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SORPTION OF ORGANIC COMPOUNDS TO SOIL AND GEOLOGIC SAMPLES THAT VARY IN MINERAL CONTENT AND DIAGENIC PROPERTIES

By

MYRNA JOYCE SALLOUM ©

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 SCIENCE

DEPARTMENT OF RENEWABLE RESOURCES

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Myrna J Sall

Permanent Address:
2513-106 A Street
Edmonton, Alberta
T6J 4S1 CANADA

Date: September 10, 1999

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 SORPTION OF ORGANIC COMPOUNDS TO SOIL AND GEOLOGIC SAMPLES THAT VARY IN MINERAL CONTENT AND DIAGENIC PROPERTIES by MYRNA JOYCE SALLOUM in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Soil Science.

M. J. Dudas

M. J. Dudas (co-supervisor)

W. B. McGill (co-supervisor)

C. M. Preston

C. M. Preston (external examiner)

Salim Abboud

S. A. Abboud

M. R. Gray

Y Feng

Y. S. Feng

Date: September 9, 1999

To those who believed in me

ABSTRACT

This dissertation examines the sorbent properties that govern sorption of surfactants and 1-naphthol in soil and geologic samples. Triton X-100 and Dowfax 8390 were equilibrated with several soil and geologic materials. Dowfax 8390 (anionic) did not sorb to any of the samples. Alternatively, Triton X-100 (nonionic) sorbed to all the samples. X-ray diffraction (XRD) revealed that the ethoxylate tail of Triton X-100 intercalates with montmorillonite. The Black Shale sample, which is predominately organic, also sorbed a large amount of Triton X-100. This suggests that additional mechanisms beyond the clay-ethoxylate tail interaction are occurring. Therefore, neither clay mineral nor organic matter (OM) content alone are suitable for predicting nonionic surfactant sorption.

Elemental analysis, cross polarization magic angle spinning ^{13}C nuclear magnetic resonance (CPMAS ^{13}C NMR) spectroscopy, and 1-naphthol sorption were used to describe the organic carbon character of several soil and geologic materials. The 1-naphthol sorption data poorly correlated with the H/C atomic ratio and carbon character as measured by CPMAS ^{13}C NMR. An examination of the humic acid and humin fractions revealed that the humin samples had larger 1-naphthol K_{oc} values than the whole samples. The 1-naphthol K_{oc} values for the humic acids differed from that of the whole samples. The correlation between the CPMAS ^{13}C NMR data and 1-naphthol sorption for the humic acids improved, however, there were still discrepancies between the H/C and 1-naphthol sorption data.

These data suggest that the orientation or molecular geometry of OM contributes to 1-naphthol sorption. A mass balance analysis confirmed that the sum of the fractions sorbed more 1-naphthol than the whole, reaffirming the OM molecular geometry hypothesis and further supporting that accessible organic carbon should be examined rather than total organic carbon. Manipulation of mineral-bound OM molecular geometry with different electrolyte cations and ionic strength values was attempted. The 1-naphthol K_{oc} values did not differ with solution conditions suggesting that the molecular geometry of mineral-bound OM can not be altered using solution conditions. Nonetheless, it appears that OM molecular geometry governs sorption reactions, however, it is unclear what factors or combination of factors determine the molecular geometry of mineral-bound OM.

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GLOSSARY OF TERMS AND ABBREVIATIONS

b	Langmuir model parameter (mg/g) that describes the sorption maximum
BCFF	Black Chernozemic fine fraction
C_o	Initial concentration (mg/L) of the sorbate in batch equilibration studies
C_e	Concentration (mg/L) of the sorbate after reaching an apparent equilibrium with the sorbent. C_e is also plotted on the x axis of a sorption isotherm.
CMC	Critical micelle concentration (mol/L)
ΔCMC	The difference between effective CMC and CMC, expressed in mol/L
CPMAS ^{13}C NMR	Cross polarization magic angle spinning ^{13}C nuclear magnetic resonance
ΔK_{oc}	Expressed in units of mL/g, ΔK_{oc} is the difference between the amount of 1-naphthol sorbed versus that of the source soil or geologic sample
DD	Dipolar dephasing: a delay is inserted into the NMR routine that allows the signal from non protonated carbons to relax (with the exception of methyl carbons) prior to data collection
effective CMC	Critical micelle concentration (mol/L) of soil-surfactant systems
FA	Fulvic acid
f_{oc}	The fraction of organic carbon in the sorbent
HA	Humic acid
Humin	The solid material remaining after exhaustive extraction with 0.1M NaOH
K_d	Sorption coefficient (mL/g) that describes the distribution of the sorbate between the soil and water phases

$K_{Freundlich}$	Freundlich model parameter (mL/g or L/g). $K_d = K_{Freundlich}$ when n=1
$K_{Langmuir}$	Langmuir model parameter (L/g or mL/g) related to binding energy
K_{Linear}	Slope of the linear sorption isotherm. K_{Linear} also equals K_d
K_{oc}	Organic carbon normalized sorption coefficient (mL/g)
K_{ow}	Octanol-water partition coefficient
Molecular Geometry	The physical organization and distribution of organic matter in solution or on the surface of a clay mineral
n	Freundlich model parameter (unitless)
normalized ΔCMC	ΔCMC normalized for soil to solution ratio (mole surfactant/g sorbent)
Sorption	Generic description for the uptake of a compound or group of compounds from the liquid to the solid phase
Sorbent	The soil or geologic sample (solid phase) that participates in sorption
Sorbate	The compound that is taken up by the solid phase
x/m	Expressed as mg/g, x/m is the y axis of a sorption isotherm and is the mass of solute sorbed per mass of sorbent

CHAPTER 1

GENERAL INTRODUCTION

The presence and persistence of organic chemicals in the environment is of continual concern. The risk associated with contamination of pristine areas through movement within the environment, and into the food chain, has caused current practices to be modified to avoid further contamination of our environment. Unfortunately accidental and non accidental environmental contamination occur on a daily basis world wide, despite the growing awareness of the associated hazards with organic contaminants. A large majority of the persistant compounds in the environment are nonionic and nonvolatile. The main fate of these contaminants is binding or sorption to soil/geologic materials (Weber and Miller, 1989). Contaminant-soil binding is so resilient, that the removal or desorption of organic chemicals is slow and one may question if it at all occurs.

Current remediation strategies are prohibitively expensive and often leave the soil in a disrupted or destroyed state. These remedial efforts, whether biological, chemical, or physical in nature have been hindered due to the strong association of organic compounds with the soil. The mechanism of organic chemical uptake by soils is still a subject of debate despite the attempts of past and current research programs (Beck *et al.* 1993; Luthy *et al.*, 1997). One is still faced, however, with the removal of contaminants from the soil to satisfy current standards, and alleviate the perceived risk associated with the presence and persistence of contaminants.

It has been suggested that "facilitators", such as surface active agents (surfactants), be used to enhance the desorption process. Synthetic surfactant use in efforts to improve contaminant removal from soils is gaining in popularity with scientists and engineers engaged in environment related areas, however, their use is considered to be in the experimental stages (Peters *et al.*, 1992). This is undoubtedly due to the variation in soils, contaminants, and the surfactants used since, as of 1992, there were over 13 000 synthetic surfactants available (Currie *et al.*, 1992). Consequently, there is a need for systematic study of soils varying in sorption properties, and of surfactants varying in properties as well as the controlling interactions with soil colloids and organic contaminants.

This introductory chapter is organized to provide the reader with the background material required for the subsequent chapters. The next section reviews surfactants and the pertinent information regarding their use in soil remedial programs. Following this, is a brief review of contaminant and soil interactions. Each individual chapter provides a more detailed introduction dealing with the specific issues studied within that chapter. The main thesis objectives follows the section on contaminant and soil interactions.

