National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

UNIVERSITY OF ALBERTA

SOIL ORGANIC MATTER AND GRANULAR STRUCTURE IN SELECTED ALBERTA MOLLISOLS

BY

ZHENGQI C ©

A THESIS SUBMITTED TO
THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY
IN
SOIL GENESIS AND CLASSIFICATION

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

SPRING, 1995

National Library of Canada
Acquisitions and Bibliographic Services Branch
395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale du Canada
Direction des acquisitions et des services bibliographiques
395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

THE AUTHOR HAS GRANTED AN IRREVOCABLE NON-EXCLUSIVE LICENCE ALLOWING THE NATIONAL LIBRARY OF CANADA TO REPRODUCE, LOAN, DISTRIBUTE OR SELL COPIES OF HIS/HER THESIS BY ANY MEANS AND IN ANY FORM OR FORMAT, MAKING THIS THESIS AVAILABLE TO INTERESTED PERSONS.

L'AUTEUR A ACCORDE UNE LICENCE IRREVOCABLE ET NON EXCLUSIVE PERMETTANT A LA BIBLIOTHEQUE NATIONALE DU CANADA DE REPRODUIRE, PRETER, DISTRIBUER OU VENDRE DES COPIES DE SA THESE DE QUELQUE MANIERE ET SOUS QUELQUE FORME QUE CE SOIT POUR METTRE DES EXEMPLAIRES DE CETTE THESE A LA DISPOSITION DES PERSONNE INTERESSEES.

THE AUTHOR RETAINS OWNERSHIP OF THE COPYRIGHT IN HIS/HER THESIS. NEITHER THE THESIS NOR SUBSTANTIAL EXTRACTS FROM IT MAY BE PRINTED OR OTHERWISE REPRODUCED WITHOUT HIS/HER PERMISSION.

L'AUTEUR CONSERVE LA PROPRIETE DU DROIT D'AUTEUR QUI PROTEGE SA THESE. NI LA THESE NI DES EXTRAITS SUBSTANTIELS DE CELLE-CI NE DOIVENT ETRE IMPRIMES OU AUTREMENT REPRODUITS SANS SON AUTORISATION.

ISBN 0-612-01679-X

Canada

UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR: Zhengqi Chen

TITLE OF THESIS: Soil Organic Matter and Granular Structure in Selected Alberta Mollisols

DEGREE: Doctor of Philosophy

YEAR THIS DEGREE GRANTED: 1995

Permanent Address:
c/o: Dr. S. Pawluk
Department of Soil Science
University of Alberta
Edmonton, Alberta
Canada, T6G 2E3

Date: March 10, 1995

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled SOIL ORGANIC MATTER AND GRANULAR STRUCTURE IN SELECTED ALBERTA MOLLISOLS submitted by ZHENGQI CHEN in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in SOIL GENESIS AND CLASSIFICATION.

S. Pawluk (supervisor)

W.B. McGill

M. J. Dudas

M.J. Dudas

Arnost Horak

A. Horak

R. Protz

R. Protz (external examiner)

Date: March 1, 1995

To my parents and Ping

Abstract

A comparative study of two Mollisols in central Alberta was conducted to investigate the ge [illegible] anular structures in Raven soil, an Orthic Humic Gleysol, and in Malmo soil, a [illegible] Black Chernozem. Micromorphological investigations, clay minerals and organo-clay complexes, aggregate distribution and stability, monosaccharide composition and soil leachate properties were also compared for both soils. Humic substances in the sola of both soils were also compared for their distribution, composition and structure using x-ray diffraction, conventional and dipolar-dephasing solid state ^{13}C NMR, and alkaline CuO digestion methods. Sorption of environmental contaminants by pedogenically modified humic substances was also investigated using isotherm methods with batch equilibrium.

The results indicated that stronger organo-clay complexation occurred in the Ah horizon of the Raven soil. Stronger development of soil microfabric was attributed to freeze/thaw processes that appeared to be more active in the Raven soil where strong gleying was more evident than in the Malmo soil. Neutral sugar composition indicated greater contribution of microbial polysaccharides in Ah and AB horizons of the Raven soil than in the solum of the Malmo soil. The strong freeze/thaw activity in the Orthic Humic Gleysol apparently overrode the chemical and biological advantages evident in the Gleyed Black Chernozem, and likely led to genesis of a stronger granular structure that had a 'shot-like' appearance.

Results from humic substance studies revealed that distribution of humic acid yields is related to soil vegetation. Humic acid carbon content increased with soil depth while the hydrogen content decreased. Humic acids became more aromatic with soil depth. Formation of polynuclear aromatic rings was likely one of the mechanisms responsible for the higher aromaticity. The p-hydroxyl phenols in humic acid digest became progressively more dominant as soil depth increased. A predominance of p-hydroxyl phenols in humic acid digest has been proposed as an indicator of humic acids from mineral horizons. Sorption experiments for humic substances showed a linear relationship between Koc of α-naphthol and the aromaticity of humic acids. The Koc values obtained in this experiment demonstrated considerable deviation from those calculated from prediction models using Kow which suggests the prediction models should be refined to include these structural and compositional properties. The overall results indicated a strong pedogenic link in substance transformation and structural formation in soils.

Acknowledgments

My earnest appreciation goes to my supervisor, Dr. S. Pawluk, for his insight in pedology, for his consistent encouragement and support throughout my study. His inspiration and versatility made my Ph. D. program an enjoyable, learning experience. His master touch on every draft of the manuscript has contributed immensely to this thesis.

I would like to thank Dr. W.B. McGill for his friendship, for his philosophic research thinking and valuable time in many discussions over the years. Dr. M.J. Dudas is acknowledged for his brilliant suggestions during the major development of this project. Dr. R. Protz from University of Guelph is gratefully acknowledged not only for his critical review of the thesis, but also for sharing his ideas of research frontiers while serving as the external examiner. Dr. A. Horak is acknowledged for kindly serving as my outside-department committee member. My appreciation is also extended to Drs. P. Crown, J.A. Robertson, Y. Feng, N.G. Juma, D.S. Chanasyk and S.A. Abboud for their interest in my research.

I am grateful to M. Abley for sharing with me his expertise in computer programming and soil thin section preparation, to P. Yee for valuable help in the laboratory, to G. Braybrook of the Geology SEM laboratory for microanalyses. I also offer my thanks to C. Figueiredo, J. Konwicki, T. Martin, S. Nakashima and C. Nguyen for their valuable help.

All the FOP members are appreciated for making this department like home. Among those I would like to most honorably mention are L. Poulsen, S. Gonzalez, N. Sawatsky, R. Pradhan, S. Luther, M. Salloum, C. Gomez, M. Bullock, Z. Zhang, Drs. B. Xing, J.M. Arocena, M. Rutherford and M. Zhang.

Special thanks are extended to Dr. T. Nakashima and Mr. G. Bigam from the NMR laboratory, Chemistry Department, for letting me share their knowledge in NMR techniques, to Dr. P. Sanborn for permitting me to use some background data of the Malmo soil.

The Natural Sciences and Engineering Research Council of Canada (NSERC) provided financial support for this research. The Government of Alberta provided me with the Province of Alberta Graduate Fellowship.

My deep appreciation goes to my wife, Ping, for her support and love at all times. I also express my gratitude to my parents, mother-in-law, sisters and brothers, sisters- and brothers-in-law, and my friend M. Wang, for their love and support.

Table of Contents

Content **Page**

Chapter I. General Introduction

Chapter II. Granular Structures in Two Alberta Mollisols ---micromorphblology, mineralogy, physical properties and lysimetry

Content **Page**

Chapter III. Structural Variations of Humic Acids in Two Sola of Alberta Mollisols

Chapter IV. Variations in Nature of Organic Geopolymers and Their Relationship with Sorption of Organic Contaminants

Chapter V. Synthesis

Appendix

Figure **Page**

List of Tables

ble Page

Chapter I
General Introduction

A unique granular structure (shot structure), present as nearly perfect spherical discrete units in the lower Ah and upper AB horizons, was reported for the Raven soil series, a Humic Gleysol (Peters and Bowser, 1960). Its genesis is unknown. Similar structures but less developed were also observed in Black Chernozems, such as Malmo series, in Alberta (Sanborn and Pawluk, 1983). A comparative study of the above soils was initiated to further our understanding about the genesis of these structural units. Such information may assist in the development of new management systems that enhance structural development and improve soil productivity.

Soil organic matter (SOM) accumulation and complexation are common processes during pedogenesis of Humic Gleysols and Black Chernozems (Agriculture Canada Expert Committee on Soil Survey, 1987), leading to formation of granular structure in their Ah horizons. The thick, dark Ah horizons with well developed granular structures and high SOM content make these soils ideal for the study of 'SOM-soil structure' relationships. The SOM associated with soil structural development is also considered as a key component that dictates the fate of organic contaminants in soils. This chapter will provide a brief review of the literature pertinent to this research project.

I.1. Soil Organic Matter

SOM is composed of decomposing plant and animal residues, metabolic by-products formed by soil organisms, soil microorganisms themselves, and resistant soil humus. Modern-day concepts of SOM generally recognize SOM as two major types of organic compounds: (i) nonhumic substances, consisting of compounds belonging to the well-known classes of organic chemistry, and (ii) humic substances, a series of amorphous, polyelectrolyte-like, high molecular-weight, brown to black substances formed by secondary synthesis reactions (Stevenson, 1982; Oades, 1989, Schnitzer, 1991).

Humic substances no longer exhibit specific chemical and physical characteristics normally associated with well-defined organic compounds but are more resistant to biological degradation. They represent the bulk of SOM.

I.1.1. *Classification of SOM*

Though many kinds of classification of SOM were attempted in the past, two systems appear to have survived to date: an ecological classification and a chemical (or fractionation) classification.

Ecological classification of SOM

The ecological classification of SOM, is primarily based on micromorphological attributes such as degree of decomposition and extent of mixing between SOM and soil mineral substances. According to Bal (1982), this classification evolves largely from the early microscopic investigation by Müller during his pioneering study of forest soils. Many of the concepts developed by Müller were later illustrated extensively and further developed by Kubiena (1953) who classified various SOM into 17 humus forms in three ecological environments: sub-aqueous, semi-terrestrial, and terrestrial ecosystems. The term 'humus form', as defined by Kubiena (1953), always refers to humus formation as a whole, not only to particular chemical or physical characteristics, but also to a particular profile development with all its horizons, their internal fabrics, and totality of their life. Thus a humus form is comprised by a particular sequence of several 'horizons', such as L, F, H, Ah. Each individual horizon was referred to as a particular 'humus type' by Jongerious and Schelling (1960). Concepts of humus form and humus type defined by Kubiena (1953) and other foregoing authors, are different from that of Russell (1973). The former is frequently followed by soil micromorphologists (Babel, 1975; Bal; 1982; and Rusek, 1985) and is therefore used in the following chapters of my thesis.

Three humus forms (mor, moder, mull) belonging to Kubiena's terrestrial humus forms are frequently referred to by pedologists (Duchaufour, 1982; Buol et al, 1989). As noted by Babel (1975), most humus forms are typified by a special horizon. Mor has a strongly developed F horizon with structurally well preserved, little comminuted or decomposed SOM developed under coniferous forest with low microbial activity. Moder is typified by a loose mixture of extensively comminuted plant remains, mineral fragments and numerous droppings of small soil fauna under deciduous and coniferous forests or in young soils. It is largely associated with a well developed H horizon in a forest soil or a moder Ah in a young soil as a result of mesofaunal activity. Mull designates a humus form with advanced humification where a characteristic Ah horizon is predominant. The SOM in mull Ah is largely present as amorphous, dark colored colloidal materials and is intimately mixed with mineral substances to form humus-mineral complexes through the activity of some earthworm species under deciduous forest (Kubiena, 1953; Babel, 1975; Rusek, 1985). Another type of Ah horizon characterized by rhizogenous organo-mineral complexes in grassland soils is termed as sward (Buol et al. 1989) and closely resembles Chernozemic Ah horizons of the Canadian Soil Classification System (Agriculture Canada Expert Committee on Soil Survey, 1987). According to Kubiena (1953) and Duchaufour (1982) soil aggregation through incomplete mixing of SOM and soil minerals is less stable as compared to mull and sward. As pointed out by Rusek (1985) and Pawluk (1985), genesis of a particular humus form is usually related to multiple, progressive faunal processes of many biotic components.

The ecological SOM classification emphasizes the totality of SOM and the integrity of its environment of formation. Inclusion of the complete soil morphological components makes this system very useful for studying the dynamics of SOM in terrestrial environments and for deducing the genetic links of soil processes.

Chemical fractionation of SOM

Knowledge of chemical fractionation of humus largely came from the persistent pursuit of the chemical nature of various forms of humus during early humus study. Humic substances are chemically fractionated into three basic operational fractions according to their solubilities in alkaline and acid solutions. These include: (i) fulvic acids (FA), soluble in both alkaline and acid solution; (ii) humic acids (HA), soluble in alkaline solution but not in acidic solution; and (iii) humin (HM) that is not soluble in either alkaline or acidic solution, where traditional extraction procedures are employed (Kononova, 1966, Stevenson, 1982).

Chemically, the FAs contain more O and less C, N, S, are more acidic, and have a lower molecular weight range with less condensed/polymerized structure than HAs and HMs. The HM is considered to be a form of HAs tightly bonded to mineral matrix in soils or sediments (Schnitzer, 1991). Other sources suggest a relatively young nature for HM where it is more closely associated chemically to plant and microbe constituents than HAs (Stevenson, 1982; Almendros and Sanz, 1991; 1992). Humus in this operational approach generally has a narrower meaning than in the ecological approach.

I. 1. 2. *Formation of SOM—Humification*

SOM accumulation is achieved through humification processes in soil. Duchaufour (1982) defined humification as 'all the processes that transform SOM from fresh organic matter into humus'. SOM coming largely from plants is considered as 'inherited' while that derived from microbial transformation is termed as 'neoformed' SOM.

Biological synthesis of humus

In most soils, the persistent search by microorganisms for energy and building blocks tied up in SOM is the driving force behind nearly all the cycling reactions involved with organic compounds (McGill and Cole, 1981). Thus, the structural bio-stability of organic components and their physical availability to microbes determine their fate in the C transformation in soils.

Plant and animal residues are the primary source for SOM. When the dead tissue enters the soil, organic components of varying bio-stability are attacked by soil microfauna and microflora. The initial invasion of organic debris by soil microflora is greatly assisted by soil fauna that physically comminute plant debris and subsequently create a greater surface area and access to the internal surface for colonization by soil microflora. As a result of faunal activity, the speed of humification may be increased up to tens or hundreds of times (Kononova, 1966; Duchaufour, 1982). Soil fauna such as collembola and oribatid mites, are noted as pioneers in comminuting organic debris in moder and mull-like moder humus of young soils (Kubiena, 1953). Their activities change the plant fragments into amorphous, colloidal faecal pellets.

Biodegradation by microflora consists of a series of progressive depletion of the chemical energy by heterotrophic organisms. Simple sugars, amino acids and simple organic acids are readily metabolized by zymogenous organisms. Complex organic substances such as polysaccharides, lipids and proteins are consumed by microorganisms capable of producing necessary extracellular enzymes. Lignin is considered as the primary source for humic substances in soils and sediments (Kononova, 1966, Duchaufour, 1982; Ertel and Hedges, 1985). Natural lignin generally has a compact structure that is insoluble in water. The basic structure has phenylpropane units with various substitutions in the aromatic ring. Three monomers (p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) are recognized in lignin chemistry. The internal monomer linkages are a variety of C-C and C-O bonds with β-aryl ether linkages predominant. Specifically, lignin is synthesized via a free-radical condensation mechanism and is not under strict enzymatic control (Zeikus, 1982; Kirk and Farrell, 1987), resulting in its recalcitrance in soils.

Three theories of biological humus formation are proposed in humus chemistry: the 'lignin theory', 'polyphenol theory' and 'sugar-amine condensation theory'. Stevenson (1982) outlined these three theories in Fig. 1:

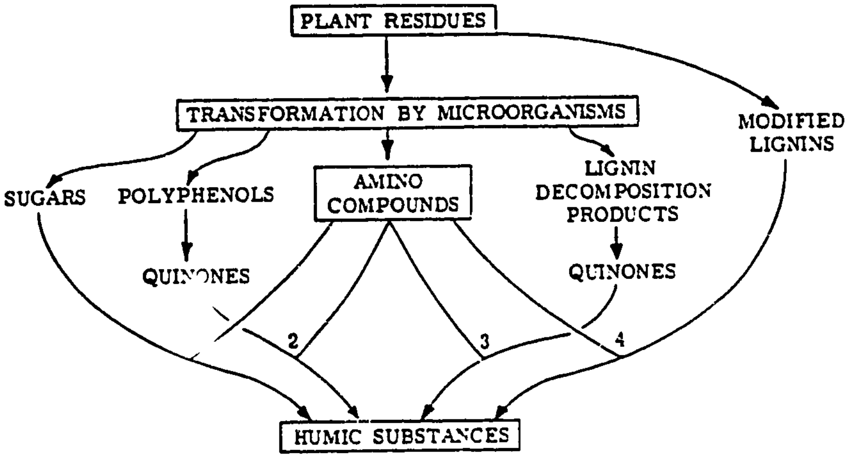


Fig. 1. Mechanisms for the formation of soil humic substances (From Stevenson, 1982).

The popular 'polyphenol theory' is outlined in pathway 2 and 3 where plant residues are transformed into quinone compounds either from microbially decomposed lignin products or from aliphatic compounds transformed into polyphenols by microbes. The condensation of quinones with amino compounds form humic compounds. The 'lignin theory' is illustrated by pathway 4 where amino compounds react with modified lignin to form humus. The 'sugar-amine condensation theory' follows pathway 1 where reducing sugar condenses with amino compounds to form humic substances through 'browning reaction'.

Stevenson (1982) and Flaig et al. (1975) considered the classic 'lignin theory' obsolete, and the importance of the 'sugar-amine condensation theory' on humus formation in soils to be unclear. The current popular 'polyphenol theory' considers quinones of lignin origin or neoformed by soil microbes, to be the major building blocks for humic substances (Flaig et al. 1975). Three stages are proposed by Stevenson (1982) for the 'polyphenol theory' as follows: (i) fungi attack simple carbohydrates, proteins and cellulose in the medullary rays, cambrium, and cortex of plant residues;
(ii) Cellulose of the xylem is decomposed by aerobic myxobacteria. Polyphenols synthesized by myxobacteria are oxidized to quinones by polyphenoloxidases, and the quinones subsequently react with N compounds to form brown humic substances;
(iii) Lignin is decomposed. Phenols released during decomposition also serve as source materials for humus synthesis.

While this theory appears to be supported by considerable experimental and theoretical evidence (Flaig et al. 1975), it seems that the complexity of humus can not be explained just by one mechanism of formation. In addition, the 'polyphenol theory' appears to be vague on the aspect of where the reactions take place. A modified version of the 'polyphenol theory' by Varadachari and Gosh (1984) is more comprehensive. A few important contributions of Varadachari and Gosh (1984) are that they clearly indicated that humus can not be synthesized within living cells but is largely formed in the dead cells; the modified polymeric fragments of lignin are also able to participate in oxidative polymerization with polyphenols; and the phenols can polymerize by themselves in situations where no N compounds are available. These modifications are valid and appear to be in accordance with quite a few findings from other humus studies (especially those supporting abiotic catalysis) that contradict the original 'polyphenol theory' by Flaig et al. (1975) and Stevenson (1982). In many modern humus studies, chemical structures of lignin components were repeatedly detected by a number of workers (Ertel and Hedges, 1985; Kögel-Knabner et al. 1988; 1990; Hempfling and Schulten, 1991) and these lignin compounds were recognized as structural components of humus (Schnitzer, 1991).

The microorganisms capable of attacking lignin are eucaryotic microbes, procaryotic microbes and lignocellulose-destroying animals. According to Zeikus (1982), white-rot fungi are capable of completely oxidizing the lignin structure to CO_2 and H_2O, while brown-rot fungi only partially modify the lignin structure (largely oxidative demethylation of phenolic and nonphenolic units). In soil ecosystems, the white-rot species are usually associated with well aerated, acid litter of mor that is typical for coniferous vegetation. White rot fungi produce little humus when they grew in lignified plant materials (Martin and Harder, 1971). Instead, some fungi of the Imperfecti group are capable of degrading lignin and cellulose and significantly contribute to humus synthesis in soils. The brown-rot fungi operating in eutrophic moder or mull with neutral pH under grass or deciduous forest are also capable of contributing to humus biosynthesis (Duchaufour, 1982).

The mode of organic matter addition is another factor affecting biological humification. In grassland ecosystems, up to 2/3 of grass biomass are deposited in soil as extensive root systems (Oades, 1989; Pawluk and Bal, 1985). Intimate contact of the fine grass roots and mineral matrix in the rhizosphere establishes a less aerated condition. Localized contact of microbial metabolites, such as polysaccharides, phenolic compounds, and N compounds, apparently favors humification. In forest ecosystems, organic substances are usually transferred into mineral soils through leaching or fauna mixing. The rich Ca supply in grassland soil has both a stabilization and a protective effect on SOM (Duchaufour, 1982). Coupled with cool temperature and a rich Ca supply from parent geological materials, grassland soils usually go through slow humification that is most effective in biological humus formation (Duchaufour, 1982, Stevenson, 1982; Pawluk and Bal, 1985).

Abiotic synthesis of humus

In contrast to biological synthesis of humus, abiotic synthesis of humus has only been recognized during the past 35 years.

Early studies by Wang et al. (1978) indicated that humic substances can be formed through abiotic processes through surface catalysis by a variety of inorganic soil components. The mechanism is known as surface oxidative polymerization and polycondensation processes through free radical reaction (Pinnavaia et al. 1974; Mortland and Halloran, 1976; Wang et al. 1986; McBride et al. 1988). The rates of polymerization/polycondensation are dependent on the nature of inorganic substances in soils. Sesquioxides have the strongest catalyzing effect. For clay minerals, the catalytic power changes in the order of 2:2 type>2:1 type> 1:1type >quartz (Wang et al. 1986). Two types of structural defects in clay minerals reported by Wang et al. (1986), most likely belong to 'linear dislocations', which according to Moore (1983), are very reactive sites for surface catalysis. These may be the major catalytic sites for pure clay deprived of sesquioxide coatings. Clay minerals containing Fe in their octahedral sheet are stronger catalysts than other clay minerals. Primary minerals are also capable of catalyzing polymerization of phenolic and benzoic compounds but their catalytic powers are variable and are generally about half the speed of clay minerals (Shindo and Huang, 1985; Wang et al. 1986). Though the reaction rates of abiotic catalysis are generally slower than enzymatic reactions, abiotic catalysis appears to play a dominant role in humification in mineral soils because of the absolute dominance of reactive mineral surfaces (Wang et al. 1986; Samir et al. 1994).

I.1.3. *Chemical structure of humus*

The model structure of humus recorded by Kononova (1966) included a strongly aromatic model presented by Fuchs and a less aromatic model without polynuclear rings as suggested by Dragunov. The hypothetical structure by Flaig (recorded by Stevenson, 1982) also has high aromaticity and high quinone components. In the current literature, a strongly aromatic hypothetical model by Stevenson (1982) largely bridged by aryl C-C, C-O-C, and C-N-C bonds and a spongy-like, much less aromatic model (Schultan et al. 1991) are presented. These models are controversial and were based on deduction following data collected by very different methods. Models up to the time of Stevenson (1982) were derived largely from the degradative study of humus, largely the HA fraction. The model of Schultan et al. (1991) was principally derived using ^{13}C NMR and pyrolysis-field ionization mass spectral (PI-MS) methods, mostly from bulk SOM and limited HA and HM observations. These models require further study using a greater range of humus substances and should be refined with a pedogenic approach for humus formation.

Genesis and structure of humic substances have also been studied by measuring the amount and characterizing the type of their aromatic components released by various digestion methods (Schinitzer, 1978; Stevenson, 1982; Hayes and Himes; 1986; Schnitzer, 1991). The ratios of three groups (syringyl, vanillyl and cinnamyl) of lignin-derived phenolic compounds were used by Ertel and Hedges (1984) to study possible vegetational origin of humic substances. The acid/aldehyde ratio of the vanillyl phenol group has been used as an index to estimate microbial alteration of lignins during humification (Ertel and Hedges, 1985; Kogel-Knabner et al. 1990; Lowe, 1992). Other methods, such as x-ray diffraction, ^{13}C NMR, FTIR, spectrometric methods, acid hydrolysis, and PI-MS methods are also frequently used to deduce the structure of humic substances (Schnitzer, 1978; Stevenson, 1982; Wilson, 1991; Schulten and Leinweber, 1991; Schnitzer et al. 1991).

Knowledge of abiotic processes is almost exclusively developed from laboratory experimentation with well defined chemicals and minerals. In a real soil system, however, the situation is drastically different. If extrapolated from Martin and Haider (1980), Wang and Huang (1989), and Wang et al. (1986), it is logical to state that presence of many kinds of phenolic and benzoic compounds will have a synergetic impact on polymerization of precursors; participation of soil N compounds may largely enhance the polymerization reaction; and presence of Fe, Mn, and Al coatings, as well as clay coatings may significantly raise the catalytic power of silt- and sand- size primary minerals. Soil organic layers and mineral horizons appear to be quite different environments for humification. There is a serious gap in knowledge about humus formation in and across the organic-mineral interface in soils. Thus, a comparative investigation of SOM in the organic horizons versus those in the mineral horizons may add insight to the genesis of humic substances in soils. As a prime factor in soil aggregation, the structural variation of humic substances may have a different impact on soil structural formation.

I.1.4. *Connection of SOM to environmental aspects of soil*

Recent environment protection studies indicated SOM is also a prime factor for sorption of nonionic organic pollutants (Xing et al. 1993; 1994a). The mechanism of sorption is largely through the partitioning of pollutants between the aqueous and solid phases. Various linear partitioning equations have been proposed for predicting K_{OC}, the organic C normalized partition coefficient of bulk soil or sediment samples (Chiou et al. 1979; Briggs, 1981; Chiou et al. 1983), where SOM was treated as a homogenous phase that presumably could be approximated by simple organics such as octanol.

New research findings reflect the complexity of organic sorbents in soils and sediments. Among the many properties of the organic phase, polarity and aromaticity seem to play a crucial role in partitioning of organic pollutants in the aqueous-soil, or aqueous-sediment interfaces. Gauthier et al (1987) reported that structural (aromaticity) and compositional variations of humic substances had an impact on K_{OC}. Xing et al. (1994b) showed that K_{OC} values predicted with the linear partition models produced large deviations from lab-measured data. Instead, they found that the ratio of percent elemental composition, (O%+N%)/C%, of a given organic sorbent, can be used for a more accurate prediction of K_{OC} values for sorption of the nonionic organic pollutants.

I.2. Soil Structure

Soil structure is primarily related to SOM that acts as a dominant aggregating agent. However, the persistence of SOM largely depends on its position within the soil structure.

Brewer (1976) defined soil structure as 'the physical constitution of soil materials as expressed by the size, shape and arrangement of solid particles, voids, including both primary particles to form compound particles and the compound particles themselves'. Today's soil structure classification (Buol et al. 1989) is rooted in Russian classification (Zakharov, 1927, as recorded by Buol et al. 1989) using shape, size and other morphological characteristics of aggregates.

Soil structures are classified into three groups: (i) cubelike, where the arrangement of soil materials is roughly equal along the three dimensions (This includes the block-like and spheroid structures. The spheroid structure includes granular and crumb structures.); (ii) plate-like, where the arrangement is largely horizontal; and (iii) prism-like, where the arrangement is dominantly vertical (Buol et al. 1989). This classification is adequate for general purposes (Russell, 1973). The Canadian system for classifying soil structure (Agriculture Canada Expert Committee on Soil Survey, 1987) is generally the same as the above system.

I.2.1. *Factors affecting soil structure formation*

Factors affecting soil structural development have been reviewed by many authors (Emerson, 1959; Harris et al. 1966; Tisdal and Oades, 1982; Kay, 1990; Oades, 1993). These factors can generally be grouped as abiotic factors (clay minerals, sesquioxides, exchangeable cations), biological factors (SOM, actions of plant roots, soil fauna and soil microorganisms) and environmental factors (temperature, moisture) that usually influence soil structure through interactions of moisture and temperature. These factors are usually inter-related during pedogeneses.

Early soil aggregation theory is principally based on the dispersion-flocculation concepts of colloidal chemistry (Jenny, 1980). Clay separates in soils are the only mechanical fraction that possesses colloidal properties. It is well known that the presence of adequate clay minerals is a basic requirement for formation of water-stable aggregates (Harris et al. 1966; Russell, 1973; Oades, 1993). Contributions of both soil clay minerals and SOM have been emphasized in the popular model by Emerson (1959), who suggested that individual clay particles adhere to one another to form small domains. The soil domains are subsequently linked to each other or to larger quartz grains by SOM. Later work by Edwards and Bremner (1967) indicated the important role of polyvalent cations in bridging negatively charged clay minerals and organic molecules to form stable microaggregates. Progress in studies of SOM and soil structure led Tisdal and Oades (1982) to develop a hierarchical model that recognized a wide range of aggregating substances, in particular SOM of variable microbial resistance, for different levels of aggregation. The impact of environmental factors on soil structural development is usually through freeze/thaw and wet/dry processes in soils. Van Vliet-Lanoe et al. (1984), Coutard and Mücher (1985) demonstrated with European soils that freeze/thaw action can reorganize soil materials into granular and platy structures. The freeze/thaw impact on Canadian soils was pointed out by Pawluk (1985) who later demonstrated that granular structure can be regenerated from structureless, ultrasonically dispersed soil materials of Black Chernozems in Canada (Pawluk, 1988).

The foregoing research is generally reflected in the framework of our current understanding about soil structure formation. The hierarchical model by Tisdal and Oades (1982) was evaluated by a number of workers and found applicable for North American soils (Elliott, 1986; Miller and Jastrow, 1990; Kay, 1990). For the

ing to the specific pedoclimatic conditions. The hierarchical model based
ı soils needs verification if it is to be used for Canadian soils that are
ıder much colder climatic conditions and with less weathered soil parent
aterials as compared to the Australian soils.

methods to study soil structure

cal methods such as aggregate size distribution and water stability are
oyed for measurement of the physical size of soil structural units (Kemper
ı, 1986). Chemical extraction methods, such as those ultilizing sodium
ium periodate-perborate, and sodium pyrophosphate are usually used to
es of aggregating substances (Greenland, 1965a, 1965b; Cheshire, 1979;
l. 1983; Churchman and Tate, 1986; Shipitalo and Protz, 1989).

es investigating the interaction between clay minerals and SOM revealed
hanisms for aggregation. With large surface areas, swelling clays, such as
ıerals, are more effectively involved in aggregation than non-expandable
(Greenland, 1965a; Harris et al. 1966; Turcheck and Oades, 1979; Theng,
; et al. 1986, 1992). The importance of smectite is largely related to its
fect on the SOM and its ability to form stable organo-clay complexes. This
effect was considered to be largely responsible for development of stable
hernozem soils (Dudas and Pawluk, 1969; Duchaufour, 1982). Studies
andard clay minerals and defined organic polymers, demonstrated that
ral complexation was influenced by charge properties both of clay minerals
polymers, saturation cations, ionic strength of media, and molecular weight
ation of the organic substances (Parifitt and Greenland, 1970a, 1970b; Gu
1992). These effects were similar to the interactions reported between clay
humic substances (Theng and Scharpenseel, 1975), or soil polysaccharides
Greenland, 1970b; Gu and Hover, 1992). These two types of SOM
are actively involved in soil aggregation (Cheshire, 1979, Stevenson, 1982;
ades, 1982; Emerson et al. 1986; Oades, 1993)

omorphological methods are ideal tools for the study of soil structure. One
advantages of soil micromorphology is that artificial disturbance to the soil
nimized so that the study can be carried out as Kubiena (1938) stated 'in
situ'. Investigations guided by defined morphological boundaries with 'true
', rather than ground 'bulk soil material', is conducted at the most

appropriate scales of resolution. Soil is a natural, anisotropic body and this anisotropy is best explored by investigation of microstructure through techniques of soil micromorphology (Kooistra, 1990). Many vital pedogenic characteristics associated with soil development processes can be deduced from micromorphological analyses using the most appropriate scales of resolution. Resolution utilized in soil micromorphological investigations can extend to submicroscopic and finer scales by coupling microscopic techniques with other techniques such as SEM, EDX and micro x-ray diffraction. Systematic illustrations of structure at the microscopic level were presented by Brewer (1976), Brewer and Sleeman (1988). The 'related distribution pattern' (RDP) of coarse and fine structural units is an important and very practical aspect for soil structure study. Brewer and Pawluk (1975) proposed eight types of RDPs, which were further grouped into four fabric sequences (granic, fragmic, chlamydic, and iunctic) according to their genetic relationships (Brewer, 1979; Pawluk, 1983). This grouping proved quite applicable for microfabric descriptions of Alberta soils (Pawluk, 1983) where the granic sequence is dominant in various humus forms in western Canada. A broad discussion of Alberta Chernozems and other Mollisols in North America was presented by Pawluk (1985), and Pawluk and Bal (1985). Micromorphology related specifically to SOM was presented by Babel (1975, 1985), Altemuller and van Vliet-Lanoe (1990). However, application of these complicated techniques to SOM studies are usually difficult and needs further development.

I.3. Summary

The importance of SOM to soil genesis has been considered since the origin of soil science through the consideration of vegetation or biota as a factor of soil formation. It is the participation of vegetation and other biota as a whole that principally separates the pedogenic processes from the geogenic processes. The functions of SOM in soils can be summarized as: (i) a nutritional function, as a major source of N, P and S for plants; (ii) a biological function, primarily as a food and energy source that regulates the ecological dynamics of the soil biota; and (iii) a physical function, in promoting soil structure thus affecting many soil physical properties. From a pedogenic viewpoint, the second and third functions are most pertinent because they are strongly related to the dynamics of soil aggregation and therefore affect soil horizon differentiation. It is in this sense that Duchaufour (1982) claimed 'humus (SOM) occurs as the connecting link between the living and mineral worlds, where it integrates all the environmental factors'.

The study of humic substances is almost as old as soil science and uncertainty of knowledge, in particular as applied to humus structure, is apparent (McKeague et al. 1986; Schnitzer, 1991; Wershaw, 1992). It is not uncommon in the literature to find a large number of SOM studies using soil samples coming from individual horizons that have no apparent genetic link. Much confusion about humus concepts can be directly or indirectly associated with uncertainty about humus structures. It is because of this that Schnitzer (1991) set the structural investigation of SOM as a 'very high priority' for future pedological studies. Detailed investigations of SOM across the upper surface mineral horizons is an ideal way to follow the change of SOM from organic to mineral soil environments.

SOM plays a primary role in genesis of soil structure. But organo-clay complexation does not automatically lead to structural formation. It appears that soil structure formation can be generally divided into two stages: aggregation, and stabilization. The former is generally driven by mechanical forces of various origins (freeze/thaw, wet/dry, mixing and compression within soil fauna, and pressure of growing plant roots). The latter is generally related to type and amount of clay minerals, structure and distribution of SOM, sesquioxides and polyvalent cations. These two processes work together to form stable aggregates. When there is only aggregation and no stabilization, soil aggregates will be unstable. This is supported by observations where there is a lack of SOM, aggregates formed by freeze/thaw or earthworm activity are not stable (Baver et al. 1972). On the other hand, stabilization without aggregation can produce structureless soil materials. For example some dark Ah horizons (such as anmoor, and some Vertisol Ah horizons) rich in organo-mineral complex remain massive (Duchaufour, 1982; Pawluk and Bal, 1985).

The SOM involved in soil structure formation also has a crucial impact on the fate of non-ionic aromatic organic contaminants in soils. Soils are usually in the immediate vicinity of pollution sources in the terrestrial environments. Thus the structural and compositional variations of SOM likely have an immediate influence on the fate of the nonionic aromatic organic pollutants. Humic substances represent the bulk of SOM. However, information on their structural and compositional nature within a continuous vertical section is scarce. Lack of such information may hinder the understanding of the early stage interactions between organic pollutants and soils or sediments during contamination events.

I.4. Themes and Objectives

Following the foregoing review, three research themes are proposed:

1. Genesis of granular structures is related to soil clay mineralogy, cation and sesquioxides composition, and is reflected in soil microfabrics. SOM is the primary factor that affects soil granular structure development. Complexation of mineral and organic substances is the major reason for aggregation. The complexation processes are mediated by frost action and soil fauna.

2. The properties of SOM reflect pedogenesis. Consequently, the distribution, structure and composition of SOM will vary with soil depth. SOM in organic layers will be different from those in mineral soil environments.

3. SOM is the primary soil component that reacts with non-ionic aromatic organic environmental contaminants. Pedogenically modified SOM vary in their capacity for sorption of environmental contaminants.

The general purpose of this study is to investigate the possible pedogenic mechanisms of granular structure formation in relation to SOM, and to characterize SOM in the Raven soil, an Orthic Humic Gleysol, and Malmo soil, a Gleyed Black Chernozem. Since the SOM associated with structural development also serves as a crucial factor in determining the behavior of nonionic organic contaminants in soils, effect of SOM on sorption of environmental contaminants will be assessed.

Specific objectives are:

1. To investigate the distribution and stability of soil aggregates in the sola of the Raven and Malmo soils and to relate this to soil environment, soil mineralogy, organo-clay complexation, soil microfabric, SOM (humic acids and polysaccharides) and soil lysimetry in order to probe their genesis.

2. To investigate the distribution, structure and composition of humic substances and their relationship to pedogenesis in the sola of Raven and Malmo soils. The aromatic precursors for SOM formation will be studied to probe the nature of their genesis.

3. To see if pedogenic modification of the SOM will have an impact on sorption of selected environmental contaminants.

I. 5. The scope of the thesis

This thesis is composed of five chapters. Chapter I is the general introduction and provides background information of this dissertation research. Chapter II reports on the pedogenic investigation of granular structures and SOM. Chapter III presents a detailed study on structural and compositional properties of SOM in the two soils. Chapter IV extends the SOM impact on contaminant sorption behavior. Chapter V provides an overall summary and synthesis of the thesis.

Reference

Agriculture Canada Expert Committee on Soil Survey, 1987. The Canadian System of Soil Classification. 2nd edition, Agri. Can. Publ. 1646, Ottawa.

Almendros, G., and Sanz, J. 1991. Structural study on the soil humin fraction---boron trifluoride-methanol transesterification of soil humin preparations. Soil Biol. Biochem. 23(12):1147-1154.

Almendros, G., and Sanz, J. 1992. A structural study of alkyl polymers in soil after perborate degradation of humin. Geoderma, [illegible]3:79-95.

Altemuller, H.J. and van Vliet-Lanoe, B. 1990. Soil thin section fluorescence microscopy. in L.A. Douglas (ed). Soil Micromorphology. Elsevier Sci. Publishers B.V., Amsterdam. Netherlands. p.565-579.

Babel, U. 1975. Micromorphology of soil organic matter. in J.E. Gieseking (ed). Soil Components. Vol. 1. Organic components. Springer, Berlin. 369-473.

Babel, U. 1985. Basic organic components. in P. Bullock, N Fedoroff, A. Jongerius, and G. Stoops (ed). Handbook for Soil Thin Section Description. Waine Research Publications. Wolverhampton. p.74-83.

Bal, L. 1982. Zoological ripening of soils. Centre for Agriculture Publishing and Documentation, Wageningen, 365p.

Baver, L.D., Gardner, W.H. and Gardner, W.R. 1972. Soil Physics. 4th edition. John Wiley & Sons Inc. New York.

Brewer, R. 1976. Fabric and Mineral Analysis of Soils. Robert E. Krieger Publishing Co. Inc. New York.

Brewer, R. 1979. Relationships between particle size, fabric and other factors in some Australian soils. Aust. J. Soil. Res. 17:29-41.

Brewer, R. and Pawluk, S. 1975. Investigations of some soils developed in hummocks of the Canadian sub-arctic and southern-arctice regions. 1. morphology and micromorphology. Can. J. Soil Sci., 55:304-311.

Brewer, R. and Sleeman, J.R. 1988. Soil Structure and Fabric. CSIRO Australia, Adelaide

Briggs, G.G. 1981. Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. J. Agric. Food Chem. 29:1050-1059.

Buol, S.W., Hole, F.D. and McCracken, R.J. 1989. Soil Genesis and Classification. 3rd edition. Iowa State University Press, Ames. USA.

Cheshire, M.V. 1979. Nature and Origin of Carbohydrates in Soils. Academic Press, London.

Cheshire, M.V., Sparling, G.P. and Mundie, C.M. 1983. Effect of periodate treatment of soil on carbohydrate contents and soil aggregation. J. Soil Sci. 34:105-112.

Chiou, C. T., Peters, L.J., and Freed, V.H. 1979. A physical concept of soil-water equilibrium for nonionic organic compounds. Science. 206:831-832.

Chiou, C.T., Porter, P.E. and Schmedding, D.W. 1983. Partition equilibra of nonionic organic compounds between soil organic matter and water. Environ. Sci. Technol. 17:227-231.

