horizons in the profile include porosity, parent material, topography and biota .

2.3.2 Electron microprobe studies of carbonate nodules and the soil matrix

Quantitative data for Ca, Mg, Al, and Si were obtained by electron microprobe analysis on different parts of the nodule, and within the matrix itself (Table 7).The nodule types investigated were disorthic. According to Wieder and Yaalon (1974), disorthic nodules are those which have sharp boundaries and are subjected to some pedoturbation, but have a fabric resembling the surrounding matrix. Except for the Trott Park and Claremont samples, the increase of Ca in the nodule was generally inversely proportional to the amount of Al and Si present. By assigning Ca to calcite and Al and Si to the clay minerals (illite and kaolinite), interrelationships of carbonates and non-carbonates could easily be followed.

In Strathalbyn, Grace (i), Grace (ii), Grace (iii), and Dublin the concentration of calcite was higher in the centre of the nodules. The amount of Al-silicate clay increased towards the fringes and in the matrix (Fig. 5). The results are consistent with those of Wieder and Yaalon (1974) and Suprychev (1963). Wieder and Yaalon found that during carbonate nodule formation, the concentration of calcite was higher in the centre of the nodule, and non-carbonate clay was expelled to the fringe and into the matrix. Suprychev's chemical analysis of calcareous concentrations in a loess-like clay loam soil showed an increase of

Table 7. Microprobe determination of Al, Mg, Ca, and Si content in carbonate nodules and soil matrix.

Soils	Nodule types		Al(%)	Mg(%)	Ca(%)	Si(%)
Clarendon		—	—	—	—	—
Claremont	Disorthic	Nodule	18.6	0.2	10.7	66.0
		Soil	18.4	1.6	15.2	50.1
Dublin	Disorthic	Nodule	1.7	3.7	47.5	4.6
		Soil	7.0	1.2	25.0	14.2
Grace (i)	Disorthic	Nodule	4.5	9.8	34.2	11.0
		Soil	5.2	1.4	6.3	11.4
Grace (ii)	Disorthic	Nodule	2.3	3.3	45.3	4.5
		Soil	8.3	1.4	27.5	16.3
Grace (iii)	Disorthic	Nodule	4.2	1.4	48.8	4.3
		Soil	10.9	1.8	13.6	26.0
Strathalbyn	Disorthic	Nodule	0.2	0.1	42.6	0.5
		Soil	12.5	0.0	0.1	12.4
Trott Park	Disorthic	Nodule	5.5	2.0	40.4	10.0
		Soil	1.6	0.2	40.8	3.1

(—) Carbonate nodule was absent in the 0-10 cm depth of the Clarendon soil

Fig.5 X-ray images showing distribution of calcium and silicate in a carbonate nodule and the matrix (Strathalbyn soil).

A (Nodule)

B (Calcium)

C (Silicate)

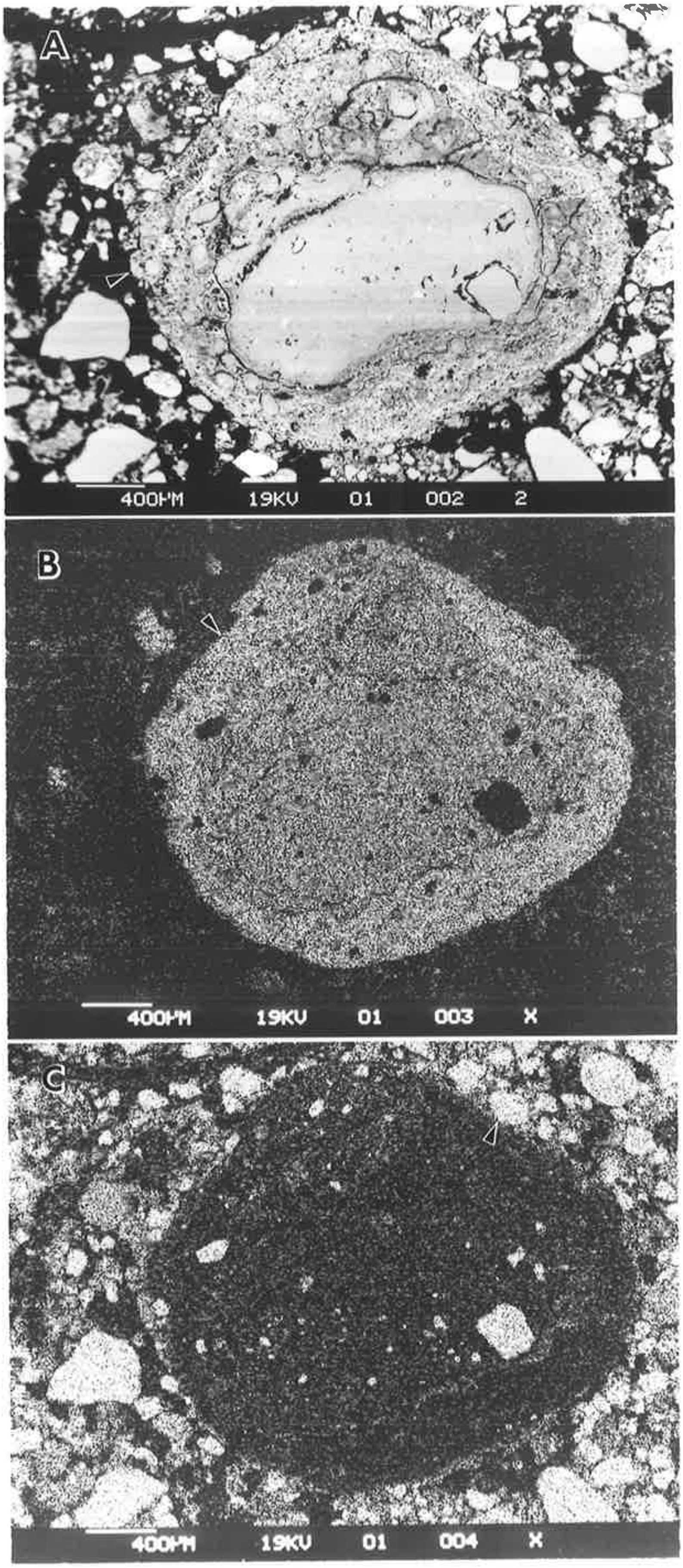
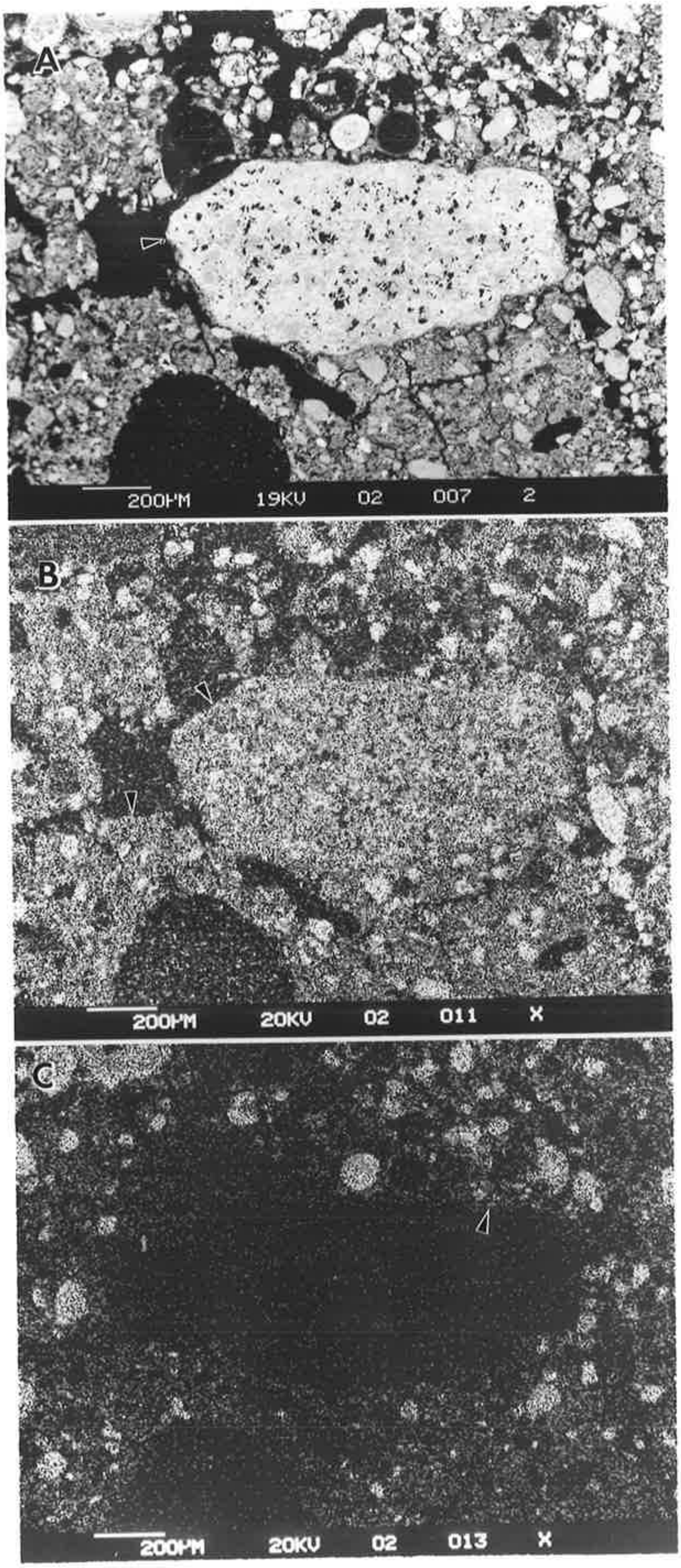

A
400HM 19KV 01 002 2
B
400HM 19KV 01 003 X
C
400HM 19KV 01 004 X

Fig.6 X-ray images showing distribution of calcium and silicate in a carbonate nodule and the matrix (Trott Park soil).

A (Nodule)

B (Calcium)

C (Silicate)


A
200µM 19KV 02 007 2
B
200µM 20KV 02 011 X
C
200µM 20KV 02 013 X

carbonate at the centre and an increase of Al_2O_3 and MgO at the periphery.

At Trott Park, calcium carbonate was present as very fine grains evenly distributed throughout the soil matrix. The microprobe data showed an almost equal distribution of Ca in the nodule and in the soil matrix (Fig. 6).

2.3.3 X-ray diffraction study of carbonate nodules

X-ray diffraction studies showed high concentrations of calcite in the centre of the carbonate nodules and an increase of Al-silicate in the periphery. The result confirms the general trends identified in the electron microprobe study. Several workers have suggested that a high concentration of calcium in the centre of the nodule is related to the increase in density brought about by repeated wetting and drying cycles in the surface horizons of the soil profile (Blokhuis et al., 1969; Wieder and Yaalon, 1974).

2.3.4 PHYSICAL PROPERTIES OF SOIL

2.3.4.1 Dispersible clay

Dispersible clay was measured after shaking the soil water suspension for increments of time from 0 to 168 h. After 168 h of shaking duplicate samples were dialysed against distilled water and dispersible clay was measured.

No simple correlation existed between the dispersible clay and $CaCO_3$ content of the soils under investigation. Dispersible clay increased with the time of shaking, and maximum dispersion occurred after 16 hours in Strathalbyn and Grace (i), and after 48 hours in Trott Park, Claremont, Dublin, Grace (ii), and Grace (iii). The amount of dispersible clay then decreased with continued shaking. In the Clarendon soil maximum clay dispersion occurred after 16 hours, and remained constant with continued shaking (Fig. 7).

The initial increase in dispersible clay may be the result of mechanical disturbance enhancing the dispersion process, and the low electrolyte concentration in the soil suspension. An increase in electrical conductivity and Ca^{2+} in the suspension occurred as the time of shaking increased. This resulted in a reduction of the dispersible clay (Table. 8, 9).

Dialysis of the suspension after 168 hours of shaking caused a decrease in the concentration of Ca^{2+} in the solution, and was accompanied by an increase in dispersible clay,

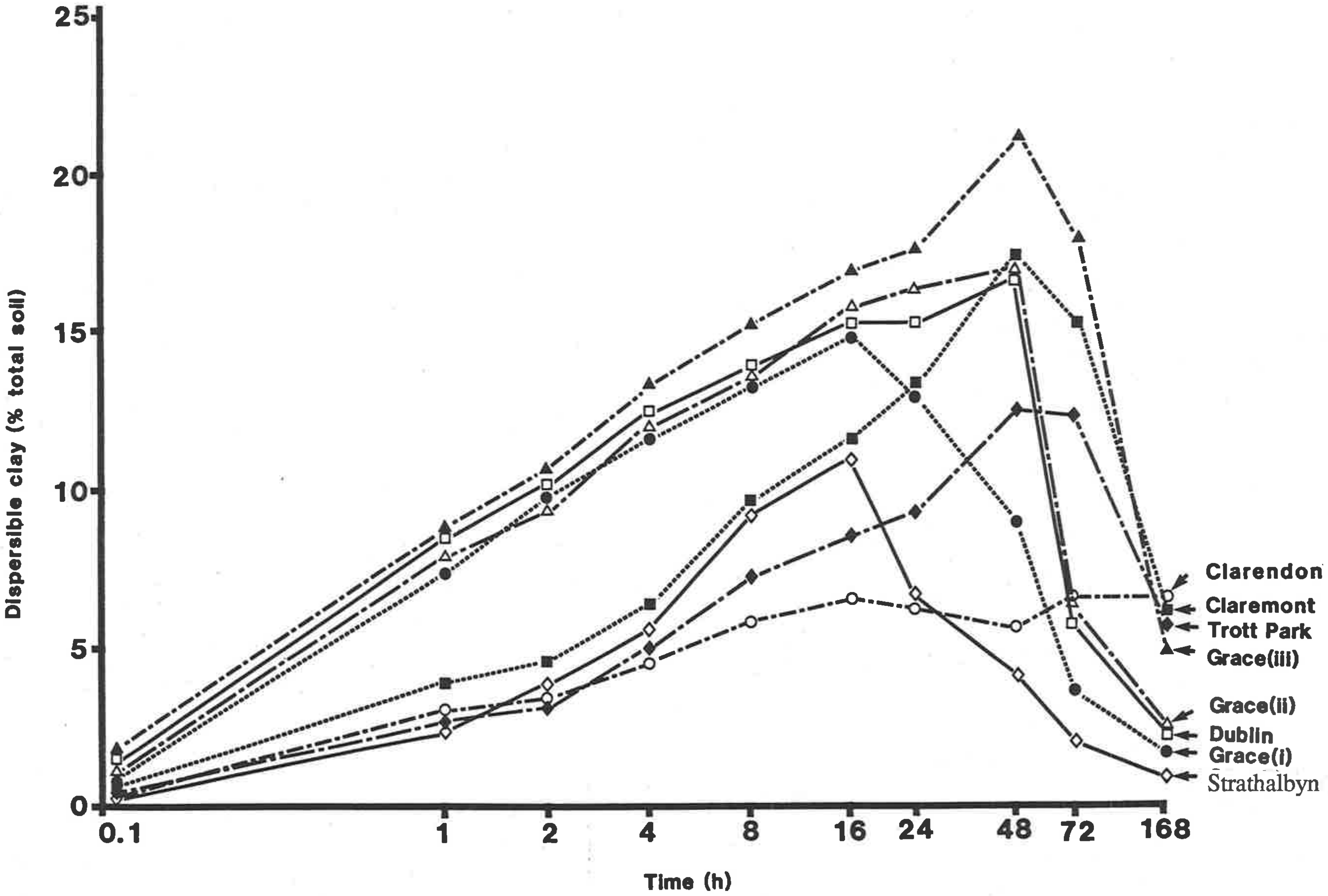


Fig.7 Dispersible clay after different times of shaking

Table 8. Electrical conductivity ($\mu S\ cm^{-1}$) of soil at different times of shaking
(1: 20 soil/water suspension)

	Time of shaking (hour)									
Soils	0	1	2	4	8	16	24	48	72	168
Clarendon	30	50	52	64	81	88	110	123	136	150
Claremont	32	77	82	90	106	110	118	121	153	166
Dublin	65	76	78	80	86	95	100	100	126	153
Grace (i)	78	84	85	90	103	111	115	126	133	156
Grace (ii)	71	85	86	91	105	113	118	122	146	193
Grace (iii)	71	82	85	88	98	108	105	109	120	146
Strathalbyn	44	67	75	80	96	100	118	121	146	185
Trott Park	53	80	80	85	93	96	106	110	127	153

Table 9. Water soluble calcium ($\mathrm{me\,l^{-1}}$) in soil at different times of shaking
(1:20 soil/water suspension)

	Time of shaking (hour)									
Soils	0	1	2	4	8	16	24	48	72	168
Clarendon	0.012	0.054	0.053	0.051	0.066	0.102	0.291	0.534	0.593	0.674
Claremont	0.018	0.034	0.035	0.035	0.035	0.045	0.069	0.130	0.262	0.740
Dublin	0.139	0.196	0.208	0.215	0.303	0.326	0.414	0.497	0.634	0.953
Grace (i)	0.139	0.172	0.180	0.169	0.297	0.319	0.413	0.554	0.681	1.100
Grace (ii)	0.074	0.109	0.117	0.113	0.121	0.142	0.195	0.309	0.450	0.854
Grace (iii)	0.123	0.156	0.136	0.146	0.156	0.172	0.225	0.275	0.377	0.874
Strathalbyn	0.034	0.073	0.070	0.070	0.108	0.243	0.386	0.663	0.837	1.230
Trott Park	0.069	0.074	0.069	0.064	0.065	0.065	0.089	0.125	0.167	0.548

suggesting a dominant role for Ca^{2+} on clay dispersion (Table 10). Quirk (1978) also suggested that after addition of lime, the electrolyte concentration of a stable suspension is increased and the particles coalesce to form loose floccs. This process of flocculation is usually reversed by lowering the electrolyte concentration. During dialysis of the Clarendon soil suspension, the electrical conductivity and the concentration of Ca^{2+} increased gradually, reducing the dispersible clay. The reduction in dispersible clay could be associated with the release of electrolytes in amounts greater than the critical coagulation concentration. The influence of free electrolytes generated in the soils on the dispersion of soil clays has been recognized by Rowell and Shainberg (1979), Shainberg et al. (1981a), Rengasamy (1982).

For all eight soils the dispersible clay after dialysis was lower than the total clay obtained by mechanical analysis. This is in accord with the findings of Rengasamy (1982), that water stable micro-aggregates were present in these soils, and only the unbound clay particles dispersed after dialysis.

When $CaCO_3$ exists in nodule form or as coarse particles, its effectiveness in aggregate stabilization by cementation or the flocculation of clay particles through an electrolyte effect is reduced. The low solubility of $CaCO_3$ in soil may also result from the interaction between the surface of the calcium carbonate and dissolved compounds, presumably silicates, producing a surface coating of calcium silicate (Lahav and Bolt, 1963). However if the suspension is shaken abrasion of particles occurs, Ca^{2+} concentration in the suspension increases due to $CaCO_3$ dissolution, and flocculation of clay results.

The surface area of soil carbonates varies enormously, consequently Ca released into soil solution does not correspond to the amount of $CaCO_3$ present in the soil (Abedi and Talibudeen, 1974). Hollford and Mattingly (1975) suggested that the surface area of $CaCO_3$ is an inverse function of the $CaCO_3$ percentage.Variations in particle size, and hence surface area of $CaCO_3$ complicate predictions of clay dispersion made simply on the basis of $CaCO_3$ contents.

Tabl 10. Dispersible clay, electrical conductivity and water soluble calcium of the soil after dialysis of the 1:20 soil/water suspension.

Soils	Dispersible clay (% of total soil)	Electrical conductivity (µS cm^{-1})	Water soluble calcium (me l^{-1})
Clarendon	5.0	190	1.06
Claremont	19.3	30	0.02
Dublin	17.9	65	0.31
Grace (i)	16.7	70	0.15
Grace (ii)	18.6	80	0.16
Grace (iii)	17.6	65	0.17
Strathalbyn	17.0	70	0.07
Trott Park	7.6	85	0.15

2.3.4.2 Consistency limits

The soils high in organic matter also had high liquid and plastic limits (Table 11). According to the position of the soils with respect to the A-line on the Casagrande plasticity chart ,Trott Park and Clarendon were of medium plasticity, and Strathalbyn, Dublin, Claremont, Grace (i), Grace (ii), Grace (iii) belonged to the low plasticity group (Fig. 8).

Medium plasticity in Trott Park and Clarendon resulted from the high organic matter contents. The relationships between plasticity index and organic matter, and/ or total nitrogen were highly significant (Table 12). The results support the findings of Baver (1930), that soil organic matter is responsible for higher upper and lower plastic limits, and suggested that the presence of organic matter with a relatively high water absorption capacity was responsible for the high plasticity limit. Baver (1930) also suggested that low plasticity was associated with low organic matter and the presence of $CaCO_3$ as coarse particles. Stakman and Bishay (1976) observed that not only the total amount, but the distribution of $CaCO_3$ over the particle fractions could influence the plasticity limits in calcareous soils.

2.3.4.3 Dispersion index

On the basis of the Emerson (1967) dispersion test, the soils had following dispersion indices:

Soils	Dispersion index
Trott Park, Clarendon, Grace (i) and Strathalbyn	1
Grace (ii), Grace (iii), Dublin	2
Claremont	3

2.3.4.4 Hydraulic conductivity and bulk density

Trott Park and Clarendon had the highest hydraulic conductivity and lowest bulk density (Table 13).

2.3.4.5 Available water

Plant available water was calculated as the difference between water contents at -10 KPa and -1500 KPa. Strathalbyn had the lowest (4%) and Clarendon soil had the highest (10%) available water (Table 14).

Table 11. Plastic limit and Liquid limit of the soil

Soils	Plastic limit (%W/W)	Liquid limit (%W/W)
Clarendon	27.8±0.4	36.0±0.0
Claremont	21.0±0.5	26.2±0.0
Dublin	16.9±0.0	21.5±0.0
Grace (i)	20.6±0.3	28.2±0.0
Grace (ii)	20.1±1.1	26.8±0.0
Grace (iii)	20.6±0.0	25.5±0.0
Strathalbyn	17.4±0.0	24.5±0.5
Trott Park	29.0±0.0	34.5±0.4
LSD (P<0.05)	1.86	0.71
(P<0.01)	2.71	1.04
(P<0.001)	4.08	1.57

Table 12. Relationship between plasticity index and Organic carbon, $CaCO_3$, Nitrogen, and clay content of the soil.

Soils	Liquid limit (%W/W)	Plastic limit (%W/W)	Organic carbon (%)	$CaCO_3$ (%)	Total nitrogen (%)	Total clay (%)
Clarendon	36.0	27.8	3.3	0.5	0.28	34.6
Claremont	26.2	21.0	2.2	11.0	0.21	28.8
Dublin	21.5	16.9	1.4	19.5	0.10	22.2
Grace (i)	28.2	20.6	2.4	23.0	0.22	20.0
Grace (ii)	26.8	20.1	2.1	14.5	0.19	24.4
Grace (iii)	25.5	20.6	2.7	11.0	0.24	23.8
Strathalbyn	24.5	17.4	1.7	14.0	0.17	24.7
Trott Park	34.5	29.0	3.9	37.0	0.44	18.5
Correlation coeff-cient			0.908	-0.017	0.839	-0.153
Significance			**	ns	**	ns

**=Significant at 0.1% level, n.s.=not significant

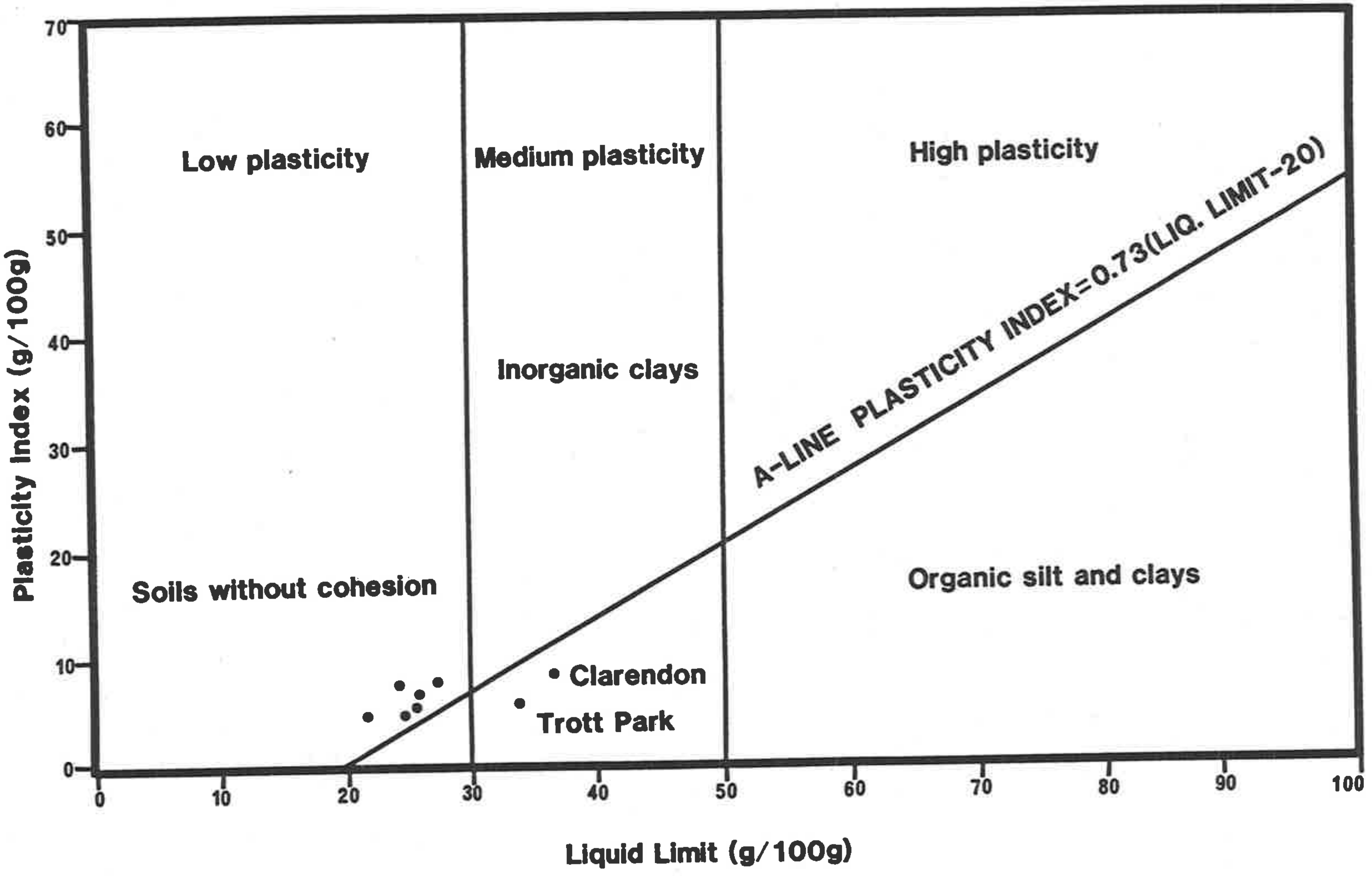


Fig. 8 Plasticity chart (Casagrande, 1948)

Table 13. Soil hydraulic conductivity and bulk density

Soils	Hydraulic conductivity (cm h^{-1})	Bulk density (g cm^{-3})
Clarendon	64.2± 2	0.93±0
Claremont	46.3± 6	1.25±2
Dublin	34.9±13	1.30±1
Grace (i)	48.8± 8	1.07±0
Grace (ii)	31.4±10	1.26±0
Grace (iii)	29.2± 5	0.97±1
Strathalbyn	10.3± 5	1.20±2
Trott Park	66.3± 0	0.83±1
LSD (P<0.05)	10.0	0.12
(P<0.01)	13.4	0.17

Table 14. Water retention (% W/W) at different water potentials (KPa)

Soils	-10	-33	-500	-1000	-1500	Available water (%)
Clarendon	26.3	19.8	17.3	17.0	16.2	10.1
Claremont	30.3	25.6	23.2	22.8	22.5	7.8
Dublin	20.8	17.1	16.4	16.0	15.5	5.3
Grace (i)	22.6	20.1	19.9	18.6	17.5	5.1
Grace (ii)	23.5	20.4	18.4	18.0	17.6	5.9
Grace (iii)	24.2	21.2	19.8	19.5	18.9	5.3
Strathalbyn	19.3	19.0	16.9	15.1	14.9	4.4
Trott Park	30.3	24.1	22.5	22.0	21.6	8.7
LSD (P<0.05)						1.4
(P<0.01)						2.0

2.3.4.6 Soil friability

Utomo and Dexter (1981) proposed the following arbitrary classification for the magnitude of K (soil friability).

$K < 0.05$	not friable
$K = 0.05\text{-}0.10$	slightly friable
$K = 0.10\text{-}0.25$	friable
$K = 0.25\text{-}0.40$	very friable
$K > 0.40$	mechanically unstable

On the basis of this classification all eight soils had the following magnitude of K:

Clarendon	K= 0.19	friable
Claremont	K= 0.04	not friable
Dublin	K= 0.14	friable
Grace (i)	K= 0.21	friable
Grace (ii)	K= 0.19	friable
Grace (iii)	K= 0.11	friable
Strathalbyn	K= 0.15	friable
Trott Park	K= 0.28	very friable

From the results it can be seen that soil density, plastic limit, hydraulic conductivity and water holding capacity are primarily dependent on the organic matter content of the soil. As the organic matter increased soil density decreased, plastic limit, hydraulic conductivity and water holding capacity increased. Among the soil constituents which are known to influence soil physical conditions, the role of organic matter has been much emphasised (Low, 1955; Russell, 1971). Organic matter was found to influence soil compactibility (Soane et al., 1972), bulk density and porosity (Davies, 1975), plastic limits (Baver, 1930; Boekel, 1965) and aggregation (Greacen, 1958).

2.3.4.7 Aggregate stability

Soils high in organic matter content had more water stable macroaggregates (>250 µm in diameter) than soils low in organic matter. An increase in particles 50-250 µm diameter was observed in soils of low organic matter content (Fig. 9).

Soil organic matter increased the stability of soil aggregates, presumably due to an enhanced growth of actinomycete and fungal mycelium, and to the production of microbial metabolites (Fig. 10). It was suggested that the stability of aggregates (particularly the stability of macro-aggregates) in many soils is dependent on the presence of organic matter (Clement, 1975; Eagle, 1975; Hamblin and Davies, 1977; Douglas and Goss, 1982; Chaney and Swift, 1984).

Calcium carbonate was responsible for stabilizing aggregates 50-250 µm in diameter. The results confirm the findings of Shanmuganathan (1983), that the addition of compounds capable of releasing Ca^{2+} into the soil solution coagulates clay into particles 50-250 µm diameter.

2.3.4.8 Relation between aggregate stability, organic matter and $CaCO_3$ content of the soil

There was a correlation between the percentage of water-stable aggregates (1000-2000 µm in diameter) and total carbon of the soil (r^2=0.73, Fig. 11). The correlation between total nitrogen and the percentage of soil aggregates (1000-2000 µm in diameter) was less (r^2=0.50). Correlation between $CaCO_3$ and the percentage of aggregates (1000-2000 µm in diameter) also was less (r^2=0.50).

In all soils the C:N ratios were narrow. The C:N ratios were lowest in Trott Park soil (9) and highest in Dublin soil (14). The results indicate that aggregate stability is primarily dependent on the total organic matter content of the soil.

These results suggest that calcium carbonate is involved in stabilizing aggregates <250 µm diameter, but does not appear to stabilize aggregates >250 µm diameter, unless sufficient organic matter is present in the soil. Positive correlations between aggregate stability and organic matter content have been reported by several authors (Rost and Rowles, 1941; Kemper and Koch, 1966; Clement, 1975; Tisdall and Oades, 1982; Chaney and Swift, 1984).

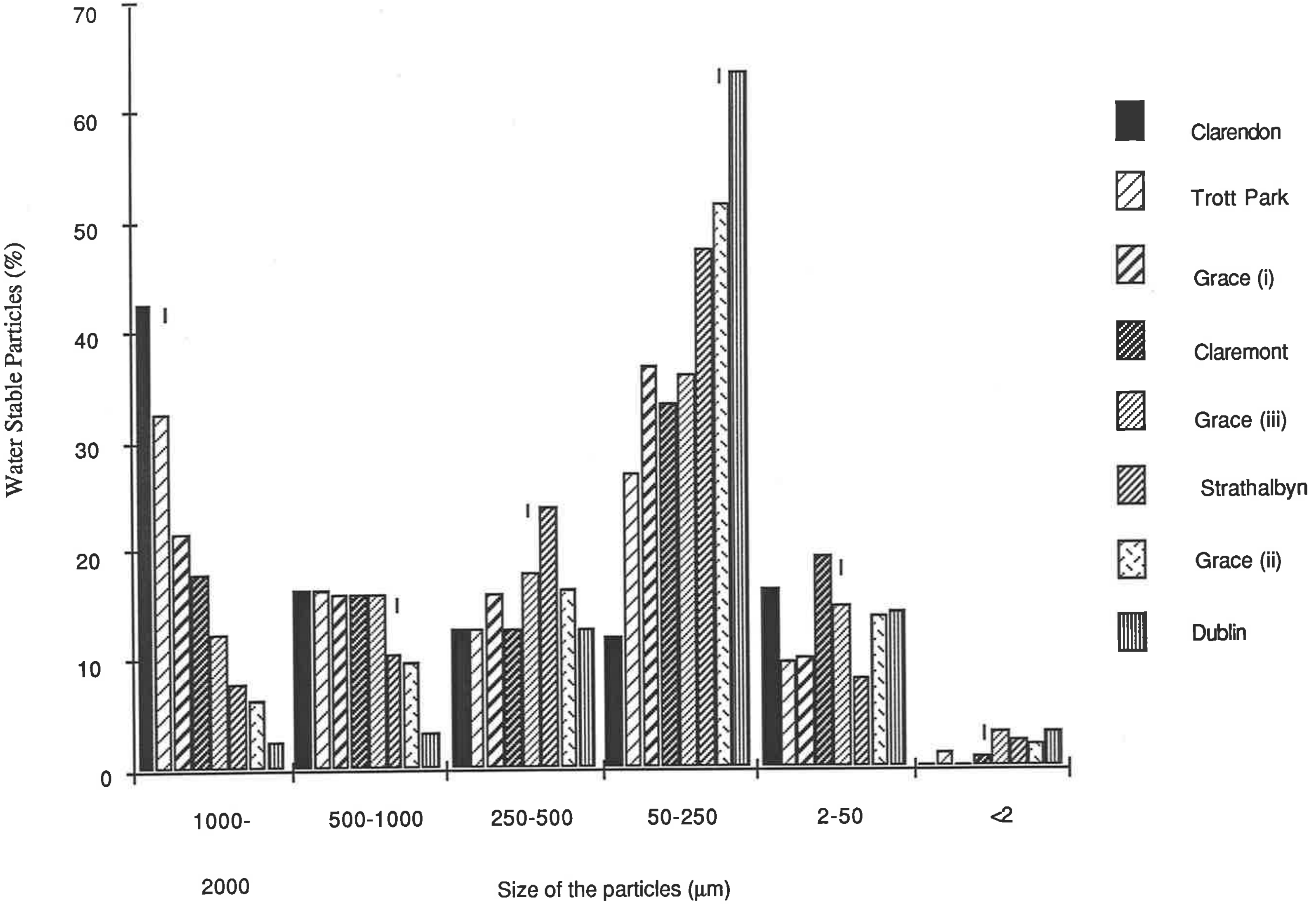
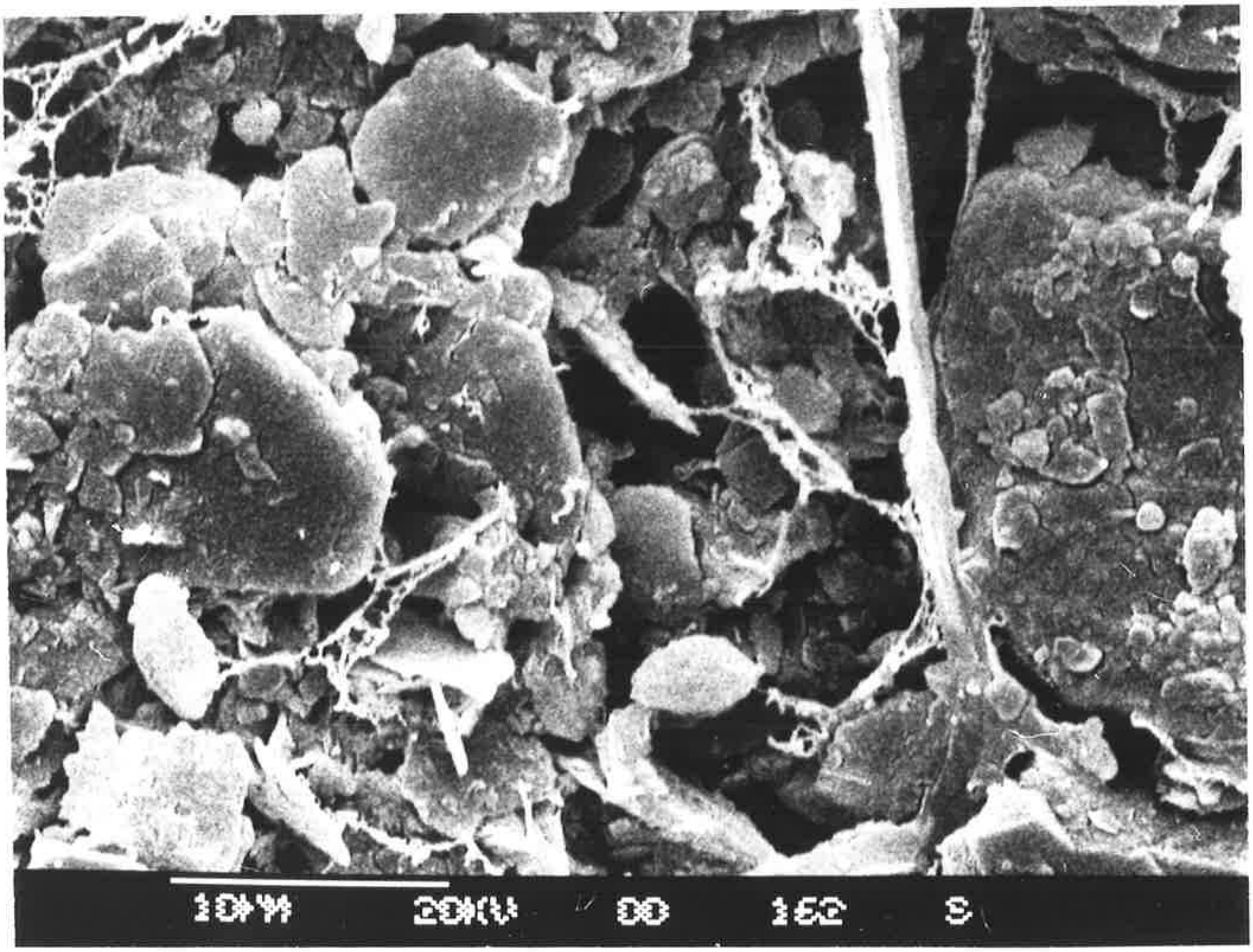


Fig. 9 The size distribution of water stable particles in eight calcareous soils. Vertical bar, $P<0.05$.