SURFACTANTS

Surfactant molecules are amphiphilic, containing both a polar and non-polar component. Traditionally, surfactants have been used as: detergents, drug carriers, food additives, in organic synthesis, and in froth and flotation petroleum recovery techniques (Atkins, 1990). Due to their ability to enhance the apparent aqueous concentration of organic contaminants, their popularity in soil and groundwater remediation is increasing (West and Harwell, 1992). Detergents are surface active, however, they may solubilize as well as disperse some materials. Furthermore, detergents are surfactants but not all surfactants behave as detergents. Each class of surfactant contains different types of molecular constituents but all concentrate at the interfacial region between phases such as the air-water or the oil-water interface (Attwood and Florence, 1983; West and Harwell, 1992). When a surfactant molecule is dissolved in water, it disrupts the structure of liquid water by distorting the hydrogen bonds between water molecules (Shinoda and Hutchinson, 1962; Attwood and Florence, 1983). The entropy decreases, thereby making the dissolution of the surfactant molecule a thermodynamically unfavorable process. This causes surfactant monomers to accumulate mainly at the surface of liquid water with the non-polar groups oriented away from the water. This accumulation results in a lowering of the surface tension. As the number of monomers in solution increases, the subsequent solvent disruption also increases until a critical point of monomer concentration is reached. At this critical concentration, the hydrophobic groups cluster together to reduce the demands of the surfactant monomers on the water molecules. These clusters are referred to as micelles. Micelles are thermodynamically stable and reversible (Shinoda and Hutchinson, 1962) as their formation minimizes the free energy of the system (Rosen, 1989). The concentration at which micelles form is known as the critical micelle concentration (CMC). Below this concentration, surfactant molecules exist as monomers and above the CMC, they exist as both micelles and monomers as depicted in Figure 1-1 (Rosen, 1989; Attwood and Florence, 1983). After the CMC is reached, the number of micelles in solution increases with surfactant concentration. A common approach to determine the CMC is by measuring the surface tension over a range of surfactant concentrations. Once the CMC is reached, subsequent surfactant addition does not result in a further lowering of the surface tension (Rosen, 1989). The CMC of a surfactant is affected by: surfactant molecular structure, the temperature of the solution and the presence of electrolytes, organic compounds, or a second phase (Rosen, 1989) such as soil colloids. Typical CMC values in aqueous systems range from 0.10 to 10 mM (West and Harwell, 1992).

Based on the charge of the polar head group, surfactants are categorized into four major classes: anionic, cationic, nonionic and zwitterionic (amphoteric). Surfactants that contain more than one polar or non-polar constituent are referred to as twin-head, dimeric or co-surfactants (Rouse *et al.* 1993; Currie *et al.* 1992). Nonionic and anionic surfactant classes are candidates with the greatest potential for aiding in contaminant desorption from soils because cationic and zwitterionic surfactants have a greater tendency to react with soil minerals. Cationic surfactants have been reported to promote sorption and retard contaminant transport by altering soil surfaces (Wagner *et al.*, 1994). Some anionic surfactants may, however, precipitate in soils with high ionic strengths or adsorb to oxides or positively charged sites of soil organic matter in soils with low pH values. Secondly, most anionic surfactants are prepared in a sodium salt form and the addition of large quantities to soils may disperse soil aggregates. Regardless of class, all surfactants interact with the soil solid phase in one manner or another.

In aqueous solution, surfactants form stable micelles with a hydrophobic core. Micelles behave as "pseudophases" that organic contaminants partition into (Shinoda and Hutchinson, 1962; Attwood and Florence, 1983; Rosen, 1989). Surfactant-enhanced solubilization results in the formation of a thermodynamically stable, isotropic solution (Attwood and Florence, 1983) containing micelles that can accommodate a characteristic amount of solute (Rosen, 1989). There are many ways that a solute can interact with micelles. For instance, solutes can become sequestered within: the hydrophobic core (micelle interior), the palisade region between the tails and the polar head group, and the surfactant head groups on the micelle surface (Currie *et al.*, 1992). Organic contaminants, however, primarily associate with the hydrophobic core of a surfactant micelle (Kile and Chiou, 1989; Edwards *et al.*, 1991). The amount of solute that can be partitioned into the micelle, often referred to as the solubilizate, is a function of surfactant structure, aggregate number, micelle geometry, ionic strength, temperature, aqueous chemistry, solubilizate chemistry, and solubilizate size (Attwood and Florence, 1983).

Surfactant molecules are subject to uptake by soil colloids. Therefore, when using surfactants in soil, one must determine the amount of surfactant that is sorbed, then add a compensating amount of surfactant to reach the CMC, such that solubilization can occur. Surfactants can interact with soil components in many ways. These mechanisms include: the adsorption of surfactants on specific mineral and organic matter sites, the formation of a surfactant monolayer at the organic/aqueous interface, and partitioning into the bulk organic matter of the soil (Edwards *et al.*, 1992). Even though the types of interactions are known, a method to predict the quantity of surfactant uptake by soil does not exist, nor does any correlation with the amount of particular soil constituents. Hence, it is currently difficult to assess the economic feasibility of using this method on a large scale.

CONTAMINANT AND SOIL INTERACTIONS

As mentioned in the introductory paragraphs, the fundamental understanding of contaminant-soil interactions is required to improve current remedial methods and to determine the feasibility of surfactant facilitated desorption. For instance, if the contaminant is trapped or sequestered in the organic matter matrix, then surfactant soil washing or flushing, or any other remedial attempt may be unsuccessful. Furthermore, soil-bound contaminants are often unavailable for microbial degradation (Rijnaarts *et al.*, 1990; Scow and Hutson, 1992; Weissenfels *et al.*, 1992;). Bioavailability limitations also encourage the resolution of the fundamental mechanisms involved.

Early studies that examined the fate of applied chemicals to soil environments observed that organic contaminant sorption was proportional to the amount of organic carbon in the soil (Lambert *et al.*, 1965; Hance, 1965; Doherty and Warren, 1969). Subsequent work established that there was a linear relationship between organic matter content and the amount of contaminant that was sorbed by the soil (Karickhoff *et al.*, 1979) and it is currently accepted that sorption of organic contaminants is proportional to the total organic carbon content of the soil or geologic sample (Luthy *et al.*, 1997). This realization has led to the widespread use of organic carbon normalized sorption coefficients (K_{oc}) when making comparisons amongst soil and geologic samples. It is suggested that with the use of empirical equations, the value of K_{oc} can be predicted from the value of the contaminants' octanol-water partition coefficient (K_{ow}: Chiou, 1989) despite reports this method is not widely applicable (Mingelgrin and Gerstl, 1983; Garbarini and Lion, 1986).

More recently, it has been reported that the sorbent characteristics, such as organic matter quality, are important indicators of contaminant sorption (Grathwohl, 1990; Xing *et al.*, 1994; Ganaye *et al.*, 1997). Grathwohl (1990) reported that sorption of chloroaliphatic chemicals was inversely proportional to the amount of oxygen in the sorbent and suggested that the degree of weathering, in cooperation with the amount of organic matter, dictated the amount of sorption. Xing *et al.* (1994) reported that contaminant sorption increased as did the aromatic carbon content of the sorbent. This result was corroborated by Chen *et al.* (1996) and Ganaye *et al.* (1997). Consequently, sorbent characteristics have been given more attention than in past studies.

MAIN THESIS OBJECTIVES

The limited knowledge of surfactant sorption behavior in soil/geologic environments prohibits widespread application , especially at the pilot or field scale. Furthermore, the uncertainty surrounding the sorption of organic contaminants confounds the application of surfactants to contaminated areas. To improve the understanding of sorption processes of surfactants and contaminants in soil systems, I chose an independent set of pristine soil/geologic samples that included samples from: two surface soils, one subsurface soil, two parent materials and one peat sample. A weathered, contaminated surface soil was included in the sorption studies described in Chapters 3 and 4, and pure clay minerals were used for detailed studies in Chapter 2. The surfactants included Dowfax 8390 (anionic) and Triton X-100 (nonionic) and the contaminant probe was 1-naphthol. The main objectives of my dissertation are to:

1) Examine the sorption of two surfactants with a variety of soil and geologic samples that varied in mineralogical and chemical characteristics.

2) Characterize the organic matter of a variety of soil and geologic samples and correlate this to the 1-naphthol sorption data.

3) Assess the use of organic matter fractions as surrogates for whole soil and geologic samples in contaminant sorption studies.

4) Examine 1-naphthol sorption to mineral-bound organic matter under various aqueous solution conditions.

This dissertation contains six chapters. Chapter 2 reports on the sorption of surfactants to soil/geologic samples that vary in mineralogical and organic matter content. Chapter 3 examines the relationships from Xing *et al.* (1994) and Chen *et al.* (1996) that suggest that sorption behavior for a given soil/geologic sample can be predicted from cross polarization magic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance (NMR) spectra. Chapter 4 is a continuation of the experiment presented in Chapter 3 but with organic matter fractions (humic acid and humin) as sorbents. This chapter also evaluates the use of organic matter fractions as surrogates for whole samples. Chapter 5, examines 1-naphthol sorption to two different types of organo-mineral complexes, that were isolated from soil/geologic samples. The sorption experiments were performed under varying solution (electrolyte cation and ionic strength) conditions. This chapter also compares the amount of 1-naphthol K_{oc} of the whole sample versus that calculated from the carbon distribution and K_{oc} value of each sample. The last chapter (6) summarizes my findings, acknowledges the advances made via this research, and suggests areas of future research.

