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THE NATURE OF ORGANIC MATERIALS AND THEIR ROLE IN MICROSTRUCTURAL DEVELOPMENT IN SELECTED CHERNOZEMIC SOILS AS AFFECTED BY MANAGEMENT PRACTICES

BY

ALLAN BRIAN GAJDOSTIK ©

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND REASEARCH IN
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled THE NATURE OF ORGANIC MATERIALS AND THEIR ROLE IN MICROSTRUCTURAL DEVELOPMENT IN SELECTED CHERNOZEMIC SOILS AS AFFECTED BY MANAGEMENT PRACTICES submitted by ALLAN BRIAN GAJDOSTIK in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in SOIL GENESIS AND CLASSIFICATION.

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M.J. Dudas

N.W. Rutter

Date: June 23, 1992

To my mother and father

Abstract

While the quantitative effect of agricultural management on the the soil organic matter has been well documented in the Brown soil zone of southern Alberta, there is still a lack of information regarding its qualitative effects. The first part of this study examined the influence of long-term management systems, native grassland, 60 years of alternate wheat-fallow rotation, and 70 years of irrigated cereal and specialty crop production, on the organic matter and aggregate stability using chemical, physical, chromatographic, and spectroscopic techniques. Despite twofold differences in the organic C concentration between native grassland and corresponding cultivated sites, the FTIR and ^{13}C NMR spectra of the humic acids (HAs) were similar, indicating no major effect of management on the chemistry of the HAs. HAs from irrigated sites had higher contents of carboxyl and peptide groups, as compared to native and cultivated HAs; the higher carboxyl component in irrigated sites indicated the OM was more completely humified. It is concluded that in a particular soil type, changes in amounts and nature of added photosynthate do not change the composition of the organic matter which is controlled by the microbial biomass and interactions of the endproducts of biomass activity with the inorganic phase of the soil.

The second part of this study determined if the degree of microstructural development had progressed sufficiently to justify the classification of these soils as Chernozems. As well, the effects of tillage and irrigation on microfabrics of these soils was evaluated. Management practices, soil faunal activity, and freeze-thaw processes have resulted in considerable diversity in microstructures of the A horizons from the Chernozemic soils studied. These fabrics depart significantly from the mullgranic sequence of fabrics considered typical for soils of the Chernozemic order. Undisturbed Brown Chernozemic Ah horizons have been modified by frost processes to produce a moderately well developed platy microstructure and a humus form that should be described as mull-like moder. Cultivated sites display a spongy and fragmental microstructures, the result of tillage in the fallow year of the rotation. Irrigated sites show well developed spongy microstructure, the result of abundant earthworm activity, and plasmic fabric that is quite uniform in composition and is tending towards mull-like plasma that is typical of Alberta Chernozems.

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INTRODUCTION

There is sufficient data in the literature to justify the statement that cultivation leads to a significant loss of organic matter from soils. However, soils differ markedly in their rates of organic matter loss (Dalal and Mayer 1986a, b). For example, Dalal and Mayer (1986b) found that organic carbon lost from five Vertisols varied from 31 to 59% after 25 years of continuous cultivation of cereal cropping in southern Queensland. The loss of organic matter (OM), usually measured in terms of total organic carbon and nitrogen, is quite rapid initially but decreases as the quantity of organic matter tends toward a new equilibrium level over a period of several decades. It is not unusual for the top ten cm of a cultivated soil to retain half its original OM content based on OM concentrations of virgin sites (Oades et al. 1988). While such losses have been well documented and related to changes in biology and fertility, and various physical parameters, information is lacking on the inherent nature of and changes in the composition of organic materials in soils which have been cultivated regularly compared with the original undisturbed situation.

The maintenance of soil fertility and soil structure is essential to stable cropping systems. In this respect, OM serves a vital role in soils; it is a source of nutrient elements that are released through mineralization, and it contributes to binding mineral matter into stable aggregates, thus maintaining a favorable soil structure.

McGill et al. (1981) postulated that various organic fractions in soils decompose at different rates depending on their chemistry and microbial accessibility. The most resistant fractions, which are assumed to contain a greater proportion of aromatic rings, have a turnover time of about 500 years, whereas the less resistant "humads" have a turnover time around 20 years (McGill et al. 1981). Therefore, the organic carbon remaining after 60 years of wheat-fallow rotation might be expected to be enriched in the resistant fractions.

Brown Chernozemic soils as defined by the Canadian System of Soil Classification (1987) are soils with a chernozemic A horizon with color values darker than 5.5 dry and 3.5 moist; and chromas less than 3.5 moist. In cultivated Brown Chernozems the Ap horizon must be thick enough and retain sufficient chromophores to provide 15 cm of surface material that meets the color criteria above. One of the more common features that define a chernozemic A horizon is the presence of a well developed granular structure and spongy microstructure (granic and /or granoidic related distribution) Kubiena 1970; Pawluk and Bal 1985; Brewer and Sleeman 1988. Preliminary micromorphological investigations (Pawluk and Bal 1985) suggest that such microstructures are either weakly developed or lacking in Brown Chernozemic soils. These soils where medium to fine in texture tend to slake and form surface crusts and readily erode when cultivated (Figure 1.1). The relationship between microstructure and the sensitivity of these soils to tillage have not been investigated.

In order to address the above mentioned issues it was felt the following objectives should be pursued: (i) to ascertain any differences in the chemical nature of the organic fraction from selected Brown Chernozemic soils after 60 years of an alternate wheat-fallow rotation as compared to that in the undisturbed virgin state, (ii) to determine if the degree of microstructural development is sufficient to justify the classification of these soils as Chernozems, (iii) to determine if the degree of humification and organo-clay complexing have progressed enough to produce mull-like plasmic fabrics, which are considered typical for soils of the Chernozemic order, and (iv) determine the effects of cultivation and irrigation on microfabrics of the above soils.

Figure 1.1 Surface clods from a cultivated Brown Chernozem near Foremost, Alberta.

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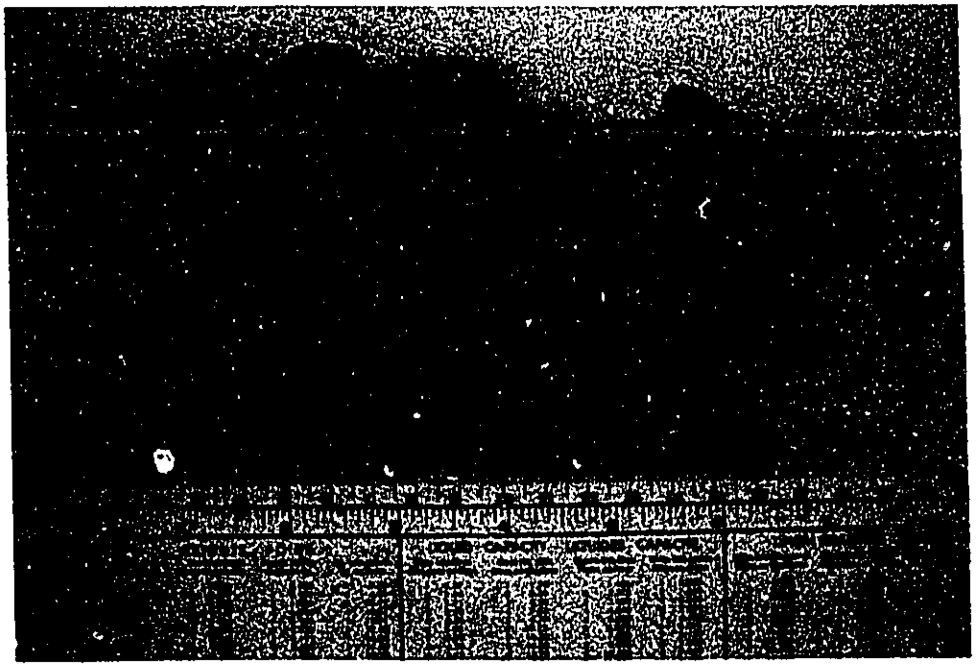

Figure 1.1 Surface clods from a cultivated Brown Chernozem near Foremost, Alberta.

Chapter 2
LITERATURE REVIEW

2.1 The nature of organic materials and their role in aggregate stabilization

2.1.1 Soil structure and crop growth

Soil structure can be defined as "the spatial heterogeneity of the different components or properties of soil" (Dexter 1988). This definition accommodates the many different aspects of soil structure which manifest themselves at many different levels of abstraction in soil. Soil structure is expressed by the size, shape, and arrangement of the solid particles and voids, including both the primary particles and the compound units formed from the primary particle (Brewer 1976). Fabric is the element of structure that deals with the arrangement.

Ideal structure for crop growth on loams and clays depends on the presence of pores for water storage available to plants (pore diameter 0.2-2.5 μm), pores for transmission of water and air (pore diameter 25-100 μm), and pores large enough for roots to grow in (pore diameter > 100 μm) (Oades 1984). A desirable range of pore sizes for a cultivated layer occurs when most of the clay fraction is flocculated into microaggregates, those < 250 μm diameter, and then these microaggregates and other components bound into macroaggregates, those > 250 μm diameter (Oades 1984). Several researchers have shown that the optimum seedbed is composed of aggregates with a range of sizes between 1 and 5 mm diameter in the vicinity of the seed (Russell 1973). For crops with very fine seeds, smaller aggregates than this may be necessary to prevent the seeds from falling down through the inter-aggregate pores. However, it is important that there is always $< 15\%$ fine material (< 250 μm) which can block the larger pores (Dexter 1988). The optimum seedbed provides adequate seed-soil contact for water supply, for swelling and germination, and also adequate aeration.

2.1.2 Creation of soil structure

Macroaggregates can be formed in homogeneous soil by wetting and drying cycles. When soil colloids shrink, cracks normally appear and these cracks define the boundaries of the aggregates or peds. With each wetting of the soil, swelling pressures tend to consolidate the aggregates, but the cracks which define the boundaries between aggregates tend to remain as planes of weakness. Subsequent wetting and drying of each aggregate occurs through the surface defined by the cracks. This is accompanied by a translocation of clay towards the outer part of the aggregate (Dexter 1988). This means the outer part will have a clay content higher than the average for the aggregate, and a porosity which is less than the mean for the aggregate. On each wetting and drying cycle, the features which define the aggregates, such as inter-aggregate cracks and intra-aggregate heterogeneity, become more pronounced until, after a number of years, an equilibrium level of "natural" aggregation is achieved (Dexter et al. 1988).

Clods ("aggregates" > 25 mm) are, in many soils, the result of compaction by agricultural machinery. The compaction pressure applied can fuse smaller structural units together to form larger, rigid groupings. With compression, densification of the soil can extend through the whole soil volume and through all hierarchical (size) orders as has been shown by the reductions in porosity of clay domains under the action of external pressure (Smart 1975).

2.1.2.1 Fragmentation processes

Fragmentation of larger structural units (of higher hierarchical order) to produce smaller structural elements (of lower hierarchical order) is a product of mechanical stress (Dexter 1979). The stress may be applied externally by, for example, a tillage implement. Fragmentation will result when the stress reaches a level equal to the soil strength. The clod or ped can fracture along planes of weakness and hence "liberate" the "imprisoned aggregates". The fracture may be either by shear or by tensile soil failure. Tensile failure is more efficient and is probably more common in the field (Dexter 1979).

With tensile failure of a compound particle (an aggregate) of a given hierarchical order, the failure surface tends to run around and between the particles (aggregates) of the next lower hierarchical order leaving them essentially intact (Dexter 1987). This is because aggregate tensile strength decreases with increasing aggregate size, i.e. higher hierarchical order (Braunack et al. 1979; Hadas 1987). Consequently, externally applied tensile stress tends to destroy only the highest hierarchical order present.

The drying of a wet soil with high shrink/swell capacity is used to describe how desiccation cracks form. Initially, shrinkage is accommodated by vertical (downwards) movement of the surface. Eventually, tensile stresses, acting in the horizontal direction, become equal to the tensile strength of the soil and vertical desiccation cracks occur (Towner 1987). Slow drying tends to produce wide cracks at large spacings, while rapid drying tends to produce numerous cracks that are narrower with smaller spacings between them. These cracks tend to produce a hexagonal-shaped pattern on the soil surface. In crops, though, they may run half way between the rows of plants where the soil is wettest and hence weakest and has a much lower root density than within the row (Sharma and Verma 1977).

When the primary cracks reach a certain width (probably around 5 mm), air convection currents dry the soil at the vertical crack faces (Ritchie and Adams 1974). The tensile stresses induced in the vertical crack walls can induce secondary (horizontal) cracks. Further drying can produce tertiary cracking.

The volumes of soil delineated by the cracks would be turned up as clods upon tillage of such a soil. The clods produced by such desiccation cracking are generally too large and impractical for seedbeds and must be broken down further by application of mechanical stresses. These stresses can be formed externally by tillage implements, internally by weathering (wetting and drying) processes or by a combination of the two, e.g. a few days of weathering followed by mechanical tillage.

2.1.3 Stability of soil structure

2.1.3.1 Stability in water

The architectural arrangement described, whether natural or created by tillage, should be stable to disruption on wetting. When an unstable air-dried aggregate is wetted rapidly it breaks down into smaller sub-units (destruction of one or more hierarchical orders) that may be aggregates from which clay particles may or may not be detached (dispersed); this has been termed slaking by Emerson (1977). Slaking is common and occurs in a wide range of soils where the aggregates are not strong enough to withstand the pressure of entrapped air or the pressure due to unequal swelling (Oades 1984). In the field, slaking of aggregates occurs mainly in surface layers since those below the surface are protected from air-drying and from rapid wetting (Tisdall and Oades 1982). Severe slaking with little or no dispersion is serious, particularly where soils are irrigated, because the slaked layers impede water infiltration and emergence of seedlings.

The destruction of a given hierarchical order automatically destroys all higher hierarchical orders. The ultimate example is the dispersion of clay platelets in a soil in the presence of a "dilute" electrolyte solution. If the organization of clay platelets, which form the lowest hierarchical order, is lost, then all the other hierarchical orders are also lost (Dexter 1988). The particles of clay are released slowly and appear as a spreading cloud around the aggregate (Arnold 1978). In the field the dispersed clay can block small pores that transmit or store water, and slaking and dispersion together produce undesirable structures such as surface crusts (Tisdall and Oades 1982). Swelling and dispersion are a function of the exchangeable ions associated with the clay, e.g., sodium and calcium, and electrolyte concentration.

2.1.3.2 Swelling and dispersion

Organic materials influence the surface properties of clay minerals which in turn influence flocculation and dispersion of the clay platelets. Organic anions are known to form strong complexes with metal ions. Dispersion of clays can result in a manner analogous to that of sodium hexametaphosphate. Oades (1984) has indicated that at least two factors are involved: (a) complexing of trivalent and divalent metal ions reduces their concentrations in solution and (b) the sorbed organic anions increase the negative charge on colloid surfaces thus increasing the diffuse double layer and favoring the dispersion of clay platelets.

The influence of organic materials on the dispersion of clay platelets has been described by Gillman (1974) in soils developed from basalt. Weathering of the ferromagnesian minerals produced a clay fraction abundant in oxides. At depth the clay dispersed as a colloid with a net positive charge, that is the zero point of charge (ZPC) of the clay was higher than the pH of the soil. Closer to the soil surface where the organic carbon content was higher the ZPC matched the pH of the soil and there was little dispersible clay. At the 20-30 cm depth interval substantial quantities of dispersible clay were present as the ZPC was lowered below the pH of the soil through sorption of negatively charged polymeric material (Oades 1984).

2.1.4 Aggregate stability as related to organic carbon content

Over the past few decades there have been numerous correlations between organic carbon content in soils and water-stable aggregation. The correlations have not always been great for any or all of the following reasons: (i) only part of the organic fraction is responsible for aggregate stabilization, (ii) there is a content of organic carbon above which no further increase in aggregate stability is observed, (iii) it is the position rather than the total amount of organic matter that is important, (iv) organic materials may not be the major binding agents, and (v) some of the aggregate stability in virgin soils is related to the spacial arrangement of organic and inorganic constituents such that particle reorganization associated with the first disturbance of virgin sod leads to a decline in the stability of aggregates (Malik et al. 1965; Low 1972; Tisdall and Oades 1980b). The stability is sometimes better related to free organic materials than to total organic carbon because this fraction acts as a substrate for microbial production of organic glues (Oades 1967), and because this fraction is a measure of roots and fungal hyphae.

Management of a soil can change the quantity of organic materials by 25 to 50 per cent and there is sufficient data to show this change can occur under different climates (Low

1972; Turchenek and Oades 1979; Lal et al. 1979; Dalal 1989; Arshad et al. 1990). Cultivation is exploitive and causes a decline in the quantity of organic materials. This decline is accentuated if fallow is included in the rotation where the soil is cultivated to ensure no plant growth (Ramig and Mazurak 1964; Ridley and Hedlin 1968; Emmond 1971; Martel and Paul 1974). Where the soil is cultivated often, aggregates are frequently exposed to physical disruption by rapid wetting and raindrop impact as well as to shearing by implements. The overall effect is to expose inaccessible organic substrates to microorganisms, increase the rates of annihilation and oxidation and therefore, the loss of organic materials (Martel and Paul 1974; Adu and Oades 1978). The rate of decline in organic matter, however, is not the same on all soil types. Skjemstad and Dalal (1987) proposed that clay soils containing dark colored humus will lose organic carbon more slowly upon cultivation than those with a large proportion of light colored humus. Dark colored humus is more completely humified with more aromatic and carboxyl groups and displays the most recalcitrance to degradation. Organic matter that is much less humified and low in aromatic and carboxyl groups will also be low in chromophores and produce low Munsell values and will offer less resistance to enzymatic attack (Skjemstad and Dalal 1987).

Organic matter can accumulate under good pastures and native grassland because the annual addition of phytomass is greater than under field crops, i.e. cereals and oilseeds. The number of stable aggregates increases under lush grass pastures and native grassland communities. This can be attributed to the perennial nature of the plant communities, length of root, vesicular-arbuscular (VA) mycorrhizal hyphae (Tisdall and Oades 1980b), and because abundant decomposable organic residues accumulate in the A horizon.

The interactions between organic polymers and mineral surfaces are complex but the mechanisms are known and have been reviewed by Greenland (1965a, 1965b, 1971) and Mortland (1970).

2.1.5 Mechanisms of clay-organic interactions

2.1.5.1 Interactions of humic and fulvic acids with surfaces of phyllosilicates

Most of the organic matter in soils is present as negatively charged polymeric material (Greenland 1971). As mentioned earlier, organic anions are normally repelled from the surface of negatively charged clay platelets. Some adsorption can occur if polyvalent exchangeable cations are present. Bonding in this way through an exchangeable cation is referred to as formation of a "cation bridge". Basically the process involves replacement of a water molecule from the hydration shell of the exchangeable cation by an oxygen of an anionic group, such as carboxylate or phenate, from the organic polymer. Charge neutrality at the surface is maintained by the cation formerly satisfying the charge of the organic functional group entering the exchange complex of the clay mineral (Greenland 1971). Yariv, Russel, and Farmer (1966), using infrared spectroscopy, showed that benzoate ion can be directly coordinated to the exchangeable cation, Figure 2.1-1 (a), usually however, a water molecule remains to from a hydrogen bond between cation and anion, Figure 2.1-1 (b).

Humic and fulvic materials adsorbed by only a bridge linkage with a divalent cation will be rather easily displaced by leaching the soil with the salt of a monovalent metal (Greenland 1971). The displacement of small amounts of humic and fulvic materials when calcium saturated clays are leached with ammonium chloride indicates some associations of organic materials with clays by this mechanism. Displacement of the organic components will occur less readily if exchangeable cations such as iron and aluminum, which can be strongly coordinated by the organic molecule, are present (Mortland 1970). A reagent able to complex the iron or aluminum with a strength at least on the same order of magnitude as the humic or fulvic acid is necessary for displacement (Greenland 1971).

The figure has been omitted due to copyright restrictions.

Figure 2.1-1 (from Greenland 1971).

In addition to coordination with exchangeable cations, other bonding forces can be active between organic anions and clay minerals. Hydrogen bonding is an important bonding process in many clay-organo complexes. It becomes very important in large molecules and polymers where additive bonds of this type together with a large molecular weight can produce a stable complex (Mortland 1970). The water bridge entails the linking of a polar organic molecule to an exchangeable metal cation through a water molecule in the primary hydration shell. This type of bond has been confirmed for montmorillonite complexes with pyridine (Farmer and Mortland 1966), ketones (Parfitt and Mortland 1968), benzoic acid and nitrobenzene (Yariv et al. 1966), and organic polymers (Parfitt 1969). Evidence is shown in the infrared spectrum by a lowering of the OH stretching frequencies of water due to the hydrogen bond formation. Its importance is greatest where the cation in question has a high solvation energy and consequently retains its primary hydration shell in spite of the intrusion of neighboring polar organic molecules (Mortland 1970). An example to illustrate this point is in the adsorption of acetone by Na^+- and Mg^{2+}-montmorillonite. Parfitt and Mortland (1968) showed for a given set of conditions the ketone to be directly coordinated to the Na^+, but indirectly coordinated to the Mg^{2+} through a water bridge linkage. Where special treatments have been used to dehydrate the cation direct ion-dipole interaction will occur.

If water molecules are displaced completely from the clay-organo system van der Waals or physical forces (London dispersion) can be significant. These result from attraction between oscillating dipoles in adjacent atoms. They decrease rapidly with distance between the interacting species. They do become quite significant in clay-organo complexes, particularly for organic compounds of large molecular weight (Greenland 1965a). The magnitude of each point of contact is small but because these interactions are additive their contribution to the total adsorption energy may be quite large. Greenland (1965a) suggested an increment of 400 cal per mole for each CH_2 segment of *n*-alkylammonium ion. With the large cations he suggests that van der Waals interactions dominate the adsorption process.

Once clay and organic material have been dried together so that these additional adsorption mechanisms are involved, they are not likely to be reversed. The probability of desorbing the molecule concurrently from each point of contact along the clay mineral surface is low (Greenland 1971). Extensive drying will thus increase the bonding between clay and humic materials. However, preliminary drying will assist in separating non-humified organic constituents not associated with the clay fraction from the remaining clay-organo complex (Ford et al. 1969). Drying, including air-drying, should be avoided as a pretreatment to extracting humic and fulvic materials from soils.

2.1.5.2 Interaction of humic and fulvic acids with hydrous oxides and edges of clay platelets

Positively charged sites normally exist on iron oxyhydroxides and aluminum hydroxides below pH 8 (Parks 1965) due to protonation of hydroxyl groups. Organic anions can therefore be associated with oxides by simple coulombic attraction. The adsorption of organic anions is readily reversed by exchange with chloride. This type of coulombic association is referred to as non-specific adsorption or more appropriately as anion exchange adsorption (Greenland 1971) (Figure 2.1-2).

The figure has been omitted due to copyright restrictions.

Figure 2.1-2 (from Greenland 1971).

In addition to anion exchange reactions, specific adsorption of anions by hydrous iron and aluminum oxides normally occurs. In this type adsorption the anion penetrates the coordination shell of an iron or aluminum atom in the surface of the hydroxide (Greenland

1971) and is thus incorporated with the surface hydroxyl layer (Figure 2.2). The difference between anion exchange reactions and this type of adsorption is the anion cannot be displaced from the complex produced simply by leaching the soil with a solution containing a non-specifically adsorbed anion such as chloride. Also, the process is not sensitive to electrolyte concentration, although it is sensitive to pH (Greenland 1965a). An adsorption maximum or inflection occurs in the adsorption-pH curve at or near the pH corresponding to the pKa value of the acid formed by the anion. Hingston et al. (1967, 1968) use the term specific adsorption or ligand exchange to describe this adsorption process. Ligand exchange would seem the more appropriate term.

A vast number of carboxylic acids are strong ligands for iron and aluminum ions (Schnitzer 1969). It would be expected then, that humic and fulvic acids would partake in ligand exchange reactions of the type describe by Hingston et al. (1967, 1968). Maximum adsorption should be observed near pH 5 since the carboxyl groups of humic acids have pKa values around this pH (Posner 1966). A very strong bond will form between oxides and humic materials if several carboxyl or other functional groups participate, even if they are distanced from each other on the molecule and interact with different ions in the surface of the hydroxide (Greenland 1971). Many other studies dealing with the bonding of metallic cations by humic and fulvic acids have shown that the metal cations tend to be strongly bonded to the carboxyl groups (Kononova 1966).