Fig. 10 Scanning electron micrographs of fungal hyphae binding soil particles into water stable aggregates (Clarendon soil).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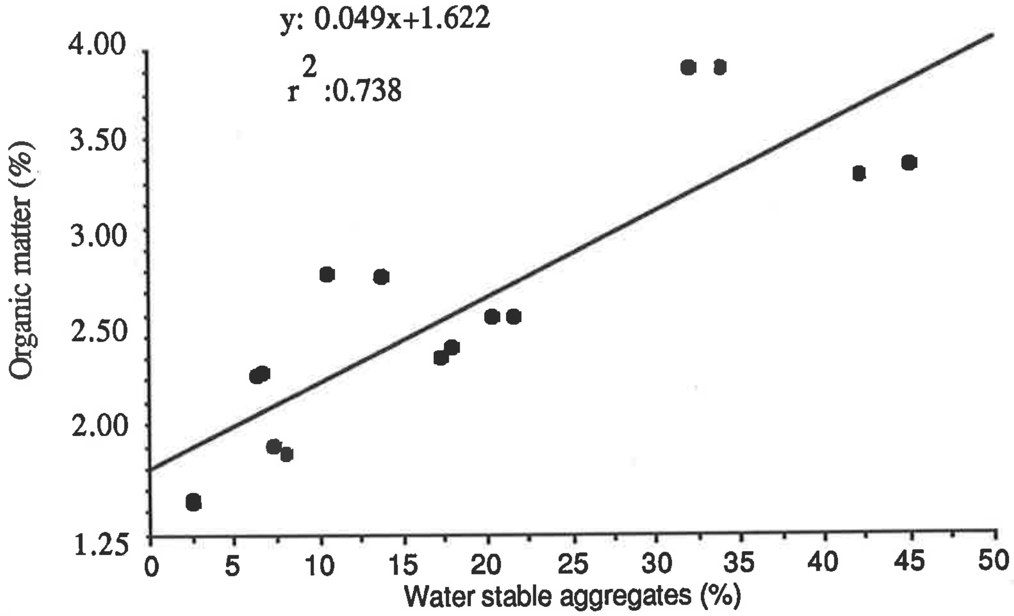

Fig. 11 Relationship between organic matter and % water stable particles (1-2 mm diameter)

2.3.5 Particle size distribution after removal of $CaCO_3$ and organic matter from the soil

Particle size distributions for the eight soils before and after removal of organic matter and $CaCO_3$ are presented in Table 15. Removal of either $CaCO_3$ or organic matter increased the silt and clay content, and decreased the sand fraction in all soils. Combined removal of organic matter and $CaCO_3$ further decreased the sand fraction and correspondingly increased the silt and clay fraction in the Strathalbyn, Clarendon, Claremont, Dublin , Grace (ii), and Grace (iii) soils. No change occurred in the clay fraction after combined removal of organic matter and $CaCO_3$ in the Trott Park and Grace (i) soils, but there was a decrease in the sand fraction accompanied by a subsequent increase in the silt fraction.

Removal of organic matter resulted in an increase in the clay which was previously part of the coarse fraction (>50 µm). This confirms the findings of Arshad et al. (1980), who observed an increase in clay size particles after removal of organic matter.

Combined removal of $CaCO_3$ and organic matter resulting in further increase of silt and clay indicates that there was an interaction between clay, $CaCO_3$ and organic matter. Involvement of complexes of Clay—Metal—Organic matter in aggregation was indicated by Edwards and Bremner (1967), Hamblin (1977), Turchenek and Oades (1978). It was suggested that organo-mineral associations act as binding agents in aggregation, especially those less than 250 µm in diameter.

2.3.6 Determination of water-stable aggregates after chemical pretreatment of soil

Water-stable aggregates were determined on Trott Park and Clarendon soils after chemical treatment of soil aggregates >4 mm in diameter. These two soils were selected for further investigation on the basis of their higher aggregate stability.

Particle size distribution of soil aggregates in the Clarendon and Trott Park after NaCl, $Na_4P_2O_7$, HCl and H_2O_2 treatments are given in Fig. 12 and 13.

Sodium pyrophosphate: $Na_4P_2O_7$ reduced the percentage of water-stable particles >2000 µm in diameter in both Clarendon (from 85% to 79%) and Trott Park (from 56% to 43%) soils with an accompanied increase in clay size particles.

Tabel 15. Particle size distribution of soil before and after removal of $CaCO_3$ and organic matter.

Soils	Treatment	Sand(%) (250-2000 μm)	Fine sand(%) (50-250 μm)	Silt(%) (2-50 μm)	Clay(%) (<2 μm)
Clarendon	Control	30.15	44.25	13.85	11.75
	$CaCO_3$ removal	16.85	51.30	17.35	14.50
	Organic matter removal	5.15	35.00	30.10	29.75
	Org. matter and $CaCO_3$ removal	4.50	29.41	31.73	34.36
Claremont	Control	15.20	53.55	17.65	13.60
	$CaCO_3$ removal	14.85	49.30	22.00	13.85
	Organic matter removal	13.75	36.40	26.75	23.10
	Org. matter and $CaCO_3$ removal	6.22	9.18	55.75	28.85
Dublin	Control	12.90	62.25	12.50	12.35
	$CaCO_3$ removal	8.95	54.95	20.00	16.10
	Organic matter removal	10.60	48.15	19.75	21.50
	Org. matter and $CaCO_3$ removal	8.92	37.28	31.60	22.20
Grace (i)	Control	17.20	62.05	8.90	11.85
	$CaCO_3$ removal	5.00	59.50	20.40	15.10
	Organic matter removal	8.75	47.75	23.25	20.25
	Org. matter and $CaCO_3$ removal	3.36	48.64	29.05	19.95
Grace (ii)	Control	13.15	61.10	13.15	12.60
	$CaCO_3$ removal	7.00	48.00	28.00	17.00
	Organic matter removal	8.85	41.30	27.60	22.25
	Org. matter and $CaCO_3$ removal	6.06	28.69	40.80	24.45
Grace (iii)	Control	9.90	70.00	8.10	12.00
	$CaCO_3$ removal	7.95	49.80	28.75	13.50
	Organic matter removal	9.50	41.75	25.15	23.60
	Org. matter and $CaCO_3$ removal	6.68	32.32	37.20	23.80
Strathalbyn	Control	21.90	58.50	7.35	12.25
	$CaCO_3$ removal	18.45	53.20	14.75	13.60
	Organic matter removal	18.95	43.60	16.35	21.10
	Org. matter and $CaCO_3$ removal	17.94	26.76	30.60	24.70
Trott Park	Control	18.80	66.85	9.75	12.60
	$CaCO_3$ removal	4.45	64.05	16.65	14.85
	Organic matter removal	4.20	46.70	29.10	20.00
	Org.matter and $CaCO_3$ removal	1.38	39.42	40.70	18.50

The control soils did not have any chemical pre-treatment.

Hydrochloric acid: 0.02 M HCl reduced the percentage of water-stable particles >2000 μm in diameter in both soils. The effect was similar to the pyrophosphate treatment.

Treatment of soil aggregates with 0.1 M HCl reduced water-stable particles > 2000 μm diameter from 85 % to 62 % in Clarendon soil, and from 56% to 20% in Trott Park soil. The effect was greater than either pyrophosphate or 0.02M HCl treatment. Because of the high $CaCO_3$ content, soil from Trott Park was more sensitive to 0.1M HCl treatment than soil from Clarendon.

Hydrogen peroxide: A massive reduction of soil aggregates (>2000 μm diameter) occurred due to H_2O_2 treatment in both Trott Park and Clarendon soils, with an accompanied increase of particles <250 μm in diameter.

Soil aggregates were more vulnerable to 0.1M HCl treatment than either 0.02M HCl or 0.1M $Na_4P_2O_7$ treatment, indicating that the aggregates had some cementing materials which were resistant to both dilute acid and pyrophosphate.

Pyrophosphate has been used to remove polyvalent cations linking the soil minerals and organic polymers (Clapp and Emerson, 1965; Stefanson, 1971). Bruckert (1982) suggested that pyrophosphate dissolves calcium humates by complexing the calcium, and destroying micro-aggregates by displacing the clay and colloidal cements. Due to the large range of organic molecules capable of forming cationic bridges, the exact nature of the organic compounds removed by pyrophosphate is not understood. The cation bridges are supposedly destroyed by $Na_4P_2O_7$, although this has not been demonstrated conclusively.

A decrease in the percentage of aggregates (>2000 μm diameter) with 0.1M HCl treatment presumably resulted from the removal of Ca^{2+} from the coordination complexes of clay and organic matter. Although treatment of soil aggregates with 0.1M HCl caused a substantial decrease in aggregates with an accompanied increase in particles <250 μm diameter, 0.1M HCl was not able to break down the stability of aggregates completely. Possibly inadequate quantities of the acid were added, or insufficient time was allowed for effective reaction with all the potential sites in the soil. According to Mehta et al. (1960), aggregates containing $CaCO_3$ remained stable even after 8h treatment with 6N HCl.

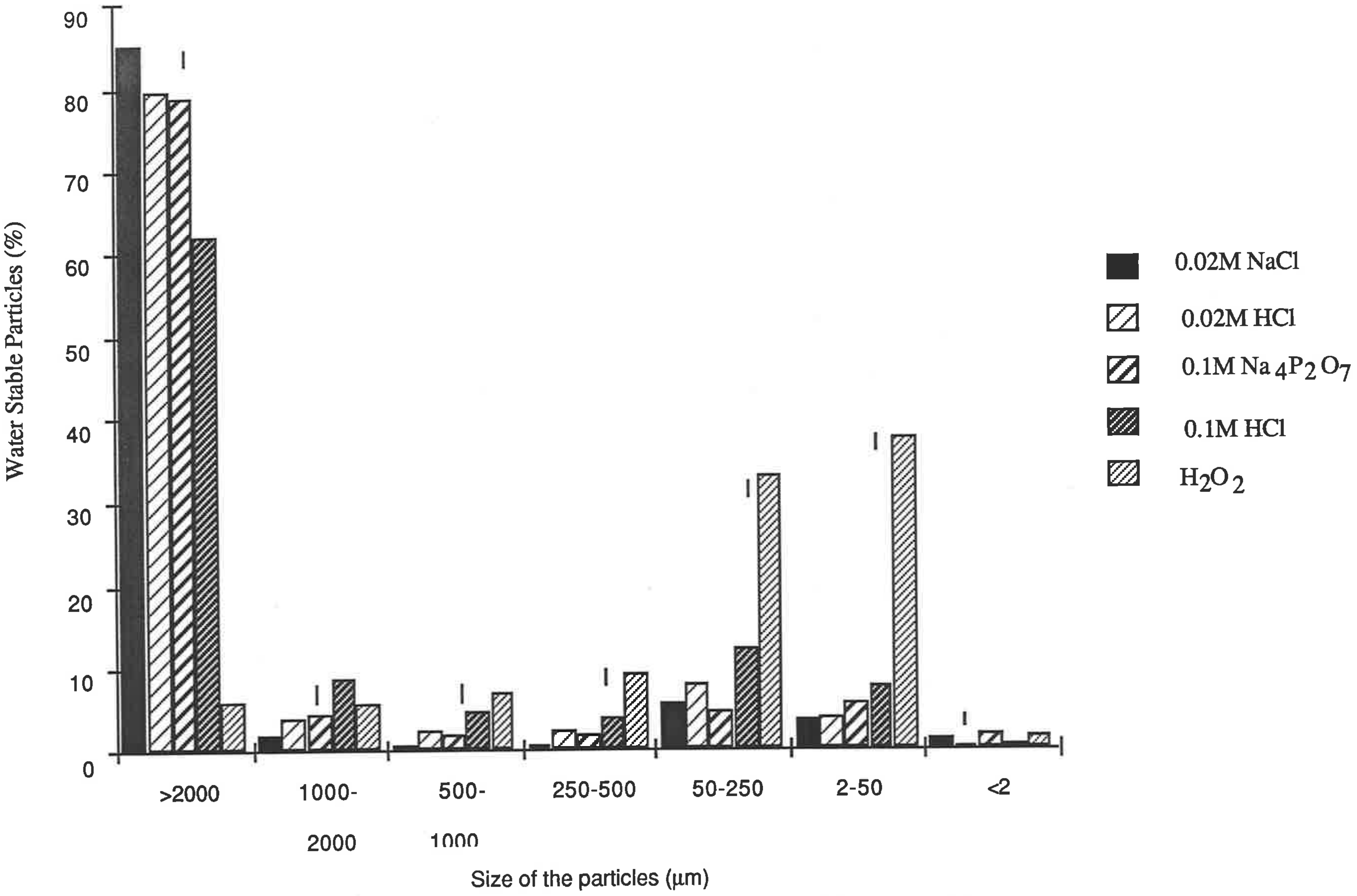

Fig. 12 The size distribution of water stable particles after chemical treatment (Clarendon soil)
Vertical bar, $P<0.05$.

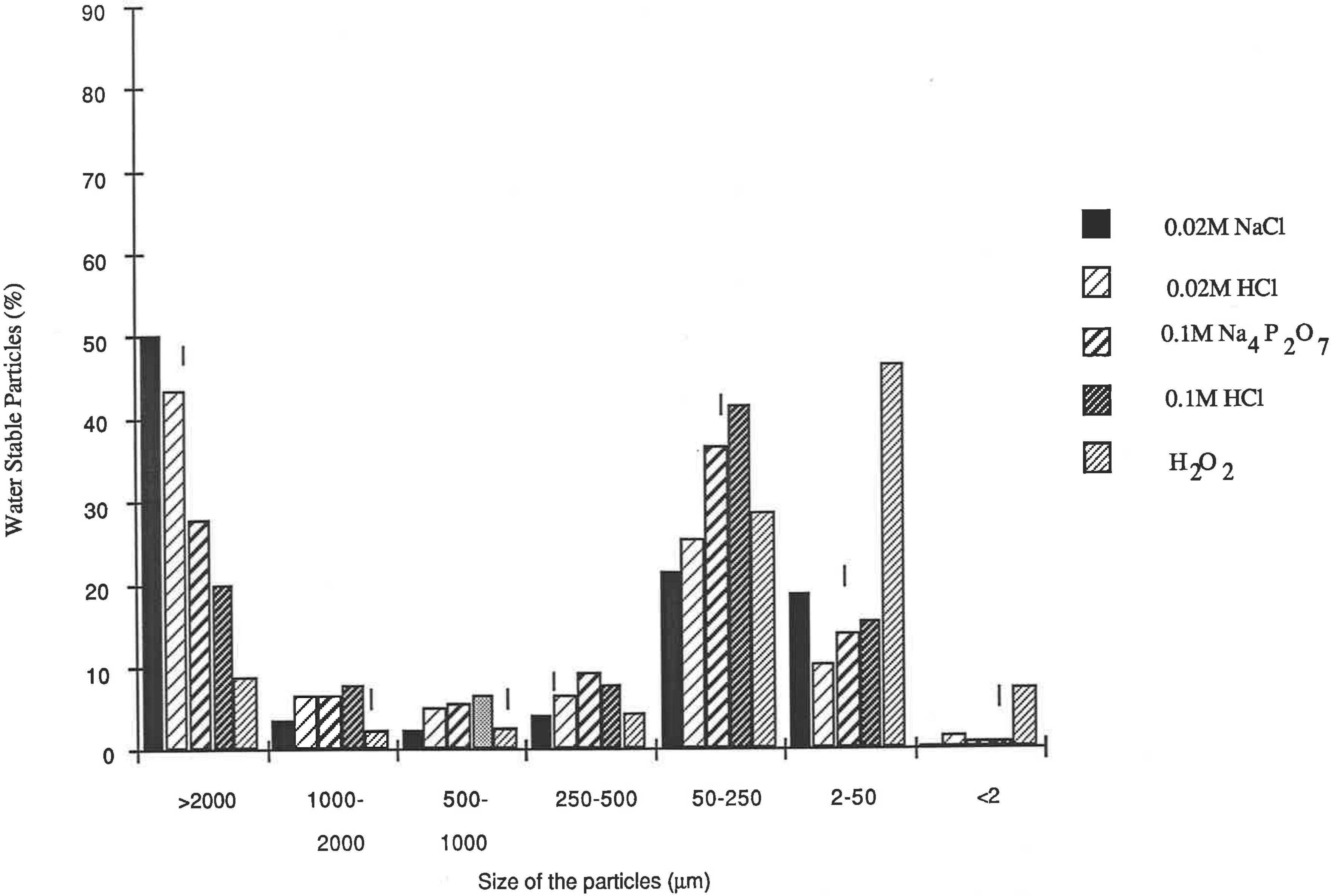

Fig. 13 The size distribution of water stable particles after chemical treatment (Trott Park soil) Vertical bar, $P<0.05$.

The results suggested that aggregates formed in the presence of calcium and organic matter were very stable, and severe chemical reaction is necessary to disrupt the stability.

Reduction in soil aggregates in both soils due to H_2O_2 treatment suggested that aggregate stability (>2000 μm diameter) was primarily dependent on the organic matter, where calcium has an additive effect.

2.4 CONCLUSIONS

The results of the investigation indicate that the distribution of lime and the presence of carbonate nodules in the soil profile is primarily dependent on the rainfall of the area, although other factors (e.g. porosity, parent material, topography etc) can influence the process.

The rate of dissolution of $CaCO_3$ decreases with the increase in particle size, hence when $CaCO_3$ is present as coarse particles in the profile, its effect on clay dispersion and aggregate stability is inhibited.

The examination of the eight different soils has given rise to the following suppositions:

1. $CaCO_3$ in solution (as Ca^{2+}) reduces dispersible clay by flocculating clay into particles 50-250 μm diameter.
2. Macroaggregate stability (>250 μm diameter) in calcareous soils is primarily dependent on the organic matter content of the soil.
3. Soils in high rainfall areas were usually high in organic matter content and also had more water-stable macroaggregates presumably due to complexes of Clay—Ca^{2+}—Organic matter.
4. Soil physical properties (e.g. bulk density, plastic limit, hydraulic conductivity and water holding capacity etc.) are primarily dependent on the organic matter content of the soil.

CHAPTER 3

THE EFFECT OF GYPSUM AND CALCIUM CARBONATE ON THE DECOMPOSITION OF ^{14}C-GLUCOSE AND THE AGGREGATE STABILITY OF SOILS

3.1 INTRODUCTION

The addition of calcium compounds to soil can increase the stability of soil aggregates by reducing swelling and/or dispersion, by lowering the exchangeable sodium percentage (ESP), and increasing the electrolyte concentration (Greene and Ford, 1985). Due to its low solubility, the application of calcium carbonate to soil usually does not improve the soil physical conditions rapidly, however there are indications that beneficial effects could arise over a prolonged period (Shanmuganathan, 1983). Gypsum which is more soluble, improves soil structure by flocculating clay particles and stabilizing aggregates 50-250 μm diameter (Shanmuganathan and Oades, 1983). No quantitative information is available that demonstrates that the application of calcium salts to soil increases the percentage of water stable particles > 250 μm diameter.

The water stability of aggregates (particularly the stability of macro-aggregates) in many soils is dependent on the presence of organic material (Clement, 1975; Eagle, 1975; Hamblin and Davies, 1977; Douglas and Goss, 1982; Chaney and Swift, 1984). The beneficial effect of organic matter on soil aggregation is usually attributed to an enhanced growth of actinomycete and fungal mycelium, and to the production of microbial metabolites. In general, the more readily available an organic substance is to microbial attack, the greater is its favourable effect on soil granulation (Martin and Waksman, 1940). It has also been stated that increased microbiological activity could also result in the loss of organic matter, especially after cultivation (Rovira and Greacen, 1957). Materials which are decomposed slowly tend to exert their binding effect over a longer period of time (Meredith and Kohnke, 1965; Tisdall and Oades, 1982). The balance between aggregation and disaggregation is related to the resistance and availability of the aggregating agents to microbial decomposition.

Calcareous soils are generally well aggregated, and the accumulation of organic matter per unit of surface area is much higher in comparison with non-calcareous soils, from which one can infer that humic compounds are more resistant to biodegradation in the presence of calcium (Duchaufour, 1982). However, no experimental evidence exists to substantiate this view.

The results presented in chapter 2 show that in soils poor in organic matter, the presence of $CaCO_3$ reduced dispersible clay by stabilizing aggregates 50-250 µm diameter. The stability of aggregates (especially macroaggregates) was primarily dependent on the organic matter content of the soil. It was also observed that the accumulation of organic matter was high in soils when they were saturated with Ca^{2+}. It was decided to investigate the effect of gypsum and calcium carbonate on the decomposition of ^{14}C-glucose and aggregate stabilization.

3.2 MATERIALS

A representative sample (0-10 cm) of the Urrbrae fine sandy loam (permanent pasture), a Red-brown earth was collected. The soil was air dried and passed through a 2 mm sieve. Some characteristics of the soil are listed in Table 16.

3.3 EXPERIMENTAL

3.3.1 Application of gypsum and calcium carbonate. Gypsum and calcium carbonate were applied at the rate of 10 t ha^{-1}. Some characteristics of the gypsum and calcium carbonate are shown in Table 17.

3.3.2 Preparation of ^{14}C-glucose solution

An aliquot of 300 µl of uniformly labelled ^{14}C-glucose, with a specific activity of 37 MBq/cm^3 (supplied by the Radio Chemical Centre, Amersham, England) was diluted in 100 cm^3 distilled water containing 12g of unlabelled glucose. The resulting solution contained 111KBq of ^{14}C-glucose and 120 mg glucose per cm^3.

3.3.3 Determination of total unlabelled CO_2-C

The amount of CO_2-C absorbed in NaOH was calculated by titrating 2 cm^3 of absorbent (1M NaOH) against 1M HCI to bring the pH from 8.3 to 3.7 (less the amount

Table 16. Properties of the (0-10 cm) Urrbrae f.s.l. soil (permanent pasture)

pH (1:5, soil/water ratio)	5.4
$CaCO_3$ (%)	Absent
Organic carbon (%)	2.04
Cation-exchange capacity (Cg-1)*	6.20
Exchangeable Na (Cg-1)	0.02
Exchangeable K (Cg-1)	0.85
Exchangeable Mg (Cg-1)	0.65
Exchangeable Ca (Cg-1)	3.00
Water holding capacity (%W/W)	45.0
Clay (%)	19.4
Silt (%)	31.3
Fine sand (%)	43.8
Coarse sand (%)	2.0
Clay mineralogy	Kaolinite and Illite

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*C= Coulomb= 6.2 x 10^{18} electron charges

(1C g^{-1} = 1 meq 100 g^{-1} approx).

Table 17. Some characteristics of the calcium compounds

Particle size distribution (%W/W) (dry sieving of 200 g)

Size (µm)	Gypsum	Calcium carbonate
>2000	0.2	0.7
2000-1410	1.9	1.3
1410- 500	16.3	8.6
500- 250	40.4	16.5
250- 150	18.8	15.4
150- 105	8.0	12.9
105- 90	2.2	4.3
90- 75	1.4	4.1
75- 64	0.9	6.8
64- 45	1.2	6.8
<2	8.7	22.2
pH (1:5/solid:water ratio)	7.3	8.0
E.C. (µS cm^{-1}) (1:5/ solid: water ratio)	3000	2730
$CaCO_3$	2.3	97.1

required for the blank). Titrations were performed with an automatic titrator (Radiometer, Copenhagen, PHM 82 Standard pH meter, TTT 80 Titrator and Autoburette ABU 80).

3.3.4 Determination of $^{14}CO_2$

An aliquot of 0.1 cm^3 of the absorbent was added to 10 cm^3 of Luma gel scintillation cocktail in vials of known background counts, and 0.9 cm^3 of distilled water was added. The contents of the vials were shaken vigorously until a clear solution was obtained. Samples were then counted in the scintillation counter (Hewlett Packard Model TRI-CARB 460 CD). 10µl of standard ^{14}C-benzoic acid of known counts were added as the internal standards to six vials, and the average recovery of the ^{14}C-internal standard was used to calculate the amount of $^{14}CO_2$.

3.3.5 Determination of ^{14}C in soil

^{14}C in the soil was determined by a modified wet-combustion method (Amato, 1983). Soil, 0.5g (<1mm, ground in a Tema mill and oven-dried at 60°C) was weighed into digestion tubes through a long neck glass funnel. Combustion mixture (6 cm^3) (Dalal, 1979) was quickly added to the bottom of the tube with a "Dispensette" dispensor, a glass rod support was placed into the digestion tube with a 10 cm^3 graduated tube containing 5 cm^3 1M NaOH, and the tube was immediately stoppered with a Subaseal.

After addition of combustion mixture, the tubes were allowed to stand at room temperature for 30 minutes. Blanks and standards (sucrose-benzoic acid containing 50 mg CO_2, radioactivity 5420 dpm), were prepared in a similar manner and included with every batch digested. The tubes were placed in a heating block for 1h at 130°C, cooled and held overnight at room temperature. The NaOH absorbing tubes were removed from the digestion tube, and the volume was made up to 10 cm^3 by adding distilled water. The contents were mixed and an aliquot of 0.1 cm^3 of the 1M NaOH absorbent was added to 0.9 cm^3 of distilled water in 20 cm^3 glass scintillation vials. After addition of 8 cm^3 of Luma gel scintillation cocktail, the vials were shaken vigorously, wiped clean and placed in the scintillation counter. The radioactivity measured was corrected for background and efficiency.

3.3.6 Treatment

Two experiments were designed

(1) to determine the effect of gypsum and calcium carbonate on the decomposition of ^{14}C-glucose,

and (2) to determine the effect of gypsum and calcium carbonate on the stability of soil aggregates and clay dispersion with or without addition of ^{14}C-glucose.

The following treatments were given to two hundred and seventy vials (100 cm^3 capacity) each containing 60g soil (oven-dry equivalent). The vials were kept at a constant temperature of 20°C±1.

Treatment No.	Experiment 1 No. of vials	Experiment 2 No. of vials	Treatment
1	21	27	Control (60g soil+ 2cm^3 H_2O)
2	21	18	$CaCO_3$ (60g soil+ 0.6 g $CaCO_3$ +2 cm^3 H_2O)
3	21	18	$CaSO_4.2H_2O$ (60g soil+ 0.6 g $CaSO_4.2H_2O$ + 2 cm^3 H_2O)
4	21	27	^{14}C-glucose (60g soil+ 2 cm^3 ^{14}C-glucose solution)
5	21	27	^{14}C-glucose+$CaCO_3$ (60g soil+ 2 cm^3 glucose solution + 0.6 g $CaCO_3$)
6	21	27	^{14}C-glucose+ $CaSO_4.2H_2O$ (60g soil+ 2 cm^3 ^{14}C-glucose solution+ 0.6 g $CaSO_4.2H_2O$)

Appropriate amounts of distilled water were added to each vial to bring the soils to 75% water holding capacity, and the contents of the vials were thoroughly mixed with a spatula.

3.3.6.1 *Experiment 1*

^{14}C-glucose with or without $CaCO_3$ or $CaSO_4.2H_2O$ was incubated for 120 days. Each vial was placed in a 1000 cm^3 confectionary jar with screw top lid. Distilled water (10 cm^3) was placed in each jar to maintain humidity. Three jars from each treatment were reserved exclusively for the determination of the total release of CO_2. Released CO_2 was absorbed in 20 cm^3 of 1M NaOH, which was replaced every 12 hours for the first seven days. The NaOH absorbing tubes were then replaced on a daily basis for 3 weeks, and then at the 9th and 17th week of incubation.

For the estimation of residual ^{14}C in soil, three vials from each treatment were collected at weeks 1, 4, 8, 12, 52 and 104.

3.3.6.2 *Experiment 2*

Fifteen of the vials from each treatment were incubated for three months as described above, and one set was left for incubation for a period of two years.

Twelve vials from treatment 1, 4, 5 and 6 were not sealed, and were subjected to two wetting and drying (W.D.) cycles per month, for three months. The vials became dry at about two weeks, and were rewetted in each cycle with distilled water to bring the contents to 75% water holding capacity.

For the determination of water stable aggregates and dispersible clay in the incubated soils, 3 vials from each treatment were collected at day 2, and then at weeks 2, 4, 8, 12 and 102.

For soils subjected to wetting and drying cycles, water stable aggregates and dispersible clay were determined after 0, 2, 4 and 6 W.D. cycles.

3.4 RESULTS AND DISCUSSION

3.4.1 Experiment 1

3.4.1.1 Incubation of ^{14}C-glucose with or without calcium compounds

Mineralization curves for ^{14}C-labelled glucose (with or without the addition of $CaCO_3$ and $CaSO_4$) are presented in Fig. 14, 15 and Table 18.

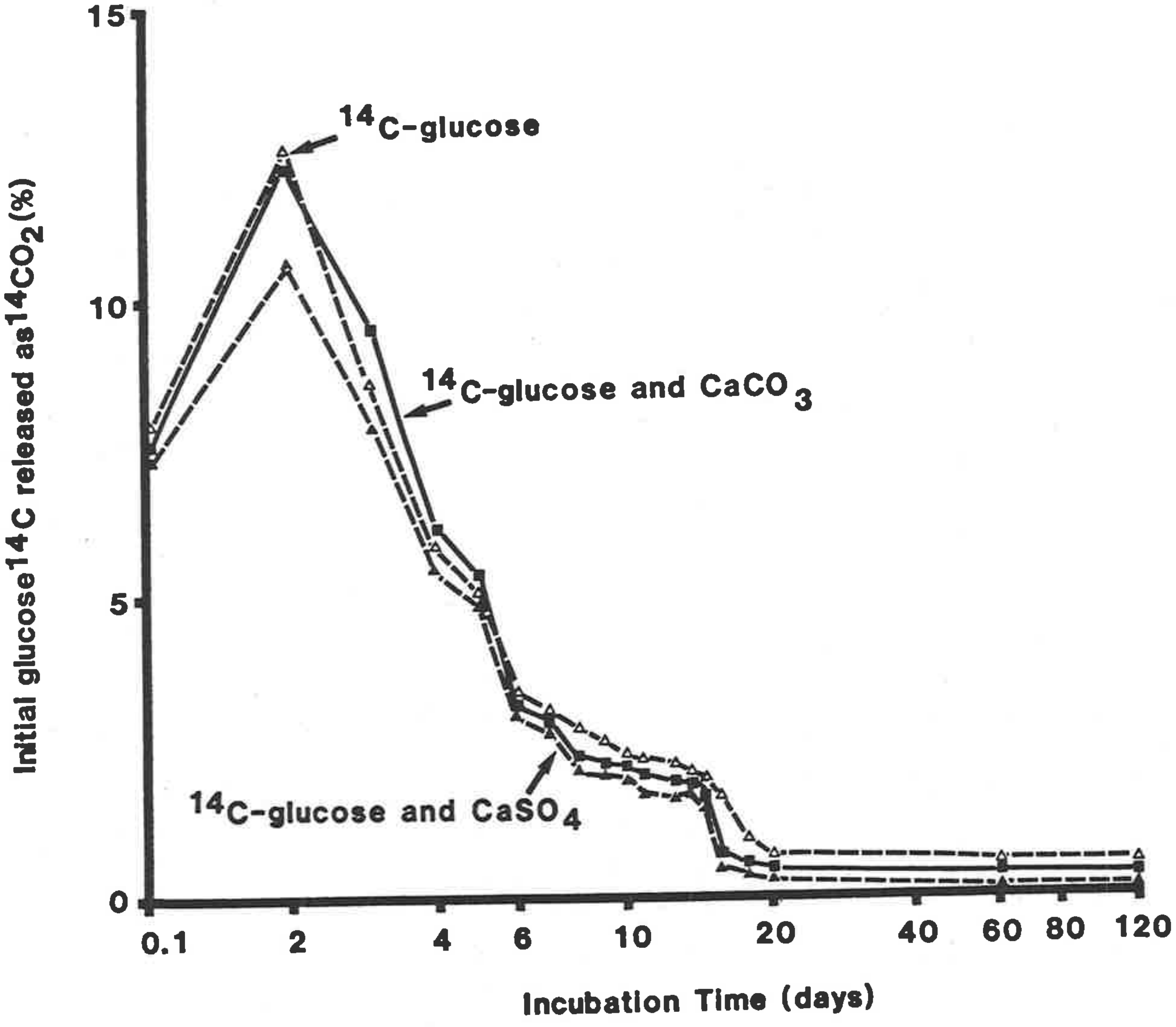


Fig.14 Release of $^{14}CO_2$ during incubation of ^{14}C-glucose

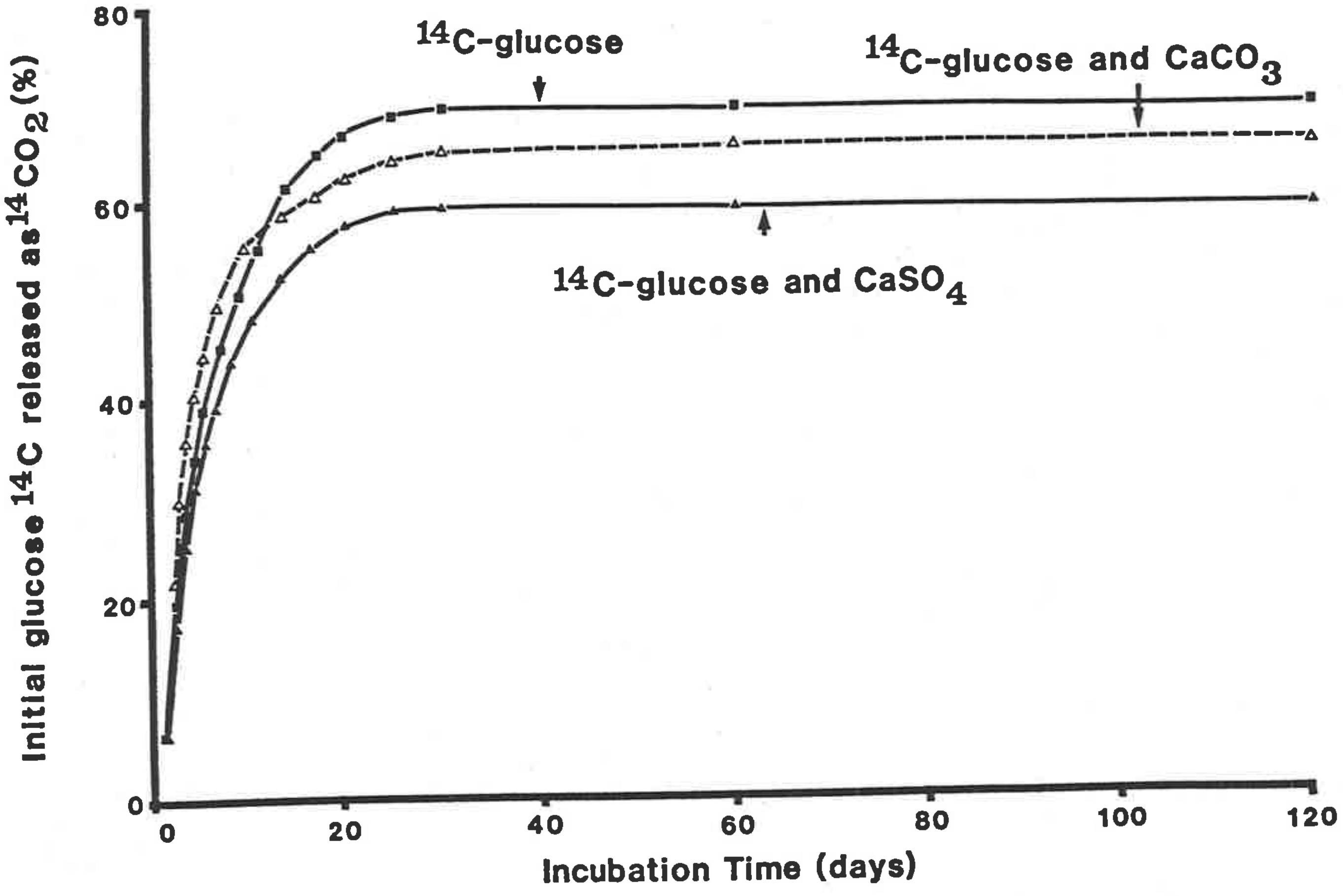


Fig.15 Cumulative release of $^{14}CO_2$ during the incubation of ^{14}C-glucose

Table 18. Rate of release of unlabelled (12C) CO_2 (mg C/ day / 100 g soil) from the Urrbrae fsl after addition of ^{14}C-glucose and calcium compounds.

Incubation period (days)	^{14}C-glucose	^{14}C-glucose+$CaCO_3$	^{14}C-glucose+$CaSO_4$
1	7.69	7.65	7.18
2	12.55	12.42	10.59
3	8.60	9.50	7.90
4	5.86	6.10	5.48
5	4.96	5.00	4.96
6	3.10	3.00	3.00
7	3.00	2.93	2.85
8	2.76	2.25	2.22
9	2.52	2.23	2.16
10	2.29	2.16	2.01
11	2.25	2.00	1.74
12	2.19	1.95	1.74
13	2.15	1.89	1.58
14	1.95	1.94	1.76
15	1.81	1.78	1.70
16	1.54	0.50	0.43
17	1.47	0.50	0.34
18	0.95	0.41	0.32
19	0.55	0.37	0.28
20	0.50	0.35	0.27
21	0.38	0.36	0.24
60	0.30	0.24	0.19
120	0.30	0.22	0.18

The pattern of decomposition of ^{14}C-glucose was similar in all treatments. The curves (Fig.14) representing the release of $^{14}CO_2$ from glucose mineralization consist of primarily three phases (Sorenson and Paul, 1971; Ahmed, 1981).

(i) rapid phase (less than 5 days) involving the oxidation of glucose, (ii) relatively slow phase (5-20 days), consisting of heterogeneous metabolic products decaying at different rates, and (iii) the slowest phase (more than 20 days) involving the decay of more or less homogeneous and stable products of decomposition.

During the initial 5 days of incubation there was increased $^{14}CO_2$ production in the ^{14}C-glucose+$CaCO_3$ treatment, in comparison to soils treated with ^{14}C-glucose or ^{14}C-glucose+$CaSO_4$ (Fig.14). Production of $^{14}CO_2$ declined for the remaining incubation period (115 days) compared to the soil treated with ^{14}C-glucose only. The rate of release of $^{14}CO_2$ from soil treated with ^{14}C-glucose+$CaSO_4$ was lower than all other treatments during the entire incubation period.

