

ULTRASONIC DISPERSION OF CLAY FROM SOIL AGGREGATES  
IN RELATION TO CARBOHYDRATE CONTENT

BY

LESLEY G. FULLER

A Thesis  
Submitted to the Faculty of Graduate Studies  
in Partial Fulfillment of the Requirements  
for the Degree of

Doctor of Philosophy

Department of Soil Science  
University of Manitoba  
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ULTRASONIC DISPERSION OF CLAY FROM SOIL AGGREGATES  
IN RELATION TO CARBOHYDRATE CONTENT

BY

LESLEY G. FULLER

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

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## ABSTRACT

Soil aggregates are complex structural units which exhibit various levels of organization reflecting diverse arrangements of soil particles and binding agents. Current methods of measuring aggregate stability involve subjecting aggregates to unknown and rather arbitrary energies of disruption, and thus do not adequately reflect the hierarchical nature of soil aggregates.

The approach taken in this work involved subjecting soil aggregates to various intensities of high frequency sound waves. Subjection of soil aggregates to increasing levels of ultrasonic energy resulted in increased dispersion of clay from the aggregate. The plot of clay remaining in an aggregated state (total aggregate clay minus dispersed clay) versus applied ultrasonic energy resulted in characteristic stability curves for each aggregate size fraction. These stability curves could be described by a first-order decay model commonly used in kinetic studies. Linearization of this exponential function provided a means to evaluate the curves. The slope of the straight line, referred to as the stability constant ( $k$ ), represents the average decrease in aggregated clay with a given increase in applied ultrasonic energy. Another parameter,  $E_{1/2}$ , can be calculated from the stability constant and is analogous to a half-life of a first-order kinetic plot. The  $E_{1/2}$  value indicates the energy input required to disperse one-half of the total aggregate clay.

Aggregate stabilities of four aggregate size fractions (ASF) obtained from a prairie-forest ecotone were determined. The lowest  $E_{1/2}$  values (51 to 98 kJ L<sup>-1</sup>) occurred for the ASF of the Ae horizon of the Orthic Gray Luvisol found under a mature aspen forest. Aggregates of the Ah horizon of the Orthic Black, found under prairie, possessed  $E_{1/2}$  values ranging from 161 to 224 kJ L<sup>-1</sup>. The greatest  $E_{1/2}$

values (280 to 504 kJ L<sup>-1</sup>) occurred for the macroaggregates of the Ahe horizon of the Orthic Dark Gray occurring within the recently established aspen forest. The relation between E<sub>1/2</sub> value and hexose carbon content of the aggregates was not consistent over the soils of the prairie-forest ecotone. The effect of carbohydrate on the dispersibility of clay from aggregates differed among these three soils.

Aggregates from cultivated sites possessed lower E<sub>1/2</sub> values (95 to 334 kJ L<sup>-1</sup>) compared to aggregates obtained from a permanent prairie (228 to 433 kJ L<sup>-1</sup>). Lower levels of ultrasonic energy were therefore required to disperse a given proportion of clay from cultivated aggregates when compared with aggregates from the adjacent prairie. Thus, bonds responsible for aggregating clay particles were more easily broken in cultivated aggregates.

A significant linear relationship between aggregate hexose content and E<sub>1/2</sub> value was observed. Thus, aggregates possessing greater amounts of carbohydrate were better able to resist dispersion of clay by ultrasound. Non-soluble hexose accounted for 72% of the variation in E<sub>1/2</sub> values among all ASF in both depths studied.

Hexose carbon associated with the clay fraction was not distributed uniformly throughout the aggregate in the prairie soil. Approximately three times as much hexose occurred in association with clays retained within the aggregate at energy levels between 100 and 500 kJ L<sup>-1</sup> compared to clays retained at energy levels of 100 kJ L<sup>-1</sup> or less. Cultivated aggregates possessed much less hexose in association with the clays retained at the higher energy levels. Therefore, carbohydrate located at various positions within the aggregate may play different roles in stabilization of the aggregate as a whole.

The significant relationship between hexose content and dispersion of clay from soil aggregates indicates that clay-carbohydrate interactions are important in the

aggregation process. Flocculation of montmorillonite in the presence of a glucose polymer (dextran) was observed in this study. Factors affecting clay flocculation included polymer molecular weight, polymer/clay ratio (w/w), nature of exchangeable cation, and ionic strength of the suspension to which polymer was added. Flocculation of Ca-montmorillonite was enhanced when the clay had initially been coagulated by addition of salt. In all cases, Mg-montmorillonite suspensions did not flocculate, but rather remained stabilized in the presence of dextran polymers. This was attributed to a greater polymer collapse on the surface of Mg-montmorillonite thus preventing flocculation.

This study demonstrated a significant relationship between aggregate hexose content and aggregate stability as measured by ultrasonic dispersion of clay over a wide range of disruptive energies. Thus, the dispersibility of clay within an aggregate was related to the hexose-carbohydrate content of the aggregate. However, the relationship between hexose content and aggregate stability was not necessarily the same among soils of differing pedogenesis. The nature of the exchangeable cations on the clay exchange sites; the presence or absence of a coagulant; polymer molecular weight; and polymer/clay ratio affect the ability of polysaccharides to bridge adjacent clay particles.

## **DEDICATION**

To my wife Cindy for her love and support through the good times and bad

Thank you Cindy from the bottom of my heart

To my three daughters, Andrea, Mandy, and Bethany



**CHAPTER 1****INTRODUCTION**

The formation of stable soil aggregates is a complex subject matter. Aggregate constituents and aggregation processes can vary considerably leading to many types of particle-particle interactions and organization within soil aggregates. As a result, the factors involved in formation of stable soil aggregates remain to be clarified.

Of the many possible binding agents present in soil, soil carbohydrates have been implicated in the formation and stabilization of soil aggregates. Carbohydrate content of soil aggregates has often been related to mean weight diameter of aggregates or percentage water stable aggregates. However, the role soil carbohydrates play in the aggregation process is not adequately understood. Part of the reason for this are the methods in which aggregates have been studied and the means by which aggregate stability has been defined.

Aggregate stability measurements have often been used to infer possible aggregation mechanisms. Most stability measurements involve subjecting aggregates to an unknown and rather arbitrary disruptive energy thereby separating "stable" aggregates from "unstable" aggregates. This approach does not adequately address the variety of particle arrangements within the complex structure of the aggregate. To further the investigation of the role carbohydrates play in stabilizing aggregates, a method of studying aggregates in terms of increasing disruptive energy is required. Studying aggregate breakdown as a function of applied disruptive energy permits the researcher to consider variations in the strength of bonding between particles and the binding agents responsible for those bonds. Such an approach would take into consideration the complex nature of aggregate structure.

Aggregation has been described as "flocculation plus" (Hillel 1982). The

combination of clay particles into discrete structural units is a necessary first step in the formation of stable aggregates. Dispersibility of clay within soil aggregates is related to the degree of flocculation and strength of the particle interactions. Dispersion of clay from soil aggregates leads to decreased aggregate stability, increased erodibility, and soil crusting (Brubaker et al. 1992). The role carbohydrate polymers play in the flocculation of clay particles remains to be clarified.

The main objective of this study was to develop a means of describing aggregate stability as a function of applied disruptive energy and to relate this stability to the carbohydrate content of the aggregates. The study consisted of three components. First, development of the method and testing on soils obtained from a prairie-forest ecotone. Second, evaluation of the method in distinguishing long-term cultivation effects on soil aggregates; and thirdly, a study of the effect of a carbohydrate polymer on the flocculation of a typical soil clay.

**CHAPTER 2****LITERATURE REVIEW****2.1 Introduction**

Soil structure has been defined as "the arrangement and organization of the particles in the soil" (Hillel 1982). This definition suggests a spatial arrangement of soil particles which has been emphasized by Dexter (1988) who defined soil structure as "the spatial heterogeneity of the different components or properties of soil". A more detailed definition of soil structure was provided by those who utilize soil structure for purposes of soil classification: "Soil structure refers to the aggregation of primary soil particles into compound particles that are separated by surfaces of weakness" (Canada Soil Survey Committee 1978). This latter definition suggests the presence of a structure-forming process which affects soil morphology. Primary particles are joined to form secondary units called compound particles. This "joining" occurs via aggregation processes which are responsible for morphology as well as stability as suggested by the presence of surfaces of weakness. Soil structure is therefore a complex soil property linking spatial considerations with physicochemical processes to produce a more or less stable morphology.

From an agronomic point of view, favorable soil structure is an essential component of productive soils as it affects plant growth through direct and indirect means. Soil structure and aggregation directly influence plant growth by affecting water retention and movement, gas exchange in the rhizosphere, and mechanical resistance to root extension or seedling emergence. Properties such as bulk density, texture, aggregation, aggregate stability, and pore size distribution indirectly affect plant growth through their effect on soil water, aeration, temperature, and mechanical resistance (Letey 1985).

The maintenance of favourable soil structure and aggregation also has an influence on environmental quality. Soil erosion, by wind and water, has received much attention with respect to its effect on the future productivity of soils. In addition to this, soil erosion by water also has an impact upon sedimentation of lakes and streams. Suspended soil material may also contribute to the eutrophication of lakes within agricultural watersheds. Phosphorus associated with particulate matter in runoff constitutes 75 to 90% of P transported from cultivated land (Sharpley et al. 1987). The growth of the alga *Selenastrum capricornutum* utilizing bioavailable P associated with runoff sediments has been documented (Sharpley et al. 1991). Maintenance of stable aggregates which resist erosion as well as enhance water infiltration and retention will minimize transport of nutrients associated with suspended solids.

Soil aggregates have been grouped into two general categories based on size. These are macroaggregates (>250  $\mu\text{m}$  in diameter) and microaggregates (<250  $\mu\text{m}$ ) (Tisdall and Oades 1982). The pore size between aggregates depends on aggregate size (Oades 1984). Aggregates > 1000  $\mu\text{m}$  in diameter are associated with pore diameters > 100  $\mu\text{m}$ . These pores are responsible for adequate soil aeration, rapid water movement, and enhanced root growth. Aggregates with diameters between 250 and 1000  $\mu\text{m}$  are associated with pore diameters of 25 to 100  $\mu\text{m}$ . These pores are involved in gas exchange and they are also responsible for the conduction of capillary water through the soil. Aggregates < 250  $\mu\text{m}$  in diameter are associated with pore diameters of < 2.5  $\mu\text{m}$ . These pores are essential for retaining plant available water in soils. Particle diameters of < 2  $\mu\text{m}$  are associated with pore diameters of < 0.2  $\mu\text{m}$ . The water in these pores exists as bound water and is not readily available for plant use (Oades 1984). Aggregate size distribution therefore has an impact on pore size distribution which in turn plays a primary role in determining water movement and retention, as well as gas exchange within the soil.

Resistance to wind erosion is also related to aggregate size. Aggregates with a minimum diameter of 840 to 1000  $\mu\text{m}$  are considered to be resistant to wind erosion (Chepil 1958, Dormaar 1987). Wind erosion contributes to loss of soil and nutrients from field soils. The quality and value of wind-erodible aggregates is such that the cost of replacing nutrients and organic matter is substantial (Dormaar 1987).

The study of aggregation and of the factors involved in formation of stable aggregates is therefore important for both agronomic and environmental reasons.

## **2.2 Aggregate Structure**

The principal inorganic components involved in aggregation include sand and silt particles (50 to 2000  $\mu\text{m}$  and 2 to 50  $\mu\text{m}$ , respectively) such as quartz, feldspars and micas. Clay size particles ( $< 2 \mu\text{m}$ ) include the common clay minerals such as smectites, vermiculite, mica, illite and kaolinite. The binding of these individual components into a structural unit is facilitated by organic and inorganic binding materials. Organic materials consist of humified matter as well as biopolymers such as polysaccharides. Inorganic binding materials consist primarily of Fe and Al oxides and  $\text{CaCO}_3$  (Oades 1984).

The diversity of the principal components provides for a wide variety of particle-particle interactions and organo-mineral associations within the aggregate. This fact was recognized by Emerson (1959) who proposed a model for aggregate structure which incorporated various arrangements of principal components and binding materials (Figure 2.1). Primary sand and silt particles were envisioned to be bridged by clay domains resulting in a structural unit called an aggregate. These clay domains in turn were held together by various means and in various arrangements. Emerson's model therefore depicted a structure with various levels of organization. This organizational aspect of aggregate structure has recently led to current theories on the hierarchical nature of soil aggregates (Tisdall and Oades 1982; Hadas 1987; Dexter 1988).

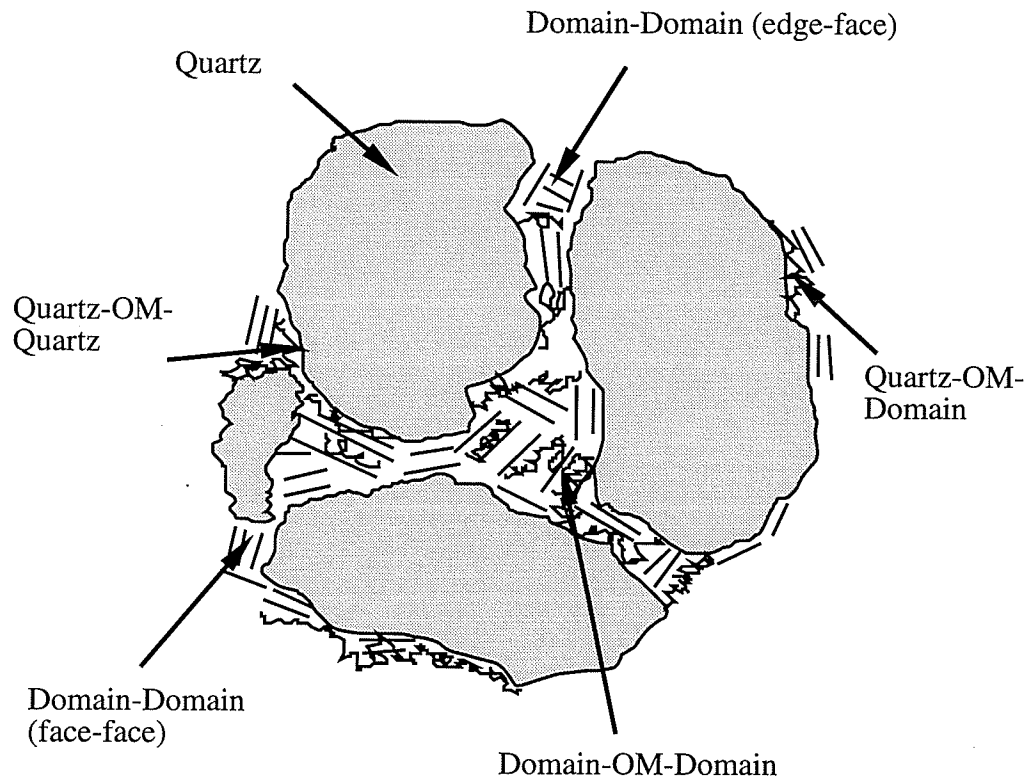


Figure 2.1. Structure of an aggregate depicting various particle-particle interactions (Emerson 1959).

### 2.2.1 The Hierarchical Nature of Soil Aggregates

Tisdall and Oades (1982) recognized the validity of Emerson's model of aggregate structure. They suggested that water-stability of aggregates depends on the presence of organic binding agents. Based on data for "red-brown earths", they suggested four stages of aggregation expressed in terms of dimensions of the structural units at each stage. These stages included  $< 0.2 \mu\text{m} \rightarrow 0.2 \text{ to } 2.0 \mu\text{m} \rightarrow 2 \text{ to } 20 \mu\text{m} \rightarrow 20 \text{ to } 250 \mu\text{m} \rightarrow > 2000 \mu\text{m}$ . The organization of these structural units into an aggregate was postulated to be controlled by organic binding agents which differed with respect to their persistence within the aggregate.

The first two stages involve interactions of clay particles, clay domains and quasi-crystals. The observation of clay mineral systems by electron microscopy reveals regions with parallel oriented plates. These regions are about 1 to 2  $\mu\text{m}$  thick. Clay domains and quasi-crystals are packets of clay particles consisting of fairly regular stacking of crystal units (Sposito 1989). The term "domain" is reserved for 2:1 clay minerals showing only inter-crystalline swelling while "quasi-crystal" is reserved for 2:1 clay minerals which show intra-crystalline swelling (Quirk & Aylmore 1971).

Smectite saturated with divalent cations form quasi-crystals through outer-sphere complexation of the aqua-ion,  $\text{M}(\text{H}_2\text{O})_6^{2+}$ , by opposing siloxane cavities (Sposito 1989). These octahedral aqua-ions are oriented with their principal symmetry axis perpendicular to the siloxane surfaces of the opposing smectite layers. The siloxane surface consists of the basal oxygen atoms of the tetrahedral sheet of a clay mineral. These oxygen atoms form distorted hexagonal cavities which are referred to as siloxane cavities (Sposito 1989).

The number of individual clay plates per quasi-crystal depends on the exchangeable cation present. Schramm and Kwak (1982) used viscosity and light-transmission measurements to study the nature of quasi-crystals within dilute suspensions of montmorillonite. The number of clay platelets per quasi-crystals of homoionic clays were expressed relative to the number of clay platelets per quasi-crystal of Li-montmorillonite (Table 2.1).

Table 2.1. Relative number of plates per quasi-crystal,  $N/N_{\text{Li}}$ , for homoionic clays (Schramm and Kwak 1982).

	Li	Na	K	Mg	Ca
$N/N_{\text{Li}}$	1.0	1.3-1.7	1.4-2.7	2.9-4.2	5.0-7.0

Ca-saturated montmorillonite possesses more platelets per quasi-crystal than the

other homoionic clays studied. The number of platelets per quasi-crystal of Ca-saturated montmorillonite is generally believed to be between 4 and 8 (O'Connor & Kemper 1969). Li-saturated montmorillonite is believed to exist as fully separated clay platelets (Schramm & Kwak 1982). Schramm and Kwak (1982) demonstrated a rapid decline in number of platelets per quasi-crystal of Ca-saturated montmorillonite following exchange with either Li, Na, or K. When Mg was exchanged for Ca there was a more gradual decrease in number of platelets per quasi-crystal.

Structural units in the size range 2-20  $\mu\text{m}$  are referred to as clusters (Dexter 1988). These units have only recently been recognized as building blocks for microaggregates and not much is known about them. It is believed that clusters form mainly through interactions among domains, quasi-crystals, and fine silt particles of primary minerals. However, the formation of clusters mainly involves interaction between clay domains and/or quasi-crystals.

The interaction of clay domains and/or quasi-crystals occurs mainly through the processes of coagulation and flocculation. Coagulation is the process by which a stable clay suspension is destabilized by reduction of the repulsive forces arising from interacting double layers (LaMer 1964). One way by which this can occur is by the addition of electrolyte to a stable clay suspension. The counter-ions of the electrolyte act to screen the electrostatic repulsion between negatively charged clays. This screening permits clay domains and quasi-crystals to approach close enough for short-range Van der Waals attractive forces to "coagulate" the clay particles. Coagulation may occur in face-to-face or edge-to-face orientations of domains and/or quasi-crystals. Face-to-face interaction occurs via a cation bridge between negative faces (Harris et al. 1966). This mechanism is also responsible for organization of clay platelets into domains or quasi-crystals. Edge-to-face orientation is possible through electrostatic attraction between a negatively charged face and a positively charged edge-hydroxyl (Emerson 1959).



The interaction of domains and quasi-crystals may also occur through bridging by an organic polymer. Flocculation is the process whereby a stable clay suspension is destabilized by a chemical bridging mechanism which enmeshes the particles in a three-dimensional floc network (LaMer 1964). The term "flocculation" is generally reserved for the bridging of colloidal particles by organic polymers (Theng 1979).

The interaction of clay particles through the action of bridging polysaccharides and humic material is important for cluster formation (Tisdall & Oades 1982; Dormaar & Foster 1991). The formation of stable clusters is the first step towards formation of stable micro- and macroaggregates.

Structural units 2 to 20  $\mu\text{m}$  in diameter are believed to be held together by persistent organic binding agents (Tisdall and Oades 1982). The binding agents include humic substances in association with clays and Fe and Al sesquioxides. However, binding of clay domains into clusters has also been shown to occur via organic binding agents derived from microbial colonies within the cluster (Dormaar and Foster 1991). Extracellular polysaccharides have been shown to be involved in cluster formation (Foster 1988). The high affinity of organic materials for clays within clusters is responsible for stabilization of a large portion of organic matter within Chernozemic soils (Turchenek and Oades 1978; Anderson 1979; Anderson and Paul 1984).

Sodium salt solutions effective for extraction of organic matter from soils (e.g.  $\text{Na}_2\text{P}_2\text{O}_7$  and  $\text{NaOH}$ ) are also very effective for dispersion of soil particles. These solutions have the ability to complex or precipitate polyvalent metals. These observations led Edwards and Bremner (1967) to suggest that microaggregate formation is the result of polyvalent metal bridging between organic polymers and clay particles. They suggested that clay-polyvalent metal-organic matter complexes (represented as C-P-OM) are the basic structural units of microaggregates. These units can be considered to represent compound particles of clay size ( $< 2 \mu\text{m}$ ) which are combined into larger units indicated

as  $(\text{C-P-OM})_x$ . These latter units may be considered to be clusters which combine to form microaggregates indicated as  $[(\text{C-P-OM})_x]_y$  (Edwards and Bremner 1967). This microaggregate theory proposed by Edwards and Bremner (1967) reflects the hierarchical ordering already discussed. The aggregation mechanism was believed to be constant over the various hierarchical levels. Polyvalent metal bridging between clays and humified organic matter was invoked to explain the aggregation process.

The role of organic binding agents in microaggregate formation has been emphasized by Tisdall and Oades (1982) and Oades (1984). Aggregates 20 to 250  $\mu\text{m}$  in diameter consist largely of particles 2 to 20  $\mu\text{m}$  (clusters) bonded together by persistent organic materials as well as inorganic agents such as crystalline oxides and disordered aluminosilicates (Tisdall and Oades 1982). The persistent organic materials are thought to consist of humic material associated with iron and aluminum. Organic materials have been shown to complex iron and aluminum and this complexation is believed to contribute to aggregate stability (Giovannini and Sequi 1976a,b; Goh and Huang 1986).

Resistant fragments of bacterial cells and colonies as well as extracellular polysaccharides are also thought to be active in microaggregate formation (Foster 1988; Dormaar and Foster 1991). Strongly sorbed polysaccharides are believed to be part of the persistent organic materials responsible for microaggregation (Tisdall and Oades 1982). Substantial losses of organic matter from soils can occur before the organic binding agents within microaggregates are degraded (Oades 1984).

The combination of two or more clusters leads to microaggregate formation (Tisdall and Oades 1982; Dexter 1988). The organic binding agents within these microaggregates are persistent humic materials as well as protected polysaccharide material (Edwards and Bremner 1967; Tisdall and Oades 1982). The persistence of the organic binding agents causes these microaggregates to be resistant to short-term effects of agricultural practices.

Aggregates larger than 250  $\mu\text{m}$  in diameter are considered to be macroaggregates and consist of clusters and microaggregates. Unlike microaggregates, macroaggregates are susceptible to slaking when rapidly immersed in water (Oades 1984). Slaking of macroaggregates yields stable microaggregates as bonds within microaggregates tend to be stronger than bonds between microaggregates (Oades 1984, Dexter 1988).

Macroaggregate formation is believed to occur via roots and fungal hyphae acting to enmesh microaggregates (Tisdall and Oades 1982; Oades 1984). These organic binding agents are more transient and temporary in nature and are therefore susceptible to changes in agricultural practices. Other binding agents include crystalline as well as non-crystalline iron and aluminum oxides (Oades 1984). The number of stable macroaggregates declines with organic matter content as roots and hyphae are decomposed and not replaced during fallow periods (Oades 1984). However, macroaggregates do remain under fallow suggesting that other means of macroaggregation are possible. The role of clusters in bridging macroaggregates should not be overlooked. These smaller units and their associated binding agents may play a significant role in development of macroaggregate structure (Emerson 1959). Particle-particle bonding within a cluster tends to be stronger than bonding between clusters and larger structural units (Dexter 1988). Slaking of macroaggregates upon wetting can be expected to be the result of breakage of the weakest bonds occurring between clusters or between clusters and larger structural units within the aggregate.

The types of particle interaction within soil aggregates include various possible arrangements. The mechanisms responsible for these interactions will depend on the hierarchical order under consideration. The coagulation of clay particles to form clay domains and quasi-crystals (Schramm and Kwak 1982) is very different from physical enmeshment of microaggregates by plant roots and fungal hyphae to form macroaggregates (Tisdall & Oades, 1982). Therefore, it is important to keep in mind the

hierarchical order when discussing aggregation mechanisms.

The concept of the hierarchical order within soil aggregates has been developed further by Hadas (1987). Hadas found, by examining various sizes of aggregates, that "soil exhibits specific structural states organized hierarchically". By utilizing a brittle fracture technique to measure the tensile strength of aggregates, Hadas found that soil possesses different states of aggregation. Structural units of a lower hierarchical order are contained within units of a higher order and act both as building blocks and cementing agents. Each order possesses an internal strength which diminishes from lower order structural units to higher order structural units. This internal strength of each order is a function of the type and amount of aggregating mechanisms prevalent at that order.

### 2.2.2 Fractal Theory And Soil Aggregation

Recently there has been interest in the application of "Fractal Theory" to soil aggregation (Perfect and Kay 1991). Fractal theory describes systems which are made up of parts that resemble the whole system (Feder 1988). These individual parts are referred to as "fractals" and are defined as "a rugose object whose rugosities show up at any length scale" (Jullien and Botet 1987). Fractal theory may be suitable for describing the hierarchical nature of soil aggregates since "fractals" form a hierarchy in which each level is related to the levels above and below.

In nature there exists a relationship between the number and size of objects within a hierarchical system (Mandelbrot 1982). This relationship can be expressed by the power-law relation:

$$N_{>x} = k(x)^{-D} \quad (1)$$

where,  $N_{>x}$  is the cumulative number of objects with a dimension greater than  $x$ ,  $k$  is a

constant, and  $D$  is a parameter which depends on the irregularity of the objects as well as the degree of fragmentation of the objects.  $D$  is referred to as the "fractal dimension" and has been utilized to describe aggregate size distributions (Perfect and Kay 1991).

Using fractal theory, Perfect & Kay (1991) investigated the relationship among fractal dimension, energy input, and probability of failure. The fractal dimension was shown to increase with increasing length of time under corn production at a given energy level indicating increased aggregate fragmentation under corn. The lowest values of  $D$  occurred for the continuous bromegrass system. Also, the probability of failure for a given aggregate size was much less under bromegrass than under corn. Increasing the level of energy input by wet-seiving resulted in increased levels of fragmentation for aggregates  $> 0.50$  mm. Fractal dimension was therefore dependent upon energy input and the probability of failure for a given aggregate size.

Aggregate sizes less than approximately 0.50 mm showed no difference in the probability of failure under bromegrass or corn production. This is consistent with the model of Tisdall & Oades (1982) who suggested that microaggregates are not affected by cropping history.

Perfect & Kay (1991) suggest that the degree of fragmentation associated with a given energy input appears to be determined by the rate of change in the probability of failure with change in aggregate size. Therefore, the change in the probability of failure with increasing or decreasing aggregate size will determine the fragmentation experienced by the soil at various levels of energy application.

In summary, it can be said that soil aggregates are complex structures which possess a hierarchical ordering of structural units. The association of clay particles, organic and inorganic binding agents, and primary silt and sand grains as suggested by the earliest models of aggregate structure leads to formation of structural units possessing

inherent stability. These units act as building blocks for larger units which in turn possess an inherent stability which depends on the mechanism by which smaller units are aggregated to form the larger unit.

Generally, there is a decrease in aggregate stability with an increase in aggregate size. Application of disruptive energy to an aggregate size fraction results in fragmentation which depends upon the probability of failure for that aggregate size. This probability of failure depends on the mechanisms involved in maintaining structural integrity. Therefore, studies of aggregate breakdown can be utilized to infer aggregation mechanisms.

There is a need to relate the presence of aggregate binding agents to the stability of the various hierarchical levels within soil aggregates. Present methods used to study aggregate stability do not adequately address the relationship between hierarchical level and the presence of binding agents such as carbohydrates. A method which relates aggregate stability to breakdown of various structural units within the aggregate would provide a means to address the relationship between binding agents and structural stability at each hierarchical level.

## **2.3 Carbohydrates and Soil Aggregation**

### **2.3.1 Carbohydrates Present In Soil**

Carbohydrate constitutes between 5 and 25% of soil organic matter with an average of approximately 10% (Cheshire 1977). Carbohydrate may exist as free monomers, dimers, oligomers or polymers within the soil but the majority are adsorbed to soil components (Stevenson 1982).

Qualitatively, the variety of monomer units found in soil is quite limited. Cheshire (1977) describes five types: hexoses, pentoses, methylpentoses, uronic acids, and hexosamines. The most prevalent are the hexoses: glucose, galactose, and mannose.

These three monomers comprise 65 to 90% of the total carbohydrate (Swincer et al. 1968; Cheshire 1977; Dormaar 1984; Baldock et al. 1987). The next most abundant are the pentoses: ribose, arabinose, xylose, which comprise between 15 and 25% of the total carbohydrate. The deoxyhexoses (fucose and rhamnose) comprise between 3 and 9% while the uronic acids and hexosamines constitute the remaining portion of total soil carbohydrate. The contribution made to the total carbohydrate content by each sugar monomer remains relatively constant irrespective of cropping treatment, soil type and climatic conditions (Baldock et al. 1987).

Cheshire et al. (1979) studied the nature of glycosidic linkages present in soil polysaccharide. Hexose sugars were found to be present in 1→3 and 1→4 linkages with significant amounts of 1→6 linkages. Pentose sugars were predominantly present in 1→4 linkages.

Soil carbohydrate originates from both plant and microbial polysaccharides. Addition of  $^{14}\text{C}$  - labelled substrate to soil followed by incubation results in transfer of  $^{14}\text{C}$  to newly synthesized sugars. The dominant sugars synthesized are glucose, galactose, mannose and minor amounts of rhamnose (Cheshire 1977). Very little arabinose or xylose is synthesized. Based on these observations, the ratio of galactose + mannose/arabinose + xylose has been used to infer the origin of soil carbohydrates (Oades 1984; Baldock et al. 1987). Microbes produce galactose and mannose while plants produce substantial quantities of the pentoses, arabinose and xylose. A wider ratio of galactose + mannose to arabinose + xylose indicates a microbial origin of the soil carbohydrate.

The concentration of carbohydrate is usually greatest in the clay, less in the silt, and lowest in the sand fraction (Cheshire and Mundie 1981; Cheshire et al. 1990). In  $^{14}\text{C}$  glucose-amended soil, Cheshire and Mundie (1981) showed that 55% of the sugars (predominantly hexoses) occurred in the clay, 36 - 42% in the silt, 2-3% in the fine sand

and 1 - 6% in the coarse sand. The three major plant sugars, glucose, arabinose and xylose, were the predominant sugars in the coarse sand and accounted for 90% of the neutral sugars present in that size fraction. In the clay fraction, galactose and mannose were usually present in almost twice the concentrations of arabinose and xylose.

Rhamnose and fucose were always present in the least amount and occurred mostly in the clay fraction. Approximately 90% of metabolic carbohydrate products of glucose occurred in the clay and silt fractions. The ratio of galactose + mannose to arabinose + xylose was highest in the clay fraction and lowest in the sand fractions. It appears that carbohydrate associated with fine fractions originates mainly from microbial sources whereas plant carbohydrates are found in coarser particle-size fractions (Turchenek and Oades 1979; Cheshire and Mundie 1981).

The addition of  $^{14}\text{C}$ -labelled plant material to soil results in a transfer of  $^{14}\text{C}$  mainly to coarse particle-size fractions initially (Cheshire and Mundie 1981). Incubation of cereal rye straw or ryegrass leaf resulted in a concentration of sugars characteristic of plant remains in the sand-size fraction after one year (Cheshire and Mundie 1981). Four years later the silt fraction contained the highest fraction of labelled sugar. However, long term incubation of  $^{14}\text{C}$ -labelled barley straw in soil for up to 18 years resulted in the highest concentration of labelled sugars in the clay fraction (Cheshire et al. 1990). Short-term changes in carbohydrate distribution following two years of cropping to barley and alfalfa, was shown to occur mainly in the sand fraction (Angers and Mehuys 1990). With time, plant polysaccharides are decomposed and microbial polysaccharides synthesized resulting in a transfer of  $^{14}\text{C}$  to finer particle-size fractions. Soil polysaccharides are therefore mainly products of microbial activity being subjected to continual degradation and resynthesis (Keefer and Mortensen 1963).