Although most available evidence indicates that hydrous oxides of iron and aluminum are the most important species involved in the interaction between secondary minerals and organic compounds in soils, silica and even quartz are not necessarily inactive in this respect. Holt and Went (1960) and Baumann (1963) have shown that silicic acid interacts strongly with organic polymers.

It seems probable that hydrous oxides would provide more available sites for adsorption to humified organic material than the surfaces of phyllosilicates. Very fine crystalline oxides of iron (e.g. goethite, lepidocrocite), aluminum, and silicon are known to be widely distributed in soils and have extensive, active surfaces which are normally hydrated so that they can participate in adsorption reactions similar to those of hydrous oxides. If the crystals are of relatively small size, 0.1 μm or less, the "activity" of the crystals will be very high (Greenland 1971).

Non-crystalline hydrous oxides have very extensive and active surfaces (Greenland 1971) However, such hydroxides possess limited stability and eventually are converted to more stable crystalline forms. Schwertmann (1965) and Schwertmann and Fischer (1966) have found that the amounts of non-crystalline iron hydroxides in soils are greater than would be expected from laboratory studies on the crystallization of such materials in relatively pure systems. Schwertmann (1966) and Schwertmann et al. (1968) subsequently showed that non-crystalline ferric hydroxide gels are exceptionally stable in the presence of soil organic matter and citrate ions. Schwertmann has suggested that the sorption of organic ions is responsible for the stability of non-crystalline iron hydroxides in soils. It is also probable that the sorption of organic anions is responsible for the observation that "free iron oxides" in many surface soils do not appear to carry a net positive charge (Deshpande et al. 1964).

2.1.6 *Aggregate organization*

Edwards and Bremner (1967) proposed that macroaggregates (> 250 μm diameter) consist of complexes of clay mineral-polyvalent metal cation-organic matter (C-P-OM) in which clay minerals are bonded to humified organic matter via a bridge of polyvalent metals. Units of C-P-OM were aggregated to give $(\text{C-P-OM})_x$, both of which were < 2 μm diameter. Further aggregation led to microaggregates of $\{(\text{C-P-OM})_x\}_y$ which were < 250 μm diameter. Bonds of C-P-C and OM-P-OM may also occur.

Muneer and Oades (1989) discussed the role of bridges of polyvalent cations in aggregation of soils. The aggregation model they proposed is based on that of Tisdall and Oades (1982), but indicate that cation bridging mechanisms are involved in the stability of aggregates both greater and less than 250 μm diameter.

At the submicron scale, Ca^{2+} is involved in the stability of quasi-crystals and domains. At a similar scale, Ca^{2+} is implicated in crosslinking functional groups in humic macromolecules (Muneer and Oades 1989).

In the microaggregate range, Ca^{2+} is involved in linking clay domains to humic components (clay-Ca^{2+}-OM). These units are further aggregated to produce (clay-Ca^{2+}-OM)$_x$ where x=3-10, in the manner described by Edwards and Bremner (1967). When x=12-50, the aggregates have diameters from 50-250 μm (Muneer and Oades 1989). Such microaggregates are then bound together by plant roots and fungal hyphae into stable aggregate with diameters of several mm.

2.1.7 *Aggregate hierarchy*

There is abundant evidence at present to indicate that stable aggregates with diameters of a few millimeters are not simply a random arrangement of the various particles responsible for the texture of the given soil. The first essential element for stable aggregate formation is flocculation of clay platelets.

Emerson (1977) suggested that parallel clay platelets (5 μm diameter) are assembled closely enough (0.1-1.3 μm apart) to behave as a hydrated unit called a domain. In his model organic materials stabilize the aggregate mainly by forming and strengthening bonds between domains and between quartz grains and domains, though the quartz grains may be linked directly to the organic fraction.

Quirk and Aylmore (1971) used the term quasi-crystals to describe the regions of parallel alignment of individual platelets of aluminosilicates in montmorillonite, that exhibit intra-crystalline expansion; they used the term domain to describe the regions of parallel alignment of crystals for illite and other clay minerals with fixed lattices, that exhibit inter-crystalline expansion only.

Quasi-crystals or domains < 2 μm diameter are often floccules consisting of clay platelets that come together to form a fluffy mass. Initially the platelets are not parallel but rather edge-to edge to form a card-house structure (Quirk 1978). On drying the system tends to lower its entropy enabling the platelets to become parallel to each other. The crystals can then be joined into larger units with interlamellar regions 2.5-4.1 nm between the crystals (Murray and Quirk 1979). In surface soils perfect alignment of the clay platelets probably occurs rarely so that the arrangement within particle< 2 μm diameter is somewhere between that of a card-house structure and that of a crystal. The platelets are held together by coulombic attraction, hydrogen bonding, and van der Waals forces.

Some particles < 2 μm diameter have been shown to be aggregates of very fine material held together by organic materials and iron oxides. In particles < 2 μm diameter, organic material is sorbed onto the surfaces of clays and held firmly by the various bonds described earlier.

The necessity to oxidize soil organic materials in particle size determinations is well known. The standard peroxidation treatment not only releases clay from microaggregates but also releases much of the very fine clay, i.e. < 0.08 μm diameter. The specific surface area of clay fractions is increased manyfold over the same fractions that were left untreated (Turchenek and Oades 1978). In order to account for these very large increases in surface areas of clay fractions either the organic materials coat quasi-crystals and domains and render them inaccessible to N_2 gas when it is used to determine surface areas, or fine clay is embedded in a matrix of organic matter (Oades 1984).

Aggregates 2-20 μm diameter are composed of tiny aggregates < 2 μm diameter bonded together so intensely by persistent organic bonds that they are not disrupted with tillage. Tisdall and Oades (1982) have indicated that some aggregates 2-20 μm diameter under old pasture growth were resistant to ultrasonic vibration for 5 minutes. Aggregates 2-20 μm diameter, obtained by ultrasonic dispersion or trituration from soils with high contents of clay and high base status, often have high contents of organic carbon (Oades and Ladd 1977; Turchenek and Oades 1978). This organic-rich fraction is highly water-stable in chernozemic soils and soils under old pasture growth (Pokotilo 1967; Turchenek and Oades 1978).

Tisdall and Oades (1982) presented a transmission electron micrograph of an ultra-thin section of soil from the rhizosphere in which aggregates 2-20 μm diameter consisted of fine aggregates < 2 μm diameter bound tightly together. Fordham and Norrish (1979) also described aggregation at this level as particles bound together via strands of glutinous material that was likely organic in nature. It was also noted by the authors that some aggregates 2-20 μm diameter were believed to be just oversized floccules of clay.

The same micrograph from Tisdall and Oades also showed individual bacteria and colonies of bacteria surrounded by a capsule of carbohydrate to which particles of fine clay appeared firmly attached. The fact that such associations between live bacterial cells and clay platelets appear to form aggregates 2-20 μm diameter is supported by the work of Ladd et al. (1977) and Ahmed (1981), who found a substantial part of the microbial biomass existed in the silt-size fraction. Since only about 2 percent of the organic matter in soils consists of biomass (Jenkinson and Rayner 1977), silt-size aggregates consisting of living bacteria must be newly formed aggregates. However, aggregates formed from bacterial colonies only represent a small number of particles stabilized by microbial debris since fungi contribute much more to soil biomass than do bacteria (Paul and van Veen 1978).

Tisdall and Oades (1982) stated that aggregates 20-250 μm from red-brown earths are stable to rapid wetting and are also not disrupted by agricultural practices. They can, however, be broken by ultrasonic vibration. Aggregation at this level involves bonding by various binding agents that include persistent organic materials and crystalline oxides and disordered aluminosilicates. The aggregates 20-250 μm diameter are quite stable partially because they are still relatively small but also, and more importantly, they involve several different types of stabilizing agents whose effects are additive over the whole unit. The individual bonds must be rather strong because the aggregates in this size range contained less than one-half as much organic carbon as the considerably less stable aggregates > 250 μm diameter as reported by the authors.

Stable aggregates 250-2000 μm diameter (macroaggregates) and those > 2000 μm in red-brown earths with high accumulations of organic carbon, more than 2 percent, are composed of microaggregates, mineral grains, and undecomposed organic fragments held together by a complex network of roots and associated fungal hyphae. Because the stability of such macroaggregates is controlled by root growth, agricultural management will have a dramatic impact on the organization and stabilization of the larger soil units.

An idealized model from Tisdall and Oades (1982) can be drawn to show that an aggregate of soil is made up of structural units of incremental sizes bound together by various binding agents (Figure 2.1-3).

Natural surface soil is not likely to exhibit such discreteness in structural units as has been indicated here. Considerable overlap between the proposed stages is a more realistic scenario in the development of an aggregate several millimeters in diameter. Nevertheless, there is sufficient evidence, particularly by the Australian researchers, to justify the proposed levels of aggregate hierarchy. Their evidence also indicates there is not a smooth continuum of sizes of stable aggregates and that structural integrity of the units at each stage is associated with a dominant binding agent.

2.1.8 Classification of organic binding agents

The organic binding agents implicated in stabilizing aggregates can be considered as three main groups based on the age and stage of decomposition of the organic materials. The types of binding agents govern the age, size, and stability of aggregates (Tisdall and Oades 1982). The three groups of organic binding agents to be discussed are labile, temporary or seasonal, and persistent.

2.1.8.1 Labile binding agents

Labile binding agents are organic materials that are rapidly decomposed by microorganisms. The most important group are the polysaccharides including microbial polysaccharides produced when organic materials are added to soil and those associated with roots and the microbial biomass in the rhizosphere (Russel 1973; Oades 1978). Polysaccharides are produced rapidly (Harris et al. 1966; Aspiras et al. 1971) and are degraded rapidly; this is why they are referred to as labile components.

The figure has been omitted due to copyright restrictions.

Figure 2.1-3 (from Tisdall and Oades 1982).

Tisdall and Oades (1982) introduced an important generalization with respect to the dynamics of stable aggregates in soil after the addition of organic materials. Readily utilizable energy substrates, such as glucose, increase stable aggregation which is transient (few weeks) because the carbon source is readily metabolized. Less readily utilizable substrates, such as grass tissue, produces a gradual increase in stable aggregates that lasts for several months. More recalcitrant materials, cellulose for example, slowly give rise to limited stability that persists for several months.

As the growth of plants proceeds, all three interactions operate so there is an increase in stable aggregates that lasts for the season because roots and associated hyphae are decomposed slowly (Tisdall and Oades 1980a). A portion of the polysaccharides can be protected from microbial degradation by association with metal ions and/or by sorption on the surfaces of clay minerals (Martin 1971; Griffiths and Burns 1972). These components and their binding action would then persist for several years.

The most convincing evidence that polysaccharides function as stabilizing agents in soil aggregates arose from the use of periodate as a selective oxidant for polysaccharides.

Soils to which organic materials were added and soils that were cultivated frequently and subsequently had low contents of organic matter were shown to have significant decreases in aggregate stability after periodate oxidation (Greenland et al. 1962; Stefanson 1971). However, it has also been observed that in some soils, destruction of polysaccharides has no influence on the level of aggregation; this means that other organic binding agents and/or inorganic cements are active.

The association of polysaccharides (be they bacterial, fungal, or affiliated with plant roots) with clay domains has been clearly illustrated by electron microscopy (Jackson et al. 1946; Foster and Rovira 1976; Tisdall and Oades 1979). These people showed convincingly the attachment of clay platelets to capsular or exuded polysaccharides.

Tisdall and Oades (1982) remind us to keep in mind the scale at which this association takes place. The polysaccharides bind clay-size particles together into aggregates that are in the order of 10 μm diameter. It seems rather unlikely that modest quantities of polymers with chain lengths of a few hundred ångströms would be significant in binding microaggregates into larger units with diameters of several millimeters.

Inconsistencies in the literature on the role of polysaccharides in stabilizing aggregates can be explained when one considers the size of aggregates investigated. Greenland et al. (1962) and Stefanson (1971) assessed the effects of treatments on small aggregates, i.e. those with diameters less than 50 μm. Tisdall and Oades (1980b) evaluated the effects of periodate on aggregates with diameters up to 10 mm. They found that aggregates with diameters greater than 50 μm were not affected by the periodate treatment. Mehta et al. (1960) looked at 2-4 mm aggregates and Webber (1965) examined > 250 μm aggregates; both groups of researchers concluded that periodate-sensitive components were not responsible for stabilizing macroaggregates. The integrity of large aggregates is not affected by periodate and it suggests that polysaccharides are not involved in stabilizing aggregates with diameters of several millimeters. It does, however, suggest that polysaccharides stabilize aggregates less than 50 μm in diameter and domains of clay (Tisdall and Oades 1982). Polysaccharides, it would seem, would have less relative importance in soils with high proportions of organic carbon such as those under permanent tall grass.

2.1.8.2 Temporary or seasonal binding agents

Temporary or seasonal binding agents are roots and fungal hyphae, particularly vesicular-arbuscular (VA) mycorrhizal fungal hyphae (Tisdall and Oades 1979; Tisdall 1991). These binding agents build up in the soil within a few weeks or months as the root systems and associated hyphae grow. They persist for the growing season and up to several years and are greatly affected by management of the soil (Tisdall and Oades 1979, 1980a, 1980b; Tisdall 1991). The seasonal binding agents are likely associated with younger macroaggregates and can be equated with the organic skeleton grains described by Bal (1973).

2.1.8.2.1 Roots

Roots supply decomposable organic residues to soil and support a large microbial population in the rhizosphere. As well, the roots of some plants, especially grass species, act as binding agents themselves. They enmesh fine aggregates into quite stable macroaggregates, even after the root has died (Clarke et al. 1967).

Residues released into the soil by roots are in the form of fine lateral roots, root hairs, sloughed-off cells from the root-cap, dead cells, mucilages, lysates and water-soluble carbohydrates (Rovira and McDougal 1967; Shamoot et al. 1968; Martin 1971; Dickinson 1974; Oades 1978). The amount of organic carbon released by roots is related to the length of root (Shamoot et al. 1968). The root systems and associated fungal hyphae of grass species are quite extensive especially in more moisture bioclimatic zones; the top few centimeters of soil would be considered all rhizosphere.

Electron micrographs of the rhizosphere showed that clay domains along the root tend to be oriented parallel to the axis of the root; the percentage of oriented particles increases with the age of the root and proximity to the root surface (Blevins et al. 1970; Foster and Rovira 1976). The clay domains had probably been reoriented by the expanding roots and by localized drying around the root, from randomly oriented positions to those of minimum energy (Aylmore and Quirk 1959).

Plants may also increase aggregate stability by providing a steady supply of carbon and other nutrients for microorganisms. This would then lead to a food supply for the mesofauna, which in turn would serve as a source for earthworms enabling populations to build up. Earthworm casts generally contain more organic carbon than the surrounding soil and the casts from soil under pasture were more stable than the surrounding soil (Swaby 1950). Earthworms can stabilize soil structure by ingesting soil and mixing it intimately with humified organic materials in its gut (Swaby 1950; Barley 1959).

2.1.8.2.2 Hyphae

Allison (1968) suggested that fine roots dry the soil locally as they grow through soil, thereby assisting with the formation of aggregates which are then stabilized by microbial polysaccharides. Other researchers have suggested that fungal hyphae form macroaggregates which are then stabilized by the hyphae or other microorganisms (Elliott and Coleman 1988; Gupta and Germida 1988; Chenu 1989). Scanning electron micrographs of virgin soil rhizospheres have shown that fungal hyphae entangled particles into macroaggregates which were stabilized by amorphous material, likely polysaccharide (Gupta and Germida 1988). Elliott and Coleman (1988) speculated that roots and fungal hyphae physically form macroaggregates and that microorganisms at the center of each macroaggregate produce polysaccharides that further add to the stability of the macroaggregate. Working with pure clay and saprophytic fungi Chenu (1989) suggested that the fungi reorganize the clay platelets into aggregates and then stabilize these aggregates with extracellular polysaccharides. The results of Aspiras et al. (1971) and Tisdall and Oades (1980b) support the hypothesis that fungal hyphae can form and stabilize aggregates, but suggest that the fungal polysaccharides can also stabilize existing macroaggregates. Hence in the field, extracellular polysaccharides of fungi probably stabilize existing aggregates (possibly formed by roots), and their polysaccharides can probably also form and stabilize new macroaggregates.

The sorption of clay platelets to fungal hyphae affects the stability of aggregates not only through the strength and persistence of bonds in soil, but also through the ability of the hyphae to grow and survive in the soil (Stotzky 1986). Particles of fine clay ($< 0.2\ \mu m$) are found to align parallel to fungal hyphae and stick firmly to the hyphae by mucilage of polysaccharide (Tisdall and Oades 1979; Foster 1988).

On agar plates, saprophytic fungi often produce an extracellular viscous mucilage composed of polysaccharide-proteins and glycoproteins which are structurally related to those in the cell wall (Chenu 1989). Low concentrations (0.5% or less) of such polysaccharides isolated from pure cultures sorb strongly to particles of clay or soil (Chenu 1989). Usually the higher the molecular weight of the polysaccharide, the more stable the aggregate (Tisdall 1991). Scleroglun, an extracellular polysaccharide produced on artificial media by a saprophytic fungus *Sclerotum*, is a neutral glucose polymer with a molecular weight of 1.5×10^6, and forms a viscous solution or gel in water (Chenu 1989). This polysaccharide was adsorbed on the surfaces of platelets of montmorillonite or kaolinite, probably via hydrophobic bonds; the adsorbed polysaccharide formed aggregates but did not enter the interlamellar region of Ca^{2+}-montmorillonite (Mortland 1986; Chenu 1989).

Extracellular bacterial polysaccharides stabilized aggregates of soil but the effect persisted for longer when polyvalent cations, e.g. Al^{3+} or Ca^{2+}, were present which suggests that negatively charged polysaccharides were bound to a negatively charged clay platelet by bridges of polyvalent cations (Martin 1971). Such bridges also appear to form between fungal hyphae and platelets of clay (Tisdall 1991). The bonds formed by these bridges are not destroyed by periodate alone, but are destroyed by sequential treatment with periodate and pyrophosphate, and may lead to higher levels of, and more persistent stable aggregates (Martin 1971; Emerson et al. 1986; Muneer and Oades 1989).

Polyvalent cations for such bonds could come from crystals of calcium oxalate or calcium carbonate often seen on the surfaces of hyphae or from mineral soil (Foster 1988). Localized wetting of the crystals or soil close to the hyphae could dissolve polyvalent cations, making them available for bridges between hyphal polysaccharides and platelets of clay (Tisdall 1991).

Although most hyphae can enter finer pores more readily than can roots or root hairs, fungal hyphae are found in the outer regions of a macroaggregate, where most of the pores are large; bacteria are generally found in the center where most of the pores are small (Foster 1988). This is attributable to the fact that fungal hyphae are aerobes, are larger (2-27 μm diameter) than bacteria (mean 0.5 μm), and can grow in drier soils than can bacteria

(Tisdall 1991). This may limit the size of macroaggregates to several mm in diameter, and may be why macroaggregates from soils under pasture are rounder than those from tilled soils (Dexter 1985). The surface stable macroaggregates are rougher and more friable than those from tilled soil (Chan 1989). This is likely due to the attachment of microaggregates to a loose network of fungal hyphae in a stable macroaggregate which is easily crushed or broken by tillage (Tisdall 1991).

2.1.8.3 *Persistent binding agents*

Persistent binding agents consist of degraded, aromatic humic material associated with the amorphous iron, aluminum, and aluminosilicates to form the large organo-mineral fraction of soil which constitutes 52-98 percent of the organic matter in soils (Greenland 1965b); Hamblin 1977; Turchenek and Oades 1978). The persistent binding agents include complexes of clay-polyvalent metal-organic matter, C-P-OM and $(C\text{-}P\text{-}OM)_X$, both of which are < 250 μm diameter as described by Edwards and Bremner (1967) and Muneer and Oades (1989), and probably include the skeleton grains described by Bal (1973).

Persistent binding agents are probably derived from the resistant fragments of roots, hyphae, bacterial cells and colonies (i.e. seasonal binding agents) developed in the rhizosphere. The humic material is thought to be in the center of the aggregate with platelets of fine clay sorbed onto it (Foster 1978; Turchenek and Oades 1978) rather than the humic material sorbed onto clay surfaces (Greenland 1965b). However, persistent binding agents have not yet been defined chemically (Tisdall and Oades 1982). It is likely that a precise chemical formula cannot be defined in the same way that a formula for humic acid cannot be defined. A small percentage of the binding by persistent materials can be broken with ultrasonic vibration (Edwards and Bremner 1967). In Chernozemic soils, especially those with a high percentage of organic carbon, aggregates 1-20 μm diameter containing organo-mineral complexes resist limited ultrasonic vibration (Hamblin 1977; Tate and Churchman 1978; Turchenek and Oades 1978). Also included in this group are strongly sorbed polymers such as polysaccharides and humic components stabilized by association with metals (Figure 2.1-4). Multifunctional organic anions associated with di- and trivalent metal cations will act as stabilizing agents.

The figure has been omitted due to copyright restrictions.

Figure 2.1-4 (from Tisdall and Oades 1982).

2.2 Soil fauna and soil structure

2.2.1 Fecal pellets as soil aggregates

Several authors (Hopp 1946; Ponomareva 1950; van de Westeringh 1972) have reported that up to 50 percent of the aggregates in surface horizons of temperate pasture soil are recognized as earthworm casts. In mull-type forest soils in Europe Kubiena (1953) and Dobrovol'skii and Titkova (1960) recognized nearly all the aggregates of the A_1 horizon as earthworm casts or residues of casts.

Microstructure of the Mollic epipedon from Typic Cryoborolls (Orthic Black Chernozems) on morainal parent material within the Black soil zone of Alberta, Canada has been reviewed extensively by Pawluk and Bal (1985) and Pawluk (1985). In the fabric descriptions of Pawluk and Bal (1985) fecal pellets are ubiquitous, comprising the majority of the granic units. Similarly Pawluk (1985) observed the humigranic and mullgranic units within fabrics of the Ah horizon to be largely fecal pellets varying in size from 30 μm to 2 mm. Pawluk and Bal (1985) clearly state the microstructure is developed from excrement and burrowing activity of a very diverse population of soil fauna and through plant root growth. Springtails (Collembola) play a key role in structure development in these soils. Their modexi, 30-65 μm in size, dominate the A_1 (15-30 cm thick) horizon where they consist of humic materials in some zones and mixed and complexed humic and mineral material in other zones (Pawluk and Bal 1985). Mite (Acari) modexi of about 30 μm in size consisting of humic material are found almost exclusively where decomposing root and stem tissue is present. Fecal pellets of Millipedes (Diplopoda), about 500 μm in diameter, and Diptera larvae, 600-750 μm size, are also prominent in the fabric of these soils (Pawluk 1985). Intimately mixed mineral and organic components characteristic of the pellets of Potworms (Enchytraeidae) are found to make up about 10 percent of the fabric in certain zones (Pawluk and Bal 1985). Earthworm (Lumbricidae) fecal material also exhibiting the characteristic mixing of organic and mineral components, is more common in the lower section of the A_1 (30-90 μm thick) where the largest modexi reach 1000-1800 μm in diameter.

2.2.2 *Stability of earthworm casts*

Lee and Foster (1991) in their review note the importance to distinguish between the structural stability of freshly deposited casts, which are generally less stable than that of other soil aggregates, and the increase in stability with increasing time after deposition. The stability of earthworm casts depends largely on the nature and concentration of organic matter they contain (Lee and Foster 1991). Swaby (1950) suggested an increase in the stability of casts was the result of gums produced by bacteria in the soil as it passed through the gut and that the production of these gums was promoted by the presence of organic materials in the ingested soil that favored the multiplication of bacteria.