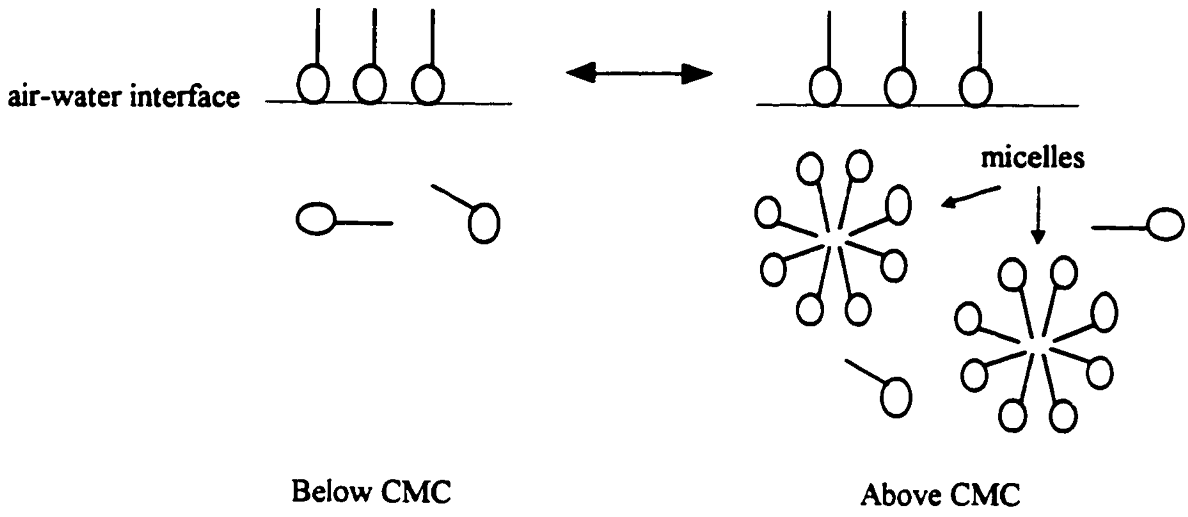

Figure 1-1: An illustration of surfactant monomers below and above the CMC

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CHAPTER 2[1]

SURFACTANT SORPTION TO SOIL AND GEOLOGIC SAMPLES WITH VARYING MINERALOGICAL AND CHEMICAL PROPERTIES

INTRODUCTION

The practices of previous and current generations have left behind a legacy of contaminated lands. The use of surfactants in the remediation of contaminated areas is advocated as a promising technology, however, its use may be restricted due to surfactant uptake by soil colloids. The majority of surfactant research has focused on: surfactant solubilization of contaminants, surfactant enhanced mobilization, surfactant facilitated desorption and bioremediation. Only a limited number of recent literature accounts examine surfactant sorption to natural colloids (Liu *et al.*, 1991; Liu *et al.*, 1992; Brownawell *et al.*, 1997; Kibbey and Hayes, 1997; Urano *et al.*, 1984; Cano and Dorn, 1996a; 1996b). The abundance of surfactant types and differences among soil colloids makes it difficult to study the surfactant-sorbent interaction on a fundamental level, however, it is the loss of surfactant to environmental surfaces that increases the amount of surfactant required for the remedial process to be successful. The economic implications alone warrant further understanding of surfactant sorption processes.

The critical micelle concentration (CMC) that compensates for surfactant uptake by natural colloids is known as the "effective CMC" and varies with soil/surfactant type as well as the soil to solution ratio (Liu *et al.*, 1991; Liu *et al.*, 1992). The effective CMC increases with the quantity of surfactant sorbed to the soil. Despite recent efforts, the quantity of surfactant sorption can not be predicted based on sorbent attributes. Urano *et al.* (1984) and Liu *et al.* (1992) observed that sorption of nonionic surfactants was proportional to the content of organic matter in the sorbent. Other reports suggest that uptake of nonionic surfactants is related more to mineral content than organic matter

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[1] A version of this chapter has been submitted for publication in Environ. Toxicol. Chem.
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(Brownawell *et al.*, 1997; Cano and Dorn, 1996a; 1996b). Alternatively, anionic surfactants have been observed to be less reactive than nonionic surfactants towards sediment samples (Rouse *et al.*, 1993).

I investigated the use of sorbent properties to predict surfactant uptake. The main objectives were to: 1) examine the sorptive behavior of two different surfactants to a variety of soil and geologic samples, 2) determine the effective CMC for a variety of samples, and 3) correlate the effective CMC with mineralogical and/or chemical characteristics of the sorbent. Surfactants were selected from two different classes (nonionic and anionic) and have been reported to enhance the aqueous solubility of hydrophobic organic contaminants (Edwards *et al.*, 1991; Rouse *et al.*, 1993).

MATERIALS AND METHODS

Collection and handling of samples

Samples were chosen to include a wide range of characteristics. I included three soil samples: two Chernozemic A horizons, Solonetzic B horizon; two geologic parent materials and two pure clay minerals. The Black Chernozemic sample (A horizon - Malmo soil series) was collected from the Ellerslie Research Station located south of Edmonton, Alberta. The Brown Chernozemic sample (A horizon - Chin soil series) was obtained near Lethbridge, Alberta. Both of these soil samples are high in native organic matter. The third soil sample, a Black Solonetz (B horizon - Duagh soil series), was acquired just north-east of Edmonton, Alberta. All soil samples were developed on glacial till and/or lacustrine material and contain smectite clays. The two geologic samples included a weathered, Cretaceous age, black Shale, sampled along the banks of Blackmud Creek, located south of Edmonton, Alberta and an aeolian Sand collected near Bruderhiem, Alberta. The soil and geologic samples were air dried and passed through a 2 mm sieve. The clay standards, Ca-saturated montmorillonite (STx-1) and kaolinite (KGa-1b) were purchased from the Source Clay Minerals Repository in Columbia, Missouri. All samples were ground to pass a 106 μm sieve prior to sorption experiments.

Measurement of sorbent properties

Total carbon was measured by high temperature (900°C) combustion (Leco Furnace) followed by infra-red quantification of the evolved CO_2. Inorganic carbon was determined by acidifying the sample, collecting the evolved CO_2 in a KOH trap, and quantifying the amount of inorganic carbon by back titration with dilute acid (Bundy and Bremner, 1972). Organic carbon was calculated by difference. Cation exchange capacity (CEC) was measured as outlined by Mckeague (1978). Sand, silt, and clay fractions were isolated by sonification and sedimentation (de Kimpe, 1993).

Surfactant Solutions

Triton X-100 was purchased from ICN Biomedicals in Aurora, Ohio. Dowfax 8390 was provided by Dow Chemical Company in Midland, Michigan. The Dowfax 8390 sample was received at a concentration of 35% by weight. Both surfactants were used as received. Surfactant solutions were prepared by dilution with a 0.01 M K_2SO_4 solution (pH adjusted to 6.5) that contained 10^{-4} M $HgCl_2$ to inhibit microbial degradation. Surfactant solutions were stored at 4°C when not being used in sorption experiments.

Sorption Experiments

The sorbent was placed in a 50 mL PYREX® glass centrifuge tube at a soil to solution ratio that would result in 20-80% of surfactant loss from solution, consequently, the soil to solution ratio varied from 1:40 to 1:400. Sorbent mass was determined on an oven-dry basis. Five glass beads (6mm in diameter) were then added to the test tube followed by the addition of 45 mL of surfactant solution. The tubes were sealed with PTFE lined screw caps and allowed to equilibrate at room temperature on a rotating mixer (20 revolutions/minute) for approximately 48 hours (preliminary tests indicated that apparent equilibrium was reached well before this time). After the 48 hour time period, the test tubes were removed from the mixer and allowed to settle overnight. The samples were then centrifuged for 30 minutes at 1750 x g. The supernatant was removed and stored at 4°C in glass vials until further analysis.

Surface Tension Measurements

Surface tension measurements were performed using a semi-automatic Fisher Scientific Surface Tensiomat®. The apparent surface tension of each sample was measured in triplicate. The platinum-iridium ring was rinsed with deionized water for each replicate measurement. Between samples, it was rinsed with deionized water, followed by acetone and then passed through a flame until it was orange-red in colour. A correction factor that considered ring geometry and temperature was calculated with an equation provided by the manufacturer and applied to obtain surface tension values. The CMC and effective CMC were taken to be the inflection point of a curve of surface tension versus the log of surfactant concentration (Liu *et al.*, 1991). To facilitate the comparison among the sorbents, I have used ΔCMC, defined as:

$$\Delta CMC = effective\ \ CMC - CMC \tag{2-1}$$

Quantification of Triton X-100

The release of dissolved organic carbon from some of the samples prevented the use of direct ultraviolet spectroscopy to measure the quantity of Triton X-100 in solution. Therefore, a modified version of the cobalt thiocyanate active substance (CTAS) method was used (Valoras and Letey, 1968; Boyer *et al.*, 1977; Inaba, 1987; Dubey *et al.*, 1995). This method is based on the principle of phase transfer. Ethoxylated surfactants form a stable complex with the ammonium cobalt thiocyanate salt to form the CTAS (Warner *et al.*, 1979). In the absence of ethoxylated surfactants, the salt remains in the aqueous phase, alternatively, the presence of surfactant results in the formation of the CTAS which is soluble in the organic phase. Therefore, the amount of CTAS in the organic phase is directly proportional to the amount of surfactant in the sample. The CTAS method used in this study entailed the addition of 30 mL of surfactant solution (high concentrations were diluted prior to this step), 30 mL of the cobalt thiocyanate reagent (2.6 M of ammonium thiocyanate and 0.10 M of cobalt (II) nitrate hexahydrate) and 5 mL of dichloromethane into a 250 mL separatory funnel. The mixture was shaken for approximately one minute, then 30 mL of a saturated sodium chloride solution was added and the layers were allowed to separate for approximately 10 minutes. The dichloromethane layer was removed and the absorbance measured at 320 nm on a Unicam SP1800 ultraviolet spectrometer. For samples that did not release dissolved organic carbon, both the CTAS and direct UV method were used and no difference was observed between the results from each method (data not shown).