The majority of soil polysaccharides are generally not available for microbial metabolism. This stability of soil polysaccharides is related to chemical and physical



unavailability rather than chemical composition or complexity (Cheshire 1977). Possible means of polysaccharide stabilization within soil include adsorption on clays, particularly montmorillonite (Lynch and Cotnoir 1956); complex formation with metals (Martin et al. 1966) and tanning by humic substances (Cheshire 1977). All three mechanisms remove polysaccharide from solution thus preventing degradation by polysaccharase enzymes.

Free polysaccharides extracted from soil by water or water-ethanol solution usually comprise much less than 1% of the total soil polysaccharides (Table 2.2). However, sonification in water at 20°C extracts about 8% of total polysaccharide.

Table 2.2. Percentage of total polysaccharide in a sandy loam soil removed with various extractants (Cheshire 1977).

Extractant	Percentage of total polysaccharide
Water (20°C)	0.5
Water (20°C with sonification)	8.0
Water(80°C)	2.9
0.05M H <sub>2</sub> SO <sub>4</sub>	1.0
0.2M NaOH	42
0.2M NaOH (with sonification)	69
0.1M EDTA (pH 7)	66
0.2M Acetylacetone (pH 8)	64

The effectiveness of the chelating extractants EDTA and acetylacetone provides evidence for the occurrence of metal-polysaccharide complexes. The presence of insoluble salts of Ca<sup>2+</sup> and Mg<sup>2+</sup> has been suggested by Barker et al. (1967). The formation of Al, Fe, Cu, and Zn-polysaccharide complexes has been shown to retard decomposition of a microbial polysaccharide (Martin et al. 1966). The order of

effectiveness was  $\text{Cu} > \text{Zn}$  and  $\text{Fe} > \text{Al}$ .

Sonification causes an increase in the extractability of polysaccharide by acting to expose organic materials which were previously protected (Table 2.2). A study of C mineralization in soil size fractions following sonification was conducted by Gregorich et al. (1989). A substantial increase in mineralization of C associated with sand, silt, and clay fractions occurs with aggregate breakdown caused by sonification. Subjection of macroaggregates (1 to 2 mm) to increasing ultrasonic energy levels resulted in increased levels of potentially mineralizable C in the sand-sized fraction while the mineralization rate stayed the same. In the clay-sized fraction, however, the levels of potentially mineralizable C decreased but the mineralization rate increased. Gregorich et al. (1989) suggest that labile material previously sequestered in the clay fraction had been exposed. They suggest this labile material may be composed primarily of polysaccharide material. Sonification may therefore release polysaccharide segments held by Van der Waal's forces to clay surfaces.

### 2.3.2 Carbohydrates as Aggregate Stabilizing Agents.

The interest in soil polysaccharides arises mainly from evidence suggesting these polymers act to stabilize soil aggregates. Some of the earliest evidence to suggest that polysaccharides may be involved in soil aggregation was the observed favorable influence of microbial and microbial products on soil aggregation (Martin and Waksman 1940; Martin and Anderson 1942; McCalla 1942).

Addition of microbial-produced polysaccharides or inoculation of bacteria into soil has been shown to be effective in binding soil particles (Martin 1945, 1946). A 50% increase in aggregates  $> 0.1$  mm in diameter in silt loam soils occurred with addition of only 0.02% (w/w) of a polysaccharide produced by *Agrobacterium radiobacter* (Rennie et al. 1954). Polysaccharides produced by *Arthrobacter viscosus* and *Azotobacter indicus*

were able to cause an increase in the aggregation of the  $< 50 \mu\text{m}$  soil particles of 30 - 70% in a sandy loam soil (Martin and Richards 1969). Most microbial polysaccharides are able to cause an increase in aggregation with concentrations of only 0.02 to 0.2 wt% (Clapp et al. 1962; Martin and Richards 1969, Martin 1971). Even though microbial polysaccharides had been shown to increase aggregation, it was not known whether these polysaccharides existed in soil.

The isolation of soil microorganisms capable of producing aggregate-stabilizing polysaccharides provided further evidence that polysaccharides were indeed involved in soil aggregation (Martin 1945; Bernier 1958; Webley et al. 1965). The addition of crude polysaccharide preparations extracted from soil have also been shown to have a favorable effect on aggregation of other soils (Rennie et al. 1954; Whistler and Kirby 1956). Recently, significant differences in aggregate stability of an eroded catena were measured in Manitoba. Aggregates at the bottom of the slope were more stable, possessing greater amounts of clay and polysaccharides of microbial origin. The persistence of microbial metabollites was deemed to have occurred due to the large amount of effective stabilizing surfaces available for clay-organic interaction and the provision of niches for the occlusion of polysaccharides (Janzen 1987; Janzen et al. 1988).

Statistically significant correlations between soil polysaccharide content and degree of aggregation suggested that soils containing higher amounts of polysaccharide exhibited better aggregated structure (Rennie et al. 1954; Acton et al. 1963; Webber 1965; Cheshire et al. 1983; Angers and Mehuys 1989; Haynes and Swift 1990). Many statistically significant correlations however did not yield a high correlation coefficient. This may be related to the difficulty in measuring soil polysaccharide, differences in the ability of various microbial polysaccharides to bind soil particles, the presence of other binding agents, or inability of the stability measurement to reflect the action of polysaccharide in aggregate stabilization. The distribution of polysaccharide within and

around soil aggregates may also be important such that only a portion of the polysaccharide may actually be controlling stability (Swincer et al. 1969).

The hypothesis that only a portion of soil polysaccharide may be responsible for aggregation is recently becoming more popular. Correlations between aggregate stability and hot-water extractable polysaccharide (Haynes and Swift 1990), heavy-fraction carbohydrate (Roberson et al. 1991) and periodate-oxidized carbohydrates (Cheshire et al. 1983) suggest that only a portion of total carbohydrates may be the effective aggregating agent. Baldock et al. (1987) could not explain differences in aggregate stability across cropping sequences by structural deterioration induced by periodate alone or by total carbohydrate content. They suggest that some portion of total carbohydrate may have been responsible for the management-induced changes in aggregate stability they observed.

The strongest evidence to suggest that polysaccharides are involved in aggregate stability arises from the decrease in stability following treatment with periodate. Periodate acts to oxidize materials containing adjacent *cis*-hydroxyls (Bobbitt 1956) and is therefore suited to oxidation of carbohydrates. One of the earliest uses of periodate to study polysaccharides in soil aggregates was conducted by Mehta et al. (1960). They showed that the increased strength of synthetic aggregates due to added polysaccharides could be eliminated by prolonged immersion of aggregates in  $\text{NaIO}_4$  followed by raising the pH to 10 using  $\text{Na}_2\text{B}_4\text{O}_7$ . The tetraborate is used to destroy partially oxidized polysaccharides. However, the periodate-borate treatment was unable to affect the stability of aggregates from a forest soil or from Rendzina soils (soils rich in free  $\text{CaCO}_3$ ). It was suggested that polysaccharides were not the principal stabilizing agents in forest and  $\text{CaCO}_3$  rich soils.

Treatment of aggregates with 0.05 M  $\text{NaIO}_4$  for 6 h resulted in appreciable reduction in stability of cultivated aggregates; whereas, aggregates from an "old

grassland" were slightly affected (Clapp and Emerson 1965). Increasing the length of time of the periodate treatment to 24 h resulted in further breakdown of old grassland aggregates but not of cultivated aggregates suggesting the cultivated aggregate breakdown was complete after 6 h. Pyrophosphate treatment in combination with periodate treatment caused complete destruction of old grassland aggregates. Clapp and Emerson (1965) suggest the pyrophosphate is able to release organic polymers coordinated with polyvalent cations. They state, "...there are two types of organic polymers holding the crumbs together, one coordinated with the exchangeable cations and the other H-bonded".

Clapp and Emerson (1965) also studied a soil with 34%  $\text{CaCO}_3$  equivalent. Subjection of this soil to periodate treatment had no effect on the stability of the aggregates. After removal of  $\text{CaCO}_3$  using 0.1 N HCl, followed by periodate treatment, there was a marked decline in stability. However, the stability of the aggregates after HCl treatment and prior to periodate treatment was no different than the aggregates containing  $\text{CaCO}_3$ . Therefore, it appeared that  $\text{CaCO}_3$  was not the stabilizing agent or that it at least could not act alone. Clapp and Emerson (1965) also found that forested soil was not susceptible to aggregate breakdown following periodate treatment. Their work therefore suggests that polysaccharides are important stabilizing agents in cultivated aggregates but may play a secondary role in forest and "old grassland" soils. Polysaccharide apparently does not have the same impact in widely different soils. The marked variation in aggregation and aggregate stability among various soil types suggests that mechanisms of aggregate stabilization differ markedly across soil types (Strickland et al. 1988).

The effect of maize root growth on aggregate stability was studied by Reid and Goss (1981) who showed that the stability of moist soil aggregates in the rhizosphere substantially decreased relative to fallow control aggregates. However, upon air-drying of the aggregates the stability of the rhizosphere aggregates was restored through the action

of periodate sensitive material. This restoration of stability upon drying also occurred when the plant was allowed to dry the soil by evapotranspiration (Reid and Goss 1982). The authors suggest, when soil water remains at relatively high potential for a long time, polysaccharides may be degraded to the detriment of aggregate stability in the rhizosphere. However, the adsorption of periodate-sensitive polysaccharides onto soil mineral surfaces during drying seemed to benefit aggregate stability and counteract detrimental consequences of maize roots.

The length of time aggregates are subjected to periodate treatment affects the amount of carbohydrate oxidized (Cheshire et al. 1983). Treatment of a sandy loam soil with 0.02 M NaIO<sub>4</sub> for 6 h resulted in oxidation of 30% of the total carbohydrate present. After 24 h approximately 50% remained and after 48 h about 36% of the carbohydrate remained (Cheshire et al. 1983). The time required to oxidize greater than 80% of the carbohydrate was approximately 1200 h. However, increasing the concentration of the periodate to 0.05 M resulted in increased oxidation of carbohydrate (49 and 27% remaining after 6 and 48 h, respectively). Short periodate treatment usually does destroy part of the aggregation which can be considered to depend on polysaccharides. The persistence of carbohydrate in periodate-treated soil means that the remaining aggregation could be attributed to polysaccharide or perhaps the carbohydrate was protected by the aggregate (Cheshire et al. 1983). These authors also showed a direct relationship between residual carbohydrate following periodate treatment and degree of aggregation. Progressive oxidation of carbohydrate resulted in a corresponding increase in the proportion of particles < 45 µm.

Generally speaking, the removal of readily-oxidized soil polysaccharides by periodate treatment results in aggregate disruption (Cheshire et al. 1984). The role of the less readily-oxidized polysaccharide in aggregate stability remains to be determined. However, exceptions do occur indicating that polysaccharide may behave quite differently

in various soils. Constituents such as lipids may be active in aggregate stabilization, particularly in forest soils. Water stability of aggregates has been shown to be related to the presence of unbound organic matter that was aliphatic and hydrophobic in nature (Dinel et al. 1992). Water repellency was believed to contribute to the increased stability.

Significant inverse linear relationships between residual polysaccharide content following 168 h of treatment with 0.02 M periodate and degree of aggregate disruption as measured by a turbidimetric procedure for 15 soils were shown by Cheshire et al. (1984). In most cases a disruption of only 79% (relative to 100% for sonicated soil) was predicted when all polysaccharides were removed. Shaking the soil in 0.02 M NaCl/0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> resulted in a disruption of 47% compared to 66% for the 0.02 M NaIO<sub>4</sub>/0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> treatment. Therefore, removal of polysaccharides caused only an extra 19% disruption. The authors suggest that if polysaccharides are responsible for the remaining aggregation after 168 h of periodate treatment, the mechanism may differ from that of the periodate-sensitive material. In conclusion, they state that periodate oxidation affected each soil in its own characteristic manner.

Two stages to the formation of stable soil aggregates have been proposed by Chaney and Swift (1986 ab). The first stage is referred to as the "aggregation phase" involving microbial polysaccharides. The second stage, or the "stabilizing phase" involves humic substances as binding agents. This view of aggregate formation recognizes the contribution of non-carbohydrate material to stabilization of aggregates. Haynes and Swift (1990) suggest there are active and inactive carbohydrates within soil aggregates. They proposed that only a portion of the total acid hydrolyzable carbohydrate may be responsible for aggregation, particularly over the short term. The fraction of carbohydrate extractable with hot water (80°C for 16 h) was shown to correlate well with aggregate stability (Haynes and Swift 1991). Short-term increases in aggregate stability following planting of grass to previously cultivated soils corresponded to hot-water

extractable carbohydrate while no change in organic C was discernible (Haynes and Swift 1990).

Densimetric separation of soil carbohydrate has been used to study the effect of cover-crops on aggregation in an orchard soil (Roberson et al. 1991). Permanent grass and barley or wheat cover-crops significantly increased saturated hydraulic conductivity and acid-extractable heavy-fraction carbohydrates (carbohydrates in soil denser than  $1.7 \text{ g mL}^{-1}$ ). Heavy-fraction carbohydrates were significantly correlated with aggregate stability and saturated hydraulic conductivity while light-fraction carbohydrates and organic C were not. Initial improvement in soil structure by cover crops was explained by the increase in heavy-fraction carbohydrates. The authors suggest that the amount of heavy-fraction carbohydrate in each treatment may reflect the amount of C that was available to polysaccharide-synthesizing microorganisms.

In summary, it is evident that polysaccharides are present in soils possessing stable aggregates and destruction of polysaccharide coincides with aggregate breakdown. However, the exact nature of the role polysaccharides play in the aggregation process is still uncertain. It is now necessary to determine whether polysaccharides contribute to aggregate stability over a wide range of disruptive energies. The role polysaccharides play in stabilization of structure particularly at lower hierarchical levels within the aggregate remains to be clarified.

## **2.4 Clay-Polysaccharide Interactions**

Organic polymers, such as polysaccharides, are long chains with varying degrees of flexibility, solubility, structural conformation, and functionality. Hence, polymer adsorption depends very much on the nature of the polymer.

Uncharged polymers do not experience electrostatic attraction to clays but rather are adsorbed via Van der Waal's forces. Flexible uncharged polymers exist as random



coils in solution. Upon adsorption they tend to spread out over the clay surface as contiguous adsorbed segments (called "trains") separated by "loops" which extend away from the surface (Theng 1982). The adsorption process causes an increase in the system entropy as solvent molecules are displaced by polymer (Parfitt and Greenland 1970a).

The energy of interaction for individual Van der Waal's forces is low; however, as Van der Waal's forces are additive, many surface contacts leads to a strong energy of interaction . The energy with which the polymer is adsorbed therefore depends on the number of surface-segment contacts. Uncharged polymers tend to have approximately 30 to 40% of the total number of segments in the polymer chain adsorbed to the mineral surface (Theng 1982). This leaves about 60 to 70% of the segments extending away from the mineral surface and able to contact other mineral particles.

The adsorption isotherms for neutral polymers, such as dextran, tend to be of the "high affinity" type (Parfitt and Greenland 1970 ab; Greenland 1963; Olness and Clapp 1975; Chenu et al. 1987). Adsorption of the polymer is essentially irreversible since the likelihood of desorption of all trains at the same time is small (Theng 1982).

Polymer concentration relative to clay concentration is an important consideration determining whether flocculation will occur. If the polymer concentration is high, the clay surfaces become saturated with adsorbed polymer. This results in the development of an osmotic pressure between adjacent clay particles and hence the clays remain in a dispersed state (Lafuma et al. 1991). Inter-polymer steric repulsive forces also contribute to stabilization of the clay suspension at high polymer concentrations. However, a lower polymer concentration will result in unsaturated clay particles. Free energy of adsorption is gained when two or more clay particles share polymer chains. The result is flocculation, the first step in cluster formation. Therefore, a given polymer may act as a "bumper" causing stabilization of the clay suspension, or as a "sticker" by inducing flocculation (Lafuma et al. 1991).

Flocculation occurs when the adsorbed layers of polymer are thick enough to extend beyond the electrostatic barrier between particles (Lafuma et al. 1991). For clays, it is necessary for polymer loops and tails to extend beyond the thickness of the diffuse double layers of adjacent clay particles. Therefore, molecular weight and conformation of the polymer, the extent of polymer collapse, degree of surface coverage, and ionic strength of the suspending medium all play a role in the strength and range of attractions and repulsions (Lafuma et al. 1991). This implies a relationship exists between the range of electrostatic repulsions and the size of the polymers that can bridge clay particles.

The adsorption behaviour of charged polymers differs from that of uncharged polymers. The main difference is the effect of pH and ionic strength on the surface charge and structural conformation of the polymer in solution. Positively charged polymers are adsorbed to negatively charged clays by electrostatic attraction. The energy of attraction is greater than for individual Van der Waal's attractive forces resulting in a rapid collapse of polymer on the mineral surface with relatively few short loops (Theng 1982). The proportion of adsorbed segments is commonly > 70%. These polymers may be most useful in charge neutralization leading to coagulation of clay particles.

Negatively charged polymers are repelled by negatively charged clay particles. However, adsorption is possible where clay edges are protonated at low pH and therefore possess positive edge sites. Anion exchange of polymer carboxyl groups with positive edge sites may also result in adsorption (Emerson 1963). The formation of polyvalent cation bridges between negatively charged clays and polyanions is another means of adsorption (Harris et al. 1966; Theng 1982). Differences in adsorption of anionic fulvic acid by montmorillonite saturated with various cations suggests that cationic bridging may be the most important means of polyanion adsorption (Theng 1976). The affinity of fulvic acid for the clay was related to the ionic potential of the saturating cation. Greater adsorption occurred for cations with greater ionic potential (i.e. valency/radius ratio). In

general, negatively charged polymers are adsorbed by only a few segments and possess extended loops and "tails" (Theng 1982).

Polysaccharide adsorption by montmorillonite largely depends on surface charge, molecular weight, structural conformation, and polymer solubility (Chenu et al. 1987). The adsorption of dextran by kaolinite and montmorillonite has been studied by a number of researchers (Clapp et al. 1968; Parfitt & Greenland 1970b; Clapp & Emerson 1972; Olness & Clapp 1973, 1975; Chenu et al. 1987). Parfitt and Greenland (1970b) showed that dextran adsorption was influenced by molecular weight and polarizing power of the cation on the exchange complex of the clay. Dextrans with molecular weights of 11,200 and 100,000 were not adsorbed by Na-, Al-, or Ca-saturated montmorillonite. However, a dextran of molecular weight  $2 \times 10^6$  was adsorbed to the extent of about 100 to 110 mg g<sup>-1</sup> of Ca- and Al- saturated montmorillonite. Adsorption of dextran by Na-saturated montmorillonite reached a maximum of about 250 mg g<sup>-1</sup>. The initial slope of the adsorption isotherms decreased with increasing polarizing power of the cation. The decrease in adsorption energy when more strongly polarizing cations are present may be due to the fact that adsorption of the polysaccharide takes place in the presence of water. The affinity of the polymer for the clay is determined by polymer adsorption and water desorption. Adsorption energy is therefore the net result of polysaccharide adsorption and water desorption (Parfitt and Greenland 1970b). An earlier study by Parfitt and Greenland (1970a) found a decrease in the initial slope of the adsorption isotherm for poly(ethylene glycol) with an increase in polarizing power of the exchangeable cations. They suggest the adsorption energy for the polymer is mainly from the net gain of translational entropy associated with the desorption of water. Dextran adsorption can likely be explained by the same mechanism.

Olness and Clapp (1973) studied adsorption of two polysaccharides by montmorillonite and the effect of adsorption on crystal expansion and collapse. They

studied dextran (B-512F produced by *Leuconostoc mesenteroides*) and a commercial polymer called polytran. Both polymers had a molecular weight of approximately  $2 \times 10^6$ . Dextran consists of glucose units linked by an  $\alpha(1 \rightarrow 6)$  linkage while polytran has 75% of its glucose units linked by  $\beta(1 \rightarrow 6)$ . The maximum adsorption of dextran was  $440 \text{ mg g}^{-1}$  clay and that of polytran  $620 \text{ mg g}^{-1}$  clay. Adsorption of either polymer by montmorillonite resulted in expanded crystals as revealed by X-ray diffractometry. The peak representing a collapsed crystal spacing (9.8 to  $9.9 \text{ \AA}$ ) diminished in intensity as the polymer content of the complexes increased. Above  $200 \text{ mg dextran g}^{-1}$  clay, the peak for the collapsed structure disappeared and the expanded structure peak (13.6 to  $14.6 \text{ \AA}$ ) increased in intensity. Spacings  $> 15 \text{ \AA}$  were not evident.

Adsorption of B512F and Polytran on Na-montmorillonite was complete when the clay/polymer ratio (w/w) was  $\geq 10$ . Clay/polymer ratios  $< 10$  resulted in incomplete adsorption of the polymers; however, the total amount of polymer adsorbed continued to increase to a maximum. The maximum adsorption, at a clay/polymer ratio of 1, was  $445 \text{ mg B512F g}^{-1}$  clay and  $600 \text{ mg Polytran g}^{-1}$  clay. Olness and Clapp (1975) suggest that the number of available primary hydroxyl groups determine the length of the adsorption segment required to form a stable complex.

Adsorption of dextran and scleroglucan by kaolinite and montmorillonite was studied by Chenu et al. (1987). Maximum adsorption of dextran on Na-montmorillonite was  $25 \text{ mg g}^{-1}$  clay and on Ca-montmorillonite was  $20 \text{ mg g}^{-1}$  clay. These values are much lower than those reported by Olness & Clapp (1975) and Parfitt & Greenland (1970 b) who demonstrated a maximum adsorption of dextran on Na-montmorillonite to be 443 and  $457 \text{ mg g}^{-1}$  clay, respectively.

In summary, it is evident that glucose polymers are adsorbed on clay minerals to varying extents depending on the nature of the saturating cation and polymer structure. Adsorption isotherms for glucose polymers on clays are well established. However, it

remains to be determined whether this adsorption actually contributes to flocculation or whether the glucose polymers simply exist as collapsed structures on the mineral surface. The effect of polymer/clay ratio on clay flocculation also needs to be clarified. The presence of a coagulant may also affect the flocculation of clay minerals as the thickness of the diffuse double layer will dictate the size of polymer that is able to bridge clay particles.

**CHAPTER 3****ULTRASONIC DISPERSION OF SOIL AGGREGATES  
OBTAINED FROM A PRAIRIE-FOREST ECOTONE****3.1 Background**

Aggregate stability has been defined as the resistance of aggregates to breakdown when subjected to potentially disruptive forces (Hillel 1982). This definition suggests that two factors affect aggregate stability: the "resistance of aggregates" which is related to the inherent stability of the aggregate due to aggregation mechanisms, and the "disruptive force" used to break down the aggregate.

Aggregate stability measurements have been used to infer aggregate structure and aggregation mechanisms (Hamblin and Greenland 1977; Chaney and Swift 1986b; Elliot 1986). Such inferences must be understood in the context of: (1) the nature of the force used to disrupt the aggregate (e.g., wet-sieving, droplet impact, sonification, etc.), and (2) the magnitude of the applied force. Differences in aggregate stability measurements may arise because different methods emphasize different aspects of structural stability (Matkin and Smart 1987).

The most common method of assessing aggregate stability is Yoder's (1936) wet-sieving method and its modifications. Other methods include the drop method of McCalla (1944), optical transmission of soil suspensions (Abu-Sharar 1988), wet-sieving/turbidimetry combination (Pojasok and Kay 1990), and penetration of aggregates with a micropenetrometer (Grant et al. 1985).

These methods mentioned above, subject aggregates to an arbitrary and unknown energy level. A standard method using controlled energy levels is needed so that aggregate stability can be described as a function of the magnitude of the disruptive

force. The main advantage of such a method is its use in the study of binding agents held within aggregates at various bond strengths.

Previous aggregation studies have used ultrasound to disperse soil aggregates eliminating the need for chemical pretreatment (Edwards and Bremner 1967a). Clay dispersion following application of ultrasonic energy has been shown to increase with increasing energy level (North 1976; Gregorich et al. 1988). Ultrasonic dispersion of clay from aggregates treated with various polymers was shown to increase with increasing duration of sonification and could be described using a first-order model (Moen and Richardson 1984).

The use of ultrasonic energy to disrupt soil aggregates and to define a stability-energy relationship involves two assumptions. The first is that dispersed clay is an appropriate measure of aggregate breakdown; this assumption has been used in various stability measurements (Goh et al. 1987; Pojasok and Kay 1990). The second assumption is that all aggregated clay can be released using sonification at high energy levels (Gregorich et al. 1988).

Soil carbohydrates may be an important component of stable aggregates. The importance of carbohydrates to aggregation has been suggested by changes in water-stable aggregation following treatment with periodate (Cheshire et al. 1983, 1984). The presence of carbohydrates within water stable aggregates and correlations with aggregate mean weight diameter indicate that these organic biomolecules contribute to aggregate stability. However, the role played by soil carbohydrates in the aggregation process is uncertain. The association of carbohydrates of microbial origin with finer soil particles (silt and clay) suggests that carbohydrates may play an important role in the flocculation of clays. It is necessary to determine whether carbohydrates contribute to resistance to clay dispersion when aggregates are subjected to increasing energies of disruption.

This study had two objectives. First, to examine the potential use of ultrasonic energy to describe a stability-energy relationship for natural aggregates of specific sizes collected from different soils. Secondly, to determine if a stability-energy relationship could be used to study the role of soil carbohydrates in the aggregation process.

### 3.2 Materials and Methods

#### Soils

The soils used in this study were an Orthic Black (Oxbow), an Orthic Dark Gray (Whitewood) and an Orthic Gray Luvisol (Waitville) (Table 3.1). All the soils occur

Table 3.1. Selected properties of soils from which aggregate size fractions were obtained.

Soil	Horizon	Depth (cm)	pH†	Organic Carbon ----- (g kg <sup>-1</sup> ) -----	Total Hexose Carbon	Texture‡
Oxbow	Ah	0 - 10	6.2	83	2.5	CL (31)
	Bm	10 - 20	7.0	36	0.9	CL (36)
Whitewood	Ahe	0 - 12	5.5	46	1.6	L (21)
	Bt	12 - 23	6.2	22	0.9	CL (38)
Waitville	Ae	0 - 13	5.9	8	0.4	L (13)
	Bt	13 - 40	5.6	12	0.3	C (48)

† pH was determined in a 1:1 soil:0.01 M CaCl<sub>2</sub> mixture.

‡ The number in parentheses indicates % clay of the whole soil.

under native vegetation and have never been cultivated. The soils were sampled along an 81-m long transect which represented a change from a prairie ecosystem (Oxbow) to an aspen-forest ecosystem (Whitewood and Waitville) (Fuller 1989). Transition from an Orthic Black through an Orthic Dark Gray and finally to an Orthic Gray Luvisol is accompanied by decreased organo-mineral association within A horizons (St. Arnaud



and Whiteside 1964). These soils were chosen to evaluate the potential for using ultrasonic dispersion to detect changes in organo-mineral association responsible for soil aggregation.

### Collection of Aggregates

Bulk soil samples were collected from A and B horizons of all three soils, air dried, and gently passed through a 9.5-mm sieve to remove large clods. To ensure the aggregates remained in their native state, they were not crushed. Aggregates were dry-sieved on an automatic sieving device. The sieving time was 15 s with a sieve loading rate of  $0.60 \text{ g cm}^{-2}$ . The four aggregate size fractions (ASF) collected were 2.0 to 9.5 mm, 0.85 to 2.0 mm, 0.25 to 0.85 mm, and  $<0.25$  mm. The 2.0 to 9.5 mm ASF was chosen because 2.0 mm is the accepted break between fine and medium granular structure (Agriculture Canada Expert Committee on Soil Survey 1987). Aggregates with a diameter  $> 0.85$  mm are generally considered to be resistant to wind erosion (Chepil 1958). Those with a diameter of 0.25 to 0.85 mm are associated with water conducting and aeration pores and are therefore necessary for proper water and air movement through the soil (Oades 1984). Aggregates  $< 0.25$  mm, referred to as microaggregates, are associated with pores that are important in water retention (Oades 1984).

### Sonification of Aggregates

Sonification of the aggregates involved placing 1.0 g of air-dry aggregates of a given ASF into a 50-mL beaker. The beaker was held by a clamp on a burette stand at an angle of approximately  $20^\circ$  from the horizontal. A 100-mL burette was held in place above the beaker containing the aggregates with its tip contacting the side of the beaker. The droplets of deionized water ran down the side of the beaker and wet the aggregates

from below. This procedure minimized aggregate disruption by explosion due to air-entrapment and slaking. Deionized water was added at a rate of about  $2 \text{ mL min}^{-1}$  until the aggregates were saturated and covered with water (about 5 to 6 mL). The rate was then increased to approximately  $7 \text{ mL min}^{-1}$ . A total of 25 mL of deionized water was added in this manner to give a water:soil ratio of 25 (Figure 3.1).

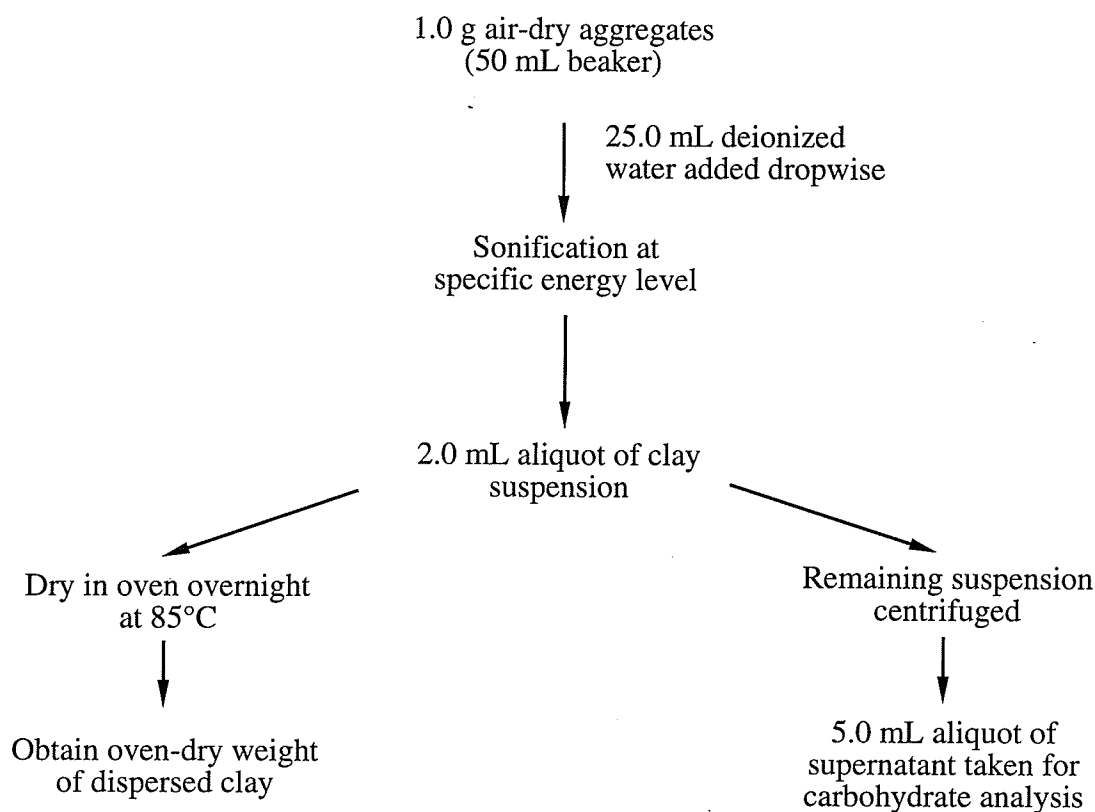


Figure 3.1. Flow chart depicting the procedure used in sonifying aggregate size fractions to obtain dispersed clay and solubilized carbohydrate at a given energy level.