The cumulative release of $^{14}CO_2$ demonstrates that soils treated with ^{14}C-glucose+$CaCO_3$ or ^{14}C-glucose+$CaSO_4$ had significantly ($P<0.05$) inhibited release of $^{14}CO_2$, from mineralization of ^{14}C-glucose (Fig.15). The mineralization of ^{14}C-glucose was reduced by 4% in the soil treated with ^{14}C-glucose+$CaCO_3$ and by 14% in the soil treated with ^{14}C-glucose+$CaSO_4$. Therefore, 10% more of the added ^{14}C-glucose was prevented from mineralization in the $CaSO_4$ treatment.

Application of $CaCO_3$ enhanced the release of $^{14}CO_2$ in the early stage of incubation when compared with the control. However subsequent $^{14}CO_2$ production was progressively suppressed. The stimulating effect of $CaCO_3$ on ^{14}C labelled glucose decomposition is thus transient and the long term effect is one of stabilization. The delayed effect of $CaCO_3$ on reducing the mineralization was probably due to its low solubility. The increase in pH (Table 19) resulting from addition of $CaCO_3$ could initially promote the mineralization of ^{14}C-glucose, but it appears that the effect is of short duration (Jenkinson, 1977).

Reduced mineralization of ^{14}C-glucose in presence of calcium may be the result of the stabilizing effect of calcium on the decomposed products of organic matter that are resistant to further decomposition by microorganisms. Microorganisms are responsible for the production of a variety of linear organic polymers; e.g. low molecular weight humic substances and various polysaccharides, or polyuronides. These are produced by many species of bacteria, fungi, actinomycetes and yeasts (Forsyth and Webley, 1949). It has been shown that the decomposition of microbial or plant polysaccharides was reduced by interaction with organic and inorganic constituents in the soil, (Martin, 1971; Cheshire et al.,1974) such as adsorption of polysaccharides onto clay surfaces, and the formation of polysaccharide-metal complexes (Swincer et al, 1969; Martin et al., 1974). These interactions either inhibit the activity of extracellular enzymes or increase the insolubility of the polysaccharides, restricting their availability to soil microorganisms (Cheshire, 1977).

Table 19. Soil pH during incubation of ^{14}C-glucose, with or without calcium compounds (1:5 soil/water ratio)

Treatment No.	Treatment	1 week	4 weeks	8 weeks	12 weeks	17 weeks
1	Control	5.6	5.6	5.6	5.4	5.4
2	$CaCO_3$	6.7	7.0	7.0	7.0	7.0
3	$CaSO_4$	5.4	5.6	5.3	5.2	5.2
4	^{14}C-glucose	6.0	6.0	6.0	5.8	5.8
5	^{14}C-glucose+$CaCO_3$	6.9	6.8	6.7	6.8	6.6
6	^{14}C-glucose+ $CaSO_4$	5.5	5.6	5.5	5.5	5.4

Organic matter is stabilized by calcium, the removal of which leads to destabilization. Gaiffe et al. (1984) demonstrated that the gradual removal of the exchangeable calcium held by the organo-mineral complexes of an organic soil resulted in the destabilization of the organo-mineral complex by H^+, produced by the biodegradation of the most labile portion of the organic matter. The clay humus complex gradually dissociates, leading to the destruction of aggregates and organo-mineral complexes. The organic matter released presumably became biodegradable due to the shortage of calcium which acted as a flocculating or binding agent.

3.4.1.2 Residual ^{14}C in the soil during the incubation of ^{14}C-glucose with or without $CaCO_3$ or $CaSO_4$

The curves for residual ^{14}C in the treatments during the two years of incubation of ^{14}C-glucose are presented in Fig.16.

After 12 weeks of incubation more than 50% of the initial ^{14}C had been lost as $^{14}CO_2$. The residual ^{14}C after two years of incubation was 25% in the soil treated with ^{14}C-glucose, 28% in the soil treated with ^{14}C-glucose+$CaCO_3$ and 30% in the soil treated with ^{14}C-glucose+$CaSO_4$. Treatments with ^{14}C-glucose+$CaCO_3$ or ^{14}C-glucose+$CaSO_4$ had significantly ($P<0.05$) more residual ^{14}C than the treatment with ^{14}C-glucose only.

The increase in residual ^{14}C may be the result of complexes of clay-Ca^{2+}-organic matter. Such complexes may influence the rate of decomposition of organic matter due to the inability of microbial enzymes to hydrolyse the complexes.

3.4.2 Experiment 2

3.4.2.1 Particle size distribution of soils incubated at 75% water holding capacity

Addition of $CaCO_3$ or $CaSO_4$ to the soil did not show any effect on the stability of macroaggregates (250-2000 µm diameter), and therefore was not implicated in cementation. Soils treated with $CaCO_3$ or $CaSO_4$ significantly ($P<0.05$) increased the percentage of soil particles of 50-250 µm diameter,with a concomitant decrease in the percentage of particles <50 µm diameter (Fig.17,18, 19, 20, 21, and 22). $CaSO_4$ was more effective than $CaCO_3$ in flocculating clay, because of the higher solubility of the gypsum (Table 20). The results are in accord with the findings of Shanmuganathan (1982), who demonstrated that application of gypsum to soil decreased the proportion of clay sized particles, and increased the proportion of particles 50-250 µm diameter.

The application of ^{14}C-glucose to soil (with or without $CaCO_3$ or $CaSO_4$) significantly ($P<0.05$) increased the percentage of aggregates of 1000-2000 µm diameter with an accompanied decrease of particles <250 µm diameter. The maximum percentage increase of macroaggregates (1000-2000 µm diameter) had occurred by the fourth week of incubation. From the fourth week the proportion of water stable soil aggregates gradually declined.

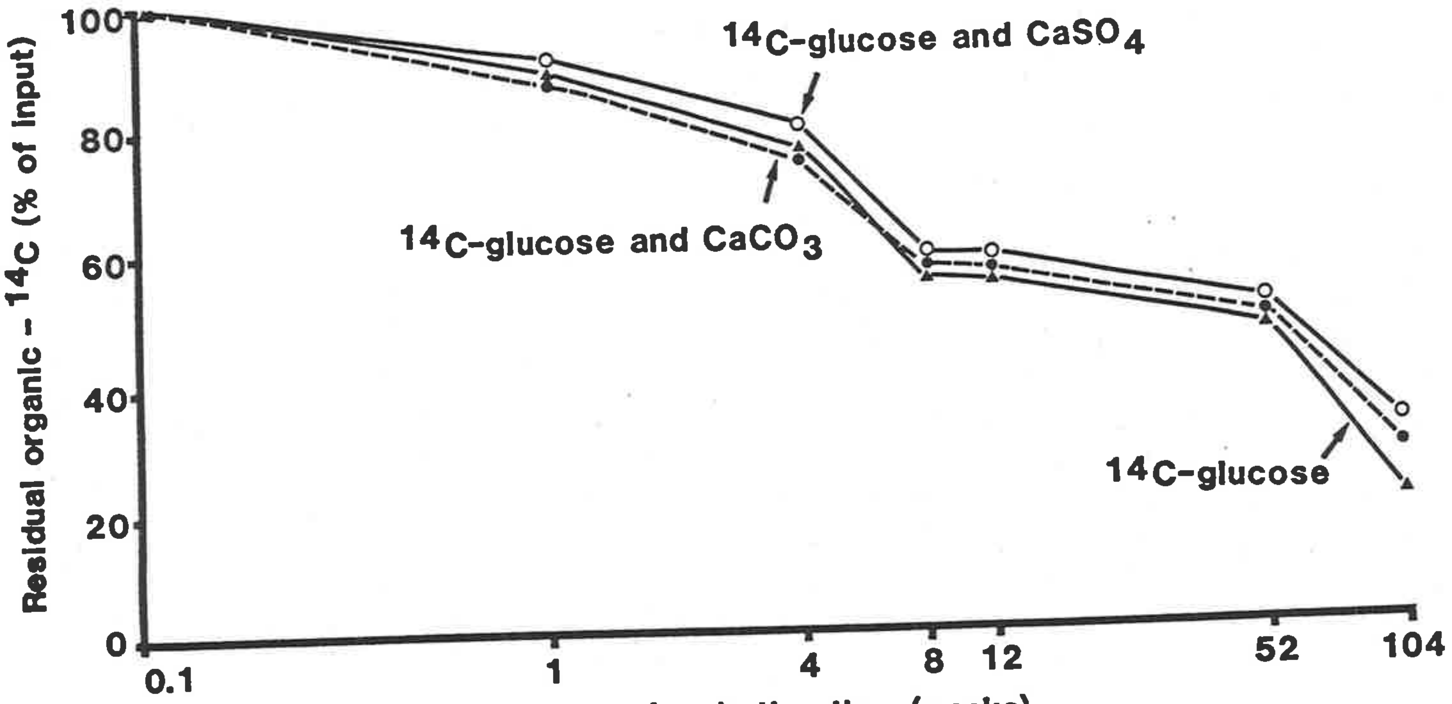


Fig.16 Residual ^{14}C during the incubation of ^{14}C-glucose

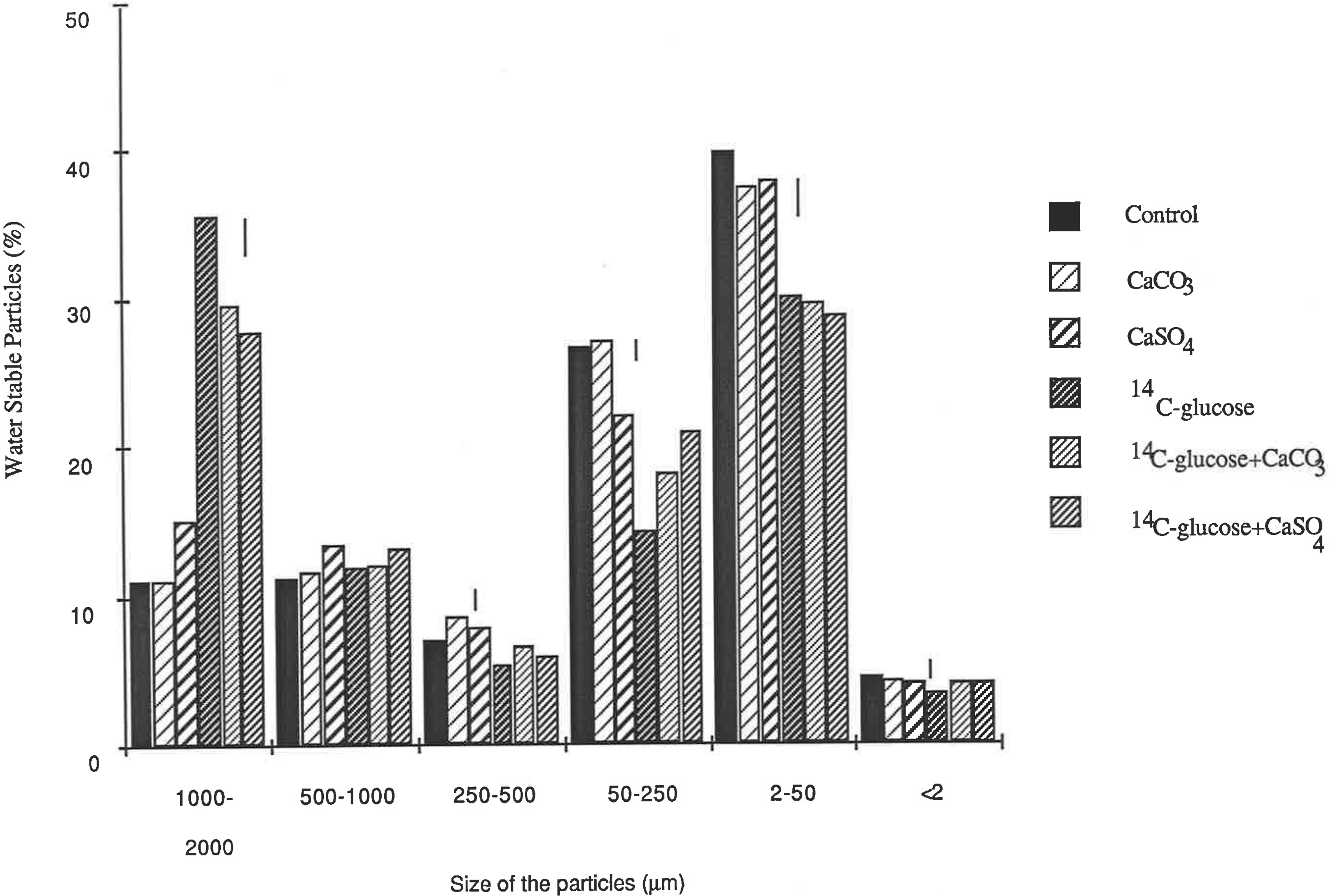


Fig. 17 The size distribution of water stable particles after day two of incubation of ^{14}C-glucose. Vertical bar, $P<0.05$.

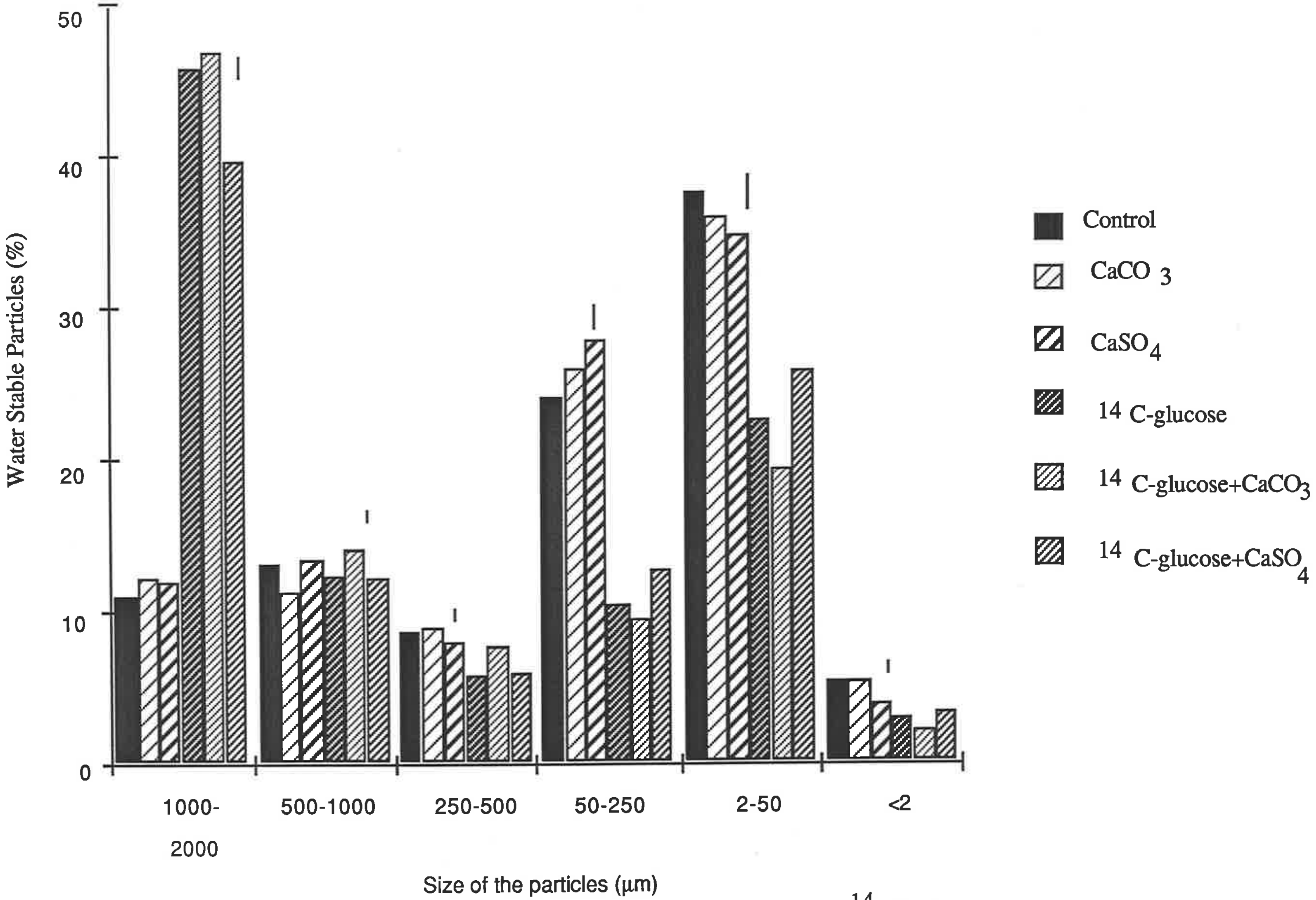


Fig. 18 The size distribution of water stable particles after two weeks incubation of ^{14}C-glucose.
Vertical bar, $P<0.05$.

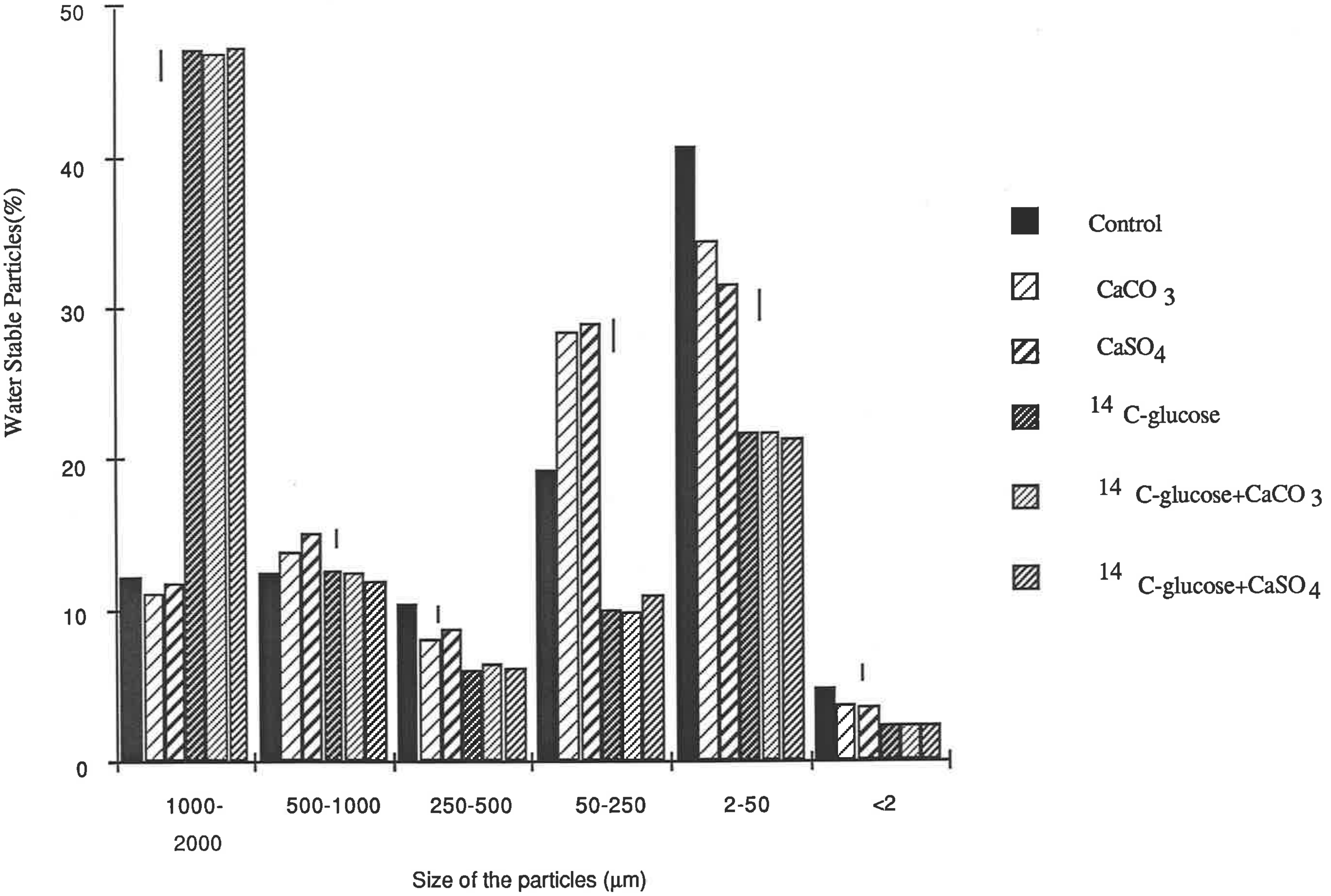


Fig. 19 The size distribution of water stable particles after four weeks incubation of ^{14}C-glucose. Vertical bar, $P<0.05$.

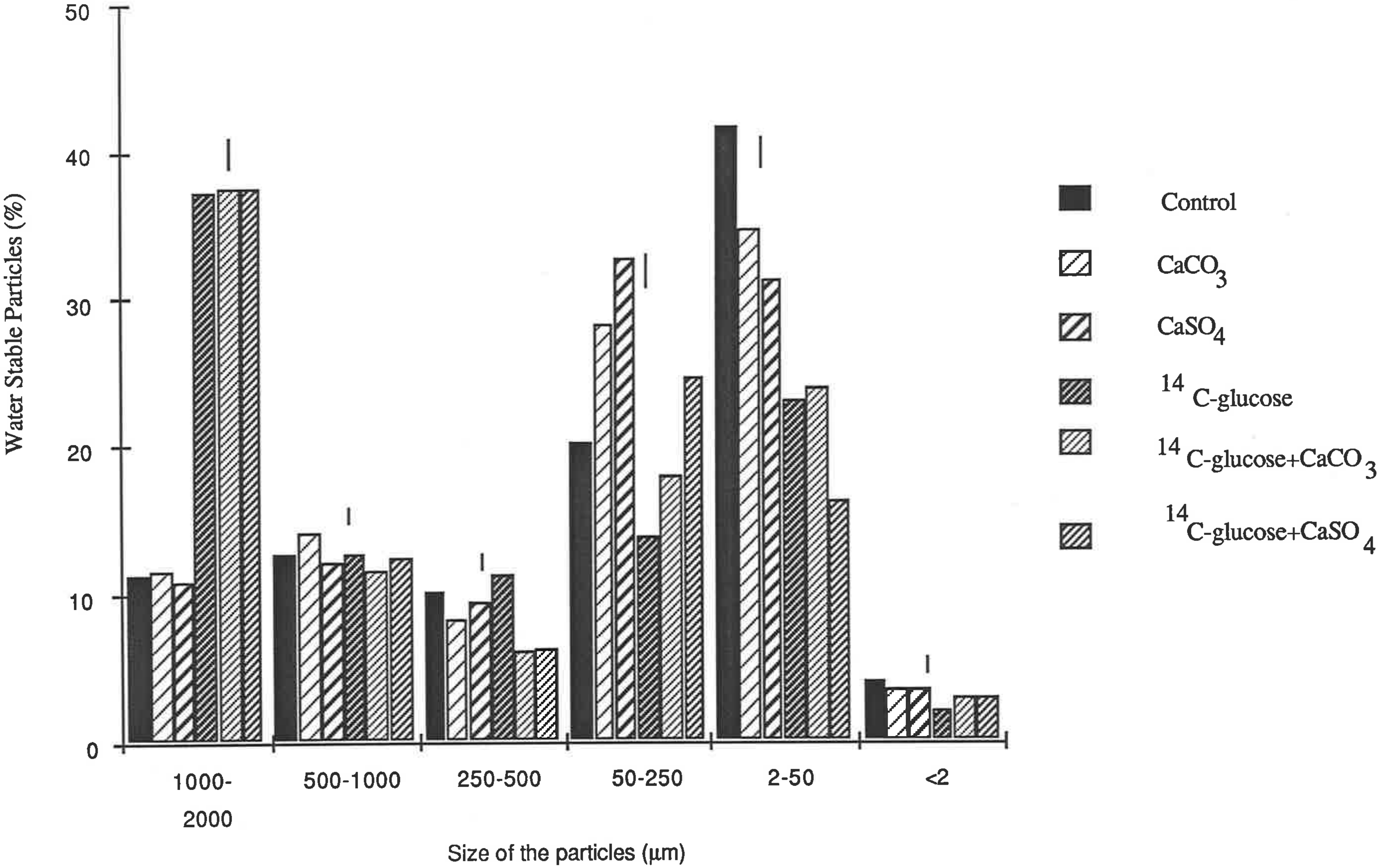


Fig. 20 The size distribution of water stable particles after eight weeks incubation of ^{14}C-glucose. Vertical bar, $P<0.05$.

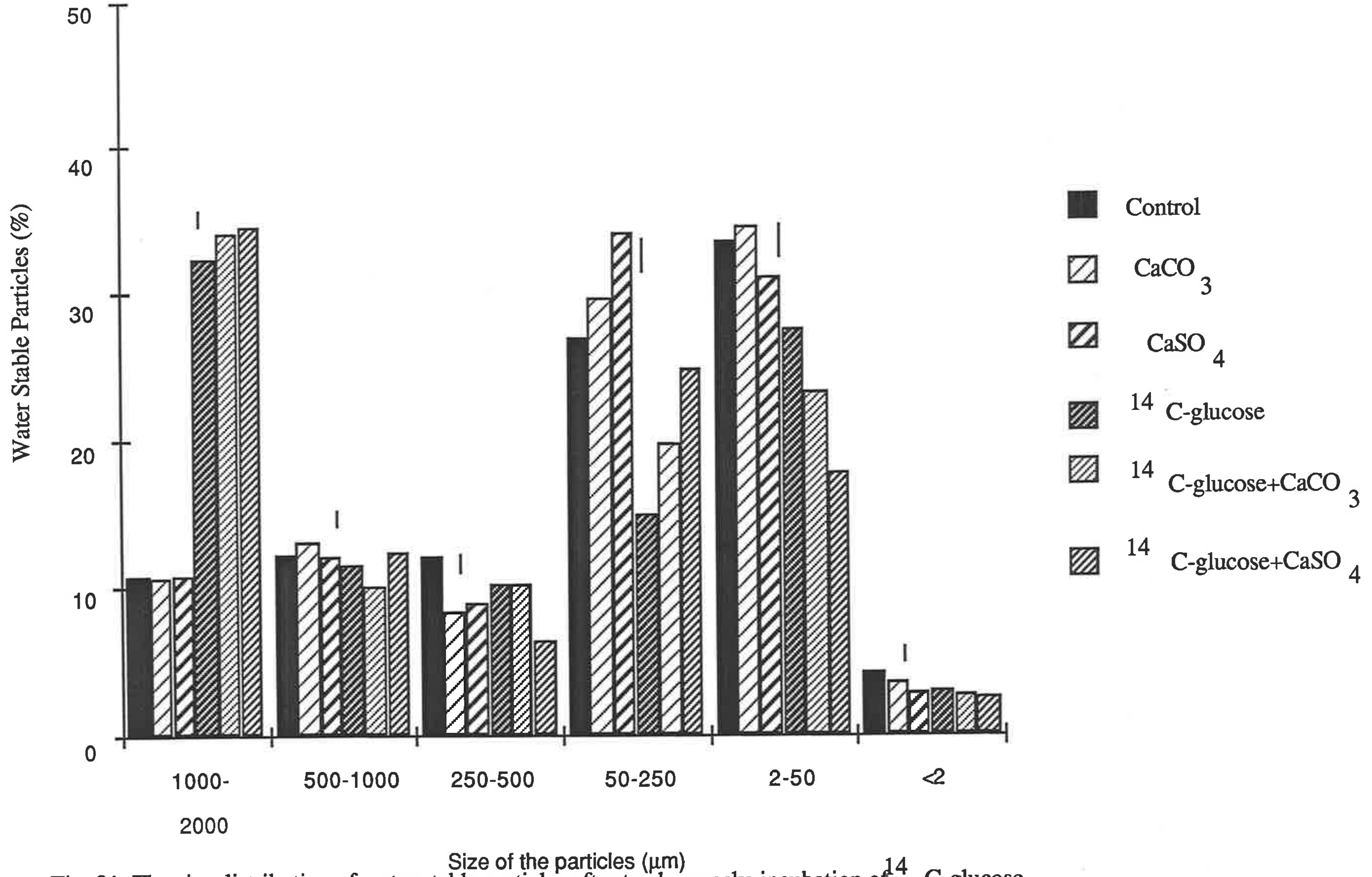


Fig. 21 The size distribution of water stable particles after twelve weeks incubation of ^{14}C-glucose. Vertical bar, $P<0.05$.

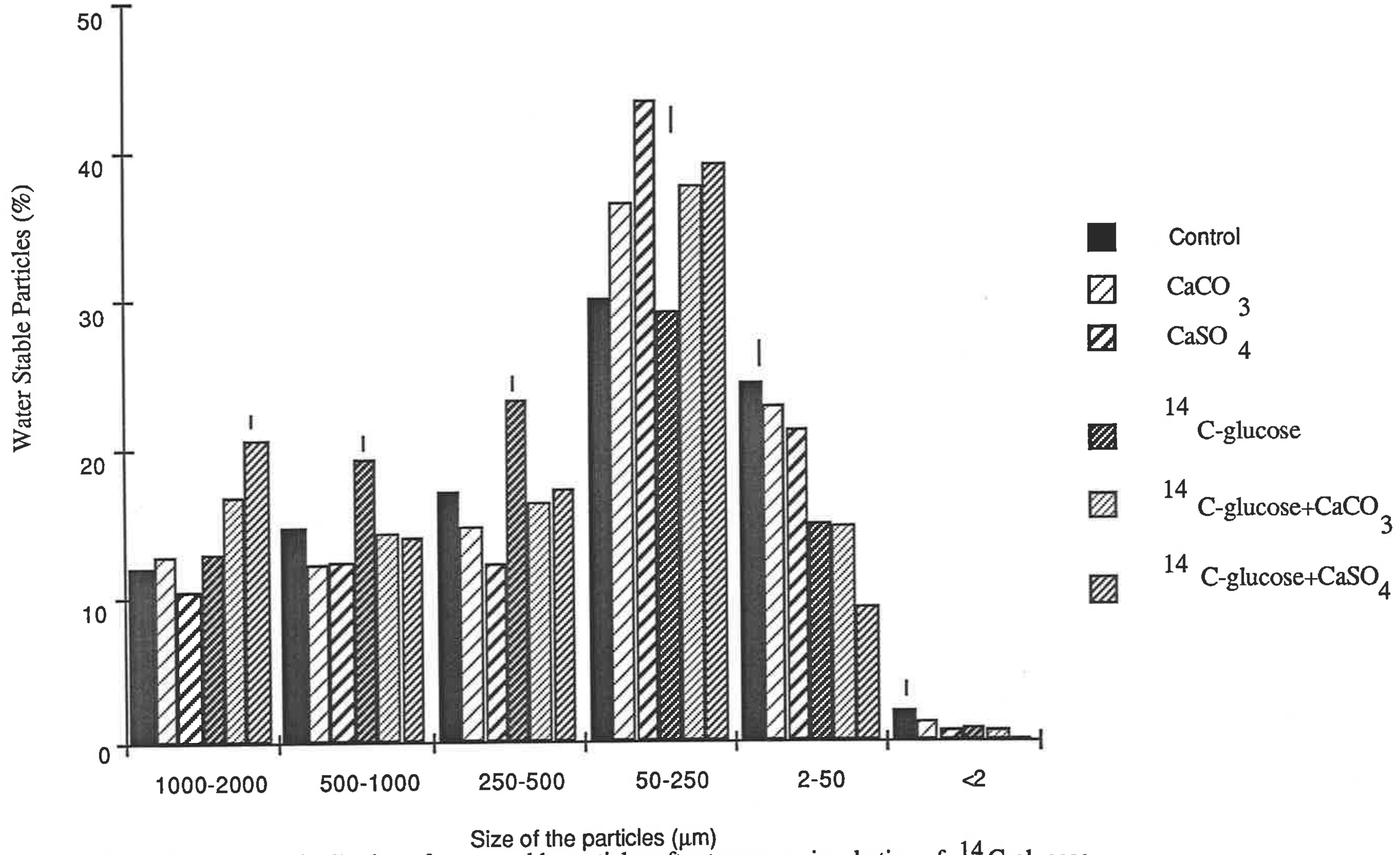


Fig. 22 The size distribution of water stable particles after two years incubation of ^{14}C-glucose. Vertical bar, $P<0.05$.

Table 20. Electrical conductivity (μS cm^{-1}) of soil during incubation of ^{14}C-glucose, with or without calcium compounds (1:5 soil/water ratio)

Treatment No	Treatment	1 week	4 weeks	8 weeks	12 weeks
1	Control	284	284	330	397
2	$CaCO_3$	650	680	685	690
3	$CaSO_4$	1136	1363	1420	1363
4	^{14}C-glucose	227	170	170	227
5	^{14}C-glucose+$CaCO_3$	645	650	645	645
6	^{14}C-glucose+$CaSO_4$	1249	1249	1136	1306

Soils treated with ^{14}C-glucose or ^{14}C-glucose+$CaCO_3$ had more water stable macroaggregates (1000-2000 μm diameter) between the second and fourteenth day of incubation, than the soil treated with ^{14}C-glucose+$CaSO_4$. However this difference in aggregate stability was insignificant between week four and eight. The stability of soil aggregates (1000-2000 μm diameter) declined in all treatments after fourth week of incubation. From week twelve to week one hundred and four, soils treated with ^{14}C-glucose+$CaCO_3$ or ^{14}C-glucose+$CaSO_4$ still had a greater percentage of aggregates of 1000-2000 μm diameter compared to the soil treated with ^{14}C-glucose only.

3.4.2.2 Effect of ^{14}C-glucose with or without $CaCO_3$ or $CaSO_4$ on the aggregate stability after wetting and drying cycles

The addition of ^{14}C-glucose, ^{14}C-glucose with $CaCO_3$ or $CaSO_4$ significantly increased the percentage of aggregates 1000-2000 μm diameter (Fig. 23, 24, 25 and 26). Maximum aggregate stability (1000-2000 μm diameter) was observed after one wetting and drying cycle. The percentage of macroaggregates (1000-2000 μm diameter) then declined gradually in all the treatments.

Significant increases in the percentage of water stable aggregates (1000-2000 μm diameter) were noted in soils treated with ^{14}C-glucose or ^{14}C-glucose+$CaCO_3$ during the first two wetting and drying cycles, compared to soil treated with ^{14}C-glucose+$CaSO_4$. However after six wetting and drying cycles, treatments with ^{14}C-glucose+$CaCO_3$ or ^{14}C-glucose+$CaSO_4$ had a significantly higher percentage of aggregates (1000-2000 μm diameter) than the treatment with ^{14}C-glucose only. Comparing the ^{14}C-glucose+$CaCO_3$ and ^{14}C-glucose+$CaSO_4$ treatments, ^{14}C-glucose+$CaSO_4$ was more efficient in soil aggregation.

These results established that the addition of ^{14}C-glucose to soil (with or without $CaCO_3$ or $CaSO_4$) increases the stability of macroaggregates (1000-2000 μm diameter), probably as a result of increased microbial activity (Clement, 1975; Eagle, 1975; Hamblin and Davies, 1977; Douglas and Goss, 1982; Chaney and Swift, 1984). However the loss of ^{14}C-glucose by mineralization gradually reduced the stability of macroaggregates (Low, 1954; Rovira and Greacen, 1957; Clement and Williams, 1958; McCalla, 1959; Martel and Paul, 1974; Adu and Oades, 1978). This decrease was more evident in the soil treated with ^{14}C-glucose only.

The decomposition of ^{14}C-glucose was slow in presence of calcium, and the Ca-organic binding agents were effective over a long period of time (Browning and Milam, 1941; Meredith and Kohnke, 1965; Tisdall and Oades, 1982). It seems that the balance between aggregation and disaggregation is related to the resistance and availability of the aggregating agents to microbial decomposition.

Wetting and drying cycles accelerated both formation and degradation of aggregates, when compared to aggregates formed during incubation at 75% water holding capacity. Wetting and drying cycles can build up soil aggregates by particle orientation and enhancement of microbial activity . On the other hand, continued wetting and drying cycles increase the surface area or porosity due to fragmentation of aggregates. Organic matter not previously accessible to microbial attack becomes biodegradable (Broadbent et al., 1964; Adu and Oades, 1978a; Tisdall et al., 1978). Therefore, the beneficial effect of wetting and drying cycles on soil aggregation could not be sustained unless organic matter is added to the soil regularly.

3.4.2.3 Dispersible clay

Incubation of soil after the addition of $CaCO_3$ or $CaSO_4$ (with or without ^{14}C-glucose) significantly decreased the percentages of dispersible clay (Fig.27). The treatments ^{14}C-glucose+$CaCO_3$ or ^{14}C-glucose+$CaSO_4$ were more effective in reducing dispersible clay than the treatments $CaCO_3$ or $CaSO_4$ alone.

With wetting and drying cycles, treatments ^{14}C-glucose+$CaCO_3$ or ^{14}C-glucose+$CaSO_4$ showed significant decreases in the percentages of dispersible clay (Fig.28).