Quantification of Dowfax 8390

A Waters 510 High performance liquid chromatograph equipped with a Waters 481 ultraviolet detector was used for Dowfax 8390 quantification. A flow rate of 1.8 mL/min, a mobile phase of 50% HPLC grade acetonitrile (Fisher Scientific) and a 150 x 4.6 mm Supelcosil™ C18 reverse phase column (Sigma-Aldrich Canada) were used. Dowfax 8390 was measured at 254 nm and quantified using the total peak areas with respect to that of external standards.

Removal of Soil Organic Matter

In one experiment, the soil organic matter was removed from a sub-sample of the Black Chernozemic soil sample. This was done by repeated additions of concentrated hydrogen peroxide in combination with gentle heating. Once foaming ceased, the sample was gently heated to dryness, washed with deionized water, and centrifuged. Rinsing was repeated two more times after which the sample was air dried and ground to pass a 106 µm sieve.

X-Ray Diffraction

Ca-saturated montmorillonite was reacted with Triton X-100 at below CMC (0.1 mM), or above CMC (4 mM). A treatment with no Triton X-100, and only 0.01 M K_2SO_4 served as a control. The experiment continued as outlined in the surfactant sorption methodology. After centrifugation, the supernatant was removed and the sorbent was analyzed by x-ray diffraction (XRD) to determine the distance or d-spacing between adjacent clay minerals. Oriented specimens of the samples were analyzed at 0% relative humidity on a Philips diffractometer (Model 1710, Philips Electronics Ltd., Scarborough, Ont) equipped with a LiF curved crystal monochromator using CoKα radiation generated at 50kV and 25 mA. Step sizes of 0.05° 2θ and an accumulation time of 2 seconds $step^{-1}$ were used for data acquisition.

Model Fitting and Statistical Tests

The isotherms for Triton X-100 sorption to the soil and geologic samples vary in shape, therefore, two isotherm models were used because the variation in shape would not be satisfied by one model alone. The first model applied to the data was the linear form ($x/m = K_{Linear}\, C_e$) where: x/m represents the quantity of solute sorbed per mass sorbent (mg/g), C_e is the equilibrium concentration (mg/L) and K_{Linear} is a constant related to sorbate affinity for the sorbent (L/g). The Langmuir model was the second model applied to the data ($x/m = K_{Langmuir}\, b\, C_e / (1 + K_{Langmuir}\, C_e)$) where: x/m and C_e are the same as the linear model, $K_{Langmuir}$ is a constant related to binding energy (L/mg), and b represents the maximum in sorption to the solid (mg/g). Linear and Langmuir isotherm curve fitting was performed using Origin™ version 4.1 at $p \leq 0.05$.

The fit of the linear versus Langmuir model was tested by calculating the F statistic from the difference of the residual sum of squares between the models divided by the residual mean square for the non linear model (Robinson, 1985). The calculated F values were compared to tabular F values at $p \leq 0.001$ with 1 and n-p degrees of freedom, where n is the number of observations and p is the number of parameters in the more complex model. If the calculated F value is less than the tabulated F value, use of the more complex model (Langmuir) is not justified by the data (Robinson, 1985).

RESULTS

Sorbent and Surfactant Properties

The soil and geologic sorbents exhibit varying carbon (1.63% to 51.23%) and clay contents (2% to 70%). Although the clay content varies, the mineralogical compositions of the clay fractions are similar among these samples (Table 2-1). The CMC for Dowfax 8390 was four-fold higher than that of Triton X-100 (Table 2-2).

Dowfax 8390 Effective CMC and ΔCMC

The effective CMC was determined from the inflection point of the surface tension-log surfactant concentration curve. For the Black Chernozemic sample, there was no difference between the CMC and effective CMC. However, the surfactant surface tension after reacting with soil became constant at a lower value than the surfactant in the absence of soil (Figure 2-1). This may be attributed to the production of dissolved organic carbon in these samples as the presence of electrolytes, and/or low molecular weight organic compounds may alter the observed surface tension value (Liu *et al.*, 1992; Gunde *et al.*, 1992). These measurements did not detect a change in the CMC for Dowfax 8390 after sorption to soil or geologic samples. An effective CMC was not detected with all other sorbents. Hence, for Dowfax 8390, the effective CMC = CMC and the ΔCMC = 0 for all samples used in this study.

Triton X-100 Effective CMC and ΔCMC

The ΔCMC for Triton X-100 was positive after equilibration with the sorbents. Figure 2-2 displays the typical displacement of the CMC in the presence of soil material. In the studies reported here, the sorbent to solution ratios vary for each sorbent-surfactant reaction. Liu *et al.* (1992) reported that the value of the effective CMC was dependent on the sorbent to water ratio. To compare the ΔCMC data among samples properly, the values were normalized to soil mass by dividing the ΔCMC by sorbent mass and multiplying the volume of surfactant used to yield mole of surfactant sorbed/g sorbent (mol surf/g sorbent). The resulting mol surf/g sorbent value is independent of the soil to solution ratio used in the batch equilibration procedure. These values are displayed in Table 2-3. The mol surf/g sorbent value is lowest for kaolinite and highest for montmorillonite. The Solonetz and Shale samples also sorbed appreciable amounts of Triton X-100. There appears to be a relationship between the sorbent clay content and mineralogy with the mol surf/g sorbent value. Furthermore, the mol surf/g sorbent values of the Black, Brown, and Solonetz samples do not support a correlation with organic carbon.

Sorption Isotherms

The uptake of Dowfax 8390 was not detected by any of the sorbents used in this study. This data corroborates the results from other work in our laboratory with contaminated soil samples, and a study by Rouse *et al.* (1993). Alternatively, Triton X-100 uptake was observed with all the sorbents. The isotherms for Triton X-100 vary in shape and the linear isotherm r^2 values range considerably among sorbents (Table 2-4). The samples with organic matter contents greater than 1% (Black, Brown, Shale, and Solonetz) have linear isotherms with similar r^2 values (between 0.84 and 0.88). Alternatively, the samples containing little or no organic carbon (Sand, Kaolinite, Montmorillonite) have linear isotherms with lower r^2 values (0.64, 0.75, and 0.48 respectively). The difference in F values from the model discrimination test indicates that the sorption isotherm data are best described using the Langmuir model (Table 2-4). The difference in F values is considerably larger for those sorbents containing low or no organic matter. In a subsequent experiment, the organic matter from the Black Chernozemic soil sample was removed to examine the role of organic matter in Triton X-100 sorption (Figure 2-3). Both the mol surf/g sorbent value and isotherm non linearity increased from that of the original sample (Tables 2-3 and 2-4). Isotherm non linearity increases in the absence of organic matter. Furthermore, the difference in F values from the model discrimination test is more than three times greater for the Black after organic matter removal.

X-Ray Diffraction of Triton X-100 and Montmorillonite

The x-ray diffractograms of 3 different treatments are depicted in Figure 2-4. Pattern A is of the control (montmorillonite reacted with 0.01M K_2SO_4) and reveals a d-spacing of 1.01 nm, as is expected for a 2:1 clay mineral in the absence of water (Brindley, 1984). The peak in pattern B is diffuse and broader than that observed in pattern A but still has an average d-spacing of 1.01 nm. Such a broad peak suggests incomplete intercalation, with some minerals contracted and some minerals remaining partially expanded (MacEwan and Wilson, 1984).

Large applications of surfactant to montmorillonite (Pattern C) yielded a d-spacing of 1.43 nm whereas the control sample yielded a sharp peak at 1.01 nm. If the surfactant was being sorbed into the interlayer space of the mineral, then the increase in d-spacing would be in proportion to the size of the surfactant. The thickness of the ethoxylate group is equal to the sum of: 1 C-C bond and 2 C-H bonds. The O-H bond is shorter than the other two bonds, thus the maximum thickness of the molecule will be determined from the C-C and C-H bonds. Using bond lengths from Streitwieser and Heathcock (1985), the thickness is: $d = (0.154 \text{ nm} + 2\,(0.11 \text{ nm})) = 0.374 \text{ nm}$. Based on the molecular size of the ethoxylate tail and the mineral structure of montmorillonite, the resulting d-spacing should be 1.384 nm. The theoretical value is in good agreement with the observed value of 1.43 nm.