Churchman, G.J. and Tate, K.R. 1986. Aggregation of clay in six New Zealand soil types as measured by disaggregation procedures. Geoderma. 37:207-220.

Coutard, J.P. and Mücher, H.J. 1985. Deformation of laminated silt loam due to repeated freezing and thawing cycles. Earth Surface Processes and Landforms. 10:309-319.

Dudas, M.J. and Pawluk, S. 1969. Naturally-occurring clay-organo complexes in Alberta Chernozems. Geoderma. 3:5-17.

Duchaufour, P. 1982. Pedology: pedogenesis and classification. English version translated by (T.R. Paton). George Allen & Unwin. London.

Edwards, A.P. and Bremner, J.M. 1967. Microaggregates in soils. J. Soil Sci. 18:67-73.

Elliott, E.T. 1986. Aggregate structure and carbon, nitrogen, and phosphorus in native and cultivated soils. Soil Sci. Soc. Am. J. 50:627-633.

Emerson, W.W. 1959. The structure of soil crumb. J. Soil Sci. 10:235-244.

Emerson. W.W., Foster, R.C. and Oades, J.M. 1986. Organo-mineral complexes in relation to soil aggregation and structure. in P.M. Hung and M. Schnitzer (ed), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., pp.521-548.

Ertel, J.R. and Hedges, J.I., 1984. The lignin component of humic substances: distribution among soils and sedimentary humic fulvic and base-insoluble fractions. Geochimica et Cosmochimica Acta, 48: 2065-2074.

Ertel, J.R. and Hedges, J.I. 1985. Sources of sedimentary humic substances: vascular plant debris. Geochimica et Cosmochimica. Acta. 49:2097-2107.

Flaig, W., Beudelspacher, H. and Rietz, E. 1975. Chemical composition and physical properties of humic substances. in J.E. Gieseking (ed). Soil Components. Vol. 1. Organic components. Springer-Verlag New York Inc. New York. pp. 1-211.

Gauthier, T.D., Seitz, W.R., and Grant, C.L. 1987. Effects of structural and compositional variations of dissolved humic materials on pyrene K_{OC} values. Environ. Sci. Technol. 21:243-248.

Greenland, D.J. 1965a. Interaction between clays and organic compounds in soils. Part I. Mechanisms of interaction between clays and defined organic compounds. Soil and Fert. 28:415-425.

Greenland, D.J. 1965b. Interaction between clays and organic compounds in soils. Part II. Adsorption of soil organic compounds and its effect on soil properties. Soil and Fert. 28:521-532.

Gu, B. and Doner, H.E. 1992. The interaction of polysaccharides with Silver Hill illite. Clays and Clay Minerals. 40:151-156.

Harris, R.F., Chesters, G., and Allen, D.N. 1966. Dynamics of soil aggregation. Adv. Agron. 18:107-160.

Hayes, M.H.B. and Himes, F.L., 1986. Nature and properties of humus-mineral complexes. in P.M. Hung and M. Schnitzer (ed), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., pp. 103-158.

Hempfling, R. and Schulten, H.-R., 1991. Pyrolysis-(gas chromatography/) mass spectrometry of agricultural soils and their humic fractions. Z. Pflanzenernahr. Bodenk., 154: 425-430.

Jenny, H. 1980. The Soil Resource: origin and behavior. Springer-Verlag New York Inc. New York.

Jongerious, A. and Schelling, J. 1960. Micromorphology of organic matter formed under the influence of soil organisms, especially soil fauna. in 7th Int. Congress of Soil Science. Madison, Wis. p.702-710.

Kay, B.D. 1990. Rates of change of soil structure under different cropping systems. Adv. Soil Sci. 12:1-52.

Kemper, W.D. and Rosenau, R.C. 1986. Aggregate stability and size distribution. in A. Klute (ed). Methods of Soil Analysis. Part. I.Physical and mineralogical methods. 2nd edition. ASA, SSSA. Madison, Wis. p.425-440.

Kirk, T.K. and Farrell, R.L. 1987. Enzymatic 'combustion': the microbial degradation of lignin. Ann. Rev. Microbiol. 41:465-505.

Kögel-Knabner, I., Zech, W. and Hatcher, P.G., 1988. Chemical composition of the organic matter in forest soils: the humus layer. Z. Pflanzenernahr. Bodenk., 151: 331-340.

Kögel-Knabner, I., Hatcher, P.G. and Zech, W., 1990. Decomposition and humification processes in forest soils: implications from structural characterization of forest soil organic matter. Trans. 14th Int. Congress Soil Sci., Kyoto, Vol. 5, pp. 218-223

Kononova. M.M. 1966. Soil Organic Matter: its nature, its role in soil formation and soil fertility. 2nd English edition. Pergamon Press, Oxford.

Kooistra, M.J. 1990. The future of soil micromorphology. in L.A. Douglas (ed). Soil Micromorphology: a basic and applied science. Elsevier, Amstodam. p.1-8.

Kubiena. W.L. 1938. Micropedology. Collegiate Press Inc. Ames. Iowa.

Kubeana, W.L. 1953. The Soils of Europe. Thomas Murby and Co., London.

Lowe, L.E. 1992. Bound phenolic acids in terrestrial humic acids. Sci. Total Environ. 117/118: 187-195.

Martin, J.P. and Haider, K 1971. Microbial activity in relation to soil humus formation. Soil Sci. 111:54-63.

Martin, J.P. and Haider, K. 1980. A comparison of the use of phenolase and perioxidase for synthesis of model humic acid-type polymers. Soil Sci. Soc. Am. J. 44:983-987.

McBride, M.B., Sikora, F.J. and Wesselink, L.G. 1988. Complexation and catalyzed oxidative polymerization of catechol by aluminum in acidic solution. Soil Sci. Soc. Am. J. 52:985-993.

McGill, W.B. and Cole, C.V. 1981. Comparative aspects of cycling of organic C, N, S, and P through soil organic matter. Geoderma, 26:267-286.

McKeague, J.A., Cheshire, M.V., Andreux, F. and Berthelin, J. 1986. Organo-mineral complexes in relation to pedogenesis. in in P.M. Hung and M. Schnitzer (ed.), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., pp. 549-592.

Miller, R.M. and Jastrow, J.D. 1990. Hierarchy of root and mycrorrhizal fungi interactions with soil aggregation. Soil Biol. Biochem. 22:579-584.

Moore, W.J. 1983. Basic Physical Chemistry. Prentice-Hall, Inc., New Jersey.

Mortland, M.M. and Halloran, L.J. 1976. Polymerization of hydroquinone by primary soil minerals. Soil Sci. 139: 505-511.

Oades, J.M. 1989. An introduction to organic matter in mineral soils. in J.B. Dixon and S.B. Weed. (ed.). Minerals in Soil Environment. 2nd edition. SSSA Inc. Madison, USA. p.89-160.

Oades, J.M. 1993. The role of biology in the formation, stabilization and degradation of soil structure. Geoderma, 56:377-400.

Parfitt, R.L. and Greenland, D.J. 1970a. The adsorption of poly(ethylen glycols) on clay minerals. Clay Mineral. 8:305-315.

Parfitt, R.L. and Greenland, D.J. 1970b. The adsorption of polysaccharides by montmorillonite. Soil Sci. Am. Proc. 34:862-866.

Pawluk, S. 1983. Fabric sequences as related to genetic processes in two Alberta soils. Geoderma, 30:233-242.

Pawluk, S. 1985. Soil micromorphology and soil fauna: problems and importance. Quaestiones Entomologicae. 21:473-496.

Pawluk, S. 1988. Freeze-thaw effects on granular structure reorganization of soil materials of varying texture and moisture content. Can. J. Soil Sci., 68:485-494.

Pawluk, S. and Bal, L., 1985. Micromorphology of selected mollic epipedons, in L.A. Douglus and M.L. Thompson (ed.), Soil Micromorphology and Soil Classification. SSSA. Spec. Publ. 15, Madison, Wis., pp. 63-83.

Peters, T.W. and Bowser, W.E. 1960. Soil survey of the Rocky Mountain House Sheet. University of Alberta Bull. No. 55-1. Alberta soil survey report No. 19. University of Alberta. Edmonton, Alberta.

Pinnavaia, T.J., Hall, P.L., Cady, S.S. and Mortland, M.M. 1974. Aromatic radical cation formation on the intracrystal surfaces of transition metal layer lattice silicates. J. Physical Chemistry. 78(10):994-999.

Rusek, J. 1985. Soil microstructures---contributions on specific soil organisms. Quaestiones Entomologicae. 21:497-514.

Russell, E. W. 1973. Soil Condition and Plant Growth. 10 edition. Longman, London.

Samir, P., Bollag, J.-M. and Huang, P.M. 1994. Role of abiotic and biotic catalysts in the transformation of phenolic compounds through oxidative coupling reactions. Soil Biol. Biochem. 26(7):813-820.

Sanborn, P. and Pawluk, S., 1983. Process studies of a Chernozemic pedon, Alberta (Canada). Geoderma, 31: 205-237.

Schnitzer, M. 1991. Soil organic matter---the next 75 years. Soil Sci., 151(1): 41-58.

Schnitzer, M. 1978. Humic substances: chemistry and reactions, in M. Schnitzer and S.U. Khan (ed.), Soil Organic Matter. Elsevier Scientific Publishing Company, Amsterdam, pp. 1-64.

Schnitzer, M., Kodama, H. and Ripmeester, J.A. 1991. Determination of aromaticity of humic substances by x-ray diffraction analysis. Soil Sci. Soc. Am. J., 55: 745-750.

Schulten, H.-R. and Leinweber, P. 1991. Influence of long-term fertilization with farmyard manure on soil organic matter: characteristics of particle-size fractions. Biol. Fertil. Soil. 12:81-88.

Schulten, H.-R., Plage, B. and Schnitzer, M. 1991. A chemical structure for humic substances. Naturwissenschaften, 78: 311-312.

Shino, H. and Huang, P.M. 1985. Catalytic polymerization of hydroquinone by primary soil minerals. Soil Sci. 139:505-511.

Shipitalo, M.J. and Protz, R. 1989. Chemistry and micromorphology of aggregation in earthworm casts. Geoderma, 45:357-374.

Stevenson, F.J. 1982. Humus Chemistry, Genesis, Composition, Reactions. John Wiley & Sons, New Yowk.

Theng, B.K.G. 1982. Clay-polymer interactions: summary and perspectives. Clays and Clay Minerals. 30:1-10.

Theng, B.K.G. and Scharpenseel, H.W. 1975. The adsorption of the ^{14}C-labelled humic acids by montmorillonite. in Proceedings in the international clay conference 1975. Applied Publishing Ltd. Wilmette, Illinois. p.643-653.

Theng, B.K.G., Churchman, G.J., and Newman, R.H. 1986. The occurrence of interlayer clay-organic complexes in two New Zealand soils. Soil Sci.,145 (5):262-266.

Theng, B.K.G., Tate, K.R., and Becher-Heidmann, P. 1992. Towards establishing the age, location, and identity of the inert soil organic matter of a spodosol. Z. Pflanznernahr. Bodenk., 155:181-184.

Tisdal, J.M. and Oades, J.M., 1982. Organic matter and water stable aggregates in soils. J. Soil Sci., 33:141-163.

Van Vliet-Lanoe, B., Coutard, J.P., and Pissart, A. 1984. Structures caused by repeated freezing and thawing in various loamy sediments: A comparison of active, fossil and experimental data. Earth Surface Processes and Landforms, 9:553-565.

Varadachari, C. and Ghosh, K. 1984. On humus formation. Plant Soil. 77:305-313.

Wang, M.C. and Huang, P.M. 1989. Pyrogallol transformations as catalyzed by nontronite, bentonite, and kaolinite. Clay and Clay minerals. 37(6): 525-531.

Wang, T.S.C., Hung, P.M., Chou, C.H. and Chen, J.H. 1986. The role of soil minerals in the abiotic polymerization of phenolic compounds and formation of the humic substances, in P.M. Hung and M. Schnitzer (ed.), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., pp. 251-281.

Wang, T.S.C., Li, S.W. and Feng, Y.L. 1978. Catalytic polymerization of phenolic compounds by clay minerals. Soil Sci. 126:15-21.

Wershaw, R.L. 1992. Membrance-micelle model for humus in soils and sediments and its relation to humification. Open File Report 91-513, US Geological Survey, Denver, Colorado.

Wilson, M.A. 1991. Analysis of functional groups in soil by nuclear magnetic resonance spectroscopy, in K.A. Smith (ed.), Soil Analysis: Modern Instrumental Techniques, 2nd edition, Marcel Dekker Inc., New York, pp. 601-645.

Xing, B., McGill, W.B., Dudas, M.J., Hepler L.G., and Dobrogowska, C. 1993. Thermodynamic parameters for pentachlorophenol sorption on montmorillonite in aqueous suspensions. Chemosphere. 26:1311-1324.

Xing, B., McGill, W.B. and Dudas, M.J. 1994a. Sorption of α-naphthol onto organic sorbents varying in polarity and aromaticity. Chemosphere. 28(1):145-153.

Xing, B., McGill, W.B. and Dudas, M.J. 1994b. Cross-correlation of polarity curves to predict partition coefficients of nonionic organic contaminants. Environ. Sci. Technol., 28:1929-1933.

Zeikus, J.G. 1982. Lignin metabolism and the carbon cycling---polymer biosynthesis, biodegradation, and environmental recalcitrance. Adv. Microb. Ecol. 5:211-243.

Chapter II

Granular Structures in Two Alberta Mollisols: micromorphology, mineralogy, physical properties and lysimetry

INTRODUCTION

The similarity of the shot structure in the Raven soil and granular structure in the Malmo soil as reviewed in Chapter I, initiated a comparative study of their genesis. The study of soil structures can be approached with an evaluation of their mineral matrix composition and organic components, especially the humic substances and polysaccharides that are usually involved in soil aggregation (Kononova, 1966; Tisdal and Oades, 1982, Emerson et al. 1986). Soil micromorphological investigation dealing with the spatial relationship of structural constituents is most suitable for study of soil structure. Micromorphological observations suggest that granular structures in similar European soils largely originate from the activity of soil fauna, especially enchytraeid and earthworms (Kubiena, 1953; Bal, 1982). In the western Canadian soils, a number of different soil fauna are also involved in the genesis of granular structure in Ah horizons (Pawluk, 1985, Pawluk and Bal, 1985). Repeated freezing/thawing has also been reported as contributing to aggregation, although structural units formed by soil fauna and those by repeated freezing/thawing are usually difficult to differentiate (Pawluk, 1985). The presence of associated micromorphological features such as banded structures (Pawluk, 1988), conglomeric and orbiculic fabrics (Fox, 1979), and related voids forms, such as joint planes, smooth metavughs, and vesicles (Pawluk, 1988), are characteristic of the latter. Factors affecting soil structural development were reviewed in Chapter I.

This study is designed to determine whether the macrostructural differences in the Raven and Malmo soils are reflected in the following: micromorphological and mineralogical properties, distribution and stability of soil aggregates, neutral sugar distribution, and leachate chemistry of the two soils. The genesis of the granular structures in the two soils is also compared.

MATERIALS AND METHODS

Site description

Soil samples were collected from the Raven series, an Othic Humic Gleysol developed in a level to depressional area near Banalto (approximately 52°23' N latitude and 114°42' W longitude), and a Malmo soil, a Gleyed Black Chernozem at the Ellerslie Research Station (approximately 53°25' N latitude and 113°33' W longitude), University of Alberta. Classification of soils was according to the Canadian System of Soil Classification (Agriculture Canada Expert Committee on Soil Survey, 1987). The Raven soil (Table 2-1) is developed under a grassland plant community and has a thick Ah horizon and shot structure in its lower Ah and AB horizons. The Malmo soil is developed under open aspen woodland with a dense grass and forb understory. It has a well developed organic layer and thick Ah horizon dominated by granular structure (Sanborn and Pawluk, 1983).

Soil Characterization

Routine soil analyses were conducted on air-dried samples after passing through a 2.0 mm sieve. Particle size distribution was determined by the pipette method (McKeague, 1978; Gee and Bauder, 1986). Soil pH was measured in deionized water at 1:2 weight to volume ratio. The exchangeable cations were displaced with buffered 1N NH_4OAc (pH 7) and Ca^{++}, Mg^{++}, K^+, and Na^+ were determined with a Perkin-Elmer model 2380 atomic absorption spectrophotometer (AAS). Total CEC of soils was calculated from the measured amount of exchangeable NH_4^+ adsorbed as determined with an autoanalyzer. Soil subsamples were further ground (< 0.25 mm) for determination of soil organic carbon (modified Walkley-Black methods by Nelson and Sommers, 1982), total N content (semimicro-Kjeldahl method), carbonate content (Bundy and Bremner, 1972), and extractable Fe and Al (McKeague, 1978).

Clay mineralogy

Clay (< 2 μ) was separated from soil samples from major horizons of the two soils by wet sieving and gravity sedimentation (Jackson, 1979) after soil samples of 25 g were ultrasonically dispersed in 250 mL of distilled water using a Braun-sonic 1510 (B. Braun, Melsungen, USA) vibrator probe (tip diameter 1.9 cm) for 6 min (2 times for 3 min) at 380 watts (Edwards and Bremner, 1967). No chemical pretreatments were used. The clay mineral identification was conducted by XRD analyses using a Philips PW1730 x-ray generator with Co-Kα radiation generated at 50 kV and 25 mA and focused with a LiF monochromator. The scanning step was 0.053° 2θ every 2 seconds. The clay samples were separately saturated with Ca^{++} and K^+ and slides were prepared according to the paste method (Theisen and Harward, 1962). The K-saturated slides

Table 2-1. Macromorphology of soils

Horizon	Depth (cm)	Color (moist)	Texture	Structure	Consistence	Boundary
			Raven soil			
Sod layer	0-10	nd	SiC	str fine gran	nd	abrupt wavy
Ah1	10-17	10 YR 2/2	SiC	str fine gran	pla, sli sti	clear wavy
Ah2	17-24	10 YR 2/2	SiC	str, fine gran	pla, sli sti	clear wavy
AB	24-36	10 YR 3/2-3/3	SiC	str fine gran	pla, sli sti	clear wavy
Bg	36-52	10 YR 4/3-5/3 matrix, 2.5Y 5/6 mottles	SiC	mod fine sub to gran	pla, sli sti	clear wavy
Ckg	>52	2.5 Y 5/2 matrix, 2.5 Y 4/6 mottles	SiC	massive	pla, sli sti	nd
			Malmo soil			
LF	18-13	7.5YR 3/2	nd	matted litter	nd	abrupt smooth
FH	13-15	5YR 3/3	nd	fibrous-amorph	nd	clear smooth
H	5-0	5YR 2/2	nd	amorph	nd	abrupt smooth
Ah1	0-10	10YR 2/1	SiC	str gran	sli firm	gradual wavy
Ah2	10-29	10YR 3/1-4/1	SiC	str med-fine gran	sli firm	clear wavy
Ah3	29-35	2.5Y 3/2	SiC	str fine gran, fine sub	firm	abrupt brocken
ABgj	35-42	2.5Y 5/2 matrix, 2.5Y 5/6 mottles	SiC	wk fine pl, wk fine gran.	firm	abrupt brocken
Bmgj	42-57	2.5Y 4/2 matrix, 2.5Y 4/4 mottles	SiC	mod fine sub	v. firm	gradual wavy
Ckgj	103+	2.5Y 4/2 matrix, 2.5Y 5/4-5/6 mottles	HC	massive	v. firm	nd

Abbreviations: nd=not determined, SiC=silty clay, HC=heavy clay, str=strong, gran=granular, mod=moderate, sub=subangular blocky, amorph=amorphous, pl=platy, pla=plastic, sli=slightly, sti=sticky, v.=very.

were scanned after heating to 105°C and run at 0% and 54% r.h. They were further heated to 300°C and 550°C and run at 0% r.h. Ca-saturated slides were scanned at room temperature at 54% r. h. and then at 0% r.h. after ethylene glycol or glycerol solvation (Warren and Dudas, 1992; Xing and Dudas, 1994). The scanned ranges were 3-36° 2θ for K-saturated samples heated to 105°C and Ca-saturated samples that were equilibrated at 54% r.h., and 3-19° 2θ for other treatments.

Micromorphology

Undisturbed soil monoliths were sampled with Kubiena boxes (Kubiena, 1953) and air-dried in the laboratory. The dried monoliths were impregnated with 3M Scotchcast electrical resin and 30 μm thick thin-sections were prepared with the aid of a Logitech polisher for the entire vertical section of the pedon in the Raven soil and the upper section (LF to Ah3) in the Malmo soil. Thin-section descriptions followed the terminology defined by Bullock et al. (1985) for microstructure, Brewer (1976) for void, pedofeature and plasma fabric, and Brewer and Pawluk (1975) and Pawluk (1983) for related distribution patterns (RDPs). General terminology for frequency, size, shape and smoothness of micromorphological components also followed Bullock et al. (1985). Optical recognition of mineral grains was carried out according to Kerr (1977). Descriptions were made with the aid of a Zeiss microscope and image analyses for selected fabric features were conducted with an attached Mop-Videoplan interactive image analysis system (Pawluk, 1988). The semi-quantitative energy dispersive x-ray analysis (EDX) for selected micromorphological features was conducted with the aid of a Cambridge Stereoscan 250 scanning electron microscope (SEM) equipped with a Tracor Northern x-ray analyzer.

Aggregate analysis

Wet sieving of soil aggregates was performed on field-moist samples and air-dried samples after passing through a 8 mm sieve. The soil samples were sieved with a set of six sieve nests (4.0, 2.0, 1.0, 0.5, 0.25, 0.125 mm) at an oscillating aptitude of 2.5 cm, 60 rotation per min for 30 min. The aggregates left on the sieve after 30 min were washed down quantitatively with distilled water and collected in pre-weighed drying tins and then oven-dried and weighed. Percentage of dry weight of each aggregate group over the total dry weight of soil was calculated. No correction for sands was conducted as microscopic observation showed a low content of sand particles for each aggregate group and the particle size analysis indicated that the two soils had low sand contents throughout the pedons (<10%). The samples were analyzed in triplicate. Statistical analyses for the aggregate data were conducted using SAS software (SAS Institute Inc., 1987).

Carbohydrate

Finely ground (< 0.149 mm) soil samples were hydrolyzed for 24 hours at 80°C with 3N H_2SO_4 following the procedure of Angers et al. (1988). The hydrolyzate was neutralized with saturated $Ba(OH)_2$ solution to pH7 and centrifuged at 12100 g to remove $BaSO_4$ precipitate. The neutralized supernatant eluted through the H^+-exchanged Fisher Resin 101 to remove interference cations, then through the acetate-exchanged Fisher Resin 201 to separate uronic acids from neutral sugars (Cheshire, 1979; Shaw and Pawluk, 1986). Aliquots of the neutral sugar solution were filtered through 0.22 μ nylon syringe filter to remove particulates then stored in polypropylene plastic bottles at 4°C till analyses. Contents of seven monosaccharides (fucose, arabinose, rhamnose, galactose, glucose, xylose and mannose) were quantified by HPLC. The high performance anion chromatography was performed using a Dionex 4500i system (Sunnyvale, Calif.) with pulse amperometric detection. The analytical column was a CarboPac™ PA1 column. A gradient elution using deionized water as the basic mobile phase, and 0.1N NaOH as the gradient former, was conducted at a flow rate of 1.0 mL/min.

Leachate

Three lysimeters were installed in the Raven soil at 0-10cm (Sod layer), 0-24 cm (Sod layer to Ah2 horizon) and 0-36 cm (Sod layer to AB horizon) in Sept. 1990. Two lysimeters were also installed in the Malmo soil, one through the organic horizons (LF to H layer) and the other to the middle of the Ah horizons (LF layer to Ah2) following the procedure of Sanborn and Pawluk (1983). The lysimeters were made up of plastic tubing with diameter of 10 cm. Leachate samples were collected in May (Spring), June and August (Summer) and September and October (Fall) at the Raven soil in 1991 and 1992. Samples at the Malmo site were collected only in 1992. The samples were stored in a cool box containing bags of ice during transportation and the electric conductivity (EC) and soil pH were measured immediately after returning to the laboratory. Cation concentrations were measured with AAS. Anions were determined with an anion exchange column using a Dionex HPLC system. Amount of soluble organic carbon (SOC) in the filtered leachates was measured with an Astro instrument (Model 2001 System 2) equipped with an infrared analyzer sensitized to CO_2 that is converted from samples through ultra-violet promoted persulfate oxidation (Astro International Corporation, 1990).

RESULTS AND DISCUSSION

Analytical properties

The two soils have high clay and low sand contents. The upper sections are enriched with organic matter that decreases gradually with depth in the Raven soil but abruptly in the Malmo soil. Soil reaction is neutral throughout the sola for both soils. Exchangeable [illegible] dominates their exchange complexes, followed by Mg^{++}, and minor amount of K [illegible]ble 2-2). The sodium pyrophosphate extractable Fe and Al compounds are [illegible] solum, especially in the Ah2 and AB horizons, of the Raven soil than [illegible] soil. These organic-bonded sesquioxides have lower concentrations in the lower section of both soils (Table 2-3). The acid-ammonium oxalate extractable Fe and Al are higher in the Sod to Ah2 horizons of the Raven soil and decease with depth. In the Malmo soil, these types of Fe compounds have lower concentrations in the lower Ah to ABgj horizons, and concentration of the Al compounds decrease with depth. Variation in concentration of the sodium dithionite-citrate-bicarbonate (NaDCB) extractable Fe is low in the Raven soil; their contents are lower in the upper solum of the Malmo soil. There is a small decrease in NaDCB extractable Al with depth in the Raven soil but no apparent variation in the Mamlo soil.

Micromorphology

The surface of the Raven soil was covered by phyto-units of grass which are mixed with faecal pellets of dipterous larvae, collembola, and very seldom, oribatid mites (Fig.2-1a and 2-1b). Large (0.5-1.0mm) crumbs and granules of mull composition that are likely earthworm casts, and smaller (35-80μ), discrete, organic, faecal pellets, dominantly of collembola, form a complex microstructure with bimodal distribution (Fig.2-1c and 2-1e). Several large aggrotubules likely of similar origin to the large crumbs and granules were also observed. Soil materials are well homogenized and have dense skeli-porphyric RDP and weak to moderate skeli-mosepic plasma fabric that is strongly masked by dark colloidal humic substances (Fig.2-1d, 2-1e, 2-1h). There are a few yellowish sedimentary nodules contributing a very minor matrigranic fabric component in the Sod layer. The nodules are very dense, and have skeli-masepic plasma

Table 2-2. Chemical and physical properties of soils

Horizon	Depth (cm)	Sand (%)	Clay (%)	Org. C. (g/100g)	N (g/100g)	C/N	pHw‡	TCEC (cmol/kg)	Exchangeable cations (cmol/kg)				CaCO$_3$ (g/100g)
									Ca^{++}	Mg^{++}	K^{+}	Na^{+}	
							Raven soil						
Sod	0-10	10	45	6.47	0.56	12	6.9	43.5	30.4	7.06	0.72	0.07	0.3
Ah1	10-17	8	43	4.57	0.41	11	6.5	41.7	25.1	6.30	0.57	0.09	0.0
Ah2	17-24	10	42	3.09	0.29	11	6.3	37.8	22.7	6.07	0.65	0.12	0.0
AB	24-36	9	45	1.39	0.14	10	6.5	32.7	21.5	6.61	0.63	0.11	0.0
Bg	36-52	10	44	0.56	0.07	8	7.7	27.8	25.2	7.06	0.58	0.10	0.8
Ckg	52+	1	53	0.44	0.06	8	8.2	27.3	29.9	7.31	0.48	0.11	1.3
							Malmo soil #						
LF	18-13	n.d.*	n.d.	48.5	1.80	27	7.2	138.6	70.4	22.5	3.20	0.40	n.d.
FH	13-5	n.d.	n.d.	39.4	2.20	18	6.9	140.7	74.6	21.7	2.6	0.40	n.d.
H	5-0	n.d.	n.d.	41.1	2.40	17	6.6	159.9	76.2	20.0	1.20	0.10	n.d.
Ah1	0-10	9	48	5.9	0.53	11	6.1	54.2	68.6	28.8	2.40	0.10	n.d.
Ah2	10-29	10	46	2.1	0.15	14	6.6	40.6	61.3	36.2	1.70	0.20	n.d.
Ah3	29-35	9	49	0.5	0.08	6	6.7	35.9	58.8	39.0	1.90	0.30	n.d.
ABgj	35-42	11	42	0.3	0.06	5	6.9	24.1	60.6	34.9	1.70	0.40	n.d.
Bmgj	42-57	7	53	0.5	0.07	7	7.3	39.1	60.1	32.5	1.50	0.30	0.0
Ckgj	103+	3	63	0.6	0.06	10	7.8	51.1	73.4	22.1	1.20	1.20	1.1

‡: pHw = pH values in 1:2 water suspension.

#: data adopted from Sanborn and Pawluk (1983) or Sanborn (1981) for Malmo soil.

*: n.d.= not determined.

Table 2-3. Extractable Fe and Al content (g/100g soil) in two soils

Horizon	Fe_p†	Fe_o‡	Fe_d¶	Al_p	Al_o	Al_d
			Raven soil			
Sod	0.22	0.22	0.90	0.22	0.52	0.19
Ah1	0.29	0.24	0.89	0.32	0.52	0.17
Ah2	0.36	0.22	0.82	0.53	0.50	0.24
AB	0.38	0.18	0.90	0.60	0.46	0.08
Bg	0.12	0.14	0.84	0.12	0.25	0.10
Ckg	0.04	0.08	0.91	0.05	0.16	0.12
			Malmo soil#			
Ah1	0.37	0.31	0.44	0.34	0.20	0.09
Ah2	0.10	0.21	0.46	0.11	0.17	0.09
Ah3	0.11	0.23	0.87	0.13	0.13	0.10
ABgj	0.13	0.26	0.90	0.14	0.12	0.09
Bmgj	0.09	0.27	1.14	0.10	0.13	0.10
BCkgj	0.06	0.32	1.07	0.08	0.10	0.06
Ckgj	0.07	0.32	1.12	0.10	0.09	0.06

†: p=sodium pyrophosphate extraction.
‡: o=acid ammonium oxalate extraction.
¶: d=sodium dithionite-citrate-bicarbonate extraction.
#: data of Malmo soil were adopted from Sanborn (1981)

fabric (Fig.2-1f and 2-1g). They are likely B horizon materials brought up by burrowing soil animals.

The Ah1 horizon has a mixed mullgranoidic to metafragmoidic fabric that is associated with a dominantly subangular blocky microstructure (Fig.2-2a). Towards the middle and lower section of the Ah1 horizon, there is an increase in metafragmic fabric components and a decrease in mesofaunal faecal pellets. The Ah2 horizon has a mixed mullgranic to metafragmic fabric comprised of accommodating to partially accommodating subangular blocky or granular structural units. A concentric basic distribution pattern (BDP), as defined by Brewer (1976), of these metafragmic units delineates an 'orbiculic' secondary fabric (Fox, 1979) that dominates the Ah2 to AB horizons (Fig.2-2b). Circular arrangement of the quartz skeleton grains is evident in these horizons (Fig. 2-2d). Typical structural units in the Ah2 and AB horizons are dense and poorly homogenized. Some aggregates contain diffuse Fe nodules in the centre that are encompassed by a mull edge forming another secondary

Fig 2-1. Micromorphological features in Sod layer of the Raven soil:

A. Melanized phytogranic units, large, equant, smooth fly larvae faecal pellets containing fibrous phyto-tissue, and micro-meso, equant to oblate, smooth collembola faecal pellets of amorphous organics. Upper Sod layer, plain light (PL), frame length (FL)=5.73mm.

B. Abundant collembola faecal pellets (45-70μ) mixed with semi-decomposed fibrous grass tissue, ellipsoidal oribatid mite faecal pellets (35μ) are of rare occurrence at the bottom right corner. Upper Sod layer, PL, FL=0.72mm.

C. Mullgranic units formed by dense, well homogenized earthworm faecal pellets of 1120-1750μ, surrounded by smaller humigranic units, largely collembola faecal pellets of 42-80μ, and form typical bimodal distribution in middle Sod layer, PL, FL=5.73mm.

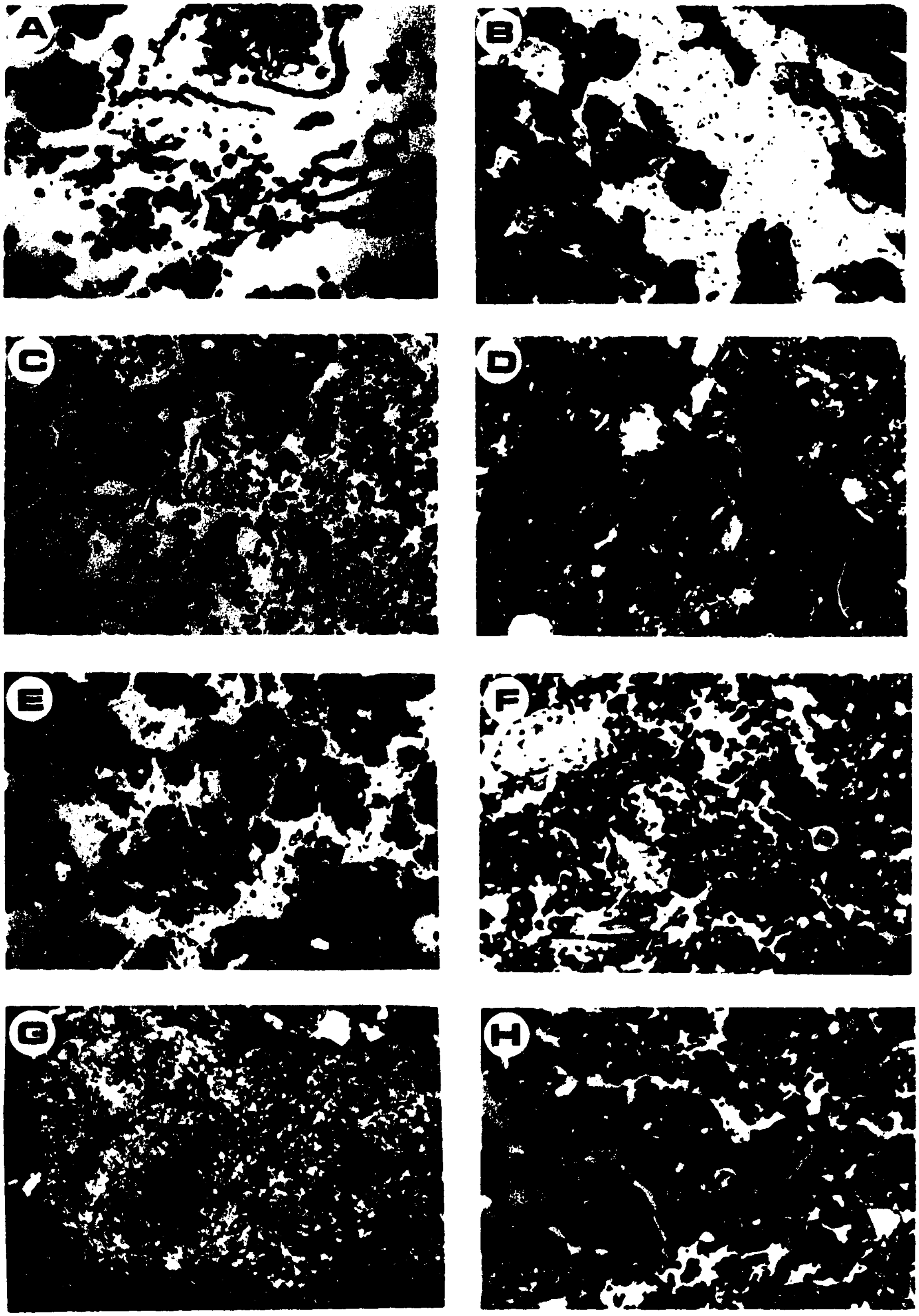
D. Weak to moderate vo-skeli-mosepic plasma fabric, strong masking by humic substances, and mammillated metavugh of earthworm faecal pellets in Fig. C, crossed polarizers (XPL), FL=0.72mm.

E. Dominantly equant to oblate, smooth collembola faecal pellets (30-80μ) composed of well humified, isotropic organic substance in bimodal distribution of Fig. C, partially crossed polarizers (PPL), FL=0.72mm.

F. Very few yellowish matrigranic sedimentary nodules are also present in the middle Sod layer, PPL, FL=5.73mm.

G. Enlarged portion of Fig.F: skeli-bimasepic plasma fabric for the sedimentary nodules containing reddish Fe nodules. XPL, FL=0.72mm.

H. Large aggrotubules with dense earthworm cast (3mm) continuous infilling. The cast is strongly masked by humic substance and is well homogenized. Upper Sod layer, PPL, FL=5.73mm.


A
B
C
D
E
F
G
H

'matriconglomeric' fabric (Fox, 1979). A few vesicles and metavughs dominate their intra-aggregate voids and these structural units have smooth lower boundaries (Fig.2-2b, 2-2e, 2-2f, 2-2g, 2-2h). Semi-quantitative EDX analyses on a few representative areas (50μ by 50μ each) show that Fe content is about two to three times higher in the center zones than in the edge portion of the typical metafragmic and conglomeric units. A sharp decrease in faunal features is most evident in the Ah2 and AB horizons.

The upper Bg horizon has a spongy microstructure and the lower Bg grades to a spongy-vughy microstructure with an increase in the abundance of interconnected and isolated vughs and vesicles (Fig.2-3a, 2-3b). The Ckg horizon has a dominant vughy microstructure and crystic plasma fabric (Fig.2-3c, 2-3d). Ortho-Fe nodules are abundant. In some zones, weakly developed aggregates are mixed with vughy groundmass, resulting in minor zones of spongy to vughy intergrade microstructure. In these zones, some granules of a mull nature are imbedded in the groundmass. These granules contain more silt-size mineral grains (dominantly quartz) than the groundmass (Fig.2-3e). Detailed micromorphological descriptions for Raven soil are given in Appendix Ia.

The upper section of the Malmo soil is characterized by coarse phyto-units and abundant and diverse faunal features such as faecal pellets of oribatid mites, collembola, beetle larvae, millepedes, and dipterous larvae (Fig.2-4a, 2-4b, 2-4c, 2-4d, 2-4e). The size of oribatid mite faecal pellets ranges from 28 to 80μ depending on microhabitats (Fig.2-4b and 2-4c). The size of phyto-units decreases in the transitional FH layer where abundance of faunal faecal pellets increases (Fig.2-4e). The H layer is dominated by fine humigranic-granoidic complex fabric, largely comprised of mesofaunal faecal pellets or casts; the size and abundance of phytogranic components are substantially decreased (abundance <5%) (Fig.2-4g, 2-4f).

The upper Ah horizon of Malmo soil shows considerable heterogeneity in composition and in its microfabric which is generally a separated modergranic-fragmic complex (Fig.2-4h). Better mixing of plasma was observed in the lower section of Ah1 to Ah2 horizons where mullgranoidic or banded mullgranoidic fabrics prevail (Fig.2-5a, 2-5b, 2-5c). Some of the aggregates, likely earthworm faecal pellets, are re-arranged towards banded mullgranoidic fabric (Fig.2-5b). The Ah2 horizon is also abundant in chambers where faecal pellets of collembola dominate (Fig.2-5d). The general microstructure of the middle to lower Ah2 is a complex formed by large mullgranic and humigranic units similar to that in the Sod layer of the Raven soil (Fig.2-5c). The Ah3 horizon has a separated complex fabric of banded mullgranoidic and mullgranic fabric

Fig. 2-2. Micromorphological features in the Ah and AB horizons of Raven soil:

A. Mullgranoidic to fragmoidic intergrade fabric in Ah1: weak to moderate mosepic plasma fabric, strong masking by humic substances, ortho-Fe nodules in centre of some aggregates, short craze planes with weak horizontal orientation are dominant interaggregate voids and orthovughs are major intra-aggregate voids. XPL, FL=2.86mm.

B. Orbiculic fabric in Ah2: The concentric arrangement of the subangular blocky aggregates that are accommodated or partially accommodated to each other in arrangement. Also noted is a significant decrease in abundance of smaller humigranic faecal pellets. PL, FL=5.73mm.

C. Same view as Fig. B: Weak skeli-mosepic plasma fabric, inter-aggregate voids are similar to Ah1. However, metavughs and vesicles are the dominant intra-aggregate voids. PPL, FL=5.73mm.

D. Patches of circular arrangement of mineral grains in the orbiculic fabric zone presented in Fig.C, XPL, FL=2.86mm.

E. Typical subangular blocky to granular intergrade aggregates in lower Ah2 and most part of AB horizons. The units are dense, partially accommodating and are poorly homogenized. Fe nodules are discernible at the centre of the aggregates and they also have smooth lower boundary. Short craze planes and slightly interconnected metavughs dominate the inter-aggregate voids while a few vesicles and smaller metavughs are major intra-aggregate voids. XPL, FL=5.73mm.