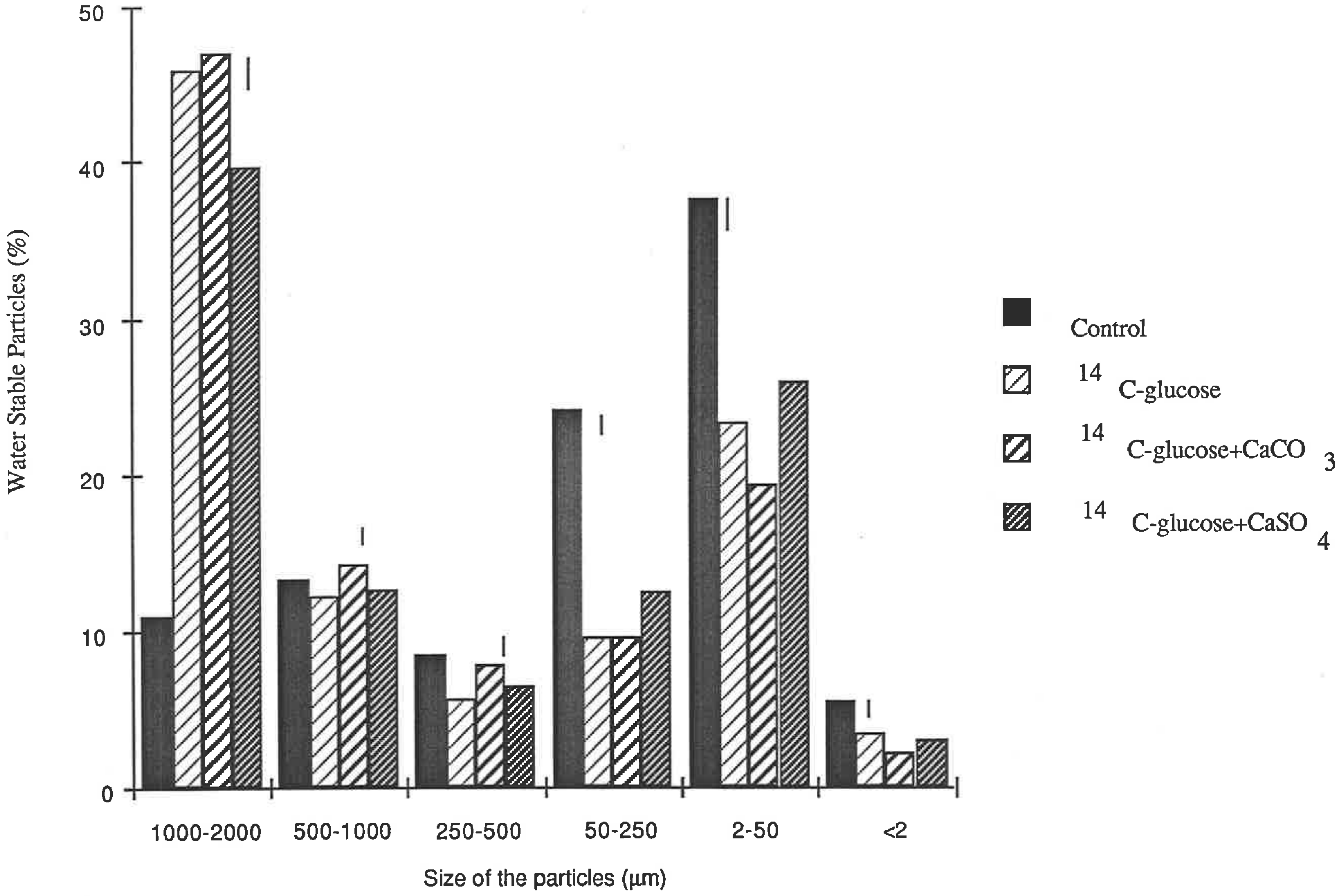


Fig. 23 The size distribution of water stable particles at zero wetting and drying cycle of soil. Vertical bar, $P<0.05$.

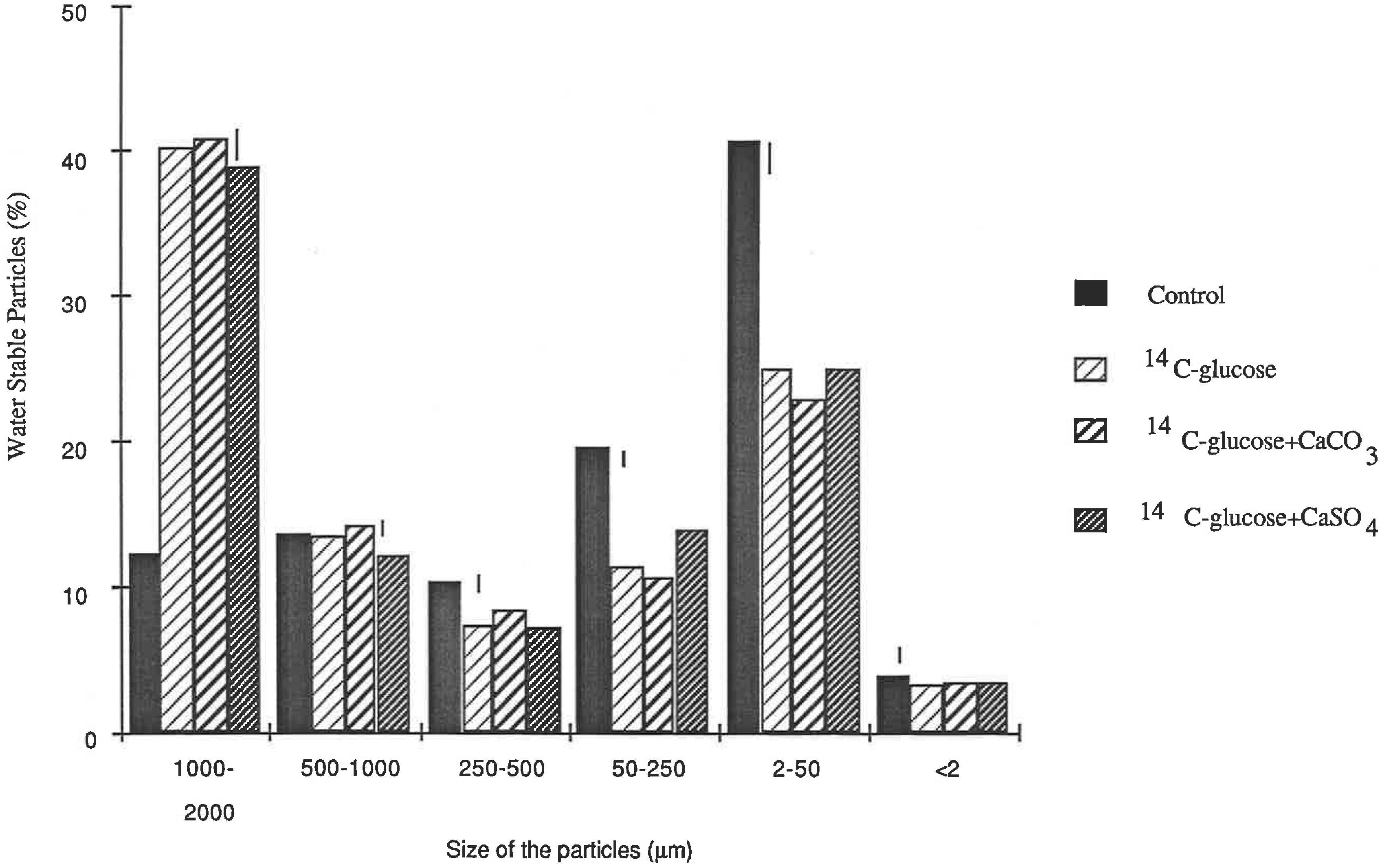


Fig. 24 The size distribution of water stable particles after two wetting and drying cycles of soil. Vertical bar, $P<0.05$.

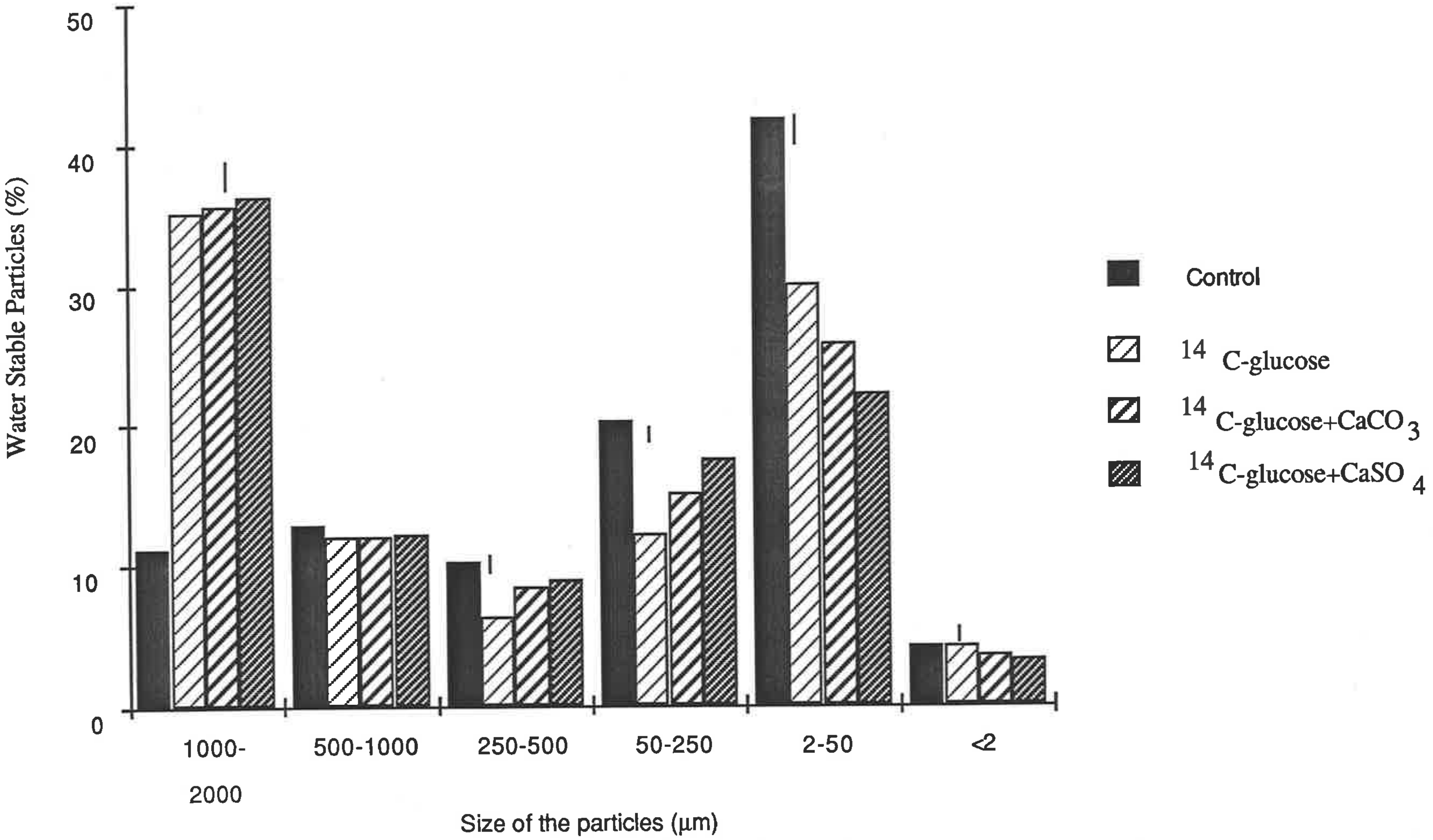


Fig. 25 The size disrtibution of water stable particles after four wetting and drying cycles of soil.
Vertical bar, $P<0.05$.

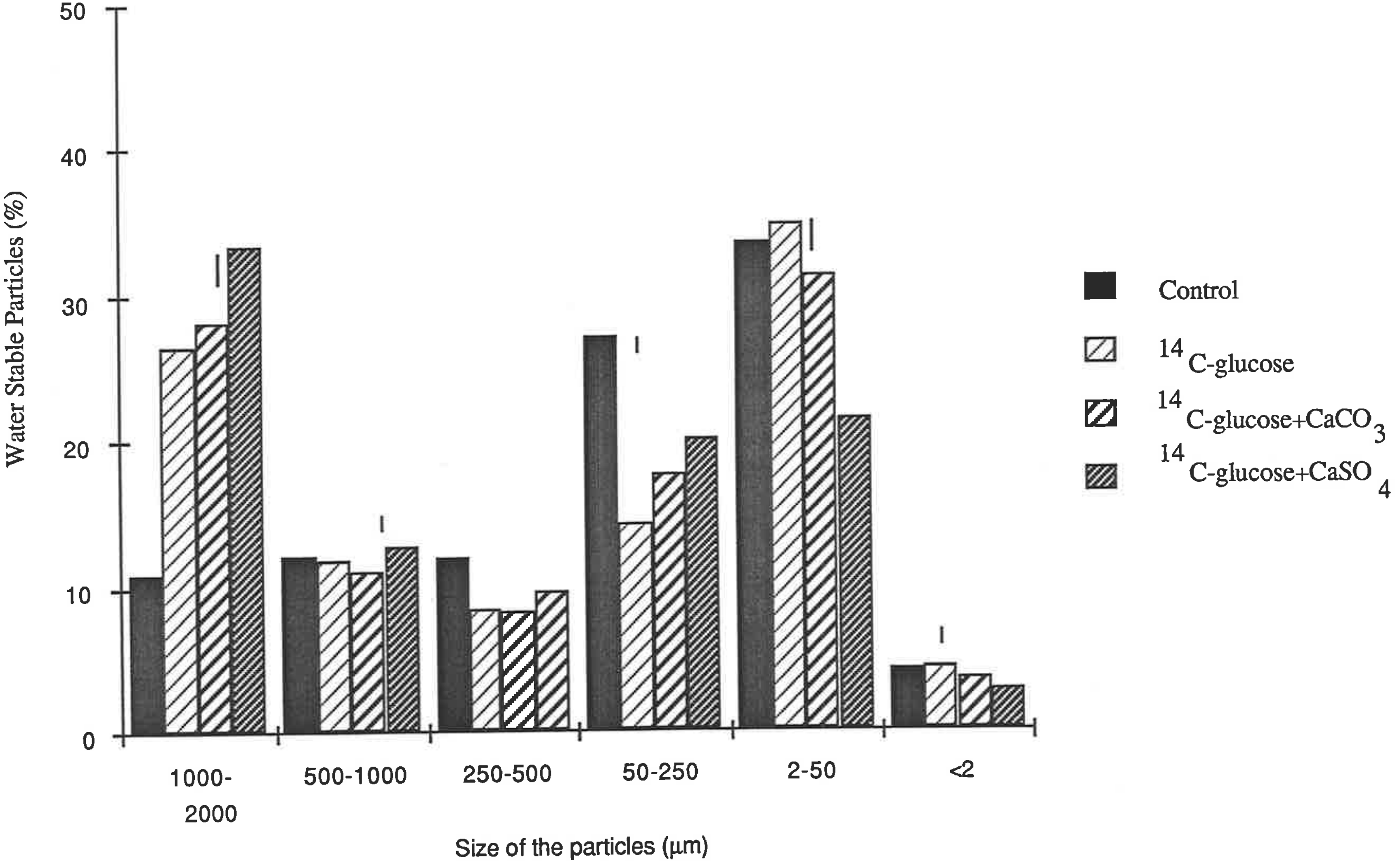


Fig. 26 The size distribution of water stable particles after six wetting and drying cycles of soil. Vertical bar, $P<0.05$.

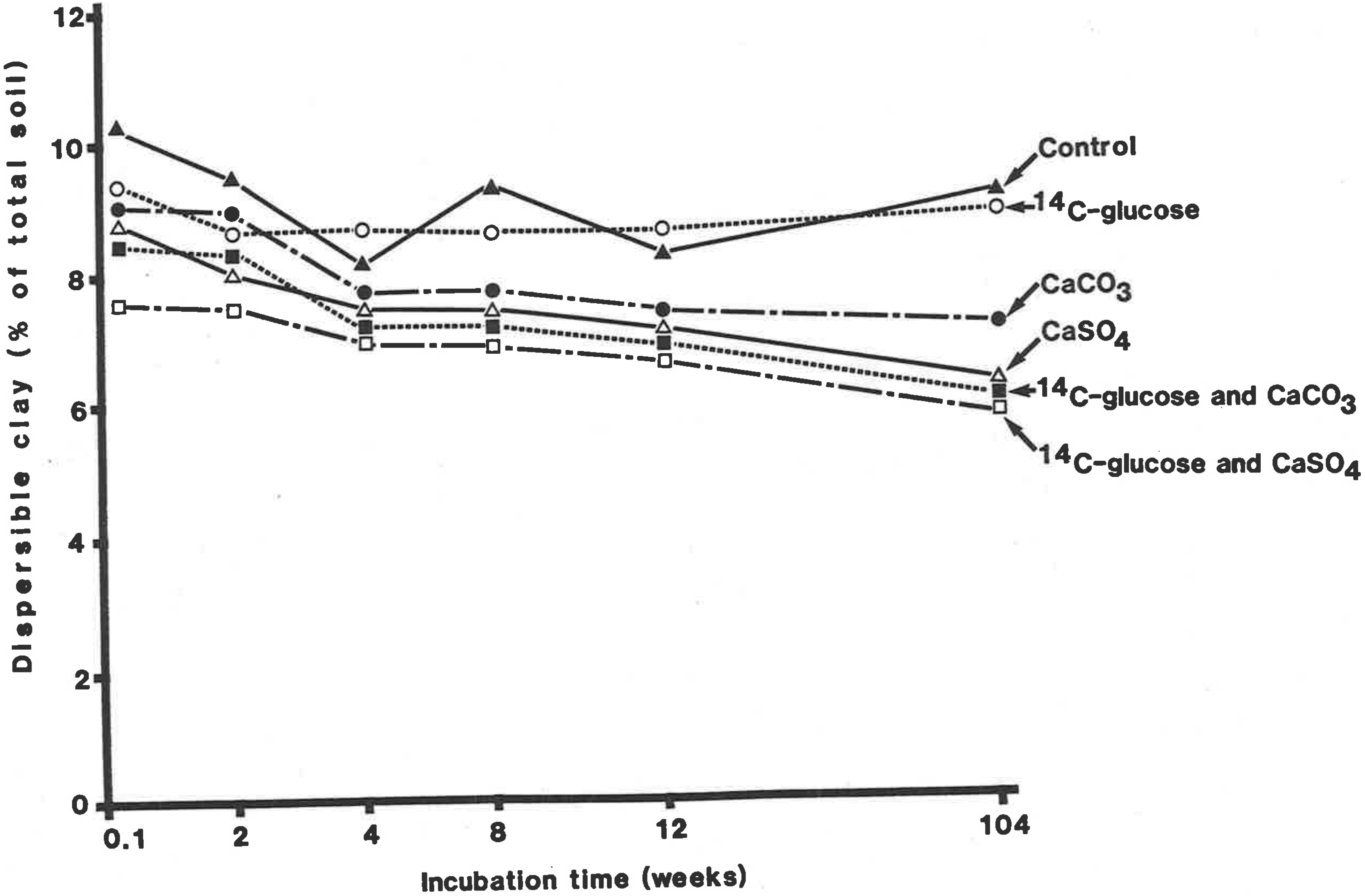


Fig. 27 Dispersible clay after the addition of ^{14}C-glucose, $CaCO_3$ and $CaSO_4$ in the soil

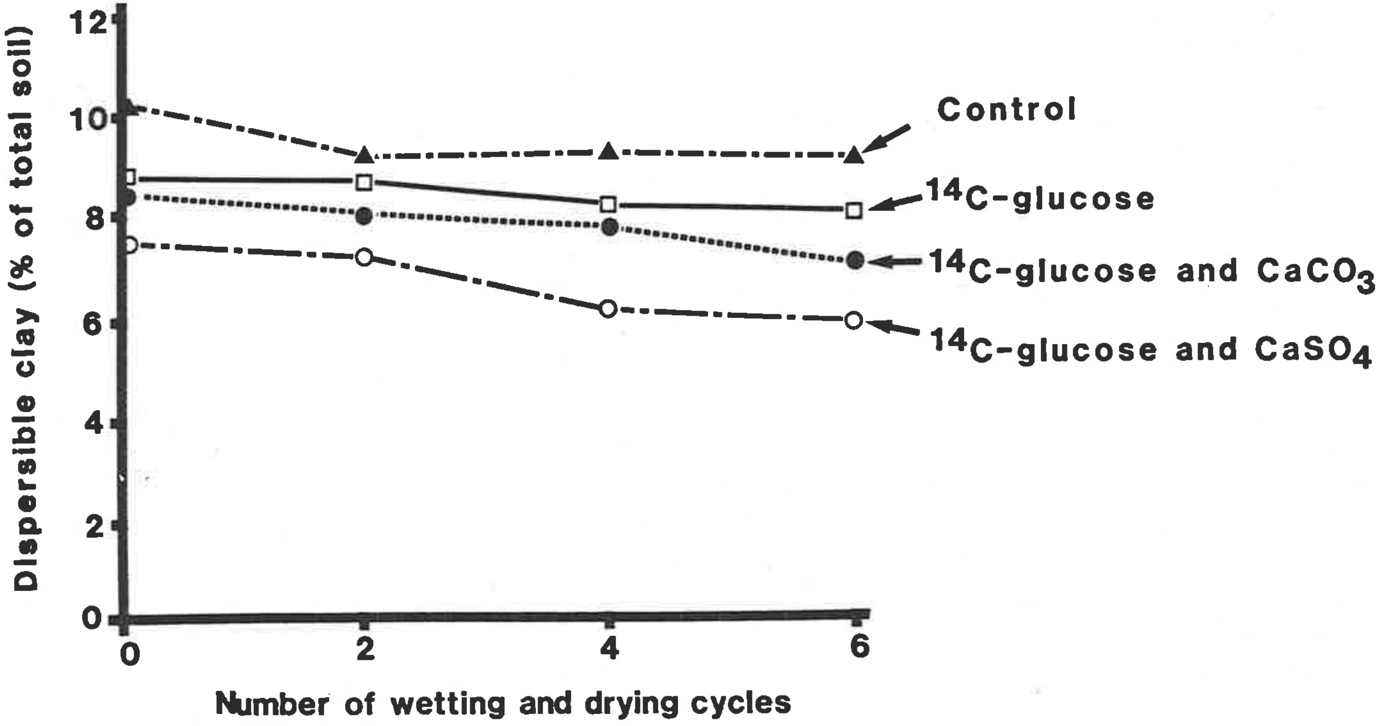


Fig.28 Influence of ^{14}C-glucose, $CaCO_3$ and $CaSO_4$ on dispersible clay of soils at different wetting and drying cycles

3.5 CONCLUSIONS

Both $CaCO_3$ and $CaSO_4$ reduced the loss of ^{14}C by mineralization of ^{14}C-labelled glucose. $CaSO_4$ was more efficient in preserving organic matter than $CaCO_3$, presumably due to the higher solubility of $CaSO_4$. Soluble Ca^{2+} inhibited the release of $^{14}CO_2$ and also conserved more residual ^{14}C from decomposition, presumably due to the interaction of Ca^{2+} with humic substances.

Application of $CaCO_3$ or $CaSO_4$ reduced dispersible clay, and stabilized particles 50-250 µm diameter range.

Incorporation of ^{14}C-glucose to the soil, with or without the addition of $CaCO_3$ or $CaSO_4$, increased the percentage of macroaggregates (1000-2000 µm diameter). Macroaggregates formed in the presence of glucose and calcium were stable for a longer time than aggregates formed in the presence of glucose only.

CHAPTER 4

THE ROLE OF CALCIUM AND ORGANIC MATTER ON THE STABILITY OF SOIL AGGREGATES

4.1 INTRODUCTION

Polysaccharides produced by the decomposition of organic materials can act as glues in soil aggregation. This mechanism has been reviewed by several authors (e.g. Swincer et al, 1968; Martin, 1971; Cheshire, 1979). The most convincing evidence that polysaccharides may function as glues in soil aggregates arose from the use of periodate as a selective oxidant for polysaccharides. Greenland et al. (1962) observed that the stability of aggregates from Red-brown earths was completely destroyed by periodate treatment, whereas the strength of surface crumbs from old grass land and from Rendzinas was reduced only slightly by periodate treatment. Clapp and Emerson (1965) observed that there was no effect of periodate oxidation on soils containing $CaCO_3$ unless preceded by pyrophosphate treatment. Tisdall and Oades (1980b) assessed the influence of periodate on aggregates with diameters upto 10 mm, and found that aggregates with diameters greater than 50 μm were unaffected by treatment with periodate. They also suggested that polysaccharides stabilize aggregates which are less than 50 μm in diameter, and also flocculate clay. Mehta et al. (1960) examined 2-4 mm aggregates and Webber (1965) > 250 μm aggregates, and both groups of workers found that periodate-sensitive materials were not responsible for stabilizing macroaggregates.

The stability of microaggregates is enhanced by multivalent cations, which act as bridges between organic colloids and clays. Edwards and Bremner (1967) suggested that macroaggregates (>250 μm diameter) consist of complexes of clay-polyvalent metal-organic matter (C—P—OM), where clay is bonded to humified organic matter through polyvalent metals.

The main evidence supporting the role of cation bridges has been based on increased disaggregation after treatment of soil with complexing agents, or often treatment with acids (e.g. Hamblin and Greenland , 1977). The complexing agent most commonly used has been pyrophosphate. Dilute sodium pyrophosphate solution disrupts clay particles bound together by an organic polymer bridged to the clay surface by polyvalent cations. Stefanson (1971) found that aggregates taken from a solonized brown soil exhibited a high level of stability after treatment with sodium periodate, however treatment with sodium pyrophosphate resulted in a complete loss of stability.

The results of chapter 2 and 3 demonstrated that organic matter was the major agent responsible for the stability of soil macroaggregates (>250 µm in diameter). In chapter 3, it was observed that macroaggregates formed in the presence of glucose and calcium were more stable than aggregates formed in the presence of glucose only, indicating that there was possibly an interaction between decomposition products of ^{14}C-glucose and soluble calcium, which may be responsible for the stability of soil aggregates. It was also observed that the addition of ^{14}C-glucose and calcium reduced the electrical conductivity of the soil solution, compared to the electrical conductivity obtained after the additon of $CaCO_3$ or $CaSO_4$ alone, suggesting that some of the Ca^{2+} was complexed by products of decomposition of glucose.

The following experiment was designed to investigate the effect of continued addition of glucose on the (a) water soluble and exchangeable calcium, (b) stability of soil aggregates after chemical treatments, and (c) extraction of organic matter from soils treated with or without calcium.

4.2 MATERIALS

A representative sample (0-10 cm) of the Urrbrae fine sandy loam (permanent pasture), a Red-brown earth was used. Soil properties are listed in chapter 3 (Table 16).

4.3 EXPERIMENTAL

4.3.1 Treatment

The following treatments were given to one hundred and eighty vials (100 cm^3

capacity) each containing 50 g soil (oven-dry equivalent). The vials were kept at a constant temperature of 20°C±1. All treatments were replicated three times.

Treatment No.	Number of vials	Treatment
1	18	Control (50g soil+ H_20)
2	18	$CaCO_3$ (50g soil+ 116 mg $CaCO_3$+ H_2O)
3	18	$CaSO_4 . 2H_2O$ (50g soil+ 200 mg $CaSO_4$+ H_2O)
4	18	Glucose (50g soil+glucose solution)
5	18	Glucose+$CaCO_3$ (50g soil+glucose solution + 116 mg $CaCO_3$)
6	18	Glucose+$CaSO_4 . 2H_2O$ (50g soil+glucose solution + 200 mg $CaSO_4 . 2H_2O$)

4.3.2 Application of glucose

10% Glucose solution (W/W) was prepared (i.e. $1cm^3$ of the solution contained 0.1g glucose). Initially 0.5g glucose (5 cm^3 glucose solution) was added to treatments 4, 5 and 6. The contents of the vials were mixed thoroughly. Appropriate amounts of distilled water were then added to each vial to bring the soils to 75% water holding capacity.

All treatments were subjected to two wetting and drying (W.D.) cycles per month, for 6 months. The vials became dry about every two weeks, and were rewetted each cycle with distilled water to bring the contents back to 75% water holding capacity. A further 5 cm^3 glucose solution was added at the end of 2, 4, 6, 8 and 10 WD cycles.

4.3.3 Application of $CaCO_3$ and $CaSO_4 . 2H_2O$

There was one application of calcium in the form of $CaCO_3$ and $CaSO_4.2H_2O$, calculated to give 1t ha^{-1} calcium.

4.3.4 Chemical Pre-treatment of Aggregates

Sodium chloride, sodium pyrophosphate and hydrochloric acid.

Air-dried soil (>4 mm ; 20 g) was immersed for 6 h in 120 cm^3 0.02 M NaCI, 0.1 M $Na_4P_2O_7$, pH 10 (Stefanson 1971). All solutions contained a crystal of thymol to inhibit biological activity. Similarly, soil aggregates were immersed for 1 h in 120 cm^3 0.1 M HCI or 0.02 M HCI. The soil was then drained for 2 h, and the size distribution of water-stable particles determined.

4.3.5 Extraction of organic matter from soil

Humic acid was extracted from soil by 0.5 M NaOH as described by Stevenson (1965). Duplicate samples were extracted by 0.5 M NaOH, after treatment with 1M HCl.

4.3.6 Water soluble, exchangeable and EDTA extractable Ca^{2+}

Soil (one gram)

↓

Water soluble calcium

Soil+100 cm^3 water. 2 h end over end shaking. Centrifuged at 3000 rpm for 1 h.

↓

Exchangeable calcium

Extracted with 1M NH_4Cl in 60% V/V ethanol and water at pH 8.5 (Heanes, 1981)

↓

EDTA calcium

The soil was extracted for 24 h on a gyrotary shaker at 200 rpm with 50 cm^3 0.05M NH_4 EDTA (pH 9.1). To minimize the contribution from clay minerals all extracts were centrifuged at 8000 rpm for 2 h prior to analysis. After destroying organic matter with alkaline hypobromite (Mitchell and Smith, 1974), extracts were analysed for calcium (McBride, et al., 1983).

4.4 RESULTS AND DISCUSSION

4.4.1 Effect of glucose, $CaCO_3$ and $CaSO_4.2H_2O$ on water stable aggregates

There was a marked increase in the percentage of water stable aggregates >2000 µm diameter after the addition of glucose or glucose+calcium to soil, however the histograms show clearly that soils treated with glucose+calcium had more water stable aggregates >2000 µm diameter than soil treated with glucose only (Fig. 29, 30, 31, 32, 33 and 34).

The addition of $CaCO_3$ and $CaSO_4$ significantly decreased the percentage of particles >250 µm diameter, with an accompanied increase of particles 50-250 µm. Both $CaCO_3$ and $CaSO_4$ also substantially decreased the proportion of the clay size particles.The results confirm the findings of chapter 2 and 3, that calcium was not implicated in macroaggregation, but in stabilizing particles 50-250 µm in diameter.

There are conflicting statements in the literature concerning the effects of $CaCO_3$ on soil structure, particularly aggregation. $CaCO_3$ is known to promote the breakdown of large aggregates, giving rise to more smaller aggregates, which are referred to as microaggregates (<250 µm in diameter) in this thesis. Both $CaCO_3$ and $CaSO_4$ are effective in stabilizing microaggregates (Rost and Rowles 1940; Peele 1936 and others). The results presented here confirm such observations.

The addition of glucose to soil increased the percentage of water stable aggregates due to increased microbial activity. The organic colloidal material, produced largely through microbial activity, together with clay is responsible for the stability of soil aggregates (Rost and Rowles, 1941; Kemper and Koch, 1966; Williams, 1971; Hamblin and Davis, 1977; Douglas and Goss, 1982; Chaney and Swift, 1984). Relatively high stability of soil macroaggregates (>2000 µm diameter) in soils treated with glucose+calcium is probably the result of microbial growth and production of metabolites from the decomposition of glucose complexed with calcium and clays. Soil aggregates formed in the presence of glucose and calcium were more stable than aggregates formed in presence of glucose only, as was also observed in chapter 3 (3.4.2.1 and 3.4.2.2).

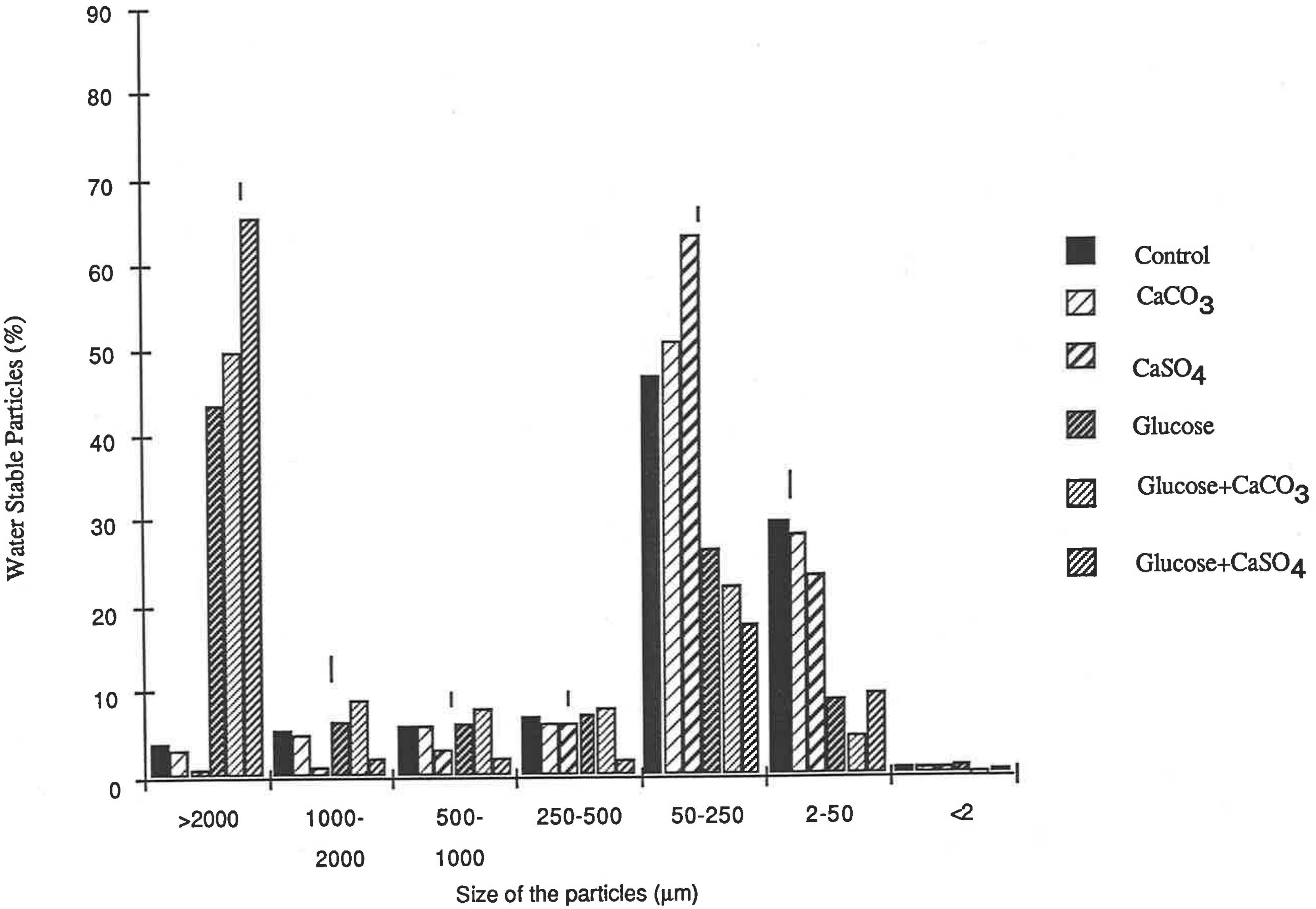


Fig. 29 The size distribution of water stable particles after the addition of 1% glucose in the soil. Vertical bar, $P<0.05$.

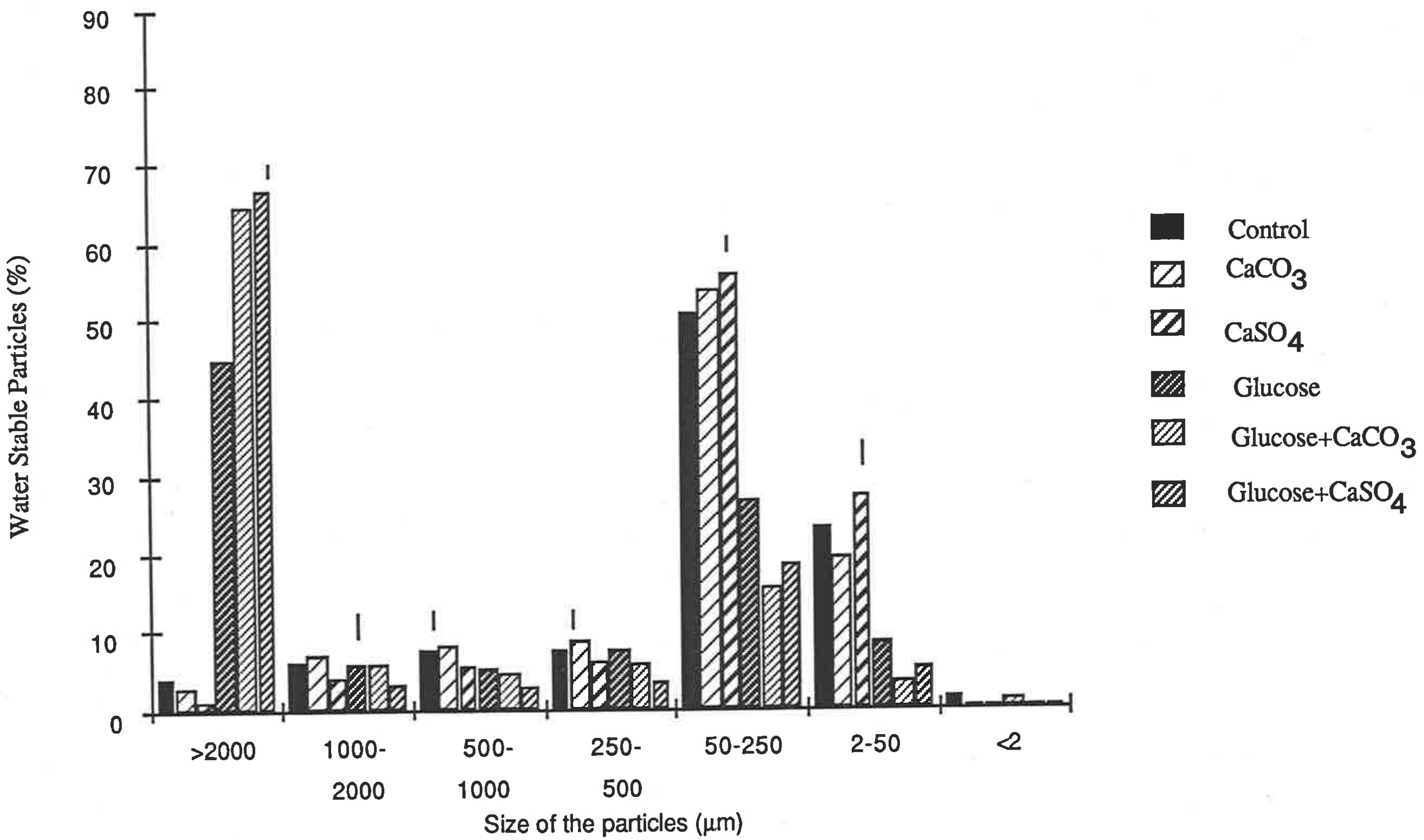


Fig. 30 The size distribution of water stable particles after the addition of 2% glucose in the soil. Vertical bar, $P<0.05$.