Tests of aggregate stability on earthworm casts, water drop impact method or wet sieving, have shown that casts are often more stable, but sometimes less stable than other soil aggregates (Lee and Foster 1991). The physical degradation and breakdown of earthworm casts is related to their tensile strength, which determines their resistance to crushing forces, raindrop impact, and their water stability. McKenzie and Dexter (1987) determined the tensile strength of casts of *Aporrectodea rosea*, using a relationship established by Dexter and Kroesbergen (1985) between the force required to crush as cast and the diameter of the cast. There is a correlation between the matric potential at which the cast is produced and the tensile strength. It was shown that the tensile strength of dried casts was about 2-5 times that of similar sized dried soil aggregates, regardless of the matric potential at which the casts were deposited. The greater stability of earthworm casts a few days old is attributable to fungal hyphae, probably invading from the surrounding soil, since most of the hyphae observed in fresh casts are devoid of cytoplasm (Lee and Foster 1991). A lack of longer-range binding materials may account for the generally low mechanical strength of freshly deposited casts (Marinissen and Dexter 1990).

In the work of Shaw and Pawluk (1986), direct microscopic examination in addition to chemical analyses of casts of *Lumbricus terrestris, Octolasion tyrtaeum,* and *Aporrectodea turgida,* obtained from three soils of differing particle size distribution, showed that in all three species' casts aggregate stability was enhanced. All casts studied demonstrated increased orientation of clay domains, while the chemical analyses strongly supported the concept that a favorable granular fabric is associated with concentration of clay-bound neutral sugars in the modexi. It was concluded, however, that the presence of some other organic binding agent was necessary to account for some of the observed aggregate stability; this binding agent was thought to be mucopolysaccharides derived from mucus secreted into the gut.

2.2.3 Synergistic effect of mixed species populations of earthworms

In the investigations of Shaw and Pawluk (1986), mentioned above, *L. terrestris* is an anecic species that removes large quantities of litter from the surface into its burrows, while *O. tyrtaeum* and *A. turgida* are endogeic species. The fabric was found to be profoundly influenced by *L. terrestris* in the immediate vicinity of the burrow walls, but where the species was present on its own the remainder of the soil volume was little affected. Phytogranic and phorphyric fabric types, which occurred only in localized areas where *L. terrestris* was active alone, were present throughout the soil where the geophages were also present (Shaw and Pawluk 1986). Where *L. terrestris* was found in association with the endogeic species (geophages) the latter ingested and transported much of the litter carried into the soil by *L. terrestris,* depositing their casts in their burrows or other voids in the soil. The combined activities of the two ecological groups produced granic fabric types in the SL and SiCL soils and enhanced fusion of the matrix in the CL soil (Shaw and Pawluk 1986).

There are implications here for programs of earthworm introduction directed at improving soil structure. A mixture of anecic and endogeic species should be the aim of such an introduction (Lee and Foster 1991).

2.3 Humus formation

2.3.1 Introduction

The synthesis of humus in the soil environment has been studied by many researchers and as a result many different theories for humus synthesis have been put forth (Felbeck 1971; Flaig 1975; Kononova 1966; Stevenson 1982). However, though each is successful from a particular point of view, none can explain all aspects of humus formation on its own merits. The polyphenol theory of Stevenson (1982) was the first comprehensive venture at explaining humus synthesis. However, Stevenson (1982) himself was fully aware of the shortcomings of the scheme outlined in his theory, and felt it was "not completely satisfactory". A theory of humus formation that is slightly different from the polyphenol theory was proposed by Varadachari and Ghosh (1984); it differs in the infrastructure of the biochemical processes. The theory is similar to the polyphenol theory in that the synthesis of polyphenols is regarded as the essential step of humus formation. A schematic representation of the processes involved in the proposed outline are presented in Figure 2.3-1.

The figure has been omitted due to copyright restrictions.

Figure 2.3-1 (from Varadachari and Ghosh 1984).

2.3.2 Synthesis of humus-building units

The modification of lignin in the soil is the result of lignin serving as an energy source for a specific group of microorganisms. In order for this occur it is necessary for the molecule to first permeate into the organism. Since penetration into the organism is not possible the lignin polymer must be depolymerized to yield smaller units that are much more soluble and can thus diffuse through the microbial cell wall (Alexander 1977). Splitting of the lignin polymer takes place along the aryl ether linkages or along the C-C bonds linking adjoining aromatic cores (Flaig 1975). According to Alexander (1977) such splitting is affected by lignase, an extracellular enzyme(s). Prior to serving as a source of C, these substituted aromatic structures may undergo a number of biochemical transformations within the cell: (i) aromatic methyl ethers are demethylated to the corresponding hydroxy derivative, (ii) terminal side chains can be oxidized to form COOH groups, and (iii) COOH groups may be oxidatively decarboxylated (Evans 1963). That these biochemical reactions are intracellular processes is well known to soil biochemists (Evans 1963; Hurst and Burges 1967). This is the important difference between the theory of Varadachari and Ghosh (1984) and Stevenson's polyphenol theory (1982), according to which such transformations "occur within or on exposed edges of intact molecules by extracellular enzymes produced by fungi". Thus, grouping the sources of the polyphenols into those from lignin and those from microorganisms, as has been done in the polyphenol theory, is not appropriate (Varadachari and Ghosh 1984). Polyphenols have to be synthesized by the microorganisms and within the microbial cells and as such they are all "microbial" polyphenols differing only in their carbon precursors which may be lignin or carbohydrates or any other C-containing compound (Varadachari and Ghosh 1984).

The initial step in humus genesis may involve release of the dilignol component (guaiacylglycerol-B-coniferyl ether, dehydrodiconiferyl ether, and dl-pinoresinol) and the formation of the primary phenylpropane (C_6-C_3) units (Stevenson 1982). For example, the decomposition of guaiacyl-B-coniferyl ether leads to the formation of guaiacylglycerol, coniferyl alcohol, coniferylaldehyde, ferulic acid, and other structurally related phenolic components as shown in Figure 2.3-2. The C_6-C_3 units then undergo oxidation in the side chain position to yield numerous low-molecular-weight aromatic acids and aldehydes (Figure 2.3-3). Some common degradation products include vanillin, vanillic acid, syringealdehyde, syringic acid, *p*-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, protocatechuic acid, and gallic acid (Stevenson 1982).

The figure has been omitted due to copyright restrictions.

Figure 2.3-2 (from Schubert 1965).

The figure has been omitted due to copyright restrictions.

Figure 2.3-4 (from Varadachari and Ghosh 1984).

Polysaccharides, like lignin, must first be cleaved into smaller, soluble molecules before they can permeate the cell. These may then be partly converted to aromatic compounds by certain specific organisms. This aromatization must precede the synthesis of humic polymers from non-aromatic sources such as carbohydrates (Varadachari and Ghosh 1984). The aromatic compounds which include numerous phenols and quinones are formed via (a) the shikimic acid pathway and (b) the acetate pathway (Birkinshaw 1965).

2.3.3 Formation of humic polymers

Phenolic acids and quinones produced from lignin and carbohydrates by microorganisms together with the oxidizing enzymes are expelled from the cell after its lysis. Under the influences of these enzymes, condensation occurs between the phenols themselves and between the phenols and amino acids (Flaig 1964). The condensing phenols include those synthesized by organisms and as well as the phenolic units of lignin (both monomeric and polymeric). Like all other phenol condensation reactions the mechanism of polymerization is a free radical one (Brown 1967). Coupling occurs at the *o*- and *p*-positions to the hydroxyl group and also through the oxygen (Nonhebel and Walton 1974) as shown (Brown 1967) in Figure 2.3-4c. With amino acids compounds such as those shown in Figure 2.3-4d may be formed (Flaig et al. 1975).

Polymerization may cause loss of COOH groups, e.g. oxidation of vanillic acid by laccase yields a series of diphenyl compounds as illustrated in Figure 2.3-4e, some of which have been decarboxylated (Brown 1967). Since polymerization causes loss of COOH groups, it seems logical that the more polymerized material will have less COOH groups per unit weight as compared to the less polymerized material (Varadachari and Ghosh 1984). This would explain why fulvic acids (FAs), which are smaller polymers, have more COOH groups per unit weight (Schnitzer and Ghosh 1979) than humic acids (HAs), which are larger polymers. Since HAs are larger molecules than FAs, one can conclude that FAs are only less polymerized forms of HAs and do not necessarily contain more aliphatic groups than HAs (Varadachari and Ghosh 1984). The E_4/E_6 ratio which has been used as evidence to elucidate the more aliphatic character of FA over HA, is simply a measure of polymer size (Varadachari and Ghosh 1984) and not of aliphatic/aromatic ratio in the humus structure (Chen et al. 1977). Support for the view that FAs are less polymerized forms of humic substances comes from the fact that they predominate under conditions where free radical polymerization is depressed, i.e. in Podzolic B horizons, in an anaerobic environment, and where excess water is present (Schnitzer and Ghosh 1979).

2.4 Summary of Literature review

From the pragmatic point of view, it is reasonable to consider microaggregates as those being less than 250 μm diameter; and macroaggregates as being greater than 250 μm diameter. The microaggregates are stabilized against disruption by rapid wetting and mechanical disturbance, including cultivation, by several mechanisms in which organo-mineral complexes play the dominant role. Polysaccharides are also significant in this respect also. The stabilization of microaggregates appears to be relatively permanent and seems to be independent of changes in the organic carbon content of the soil caused by different management practices (Tisdall and Oades 1982).

Conversely, the stability of macroaggregates requires live roots and their associated fungal hyphae. Numbers of stable macroaggregates decline rapidly as organic carbon content declines; roots and hyphae are decomposed and subsequently not replaced in sufficient quantities with monoculture crop systems. The stabilization of macroaggregates is controlled by management and increases under lush pastures and native grassland ecosystems. Arable cropping leads to a dramatic decline in stabilization of macroaggregates and is further accentuated when fallow is included as part of the crop rotation.

There is ample evidence of the beneficial effects of faunal activity on soil structure. The majority of soil aggregates in the Ah horizon (Mollic epipedon) of Orthic Black Chernozems (Typic Cryoborolls) are recognized as faunal modexi. Orthic Brown Chernozems (Aridic Haploborolls) also contain aggregates that are the result of faunal activity, however, the numbers of fecal pellets are seriously depressed due to the lack of moisture in the region.

Earthworm casts are frequently more stable but sometimes less stable than other soil aggregates. The burrows of some common earthworm species open at the surface and have a predominantly vertical orientation, while those of other species rarely open at the surface and have a predominantly horizontal orientation (Lee and Foster 1991). Maximum contribution to aggregate stabilization and formation of mullgranic units of fabric results from populations of earthworms that include species from both these groups.

Lignin and carbohydrates, the chief sources of C for soil microorganisms, are first broken down by extracellular enzymes into smaller units. The soluble units are converted by organisms into phenolic compounds that serve as the precursors to humus. Phenolic acids and quinones produced by the microorganisms together with oxidizing enzymes are discharged from the cell where they polymerize (polycondense) by a free radical mechanism to form humus (Varadachari and Ghosh 1984).

Chapter 3
MATERIALS AND METHODS

3.1 Materials

3.1.1 The study areas

The A horizons of four representative undisturbed (virgin) and four cultivated, fine-textured Brown Chernozemic pedons were selected for this study. As well, the A horizons of four irrigated, fine-textured Dark Brown Chernozemic pedons were included. The locations of the sites are shown in Figure 3.1-1. The virgin and cultivated sites are located southeast of Foremost, Alberta. Sites 1 and 2 are located approximately at 49° 23' 35"-24' 12" N latitude, 111° 15' 28"-16' 14" W longitude (E 1/2, Sec. 22, Tp. 5, R. 10, W4,) while at Sites 3 and 4 virgin and cultivated sites are located at 49° 17' 24-48" N latitude, 111° 14' 9-46" W longitude (virgin sites on the NE 1/4 of Sec. 11, Tp. 4, R. 10, W4 and the cultivated sites on the SE 1/4 Sec. 14, Tp. 4, R. 10, W4. The four irrigated sites are located 6.4 km north and 3.2 km west of the town Coaldale, Alberta at 49° 46' 48"-47' 12" N latitude, 112° 39' 30"-40' 9" W longitude (NW 1/4, Sec. 33, Tp. 9, R. 20, W4).

3.1.2 Parent materials and landforms

The parent material in the Foremost area, which is located on the Milk River Sheet, is a Quaternary deposit of calcareous till (Westgate 1968). The Pakowki drift is a heavy loam texture at sites 1 and 2 and clay loam texture at sites 3 and 4 (Westgate 1968). The color of the oxidized tills in the area are grayish yellow brown (10YR 5/2) and dull yellow orange (10YR 6/3).

The landform at the first two sites is described as gently undulating ground moraine with a few undrained depressions. The elevation in this area is approximately 884 m above sea level (Westgate 1968). Sites 3 and 4 have been developed on the undulating to gently rolling Etzikom end moraine, occurring in linear or curvilinear belts that are aligned in a common direction (Westgate 1968). The elevation here is approximately 895 m above sea level (Westgate 1968).

The surficial geologic features in the Coadale area are also the result of glaciation. The Coaldale series is developed on a glaciolacustrine deposit. The material is fine-textured silty clay loam, weakly calcareous, and free of coarse fragments. The landform is described as a lake basin with level topography. The elevation here is approximately 862 m above sea level.

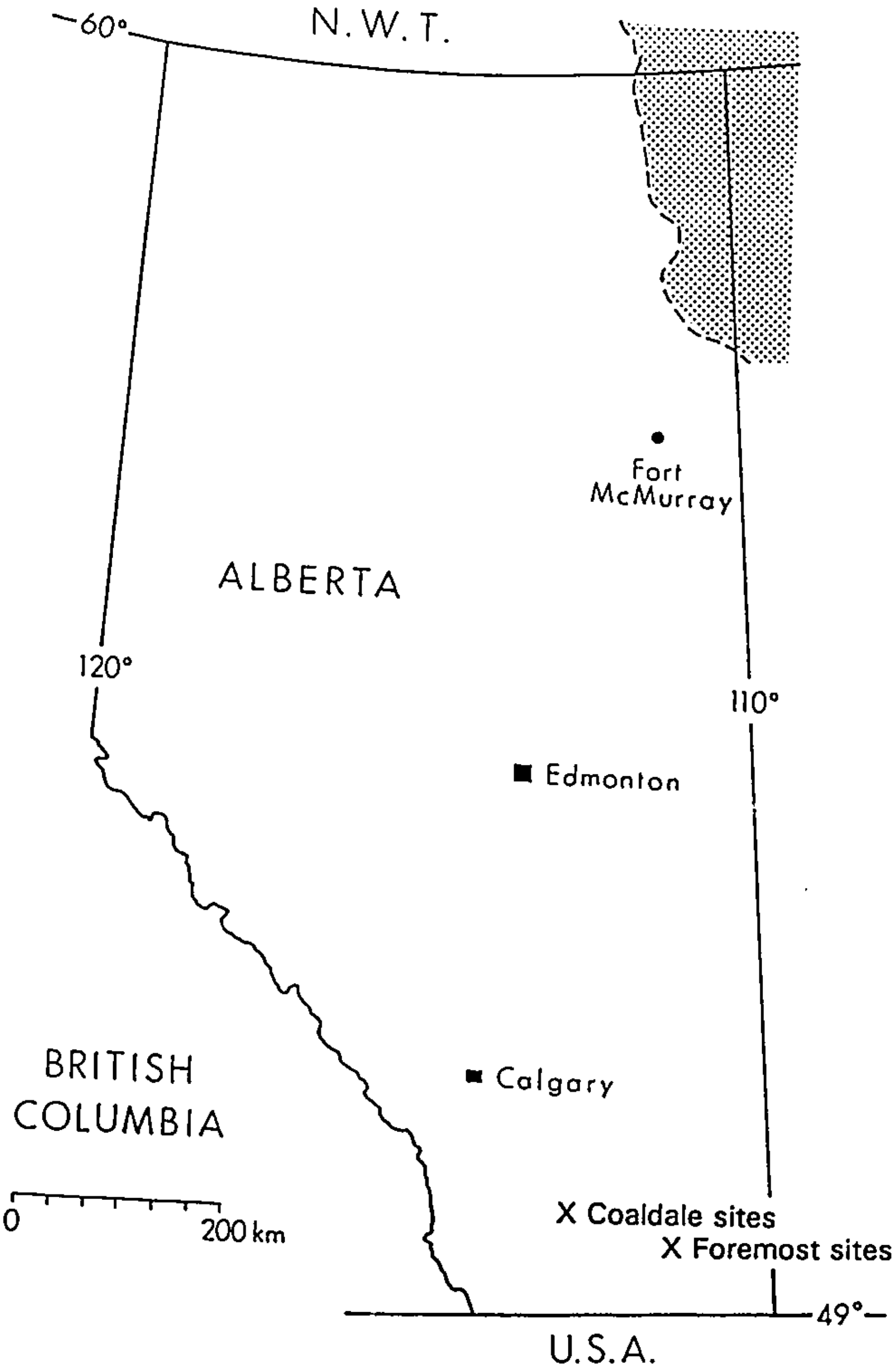

Figure 3.1-1 Location map of the study area.

3.1.3 Vegetation

The vegetation of the entire Milk River Sheet, with the exception of the Cypress Hills area, is typical prairie, and supports a semi-arid prairie flora. In general, there is a gradual change in flora from west to east. The decrease in precipitation towards the east favors more xerophytic plant species. However, the climatic change within the sheet is not sufficient to cause the disappearance of species; rather, there is a gradual shift in the relative abundance of species.

There are two main species of grasses in the area. blue grama grass (*Bouteloua gracilis*), a low growing, fine-leaved grass with a curved head that turns a deep purple on curling; and common spear grass (*Stipa comata*) the common name derived from the long curled awn with minute barbs along its edges; a distinguishing feature of this grass (Wyatt et al. 1941). Other species of grasses important in the area include the following: June grass (*Koeleria cristata*), a fine-leaved grass with a compressed panicle type head; Sandberg's bluegrass (*Poa secunda*), a small low growing tufted grass having good forage value; bluejoint (*Agropyron Smithii*), now known as western wheatgrass, a medium sized rather coarse-stemmed grass having a true spike head (this specie is more common in small local depressions than on upslope positions); plains reedgrass (*Calamagrostis montonensis*), a specie similar to June grass but slightly larger; and green spear grass (*Stipa viridula*), a low growing awned grass slightly smaller and having much smaller awns than common spear grass (Wyatt et al. 1941). Smooth wheatgrass (*Agropyron pauciflorum*) is fairly common on upslope positions but does not occur in depressions since it tolerates very little salt. Tufted hairgrass (*Deschampsia caespitosa*) is often associated with bluejoint in the local depressions.

Two species of club moss are also quite common to this region. Common club moss (*Selaginella densa*), a small low growing club moss that spreads in patches over the ground surface to the exclusion of forage plants; and prairie phlox (*Phlox Hoodii*), a more upright moss that lacks the creeping quality of common club moss (Wyatt et al. 1941).

The native vegetation in the area surrounding the town of Coaldale is no longer present as most of the land has been under irrigated crop production for 70 years or more. The original vegetation of the area can be found 14 km north of the town on coulee slopes, valley bottoms, and the edges of water bodies. The native vegetation would likely have been included in the Mixed Prairie Grassland Association. The literature indicated that five grass species were the most common in this area: blue grama grass (*Bouteloua gracilis*); June grass (*Koeleria cristata*), plains reed grass (*Calamagrostis montanensis*), bluejoint or bluestem (*Agropyron Smithii*), and northern wheatgrass (*Agropyron dasystachyum*) (Wyatt et al. 1939). Bluejoint was especially common in small local depressions and often formed a fairly dense mat, almost to the exclusion of other grasses (Wyatt et al. 1939).

Common spear grass (*Stipa comata*), green spear grass (*Stipa viridula*), and Sandberg's bluegrass (*Poa secunda*) would also have been present but in lesser amounts.

The two mosses mentioned earlier, common club moss (*Selaginella densa*) and prairie phlox (*Phlox Hoodii*) were also known to exist in this area as well (Wyatt et al. 1939).

3.1.4 Climate

The climate of the Foremost area is generally characterized as subarid and continental with moderately long, bright, warm summers and bright, cold winters. Although this locale is a considerable distance from the Rocky Mountains, warm Chinook winds frequently blow from the west during the winter months, resulting in snowmelt and rather mild winter conditions. The mean annual temperature (MAT) for the 8 sites, inferred from the MAT at Foremost, is 4.8^{o}C, July being the warmest month, 18.9^{o}C, and January the coldest month at -11.6^{o}C (Figure 3.1-2a).

Precipitation normals for a thirty year period (1951-1980) shows that Foremost receives 356 mm of precipitation annually. The May to September precipitation, 182 mm, accounts for more than 50% of the annual total which is favorable for crop production (Figure 3.1-3a). This is however, offset by high yearly variability and uneven distribution.

The climate of the Coaldale area is similar to that of Foremost except that the moisture subclass is semiarid. The proximity to the Rocky Mountains, in addition to the warm chinook winds, adds further to the mild temperatures and melting snow during the winter months. The MAT for the four sites, inferred from the MAT at Coaldale, is 5.2^{o}C, again, July being the warmest month, 18.5^{o}C, and January the coldest month at -10.8^{o}C (Figure 3.1-2b).

Annual precipitation for Coaldale is 390 mm, a bit higher than that for Foremost, but enough so that this area is included in the semiarid moisture subclass. The May to September precipitation, 193 mm, accounts for 50% of the annual total, which, again, is favorable for crop production (Figure 3.1-3b). However, most of the water for field crops is provided through irrigation. Nevertheless rainfall provides an important source of soil moisture early in the spring, freeing farmers from the task of "sprinkling" crops up.

Figure 3.1-2a Mean monthly temperature recorded at the Foremost meteorological station (long-term average, 1951-1980 Environment Canada).

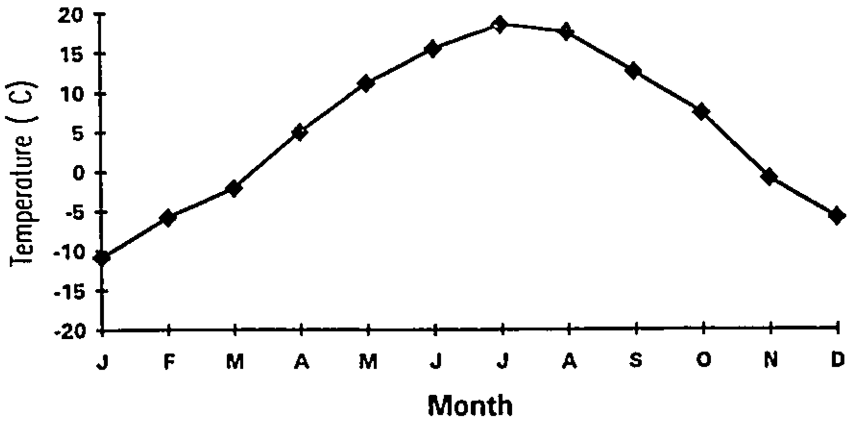

Figure 3.1-2b Mean monthly temperature recorded at the Coaldale meteorological station (long-term average, 1951-1980 Environment Canada).

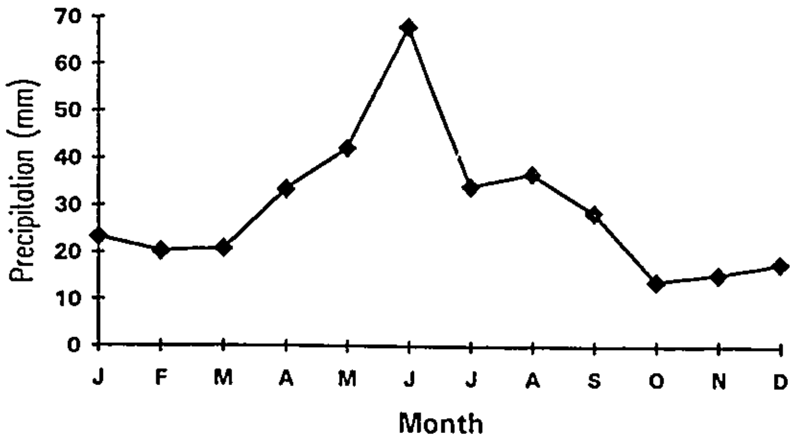

Figure 3.1-3a Mean monthly precipitation recorded at the Foremost meteorological station (long-term average, 1951-1980 Environment Canada).