F. Granular structure in lower Ah2 and AB horizons: The aggregates are dense and lack homogenization. Presence of Fe nodules in the centre of some aggregates with mull outer portion form matriconglomeric fabric. Compound packing voids are dominantly inter-aggregate voids between densely packed soil materials. Few vesicles and metavughs are present as major intra-aggregate voids. PPL, FL=5.73mm.

G. Enlarged matriconglomeric fabric in Fig.F, note the edges of the original granular units that are weakly separated from the mull outer portion. PL, FL=2.86mm.

H. Same area as Fig. G: dense porphyric related distribution inside the matriconglomeric units, note the cementation by the diffuse Fe nodule in the central zone of the granule, and very few micro to meso vughs in the granule. XPL, FL=2.86mm.

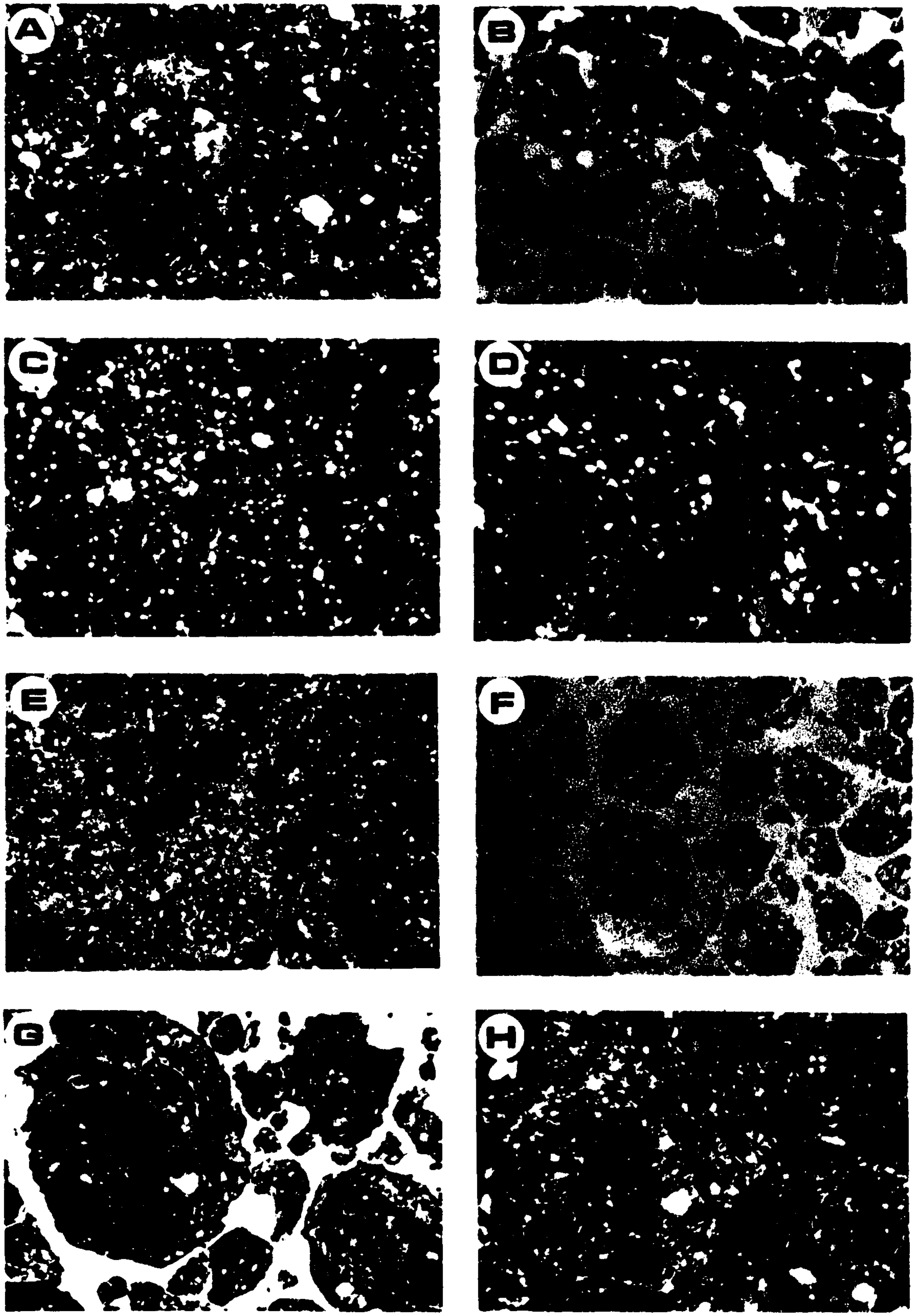

A
B
C
D
E
F
G
H

Fig. 2-3. Micromorphological features in the Bg and Ckg horizons of Raven soil:

A. Spongy and granular intergrade microstructure in the upper Bg; dominantly metafragmoidic and mullgranoidic units of 420-850μ, separated dominantly by interconnected vughs or compound packing voids. Vesicles are common within the granules, some granules have conglomeric fabric. PL. FL=5.73mm.

B. Spongy to vughy intergrade microstructure in lower Bg: Moderately formed matrigranoidic units (140-700μ) are weakly separated, indicating an intermediate stage of aggregate development, likely by freeze/thaw effects. Note vesicles are frequent within aggregates and ortho Mn/Fe nodules are discernible. PL, FL=5.73mm.

C. Vughy microstructure in Ckg: Mineral groundmass is weakly separated by vughs and vesicles; some ortho Fe nodules are noticeable. XPL, FL=5.73mm.

D. Crystic plasma fabric in the Ckg horizon. XPL, FL=0.72mm.

E. Zones of spongy-vughy complex microstructure in Ckg: Weakly formed aggregates; earthworm faecal pellets (600-1100μ) containing more sand- and silt-sized quartz grains and strongly masked by humic substances, are imbedded in the mineral groundmass of crystic plasma fabric. XPL, FL=5.73mm.

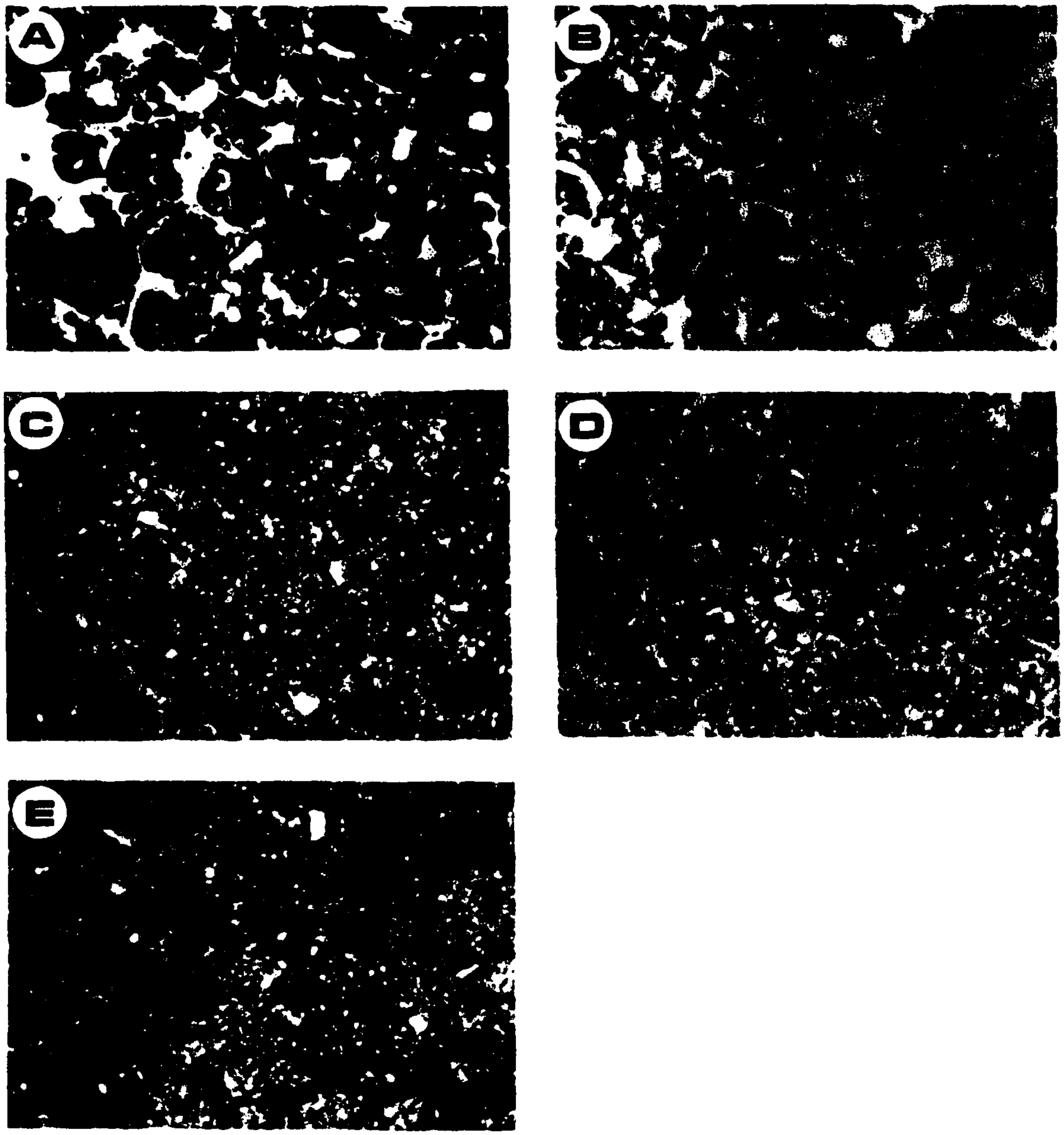

A
B
C
D
E

Fig. 2-4. Micromorphological features in the organic layers and Ah horizons of Malmo soil:

A. Phytogranic units in LF layer: Largely leaf vessels (280-8700μ), stems and bark debris (364-2200μ) mixed with minor amount of faecal pellets (dominantly 35-70μ) of mesofauna. PL, FL=5.73mm.

B. Ellipsoidal faecal pellets (53-80μ) of oribatid mites, exclusively isotropic, amorphous organic substances, in the centre of woody fragments. Outside the woody fragment are aged collembola faecal pellets of various shapes. PL, FL=0.72mm.

C. Beetle larvae faecal pellets (50-90μ), containing small fibrous tissue, are found in the upper cavity of woody fragments. In the middle and lower feeding cavities are ellipsoidal faecal pellets (28-50μ) of small oribatid mites. Outside the woody fragment are aged collembola faecal pellets of various shape. LF layer, PL, FL=2.86mm.

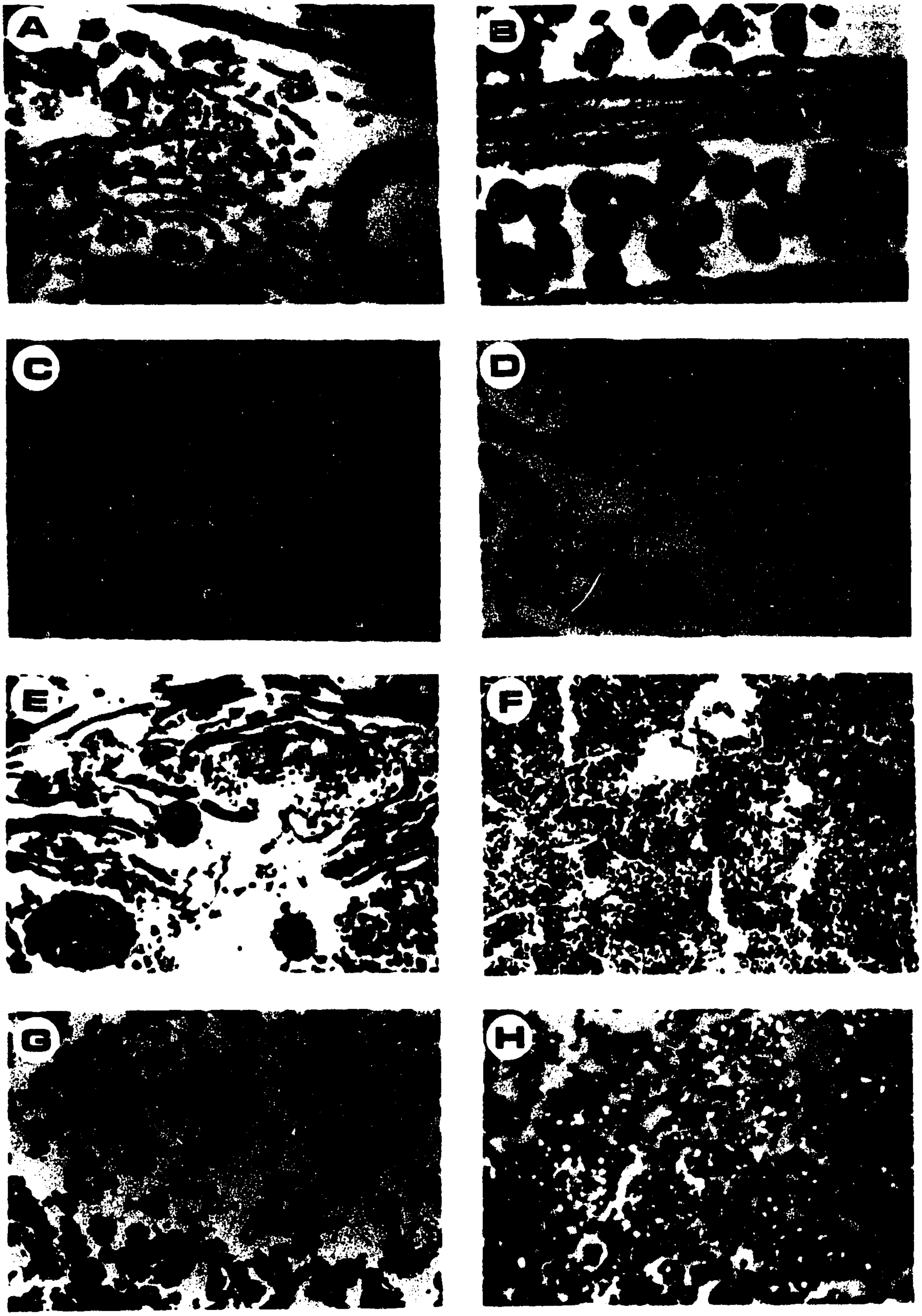
D. Spherical faecal pellets (580-650μ) of millepede, composed of porous, mull substance. LF layer, PL, FL=5.73mm.

E. Spherical faecal pellets of fly larvae, containing woody fragments. FH layer, PL, FL=5.73mm.

F. Fine spongy and vughy microstructure of the H layer: organic faecal pellets largely of mesofauna form loose patches (about 560μ), separated by craze planes. There are very few well melanized, small phytofragments present. PL, FL=5.73mm.

G. Enlarged view of Fig.F: Humigranoidic fabric dominantly comprised of isotropic faecal pellets and casts of mesofauna. PL, FL=0.72mm.

H. Mixed crumbs, granules and subangular blocky aggregates with heterogeneous plasma compositions in the upper Ah1, PPL, FL=5.73mm.


A
B
C
D
E
F
G
H

zones (Appendix Ib). Yellowish sedimentary nodules, similar to those in the Raven soil, are also observed to be assembled into the banded mullgranoidic fabric (Fig.2-5e). Some zones in the Ah3 horizon showed a unique obliquely banded mullgranoidic fabric (Fig.2-5g). However, platy aggregates in the banded mullgranoidic fabric zones have silasepic to weak mosepic plasma fabric and are identical to those in the mullgranic zones (Fig.2-5f and 2-5c). Mullgranoidic to porphyric intergrade fabric is observed in the lower Ah3 horizon and some aggregates are re-arranged into minor conglomeric-porphyric fabric units (Fig.2-5h). A detailed micromorphological description for Malmo soil was outlined in Appendix Ib.

The granic sequence generally dominates the overall fabrics in the Sod layer of the Raven soil and the Ah horizon of the Malmo soil where a banded mullgranoidic fabric component is frequently observed as well. The Ah and AB horizons of the Raven soil is dominated by the metafragmic fabric sequence. In the Raven soil, change in dominant fabric sequence is as follows: matriporphyric (Ckg), matriporphyric to metafragmoidic (Bg), metafragmic (AB to Ah2), metafragmic to metafragmoidic (Ah1), mullgranic, humigranic, and phytogranic (Sod layer), proceeding from the parent materials to the surface of the soil, thus representing a shift from physical processes to biological processes, although mixing of these fabric components in localized zones appears unavoidable. A few sedimentary nodules are scattered throughout the soil above the B horizons in both soils and are responsible for minor areas of matrigranic fabric. These are likely mineral matrix brought up by soil fauna into the upper horizons from the B horizon which has a similar porphyriskelic RDP and skeli-masepic to skeli-omnisepic plasma fabrics. The presence of these nodules reflects the youthful nature of the two Alberta Mollisols and are characteristic of western Canadian soils as observed by Pawluk (1985) and Pawluk and Bal (1985). Dominance of the metafragmic fabric in the Ah2 and AB horizons of the Raven soil is a reflection of freeze/thaw effects. The presence of vesicles and metavughs, the circular arrangement of the fine sand- to silt-size mineral grains, and the associated secondary fabrics (orbiculic and conglomeric) tend to support this possibility since these fabric features are typical of soils subjected to frost influence (Fox, 1979; Pawluk, 1988). The dense appearance, poorly homogenized plasma composition, and smooth lower boundary of typical aggregates in the Ah2 and AB horizons closely resemble aggregates generated by freeze/thaw effects (Van Vliet-Lanoe et al. 1984; Pawluk, 1988). Bullock et al. (1985) stated that excrements of soil fauna are usually unaccommodated in their arrangement. Thus the genesis of the 'shot structure' in the Ah2 and AB horizons in Raven soil is likely a result

Fig. 2-5. Micromorphological features in the Ah horizons of Malmo soil:

A. Middle Ah1: Large aggrotubule (6.2 mm) of earthworm casts is infilling the inter-aggregate space of crumbs and granules. Some platy aggregates are rearranged into minor banded mullgranoidic fabric zones. PPL, FL=5.73mm.

B. Banded mullgranoidic fabric in Ah2: Aggregates are rearranged into banded mullgranoidic intergrade fabric (right side of picture) likely by freeze/thaw. An earthworm cast (left side of picture) is incorporated into platy aggregates. PPL. FL=5.73mm.

C. Mullgranoidic fabric in Ah2 horizon: Isotropic faecal pellets of mesofauna are distributed in the inter-aggregate spaces of larger aggregates (560-2000µ) with strong masking by humic substances. The latter have silasepic to insepic plasma fabrics. PL, FL=5.73mm

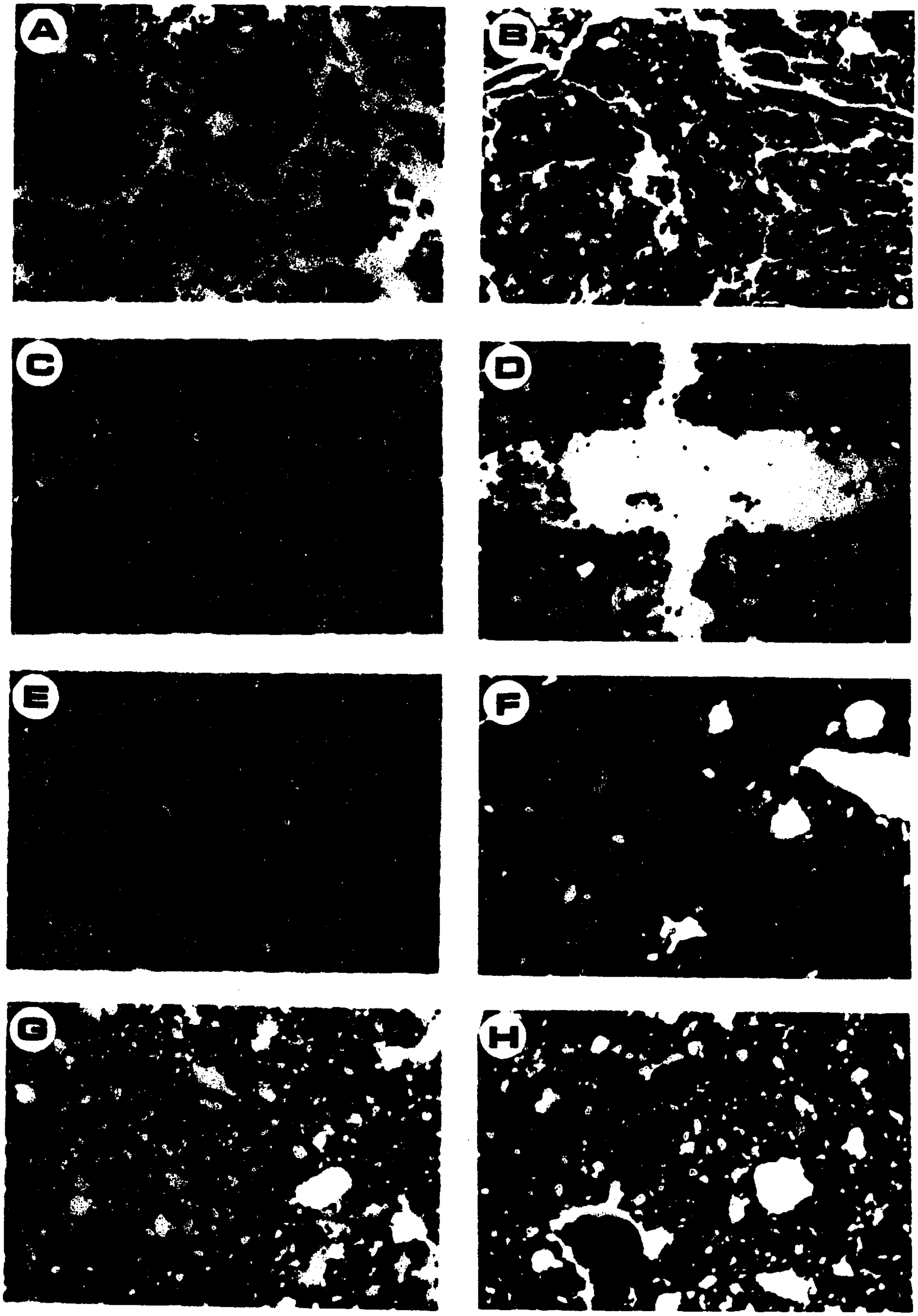
D. Ellipsoidal chamber connected with a vertical portion of a large craze plane in Ah2; faecal pellets present in the chamber are exclusively of collembola. PPL, FL=5.73mm.

E. Banded mullgranoidic porphyric fabric in Ah3: note the sedimentary nodules are incorporated into the platy structure. The dominant inter-aggregate voids are sub-horizontal joint planes. PPL, FL=5.73mm.

F. Enlarged portion of Fig.E: Humigranic units, likely collembola faecal pellets, are arranged into the platy aggregates likely by freeze/thaw. Note there is a lack of clay orientation. PPL, FL=0.72mm.

G. Obliquely banded porphyric fabric in Ah3: series of subparallel oblique bands of dominantly 1000-1700µ long, likely formed by upward frost pressure. PPL, FL=5.73mm.

H. Ortho-mullconglomeric-porphyric fabric components in Ah3: Quartz grain (560µ, middle-right position), and mullgranic unit of 840µ (upper middle position) are densely surrounded by mull substance, forming ortho-mullconglomeric-porphyric fabric components likely by freeze/thaw. PPL, FL=5.73mm.


A
B
C
D
E
F
G
H

of soil physical processes. Presence of diffuse Fe nodules in the centre of some matriconglomeric units is likely related to the cementation effects of Fe colloids during the initial stage of aggregation due to psuedo-gley processes. These Fe cemented aggregates are further stabilized through addition of the mull materials along the edge of conglomeric units observed in the Bg and Ah2 horizons of the Raven soil. Image analysis for the metafragmic units and conglomeric units in the Ah2 to AB horizons showed a range of 'form PE' values from 0.825 to 0.836, similar to the values for the structural units generated by repeated freeze/thaw (Pawluk, 1988). The sharp decrease or lack of humigranic faecal pellets in the Ah2 to AB horizons as compared to the Sod layer also suggests that the metafragmic and conglomeric units are not likely of biological origin. Increased faunal activity in the Sod layer is reflected by the increased abundance of their faecal pellets. The well homogenized earthworm faecal pellets are reflected by the presence of mammilated metavughs (Brewer, 1976; Mermut, 1985).

The presence of the platy microstructures in the banded mullgranoidic zones in the Ah horizon of the Malmo soil, is likely related to the influence of freeze/thaw as well. Pawluk (1988) showed that extended freeze/thaw processes can produce banded mullfragmoidic and mullgranic fabrics similar to those found in Chernozemic Ah horizons. Dominance of the joint subhorizontal planar voids is characteristic of freeze/thaw effects (Pawluk, 1988). An 'obliquely banded-mullgranoidic fabric' in the lower Ah horizon of Malmo soil is probably related to a localized freeze heave developed by vertical frost pressure. The effect of freeze/thaw in the Ah horizon is generally confined to the re-arrangement and re-organization of the existing structural units such as earthworm faecal pellets and sedimentary nodules. The similar plasma fabric and good homogenization of plasma constituents in the banded mullgranoidic zones and the nonmodified mullgranic/granoidic zones imply a coupled influence of both soil fauna and frost action. As suggested by Pawluk and Bal (1985), it is likely that participation of multiple pedogenic forces of biological and physical nature are responsible for the formation of these complex fabrics. In comparison to the Raven soil, the microfabrics in Malmo soil reflect a greater diversity of soil fauna under the grass-forest vegetation. Kobikova and Russek (1976) suggest faecal pellets of collembola and oribatid mites contribute humigranic units of 35-90 μ size to soil fabric. These units closely approximate the size and shape of the humigranic units in the soils of this study. Dominant occurrence of collembola faecal pellets in the organic layers and the upper Ah horizon support the ubiquitous role of collembola in comminuting the litter. Collembola faecal pellets are present in both Malmo and Raven soils with greatest abundance as discrete humigranic units, as fused humigranoidic units, or as isotropic humigranic components imbedded in the modergranic units made up of dipterous larvae faecal pellets or mullgranic earthworm faecal pellets. Oribatid mite activity is largely restricted to the woody tissue and their faecal pellets are most evident in the LF layer of the Malmo soil. They are rarely observed in the Raven soil. This is in contrast to some forest soils in British Columbia where oribatid mites were reported as the predominant decomposer (Fox et al. 1994).

Mineralogy

The mineral composition of these two soils is quite similar in the major horizons. Sand and silt fractions are dominated by quartz that accounts for more than 90% for the orthogranic units according to petrographic observations using optical criteria outlined by Kerr (1977) and frequency approximation by Bullock et al. (1985). Clay mineral composition is dominantly smectite, with lesser amounts of mica and kaolinite (Fig.2-6 and Fig.2-7). Smectite clay shows a 001 reflection of 1.0 nm for K-saturated samples run at 0% r.h. after room temperature, 300°C and 550°C treatments. The spacing expands to 1.2 to 1.4 nm after equilibrating at 54% r.h. An expansion to about 1.8 to 1.7 nm for the Ca-saturated sample after glycerol solvation compared to expansion to 1.6-1.7 nm after ethylene glycol solvation, indicates the smectite mineral is largely montmorillonite. Sharp 1.0 nm 001 reflection for all treatments suggests the presence of mica. A well resolved secondary peak at 0.50 nm indicates that the mica mineral is most likely muscovite. Presence of hydrous mica and/or soil vermiculite is evident since the 1.0 nm peak for the Ca-saturated clay is smaller than for the K-saturated clay. Presence of kaolinite is evidenced with the 0.72 nm peak that is stable to all the treatments except for K-550°C where its crystal lattice collapses. Lack of symmetry of the 0.72 nm peak is likely due to co-reflection of a secondary peak of chlorite at about 0.71 nm. The significant difference in intensity of the 0.72 nm peak between the K-550°C treatment and other treatments indicates kaolinite is the major contributor to this peak and chlorite co-reflection forms only a small shoulder of minor importance. Minor amount of chlorite is also evident from the very weak peak at 1.42 nm for all treatments (especially, for the K-550 °C and K-300°C treatments) for major horizons in both soils. Moderate enhancement of the 1.42 nm reflection by the Ca-glycerol treatment, as compared to other treatments, reveals possible contribution from soil vermiculite and/or beidellite. The small peak at 0.33 nm arises from clay-sized quartz. These clay mineral assemblages are typical of Alberta soils (Warren and Dudas, 1992).

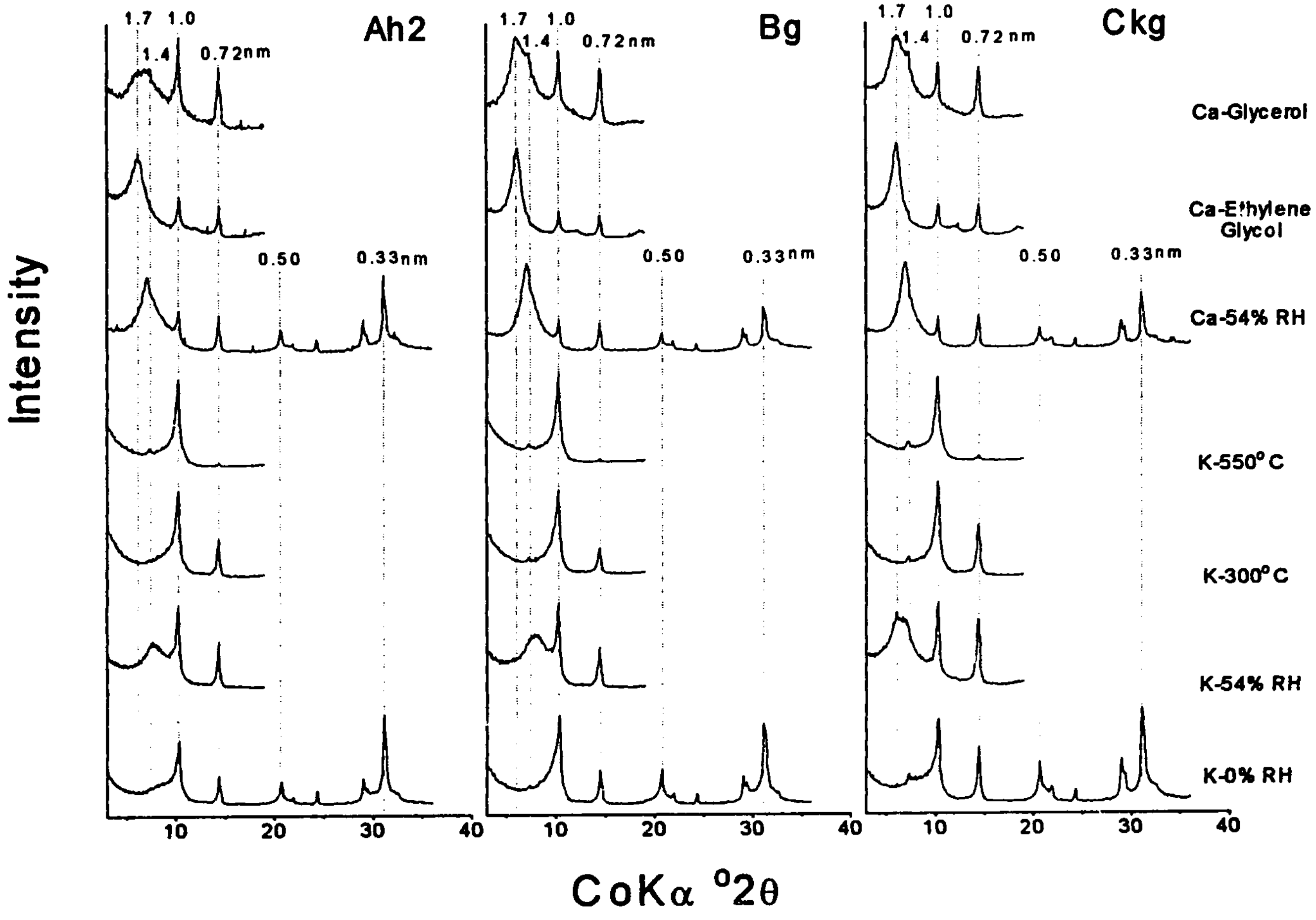


Fig.2-6. X-ray diffractograms of K- and Ca-saturated clay in the Raven soil

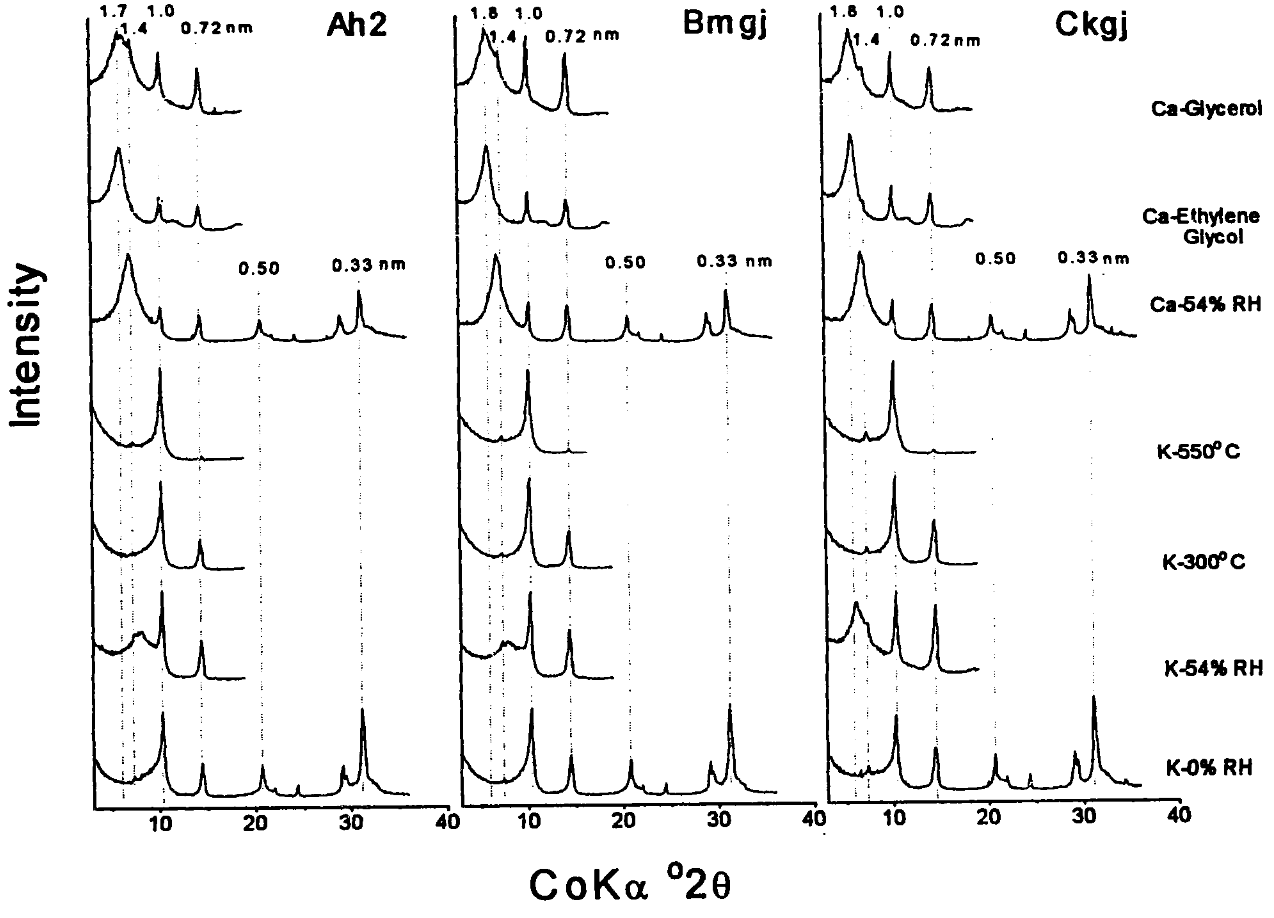


Fig.2-7. X-ray diffractograms of K- and Ca-saturated clay in the Malmo soil.

and Al oxides by acid ammonium oxalate extraction (McKeague, 1978)
r results. Repeated sodium dithionite-citrate-bicarbonate (NaDCB)
her improved the resolution. The best resolution resulted from a
$_2$-NaDCB treatment (Fig.2-8). Thus the smectite is present largely as
mplex in the Ah2 horizon. To probe the nature of the organic substances
lay complex, a repeated sodium pyrophosphate extraction followed with
trifugation (39,100 g for 15 min) was also employed to remove humic
ic acids. This treatment considerably improved the resolution of the
1.8 nm) for the Ca-saturated sample that had been subjected to glycerol
all peak at 0.86 nm is probably an artifact resulting from residual $P_2O_7^{4-}$
mpletely removed by centrifuge washing.
differences in resolution of the smectite peaks (1.8 nm) for glycerol
also observed for the Malmo soil but to a lesser extent (Fig.2-8).
smectite in the Ah2 horizon responded differently to similar extraction
ntioned previously. The untreated organo-clay complex in the Ah2
Malmo soil had better resolution at 1.8 nm as compared to the Ah2
Raven soil. The H_2O_2 treatment resulted in the best improvement in
cid ammonium oxalate extraction, NaDCB extraction, sodium
extraction, and the combined H_2O_2-NaDCB treatment similarly
harpness of the smectite peak at 1.8 nm after glycerol solvation (Fig.2-

ineral diffractograms indicate complexation of organics on the edges of
als in Ah2 horizons of both soils. There does not appear to be interlayer
since reflection greater than 1.8 nm that were reported for interlayer
heng et al. 1986, 1992) was not observed in this study. The organo-clay
tion prevented complete penetration of glycerol in the Ca-saturated clay
llowed the complex to only partially swell; this produced a poorly
at 1.8 to 1.6 nm for the organo-clay in the Ah2 horizon of the Raven soil.
provement for the 1.8 nm peak by 30% H_2O_2 treatment suggests some of
bstances are spatially protected against oxidation by H_2O_2 by inorganic
rtial improvement in peak intensity by acid-ammonium oxalate extraction

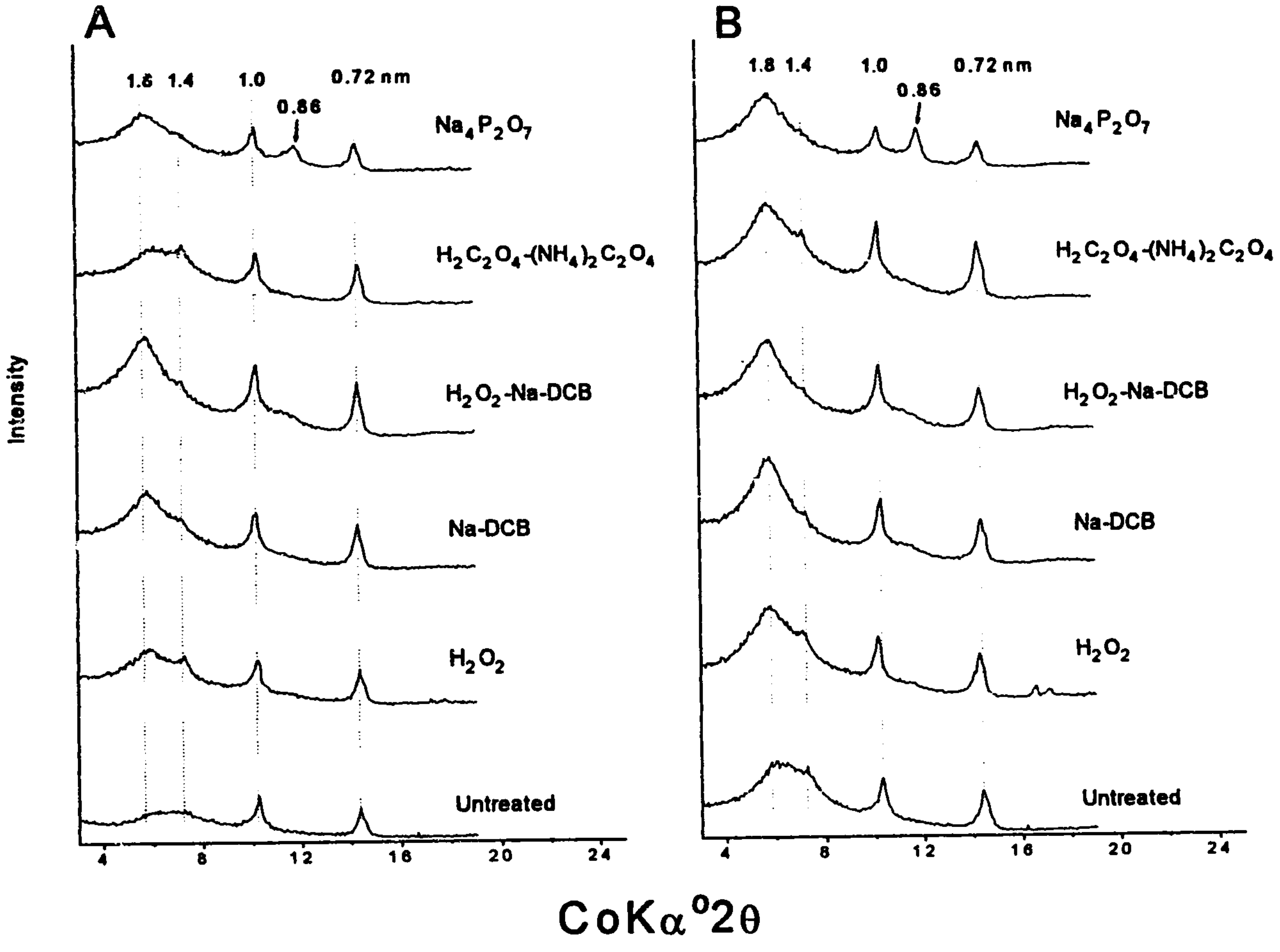


Fig. 2-8. X-ray diffractograms of the Ca-glycerol treated organo-clay complexes after various chemical treatments, Ah2 horizons of the Raven (A) and the Malmo (B) soils.

implies some interaction with amorphous Fe, Al oxides or hydroxides may have occurred to a limited extent. Further improvement with NaDCB extraction suggests that some Fe, Al in micro-crystalline forms also participated in the complexation or that more tightly bonded organics are also released by partial dissolution of Fe and Al from clays as suggested by Pawluk (1972). The most improved resolution obtained after combined H_2O_2-NaDCB extraction confirmed the involvement of Fe, Al in microcrystalline forms in complexation and the protective nature of these forms of sesquioxides against the decomposition of organic substances by H_2O_2 oxidation. Improvement of the 1.8 nm peak by repeated extractions of organics with $Na_4P_2O_7$ indicates that some of the organic matter in the complex is made up of alkaline soluble humic substances (humic acids and fulvic acids). Since this extraction led only to limited resolution of the 1.8 nm peak as compared to the combined H_2O_2-NaDCB treatment, it is likely the remaining organic fraction in the complex is humin. The organic matter in most dark colored mollic epipedons is dominantly humin and humic acids (Kononova, 1966; Duchaufour, 1982). Allison (1973) and Duchaufour (1982) reported that the good structure of mollic epipedons is largely attributable to clay-humus complexation.