DISCUSSION

The behavior of Dowfax 8390 and Triton X-100 with several soil and geologic samples were observed to be different. These differences are attributed to surfactant charge. Dowfax 8390 is dianionic, therefore, it should be electrostatically repelled by soil constituents and not sorb as much as other surfactants, particularly those from the nonionic class. Evidence from this study and by Rouse *et al.* (1993) support the hypothesis of surfactant repulsion by the sorbent as an explanation for undetectable surfactant uptake. The lack of sorption is an advantage for surfactant facilitated soil remediation as Dowfax 8390 sorption to soil/geologic material will be minimal.

Alternatively, Triton X-100 was observed to react with all sorbents tested. Because Triton X-100 is nonionic, it is likely to react with natural particles via hydrogen bonding or van der Waals forces. The value mol surf/g sorbent was observed to be greatest for the samples with large quantities of clay minerals. A comparison between the two surface soil samples (Black and Brown) reveals that the Brown sample, which contains less organic matter, sorbed more than the Black sample. The Solonetzic soil sample also provided similar evidence for the mineral portion of the sample as the dominant contributor to sorption of Triton X-100. Furthermore, isotherm non linearity increased with a decline in organic carbon content (Table 2-4). Additionally, the value of mol surf/g sorbent and isotherm non linearity increased when the organic matter was removed from the Black sample. Finally, statistical analyses indicate that the data are described better with the Langmuir model, noting that the difference in F values was greatest for samples that do not contain large amounts of organic carbon. From these observations, it appears that mineral surfaces are more favorable for Triton X-100 sorption and may be blocked by organic matter.

The XRD data provide strong evidence that Triton X-100 intercalates with montmorillonite, even at low concentrations. These findings agree with Law and Kunze (1966) and Platikanov et al. (1977) who reported intercalation of similar nonionic surfactants with montmorillonite. Evidence from the XRD study supports the conclusion that the ethoxylate chain enters the interlayer spaces of montmorillonite. Furthermore, Cano and Dorn (1996a) reported an increase in alcohol ethoxylate surfactant sorption with the clay content of four different sediments. Brownawell *et al.* (1997) reported that sorption quantity and isotherm non linearity increased with the number of ethoxylate groups in the surfactant. These accounts in conjunction with our own data suggest that the ethoxylate chain intercalates with expanding clay minerals.

The Shale sample interacted strongly with Triton X-100 but contains only 18% clay sized particles. This sample is high in organic matter and low in mineral content, hence, the mineral fraction may not be as accessible as in the other sorbents, yet the mol surf/g sorbent was observed to be greater than that of the Solonetzic sample. This implies that the ethoxylate tail-clay interaction may not be the prominent mechanism between Triton X-100 and the Shale sample. The branched alkyl chain or the aromatic portion of the surfactant may interact with the organic phase of the Shale sample. The linear isotherm correlation coefficient is the highest for the shale, also supporting the notion of another type of sorption mechanism. Narkis and Ben-David (1985) studied the sorption of nonionic surfactants to activated carbon and montmorillonite. They concluded that nonylphenol ethoxylated surfactants interact with montmorillonite via the hydrophilic portion (ethoxylate chain) and with activated carbon via hydrophobic groups. This report in conjunction with our observations, support the concept that Triton X-100 may have sorbed to the Shale sample by another means that can not be described by the ethoxylate chain-clay mineral interaction.

Urano *et al.* (1984) reported a linear relationship between alcohol ethoxylate surfactant sorption and sediment organic carbon content, however, I did not find such a correlation, nor did Brownawell *et al.* (1997). Cano and Dorn (1996a; 1996b) observed a linear relationship between the alcohol ethoxylate surfactant sorption and the clay content of four sediments. Again, results from our study and that of Brownawell *et al.* (1997) contradict a linear relationship between surfactant sorption and clay content but reveal that it is the content of expanding clays, rather than total clay content that is related to surfactant sorption.

Brownawell *et al.* (1997) suggest that the presence of expanding 2:1 clay minerals prevented the strong correlation observed by Urano *et al.* (1984). I suggest that neither clay nor organic matter content alone is a suitable attribute to predict alcohol ethoxylate surfactant sorption to soil and geologic samples. The increase in the mol surf/g sorbent for the Black sample after the majority of the organic matter was removed supports the hypothesis that there is a strong correlation between alcohol ethoxylate surfactants and the mineral portion of soil samples and implies that organic matter may impede this sorption reaction. However, the high mol surf/g sorbent value for the Shale sample suggests that Triton X-100 can sorb via other mechanisms. Therefore, it may not be clay or organic matter alone that governs these sorption reactions, but a combination of both. Finally, it is evident that sample characteristics are of great importance when attempting to predict alcohol ethoxylate surfactant uptake, especially if the sample contains both organic matter and expanding clay minerals.

Table 2-1 : Selected Sorbent Properties

Sample	OC (g/100g)	CEC (cmoles(+)/kg)	sand (g/100g)	silt (g/100g)	clay (g/100g)	clay minerals (in relative order of abundance)
Black Chernozem	4.83	36	30	55	15	montmorillonite, kaolinite, and mica[a]
Brown Chernozem	1.72	22	58	26	16	montmorillonite, kaolinite, and mica[a]
Sand	0.055	2	97	1	2	not determined
Shale	51.23	101	nd	nd	nd	montmorillonite, kaolinite, and mica[b]
Solonetz	1.63	41	5	25	70	montmorillonite, kaolinite and mica[c]
Kaolinite	0.00	8	0	0	100	kaolinite
Montmorillonite	0.00	84	0	0	100	montmorillonite

a = from Qualizza (1994), b = from Pawluk and Bayrock (1969), c = from Kohut (1994)

Table 2-2 : Pertinent Surfactant Properties

Surfactant	Chemical Formula	Surfactant Class	CMC[a] (mol/L)
Dowfax 8390	$C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$	Anionic	8.0×10^{-4}
Triton X-100	$C_8H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$	Nonionic	2.0×10^{-4}

a = measured in this study

Table 2-3: Triton X-100 effective CMC and ΔCMC

Sample	effective CMC (mol/L)	ΔCMC (mol/L)	normalized ΔCMC for soil to solution ratio (mol surf/g sorbent)
Black	6.31×10^{-4}	4.31×10^{-4}	4.4×10^{-5}
Black - OM	8.91×10^{-4}	6.91×10^{-4}	7.7×10^{-5}
Brown	1.26×10^{-3}	1.06×10^{-3}	5.4×10^{-5}
Sand	5.01×10^{-4}	3.01×10^{-4}	1.3×10^{-5}
Shale	1.00×10^{-3}	8.00×10^{-4}	2.9×10^{-4}
Solonetz	1.12×10^{-3}	9.20×10^{-4}	2.0×10^{-4}
Kaolinite	2.50×10^{-4}	5.00×10^{-5}	2.1×10^{-6}
Montmorillonite	1.32×10^{-3}	1.12×10^{-3}	5.40×10^{-4}

OM = organic matter

Table 2-4: Triton X-100 isotherm parameters and statistical analysis

Sample	K_{Linear} (L/g)	Linear isotherm r^2	$K_{Langmuir}$ (L/mg)	b (mg/g)	Langmuir isotherm r^2	(F calc - F table)[a]	n
Black	42.77	0.880	4.59	53.72	0.972	40.49	7
Black - OM	36.64	0.714	4.36	66.13	0.964	148.06	9
Brown	57.54	0.872	1.12	115.92	0.974	40.59	7
Sand	4.11	0.644	7.83	8.34	0.997	259.23	6
Shale	174.85	0.882	1.45	359.97	0.959	519.55	9
Solonetz	132.04	0.844	1.40	289.94	0.958	1638.73	9
Kaolinite	3.69	0.746	3.18	7.17	0.978	38.97	9
Montmorillonite	187.52	0.482	7.79	596.72	0.982	36.69	9

OM = organic matter

n = number of observations,

a = a positive difference in F values indicates the Langmuir model is justified by the data