The beaker was then immediately immersed in an ice bath and the aggregate-deionized water mixture sonified at a specific energy level. Following sonification, a 2-mL aliquot of clay suspension was removed from the top 1 cm of the suspension after allowing sand and silt size particles to settle out. A pipette-aid was used to prevent

potential mixing of the suspension using a hand-held bulb. The 2-mL aliquots were placed in preweighed aluminum weighing dishes and dried overnight in an oven at 85°C. The oven-dry mass of clay was expressed as a percent of total oven-dry mass of the initial aggregates. To determine whether saturation time affected the amount of clay dispersed at a given energy level, the water-aggregate mixtures were allowed to stand for 0, 30, 60 and 120 min prior to sonification.

Ultrasonic energy was applied using a Braun-Sonic 2000 sonifier with either a 9.5-mm or a 19-mm-diameter probe. The energy supplied by the probe to the suspension was 2.79 times less than the energy indicated on the probe meter (Appendix A). This correction factor was found to be constant over a range of meter readings and duration of sonification ( $2.79 \pm 0.08$ ). The correction factor was determined by calibration of the probe according to North (1976) and agreed with a value of 2.61 calculated for a similar probe used by Gregorich et al. (1988). The energy levels were calculated as Watts x seconds per mL of water and expressed in  $\text{kJ L}^{-1}$  using the meter reading wattage rather than the corrected wattage to be consistent with previous studies (Gregorich et al. 1988; Christensen 1985). Energy levels applied were 0, 100, 200, 300, 400, 500, and 1000  $\text{kJ L}^{-1}$  for all ASF except for the ASF of the Waitville Ae which were subjected to energy levels of 0, 25, 50, 75, 100, 200, and 1000  $\text{kJ L}^{-1}$ . Lower energy levels were required to generate stability curves for this horizon because the aggregates were more fragile. Sonification was done in duplicate with a new sample for each energy level. The 9.5-mm probe was used for all energy levels except 1000  $\text{kJ L}^{-1}$  where the 19-mm probe was used to ensure that all the aggregated clay was dispersed.

The data were fitted to a first-order decay model described by the equation,

$$A = A_{\max}e^{-kE} \quad (1)$$

where,

$A$  = clay remaining in aggregated form at energy level  $E$

$A_{\max}$  = total aggregated clay in the ASF

$k$  = constant ( $L \text{ kJ}^{-1}$ )

$E$  = applied ultrasonic energy ( $\text{kJ L}^{-1}$ ).

The above equation was transformed into a linear form by taking the natural log of both sides of the equation to give,

$$\ln A = \ln A_{\max} - kE. \quad (2)$$

A plot of  $\ln A$  vs.  $E$  yields a straight line with slope  $k$ . Two useful parameters to describe the decay curve were obtained from the regression of  $\ln A$  vs  $E$ . The first is  $k$ , henceforth referred to as the "stability constant". This stability constant is analogous to the rate constant of a first-order kinetic plot and describes the average release of aggregated clay upon application of a given level of energy. The second useful parameter for describing stability of aggregates is the  $E_{1/2}$  value. This value is analogous to a half-life value and describes the energy required to release one-half of the clay from the aggregates. The  $E_{1/2}$  value is calculated in the same manner as a half-life (Eq. 3).

$$E_{1/2} = 0.693/k \quad (3)$$

### Carbohydrate Analysis

The remaining suspension was centrifuged at 24000 g for 20 min. A 5-mL

aliquot of the supernatant was then removed for hexose determination by the anthrone method of Brink et al. (1960) using glucose as the standard. The hexose determined at this point is referred to as "solubilized hexose". Total hexose was also determined for each ASF using the anthrone method following acid hydrolysis of the aggregates in 1.5 M H<sub>2</sub>SO<sub>4</sub> at 85°C for 16 h (Angers et al. 1988). Total hexose analyses were measured in triplicate. Organic carbon in whole soil and each ASF was analyzed by a modified Walkley-Black method (Yeomans and Bremner 1988).

### 3.3 Results and Discussion

The effect of saturation time on the amount of clay dispersed at a given energy level was not significant ( $P = 0.05$ ) (Table 3.2). Hence, saturation time is not a critical factor at least within the first two hours of saturation.

Increasing the amount of applied energy resulted in increased amounts of dispersed clay and therefore less clay remained in an aggregated state. The plot of aggregated clay as a function of applied energy resulted in characteristic stability curves for each ASF (Figure 3.2). All  $r^2$  values, with a few exceptions (Waitville Bt 0.85 to 2.0 mm; Waitville Ae 2.0 to 9.5 mm), indicate a very good fit of the data to a first-order plot ( $P < 0.05$ ) (Table 3.3). Thus, Equation 2 was used to obtain  $k$  and  $E_{1/2}$  values (Figure 3.3).

The lower  $r^2$  values for the Waitville Ae aggregates are a reflection of their lower inherent stability. This soil has experienced eluviation of clay from the Ae horizon as evidenced by the Bt horizon immediately below which possesses an accumulation of illuvial clay. Loss of clay, lower organic matter levels and perhaps a lower exchangeable Ca/Mg ratio (Fuller 1989) in the Ae horizon result in less stable aggregates. These aggregates are more susceptible to initial breakdown upon addition of water and hence the first-order model does not fit the data as well.

The stability curves of all ASF suggest there was a relatively large amount of clay contained within aggregates which was easily dispersed. After the initial application of energy ( $100 \text{ kJ L}^{-1}$ ) no visible macroaggregates remained. Gregorich et al. (1988) suggested that release of clay at low energy levels was probably related to the loss of material between microaggregates responsible for binding microaggregates into macroaggregates. Application of comparatively low levels of ultrasonic energy is therefore sufficient to break particle-to-particle bonds responsible for

Table 3.2. The effect of saturation time on the amount of clay dispersed for a particular aggregate size fraction (ASF) at a given ultrasonic energy level.

Soil	Horizon	ASF (mm)	Energy ( $\text{kJ L}^{-1}$ )	Saturation time† (min)	Dispersed clay‡ ( $\text{g kg}^{-1}$ )
Oxbow	Ah	0.25-0.85	500	0	246a
				30	261a
				60	265a
				120	260a
			100	0	170a
				30	169a
				60	166a
				120	156a
Oxbow	Bm	0.85-2.0	500	0	342a
				30	340a
				60	356a
				120	347a
			100	0	308a
				30	312a
				60	302a
				120	307a
Waitville	Bt	2.0-9.5	100	0	410a
				30	429a
				60	418a
				120	401a

† Length of time the aggregates remained saturated prior to sonification

‡ Means followed by the same letter are not significantly different ( $P = 0.05$ )

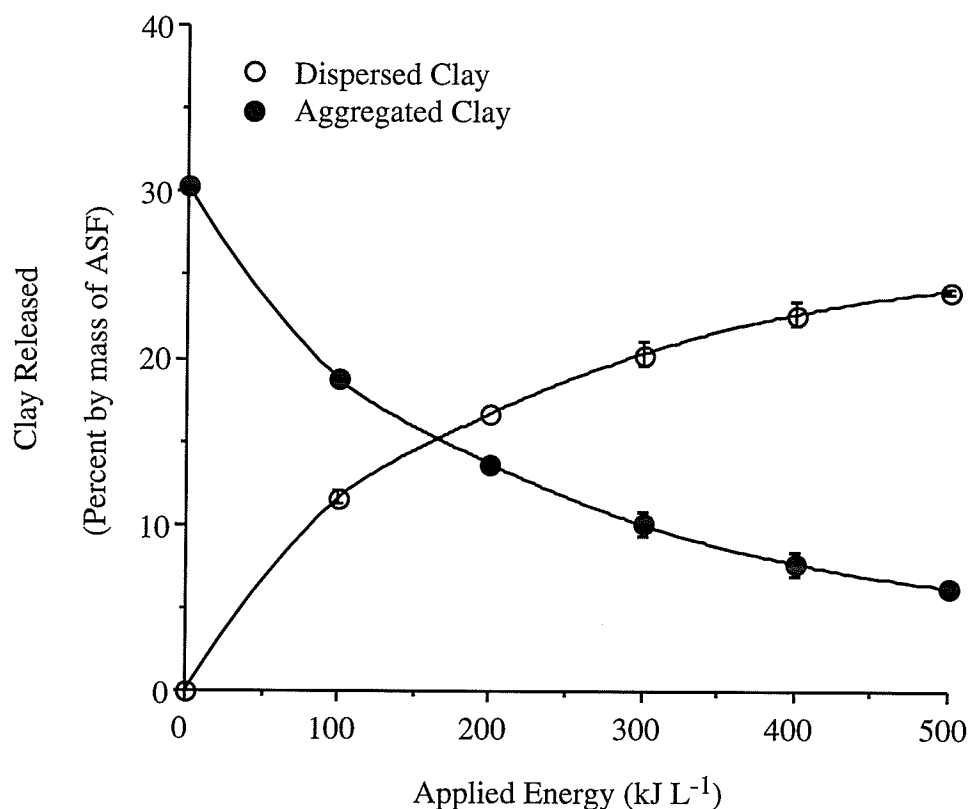


Figure 3.2. Dispersion of clay as a function of applied ultrasonic energy (data for the < 0.25 mm ASF of the Oxbow Ah horizon). Error bars indicate the standard error of the mean.

macroaggregation. Higher energies were required to disperse clay from the remaining microaggregates. This clay was dispersed at a decreasing rate, as indicated by the declining slope of the curves (Figure 3.2 and 3.3). Microaggregation has been hypothesized to be the result of cation bridging between clay particles and organic polymers (Edwards and Bremner 1967b). The need to increase applied energy to cause release of clay from microaggregates suggests a gradation in the strengths of particle-to-particle bonding. This may be related to variation in bridging cations and/or functional

Table 3.3.  $E_{1/2}$  values and coefficient of determination,  $r^2$ , ( $P < 0.05$ ) as determined from the linearized stability curve (Eq. 2) of each ASF.

Horizon	ASF (mm)	$E_{1/2}$ (kJ L <sup>-1</sup> )	$r^2$
Oxbow Ah	2.0-9.5	161 (23) <sup>†</sup>	0.83
	0.85-2.0	165 (12)	0.95
	0.25-0.85	187 (8)	0.98
	< 0.25	224 (12)	0.97
Oxbow Bm	2.0-9.5	135 (21)	0.80
	0.85-2.0	118 (14)	0.87
	0.25-0.85	124 (11)	0.92
	< 0.25	N.D <sup>‡</sup>	N.D
Whitewood Ahe	2.0-9.5	280 (35)	0.85
	0.85-2.0	343 (44)	0.86
	0.25-0.85	502 (98)	0.71
	< 0.25	191 (8)	0.98
Whitewood Bt	2.0-9.5	111 (18)	0.79
	0.85-2.0	115 (16)	0.84
	0.25-0.85	118 (14)	0.86
	< 0.25	N.D	N.D
Waitville Ae	2.0-9.5	64 (16)	0.61
	0.85-2.0	51 (8)	0.80
	0.25-0.85	98 (21)	0.69
	< 0.25	73 (9)	0.87
Waitville Bt	2.0-9.5	144 (30)	0.70
	0.85-2.0	132 (49)	0.48
	0.25-0.85	N.D	N.D
	< 0.25	N.D	N.D

<sup>†</sup> Values within parentheses are standard errors as determined by linear regression.

<sup>‡</sup> Not determined.



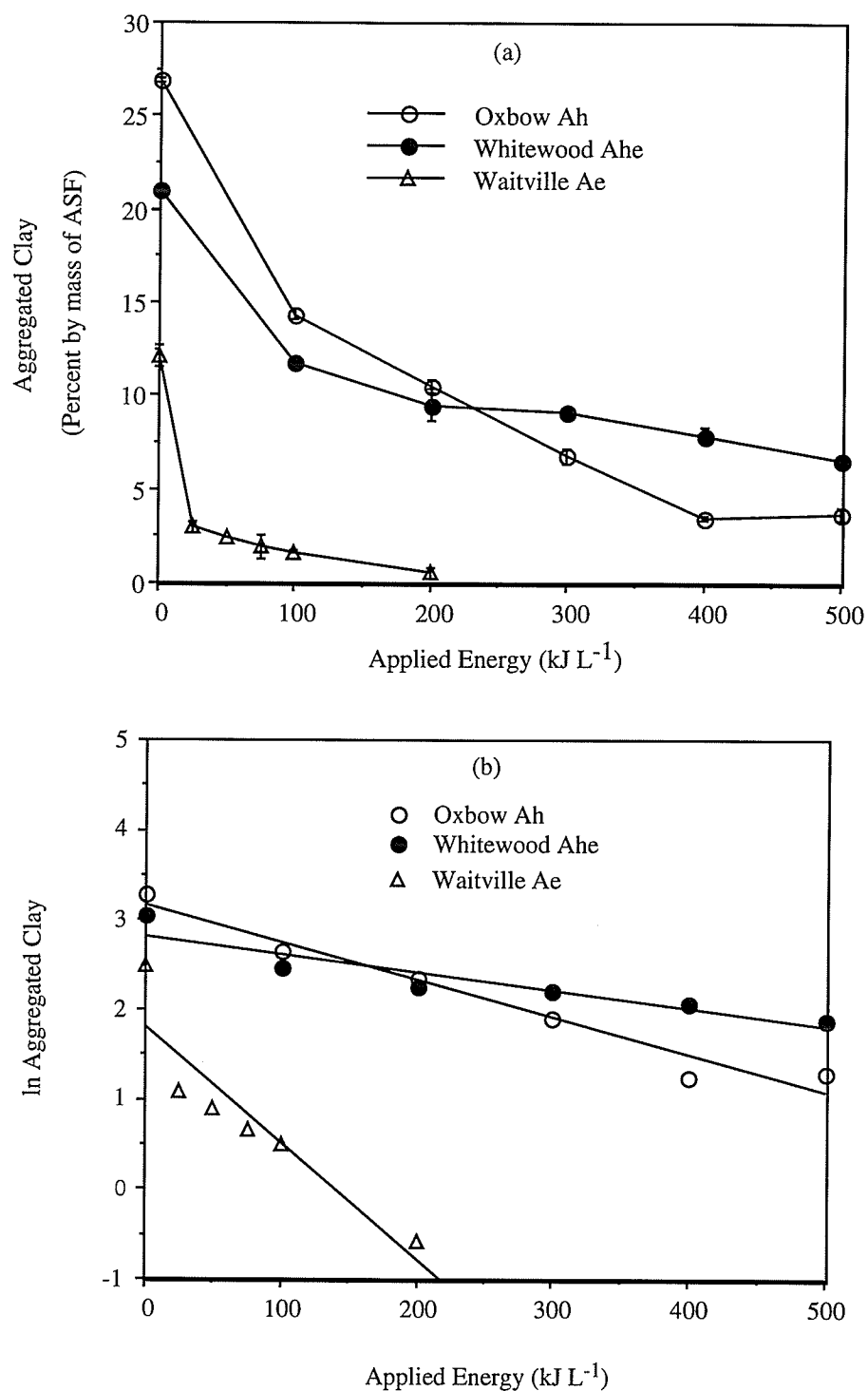


Figure 3.3. (a) Stability curves for the 0.85 - 2.0 mm ASF of the Oxbow Ah, Whitewood Ahe, and Waitville Ae horizons; (b) linearized form of the same data.

groups active in the aggregation process. Variation in the strength of bonding and aggregation is consistent with the aggregate model of Emerson (1959) who proposed various bonding mechanisms in the aggregation of primary particles.

Regression analysis of solubilized hexose as a function of dispersed clay at each energy level displayed significant ( $P < 0.05$ )  $r^2$  values (Table 3.5). A significant relationship existed between dispersed clay and solubilized hexose particularly for the Chernozemic soils (Figure 3.4) ( $P < 0.05$ ). The increase in solubilized hexose is most likely related to an increase in exposed surface area of the clays as dispersion increased. More of the surface-associated carbohydrate would be exposed to the solution as the system became more dispersed. It is not possible to determine from the data if this solubilized carbohydrate is directly responsible for binding clay particles; however, it is evident that dispersion of clay corresponds with solubilization of carbohydrate.

The Whitewood Ahe macroaggregates were able to resist dispersion of clay to a greater extent than the corresponding aggregates within the Oxbow Ah and Waitville Ae horizons as indicated by the higher  $E_{1/2}$  values (Table 3.3). The  $E_{1/2}$  values for the microaggregates ( $< 0.25$  mm) were similar in the Ah and Ahe horizons but much lower in the Ae horizon.

Differences in the  $E_{1/2}$  values for the three A horizons indicate that the means by which clay was retained within the aggregates were not the same in these horizons. The Chernozemic A horizon aggregates (Oxbow Ah and Whitewood Ahe) possessed greater stability than the Luvisolic Ae horizon aggregates. The greater organic matter and carbohydrate content of the Ah and Ahe horizons relative to the Ae horizon would contribute to aggregate stabilization through bridging of clay particles.

Table 3.4. Total hexose carbon in aggregate size fractions (ASF) of three soils and hexose carbon solubilized by the 0 kJ L<sup>-1</sup> and 1000 kJ L<sup>-1</sup> treatments.

Soil	Horizon	ASF	Total Hexose Carbon	Solubilized Hexose Carbon	
		(mm)		0 kJ L <sup>-1</sup>	1000 kJ L <sup>-1</sup>
				(g kg <sup>-1</sup> )	
Oxbow	Ah	2.0-9.5	2.01 bA <sup>†</sup>	0.06 aA	0.26 bA
		0.85-2.0	4.40 aA	0.05 aA	0.24 bA
		0.25-0.85	4.92 aA	0.03 aA	0.34abA
		< 0.25	5.44 aA	0.05 aA	0.38 aA
Whitewood	Ahe	2.0-9.5	2.68 cA	0.02 aA	0.19 aA
		0.85-2.0	2.98 cB	0.03 aB	0.18 aA
		0.25-0.85	3.60 bB	0.03 aA	0.24 aA
		< 0.25	4.72 aB	0.02 aA	0.23 aB
Waitville	Ae	2.0-9.5	0.84 aB	0.03 aA	0.08 aB
		0.85-2.0	0.66 aC	0.03 aB	0.09 aB
		0.25-0.85	0.86 aC	0.02 aA	0.09 aB
		< 0.25	0.90 aC	0.02 aA	0.10 aC
Oxbow	Bm	2.0-9.5	0.65 cA	0.01 aA	0.14 aA
		0.85-2.0	0.74 bcA	0.03 aA	0.12 aA
		0.25-0.85	0.92 bA	0.03 aA	0.14 aA
		< 0.25	1.71 aA	-	-
Whitewood	Bt	2.0-9.5	0.62 aA	0.02 aA	0.13 aB
		0.85-2.0	0.87 aA	0.02 aA	0.16 aA
		0.25-0.85	1.02 aA	0.02 aA	0.18 aA
		< 0.25	1.31 aA	-	-
Waitville	Bt	2.0-9.5	0.35 cB	0.02 aA	0.09 aC
		0.85-2.0	0.67 bcA	0.04 aA	0.13 aA
		0.25-0.85	0.92 bA	-	-
		< 0.25	1.65 aA	-	-

<sup>†</sup> Different lowercase letters indicate significant differences ( $P < 0.05$ ) among ASF within a horizon. Different uppercase letters indicate significant differences ( $P < 0.05$ ) between A or B horizons within an ASF.

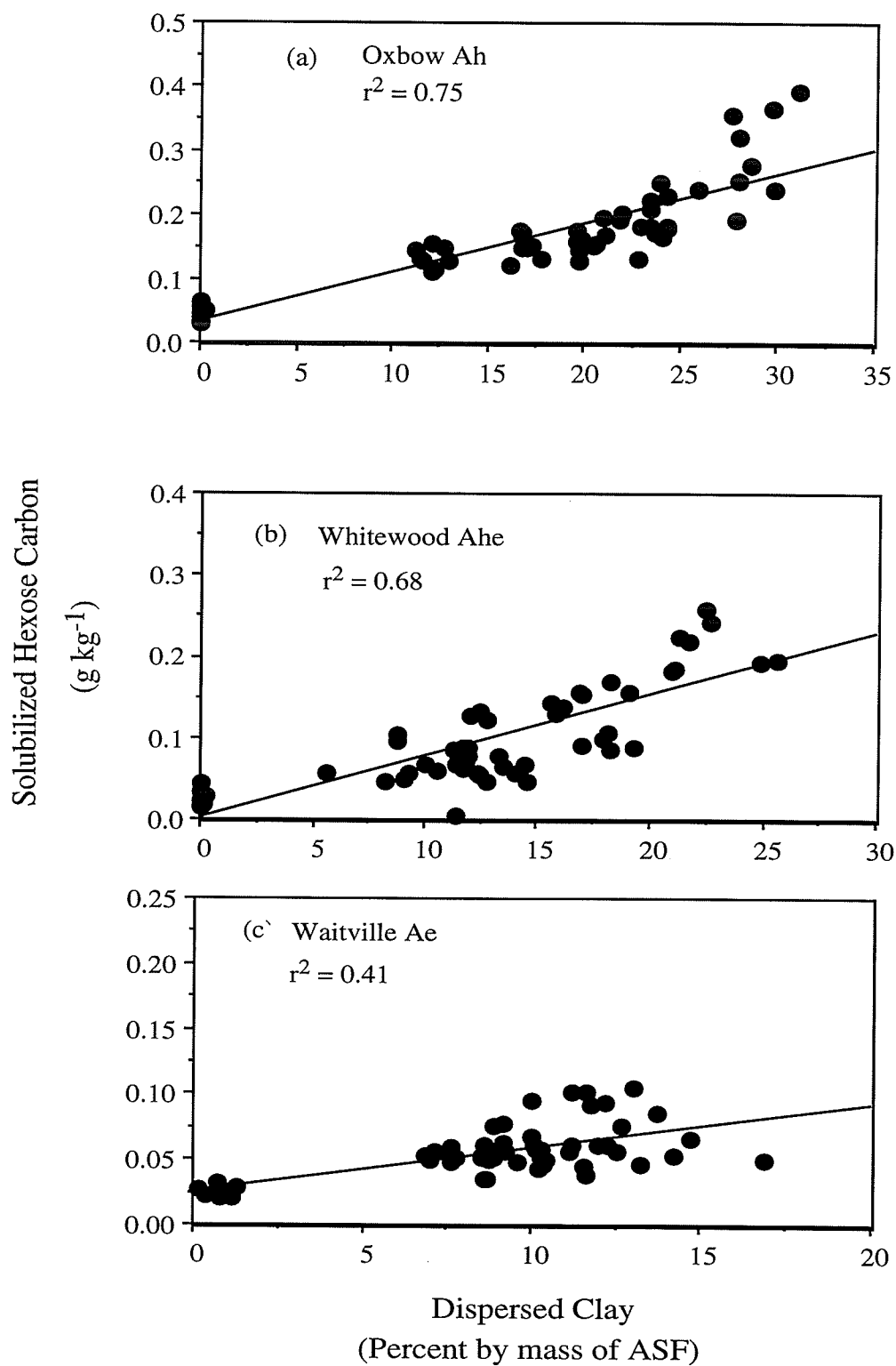


Figure 3.4. Solubilized hexose carbon plotted as a function of dispersed clay for all ASF within the Oxbow Ah, Whitewood Ahe, and Waitville Ae horizons ( $P < 0.001$ ).

Table 3.5. Coefficients of determination ( $P < 0.05$ ) for the regression of solubilized hexose carbon as a function of dispersed clay at each energy level for A horizon aggregates.

ASF (mm)	Oxbow Ah	Whitewood Ahe	Waitville Ae	All A Horizons
2.0-9.5	0.78	0.79	0.47	0.72
0.85-2.0	0.91	0.62	0.52	0.76
0.25-0.85	0.80	0.79	0.84	0.85
< 0.25	0.88	0.94	0.72	0.89

The change in the stability of the A horizon aggregates should be interpreted in the context of the transition from prairie to aspen forest since a change in vegetation and biomass distribution will affect organic matter dynamics in the soil. There has been an initial increase in aggregate stability under the newly established forest (Ahe horizon) followed by a dramatic decline under the mature forest (Ae horizon). The increase in aggregate stability in mull A-horizons under forest has been found by Mehta et al. (1960) and Clapp and Emerson (1965). Clapp and Emerson (1965) found that aggregates collected from a forest soil exhibited greater stability and resistance to periodate in combination with borate or pyrophosphate than aggregates from a grassland soil. No explanation for this enhanced stability was provided. The forest soil studied by Clapp and Emerson (1965) possessed a mull A-horizon with 6.9% organic carbon and a pH of 6.7. The Whitewood Ahe also was a mull A-horizon with relatively high organic carbon content. The greater stability of the Ahe horizon relative to the Ah horizon does not reflect the decrease in organic matter and carbohydrate content of the former. This greater stability may be related to the fact that the Ahe horizon has experienced eluviation of clay-organic matter complexes. It is reasonable to expect that the clay held within aggregates with the weakest particle-to-particle bonds would be eluviated first resulting in passive enrichment of aggregates with clay held by strong

particle-to-particle bonds. The presence of fungal hyphae may also contribute to the enhanced stability of a forest mull horizon (Tisdall and Oades 1982).

The Waitville Ae horizon was not a mull horizon but rather was a strongly leached horizon with little organic matter or clay present. The lack of organo-mineral association in such a horizon (St. Arnaud and Whiteside 1964) would result in aggregates with low stability.

The B horizon data indicated little difference among the  $E_{1/2}$  values of the aggregate size fractions within a horizon or among the three B horizons. The illuvial clay in the Bt horizons was as easily dispersed as the clay within the Bm horizon. This seems reasonable since illuvial clay exists as cutans on ped surfaces and therefore would be subject to dispersion more so than clay contained within the interior of a ped. Apparently, a high clay content alone is not sufficient to ensure greater aggregate stability when organic matter levels are low. The interaction of the organic fraction with clays in the Ah and Ahe aggregates is essential for aggregate stability.

The total hexose concentration increased with decreasing aggregate size except in the Ae horizon where the concentration was similar among all aggregate size fractions (Table 3.4). A similar, inverse relationship was also observed by Baldock et al. (1987). Carbohydrate concentration has generally been found to be greatest in the clay size fraction, less in the silt, and least in the sand-sized fraction (Cheshire and Mundie 1981; Catroux and Schnitzer 1987; Angers and Mehuys 1990). If small size aggregates are composed predominantly of clay-sized particles as suggested by Tisdall and Oades (1982), then small aggregates should have a greater concentration of carbohydrate.

The values for total hexose were higher than those reported by Angers and Mehuys (1990) and by Dormaar (1983). The hexose C content of aggregates in this study ranged from 2.0 to 5.4 g kg<sup>-1</sup> in the native prairie soil. Dormaar (1983)

studied a native prairie soil in Alberta and found polysaccharide C within aggregates to range from 2.0 to 2.8 g kg<sup>-1</sup>. The lower values found in Dormaar's study can be attributed to lower amounts of organic C in the Dark Brown of that study. The proportion of organic C as hexose C in this study (on a whole soil basis) ranged from 2.5 to 5.0% and is consistent with values in the two studies mentioned above (Table 3.1).

Destruction of aggregates by sonification at 1000 kJ L<sup>-1</sup> caused solubilization of hexose from the aggregates (Table 3.4). This solubilized hexose carbon ranged from about 0.08 to 0.38 g kg<sup>-1</sup> and comprised approximately 5 to 10% of the total hexose carbon within A-horizon aggregates and approximately 20% in B-horizon aggregates. Cheshire (1977) was able to extract 8% of the total carbohydrate from a sandy loam soil by sonification in water at 20°C. Following sonification, the association of organic matter with clay and silt particles has been shown to comprise greater than 80 to 90% of the total soil carbon (Christensen 1985).

Carbohydrate was also solubilized from the aggregates when no ultrasonic energy was applied (Table 3.4). The hexose carbon solubilized at 0 kJ L<sup>-1</sup> comprised < 0.06 g kg<sup>-1</sup>. The aggregates with the greatest concentration of hexose released more soluble hexose at 1000 kJ L<sup>-1</sup>. Some of the stable carbohydrate within A horizons is likely to be associated with organic components within the aggregates. The lower content of organic matter in the B horizon would reduce stabilization of carbohydrate in the organic fraction. Therefore a greater proportion of the total carbohydrate would be subject to solubilization. This was indeed the case (Table 3.4).

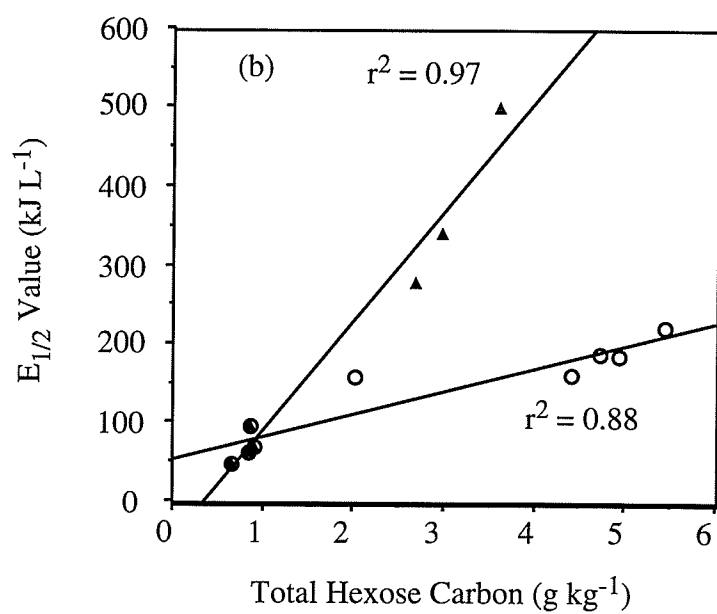
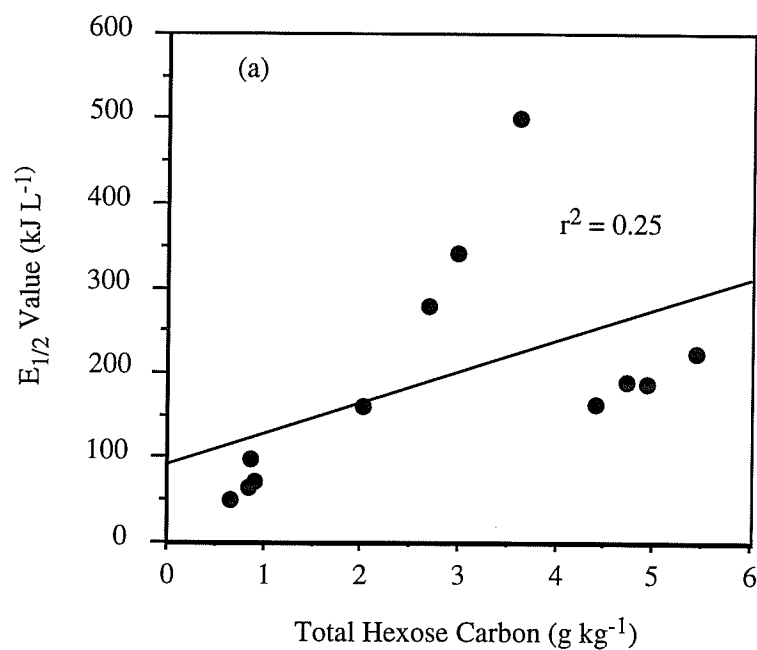
The occurrence of a relatively small but easily mineralizable organic fraction within soil aggregates dispersed by ultrasound has been shown by Gregorich et al. (1989). They suggested this material was physically protected polysaccharides. The present study also revealed the presence of a relatively small fraction of physically

protected carbohydrate which could be released by sonification. However, the majority of the hexose contained within these aggregates was so strongly associated with mineral and/or organic matter surfaces that sonification at  $1000 \text{ kJ L}^{-1}$  did not release this hexose.

The effect of cultivation on the carbohydrate content of particle-size fractions generally causes decreased levels of carbohydrate in sand and silt fractions with little change in clay fractions (Dalal and Henry 1988; Angers and Mehuys 1990). This redistribution of carbohydrate in particle-size fractions following cultivation also implies the presence of relatively labile and more stable fractions of soil carbohydrate. The most stable fraction is associated with clays while the carbohydrate associated with coarser fractions tends to be more labile. Polysaccharide adsorbed to montmorillonite is generally not susceptible to oxidation under conditions where free solution polysaccharide is easily oxidized (Emerson et al. 1986). Therefore, the carbohydrate remaining associated with surfaces following dispersion of soil aggregates was likely to be a part of the stable carbohydrate fraction associated with clay and organic colloid surfaces.