Formation of organo-clay edge complexes also appeared to prevent the complete rehydration of K-saturated samples to 1.2-1.4 nm for the Ah2 and Bg horizons as compared to the Ckg horizon of the Raven soil (Fig.2-6). Similar phenomena were also noted for the organo-clay in major horizons of the Malmo soil (Fig.2-7). This pattern is also evident in the diffractograms of organo-clay complexes from both Ah2 horizons for Ca-54% r.h. treatment. The XRD diffractograms for Ah2 horizons of both soils indicated strongest organo-clay complexation, so they were treated with 30% H_2O_2 for removal of organic matter. This treatment likely improved rehydration of the K-saturated samples in the Ah2 horizons for both soils (Fig.2-9). Alternatively, this change in diffractogram may also have resulted from the improved detectability of smectite after removal of the organic matter by the H_2O_2 treatment.

Influence of organo-clay complexation on soil aggregation was also observed at the microscopic level. Micromorphological observations showed faint interference colors of clay domains as a result of considerable masking by well humified organic substances for the entire range of aggregate sizes in the Ah2 horizons of both soils. Penetration into clay domains by colloidal organic substances appeared to have caused poor orientation of clays during aggregation, resulting in a dominance of silasepic to mosepic plasma fabrics. Retention of soil organic matter through humification and

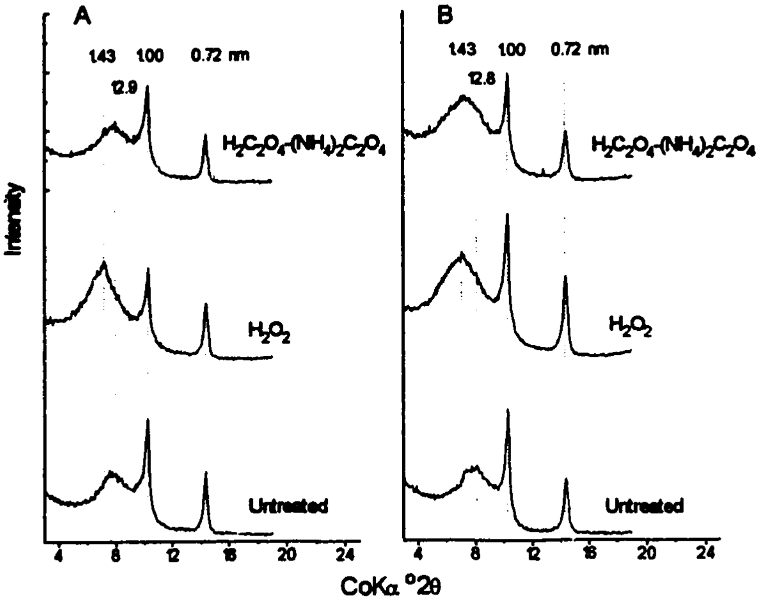


Fig. 2-9. X-ray diffractograms of the K-54% r.h. treated organo-clay complexes, before and after removal of organic matter by H_2O_2 and of amorphous sesquioxides by $H_2C_2O_4(NH_4)C_2O_4$, Ah2 horizons of the Raven (A) and the Malmo (B) soils.

complexation was previously reported for Black Chernozemic soils in Alberta (Dudas and Pawluk, 1969). Dudas and Pawluk (1969) observed the presence of organo-clay edge complexation but no interlayer complexation in Ah horizons of Alberta Chernozems. Participation of Fe, Al in microcrystalline forms, as revealed in this study, appears to be related to tighter organo-clay complexation in the Ah2 horizon of Raven soil. This is also in agreement with the analytical data for the extractable Fe and Al compounds in the two soils (Table 2-3). The Raven soil has more organic-complexed Fe and Al in the solum than the Malmo soil.

Theng et al. (1986, 1992) reported the occurrence of interlayer organo-smectite complexation for two New Zealand Spodic soils. They proprosed three conditions for interlayer organo-clay complexation: (i) presence of smectite minerals; (ii) acidic soil reaction; and (iii) accumulation of organic matter associated with low microbial activity. An acidic soil reaction rarely occurs in Chernozemic soils. High base saturation and dominance of Ca^{++} on the exchange complex and near neutral pH are more characteristic of Chernozemic soils.

Aggregate

To avoid cumbersome statistical discussion, the major trends of the aggregate properties are presented. Aggregate distribution for field-moist samples varied widely among soil horizons. In the Sod layer of the Raven soil, large aggregates of 8.0-4.0 mm size are dominant. These aggregates appeared to be bound largely by plant roots. Aggregates in the 8.0-2.0 mm sizes make up more than 50% of the total dry weight of the soil in the Sod layer. Aggregates in the 2.0-0.50 mm size range dominate in the Ah1, Ah2, and Bg horizons. This is in agreement with micromorphological observations. Aggregates in the Ckg horizon are distributed evenly in the 8.0, 4.0-2.0, 2.0-1.0, and 1.0-0.50 size range (Fig.2-10).

A similar shift in distribution with soil depth is also observed for the Malmo soil but the aggregates are slightly larger and there are more aggregates in the 4.0-2.0 mm size range as compared to the Raven soil (Fig.2-11). Generally, field-moist samples of the Ah horizons from both soils are largely water-stable.

Air-dried samples showed greater variations with soil depth than the field-moist samples. About 30% of the aggregates were in the 8.0-4.0 mm size range in the Sod layer of the Raven soil. Aggregates of this size range decrease progressively with soil depth and were absent in the Bg and Ckg horizons. Aggregates in 4.0-2.0, 2.0-1.0, 1.0-0.5 mm size groups also showed a similar reduction with soil depth. Aggregates of 1.0-0.50 mm size are dominant in the Ah1 to AB horizons, although content of aggregates in the 2.0-1.0 mm and 0.50-0.25 mm size range was also high. Smaller aggregates (< 0.50 mm) make up the major fraction in the Bg and Ckg horizons, likely as a result of disintegration of larger, unstable aggregates (Fig.2-10).

A similar reduction with depth was observed for large aggregates of the air-dried samples from the Malmo soil (Fig.2-11). The 8.0-4.0 mm aggregate size that is dominant in the Ah1 horizon showed the greatest reduction with soil depth and were absent in the Ckgj horizon. Aggregates of 1.0-0.50 mm size are dominant from the Ah2 to the Ckgj horizon. Aggregates in 4.0-2.0 and 2.0-1.0 mm size ranges are more evenly distributed with soil depth as compared to the Raven soil. Similarly, there are also more finer aggregates (< 0.50 mm) in the Ckgj horizons than in the upper horizons.

Comparison of results for field-moist samples with air-dried samples also showed a relationship to soil depth. In the Sod layer (Raven soil) and Ah1 horizon (Malmo soil), both field-moist and air-dried samples have similar distribution patterns. Air-dried samples consistently have fewer large aggregates (> 1.0 mm) and more small aggregate (< 0.50 mm) than field-moist samples with increase in depth. The largest

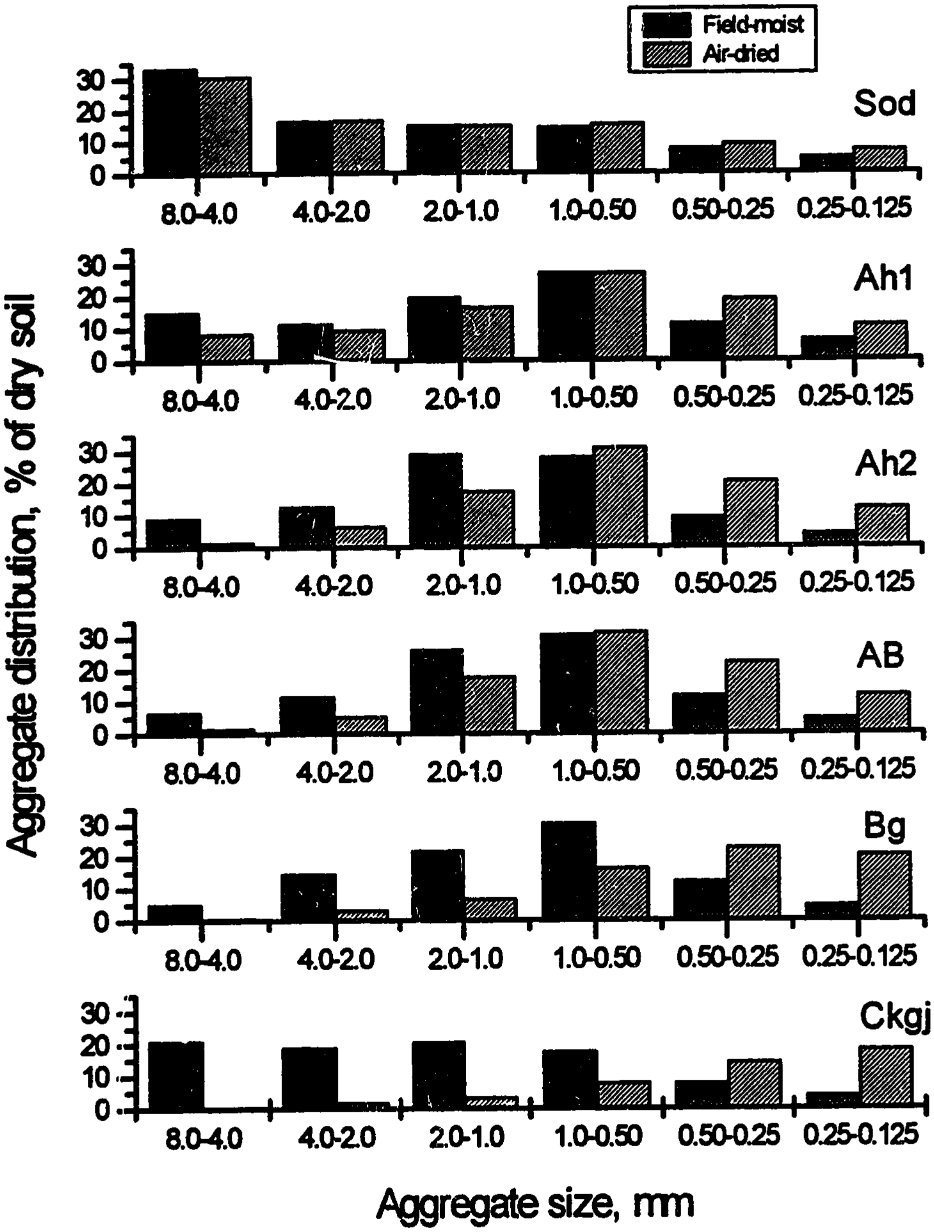


Fig. 2-10. Distribution of aggregates in the Raven soil as influenced by sample moisture.

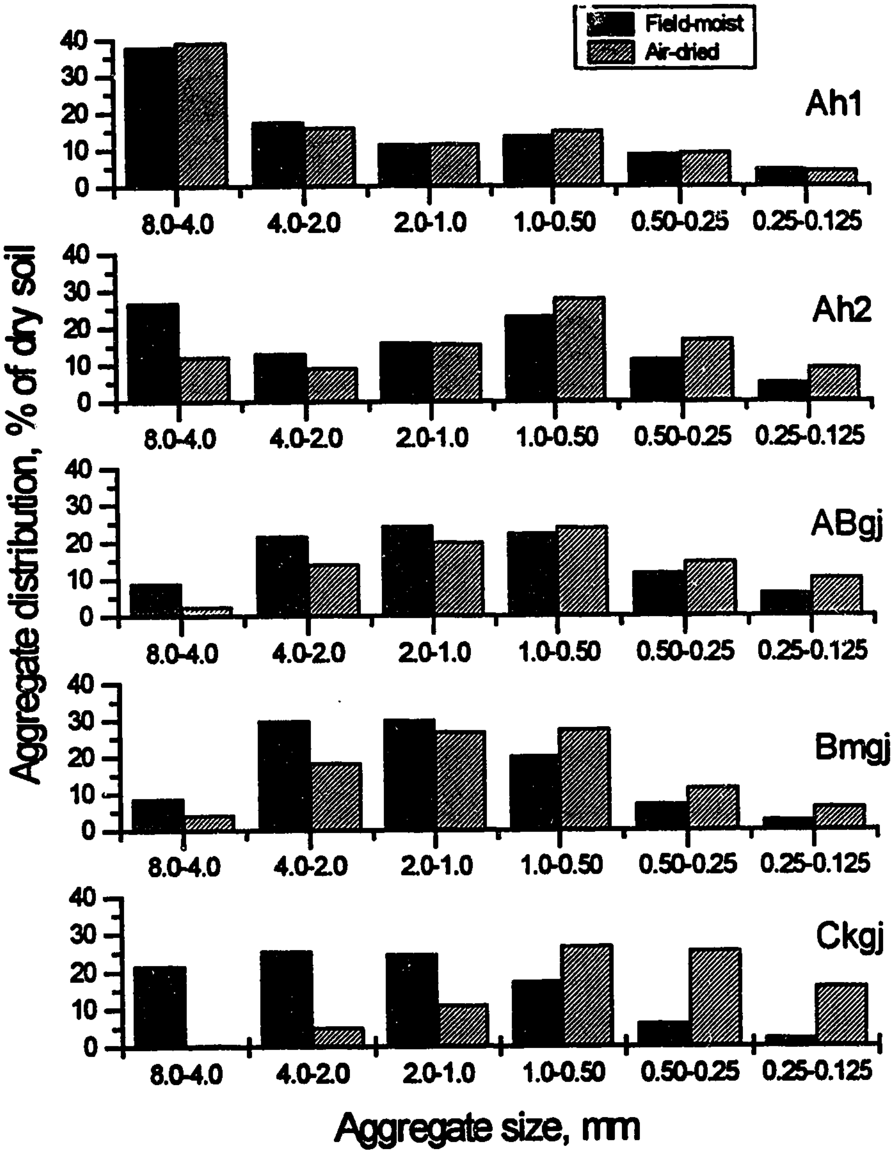


Fig. 2-11. Distribution of aggregates in the Malmo soil as influenced by sample moisture.

change in aggregate distribution occurred in the C horizons for both soils. Air-dried samples below the AB horizon (Raven soil) and ABgj horizon (Malmo soil) were observed to very rapidly wet and slake in the laboratory. Air-dried samples from the upper horizons of both soils showed much slower wetting rates. Aggregates in the upper most horizons (Sod layer of Raven soil and Ah1 horizon for Malmo soil) also exhibited some hydrophobic properties where wetting could not be completed in less than 5 minutes whereas aggregates from the B and C horizons became wet quickly upon contact with water and slaked within one minute of wetting.

According to Haynes and Swift (1990), moisture is the most important factor affecting wet-sieving and the moisture effect on sieving is related to soil organic matter content. Similar observations were noted for samples of this study and could be related to change in depth of sampling. There is more SOM in the upper sola of both soils as indicated by their percent organic C values (Table 2-2). If the upper sola also contain more humic acids, the aggregates will be more stable. Humic acids are reported to reduce wetability of the smectite-humic acid complex (Jouany, 1991) and soil aggregates (Giovannini et al, 1983).

It appears that the classic Yoder method is suitable for studying the erodability of soil aggregates in surface horizons. Disaggregation during wet sieving arises from both slaking by water and disaggregation by mechanical oscillation. Air-drying a sample induces a severe 'trapped-air effect' that can cause strong disaggregation. Aggregates other than those in the uppermost horizons are not likely to be subjected to such dramatic effects under natural conditions. For this reason, aggregate distribution data for field-moist samples should be considered a more appropriate measurement for aggregate distribution in lower soil horizons. Wet-sieving analysis for air-dried samples can give an indication of both stability and distribution. That is likely why wet-sieving data for field-moist samples showed better agreement with micromorphological observations than the latter since micromorphological observations more closely approximate in situ conditions, and reflect aggregate distribution, rather than aggregate water-stability.

Neutral sugar

Content of neutral sugars generally decreases with soil depth for both pedons (Table 2-4). The ratio of (galactose+mannose)/(arabinose+xylose) ranges from 1.0 to 3.8 and decreases with soil depth in the mineral horizons. The ratio increases from organic layers to mineral horizons in the Malmo soil. In the Raven soil, the ratios

Table 2-4. Composition of neutral sugar (mg/g) in the acid digest of two soils

Horizon	Fucose	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose	Sum	$\frac{\text{Galactose+Mannose}}{\text{Arabinose+Xylose}}$
				Raven soil					
Sod layer	0.306	0.589	0.546	1.29	1.12	0.246	1.85	5.96	3.8
Ah1	0.146	0.439	0.355	0.606	0.588	0.239	1.06	3.43	2.4
Ah2	0.086	0.222	0.197	0.289	0.237	0.121	0.623	1.77	2.7
AB	0.055	0.129	0.099	0.294	0.310	0.109	0.291	1.28	2.5
Bg	0.015	0.045	0.026	0.057	0.024	0.027	0.089	0.284	2.0
Ckg	0.011	0.030	0.014	0.049	0.048	0.026	0.033	0.212	1.5
				Malmo soil					
LF	1.35	10.6	3.22	7.65	12.8	5.17	9.01	49.8	1.1
FH	1.42	5.03	3.56	6.02	6.54	3.08	9.98	35.6	1.9
H	2.29	6.12	3.60	8.37	18.3	3.70	8.85	51.2	1.7
Ah1	0.296	0.617	0.452	0.567	1.08	0.169	1.40	4.58	2.5
Ah2	0.119	0.193	0.121	0.463	0.626	0.185	0.436	2.14	2.4
Ah3	0.022	0.046	0.027	0.098	0.134	0.059	0.085	0.472	1.7
ABgj	0.017	0.055	0.033	0.098	0.126	0.053	0.073	0.454	1.6
Bmgj	0.018	0.049	0.029	0.090	0.135	0.048	0.085	0.455	1.8
Ckgj	0.002	0.006	0.005	0.010	0.011	0.006	0.003	0.044	1.0

appear larger as compared to mineral horizons of the Malmo soil.

The sharp reduction of neutral sugar yield from the AB to the Bg horizon in the Raven soil corresponds to the change from 'shot structure' to subangular blocky structure (Table 2-1). An abrupt change in the total amount of neutral sugar occurs in the Malmo soil between the Ah2 and Ah3 horizons, where the (galactose+mannose)/(arabinose+xylose) ratio decreased sharply. This also corresponds to an increase in subangular blocky units (Table 2-1). Change in sugar content is more gradual in the Raven soil as compared to the Malmo soil. This parallels the total organic C distribution for both sola (Table 2-2). A sharp reduction of suger yield and the sugar ratio was also observed between the B and the C horizons for both soils.

The percent content of individual sugar components showed relatively more galactose and mannose and less glucose in the Raven soil as compared to the mineral horizons in Malmo soil (Table 2-5). According to Cowie and Hedges (1984), the woody tissues are richer in glucose while grass may have considerably less glucose. Thus this difference may be related to the vegetational difference at the two sites. There is a slight increase in percent xylose content with soil depth in both soils and it may largely come from the deep roots that are usually the major source of C at lower depths (McKeague et al. 1986). Microorganisms have very low xylose content (Cowie and Hedges, 1984).

Variations in percent content of monosaccharide components have been used as an indicator of the origin of polysaccharides in soils (Oades, 1984) and in broader bio-ecosystems (Cowie and Hedges, 1984). Oades (1984) has used the (mannose+galactose)/(arabinose+xylose) ratio because microbial populations usually synthesize little or no arabinose and xylose that are major components of plant polysaccharides. A ratio < 0.5 is typical for plant polysaccharides while a ratio>2.0 is characteristic of microbial polysaccharides. The Raven soil has a ratio >2.0 for the entire solum, thus its polysaccharides are largely of microbial origin. In contrast, only the ratios in upper and middle Ah horizon of the Malmo soil are >2.0 and support a microbial origin; the major portion of the solum has values ranging between 1.0-2.0, indicating a likely mixed origin for its polysaccharides (Table 2-4). Polysaccharides are significant aggregating substances (Cheshire, 1979, Stevenson, 1982). The microbial polysaccharides are particularly effective for formation of stable aggregates (Emerson et al. 1986). Chaunel et al. (1994) suggested that microbial polysaccharides may form long range polymer bridges that maintain water stability of soil aggregates. Thus the origin of granular structure in both soils also bears microbial relevance.

Table 2-5. Percentage ratio of monosaccharide components in total monosaccharide yield in the acid digest of two soils

Horizon	Fucose	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose
			Raven soil				
Sod layer	5.1	9.9	9.2	21.6	18.8	4.1	31.1
Ah1	4.3	12.8	10.4	17.7	17.1	7.0	30.8
Ah2	4.9	12.5	11.1	16.3	13.4	6.8	35.2
AB	4.3	10.0	7.7	22.9	24.1	8.5	22.6
Bg	5.3	15.7	9.1	20.2	8.5	9.6	31.3
Ckg	5.2	14.2	6.5	23.1	22.8	12.4	15.7
			Malmo soil				
LF	2.7	21.3	6.5	15.3	25.7	10.4	18.1
FH	4.0	14.1	10.0	16.9	18.4	8.7	28.0
H	4.5	11.9	7.0	16.3	35.7	7.2	17.3
Ah1	6.5	13.5	9.9	12.4	23.6	3.7	30.6
Ah2	5.6	9.0	5.6	21.6	29.2	8.6	20.4
Ah3	4.7	9.8	5.8	20.8	28.4	12.4	18.0
ABgj	3.7	12.0	7.2	21.7	27.8	11.7	16.0
Bmgj	4.0	10.8	6.5	19.8	29.7	10.6	18.7
Ckgj	4.8	14.8	10.9	23.2	24.3	14.5	7.0

Lysimetry

The pH values of leachates from lysimeters are in the neutral range (6.6-7.2) for the upper horizons of the Raven soil (Table 2-6). The EC values range from approximately 8×10^{-2} to 15×10^{-2} dS/m and decrease with soil depth in spring and fall samples, but increase with depth for the summer samples. Ca^{++} is the dominant cation in the leachate followed by lower concentrations of Mg^{++} and Na^{+} for all seasons. The K^{+} concentration is lowest. Distribution of cations shows seasonal variations. Cation concentrations decrease with soil depth in spring but are quite variable in summer and fall. Amount of soluble organic C (SOC) in the leachate varies between 10 to 45 µg C/mL, and decreases with soil depth.

Lysimeter leachates from the Malmo soil show considerable differences compared to the Raven soil. The pH values are higher (7.2-7.7). The EC values for Malmo soils range from 96 to 165×10^{-2} dS/m and are about 10 to 20 times higher than those of the Raven soil. The cation composition for Malmo soils is dominantly Ca^{++} and K^{+}, followed by Mg^{++} and Na^{+}. The concentration of K^{+} is about 50-70 times, Ca^{++} about 6-9 times, and Mg^{++} about 4-8 times higher as compared to values for the Raven

Table 2-6. Leachate properties of two soils, 1992

Sample	pH	EC	Cation composition (µg/mL)				Anion composition (µg/mL)			SOC
		(dS/m)	Ca^{++}	Mg^{++}	K^{+}	Na^{+}	Cl^{1-}	SO_4^{2-}	NO_3^{1-}	(C µg/mL)
					Raven soil					
May										
Sod	7.17	$10.5*10^{-2}$	12.6	3.68	1.05	1.02	0.72	1.21	0.24	33.8
Sod-Ah2	7.05	$9.09*10^{-2}$	9.35	2.12	0.87	3.26	0.69	2.91	0.06	16.5
Sod-AB	7.06	$7.89*10^{-2}$	7.60	1.49	0.50	2.37	1.00	1.50	0.20	11.0
June										
Sod	6.80	$14.9*10^{-2}$	9.20	2.23	0.62	2.39	0.58	0.28	0.08	33.6
Sod-Ah2	6.60	$13.4*10^{-2}$	8.65	2.57	0.90	2.18	0.54	0.97	0.06	31.8
Sod-AB	7.18	$18.5*10^{-2}$	9.25	1.96	0.31	2.14	0.99	0.89	0.08	28.4
Aug.										
Sod	7.04	$8.11*10^{-2}$	10.4	2.46	1.59	2.73	0.66	0.63	0.22	43.6
Sod-Ah2	6.98	$9.73*10^{-2}$	9.85	2.40	1.27	2.12	0.63	0.73	0.01	37.0
Sod-AB	7.14	$15.7*10^{-2}$	12.1	2.30	0.41	2.15	0.63	0.62	0.04	27.9
Sept.										
Sod	6.64	$10.1*10^{-2}$	11.2	2.17	1.12	2.18	1.15	4.70	4.35	45.1
Sod-Ah2	6.76	$7.15*10^{-2}$	10.8	4.01	0.63	2.66	0.32	0.71	0.02	33.1
Sod-AB	6.78	$8.00*10^{-2}$	7.80	1.87	1.42	2.43	1.00	0.50	0.10	21.7
					Malmo soil					
June										
LF-H	7.62	$146*10^{-2}$	51.0	8.30	54.6	2.44	18.0	75.0	90.0	110
LF-Ah2	7.70	$165*10^{-2}$	64.0	13.9	34.9	2.83	19.0	65.0	75.0	92.5
Aug.										
LF-H	7.19	$118*10^{-2}$	68.5	11.3	75.5	2.65	25.0	57.0	229	82.1
LF-Ah2	7.42	$95.8*10^{-2}$	66.0	14.6	39.0	2.51	7.90	73.7	127	78.1
Sept.										
LF-H	7.18	$159*10^{-2}$	93.5	16.1	92.5	3.31	20.0	34.0	322	79.1
LF-Ah2	7.48	$110*10^{-2}$	72.5	15.5	45.2	2.74	15.0	49.0	150	66.5

soil. Concentration of K^+ and Ca^{++} decrease with soil depth but Mg^{++} concentration is variable. The values for Na^+ are similar for both soils. SOC values in the Malmo soil range from 66.5 to 110 μg C/mL, and are much higher than for the Raven soils. These values decrease with soil depth.

Dominance of Ca^{++} in lysimeter leachates for the Raven soil is characteristic of grassland soils (Pawluk, 1986). Predominance of K^+ in canopy drip and soil lysimeter leachate is typical for forest soils as reported by Howitt and Pawluk (1985) for Gray Luvisol and Arocena et al. (1992) for Podzols in Alberta. The high content of both Ca^{++} and K^+ in the lysimeter solution for the Malmo soil may be a reflection of grass-forest vegetation of the Parkland area. As pointed out by McKeague (1986), cation composition in leachates may influence the stability of organo-clay complexes and subsequently affect aggregation dynamics in soils. The stability of organo-mineral complexes of Mollisols is considered to be largely related to abundant Ca^{++} supply that regulates the amount of soil humic substances in the coagulated state that binds it to negatively charged soil clays in grassland soils (Kononova, 1966; Duchaufour, 1982; McKeague et al. 1986). The chemical properties of the leachates reported here are favorable for soil aggregation in both soils.

SUMMARY AND CONCLUSION

The results of this study indicate a major impact of freeze/thaw processes on the genesis of the 'shot structure' in Raven soil. The more pronounced freeze/thaw effects in the Raven soil as compared to the Malmo soil, probably reflects a greater degree of water-saturation in the former soil, which is an Orthic Humic Gleysol developed in a level to depressional area with a high water table. Saturation above field capacity is optimum for best development of freeze/thaw fabric (Coutard and Mücher, 1985; Pawluk, 1988). Processes of psuedogley apparently contributed to the initiation of granulation by supplying Fe compounds to the process. Stabilization by a mull-like matrix along the outer edges of the aggregate and formation of various conglomeric units through freezing/thawing further contributed to development of the shot structure. The pH, EC, cation composition and SOC values indicate stronger nutrient cycling in the Malmo soil. The higher Ca^{++} and K^+ input, higher SOC values and large EC values of the leachates in Malmo soil are apparently more favorable for soil aggregation as compared to the Raven soil. Better homogenization of the matrix substances also indicates a stronger faunal impact on soil aggregation in the Ah horizon of the Malmo soil. However, granular structures are better developed in the Raven soil than in the Malmo soil, reflecting a dominant influence of freeze/thaw processes in the former as regulated by drainage as an important factor in their genesis.

Soil fauna have apparently contributed to granular structure formation in both the Raven and Malmo soils but the strongest faunal impact is in the Malmo soil. However, freeze/thaw processes seem to override the soil faunal influence during genesis of the 'shot structure'. Thus physical and physiochemical processes rather than biological processes are likely largely responsible for the genesis of the 'shot structure' in the Raven soil. Even though the Raven soil has less faunal activity and biocycling, the wetter conditions may enhance the build-up of polysaccharides and lipids by retarding the rate of oxidation and decomposition of the complex organic structures (Duchaufour, 1982; Dinel et al. 1990). The Ah horizons of both soils have considerable microbial polysaccharides but a greater abundance in the solum of the Raven soil may also be related to the genesis of the conglomeric secondary fabric in 'shot structures' in its Ah and AB horizons. For this reason, the biochemical influence in aggregation can not be completely excluded. The two soils have identical mineralogical assemblages but the stronger organo-clay complexation in the Ah horizon of the Raven soil is also likely responsible for stronger stabilization. Results of this study have applicable significance in that an enhancement of the freeze/thaw process by maintaining a high moisture content, coupled with adequate microbial polysaccharides and Ca supply may lead to development and conservation of strong granular structures.

REFERENCE

Agriculture Canada Expert Committee on Soil Survey, 1987. The Canadian System of Soil Classification. 2nd edition, Agri. Can. Publ. 1646, Ottawa.

Allison, F.E. 1973. Soil Organic Matter and Its Role in Crop Production. Elservier Science Publication Co. New York.

Angers, D.A., Nadeau, P., and Mehuys, G.R. 1988. Determination of carbohydrate composition of soil hydrolysates by high-performance liquid chromatography. Journal of Chromatography. 454:444-449.

Astro International Corporation. 1990. Astro model 2001 system 2: computer controlled multi-method automated laboratory total organic carbon analyzer operations manual. League City, Texas.

Arocena, J.M., Pawluk, S. and Dudas, M.J. 1992. Genesis of selected sandy soils in Alberta, Canada as revealed by microfabric, leachate- and soil composition. Geoderma, 54:65-90.

Bal, L. 1982. Zoological ripening of soils. Centre for Agriculture Publishing and Documentation, Wageningen.

Brewer, R. 1976. Fabric and Mineral Analysis of Soils. Robert E. Krieger Publishing Company, Huntington, N.Y.

Brewer, R. and Pawluk, S. 1975. Investigations of some soils developed in hummocks of the Canadian sub-arctic and southern-arctic regions. I. Morphology and micromorphology. Can. J. Soil Sci. 55:301-309.

Bullock, P., Fedoroff, N., Jongerius, A., Stoops, G., Tursina, T. and Babel, U. 1985. Handbook for Soil Thin Section Description. Waine Research Publications. Wolverhampton, England.

Bundy, L.G. and Bremner, J.M. 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Sci. Soc. Am. Proc., 36:273-275.

Chenul, C., Guerif, J. and Jaunet, A.M. 1994. Polymer bridging: a mechanism of clay and soil structure stabilization by polysaccharides. in J.E. Etchevers et al. (ed). Symposia of the 15th World Congress of Soil Science. Vol. 3A. International Society of Soil Science. Acapulco, Mexico.

Cheshire, M.V. 1979. Nature and Origin of Carbohydrates in Soils. Academic Press, London.

Coutard, J.P. and Mücher, H.J. 1985. Deformation of laminated silt loam due to repeated freezing and thawing cycles. Earth Surface Processes and Landforms, 10:309-319.

Cowie, G.L., and Hedges, J.I. 1984. Carbohydrate sources in coastal marine environment. Geochimica et Cosmochimica Acta. 48:2075-2087.

Dinel, H., Schnitzer, M. and Mehuys, G.R. 1990. Soil lipids: origin, nature, content, decomposition, and effect on soil physical properties. in J.-M. Bollag and G. Stotzky (ed.) Soil Biochemistry, Vol. 6. Marcel Dekker, Inc. New York. p. 397-429.

Duchaufour, P. 1982. Pedology: Pedogenesis and Classification. (English version tranlated by T.R. Paton). George Allen & Unwin, London.

Dudas, M.J. and Pawluk. S. 1969. Naturally occurring organo-clay complexes of orthic Black Chernozems. Geoderma, 3:5-17.

Edwards, A.P. and Bremner, J.M.. 1967. Dispersion of soil particles by sonic vibration. J. Soil Sci. 18:47-63.

Emerson, W.W., Foster, F.C., and Oades, J.M. 1986. Organo-mineral complexes in relation to soil aggregation and structure. in P.M. Huang and M. Schnitzer (ed.), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., p 521-545.

Fox, C.A. 1979. The soil micromorphology and genesis of the Turbic Cryosols from the MacKenzie River valley and Yukon Coastal plain. Ph. D. thesis. The University of Guelph. Guelph, Ontario.

Fox, C.A., Preston, C.M., and Fyfe, C.A. 1994. Micromorphological and ^{13}C NMR characterization of a humic, lignic, and histic Folisol from British Columbia. Can. J. Soil Sci.

Gee, G.W. and Bauder, J.W. 1986. Particle size analysis, in A. Klute (ed.) Methods of Soil Analysis, part 1---physical and mineralogical methods, 2nd edition, American Society of Agronomy, Inc., Soil Science Society of America, Inc. Publisher, Madison, Wisconsin, USA. pp. 383-409.

Giovannini, G., Luchesi, S., and Cervelli, S. 1983. Water repellent substances and aggregate stability in hydrophobic soils. Soil Sci. 41:73-83.

Haynes, R.J. and Swift, R.S. 1990. Stability of soil aggregates in relation to organic constituents and soil water content. J. Soil Sci. 41:73-83.

Howitt, R.W. and Pawluk. S. 1985. The genesis of a Gray Luvisol within the boreal forest region II. Dynamic pedology. Can. J. Soil Sci. 65:9-19.

Jackson, M.L. 1979. Soil Chemical Analysis --- Advanced Course. 2nd ed. Jackson, M.L., Madison, WI.

Jouany, C. 1991. Surface free energy components of clay-synthetic humic acid complexes from contact-angle measurements. Clay and Clay Minerals. 39:43-49.

Kobikova, J. and Rusek, J. 1976. Development of Xerothermic Rendzinas: a study in ecology and soil microstructure. Academic Praha.

Kononova, M.M., 1966. Soil Organic Matter: Its Nature, Its Role in Soil Formation and in Soil Fertility. 2nd English edition. Pergamom Press, Oxford.

Kubiena, W.L. 1953. The Soils of Europe. Thomas Murby and Co., London.

Kerr, P.F. 1977. Optical Mineralogy. 4'th edition. McGraw-Hill Inc. U.S.A.

McKeague, J.A. (ed). 1978. Manual of Soil Sampling and Methods of Analysis. Canadian Soil Survey Committee, Canadian Society of Soil Science. Ottawa, 2nd edition.

McKeague, J.A., Cheshire, M.V., Andreux, F, and Berthelin, J. 1986. Organo-mineral complexes in relation to pedogenesis. in P.M. Huang and M. Schnitzer (ed.), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., pp. 549-592.

Mermut, A.R. 1985. Faunal influence on soil microfabrics and other soil properties. Quaestiones Entomologicae, 21:595-608.

Nelson, D.W. and Sommers, L.E., 1982. Total carbon, organic carbon, and organic matter. in A.L. Page, R.H., Miller, D. R. Keeney (ed.), Methods of Soil Analysis, Part 2---Chemical and microbiological properties. 2nd edition. American Society of Agronomy, Inc., Soil Science Society of America, Inc. Publisher, Madison, Wisconsin, USA. p. 536-577.

Oades, J.M. 1984. Soil organic matter and structural stability: mechanisms and implications for management. Plant and Soil. 76:319-337.

Pawluk, S. 1972. Measurements of crystalline and amorphous iron removal in soils. Can. J. Soil Sci. 52:119-123.

Pawluk, S. 1983. Fabric sequences as related to genetic processes in two Alberta soils. Geoderma, 30:233-242.

Pawluk, S. 1985. Soil micromorphology and soil fauna: problems and importance. Quaestiones Entomologicae. 21:473-496.

Pawluk, S. 1986. Vegetation and management effects upon some properties of Black Chernozemic soils of Edmonton region. Can. J. Soil Sci. 66:73-89.

Pawluk, S., 1988. Freeze-thaw effects on granular structure reorganization of soil materials of varying texture and moisture content. Can. J. Soil Sci., 68:485-494.

Pawluk, S. and Bal, L., 1985. Micromorphology of selected mollic epipedons, in L.A. Douglus and M.L. Thompson (ed.), Soil Micromorphology and Soil Classification. SSSA. Spec. Publ. 15, Madison, Wis., p. 63-83.

Sanborn, P. 1981. Master Thesis. Department of Soil Science, University of Alberta. Edmonton, Alberta.

Sanborn, P. and Pawluk, S., 1983. Process studies of a Chernozemic pedon, Alberta (Canada). Geoderma, 31: 205-237.

SAS Institute Inc., 1987. SAS/STAT guide for personal computers. version 6 ed., Cary, NC, USA.

Shaw, C. and Pawluk, S. 1986. The development of soil structure by *Octolasion tyrtaeum, Aporrectodea turgida* and *Lumbricus terrestris* in parent materials belonging to different textural classes. Pedobiologia, 29:327-339.

Stevenson, F.J., 1982. Humus Chemistry, Genesis, Composition, Reactions. John Wiley & Sons, New Yowk.

Theisen, A.A. and Harward, M.E. 1962. A paste method for preparation of slides for clay mineral identification by x-ray diffraction. Soil Sci. Soc. Am. Proc. 26:90-91.

Theng, B.K.G., Churchman, G.J., and Newman, R.H. 1986. The occurrence of interlayer clay-organic complexes in two New Zealand soils. Soil Sci.,145 (5):262-266.

Theng, B.K.G., Tate, K.R., and Becher-Heidmann, P., 1992. Towards establishing the age, location, and identity of the inert soil organic matter of a spodosol. Z. Pflanznernahr. Bodenk., 155:181-184.

Tisdal, J.M. and Oades, J.M. 1982. Organic matter and water stable aggregates in soils. J. Soil Sci. 33:141-163.

Van Vliet-Lanoe, B., Coutard, J.P., and Pissart, A. 1984. Structures caused by repeated freezing and thawing in various loamy sediments: A comparison of active, fossil and experimental data. Earth Surface Processes and Landforms. 9:553-565.

Warren, C.J., and Dudas, M.J. 1992. Acidification adjacent to an elemental sulfer stockpile: I. Mineral weathering. Can. J. Soil Sci. 72:113-126.

Xing, B., and Dudas, M.J. 1994. Characterization of clay minerals in White Clay Soils, People's Republic of China. Soil Sci. Soc. Am. J. 58:1253-1259.

Chapter III
Structural Variations of Humic Acids in Two Sola of Alberta Mollisols*

INTRODUCTION

Humic acids (HAs) have a profound impact on the genesis of Mollisols. The formation of granular structure, which is characteristic of mollic epipedons, is related to the aggregation effects by HAs (Kononova, 1966; Tisdal and Oades, 1982), together with the activity of soil fauna (Pawluk and Bal, 1985; Thompson et al., 1990) and freeze-thaw effects (Pawluk, 1988). The properties of HAs from a wide range of soils have been documented in the literature (Kononova, 1966; Schnitzer, 1978; Stevenson, 1982; Hayes and Himes, 1986; Schnitzer, 1991). In order to evaluate the contribution of HAs to pedogenesis, it is highly desirable to investigate the whole solum. To the authors' knowledge, systematic comparisons of HAs from the whole solum were rarely documented in the literature, partly because of the difficulties in extracting adequate amount of HAs from subsoil horizons where the organic matter content is usually low.