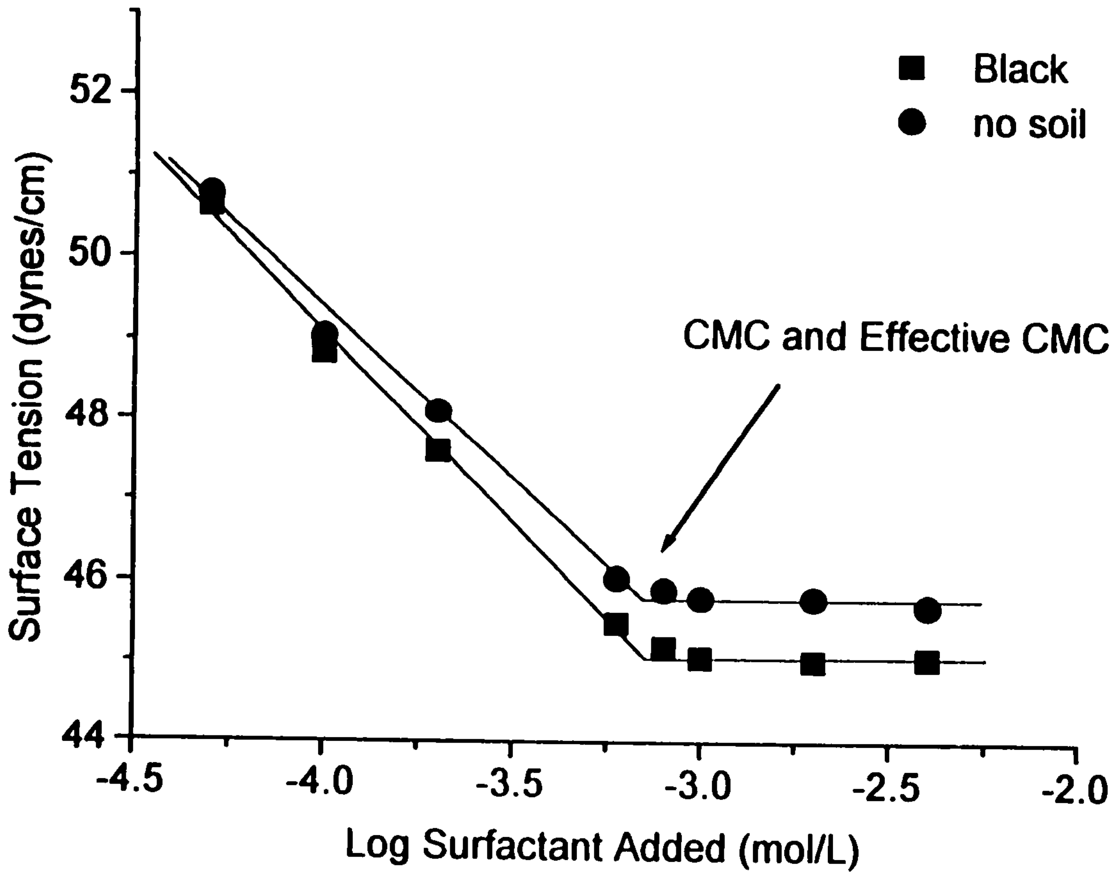


Figure 2-1: Effective CMC for Dowfax 8390 equilibrated with the Black Chernozemic Soil Sample

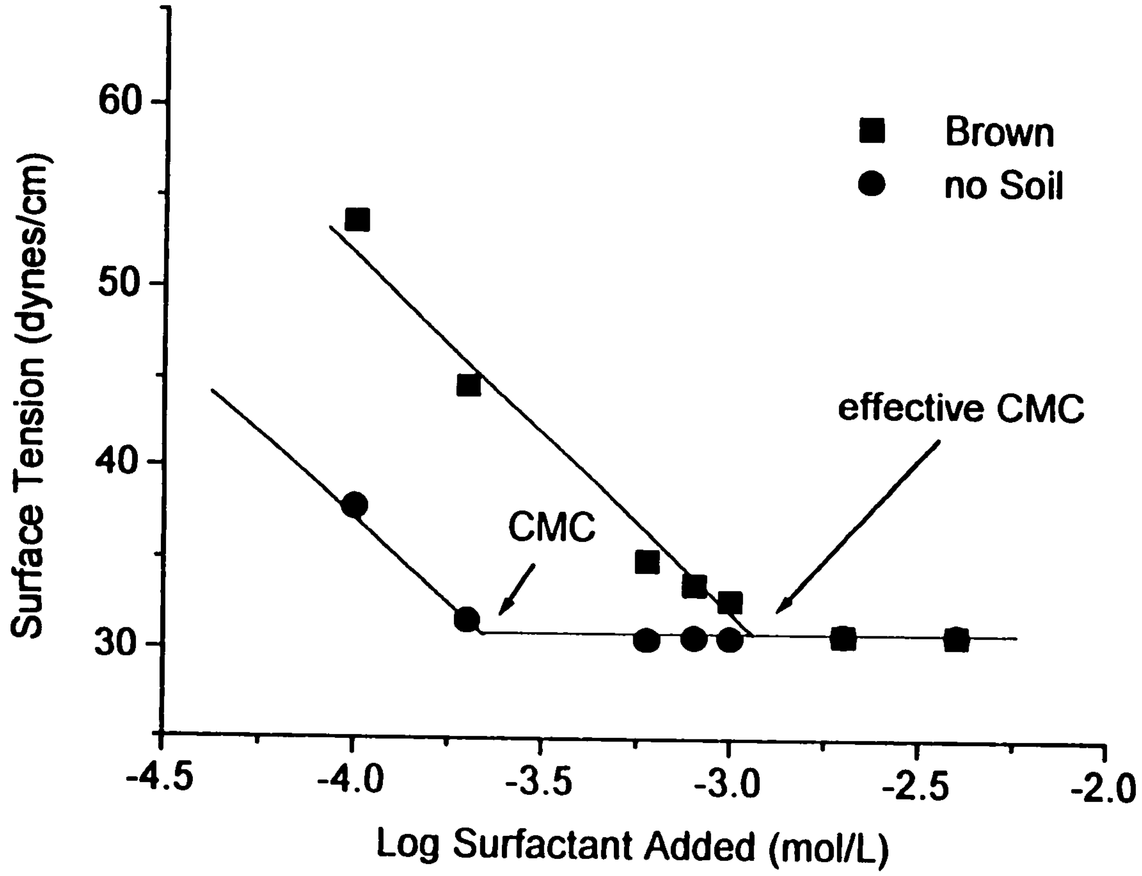


Figure 2-2: Effective CMC for Triton X-100 equilibrated with the Brown Chernozemic Soil Sample

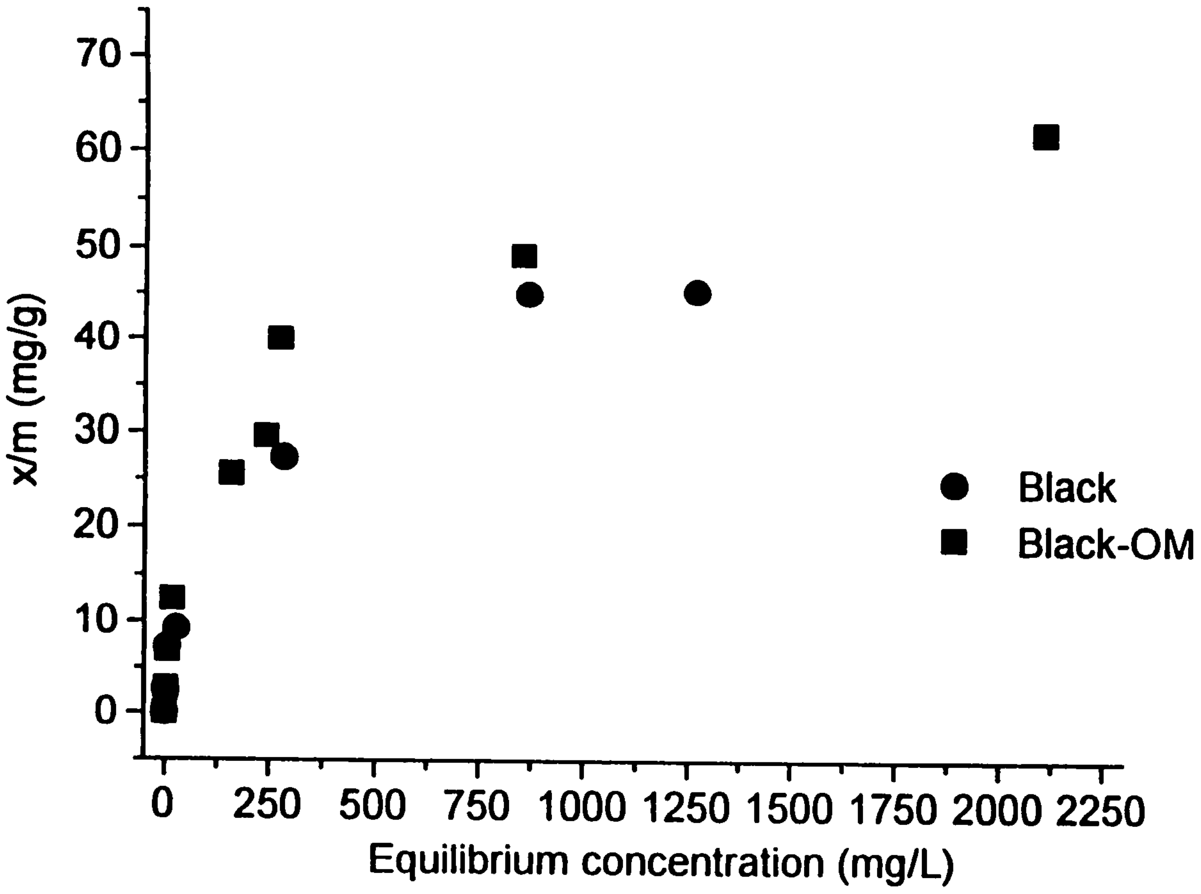
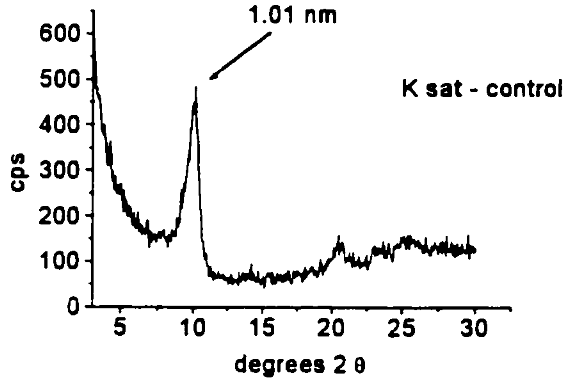