Carbohydrates have been reported to be essential to the maintenance of stable aggregates (Cheshire et al. 1984; Angers and Mehuys 1989). It would seem reasonable to suspect aggregates with greater  $E_{1/2}$  values to possess greater amounts of carbohydrate material. Regression analysis of total hexose carbon vs.  $E_{1/2}$  values of all A horizon ASF yielded a  $r^2$  value of 0.25 (Figure 3.5a). This low  $r^2$  value was mainly due to the relatively high  $E_{1/2}$  values for the Whitewood Ahe macroaggregates. However, it is possible to show two linear trends in the data (Figure 3.5b). The first regression ( $r^2 = 0.97$ ;  $P < 0.05$ ) includes predominantly macroaggregate data for the Whitewood and Waitville soils. The second regression ( $r^2 = 0.88$ ,  $P < 0.05$ ) includes data for the Oxbow Ah horizon found under prairie. The microaggregates of both the





- ▲ Forest ASF (excluding Wh <0.25mm ASF)
- All ASF (excluding Wh macroaggregates)

Figure 3.5. (a)  $E_{1/2}$  plotted as a function of total hexose carbon ( $P < 0.10$ ); and (b) two possible linear trends in the data ( $P < 0.001$ ).

Oxbow Ah and the Whitewood Ahe fall along the second regression line. The Whitewood Ahe microaggregates had similar properties as the Oxbow Ah microaggregates suggesting the microaggregates were less vulnerable to changes following forest invasion of prairie. These linear trends suggest a significant relationship between dispersion of clay by ultrasound and carbohydrate content. However, this relationship may not necessarily be the same among different soils and/or aggregate sizes. Strickland et al. (1988) have suggested that different soils show variation in aggregation and aggregate stability because mechanisms of aggregate stabilization differ markedly across soil types. The effect of carbohydrate on soil aggregate stability appears to be quite different for macroaggregates under forest compared to aggregates found under prairie.

### 3.4 Summary

The objectives of this study were (i) to develop a method to describe aggregate stability-energy relationships using ultrasonic dispersion and (ii) to examine the role played by carbohydrate in soil aggregation. Study soils included an Orthic Black, Orthic Dark Gray, and Orthic Gray Luvisol, representing the change from a prairie ecosystem to an aspen-forest ecosystem. Aggregate size fractions (ASF) from these soils were sonified, and dispersed clay and solubilized carbohydrate measured at energy levels ranging from 0 to 1000 kJ L<sup>-1</sup>. Ultrasonic dispersion of aggregated clay resulted in characteristic "stability curves" for each ASF which obeyed a first-order decay curve and provided two parameters describing the release of clay from soil aggregates with increasing levels of applied energy: the "stability constant"  $k$  and the  $E_{1/2}$  value, which are analogous to a first-order rate constant and half-life, respectively.  $E_{1/2}$  values ranged from 51 to 502 kJ L<sup>-1</sup>. These values were smallest for the Ae horizon of the Orthic Gray Luvisol and greatest for the macroaggregates of the Ahe horizon of the

Orthic Dark Gray. The development of a stability-energy relationship for aggregates provides a means to study the role of binding agents, such as carbohydrate, in the aggregation process.

Total hexose concentration within aggregates increased with a decrease in aggregate size. Macroaggregates found in the Orthic Dark Gray (Whitewood) under forest were the most resistant to ultrasonic dispersion. Upon complete destruction of aggregates by sonification, only a minor amount (5-10%) of the total hexose contained within the aggregates was solubilized. The remaining hexose was strongly associated with surfaces.

The wide range in  $E_{1/2}$  values of A horizon aggregates, collected from the prairie-forest ecotone, indicated that the aggregates varied in their ability to resist dispersion by ultrasound. Therefore, mechanisms responsible for maintaining clay within these aggregates either differed in magnitude or in nature. Aggregate formation and stabilization may therefore be soil specific and the environment and pedogenic history of the soil may play a role in determining the aggregation mechanisms and processes responsible for aggregate stabilization.

Total hexose carbon did not correlate well with  $E_{1/2}$  values of aggregates from these widely differing soils. The relationship between clay dispersion and hexose carbon content was different between prairie and forest aggregates.

This approach provides a means to describe a stability-energy relationship for a given aggregate size fraction. Standardizing the procedure and calibrating the ultrasonic probes make this method useful for comparing different soils and treatments in various laboratories by providing a means to describe aggregate stability as a function of applied ultrasonic energy.

## CHAPTER 4

### CULTIVATION EFFECTS ON CARBOHYDRATE CONTENT AND DISPERSIBLE CLAY OF SOIL AGGREGATES

#### 4.1 Background

The effect of cultivation on soil carbohydrates is mainly of a quantitative rather than qualitative nature. Studies have revealed that the sugar residues present in soil are not influenced by cropping treatments. The usual monosaccharides include glucose, galactose, mannose, arabinose, xylose, fucose and rhamnose. The relative proportions of the monosaccharides remain relatively constant under forage, annual crop, or fallow (Dormaar 1984; Baldock et al. 1987; Benzing-Purdie and Nikiforuk 1989; Angers and Mehuys 1990).

Cultivation of soils, that were under pasture or forage for long periods of time, results in a decline in carbohydrate contents when annual cropping is imposed on the soil (Swincer et al. 1968; Dormaar 1983, 1984; Dalal and Henry 1988). In Australia, a reduction of 66% in carbohydrate concentration occurred for fine sandy loam soils subjected to a wheat-fallow rotation (Swincer et al. 1968). Declines in the carbohydrate contents of soil aggregates under continuous wheat and wheat-fallow management relative to the native prairie were reported by Dormaar (1983). Cereal production in Australia resulted in a decrease in soil carbohydrate contents by as much as 46% relative to virgin soils (Dalal and Henry 1988).

The proportion of aggregate C present as monosaccharide C for native prairie was found to vary from 6.9 to 7.6% while for the continuous wheat it varied from 3.6 to 5.5% and from 1.8 to 5.1% and 1.6 to 6.7% for the wheat and fallow of the wheat-fallow rotation (Dormaar 1984). Contrary to this, Dalal and Henry (1988) found the percentage of total soil C present as carbohydrate C to be higher in cultivated soils.

Others have found no difference in proportion of carbohydrate C in total organic C across cropping treatments (Baldock et al. 1987).

Although the relative proportions of monosaccharides remained relatively constant across cropping treatments, the ease of extraction and molecular weight distribution of polymers have been found to vary (Swincer et al. 1968). An "old pasture" soil contained about three times as much soil carbohydrates as the same soil subjected to a wheat-fallow rotation. The soil under pasture possessed 2 to 3 times more carbohydrates of molecular weight  $> 100,000$  compared to the wheat-fallow soil which possessed more carbohydrate in the  $< 4000$  and  $4000$  to  $100,000$  molecular weight ranges. The authors suggest a relationship between ease of extraction and molecular weight of the polymer. Larger polymers were expected to be less extractable and were thought to be active in aggregate stabilization. Under pasture there was more than three times as much carbohydrates bound to the soil colloids in such a way that it was not readily released. The abundance of humic substances of apparent molecular weight  $> 100,000$  in water-stable aggregates has also been observed by Dell'Agnola and Ferrari (1971). Cultivation apparently causes a shift towards smaller molecular weight polymers.

Root exudation and physical enmeshment of soil particles by roots are believed to contribute to aggregate formation in the rhizosphere. The amount of rhizodeposition of assimilated  $^{14}\text{C}$  has been shown to be twice as great under brome grass than under corn (Davenport and Thomas 1988). The root system of ryegrass consists of an extensive system with fine roots. The ryegrass root system has been shown to be more efficient than that of white clover in stabilizing aggregates of a loam soil (Tisdall and Oades 1979). This increased stabilization within the ryegrass rhizosphere was evident after 8 weeks of ryegrass growth and continued to increase up to 16 weeks of growth. Aggregates  $50$  to  $250\ \mu\text{m}$  in diameter were bound into aggregates  $> 2000\ \mu\text{m}$  in

diameter. Aggregate stabilization was related to the length of root in the total soil (Tisdall and Oades 1979). Treatment of the stabilized aggregates under ryegrass with periodate caused reduction in aggregate stability but not to the extent of an unplanted control (Tisdall and Oades 1979). The stabilization of aggregates under ryegrass was attributed to a larger population of vesicular-arbuscular mycorrhizal hyphae in the soil. Electron micrographs revealed hyphae covered with amorphous material, probably polysaccharide, to which clay particles appeared firmly attached (Tisdall and Oades 1979).

Root growth of ryegrass and lucerne increased stability of aggregates (relative to unplanted control) of a sandy loam soil in both moist and dry states after 42 d of growth (Reid and Goss 1981). The beneficial effects were associated with periodate-sensitive materials produced in the rhizosphere. Growth of maize, tomato, and wheat for 25 d decreased the stability of moist aggregates but these deleterious effects were not apparent after air-drying. The increased stabilization upon air-drying was related to the presence of periodate-sensitive materials.

The loss of stable aggregates from bromegrass soils due to initiation of grain-corn production occurred rapidly within 1 to 2 years (Baldock and Kay 1987). The accumulation of aggregating agents under bromegrass production relative to losses due to grain-corn production is suspected to be a slower process (Baldock and Kay 1987). The rebuilding of good structure takes much longer than it does to destroy good structure (Low 1955; Tisdall and Oades 1980). It has been argued that soil under cropping may never be like soil under native prairie (Dormaar 1984).

Short term changes in soil carbohydrate content following cropping of a clay soil (Orthic Humic Gleysol) to barley and alfalfa for 2 years have been correlated with increased aggregate mean weight diameter (Angers and Mehuys 1989). Periodate treatment confirmed the involvement of carbohydrate in stabilization of aggregates.

However, the significant correlation ( $P < 0.001$ ) yielded a correlation coefficient of only 0.63 implying the involvement of other binding agents. Tetraborate treatment was able to remove any stabilizing agent remaining after periodate treatment. Angers and Mehuys (1989) suggest that more-humified organic substances also contributed to the significant crop effect on aggregate mean weight diameter. The presence of periodate-sensitive materials within water-stable aggregates of various cropping treatments has also been documented by Baldock and Kay (1987). They suggest that non-carbohydrate material is involved in aggregate stabilization. They also argue that differences in structural stability observed across cropping treatments could not be explained by the presence of periodate-sensitive materials alone.

Densimetric and particle-size fractionation of soils have been utilized to study long-term (Dormaar 1984; Dalal and Henry 1988) and short-term (Angers and Mehuys 1990) effects of cultivation and cropping history on soil carbohydrate. Densimetric separation of soil carbohydrate revealed that the proportion of carbohydrate in the light-fraction ( $< 2 \text{ Mg m}^{-3}$ ) ranged from 27 to 43% for virgin soils. Cultivation resulted in a decline of light fraction carbohydrate by as much as 60% (Dalal and Henry 1988). The light fraction C was enriched in carbohydrate C relative to whole soil and heavy fraction C due to a greater proportion of coarse organic matter containing partly decomposed plant residues. Roberson et al. (1991) suggest that heavy fraction rather than light-fraction carbohydrate is responsible for aggregate stabilization.

The distribution of carbohydrates is generally greater in the clay fraction, less in the silt and lowest in the sand fraction (Cheshire and Mundie 1981; Catroux and Schnitzer 1987; Angers and Mehuys 1990). However, considerable variation in particle-size distribution among soils may occur (Dalal and Henry 1988). Following 20 years of cultivation, the sand and silt fractions lost substantial amounts of carbohydrate while the clay fraction was least affected. However, in terms of carbohydrate-C

enrichment, the sand fraction was more enriched following cultivation. The clay fraction was depleted in carbohydrate-C in light-textured soils (< 20% clay) and was enriched in heavy-textured soils (> 75% clay).

Two years of cropping to barley and alfalfa resulted in greater carbohydrate contents of whole soil (Angers and Mehuys 1990). This effect could be attributed to increased carbohydrate contents in the sand fraction (46 to 83%). Therefore, it appears that short-term effects of cropping on carbohydrate contents occurs mainly in the sand fraction. Decomposition of these plant and microbial residues results in transfer of carbohydrate to finer fractions via microbial synthesis of new carbohydrates. The extent to which this carbohydrate redistribution has affected aggregation both quantitatively (ie. proportions in each ASF) and qualitatively (ie. mechanistically) is not well documented.

The dispersion of clay from soil aggregates presents problems due to aggregate breakdown and pore blockage. The importance of dispersible clay as a measure of soil structural integrity has recently been emphasized (Brubaker et al. 1992). The evaluation of the energy level at which clay disperses and the proportion of clay dispersed at varying energy levels would provide important information about the nature of aggregate breakdown.

The objective of this study was to examine the role of polysaccharide in the aggregation process by subjecting soil aggregates to ultrasonic dispersion and relating the amount of hexose within each ASF to the dispersion of clay. The effect of long-term cultivation of a prairie soil was examined by comparing aggregates under prairie with those from adjacent cultivated soils.



## 4.2 Materials and Methods

### Soils

This study focused on the long-term effect of cultivation on a medium-textured glacial-till derived soil. The soil studied was an Orthic Black of the Oxbow Association. Orthic profiles that possessed similar solum thicknesses, B horizon development and A horizon thickness were sampled. This insured that the effect of cultivation on a particular subgroup could be evaluated. Three field replicates were taken from separate profiles at three sites. The 0-7 and 7-14 cm depths were sampled from A horizons. Some properties of the soils are indicated in Table 4.1.

Table 4.1. Selected chemical and physical properties of the soil in this study.

Site	Sand	Silt	Clay	pH†	Organic Carbon	Hexose Carbon‡
	----- % -----				----- g kg <sup>-1</sup> -----	
	0-7 cm depth					
Pr	36.3§	32.4	31.3	6.6	40.0	3.4
C1	45.7	27.3	27.0	7.1	19.2	1.6
C2	44.5	29.1	26.4	7.1	18.5	1.4
	7-14 cm depth					
Pr	42.1	27.8	30.1	6.7	25.6	2.3
C1	43.5	28.5	28.0	7.3	17.4	1.4
C2	44.9	29.1	26.0	7.1	17.5	1.4

<sup>†</sup> pH was determined on a 1:1 soil:0.01 M CaCl<sub>2</sub> suspension.

<sup>‡</sup> Assumes a hexose-C content of 40% by weight based on the chemical formula for glucose.

<sup>§</sup> Particle-size analysis and pH were conducted on a composite sample of three field replicates.

### Site Descriptions

Sites were selected where the management of the soil since the time of breaking was known (Table 4.2). Three sites were sampled. The first (Pr) was a native prairie site which had never been cultivated. The native vegetation was dominated by northern

wheatgrass (*Agropyron dasystachyum*), speargrass (*Stipa comata*), rough fescue (*Festuca scabrella*), and pasture sage (*Artemisia frigida*). Blue gramma (*Bouteloua gracilis*) and the non-native crested wheatgrass (*Agropyron cristatum*) were also present. The site had not been grazed by cattle for the past 6 years.

Table 4.2. Management history of the study sites.\*

Site	Year of Breaking	CF†	CCF‡	CW§
Prairie (Pr)	--	--	--	--
Cultivated (C1)¶	ca. 1905	1905-1958	1958-1982	1982-present
Cultivated (C2)††	ca. 1905	1905-1982	--	1982-present

\* History according to the landowner.

† Cereal-fallow rotation (wheat or barley).

‡ Cereal-cereal-fallow rotation (wheat or barley).

§ Continuous wheat with minimum tillage.

¶ Tillage using sweep cultivator; minimum tillage practiced.

†† Tillage by discing.

The cultivated sites were adjacent to the prairie. It was estimated by the landowner that breaking of these sites occurred in the years 1905 to 1906. The management of the second site (C1) included a cereal-fallow rotation (wheat or barley) from the time of breaking until approximately 1958. From 1958 to 1982 the site had a cereal-cereal-fallow rotation and from 1982 to present it has been continuously cropped to wheat. Since 1958, this site was managed using minimum tillage avoiding fall tillage as much as possible. A cultivator with sweeps was used in fallow years.

The management of the third site (C2) included a cereal-fallow rotation (wheat or barley) from the time of breaking until 1982. Fall tillage was accomplished by discing in the crop year resulting in little trash cover. Tillage in the fallow year was also accomplished by discing. From 1982 to present this site has had a continuous wheat rotation in the same manner as site C1. Thus, in terms of tillage intensity, these soils can be ranked in the order  $C2 > C1 > Pr$ .

### Collection of Aggregate Size Fractions

The soil samples in this study were treated in the same manner described in section 3.2. The same method of sieving was used as described in section 3.2 and the same aggregate size fractions were collected (2.0 to 9.5, 0.85 to 2.0, 0.25 to 0.85, and <0.25 mm).

### Sonification

The method of sonification used has been described previously (section 3.2). However, the energy level used to obtain  $A_{\max}$  in this study was  $1500 \text{ kJ L}^{-1}$ . The data were described by the first-order decay model of Equations 1 and 2 of chapter 3. The values of  $E_{1/2}$  were calculated for each aggregate size fraction (ASF) as described previously in chapter 3.

### Carbohydrate Analysis

Hexose carbohydrate was determined using the anthrone colorimetric method of Brink et al. (1960) following acid hydrolysis of the aggregates in  $1.5 \text{ M H}_2\text{SO}_4$  at  $85^\circ\text{C}$  for 16 h (Angers et al. 1988). Glucose was used as the standard. Hexose solubilized during sonification of aggregates was determined as described in section 3.2.

The effect of cultivation on clay-associated hexose was also studied for the 0-7 cm depth of the soils from the Pr and C2 sites. The experimental approach involved sonifying aggregates at  $100 \text{ kJ L}^{-1}$ , decanting the dispersed clay, re-sonifying the remaining residue at  $500 \text{ kJ L}^{-1}$  (water:soil ratio of 25) and decanting the dispersed clay again (Figure 4.1). In this manner, clay retained within aggregates at low energy levels ( $100 \text{ kJ L}^{-1}$ ) could be separated from clay retained within aggregates at intermediate energy levels (100 to  $500 \text{ kJ L}^{-1}$ ). The decanted clay was centrifuged at  $24000 \text{ g}$  for 20

min and then dried in an oven at 40°C. One gram of clay, thus collected, was subjected to acid hydrolysis in 10 mL of 1.5 M H<sub>2</sub>SO<sub>4</sub> for 16 h. Hexose within the hydrolysate was determined using the anthrone procedure (Brink et al. 1960) using glucose standards.

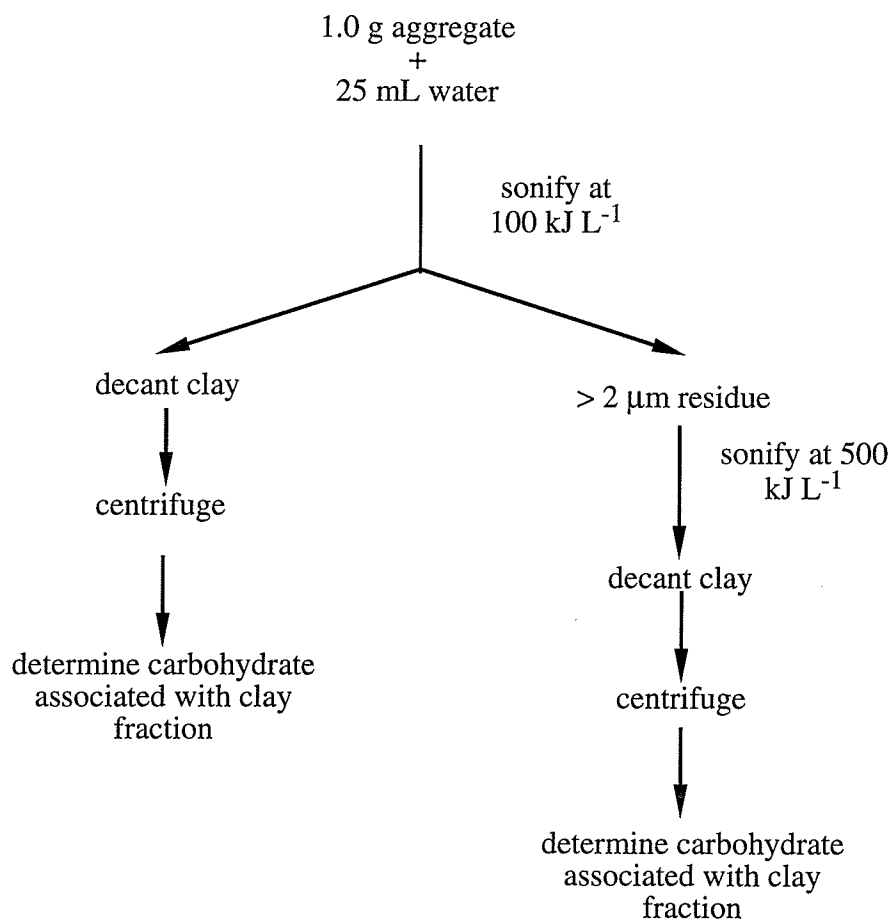


Figure 4.1. Flow chart depicting the procedure used to separate clay fractions from an ASF.

### Miscellaneous Analyses

Particle-size analysis on whole soil samples was conducted by the pipette-method after treatment with hydrogen peroxide to remove organic matter. These samples contained no  $\text{CaCO}_3$  so pretreatment with HCl was not required.

Organic carbon was determined using a modified Walkley-Black method (Yeomans and Bremner 1988).

### Statistical Analysis

Analysis of variance was conducted separately for the 0-7 cm and 7-14 cm depths. The ANOVA was conducted only after homogeneity of variance was established among the three sites. Data which exhibited non-homogeneity of variance among sites were subjected to log transformation prior to the analysis of variance. Log transformation successfully ensured homogeneity of variance (Steel and Torrie 1980).

## 4.3 Results and Discussion

### Aggregate Size Distribution

The distribution of aggregate size fractions (ASF) on a percentage weight basis was significantly different between the Pr and C2 sites in the 0-7 cm depth (Table 4.3). The soils of the C2 site possessed significantly less 2.0 to 9.5 mm aggregates and significantly more <0.25 mm aggregates relative to the soils of the Pr site. There was no net change in the proportion of aggregate size fractions 0.85 to 2.0 and 0.25 to 0.85 mm between the C2 and Pr site. No significant differences were found in aggregate distribution between the 0-7 cm depths of the C1 and Pr sites.

Table 4.3. Aggregate size distribution at each study site.

ASF† (mm)	Site		
	Pr	C1	C2
	-----(% w/w)-----		
		<i>0-7 cm depth</i>	
2.0-9.5	23.8 (0.7)‡	24.7 (3.0)	13.2 (0.5)
0.85-2.0	14.6 (0.6)	13.5 (1.6)	10.6 (0.5)
0.25-0.85	28.7 (0.5)	29.0 (0.6)	31.1 (0.7)
< 0.25	32.9 (1.0)	32.8 (4.2)	45.1 (0.4)
		<i>7-14 cm depth</i>	
2.0-9.5	26.1 (0.6)	35.7 (4.2)	31.8 (2.2)
0.85-2.0	14.8 (0.5)	17.8 (1.5)	16.7 (1.0)
0.25-0.85	28.9 (0.5)	24.8 (1.6)	26.0 (0.9)
< 0.25	30.2 (1.0)	21.7 (3.9)	25.5 (1.7)

† ASF = aggregate size fraction.

‡ Numbers in parentheses indicate standard error of the mean. Mean of three field replicates.

LSD<sub>0.05</sub> among sites (0-7 cm depth) = 2.4.

LSD<sub>0.05</sub> among sites (7-14 cm depth) = 3.0.

In the 7-14 cm depth there was no significant difference in aggregate size distribution between the Pr and C2 sites. However, the C1 site possessed significantly more 2.0 to 9.5 mm aggregates and less <0.25 mm aggregates relative to the soils of the Pr site. At all three sites, the 0.85 to 2.0 mm ASF comprised the smallest proportion of soil less than 9.5 mm in diameter (in both depths).

The aggregate size distribution can be expected to be altered by tillage. The increase in <0.25 mm ASF at the expense of the 2.0 to 9.5 mm ASF in the C2 site (0-7 cm depth) suggests that the tillage of the C2 site has caused destruction of the largest aggregates. The absence of this effect at the C1 site suggests that the sweep cultivator and minimum tillage has a less drastic effect on macroaggregate breakdown. Since the C1 and C2 sites have been managed in a similar manner in recent years (Table 4.2), it is not possible to explain differences between these soils on the basis of roots and fungal hyphae as emphasized by Tisdall and Oades (1982). Differences in particle size

distribution among the three sites are minimal and therefore cannot be used as an explanation for the differences in aggregate size distribution (Table 4.1).

### Aggregate Stability

Aggregate stability as determined by ultrasonic dispersion showed differences among the three sites (Figures 4.2 and 4.3). The macroaggregates of the C1 site were less stable than those of the Pr site but more stable than the same aggregates at the C2 site. The macroaggregates of the 0-7 cm depth of the cultivated soils showed a decrease in stability as indicated by an increase in the slope of the regression lines. This shows that the ability to withstand disruption by sonification relative to the macroaggregates of the Pr site is substantially less (Figure 4.2 a,b,c). The increased negative slope indicates that at a given energy level there was less clay remaining in an aggregated state (ie. more clay dispersed) for the cultivated macroaggregates. Therefore, less clay remains aggregated at each energy level within these cultivated macroaggregates and hence the potential for clay dispersion is greater compared with prairie macroaggregates.

The microaggregates in the 0-7 cm depth did not show the same differences in stability as the macroaggregates (Figure 4.2 d). The slope of the regression line has become more negative for the cultivated microaggregates but only slightly so. Therefore, the stability of the microaggregates was less influenced by differences in soil management than was that of the macroaggregates.

Microaggregation theory suggests that microaggregates are not influenced by agricultural practices (Tisdall and Oades 1982; Oades 1984). These data indicate that agricultural management has affected the stability of microaggregates to a certain extent but this effect is much less than that observed for macroaggregates. Long-term cultivation has reduced the ability of microaggregates to withstand ultrasonic vibration.

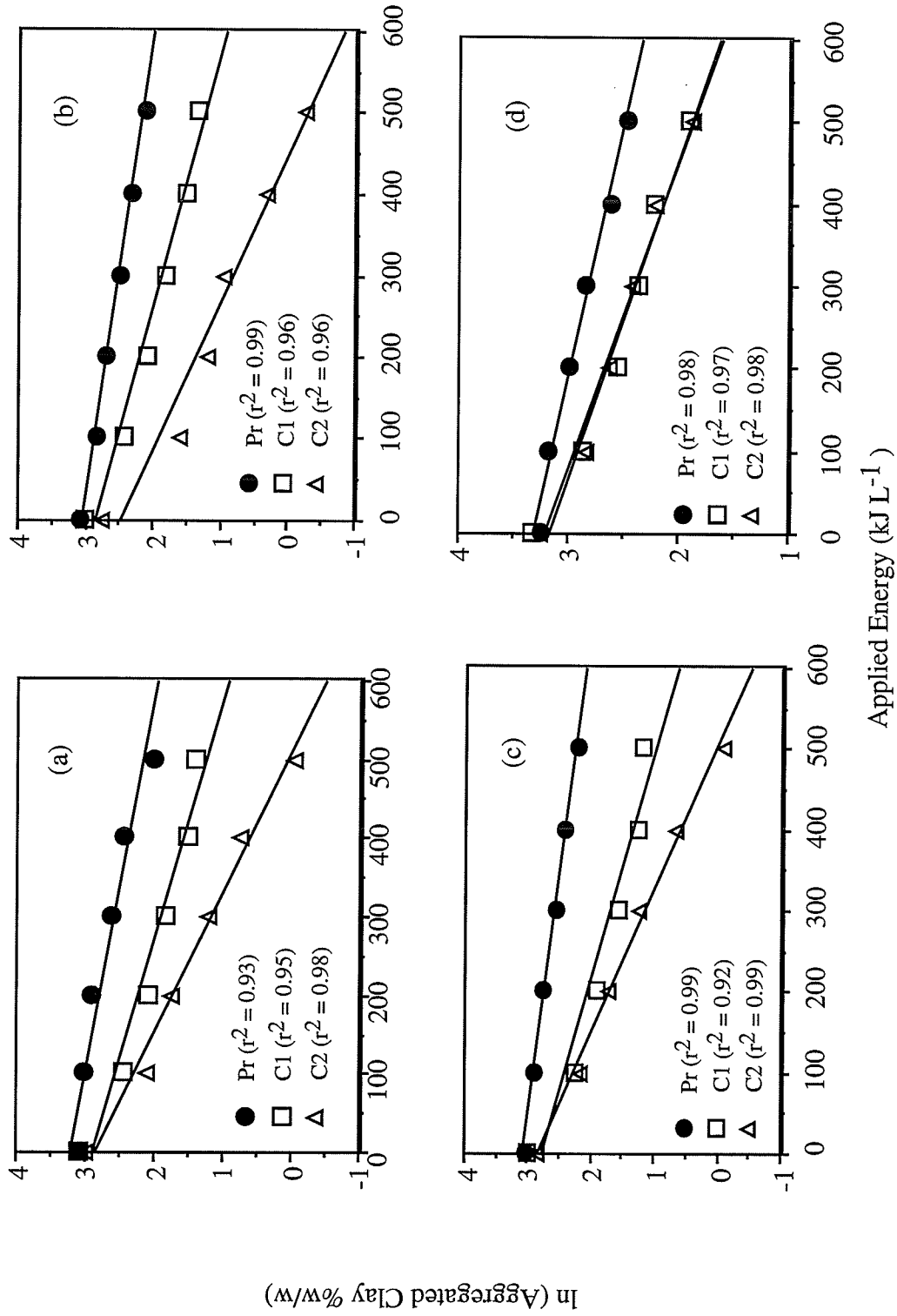


Figure 4.2. Linearized form of the stability curves of all ASF (0-7 cm depth); (a) 2.0-9.5 mm; (b) 0.85-2.0 mm; (c) 0.25-0.85 mm; (d)  $< 0.25$  mm.



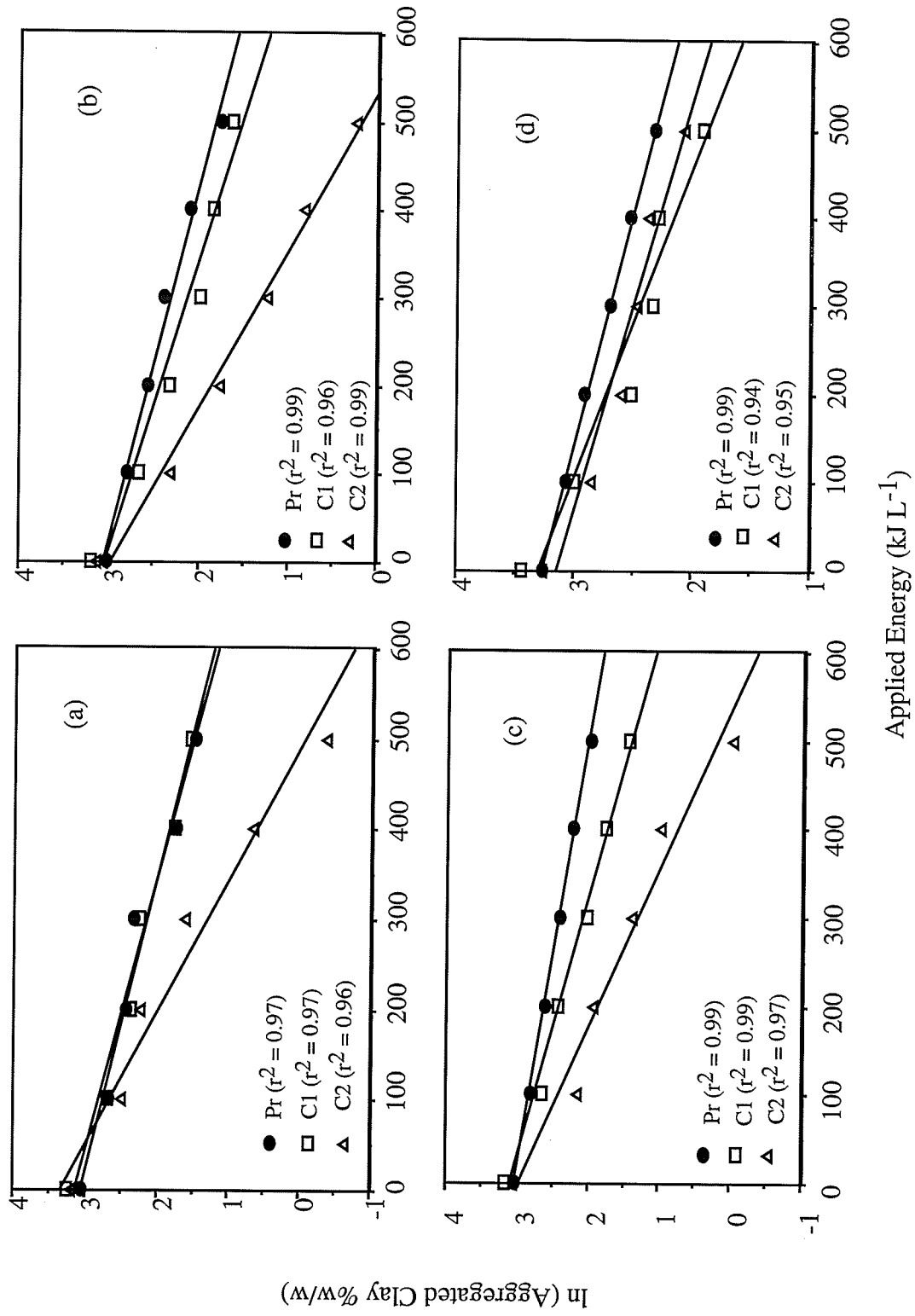


Figure 4.3. Linearized form of the stability curves of all ASF (7-14 cm depth); (a) 2.0-9.5 mm; (b) 0.85-2.0 mm; (c) 0.25-0.85 mm; (d)  $< 0.25$  mm.