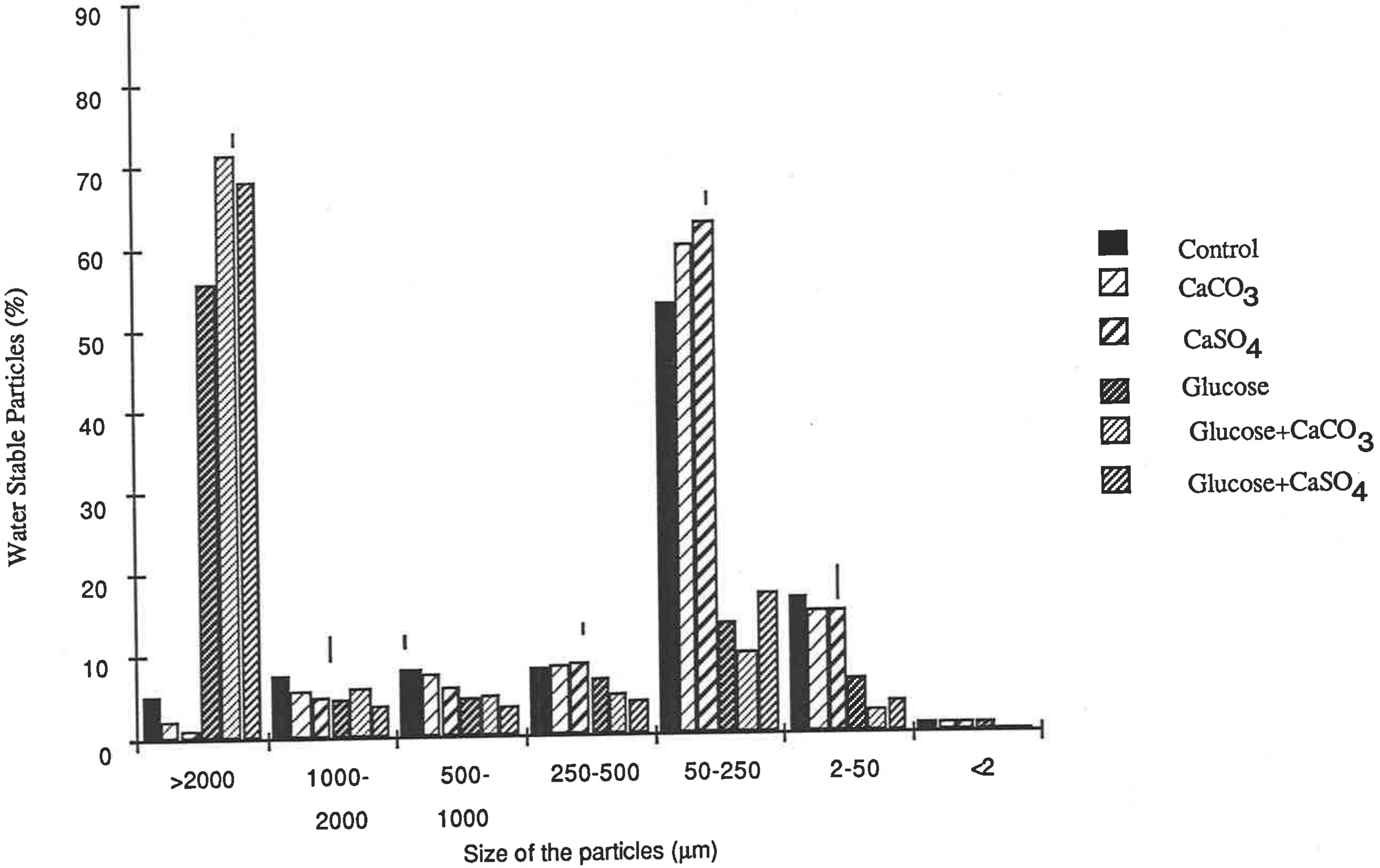


Fig. 31 The size distribution of water stable particles after the addition of 3% glucose in the soil. Vertical bar, $P<0.05$.

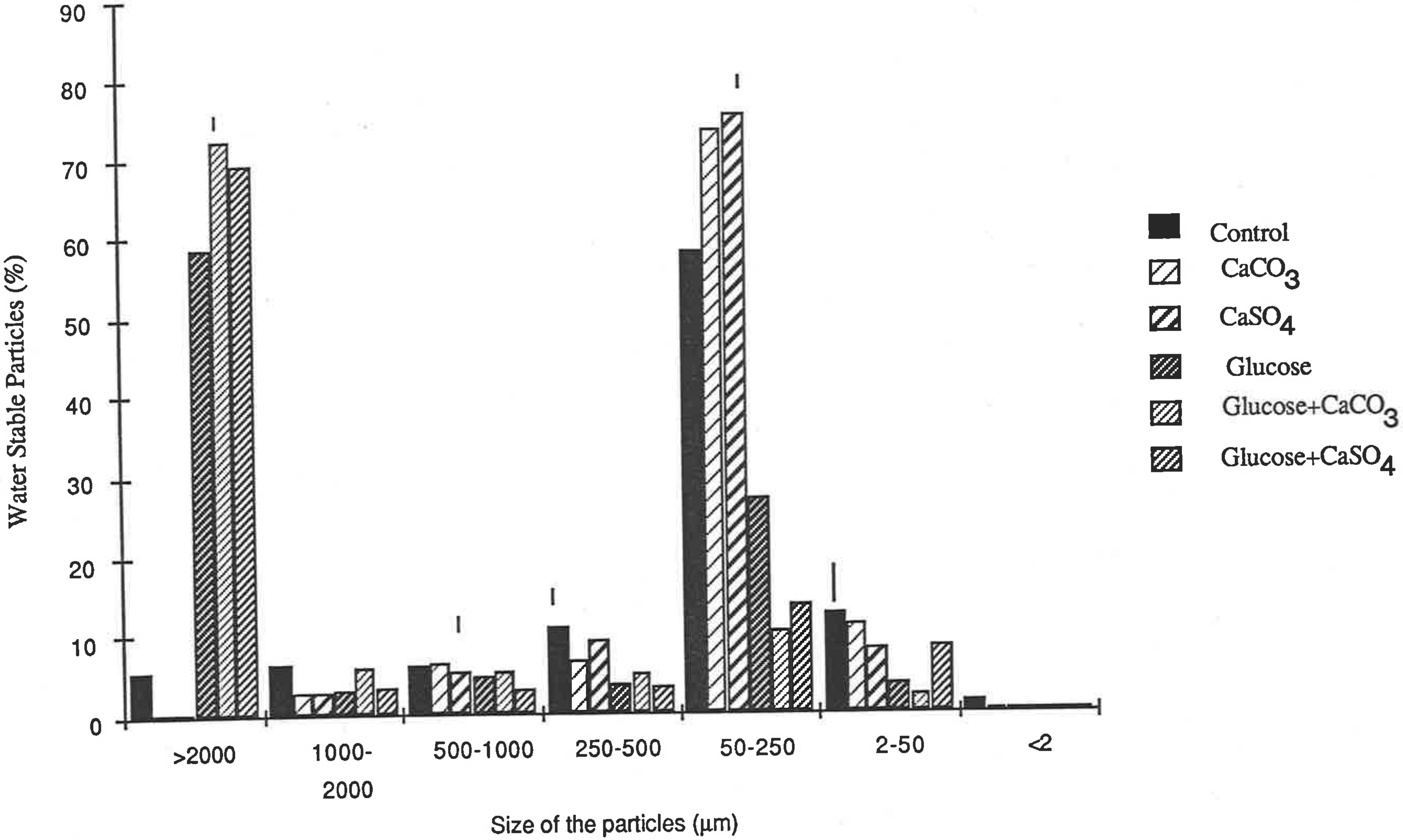


Fig. 32 The size distribution of water stable particles after the addition of 4% glucose in the soil. Vertical bar, $P<0.05$.

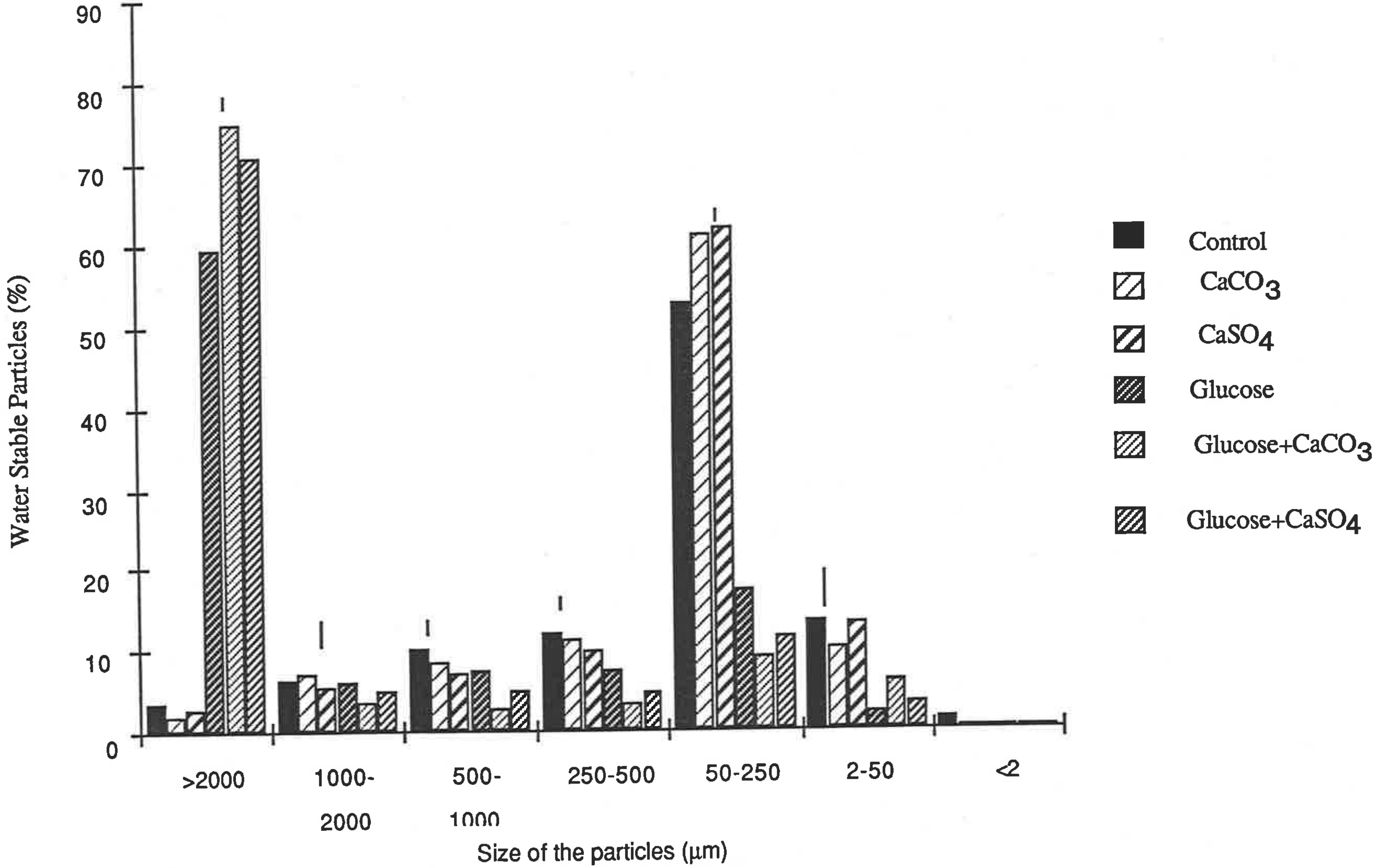


Fig.33 The size distribution of water stable particles after the addition of 5% glucose in the soil. Vertical bar, $P<0.05$.

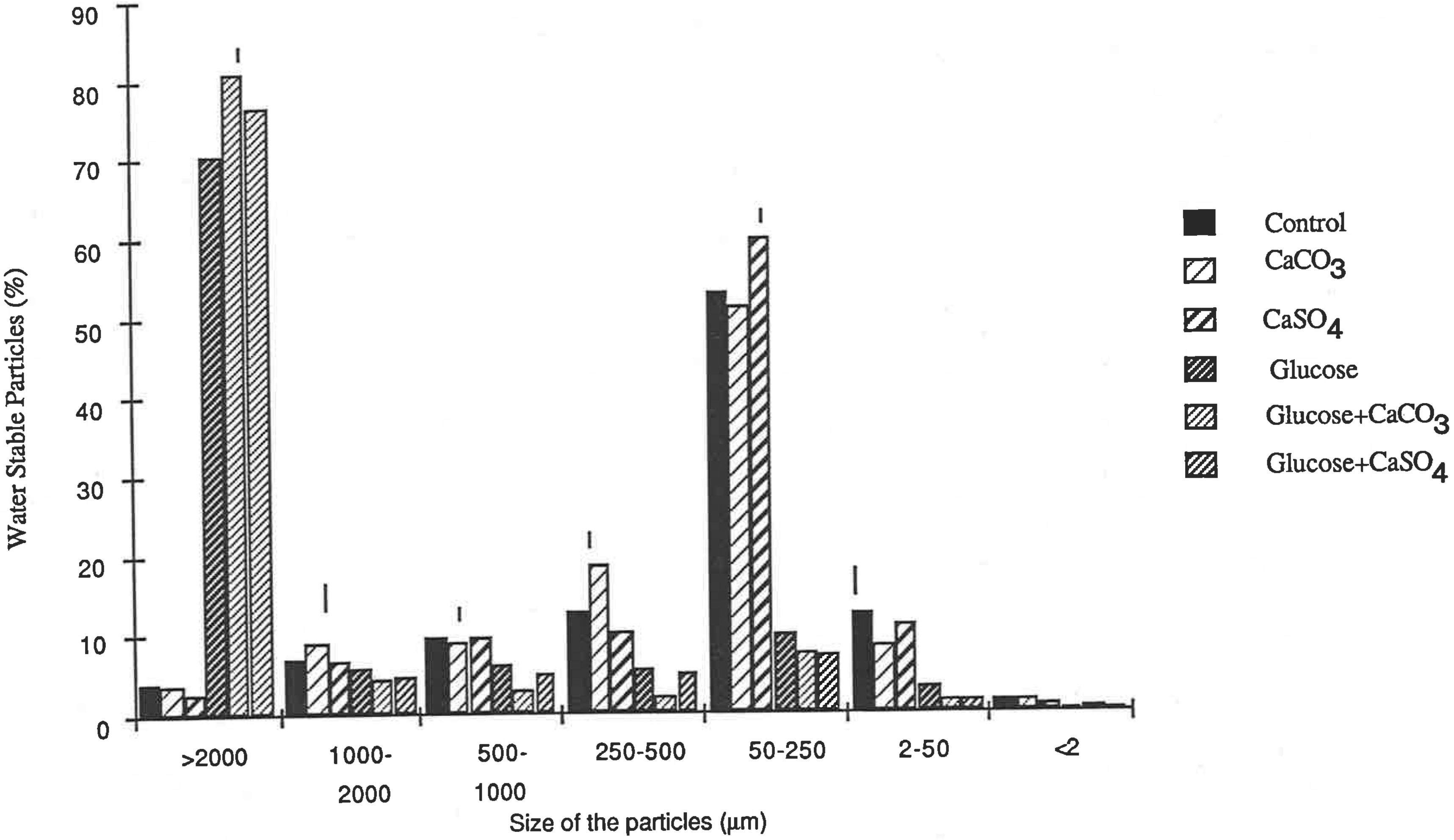


Fig. 34 The size distribution of water stable particles after the addition of 6% glucose in the soil. Vertical bar, $P<0.05$.

4.4.2 Determination of water stable aggregates after chemical treatments

After the addition of 6% glucose to soil, water stable soil aggregates were determined (after 12 W.D.cycles). This was followed by 0.02M NaCl. 0.1M $Na_4P_2O_7$, 0.02M HCl and 0.1M HCl treatments on soil aggregates of size <4.7 mm in diameter.

Treatment of soil aggregates with 0.1M $Na_4P_2O_7$, 0.02M HCl or 0.1M HCl decreased the number of particles >250 µm diameter, with an accompanied increase of particles <250µm diameter. After each treatment, the soils to which glucose+calcium were added contained more water stable macroaggregates (>2000 µm diameter), when compared to soils to which a single treatment of glucose or calcium were applied (Fig. 35,36, and 37).

Comparison of treatments with 0.1M $Na_4P_2O_7$, 0.02M HCl and 0.1M HCl (on the basis of effectiveness in reduction of the stability of macroaggregates) on the stability of soil aggregates showed a decreasing order of efficiency 0.1M HCl > 0.02M HCl > 0.1M $Na_4P_2O_7$.

Disruption of soil aggregates from pyrophosphate treatment was less than the 0.1M HCl treatment, indicating that pyrophosphate resistant stabilizing materials were present in the soil. The results presented here confirm the findings in chapter 2, that soil aggregates in calcareous soils were stabilized by materials not extracted by pyrophosphate (2.3.6). Pyrophosphate has been used to disrupt clay particles bound together by organic polymers bridged to the clay surfaces by polyvalent cations. Significant decreases in the percentages of soil aggregates (>2000 µm diameter) by 0.1M HCl treatment was probably due to partial breakdown of cation bridges, by removing Ca^{2+} bridging the soil minerals and organic polymers.

4.4.3 Dispersible clay

Treatments involving gypsum were more efficient than others in reducing dispersible clay (Fig.38). This is probably due to the greater solubility of $CaSO_4.2H_2O$ giving a higher electrolyte concentration (Table 20). When $CaCO_3$ or $CaSO_4.2H_2O$ reduced clay dispersion, the addition of glucose increased dispersible clay. The result is in accord with the findings of Gupta et al. (1984), who suggested that when $CaCO_3$ reduced clay dispersion, additions of organic matter enhanced dispersible clay.

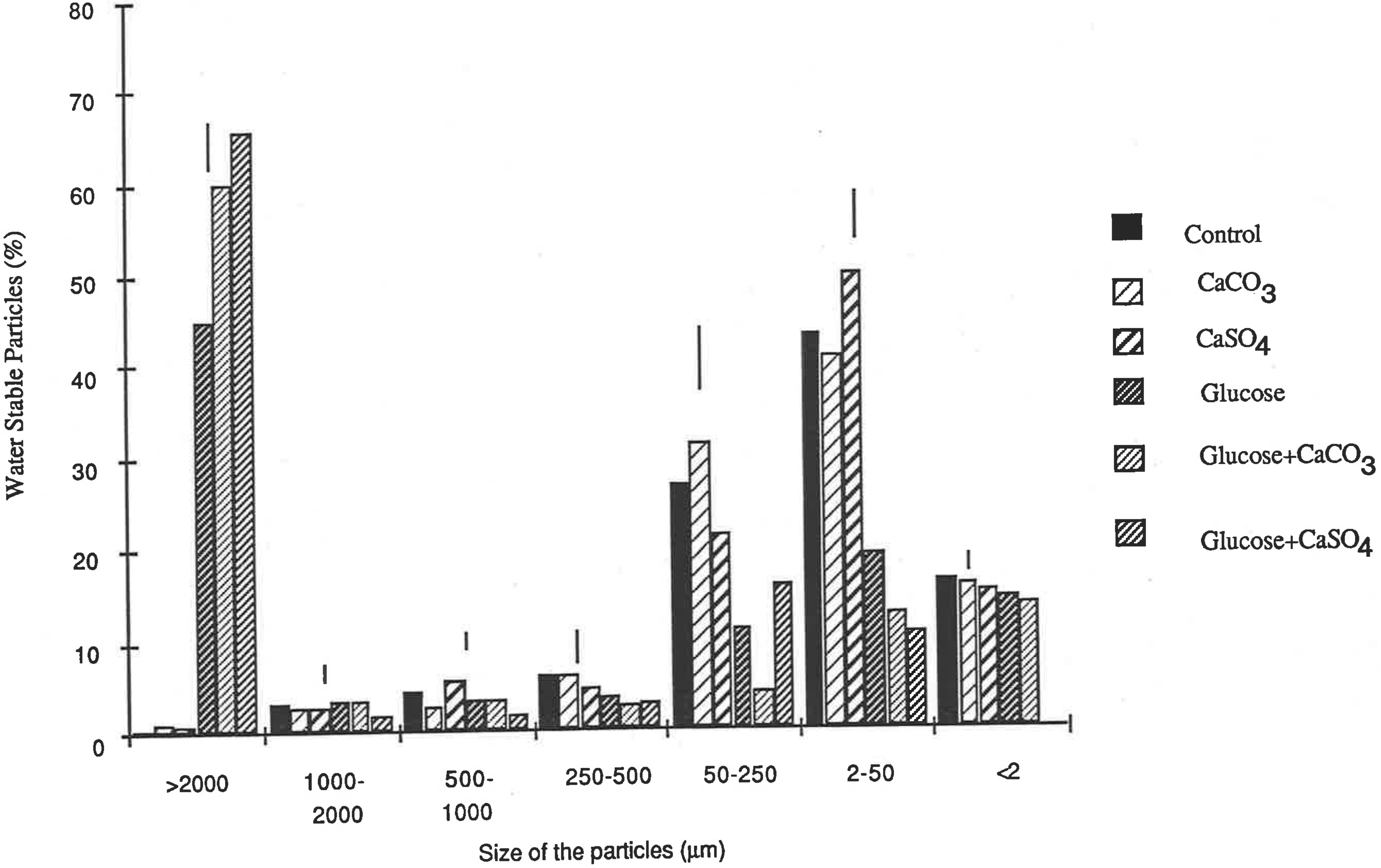


Fig. 35 The size distribution of water stable particles of soil after 0.1M $Na_4P_2O_7$ treatment. Vertical bar, $P<0.05$.

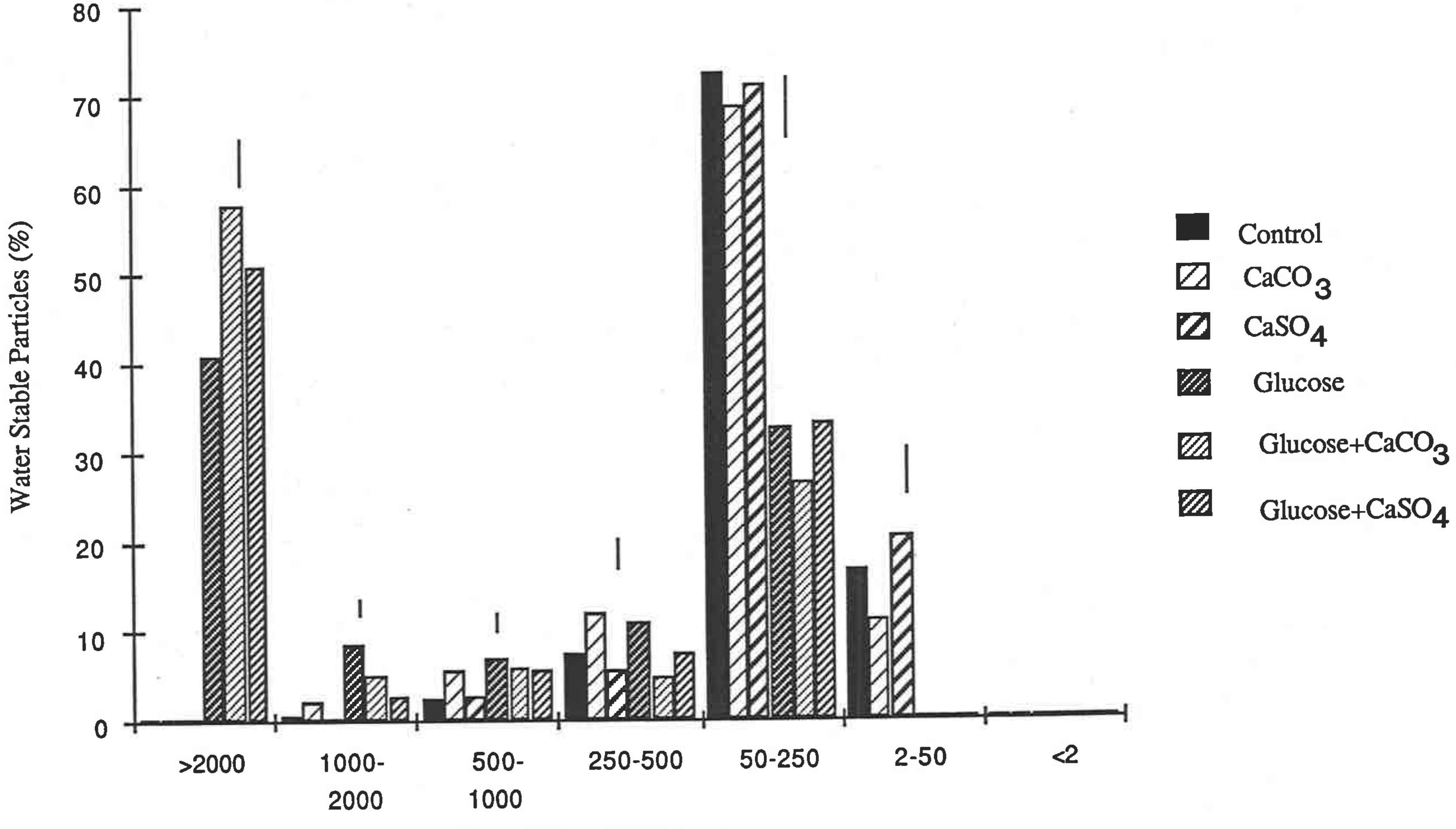
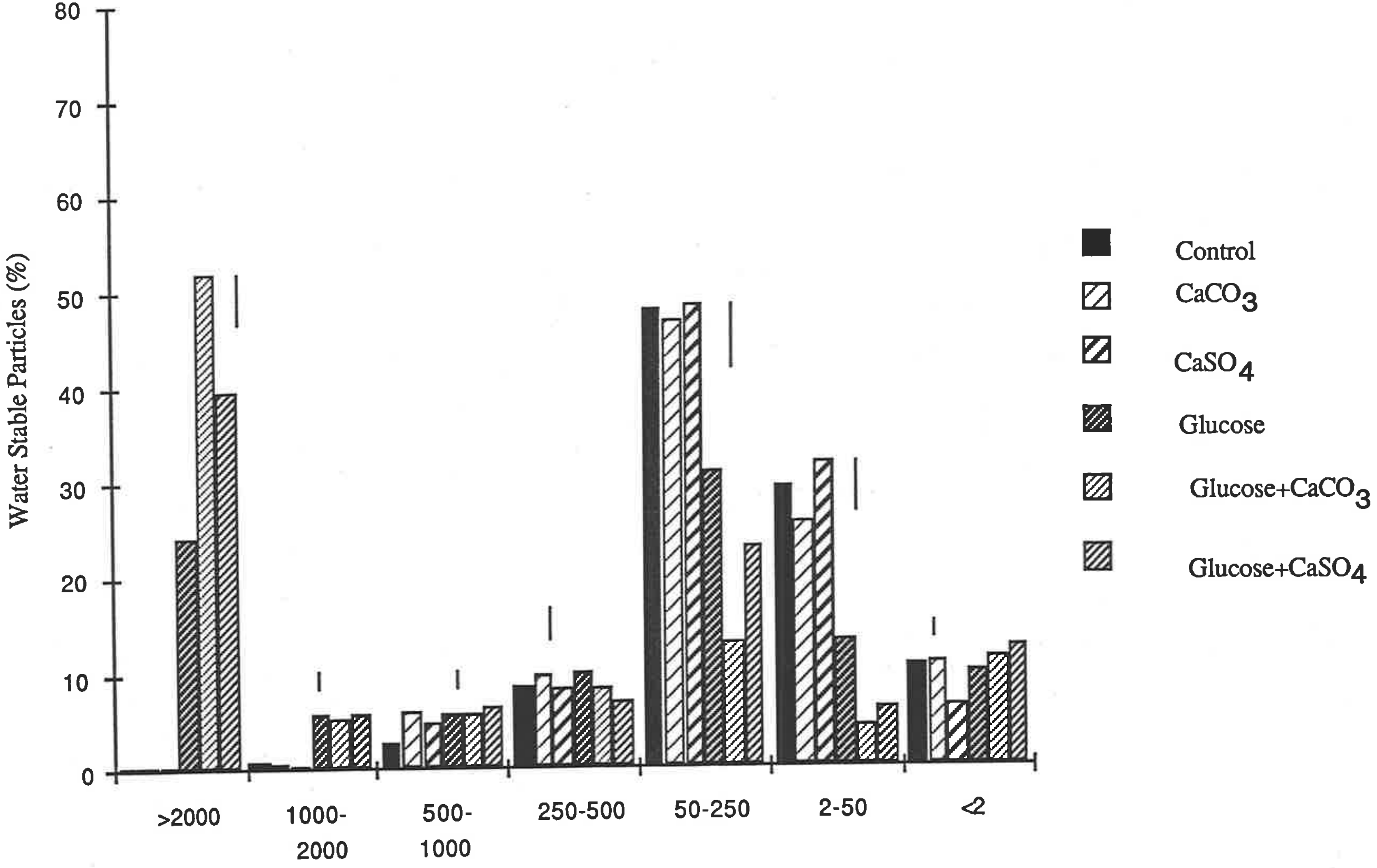


Fig. 36 The size distribution of water stable particles of soil after 0.02M HCl treatment. Vertical bar, $P<0.05$.



Size of the particles (µm)

Fig. 37 The size distribution of water stable particles of soil after 0.1M HCl treatment. Vertical bar, $P<0.05$.

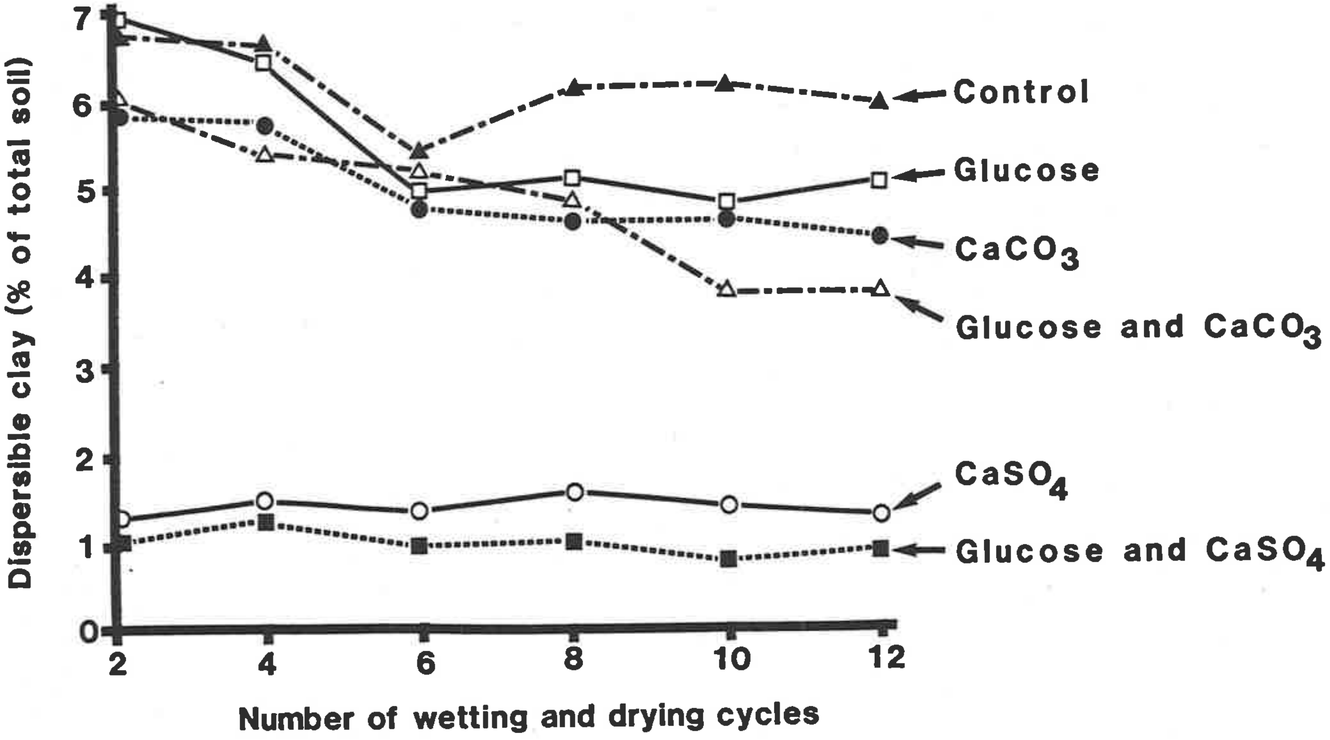


Fig. 38 Influence of glucose, $CaSO_4$ and $CaCO_3$ on dispersible clay of soils at different wetting and drying cycles

4.4.4 Water soluble, exchangeable and EDTA extractable calcium after the addition of glucose, $CaCO_3$ and $CaSO_4.2H_2O$ to the soil.

The electrical conductivity of soils was reduced after the addition of glucose+calcium when compared to soils to which only calcium was added (Table 21). The reduction of electrical conductivity was small after the initial addition of glucose, but gradually decreased with each subsequent addition of glucose. This indicates that some of the soluble calcium became insoluble by complexing with decomposition products from glucose.

The above findings were confirmed by determining water soluble, exchangeable and EDTA extractable calcium. The results in Table 22, show that the water soluble, exchangeable and EDTA extractable calcium were lower in soils treated with glucose+calcium compared to soils treated with calcium only.

4.4.5 Extraction of organic matter from soil

Humic acid was extracted after the addition of 6% glucose to soil (after 10 W.D. cycles). Humic acid extracted from soil by 0.5M NaOH was less in soils to which calcium was added (Fig.39). There was about 18% less humic acid in calcium treated soils compared to the control. Similarly 12% less humic acid was extracted in soils treated with glucose+calcium compared to soil treated with glucose only.

Acid pretreatment of soil increased the efficiency of extraction of humic acid by about 32% in soil treated with glucose and 55% in soils treated with calcium or glucose+calcium.

The presence of Ca in the form of $CaCO_3$ or $CaSO_4$ reduced the efficiency of humic acid extraction by NaOH. As a general rule, extraction of soil with 0.1 or 0.5M NaOH leads to the recovery of approximately two-thirds of the soil organic matter. However in many soils, calcium and other polyvalent cations are responsible for maintaining organic matter in a flocculated and insoluble condition. Oades (1987) suggested that when humic polymers are saturated with polyvalent cations, they shrink due to association of ionisable groups and cross linking of polymers by interaction of functional groups and polyvalent cations. This corss-linking results in smaller, denser and more rigid molecules. It was indicated that such molecules would be more stable to both chemical and biological attack. Leaching of the soil

Table 21. Soil pH and electrical conductivity after the addition of glucose and calcium to soil (1:5 woil/water suspension)

	Glucose added (%)					
	1	2	3	4	5	6
Treatment	**Electrical conductivity (µS cm^{-1})**					
Control	135	180	180	220	240	200
$CaCO_3$	180	200	200	270	300	300
$CaSO_4.2H_2O$	950	1100	1000	1000	1100	1200
Glucose	85	80	70	80	75	80
Glucose+$CaCO_3$	130	125	110	115	120	120
Glucose+$CaSO_4.2H_2O$	900	950	1000	900	900	1000
	pH					
Control	5.6	5.2	5.3	5.2	5.3	5.1
$CaCO_3$	6.8	6.6	6.7	6.5	6.5	6.3
$CaSO_4.2H_2O$	5.1	5.0	5.1	5.0	5.0	4.9
Glucose	5.9	6.0	6.0	5.9	6.1	5.9
Glucose+$CaCO_3$	7.0	6.9	6.9	6.8	6.8	6.6
Glucose+$CaSO_4.2H_2O$	5.5	5.4	5.4	5.4	5.4	5.2

Table 22. CALCIUM EXTRACTED BY WATER, SALT AND A COMPLEXING AGENT

Glucose added (%)	Treatment 1 Control	 2 Glucose	 3 $CaCO_3$	 4 Glucose+$CaCO_3$	 5 $CaSO_4$	 6 Glucose+$CaSO_4$
WATER SOLUBLE Ca^{2+} ($C\ g^{-1}$)						
1	0.08	0.08	0.13	0.12	1.25	1.10
2	0.10	0.08	0.15	0.13	1.23	1.00
3	0.10	0.08	0.15	0.13	1.20	1.00
4	0.13	0.08	0.20	0.14	1.10	1.00
5	0.13	0.08	0.25	0.14	1.23	1.00
6	0.13	0.08	0.25	0.14	1.18	1.00
EXCHANGEABLE Ca^{2+} ($C\ g^{-1}$)						
1	1.45	1.45	2.45	1.75	2.35	1.65
2	1.45	1.45	2.30	1.65	2.30	1.70
3	1.40	1.45	2.35	1.65	2.25	1.85
4	1.35	1.50	2.25	1.65	2.40	1.95
5	1.40	1.50	2.25	1.60	2.20	1.75
6	1.40	1.50	2.25	1.60	2.20	1.70
EDTA EXTRACTABLE Ca^{2+} ($C\ g^{-1}$)						
1	0.79	0.95	1.11	1.00	1.35	1.06
2	0.83	0.96	1.18	0.93	1.30	1.04
3	0.83	1.03	1.32	0.84	1.33	1.03
4	0.70	0.76	0.79	0.71	1.08	0.79
5	0.71	0.90	0.94	0.70	1.10	0.81
6	0.71	0.95	0.94	0.71	1.10	0.86

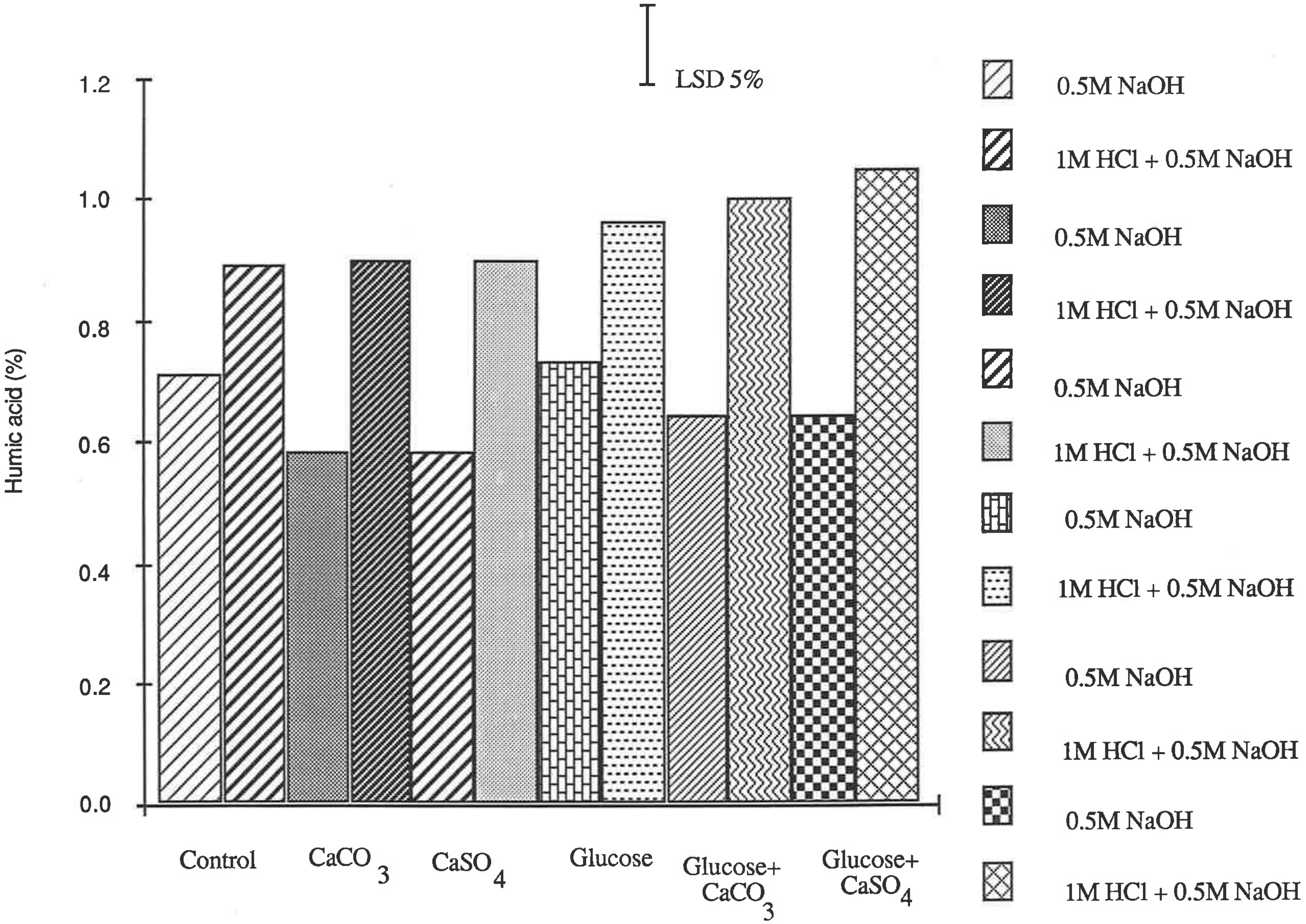


Fig.39 Extraction of organic matter from soil before and after treatment with 1M HCl.

with dilute HCl, which removes Ca and other polyvalent cations, increases the efficiency of extraction of organic matter with alkaline reagents.