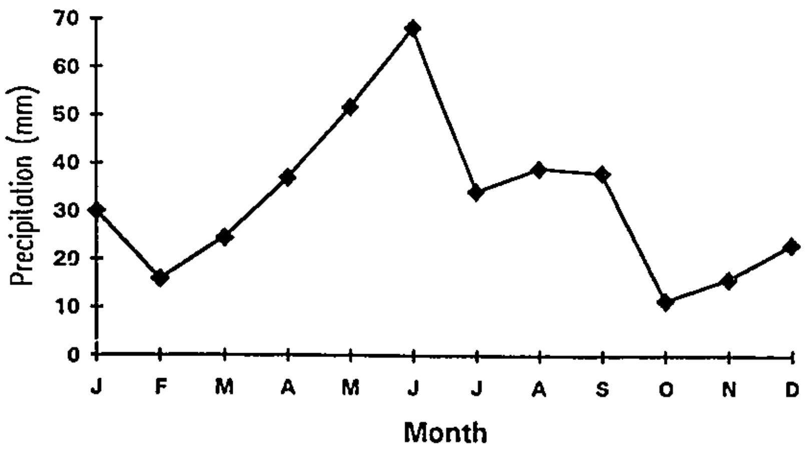

Figure 3.1-3b Mean monthly precipitation recorded at the Coaldale meteorological station (long-term average, 1951-1980 Environment Canada).

3.1.5 Farming practices

Dryland crop production characterizes the type of farming practiced on cultivated land in the Foremost and surrounding area. There are however, blocks of land on the Milk River sheet still uncultivated. The area south and east of Manyberries, an area south of Milk River east of Deadhorse coulee and extending as far east as Pinhorn, and the area from Pinhorn extending eastward, up to and including, the Wildhorse area. These areas are home to some vast tracts of native rangeland used for grazing cattle.

As can be interpreted from the climatological data, the Foremost area is well supplied with warm dry weather. This is reflected in the type of crop rotation ensued by grain and oilseed producers; an alternate wheat-fallow rotation has been the norm for 60 years or more. This rotation is quite popular because many firmly believe that moisture is conserved in the fallow year; soil N and P are replenished via mineralization of organic matter, thus eliminating the need for commercial fertilizers; and a high level of weed control is sustained. Some of the more agronomically conscious and innovative producers have experimented with continuous cropping, minimum tillage, and/or no-till in the non crop year. Their modern view of crop production and long-term productivity has proven to be monetarily and scientifically sound. However, many producers still maintain an exploitive wheat-fallow rotation for reasons that can only be described as archaic.

As mentioned earlier, the Coaldale area has been under irrigated crop production since 1921 or earlier. This area is intensively farmed with high levels of inputs, i.e. fertilizers, chemicals, etc., high application rates of water, and aggressive tillage. Crops grown in the area generally include sugar beets, soft white wheat, beans, canola, vegetables, and barely/corn silage.

Abundant water is supplied to growing crops via irrigation systems. The two most popular systems in this area are wheel lines and center pivots. The water can be applied rather quickly with either system; a requirement for any system in southern Alberta because evapotranspiration rates are quite high.

The tillage, as can be expected, is quite intense on irrigated land. In the spring, 2-3 passes with a cultivator followed by 2-3 passes with a harrow/packer drawbar are typical for seedbed preparation of fine-seeded crops such as sugar beets. Plowing also plays a major role in the cultivation requirements for these producers. Plowing to depth of 20-26 cm is performed in the fall on land that is to be planted in sugar beets in the spring; it is also done after the beet harvest to "loosen" the soil that has been compacted by trucks and irrigation water. After soft white wheat has been harvested spiking and disking operations are done to "loosen" the soil and bury the stubble respectively.

The land, on which the four sites are located is owned by the Unger family. These people have raised some impressive crops. Semi-dwarf feed barley has yielded over 150 bushels per acre and the sugar beets have been near the 30 tonne per acre mark. These producers, follow a three year rotation that includes soft white wheat-beans-sugar beets. In addition to the aggressive tillage already mentioned, subsoil fracturing has been incorporated into the tillage program on this farm. They have found improved percolation of water down to depths of 60-70 cm. The Unger's apply about 30 cm of water to soft white wheat over the growing season and about 50-60 cm of water to the sugar beets.

3.2 Methods

3.2.1 Pedon description and soil sampling

A pit with dimensions of 1 x 1 x 1.7 m was dug on the native rangeland at site 1 (Foremost) for a detailed profile description. A similar size pit was dug on the Coaldale series near site 2 for a detailed profile description.

At each location soil samples of *ca* 5 kg were collected from the top 0-10 cm of Ah horizons of native sites and 0-10 cm of Ap horizon of cultivated and irrigated sites. Upon returning to the laboratory, *ca* 400 g of field-moist, intact subsamples were passed with minimum pressure through a 6.3 mm sieve, air-dried, and saved for wet sieving (aggregate stability). The remainder of the original sample was air-dried and ground to pass a 2 mm sieve after removal of root detritus. This fine-earth fraction was then used in subsequent analyses.

Two undisturbed intact cores, for micromorphological studies, were extracted from depths of 0-10 cm and 7.5-18 cm at each site. The dimensions of the cores were approximately 7.5 x 10 cm. Upon return to the lab the cores were immediately placed in an oven at 65^oC for 2 weeks to dry.

3.2.2 Routine chemical analyses

All routine chemical analyses were conducted according to procedures outlined by McKeague (1978), unless otherwise noted. Soil pH was measured in H_2O and 0.01 M $CaCl_2$, using a Beckman Electromate pH meter; the soil to solution ratio was 1:2. Organic carbon was determined by the wet oxidation, Walkley-Black, procedure, using the *o*-phenanthroline-ferrous complex as the indicator. Total nitrogen and phosphorous was determined by the Technicon AutoAnalyzer II, Industrial Method No. 334-74W/B$^+$ after micro-Kjeldahl digestion. Mineral N was determined by the indolphenol blue method utilizing the autoanalyzer after extraction with 2 N KCl. Cation exchange capacity (CEC) and exchangeable cations were determined by the NH_4OAc method. Quantities of exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+, in 1 N NH_4OAc buffered at pH 7.0, were obtained by atomic absorption spectroscopy. The CEC was calculated from the amount of adsorbed NH_4^+ displaced by an acidified 10% NaCl solution. The excess electrolyte was washed out with 95% ethanol instead of 99% isopropanol. Exchangeable acidity was determined by the barium acetate method (McKeague 1976). Free (non-silicate) Fe, Al, and Si were extracted using the dithionite-citrate-bicarbonate method with subsequent analysis of the by atomic absorption spectroscopy.

3.2.3 Physical analyses

Particle-size analysis was accomplished by the hydrometer method after H_2O_2 treatment to destroy organic matter. Bulk density was determined by the core method using a 7.5 cm diameter core sampler (McKeague 1978). Aggregate stability was performed by the wet sieving method as described by Kemper and Rosenau (1986). Briefly, triplicate 35 g samples of < 6.3 mm diameter material were placed on the top of a stack of 6 sieves, 4, 2, 1, 0.5, 0.25, and 0.124 mm openings, arranged in decreasing size and the sieve stack was gently moved up and down for 30 min while immersed in water.

3.2.4 Clay mineralogy

Subsamples from half the sampled sites were dispersed in distilled water using ultrasonic vibration (Genrich and Bremner 1972) and the clay-size fraction (< 2.0 μm) separated by successive dispersion and gravity sedimentation. Phyllosilicate minerals present in the clay separates were identified from X-ray diffractograms of oriented specimens. Subsamples of the clay-size fraction were saturated with Ca^{2+} and K^+ by repeated treatments with 1 N solutions of the respective chloride salts. Samples were washed free of excess electrolyte by repeated dispersion in deionized water and centrifugation. Oriented specimens of the electrolyte free Ca^{2+}- and K^+-saturated clay separates were prepared using the paste method of Thiesson and Harward (1962) and subjected to seven pretreatments as described by Dudas and Pawluk (1982). Diffraction patterns were obtained on a Philips step-scanning diffractometer using a step size of 0.05^o 2θ and an accumulation time of 2 seconds·step^{-1}. All samples were irradiated with CoKα radiation (λ = 0.17903 nm) generated at 50 kV and 25 mA.

3.2.5 Micromorphology

The oven-dried cores were impregnated under vacuum with Scotchcast epoxy resin. Vertically oriented thin sections (5 x 7 cm) were prepared from each of the impregnated cores with the aid of a Logitech polishing machine. The thin sections were then examined under a Zeiss photomicroscope and micromorphological descriptions prepared according to the terminology of Brewer and Sleeman (1988) and Bullock et al. (1985).

3.2.6 Organic fraction characterization

3.2.6.1 Organic matter extraction and purification

A modified method of Schnitzer and Schuppli (1989) was used for this purpose. Air-dry soil, 5 x 100 grams, was weighed into 1000-ml beakers and 500 ml of unadjusted 0.1 M $Na_4P_2O_7 \cdot 10\ H_2O$, pH 9.4-9.6, added to the beakers. The suspension was stirred and then dispersed using ultrasonic vibration (Genrich and Bremner 1972). After 24 h, the dark-colored extracts were decanted into 250-ml centrifuge bottles and centrifuged at 1800 rpm for 20 min. At this stage, the dark-colored extracts still contained suspended clays. In order to remove most of the clays, the extracts were decanted from the 250-ml bottles into 50-ml polypropylene centrifuge tubes and centrifuged at 15 000 rpm for 25 min. After this treatment, a small buff-colored plug was present at the bottom of the tube. The extracts were decanted into a beaker and acidified with 2 M HCl to pH 2.0 and allowed to stand at room temperature for 24 h. The supernatant, fulvic acid (FA), was then separated from the coagulate humic acid (HA), by centrifugation at 15 000 rpm for 25 min.

Half the HA samples were purified, i.e. ash contents reduced to < 5%, by methods according to Schnitzer and Schuppli (1989). HA was shaken three times in succession for 24 h at room temperature with an HCl-HF solution (5 ml conc. HCl + 5 ml 49% HF + 990 ml deionized H_2O) in 50-ml centrifuge tubes at a ratio of 0.3 g HA to 30 ml HF-HCl. The number of HCl-HF treatments was limited to three in order not to dissolve too much OM. Prolonged treatment with dilute HCl-HF solutions leads to significant losses of nitrogenous components and carbohydrates (Schnitzer and Schuppli 1989). The HA was then separated by centrifugation at 17 500 rpm for 30 min, washed with deionized H_2O, and freeze-dried in a vacuum desiccator.

The remaining HA samples were treated with a powerful reductant in order to remove paramagnetics, primarily Fe^{3+}, with the intention of improving the quality of ^{13}C NMR spectra. The HA samples were first treated two times in succession with the prepared HCl-HF solution. One gram of HA was then reduced with freshly prepared 0.05 M stannous chloride ($SnCl_2 \cdot 2H_2O$) solution, shaken for 1 h, and centrifuged at 17 500 rpm (Arshad et al. 1988). The HA was then washed once with 0.05 HCl and twice with deionized H_2O.

3.2.6.2 FTIR spectra

FTIR spectra were recorded on KBr pellets, consisting of 1 mg of sample and 200 mg of KBr, from 4000 to 400 cm^{-1}, on a Beckman 4250 IR double beam spectrophotometer to provide key information on the structural arrangement of oxygen-containing functional groups, the occurrence of protein and carbohydrate constituents, and the presence of inorganic impurities, i.e. clay, in isolated humic acids.

3.2.6.3 Solid-state ^{13}C NMR spectra

Of the methods developed in recent years, ^{13}C NMR spectroscopy is probably the most useful for the characterization of soil organic matter and its components (Schnitzer 1990). The spectrum provides resolution and an inventory of the different forms of carbon in the humic acid. The ^{13}C NMR spectrum indicates the presence in the humic acid of a wide variety of components and structures whose determination by other methods would either be laborious and time-consuming or not possible at all.

^{13}C CP/MAS NMR spectra were recorded at a frequency of 45.28 MHz on a Brucker CXP-180 NMR spectrometer equipped with a Doty Scientific probe. Single-shot cross-polarization contacts of 2 ms were used with matching radio-frequency field amplitudes of 75 kHz. Up to 92 000 500 W decays were co-added with a delay time of 1 sec. These were zero-filled to 4000 data points before Fourier transformation. Magic angle spinning rates were 4 kHz and the line broadening was 50 Hz.

3.2.6.4 Preparation of samples for carbohydrate analysis

Exactly 20.0 grams of < 100 mesh soil was hydrolyzed for 24 h at 80°C in 20.0 ml 3 N H_2SO_4; addition of water was necessary to compensate for evaporation loss. The suspension was then filtered with suction through a GF/A glass microfibre filter. The hydrolysates were neutrailized to pH 7 with $Ba(OH)_2$. The suspension was shaken and centrifuged at 15 000 rpm to remove the the barium sulfate precipitate. Metallic cations and any remaining anions were removed by passing the solution through cation and anion exchange columns as described by Shaw (1984). The clear sugar solution was stored at 4^oC until analysis. Five neutral sugars, glucose, galactose, mannose, arabinose, and xylose, were quantified by HPLC.

3.2.6.5 Separation and quantification of neutral monosaccharides

Anion exchange chromatography was performed using the Dionex 4500i system with pulsed amperometric detection (gold).

Anion exchange chromatography has been used extensively for analysis of acidic carbohydrates or glycopeptides. It is not a technique commonly associated with analyzing neutral carbohydrates. However, examination of the pKa values of the neutral monosaccharides shows that carbohydrates are weak acids. The pKa values for glucose, galactose, mannose, and xylose are 12.28, 12.39, 12.08, and 12.15 respectively. At high pH (12-13) they will be either partially or completely ionized and thus can be separated by anion exchange chromatography.

Pulsed amperometric detection utilizes a repeating sequence of three potentials, E_1, E_2, and E_3 which are applied for specific durations; t_1, t_2, and t_3 respectively. Best results are obtained when E_1 is close to the glucose oxidation peak, E_2 is at a high positive potential to electrochemically clean the electrode surface, and E_3 is at a negative potential to reduce gold oxide to back to gold. The three potentials used here were 0.05 v, 0.60 v, and -0.80 v while the three pulse durations were 300 ms, 300 ms, and 480 ms respectively. The output range was 300 nA.

The analytical column was a CarboPac™ PA1 (250 x 4 mm I.D.) (P/N 35391) column developed for carbohydrate separations. This column is based on pellicular MicroBead technology. A CarboPac guard column (25 x 3 mm I.D.) (P/N 37141) was placed in front of the analytical column. The separation was performed isocratically using 10% 0.1 N NaOH + 90% deionized H_2O at a flow rate of 1.0 ml/min. Confirmation of peak identities was accomplished by comparing retention times of samples to those of standard solutions of the five neutral sugars. As well, samples were spiked with standards for added confidence in peak identity.

Chapter 4
RESULTS AND DISCUSSION

4.1 Morphology

The Ah horizon morphology of the native Orthic Brown Chernozem (Table 4.1-1a) is atypical for soils of the Chernozemic order. From the description it can be seen that the Ah horizon is low in chromophores and lacks in development and thickness. The humus is light colored, brown (10YR 4/4), and the organic matter accumulations, for the most part, are confined to the top 6 cm. Below this depth, the color change is so gradual that it is difficult to distinguish the boundary between the A and B horizon. The grade of structure is weak; that is, there is a low degree of distinctness of aggregation in the A horizon - the feature that best exemplifies the Brown Chernozemic great group. The granular structure, that is so characteristic of Chernozemic A horizons, is not clearly discernable in the Brown soils of southeastern Alberta.

The A horizon site 1 had sufficient thickness to meet the 10 cm minimum requirement for thickness as outlined by the CSSC (1978). However, examination of sites on native rangeland in the area revealed consistently thin surface horizons; thicknesses were in the range of 6 to 12 cm. More often than not A horizons did not provide sufficient thickness to meet the minimum requirement as defined for Chernozemic A horizons.

Morphological data for Ap horizons of cultivated sites were only noted in the field and are not described. In discussions with the people at Soil Survey, who are at present mapping this area, it was their feeling that approximately two thirds of the cultivated soils fail to provide 15 cm of surface material that has a color value darker than 5.5 dry. Field observations indicate the structure of the Ap horizon is not granular *per se*, rather it is composed of clods, soil units > 25 mm, and smaller units that resemble crumbs. These "crumbs", however, are really fragments of larger soil units, i.e. clods; "natural" aggregates are rounder and more friable than tillage-induced fragments. During spring it is not uncommon for clods and surface crusts to occupy notable areas of cultivated fields, especially where the soils are fine- to medium-textured.

With respect to the 15 cm of surface material in cultivated Ap layers - if the original Ah horizon is only 7 to 10 cm thick depending on slope position, the mixed Ap layer may be composed of 5 to 8 cm of B horizon depending on tillage depth.

Table 4.1-1a Profile description of the native Orthic Brown Chernozem at site 1, Foremost.

Horizon	Depth (cm)	Description
Ah	0-10	Brown (10YR 4/4 d); loam; weak, fine to medium, subangular blocky and weak, fine to medium granular; slighly hard; abundant, very fine, random, inped and exped roots; gradual, wavy boundary; 8-10 cm thick.
Bm	10-40	Dull yellowish brown (10 YR 5/3 d); loam; weak to moderate, fine to medium prismatic and weak to moderate, fine to medium, subangular blocky; hard; plentiful, very fine, vertical, inped and exped roots; clear wavy boundary; 20-30 cm thick.
Cca	40-75	Dull yellow orange (10 YR 6/3 d); loam; massive; very hard; few, very fine, vertical roots; strongly calcareous; gradual vavy boundary; 30-47 cm thick.
Ck	75+	Yellowish brown (2.5 Y 5/3 d); loam; massive; very hard; very few, very fine, vertical roots; moderately calcareous.

Table 4.1-1b Profile description of the Orthic Dark Brown Chernozem at Coaldale.

Horizon	Depth (cm)	Description
Ap1	0-15	Very dark grayish brown (10YR 3/2 m), dark grayish brown (10YR4/2 d); silty clay loam; moderate, medium, subangular blocky and moderate to strong, fine granular; very friable; clear, wavy boundary; 13-15 cm thick; mildly alkaline.
Ap2	15-23	Dark brown (10YR 3/3 m); silty clay loam; moderate, fine subangular blocky and moderate, fine granular; very friable; clear, wavy boundary; 8-10 cm thick; mildly alkaline.
Bm1	23-38	Dark brown (10YR 3/4 m); silty clay; moderate, fine to medium, subangular blocky; friable; clear wavy boundary; 13-20 cm thick.
Bm2	38-47	Dull yellowish brown (10YR 4/3 m); silty clay loam; weak to moderate, medium to coarse prismatic and weak, medium, angular blocky; friable; gradual, smooth boundary; 9-12 cm thick; mildly alkaline.
Cca	47-84	Dark grayish brown (10YR 4.5/2 m); silty clay loam; massive; friable; moderately calcareous; gradual wavy boundary; 32-42 cm thick.
Ck	84-100+	Dull yellowish brown (10YR 4/3 m); silty clay loam; massive; friable; weakly calcareous.

In contrast to the virgin and cultivated Brown Chernozemic soils, morphology of the A horizon from the Dark Brown Chernozem is typical of Chernozemic soils in more moist bioclimatic zones of the province (Table 4.1-1b). The Ap1 horizon has a dark grayish brown (10YR 3/2 m) color. The gray component is due to finely disseminated $CaCO_3$ and carbonate nodules brought up via plowing from the weakly calcareous solum and mixed with existing Ap material. The two Ap horizons are higher in chromophores as evidenced by the darker color values and lower chromas; attributable to more plentiful and darker colored humus accumulations.

Field observations revealed a thick A horizon with a well developed, fine granular structure that was friable and "fluffy". The grade of structure was moderate and strong, i.e. the aggregates were well formed and had a moderate to strong degree of distictness. Clods were present on the surface but their numbers and size were dramatically reduced as compared to the cultivated sites for Brown Chernozemic soils.

The combined thickness of the two Ap horizons is about 23 cm; thicker than normal. The thickness of the original Ah horizon on this lake basin is not kown because this land was cultivated before the soil survey was conducated However, it was noted in the field the present plow depth reaches into the B horizon. This means the Ap layer is thicker than the original Ah horizon.

4.2 Chemical and physical properties

Particle-size analysis indicates an enrichment in clay in the B horizon in all cultivated sites as compared to corresponding native Ah horizons (144-188 vs. 100-123 $g{\cdot}kg^{-1}$) (Table 4.2-1). The Ah horizons from the virgin pedons have similar ranges of sand (348-402 $g{\cdot}kg^{-1}$) and silt (479-531 $g{\cdot}kg^{-1}$), while the cultivated A horizons show more variability in sand (252-426 $g{\cdot}kg^{-1}$) and silt (430-560 $g{\cdot}kg^{-1}$) composition. Texturally these sites border on medium-textured silt loam and loam classes.

A horizons from irrigated pedons have nearly the same proportions of sand, silt, and clay at all sites. This was anticipated since the pedons are located on the Coaldale lake basin. The sand content is low, ≤ 15%, while the silt and clay fractions dominate the particle-size distribution, consequently, these Ap horizons are classified as silty clay loam in texture.

Table 4.2-1 Particle-size data for the A horizons.

Treatment		Sand	Silt	Clay
			$g \cdot kg^{-1}$	
Native	Site 1	402	498	100
	2	348	531	121
	3	398	479	123
	4	387	495	118
Cultivated	Site 1	342	484	174
	2	340	484	182
	3	252	560	188
	4	426	430	144
Irrigated	Site 1	150	506	344
	2	146	508	346
	3	135	507	358
	4	140	509	351

Bulk density (D_b) showed little change in cultivated sites as compared to virgin sites in the 1.2-8.9 cm depth interval except at site 3 where the D_b increases slighly from 1.23 to 1.35 $Mg \cdot m^{-3}$ (Table 4.2-2). Bulk density was consistently higher at all tilled sites in the 8.9-16.5 cm depth interval compared to virgin sites, suggesting a certain degree of tillage compaction had taken place in this zone. Bulk density was consistently low at all irrigated sites, hence supporting the field observation of a "fluffy" Ap horizon. Reasons for the low bulk density values under this management include inherent high porosity of fine-textured glaciolacustrine parent material and the fact that soil above the plow depth is turned over and thus, is modified to a greater degree by freeze-thaw processes. In the spring, soil within the plow depth will be loose, granular, and very friable.

Table 4.2-2 Bulk density of the A horizons at two depth intervals.

		Db* (Mg·m^{-3}) at 2 depths	
		1.2-8.9 cm	8.9-16.5 cm
Native	Site 1	1.26	1.33
	2	1.21	1.28
	3	1.23	1.30
	4	1.27	1.33
Cultivated	Site 1	1.28	1.40
	2	1.26	1.46
	3	1.35	1.44
	4	1.25	1.43
Irrigated	Site 1	1.14	1.17
	2	1.21	1.24
	3	1.10	1.11
	4	1.10	1.15

* bulk density

X-ray diffraction analysis indicated that total clay separates consisted dominantly of smectite and mica with considerably lesser amounts of kaolinite and chlorite (Figure 4.2-1). Both montmorillonite and beidellite were identified in all clay samples by the glycerol-solvated specimen with the former smectite consistently dominant in abundance (Dudas and Pawluk 1982). Diffractograms of K^+-saturated specimens showed that dioctahedral mica (muscovite) to be more abundant than trioctahedral species as evidenced by the strong (002) reflection at 0.498 nm relative to intensities of first order basal reflections (Fanning and Keramidas 1977).