Cultivation has not had the same effect on aggregate stability and dispersible clay within the 7-14 cm depth. The macroaggregates of the C1 site possess a similar stability as the macroaggregates under prairie (Figure 4.3 a,b,c). However, the macroaggregates of the C2 site are less stable than macroaggregates from both the Pr and C1 sites.

The microaggregates of the 7-14 cm depth show little difference with respect to aggregate stability and clay dispersibility (Figure 4.3 d). Once again the data indicate that microaggregate stability has not been influenced to the same extent by cultivation as has macroaggregate stability.

The  $E_{1/2}$  values provide a numerical and physical evaluation of the regression lines (Table 4.4). These values indicate the average energy input required to disperse one-half of the clay within the aggregate. The  $E_{1/2}$  values therefore reflect differences in the slope of the regression lines and thus permit a comparison of the dispersibility of clay within aggregates. The data for the 0-7 cm depth indicate a decrease in  $E_{1/2}$  values for macroaggregates under cultivation relative to those under prairie. The order of stability for all macroaggregates in the 0-7 cm depth is  $Pr > C1 > C2$ . This corresponds to a decrease in tillage intensity of the sites.

The microaggregates under cultivation also have lower  $E_{1/2}$  values but the decrease relative to prairie is not as great as for the macroaggregates. At all three sites the microaggregates possess the greatest stability of all ASF studied. The greater stability of smaller structural units in the hierarchical ordering of soil aggregates can be seen (Hadas 1987; Dexter 1988).

The  $E_{1/2}$  values for aggregates of the 7-14 cm depth were lowest at the C2 site. Stability of macroaggregates is similar for the prairie and C1 site but much less at the C2 site. Microaggregate stability in the 7-14 cm depth is similar among all three sites. Once again, microaggregates possess the greatest stability.

Table 4.4.  $E_{1/2}$  values of aggregate size fractions at three sites.

ASF (mm)	Site		
	Pr	C1	C2
	-----( $\text{kJ L}^{-1}$ )-----		
<i>0-7 cm depth</i>			
2.0-9.5	334 (34) <sup>†</sup>	209 (38)	119 (16)
0.85-2.0	382 (35)	213 (52)	120 (7)
0.25-0.85	425 (64)	190 (61)	118 (19)
< 0.25	433 (52)	263 (7)	271 (23)
<i>7-14 cm depth</i>			
2.0-9.5	228 (13)	212 (44)	95 (8)
0.85-2.0	281 (3)	229 (20)	124 (5)
0.25-0.85	339 (37)	210 (52)	118 (26)
< 0.25	370 (24)	249 (48)	334 (19)

<sup>†</sup> Numbers in parentheses are standard errors of the mean of three field replicates.

LSD<sub>0.05</sub> among sites (0-7 cm) = 57; (7-14 cm) = 44.

LSD<sub>0.05</sub> among ASF (0-7 cm) = 66; (7-14 cm) = 51.

The management of the C1 and C2 sites has been the same since 1982. Both sites have had continuous wheat production since 1982 utilizing a sweep cultivator as the tillage implement. Minimum tillage with residue maintenance has been conducted at both sites during this time period. The similarity in management for the past 10 years rules out management since 1982 as the reason for differences in aggregate stability observed between the two sites.

Differences between the C1 and C2 sites arise in the long-term management prior to institution of continuous wheat (Table 4.2). The C2 site has had more fallow years than the C1 site and the method of tillage also differed before 1982. The C2 site was tilled by discing with no attempt to maintain trash cover. Method of tillage has an effect on the amount of crop residue left after tillage. The effect of tillage implement on average residue cover reduction for wheat, sorghum, and sunflower has been shown to

be 65%, 19%, and 12% for disc, blade and chisel tillage, respectively (Sallaway et al. 1988). The absence of residue cover has left the soil at C2 exposed to wind and water erosion. Discing is also known to cause a shift in aggregate size distribution towards smaller aggregate size fractions more than other tillage implements (Braunack and McPhee 1991). The amount of erodible aggregates of a silt loam soil tended to decrease following tillage with a blade rodweeder or sweep cultivator but increased following discing (Smika and Greb 1975). The percentage aggregation of the same silt loam soil decreased from 70% aggregation to 50% following five tillage operations with a sweep cultivator but dropped from 70% aggregation to 30% with a disc implement (Smika and Greb 1975). Therefore, the long-term use of discing with little residue maintenance and intensive tillage may be, at least in part, responsible for the reduction in aggregate stability between the two cultivated sites.

It appears that the type of management before institution of continuous wheat may have far reaching effects on the aggregate size distribution and aggregate stability of the C1 and C2 sites. If the prairie is considered to be a baseline for comparison, then it is evident that long-term cultivation has reduced the stability of aggregates, particularly in the 0-7 cm depth. Continuous wheat management with minimum tillage since 1982 has failed to return the stability of the aggregates to levels found in the prairie site. The build-up of good soil structure and aggregate stability takes much longer than their decline under cultivation (Low 1955; Dormaar 1984; Baldock and Kay 1987).

The soil which had been subjected to greater fallow frequency and tillage by discing (C2) consistently showed the lowest macroaggregate stability within both depths. The potential for aggregate disruption at this site is greater since less energy is required to disperse an equivalent proportion of clay from aggregates. Therefore, this site will be more susceptible to structural breakdown by raindrop impact and dispersion

of clay, resulting in pore blockage leading to crusting, lower water infiltration and subsequent erosion.

The C1 site, which has had less fallow over the long term and tillage with a sweep cultivator, has also experienced a reduction in macroaggregate stability in the 0-7 cm depth relative to the prairie. However, the C2 site consistently exhibited lower aggregate stability. The deterioration of soil structure with increasing fallow frequency is evident in this study and supports findings of others (Tisdall and Oades 1982; Oades 1984). More importantly, the effects due to difference in management between the cultivated sites appears to remain after 10 years of continuous wheat with minimum tillage. Long-term management history therefore has an impact on shorter-term aggregate stabilization and structural improvement.

It is important to recognize that aggregate size distribution was similar for the Pr and C1 sites. However, an increase in the  $< 0.25$  mm ASF at the expense of the 2.0 to 9.5 mm ASF in the 0-7 cm depth of the C2 site has occurred. The C2 site has not only experienced a decline in the stability of aggregates but the proportion of macroaggregates has also been reduced. These macroaggregates contain pores responsible for water and gas movement through the soil. The similar aggregate size distribution between the Pr and C1 sites suggests that pore-size distribution may be similar. However, the potential for structural deterioration is greater for C1 aggregates and even more so for C2 aggregates. Structural deterioration will result in changes in pore size distribution which in turn will affect water infiltration and retention as well as gas movement within the soil.

In general, microaggregation has been less influenced by long-term cultivation. However, a negative impact is still apparent in cultivated sites, particularly in the 0-7 cm depth.

### Carbohydrate Content of Soil Aggregates

The hexose content of all ASF has declined in the cultivated soils to approximately 40 to 50% of the levels found within prairie ASF (Tables 4.5 and 4.6). This is true for both the 0-7 and 7-14 cm depths. Differences in management between the C1 and C2 sites did not result in differences in the hexose concentration of ASF in either depth. The hexose contents of ASF are about 1.5 to 2 times greater than levels of polysaccharide found in a Dark Brown studied by Dormaar (1983). This difference can be attributed to greater organic matter levels found in the soil of the present study. This soil belongs to the Black great group of the Chernozemic order.

The ASF with the greatest hexose content was the microaggregate fraction, <0.25 mm, in both depths for all three sites. The 2.0 to 9.5 mm ASF within the 0-7 cm under prairie also possesses higher levels of hexose relative to other macroaggregates. The greater concentration of hexose within the smallest ASF is consistent with earlier reported findings for the prairie-forest ecotone soils (Fuller and Goh 1992) and those of Baldock et al. (1987) who showed an increase in carbohydrate content with decreasing aggregate size. The greatest amount of biomass C has been shown to occur within microaggregates and decreased with increasing aggregate size (Seech and Beauchamp 1988). However, Dormaar (1983) showed declining polysaccharide concentrations with decreasing aggregate size for both prairie and cultivated soil. The reason for this may be related to the lower clay content of the soil in Dormaar's study which averaged 18% compared with an average of 28% in this study. Microaggregates tend to be enriched in clay relative to macroaggregates (Tisdall and Oades 1982) and therefore soil with lower clay content may not provide the same protection of polysaccharide within the microaggregate structure.

Table 4.5. Hexose carbon and total organic carbon within four aggregate size fractions from the 0-7 cm depth of the three study sites.

Site	Total organic carbon	Hexose carbon	Non-hexose carbon	Soluble hexose carbon†
----- (g kg <sup>-1</sup> ) -----				
<i>2.0-9.5 mm ASF</i>				
Pr	66.7 aA‡	4.24 aAB	62.5 aA	0.53 aA
C1	40.4 bA	1.83 bA	38.6 bA	0.10 cB
C2	41.3 bB	1.89 bB	39.4 bA	0.18 bA
<i>0.85-2.0 mm ASF</i>				
Pr	64.6 aA	3.50 aC	61.1 aA	0.42 aB
C1	39.7 bA	1.69 bAB	38.0 bA	0.12 cAB
C2	32.4 cC	1.44 cC	31.0 cA	0.19 bA
<i>0.25-0.85 mm ASF</i>				
Pr	61.9 aA	3.67 aBC	58.2 aA	0.44 aAB
C1	39.4 bA	1.53 bB	37.9 bA	0.10 cB
C2	34.9 cC	1.67 bBC	33.2 cA	0.13 bB
<i>&lt; 0.25 mm ASF</i>				
Pr	67.2 aA	4.52 aA	62.7 aA	0.52 aA
C1	44.0 bA	1.94 cA	42.1 bA	0.13 cA
C2	47.0 bA	2.34 bA	44.7 bA	0.22 bA

† Hexose solubilized during sonification at 1500 kJ L<sup>-1</sup>.

‡ Lowercase letters indicate significant differences among sites within an ASF. Uppercase letters indicate significant differences among ASF within a site. Means followed by the same letter are not significantly different (P = 0.05).

The decline in hexose concentration within ASF follows closely the decline in organic carbon and non-hexose organic carbon upon cultivation (Tables 4.5 and 4.6). Correlation of hexose carbon with organic carbon resulted in a correlation coefficient of  $r = 0.96$  ( $P < 0.001$ ) (Figure 4.4). Correlation of hexose carbon with non-hexose organic carbon (organic carbon - hexose carbon) was also highly significant with a correlation coefficient of  $r = 0.95$  ( $P < 0.001$ ). Therefore the total amount of hexose in soil aggregates is closely correlated with the amount of organic carbon present.

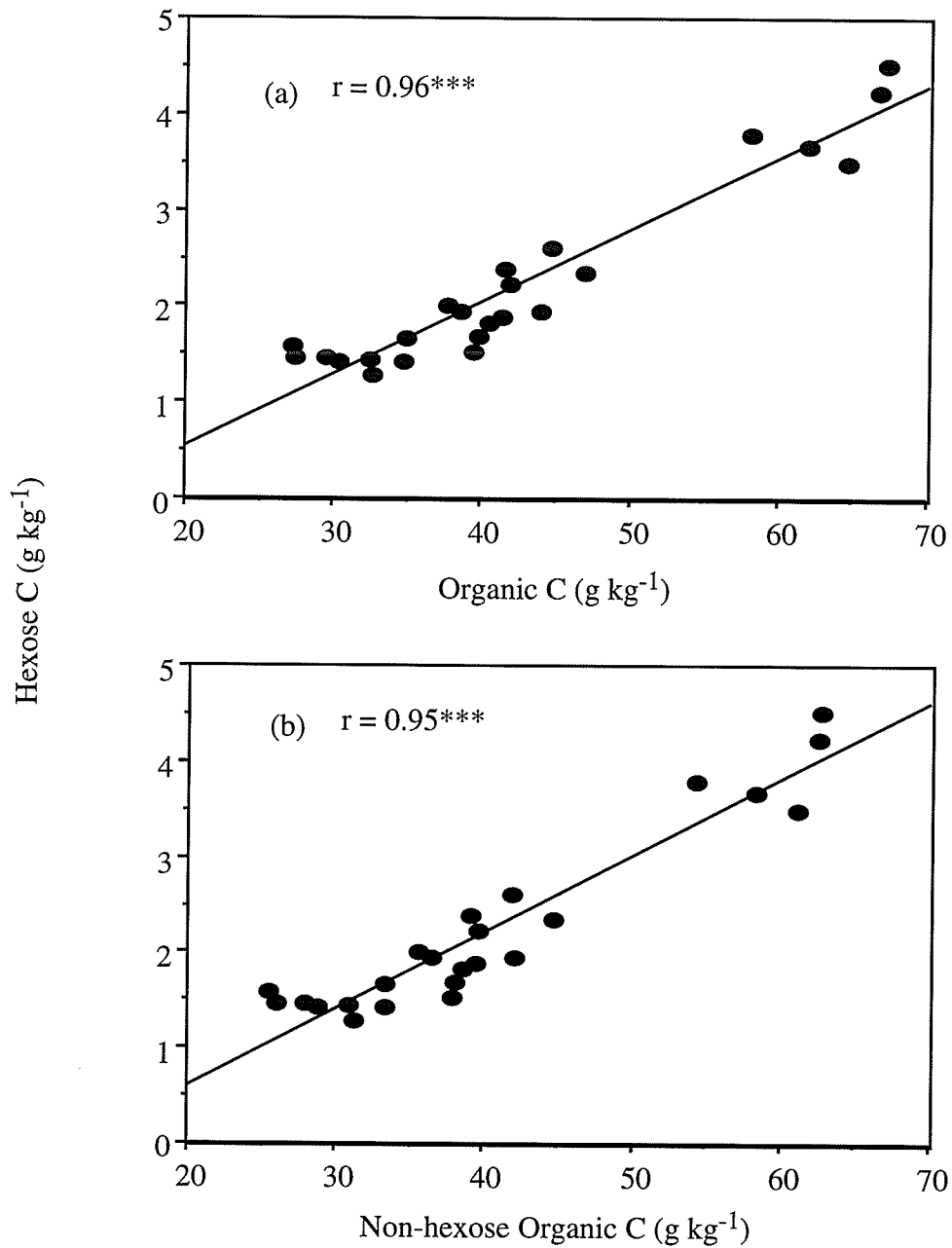


Figure 4.4. Correlation of hexose carbon with (a) organic carbon; and (b) non-hexose organic carbon (\*\*\*) indicates correlation significant at  $P < 0.001$ ).

Despite the correlation between organic carbon and hexose carbon, the proportion of total organic carbon existing as hexose carbon within a given ASF was



Table 4.6. Hexose carbon and total organic carbon within four aggregate size fractions from the 7-14 cm depth of the three study sites.

Site	Total organic carbon	Hexose carbon	Non-hexose carbon	Soluble hexose carbon†
----- (g kg <sup>-1</sup> ) -----				
<i>2.0-9.5 mm ASF</i>				
Pr	41.5 aB‡	2.39 aBC	39.1 aB	0.54 aA
C1	32.5 bB	1.28 bC	31.2 bB	0.11 cB
C2	34.7 bB	1.43 bB	33.3 bAB	0.20 bB
<i>0.85-2.0 mm ASF</i>				
Pr	41.9 aB	2.22 aC	39.7 aB	0.26 aC
C1	27.1 cC	1.60 bB	25.5 cC	0.09 cBC
C2	30.0 bC	1.42 bB	28.9 bBC	0.20 bB
<i>0.25-0.85 mm ASF</i>				
Pr	44.6 aB	2.60 aB	42.0 aB	0.28 aC
C1	27.4 bC	1.47 bBC	25.9 bC	0.07 cC
C2	29.4 bC	1.46 bB	27.9 bC	0.21 bAB
<i>&lt; 0.25 mm ASF</i>				
Pr	58.1 aA	3.80 aA	54.3 aA	0.38 aB
C1	37.6 bA	2.02 bA	35.6 bA	0.15 cA
C2	38.5 bA	1.94 bA	36.6 bA	0.26 bA

† Hexose solubilized during sonification at 1500 kJ L<sup>-1</sup>.

‡ Lowercase letters indicate significant differences among sites within an ASF. Uppercase letters indicate significant differences among ASF within a site. Means followed by the same letter are not significantly different (P = 0.05).

significantly greater under prairie when compared with the cultivated sites (Table 4.7).

The values ranged from 5.3 to 6.8% under prairie and 3.9 to 6.0% within cultivated soils. These values are consistent with those reported by Dormaar (1984) who also found a greater proportion of total organic carbon present as carbohydrate carbon under a prairie soil relative to the same soil subjected to continuous wheat or wheat-fallow rotations. Swincer et al. (1968) also found a decrease in the proportion of carbohydrate carbon for a soil under wheat-fallow rotation relative to an "old pasture" soil. The lower proportion of hexose carbon in cultivated soils implies that hexose is preferentially decomposed following tillage of a virgin soil. This is reasonable since

tillage exposes previously protected organic matter (Rovira and Greacen, 1957; Gregorich et al. 1989). The carbohydrate thus exposed would be expected to be readily decomposed.

The proportion of organic carbon present as hexose carbon was not significantly different among ASF within each site. The similar proportion of hexose within the organic fraction among various ASF suggests that the balance between decomposition and resynthesis of hexose by the microbial population relative to other organic fractions must have been similar among the various ASF at each site.

The ratio of non-hexose carbon to hexose carbon within the 0-7 cm depth was significantly lower for the prairie ASF (Table 4.7). There were no significant differences among ASF within sites for either of the two depths studied. Cultivation has resulted in a greater decrease in hexose carbon relative to non-hexose carbon within the 0-7 cm depth. There was no difference among the C1 and C2 sites (0-7 cm depth) except for the 0.25 to 0.85 mm ASF where a greater proportion of non-hexose carbon occurred in the C1 ASF.

Application of ultrasonic energy to soil aggregates resulted not only in dispersion of clay but also in the solubilization of hexose (Figures 4.5, 4.6, 4.7). Correlation of solubilized hexose with dispersed clay yielded high correlation coefficients for the aggregate size fractions obtained from the prairie site (Table 4.8). This increase in the amount of hexose solubilized during sonification indicates that as more clay is dispersed there is a corresponding increase in the amount of hexose exposed to the solution. This will be the result of an increase in exposed aggregate surface area and hence more hexose becomes solubilized.

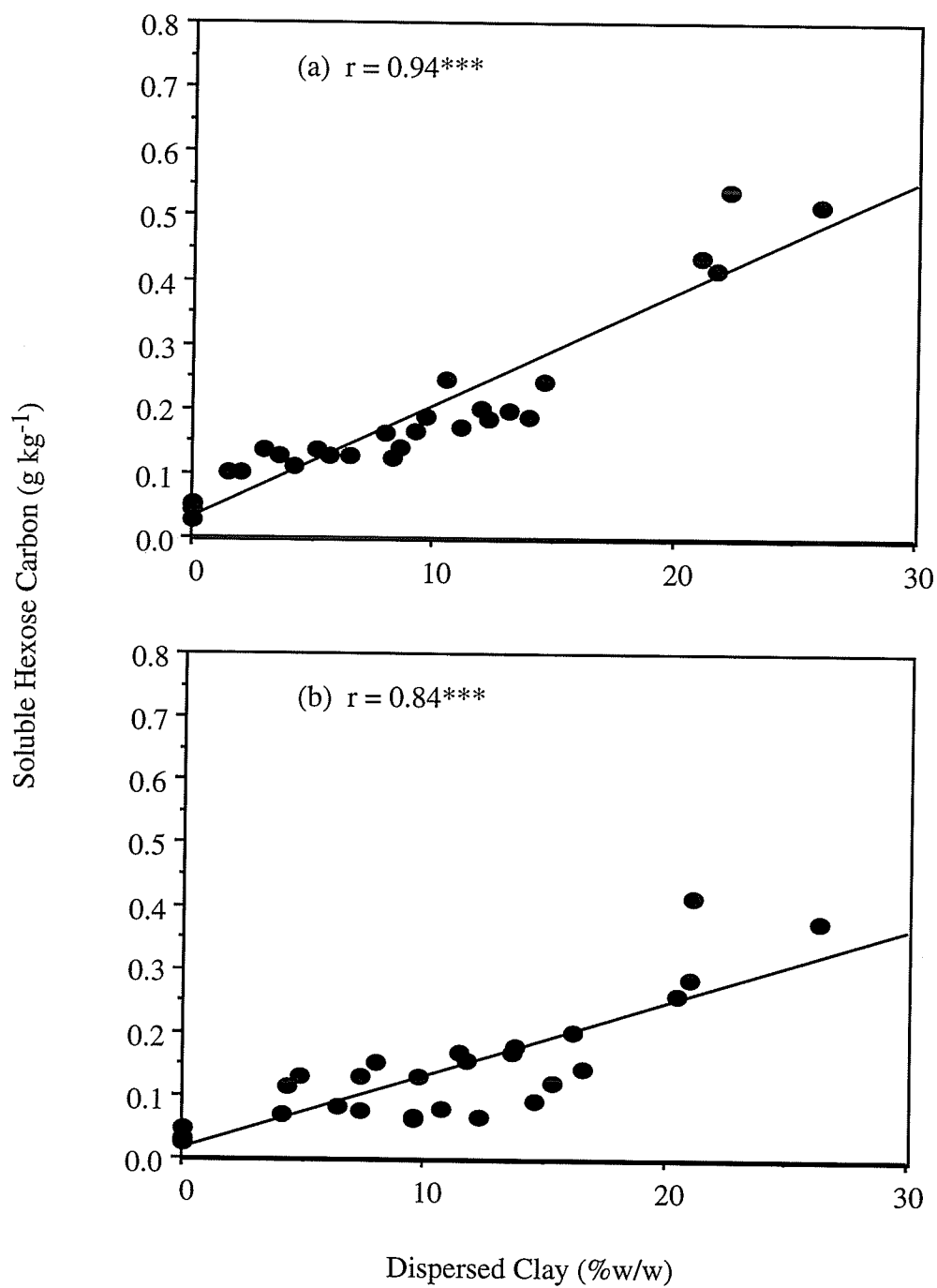


Figure 4.5. Correlation of solubilized hexose carbon with dispersed clay for ASF of the Pr site; (a) 0-7 cm depth; (b) 7-14 cm depth (\*\*\*) indicates correlation significant at  $P < 0.001$ ).

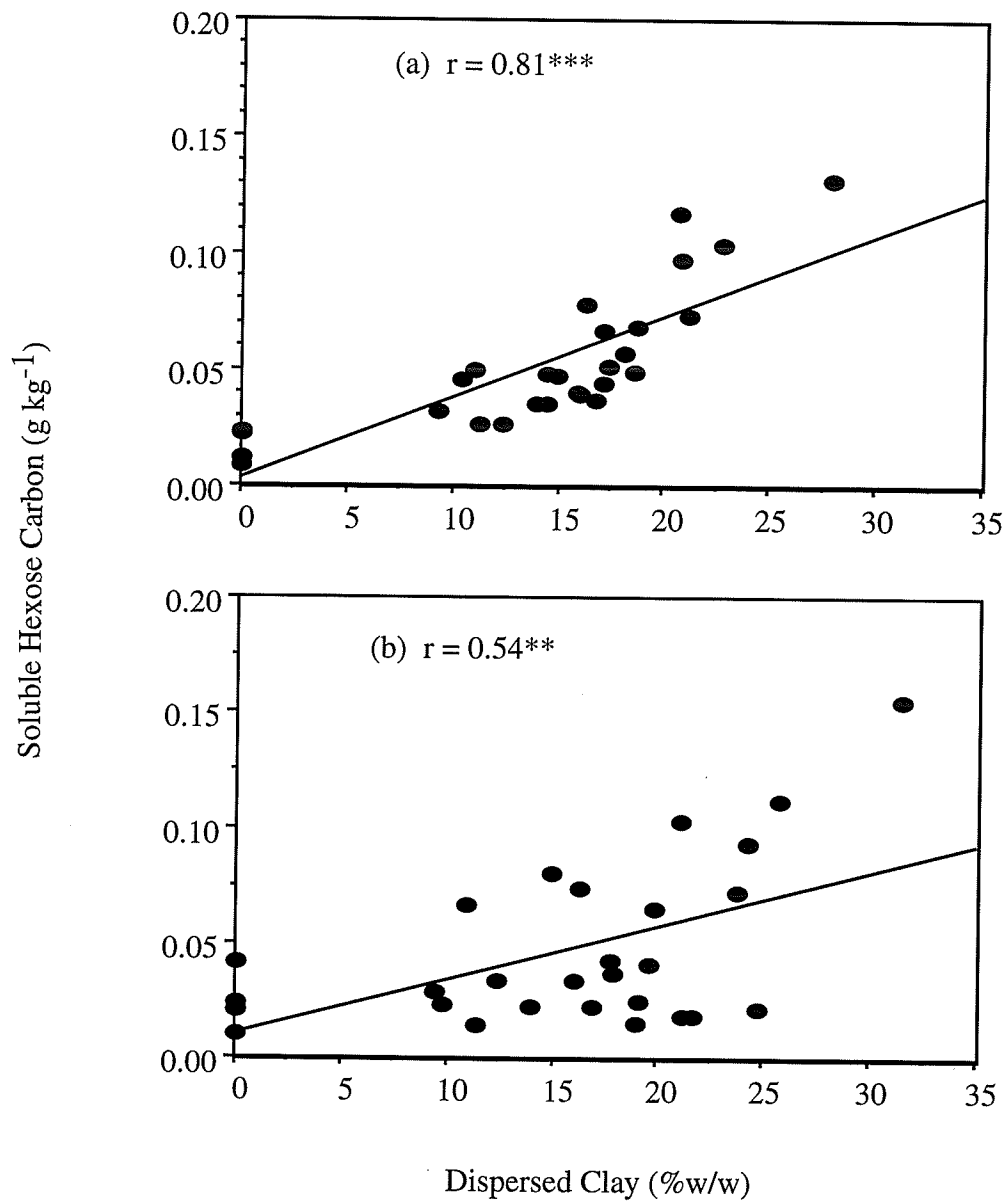


Figure 4.6. Correlation of solubilized hexose carbon with dispersed clay for ASF of the C1 site; (a) 0-7 cm depth; (b) 7-14 cm depth (\*\* and \*\*\* indicate correlation significant at  $P < 0.01$  and  $P < 0.001$ , respectively).

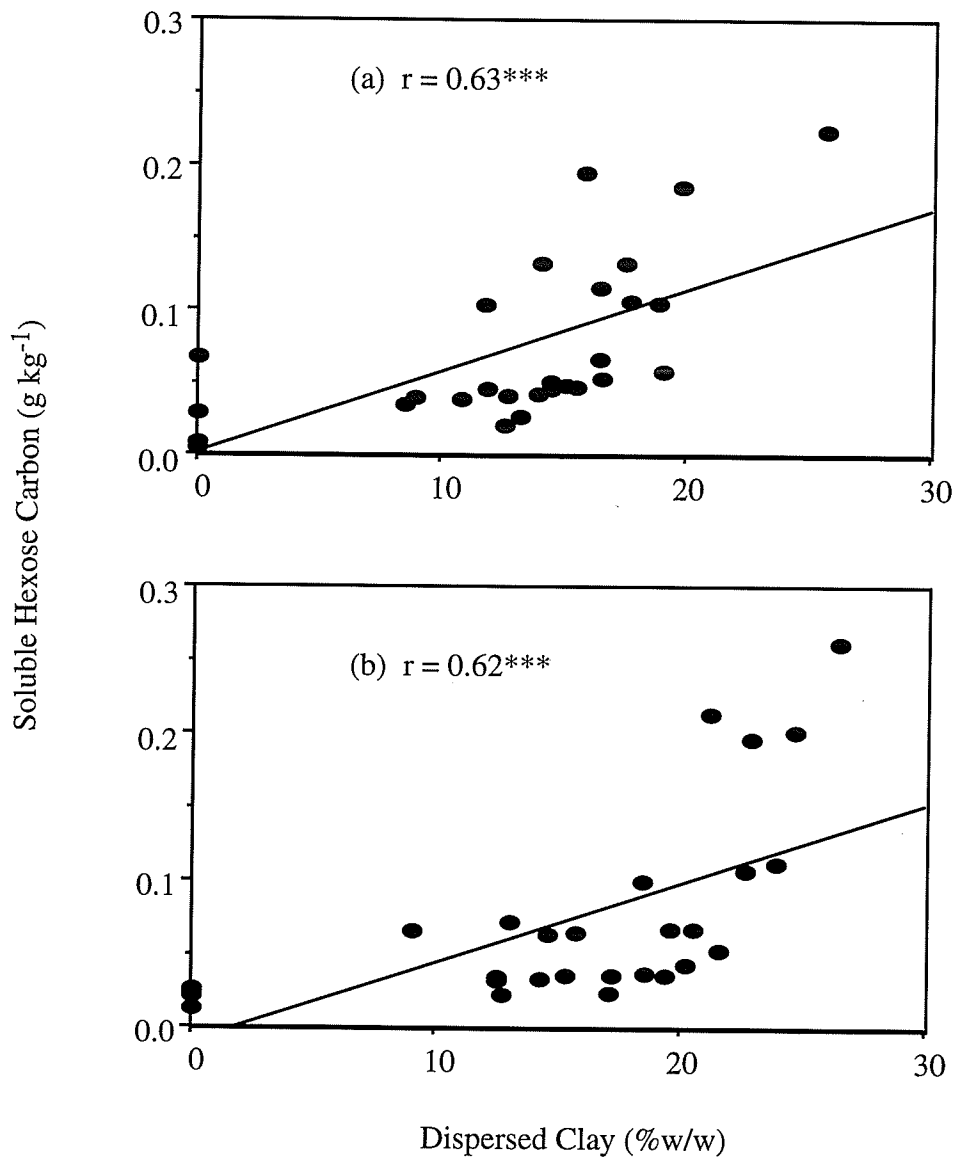


Figure 4.7. Correlation of solubilized hexose carbon with dispersed clay for ASF of the C2 site; (a) 0-7 cm depth; (b) 7-14 cm depth (\*\*\*) indicates correlation significant at  $P < 0.001$ ).

The correlation coefficients were generally lower for the cultivated sites. The poorer correlation in cultivated sites may imply that hexose is not as uniformly distributed throughout the aggregate as compared to prairie aggregates or that the hexose is retained within the aggregate by different means. Hence increasing exposed

Table 4.7. Hexose carbon as a percentage of total organic carbon and the ratio of non-hexose carbon to hexose carbon within four aggregate size fractions from the three study sites.