Equal amounts of glucose were added to soils treated with glucose with or without calcium. However, the amount of humic acid extracted from the soil treated with glucose+calcium was about 23% more than the soils treated with glucose only. The results confirm the findings in chapter 3, that mineralization of glucose is reduced in the presence of calcium (3.3.1.1).

4.5 CONCLUSIONS

Application of $CaCO_3$ and $CaSO_4.2H_2O$ decreased the proportion of particles >250 µm diameter, with an accompanied increase in the proportion of particles of 50-250 µm diameter.

Organic matter was the main binding agent of soil macroaggregates (>250 µm diameter), but there was an additive effect of calcium. The stability of soil macroaggregates in the presence of calcium and glucose probably originates from complexes of clay—Ca^{2+}—organic matter, where clay is bonded to humified organic matter through Ca^{2+}.

Macroaggregates formed in the presence of glucose (with or without calcium) were little affected by pyrophosphate treatment, indicating that soil aggregates >250 µm diameter contained pyrophosphate resistant material.

The addition of glucose to soil decreased the water soluble, exchangeable and EDTA extractable calcium. This indicates that soluble calcium was complexed by products of glucose decomposition and are strongly held by the soil.

Calcium inhibited the extraction of humic acid by NaOH. However acid pretreatment increased the efficiency of extraction of organic matter with NaOH, indicating the involvement of Ca^{2+} in cation bridges.

Equal amounts of glucose were added to soils with or without added calcium. The amount of humic acid extracted from soil by NaOH after acid treatment was higher in soils treated with glucose+calcium compared to soil treated with glucose only, indicating that calcium was involved in protecting recently formed organic materials in the soil.

CHAPTER 5

THE ROLE OF CALCIUM ON THE DECOMPOSITION OF ^{14}C-LABELLED PLANT MATERIAL AND SOIL AGGREGATE STABILITY IN THE FIELD

5.1 INTRODUCTION

The beneficial influence of organic matter on soil physical properties has been known for a long time. Incorporation of straw increases soil organic matter contents (Rasmussen et al., 1980; Hooker et al., 1982), and also increases both microbial polysaccharide levels and aggregate stabililty (Martin, 1942; Mehta et al., 1960: Lynch and Elliott, 1983; Acton et al., 1963; Dormaar et al., 1979). The favourable effect of plant residues on aggregates is usually ascribed to an enhanced growth of actinomycete and fungal mycelium, and to the production of microbial metabolites. The role of microorganisms in the transformation of organic matter in soil is a crucial one, and the rates of turnover and mineralization of organic substrates are largely governed by the activity of the soil biomass. Inhibition of microbial activity by low or high temperature, drought, waterlogging or extremes of pH may result in the persistence in the soil of potentially decomposable and mineralizable compounds, with subsequent effects on fertility, nutrient cycling and soil structure.

Tisdall and Oades (1982) demonstrated that the water-stability of macroaggregates depends largely on roots and hyphae, and thus on growing root systems. Numbers of stable macroaggregates declined with the loss of organic matter as the roots and hyphae decomposed and were not replaced. Tisdall and Oades (1982) suggested that three main groups of organic binding agents are involved in stabilizing aggregates, based on the age and degradation of the organic matter. These binding agents are considered as transient, temporary and persist~~a~~nt. Persistent binding agents consist of degraded, aromatic humic material in association with amorphous iron, aluminium and aluminosilicates and polyvalent metal cations. The metal ions act as a bridge between clay-organic matter and organic matter-organic matter (Edwards and Bremner, 1967).

Laboratory experiments demonstrated that calcium reduced the mineralization of ^{14}C-glucose (chapter 3). It was also observed that soil macroaggregates formed in presence of organic matter and calcium were more stable both physically and chemically than the aggregates stabilized by organic matter only (chapter 3 and 4). An experiment was designed to determine whether these phenomena occur in the field.

5.2 MATERIALS

The field experiment was conducted in a paddock at the Waite Agricultural Research Institute (permanent rotation trial). The soil was a Red-brown earth of the Urrbrae fine sandy loam series. Some properties of the soil are listed in Table 23.

5.3 EXPERIMENTAL

5.3.1 Treatment

Open plastic tubes (40 cm long x 8 cm dia.) were pushed into the ground to 35 cm. The leading edge of the tubes were offset to minimise compaction of the soil during installation. Field moist soil was removed from the cylinders (0-8 cm), and pooled for mixing with pre-weighed, ^{14}C-labelled wheat straw and calcium compounds.

Calcium in the form of $CaCO_3$ and $CaSO_4$. $2H_2O$ was applied at the rate of 1 t ha^{-1}. Plant material [<0.5 cm. length, uniformly labelled ^{14}C wheat straw "L" (29.4 μc ^{14}C/g C) supplied by Landwirtschaftlich-Chemische, Bundesversuchsanstalt in wien, Austria] was applied at the rate of 2.5 t ha^{-1}.

Plant material (with or without calcium compounds) was thoroughly mixed with field moist soil. The amended soils were then returned to the cylinders, and the soil surfaces tamped gently. Treatments were placed according to a randomized design, and all treatments were replicated four times.

Table 23. Properties of the (0-10 cm) Urrbrae f.s.l. (permanent rotation trial)

pH (1:5, soil/water ratio)	5.6
E.C.μS cm^{-1} (1:5, soil/water ratio)	90
$CaCO_3$ (%)	Not present
Organic carbon (%)	1.75
Cation-exchange capacity(Cg^{-1})*	6.00
Exchangeable Na (Cg^{-1})	0.43
Exchangeable K (Cg^{-1})	1.50
Exchangeable Mg (Cg^{-1})	0.65
Exchangeable Ca (Cg^{-1})	4.62
Water holding capacity (%W/W)	32%
Clay (%)	17.8
Silt (%)	32.0
Fine sand (%)	47.6
Coarse sand (%)	2.6
Clay mineralogy	Kaolinite and illite

---

*C = Coulomb = 6.2 x 10^{18} electron charges

(1 C g^{-1} = 1 meq 100 g^{-1} approx)

Treatment No	Treatment
1	Control
2	$CaCO_3$ (2.3 t h^{-1})
3	$CaSO_4$. $2H_2O$ (5.0 t h^{-1})
4	^{14}C-labelled wheat straw (2.5 t h^{-1})
5	^{14}C-labelled wheat straw + $CaCO_3$ (2.5 t h^{-1}wheat straw +2.3 t $h^{-1}$$CaCO_3$)
6	^{14}C-labelled wheat straw +$CaSO_4.2H_2O$ (2.5 t h^{-1} wheat straw + 5.0 t h^{-1} $CaSO_4.2H_2O$)

5.3.2 Sampling and analysis of soils containing ^{14}C-wheat straw

Throughout the 8 month experiment, the soil within the tubes was maintained free of vegetation. After 1, 2, 4, 8, 16 and 32 weeks, four cylinders from each treatment were selected at random from the site grids, removed and sawn into lengths. The soil from 0-8 cm depth was removed and weighed moist, mixed thoroughly, and subsampled.

5.3.3 Residual ^{14}C

Residual ^{14}C was determined on ground, air-dried subsamples (as described in chapter two).

5.3.4 Biomass ^{14}C

Biomass- ^{14}C in the soil (0-8 cm) was determined by chloroform fumigation (Jenkinson and Powlson,1976) using soil samples within two hours after collection. Four portions of soil, each containing 30 g, were taken from each sample and placed in 100 cm^3 glass beakers; two portions were then fumigated with $CHCl_3$ and two left unfumigated. The $CHCl_3$ was purified by shaking the Analar-grade (containing ethanol as stabilizer) three times with 5% concentrated H_2SO_4. The $CHCl_3$ was then washed five times with water, dried over anhydrous K_2CO_3 and redistilled. The purified reagent was stored over anhydrous K_2CO_3 in the dark. Replicate portions of soil were taken for dry matter determinations and measurement of water holding capacity.

The fumigations were performed in large desiccators (30.5 cm dia.) lined with moist paper. Each desiccator contained a beaker with 50 cm^3 of alcohol-free $CHCl_3$, and a few anti-bumping granules. The desiccator was evacuated until the $CHCl_3$ boiled vigorously, the tap closed and the desiccator then left in the dark at 20°C for 18-24 h. The beaker of $CHCl_3$ and the paper were then removed, and $CHCl_3$ vapour extracted from the soil by repeated evacuation in the desiccator. Eight 3-min evacuations, three with a water pump, followed by five with a high vacuum oil pump, were applied. Each portion of fumigated soil was inoculated with 0.3 g of untreated air-dry soil and mixed with a spatula. The unfumigated portions of soil were not inoculated. While fumigation was in progress, the unfumigated controls were kept at 20°C in desiccators lined with moist paper.

5.3.5 Incubation procedure and analytical methods

The portions of soil were incubated for 10 days at 20°C, and the CO_2 evolution was measured. The unfumigated soils were incubated for an additional 10-day period. Each beaker of soil was placed in a wide-neck (8 cm dia.) screw-top glass confectionary jar (volume 1000 cm^3), together with 25 cm^3 of 1M NaOH in a glass vial to absorb CO_2. The jar also contained 5 cm^3 of distilled water to offset the drying effect of the alkali. Blank incubations, in which the jar contained water and alkali but no soil, were included in each experiment. The volume of the jar was sufficient to ensure that there was adequate O_2 for the whole incubation. Total CO_2 released was determined by titration (Tinsley et al., 1951), and $^{14}CO_2$ was determined by liquid scintillation counting (Adu and Oades, 1978). Soil biomass (B) was calculated from the expression $B = (X-y)/k$, where X is the CO_2-C evolved by fumigated soil over the period 0-10 days and y the CO_2-C evolved by unfumigated soil over the 10-20 days period. For mixed populations of organisms in soils, k was taken to be 0.45 (Jenkinson, 1976).

5.4 RESULTS AND DISCUSSION

5.4.1 *Residual ^{14}C in soil*

The results of the decomposition of ^{14}C-wheat straw (with or without calcium compounds) are shown in Fig. 40. Eight weeks after incorporation of plant material, more than 50% of the ^{14}C of the original input was lost from soil as $^{14}CO_2$ in all the treatments. There was no significant effect of treatments on the decomposition of ^{14}C-wheat straw at week one and two. However after two weeks, the treatment containing ^{14}C-wheat straw +$CaSO_4$ had significantly more residual ^{14}C than other treatments ($P< 0.05$). The treatment containing ^{14}C-wheat straw+$CaCO_3$ did not conserve as much organic matter as the treatment containing ^{14}C-wheat straw +$CaSO_4$, but accumulated relatively more organic matter than the treatment containing ^{14}C-wheat straw only. After 32 weeks decomposition of ^{14}C-wheat straw, the residual ^{14}C in soil treated with ^{14}C-wheat straw+$CaSO_4$, ^{14}C-wheat straw+$CaCO_3$ and ^{14}C-wheat straw was 33%, 31% and 28% respectively.

After one week of incorporation of plant material, there was less residual ^{14}C in the soil treated with ^{14}C-wheat straw+$CaCO_3$ compared to the soil treated with ^{14}C-wheat straw, however subsequently $CaCO_3$ increased the residual ^{14}C in the soil. These results suggested that the stimulating effect of $CaCO_3$ on the decomposition of ^{14}C-wheat straw is transient (which may arise due to pH, Table 24) and subsequently $CaCO_3$ stabilized decomposition products of ^{14}C-wheat straw. These results are in accord with the findings in chapter 3, that the application of $CaCO_3$ to soil enhanced the release of $^{14}CO_2$ in the early stage of incubation of ^{14}C-glucose , but subsequent $^{14}CO_2$ production was progressively suppressed.

It seems that there are two probable mechanisms which can explain the accumulation of organic matter in similar soil and climatic conditions.

(i) cation bridges: Humic materials consist of a variety of functional groups including COOH, phenolic $^{-}$OH, enolic $^{-}$OH, quinone, hydroxyquinone, lactone, ether and alcoholic $^{-}$OH (Stevenson, 1982). Humic materials mainly carry negative charges, arising from exposed —COOH and —OH groups, from which at least part of the hydrogen may be replaced by cation exchange. Negatively charged organic species are normally repelled by the negatively

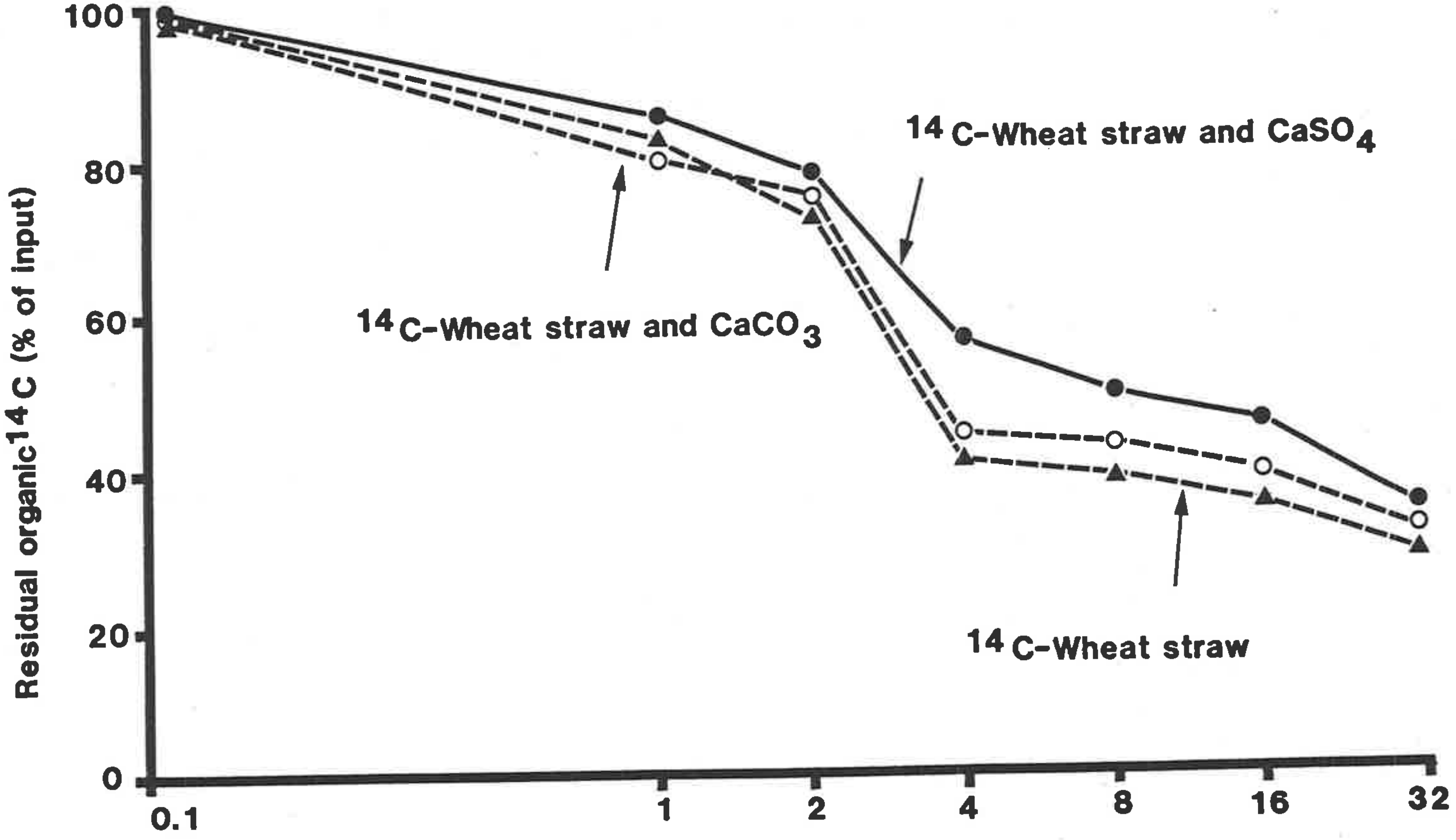


Fig. 40 Decomposition of ^{14}C-labelled wheat straw

Table 24 . Soil pH during the decomposition of ^{14}C-wheat straw , with or without calcium compounds (1: 5, soil/water ratio)

		Time of decomposition (week)					
Treatment No.	Treatment	1	2	4	8	16	32
1	Control	5.6	5.6	5.5	5.6	5.5	5.5
2	$CaCO_3$	6.9	6.9	6.5	6.4	6.0	6.0
3	$CaSO_4.2H_2O$	4.7	4.7	4.6	4.7	4.5	4.8
4	^{14}C-wheat straw	5.5	5.2	5.5	5.5	4.8	4.7
5	^{14}C-wheat straw + $CaCO_3$	7.0	7.0	6.5	6.5	5.9	5.9
6	^{14}C-wheat straw +$CaSO_4.2H_2O$	4.9	4.9	4.9	4.9	4.6	4.8

charged clay, with little or no adsorption. Binding of organic anions by clay is possible when a polyvalent cation is present on the exchange complex, in which case the cation neutralizes the negative charge on the clay, as well as the acidic group of the organic molecules to form a salt bridge (Clay—M—OOCR). It was suggested that both particulate and colloidal organic matter can undergo physical stabilization in the soil environment by association with many types of minerals and polyvalent cations (Cheshire et al., 1977), such as adsorption of polysaccharides onto clay surfaces and the formation of polysaccharide-metal complexes (Swincer et al., 1969: Martin and Haider, 1971; Martin et al., 1974).

(ii) In addition to cation bridges, organic matter can also accumulate in soil when it is present inside the soil aggregates where microorganisms do not have an access to the organic matter. Soil aggregates formed in the presence of calcium and organic matter were more stable than aggregates formed by organic matter only. Stable soil aggregates can protect organic matter from microbial attack, because some of it is probably situated in pores too fine for microorganisms to enter. Organic matter will remain inside the aggregates until the aggregates are disrupted by wetting and drying, or sheared by mechanical stress. The net effect is exposure of inaccessible organic matter to microorganisms, and to stimulate oxidation and loss of organic matter (Low, 1954; Rovira and Greacen, 1957; Clement and Williams, 1958; McCalla, 1959; Martel and Paul, 1974; Adu and Oades, 1978).

Protection of organic matter from decomposition by formation of stable soil aggregates or cation bridges is dependent on the soil physical , chemical and biological conditions. However, organic matter decomposition and soil aggregate formation usually occurs concurrently.

5.4.2 Formation of microbial biomass from decomposing plant material

5.4.2.1 *Total unlabelled biomass*

The biomass contents of soil during the decomposition of plant material are presented in Table 25 and 26. The amount of biomass was greatest after one week of incorporation of plant material, and then declined gradually with time of decomposition. The treatments had no significant effect on the biomass contents measured at week one and two. The treatment

Table 25. The biomass contents of soil calculated by fumigation with $CHCl_3$

One week after incorporation of plant material

Treatment	CO_2-C evolved, mg/100 g soil Untreated soil 0-10 days	Untreated soil 10-20 days	Fumigated soil 0-10 days	Flush of decomposion mgCO_2-C/100g soil	microbial mg C/100g soil	microbial kg C ha^{-1} 0-8 cm
Wheat straw	23.4	17.4	35.4	18.0	40.0	320
Wheat straw +$CaCO_3$	35.3	22.5	41.0	18.4	41.0	328
Wheat straw +$CaSO_4$	27.9	16.1	31.0	14.9	33.0	266
L.S.D.($P<0.05$)	9.7	5.5	6.8	9.1	20.3	162.5

Two weeks after incorporation of plant material

Treatment	Untreated soil 0-10 days	Untreated soil 10-20 days	Fumigated soil 0-10 days	Flush of decomposion mgCO_2-C/100g soil	microbial mg C/100g soil	microbial kg C ha^{-1} 0-8 cm
Wheat straw	27.6	18.8	31.3	12.5	27.3	222
Wheat straw +$CaCO_3$	21.1	15.8	27.1	11.3	25.2	201
Wheat straw +$CaSO_4$	40.2	26.2	35.6	9.3	20.8	166
L.S.D.($P<0.05$)	8.3	4.5	5.4	7.3	16.2	130.2

Four weeks after incorporation of plant material

Treatment	Untreated soil 0-10 days	Untreated soil 10-20 days	Fumigated soil 0-10 days	Flush of decomposion mgCO_2-C/100g soil	microbial mg C/100g soil	microbial kg C ha^{-1} 0-8 cm
Wheat straw	21.4	12.8	23.9	11.0	24.4	195
Wheat straw + $CaCO_3$	18.3	13.1	20.3	6.9	15.4	123
Wheat straw + $CaSO_4$	26.4	19.0	22.6	3.5	7.9	63
L.S.D.($P<0.05$)	5.6	3.7	3.5	3.6	8.1	34.3

Table 26. The biomass contents of soil calculated by fumigation with $CHCl_3$

Treatment	CO_2-C evolved, mg/100 g soil Untreated soil 0-10 days	 Untreated soil 10-20 days	 Fumigated soil 0-10 days	Flush of decomposition mgCO_2-C/100 g soil	microbial mg C/100g soil	microbial kg C ha^{-1}
	Eight weeks after incorporation of plant material					
Wheat straw	11.6	9.2	15.5	6.2	13.8	111
Wheat straw + $CaCO_3$	12.7	12.1	13.6	1.5	3.4	27
Wheat straw +$CaSO_4$	6.2	1.2	3.1	1.9	4.3	34
L.S.D.($P<0.05$)	3.9	1.7	3.2	1.9	4.2	34.3
	Sixteen weeks after incorporation of plant material					
Wheat straw	19.5	16.5	20.8	4.3	9.6	77
Wheat straw +$CaCO_3$	14.4	12.0	15.1	3.1	6.9	53
Wheat straw +$CaSO_4$	18.1	16.8	17.5	0.7	1.5	12
L.S.D.($P<0.05$)	2.8	0.9	2.3	1.9	4.2	34.3
	Thirty two weeks after incorporation of plant material					
Wheat straw	8.0	6.3	9.6	3.3	7.3	58
Wheat straw + $CaCO_3$	6.8	4.3	6.7	2.3	5.2	41
Wheat straw + $CaSO_4$	4.6	1.4	2.9	1.5	3.3	26
L.S.D.($P<0.05$)	1.4	1.6	1.5	1.0	2.3	18.3

containing ^{14}C-wheat straw+$CaCO_3$ reduced the biomass significantly by the fourth week, whereas the treatment containing ^{14}C-wheat straw+$CaSO_4$ gradually reduced the soil biomass between four to thirty two weeks of decomposition of plant material ($P<0.05$).

5.4.2.2 *Biomass ^{14}C*

The amount of ^{14}C in the biomass, and the proportion of residual ^{14}C remaining in the biomass were significantly reduced in the treatment ^{14}C-wheat straw+$CaSO_4$ (Table 27,28 and Fig. 41). The treatment comprising ^{14}C-wheat straw+$CaCO_3$ did not significantly reduce the level of ^{14}C in the biomass until the thirty second week.

The treatment containing ^{14}C-wheat straw+$CaSO_4$ had less ^{14}C in the biomass than other treatments, suggesting that Ca^{2+} reduced the microbial activity. As all the treatments in this experiment were conducted under similar soil and climatic conditons, it is most probable that calcium reduced the release of CO_2-C by bridging metabolic products of ^{14}C-wheat straw decomposition to clays or to organic colloids, thereby inhibiting release of CO_2. The results confirm the findings in chapter 3 (3.4.1.1), that decomposition of ^{14}C-glucose is inhibited in presence of calcium.

$CaCO_3$ was not as effective as $CaSO_4$ in suppressing microbial activity, presumably because of its lower solubility. Soil pH in $CaCO_3$ treated soil was neutral or near neutral which may also favour microbial activity (Table 24). However, the effect of pH on organic matter decomposition was transient (chapter 5 section 5.4.1 and chapter 3).

Several factors can affect the rate of decomposition ; such as organic-matter metal ion complexing (Martin et al., 1966), nutrient availability (Coulson and Butterfield, 1978; Stotzky and Norman, 1961), clays (Marshall, 1975) and soil physical conditions (Adu and Oades, 1978; Martin et al., 1982; Zunino et al., 1982).

Table 27. ^{14}C in soil biomass calculated by fumigation with $CHCl_3$

One week after incorporation of plant material

	$^{14}CO_2$ evolved dpm/100 g soil				
Treatment	Untreated soil 0-10 days	Untreated soil 10-20 days	Fumigated soil 0-10 days	Flush of decomposition $^{14}CO_2$ (dpm)/100 g soil	microbial ^{14}C(dpm)/100 g soil
Wheat straw	3131	1767	4394	2626	5837
Wheat straw +$CaCO_3$	3871	2010	3932	1922	4271
Wheat straw +$CaSO_4$	4220	2218	4224	2006	4457
L.S.D. ($P<0.05$)	2217	1235	938	1275	2833
			Two weeks after incorporation of plant material		
Wheat straw	2458	1268	2973	1704	3788
Wheat straw +$CaCO_3$	2953	2045	3371	1326	2946
Wheat straw +$CaSO_4$	3050	2098	2516	418	929
L.S.D. ($P<0.05$)	1351	942	1177	1251	2780
			Four weeks after incorporation of plant material		
Wheat straw	2071	1356	2241	884	1966
Wheat straw +$CaCO_3$	1702	1161	1610	449	999
Wheat straw +$CaSO_4$	1479	1093	1328	234	522
L.S.D. ($P<0.05$)	1602	613	474	509	1131

Table 28. ^{14}C in soil biomass calculated by fumigation with $CHCl_3$

Eight weeks after incorporation of plant material

	$^{14}CO_2$ evolved dpm/100 g soil				
Treatment	Untreated soil 0-10 days	Untreated soil 10-20 days	Fumigated soil 0-10 days	Flush of decomposition $^{14}CO_2$ (dpm)/100 g soil	microbial ^{14}C(dpm)/100 g soil
Wheat straw	871	682	1310	627	1395
Wheat straw +$CaCO_3$	959	614	1053	438	973
Wheat straw +$CaSO_4$	2000	1406	1734	328	729
L.S.D. ($P<0.05$)	501	421	464	213	473
Sixteen weeks after after incorporation of plant material					
Wheat straw	120	76	257	181	404
Wheat straw +$CaCO_3$	140	73	185	111	248
Wheat straw +$CaSO_4$	75	49	108	58	130
L.S.D. ($P<0.05$)	76	51	116	92	206
Thirty two weeks after incorporation of plant material					
Wheat straw	37	20	64	43	83
Wheat straw +$CaCO_3$	44	20	39	19	42
Wheat straw +$CaSO_4$	25	13	30	17	38
L.S.D. ($P<0.05$)	35	9	14	15	35

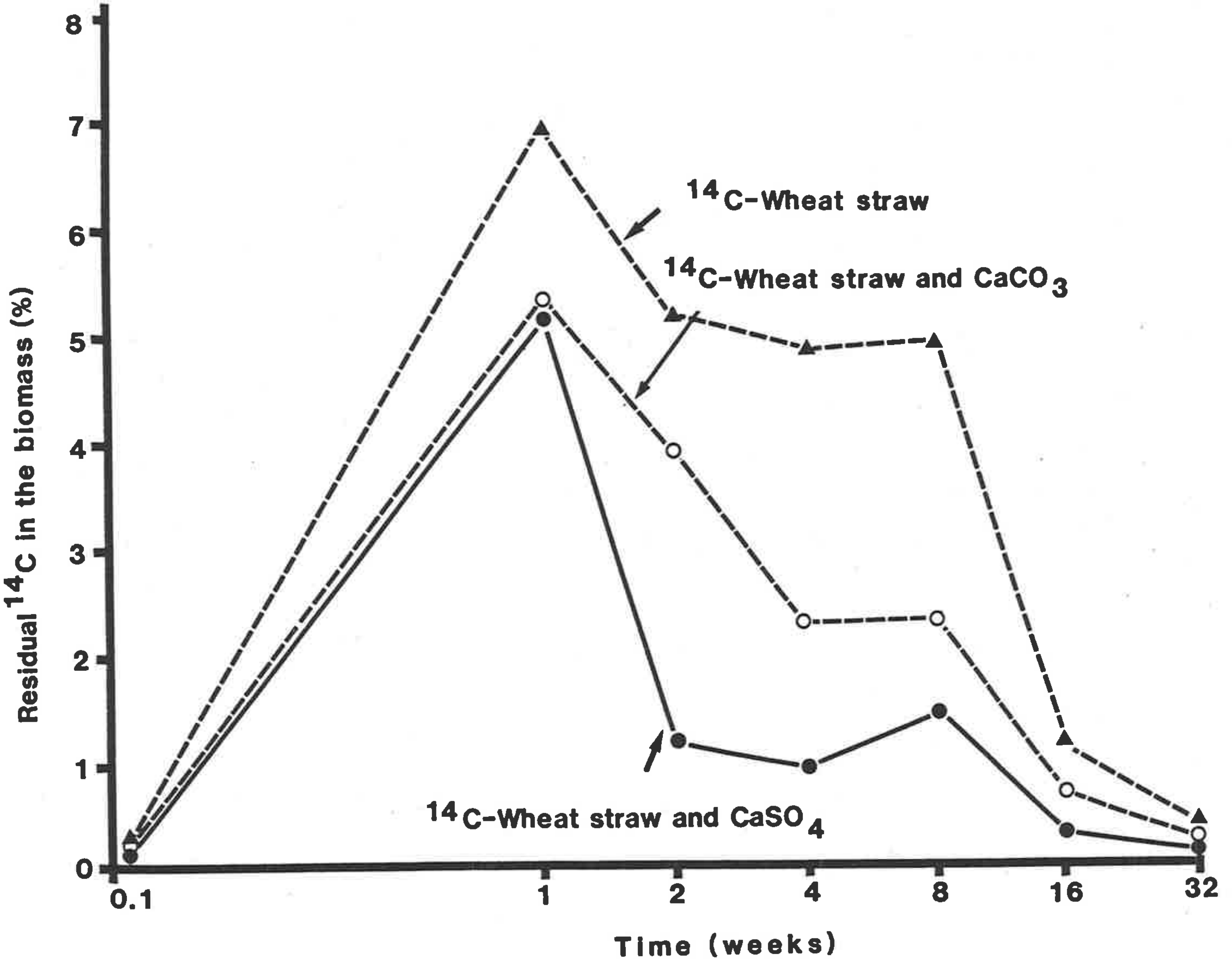


Fig.41 Residual ^{14}C in the biomass during the decomposition of ^{14}C-wheat straw

5.4.3 Water stable aggregates

Addition of ^{14}C-wheat straw (with or without $CaCO_3$ or $CaSO_4.2H_2O$) increased the stability of aggregates > 2000 µm diameter. Amounts of soil aggregates (> 2000 µm diameter) were maximal at 2 weeks in treatment 4 (^{14}C-wheat straw), and at 4 weeks in treatment 5 (^{14}C-wheat straw+$CaCO_3$) and 6 (^{14}C-wheat straw+$CaSO_4$). The percentage of water stable aggregates (>2000 µm diameter) declined gradually from this point. Soils treated with ^{14}C-wheat straw+$CaCO_3$ or ^{14}C-wheat straw+$CaSO_4$ had consistently more water stable macro-aggregates than soil treated with ^{14}C-wheat straw only (Fig. 42,43,44,45,46 and 47).

Application of calcium in the field in the form of $CaCO_3$ or $CaSO_4$. $2H_2O$ resulted in a decrease of particles <2 µm diameter, with a concurrent increase of particles 50-250 µm.

Addition of calcium without organic matter had little net effect on the stability of macroaggregates. This is in accord with the findings in chapter two; i.e. in calcareous soils with low organic matter contents most of the soil particles are in <250 µm diameter range.

Incorporation of ^{14}C-wheat straw, presumably increases both organic matter and microbial polysaccharide level, promoting subsequent increases in aggregate stability (Martin, 1982; Lynch and Elliott, 1983; Acton et al., 1963; Dormaar et al., 1979). A decrease in the percentage of macroaggregates (>2000 µm diameter) was presumably due to the loss of organic matter. However soils containing ^{14}C-wheat straw plus $CaCO_3$ or ^{14}C-wheat straw plus $CaSO_4$, had more water stable macroaggregates than soil containing ^{14}C-wheat straw only, suggesting that Ca^{2+} had a significant effect on the aggregate stability.

5.4.4 Dispersible clay

The addition of $CaCO_3$ or $CaSO_4.2H_2O$ (with or without ^{14}C-wheat straw) decreased dispersible clay, whereas incorporation of ^{14}C-wheat straw alone increased the amounts of dispersible clay (Fig. 48).

The addition of $CaSO_4.2H_2O$ (with or without ^{14}C-wheat straw) was initially more efficient in reducing clay dispersion than other treatments, but its effect gradually decreased with time. Dispersible clay in treatments containing $CaCO_3$ remained relatively constant throughout the experiment.

Gypsum was more efficient than other treatments because of its high solubility, and hence higher electrical conductivity in solution (Table 29). Initially the electrical conductivity of $CaSO_4$ treatments, was about five times higher than $CaCO_3$ treatments. However this difference in conductivity was progressively reduced due to the loss of salt through leaching from the soil surface (0-8 cm) in $CaSO_4$ treatments (Table 30).

Increases in dispersible clay probably arise from the action of organic anions released during the decomposition of the plant material. These anions may assist clay dispersion by blocking positive sites on colloid surfaces, and by complexing polyvalent cations in solution (Bloomfield, 1963; Gillman, 1974; Oades, 1984).

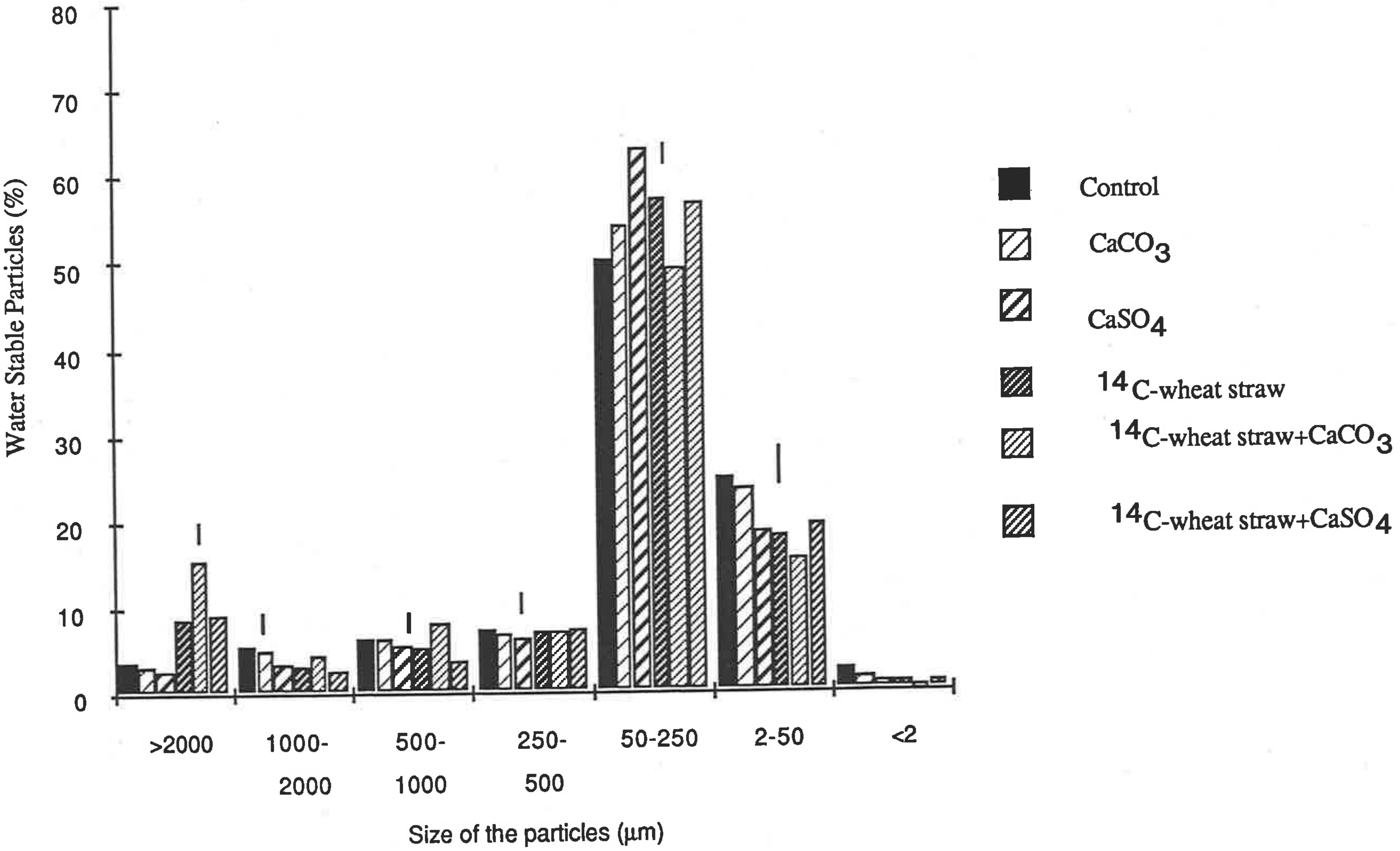


Fig. 42 The size distribution of water stable particles after one week decomposition of ^{14}C-wheat straw. Vertical bar, $P<0.05$.