Figure 2-3: Triton X-100 sorption isotherm to the Black soil sample before and after organic matter remova

Pattern A



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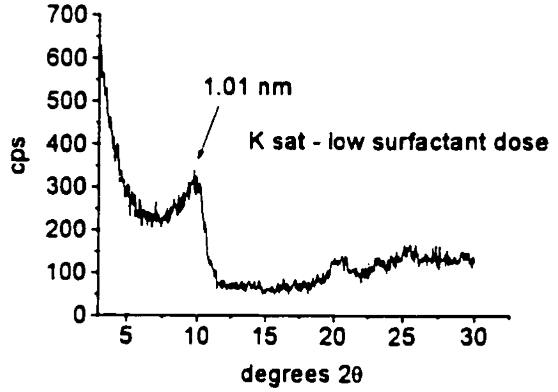

Pattern C

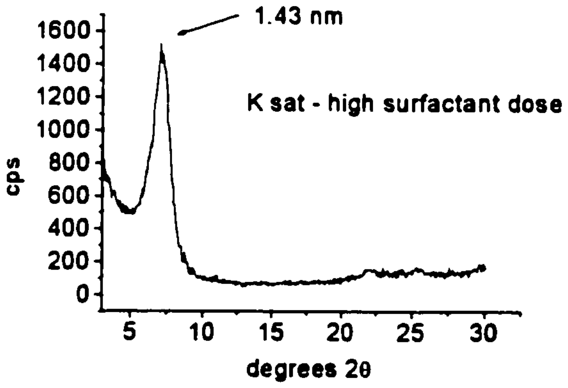

Figure 2-4: X-ray Diffractograms of montmorillonite equilibrated with: 0.01M K_2SO_4 (Pattern A), 0.1mM Triton X-100 (Pattern B) and 4.0 mM Triton X-100 (Pattern C).

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CHAPTER 3[1]

ORGANIC MATTER MOLECULAR GEOMETRY GOVERNS 1-NAPHTHOL SORPTION IN SOIL AND GEOLOGIC SAMPLES

INTRODUCTION

Sorption of xenobiotic chemicals to soils and geologic materials is impeding the rate and progress of physical, biological and chemical remediation. The current understanding of the underlying, fundamental reactions that occur between xenobiotics and natural sorbents is not well developed (Luthy *et al.*, 1997). Accordingly, the partition theory is often used to describe the extent of xenobiotic sorption to soil and geologic samples, despite evidence that it is not universally applicable (Mingelgrin and Gerstl, 1983; Isaacson and Frink, 1984). The partition theory states that contaminants dissolve into organic matter and this distribution is purely a function of the contaminants' hydrophobicity, rather than the properties of organic matter (Chiou, 1989). Furthermore, the partition theory suggests that octanol is a suitable surrogate for organic matter found in nature and that sorption of a compound can be predicted based on its partitioning behavior in octanol.

Earlier work in this laboratory (Qualizza, 1994; Xing *et al.* 1994a, b, c; Chen *et al.*, 1996) explored the variation in carbon character among samples and reported that the partition theory was unable to compensate accurately for the differences in the diagenetic properties of organic matter. It was established that young organic matter, such as that found in surface soils, sorbed less hydrophobic chemical, than older, more condensed organic matter such as that found in weathered shale samples. Other reports (Grathwohl, 1990; Ganaye *et al.*, 1997) and a recent review (Luthy *et al.*, 1997) recognize that the extent of contaminant uptake varies with the amount of aromatic carbon in the sorbent. Despite this realization, determining sorbent aromaticity is a difficult task, especially with complex sorbents, such as soils and geologic samples.

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M. J. Salloum, M. J. Dudas, and W. B. McGill

Access to sophisticated chemical techniques such as cross polarization magic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance (NMR) spectroscopy has advanced the study of organic matter ecology. CPMAS ^{13}C NMR use is progressing chemical structure definition studies of organic matter and fractions thereof from soil and geologic samples. The work of Xing *et al.* (1994b) and Chen *et al.* (1996) revealed that the amount of xenobiotic uptake was related to sample aromaticity as measured by CPMAS ^{13}C NMR spectroscopy. Therefore, for a given sample, the CPMAS ^{13}C NMR spectra can be used to calculate the amount of aromatic carbon, that would give rise to the sorption coefficient of the sample. The relationships described by Xing *et al.* (1994b) and Chen *et al.* (1996) were based on a small number of samples, however, if the partition theory is ubiquitous, then the relationships should be applicable to a wide range of soil and geologic samples. The objectives were to: 1) determine 1-naphthol sorption for a diverse range of soil and geologic samples, 2) measure the elemental composition and aromaticity of the samples, and 3) examine the consistency between the elemental, CPMAS ^{13}C NMR, and sorption data.

MATERIALS AND METHODS

Sorbents

The samples were chosen to represent a range of organic carbon characteristics. The Black and Brown Chernozemic, Black Solonetzic, Sand and Black Shale samples, as described in Chapter 2 were included in the set of samples for this study. I also included a weathered, contaminated surface soil that is now nonwettable, from the Ellerslie Research Station, located south of Edmonton (Ah horizon - Malmo soil series). This soil was contaminated with crude oil in 1973 as part of a reclamation experiment but now does not have any qualitative signs of hydrocarbon contamination nor does it smell or feel oily. The nonwettable nature of this soil sample is suggested to be due to the presence of long-chain and polycyclic aliphatic organic compounds of petroleum origin (Roy *et al.*, 1999). For detailled information on the characteristics of this nonwettable soil, the reader is referred to reports by Roy and McGill (1998) and Roy *et al.* (1999). The Pahokee Peat sample was purchased from the International Humic Substances Society (IHSS). The Peat sample was received air-dry and ground to pass a 106 µm sieve. The remaining samples were air-dried, passed through a 2 mm sieve and then ground to pass a 106 µm sieve.

C, H, and N analysis and Ash Content

C, H, and N content was measured using an EA 1108 elemental analyzer (Carlo Erba Instruments) in the Department of Chemistry, University of Alberta. Prior to elemental analysis, the samples were freeze-dried for 48 hours to remove any remaining water. The C content of the Sand sample was measured by Leco furnace. Inorganic carbon was determined by acidification of the sample, followed by collection and quantification of the evolved CO_2 (Bundy and Bremner, 1972). Organic carbon was calculated by difference. The ash content was determined by combustion to a constant weight at 750°C.

CPMAS ^{13}C NMR Spectra

The CPMAS ^{13}C NMR spectra were obtained on a Bruker AM 300 instrument in the Department of Chemistry, University of Alberta. The spectra of the soil/geologic sample were obtained using the following parameters: sample mass of 200 to 300 mg, a spectral frequency of 75.468 MHz for carbon, a HP WP 73A probe, a magic-angle spinning rate of 5 kHz, a cross polarization time of 2 ms, and a relaxation delay of 2 s. The acquisition time was 0.057 s and the number of scans varied between 512 and 24 427, depending on the signal to noise ratio. Dipolar dephasing (DD) experiments were performed on the Shale and Peat samples using the same parameters, but included a dephasing delay of 70 µs prior to data acquisition. This technique introduces a delay that allows the signal from protonated carbons to relax, prior to data acquisition (Wilson, 1987; Preston, 1996). The resulting spectrum reveals the signal of nonprotonated and methyl carbons. Carbon assignments were made as described by Xing *et al.* (1994b) using the following chemical shift ranges: aliphatic-C (0-106 ppm), aromatic-C (106-165 ppm), and carboxyl-C and carbonyl-C (165-230 ppm). The percent of each region was calculated by taking the ratio of the signal area of each range versus the total signal area (0-230 ppm).