Site	Hexose C		Non-hexose C Hexose C	
	Depth		Depth	
	0-7 cm ( % of total organic C)	7-14 cm	0-7 cm	7-14 cm
<i>2.0-9.5 mm ASF</i>				
Pr	6.6	6.0	14.7	16.3
C1	4.6	4.0	21.1	24.4
C2	4.6	4.2	20.8	23.3
<i>0.85-2.0 mm ASF</i>				
Pr	5.5	5.3	17.4	17.9
C1	4.3	6.0	22.5	15.9
C2	4.4	4.7	21.5	20.3
<i>0.25-0.85 mm ASF</i>				
Pr	6.2	5.8	15.8	16.1
C1	3.9	5.4	24.8	17.6
C2	4.8	5.0	19.9	19.1
<i>&lt; 0.25 mm ASF</i>				
Pr	6.8	6.5	13.9	14.3
C1	4.4	5.4	21.7	17.6
C2	5.0	5.1	19.1	18.9
LSD <sub>0.05</sub> <sup>†</sup>	0.9	0.9	3.3	ns
LSD <sub>0.05</sub> <sup>‡</sup>	ns	ns	ns	ns

<sup>†</sup> LSD among sites within a given ASF.

<sup>‡</sup> LSD among ASF within a given site.

Table 4.8. Correlation coefficients for the correlation of solubilized hexose with dispersed clay for individual ASF ( $P < 0.05$ ).

Site	ASF (mm)				All ASF
	2.0-9.5	0.85-2.0	0.25-0.85	< 0.25	
0-7 cm depth					
Pr	0.94	0.97	0.97	0.95	0.94
C1	0.80	0.64	0.80	0.95	0.81
C2	0.69	0.49	0.58	0.82	0.63
7-14 cm depth					
Pr	0.77	0.81	0.97	0.97	0.84
C1	0.87	0.58	0.84	0.62	0.54
C2	0.79	0.50	0.47	0.84	0.62

surface area may not necessarily result in an increase in hexose solubilization in cultivated aggregates. The dispersion of the data in Figures 4.6 and 4.7 indicates a greater variability in the amount of hexose solubilized upon dispersion of a given amount of clay for cultivated aggregates relative to prairie aggregates. The concept of different microhabitats within soil aggregates may explain the poorer relation between dispersed clay and solubilized hexose. This concept, as proposed by Hattori and Hattori (1976), suggests that the inner part of a soil aggregate is more favorable for microbial existence than the outer part. This leads to differences in microbial populations between various regions of an aggregate and as a result differences in the location of microbial metabolites such as polysaccharides.

Application of  $1500 \text{ kJ L}^{-1}$  ultrasonic energy was assumed to result in maximum clay dispersion. This level of energy has been shown to be more effective in dispersing clay than treatment with hydrogen peroxide (Gregorich et al. 1988). The amount of hexose solubilized at this energy level varies among the three sites (Table 4.6). This hexose represents that which could be solubilized upon complete dispersion of the aggregate. In both depths, the aggregates obtained from the prairie contained higher amounts of soluble hexose than the aggregates from the cultivated sites. The aggregates from the C1 site contained less soluble hexose than aggregates from the C2 site. The percentage of hexose that was solubilized at  $1500 \text{ kJ L}^{-1}$  ranged from 9.9 to 17.4, 4.9 to 9.8, and 7.7 to 14.5 for the Pr, C1 and C2 sites, respectively. Therefore, the aggregates of the prairie soils not only possessed more hexose but a greater proportion of this hexose can be solubilized. The reduction in hexose content of aggregates upon cultivation is accompanied by a decline in the proportion of soluble hexose within the aggregate.

### Regression Analysis

To determine whether hexose carbohydrate was significantly related to the dispersion of clay from soil aggregates by ultrasonic dispersion, regression of hexose vs.  $E_{1/2}$  was conducted for the three sites for the 0-7, 7-14 and 0-14 cm depths.

Previous research has shown that carbohydrate is significantly correlated with mean weight diameter of water stable aggregates (Angers and Mehuys 1989). However, the effect of carbohydrate on the dispersibility of clay from soil aggregates as a function of applied energy has not previously been studied. The use of ultrasonic vibration in this study permits the evaluation of clay dispersion as a function of applied ultrasonic energy in relation to hexose carbohydrate content of the aggregates.

Hexose was significantly related to  $E_{1/2}$  within all depths (Table 4.9, Figure 4.8). In the 0-7 cm depth, hexose, soluble hexose, and the difference between hexose and soluble hexose (non-soluble hexose) accounted for 80, 67 and 81% of the variation in  $E_{1/2}$  values, respectively. However, in the 7-14 cm depth these values dropped to 59% for hexose and 63% for non-soluble hexose. Soluble hexose was not significantly related to  $E_{1/2}$  value in the 7-14 cm depth (Table 4.9). If the data for both depths were pooled, the variation in  $E_{1/2}$  value explained by hexose, soluble hexose and non-soluble hexose was 71, 48 and 72%, respectively (Table 4.9).

Table 4.9. Coefficients of determination for the regression of  $E_{1/2}$  value with hexose.

Independent Variable	Depth		
	0-7 cm	7-14 cm	0-14 cm
Hexose	0.80***	0.59**	0.71***
Soluble Hexose	0.67**	0.18ns†	0.48***
Non-soluble Hexose	0.81***	0.63**	0.72***

\*\* Regression significant at  $P < 0.01$

\*\*\* Regression significant at  $P < 0.001$

† Regression not significant at  $P = 0.05$



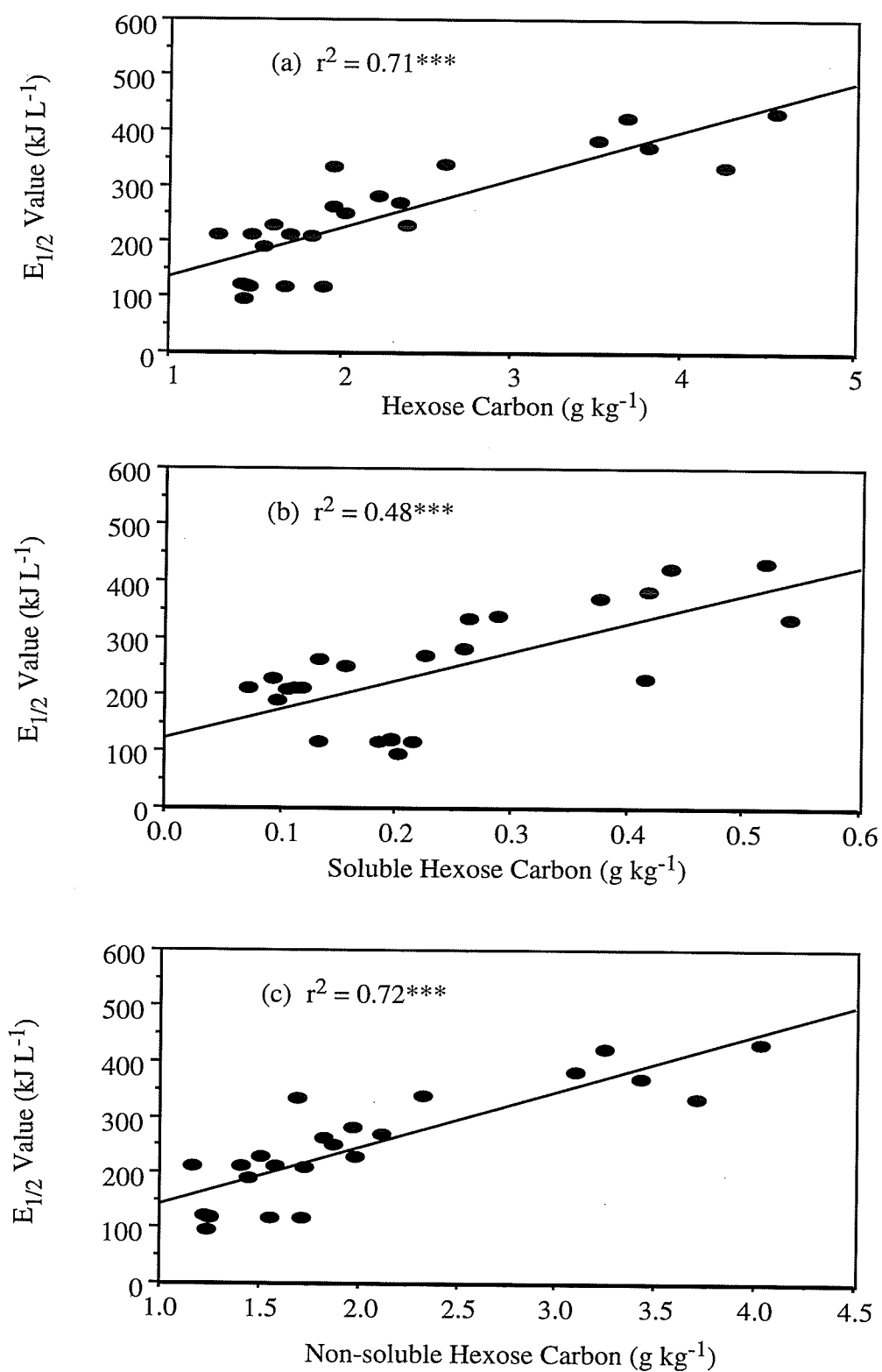


Figure 4.8. Regression of  $E_{1/2}$  value vs (a) hexose carbon; (b) soluble hexose carbon; (c) non-soluble hexose carbon.

The coefficient of determination was much lower for soluble hexose indicating that this portion of total hexose was not as strongly related to clay dispersibility within the aggregate. Hexose associated with soil surfaces following complete dispersion of the aggregate (hexose - soluble hexose) consistently showed a slightly higher coefficient of determination than soluble hexose and was able to explain the greatest amount of variation in dispersion of clay. This is consistent with the results of Roberson et al. (1991) that showed that aggregate stability was most closely related to "heavy-fraction" carbohydrate associated with soil particle surfaces. Therefore, only a portion of the total carbohydrate of soil aggregates may be responsible for aggregation.

The effect of other organic binding agents on dispersion of clay from aggregates must also be considered. The regression of  $E_{1/2}$  value as a function of organic carbon and non-hexose organic carbon (organic carbon - hexose carbon) yielded significant coefficients of determination (Table 4.10, Figure 4.9). Within the 0-7 cm depth organic carbon and non-hexose carbon accounted for 86 and 87% of the variation in  $E_{1/2}$  value. These values are greater than those of hexose and non-soluble hexose in Table 4.9. Therefore within this surface 7 cm depth there are other organic binding agents which may also contribute to aggregate stability. However, in the 7-14 cm depth the regression of  $E_{1/2}$  value with organic carbon and non-hexose organic carbon yielded much lower coefficients of determination than those obtained for the regression of  $E_{1/2}$  with hexose. Thus, hexose and non-soluble hexose were better able to explain variation in  $E_{1/2}$  value in the 7-14 cm depth. Over both depths, the amount of variation in  $E_{1/2}$  explained by organic carbon and non-hexose organic carbon amounted to 65 and 64%, respectively. Once again, hexose and non-soluble hexose were better able to explain variation in  $E_{1/2}$  value over both depths ( $r^2 = 0.71$  and  $0.72$ , respectively; Table 4.9).

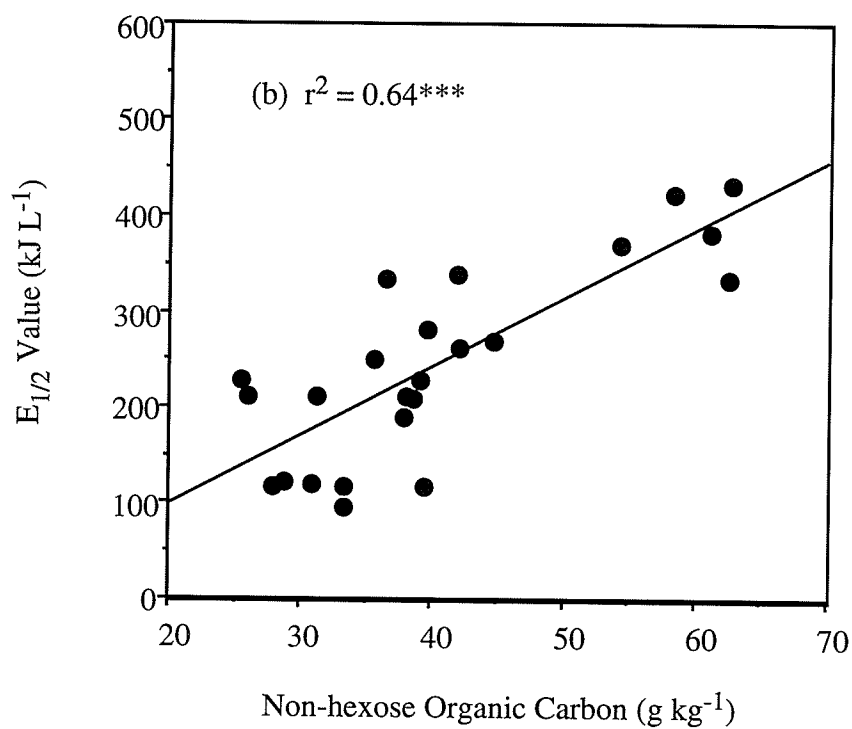
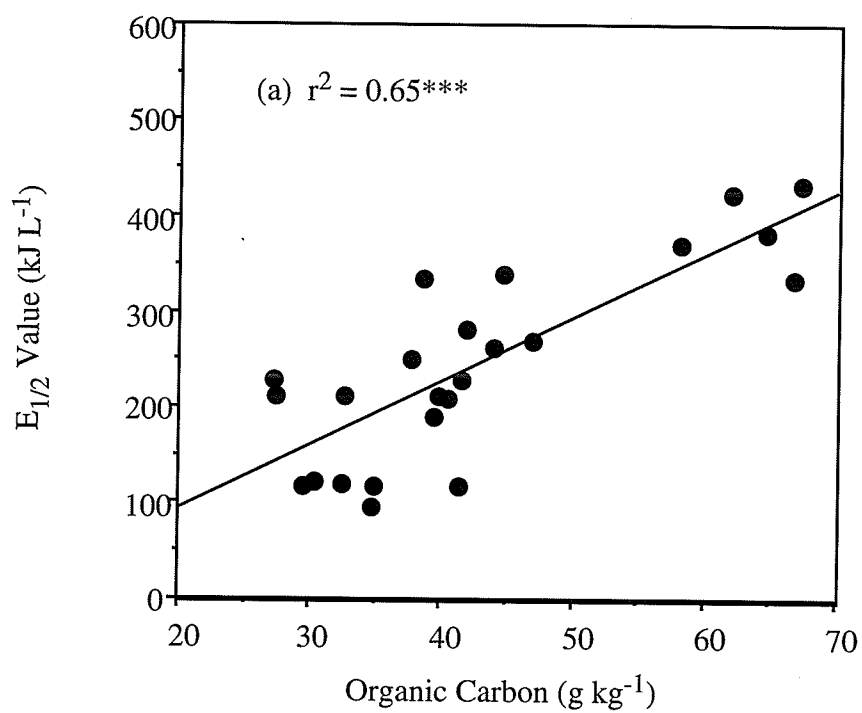


Figure 4.9. Regression of  $E_{1/2}$  value vs (a) organic carbon; and (b) non-hexose organic carbon.

Table 4.10. Coefficients of determination for the regression of  $E_{1/2}$  value with organic carbon, non-hexose organic carbon and clay content of the aggregate size fraction ( $A_{\max}$ ).

Independent Variable	Depth		
	0-7 cm	7-14 cm	0-14 cm
Organic carbon	0.86***	0.53**	0.65***
Non-hexose organic carbon	0.87***	0.52**	0.64***
$A_{\max}$	0.31 ns†	0.03 ns	0.11 ns

\*\* Regression significant at  $P < 0.01$

\*\*\* Regression significant at  $P < 0.001$

† Regression not significant at  $P = 0.05$

A closer examination of the data in Figure 4.8 reveals five data points which exhibited low  $E_{1/2}$  values (approximately  $120 \text{ kJ L}^{-1}$ ) for the amount of hexose contained within the aggregate. These points correspond to macroaggregates from the C2 site. These macroaggregates possess hexose and other organic material (Figure 4.9) which apparently do not contribute to the ability of the aggregates to resist clay dispersion by sonification. The presence of carbohydrate within soil aggregates which does not correlate with aggregate stability measurements has been documented by other researchers. Baldock et al. (1987) found no significant correlations between either the total carbohydrate content or the content of individual sugars and the stability of aggregates in soils from different cropping treatments. Baldock and Kay (1987) found that periodate treatment did reduce aggregate stability but the structural deterioration induced by periodate did not appear to account for the large differences in aggregate stability observed across cropping sequences. Webber (1965) stated that the seasonal variation in the content of polysaccharides and aggregate stability showed a marked out-of-phase relationship. These three studies indicate that the presence of carbohydrate does not necessarily result in increased aggregate stability, but rather, it is possible for carbohydrate to be present and yet not contribute to aggregate stability. The observation that periodate oxidation affects soil aggregate stability to varying degrees

indicates that carbohydrate may not behave similarly in all soils (Cheshire et al. 1984). However, many other studies (Rennie et al. 1954; Chesters et al. 1957; Cheshire et al. 1983,1984; Angers and Mehuys 1989) have shown carbohydrate to be correlated with aggregate stability and it is generally accepted that carbohydrate is active in aggregate stabilization (Martin 1971; Oades 1984). The present study indicates that exceptions do occur.

Removal of the data points for the C2 macroaggregates (in Figures 4.8 and 4.9) results in an improvement in the  $r^2$  values obtained (Figures 4.10 and 4.11). All ASF of the prairie site and the C1 site as well as the microaggregates of the C2 site exhibit a strong relationship between hexose content and resistance to clay dispersion by ultrasound. Both soluble and non-soluble hexose fractions are strongly related to  $E_{1/2}$  value; however, the non-soluble fraction is better able to explain variation in  $E_{1/2}$  values ( $r^2 = 0.76$ , Figure 4.10). Once again, this is consistent with the hypothesis of Roberson et al. (1991) who suggest that carbohydrates associated with particle surfaces (heavy-fraction carbohydrate) are more strongly related to aggregate stability than "light-fraction" carbohydrates. The heavy-fraction carbohydrates will contain both soluble and non-soluble fractions. The data of this study suggests that both fractions are related to dispersibility of clay but the non-soluble fraction is better able to explain variation in clay dispersion from aggregates.

The distribution of hexose within soil aggregates may influence the activity of hexose in the aggregation process. Swincer et al. (1969) state that "the distribution of the polysaccharides within and around aggregates is probably important, so that only a portion of an effective polymer may actually be controlling stability". With this in mind, the distribution of clay-associated hexose within aggregates was studied by subjecting aggregates from the 0-7 cm depth of the prairie and C2 site to sonification at 100 and 500 kJ L<sup>-1</sup>. The clay dispersed at each energy level was collected by repeated

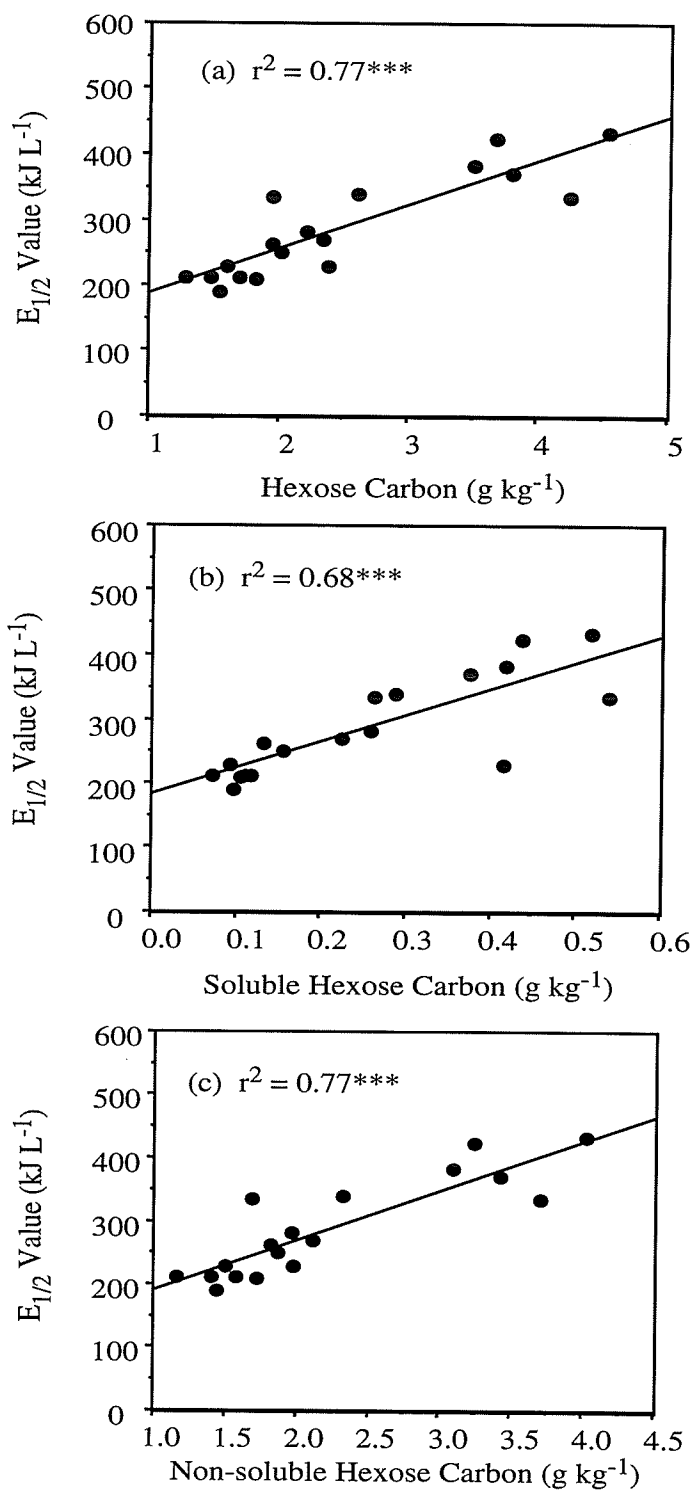


Figure 4.10. Regression of  $E_{1/2}$  value vs (a) hexose carbon; (b) soluble hexose carbon; and (c) non-soluble hexose carbon, with C2 macroaggregate data removed.

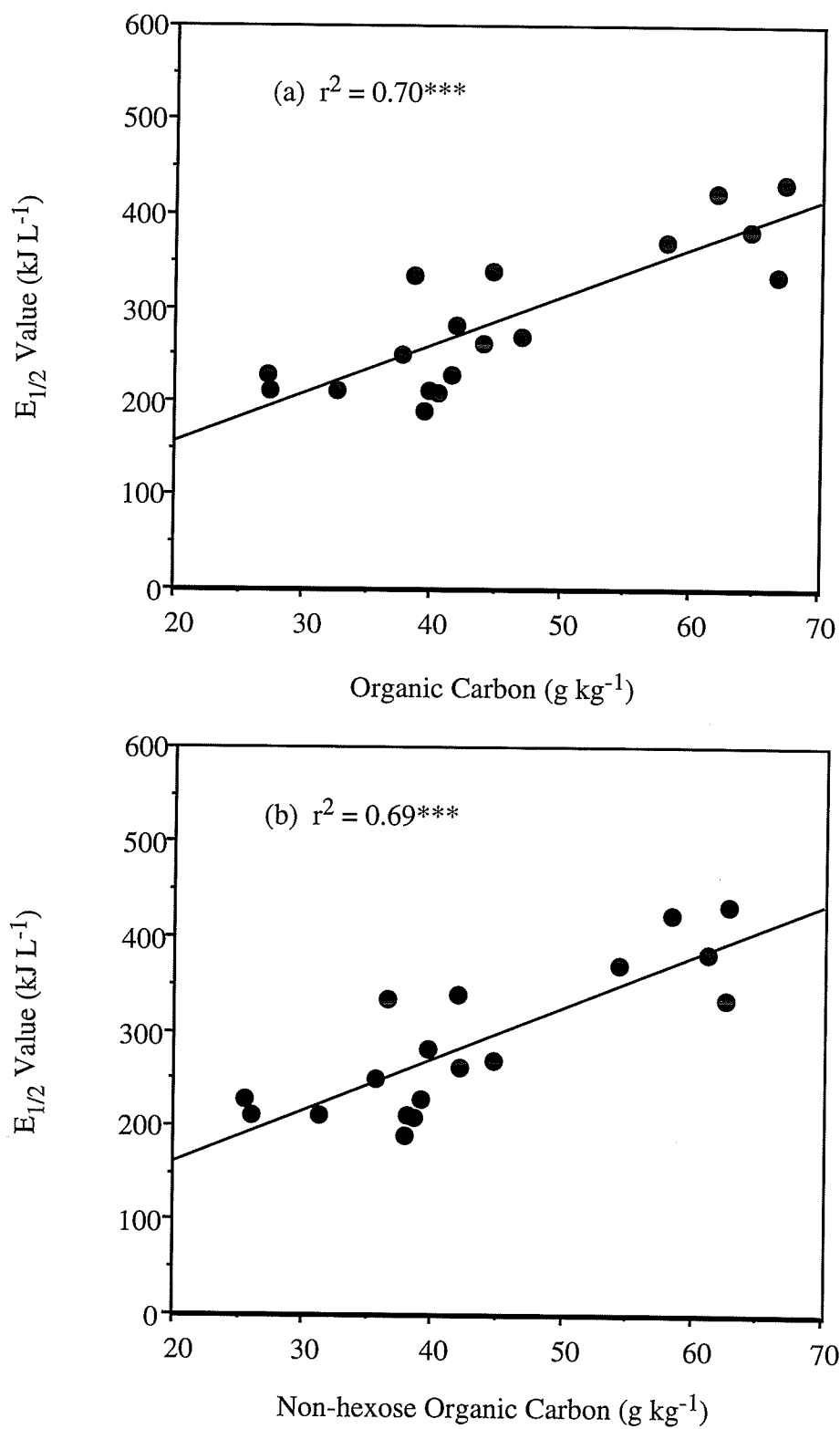


Figure 4.11. Regression of  $E_{1/2}$  value vs (a) organic carbon; and (b) non-hexose organic carbon, with C2 macroaggregate data removed.

sedimentation and decanting (Figure 4.1). The clay dispersed at  $100 \text{ kJ L}^{-1}$  represents clay which was retained within the aggregate at low energy levels and is referred to as "low-energy clay" in this study. The clay dispersed at  $500 \text{ kJ L}^{-1}$  represents clay retained within the aggregate at energy levels between 100 and  $500 \text{ kJ L}^{-1}$ . This clay is referred to as "high-energy clay". The concentration of hexose within the clay fraction was similar for the low and high energy clays within all ASF of the prairie soil (Table 4.11). The 0.85-2.0 mm ASF contained almost twice the amount of hexose per kg of clay than the other ASF. In all ASF, the concentration of clay-associated hexose was much less for the C2 site reflecting the overall decline of hexose within the whole aggregate. The concentration of hexose was similar for low and high energy clays within the 2.0-9.5 mm and 0.85-2.0 mm ASF of the C2 site. However, in the 0.25-0.85 mm and  $< 0.25 \text{ mm}$  ASF there were dissimilar amounts of hexose associated with the clay fraction: within the microaggregates there was a greater concentration of hexose associated with the high energy clays whereas the opposite was true for the 0.25-0.85 mm ASF.

Expressing the concentration of clay-associated hexose in terms of  $\text{g kg}^{-1}$  aggregate takes into consideration the amount of clay dispersed following aggregate disruption at 100 and at  $500 \text{ kJ L}^{-1}$  (Table 4.11). In prairie aggregates, a greater amount of hexose is associated with clays dispersed between 100 and  $500 \text{ kJ L}^{-1}$  compared to the cultivated aggregates. The prairie aggregates contain almost three times more hexose associated with clays retained within the aggregate at energy levels between 100 and  $500 \text{ kJ L}^{-1}$  (Table 4.11). The 2.0-9.5 and 0.85-2.0 mm macroaggregates of the C2 site exhibit similar amounts of hexose occurring in association with clays dispersed at  $100 \text{ kJ L}^{-1}$  and at  $500 \text{ kJ L}^{-1}$ . The 0.25-0.85 mm ASF of the C2 site contains more hexose associated with clays which are easily dispersed than hexose associated with clays retained at higher energy levels. The



Table 4.11. Hexose associated with the clay fraction dispersed at 100 kJ L<sup>-1</sup> and at 500 kJ L<sup>-1</sup> for all ASF within the 0-7 cm depth of the Pr and C2 sites.

Site	Energy Level (kJ L <sup>-1</sup> )		Energy Level (kJ L <sup>-1</sup> )	
	100	500	100	500
	(g kg <sup>-1</sup> clay)		(g kg <sup>-1</sup> aggregate)	
<i>2.0-9.5 mm ASF</i>				
Pr	4.60 (0.04)†	5.16 (0.24)	0.20 (0.02)	0.53 (0.03)
C2	3.96 (0.37)	4.08 (0.12)	0.35 (0.04)	0.40 (0.06)
<i>0.85-2.0 mm ASF</i>				
Pr	9.60 (0.16)	10.6 (0.8)	0.34 (0.01)	0.98 (0.04)
C2	5.20 (0.28)	4.60 (0.68)	0.35 (0.01)	0.36 (0.02)
<i>0.25-0.85 mm ASF</i>				
Pr	6.32 (0.32)	6.92 (1.12)	0.20 (0.01)	0.59 (0.02)
C2	3.24 (0.12)	0.99 (0.08)	0.25 (0.02)	0.08 (0.01)
<i>&lt; 0.25 mm ASF</i>				
Pr	4.48 (0.12)	4.36 (0.16)	0.18 (0.02)	0.51 (0.07)
C2	0.88 (0.08)	3.28 (0.28)	0.05 (0.004)	0.42 (0.004)

† Numbers in parentheses indicate standard error of the mean.

microaggregates of the C2 site exhibit a similar distribution as the prairie aggregates with more hexose associated with high energy clays. The data indicate that aggregates which exhibited greater  $E_{1/2}$  values (prairie aggregates and C2 microaggregates) tend to contain a greater proportion of hexose in association with clays which were dispersed at higher energy levels. These clays can be expected to be associated with structural units of lower hierarchical order such as clusters. The macroaggregates of the C2 site, which exhibited low  $E_{1/2}$  values despite similar amounts of hexose and organic carbon as the C1 site aggregates, possess less hexose associated with clays dispersed at higher energy levels and therefore a greater proportion of hexose associated with clays dispersed at low energy levels. This hexose associated with clays dispersed at low energy levels apparently did not contribute to stabilization of the C2 macroaggregates. Therefore, the distribution of hexose within the aggregate and the proportion of hexose

associated with clays retained at higher energy levels may be the key to understanding the action of carbohydrates in the stabilization process.

Polysaccharides associated with macroaggregates are transient in nature as periodate treatment of macroaggregates does not necessarily result in decreased macroaggregate stability (Mehta et al. 1960; Webber 1965; Tisdall and Oades 1980, 1982). Clays dispersed at  $100 \text{ kJ L}^{-1}$  are believed to be responsible for binding microaggregates into macroaggregates (Gregorich et al. 1988, 1989). The proportion of hexose associated with clays dispersed at  $100 \text{ kJ L}^{-1}$  is generally much less within the stable aggregates of this study and the presence of hexose alone does not indicate activity in macroaggregation. Tisdall and Oades (1982) state "It is unlikely that small quantities of polymers with chain lengths of a few hundred angstroms would be important in binding particles into aggregates with diameters of several millimeters". Therefore, the role of carbohydrate in macroaggregation may be indirect through stabilization of clusters which could in turn bridge microaggregates into macroaggregates (Tisdall and Oades 1979; Foster 1988; Dormaar and Foster 1991).