It is well known that simple aromatic compounds (SACs) are precursors for formation of HAs by either biological processes involving enzymatic catalysis (Kononova, 1966; Martin and Haider, 1980; Sjoblad and Bollag, 1981), or abiotic surface catalytic oxidative polymerization and polycondensation in mineral and soil suspension (Wang et al., 1986; McBride et al. 1988). The properties of SACs, especially the lignin-derived phenols, have been used to derive the origin of HAs (Ertel and Hedges, 1984; Lowe, 1992). However, it is not known whether these components of HAs retain their original characteristics as pedogenesis extends to deep depth in soils. SACs were also used to study the structure of HAs (Khan and Schnitzer, 1972; Neyroud and Schnitzer, 1974; Hayes and Himes, 1986; Kögel-Knabner et al., 1988).

Influence of humic substances on soil aggregation was substantiated in Chapter II. The objectives of this research, as outlined in Chapter I, were to compare the distribution, structure and composition of HAs and their SACs in the entire sola of two Mollisols from central Alberta.

---

* A version of this chapter is in press: Chen, Z. and S. Pawluk, 1994. Geoderma.

MATERIALS AND METHODS

Extraction of HAs from soils

Soil samples were collected from the Malmo series, a Gleyed Black Chernozem at the Ellerslie Research Station, University of Alberta, and the Raven series, an Orthic Humic Gleysol (Agriculture Canada Expert Committee on Soil Survey, 1987) developed in a level to depressional area near Banalto, Alberta. The Malmo site has an undisturbed soil formed under an open aspen-woodland stand; this soil was chosen because of its well developed organic layers and thick Ah horizon (Sanborn and Pawluk, 1983). The Raven site is developed under grassland vegetation and this soil was selected because of its thick Ah horizon. The basic soil properties are outlined in Table 3-1. The macromorphological, micromorphological, mineralogical, and other analytical properties of these two soils were outlined in Chapter II.

Table 3-1. Basic properties of soils

Horizon†	Depth (cm)	Sand (%)	Clay (%)	Org. C. (g/100g)	N (g/100g)	C/N	pHw‡	CEC (cmol/kg)
				Malmo soil #				
LF	18-13	n.d.*	n.d.	48.5	1.80	27	7.2	138.6
FH	13-5	n.d.	n.d.	39.4	2.20	18	6.9	140.7
H	5-0	n.d.	n.d.	41.1	2.40	17	6.6	159.9
Ah1	0-10	9	48	5.9	0.53	11	6.1	54.2
Ah2	10-29	10	46	2.1	0.15	14	6.6	40.6
Ah3	29-35	9	49	0.5	0.08	6	6.7	35.9
ABgj	35-42	11	42	0.3	0.06	5	6.9	24.1
Bmgj	42-57	7	53	0.5	0.07	7	7.3	39.1
Ckgj	103+	3	63	0.6	0.06	10	7.8	51.1
				Raven soil				
Sod	0-10	10	45	6.47	0.56	12	6.9	43.5
Ah1	10-17	8	43	4.57	0.41	11	6.5	41.7
Ah2	17-24	10	42	3.09	0.29	11	6.3	37.8
AB	24-36	9	45	1.39	0.14	10	6.5	32.7
Bg	36-52	10	44	0.56	0.07	8	7.7	27.8
Ckg	52+	1	53	0.44	0.06	8	8.2	27.3

†: horizon designated according to Agriculture Canada Expert Committee on Soil Survey, 1987.

‡: pHw = pH values in 1:2 water suspension.

#: data adopted from Sanborn and Pawluk (1983) for Malmo soil.

*: n.d.= not determined.

HAs from sola of the two soils were extracted under N_2 using 0.1M $Na_4P_2O_7$ with natural pH (pH 10.6). The procedures are generally those outlined by Schnitzer (1982) with slight modification to remove clays by salting out with 0.3 M KCl and removal through centrifugation before acidification. This modification was designed to avoid release of Fe compounds from Fe oxide coatings, clay minerals or organo-clay complexes into HAs during subsequent acidification since high Fe content may interfere with ^{13}C CP/MAS NMR analysis of HAs (Arshad et al., 1988). The dark clay and organo-clay coagulates were alternatively treated with 0.1M $Na_4P_2O_7$ and 0.3 M KCl under N_2 to further extract HAs until the extracts reached a light brown color. The extracts were combined and acidified with 6N HCl to pH 1 and allowed to settle for 24 hours before further centrifugation at 16,300 g for 15 minutes to separate HAs and fulvic acids. The HAs were treated three times with 0.5% (v/v) HF-HCl for 24 hours following the procedure of Schnitzer et al. (1991) to remove silicate impurities, then dialyzed with 'Spectra/Por-3 molecularporous dialysis membrane' (3,500 molecular weight cut-off, Fisher Scientific) against distilled water and deionized water to chloride free, freeze-dried under vacuum, and ground into fine powder for analyses.

Spectroscopic analysis of HAs

Fourier transform infra-red spectroscopy (FTIR)

The FTIR spectra were obtained by pressing HAs into KBr pellet and analyzing with a Nicolet SX-20 spectrometer for a spectral range of 400 to 4000 cm^{-1}. Major absorption bands were assigned as follows (Schnitzer, 1978; Stevenson, 1982): 3400-3300 cm^{-1} to O-H stretching, 2940-2900 cm^{-1} to aliphatic C-H stretching, 1725-1720 cm^{-1} to C=O stretching of COOH, 1620-1600 cm^{-1} to aromatic C=C, 1590-1517 cm^{-1} to COO^- symmetric stretching, N-H deformation, C=N stretching of amide II band; 1460-1450 cm^{-1} to aliphatic C-H, 1280-1200 cm^{-1} to C-O stretching and OH deformation of COOH, C-O stretching of aryl ethers, and 1170-950 cm^{-1} to C-O stretching of polysaccharide or polysaccharide-like substances.

X-ray diffraction (XRD)

XRD was carried out on fine powder of HAs pressed onto a glass slide at a volume of 7x17x1 mm^3 using a Philips diffractometer with Cu-Kα radiation at 50 mV and 25 mA and LiF monochromator. Scanning was conducted over a range from 3 to 90^o 2θ. The accumulation time was 1 second. Preliminary comparison with an unmounted Al slide and glass slide showed little interference of the latter in diffractograms of HAs.

^{13}C CP/MAS NMR spectroscopy

Conventional solid state ^{13}C CP/MAS NMR analysis was conducted by the Dept. of Chemistry, University of Alberta, with a Bruker AM 300 instrument, operating with CP/MAS accessory and a HP WP 73A probe, at 75 MHz frequency, 5000 kHz spinning rate, with 90° pulse width of 5.50 µs, 2 ms contact time, and 70 ms acquisition time. The chemical shift scale was determined with reference to adamantane. The spectra were integrated to determine the percentage of C from 0-220 ppm chemical shift range, which was assigned to alkyl C (0-50 ppm), O-alkyl C (50-107 ppm), aromatic C (107-165 ppm), carboxyl C (165-190 ppm) and carbonyl C (190-220 ppm) according to Malcolm and McCarthy (1986), Schnitzer et al (1991) and Wilson (1991). The dipolar-dephasing solid state ^{13}C CP/MAS NMR analysis was conducted with a dephasing period of 70 µs. Structurally speaking, signals from nonprotonated carbons in a molecule have a longer decay time than protonated carbons. Momentarily turning off the high power decoupling for a period of 70 µs diminishes the signals from protonated C, and signals from nonprotonated C are recorded (Axelson, 1985; Wilson, 1987). By comparing the conventional and the dipolar-dephasing ^{13}C CP/MAS NMR spectra for samples from different soil depths, fundamental structural change of C skeleton in HAs can be deduced.

Chemical analyses of HAs

Elemental analysis

The elemental analyses for C, H, N and O of HAs were carried out with Carlo Erba CHNS-O EA1108 elemental analyzer. The ash content was determined by heating HA samples at 740°C for 4 hours (Schnitzer, 1982).

CuO digestion

The alkaline cupric oxide digestion of HAs followed procedures of Hedges and Ertel (1982) with a minibomb under N_2. The digest was acidified to pH 1 and centrifuged at 16,300 g for 15 minutes. The residue was washed and centrifuged two times with acidified (pH 1) deionized water. The supernatant and washes were combined and extracted three times with diethylether previously treated with saturated solution of $Fe(NH_4)_2(SO_4)_2$ to remove peroxides (Hedges and Ertel, 1982). The diethylether extract was collected in a 150 mL glass beaker and placed in a large wide mouth glass bottle equipped with a plastic stopper having a N_2 inlet and air outlet to block atmospheric air entrance. The extracts were evaporated under a stream of N_2 in the fumehood. The residue was quantitatively dissolved into 4.00 mL HPLC grade methanol. The methanol solution was passed through a 0.2 μm Teflon filter. The filtrate was collected in a small glass vial with a Teflon cap and lines to ensure tight sealing, then stored in refrigerator before analysis for SACs.

The SACs in HA digests were analyzed with a DIONEX-HPLC system, with a standard C-18 analytic column, at 280 nm wavelength, at flow rate of 1.00 mL per minute. Preliminary work in our lab indicated this wavelength gave the best sensitivity for common SACs found in HAs. Reverse phase chromatography was used, with a butanol:acetic acid:water mixture, at 15:1:984 volume ratios (Vance et al., 1985), as the basic mobile phase. To achieve a desirable resolution for a range of common SACs found in the HA digest, we developed a stepwise gradient series using acetonitrile as gradient former. The gradients were 0 to 7%, 7 to 30%, 30 to 40%, 40%, and 0% acetonitrile (volume basis) for the 0 to 14 min, 14 to 30 min, 30 to 42 min, 42 to 45 min, and 45 to 60 min retention times, respectively. All chemicals were HPLC grade (Aldrich Chemical Company, Inc.). Tests with standard SACs indicated excellent linearity between peak areas and working concentrations (R^2 values ranged from 0.99 to 1.00).

RESULTS

Yields of HAs

The HA yield increased with depth in the organic layers, then dropped abruptly with depth in the mineral horizons for the Malmo soils (Fig.3-1a). In comparison, the HA yield for the Raven soils decreased less abruptly with depth (Fig.3-1b). The ratios of the amount of C extracted as HAs (HA-C) to soil organic C are shown in Fig.3-2. For the Malmo soils, more organic C was extracted as HA-C with soil depth as a result of progressive humification from LF to H layers. The highest ratio of HA-C to soil organic C was found in the Ah horizons and ranged about 40 to 50%. It decreases sharply below the Ah horizons (Fig.3-2a). Similarly, this ratio is higher in the Ah horizons of the Raven soils (Fig.3-2b). About 25 to 30% of soil organic C was extracted in Ah horizons. These values are about 10 to 20% lower when compared to those in the Ah horizons at Malmo soils. Thus the organic matter in both soils became

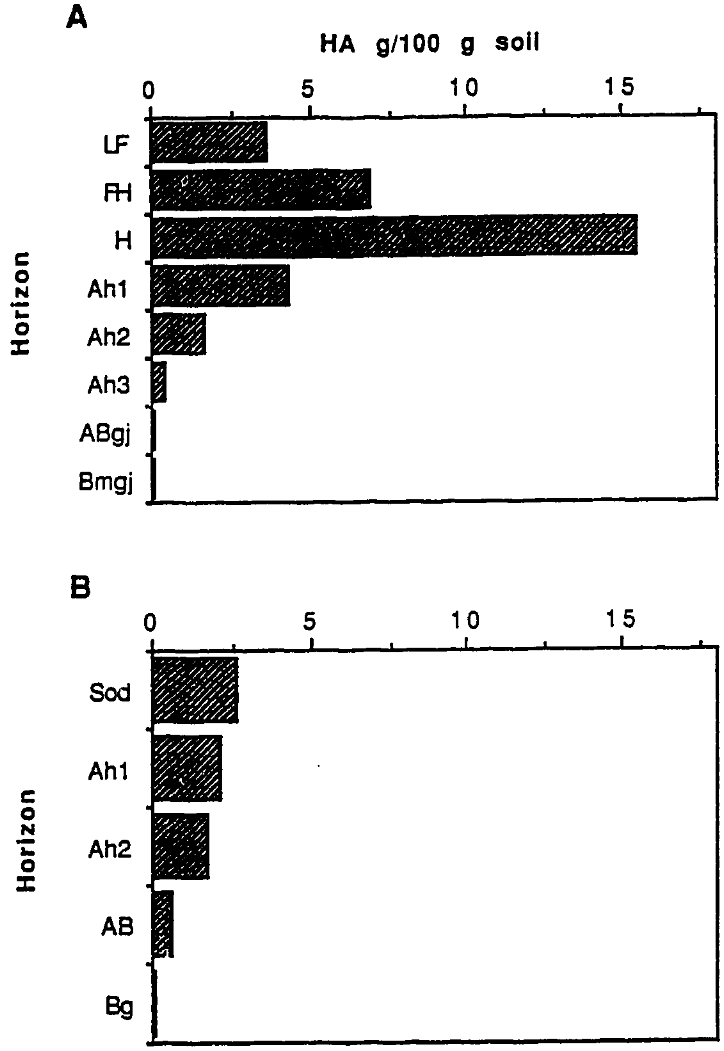


Fig. 3-1. Yield distribution of humic acids (HA) with soil depth in the Malmo (A) and the R[illegible]en (B) soils.

less extractable as HAs in the mineral horizons with increase in depth below Ah horizons.

Spectroscopic analyses

FTIR

The FTIR spectra through the solum of the Malmo soil are given in Fig.3-3. Strong absorption bands at 3400-3300 cm^{-1} (O-H stretching,, 2940-2900 cm^{-1} (aliphatic C-H stretching), 1725-1720 cm^{-1} (C=O stretching of COOH), 1620-1600

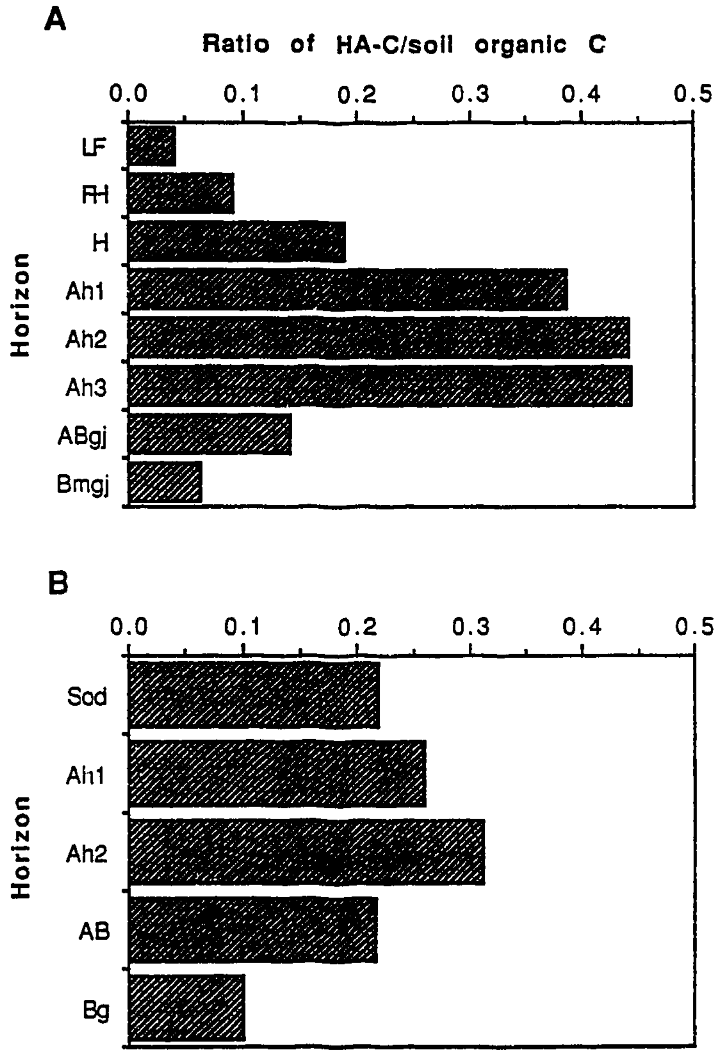


Fig. 3-2. Change of ratios of amount of carbon extracted as humic acids (HA-C) to soil organic carbon with soil depth in the Malmo (A) and Raven (B) soils.

cm^{-1} (aromatic C=C), 1280-1200 cm^{-1} (C-O stretching and OH deformation of COOH, C-O stretching of aryl ethers) are evident, and spectra closely resemble the type-1 IR spectra of typical HAs (Stevenson, 1982). The spectra for HAs in the Raven soils are generally identical to those from mineral horizons of the Malmo soils.

XRD

The XRD spectra of HAs from Malmo soils are illustrated in Fig. 3-4. Intensity of the γ-band at 0.43-0.41 nm and the G-band at about 0.35 nm differ with depth. A

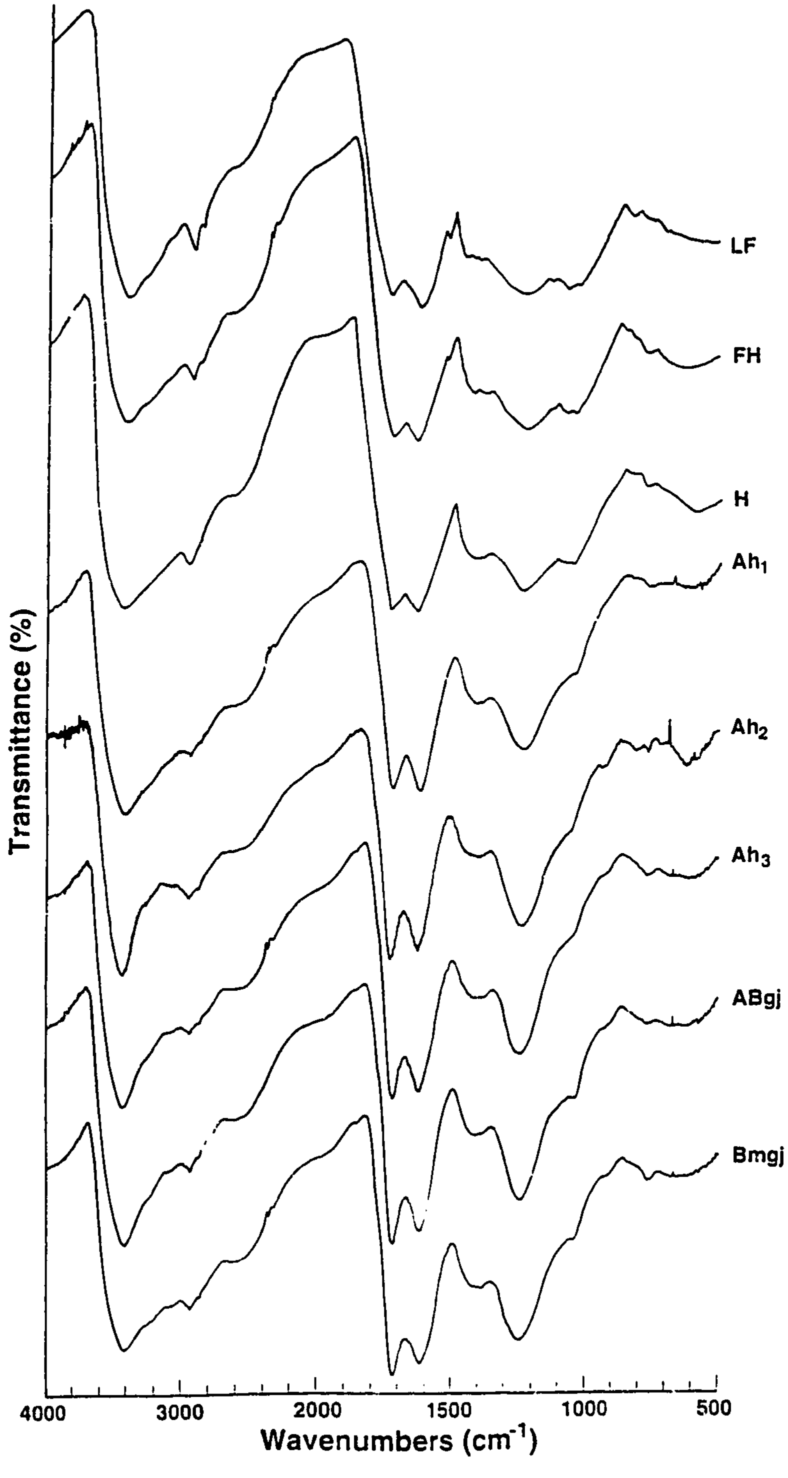


Fig. 3-3. FTIR spectra of humic acids (HAs) in the solum of the Malmo soil.

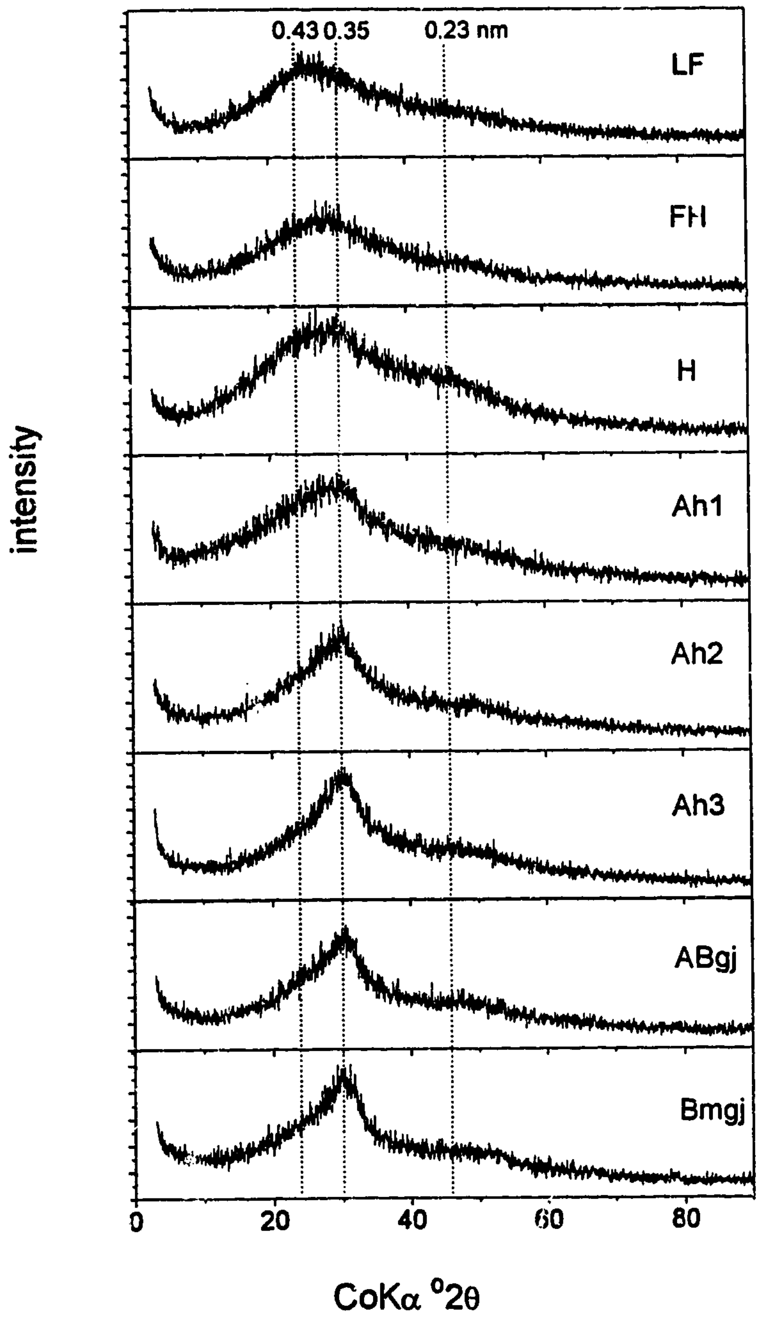


Fig. 3-4. X-ray diffractograms of humic acids (HAs) in the solum of the Malmo soil.

progressive shift from γ-band to G-band is apparent from the LF to the Ah2 horizon, below which, little change is observed. The major peaks for the H layer and Ah1 horizon are composed of both γ-band and G-band components. These spectra, from LF to Bmgj horizons, reflect a sequence from the type-V to type-II HA diffractograms that were reported for diverse soil environments (Schnitzer et al., 1991). For the Raven soil (spectra not shown), the diffractograms generally resemble that of HAs from the Ah1 horizon of Malmo soils, with a slight increase in sharpness of peaks with soil depth.

^{13}C NMR

Conventional solid state ^{13}C CP/MAS NMR spectra for a complete sequence of horizons of Malmo soil are shown in Fig.3-5. The spectra can be divided into three zones according to soil horizons. The first zone includes the organic LF to H horizons, where the distribution of C is quite diverse. The alkyl C (0-50 ppm) and O-alkyl C (50-107 ppm) account for more than 50% of the HA-C (Table 3-2). A reduction of the phenolic C (150-165 ppm) with depth is evident in the spectra within this zone. The

Table 3-2. Percentage distribution of carbon in humic acids (HAs) calculated from conventional solid state ^{13}C CP/MAS NMR spectra

Horizon	type of carbon					aromaticity†	
	alkyl (%)	O-alkyl (%)	aromatic (%)	carboxyl (%)	carbonyl (%)	f1 (%)	f2 (%)
			Malmo soil				
LF	24	29	28	12	6	28	35
FH	26	29	24	14	7	24	30
H	25	30	25	14	6	25	32
Ah1	22	22	33	15	8	33	43
Ah2	13	16	47	13	9	47	62
Ah3	10	14	51	14	11	51	68
ABgj	10	14	46	19	11	46	66
Bmgj	11	14	48	15	12	48	66
			Raven soil				
Sod	19	21	38	14	8	38	50
Ah1	13	22	35	23	6	35	49
Ah2	12	21	40	20	8	40	55
AB	13	14	45	14	14	45	63
Bg	15	19	41	14	11	41	55

†: f1= aromatic carbon/(alkyl+O-alkyl+aromatic+carboxyl+carbonyl)x100
f2= aromatic carbon/(alkyl+O-alkyl+aromatic)x100

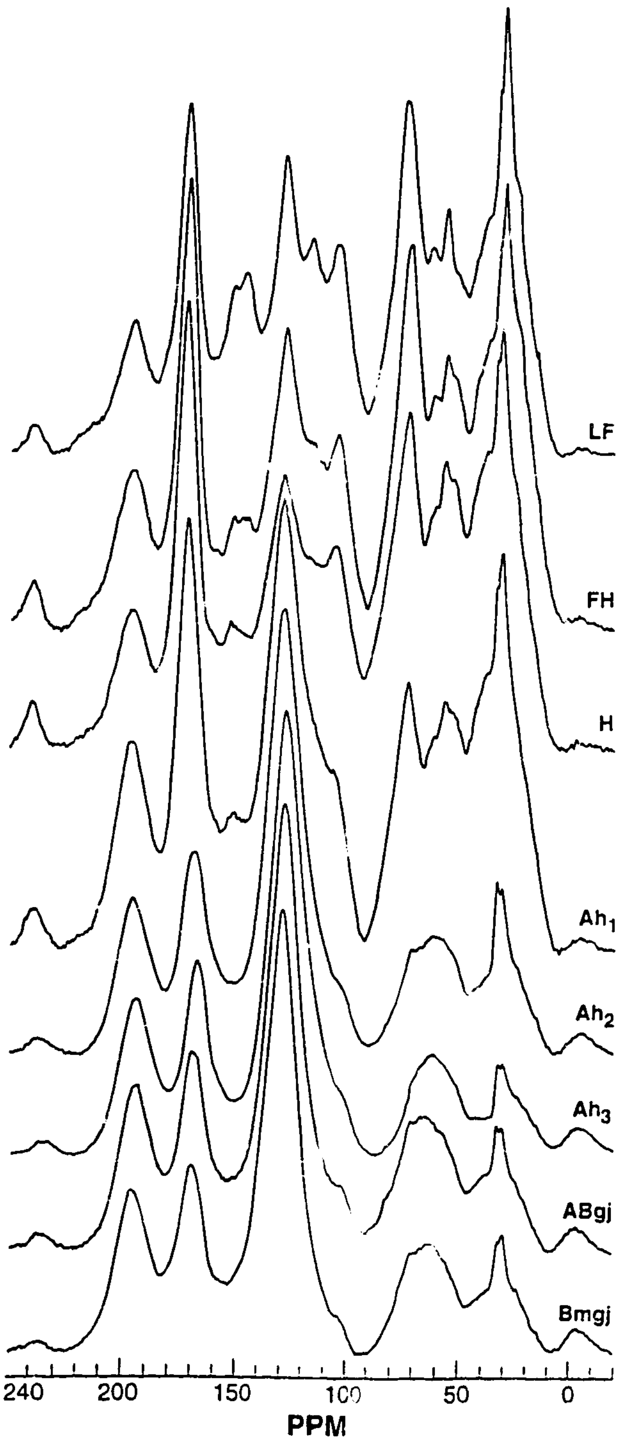


Fig. 3-5. Conventional solid state ^{13}C CP/MAS NMR spectra of humic acids (HAs) in the solum of the Malmo soil.

Ah1 horizon is a transitional zone where reduction of O-alkyl (50-107 ppm) and increase of aromatic C (107-165 ppm) are apparent. A much reduced signal of phenolic-C is still present. The third zone extends from the Ah2 to the Bmgj horizon where aromatic C dominates the entire spectra. Both the O-alkyl C, and the alkyl C are significantly diminished. Phenolic C is barely evident. Consequently, it is the most aromatic zone in the solum. Aromaticity of HAs is doubled from the first zone to the third zone (Table 3-2). This trend is much less pronounced in the Raven soils developed under grass plant communities (spectra not shown). An increase of aromaticity of about 30% is recorded in the solum of Raven soils and the alkyl C and O-alkyl C are better preserved than in the Malmo soils (Table 3-2).

Comparisons of conventional and dipolar-dephasing ^{13}C CP/MAS NMR spectra of HAs for major horizons of the Malmo soils are illustrated in Fig.2-6. Nonprotonated C gradually decreases in carboxyl C range and increases in aromatic C range from the LF to the Ah1 horizons. Within the aromatic range, phenolic C gradually diminishes and other nonprotonated aromatic C increases with depth. Nonprotonated C in the aromatic range overrides that in the carboxyl range extending from the Ah2 horizon to the Bmgj horizon, with dominant signals produced at 128 and 132 ppm. Similarly, minor increase of nonprotonated aromatic C with depth is also observed for the Raven soils (spectra not shown).

Chemical analyses

Elemental composition

The elemental composition of HAs of the two soils are given in Table 3-3. C content for the Malmo soils decreases slightly from the LF to H horizons, followed by an increase in the Ah1 and Ah2 horizons below which little change is observed. The H content shows a reverse trend to the C content. A similar change of C content is also observed in the Raven soils but the H content shows minimal change. As a result, the atomic C/H ratio increases in both soils with depth. N percentage increases with depth in the Malmo soils; a reverse trend is observed for the Raven soils. The O content slightly increases from the LF to H horizons then decreases with depth in the mineral horizons of the Malmo soils but little change is observed in the Raven soils.

CuO digestion

The SACs in the HA digest were grouped into four phenol families: p-hydroxyl phenols (protocatechuic acid, p-hydroxybenzoic acid and p-hydroxybenzaldehyde),

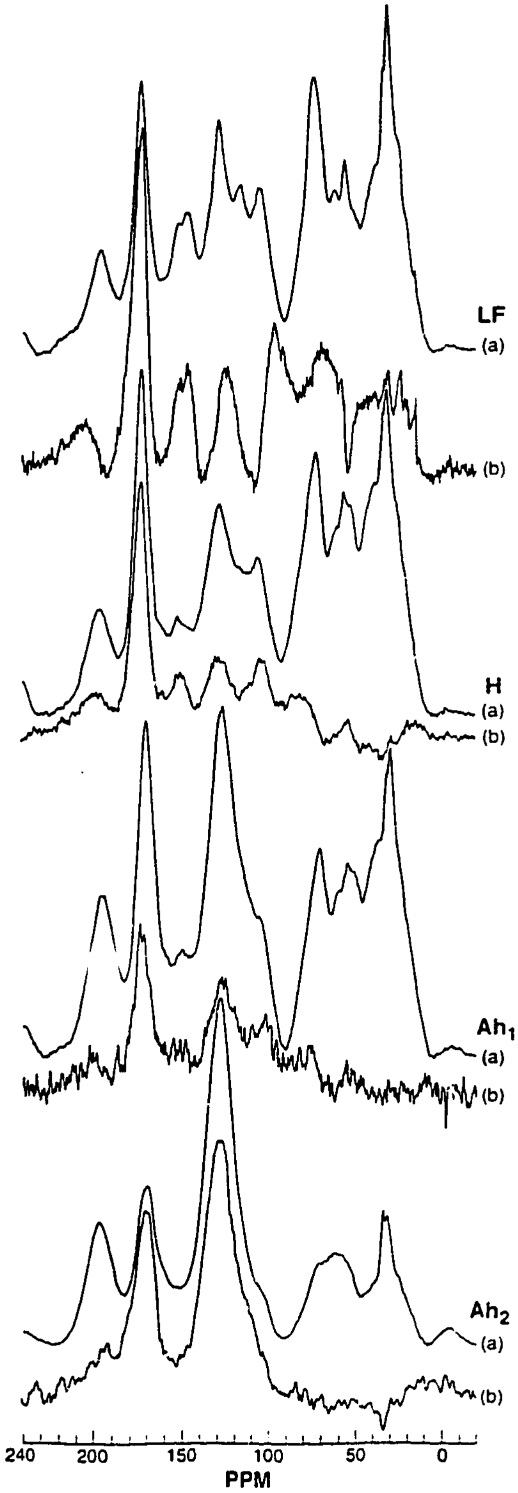


Fig. 3-6. Comparison of the conventional (a) and dipolar-dephasing solid state ^{13}C CP/MAS NMR spectra (b) of humic acids (HAs) from selected horizons of the Malmo soil.

Table 3-3. Elemental composition, atomic ratio and ash content of humic acids (HAs) from soils (moisture and ash free basis)

Horizon	C (%)	H (%)	N (%)	O (%)	Ash (%)	C/H	C/N	C/O
				Malmo soil				
LF	53.7	4.73	2.31	38.8	0.49	0.95	27.1	1.84
FH	52.2	4.14	2.85	40.2	0.26	1.05	21.4	1.73
H	50.3	4.38	2.99	41.3	0.36	0.96	19.6	1.62
Ah1	54.3	3.59	2.88	38.3	0.[illegible]	1.26	21.9	1.86
Ah2	56.8	3.04	3.51	36.2	0.63	1.55	18.9	2.09
Ah3	56.5	2.98	3.47	35.6	1.84	1.58	19.0	2.12
ABgj	56.5	3.17	3.04	36.5	4.16	1.49	21.7	2.06
Bmgj	59.9	3.50	2.86	33.1	7.44	1.43	24.4	2.41
				Raven soil				
Sod	54.5	3.56	4.24	36.2	0.37	1.28	15.0	2.01
Ah1	55.0	3.41	4.21	36.7	0.43	1.34	15.2	2.00
Ah2	55.3	3.45	3.96	37.6	0.37	1.34	16.3	1.96
AB	55.4	3.30	3.59	35.1	0.54	1.40	18.0	2.11
Bg	56.2	3.58	3.36	36.0	2.06	1.31	19.5	2.08

vanillyl phenols (vanillic acid and vanillin), syringyl phenols (syringic acid and syringaldehyde), and cinnamyl phenols (p-coumaric acid, ferulic acid, iso-ferulic acid and trans-cinnamic acid). According to Ertel and Hedges (1984), these phenol families represent four different chemical substitution patterns of SACs and may be used to calculate lignin parameters that reflect the vegetational origins of HAs. Yields of the four phenol families are shown in Table 3-4. With increase in soil depth, ratios of the syringyl phenols to vanillyl phenols, and ratios of cinnamyl phenols to vanillyl phenols decrease in the organic horizons but show little change in the mineral horizons. The ratios of p-hydroxyl phenols to vanillyl phenols increase with depth in both soils. A ratio of about 1.5 of p-hydroxyl phenols to vanillyl phenols appears to separate the HAs in most mineral horizons from those in organic layers except for the transitional Ah1 horizon that has a ratio near this value (Fig.3-7). When the ratios of p-hydroxyl phenols to cinnamyl phenols, and percent p-hydroxyl phenols in sum of the four phenol families were plotted against soil depth for the two soils, both values increased (Fig.3-8). A parallel relationship between these two parameters is apparent. The p-hydroxyl phenols account approximately for more than 50% of the sum of phenols in the mineral horizons. Thus, p-hydroxyl phenols gradually become dominant in HAs digest with soil depth. The acid/aldehyde ratios for vanillyl phenols, and those for p-hydroxyl phenols are given in Table 3-5. Both ratios increase with soil depth. Another change within the

Table 3-4. Yield for four phenol families in alkaline CuO digest of humic acids (HAs) with soil depth

Horizon	Yield (mg/g HAs) of phenol family†				
	syringyl	vanillyl	cinnamyl	p-hydroxyl	sum
			Malmo soil		
LF	0.851	1.91	1.20	2.08	6.04
FH	0.472	1.38	0.401	1.89	4.15
H	0.447	1.49	0.215	2.07	4.23
Ah1	0.181	1.07	0.097	1.57	2.92
Ah2	0.099	0.357	0.028	0.774	1.26
Ah3	0.106	0.338	0.047	0.784	1.28
ABgj	0.147	0.556	0.061	1.15	1.91
Bmgj	0.153	0.492	0.077	1.21	1.94
			Raven soil		
Sod	0.343	0.792	0.145	1.41	2.69
Ah1	0.162	0.471	0.092	1.07	1.79
Ah2	0.095	0.365	0.090	0.947	1.50
AB	0.063	0.255	0.035	0.877	1.23
Bg	0.099	0.431	0.039	1.26	1.83

†: phenol families grouped according to Ertel and Hedges (1984).

Table. 3-5. Acid/aldehyde ratio of vanillyl (Vp) and p-hydroxyl phenols (Hp) and component change of p-hydroxyl phenols with soil depth

Horizons	Acid/aldehyde ratio		(Phb+PhbA)/Prt#
	Vp	Hp	
		Malmo soil	
LF	0.39	0.9	11.4
FH	0.57	1.3	3.1
H	0.78	2.8	3.0
Ah1	1.43	4.0	2.0
Ah2	1.89	4.7	1.2
Ah3	1.61	7.5	1.0
ABgj	1.52	6.6	1.2
Bmgj	1.57	7.8	1.0
		Raven soil	
Sod	1.32	2.0	1.2
Ah1	1.51	3.0	1.1
Ah2	1.54	3.2	1.1
AB	1.63	3.7	0.7
Bg	1.44	4.3	0.8

#: Phb = p-hydroxybenzoic acid, PhbA = p-hydroxybenzaldehyde, Prt = protocatechuic acid.