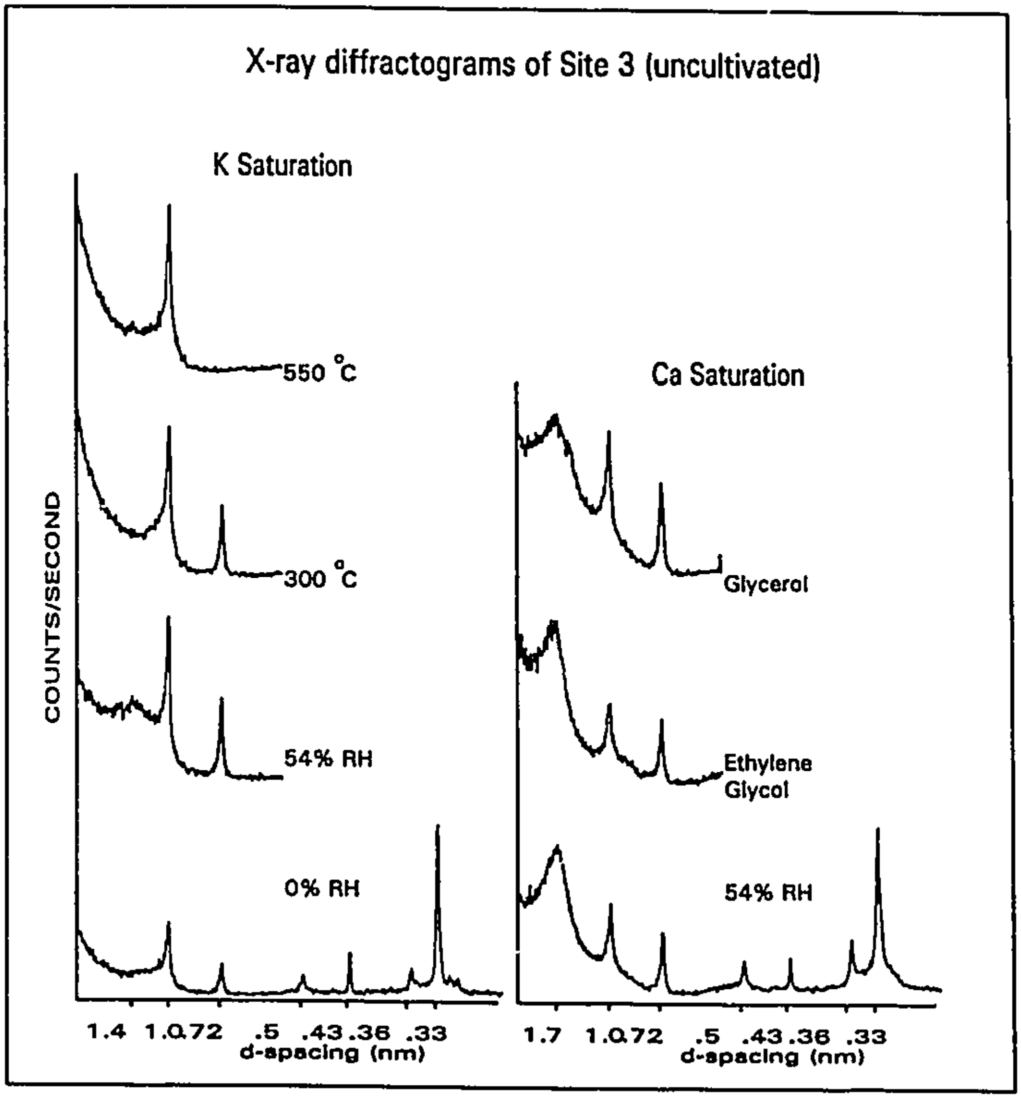

Figure 4.2-1a X-ray diffractograms obtained for Ca^{+2}- and K^{+}-saturated clay specimens from native site 3.

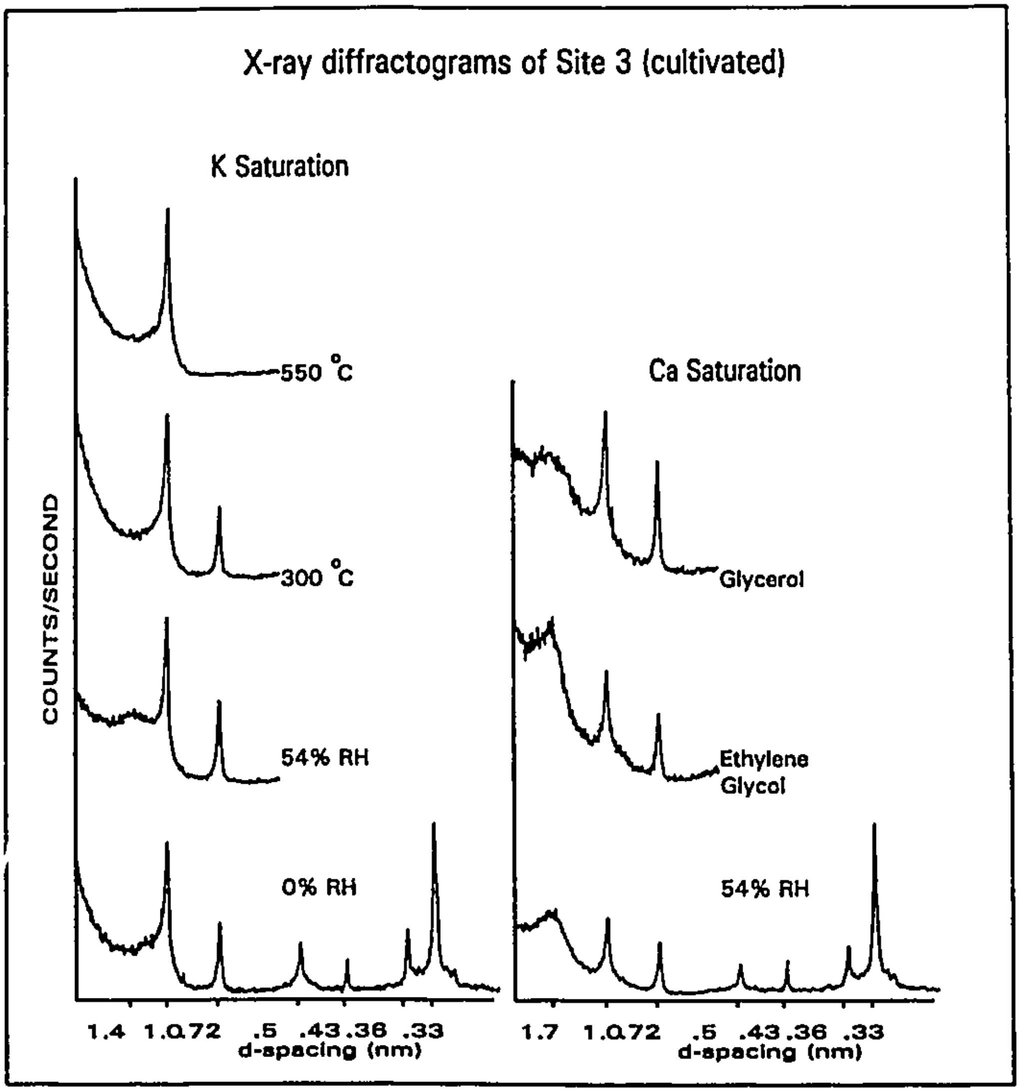

Figure 4.2-1b X-ray diffractograms obtained for Ca^{+2}- and K^{+}-saturated clay specimens from cultivated site 3.

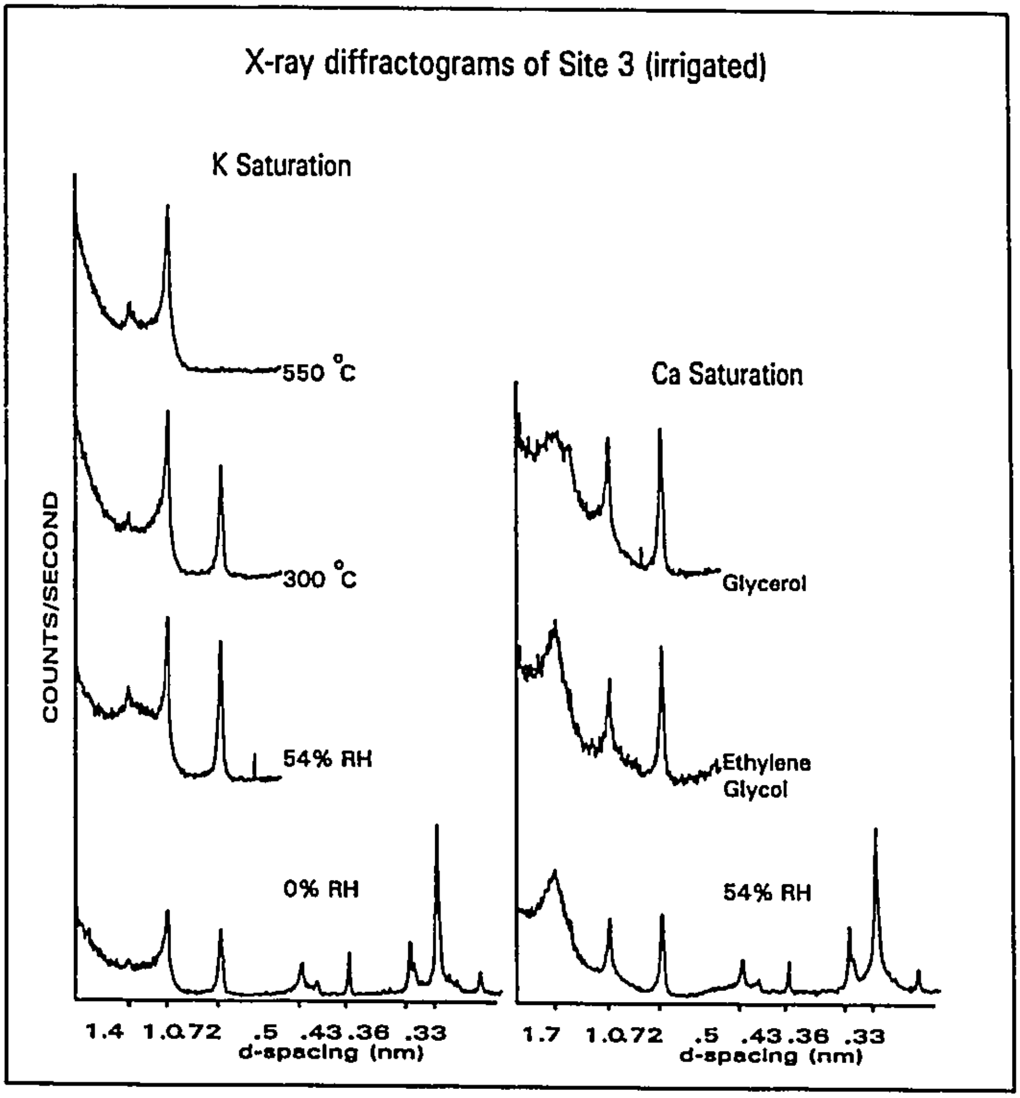

Figure 4.2-1c X-ray diffractograms obtained for Ca^{+2}- and K^{+}-saturated clay specimens from irrigated site 3.

Dissolution analysis by dithionite-citrate-bicarbonate (Table 4.2-3) revealed secondary, non-silicate Fe, Al, and Si minerals are only minor components in these soils. "Free" iron ranges from 8.4 g·kg^{-1} in a virgin Ah (site 2) up to 11.0 g·kg^{-1} in an irrigated Ap (site 1). These values indicate that the abundance of iron is sufficient to be considered an important stabilizing agent of organic materials, particularly so since sand-sized goethite is relatively absent in these soils.

Table 4.2-3 Extractable Al, Fe, and Si in whole soils.

Treatment		Al_d	Fe_d	Si_d
		g·kg^{-1}		
Native	Site 1	1.9	9.8	3.8
	2	1.7	8.4	4.3
	3	1.7	8.8	4.2
	4	1.9	9.0	3.1
Cultivated	Site 1	1.9	9.2	2.2
	2	1.9	9.1	4.0
	3	1.8	9.4	3.0
	4	1.7	8.6	1.6
Irrigated	Site 1	2.5	11.0	5.4
	2	2.2	9.9	3.3
	3	2.0	9.1	3.1
	4	2.1	10.5	2.8

All native Ah horizons exhibit a slightly acidic reaction (Table 4.2-4). The analogous cultivated sites show increased acidity; soil reaction decreases anywhere from 0.26-0.71 pH units from the corresponding virgin sites except at site 4 where the pH increases by 0.23 units. The irrigated A horizons, on the other hand, show a consistent mild to slighlty alkaline soil reaction depending on the matrix medium in which the measurement is made (Table 4.2-4).

Table 4.2-4 Some chemical properties of the A horizons investigated.

Treatment		pH		Cation Exchange					
		H_2O	$CaCl_2$	Ca	Mg	K	Na	ex acid	Total CEC
						exchange capacity			cmol (+)·kg^{-1}
Native	Site 1	6.58	6.14	74	18	2.4	0.2	5	11.6
	2	6.23	5.68	73	18	2.5	0.2	6	12.2
	3	6.68	6.23	74	19	2.3	0.2	5	13.0
	4	6.60	6.20	75	17	2.2	0.2	5	12.0
Cultivated	Site 1	6.26	5.76	72	17	2.0	0.2	8	14.4
	2	5.96	5.42	72	17	2.7	0.2	8	15.1
	3	5.97	5.52	70	18	2.3	0.2	10	16.3
	4	6.83	6.42	79	14	2.1	0.2	4	13.2
Irrigated	Site 1	7.93	7.60	74	15	8.3	1.3	1	24.2
	2	7.93	7.55	76	14	8.2	1.3	1	24.6
	3	7.96	7.63	75	14	8.5	1.3	1	24.8
	4	7.95	7.59	75	14	8.4	1.3	1	24.1

Exchangeable bases for all samples are dominated by Ca^{2+} with lesser amounts of Mg^{2+}, K^{+}, and Na^{+}. Cation exchange capacity (CEC) increases modestly in all cultivted sites from the respective native sites (Table 4.2-4). This increase in CEC with cultivation is primarily due to an increase in clay content in the "plow" depth. Irrigated Ap horizons show substantially higher CEC compared to both virgin and cultivated sites due to the high clay/low sand content of the parent material. For example, looking at the CEC from site 1 of each treatment, in the order of irrigated, cultivated, native soil, exchange capacity declines from 24.2 to 14.4 to 11.6 cm [illegible] (+)·kg^{-1} of soil, respectively.

4.3 *C, N, and P properties*

The distribution of organic carbon with depth for an undisturbed virgin site is shown in Figure 4.3-1. Accumulations of organic carbon (OC) are highest in the top 6 or 7 cm of the profile, strongly supporting the previous interpretation of the Munsell color data. The top 5 cm depth displays unexpectedly high OC values for undisturbed soils in this region of the province. This zone, however, contains high proportions of low density organic materials (< 2.0 Mg·m^{-3}) which are enriched in carbohydrate-C. These light fractions are derived from coarse organic matter containing partly decomposed plant residues (Oades 1972; Whitehead et al. 1975) and microbial debris and fungal hyphae with wide C/N ratios (Dalal and Mayer 1987), which are relatively high in carbohydrate concentration. This graph also illustrates two other important points. First, losses of organic matter (OM) in the tilled layer have always been attributed to exploitive cultivation. Few reseachers have considered redistribution of OC that results from mixing the top 12-15 cm of surface soil. Some of the loss in OC should be attributed to the dilution effect, i.e. mixing top layers of soil (0-5 cm) that contain high amounts of OC with deeper layers (soil occuring in the 8-15 cm depth interval) containing much lower proportions of OC. Secondly, the OC concentration declines rapidly from 47.2 g·kg^{-1}, at a depth of 2.5 cm, to 20.1 g·kg^{-1} at 10 cm. This sharp trend in OC raises a concern on the validity of carbon determinations (or any other element for that matter) on bulk samples, i.e. those taken from large depth intervals such as the commonly used 0-10 cm interval. For Ap horizons that have been cultivated and mixed for long periods, the determined OC value can be considered an average that is representative of the cultivation depth. For undisturbed Ah horizons, the determined value cannot be considered a mean value that is typical of an entire depth interval. In this case the sampling depth interval, 0-10 cm, is too liberal because the natural variability that exists in this depth range is exceedingly high. Sampling increments of 2.5 or

5.0 cm would be more approriate for showing trends with depth or making comparisons with other undisturbed Ah horizons.

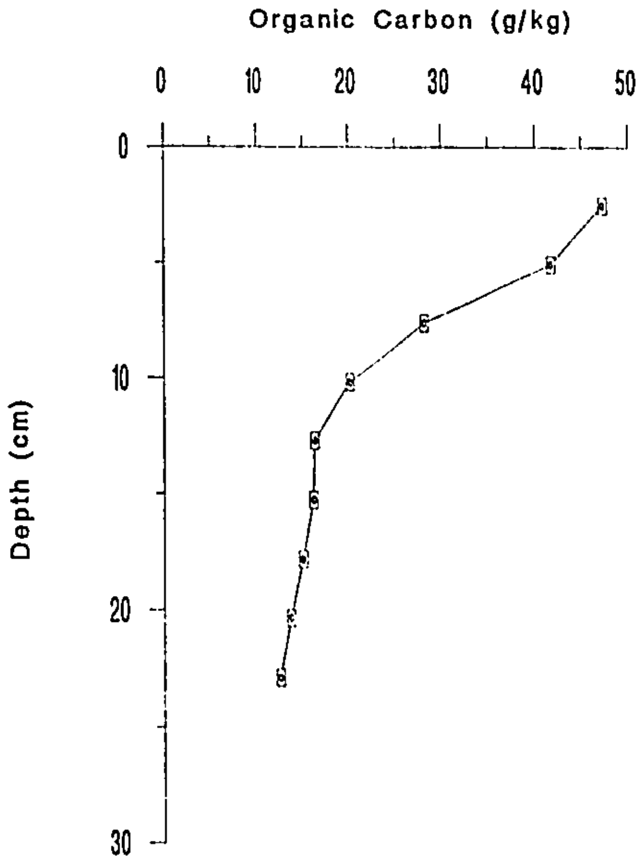

Figure 4.3-1 Organic carbon distribution with depth in native site 1.

After 60 years of wheat-fallow cultivation, total soil organic carbon, in the 0-10 cm depth, has declined by 37, 41, and 62% in sites 1, 2, and 4 respectively, relative to nearby native sites (Table 4.3-2). Site 3 showed more resilience to organic carbon decline, hence the reduction only amounted to 14% of the original OC content. The same comparison for irrigated sites cannot be made since original virgin sites were unavailable for comparison. Cultivated sites also showed declines in total N that were of the same magnitude as those in total OC. Unlike soil OC though, N concentration in cultivated and irrigated sites is highly dependent on the rate of application of commercial fertilizers. In contrast to OC and N reductions, cultivation had little influence on total soil P concentration. Irrigated sites showed consistently high levels of total P, likely due to additions of monoammonium phosphate. No distinct trends in the C/N ratio were evident. This conflicts, to a certain degree, with the results of Campbell and Souster (1982), Woods and Schuman (1988), and Bowman et al. (1990) who reported cultivation of rangeland sites resulted in narrowing of C/N ratios in soils of the Great Plains. A word of caution is in order with regard to interpreting C/N ratio data. It is well known that cultivation leads to reduced levels of soil OC, the effect on N is not as clear. This is because C is not subsequently replenished through commercial fertilizers as are N and P. Therefore, OC will decline and N will tend to remain at some constant level under arable farming. In general then, cropping virgin or rangeland Chernozemic soils coupled with additions of N fertilizer should lead to narrowing of C/N ratios.

Table 4.3-1 C, N, and P properties of the A horizons.

Treatment		OC	N	P	C/N
		—$g \cdot kg^{-1}$—		$mg \cdot kg^{-1}$	
Native	Site 1	21.5	1.8	400	11.9
	2	21.8	2.2	500	9.9
	3	23.6	1.9	400	12.4
	4	21.9	1.7	400	12.9
Cultivated	Site 1	13.6	1.1	400	12.4
	2	12.8	1.4	400	9.1
	3	20.2	1.6	500	12.6
	4	8.3	0.6	300	13.8
Irrigated	Site 1	20.2	1.8	600	11.2
	2	20.2	1.8	600	11.2
	3	27.9	2.0	600	14.0
	4	20.9	1.8	600	11.6

The degradation of OM in cultivated sites has been accelerated by: (i) stimulating short, intense bursts of microbial activity via increasing the oxygen supply to the soil, (ii) physical disintegration as a result of repeated cultivation passes to maintain the soil surface free of plant growth during the fallow year, (iii) exposing inaccessible organic substrates to microorganisms, and (iv) increasing exposure to wind and water. Thus, the degree to which exploitive cultivation alters the organic matter properties of a soil depend on such factors as the original thickness of the A horizon and its original organic matter concentration, the susceptibility of the site to erosion, and the type and intensity of cultivation practices which enhance organic matter mineralization and mix lower horizons of the profile into the surface horizon.

4.4 Carbohydrates in soil hydrolysates

Long term cultivation has also resulted in a sharp decline in carbohydrate-C (in monosaccharide form) in sites 1 and 2, with reductions of 68 and 61% respectively, however, in site 3 carbohydrate-C increased by 18% (Table 4.4-1). For sites 1 and 2 the decline in the labile fraction of soil organic C (carbohydrate-C) was larger than the decline in total organic C. Campbell and Souster (1982), Janzen (1987), and Bowman et al. (1990) also reported disproportionately higher losses of labile organic C than losses of total organic C as a result of long term wheat-fallow cultivation. Dalal and Henry (1988), however, reported carbohydrate-C did not show any higher rate of decomposition than total organic C in an Alfisol and two Vertisols used primarily for cereal production. This could be due to the fact that polysaccharide polymers are so strongly sorbed to clay minerals that they have become persistent binding agents and can not be disrupted by tillage nor can they be accessed by microorganisms. Consequently, carbohydrates in the clay fraction are no more labile than total organic C as reported by the two authors. If, on the other hand, polysaccharides are not stabilized as organo-mineral complexes they should theoretically exhibit higher lability because carbohydrates are readily utilizable sources of energy to soil microorganisms. This is likely the reason cultivated sites 1 and 2 show higher decomposition rates of labile organic C. In site 3 the net carbohydrate concentration actually increased with the wheat-fallow rotation, supporting the results of Dalal and Henry (1988). This could be due to addition of organic materials, such as wheat straw, to the soil at this site.

Table 4.4-1 Concentration of five monosaccharides in soil hydrolysates.

Sugar	Site 1		Site 2	
	Native	Cultivated	Native	Cultivated
	mg·kg^{-1} whole soil			
Glucose	1157	419	1105	624
Galactose	856	268	945	321
Mannose	783	169	802	189
Arabinose	870	299	842	317
Xylose	576	207	620	239
Total	4242	1362	4317	1690
$\frac{\text{Galactose + mannose}}{\text{Arabinose + xylose}}$	1.13	0.86	1.20	0.92

Sugar	Site 3		Site 2	Site 3
	Native	Cultivated	Irrigated	Irrigated
	mg·kg^{-1} whole soil		mg·kg^{-1} whole soil	
Glucose	584	779	443	190
Galactose	545	546	420	205
Mannose	203	400	231	186
Arabinose	449	477	392	148
Xylose	308	267	279	133
Total	2089	2469	1765	862
$\frac{\text{Galactose + mannose}}{\text{Arabinose + xylose}}$	0.99	1.27	0.97	1.39

The proportion of carbohydrate-C to total organic C in soil varies from 5 to 25% (Cheshire 1979). In a number of Australian soils, neutral monosaccharides accounted for 5 to 17% of OC (Oades 1972). Dalal and Henry (1988) reported values in the range of 5 to 16% for two Vertisols. Slightly higher values were found in this study (9-20%, not including irrigated sites) (Table 4.4-2). The carbohydrate-C, as a percentage of total soil organic C, was also higher in virgin sites 1 and 2 but lower in site 3 as compared to cultivated sites.

Table 4.4-2 Carbohydrate-C as a percentage of total organic carbon.