The greater proportion of hexose associated with clays dispersed at  $500 \text{ kJ L}^{-1}$  suggests that polysaccharides may be most active in microaggregation. Tisdall and Oades (1982) suggest strongly sorbed polymers such as polysaccharides may be responsible for microaggregate formation. These polysaccharides tend to be more persistent in nature due to stabilization by adsorption on clay surfaces and association with polyvalent cations (Martin and Richards 1969; Martin 1971). Clays dispersed from aggregates at  $500 \text{ kJ L}^{-1}$  are believed to be derived from breakdown of microaggregates (Gregorich et al. 1989). Disruption of aggregates by ultrasonic dispersion causes release of labile organic matter which is subsequently mineralized (Gregorich et al. 1989). An increase in the mineralization of clay-associated organic matter occurred following sonification at energy levels of 300 to  $500 \text{ kJ L}^{-1}$  (Gregorich

et al. 1989). These authors suggest that at these energy levels microaggregate breakdown occurs thus releasing physically protected labile organic material. They suggest the organic matter released at these energy levels and associated with the clay fraction may be sequestered polysaccharides. The occurrence of a greater proportion of hexose with clays dispersed at  $500 \text{ kJ L}^{-1}$  within stable aggregates supports the presence of sequestered carbohydrate within these aggregates. The physical protection of carbohydrates may be the result of flocculation and aggregation of clays via polysaccharide material. The formation of clay-organic matter complexes via polyvalent cation bridges has been proposed as the fundamental mechanism of microaggregation (Edwards and Bremner 1967). If this is so, an understanding of the interaction of polymer chains with exchangeable cations at clay surfaces is necessary to understand the mechanism by which polysaccharides bridge clay particles.

#### 4.4 Summary

This study has shown the effect of long-term cultivation on hexose carbohydrate content and dispersibility of clay within natural soil aggregates. Cultivation has reduced carbohydrate levels to approximately one-half the levels found within aggregates of a prairie soil. Continuous wheat management for the past 10 years following 70 years of cultivation has not returned carbohydrate levels to the same level as found in prairie aggregates.

The stability of the aggregates, as measured by ultrasonic dispersion of clay, was reduced under cultivation. The prairie aggregates possessed the greatest stability. The clay contained within the prairie aggregates was held much more strongly within the aggregate and therefore showed greater resistance to dispersion by ultrasonic vibration. The aggregates of the cultivated sites had lower  $E_{1/2}$  values indicating that clay was more easily dispersed from aggregates at lower ultrasonic energy levels than in

the adjacent prairie site. The clays within the cultivated aggregates therefore were held less strongly resulting in a greater release of clay at lower energy levels. The site which had been intensively tilled by discing throughout its history possessed the lowest  $E_{1/2}$  values suggesting that long-term tillage methods and practices may have an impact on the dispersibility of clay within soil aggregates. Subsequently, subjection of the cultivated sites to a continuous wheat rotation with minimum tillage for the past 10 years has not seen the return of aggregate stability as found under prairie. The dispersibility of the clay within cultivated aggregates remained much greater than aggregates under prairie even after continuous wheat management.

Aggregate stability was significantly related to hexose content of the aggregates. The hexose content of the aggregates was able to explain approximately 70 to 77% of the variation in  $E_{1/2}$  values. Hexose associated with surfaces, as opposed to hexose solubilized during sonification, was better able to explain variation in  $E_{1/2}$  values suggesting that carbohydrate strongly adsorbed to surfaces is the fraction of carbohydrate most responsible for aggregation of clays. However, non-hexose organic carbon was also significantly related to aggregate stability suggesting that other organic constituents also play an important role in stabilizing soil aggregates.

Clay-associated carbohydrate was not distributed uniformly throughout the aggregate in the most stable aggregates. Under prairie there was a greater proportion of hexose associated with clays which were held within the aggregate at energy levels between 100 and 500 kJ L<sup>-1</sup>. Approximately three times as much hexose occurred with these clays as with clays held within the aggregate at energy levels  $\leq 100$  kJ L<sup>-1</sup>. Aggregates with low stabilities possessed much less hexose associated with clays dispersed at the higher energy levels. Aggregates which were better able to resist dispersion of clay by sonification possessed a greater proportion of clay held within the aggregate at higher energy levels and a greater proportion of hexose associated with

these clays. It is possible that this hexose was responsible for bonding between clay particles and clusters thereby contributing to the resistance to dispersion by sonification. However, it is also possible that the hexose associated with these clays were merely adsorbed to clays which had been stabilized within the aggregate by some other means.

**CHAPTER 5****THE EFFECT OF IONIC SATURATION ON SEDIMENTATION OF  
MONTMORILLONITE IN THE PRESENCE OF A NEUTRAL  
POLYSACCHARIDE****5.1 Background**

The occurrence of carbohydrate associated with the clay fraction of soil aggregates suggests that clay-carbohydrate interactions are important in the aggregation of soil particles. Clay-carbohydrate interactions have been a source of interest ever since it has been established that carbohydrates are present within stable soil aggregates. The study of clay-carbohydrate interactions will provide insight into the factors which affect the adsorption of polymers effective in the aggregation process.

The adsorption of dextran polymers by montmorillonite has been well established by many researchers (Greenland 1963; Clapp et al. 1968; Parfitt and Greenland 1970ab; Olness and Clapp 1975; Chenu et al. 1987). The adsorption isotherms for dextran polymers generally are of the high-affinity type. These polymers interact strongly with montmorillonite surfaces possibly through the adsorption of many polymer segments or "trains". The adsorption is essentially irreversible since the likelihood is small that all adsorbed trains will be desorbed at the same time (Theng 1982). Maximum adsorption of dextran by Na-montmorillonite has been found to vary from 445 mg g<sup>-1</sup> (Olness and Clapp 1975) to as low as 25 mg g<sup>-1</sup> (Chenu et al. 1987) (Table 5.1). The wide range of adsorption maxima suggest that experimental conditions and source of clay affect dextran adsorption.

Adsorption of neutral dextran polymers by montmorillonite has been shown to depend on the molecular weight of the polymer. Generally, larger polymers are adsorbed to a greater extent than smaller ones (Parfitt and Greenland 1970b; Clapp and

Table 5.1. Dextran adsorption ( $2 \times 10^6$  molecular weight) on Na- and Ca-montmorillonite.

Clay	Adsorbed Dextran ( $\text{mg g}^{-1}$ )	Reference
Na-montmorillonite (Upton, Wyoming)	250	Parfitt and Greenland 1970b
Ca-montmorillonite (Upton, Wyoming)	100	Parfitt and Greenland 1970b
Na-montmorillonite (Clay Spur, Wyoming)	445	Olness and Clapp 1975
Na-montmorillonite (Source unknown)	25	Chenu et al. 1987
Ca-montmorillonite (Source unknown)	20	Chenu et al. 1987

Emerson 1972). Parfitt and Greenland (1970b) could not detect adsorption of dextran polymers of molecular weight 11,200 or 100,000 by Na- or Ca-saturated montmorillonite. However, a dextran of molecular weight  $2 \times 10^6$  was readily adsorbed. Clapp and Emerson (1972) found a direct relationship between the initial slope of the adsorption isotherm and the intrinsic viscosity of the polymer. Intrinsic viscosity of an uncharged polymer is directly related to its molecular weight, thus, the largest polymers showed the greatest affinity for Upton montmorillonite. If adsorption is related to the probability of polymer segments contacting the clay surface (Theng 1982), it is reasonable to expect larger polymers to be adsorbed to a greater extent than lower molecular weight polymers. An increase in adsorption with increased molecular weight has been shown for polyethylene glycol adsorption on Ca-montmorillonite (Parfitt and Greenland 1970a) (Table 5.2). The increase in free energy of adsorption ( $-\Delta G$ ) with

increasing molecular weight indicated stronger adsorption of larger polymers by Ca-montmorillonite.

Table 5.2. Thermodynamic data for the adsorption of polyethylene glycols by Ca-montmorillonite (from Parfitt and Greenland 1970a).

Molecular weight	$-\Delta G$	$-\Delta H$	$\Delta S$
	-----( $\text{cal mol}^{-1}$ )-----		(entropy units)
200	1890	1960	-0.2
300	2070	1470	2.0
400	2340	1500	2.8
600	3340	0	11.1

Dextran adsorption is also influenced by the nature of exchangeable cation present on the exchange complex (Table 5.3). Clapp and Emerson (1972) suggest that initial adsorption of polysaccharides could occur by hydroxyl groups displacing water molecules surrounding exchangeable cations as has been shown for alcohols (Dowdy and Mortland 1967). Adsorption of polyethylene glycol by montmorillonite was shown to be the result of water desorption (Parfitt and Greenland 1970a). The adsorption energy was shown to arise primarily from an increase in translational entropy associated with the desorption of water molecules (Table 5.2). Free energy of adsorption of polyethylene glycol on montmorillonite became less negative with an increase in the polarizing power of the cation (Table 5.3). Parfitt and Greenland (1970a) state: "If ion dipole interactions were controlling the reaction, then the more polarizing cations would cause stronger adsorption and the reverse order would be obtained". Direct interaction between the exchangeable cations and the polymer molecule would not be responsible for adsorption, presumably because the cations retain their hydration shells. Parfitt and Greenland (1970a) suggest that interaction between the ether oxygen of the polymer and water molecules in the primary hydration shell of the exchangeable cation was



responsible for the adsorption. A favourable contribution to the free energy of adsorption arises from the increase in entropy upon displacement of water. The initial slope of dextran adsorption isotherms decreased as more strongly polarizing cations (e.g.  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ ) were present on the exchange (Parfitt and Greenland 1970b). Displacement of water molecules around more strongly polarizing cations will be more difficult and hence the affinity of the polymer for the clay is not as strong. In other words, a Na-saturated clay should adsorb more than a Ca-saturated clay (Table 5.1). Therefore, the nature of the hydration shell of the cation and the ability of the polymer to compete with water molecules for adsorption sites will determine the affinity of the polymer for the clay. This would also explain why larger molecular weight polymers are adsorbed to a greater extent than smaller molecular weight polymers since the larger polymer is better able to compete for adsorption sites.

Table 5.3. Thermodynamic data for the adsorption of polyethylene glycol (molecular weight 300) by montmorillonite saturated with different cations (from Parfitt and Greenland 1970a).

Cation	$-\Delta G$ -----( $\text{cal mol}^{-1}$ )-----	$-\Delta H$	$\Delta S$ (entropy units)
$\text{Cs}^+$	2920	0	9.7
$\text{Na}^+$	2280	860	4.6
$\text{Ca}^{2+}$	2070	1470	2.0
$\text{Al}^{3+}$	1920	2100	-0.6

X-ray diffraction studies of polysaccharide-montmorillonite complexes have found that intercalation of Na-, Ca-, and Al-saturated Upton montmorillonite was possible (Parfitt and Greenland 1970b). However, intercalation of Ca-montmorillonite (unknown source) with dextran did not occur in the studies conducted by Chenu et al. (1987). This would explain the low adsorption maxima found for dextran by Chenu et

al. (1987). Intercalation of Na-saturated Clay Spur montmorillonite has been documented by Olness and Clapp (1975). Thus a greater amount of dextran was adsorbed in their study (Table 5.1). Obviously the source or nature of montmorillonite has an impact on adsorption characteristics of dextran.

Chenu et al. (1987) studied the adsorption of dextran and scleroglucan on montmorillonite. Using electron microscopy, they could see no modification of the clay fabric in the presence of dextran but observed a network of "organo-mineral associations" in the presence of scleroglucan. However, this alone does not indicate that dextran is not involved in flocculation of montmorillonite but rather the orientation of the clay particles differed for the two polymers.

This study was conducted to determine whether a flexible random coil polymer such as dextran is capable of facilitating flocculation of montmorillonite. Dextran is a glucose polymer linked by  $\alpha(1\rightarrow6)$  glycosidic bonds. The nature of this linkage permits free rotation about the three bonds of the glycosidic linkage (Figure 5.1). A further objective of this study was to determine whether two dextran polymers of different molecular weight were able to cause flocculation of montmorillonite saturated with either Ca or Mg.

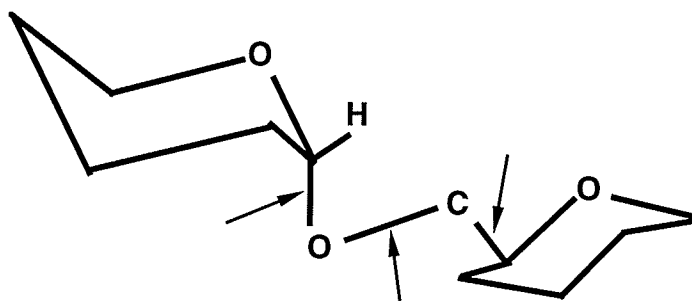


Figure 5.1.  $\alpha(1\rightarrow6)$  glycosidic linkage of dextran with arrows indicating three bonds of rotation.

## 5.2 Materials and Methods

Crook County Na-montmorillonite from Wyoming U.S.A (SWy-1) was obtained from the Source Clays Repository of the Clay Minerals Society, Columbia, Missouri. A bulk sample was dispersed using a laboratory homogenizer. The clay fraction was fractionated by repeated sedimentation and decantation. The clays were saturated with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  by addition of 0.6 M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  or 0.6 M  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . This was repeated five times to ensure complete saturation of the clays. Excess salt was removed by washing with deionized water until no positive test for chloride could be observed using 0.01 M  $\text{AgNO}_3$ .

Two dextran polymers were obtained from Pharmacia (Sweden). These polymers had a molecular weight of approximately 500,000 (T500) and  $2 \times 10^6$  (T2000).

The flocculation study was conducted using 15-mL centrifuge tubes. Sufficient clay was obtained from the stock suspensions and added to the centrifuge tubes to ensure a 2% concentration in a 10-mL final volume. The pH of the stock solution was lowered to 7.0 with dilute HCl. The dextran polymers were solubilized in deionized water so that an appropriate volume of the solution would deliver pre-determined amounts of polymer. Polymer/clay ratios of 0.001, 0.002, 0.01, 0.02, 0.1, and 0.2 (w/w) were prepared by simultaneously mixing the clay suspension with the appropriate volume of dextran solution. A control was also prepared with no polymer. The final volume was made to 10 mL and the tubes were gently shaken for 1 h to ensure thorough mixing of clay and polymer. The tubes were then set aside in a laboratory to allow sedimentation to begin. The temperature of the room remained at  $22^\circ\text{C} \pm 1^\circ\text{C}$ .

A 2% clay suspension was used because preliminary investigations showed that the boundary between the clear supernatant and clay was not distinct for clay suspensions with a concentration  $< 2\%$ . Calipers were used to measure the depth of the

sedimentation; the distance from the top of the clear supernatant to the top of the sedimenting clay was measured. Measurements were taken every 24 h. The depth of sedimentation was used to infer the extent of flocculation of the suspension. It was assumed that the larger flocs would sediment more quickly than non-flocculated clay particles.

The effect of coagulation on the flocculation of montmorillonite by the T500 dextran was studied by adding 0.01 M  $\text{CaCl}_2$  or 0.01 M  $\text{MgCl}_2$  to the clay-dextran complexes. This was accomplished in one of two manners. In the first case, the clay-dextran mixtures were prepared as described above. However, following the one-hour shaking time, the salt was added to the mixture and the tubes were shaken again for one hour. Thus the coagulant was added after the flocculant. In the second case, the salt was added to the clay suspension prior to addition of the polymer. In this case, the coagulant was added before the flocculant. Therefore, this study observed the effect of the presence of a coagulant and the effect of the order of addition of a coagulant and flocculant.

Surface area measurements using the EGME method were conducted on air-dried clay ground to pass a 100 mesh sieve (Carter et al. 1986). Cation exchange capacity was determined by saturating the exchange with Ca and displacing with Mg (Table 5.4).

Table 5.4. Cation exchange capacity and specific surface area of Crook County clay.

CEC	95 cmol(+) $\text{kg}^{-1}$	
Specific surface area:	Mean ( $10^3 \text{ m}^2 \text{ kg}^{-1}$ )	S.E. ( $10^3 \text{ m}^2 \text{ kg}^{-1}$ ) <sup>†</sup>
Ca-saturated	743	3
Mg-saturated	679	9

<sup>†</sup> Standard error of the mean of two replicates.

### 5.3 Results and Discussion

The sedimentation of montmorillonite was influenced by the presence of the T500 dextran polymer (Figure 5.2). Ca-saturated Crook County montmorillonite sedimented at a faster rate than the control when the polymer/clay ratio was  $\leq 0.01$  (or 1% polymer by weight). The curves in Figure 5.2 reach a plateau at polymer/clay ratios of 0.01 or less indicating that polymer at a concentration of 0.1% was able to cause flocculation to the same extent as a polymer at 1%. A point was reached where additional polymer no longer enhanced the sedimentation of the clay. This occurred at a polymer/clay ratio of 0.02 or less (or 2% polymer by weight). Within the first 72 h of sedimentation, the polymer at a polymer/clay ratio of 0.02 had only a slight positive effect on the depth of sedimentation relative to the control. However, after 96 h the polymer at a polymer/clay ratio of 0.02 caused increased sedimentation. Within the first 72 h of sedimentation, the polymer at ratios of 0.1 and 0.2 resulted in similar sedimentation depths as the control.

There was essentially no flocculation of the clay when  $\text{Mg}^{2+}$  was the exchangeable cation (Figure 5.2). These results for Mg-saturated montmorillonite contrast strongly with those for the Ca-montmorillonite, indicating that the polymer-clay interaction was affected by the exchangeable cation. The reason for this difference may be two-fold. First, it is possible that the affinity of the polymer for the clay surface was reduced by the presence of the more strongly polarizing Mg cations as discussed by Parfitt and Greenland (1970a). Secondly, it is also possible that polymer adsorption on the Mg-saturated clay resulted in greater collapse of the polymer on the surface, resulting in shorter and fewer loops and tails extending away from the surface and thus flocculation would be inhibited.

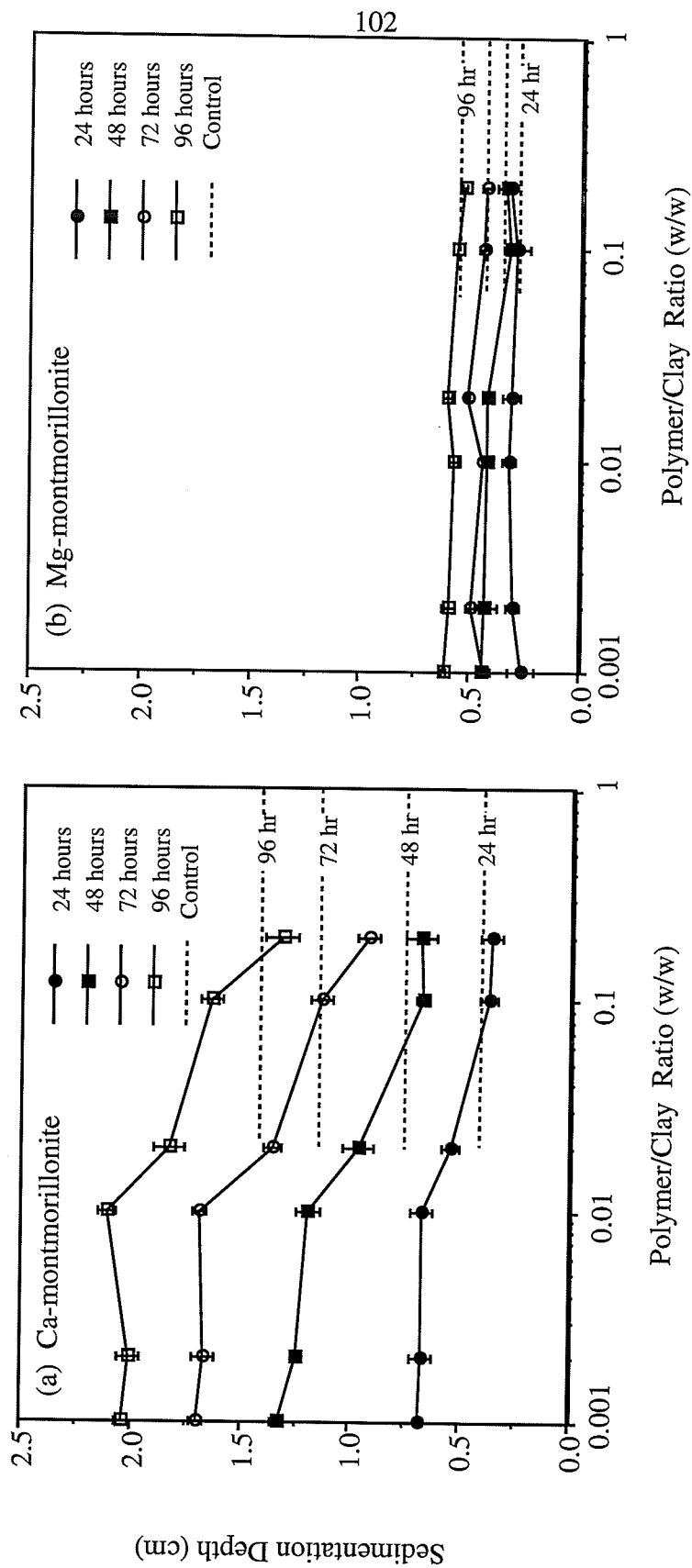


Figure 5.2. Sedimentation of (a) Ca-saturated montmorillonite; and (b) Mg-saturated montmorillonite, in the presence of dextran (T500) at various polymer/clay ratios (w/w).

Addition of the T2000 dextran polymer to Ca-saturated Crook County montmorillonite also resulted in enhanced sedimentation of the clay (Figure 5.3). The same tendency towards increased sedimentation at polymer/clay ratios of 0.01 or less occurs with the T2000 polymer. However, the data are somewhat different from that of the T500 dextran in that an increase in sedimentation at a polymer/clay ratio of 0.1 was evident. The depth of sedimentation was much less for a polymer/clay ratio of 0.2 and was less than or equal to that of the control.

The T2000 dextran did not cause flocculation of the Mg-saturated clay. The presence of Mg on the exchange sites inhibited the flocculation of this clay as it did for the smaller T500 dextran polymer.

The data for the T500 dextran polymer was typical of colloid-polymer interactions. Polymers have been used for industrial purposes as either flocculants ("stickers") or stabilizers ("bumpers"). The factor that determines whether a polymer acts as a bumper or a sticker is the concentration of polymer relative to that of the colloidal particles. If the polymer concentration is too high, the colloidal particles become saturated with the polymer and an osmotic pressure builds up between colloidal particles (Lafuma et al. 1991). In this way the colloidal particles are stabilized and the polymer acts as a bumper keeping the particles in a dispersed state. Repulsive interactions between interacting polymer loops and tails will also contribute to stabilization of the clay suspension. At a lower polymer concentration, the colloidal particles are no longer saturated and the buildup of osmotic pressure is insufficient to stabilize the suspension. If polymer loops and tails extend beyond the electrostatic barrier between charged colloidal particles, then flocculation will occur (Lafuma et al. 1991). The distance over which the electrostatic barrier extends for clay particles depends on the thickness of the diffuse double layer. Therefore, polymer size and the

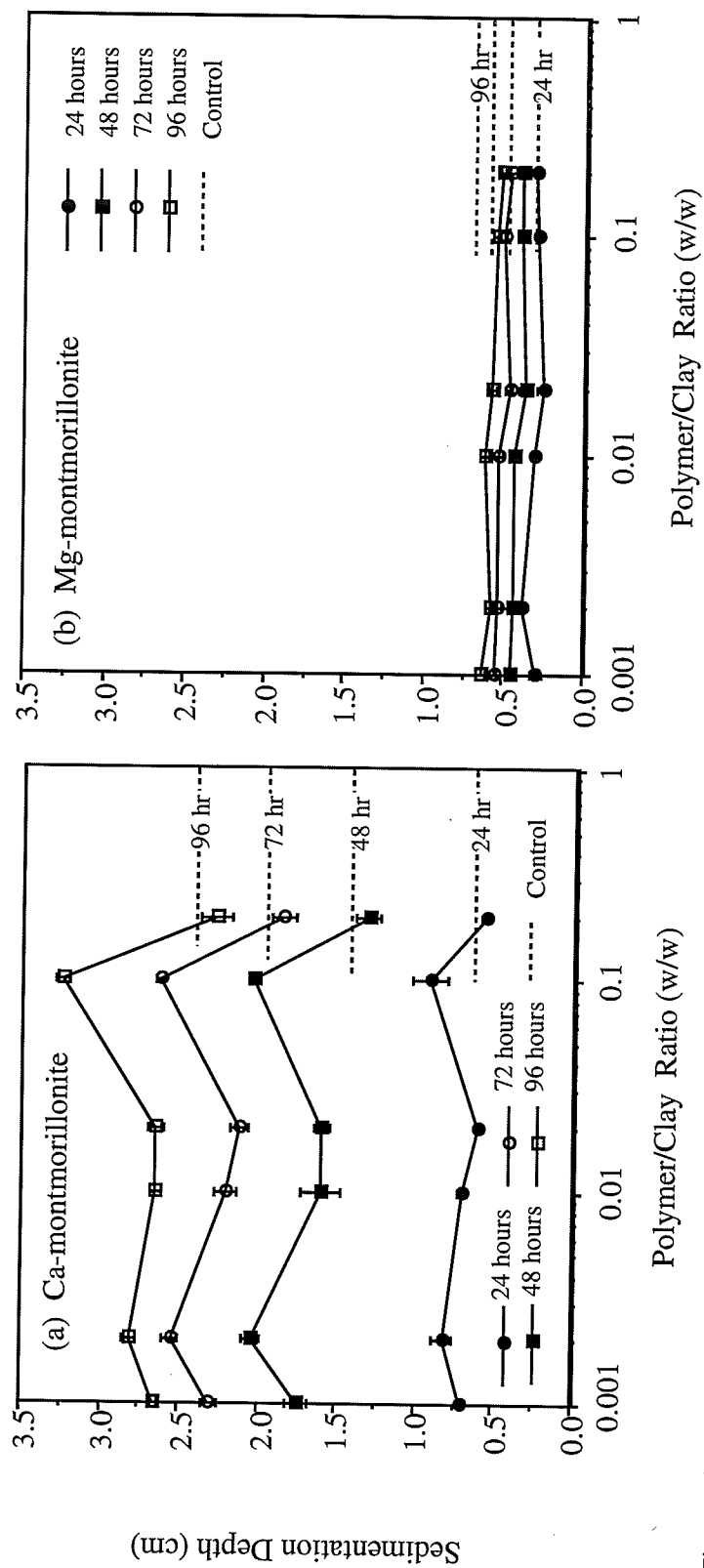


Figure 5.3. Sedimentation of (a) Ca-saturated montmorillonite; and (b) Mg-saturated montmorillonite in the presence of dextran (T2000) at various polymer/clay ratios (w/w).



length of loops and tails as well as thickness of the diffuse double layer will determine if flocculation occurs at a given polymer concentration.

Within the first 96 h, the presence of the T500 dextran at polymer/clay ratios of 0.1 and 0.2 resulted in equal or less sedimentation than the Ca-saturated control (Figure 5.2). If all the polymer was adsorbed, it would correspond to a polymer concentration of 100 and 200 mg g<sup>-1</sup> clay, respectively. This is the maximum dextran adsorbed by Ca-saturated Upton montmorillonite documented by Parfitt and Greenland (1970b). If the Ca-saturated montmorillonite is saturated with polymer at these concentrations, then the absence of flocculation relative to the control would be expected according to the reasoning of Lafuma et al. (1991) as discussed previously. However, it is likely not all of the polymer was adsorbed at these concentrations. The polymer/clay ratio at which flocculation occurred was 0.01, or 10 mg g<sup>-1</sup> clay. At this concentration there is ten times less polymer present than at the adsorption maximum found by Partitt and Greenland (1970b); however, the polymer at this concentration enhanced the depth of sedimentation of the Ca-saturated montmorillonite. This was also true for polymer/clay ratios of 0.001 and 0.002 corresponding to 1 and 2 mg g<sup>-1</sup> clay, respectively. Rennie et al. (1954) were able to show an increase in aggregation with addition of only 0.02% (w/w) of a polysaccharide produced by *Agrobacterium radiobacter*. Most microbial polysaccharides cause an increase in aggregation at concentrations of only 0.02 to 0.2% (w/w) (Clapp et al. 1962; Martin and Richards 1969; Martin 1971). Relative to the control, enhanced sedimentation in this study occurred at polymer concentrations of 0.1 to 1% (w/w). The slightly higher polymer concentrations that induced sedimentation may be attributed to the addition of polymer directly to a clay suspension whereas in the work cited previously polymer was added directly to soil.

Apparently, the T500 polymer was adsorbed in such a configuration that loops and tails extended far enough out from the surface of clay particles to overcome the

electrostatic barrier between the particles. Complete collapse of positively charged polymers are believed to occur upon adsorption (Theng 1982). However, uncharged polymers, such as dextran, are adsorbed with only part of the polymer chain attached to the surface. The adsorbed portion usually is 30 to 40% of the total number of polymer segments (Theng 1982). Therefore, the molecular weight of the polymer will determine the distance the loops and tails extend from the surface of the clay particle. Apparently, the loops and tails of the T500 dextran extend far enough to cause flocculation of the clay.

The T2000 and T500 dextran behaved similarly at polymer/clay ratios of 0.01 and 0.002 for the Ca-saturated montmorillonite. However, after 96 h of sedimentation, the T2000 polymer at a polymer/clay ratio 0.1 caused the greatest sedimentation of the Ca-montmorillonite. This is in contrast to the T500 dextran system where sedimentation depth was similar to the control at the ratio of 0.1. The greater flocculation at this polymer/clay ratio may be the result of the formation of a three-dimensional floc network as observed by Chenu et al. (1987) for scleroglucan. After 96 h, the depth of sedimentation was greatest for the system with the 0.1 polymer/clay ratio suggesting that the sedimenting units were larger than those of the control or the other treatments. This may be the result of smaller units being combined into larger units by flocculation with the larger polymer. However, increasing the polymer/clay ratio to 0.2, resulted in a decrease in the depth of sedimentation which was similar to or less than the control.

The larger polymer caused flocculation at a higher polymer/clay ratio than the smaller T500 polymer. The reason for this may be related to different molar concentrations of the two polymers at similar polymer/clay ratios. The molecular weight of the T2000 polymer is four times that of the T500 polymer. Therefore, the molar concentration for the T2000 polymer will be one-quarter that of the T500

polymer for an equivalent mass of polymer in a given volume of solvent. The osmotic pressure developed by the presence of the T2000 polymer will be less than that of the T500 polymer since osmotic pressure is directly related to the molar concentration of the solute. The lower molar concentration of the T2000 polymer compared to the T500 polymer at the same polymer/clay ratio would explain the ability of the larger polymer to flocculate the Ca-saturated montmorillonite at a higher polymer/clay ratio as repulsion of clay particles due to osmotic pressure would be decreased.

The reason for the difference in sedimentation behavior between the Ca and Mg-saturated montmorillonite is not known with certainty. However, if polymer adsorption occurs via water displacement around exchangeable cations as described by Parfitt and Greenland (1970ab), then the affinity of dextran polymers for the more strongly polarizing (higher charge density) Mg cation would be less. The more negative hydration enthalpy of Mg relative to that of Ca would make it more difficult for the polymer to displace hydration water around the Mg cation. As a result, the polymer may displace water adsorbed to the clay surface instead. A greater collapse of the polymer on the clay surface may then occur as more segment-surface contacts would be possible.

The order in which 0.01 M  $\text{CaCl}_2$  and T500 dextran were added to the Ca-saturated clay suspensions affected the sedimentation behavior of the clay (Figure 5.4). The case where no additional salt was added is indicated by the closed circles and is the same data found in Figure 5.2. When salt was added to the clay suspension after addition of dextran, the polymer no longer enhanced sedimentation (closed triangles). After 48 h, it appeared that the polymer actually inhibited sedimentation of the clays relative to the control (dashed line). Addition of 0.01 M  $\text{CaCl}_2$  solution after addition of polymer (closed triangles) either disrupted or prevented the association of polymer with clay, which was evident where no additional salt was added (closed circles).

By comparison, addition of the salt to the clay suspension prior to the addition of polymer molecules resulted in enhanced sedimentation at all polymer concentrations (Figure 5.4). Addition of salt would result in a greater shielding of colloid charge resulting in coagulation of the clays and hence the clays would approach more closely. Adding a flocculant, such as T500 dextran, now results in enhanced flocculation of the coagulated clays permitting the polymer to bridge clay particles. Even the higher concentrations of polymer resulted in flocculation of the clay suspension. Therefore, when coagulation precedes the introduction of a polymer, the probability will increase that polymer loops and tails will be present that are long enough to contact adjacent clay particles.