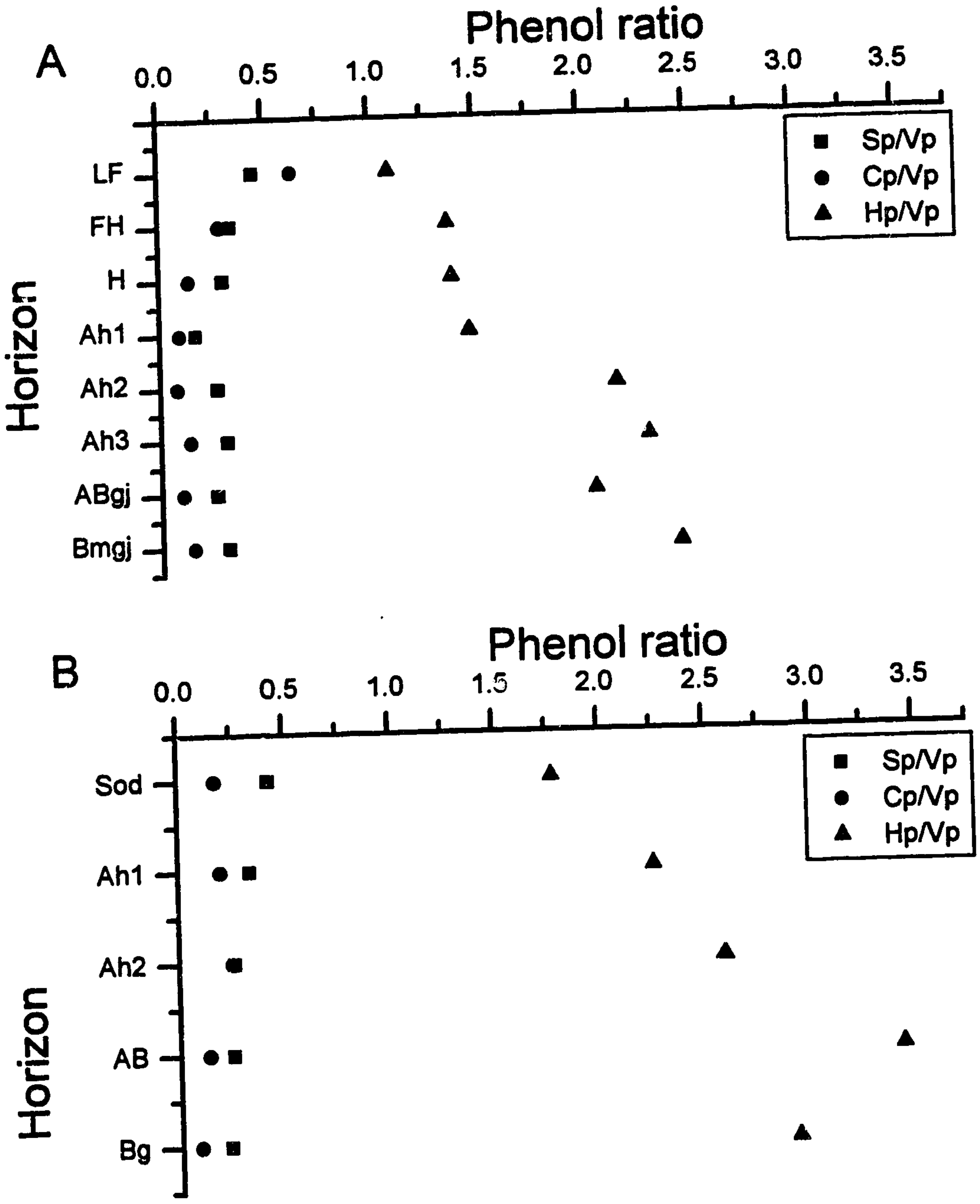


Fig. 3-7. Change of the ratios of syringyl (Sp), cinnamyl (Cp) and p-hydroxyl (Hp) phenols to vanillyl phenols (Vp) in the alkaline CuO digest of humic acids (HAs) with soil depth in the Malmo soil (A) and Raven soils (B).

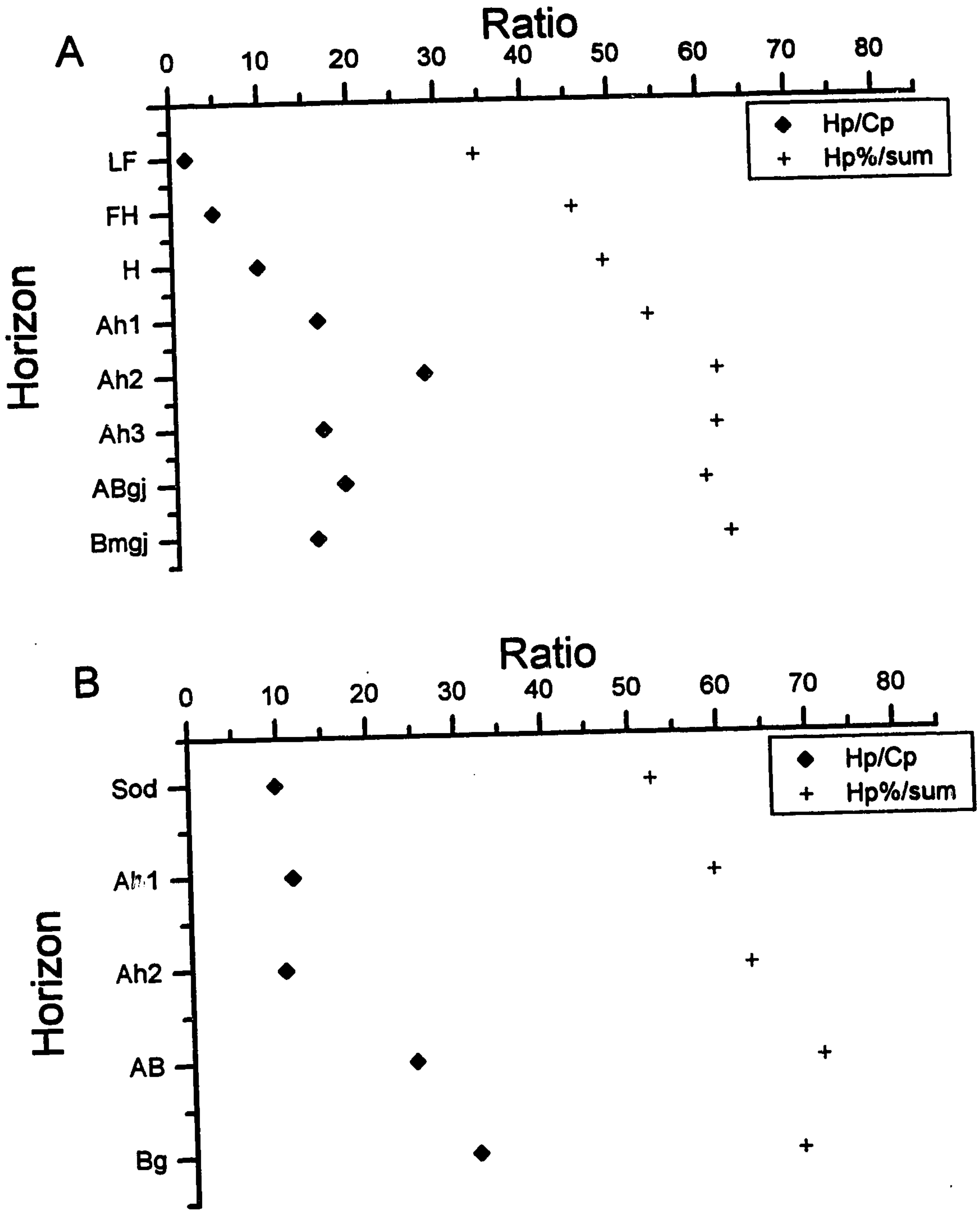


Fig. 3-8. Change of p-hydroxyl phenols (Hp) to cinnamyl phenol (Cp) ratio, and percentage of p-hydroxyl phenol (Hp%) in the sum of phenols (sum) in alkaline digest of humic acids (HAs) with soil depth in the Malmo soil (A) and Raven soil (B).

p-hydroxyl phenols is a decrease in the ratio of p-hydroxybenzoic member to protocatechuic member with soil depth in both soils.

DISCUSSION

Yields of HAs

The HA yield distribution of Malmo soil is typical of forest soils, where most of the HAs were extracted in the organic layers and upper mineral horizons. The less abrupt reduction of HA yields with soil depth in the Raven soil is a reflection of the grass plant communities under which the soil developed and a lack of organic surface layers. Organic matter is mainly added to forest soils by surface addition, thus an abrupt decrease in yield is expected (Stevenson, 1982). The yield distribution in the Raven soil with grass vegetation reflects the major mode of addition of organic matter through the grass root systems that usually humify in situ in the rhyzosphere (Stevenson, 1982). Fine grass roots usually form a close association with mineral soil in the rhyzosphere which may lead to lower extractability as HAs. An increase of HA-C from organic layers to mineral horizons of the Malmo soil is a result of increased humification. This is in agreement with findings by Kögel-Knabner et al. (1990). The HA yield values in the upper sola are greater than the organic C contents in the C horizons for both soils. The ratios of HA-C to soil organic C also progressively decreases with depth. Thus the build up of HAs in the sola is likely a result of pedogenesis, rather than inheritance from organic matter within the parent geological materials.

XRD

The XRD technique gives an estimation about the development of the aromatic network in the HA structure (Schnitzer, 1978; Stevenson, 1982). For the Malmo soil, a progressive shift from γ-band to G-band from LF to Ah2 horizons indicates a progressive development of the aromatic network in the HA structure from LF to Ah2 horizons. Lack of change below the Ah2 implies that the HAs in the lower horizons likely have similar structures. While HAs in the Ah1 horizon reflects a transitional characteristic, its peak was observed to be composed of both γ-band and G-band of about equal intensity when separated by the procedures suggested by Schnitzer et al. (1991). Such observations generally agree well with our NMR results for those horizons. Major types of HA diffractograms were reported by Schnitzer et al. (1991) for soils from a wide range of geographical and climatic environments. However, a similar diversity of HA diffractograms was also found within the solum in Malmo soils. Depth differences in HA diffractograms for the Raven soil are minor.

^{13}C NMR

The change of aromaticity of HAs with soil depth is strongly supported by both the conventional and dipolar-dephasing ^{13}C CP/MAS NMR results. To the authors' knowledge, this is the first paper that clearly presents this observation for two complete sola. A similar trend for aromaticity change of bulk soil organic matter in the sand-free fraction was also reported from a ^{13}C CP/MAS NMR study for an Australia podzol (Skjemstad et al., 1992). Reduction of O-alkyl substances (polysaccharides or polysaccharide-like substances) during humification are well known (Kögel-Knabner et al. 1990; Duchaufour, 1982; Stevenson, 1982), while the decrease of alkyl substances (lipids) in mineral horizons is not frequently reported. The shift of nonprotonated C distribution from the LF to Ah2 horizons, revealed by dipolar-dephasing spectra, indicates that polymerization and polycondensation of the C skeleton in HAs occurred with soil depth. This change is most pronounced below the Ah1 horizon for the Malmo soil, and to a lesser extent for the Raven soil. The strong signals of nonprotonated C that peaked at 128 and 132 ppm are more likely from C in polynuclear aromatic rings (Breitmaier and Voelter, 1987), and indicate polycondensation may have occurred from the Ah1 to Ah2 horizons. Such a process is likely one of the mechanisms leading to higher aromaticity in the horizons below the Ah1. Similarly, this process may also be responsible for the increase in aromaticity extending from the organic layers to the Ah1 horizon. Other authors attributed these peaks to alkyl-substituted aromatic rings (Kögel-Knabner et al., 1990). This kind of substitution can not be excluded from our spectra but may not be the dominant structure. Increase in alkyl-substituted aromatic structure should lead to a decrease in the atomic C/H ratios towards values smaller than 1 with soil depth, no matter whether the alkyl structure is branched or not. However, this is not in agreement with the C/H ratios in Table 3-3. The nonprotonated C in the phenolic range may have been transformed into polymerized or fused aromatic C in the mineral horizons since the signals of the former are apparent in organic layers but barely evident in the dipolar-dephasing spectra of the mineral horizons. It is known that phenolic substances are easily transformed into HAs under both abiotic-catalyzed (Wang et al., 1986; McBride et al., 1988) and enzyme-catalyzed conditions (Martin and Haider, 1980; Sjoblad and Bollag, 1981). Selective preservation of the polymerized and fused aromatic rings may also have occurred in the mineral horizons. The magnitude of aromaticity change with depth in these two soils is consistent with the structural change of nonprotonated C in HAs in both soils. This change is also in agreement with the XRD observation, and the increase in the atomic C/H ratios of HAs with soil depth.

Polymerization and polycondensation of HAs likely occurred mainly upon contact with mineral substances in our soils where the abiotic surface-process may have contributed to HA synthesis from the microbe-modified organic precursors. The clay mineral assemblages in the Malmo soil and the Raven soil are largely smectite. This together with a near neutral soil pH, and a pseudogley condition (formation of Fe oxide or hydroxide coatings and nodules that are stronger catalysts than clay minerals) as reported in Chapter II, tends to favor the abiotic process through surface-catalyzed oxidative polymerization and polycondensation (Wang et al., 1986; McBride et al., 1988).

The concepts of polymerization and polycondensation during humification are loosely used in the literature to explain HA formation, though fundamental differences in their structures exist. Breitmaier and Voelter (1987) have illustrated the chemical shift values for a number of nonprotonated aromatic carbons that are involved in different coupling arrangements between two single aromatic rings. The C-C coupling of nonprotonated C between two adjacent aromatic rings was described for both enzyme-involved (Sjoblad and Bollag, 1981) and abiotic oxidative polymerization processes (McBride et al., 1988). Its chemical shift value should be about 141 ppm, similar to that for C-C coupling in biphenyl structure. Alkyl-jointed nonprotonated aromatic C, mentioned by Stevenson (1982), Hayes and Himes (1986) as a HA structural component, has a chemical shift in the range of 141-144 ppm. Other nonprotonated C bridged by electron-withdrawing atoms during polymerization have resonance towards low field, such as for diphenyl amine (143 ppm), diphenyl ester (150 ppm), dibenzyl ester (139 ppm) and other type structures. While trying to establish a possible reaction scheme for the Al^{3+} catalyzed polymerization of catechol, McBride et al. (1988) found it was difficult to explain the formation of the final high molecular weight products by polymerization alone and instead suggested a strongly condensed polynuclear aromatic structure as found in northern temperate soils. Presence of polynuclear aromatic substances, such as alkylnaphthalenes, in HAs were also reported for some German soils (Hempfling and Schulten, 1991) and for some Canadian soils (Schulten et al., 1991). Our data suggest that polycondensation to polynuclear aromatic rings likely contributed to aromatization of HAs as soil depth increased. The progressive increase with depth of nonprotonated C shifting from the carboxyl range to the aromatic range is in agreement with the possible enrichment of polynuclear aromatic rings at lower soil depths rather than from the nonprotonated C_1 carbon bonded to a carboxyl C in the aromatic rings.

CuO digestion

The CuO digestion has long been used to study the aromatic components in HAs because of relatively higher yields and fewer artificial effects than other methods (Schnitzer, 1978; Stevenson, 1982). Mild degradation methods were also favored by Hayes and Himes (1986) for HA structural studies in order to minimize artifacts. Our data indicated a progressive modification of lignin derived phenols in HAs with increase in soil depth. The shift from other phenol families to p-hydroxyl phenols in HA digest indicates modification to lignin moieties as soil depth increased. This may be best reflected by the ratio of the p-hydroxyl phenols to the cinnamyl phenols that are most mobile (Ertel and Sedges, 1984). Hartley and Whitehead (1985) reported that the p-hydroxyl phenols were likely of microbial origin while other phenols were generally early derivatives from lignin degradation. Earlier work by Martin et al. (1974) also indicated that hydroxyl-substituted phenols were products of soil fungal activity. In the Malmo soils, a change of phenol components with depth suggests the HAs from organic layers are more plant-related, while those from mineral horizons, especially from Ah2 to Bmgj are more microbe-related. In the Raven soils, these trends are also apparent. The HAs in mineral horizons are apparently different from those in organic layers. In a study of the origin of HAs, Ertel and Hedges (1984) considered the p-hydroxyl phenols to be of ambiguous origin and excluded them during discussion. Our data suggest that they are characteristically dominant components of HA digest in mineral horizons. Higher ratio of these p-hydroxyl phenols as compared to other components, especially to cinnamyl phenols, should be a good indicator of further humification. These ratios also provide further molecular information related to the nature of the aromatic fraction in HAs with change in soil depth. We therefore propose that they could serve as useful pedogenic parameters in further studies of humification and in organic paleopedology.

SUMMARY AND CONCLUSION

Since the HAs were extracted from the entire soil sola, the HAs from different horizons are genetically related and thus comparable. Thus, the structural transformation of HAs with soil depth is likely the result of pedogenic processes.

Findings in this chapter showed the aromaticity of HAs to be a function of soil depth. Thus comparison of HAs from a single horizon of genetically non-related soils has limited significance. The HAs in the organic layers are less aromatic and contain less fused aromatic C, which may structurally more closely resemble a sponge-like model of HAs outlined by Hayes and Himes (1986) and later proposed by Schulten et al. (1991). The HAs in the mineral horizons may structurally be in between the above model and a more polycondensed model proposed by Stevenson (1982), though the latter model may be a bit too aromatic to fit our [illegible] Dragunov's and Fuchs's structural models recorded by Kononova (1966) lik [illegible] not fit our HAs in the mineral horizons for either lack of fused aromatic rings (Dragunov's model) or for being over aromatic (Fuchs's model). Our results also indicate greater aromaticity variations for the HAs from soils under forest-grass transition than under grass vegetation.

In conclusion, these results showed the amount, as well as the structure and composition of HAs, are functions of vegetation and soil depth. Properties of HAs changed more abruptly for soil under grass-forest communities than under grass vegetation. As soil depth increases, HAs are enriched with C and depleted of H, and the HAs become more aromatic likely through polycondensation by formation of polynuclear aromatic rings. Together with aromatization, the HAs become less lignin-like than those from organic layers and were modified to HAs typical of mineral soil horizons.

REFERENCE

Agriculture Canada Expert Committee on Soil Survey. 1987. The Canadian System of Soil Classification. 2nd edition, Agri. Can. Publ. 1646, Ottawa.

Arshad, M, A., Ripmeester, J.A. and Schnitzer, M. 1988. Attempts to improve solid state ^{13}C NMR spectra of whole mineral soils. Can. J. Soil Sci., 68: 593-602.

Axelson, D.E. 1985. Solid state nuclear magnetic resonance of fossil fuels. Multiscience Publication Limited, Minister of Supply and Services Canada (M39-16/1985E). Canada.

Breitmaier, E. and Voelter, W. 1987. Carbon-13 NMR Spectroscopy: High-Resolution Methods and Applications in Organic Chemistry and Biochemistry. 3rd, completely revised edition, VCH Verlagsgesellschaft.,Weinheim, Germany.

Ertel, J.R. and Hedges, J.I. 1984. The lignin component of humic substances: Distribution among soils and sedimentary humic, fulvic, and base-insoluble fractions. Geochimica et Cosmochimica Acta, 48: 2065-2074.

Hartley, R.D. and Whitehead, D.C. 1985. Phenolic acids in soils and their influence on plant growth and soil microbial processes, in D. Vaughan and R.E. Malcolm (ed), Soil Organic Matter and Biological Activity, Dr. W. Junk Publishers, Dordrecht, Netherlands, pp. 109-149.

Hayes, M.H.B. and Himes, F.L. 1986. Nature and properties of humus-mineral complexes. in P.M. Huang and M. Schnitzer (ed), Interactions of Soil Minerals with Natural Organics and Microbes, SSS publ. No. 17, SSSA Inc., Madison, Wis., pp. 103-158.

Hedges, J.I. and Ertel, J. R. 1982. Charaterization of lignin by gas capillary chromatography of cupric oxide oxidation products. Anal. Chem., 54: 174-178.

Hempfling, R. and Schulten, H.-R. 1991. Pyrolysis-(gas chromatography/) mass spectrometry of agricultural soils and their humic fractions. Z. Pflanzenernahr. Bodenk., 154: 425-430.

Khan, S.U. and Schnitzer, M. 1972. Permanganate oxidation of humic acids, fulvic acids, and humins extracted from Ah horizons of a Black Chernozem, a Black Solod, and a Black Solonetz soils. Can. J. Soil Sci., 54: 43-51.

Kögel-Knabner, I., Zech, W. and Hatcher, P.G. 1988. Chemical composition of the organic matter in forest soils: the humus layer. Z. Pflanzenernahr. Bodenk., 151: 331-340.

Kögel-Knabner, I., Hatcher, P.G. and Zech, W. 1990. Decomposition and humification processes in forest soils: implications from structural characterization of forest soil organic matter. Trans. 14th Int. Congress Soil Sci., Kyoto, Vol. 5, pp. 218-223.

Kononova, M.M. 1966. Soil Organic Matter: Its Nature, Its Role in Soil Formation and in Soil Fertility. 2nd English edition. Pergamom Press, Oxford.

Lowe, L.E. 1992. Bound phenolic acids in terrestrial humic acids. Sci. Total Environ., 117/118: 187-195.

Malcolm, R. L. and MacCarthy, P. 1986. Limitations in the use of commercial humic acids in water and soil research. Environ. Sci. Technol., 20(9): 904-911.

Martin, J.P. and Haider, K. 1980. A comparison of the use of phenolase and peroxidase for synthesis of model humic acid-type polymers. Soil Sci. Soc. Am. J., 44: 983-988.

Martin, J.P., Haider, K. and Saiz-Jimenez, C. 1974. Sodium analgam reductive degradation of fungal and model phenolic polymers, soil humic acids, and simple phenolic compounds. Soil Sci. Soc. Amer. Proc., 38: 760-765.

McBride, M.B., Sikora, F.J. and Wesselink, L.G. 1988. Complexation and catalyzed oxidative polymerization of catechol by aluminum in acidic solution. Soil Sci. Soc. Am. J., 52: 985-993

Neyroud, J.A. and Schnitzer, M. 1974. The exhaustive alkaline cupric oxide oxidation of humic acid and fulvic acid. Soil Sci. Soc. Amer. Proc., 38: 907-913.

Pawluk, S. 1988. Freeze-thaw effects on granular structure reorganization of soil materials of varying texture and moisture content. Can. J. Soil Sci., 68:485-494.

Pawluk, S. and Bal, L. 1985. Micromorphology of selected mollic epipedons, in L.A. Douglus and M.L. Thompson (ed.), Soil Micromorphology and Soil Classification. SSSA. Spec. Publ. 15, Madison, Wis., pp. 63-83.

Sanborn, P. and Pawluk, S. 1983. Process studies of a Chernozemic pedon, Alberta (Canada). Geoderma, 31: 205-237.

Schnitzer, M. 1978. Humic substances: chemistry and reactions, in M. Schnitzer and S.U. Khan (ed.), Soil Organic Matter. Elsevier Scientific Publishing Company, Amsterdam, pp. 1-64.

Schnitzer, M. 1991. Soil organic matter---the next 75 years. Soil Sci., 151(1): 41-58.

Schnitzer, M. 1982. Organic matter characterization. in L.A. Page, R.H. Miller and D.R. Keeney (ed.), Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties. 2nd edition, American Society of Agronomy Inc. and Soil Science Society of America, Inc. Publisher, Madison, Wis., pp.581-594.

Schnitzer, M., Kodama, H. and Ripmeester, J.A. 1991. Determination of aromaticity of humic substances by x-ray diffraction analysis. Soil Sci. Soc. Am. J., 55: 745-750.

Schulten, H.-R., Plage, B. and Schnitzer, M. 1991. A chemical structure for humic substances. Naturwissenschaften, 78: 311-312.

Sjoblad, R.D. and Bollag, J.M. 1981. Oxidative coupling of aromatic compounds by enzymes from soil microorganisms, in E.A. Paul and J.N. Ladd (ed.), Soil Biochemistry, Vol. 5. Marcel Dekker, Inc., New York, pp. 113-152.

Skjemstad, J.O., Waters, A.G., Hanna, J.V. and Oades, J.M. 1992. Genesis of Podzols on coastal dunes in southern Queensland. IV. Nature of the organic fraction as seen by ^{13}C nuclear magnetic resonance spectroscopy. Aust. J. Soil Res., 30:667-681.

Stevenson, F.J. 1982. Humus Chemistry, Genesis, Composition, Reactions. John Wiley & Sons, New York.

Thompson, M.L., Fedoroff, N. and Fournier, B. 1990. Morphological features related to agriculture and faunal activity in three loess-derived soils in France. Geoderma, 46: 329-349.

Tisdal, J.M. and Oades, J.M. 1982. Organic matter and water stable aggregates in soils. J. Soil Sci., 33:141-163.

Wang, T.S.C., Huang, P.M., Chou, C.H. and Chen, J.H. 1986. The role of soil minerals in the abiotic polymerization of phenolic compounds and formation of the humic substances, in P.M. Huang and M. Schnitzer (ed.), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., pp. 251-281.

Wilson, M.A. 1991. Analysis of functional groups in soil by nuclear magnetic resonance spectroscopy, in K.A. Smith (Editor), Soil Analysis: Modern Instrumental Techniques, 2nd edition, Marcel Dekker Inc., New York, pp. 601-645.

Wilson, M.A. 1987. NMR Techniques and Application in Geochemistry and Soil Chemistry. Pergamom Press, Oxford.

Vance, G.F., Boyd, S.A. and Mokma, D.L. 1985. Extraction of phenolic compounds from Spodosol profile: an evaluation of three extractants. Soil Sci. 140(6): 412-420.

Chapter IV

Variations in Nature of Organic Geopolymers and Their Relationship with Sorption of Organic Contaminants

INTRODUCTION

Soil organic matter associated with soil structural development also affects the sorption of non-ionic, aromatic organic pollutants. Organic geopolymers in soils and sediments are usually the prime sorbents for non-ionic organic pollutants (Hassett et al., 1981; Sun and Boyd, 1991; Xing et al., 1993; Xing et al., 1994a). Various linear partitioning equations have been proposed for predicting partition coefficients (Chiou et al., 1979; Briggs, 1981; Chiou et al., 1983; Means et al., 1980), where the organic phase was treated as homogeneous with partitioning behavior parallel to that of octanol. Organic sorbents in soils and sediments are complex, however. The aromaticity of organic substances in soil and sediments has a significant impact on sorption and partitioning of aromatic organic pollutants in the terrestrial environment (Grathwohl, 1990). These reactions usually regulate other processes (adsorption, desorption, transport and biodegradation) and determine the fate of organic pollutants. Xing et al. (1994b) showed a marked discrepancy between the laboratory-measured K_{OC} values and those predicted with the linear partition models. Instead, they proposed a mass ratio of percent elemental composition, (O%+N%)/C%, of a given organic sorbent, be used for more accurate prediction of K_{OC} values. They termed this compositional property of organic sorbents 'polarity'. Soils and sediments are usually immediate receptors of pollutants in the terrestrial environment. Thus the structural and compositional variation among organic geopolymers in soils or sediments likely influences the fate of non-ionic aromatic organic pollutants. Humic substances represent the bulk of soil organic matter (Stevenson, 1982; Schnitzer, 1978; 1991). However, information about their structural and compositional characteristics within a continuous vertical section is scarce. This may hinder understanding of interactions between organic pollutants and soils or sediments during the early stages following contamination events.

The objective of this study, as defined in Chapter I, is to investigate if pedogenic modification of the humic substances will have an impact on sorption of environmental pollutants. In addition, this study is extended to include the common organic geopolymers found in terrestrial environments. Their structural and compositional variations are related to sorption of the non-ionic aromatic organic ollutant α-naphthol. α-naphthol is a potential groundwater pollutant (Zachara et al. 984) found in coal conversion waste streams (Hassett et al., 1981) and in iodegradation processes of the insecticide carbaryl (Bollag et al., 1976).

METHODS AND MATERIALS

Extraction of HAs from soils

Soil samples were collected from the Malmo soil, a Gleyed Black Chernozem at the Ellerslie Research Station of the University of Alberta (Agriculture Canada Expert Committee on Soil Survey, 1987). The site has an undisturbed soil formed under an open aspen-[illegible] stand; this pedon was chosen because of its well developed organic layer and thick Ah horizon. The basic properties of the soils are outlined by Sanborn and Pawluk (1983); generally, they are neutral in pH, clay textured and have a high organic C content in the upper horizons. Humic acids (HAs) from sola of the soils were extracted under N_2 using 0.1M $Na_4P_2O_7$ with natural pH (pH=10.6). The procedures were generally those as outlined in Chapter III. The HAs from major horizons of Malmo soil were used for this study.

Additional soil and sediment samples used in this study, included peat, Ah horizon soils, humate deposits and shale samples as described by Xing et al. (1994b). The peat sample was collected from north of Edmonton, Alberta. It is well humified sedge of recent origin (a few hundred years). The soil samples of Ah horizons were from the Malmo soil and White clay soil respectively. The Malmo soils are formed on glacial-lacustrine deposits and are about ten thousand years of age (Sandborn and Pawluk, 1983). The White Clay soil is developed from weathered Quaternary aged sediments in P.R. China (Xing and Dudas, 1992). The humate deposits refers to the brownish carbonaceous mudstone (upper Cretaceous) from the Menefee Formation in the north of New Mexico (Siemers and Wadell, 1977). The Black shale is a Cretaceous aged weathered shale containing thin layers of soft coal and was obtained from Edmonton, Alberta. These materials represent a broad range of geological diagenesis and are also common sources of organic geopolymers in terrestrial environments. They were ground into fine powder for subsequent analyses.

^{13}C CP/MAS NMR spectroscopy

Conventional solid state ^{13}C CP/MAS NMR analysis was conducted at the Department of Chemistry, University of Alberta, with a Brucker AM 300 instrument, operating with CP/MAS accessory and a HP WP 73A probe, at 75 MHz frequency, 5,000 kHz spinning rate, with 90° pulse width of 5.50 μs, 2 ms contact time, and 70 ms acquisition ti [illegible] he 0-220 ppm chemical shift range, C atoms were assigned to alkyl C (0-50 ppm [illegible] kyl C (50-107 ppm), aromatic C (107-165 ppm), carboxyl C (165-190 ppm) and carbonyl C (190-220 ppm) according to Malcolm and MacCarthy (1986), Wilson (1991), and Breitmaier and Voelter (1987).

Elemental analysis

The elemental analyses for C, H, N and O of HAs and C, H, and N of peat, humate deposits and Blake shale were conducted with a Carlo Erba CHNS-O EA1108 elemental analyzer. The O content for peat, humate and Black shale was calculated by difference, after correction for ash content. The ash content was determined by heating samples at $740^{\circ}C$ for 4 hours (Schnitzer 1982). The C contents of Ah samples from Malmo and White Clay soils were determined with dry combustion using a LECO Carbon Determinator (CR12 Model). The H, N, and O contents were not determined for the whole soil samples because these elements are not separable from those of the phylosilicates matrix of the soils.

Sorption isotherm

Sorption isotherms were obtained with HAs, soil and sediment samples by the batch equilibrium method as outlined by Xing et al. (1994a). The α-naphthol solution concentrations ranged from 0-300 ppm for HAs to obtain linear isotherms. The solution was maintained at pH of 4.0 to limit dissolution of HAs. The α-naphthol solution concentrations ranged from 0-600 ppm and were maintained at solution pH of 6.0 for the soil and sediment samples. Background electrolyte concentration was 0.03 molar $CaCl_2$. Solution:solid (volume:weight) ratio was 100:1 for HAs from major horizons (FH, Ah1, Ah2, Ah3) of Malmo soil and 20:1 for the soil and sediment samples. Labeled α-naphthol solution was prepared by adding ^{14}C-α-naphthol to α-naphthol solutions in sufficient amounts to produce an activity of 100 Bq/mL. HA or finely powdered sediments were weighed into glass tubes that were then filled with 10.00 mL of labeled solution with minimum headspace in the tube. A minor amount of $HgCl_2$ (10^{-5} M) was used to minimize biological activity. The tubes were immediately sealed with screw-caps having Teflon liners and shaken horizontally in a LAB-line Orbit Environ-shaker at 300 rpm for 24 hours. After centrifuging at 3200 g for 30 min, 1.00 ml aliquots of supernatant solution were sampled for α-naphthol analysis by liquid scintillation counting. The difference between the initial and final concentrations of α-naphthol was attributed to sorption by sorbents. A control test for each α-naphthol concentration was also conducted and showed that the glass centrifuge tubes did not adsorb α-naphthol. The sorption (partition) coefficient, K_d, was calculated from the slope of the linear sorption isotherm ($x/m=K_dCe$). The K_{OC} value was obtained as the quotient of K_d divided by organic C fraction, f_{OC}, of samples.

Correlation analysis

Simple correlation analysis was conducted using SAS software (SAS Institute Inc., 1987). Pearson correlation coefficients were computed among the compositional and structural parameters for the samples Data of other environmentally-related biopolymers (Xing et al. 1994a), of humic substances of various origins, such as diagnostic soil horizons (Malcolm, 1990, Schnitzer et al. 1991; Ricca and Severini, 1993; and HAs in Chapter III), of different size fraction of soil aggregates (Catroux and Schnitzer, 1987), of aqueous environments (Malcolm, 1990; Malcolm and MacCarthy, 1986), and of commercial sources (Malcolm and MacCarthy, 1986), were pooled together to represent a broader range of organic biopolymers and geopolymers.

RESULTS

^{13}C NMR

Conventional solid state ^{13}C CP/MAS NMR spectra of HAs for major horizons of Malmo soil are shown in Fig.4-1. The spectra of the FH horizon reveals that the distribution of C is quite diverse. The sharp peak at 30-31 ppm is from long chain polymethylene, probably in fatty acids (Nordén and Berg, 1990). The peak at 50-60 ppm is methoxyl signal (Malcolm, 1990). The peak at 73-75 ppm is due to C_2, C_3, C_5 and at 103-105 is due to anomeric C_1 for sugar in the pyranose unit of polysaccharides (Nordén and Berg, 1990; Malcolm, 1990). In the aromatic range, peaks at 116 ppm (signal of C_2, C_6) and 150-165 ppm (signal of C_1) are from phenol structure (Breitmaier and Voelter, 1987; Malcolm, 1990). The alkyl C (0-50 ppm) and O-alkyl C (50-107 ppm) account for more than 50% of carbon in HAs in this horizon (Table 4-1). The Ah1 horizon has transitional characteristics where reduction of O-alkyl (50-107 ppm) and increase of aromatic C (107-165 ppm) are apparent. A much reduced signal of phenolic-C is still evident. The spectra of HAs extending from the Ah2 to the Bmgj horizon are similar in that their aromatic C dominates the entire spectra. Both the O-alkyl C, and the alkyl C are significantly diminished. Phenolic C is barely evident. Consequently, it is the most aromatic zone in the soil.

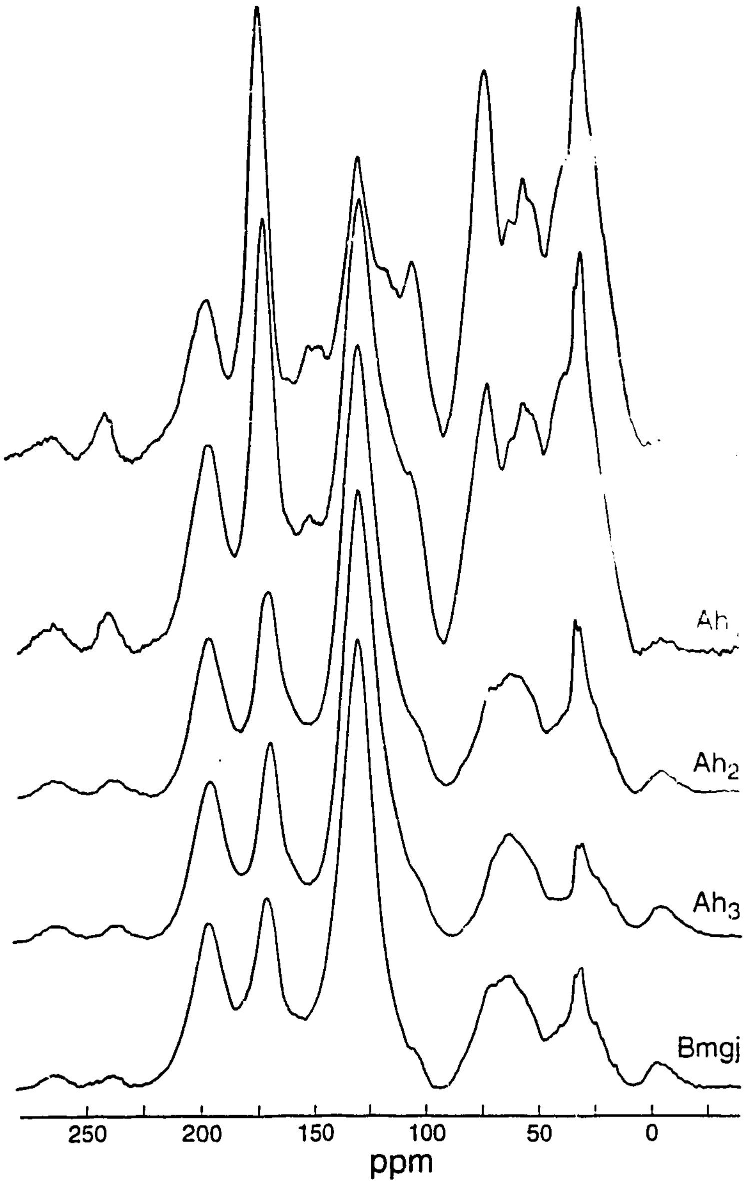


Fig. 4-1. Conventional solid state ^{13}C CP/MAS NMR spectra of humic acids in major horizons of the Malmo soil.

The conventional ^{13}C CP/MAS NMR spectra for peat, Ah horizons from White Clay soil and Malmo soil, humate deposit, and Black shale are given in Fig.4-2. These samples can be segregated into three groups according to their structures. The peat sample is typical of plant material, where the alkyl and O-alkyl make up the bulk (over 70%) of their carbon (Table 4-1). The fact that about 50% of its carbon is

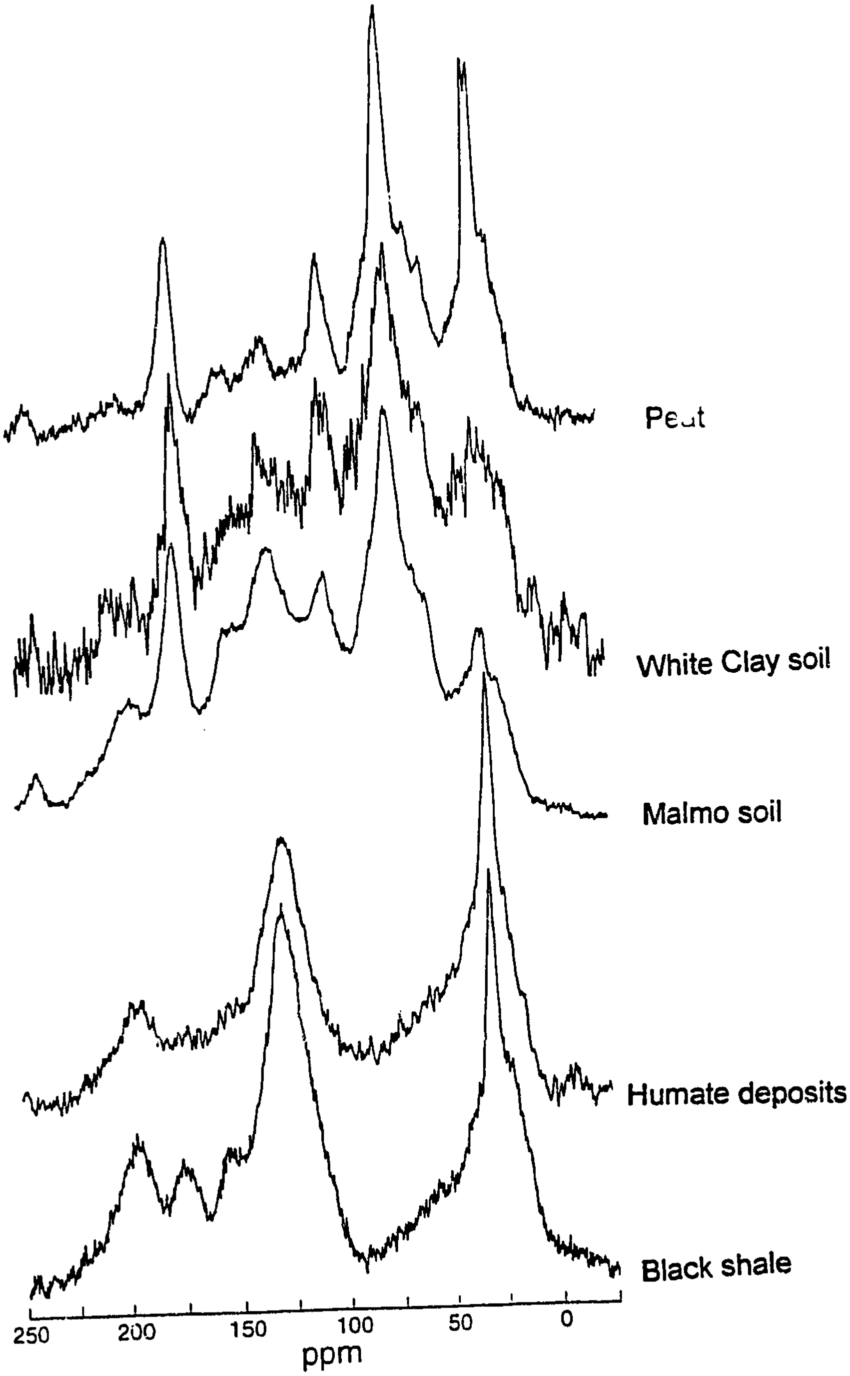


Fig. 4-2. Conventional solid state ^{13}C CP/MAS NMR spectra of organic geopolymers in selected soils and sediments.

Table 4-1. Percentage distribution of carbon in humic acids from the Malmo soil, and in soils and sediments, calculated from the conventional solid state ^{13}C CP/MAS NMR spectra.