Treatment		$\frac{\text{Carbohydrate-C}}{\text{Total organic C}}$
Native	Site 1	19.7
	2	19.8
	3	8.9
	4	ND
Cultivated	Site 1	10.0
	2	13.2
	3	12.2
	4	ND
Irrigated	Site 1	ND
	2	8.7
	3	3.1
	4	ND

Net amounts of individual monosaccharides were also lower in cultivated soils than in virgin soils in sites 1 and 2; in site 3 the trend was reversed except for xylose which was higher in the virgin Ah horizon (Table 4.4-1). Glucose was the dominant monosaccharide in soil hydrolysates except in site 3 of the irrigated treatment where galactose was slightly higher. Monosaccharide concentrations for the two irrigated sites are much lower than anticipated likely because a sizeable portion of the H_2SO_4 was consumed by the $CaCO_3$ present in these sites. Oades (1984) suggests a galactose + mannose-to-arabinose + xylose ratio of < 0.5 is typical of plant-derived carbohydrates while a ratio of > 2.0 is characteristic of microbial carbohydrates. Therfore, the corresponding monosaccharide ratios listed in Table 4.2-7 which range from 0.86 to 1.27 (not including irrigated samples) appear to indicate the presence of both plant and microbially-derived carbohydrates. The galactose + mannose-to-arabinose + xylose ratios from virgin sites 1 and 2 were significantly higher (31 and 30% respectively) than those from similar cultivated sites, while in site 3 the opposite was true; the ratio in the cultivated soil was 28% higher than the virgin sample. These results indicate the presence of significantly more microbial-derived carbohydrates in virgin sites 1 and 2 but more plant-derived carbohydrates in similar cultivated sites. For reasons unknown to the author the opposite trend exists in site 3. Arabinose and xylose (plant polysaccharides) increase in abundance, relative to galactose and mannose, upon cultivation possibly because they are left behind as the recalcitrant plant polysaccharides from crop residues (Dalal and Henry 1988). The resistance to decomposition of plant polysaccharides may be due to their role in forming stable aggregates < 20 μm diameter and are thus rendered inaccessible to microorganisms and their degradative enzymes.

4.5 Spectroscopic data

4.5.1 Infrared spectra

The FTIR spectra of humic acids extracted from native and cultivated sites are shown in Figure 4.5-1a. The spectra show a strong –OH absorption band at 3440 to 3420 cm^{-1}, a C–H absorption band from CH_3 groups at 2940 to 2920 cm^{-1}, a C–H shoulder from CH_2 groups at 2850 cm^{-1}, a C=O stretch of COOH absorption band at 1720 to 1710 cm^{-1}, an aromatic C=C absorption band at 1640 to 1610 cm^{-1}, weak –OH deformation and C–O stretching of phenolic–OH or weak COO^-–antisymmetric stretching at 1390 to 1380 cm^{-1}, a C–O stretch and –OH deformation of COOH groups at 1280 to 1200 cm^{-1}, and C–O stretching of polysaccharide or polysaccharide-like substances and/or Si–O of silicate impurities at 1050 to 1020 cm^{-1} (Steveson 1982; Novak and Smeck 1991). Virgin and cultivated spectra are essentially similar except for differences in intensities of certain bands.

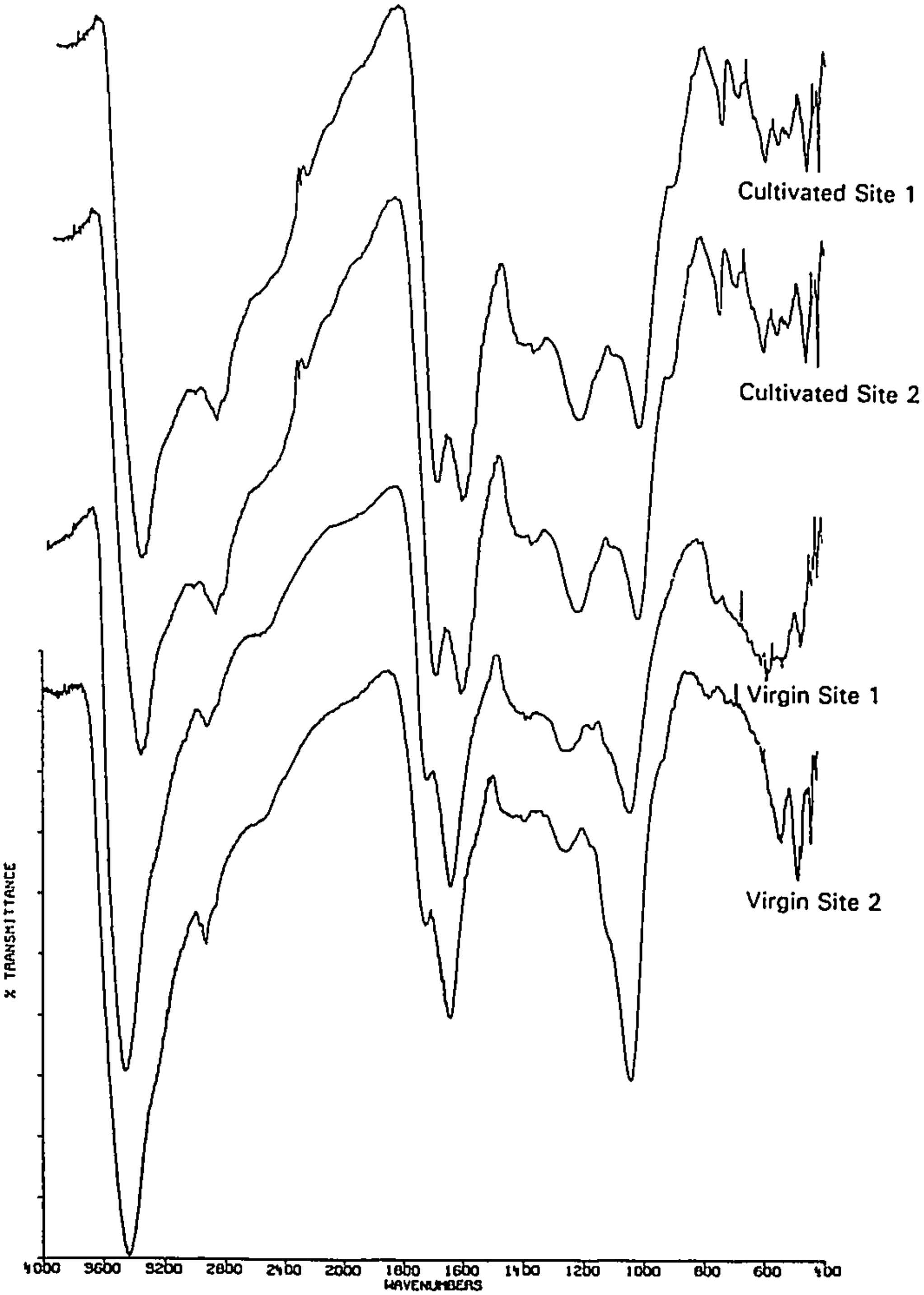

Figure 4.5-1a FTIR spectra of humic acids from virgin and cultivated sites 1 and 2.

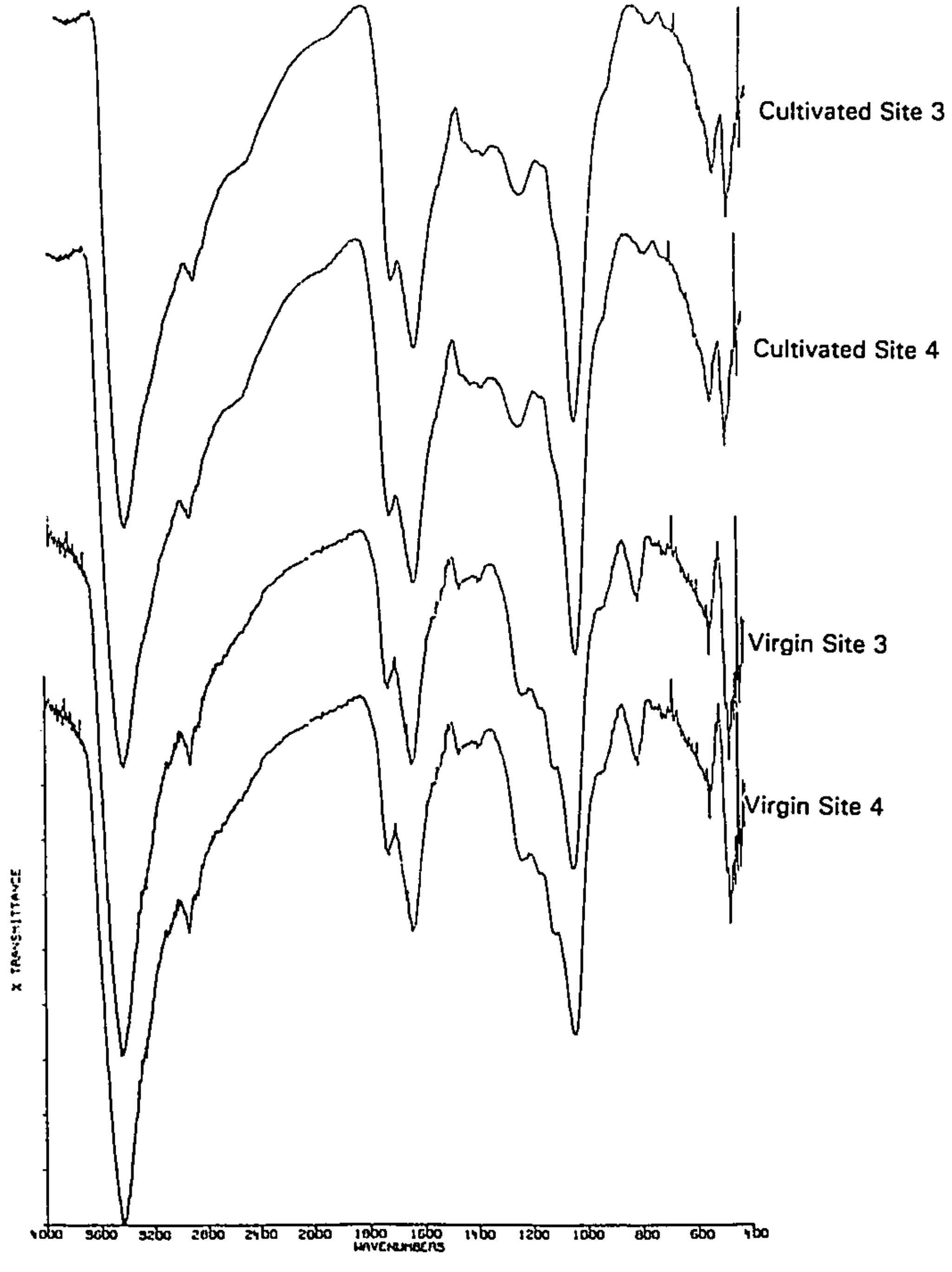

Figure 4.5-1a ... continued FTIR spectra of humic acids from virgin and cultivated sites 3 and 4.

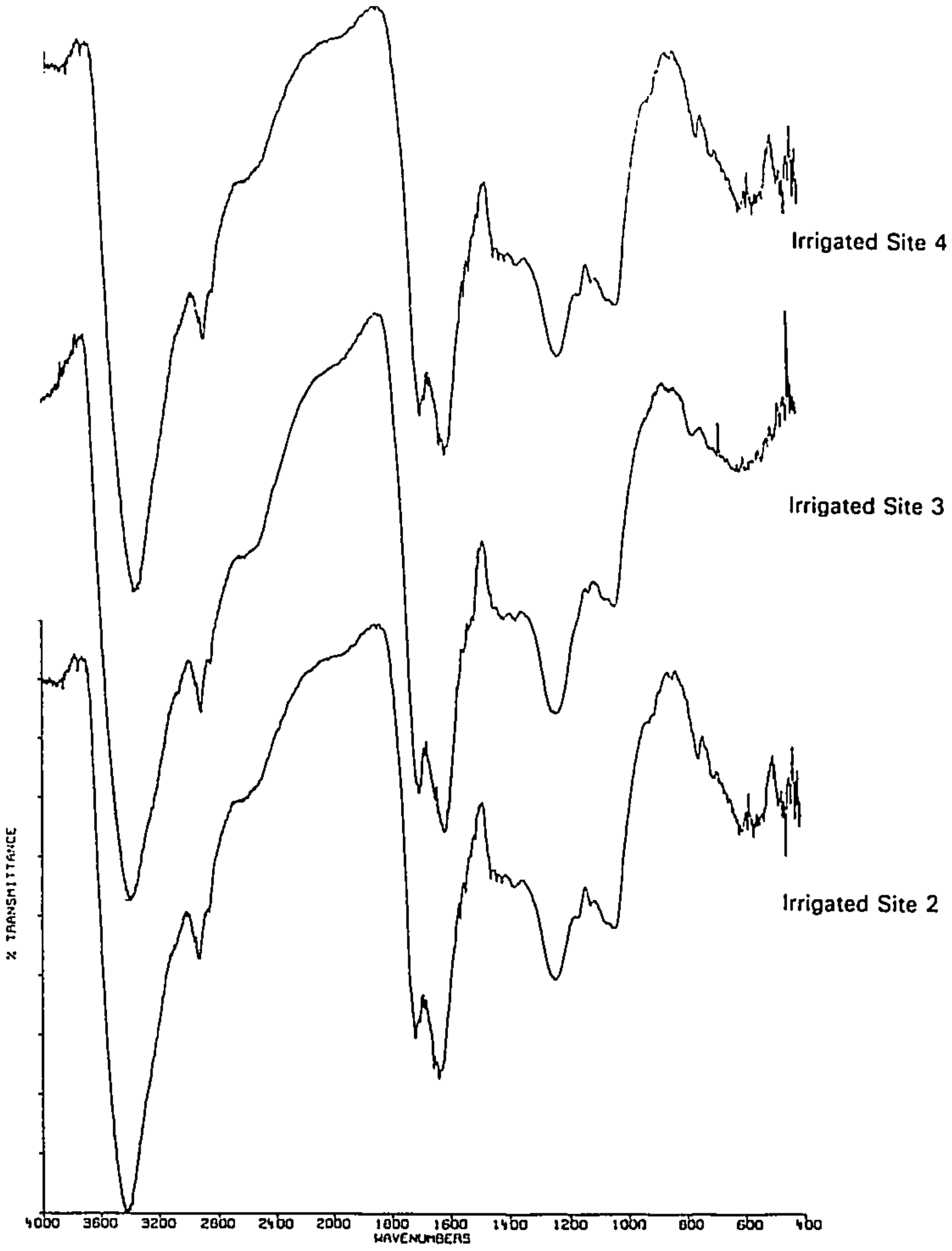

Figure 4.5-1b FTIR spectra of humic acids from irrigated sites.

The FTIR spectra show that humic acids obtained from native and cultivated sites lack significantant proteinaceous material, the amide I and II bands at 1650 and 1540 cm^{-1} are almost indiscernible in the spectra. The relatively strong absorption band at 1050 to 1020 cm^{-1}, native site 2 and both treatments in sites 3 and 4, suggests that the clay-OM complex was extracted. This is further substantiated by moderately high ash contents (data not shown), i.e. $\cong$ 15%, before further purification was accomplished. It is noteworthy that the humic acids from the cultivated sites show evidence of a higher carboxyl content than the native sites with higher absorbances at 1710 and 1240 cm^{-1} (Figure 4.5-1a). This increase in acid groups demonstrates that the material remaining in the cultivated soils after 60 years of cultivation is more completely humified and may represent the most resistant fraction of the original humic material (Skjemstad and Dalal 1987). This is in accordance with McGill et al. (1981), who proposed that resistent soil organic matter resulted from the decomposition of less recalcitrant moieties, leaving those with greatest resistance to enzymatic attack. The net result is an overall increase in recalcitrance.

FTIR spectra of humic acids extracted from irrigated sites (Figure 4.5-1b) show the same absorption bands as those from virgin and cultivated sites, plus additional bands; these include a weak band indicative of C=O stretching of amides (amide I band) and quinones at 1660 to 1650 cm^{-1}, weak COO^{-}–symmetric stretching, N–H deformation plus C=N stretching (amide II band) at 1560 to 1520 cm^{-1}, and a weak aliphatic C–H stretching band at 1460 to 1420 cm^{-1} (Stevenson 1982). The presence of amide I and II bands indicates a greater peptide content in these humic acids. A high carboxyl component is also evident in these humic acids as shown by a pronounced absorption band at 1240 cm^{-1}. This indicates that the organic material is better decomposed and more completely humified under this management regime. According to Bal (1982) the OM is better aged or ripened, attesting to the abundant earthworm fecal material as observed in thin section.

4.5.2 NMR spectra

Solid state ^{13}C CP/MAS NMR spectra of humic acids from a native and a cultivated site are shown in Figure 4.5-2. The spectra are divided into the following areas: 0-40 ppm (paraffinic C); 40-60 ppm (C in branched aliphatics, amino acids, and OCH_3 groups); 60-105 ppm (C in carbohydrates and in aliphatics containing C bonded to OH, ether oxygens, or occurring in five- or six-membered rings bonded to O); 105-150 ppm (aromatic C); 150-170 ppm (phenolic C); and 170-190 ppm (C in COOH groups) (Arshad et al. 1990).

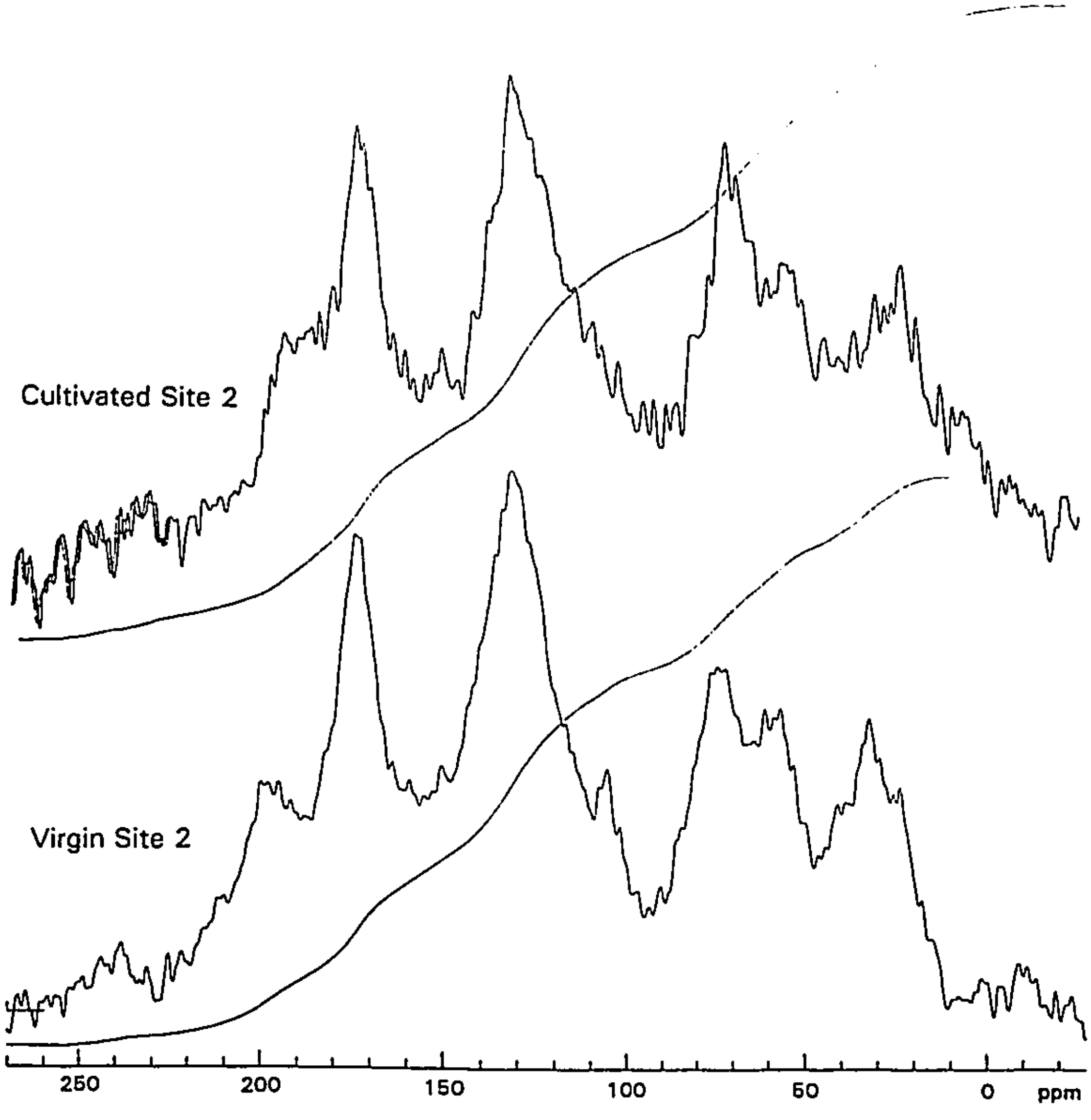

Figure 4.5-2 ^{13}C NMR spectra of humic acids from virgin and cultivated site 2.

The spectra for the native and cultivated humic acids are again similar except for differences in intensities. Both curves exhibit strong signals at 32, 57, 74, 130-132, and 174 ppm. The cultivated site also exhibits a strong signal at 27 ppm. Small signals or shoulders at 13, 16, and 18, ppm are typical of CH_3 groups; signals at 22 and 24 ppm are due to CH_2, and those near 30 ppm are characteristic of $(CH_2)_n$ in long-chain paraffinic structures (Schnitzer and Schuppli 1989). Resonances at 57 ppm are likely due to C in OCH_3 and not to C in amino acids. The strong resonances at 74 ppm arise from C in carbohydrates and other OH-substituted aliphatic structures (Schnitzer and Preston 1987). The weak signal at 105 ppm in the two spectra is likely the result of C-1 carbons of cellulose or hemicellulose (Arshad et al. 1990). Aromatic C shows a strong signal at 130-132 ppm. The small signal around 150 ppm in both curves indicates depletion in phenolic C (that is aromatic C bonded to OH groups). Lastly, the strong signal at 174 ppm results from C in COOH groups.

In comparing the relative composition of the humic materials in the two soils the general conclusion is that the humic acids are remarkably similar in composition despite profound differences in quality and quantity of inputs under the two different management systems. Particularly noteworthy is the cultivated site, where the input of organic material is negligible every second year. After 60 years of WF rotation, the OM in the cultivated site can be considered to have reached an equilibrium state and should represent the end product of biomass activity (Oades et al. 1988; Capriel et al. 1992). Only two differences in composition are worth noting. The cultivated soil appears to contain greater proportions of carbohydrates and paraffinic C. We know the former not to be true, carbohydrates were measured directly on soil hydrolysates and cultivated site 2 is depleted in net quantites of carbohydrates relative to the native soil. Schnitzer (1990), in his review, noted that ^{13}C NMR spectroscopy cannot be used for the quantitative analysis of carbohydrates in humic susbstances. Dissolution of paramagnetic ions, most notably Fe^{3+}, with dilute HCl-HF solution also removed a certain percentage of carbohydrates and nitrogenous components. Therefore, humic acids can no longer be considered as "natural" and may contain artefacts induced by the purification step. Still, it is noteworthy, the HCl-HF treatment was performed with gentle shaking at room temperature and did not remove all carbohydrates, as shown by the resonance at 74 ppm. Thus, the objective of preventing excessive losses of OM by limiting the number of HCl-HF treatments to three, was achieved.

Although peak areas were not measured it appears that no significant differences in per cent aromaticity are evident between the two treatments. This is in contrast to Turchenek and Oades (1979) who reported that the extractable OM from a soil that had been in a alternate WF rotation for 60 years was more aromatic compared to the OM in a permanent pasture. Wilson (1987) noted that aromatic components in a soil used for cereal production probably originate from the lignin of wheat straw and roots. However, if cereal lignin is a major source of aromatic materials in the WF soil, it is suprising that there is such a small resonance of the *O*-aromatic-C of phenols at 150 ppm. It is likely that this particular bond is readily oxidized in and is not a recalcitrant moiety which accumulates in soils.

Recent investigations of Oades et al. (1988) and Fründ and Lüdemann (1989) suggest that the standard NaOH extraction procedure, generally used for the isolation of humic and fulvic acids, does not separate the original humic material into fractions of largely different chemical composition. Rather it seems to dissolve the most accessible fraction of the humic material while leaving the major inaccessible fraction unchanged. These researchers concluded that the composition of NaOH extract reflects the composition of the OM in soil. Schnitzer and Schuppli (1989) found that unadjusted 0.1 M $Na_4P_2O_7$, in the pH range 9.0-9.4, was almost as efficient as 0.5 M NaOH solution for extracting HAs but takes up only 4-6% as much O_2. This means the probabilities for autooxidation and also for hydrolysis are greatly dimished.