It has already been shown that the T500 dextran polymer did not cause flocculation of Mg-saturated montmorillonite (Figure 5.2). Addition of 0.01M  $\text{MgCl}_2$  to the clay-dextran mixture did not enhance the sedimentation of the clay over that of the control (closed triangles; Figure 5.5). After 48 h, the presence of polymer at all concentrations caused the sedimentation depth to decrease relative to the control. The inhibition of sedimentation by the polymer suggests that it stabilized the suspension.

When salt was added prior to the polymer, there was essentially no increase in the depth of sedimentation except at the polymer/clay ratio of 0.001. Coagulation of the clays did not enhance the sedimentation of the Mg-saturated clay. The collapse of the polymer on the clay with few loops and tails extending beyond the electrostatic barrier of adjacent clay particles was invoked to explain the absence of flocculation in the Mg-saturated clay system. Addition of salt decreases the electrostatic barrier and the distance between clay particles is reduced. The polymer loops and tails should therefore be able to interact with adjacent clay particles. The absence of the marked sedimentation enhancement, as observed for the Ca-saturated clays for all polymer concentrations, may indicate that the adsorption of the polymer by Mg-saturated clay

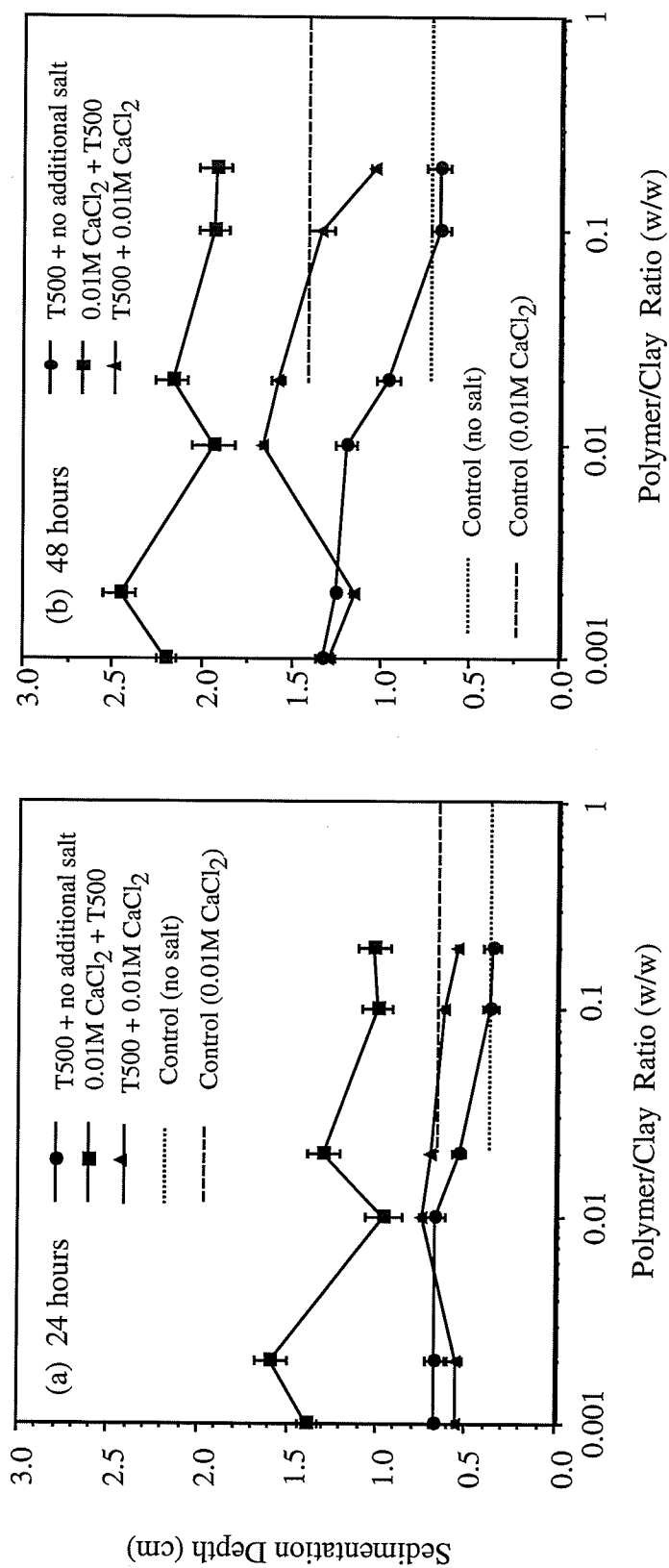


Figure 5.4. The effect of the addition sequence of 0.01 M CaCl<sub>2</sub> and T500 dextran polymer on the sedimentation of Ca-saturated montmorillonite.

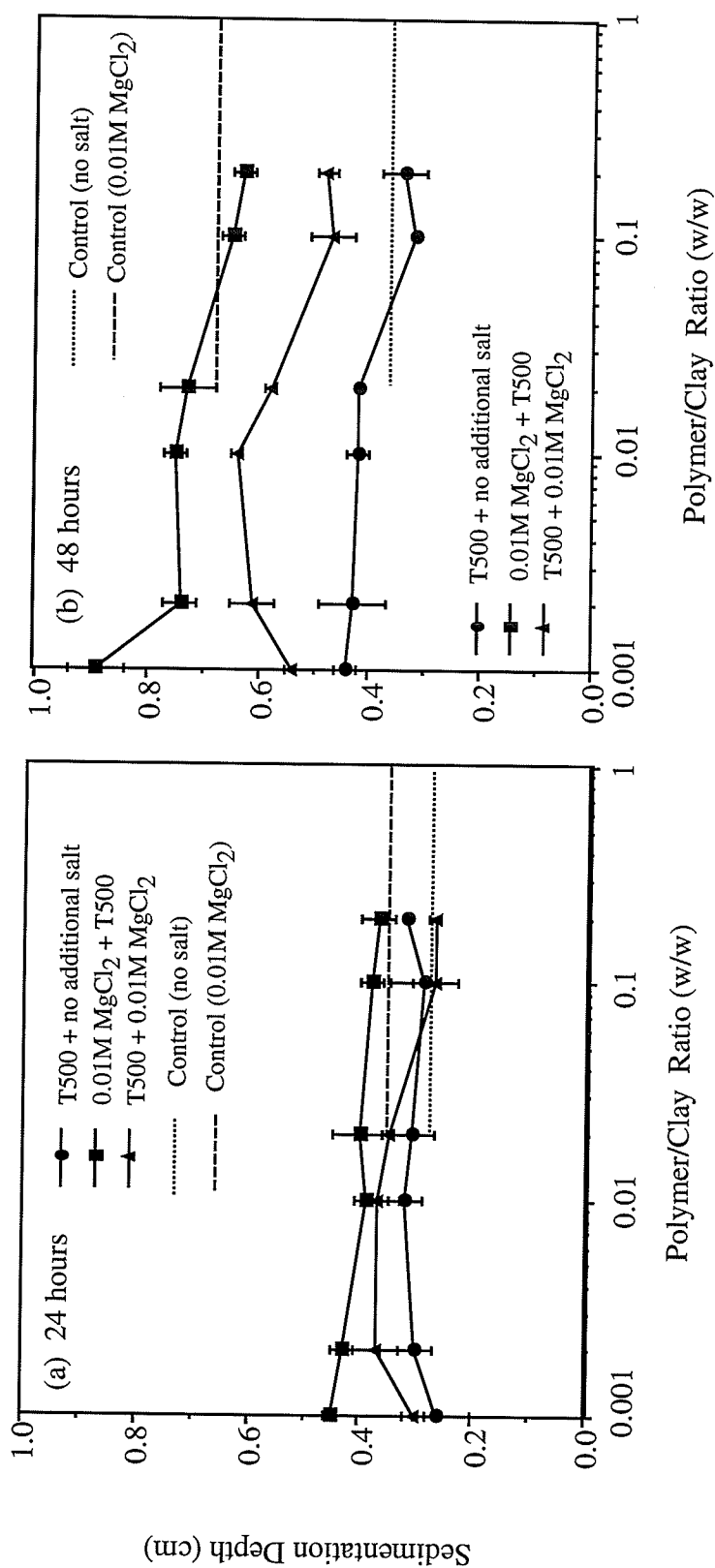


Figure 5.5. The effect of the addition sequence of 0.01 M  $\text{MgCl}_2$  and T500 dextran polymer on the sedimentation of Mg-saturated montmorillonite.

results in polymer collapse. A collapsed polymer with shorter and fewer loops and tails would not be able to bridge the coagulated clays.

The absence of a marked alteration of clay fabric upon adsorption of dextran (molecular weight of  $2 \times 10^6$ ) by Ca-montmorillonite has recently been shown by Chenu et al. (1987). They used a clay suspension concentration of 0.5%. Based on the adsorption maximum ( $25 \text{ mg g}^{-1}$ ) and the equilibrium concentration of dextran (approximately  $1.25 \text{ mg mL}^{-1}$ ; final volume 20 mL), the polymer/clay ratio at the adsorption maximum in Chenu's study is estimated to be 0.3. This corresponds to the polymer/clay ratio where sedimentation was not enhanced for either the T500 or T2000 dextran. Therefore, the absence of particle rearrangement in the presence of dextran in the study of Chenu et al. (1987) may be attributed to an excessive polymer concentration. Flocculation of the clays did not occur and the dextran polymers would have stabilized the clay suspension.

#### 5.4 Summary

The addition of dextran of differing molecular weight to Ca- and Mg- saturated Crook County montmorillonite suspensions resulted in enhanced sedimentation of the Ca-montmorillonite but not the Mg-montmorillonite. The enhanced sedimentation suggests that the polymers were able to flocculate the Ca-saturated montmorillonite. The absence of marked flocculation of Mg-saturated montmorillonite may be caused by a greater collapse upon adsorption of the polymer on the clay surface compared to that of the Ca system. The result would be an adsorbed polymer with a greater proportion of segments existing as trains and fewer as loops and tails.

The T500 dextran caused enhanced sedimentation of the Ca-montmorillonite suspension at polymer/clay ratios of  $\leq 0.01$ . Increasing the polymer concentration above this level stabilized the suspension such that sedimentation was less than or equal

to that of the control. The T2000 dextran caused a similar increase in the sedimentation of Ca-montmorillonite at polymer/clay ratios of  $< 0.01$ . However, at a polymer/clay ratio of 0.1 the T2000 dextran polymers caused greater sedimentation of the suspension. This was believed to be the result of the formation of larger flocs by formation of a network of clay-dextran complexes derived from smaller flocs.

Addition of salt to clay suspensions after the introduction of the T500 polymer resulted in the removal of the polymer effect which was evident when no salt had been added. The control, where no polymer had been added, sedimented at a similar rate as the suspensions with polymer plus 0.01 M  $\text{CaCl}_2$ . The salt either disrupted polymer-clay interactions or prevented the polymer effect. The coagulation of the polymer-clay complexes had a greater effect on sedimentation than the addition of polymer with no additional salt.

Coagulation of the Ca-montmorillonite clay suspension by addition of salt prior to addition of the polymer resulted in enhanced sedimentation at all polymer concentrations. The approach of clay particles through the action of the coagulant facilitated particle bridging by the T500 polymer and therefore flocculation was possible. However, in the case of the Mg-montmorillonite coagulation of the suspension did not result in enhanced flocculation relative to the control. This suggests that the polymer was adsorbed with a greater proportion of collapsed segments in the Mg-montmorillonite suspension. The adsorbed polymer was not able to flocculate the coagulated suspension, probably due to fewer and shorter loops and tails.



**CHAPTER 6****SUMMARY AND CONCLUSIONS**

Previous methods of measuring aggregate stability involve subjecting aggregates to unknown and rather arbitrary energies of disruption. These methods do not reflect the hierarchical nature of soil aggregates as they cause aggregate breakdown at a single level of applied disruptive energy.

The approach taken in this work involves subjecting soil aggregates to various intensities of high-frequency sound waves. Thus, aggregate breakdown and clay dispersion is observed as a function of increasing ultrasonic energy. This permits evaluation of aggregate constituents and binding agents within the complex structure of soil aggregates, thus aggregation mechanisms at various hierarchical levels within the aggregate can be studied. Moreover, an overall evaluation of aggregate stability is possible thereby allowing comparisons of aggregate stability in soils subjected to varying treatments as well as among soils of different pedological histories.

Subjection of soil aggregates to increasing levels of ultrasonic energy resulted in increased dispersion of clay from the aggregate. The plot of clay remaining in an aggregated state (total aggregate clay minus dispersed clay) versus applied ultrasonic energy resulted in characteristic stability curves for each aggregate size fraction. These stability curves could be described by a first-order decay model commonly used in kinetic studies. However, in this case, the model describes the decrease in aggregated clay as a function of applied ultrasonic energy. Linearization of this exponential function provides a means to evaluate the curves. The slope of the straight line, referred to as the stability constant ( $k$ ), represents the average decrease in aggregated clay with a given increase in applied ultrasonic energy. Another parameter,  $E_{1/2}$ , can be calculated from the stability constant and is analogous to a half-life of a first-order kinetic plot.

The  $E_{1/2}$  value indicates the energy input required to disperse one-half of the total aggregate clay. Thus, aggregate breakdown was related to energy input.

Aggregate stability of four aggregate size fractions (ASF) obtained from a prairie-forest ecotone was determined. The aggregates from the prairie-forest ecotone possessed widely differing  $E_{1/2}$  values. The lowest values (51 to 98 kJ L<sup>-1</sup>) occurred for the ASF of the Ae horizon of the Orthic Gray Luvisol found under a mature aspen forest. This horizon is a strongly leached and acidic horizon possessing little clay or organic matter. As a result, less energy was required to disperse the clay contained within the Ae aggregates. The aggregates of the Ah horizon of the Orthic Black found under prairie had  $E_{1/2}$  values ranging from 161 to 224 kJ L<sup>-1</sup>. This horizon had the highest amount of organic matter among the three A horizons studied. The greatest  $E_{1/2}$  values (280 to 504 kJ L<sup>-1</sup>) occurred for the macroaggregates of the Ahe horizon of the Orthic Dark Gray occurring within the newly established aspen forest. This Ahe horizon has experienced an increase in eluviation as well as a reduction in organic matter, carbohydrate content and clay content relative to the Ah horizon of the prairie soil. Despite the loss in organic matter and clay, the macroaggregates have experienced an increase in their ability to resist destruction by ultrasound. The microaggregates of the Ahe horizon had a similar amount of organic matter and carbohydrate as the Ah microaggregates. The shift from prairie to forest vegetation did not affect the stability of these microaggregates as the  $E_{1/2}$  value remains similar to that of the Ah microaggregates. The similarity in  $E_{1/2}$  values for the Ah and Ahe microaggregates suggests that the binding mechanisms within these aggregates are also similar. The absence of a change in organic matter content, carbohydrate content, and aggregate stability following a change from the prairie to forest ecosystem is consistent with the view that microaggregates are least affected by changes in management of the soil (Tisdall and Oades 1982; Oades 1984).

Aggregates obtained from B horizons of the prairie-forest ecotone possessed similar  $E_{1/2}$  values indicating that, despite differences in the nature of the illuvial Bt horizons and non-illuvial Bm horizon, the dispersibility of clay as a function of energy remains similar. The absence of organic binding agents in B horizons likely contributes to this similarity.

The relation between  $E_{1/2}$  value and hexose carbon content of the aggregates was not consistent across the soils of the prairie-forest ecotone. The effect of polysaccharide on the dispersibility of clay was therefore not the same in these three widely differing soils. The role of polysaccharide in aggregate stabilization is therefore soil-specific. The lower stability of the Ah aggregates despite the greater amount of carbohydrate suggests there is a critical level of carbohydrate, above which aggregate stability is not enhanced or perhaps inhibited. Changes in particle-size and organic matter dynamics among different soils appear to affect the role polysaccharides play in the aggregation process.

Sonification of aggregates resulted in solubilization of hexose carbohydrate. The proportion of total hexose carbon solubilized ranged from about 5 to 14% in A horizon aggregates and 15 to 26% in B horizon aggregates. Most of the hexose within these aggregates was strongly associated with surfaces; and sonification at  $1000 \text{ kJ L}^{-1}$  was insufficient to solubilize this surface-associated carbohydrate. However, a small fraction of the total carbohydrate can be released by sonification. There was a significant relationship between the amount of hexose solubilized and the amount of clay dispersed at each energy level. It is not known whether this solubilized carbohydrate is directly responsible for aggregation; however, as more clay was dispersed a greater amount of carbohydrate was released into solution. This is likely the result of increased dispersion of the system resulting in a greater amount of exposed surface area where solubilization could occur.

The study of the effect of cultivation of a single soil type showed that long-term cultivation results in a decrease in hexose content, organic carbon content and  $E_{1/2}$  values. The site subjected to disc tillage throughout its cultivated history had aggregates with the lowest  $E_{1/2}$  values (119 to 334 kJ L<sup>-1</sup>). The greatest  $E_{1/2}$  values occurred for aggregates under an adjacent permanent prairie (228 to 433 kJ L<sup>-1</sup>). Lower levels of ultrasonic energy were therefore required to disperse a given proportion of clay from cultivated aggregates when compared with aggregates from the adjacent prairie. Continuous wheat production with minimum tillage over the past 10 years did not restore the stability of the aggregates to levels found in the prairie. Macroaggregates of the cultivated sites had a greater reduction in  $E_{1/2}$  values than corresponding microaggregates suggesting that agricultural practices have less of an effect on microaggregate stability.

A significant relationship between aggregate hexose content and  $E_{1/2}$  value was observed. Non-soluble hexose accounted for 72% of the variation in  $E_{1/2}$  values among all ASF in both depths studied. Hexose solubilized at 1500 kJ L<sup>-1</sup> accounted for only 48% of the variation in  $E_{1/2}$  values while non-hexose organic carbon accounted for 64% of the variation in  $E_{1/2}$  values.

Hexose carbon associated with the clay fraction was not distributed uniformly throughout the aggregate in the prairie soil. In the prairie aggregates, approximately three times as much hexose occurred in association with clays retained within the aggregate at energy levels between 100 and 500 kJ L<sup>-1</sup> as with clays retained at energy levels of 100 kJ L<sup>-1</sup> or less. Cultivated aggregates possessed much less hexose in association with the clays retained at the higher energy levels. Therefore, carbohydrate located at different positions within the aggregate may play different roles in stabilization of the aggregate as a whole.

The greater proportion of hexose associated with clays held at 100 to 500 kJ L<sup>-1</sup> in stable prairie aggregates and the significant relation between aggregate hexose content and  $E_{1/2}$  value indicate that hexose contributes to stabilization of clays within the aggregate. The aggregates with the most hexose were better able to resist disruption and clay dispersion when subjected to ultrasound.

The significant relationship between hexose content and dispersion of clay from soil aggregates indicates that clay-carbohydrate interactions are important in the aggregation process. Flocculation of Ca-montmorillonite in the presence of a glucose polymer (dextran) was observed in this study. Increased rate of sedimentation occurred for polymer/clay ratios between 0.01 and 0.001 (0.1 to 1%) for the T500 polymer (molecular weight of 500,000). Increasing the polymer concentration above 1% resulted in either no increase in sedimentation rate or a decrease relative to the control. This indicates that a polymer concentration above a certain level may inhibit the aggregation process.

The larger T2000 dextran polymer (molecular weight of  $2 \times 10^6$ ) also caused increased sedimentation of Ca-montmorillonite. The behavior of this polymer differed from that of the T500 polymer in that maximum rate of sedimentation occurred at a polymer/clay ratio of 0.1 (10%). This indicates an interaction between polymer size and polymer concentration in the flocculation of Ca-montmorillonite. The larger polymer was able to cause flocculation at a higher polymer/clay ratio than the smaller polymer. This is attributed to a lower osmotic pressure for the larger polymer as compared to the smaller polymer, as the molar concentration of the larger polymer is less at an equivalent polymer/clay ratio. The results suggest that repulsion due to increased osmotic pressure and repulsive interactions between polymer segments at high polymer/clay ratios was greater than the ability of the smaller polymer to bridge

clay particles. The large polymer was able to span clay particles over greater distances and overcome repulsive forces.

The Mg-montmorillonite suspension did not sediment at a greater rate than the control in the presence of either the T500 or T2000 dextran polymer. Under the experimental conditions of this study, it is thought that the polymer was adsorbed to the Mg-montmorillonite in such a way that polymer loops and tails were shorter and fewer than when the polymer was adsorbed to the Ca-montmorillonite. Polymer collapse on the Mg-montmorillonite was more complete resulting in reduced flocculation capability.

Coagulation and flocculation were studied by altering the order in which salt and dextran were added to the clay-suspension. The order in which polymer and salt were added influenced the rate of sedimentation in the Ca-montmorillonite system. Coagulation of the clay suspension by addition of salt followed by the polymer resulted in greater depths of sedimentation. If the order was reversed, there was no increase in sedimentation rate. Coagulation was therefore necessary for flocculation to occur sufficiently to cause enhanced sedimentation. The reduction in repulsive forces between negatively-charged clay particles by the presence of a salt solution apparently enabled clays to approach close enough for the T500 polymer to span the distance between clays. This occurred at all rates of polymer but was greatest for polymer/clay ratios of  $< 0.002$  (or 0.2% polymer w/w).

Addition of salt prior to polymer (T500) to the Mg-montmorillonite system did not result in enhanced sedimentation rate relative to the polymer except at very low polymer concentration (0.1% after 48 h). However, addition of polymer (T500) prior to salt did inhibit the rate of sedimentation of the clay suspension relative to the control with salt (after 48 h). It appears that the polymer was unable to bridge Mg-saturated montmorillonite particles even when coagulation had occurred and repulsive forces had

been minimized. The extent of polymer collapse on the clay surface was such that the loops and tails were not able to bridge the distance between clays.

Factors affecting clay flocculation therefore include the molecular weight of the polymer, nature of the cation on the exchange sites of the clay, and the ionic strength of the suspension to which polymer is added. This indicates that Ca-saturated clays when coagulated are susceptible to polymer bridging when a flexible polymer of sufficient molecular weight is present at appropriate concentrations.

This study has demonstrated the use of high-frequency sound waves to study aggregate breakdown as a function of energy input. It has been shown that soil aggregates possess clay held at varying energy levels. The overall dispersibility of clay was related to hexose carbohydrate content of the aggregates. Previous studies have demonstrated a relationship between aggregate mean weight diameter or wet aggregate stability and soil carbohydrate content. However, it remained to be determined whether soil carbohydrates were directly involved in aggregate stabilization or whether they simply occurred within aggregates stabilized by some other agent. This study has demonstrated that carbohydrates are involved in aggregate stabilization by their ability to flocculate clay particles. Aggregates possessing more carbohydrates required higher levels of ultrasonic energy to cause clay dispersion. Variations in the distribution of clay-associated carbohydrates within the structure of soil aggregates has also been shown. Flocculation of clays was found to depend on the nature of the exchangeable cation, polymer molecular weight, polymer/clay ratio, and the ionic strength of the suspension; all of which are highly variable under soil conditions.

Many questions remain unanswered. It will be necessary to determine whether different carbohydrate polymers are involved in aggregate stabilization at various hierarchical levels within soil aggregates. The molecular weight of soil carbohydrate polymers and their distribution within the aggregate structure must be considered.

Further, the role of steric stabilization of clays in the presence of excess polymer must be studied in concentrated suspensions as found in soil.

Stable aggregates are essential for both agronomic and environmental reasons. Thus, the ability to study aggregate stability as a function of disruptive energy will enhance the understanding of aggregate breakdown under various natural disruptive forces such as raindrop impact and shear forces generated by tillage implements. It will now be possible to study agents responsible for maintaining particle-particle interactions at various energy levels and thus contribute to better management of soils.



## APPENDIX A

## Determination of Ultrasonic Probe Correction Factor

The ultrasonic probe was calibrated at the factory so that the meter reading x 0.5 equals power output (at high power setting) or meter reading x 0.7 equals power output (at low power setting). The actual power output generated by the probe will be less than that indicated by the meter due to energy loss as heat. A correction factor was therefore required to obtain the difference between output as indicated by the meter and output actually delivered by the probe. The correction factor for the probe was determined as suggested by North (1976). A known mass of water was sonified for varying lengths of time at two different meter settings. The following equation was used to calculate probe power output.

$$P = (m_w \times c_w) + (m_b \times c_b) \times \Delta T/t$$

where,

P	= actual power output of probe (kJ s <sup>-1</sup> )
m <sub>w</sub>	= mass of water (kg)
c <sub>w</sub>	= specific heat of water (4.19 kJ kg <sup>-1</sup> °C <sup>-1</sup> )
m <sub>b</sub>	= mass of beaker (kg)
c <sub>b</sub>	= specific heat of beaker (0.84 kJ kg <sup>-1</sup> °C <sup>-1</sup> )
ΔT	= change in temperature (°C)
t	= time (s)

Example: Sonification for 143 s resulted in a temperature rise of 13 °C.

$$\begin{aligned}
 P &= \{[(0.025 \text{ kg} \times 4.19 \text{ kJ kg}^{-1} \text{ °C}^{-1}) + (0.0271 \text{ kg} \times 0.84 \text{ kJ kg}^{-1} \text{ °C}^{-1})] \times 13 \text{ °C} / 143 \text{ s}\} \\
 &= \{[(0.104 \text{ kJ °C}^{-1}) + (0.022 \text{ kJ °C}^{-1})] \times 0.090 \text{ °C s}^{-1}\} \\
 &= 0.0113 \text{ kJ s}^{-1} \\
 &= 11.3 \text{ J s}^{-1}; \text{ since } 1 \text{ W} = 1 \text{ J s}^{-1} \\
 P &= 11.3 \text{ W}
 \end{aligned}$$

The rise in temperature of the sonified water was linear with respect to the amount of ultrasonic energy applied as indicated by the meter on the generator (Figure A1).

These data were obtained over two different meter settings and over six different durations of sonification. Therefore, the water was receiving an amount of energy which could be controlled by the meter setting and duration of sonification. However, the amount of heat loss would be expected to vary and therefore must be included in the calculation of actual probe power output.

#### Estimation of Heat Loss (H):

Heat loss was estimated from the cooling rate of the sonified water as indicated by the slope of the curve over the temperature range specified (Table A1; Figure A2). Heat loss was converted to  $\text{J s}^{-1}$  based on the mass and heat capacities of the water and beaker. The value of H was then added to the value of P calculated above to determine the actual power output of the probe (Table A2).

Table A1. Rate of cooling over specified temperature ranges and calculated heat loss.

Test No.	T <sub>max</sub> (°C)	Temperature Range (°C)	Cooling rate (°C s <sup>-1</sup> )	H (J s <sup>-1</sup> )
1	28	28 to 24	0.0020	0.25
2	31	30 to 24	0.0028	0.35
3	37	36 to 27	0.0077	0.97
4	46	45 to 30	0.0138	1.74
5	51	50 to 36	0.0216	2.73
6	56	55 to 45	0.0337	4.26

Table A2. Probe correction factor determined over two meter readings and various durations of sonification.

Test No.	Meter reading output (a) W	P + H (b) W	Correction Factor (a/b)
1	35.0	14.32	2.44
2	35.0	12.84	2.72
3	35.0	12.49	2.80
4	49.7	16.48	3.01
5	49.7	16.66	2.98
6	49.7	17.77	2.79
Mean			2.79
Standard error			0.08

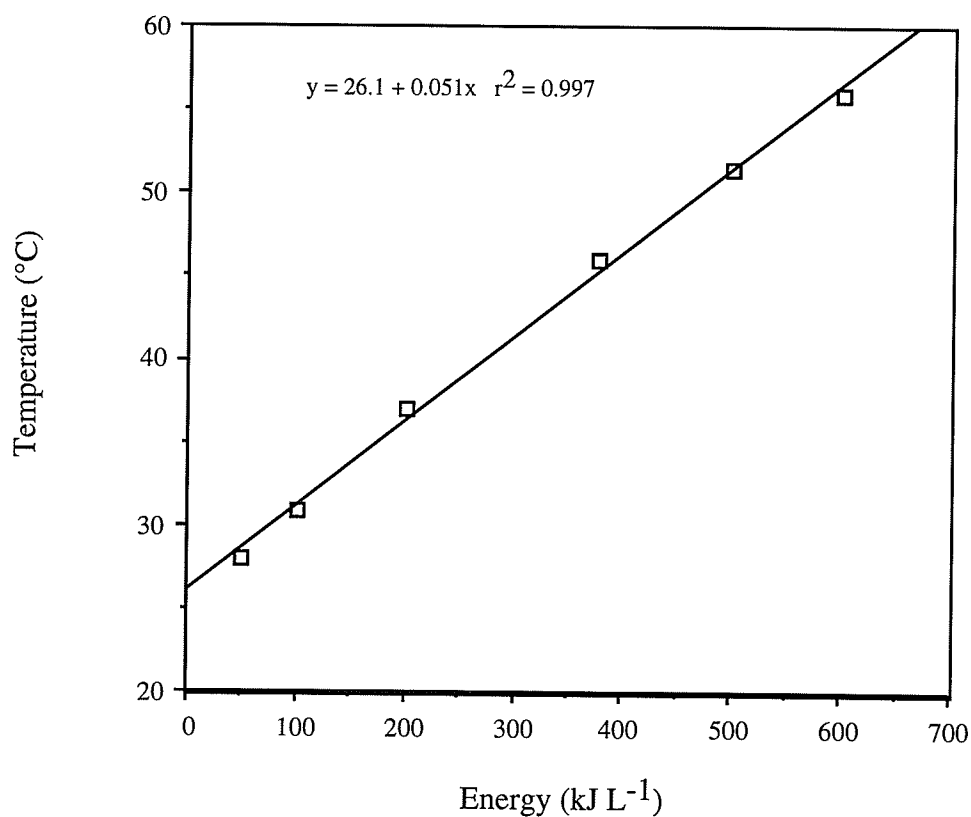


Figure A1. Rise in water temperature with increased application of ultrasonic energy input.

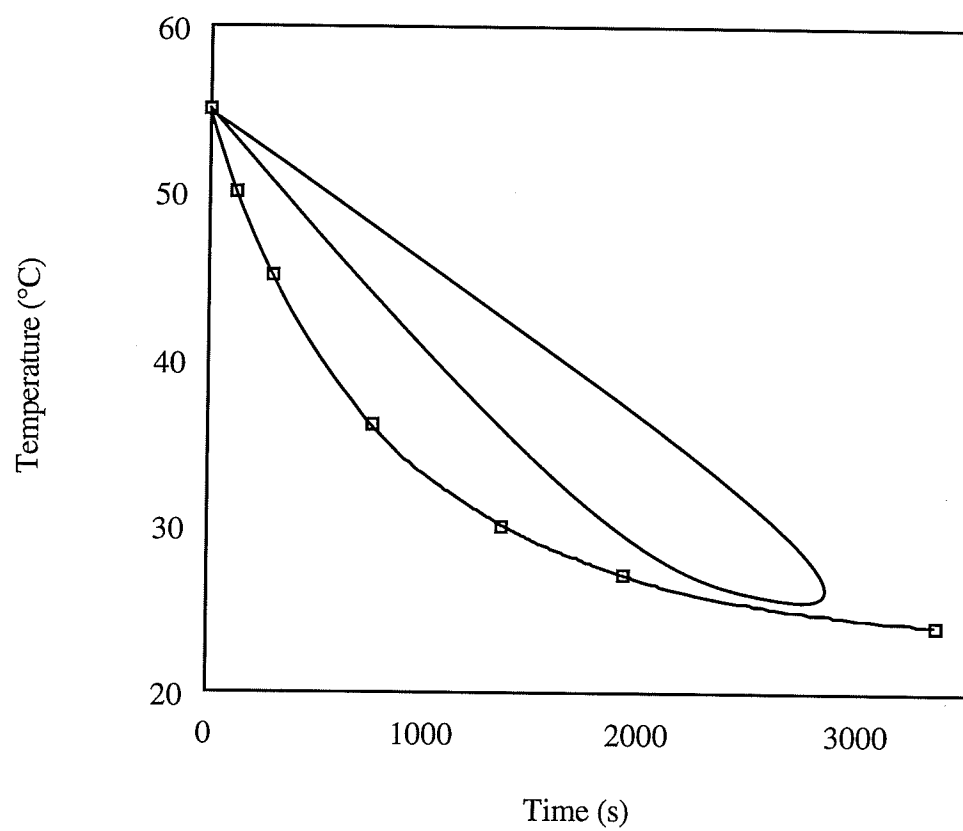


Figure A2. Cooling curve for water following sonification.

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