Samples	Type of carbon					Aromaticity#	
	alkyl (%)	O-alkyl (%)	aromatic (%)	carboxyl (%)	carbonyl (%)	f_1 (%)	f_2 (%)
			Humic acids in Malmo soil				
FH	26	29	24	14	7	24	30
Ah1	22	22	33	15	8	33	43
Ah2	13	16	47	13	9	47	62
Ah3	10	14	51	14	11	51	68
Bmgj	11	14	48	15	12	48	66
			Soil and sediment samples				
Peat	27	45	16	9	3	9	10
White Clay soil	20	42	25	10	4	25	29
Malmo soil	13	37	31	12	7	31	38
Humate deposits	33	16	36	7	8	36	42
Black shale	29	10	42	8	10	42	52

#: f_1= aromatic carbon/(alkyl+O-alkyl+aromatic+carboxyl+carbonyl carbon)x100
f_2= aromatic carbon/(alkyl+O-alkyl+aromatic carbon)x100

distributed in O-alkyl C indicates it is highly cellulitic. The surface Ah horizons of the White Clay and Malmo soils represent the second group. The signal from alkyl-C is weaker while the aromatic-C and carboxyl-C are stronger as compared to the peat sample. The spectra for humate deposits and Black shale represent the third group. They are much simpler spectra where alkyl-C and aromatic C dominate the spectra. The single sharp peak at 30 ppm indicates their alkyl-C has dominantly polymethylene structure, unlike that of peat which has about half of its alkyl-C from branched alkyl structures. The enrichment of aromatic-C makes them the most aromatic group. The oldest Black shale is most aromatic in nature.

To identify possible sideband interference, a 'total side band suppression' mode (TOSS) (Dixon, 1982) was superimposed over the conventional ^{13}C CP/MAS NMR spectroscopy. Comparisons of the TOSS and conventional ^{13}C CP/MAS NMR spectra for samples of contrasting aromaticities (a low aromatic HAs from the LF horizon of the Malmo soil, Chapter III, and a highly aromatic coke sample) are given in Fig. 4-3.

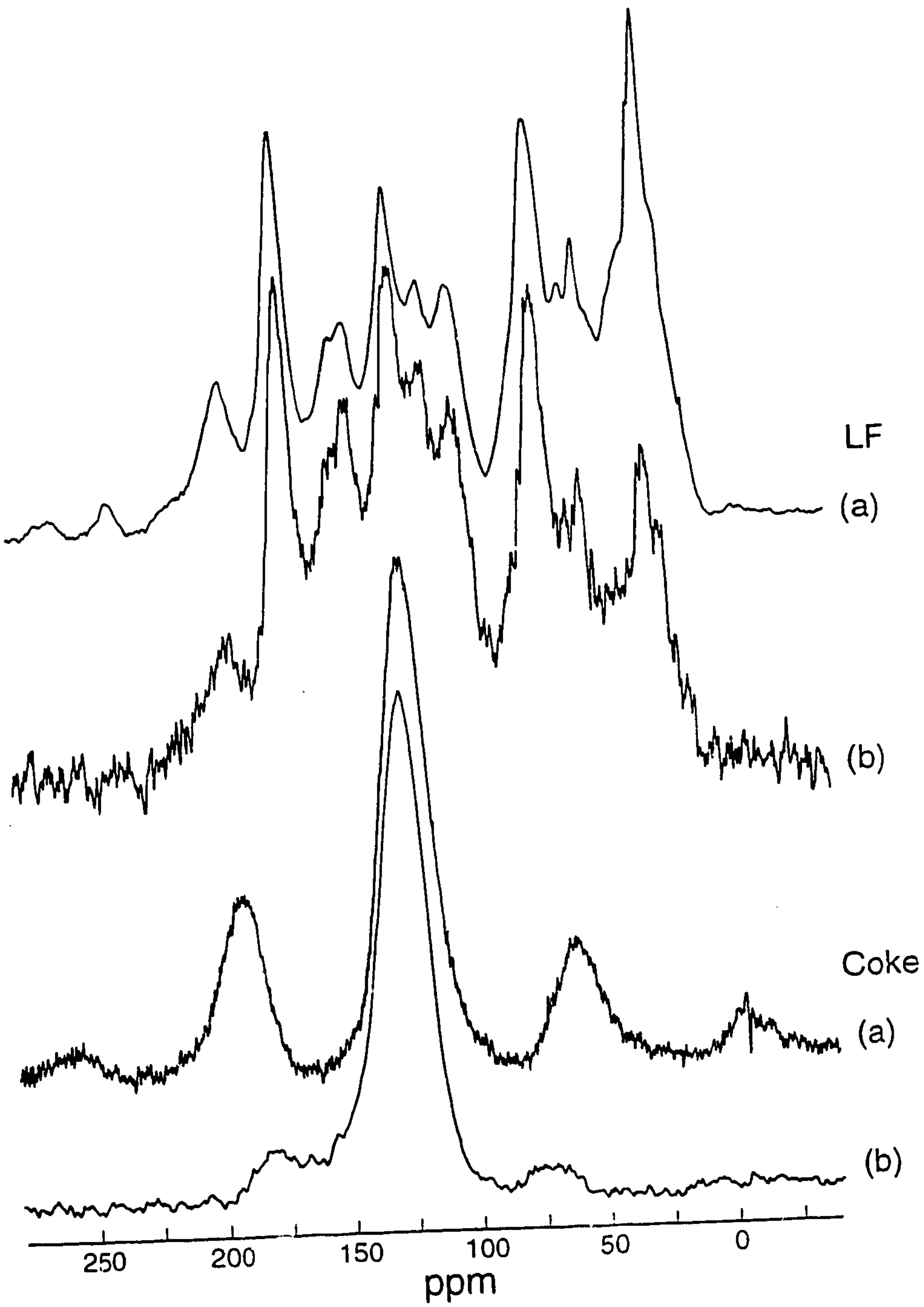


Fig. 4-3. Comparison between conventional solid state ^{13}C CP/MAS NMR (a) and TOSS spectra (b) for humic acids in the LF layer of the Malmo soil, and a coke sample of contrasting aromaticity.

The peaks for the conventional ^{13}C CP/MAS spectra of the HA sample in the LF layer of Malmo soil are legitimate peaks, each of these peaks has a corresponding peak in the TOSS spectra. The TOSS spectra tend to give weaker signals for alkyl-C but stronger signals for aromatic-C. Consequently, the aromaticity values estimated from the TOSS spectra (40%) are higher than from conventional CP/MAS spectra (24%). However, for the highly aromatic coke sample, the easily identifiable sidebands that are nearly-symmetric along the isotropic aromatic peak at 110-165 ppm in the conventional ^{13}C CP/MAS NMR spectra are removed in the TOSS spectra. Its aromaticity (85%) could be calculated only from the TOSS spectra.

Elemental composition

The elemental composition of HAs of the Malmo soil are given in Table 4-2. C content increases slightly from the organic FH layers to the mineral horizons. The H content shows a reverse trend to the C content. As a result, the atomic H/C ratio

Table 4-2. Percent elemental composition, polarity ((O+N)/C), atomic ratio (moisture and ash free basis) and ash content for humic acids from the Malmo soil, and for geo-polymers in soil and sediment samples

Sample	C	H	N	O	(O+N)/C	Ash	Atomic ratio			
	(%)	(%)	(%)	(%)		(%)	H/C	N/C	O/C	(N+O)/C
					Humic acids from Malmo soil					
FH	52.2	4.14	2.85	40.2	0.82	0.26	0.95	0.047	0.58	0.63
Ah1	54.3	3.59	2.88	38.3	0.76	0.51	0.79	0.045	0.53	0.57
Ah2	56.8	3.04	3.51	36.2	0.70	0.63	0.65	0.053	0.48	0.53
Ah3	56.5	2.98	3.47	35.6	0.69	1.84	0.63	0.053	0.47	0.52
Bmgj	59.9	3.50	2.86	33.1	0.60	7.44	0.70	0.041	0.41	0.46
					Soil and sediment samples					
Peat	53.0	5.73	4.21	37.2	0.78	42.0	1.30	0.068	0.53	0.60
White Clay soil	7.38†	nd	nd	nd	nd	nd	nd	nd	nd	nd
Malmo soil	4.53†	nd	nd	nd	nd	nd	nd	nd	nd	nd
Humate deposit	61.3	5.22	1.59	30.6	0.53	68.0	1.02	0.022	0.37	0.39
Black shale	65.4	3.20	0.00	30.0	0.46	17.0	0.59	0.00	0.34	0.34

†Value not corrected for ash.

decreases with soil depth. Parallel to C content, the N percentage increases with depth too. The O content slightly decreases with depth in the mineral horizons. The polarity, defined as the mass ratio of (N%+O%)/C% (Xing et al. 1994a), also decreases from organic layers to mineral horizons. Similarly, the atomic ratio of (N+O)/C also decreases.

The elemental composition of the soil and sediment samples shows similar trends of change due to the difference in geological diagenesis, but at a broader range (Table 4-2). The peat material composition is similar to HAs in the LF layer of the Malmo soil. The Humate deposit and Black shale have higher C content than peat and the HAs extracted from the Malmo soil. The atomic H/C ratios are highest for peat and lowest for the Black shale. The N content is higher for peat compared with Humate deposits and Black shale. These soil and sediment samples apparently have higher ash contents than HAs. The polarity values and atomic (N+O)/C ratio of the sediment samples show greater variation than HAs extracted from the Malmo soil.

Sorption isotherm

Uptake of α-naphthol solution fitted linearly for HAs (R values ranged 0.98 to 1.00) in the test condition (Fig.4-4), although the isotherms also fitted Freundlich equation (R values ranged from 0.99 to 1.00). The K_d value from linear fitting, calculated as the slope of each isotherm is shown in Fig.4-4. For each equilibrium

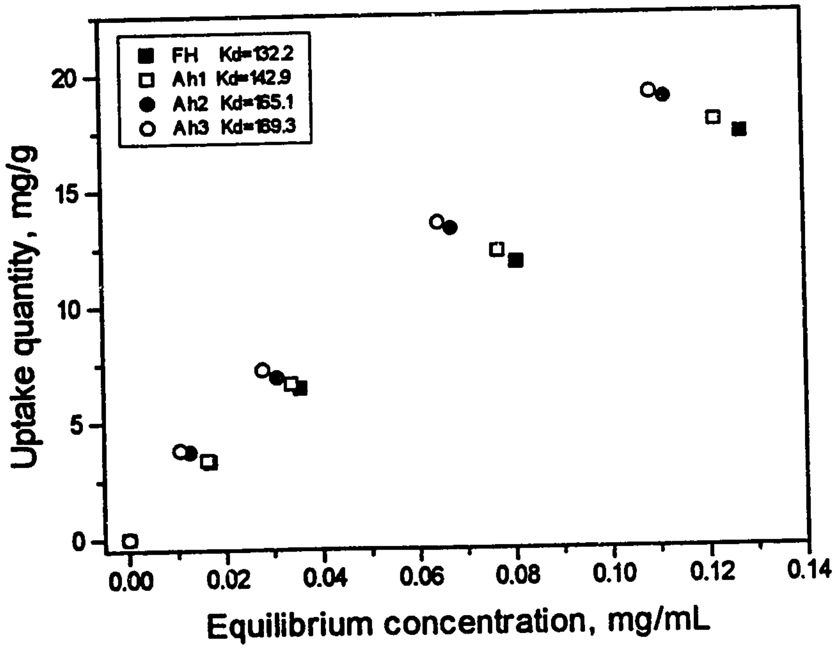


Fig. 4-4. Sorption isotherms and Kd values for α-naphthol by humic acids from Malmo soil.

concentration range, the uptake quantity showed a consistent pattern: Ah3>Ah2>Ah1>FH. This pattern parallels the aromaticity order reported for HAs. The K_{OC} values are 253, 263, 291 and 300 mL/g for HAs from FH, Ah1 Ah2 and Ah3 horizons respectively. The plot showed a linear relationship between K_{OC} and aromaticity (f_l) calculated from ^{13}C CPMAS NMR spectra (Fig. 4-5). These values are much lower than the predicted K_{OC} value from the linear equation by Means et al. (1980).

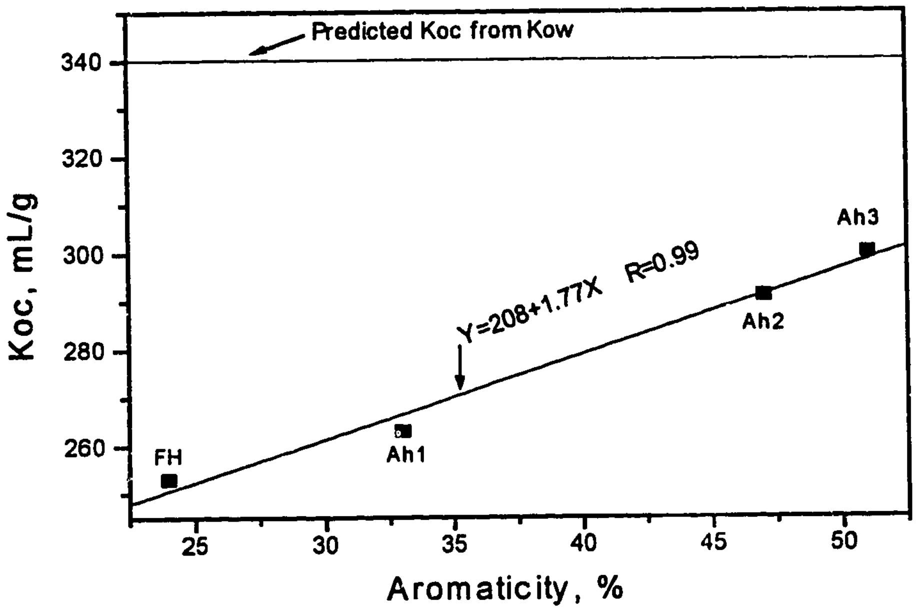


Fig. 4-5. Relationship of Koc for α-naphthol and aromaticity of humic acids from Malmo soil in comparison with the predicted value.

Sorption isotherms for the soil and sediment samples are plotted in Fig. 4-6. Both the linear equation and Freundlich equation fitted the sorption isotherms (R values ranged from 0.97 to 1.00 for the former, and from 0.99 to 1.00 for the latter). The K_d values, derived from linear regression, are 355, 74.5, 20.0, and 13.3 (mL/g) for Black shale, peat, White Clay soil, and Malmo soil respectively. Their K_{OC} values in descending order were Black shale (654) > Malmo soil (294)> White clay soil (271) > peat (231 mL/g). The values for Malmo soil, White clay soil and peat are lower than the predicted value, however, the value for Black shale is greater (Fig. 4-7). Linear regression between K_{OC} and aromaticity of the organic geopolymers in these samples yielded a higher slope but lower intercept value (R=0.82) as compared with the values observed for HA samples. The Black shale is older in age, and belongs to a more advanced stage of diagenesis relative to the unconsolidated peat and soil samples. The nature of organic geopolymers in the Black shale may be different from those in peat or soil samples, according to Grathwohl (1990). Removal of the Black shale value

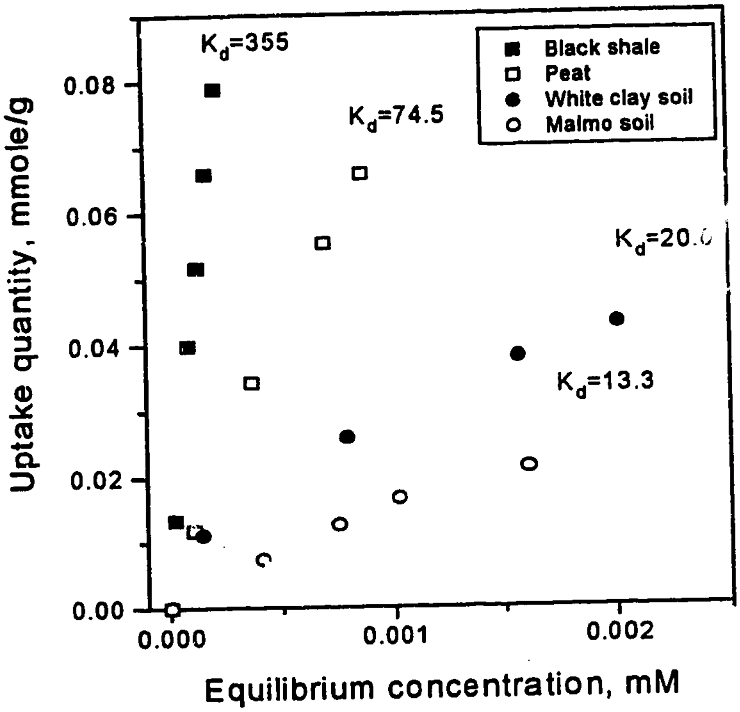


Fig. 4-6. Sorption isotherms of α-naphthol onto selected soils and sediments.

resulted in a different linear relationship (R=0.99) with an intercept value of 205 mL/g which is very close to that of HA samples. These values are apparently different from the predicted K_{OC} value by conversion K_{OC}-K_{OW} equation (Means et al., 1980).

Correlation analysis

The compositional parameters and structural parameters are generally significantly related (Table 4-3). The polarity variable, as defined by Xing et al. (1994b), and atomic ratios of (N+O)/C, H/C are positively correlated. These values are all negatively correlated with the structural parameter aromaticity determined as the percentage of aromatic-C over the sum of all the C fractions (f_1), or as the percentage of aromatic-C over the sum of alkyl-C, O-alkyl-C, plus aromatic-C (f_2) (Malcolm and MacCarthy, 1986; Malcolm, 1990; Schnitzer et al., 1991).

The atomic H/C ratio tends to give the best correlation to aromaticity among the compositional properties. The polarity and the atomic ratio of (N+O)/C have similar correlation coefficients to aromaticity. Aromaticity calculated as f_1 formula tends to give slightly higher correlation values than f_2 for polarity and atomic (N+O)/C ratio but smaller values for atomic H/C ratios. However, the correlation coefficients are generally not high, indicating other factors may also influence their relationship. The wide range of sample sources and differences in methods of aromaticity estimation may be responsible for the low correlation values. The grouped data according to the aromaticity calculation formula by Catrous and Schnitzer (1987) tend to give higher correlation values than those by Malcolm and MacCarthy (1986) and values of HAs in Chapter III, which in turn give higher correlation coefficient values than the total pooled data. For data grouped according to Catrous and Schnitzer (1987), the atomic H/C ratio is neither correlated with polarity nor atomic (N+O)/C ratios.

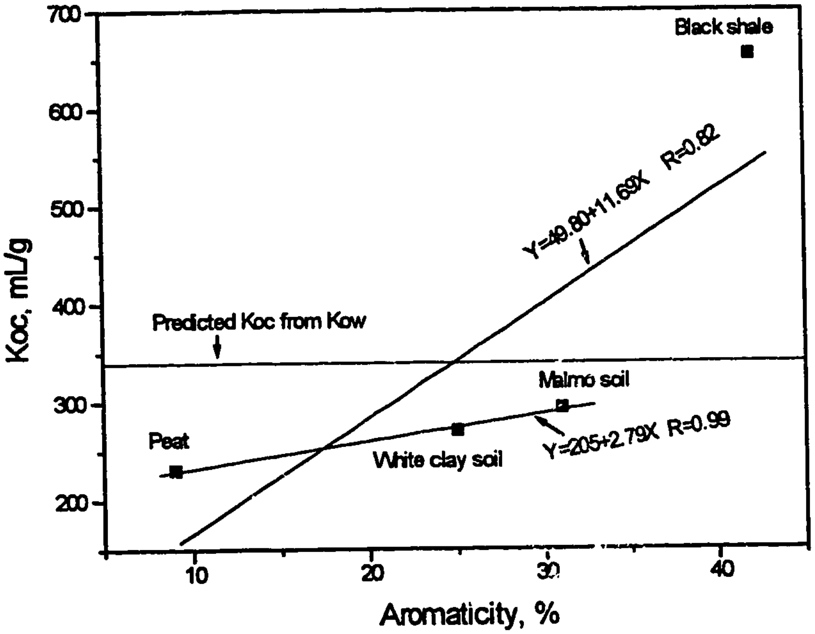


Fig. 4-7. Relationship of Koc for α-naphthol and aromaticity of selected soils and sediments in comparison with the predicted value.

Table 4-3. Pearson correlation coefficients for selected structural and compositional properties of some environmentally-related organic bio-, geo-polymers in terrestrial and aqueous bodies.

Parameters	Atomic ratio		Aromaticity	
	(N+O)/C	H/C	f_1†	f_2‡
		Tatal pooled data		
Polarity§	0.99****	0.43****	-0.48****	-0.46****
Atomic (N+O)/C		0.44****	-0.47****	-0.46****
Atomic H/C			-0.59****	-0.69****
Aromaticity fa$_1$				0.97****
		Aromaticity determined as Catrous and Schnitzer (1987)		
Polarity	0.99****	0.35^{ns¶}	-0.62**	-0.56*
Atomic (N+O)/C		0.36^{ns}	-0.62**	-0.57*
Atomic H/C			-0.84****	-0.85****
Aromaticity fa$_1$				0.99****
		Aromaticity determined as Malcolm and MacCarthy (1986)		
Polarity	0.99****	0.50***	-0.45****	-0.42**
Atomic (N+O)/C		0.50***	-0.45***	-0.42**
Atomic H/C			-0.69****	-0.73****
Aromaticity fa$_1$				0.98****

†: f_1 = aromatic C/(alkyl C + O-alkyl C + aromatic C + carboxylic C + carbonyl C) x 100
for Malcolm and MacCarthy (1986);
f_1 = aromatic C/(alkyl C + O-alkyl C + aromatic C + carboxylic C) x 100
for Catrous and Schnitzer (1987)
‡: f_2 = aromatic C/(alkyl C + O-alkyl C + aromatic C) x 100
§: polarity = (O%+N%)/C%, as defined by Xing et al. (1994b)
****, ***, **, *: significant at 0.0001, 0.001, 0.01, or 0.05 levels respectively
¶: ns: not significant

DISCUSSION

^{13}C NMR

The change of aromaticity of HAs with soil depth is strongly supported by the conventional ^{13}C CP/MAS NMR results in Fig. 4-1. Chapter III confirmed this observation with dipolar-dephasing ^{13}C CP/MAS NMR and suggested that polycondensation is likely one of the mechanisms leading to higher aromaticity in the horizons below the Ah1. The phenolic-C in the organic layers may have been transformed into the polynuclear aromatic C in the mineral horizons since the signals of the former are apparent in organic horizons but barely evident in the spectra of the mineral horizons. Presence of a phenol structure is indicated by twin peaks at 150 to 165 ppm range (C_1 signal) and at 116 ppm (C_2, C_6 signals) in the ^{13}C CP/MAS NMR spectra. The former serves as a measure for C associated with phenolic-OH group (Catrous and Schnitzer, 1987). The C_2, C_6 carbon signals in a phenolic ring usually have resonance at 116 ppm (Breitmaier and Voelter , 1987). This peak can be used to further indicate the presence of phenolic structure if another peak around 165 ppm for the C_1 carbon in phenolic ring structure also appears in conjunction with it. Such is the case for the HAs in the FH layer of Malmo soil. We make this point here to help in the identification of the phenolic structure since Malcolm (1990) pointed out a possible signal overlap at 150-170 ppm range from ester structure.

Variations of aromaticity for the soil and sediment samples indicate that the organic matter in soils or sediments are structurally different. This difference is not only present for the changes in extractable soil HAs with depth but also present at a broader range for soils and sediments with the extent of geological diagenesis. Thus organic substances in soils and sediments can not be considered as a homogenous phase as previously suggested by Chiou et al. (1979; 1983) or Means et al. (1980). The change in aromaticity follows the sequence:

Peat→Soils (White clay and Malmo soils)→Humate deposits→Black shale

The aromaticity of organic substances in soils and sediments has a significant impact on sorption and partitioning of aromatic organic pollutants in the terrestrial environment (Grathwohl 1990). It regulates other processes (partitioning, sorption and desorption) and determines the fate of organic pollutants. Studies with genetically-related samples, such as the HAs samples presented here provide an understanding of the consecutive changes that occur in the nature of HAs in soil. It also facilitates the prediction of the behavior of non-ionic organic pollutants in soils at a localized scale.

The structural variations among the soil and sediment samples provide additional information about soils and sedimentary substances. The geological diagenesis difference presented here permits a reasonable link between the variation in common terrestrial substances in relation to their structure and geological transformation of C from plant litter to coal. The aromaticity change in soil and sediments is in agreement with the view of Grathwohl (1990). Thus the nature of organic sorbents, such as aromaticity, should be incorporated into the prediction models for non-ionic organic pollutants. Xing et al. (1994b) suggested the use of polarity to predict the K_{oc} values with a cross-correlation method that includes the interactions of both the solute and sorbent phases. It is certainly an improved approach and can be easily applied to standard organic chemicals and well defined biopolymers. For soils and sediments, their polarity can not be easily obtained from elemental analysis due to an intimate association of the organics and mineral matrix that are practically not separable without a significant loss of the organic component or modification of the organic substances. In this case, aromaticity of organic substances estimated with ^{13}C CP/MAS NMR provides another possible alternative, given that there is an adequate amount of C in the samples and easy access to the instrument. A linear relationship between sorption quantity and aromaticity also facilitates the calculation of K_{OC} for the bulk of soil and sediment samples for non-ionic aromatic organic pollutants.

Estimation of aromaticity of organic substances is a crucial measurement. However, as pointed out by Dixon (1982), spinning sidebands may interfere with the analyses. The spinning sidebands are easy to identify and can be removed from integration. However, quantification may become much difficult when overlaps of spinning sidebands and isotropic bands occur. The signal intensity for the overlapped regions are either overestimated due to inclusion of the sideband or the isotropic band may be discarded by mistake as a sideband. A comparison of ^{13}C CP/MAS NMR spectra and TOSS spectra would facilitate the sideband identification and remove possible overlap problems. This combination should improve spectra interpretation with greater confidence. Some signal loss for fast-spinning atoms (such as polymethylene signal) may be inevitable (Axelson, 1985). Thus the TOSS spectrum is not suitable for structural analysis of the highly aliphatic organics and one may prefer to use the conventional ^{13}C CP/MAS NMR estimation, as was the case for the LF sample. The highly aromatic organics have about a nine-fold greater possibility to produce spinning sidebands than aliphatic organics (Dixon, 1982; Axelson, 1985). Thus their TOSS spectra may be a better reflection of the structural features and likely to give better estimation of aromaticity. Such is the case for the highly aromatic coke sample.

Compositional properties

The trends of change for C, H and O are similar for HAs in Malmo soil and for the soil and sediment samples. Change in the polarity and atomic ratios also showed similar trends for HAs with soil depth, and for the soil and sediments with the geological diagenesis difference. Such trends are likely related to aromaticity since aromaticity increases with soil depth for HAs as well as with extent of the geological diagenesis for the soil and sediment samples. The soil and sediment samples represent a much broader scale and some compositional changes, such as N content for HAs in soil is not evident for the sediment samples. The soil habitat is biologically active while the sediments (Humate deposits and Black shale) represent a biologically less active environment.

Sorption isotherm

Sorption results demonstrate a consistent relationship between uptake quantity and aromaticity of HAs. Structural variations of HAs within the soil solum likely have influenced the behavior of α-naphthol. This is in agreement with Gauthier et al (1994) and Xing et al. (1994a) whose organic sorbents bear no genetic relationships. HA samples reported in this chapter are from the same solum and are believed to be genetically-related (Chapter III). Using these HA samples facilitates the understanding and prediction of the pollutant behavior in a much more concrete manner. The rule of 'likes sorb likes' is applicable for the interactions between organic pollutants and organic sorbents. Thus the non-ionic aromatic organic pollutants are likely sorbed more strongly by well humified, more aromatic HAs in the mineral horizons while the polar or aliphatic organic pollutants may be sorbed more strongly in the highly cellulitic, less aromatic organic layers in the surface soil. Gauthier et al. (1987) used dissolved HAs for pyrene sorption. Their results were more applicable to the interaction of humic substances and pollutants during transport. Our results are more applicable for the water-solid interface system. Soil micromorphological observations showed that the humic substances are usually either bound to the mineral matrix in soils as organic-mineral complexes or as discrete humic granules in the inter-aggregate space (Pawluk and Bal, 1985, Sanborn and Pawluk, 1983; and Chapter II). Thus, partition of organic pollutants in the water-solid system is more common in soils. As for the sediment samples, their K_{OC} is also determined by aromaticity, which in turn was influenced by the extent of geological diagenesis. Those with higher aromaticity have larger K_{OC} values for non-ionic aromatic organic pollutants. Similar results were noted by Xing (1994) for toluene sorption onto these soils and sediments. The K_{OC} value of a specific non-ionic aromatic pollutant is not a fixed value for all organic sorbents. It changes with the nature of the organic sorbents. The extremely high Koc value for the Black shale sample indicated complexity in the sediment samples of advanced diagenesis. Other unknown factors, in addition to aromaticity, may have affected its sorption for α-naphthol. Further pursue is needed to understand this phenomenon.

Correlation among structural and compositional properties

The wide range of organic substances is probably one of the reasons for low correlation values. This is evident from the change in correlation coefficients obtained from grouped data as compared with the total pooled data in Table 4-3. Aromaticity calculation formulas are slightly different for the two grouped data. Use of the formula by Catrous and Schnitzer (1987) results in higher aromaticity values than those used by

Malcolm and McCarthy (1986) since the former excludes carbonyl-C (190-220 ppm) from their formula. The O content is calculated by the difference method for the former group of data while in the latter group is by direct analyses. Other variations may also contribute to a low correlation coefficient, such as diversity in organic substances as pointed out by Gauthier et al. (1987). The scope of humic substances used in the correlation analysis covered most types of humic materials reported in the literature.

The atomic H/C ratio has the best negative correlation with aromaticity for all three groups of data. Reduction in alkyl or O-alkyl moieties for aromatic bio-, and geopolymers should lead to lower atomic H/C ratios. In addition, high substitution for H by other atoms or structural moieties (rather than alkyl moiety) in the aromatic carbon may also lead to lower atomic H/C ratios. Catrous and Schnitzer (1987) pointed out that the carbon atoms in the aromatic rings are usually heavily substituted. In fact, the extent of these substitutions can be qualitatively or quantitatively investigated by various dipolar-dephasing ^{13}C CP/MAS NMR studies (Axelson, 1985; Wilson, 1987) or by combined ^{1}H-NMR and ^{13}C-NMR analyses. In addition, formation of a polynuclear aromatic structure may also lead to low H/C atomic ratios (Chapter III). This kind of structural change can also be evaluated with dipolar-dephasing ^{13}C CP/MAS NMR approach (Chapter III). However, the use of atomic H/C ratios is not feasible for samples with high carboxyl functional group content such as fulvic acids (Gauthier, 1987). The majority of organic substances presented in the pooled data for this study are HAs. Similarly, the atomic H/C ratio may show poor correlation with aromaticity for samples with high carbonyl functional group content. That is why a better correlation was obtained between the atomic H/C ratio and aromaticity (f_2 formula) since both carboxyl and carbonyl functional groups are excluded (Table 4-3). Although aromaticity has similar correlation coefficient values with either polarity or atomic (N+O)/O ratio, polarity is easier to calculate than the atomic ratio of (N+O)/C. We favor the use of the polarity variable because it has been successfully used to predict K_{OC} values in non-ionic organic sorption studies (Xing et al., 1994b). The aromaticity calculated as f_1 formula gives better correlation values with polarity or atomic (N+O)/C ratio than f_2 (Table 4-3). We favor the former because it gives a more logical estimate of aromaticity. The uncertainty as to how many carboxylic acids in the 170-190 ppm range are bound to aromatic or aliphatic moieties is the major reason for using the f_2 formula for aromaticity calculation (Schnitzer, 1991). This uncertainty should not lead to the exclusion of carboxylic C since it is not aromatic no matter what type of structure it is bound to. According to the data given by Breitmaier and Voelter (1987), possible overlap with quinone structure may occur in the carboxylic-C signal range. Thus there is a question as to whether to classify the quinone compounds as aromatic. Breitmaier and Voeiter (1987) did not place them with the aromatic compounds. They should not be considered as aromatic compounds since they do not have the continuous, planner, and conjugated π-bonds according to the criteria of Wade (1987).

CONCLUSION

Results presented in this chapter showed that the pedogenically modified HAs vary in their sorption of aromatic non-ionic pollutants. Thus a pedogenic link to HAs should be considered for environmental soil studies. Variations of HAs properties with soil depth are to some extent similar to soil and sediments differing in extent of geological diagenesis; the latter demonstrate a broader scale. The localized structural and compositional variations of HAs facilitate our understanding of interactions between organic pollutants and organic matter. Such structural change affects their interactions as sorbents for pollutants such as α-naphthol. The K_{OC} values increase linearly with aromaticity for organic geopolymers in soils and sediments. The structural features and compositional properties are strongly correlated and this provides alternative ways for calculating K_{OC} values. The H/C atomic ratio may serve as the possible alternative parameter for predicting K_{OC} for samples low in carboxyl and carbonyl contents. Improvement in currently linear prediction models for organic pollutants should be made to incorporate the structural (aromaticity) or compositional properties (polarity or atomic H/C ratio) of the organic geopolymers in soils or sediments in order to include the influence of the nature of organic geopolymers.

REFERENCE

Agriculture Canada Expert Committee on Soil Survey. 1987. The Canadian System of Soil Classification. 2nd ed., Agri. Can. Publ. 1646. Ottawa.

Axelson, D.E. 1985. Solid State Nuclear Magnetic Resonance of Fossil Fuels. Multiscience Publications Limited, Minister of Supply and Services Canada (M39-16/1985E). Canada.

Bollag, J.-M., Sjoblad, R.D., Czaplicki, E.J., Hoeppel, R.E. 1976. Transformations of 1-naphthol by the culture fitrate of *Rhizoctonia praticola*. Soil Biol. Biochem., 8:7-11.

Breitmaier, E. and Voelter, W. 1987. Carbon-13 NMR Spectroscopy: High-Resolution Methods and Applications in Organic Chemistry and Biochemistry. 3'rd, completely revised edition. VCH Verlagsgesellschaft. Weinheim, Germany.

Briggs, G.G. 1981. Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. J. Agric. Food Chem. 29:1050-1059.

Catroux, G. and Schnitzer, M. 1987. Chemical, spectroscopic and biological characteristics of the organic matter in particle size fractions separated from an Aquoll. Soil Sci. Soc. Am. J. 51:1200-1207.

Chiou, C. T., Peters, L.J., and Freed, V.H. 1979. A physical concept of soil-water equilibrium for non-ionic organic compounds. Science. 206:831-832.

Chiou, C.T., Porter, P.E. and Schmedding, D.W. 1983. Partition equilibra of non-ionic organic compounds between soil organic matter and water. Environ. Sci. Technol. 17:227-231.

Dixon, W.T. 1982. Spinning-sideband-free and spinning-sideband-only NMR spectra in spinning samples. J. Chem. Phys. 77(4):1800-1809.

Gauthier, T.D., Seitz, W.R., and Grant, C.L. 1987. Effects of structural and compositional variations of dissolved humic materials on pyrene K_{OC} values. Environ. Sci. Technol. 21:243-248.

Grathwohl, P., 1990. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: implication on Koc correlation. Eviron. Sci. Technol., 24:1687-1693.

Hassett, J.J., Banwart, W.L. Wood, S.G. and Means, J.C. 1981. Sorption of α-naphthol:implications concerning the limits of hydrophobic sorption. Soil Sci. Am. J. 45:38-41.

Malcolm, R.L 1990. Variations between humic substances isolated from soils, stream waters and groundwaters as revealed by ^{13}C-NMR spectroscopy. In Humic Substances in Soil and Crop Sciences: Selected readings. American Society of Agronomy and Soil Science Society of America Inc., Madison, WI, USA. pp. 13-35.

Malcolm, R. L. and MacCarthy, P. 1986. Limitations in the use of commercial humic acids in water and soil research. Environ. Sci. Technol. 20(9):904-911.

Means, J.C., Wood, S.G., Hassett, J.J. and Banwart, W.L. 1980. Sorption of polynuclear aromatic hydrocarbons by sediments and soils. Environ. Sci. Technol. 14:1524-1528.

Nordén, B. and Berg, B. 1990. A non-destructive method (solid state ^{13}C NMR) for determine organic chemical components of decomposing litter. Soil Biol. Biochem. 22:271-275.

Pawluk, S. and Bal, L. 1985. Chapter 4: Micromorphology of selected mollic epipedons, in L.A. Douglus and M.L. Thompson (ed.), Soil Micromorphology and Soil Classification. SSSA. Spec. Publ. 15 Madison. Wis. pp. 63-83.

Ricca, G. and Severini, F. 1993. Structural investigations of humic substances by FTIR, ^{13}C-NMR spectroscopy and comparison with maleic oligomer of known structure. Geoderma. 58:233-244.

Sanborn, P. and Pawluk, S. 1983. Process studies of a Chernozemic pedon, Alberta (Canada). Geoderma. 31:205-237

SAS Institute Inc., 1987. SAS/STAT guide for personal computers. version 6 ed., Cary, NC, USA.

Schnitzer, M. 1978. Humic substances: chemistry and reactions, in M. Schnitzer and S.U. Khan (ed.) Soil Organic Matter. Elsevier Scientific Publishing Company, Amsterdam. pp. 1-64.

Schnitzer, M. 1982. Organic matter characterization. in L.A. Page, R.H. Miller and D.R. Keeney (ed.), Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2'nd edition. American Society of Agronomy, Inc. and Soil Science Society of America, Inc. Publisher. Madison, Wis. pp.581-594

Schnitzer, M. 1991. Soil organic matter---the next 75 years. Soil Sci. 151 (1):41-58.

Schnitzer, M., Kodama, H., and Ripmeester, J.A. 1991. Determination of aromaticity of humic substances by x-ray diffraction analysis. Soil Sci. Soc. Am. J. 55:745-750.

Siemers, C.T. and Wadell, J.S. 1977. Humate deposits of the Manefee Formation (upper Cretaceous), northwestern New Mexico. Suppliment to New Geol. Soc. Guidebook. 28th Field Conf., San Juan Basin III.

Stevenson, F.J. 1982. Humus Chemistry, Genesis, Composition, Reactions. John Wiley & Sons, New York.

Sun, S and Boyd, S.A. 1991. Sorption of polychlorobiphenyl (PCP) congeners by residual PCP-oil phases in soils. J. Environ. Qual. 20: 557-571.

Wade, L.G. 1987. Organic Chemistry. Prentice-Hall, Inc., A division of Simon & Schuster. Englewood Cliffs, New Jersey, USA.

Wilson, M.A. 1991. Analysis of functional groups in soil by nuclear magnetic resonance spectroscopy. in K.A. Smith (ed), Soil Analysis: Modern Instrumental Techniques. 2'nd edition, Marcel Dekker Inc., New York. pp. 601-645.

Xing, B. 1994. Uptake of Organic Chemicals by Soils. Ph. D. thesis. Dept. of Soil Science, University of Alberta. Edmonton, Alberta. Canada.

Xing, B. and Dudas, M.J. 1992. Pedogenic properties of white clay soils of the Three River Plain, Heilongjing Province, P.R. China. Geoderma. 54:181-211.

Xing, B., McGill, W.B., Dudas, M.J., Hepler L.G., and Dobrogowska, C. 1993. Thermodynamic parameters for pentachlorophenol sorption on montmorillonite in aqueous suspensions. Chemosphere. 26:1311-1324.

Xing, B., McGill, W.B. and Dudas, M.J. 1994a. Sorption of α-naphthol onto organic sorbents varying in polarity and aromaticity. Chemosphere. 28(1):145-153.

Xing, B., McGill, W.B. and Dudas, M.J. 1994b. Cross-correlation of polarity curves to predict partition coefficients of non-ionic organic contaminants. Environ. Sci. Technol., 28:1929-1933.

Zachara, J.M., Felice, L.J., Riley, R.G., Harrison, F.L., Mallon, B., Wobber, F.J. 1984. The selection of organic chemicals for subsurface transport research. DOE/ER-0217. U.S. Dept. of Energy, Washington, D.C.

Chapter V
Synthesis

The main purpose of my dissertation research is to investigate pedogenesis of granular structure in relation to SOM, and to characterize SOM in the foregoing soils. Since the SOM associated with structural development also serves as a crucial factor in the determination of the behavior of non-ionic organic contaminants in soil, the effect of SOM on sorption of environmental contaminants was also assessed. Three research themes were proposed in Chapter I as follows:

1. Genesis of granular structures is related to soil clay mineralogy, cation and sesquioxides composition and is reflected in soil microfabrics. SOM is the primary factor that affects soil granular structure development. Complexation of mineral and organic substances is the major reason for aggregation. The complexation processes are mediated by frost action and soil fauna.
2. The properties of SOM reflect pedogenesis. Consequently, the distribution, structure and composition of SOM will vary with soil depth. SOM in organic layers will be different from those in mineral soil environments.
3. SOM is the primary soil component that reacts with non-ionic organic environmental contaminants. Pedogenically modified SOM vary in their capacity for sorption of environmental contaminants.

I. Syntheses and general conclusion

I1. On soil structure

The theme about genesis of granular structure was tested in Chapter II. The basic background information concerning the two soils was also presented in Chapter II. This arrangement presented a general understanding of the two soils in the early sections and facilitated discussion in the following chapters.