Although it is certainly premature to generalize these results which have been obtained on a few sites in the Brown soil zone, the gross composition of the OM in soils which have been managed differently and which have different soil OM levels is similar. This indicates that, changes in management, which have dramatically altered the nature and amount of photosynthate entering the soil, have had little influence on the composition of the products formed by the action of the soil biomass (Oades et al. 1988; Capriel et al. 1992). Selective decomposition of different chemical fractions of plant debris may occur during the early stages of degradation, but over the long term (60 years) these differences become minor, and the end product of biomass activity in a particular soil remains constant (Oades et al. 1988; Capriel et al. 1992). Thus, the longevity of the soil organic matter in the cultivated soil cannot be explained on the basis of a particular stable chemical fraction resulting from the selective degradation of diverse components, but we must look towards their interaction with inorganic materials and to the position of the organic molecules within certain size fractions.

There is abundant evidence suggesting clay minerals are involved in stabilizing OM, however, the stabilization is not confined to a specific chemical group, although the clay fraction is often enriched in alkyl materials (Skjemstad et al. 1986; Skjemstad and Dalal 1987; Oades et al. 1987; Oades et al. 1988). There is also the concept of non-specific adsorption, in which organic materials are attached to clay surfaces via cation bridges associated with ligand groups. Instead of concentrating on specific functional groups alone, we should consider adsorption of a hodgepodge population of organic fractions as a whole through ligand groups dominated by carboxyls (Oades et al. 1988).

All soils contain iron, some of which is in mineral lattices and as such does not interfere with resonance of ^{13}C nuclei. Still, most soils contain at least 0.5 to 1.0 per cent iron in the form of oxides, and some Podzolic Bf horizons contain several per cent Fe_2O_3. Unless the iron oxides occur as nodules, as they do in Bf horizons of Podzols, they are usually concentrated in finer fractions, i.e. $< 2\ \mu m$ diameter, along with long-chained alkyl groups (Skjemstad et al. 1986; Skjemstad and Dalal 1987). Very fine crystalline oxides of iron, such as goethite, possess extensive, active surfaces that are normally positively charged (below pH 8) and hydrated so that substantial participation in ligand exchange reactions with carboxyl functional groups would be expected. A very strong bond will form between oxides and humic materials if several carboxyl or other functional groups participate. It is this type of permanent interaction which helps explain why humic materials remaining in the cultivated soil represent the most resilient fraction of original OM. Support for this proposal is provided by the spectroscopic data. FTIR spectra indicate an enrichment in carboxyl groups in the cultivated site, this is evidenced by stronger absorption bands at 1710 and 1240 cm^{-1}. Paramagnetic iron in the cultivated HA negatively influenced the NMR spectrum by reducing the signal to noise ratio. The Fe-humate complex was so strong that two treatments with dilute HCl-HF and one treatment with stannous chloride could not remove all the iron from the HA of the cultivated site. Oades et al. (1987) also indicated a substantial interaction of carbohydrates with oxide surfaces, this from the dominace of carbohydratres in dithionite extracts. Moreover, broadening of the carbohydrate signal and spinning side bands at 70 and 195 ppm were evident in both spectra, attributable to the Sn^{+2}/Sn^{+4} ions (Figure 4.5-2).

4.6 Aggregate stability

Soils under native sod displayed appreciably greater aggregate stability as compared to corresponding cultivated soils (Table 4.6-1 and Figure 4.6-1). There were more stable macroaggregates (i.e. those > 0.25 mm) in the native sod than in cultivated soil when slaked. There was a much larger proportion of the original sample in the microaggregate size classes, 0.25-0.124 and < 0.124 mm for cultivated soils, especially the < 0.124 mm size class. With such a large percentage of the aggregates in the < 0.124 mm size fraction, it is likely that some of the slaked microaggregates were reduced to silt and clay-size particles; nevertheless, this is only speculation and can only be confirmed by using a sieve with openings of 0.053 mm on the bottom of the sieve stack. Similar research on aggregate stability by Elliott (1986) on Pachic Haplustolls, revealed macroaggregates of native sod to be more stable than those in the cultivated soil. Macroaggregates from the native sod contained higher concentrations of OC than those from cultivated soils. Loss of OM upon cultivation resulted in a smaller proportion of soil containing high nutrient macroaggregates and a larger proportion of soil containing low nutrient microaggregates. Roots and fungal hyphae may be responsible for holding macroaggregates together (Tisdall and Oades 1979; 1982; Oades 1984; Tisdall 1991). Still, the amounts of roots and hyphae present in the soil account for only a small amount of the total soil OM (Elliott 1986). Therefore, the great loss of soil OM due to long-term cultivation must come from another soil OM pool in addition to roots and hyphae.

Table 4.6-1 Size distribution of cultivated and native sod aggregtes when slaked.

	Site 1		Site 2	
Aggregate size	Virgin	Cultivated	Virgin	Cultivated
(mm)	% of dry soil			
6.3-4.0	19.4	1.4	12.6	2.8
4.0-2.0	15.7	2.7	16.5	7.0
2.0-1.0	14.1	3.8	10.8	11.3
1.0-0.5	17.6	7.1	15.4	17.3
0.50-0.25	13.3	17.1	18.6	19.3
0.25-0.124	9.8	21.7	13.6	17.4
> 0.125	89.9	53.8	87.5	75.1
MWD (mm)	1.88	0.40	1.52	0.78

Table 4.6-1 ... continued

Aggregate size	Site 3		Site 4	
	Virgin	Cultivated	Virgin	Cultivated
(mm)	% of dry soil			
6.3-4.0	17.3	2.5	5.6	1.2
4.0-2.0	17.4	4.1	9.7	3.9
2.0-1.0	15.7	5.4	14.4	5.3
1.0-0.5	16.2	9.5	21.7	11.4
0.50-0.25	12.5	14.9	16.8	20.0
0.25-0.124	9.0	19.5	14.5	20.4
> 0.125	88.1	55.9	82.7	62.2
MWD (mm)	1.85	0.53	1.06	0.48

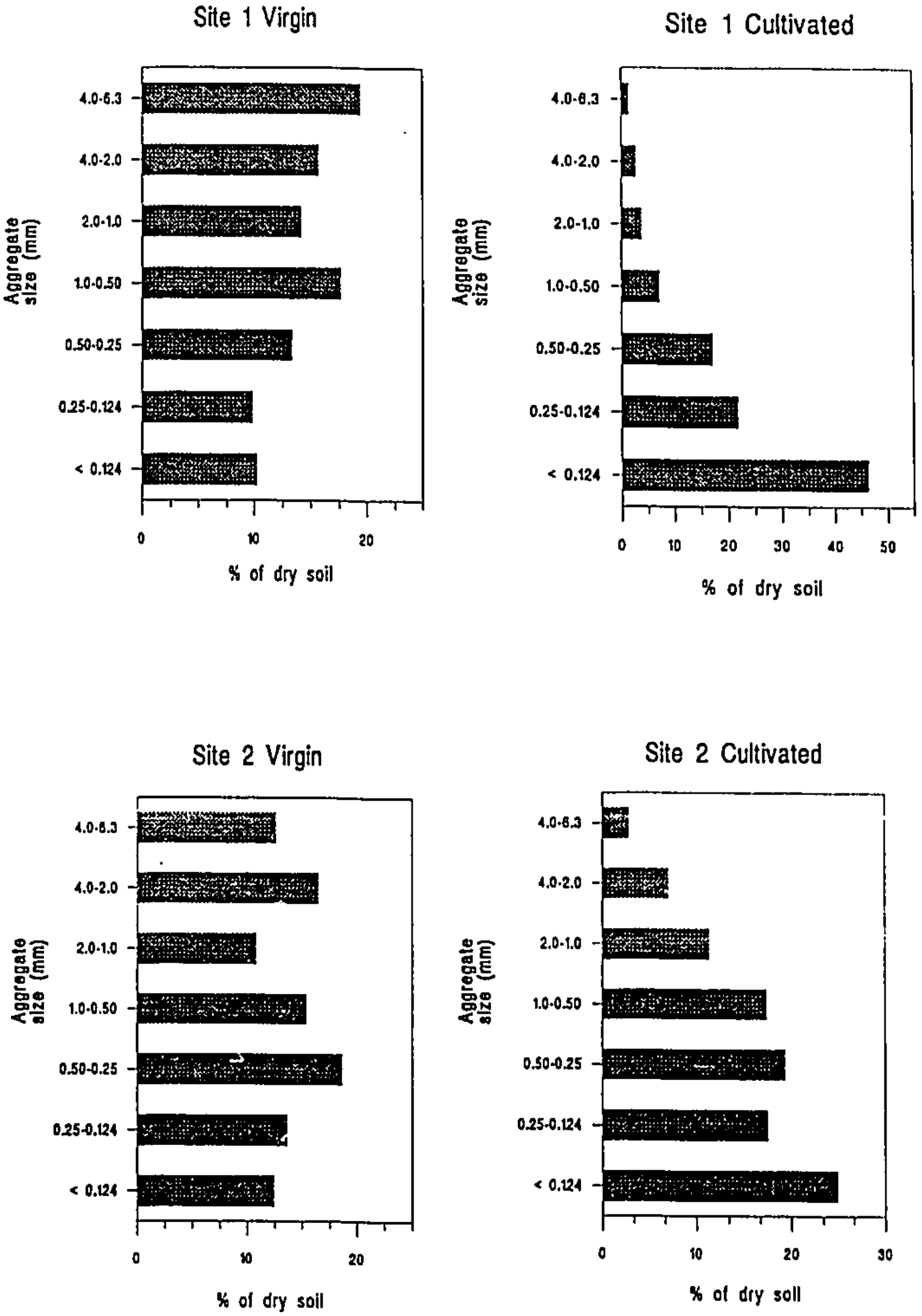

Figure 4.6-1 Size distribution of native sod and cultivated aggregates when slaked.

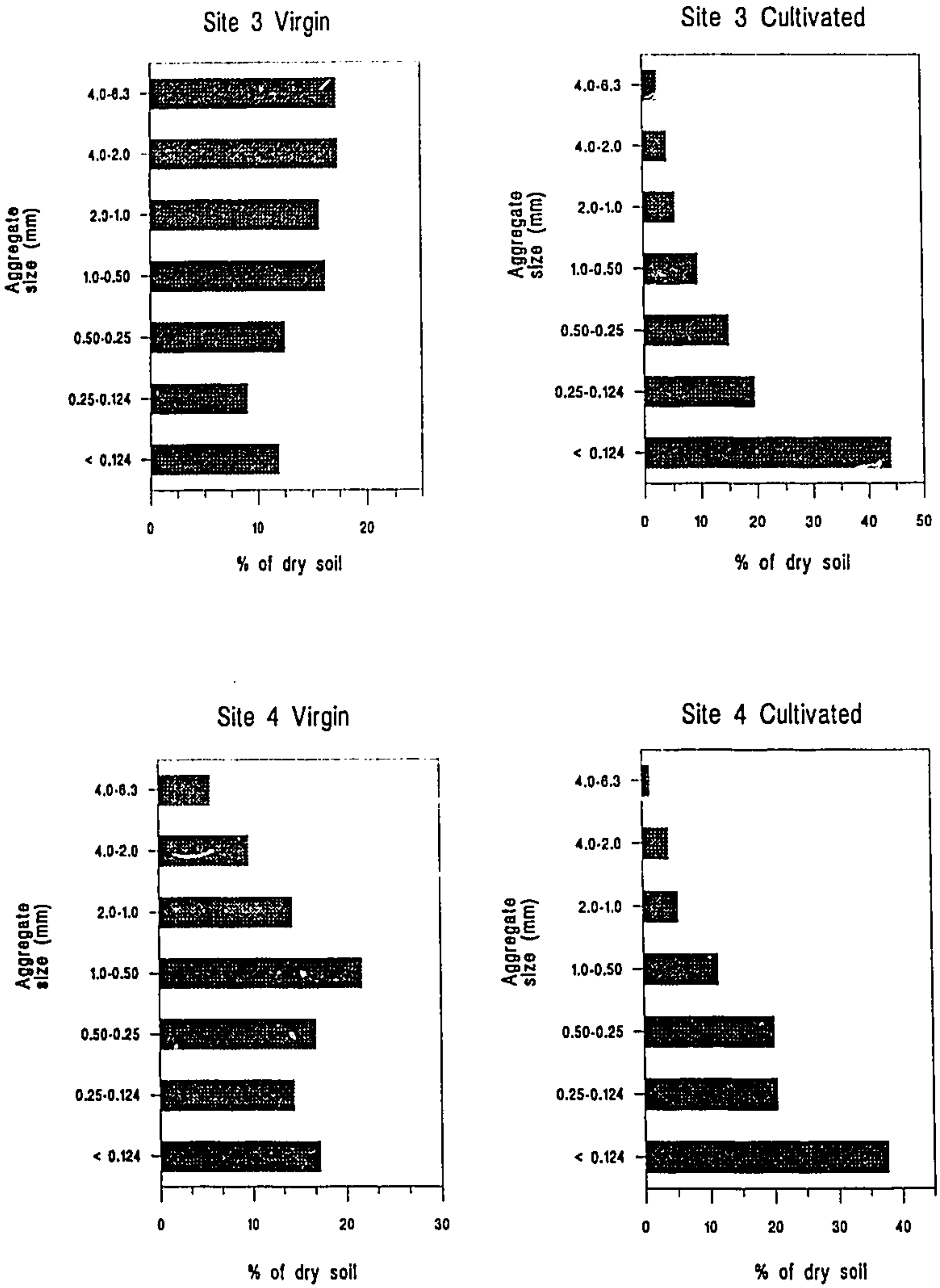

Figure 4.6-1 ... continued

Aggregate-size distribution for irrigated samples (Dark Brown Chernozemic) was distinctly different from that of native and cultivated sites (Brown Chernozemic); most of the soil was concentrated in the last four size classes (Table 4.6-2 and Figure 4.6-2). The aggregate distribution for sites 1,2, and 4 was approximately equal between the 1.0-0.5, 0.5-0.25, and < 0.125 mm size fractions (values in the range of 20.4 to 24.8 %), while the 0.25-0.124 mm size class contained 15.6 to 17.6 % of the aggregates. In site 3, 35.5% of the aggregates were in the 1.0-0.5 mm size and 19.6% were in 2.0-1.0 mm size class.

Table 4.6-2 Size distribution of irrigated aggregates when slaked.

	Site 1	Site 2	Site 3	Site 4
Aggregate size	Irrigated	Irrigated	Irrigated	Irrigated
(mm)	% of dry soil			
6.3-4.0	0.8	0.60	0.8	0.4
4.0-2.0	3.5	6.6	5.6	2.9
2.0-1.0	10.5	11.5	19.6	9.4
1.0-0.5	22.7	20.4	35.5	23.1
0.50-0.25	21.0	22.0	10.5	24.8
0.25-0.124	15.6	15.6	12.7	17.6
> 0.125	74.5	76.7	84.7	78.2
MWD (mm)	0.60	0.68	0.84	0.56

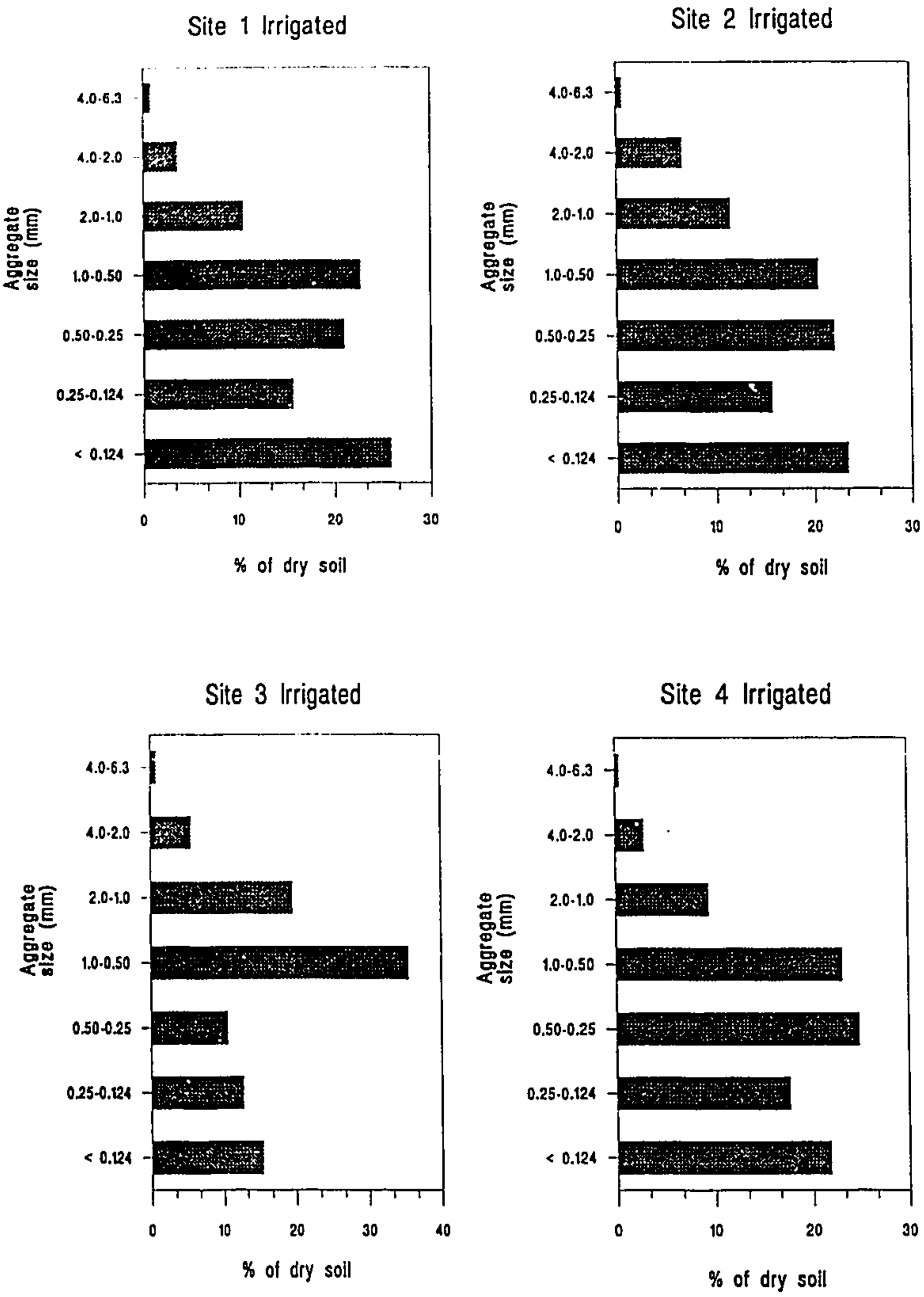

Figure 4.6-2 Size distribution of irrigated aggregates when slaked.

There are conflicting reports on the effects of air-drying on aggregate stability; both increases and decreases in aggregate stability have been observed. Churchman and Tate (1987) found that in soils under permanent pasture, with 5-10% OC, air dried aggregates were significantly more stable than the ones in the field-moist state. In contrast to this, Munroe and Kladivko (1987) observed that air drying an arable soil, with 1% OC, greatly reduced aggregate stability. Haynes and Swift (1990) showed convincingly that air drying, before wet sieving, increases the stability of long-term pasture aggregates but decreases the stability of arable aggregates; thereby explaining the past contradicting results.

Aggregate stability as determined by wet sieving of dried aggregates measures both the rapid breakdown of aggregates upon rewetting (slaking) and the subsequent breakdown of aggregates owing to the mechanical sieving action. Slaking is a very important process and is a particular problem on fine-textured cultivated soils in the Brown soil zone when periods of intense rainfall occur after the soil surface has dried out. Macroaggregates from cultivated soils, because of their lack of seasonal binding agents, are weakly bound together and drying causes incipient fracture planes to develop. Upon contact with water (in the liquid phase) the aggregates quickly rewet owing to rapid rehydration of particle surfaces. The resultant rapid release of energy causes extensive aggregate breakdown. Unequal pressures caused by differential swelling during rewetting and the presence of entrapped air in pores also promotes aggregate breakdown (Oades 1984). Weakened macroaggregates are further broken down by the mechanical action of wet sieving.

Native sod macroaggregates, in contrast, are stabilized by fine plant roots, root hairs and associated fungal hyphae (Tisdall and Oades 1982). Haynes and Swift (1990) observed that pasture aggregates rewet much more slowly than the arable ones. They attributed this to the coarse organic materials imparting partial hydrophobic properties to the dried pasture aggregate. In turn, the energy released upon rehydration is dissipated over a longer period of time (Haynes and Swift 1990). This coupled with the inherently stronger binding within the native macroaggregates means that upon rewetting, native macroaggregates are far more stable than cultivated ones. It seems plausible that drying (and contraction of the macroaggregates) enhanced the binding of fungal hyphae, humic substances, and polysaccharides thus imparting a greater stability on native macroaggregates. Although such an effect would seem just as plausible in cultivated macroaggregates, the effect is probably overcome by the disruptive forces induced by air-drying and rapid rewetting.

Acid hydrolysis does not differentiate between active and inactive carbohydrate binding agents and generally correlation coefficients for carbohydrate content and aggregate stability are similar to those for total OC content (Chaney and Swift 1984; Baldock et al. 1987). Baldock et al. (1987) found that total hydrolysable carbohydrate content was not significantly correlated with aggregate stability of samples from a Gleyed Melanic Brunisol of different cropping histories. They concluded that if carbohyrates are responsible for changes in aggregate stability, that have occured over a relatively short time period, then a specific pool must be involved. The hot and cold water-extractable carbohydrate fractions of Haynes and Swift (1990) seems to represent such a pool. They suggested that the water-extractable fraction primarily characterizes microbial mucilage. The significance of the hot water-extractable carbohydrate fraction was shown by the fact that it was much more closely correlated with aggregate stability than was hydrolysable carbohydrate or OC over a range of cropping histories. This may help to explain the situation in the third site of the Brown Chernozem. The cultivated soil has 14% less OC but 18% more carbohydrates than the native sod. The hot water-extractable carbohydrate fraction may have helped explain the difference in macroaggregate stability between the virgin and cultivated treatments in this particular site that total hydrolysable carbohydrate content did not. Nevertheless, the numbers of stable macroaggregates in the cultivated soil, which are the most reliable indicators of structural stability, are dramatically reduced after slaking. Thus, it seems there is sufficient evidence to justify the statement that plant roots and associated fungal hyphae, even though accounting for only a small proportion of the total OC content in the soil, represent the most imporant stabilizing mechanisms of macroaggregates.

4.7 Micromorphology

Distinctive and consistent associations of micromorphological characteristics were found in each of the three management regimes of A horizons of Chernozemic soils, so summary descriptions from one representative pedon of each regime are presented in Table 4.7-1. The obvious differences in microstructure, as expressed by the degree and type of aggregate development, are directly related to manangement practices, in combination with bioclimatic factors. Of the latter, earthworm activity is the most important in irrigated sites for producing spongy microstructures and partially accomodated granoidic related distributions (Figure 4.7-4a). In native grassland sites, climate is likely the most important factor governing microstructural development. The lack of significant accumulations of snow and the frequent winter chinooks may result in more frequent freeze-thaw cycles.

Table 4.7-1 Summary of micromorphological descriptions.

Site 1 Native

Microstructure

0-2.5 cm ultrafine granular

2.5-8.5 cm platy aggregates, 150-400 μm thick and up to 6.5 mm long

8.5-12.5 cm platy aggregates that increase in thickness with depth, 200-750 μm thick; also some subangular blocks, 720 μm to 5 mm wide

Related Distribution

0-2.5 cm Ortho-humo-phytogranoidic

2.5-8.5 cm Banded intergrade porphyric-matrigranoidic

8.5-12.5 cm Banded fragmoidic intergrade porphyric-matrigranoidic // fragmoidic vughy porphyric

Pedological Features

(i) Fecal pellets dark brown to black in color, 30-55 μm in size, are plentiful in the 0-2.5 cm zone and are responsible for the humi- component of the observed fabric. (ii) Some aggrotubules with matri-humigranoidic and porphyric-matri-humigranoidic fabric comprised of 30-120 μm size units are present in the 4.5 -12.5 cm depth interval. (iii) Discrete brown to dark brown isotropic organic glaebules (melanons), 10 to 15 μm up to 425 μm in size, are ubiquitous throughout the entire sampling depth.