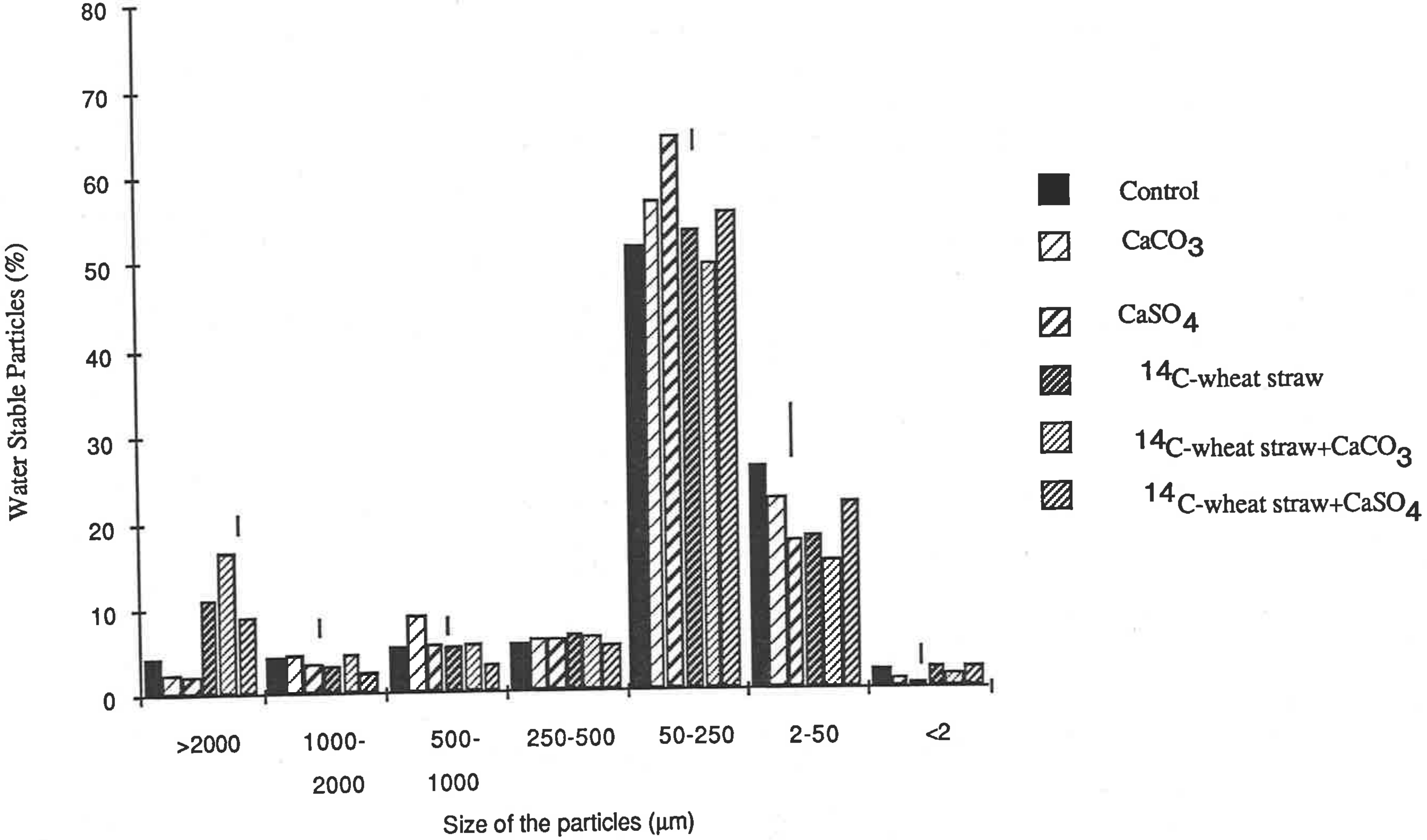


Fig. 43 The size distribution of water stable particles after two weeks decomposition of ^{14}C-wheat straw. Vertical bar, $P<0.05$.

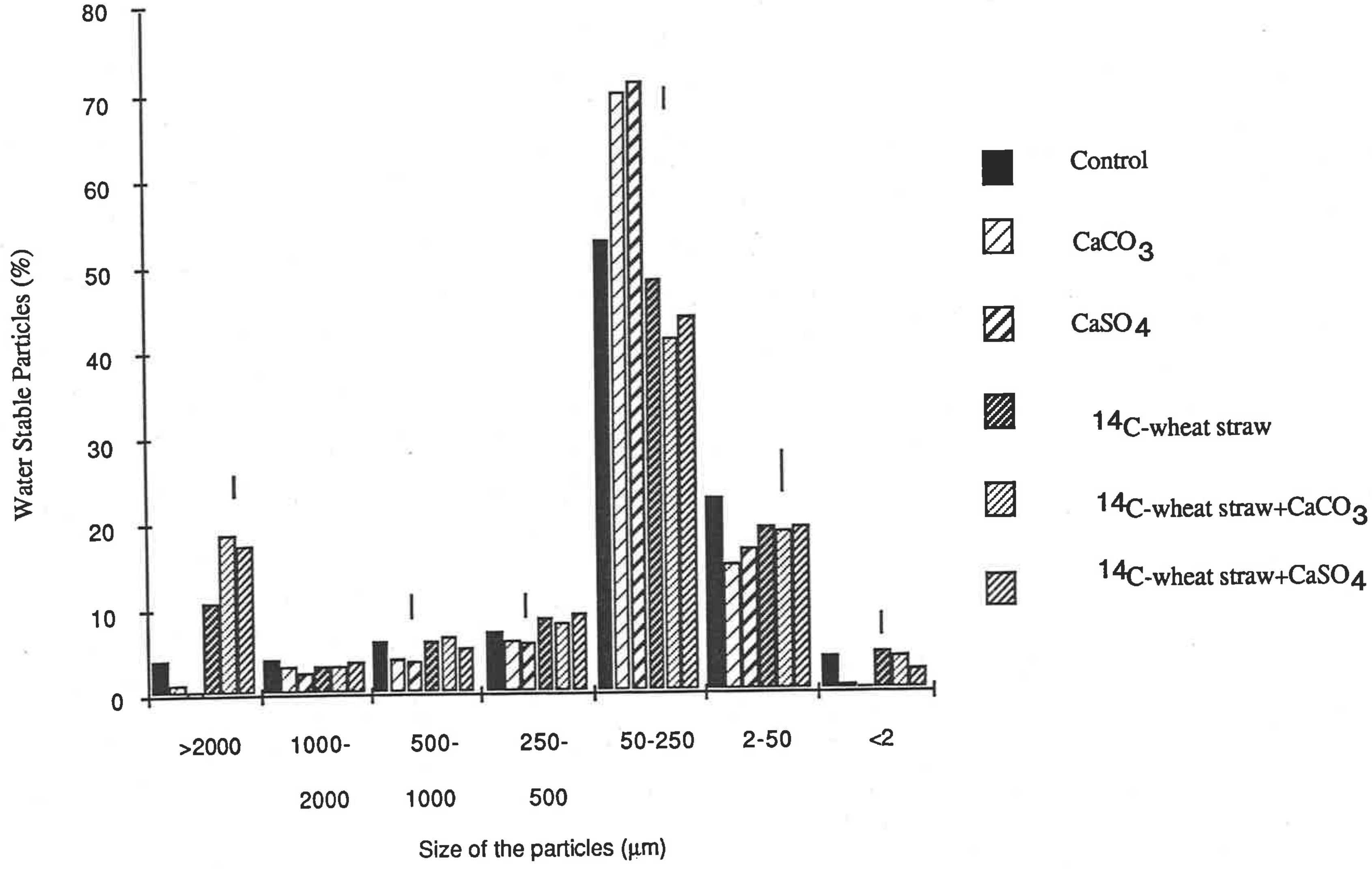


Fig. 44 The size distribution of water stable particles after four weeks decomposition of ^{14}C-wheat straw.
Vertical bar, $P<0.05$.

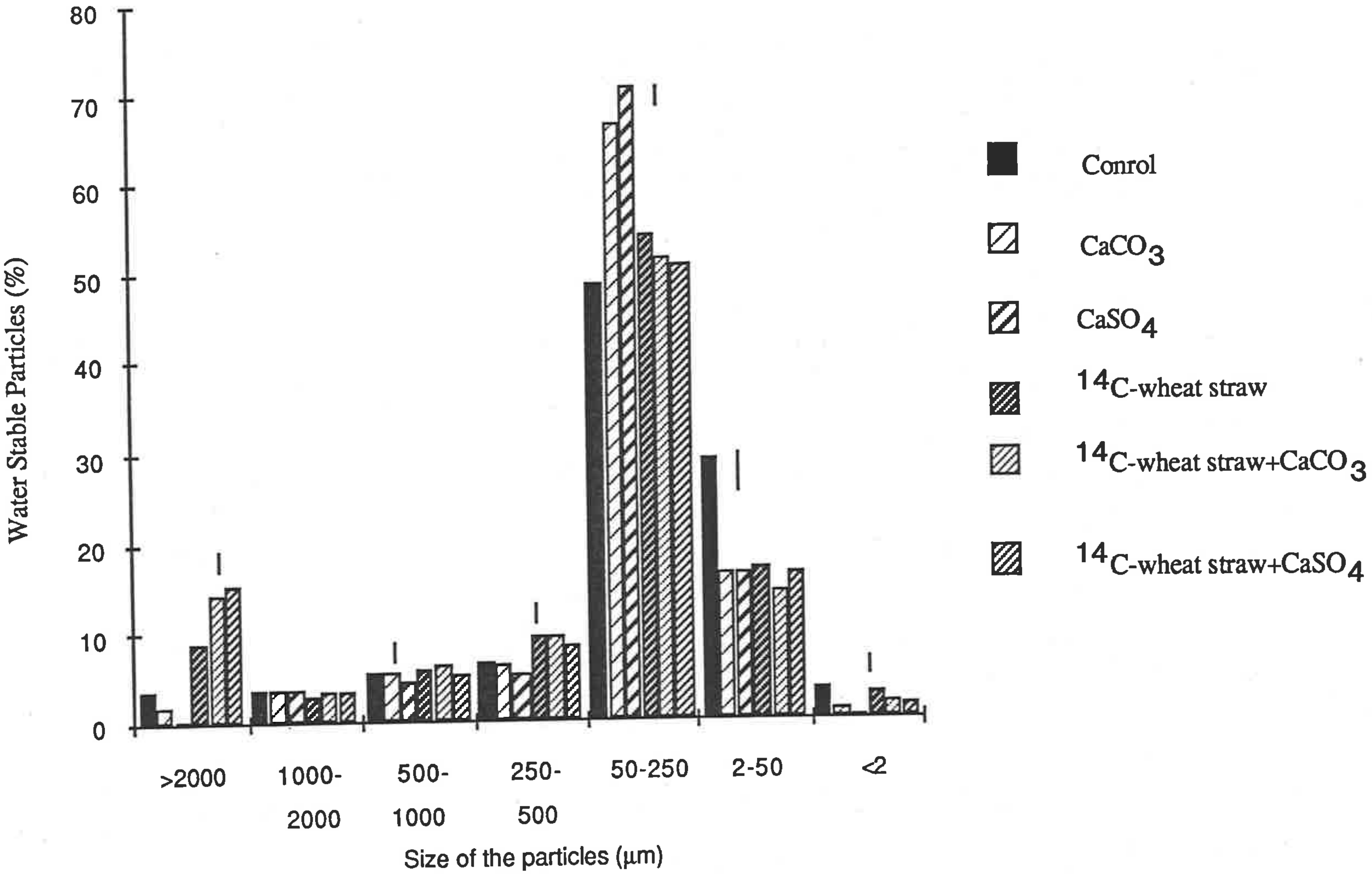


Fig. 45 The size distribution of water stable particles after eight weeks decomposition of ^{14}C-wheat straw. Vertical bar, $P<0.05$.

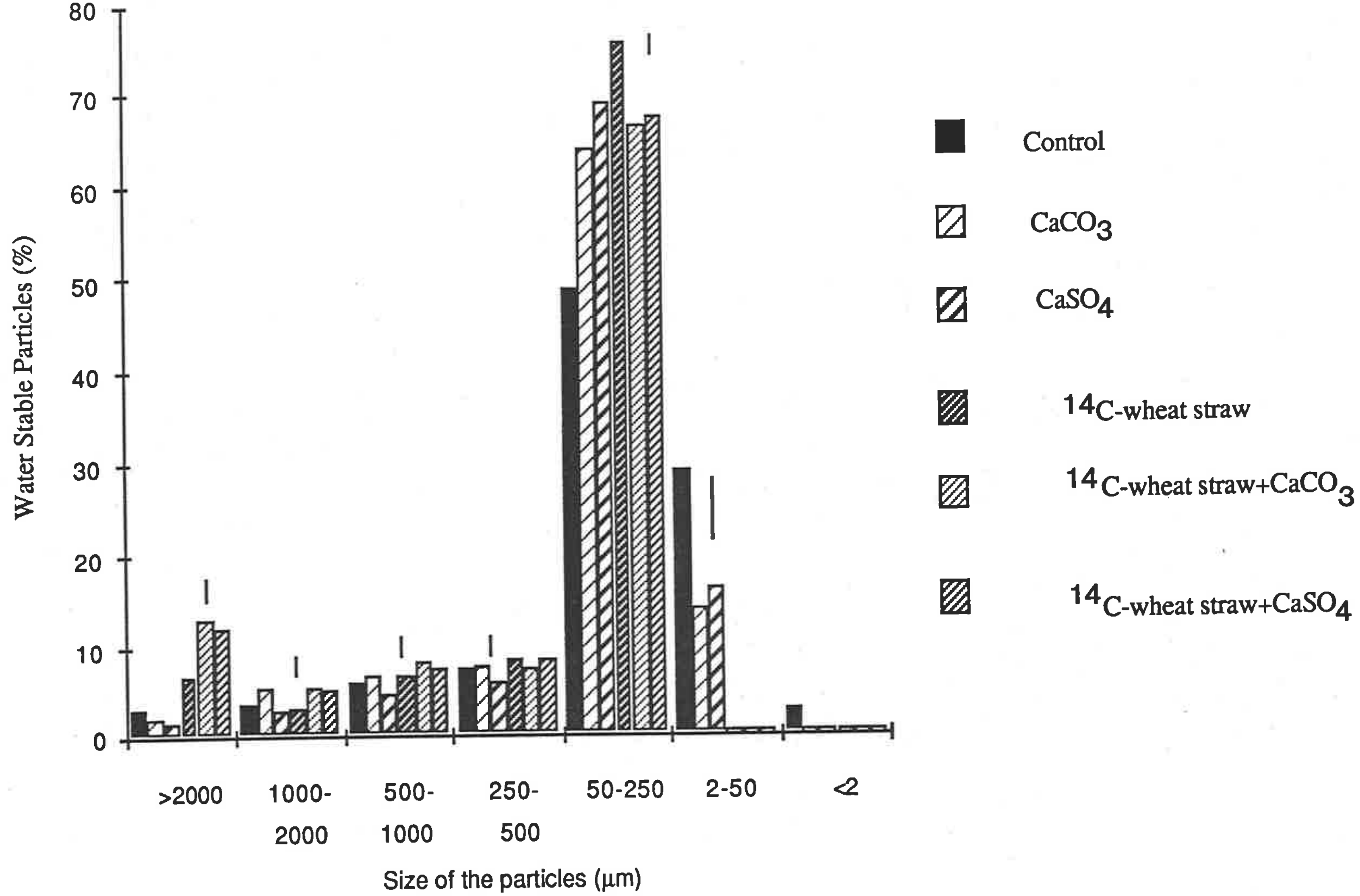


Fig. 46 The size distribution of water stable particles after sixteen weeks decomposition of ^{14}C-wheat straw. Vertical bar, $P<0.05$.

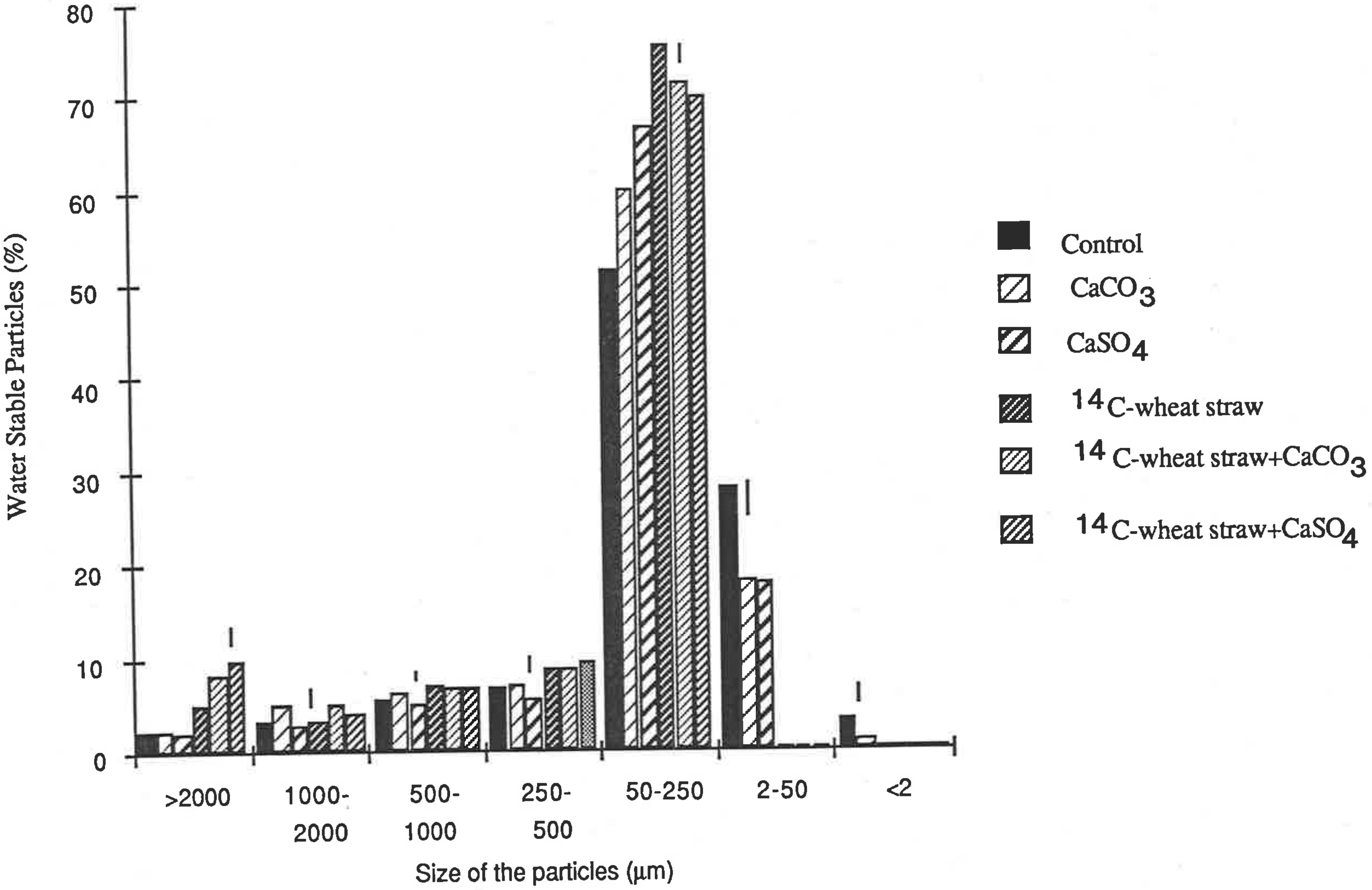


Fig. 47 The size distribution of water stable particles after thirty two weeks decomposition of ^{14}C-wheat straw.
Vertical bar, $P<0.05$.

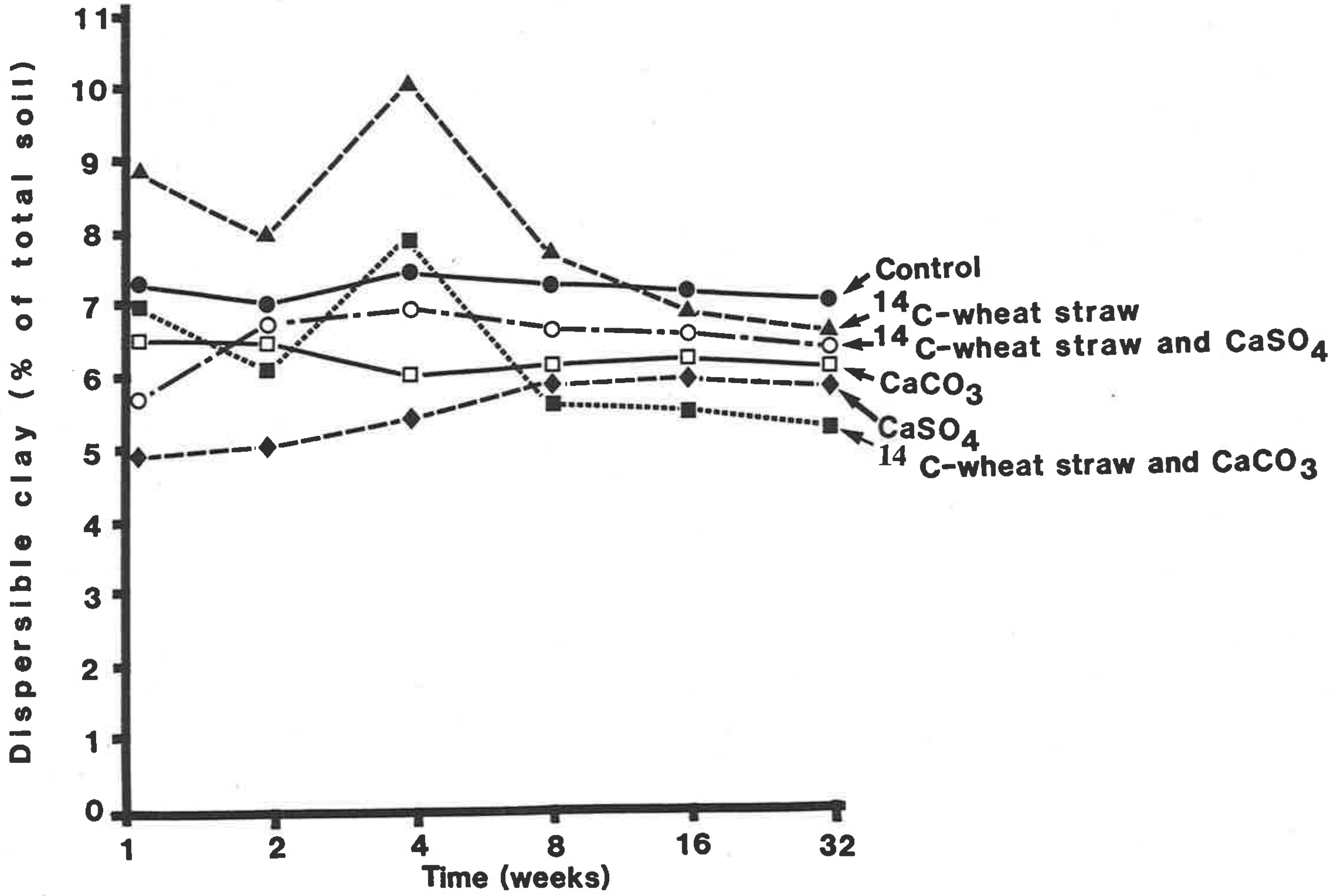


Fig.48 Dispersible clay during the decomposition of ^{14}C-wheat straw with or without calcium compounds

Table 29. Electrical conductivity (μS cm^{-1}) of soil during the decomposition of ^{14}C-wheat straw with or without calcium compounds (1: 5 soil/water ratio)

Treatment No.	Treatment	Time of decomposition (week)					
		1	2	4	8	16	32
1	Control	80	62	62	60	64	68
2	$CaCO_3$	150	120	128	104	124	120
3	$CaSO_4.2H_2O$	740	517	405	165	160	142
4	^{14}C-wheat straw	85	65	65	65	68	70
5	^{14}C-wheat straw + $CaCO_3$	147	118	126	103	118	120
6	^{14}C-wheat straw +$CaSO_4.2H_2O$	734	516	403	205	163	146

Table 30. Water soluble calcium during the decomposition of ^{14}C-wheat straw, with or without calcium compounds (mg/ 100 g soil)

Treatment No.	Treatment	Time of decomposition (week) 1	2	4	8	16	32
		0-8 cm depth					
2	$CaCO_3$	4.86	4.50	3.50	3.20	2.65	2.60
3	$CaSO_4.2H_2O$	12.50	12.50	10.60	6.00	3.10	3.00
5	^{14}C-wheat straw $+CaCO_3$	4.80	4.40	3.30	3.00	2.60	2.50
6	^{14}C-wheat straw $+ CaSO_4.2H_2O$	12.50	12.20	10.40	5.90	3.10	2.90
		8-20 cm depth					
2	$CaCO_3$	9.50	9.00	6.80	5.60	5.00	5.10
3	$CaSO_4.2H_2O$	42.00	60.00	52.75	33.10	34.20	30.20
5	^{14}C-wheat straw $+CaCO_3$	9.35	8.30	6.72	5.17	5.10	5.00
6	^{14}C-wheat straw $+CaSO_4.2H_2O$	41.50	60.00	52.25	33.00	34.00	30.00

5.5 CONCLUSIONS

The results of this experiment demonstrated that $CaSO_4$. $2H_2O$ conserved more organic matter by inhibiting mineralization of plant material. There was also less biomass-C in $CaSO_4$ treated soil than $CaCO_3$ treated and non treated soil. The mechanism by which Ca^{2+} retarded mineralization of ^{14}C-wheat straw cannot be defined precisely, but it is assumed that Ca^{2+} retarded the release of CO_2-C by bridging metabolic products of decomposed plant material to clays or to organic colloids.

$CaCO_3$ was not as effective as $CaSO_4.2H_2O$ in reducing the decomposition of plant material, presumably because of the low solubility of $CaCO_3$. The treatment containing ^{14}C-wheat straw +$CaCO_3$ accumulated relatively more organic matter than the treatment containing ^{14}C-wheat straw only; indicating that $CaCO_3$ did not accelerate the decomposition.

Addition of ^{14}C-wheat straw (with or without calcium compounds) increased the stability of aggregates >2000 µm diameter. However soil aggregates formed in the presence of plant material and calcium compounds were more stable than aggregates formed in the presence of plant material only. This indicates that Ca^{2+} has an additive effect on the aggregate stability.

$CaSO_4$. $2H_2O$ was more effective in reducing dispersible clay than $CaCO_3$ because of its higher solubility. However the efficiency of $CaSO_4$. $2H_2O$ gradually decreased due to the leaching loss of Ca^{2+} from the soil .

The implications of these results are

(i) Loss of organic matter from soil can be reduced by the addition of calcium.

(ii) Greater stability of soil structure can be obtained by the combined addition of organic matter and calcium.

(iii) Although $CaSO_4$. $2H_2O$ is more effective than $CaCO_3$ in conserving organic matter and improving soil physical properties, leaching loss of Ca^{2+} from $CaSO_4.2H_2O$ requires regular addition of $CaSO_4$. $2H_2O$ to maintain the Ca^{2+} concentration in the soil.

(iv) Due to low solubility of $CaCO_3$ it could be presumed that beneficial effects from its application to soil would arise over a prolonged period.

CHAPTER 6

GENERAL DISCUSSION AND CONCLUSIONS

6.1 Role of calcium in the mineralization of organic matter

The results in chapters 3 and 5 show clearly that calcium influences the mineralization of organic materials in the laboratory and in the field. In both cases mineralization of organic carbon (as measured by release of CO_2) was decreased in the presence of added calcium.

The mineralization of ^{14}C-glucose occurred in three phases (Fig. 14) (i) rapid phase (less than 5 days) involving the oxidation of ^{14}C-glucose, (ii) relatively slow phase (5-20 days) in which heterogeneous metabolic products decay at different rates, and (iii) the slowest phase (more than 20 days) involving the decay of more or less homogeneous and stable products of decomposition. During the rapid phase of mineralization, the release of $^{14}CO_2$ was higher in soil treated with ^{14}C-glucose+$CaCO_3$ compared with the soils treated with ^{14}C-glucose+$CaSO_4$ or ^{14}C-glucose. Subsequent production of $^{14}CO_2$ was suppressed compared to the control. Compared to the other treatments $CaSO_4$ was more efficient in reducing the release of $^{14}CO_2$ during the entire incubation period.

The cumulative release of $^{14}CO_2$ demonstrated that $CaCO_3$ stimulated the release of labelled CO_2 in the early stage of incubation, compared to soils treated with ^{14}C-glucose+$CaSO_4$ or ^{14}C-glucose (Fig. 15). Subsequently a stabilizing effect was evident, and the cumulative release curves for $^{14}CO_2$ crossed over. The presence of $CaCO_3$ eventually inhibited organic matter mineralization compared to the control. The stimulating effect of $CaCO_3$ on ^{14}C-glucose decomposition appears to be transient.

It has been suggested that liming stimulates organic matter decomposition. It is advocated that the stimulating effect of lime is the result of the shift of pH from acid to alkaline condition, which may favour microbial activity. The results in chapters 3 and 5 show that the pH of the $CaCO_3$ treated soil was about 7, and the pH of the $CaSO_4$ treated soil was about 5.5. However both $CaSO_4$ and $CaCO_3$ reduced the mineralization of ^{14}C-glucose. The delayed effect of $CaCO_3$ on reducing the mineralization was probably due to its low solubility.The results indicate that availability of calcium is more important than pH during the decomposition of organic matter. It has been demonstrated that low pH can slow down the decomposition of organic matter initially but the effect diminishes with time (Jenkinson, 1977). According to Oades (1986), 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. Thus the effect of pH on organic matter decomposition due to liming has been based on short term studies and in the longer term other factors influence the rate of decomposition (e.g. cultivation, wetting and drying, absence of stabilizing agents etc.).

Calcium increased the residual ^{14}C during the incubation of ^{14}C-glucose and the decomposition of ^{14}C-labelled wheat straw. The slow decomposition of organic matter in soil in the presence of calcium can occur by all or any one of the following proposed mechanisms. The various mechanisms require further specific studies.

(i) Organic matter forms complexes with metals of different stabilities by ion exchange, surface adsorption, chelation, and complex coagulation and peptization reactions. The complexing ability of humic acid results largely from the content of oxygen-containing functional groups, such as COOH, phenolic OH, and C=O groups of various types. Amino and imino groups may also be involved (Stevenson, 1982). Humic polymers can bind cations which influence the stereochemical arrangement of functional groups forming very stable complexes. Such complexes may reduce the rate of decomposition of the polymers in soil. Chemical studies have shown that soil organic matter commonly contains 5 to 20 percent of polysaccharides (Mehta, et al. 1960). Polysaccharides which contain uronic acid groups or cis hydroxyls at the 2 and 3 C positions (e.g. mannose), may form salts or complexes with metal cations (Mortensen, 1963). Martin et al. (1966) demonstrated that salt or complex formation of polysaccharides with metal cations markedly influenced the rate of decomposition of the polymers in soil, and suggested that the primary factor causing reduced decomposition rates was the inability of microbial enzymes to hydrolyze these complexes. The opposite effects have also been demonstrated by Gaiffe et al. (1984). The gradual removal of the exchangeable calcium held by the organo-mineral complexes of an organic soil resulted in the destabilization of the organo mineral complex by H^+, produced by the biodegradation of the most labile portion of the organic matter. The clay humus complex gradually dissociated leading to the destruction of aggregates and organo-mineral complexes. The organic matter released became biodegradable because the protective effect of calcium had been removed.

(ii) Clay particles which carry negative charges will normally repel each other. Organic colloids which possess funtional groups may be more condensed when saturated with calcium (Oades, 1987). Because both clays and organic matter are negatively charged, calcium bridges organic molecules to clay particles, forming stable aggregates. Involvement of cation bridges in the stability of aggregates <250 μm diameter has been reported by several authors (e.g. Edwards and Bremner, 1967; Tisdall and Oades, 1982).

(iii) Soil aggregates formed in presence of calcium and organic matter were more stable than aggregates formed in presence of organic matter only. Stable aggregates may protect organic matter from decomposition, because some of the organic material is situated in pores too fine for micro-organisms to enter. Organic matter contained in pores smaller than about one micron (10^{-6} m) diameter may be inaccessible to bacteria and thereby protected, although it is not adsorbed on the mineral surfaces (Rovira and Greacen, 1957). Organic matter will remain inside the aggregates until the aggregates are disrupted by wetting and drying or sheared by mechanical stress, e.g. by cultivation, root growth etc.

6.2 Influence of calcium on the microbial biomass

Microbial biomass in soil was determined by chloroform fumigation at intervals over the 32 weeks of decomposition of ^{14}C-labelled wheat straw (Chapter 5). In all treatments, the amount of biomass was greatest after one week of incorporation of plant material, and then declined gradually with time of decomposition. The treatments had no significant effect on the biomass until week two. Subsequently, soils treated with ^{14}C-wheat straw+$CaSO_4$ or ^{14}C-wheat straw+$CaCO_3$ contained less biomass compared to the soil treated with ^{14}C-wheat straw only.

There was no significant effect of treatments on the biomass during the first two weeks of decomposition of ^{14}C-wheat straw, indicating that calcium does not have a toxic effect on microorganisms. However the toxic effect of calcium on microorganisms is possible and this aspect requires further study. According to Martin et al. (1966), toxicity effects of metals on decomposition rates are transient, because some of the soil organisms are sensitive to the high salt concentration and decomposition is retarded until a population of more tolerant forms develops, or until additional types adjust to high metal levels. Low biomass in the presence of calcium may be the result of the stabilizing effect of calcium on the decomposed products of organic matter resistant to further decomposition by soil organisms. The influence of significant concentrations of Ca on the fumigation method for measuring biomass is unknown, and the lower biomass contents in the presence of Ca may be an effect on the method by which biomass is determined.

6.3 Cation Bridges

Water-stable aggregates were determined on calcareous soils, and in the soils treated with glucose with or without calcium (Chapter 2 and 4). This was followed by 0.02M NaCl. 0.1M $Na_2P_4O_7$, 0.02M HCl and 0.1M HCl, to determine the character of binding agents involved in the stability of aggregates.

Soil aggregates formed in presence of calcium and organic matter were not degraded by treatment with pyrophosphate. Therefore, the aggregates contained some binding agents which were resistant to pyrophosphate.

It is well known that polysaccharides, particularly microbially produced polysaccharides, are very effective in increasing the stability of aggregates when added to soils (Geoghegan and Brian, 1948; Swaby, 1949; Clapp et al., 1962; Martin, 1971). The loss of stability brought about by treatment of natural aggregates with dilute periodate, which oxidises polysaccharides but has little effect on other materials, confirms that in many soils polysaccharides play an important role (Greenland et al, 1962; Harris et al, 1963; Clapp and Emerson, 1965). However, in soils containing $CaCO_3$ (Greenland et al, 1962) or soil under pasture (Tisdall and Oades, 1982) aggregates remain stable after treatment with periodate, indicating that other binding agents were also involved in the stability of aggregates. Aggregates which were stable after treatment with periodate, had decreased stability after treatment with pyrophosphate. It was suggested that in those soils, polysaccharides are less important to aggregate stability than organic matter bonded to the clay particles through association with aluminium , iron or calcium (Stefanson, 1971; Hamblin and Greenland, 1977). Pyrophosphate has been used to "break" the organic matter-polyvalent cation-clay bridges. However, due to the large range of organic molecules capable of forming cationic bridges, the exact nature of the organic compounds removed by pyrophosphate is not understood. Stability of soil aggregates after pyrophosphate treatment does not indicate that cation bridges were not involved in aggregation. The complexes of clay-Ca^{2+}-organic matter may be very stable and not influenced by treatments with pyrophosphate.

If the stability of soil aggregates is the result of complexes of clay-Ca^{2+}-organic matter, then treatment of aggregates with acid should remove Ca^{2+} from the coordination complexes and result in disruption of aggregates. Soil aggregates were stable to 0.02M HCl treatment. However when the concentration of acid was increased from 0.02M HCl to 0.1M HCl substantial decreases in the percentage of aggregates (>2000 μm diameter) occurred with accompanied increase in particles <250 μm diameter compared with the 0.1M $Na_4P_2O_7$ or 0.02M HCl treatments. These results suggest that complexes of clay-Ca^{2+}-organic matter were very stable, and strong chemical reaction is necessary to disrupt the stability of aggregates. Generally 0.1M HCl will disrupt large aggregates completely. Partial breakdown of aggregates with 0.1M HCl treatment may be due to insufficient acid and/or a slow rate of reaction.

6.4 Influence of calcium on the extraction of organic matter from soil

It was observed that water soluble, exchangeable and EDTA extractable calcium were lower in soils treated with glucose+calcium compared to soils treated with calcium only (Chapter 4). Similarly humic acid (extracted by NaOH) was less extractable in soils treated with glucose+calcium compared to soil treated with glucose. Acid pretreatment of soil which removed calcium and increased the efficiency of extraction of humic acid by about 50%

indicated that some of the soluble calcium became insoluble by complexing with the decomposition products from glucose. In a review, Oades (1987) suggested that the insolubility of organic matter in NaOH is the result of cation bridges in the soil. Removal of the cations by an acid treatment increases the extraction of organic matter, often by a factor of 2.

Humic acid forms both soluble and insoluble complexes with polyvalent cations, depending upon the degree of saturation (Stevenson, 1982). Calcium can affect the solubility characteristics of humic substances possibly in three different ways. (i) When humic substances are dissolved in water, dissociation of acidic functional groups occurs and the molecule assumes a stretched configuration because of repulsion of charged groups. When calcium is added, the charge is reduced through salt formation and the molecule collapses, thereby reducing the solubility (Stevenson, 1982; Oades, 1987). (ii) Like other polyvalent cations (e.g. Fe and Al) calcium also has the potential for linking individual molecules together to produce chainlike structures. (iii) Clays and organic colloids are negatively charged, calcium is able to form coordination complexes with clays and organic molecules by neutralizing the negative charges. Such a complex may be able to reduce the solubility of organic matter in NaOH.

6.5 Model of an aggregate

6.5.1 Introduction

Several models have been proposed to describe the way in which individual mineral particles are held together to form water-stable aggregates in soil. It is worth discussing the models of an aggregate as proposed by several authors before a model of an aggregate is proposed in soil containing calcium and organic matter.