Results in Chapter II indicated that the two soils have similar clay assemblages; dominantly smectite and minor amounts of mica and kaolinite, typical of Alberta soils. Distribution of stable soil aggregates is largely in the 0.5 to 1.5 mm, and the size decreased gradually with soil depth. The stability of aggregates is high in both soils and change in stability generally follows the patterns for % organic C, HA and neutral sugar distribution in the sola of both soils. Macromorphological and micromorphological analyses indicate that the two soils are strongly structured and that the soil microfabrics generally comprise f-members and lack f-matrix in the upper sola. Presence of SOM in soil aggregates is reflected by the strong masking effect of colloidal humic substances in the aggregates and lack of plasma separation (silasepic plasma fabric) or with weak plasma separation (weak skeli-mosepic plasma fabric). Participation of biota in structural formation is reflected through abundant faecal pellets of various mesofauna and macrofauna. The thick organic horizons in the Malmo soil provide abundant food sources for soil fauna. Repeated, progressive ingestion of faunal faecal materials by following generations of the same faunal species and/or different soil fauna may form mull (Rusek, 1985). These progressive processes reflect the time factor involved in pedogenesis. Progressive cycling of faecal materials is probably one of the most common phenomena in pedogenesis, each cycle may reinforce the effect of soil structural development and horizon differentiation toward the steady state status within the specific ecosystem with which the soil is associated. Earthworms are considered to be the most important mull formers in soils (Kubiena, 1953; Russell, 1973; Rusek, 1985). The short history of their presence in Canadian soils is probably the reason for incomplete mull formation in western Canadian soils and may explain why the Ah humus type in these soils looks like a mull-like moder (Pawluk, 1985). The poor aeration and psuedogley in the Raven soil, according to Russell (1973), is not favorable for establishment of most soil fauna since they prefer a well aerated environment. This is probably why less faecal material was observed below the Sod layer in the Raven soil, even though the soil has a high % organic C content extending from the Ah to the AB horizons. The strong organo-clay complexation in the Ah horizons of the Raven and the Malmo soils suggest that complexation played a role in the aggregation of these two soils. The x-ray diffractograms showed that the complexation largely took place on the edges of smectite. This contradicts Duchaufour (1982) and Theng et al (1986, 1992) who suggested that interlayer complexation was largely responsible for the interactions between SOM and smectite. Early investigation on naturally-occurring organo-clay complexes in Alberta Chernozems (Dudas and Pawluk, 1969) showed complexation similar to that reported in Chapter II. Since typical steppe soils are approximately neutral in reaction, Chernozems do not meet the acidic conditions required for interlayer complexation to develop (Theng et al. 1986, 1992). It is of practical importance that the edge complexation observed in the current study can reduce rehydration of K-saturated and Ca-saturated clay minerals (Chapter II). This phenomenon should contribute to the stabilization of soil aggregates.

Soil is a dynamic natural body and a pedogenic study without the investigation of its dynamic properties would be insufficient. Lysimetry is well suited for the study of soil dynamic properties. Mckeague et al. (1986) suggested that cation composition of leachates is related to the dynamics of soil aggregation. The near neutral pH, and dominance of Ca in the leachate solution (Chapter II) are favorable for Ca saturation in the organo-clay complexes and stabilization of soil aggregates.

I2. On SOM

Participation of SOM in soil aggregation is evident from micromorphological and clay mineralogical observations reported in Chapter II. This prompted a detailed study of SOM as reported in Chapter III. Micromorphological evidence suggested it was mainly the colloidal humic substances that were involved in soil aggregation (Chapter II). Thus this study focused on the HA fraction. This fraction is considered to be a major participant in soil aggregation and stabilization of Chernozemic soils (Kononova, 1966; Stevenson, 1982). The study of HAs throughout the entire sola was also used to test the second research theme as outlined in Chapter I, ie. that the properties of SOM reflect pedogenesis, such that SOM in the organic layers differs from that in mineral horizons. This study was considered to be important for our understanding of the SOM transformation in the soils under investigation. Detailed published studies of SOM are usually restricted to the upper organic and Ah horizons and very few studies extended to the entire sola. Results in Chapter III indicated the distribution pattern of HAs is related to vegetation. The structure of HAs in organic layers varies from the mineral horizons. There is an increase in aromaticity of HAs with soil depth and the greatest increase was observed in the transitional Ah1 horizon under forest-grass transition vegetation. This observation was clearly evident in both sola where modern analytical techniques were applied. The reason for the increased aromaticity is mainly attributed to increased polycondensation. Extension of this study to simple aromatic compounds (SACs) in HA digest was designed to probe the molecular information related to such structural variations. It is at this level that some of the genetic links of HAs to lignin and other neoformed SACs can be resolved. The results for SACs in HA digest showed a very important trend, ie. as aromaticity increased with soil depth, more p-hydroxyl substituted phenols were found and such phenols became the predominant components of SACs in HAs digest in mineral horizons. This trend parallels the change in ratio of p-hydroxyl substituted phenols to cinnamyl phenols in the sola. A value of 1.5 for the ratio of p-hydroxyl phenols to vanillyl phenols appears to separate HAs in the organic layers from those in mineral soil environment. Within the p-hydroxyl phenols, a shift from p-hydroxybenzaldehyde to p-hydroxybenzoic acid, and then to protocatechuic acid with soil depth was also evident.

These data indicated that the HAs in the organic layers are plant-related, while those in mineral soils are microbe-related. Thus the polyphenol theory may likely be applicable in HA genesis. Based on evidence shown in this study, the modification to the polyphenol theory as suggested by Varadachari and Ghosh (1984) as discussed in Chapter I, is thus necessary so that the slightly modified lignin monomers would be included. Results in Chapter III also suggest possible participation of abiotic catalysis in HA synthesis because of the sharp increase in HA aromaticity in the Ah1 horizon of the Malmo soil. Results reported in Chapter III tend to support the second theme as defined in Chapter I from various levels of resolution. Increased aromaticity for HAs appears to parallel a decrease in alkyl-C (lipids) and polysaccharides-C content. These structural moieties of HAs have widely flexible, stretchable configurations and are more effective stabilizing agents for soil aggregates as compared to the relative rigid aromatic structural moiety of HAs. Thus an increase in aromaticity of HAs with depth is likely one of the reasons for decreased aggregate stability. The XRD behavior of clay minerals and organo-clay complexes in Chapter II also support this possibility.

I3. On sorption of pollutants by SOM

Chapter IV is a natural extension of Chapter III to include environmental issues. It is also a test of the third research theme as outlined in Chapter I. The results tend to support the research theme in that pedogenically modified SOM differs in its capacity for sorption of environmental contaminants. This is indicated by the linear relationship between the C normalized sorption coefficient (Koc) and aromaticity of HAs. To extend the observation to a broader scale, unextracted soil and sediment samples were also used. Except for the Black shale sample (the nature of its organic geopolymers needs further pursue), most samples indicated a linear relationship of Koc and aromaticity in the organic fraction of the sample. The Koc values obtained were much smaller than those calculated from the published prediction equations (Chiou et al. 1979; Means et al. 1980). An examination of polarity, atomic (O+N)/C, and atomic H/C ratios indicated these parameters are negatively correlated with aromaticity. The atomic H/C ratio gives the strongest negative relationship with aromaticity. This information showed additional mechanisms by which Koc could be linked to properties of organic components in the sorption media. Since the HAs were extracted from the sola of the soils, variations in Koc values with soil depth pointed out the short range interactions between SOM and non-ionic organic contaminants. Such information is generally missing in the literature related to environmental soil studies.

II. Advancement in knowledge

Soil is an anisotropic natural body. The soil anisotropy is best reflected by the diversity of soil microfabrics. Results reported in Chapter II have amplified our knowledge on soil anisotropy.

In the sola of both soils, soil structure ranged from massive (C), subangular blocky and granular (B), to granular and crumbs (Ah of both soils). This is associated with a change in dominant pedogenic forces from physical (C horizons) to biological/biochemical forces (upper Ah, Sod layer of Raven soil, and Ah of Malmo soil). In the Raven soil, the microfabric is essentially matriporphyric groundmass in the Ckg horizon. The granular structure (shot structure) in the AB and Ah horizons has typical metafragmic microfabric and heterogeneous plasma composition. The granular structure of biological origin in the upper section of the Raven and Malmo soils generally has humigranic to mullgranic/mullgranoidic microfabrics. These microfabric differences are beyond the resolution of field morphological description and demonstrated the diversity in the origin of granular structures. Influence of freeze/thaw on structural development has been noted in some western Canadian soils (Pawluk, 1985, 1988). However, such strong impact on aggregation in the Humic Gleysol as observed in Chapter II, has never been reported. The Orthic Humic Gleysol in many aspects is morphologically similar to the Gleyed Black Chernozem as defined in the Canadian System of Soil Classification (Agriculture Canada Expert Committee on Soil Survey, 1987). This research addressed their microfabric and genetic differences.

Findings in this research contributed to advancement in knowledge on SOM in the following aspects:

1. It is clearly established that the structure (aromaticity) and composition of HAs is a function of soil depth. Such change is associated with vegetation under which the soils developed. This change is likely the result of polycondensation and possible ways to distinguish polycondensation and polymerization is also proposed (Chapter III).

2. The HAs in organic layers and in the soil mineral environment are different in many aspects. New parameters such as ratios of (p-hydroxyl phenols)/(vanillyl phenols), (p-hydroxyl phenol)/(cinnamyl phenol), or percentage of p-hydroxyl phenols based on the sum of all phenols can be used to differentiate these two types of HAs. The ratio of (p-hydroxyl phenol)/(cinnamyl phenol) is the most sensitive.

3. Associated with the change in HA structure, the acid/aldehyde ratio in HA digest also changed. There is a general increase in this ratio for all phenol groups and

within the p-hydroxyl phenol group, the change shifts from p-hydroxylbenzoic aldehyde, to p-hydroxylbenzoic acid, then to protocatechuic acid.

The findings in structural and compositional variations of HAs in soil implies that the two currently existing models (Schulten et al. 1991; Stevenson, 1982) may be part of a continuum of HAs structure. The results suggest that there is a need to establish the pedogenic basis for SOM formation. The effects of pedogenic modification to SOM demonstrated a clear impact on sorption of environmental contaminants (Chapter IV). Information in this area of the study contributes to our understanding of SOM-contaminants interaction during the early stage of contamination events in terrestrial environment.

III. Future research needs

Soil structure is a fundamental property of soils. Knowledge of soil structural formation, ie. soil aggregation/disaggregation is a major part of pedological studies. Within the pedon, it is the type of aggregation/disaggregation that often determines type and extent of soil horizon formation that forms the morphological basis for soil classification. The type and degree of soil aggregation/disaggregation results from several soil forming processes which include SOM-mineral interaction, biota participation, physical processes such as wet/dry, and freeze/thaw, and aging. These factors may affect soil aggregation at various levels of resolution (Tisdal and Oades, 1982). Hierarchy in soil aggregation is particularly evident for soils strongly influenced by SOM as compared to soils cemented by sesquioxide (Oades, 1993). No matter what level of resolution is considered, the SOM-mineral interaction is still the crucial factor in the stabilization of soil aggregates in temperate soils. Therefore, it is not surprising that Duchaufour (1982) considered SOM as the motive force in pedogenesis. It integrates the basic soil processes (weathering, humification, and movement of soil materials) by controlling the formation of specific organo-mineral complexes on which all soil properties depend. It is also the SOM that controls the fate of non-ionic organic pollutants by sorption of pollutants.

As related to this study, the following work needs to be pursued further in future:

1. The chemical nature of the aggregating agents should be further evaluated. This can be done by using various empirical extraction methods, such as sodium chlorite for electrostatic attraction, sodium periodate for polysaccharides bonding,

sodium pyrophosphate for bonding by humic substances and organic-bonded Ca, Fe and Al (Greenland, 1965a,b; Edwards and Bremner, 1967; Churchman and Tate, 1986; Shipitalo and Protz, 1989).

2. In situ characterization of the chemical nature of aggregating agents can be conducted using ultra-thin sections and modern staining techniques (Foster, 1994) for SOM, and EDX and micro x-ray analyses (Arocena et al. 1994) for mineral cementing agents. Such results would permit more precise interpretation and visualization of soil structural development.

3. Other SOM fractions, such as humin-clay interaction, FA-HA transformation on the surface of soil mineral components and its effect on soil aggregation should also be investigated since this may contribute to soil organo-mineral complexation.

4. Methods should also be developed to compare the contribution of biological/biochemical and abiotic catalyzed synthesis of humic substances. The importance of this work appears to override its complexity. Much remains unknown about this subject.

With progress in modern technology, it appears an area of 'organic pedology' is emerging. This is evident in a few fronts: (i) in-situ study of SOM with heavy metal staining in soil ultra-thin sections (Foster, 1994; Chenul et al. 1994); (ii) the study of aromatic precursors and SOM transformation (Ertel and Hedges, 1984; Wang et al. 1986; Kögel-Knabler et al. 1988, 1990; Low, 1992; Samir et al. 1994); (iii) structural study of SOM with various ^{13}C NMR techniques (Wilson, 1987; Kögel-Knabler et al, 1988, 1990, 1992) and PI-MS methods (Hempfling and Schulten, 1991; Schulten and Leinweber, 1991). While the complexity of SOM remains a major challenge to pedologists and the need to improve instrumental techniques is apparent, progress in understanding of soil aggregation and SOM can still be achieved by focusing on the genetic link during pedogenesis and the structure-based investigation at different levels of resolution.

Reference

Agriculture Canada Expert Committee on Soil Survey, 1987. The Canadian System of Soil Classification. 2nd edition, Agri. Can. Publ. 1646, Ottawa.

Arocena, J.M., Pawluk, S. and Dudas, M.J. 1994. Iron oxides in iron-rich nodules of sandy soils from Alberta (Canada). in A.J. Ringrose-Voase and G.S. Humphreys (ed). Soil Micromorphology: Studies in management and genesis. Proc. IX. Int. Working Meeting on Soil Micromorphology. Townsville, Australia. p83-97.

Chenul, C., Guerif, J. and Jaunet, A.M. 1994. Polymer bridging: a mechanism of clay and soil structure stabilization by polysaccharides. in J.E. Etchevers et al. (ed.) Symposia of the 15th World Congress of Soil Science. Vol. 3A. International Society of Soil Science. Acapulco, Mexico.

Chiou, C. T., Peters, L.J., and Freed, V.H. 1979. A physical concept of soil-water equilibrium for nonionic organic compounds. Science. 206:831-832.

Churchman, G.J. and Tate, K.R. 1986. Aggregation of clay in six New Zealand soil types as measured by disaggregation procedures. Geoderma. 37:207-220.

Dudas, M.J. and Pawluk, S. 1969. Naturally-occurring clay-organo complexes in Alberta Chernozems. Geoderma. 3:5-17.

Duchaufour, P. 1982. Pedology: pedogenesis and classification. English version translated by (T.R. Paton). George Allen & Unwin. London.

Ertel, J.R. and Hedges, J.I. 1984. The lignin component of humic substances: distribution among soils and sedimentary humic fulvic and base-insoluble fractions. Geochimica et Cosmochimica Acta, 48: 2065-2074.

Edwards, A.P. and Bremner, J.M. 1967. Microaggregates in soils. J. Soil Sci. 18:67-73.

Foster, R.C. 1994. The ultramicromorphology of soil biota in situ in natural soils: a review. in A.J. Ringrose-Voase and G.S. Humphreys (ed). Soil Micromorphology: Studies in management and genesis. Proc. IX. Int. Working Meeting on Soil Micromorphology. Townsville, Australia. p381-393.

Greenland, D.J. 1965a. Interaction between clays and organic compounds in soils. Part I. Mechanisms of interaction between clays and defined organic compounds. Soil and Fert. 28:415-425.

Greenland, D.J. 1965b. Interaction between clays and organic compounds in soils. Part II. Adsorption of soil organic compounds and its effect on soil properties. Soil and Fert. 28:521-532.

Hempfling, R. and Schulten, H.-R., 1991. Pyrolysis-(gas chromatography/) mass spectrometry of agricultural soils and their humic fractions. Z. Pflanzenernahr. Bodenk., 154: 425-430.

Kögel-Knabner, I., Zech, W. and Hatcher, P.G. 1988. Chemical composition of the organic matter in forest soils: the humus layer. Z. Pflanzenernähr. Bodenk., 151.331-340.

Kögel-Knabner, I., Hatcher, P.G. and Zech, W. 1990. Decomposition and humification processes in forest soils: implications from structural characterization of forest soil organic matter. Trans. 14th Int. Congress Soil Sci., Kyoto, Vol. 5, pp. 218-223

Kögel-Knabner, I., de Leeuw, J.W. and Hatcher, P.G. 1992. Nature and distribution of alkyl carbon in forest soil profiles: implications for the origin and humification of aliphatic biomacromolecules. Sci. Total Environ., 117/118:175-185.

Kononova. M.M. 1966. Soil Organic Matter: its nature, its role in soil formation and soil fertility. 2nd English edition. Pergamon Press, Oxford.

Kubiena, W.L. 1953. The Soils of Europe. Thomas Murby and Co., London.

Lowe, L.E. 1992. Bound phenolic acids in terrestrial humic acids. Sci. Total Environ., 117/118: 187-195.

McKeague, J.A., Cheshire, M.V. andreux, F. and Berthelin, J. 1986. Organo-mineral complexes in relation to pedogenesis. in in P.M. Hung and M. Schnitzer (ed.), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., pp. 549-592..

Means, J.C., Wood, S.G., Hassett, J.J. and Banwart, W.L. 1980. Sorption of polynuclear aromatic hydrocarbons by sediments and soils. Enviro. Sci. Technol., 14:1524-1528.

Oades, J.M. 1993. The role of biology in the formation, stabilization and degradation of soil structure. Geoderma. 377-400.

Pawluk, S. 1985. Soil micromorphology and soil fauna: problems and importance. Quaestiones Entomologicae. 21:473-496.

Pawluk, S. 1988. Freeze-thaw effects on granular structure reorganization of soil materials of varying texture and moisture content. Can. J. Soil Sci., 68:485-494.

Rusek, J. 1985. Soil microstructures---contributions on specific soil organisms. Quaestiones Entomologicae. 21:497-514.

Russell, E. W. 1973. Soil Condition and Plant Growth. 10 edition. Longman, London.

Samir, P., Bollag, J.-M. and Huang, P.M. 1994. Role of abiotic and biotic catalysts in the transformation of phenolic compounds through oxidative coupling reactions. Soil Biol. Biochem. 26(7):813-820.

Schulten, H.-R. and Leinweber, P. 1991. Influence of long-term fertilization with farmyard manure on soil organic matter: characteristics of particle-size fractions. Biol. Fertil. Soil. 12:81-88.

Schulten, H.-R., Plage, B. and Schnitzer, M. 1991. A chemical structure for humic substances. Naturwissenschaften, 78: 311-312.

Shipitalo, M.J. and Protz, R. 1989. Chemistry and micromorphology of aggregation in earthworm casts. Geoderma, 45:357-374.

Stevenson, F.J. 1982. Humus Chemistry, Genesis, Composition, Reactions. John Wiley & Sons, New Yowk.

Theng, B.K.G., Churchman, G.J., and Newman, R.H. 1986. The occurrence of interlayer clay-organic complexes in two New Zealand soils. Soil Sci. 145 (5):262-266.

Theng, B.K.G., Tate, K.R., and Becher-Heidmann, P. 1992. Towards establishing the age, location, and identity of the inert soil organic matter of a spodosol. Z. Pflanznernahr. Bodenk., 155:181-184.

Tisdal, J.M. and Oades, J.M. 1982. Organic matter and water stable aggregates in soils. J. Soil Sci., 33:141-163.

Varadachari, C. and Ghosh, K. 1984. On humus formation. Plant Soil. 77:305-313.

Wang, T.S.C., Hung, P.M., Chou, C.H. and Chen, J.H. 1986. The role of soil minerals in the abiotic polymerization of phenolic compounds and formation of the humic substances, in P.M. Hung and M. Schnitzer (ed.), Interactions of Soil Minerals with Natural Organics and Microbes, SSSA spec. publ. No. 17, SSSA Inc., Madison, Wis., pp. 251-281.

Wilson, M.A. 1987. NMR Techniques and Application in Geochemistry and Soil Chemistry. Pergamom Press, Oxford.

Appendix I

A. Micromorphological description for the Raven soil

Horizons Description

Sod layer

Microstructure: Mixed granular to crumb, largely unaccommodated, random, ultrafine and very fine, smooth and undulating granules with strong bimodal distribution. Large granules of 0.5-1.0 mm size occur randomly and make up about 60% of the fabric. These granules are made up of either fine mineral or well homogenized mull matrix and are widely and randomly spaced. The inter-aggregate space is filled dominantly with finer (35-60 μ) humigranic units. There are undecomposed, melanized plant fragments at the surface 1.5-2 cm.

Voids: Compound packing voids and strongly interconnected vughs of variable size dominate the inter-aggregate space. Micro and macro, smooth channels of random orientation and distribution are also common. The intra-aggregate voids are dominantly rounded or subrounded, oblate, smooth and ultrafine (40-100 μ) vughs. There are very few macro chambers.

Pedological features: Many of the larger aggregates are made up of single and welded faecal pellets most likely largely those of earthworms. Many of the pellets are well homogenized and strongly resemble a mull. Their size ranges up to 1200 μ although there are many around 600 μ in size and have a distinct oval shape. Several large aggrotubles (up to 3 mm) occur randomly, likely of similar origin although discrete humic particles are still discernible internally. Some of the larger aggregates are oblate sedimentary nodules that may be lower B horizon material brought up by soil fauna. The units have a dense porphyroskeliic related distribution and the plasma has a skel-in mosepic to masepic fabric. Typic orthic nodules with diffuse boundaries commonly impregnate sedimentary nodules.

Ah1 horizon

Microstructure: upper 0-1 cm. same as Sod layer.

Below 1 cm: very dominantly moderate and strong subangular blocky. The majority of units range in size from 600-1200 μ, equant to lobate, subrounded to subangular and with undulating walls. Ultrafine (35-70 μ) discrete units of humic material are also a common occurrence but less frequent than the Sod layer.

Voids: The dominant inter-aggregate voids are craze planes showing weak horizontal orientation. A few intra-aggregate voids are dominantly micro, prolate and acicular, subrounded, undulating vughs.

Pedological features: Orthic iron nodules are present as in the Sod layer. Aggrotubules are present with loose continuous infillings of aggregate of about 600 μ size. There are large features with a few up to 6 mm in diameter and appear to contain earthworm faecal pellets. The smaller aggrotubules of about [illegible]00 μ size were likely formed by earthworms and now have loose infillings of collembola faecal pellets. The ultrafine discrete humigranic units are likely collembola faecal pellets and decreases in abundance with depth in lower Ah1.

Ab2 horizon

Microstructure: Much of the microstructure is similar to the Ah1 horizon. However towards the bottom of the layer and within a vertical zone occupying about one third of the section the aggregates become more rounded with interconnected vughs becoming dominant. Thus the microstructure intergrades to a strong very fine and fine granular. Some of the granules are well rounded and show a *concentric pattern* to both voids and skeleton grains. The matrix materials in the centre of granules are yellower and look denser while the matrix materials close to the boundary of granules are usually darker. The intra-aggregate voids are largely vesicles and metavughs.

Pedological features: Aggrotubules are much less frequent. Faecal materials are further reduced compared to Ah1.

Micromorphological description for the Raven soil (continued)

Horizons	Description

AB horizon

Microstructure: The microstructure is very similar to the Ah2 in upper section but with a higher percentage of granular units. About 30% is strong ultrafine subangular blocky that integrades to a strong ultrafine and very fine granular. The subangular blocky units are smooth to undulating and prolate to oblate in shape. The granular units are equant to oblate and smooth to undulating in shape. In the lower section of the horizon, granular units are very dominant. The units have a dense porphyroskeli related distribution and skel-mosepic plasma that is strongly masked by humic materials. The ultrafine humigranic units are less common compared to upper horizons. Similar to the above horizon, some granules have yellower matrix in the centre and darker matrix materials along the boundary of the units.

Voids: Granular units are separated by interconnected vughs. Subangular blocky units are separated by micro craze planes. There are very few channels similar to those found in the Ah horizon. The intra-aggregate voids are similar to those in the Ah2 horizon.

Pedological features: Aggrotubules and orthic iron oxide nodules are present and closely resemble those in the upper horizon. The large units loosely filling the aggrotubules appear to be earthworm faecal pellets.

Bg horizon

Microstructure: The B horizon strongly interfingers with the AB horizon. The B horizon has a spongy microstrucutre that strongly intergrades in some zones to weak and moderate ultrafine and very fine prolate to equant granules. The aggregates have a dense porphyroskelic related distribution and skel-bi-ma-mosepic, and in a few cases, omnisepic plasma fabric. The concentric pattern of aggregation similar to the Ah2 and AB horizons are also common.

Voids: Inter-aggregate voids are very dominantly smooth to undulating, moderately interconnected mesovughs. A few craze planes also interconnected vughs. Few channels of variable size are present. Intra-aggregate micro to meso vughs and vesicles are very few.

Pedological features: A few random, dense, discrete equant and lobate earthworm faecal pellets occur throughout. These are comprised of mull humus. A few orthic iron oxide nodules of variable size are also present.

Ckg horizon

Microstructure: Spongy microstructure in the upper section grading to weak granular in 40% of the zone and closely resembles the Bg horizon. The middle and lower section grades towards a very vughy microstructure. Weakly formed aggregates are discernible throughout. All materials have a dense porphyric related distribution and crystic plasma fabric.

Voids: Dominantly micro and meso, oblate to acicular, subrounded to subangular, smooth to undulating vughs. Near the transition to the B horizon, frequently short fine and medium micro craze planes interconnect the vughs resulting in the formation of weak granular units associated with the spongy microstructure. In the lower section, planar voids are less frequent resulting in a very vughy microstructure. A few rounded to subrounded smooth meso channels are also present.

Pedological features: Very few aggrotubules of macro size are evident. A few earthworm faecal pellets are imbedded in the groundmass. They are up to 800 μ in diameter, contain mull matrix and more skeletal grains than the adjoining groundmass. These could also be aggregates that moved down from the Ah horizon through planar voids that developed during drying. The alignment of these zones with those from the B horizon supports this possibility.

B. Micromorphological description for the Malmo soil

Horizons Description

LF layer

Microstructure: The upper half of the LF layer has complex microstructure largely dominated by leaf fragments (1.9 to 8.4 mm long) and very few melanized stems (1.1 to 2.8 mm diameter). About 5% of the area are occupied by largely irregular, undulating to smooth discrete humigranic units that are 45 to 70 μ in size. Very few, equate to oblate, rough to undulating granules (500 to 1400 μ) are minor components. The lower half of the LF layer also has complex structure with granular and platy components, dominated by meso to macro (420 to 620 μ), equate to prolate, smooth granules and macro to mega (700 to 5100 μ), cylindrical or platy components that resemble mull and have skeli-mosepic plasma fabric.

Voids: Dominantly simple packing voids. Series of undulating to smooth, subparrallel horizontal planes are frequent components of voids bellow leaf vessels and the platy aggregate components.

Pedological feature: Collembola faecal pellets of irregular shape and various sizes (25 to 100 μ) occur in close association with plant fragments. Very few micro to meso (20 to 80 μ), equant to oval, smooth oribatid mite faecal pellets are noted in the cavities of woody tissues. Very few, rough, faecal pellets (50-90 μ) of beetle larvae are also present in the cavities of the woody fragments. Both have isotropic plasma fabrics. Very few, equant, faecal pellets of dipterous larvae are present. The faecal pellets of millepede (580-650 μ) are largely located in the lower LF layer and are responsible for the platy and granular mull components. Faecal pellets of dipterous larvae are major source for the granules of 500-1400 μ in upper LF layer.

FH layer

Microstructure is similar to the LF layer. The size of plant fragments is reduced (dominantly 1000 to 2000 μ). There is an increase in granules of humic substances that account for about 15% of the area. These granules have isotropic plasma fabric and are dominantly in sizes ranging from 50 to 70 μ.

Voids form are similar to LF layer but there is an increase of compound packing voids due to increase in proportion of the granules of humic substances.

Pedological feature: Collembola faecal pellets are dominant. Very few, meso to macro (450 to 1300 μ), equant to oblate, undulating to smooth, faecal pellets of dipterous larvae are present as random clusters.

H layer

Microstructure: Fine spongy and vughy microstructure, dominantly composed of fused fine aggregates of 20 to 70 μ, likely aged single or disintegrated faecal pellets of mesofauna. The fused aggregates have isotropic plasma fabric. These organic aggregates account for about 20 to 30% of the area and are darker relative to those in LF and FH layers. The plant fragments are reduced in both frequency (about 5% of the area) and size (dominantly 560 to 1700 μ). They are also darker as compared to upper organic layers.

Voids: Common, rough craze planes up to 2 cm separate the organic substances into partially accommodating, loose patches. Within these loose organic patches, irregular compound packing voids are the major void components. Vughs are frequent in minor zones occupied by tightly fused organic aggregates.

Pedological features: Dominantly fused or disintegrated mesofaunal faecal pellets of 20 to 70 μ throughout the section. The exact origin of the faecal materials is difficult to estimate due to aging and disintegration. Very few, fine macro (500 to 700 μ), oblate, undulating dipterous larvae faecal pellets are also present.

Micromorphological description for the Malmo soil (continued)

Horizons **Description**

Ah1 horizon

Microstructure: Mixed crumb to granular, largely comprised of unaccommodating, equant to oblate, undulating crumbs of 1200 to 4000 μ and granules dominantly 340 to 700 μ. Both the crumbs and granules in upper Ah1 have heterogeneous plasma fabrics as separated patches of either moderate skeli-mosepic or isotropic components. They account for about 10% to 20% of the area. The random, irregular, fine granules are dominantly about 50 μ and are discrete humic substances, likely aged collembola/enchytraeid faecal pellets or their fragments, and account for about 10% to 20% of the area and are darker than those in organic horizons. Very few random plant fragments of variable size (largely 840 t[illegible]) are present. Largely platy aggregates of mull composition with weak skeli-mosepic plasm[illegible] the lower Ah1 horizon. Few, meso (50 to 300 μ), equant, prolate or irregular, yellow[illegible]entary nodules of skeli-mosepic or skeli-omnisepic plasma fabric are present in close a[illegible]

Voids: M[illegible] undulating craze planes and compound packing voids dominate the inter-aggregate spa[illegible]ter-aggregate space for the platy structure zone are short, subparallel, rough to undulating horizontal ortho-planes of 40 to 70 μ thickness. Irregular, ortho-vughs, or interconnected vughs dominate the intra-aggregate space.

Pedological features: Well homogenized aggrotubules (4.4 to 6.2 mm long) occur frequently, likely comprised of earthworm faecal pellets. Dark mesofaunal faecal pellets of 35 to 70 μ diameter (likely aged collembola/enchytraeid faecal pellets) are easily discernible in these aggrotubules. These mesofaunal faecal materials are throughout the section.

Ah2 horizon

Microstructure: Granular to spongy complex structure, largely similar to Ah1 but showing an increase of granules of 560-2000 μ with soil depth. There is a reduction of humigranic units as compared to the upper horizons. Towards the lower section, large granules (1000-1500 μ) of mull nature and small granules (20-90 μ) of humic substances form a bimodal distribution. The large granules have silasepic to insepic plasma fabrics with strong masking by humic substances and are likely earthworm faecal pellets. The small granules are isotropic and are likely collembola/enchytraeid faecal pellets. Very few, subangular to granular, undulating sedimentary nodules in various sizes (280 to 850 μ) are present. These sedimentary nodules have omnisepic plasma fabric. Very few plant fragments are also present.

Voids: A few mega, undulating craze planes (140 to 2500 μ thick) extend throughout the section. Few, macro to mega (1 to 9 mm), nearly spherical, oval or planar, smooth chambers occur connected with the craze planes or randomly in the matrix. All the chambers are loosely filled with some discrete or fused collembola faecal pellets (20 to 80 μ diameters, largely isotropic organic substance or occasionally mull) and some plant fragments. Very few root channels are also present. Compound packing voids and interconnected vughs generally dominate the inter-aggregate space. Vughs and interconnected vughs dominate the intra-aggregate space.

Pedological features: Collembola faecal pellets of variable size (28 to 70 μ), color (brown, black) and composition (isotropic organic or weak mosepic mull) are dominant pedological features. They are generally distributed as four patterns: (a) as randomly distributed in the inter-aggregate space; (b) as recognizable constituents in earthworm faecal pellets; (c) as discrete or fused faecal pellets in the chambers or root channels; and (d) as loose infillings in the aggrotubules. Few aggrotubules, likely of earthworm casts, 2.5 to 8.5 mm long, are present throughout the thin section. Earthworm faecal pellets (672 to 2800 μ) of mull composition occur throughout the section.

Micromorphological description for the Malmo soil (continued)

Horizons Description

Ah3 horizon

Microstructure: The upper part is dominated by platy structure. The aggregates are dominantly 1400 to 2250 μ long and 280 to 350 μ thick, and are largely mull of silasepic plasma fabric with strong masking by humic substances. Some slightly elongated granules are similar in sizes to the mull units in the Ah2 horizon (likely earthworm casts), and are rearranged into platy aggregates. One segment of the thin section is dominated by an 'obliquely banded' structure. Fine oblique planes separate the acicular to acicular-planar peds into oblique bands of similar sizes to platy aggregates in the upper portion. The microstructure grades to a spongy microstructure similar to Ah2. The platy aggregates and granules have the same plasma fabric as the large granules in the Ah2 horizon. Towards the lower zone of the horizon, the microstructure grades to a spongy to vughy intergrade. Very few, sedimentary nodules similar to those in the upper Ah section, appear randomly throughout.

Voids: Series of subparellel ortho-planes, and micro to macro (100 to 3100 μ long) irregular orthovughs are the dominant inter-aggregate voids in the platy structure area. Irregular orthovughs of similar size and oblique planes are the dominant inter-aggregate voids in the 'obliquely banded' area. Micro, rounded and subrounded or irregular, orthovughs are dominant intra-aggregate voids in both banded areas. In the remainder of the section, interconnected meso to macro (200 to 1700 μ) irregular orthovughs dominate inter-aggregate voids. Very few short irregular orthoplanes are minor void components. The intra-aggregate space is dominated by meso (100 to 200 μ), irregular orthovughs. In the lower section of spongy to vughy microstructure, meso to macro (dominantly 180 to 600 μ), irregular orthovughs dominate. The intra-aggregate space is dominantly irregular meso (about 100 to 200 μ) orthovughs.

Pedological features: Earthworm faecal pellets of 670 to 850 μ appear throughout. They have silasepic to insepic plasma fabrics. Few, aggrotubules of variable length (800 to 4000 μ), filled largely with earthworm casts of plasma fabrics similar to that of the earthworm faecal pellets are present. Very few, meso to macro (100 to 650 μ), equant to oblate or prolate, reddish-brown, ortho-Fe nodules are present.

Appendix II

Glossary of Terms

plasma: the fine, clay-sized constituents of soils, both organic and inorganic, crystalline and amorphous, capable of being moved, reorganized, or concentrated [illegible] the processes of soil formation.

skeleton grains: the simple crystals of mineral and individual organic fragments larger than clay-size, which are relatively stable and not readily translocated, concentrated, or reorganized by processes of soil formation.

Void terms

simple packing voids: voids due to random packing of single grains, usually irregular orthovoids approximately equant to prolate in overall dimensions as measured between adjoining grains, and strongly interconnected.

compound packing voids: due to packing of aggregates, which do not accommodate each other, they are unoriented, have random distribution, usually equant to prolate, irregular orthovoids or smoothed metavoids, strongly interconnected.

plane: simple voids that are planar according to the ratios of their principal axes, mostly formed by contraction of the soil materials.

vugh: relatively large voids other than packing voids, usually irregular in shape, and not normally interconnected with other voids of comparable size, but rather appear as discrete entities, usually unoriented and randomly distributed.

vesicle: isolated voids different from vughs in that their walls consist of regular, smooth, simple curves.

chamber: chamber differ from vughs in that their walls are regular and smoothed, they are usually interconnected through channels and have a characteristic shape, such as subspherical or arched.

microstructure: all aspects of soil structure that are revealed when a soil material is examined at a magnification of 5x or greater. It is not concerned with the internal fabric of the solid part of soil mass. Following microstructure types were defined as:

vughy structure: No separated aggregates. Mass broken up by scattered but not interconnected vughs and occasional channels and chambers.

spongy structure: Few, if any, fully separated aggregates. Much pore space; voids often strongly interconnected.

granular structure: Granules are separated by compound packing voids and do not accommodate each other.

subangular blocky structure: aggregates are separated by short planar voids on all or most sides. Vughs and small channels often occur within the aggregates which may contain groups of partially welded crumbs. Aggregate faces largely accommodate each other.

platy structure: Stacks of aggregates generally horizontally elongated and separated by planar voids. Interior voids are variable.

Complex structure: consists of mixture of two or more microstructure types. Combined terms can be used to name the complex microstructure, such as spongy-vughy microstructure.

soil fabric: the physical constitution of a soil material as expressed by the spatial arrangement of the solid particles and associated voids, including distribution patterns, orientation patterns and packing of soil materials.

related distribution pattern: the distribution pattern of like individuals with regard to the distribution of groups of individuals of a different kind.

granic: unaccommodated, typically loosely packed, discrete units without coatings on, or bridges between them.

granoidic: forms like those in granic fabric but the units are not discrete and are fused at their contacts.

fragmic: relatively densely packed, accommodated discrete units with out coating on, or bridges between units.

fragmoidic: forms like those in fragmic fabric but units are not discrete, and are fused at their contacts.

conglomeric: a compound fabric arrangement in which the primary units are discrete granic f-members (coarser units) randomly set into a groundmass of finer f-matrix materials (usually less than 2 m in size) about which the associated voids delineate a secondary fabric of elliptical to rounded framework members such as fragmic or granoidic.

orbiculic: a sorted distribution fabric where the skeleton grains or f-members are distributed in a circular or ellipsoidal arrangement.

Common prefixes:

meta-: to be smoothed, rounded.

phyto-:, of plant origin.

humi-: of humified organic substance.

mull-: of intimately mixed organic-mineral complexes, ie, of mull.

matri-: of mineral matrix materials.

Plasma fabric: refer to the organization and nature of constituents of the plasma, including extinction patterns of various kinds and arrangements (distribution and orientation patterns) of plasma grains.

isotic: isotropic or opaque, no plasma aggregates or separation.

crystic: recognizable birefringent (or isotropic) crystals, no plasma aggregation or separation.

silasepic: flecked extinction, plasma aggregates present but difficult to differentiate from silt grains, no plasma separation.

mosepic: flecked and weakly striated extinction, plasma aggregates recognizable, plasma separation is indicated as numerous patches.

vosepic: plasma separation is associated with voids.

skelsepic: plasma separation is associated with skeleton grains.

masepic: usually striated, plasma separation as elongated zones within soil material.

omnisepic: dominantly striated, complicated strongly striated plasma separation.

pedological feature: recognizable units within a soil material which are distinguishable from the associated material for any reasons, such as origin, difference in concentration of some fraction of the plasma, or differences in arrangement of the constituents (fabric).

faecal pellets: individual entities of faunal excrements.

cast: welded faecal pellets.

pedotubule: a pedological feature consisting of soil material and having a tubular external form, either single tubes or branching systems of tubes; its external boundaries are relatively sharp.

aggrotubule: a type of pedotubule composed of skeleton grains and plasma which occur essentially as recognizable aggregates within which there is no directional arrangement with regard to the external form.

nodule: a three-dimensional unit within soil matrix of the soil material, usually approximately prolate to equant in shape. It is recognized as a unit because of a greater concentration of some constituent, with an undifferentiated internal fabric.

form PE: a measurement for sphericity in image analysis, where:

$$\text{'form PE'}=(4\pi \times \text{area})/(\text{perimeter})^2.$$

For circle, 'form PE'=1; for ellipse and irregular structures, 'form PE'<1.

dipolar dephasing: a NMR technique for study ^{13}C-H dipolar interaction experienced by different carbon types by varying the time for which the decoupler is turned off. It can be used to eliminate resonances from the spectrum from carbons experiencing strong dipolar interactions.

sideband: chemical shift anisotropy due to the rigidity of solid samples.

REFERENCE

Brewer, R. 1976. Fabric and Mineral Analysis of Soils. Robert E. Krieger Publishing Company, Huntington, N.Y.

Brewer, R. and Pawluk, S. 1975. Investigations of some soils developed in hummocks of the Canadian sub-arctic and southern-arctic regions. I. Morphology and micromorphology. Can. J. Soil Sci. 55:301-309.

Brewer, R. and Sleeman, J.R. 1988. Soil Structure and Fabric. CSIRO Australia, Adelaide.

Bullock, P., Fedoroff, N., Jongerius, A., Stoops, G., Tursina, T. and Babel, U. 1985. Handbook For Soil Thin Section Description. Waine Research Publications. Wolverhampton, England.

Fox, C.A. 1979. The soil micromorphology and genesis of the Turbic Cryosols from the MacKenzie River valley and Yukon Coastal plain. Ph. D. thesis. The University of Guelph. Guelph, Ontario.

Wilson, M.A. 1987. NMR Techniques and Application in Geochemistry and Soil Chemistry. Pergamom Press, Oxford.