Plasmic Fabric

Dominant plasmic fabric is misepic with weak masking by the poorly humified organic plasma.

Notes

The presence of partly decomposed plant fragments and the abundance of discrete organic glaebules suggests the plasma is not homogeous in composition. Organic components are poorly humified and it appears that colloidal complexing between organic matter and clays is weak as there is little masking of the birefringence. Plasmic fabrics are not mull-like in character and would be more accurately described as mull-like moder. The absence of mullgranic units of fabric and fecal excrement from a diverse population of soil fauna indicates this is not an f-fabric that would be considered typical of soils of the Chernozemic order.

Table 4.7 ... continued

Site I Cultivated

Microstructure

0-6 cm 60% spongy, 40% fragments (0.5-3 mm) and clods (5-28 mm)

6-12 cm 55% fragments (0.5-5 mm) and clods (5-32 mm), 45% spongy

12-14 cm dense spongy to vughy

14-18 cm massive

Related Distribution

0-6 cm granoidic//vughy porphyric

6-12 cm porphyric-matrigranoidic//vughy porphyric

12-14 cm intergrade vughy porphyric-matrigranoidic

14-18 cm dense vughy porphyric

Pedological Features

(i) Discrete brown to dark brown isotropic organic glaebules (melanons), < 10 μm up to 100 μm in size, are ubiquitous throughout the sampling depth.

(ii) Collembola fecal pellets, 30-65 μm in size, observed in aggrotubules.

Plasmic Fabric

Dominant plasmic fabric is skel-insepic with little masking by the remaining organic plasma. Fragments, i.e. aggregates ≤ 5 mm diameter, of B horizon brought up through tillage have an omnisepic plasmic fabric.

Notes

A 5 mm thick crust overlies this section. The crust is likely a remnant of a larger clod that was fractured by tillage. Clods are often composed of fused, rounded "aggregates" 120-540 μm in size, unaggregated quartz grains, and fused tillage-induced fragments 30-80 μm in size. It appears that tillage is a suitable mechanism for mixing organic and mineral matter; reorganization of the fabric has resulted in the disappearance of the light, partly decomposed plant fragments and produced plasma that is more uniform in composition. A plow pan is found at a depth of 14 cm.

Table 4.7 ... continued

Site 3 Irrigated

Microstructure

0-3 cm 45% spongy, 35% subangular blocky (360 μm-2.9 mm in size), and 20% granular (150 μm-1200 μm in size)

3-7 cm 55% spongy, 35% subangular blocky (720 μm-8.3 mm), and 10% granular (150-1250 μm in size)

7-9.5 cm 85% spongy and 15 % granular (50-1100 μm in size)

9.5-14 cm 65% subangular blocky (720 μm-5 mm) and 35% spongy

Related Distribution

0-3 cm fragmoidic metapegrigranoidic//porphyric-fragmoidic metapegrigranoidic//fissured pegriporphyric//metapegrigranoidic

3-7 cm fragmoidic metapegrigranoidic//fragmoidic-porphyric-metagranoidic// pegrifragmoidic //fissured pegriporphyric

7-9.5 cm metapegrigranoidic//porphyric-metapegrigranoidic//vughy porphyric

9.5-14 cm fragmoidic//porphyric-pegrigranoidic//vughy pegriporphyric

Pedological Features

(i) Earthworm fecal pellets, 360-1250 μm in size with varying degrees of coalescence, comprise the spongy microstructure

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This coupled with the abundant silt content of the pedons may provide conditions that promote ice lens formation (Van Vliet-Lanoë 1985) and the development of platy structures (Sanborn and Pawluk 1988) (Figure 4.7-4b). The platy aggregates are lens-shaped and have evolved through deformation and erosion attributable to the ice lensing (Van Vliet-Lanoë 1985). The particle-size segregation often observed in the platy aggregates of Ae horizons of Gray Luvisols (Mermut and St. Arnaud 1981) is moderately expressed in the native Ah horizons. From Figure 4.7-4b it can be seen that a capping composed of silt, clay-size particles and humic constituents has developed on the top of the platelets to give a band that is a bit darker and denser at the top. According to Van Vliet-Lanoe (1985) the capping of

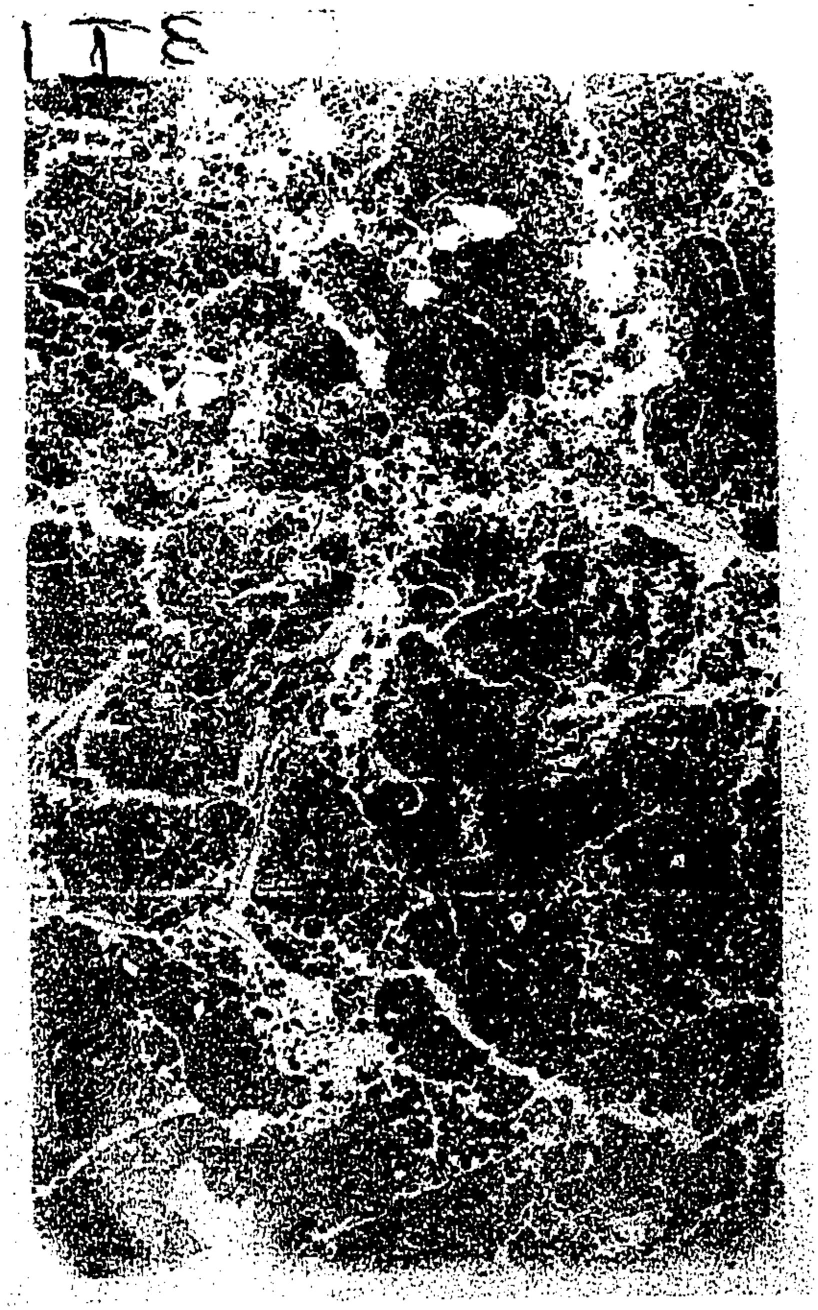

Figure 4.7-1 Fabric of 0-7 cm depth interval from Irrigated Site 3 (Orthic Dark Brown Chernozem).

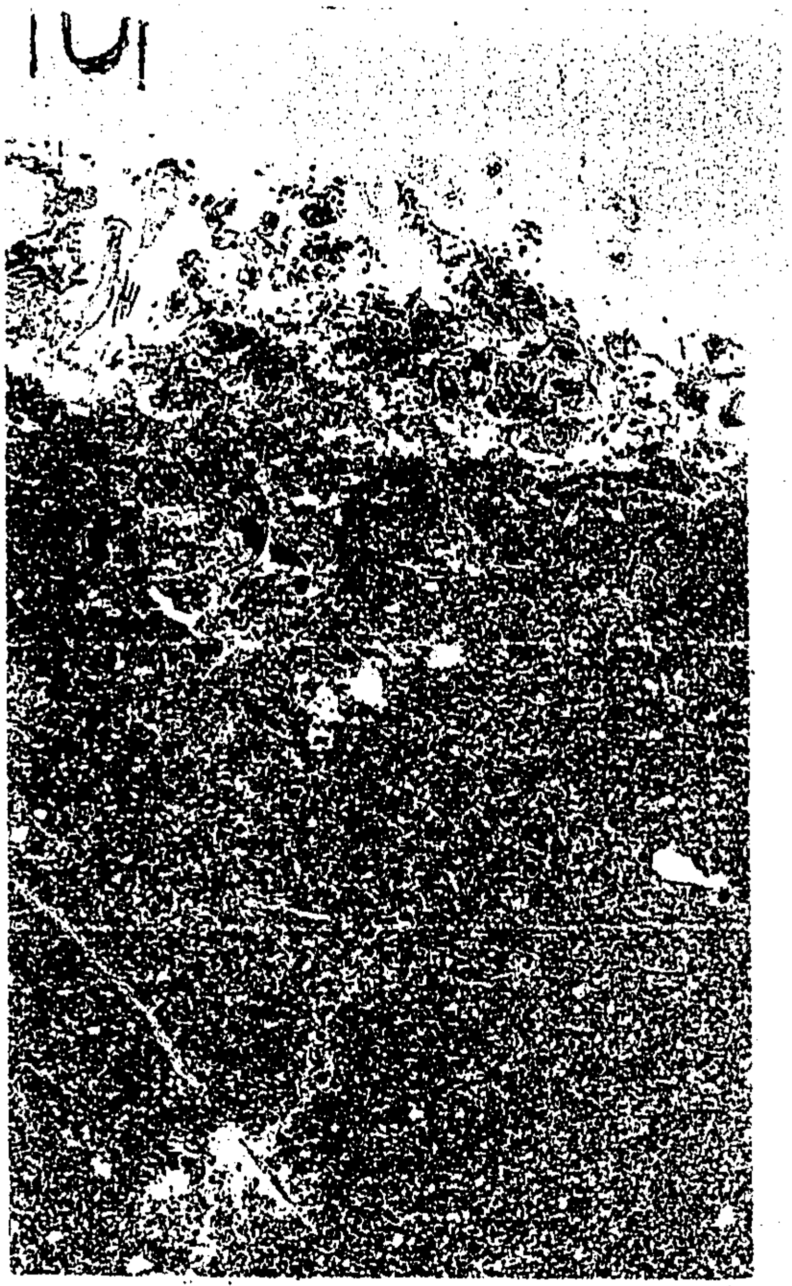

Figure 4.7-2 Fabric of 0-6 cm depth from Native Site 1 (Orthic Brown Chernozem).

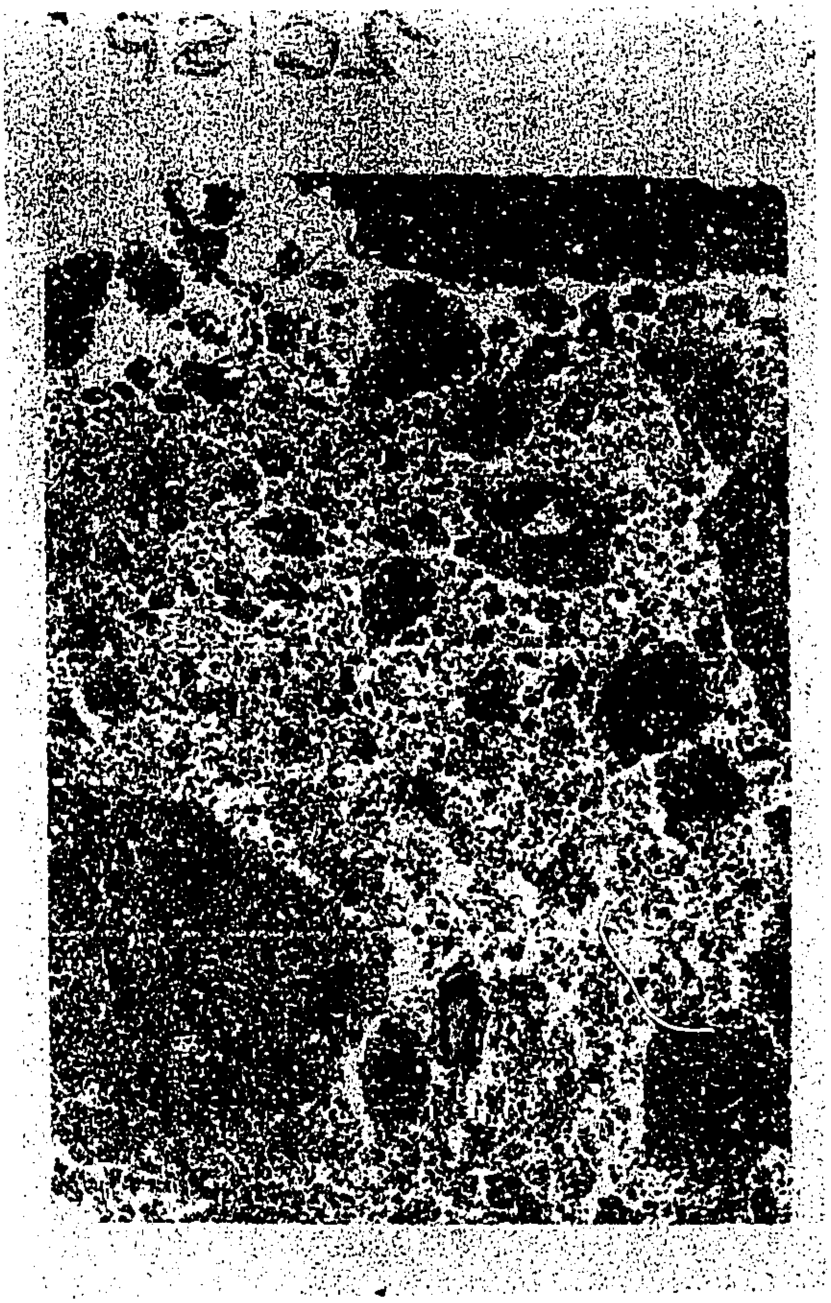

Figure 4.7-3 Fabric of 0-6 cm depth from Cultivated Site 2 (Orthic Brown Chernozem).

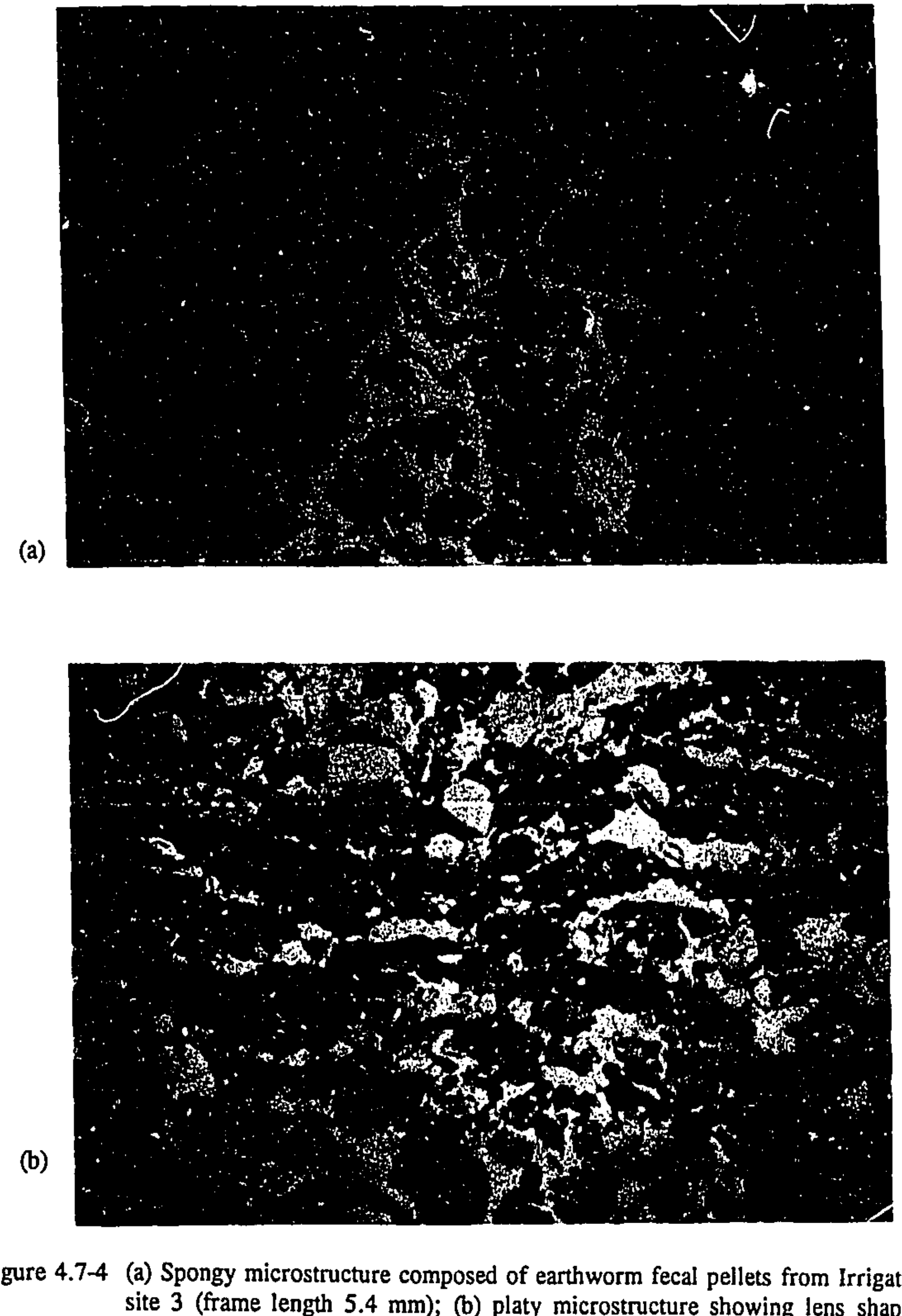

Figure 4.7-4 (a) Spongy microstructure composed of earthworm fecal pellets from Irrigated site 3 (frame length 5.4 mm); (b) platy microstructure showing lens shaped aggregates from Native site 1 (frame length 3.5 mm).

fine particles progressively developes on the top face of the aggregates due to successive phases of particle sorting by ice and of translocation on thawing. Wetting and drying cycles would also be important in this respect also. Thus, the capping of fine components on the top of the platelets likely reflects incipient eluviation in these soils.

The diverse microstructures include characteristics which depart significantly from the mull humus forms, as defined for European Chernozems (Kubiena 1953) and the immature or "proto" stage of mull development in Orthic Black Chernozems (Pawluk 1985). In mull, humic constituents are chemically complexed (bonded) to clays and clay minerals and recognizable plant residues are scarce. Kubiena (1953, 1970), Bal (1982), and Pawluk and Bal (1985) emphasized the role of soil fauna, especially earthworms, in mixing and blending organic and mineral matter, thus contributing very significantly to the mullgranic sequence fabric that is considered typical of Chernozemic A horizons. The zones of spongy microstructure in the irrigated sites are the direct result of earthworms and tend to parallel Pawluk's "proto" mull humus concept.

In the native grassland sites (Orthic Brown Chernozem), the presence of partly decomposed plant fragments and the abundance of discrete organic glaebules suggests the plasma is not homogeous in composition. Organic components are poorly humified and it appears that colloidal complexing between organic matter and clays is weak as there is little masking of the birefringence. Plasmic fabrics are not mull-like in character and would be more accurately described as mull-like moder. The absence of mullgranic units of fabric and fecal excrement from a diverse population of soil fauna indicates this is not an f-fabric that would be considered typical of soils of the Chernozemic order.

Chapter 5

CONCLUSIONS

Although research conducted during the past 60 years has provided valuable information about degradation of soil organic matter in the Brown soil zone of southern Alberta, information on the inherent nature of OM, redistribution of OC within the till layer, and losses of labile forms of OC, have not received adequate attention. Despite twofold differences in the organic C concentration between native grassland and cultivated sites investigated, the FTIR and ^{13}C NMR spectra of the humic acids were similar, indicating no major effect of management on their chemistry. The gross composition of OM in the soils under the two management systems is similar; indicating that irrespective of the composition of the inputs of photosynthate to the soil, the composition of the endproducts of decomposition of plant materials remains relatively constant (Oades et al. 1988). It is suggested that in Chernozemic soils plant materials will, over a period of several decades, be decomposed to form humified or partially humified substances. The composition of this material will depend on the environment in particular soils but will not be changed to a great extent by differences in amount of photosynthate added. Biological chemicals are decomposed at different rates with relatively short "half-lives", but over a period of decades all all added components will have been metabolized completely. Consequently, the longevity of organic materials in the cultivated sites cannot be explained on the basis of their chemistry and attention must be turned to the interaction of OM with the inorganic phase and the position of the organic molecules within aggregates. Knowledge of the distribution and position of organic materials within the geometrical arrangements of soil aggregates is required. It begins as plant debris, which becomes a focal point for soil biota and exists for a period of time as an active microsite before it is enveloped by a matrix of inorganic components, and then changes very little, unless the site is disturbed by cultivation which exposes inaccessible substrates to microbial enzymes (Oades et al. 1988).

In Brown Chernozemic soils where OM is the major binding agent, macroaggregation is controlled by management. Indeed, the native sod macroaggregates have a higher OC content and greater stability than cultivated ones. Upon air-drying, and contraction of the macroaggregates, additional intermolecular associations may well be formed between organic molecules and mineral surfaces; thus, imparting greater stability on the native sod macroaggregates. The numbers of stable macroaggregates in cultivated soils could be increased by replacing fallowing in the non crop year with "minimum tillage". It has been reported in the literature that in direct-drilled soils, roots follow old root channels (Ehlers et al. 1983.) where infective propagules of VA mycorrhizal fungi are likely concentrated. Hence, the new season's roots in direct-drilled soils could become mycorrhizal and help stabilize macroaggregates more quickly than those in conventionally tilled soils.

Microaggregation is not so sensitive to management. Therefore, it is more difficult to improve microaggregation by "normal" farming practices although systems which conserve OM will slowly improve the numbers of stable microaggregates.

Management practices, soil faunal activity, and freeze-thaw processes have resulted in considerable diversity in microstructures of the A horizons from the Chernozemic soils studied. These fabrics depart significantly from the mullgranic sequence of fabrics considered typical for soils of the Chernozemic order. Undisturbed Brown Chernozemic Ah horizons have been modified by frost processes to produce a moderately well developed platy microstructure. The inherent platy microstructure is weakly developed and very sensitive to tillage. Extensive colloidal complexing appears to be weak, likely because the OM is poorly humified. As well, fecal pellets from the indigenous soil fauna are relatively absent; consequently, the mechanism for mixing organic and mineral matter is not present in the Brown Chernozems. The fact that the OM is so poorly humified and discrete organic glaebules are ubiquitous throughout the thin sections indicates the plasma cannot be considered a mull humus form; nor can it even be considered "proto" mull. Plasmic fabrics should be described as mull-like moder.

Cultivated sites display spongy and fragmental microstructures, the result of tillage in the fallow year of the rotation. The essential role of earthworms in mixing and blending mineral and OM and forming mullgranic units of fabric is illustrated convincingly in thin sections from irrigated sites. The irrigated soils show a well developed spongy microstructure that consists of discrete and coalesced casts. Plasmic fabrics are quite uniform in composition and are tending towards mull-like plasma that is typical of Alberta Chernozems.

Irrigation has created a soil environment, in the normally dry southern region of the province, that supplies abundant organic residues and moisture that is conducive to the survival of earthworms. The ingesting action of earthworms in which mineral and dead plant residues are consumed together coupled with an abundant clay component have resulted in crumb-size casts which have contributed markedly to structural (aggregate) stability. This has been most pronounced in the 0.25-0.5 and 0.5-1.0 mm size classes.

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