Emerson (1959) proposed that crumbs are formed from units of colloidal clay, or domains , and coarser particles of silt and sand (quartz) cemented together by humus.

Quirk and Aylmore (1971) used the term quasi-crystal to describe the regions of parallel alignment of individual lamellae of aluminosilicates in montmorillonite, which exhibit intra-crystalline swelling; and the term domain to describe the regions of near parallel alignment of crystals for illite and other clays with fixed lattices, which exhibit inter-crystalline swelling only. The concept of domains provides a more realistic way of thinking about the organization of clay particles in soil than a card-house type structure. The concept is particularly useful when considering the reactions of stabilizing agents with soils.

Edwards and Bremner (1967) suggested that macroaggregates (>250 µm diameter) consist of complexes of clay-polyvalent metal-organic matter (C-P-OM) where clay is bonded to humified organic matter through polyvalent metals. Particles of C-P-OM and $(\text{C-P-OM})_x$, both of which are <2 µm diameter, form microaggregates $((\text{C-P-OM})_x)_y$ which are <250 µm diameter. Bonds of C-P-C and OM-P-OM, and even of aluminiumor iron oxide, or H-bonds may occur also. Edwards and Bremner (1967) suggested also that fragments of humifed organic matter may be bonded to a single clay particle, and that a single fragment of humified organic matter may be bonded to more than one clay particle.

Tisdall and Oades (1982) proposed a model of aggregation in a red-brown earth. In their model there were four stages of aggregation;

<2 µm—2-20 µm—20-250 µm—>2000 µm

According to Tisdall and Oades, water-stable aggregates >2000 µm diameter consist of aggregates and particles held together mainly by a fine network of roots and hyphae. Because the stability of particles >2000 µm diameter is related to the growth of roots and hyphae, the stability was primarily controlled by agricultural practices. Aggregates 20-250 µm diameter consisted largely of particles 2-20 µm diameter bonded together by various cements including persistent organic materials and crystalline oxides and highly disordered aluminosilicates. The aggregates 20-250 µm diameter were very stable partly because they were small, but also because they contained several types of binding agents, the effects of which were additive. Complexes of C-P-OM were also involved. Aggregates 2-20 µm diameter consisted of particles <2 µm diameter bonded together so strongly by persistent organic bonds that they were not usually disrupted by agricultural practices. Water stable particles <2 µm diameter were floccules of fine clay.

The models described above suggest that the most important mechanism operating in soil is probably the bridges of polyvalent cations between the surface of the clay particles or hydroxy polymers and the ligand groups of organic polymers, e.g. carboxyl groups, which exist in particles <250 µm range. Stability of aggregates >2000 µm diameter is largely dependent on the organic matter content of the soil. The effect of organic matter on the stability of aggregates is transient, because stability decreases with the loss of organic matter.

6.5.2 Model of an aggregate containing calcium and organic matter

A model of an aggregate is proposed on the basis of stability of aggregates after chemical treatments with 0.1M $Na_4P_2O_7$, 0.02M HCl and 0.1M HCl (Chapter 4). These aggregates were formed after the addition of glucose (6t ha^{-1}) and calcium (1t ha^{-1}). Stability of aggregates may vary depending on the organic matter and calcium contents of the soil.

In this model, aggregates break down in four stages, in order of the efficiency 0.1M HCl> 0.02M HCl > 0.1M $Na_4P_2O_7$.

Stage 1	2	3	4
>2000 µm	50-250 µm	<2-50 µm	<2µm

Stage 1. Aggregates >2000 µm diameter

Water stable aggregates >2000 µm diameter consist of aggregates <250 µm diameter mainly held together by organic material and the stability of aggregates declined rapidly with the decomposition of organic matter by microorganisms.

Soil containing calcium and organic matter had more water stable macroaggregates and aggregates remained stable for a longer period of time compared to soil containing organic matter only, suggesting that calcium has an additive effect on the stability of aggregates. The beneficial effect of calcium and organic matter on the stability of aggregates was presumably due to complexes of clay—Ca^{2+}—organic matter. Aggregates (>2000 µm diameter) formed by calcium and organic matter were persistent, since aggregates were stable with 0.1M $Na_4P_2O_7$ treatment (Fig. 35). Aggregates were also stable after 0.02M HCl treatment. Increase in acid concentration from 0.02M HCl to 0.1M HCl decreased the stability of aggregates significantly (Fig. 36 and 37).

Several authors suggested that persistent binding agents include complexes of clay—polyvalent metal—organic matter, C—P—OM and $(C—P—OM)_x$, both of which were

<250 µm diameter (Edwards and Bremner, 1967; Tisdall and Oades, 1982). The results of the present study suggested that such complexes were also involved in the stability of aggregates >250 µm diameter in soil containing calcium and organic matter.

In addition to cation bridges , fungal hyphae were also involved in the stability of soil macroaggregates (Chapter 2, Fig. 10). Although individual hyphae are not strong, the combined strength of all hyphae holds particles firmly so that aggregates do not slake when wetted rapidly.

Stage 2. Aggregates 50-250 µm diameter

Water stable aggregates 50-250 µm diameter consisting of particles <2 µm diameter results either from bonding clay—Ca^{2+}—organic matter or flocculation of clay particles. Addition of calcium without organic matter in soil, flocculated clay particles to aggregates 50-250 µm diameter. There was no evidence that calcium stabilized aggregates >250 µm diameter. Flocculation is largely controlled by coagulation-dispersion phenomena. Coagulation of clay particles is promoted by polyvalent exchangeable cations or high electrolyte concentrations and is reversible by exchanging cations or by dilution (van Olphen, 1977).

Treatment of aggregates with 0.02M HCl decreased the aggregates >2000 µm diameter and increased the percentage of particles 50-250 µm diameter. When the soil was treated with 0.1M HCl there was a decrease of particles 50-250 µm with an accompanied increase of particles <50 µm diameter, suggesting that cation bridges were also involved in the stability of microaggregates (<250 µm diameter).

Stage 3. Aggregates 2-50 µm diameter

Aggregates 2-50 µm diameter consist of particles <2 µm diameter, which also results from binding clay—Ca^{2+}—organic matter. Treatment of soil with HCl decreased the stability of aggregates >2000 µm and 50-250 µm diameter and increased the percentage of particles 2-50 µm diameter (Fig. 36 and 37).

Stage 4. Aggregates <2 µm diameter

Water-stable particles <2 µm diameter are often floccules where individual clay plates (which may consist of individual lamellae or groups of lamellae called sheets) come together to form a fluffy mass. Initially the plates are not parallel, but are attracted edge-to-face to form an open card-house structure (Quirk, 1978). However on drying the system tends to lower its entropy so that the plates are then paralled and if aligned perfectly will form a crystal 4 nm wide. The crystals may then be joined into larger units with silt-shaped pores 2.5 nm to 4.1 nm between the crystals (Murray and Quirk, 1979). The plates are held together by van der Waal's forces, H-bonding and coulombic attraction. However the charges of ions associated with the surface of clay are influenced by organic and inorganic materials (Greenland 1965; 1971). For example, organic materials may increase or decrease the attraction between the particles (Chapter 1). In soil containing Ca the arrangement of clay plates is largely controlled by the Ca status in soil solution, which prevents the plates from moving apart in conditions of excess water and low electrolyte concentrations (Oades, 1987).

On the basis of the above observation, a model of an aggregate is proposed, where cation bridges are the most important mechanisms in the stability of soil aggregates (Fig. 49). In this model cation bridges are involved in the stability of both micro- (<250 µm diameter) and macro-aggregates (>250 µm diameter). In addition to cation bridges, fungal hyphae, bacteria and plant materials are also involved in the stability of macroaggregates.

6.6 Role of calcium and organic matter on the physical properties of soils

No simple correlation existed between the dispersible clay and $CaCO_3$ content of the calcareous soils under investigation (Chapter 2). In all soils, the amount of dispersible clay increased initially, and then progressively decreased with continued shaking, due to the increase in electrical conductivity and Ca^{2+} in the suspension (see section 2.3.4.1). When $CaCO_3$ exists in nodular form its solubility is decreased. The low solubility of $CaCO_3$ in soil may also result from the interaction between the surface of the calcium carbonate and dissolved compounds, presumably silicates, producing a surface coating of calcium silicate (Lahav and Bolt, 1963). However, if the suspension is shaken, abrasion of particles occurs, the Ca^{2+} concentration in the suspension increases due to $CaCO_3$ dissolution, and flocculation of clay results. The surface area of nodules varies enormously, consequently Ca released into soil solution does not correspond to the amout of $CaCO_3$ present in the soil (Abedi and

Talibudeen, 1974).

Physical properties of calcareous soils (e.g. aggregate stability, bulk density, hydraulic conductivity and water holding capacity etc.) are primarily dependent on the organic matter content of the soil. For calcareous soils low in organic matter, or for soils to which calcium has been applied without addition of organic matter, there was a substantial portion of the soil stabilized in aggregates 50-250 µm range. Improvement is likely to be achieved on poorly structured soils by the combined application of calcium and organic matter.

6.7 Selection of gypsum or calcium carbonate as a source of calcium

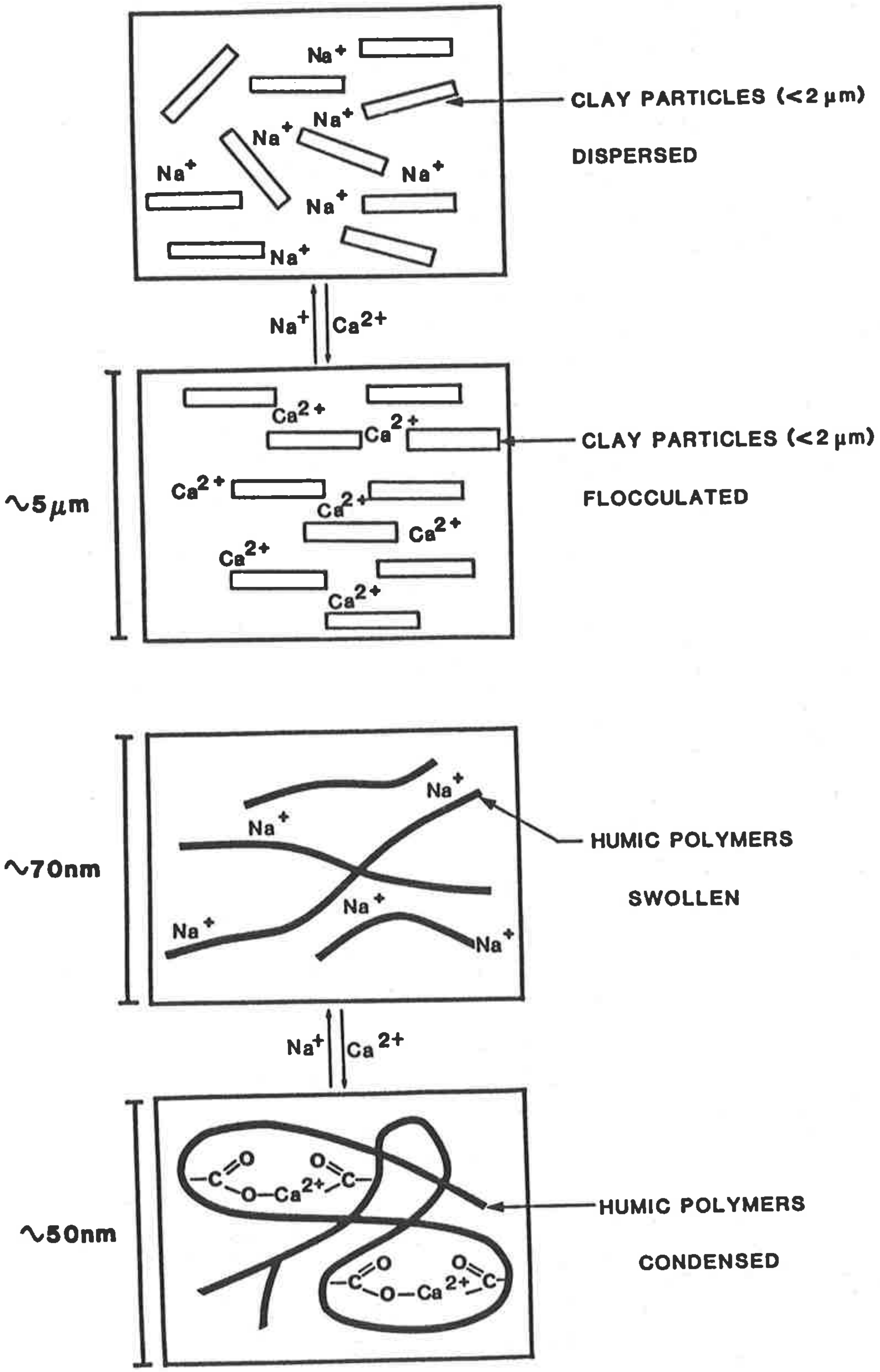
Compared to gypsum, calcium carbonate was not efficient in (a) improving soil physical properties, and (b) reducing the decomposition of organic matter. $CaSO_4$ was more effective in improving soil physical properties than $CaCO_3$ because of its greater solubility. However the efficiency of $CaSO_4$ gradually decreased due to the leaching loss of Ca^{2+} form the soil (Table 29). Therefore regular addition of $CaSO_4$ is required to maintain the Ca^{2+} concentration in the soil. Particle size, which affects the solubility of $CaCO_3$ is an important factor when calcium carbonate is considered. On the other hand the cost involved in obtaining the very fine $CaCO_3$, and the considerable time involved to obtain any beneficial effects may limit economic use.

6.8 Conclusions

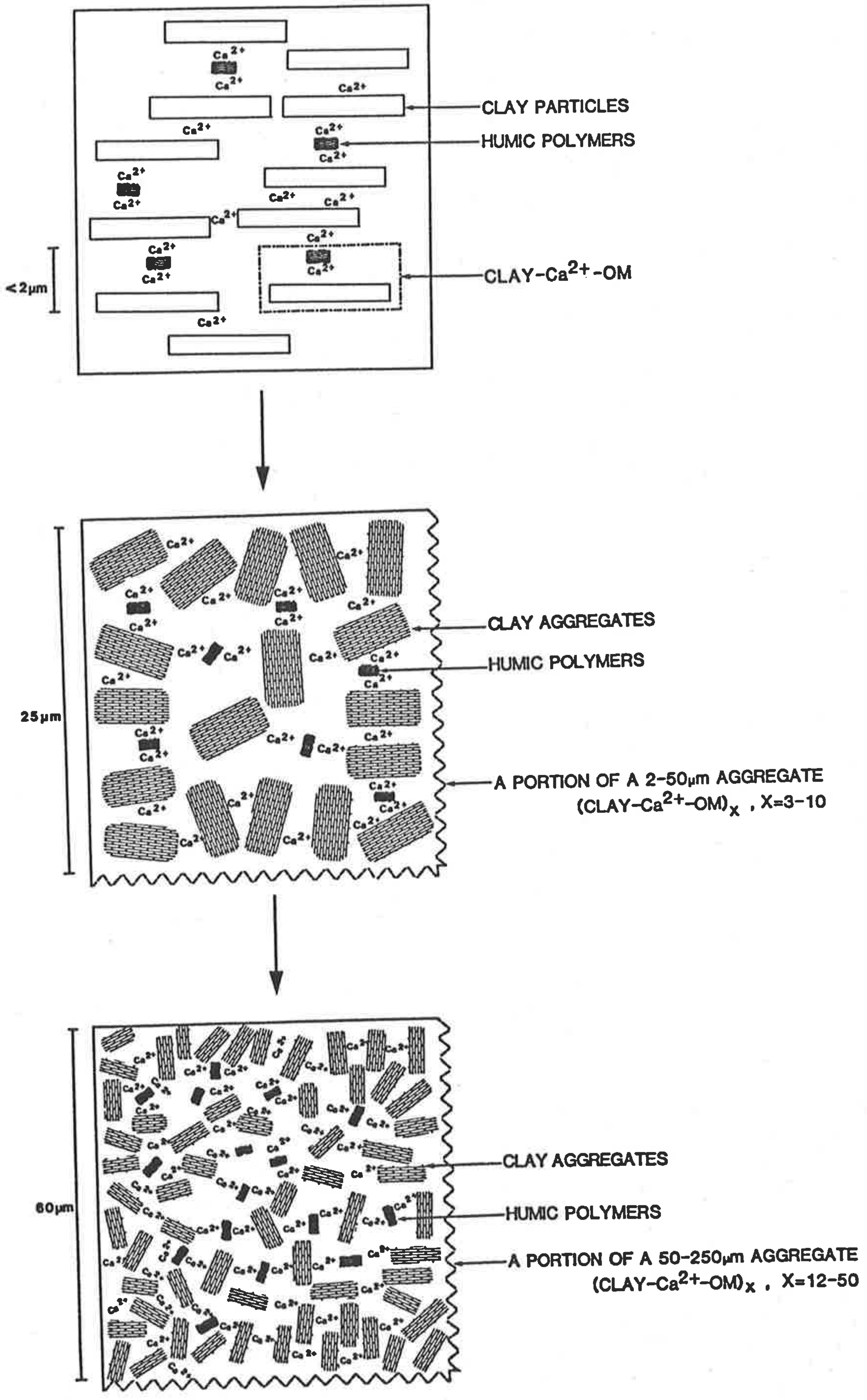
The results of the present study agree with the old concept that calcium stabilizes soil structure by cation bridging (e.g. Peterson, 1947; Russell, 1950), and calcium also reduces the decomposition of organic matter (Duchefaour, 1982). Cation bridges are probably one of the reasons for higher organic matter contents in calcareous soils, compared with noncalcareous soils. However, the presence of $CaCO_3$ in the soil does not necessarily mean that organic matter will be conserved. Calcium will react with clays and organic materials only when it is present as Ca^{2+} in solution. The solubility of $CaCO_3$ is reduced when it is present in nodular form (see chapter 2). The presence of Ca in the nodule is largely controlled by the local conditions (e.g. rainfall, temperature, porosity etc.). Therefore soils occurring in an environment not favourable for dissolution of $CaCO_3$ do not favour conservation of organic matter.

Summarizing, although all the evidence suggests that cation bridges are involved in the stability of soil structure, little is known about the exact mechanisms. Further study is needed to explore this complex and important mechanism of soil structural stability. This knowledge may help to improve the efficiency of present soil management practices.

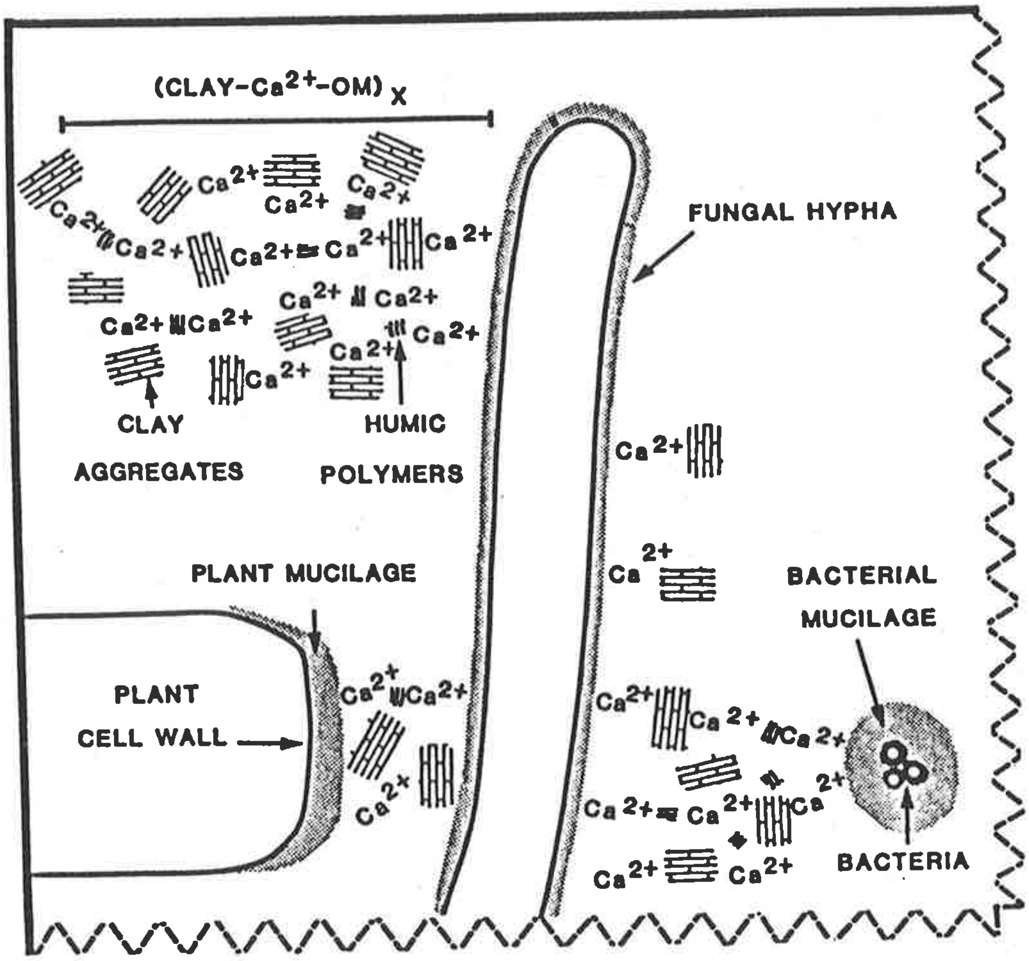
Fig. 49 Model of an aggregate containing calcium and organic matter.


Na+
Na+
Na+
Na+
Na+
Na+
Na+
CLAY PARTICLES (<2 µm)
DISPERSED
Na+
Ca2+
~5µm
Ca2+
Ca2+
Ca2+
Ca2+
Ca2+
Ca2+
Ca2+
CLAY PARTICLES (<2 µm)
FLOCCULATED
~70nm
Na+
Na+
Na+
Na+
Na+
HUMIC POLYMERS
SWOLLEN
Na+
Ca 2+
~50nm
—C=O —O—Ca2+—O=C—
—C=O —O—Ca 2+—O=C—
HUMIC POLYMERS
CONDENSED

A


CLAY PARTICLES
HUMIC POLYMERS
CLAY-Ca2+-OM
<2µm
Ca2+
CLAY AGGREGATES
HUMIC POLYMERS
25µm
A PORTION OF A 2-50µm AGGREGATE
(CLAY-Ca2+-OM)x , X=3-10
CLAY AGGREGATES
HUMIC POLYMERS
60µm
A PORTION OF A 50-250µm AGGREGATE
(CLAY-Ca2+-OM)x , X=12-50

B



A PORTION OF A >250μm AGGREGATE

C

Appendix-A. Macromorphological descriptions of soils

Clarendon

Landscape: Hilly uplands with dissected lateritic tablelands, forest and woodland areas, blocks of pine plantings and remnants of native forest.

Location: 138°40'E, 35°04'S

Climate: Mean annual reainfall 550-1100 mm
Mean annual evaporation 1750 mm

Mean altitude: 200 m

Native vegetation: Open forest, subdominant E.obliqua-E.bazteri.

Morphology depth (cm)	Description
0-10	Very dusky red (2.5YR 2/3) silty clay loam, friable, crumb structure, few earthworms, many roots, few rock fragments and slates, effervesces weakly; diffuse to
10-20	Dark reddish brown (2.5 YR 2/4) silty clay loam, friable, crumb structure, few rock fragments, effervesces weakly; gradational to
20-30	As above but medium clay, 5% carbonate nodules, effervesces strongly; gradational to
30-50	As above but dusky red (2.5YR 3/2), effervesces strongly; clear to
50-120	Soft layer of carbonate deposition.
120	and onward calcareous schist.

Claremont

Landscape: Hilly uplands, forest and woodland areas and remnants of native vegetation.

Location: 138°38'E, 34°58'S

Climate: Mean annual rainfall 600-700 mm

Mean annual evaporation 1500 mm

Morphology depth (cm)	Description
0-10	Very dark reddish brown (7.5R 2/3) light clay, strong, crumb grading to strong granular and subangular blocky. A few rock nodules and many grass roots. Effervesces moderately; continuing to
10-20	Very dark reddish brown (7.5YR 3/2) light clay, friable, crumb structure, effervesces moderately; gradational to
20-40	Reddish yellow (5YR 7/6) light medium clay, apedal, 5% carbonate nodules, effervesces strongly; gradational to
40-50	Yellowish red (5YR 5/6) light clay, apedal, effervesces strongly.
50	and onwards hardpan.

Dublin

Landscape: An undulating plain with occasional dunes, used for rotation cereal cultivation and livestock grazing.

Location: 138°32'E, 34°26'S

Climate: Mean annual rainfall 400-450 mm

Mean annual evaporation 1800 mm

Mean altitude: 80 m.

Morphology: depth (cm)	Description
0-10	Dark brown (7.5YR 3/4) silt loam, apedal, hard, effervesces strongly; diffuse to
10-30	Dark brown (7.5YR 4/6) clay loam, apedal, hard, effervesces strongly; diffuse to

30-40	Dark brown (7.5YR 5/6) clay loam, apedal, weakly coherent, 5% carbonate nodule, effervesces strongly; gradational to
40-50	Strong brown (7.5YR 5/8) silty clay, apedal, weakly coherent, 5% carbonate nodules, effervesces strongly; gradational to
50-90	Dark brown (7.5YR 5/6) light clay, apedal, weak to moderately coherent, some soft and concretionary carbonate, effervesces strongly; diffuse to
90-100	Reddish yellow (7.5YR 6/6) light clay, apedal, weak to moderately coherent, a little soft carbonate nodule, effervesces strongly; diffuse to
100-120	Strong brown (7.5YR 5/8) light clay, apedal, weak to moderately coherent, 5% carbonate nodule, effervesces strongly; continuing to
120-140	Yellowish red (5YR 4/8) light clay, apedal, moderately coherent, effervesces strongly; continuing to
140-150	as above except 5% carbonate nodule.

Grace (i)

Landscape: An undulating plain used for rotation cereal cultivation and livestock grazing.

Location: 138°32'E, 34°26'S

Climate: Mean annual rainfall 400-450 mm

Mean annual evaporation 1800 mm

Mean altitude: 80 m.

Morphology:

depth (cm)	Description
0-20	Dark reddish brown (5YR 3/4) silt loam, moderate, crumb structure, brittle (dry), many roots, effervesces strongly ; diffuse to
20-50	Yellowish red (5YR 4/6) clay loam, crumb grading to weak to moderate, effervesces strongly; clear to

50-60	Dark brown (7.5YR 4/6) light clay, weak subangular blocky, 5% carbonate nodule, effervesces strongly; gradational to
60-70	Dark brown (7.5YR 4/6) light medium clay, weak subangular blocky, 5% carbonate nodule, effervesces strongly; gradational to
70-90	Yellowish red (5YR 5/6) light medium clay, hard, medium subangular blocky, effervesces strongly; gradational to
90-130	Yellowish red (5YR 5/6) medium clay, hard, medium subangular blocky, 5% carbonate nodule, effervesces strongly; gradational to
130-150	As above

Grace (ii)

Landscape: An undulating plain used for rotation cereal cultivation and livestock graziang.

Location: 138°32'E, 34°26'S

Climate: Mean annual rainfall 400-450 mm

Mean annual evaporation 1800 mm

Mean altitude: 80 m.

Morphology depth (cm)	Description
0-10	Dark reddish brown (5YR 3/3) loam, weak, granular, effervesces strongly; clear to
10-20	As above, but clay loam; diffuse to
20-40	Yellowish red (5YR 4/6) light clay, weak, granular, effervesces strongly; duffuse to
40-60	Strong brown (7.5YR 5/6) light clay, weak, granular, 5% carbonate nodules, effervesces strongly; diffuse to
60-80	As above, but 10% carbonate nodules; diffuse to
80-90	As above, but medium clay; gradational to

90-130	Reddish yellow (7.5YR 6/6) medium clay, weak, granular, 10% carbonate nodules, effervesces strongly; diffuse to
130-160	Strong brown (7.5YR 5/6) medium clay, 20% carbonate nodules, effervesces strongly; continuing to

Grace (iii)

Landscape: An undulating plain used for rotation cereal cultivation and livestock grazing.

Location: 138°32'E, 34°26'S

Climate: Mean annual rainfall 400-450 mm
Mean annual evaporation 1800 mm

Mean altitude: 80 m.

Morphology depth (cm)	Description
0-20	Dark brown (7.5YR 3/4) silt loam, moderate, crumb structure, few roots, effervesces weakly; diffuse to
20-40	As above, weak medium subangular blocky, 5% carbonate nodules, effevesces strongly; gradationl to
40-50	Strong brown (7.5YR 5/8) silt clay loam, weak, medium subangular blocky, 5% carbonate nodules, effervesces strongly; gradationl to
50-70	As above, but silty clay; gradational to
70-110	Strong brown (7.5YR 5/8) light clay, hard, medium subangular blocky, 5% carbonate nodules, effervesces strongly; gradational to
110-140	As above, but light medium clay and no visible carbonate nodules; continuing to
140-150	Reddish yellow (7.5YR 6/6) light medium clay, hard, medium subangular blocky, 5% carbonate nodules, effervesces strongly.

Strathalbyn

Landscape: An undulating plain on tillite with areas of calcrete merging into alluvial fans. The cover is open parkland is used for livestock grazing; the cropland for rotation cereal cropping and livestock grazing.

Location: 138°58'E, 35°14'S

Climate: Mean annual rainfall 350-750 mm
Mean annual evaporation 1750-1800 mm

Altitude: 140 m.

Native vegetation: Open woodland, minor E. odorata.

Morphology depth (cm)	Description
0-10	Dark brown (7.5YR 4/4) silt loam, weak, crumb structure, 5% carbonate nodules, few roots, effervesces strongly; diffuse to
10-20	Light brown (7.5YR 6/4) silt loam, weak, crumb structure, 60% carbonate nodules, effervesces strongly; diffuse to
20-30	Pink (7.5YR 8/4) clay loam, apedal, weakly coherent, 30% carbonate nodules, effervesces strongly; gradational to
30-40	As above, but yellow (10YR 8/6); gradational to
40-60	As above, but silty clay loam, 20% carbonate nodules; gradational to
60-80	As above, but fine sandy clay, 40% carbonate nodules.
80	and onwards carbonate pans.

Trott Park

Landscape: Fans with areas of calcrete on the surface, merging into a gently undulating plain with occassional laterite-capped tableland remnants. Cliffs alternate with beaches and dunes along the coastline. There are three major forms of cover; cropland pastures in the plain; horticultural plantations on the fans and open parkland over grazed pastures on the steeper slopes.

Location: 138°32'E, 35°12'S

Climate: Mean annual rainfall 500-800 mm

Mean annual evaporation 1700 mm

Mean altitude: 40 m.

Morphlogy depth(cm).	Description
0-10	Very dark brown (10Yr 2/3) light clay, friable, crumb structure, few earthworms, many roots, 5% carbonate nodule, effervesces strongly; gradational to
10-20	As above but light medium clay; gradational to
20-30	As above but medium clay, 5% carbonate nodule; continuing to
30-40	As above, but 10% carbonate nodule.
40	and onwards carbonate pans.

Appendix-B. Micromorphological characteristics of soil matrix and carbonate nodules of the surface horizons (0-10 cm depth).

Two types of soil fabric were identified:

(i) Calciapic- and argillasepic fabric with a significant proportion (15-40 %) of silt-size grains of carbonates (Mulders, 1969),

and (ii) Porphyroskelic fabric in which the plasma occurs as a dense ground mass in which skeleton grains are set after the manner of phenocrysts in a porphyritic rock (Stace et al., 1968).

Clarendon: The microstructure was generally compact, and contained angular and subangular quartz grains and few rock nodules. Interconnected vughs and channels. The plasmic fabric was porphyroskelic with skew planes (Fig. 50 A)

Claremont: The microstructure was compact. The skeleton was more abundant than the plasma plus voids, and consisted of angular and subangular quartz grains. Rock nodules and remnants of plant materials and a small amount of feldspars were also present. Voids were irregular, interconnected vughs and channels. The plasmic fabric was porphyroskelic(Fig. 50B).

Dublin: The microstructure was mainly loose with locally compact zones. Randomly distributed angular and subangular quartz grains, few feldspars present. Irregular vughs and voids and some of them connected forming channels. The plasmic fabric was calciasepic porphyroskelic (Fig. 50C). Carbonate nodules were of two types:

(i) undifferentiated nodules with a sharp boundary, and

(ii) sharply outlined nodules.

Grace (i): The microstructure was mainly compact, with locally loose zones. Poorly sorted subangular quartz grains. Remnants of plant materials and presence of feldspars were recorded. Interconnected vughs and voids. The plasmic fabric was calciasepic (Fig. 50D). Carbonate nodules were of two types:

(i) undifferentiated nodules with a sharp boundary, and

(ii) sharply outlined nodules.

Grace (ii): The microstructure displayed a principally loose arrangement. The skeleton grains were predominantly angular and subangular quartz. The plasmic fabric was calciaspic prophyroskelic. Voids were irregular, interconnected vughs and channels. Carbonate nodules were sharply outlined with embedded skeleton grains few or absent (Fig. 50E).

Grace (iii): The microstructure was generally compact with poorly sorted subangular quartz grains, few rock nodules, voids and vughs , some of them interconnected. The plasmic fabric was calciasepic porphyroskelic. Carbonate nodules were sharply outlined (Fig.50F).

Strathalbyn: The microstructure was mainly loose. The skeleton consists of small subangular and subrounded to medium quartz grains. Interconnected vughs and voids. The fabric was calciasepic (Fig. 50G) . Carbonate nodules were of two types:

(i) undifferentiated nodules with a sharp boundary and

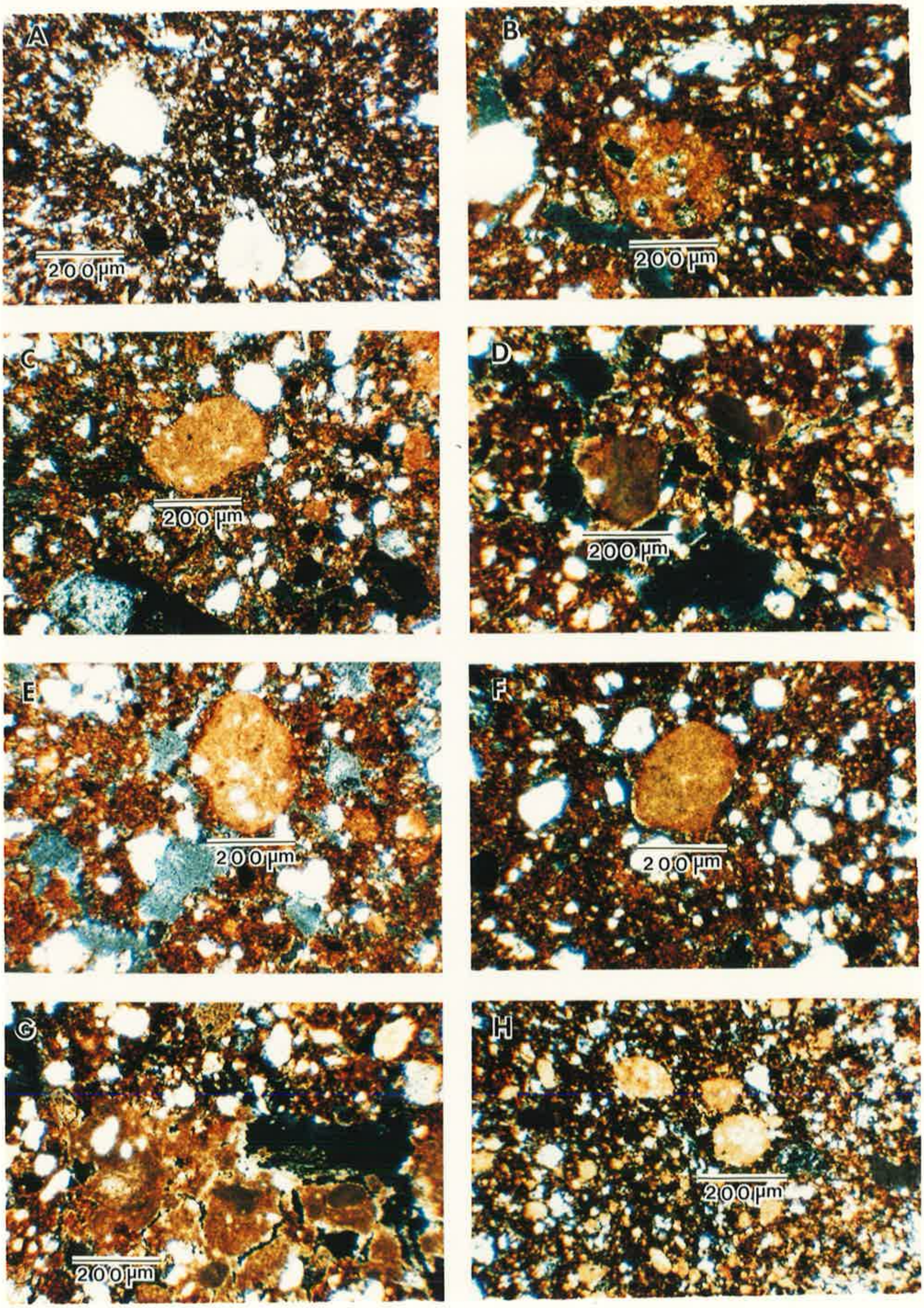
(ii) sharply outlined nodules without or with a few embedded skeleton grains.

Trott Park: The dominant microstructure was loose with locally compact zones. Randomly distributed, angular to subangular poorly sorted quartz grains and remnants of plant materials. A few rock nodules and feldspar were also present. Voids were irregular, interconnected vughs and voids forming big channels. The fabric was calciasepic. Carbonate nodules have round and irregular boundaries (Fig. 50H).

The carbonate occurred primarily in nodule form in the Strathalbyn, Dublin, Grace (i), Grace (ii), Grace (iii) and Waite profiles. At Trott Park, carbonate was present in the form of microcrystals. Clarendon soil did not contain any carbonate nodules in the surface horizon.

The physical and chemical nature and the behaviour of soil materials depend upon the size, shape, and arrangements of soil particles. These result from the modification of the parent rock, or parent material, by soil-forming processes. The presence of calcium carbonate in nodule form indicates a reduction in solubility and hence the effectiveness of $CaCO_3$ on aggregate stability is diminished. Usually, well aggregated calcareous soils tend to have less carbonate nodules in the soil profile than poorly aggregated soils (Blokhuis et al., 1969).

Fig. 50 Micromorphology of carbonate nodules and matrix


A
200 µm
B
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C
200 µm
D
200 µm
E
200 µm
F
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G
200 µm
H
200 µm

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