Sorption Experiments

1-naphthol (99%+) and 1-naphthol-1-^{14}C (7.7mCi/mmol) were purchased from Sigma Chemical Co. and used as received. Analysis of the 1-naphthol by Gas Chromatography with Flame Ionization Detection did not reveal the presence of impurities. The sorption experiments were conducted as batch equlibrations as described by Xing *et al.* (1994a) and Chen *et al.* (1996). 1-naphthol and 1-naphthol-1-^{14}C were prepared in a 0.01M $CaCl_2$ solution (pH adjusted to 6.5) that included 10^{-4} M of $HgCl_2$ to prevent biological degradation of the sorbate. Solutions contained total 1-naphthol concentrations of 100 to 600 mg/L labeled with an activity of 100 Bq mL^{-1} (~6000 dpm). The soil or geologic sample along with 5 glass beads (6mm in diameter) were placed into 16 x 100 mm KIMAX® test tubes at soil to solution ratios that would result in 20-80% loss of sorbate (1:5 to 1:120). The 1-naphthol solution was added and the test tubes were sealed with a PTFE lined screw cap. The samples were placed on a rotating shaker (20 rpm) and mixed for 48 hours at room temperature (22°C ± 1°C). The samples were then removed from the shaker, and centrifuged at 1000 x g for 30 minutes. A 2 mL aliquot was removed from the supernatant and placed in a 20 mL glass scintillation vial containing 10 mL of Optiphase 'Hisafe3' Scintillation cocktail (Fisher Scientific) and counted on a Packard Tricarb® 2000CA Liquid Scintillation Analyzer. Reports from the literature (Xing *et al.*, 1994a; Chen *et al.*, 1996) and preliminary tests confirmed that 1-naphthol did not sorb to the test tubes. Hence, all sorbate losses from solution were attributed to 1-naphthol sorption to the sample, and sorption was calculated from the change in solution ^{14}C activity.

Sorption Coefficients (K_d, K_{oc})

For linear isotherms, K_d is the ratio of a substance's concentration in the sorbent and water phases (Schwarzenbach *et al.*, 1993). This ratio is displayed in equation (3-1), where C_s is the concentration of sorbate on the solid phase and C_e is the solution concentration of the substance after reacting with the solid (equilibrium concentration).

$$K_d = \frac{C_s}{C_e} \tag{3-1}$$

Because the concentration on the soil phase is determined by difference, equation (3-1) becomes:

$$K_d = \frac{(C_o - C_e)volume}{C_e mass} \tag{3-2}$$

where C_o is the initial concentration of the sorbate, volume and mass are the solution volume and sorbent mass used in the batch equilibration, respectively. Manipulation of equation (3-2) produces:

$$K_d = \left(\frac{C_o}{C_e} - 1\right)\frac{volume}{mass} \tag{3-3}$$

Rearranging equation (3-3) creates a linear form (equation (3-4)) that allows the calculation of K_d from the slope of a plot of C_o versus C_e.

$$C_e = \frac{C_o}{K_d\left(mass/volume\right) + 1} \tag{3-4}$$

Using equation (3-4) may decrease the error associated with calculating K_d because C_o and C_e values are directly measured whereas other methods, such as the isotherm method, entail the use of differences rather than measured quantities. Hence, equation (3-4) was used to calculate the value of K_d in this paper.

It is well accepted that partitioning of organic compounds to soil and geologic samples is proportional to the quantity of organic carbon in the sample (Chiou, 1989). Therefore, the K_d values were normalized to organic carbon content to facilitate comparisons among sorbents. The organic carbon normalized sorption coefficient, (K_{oc}), is calculated using equation (3-5) where f_{oc} is the fraction of organic carbon present in the sample (Karickhoff *et al.*, 1979).

$$K_{oc} = \frac{K_d}{f_{oc}} \tag{3-5}$$

Statistical Analysis

Linear regression analysis for the K_d determination was performed using Origin™ version 4.1. PROC GLM and least significant difference (LSD) tests were performed using the SAS® System software version 6.11. Both the regression analysis and LSD separation tests were performed at $\alpha=0.05$, unless otherwise stated.

RESULTS

Sorbent Properties

The sorbent properties are listed in Table 3-1. Oxygen analysis was not performed on the mineral samples because it is difficult to distinguish between organic and mineral oxygen. The elemental data for the sorbents reveal a range of C, H, and N contents. With the exception of the Brown and Solonetzic samples, the H/C ratios are consistent with the diagenetic properties of these materials. When organic matter is degraded, it becomes more condensed, resulting in a decrease of the H/C ratio (Grathwohl, 1990; Huang and Weber, Jr., 1997). The Shale sample has the lowest H/C ratio, and is more condensed than any of the other samples. The nonwettable Black sample has a lower H/C ratio than the Black sample, and may be a result of the presence of weathered, residual hydrocarbons that have become polymerized into the organic matter. The H/C ratio of the Peat is lower than that of the mineral soils and is consistent with its being well humified (Lyon, 1995). The H/C ratios for the Brown and Solonetz, are uncharacteristic of soil/geologic samples in general. I am confident in the measured values and can only offer that the presence of mineral hydrogen may have resulted in the large H/C values because silicate minerals contain hydroxyl groups along the broken edges (McBride, 1994). The low carbon contents of the Brown and Solonetzic soil samples may have magnified the presence of inorganic hydrogen in the H/C ratio more than the other samples in this study.

CPMAS ^{13}C NMR spectra

The aromatic-C contents are similar for the Black, Brown, Shale and Solonetzic samples (Table 3-2). A CPMAS ^{13}C NMR spectrum was not obtained for the Sand sample because the low carbon content would not yield an adequate signal to noise ratio. The Peat and nonwettable Black samples produced the lowest and highest signals in the aromatic region respectively. The increase in the aromatic-C signal in the nonwettable sample over that of the Black sample is consistent with the hydrocarbon contamination. In a DD CPMAS ^{13}C NMR spectrum, the signal from carbon atoms directly bonded to hydrogens diminishes quickly (Hatcher, 1987). Furthermore, methyl carbons, due to rotational motion, require longer times for the signal to decline (Alemany *et al.*, 1983). It is suggested that a delay time of 55 μs should reveal only the signal from methyl and nonprotonated carbons. Both the conventional and DD spectra of the Shale and Peat samples are displayed in Figure 3-1. The Shale sample contains a large amount of nonprotonated carbon, for the signal remained after the 70 μs dephasing delay. There was only a small decline in the aliphatic region, indicating that this sample contains an appreciable amount of methyl carbon. The DD CPMAS ^{13}C NMR spectrum for the Peat sample only displays a decrease in the aliphatic region, likely due to the presence of $-CH_2$ and -CH carbon (Alemany *et al.*, 1983).

Sorption Coefficients

The soil/geologic samples produced linear sorption isotherms (Figure 3-2) and a wide range of 1-naphthol sorption coefficients. The Black, Brown, and Solonetzic samples produced similar sorption isotherms. The K_d value is smallest and greatest for the Sand and Shale samples respectively (Table 3-3) and corresponds to the amount of organic carbon content in each sample. The K_{oc} values vary considerably among samples and were found to be significantly different at $p<0.01$. The 1-naphthol K_{oc} value was not calculated for the Sand sample because low quantities of f_{oc} are susceptible to more error due to difficulty in obtaining accurate measurements of low organic carbon quantities (Rutherford, *et al.*, 1992). The range of K_{oc} values can be attributed to differences in organic carbon character and is consistent with the general diagenetic properties of the samples. For instance, the K_{oc} value is highest for the weathered black Shale sample, whereas the younger, surface soil samples generated lower K_{oc} values. Because the nonwettable Black sample has a history of hydrocarbon contamination, one would expect the 1-naphthol K_{oc} value to be higher, however, the opposite was observed. The Solonetz and Brown samples also sorbed appreciable amounts of 1-naphthol as indicated by the high values of K_{oc}.

DISCUSSION

The variation in 1-naphthol K_{oc} values is attributed to the differences in carbon character of the soil and geologic samples. This is consistent with earlier findings (Xing *et al.*, 1994b; Chen *et al.*, 1996) and other reports in the literature (Grathwohl, 1990; Ganaye, *et al.*, 1997). The Shale sample sorbed the most 1-naphthol and is consistent with the chemical characterization as the H/C value is indicative of highly aromatic, condensed organic matter. Furthermore, the DD-CPMAS ^{13}C NMR spectrum indicates that this sample contains mostly nonprotonated carbon and supports the measured 1-naphthol K_{oc} value. The Peat sample sorbed much less 1-naphthol than the Shale sample, but again, is consistent with the chemical data. The Peat sample has a higher H/C ratio, low percentage of aromatic carbon, and the DD-CPMAS ^{13}C NMR spectrum reveals a large amount of protonated, aliphatic carbon. Based on chemical characteristics alone, the Peat sample should not sorb as much 1-naphthol as the Shale, and concurs with the 1-naphthol K_{oc} values reported here.

The chemical differences between the Black and nonwettable Black sample are consistent with the contamination history. The H/C value is lower for the nonwettable sample and suggests that the organic matter phase of this sample is more condensed. The nonwettable

Black sample has a higher proportion of aromatic carbon, however, the 1-naphthol K_{oc} value is lower. The aromatic carbon content of the nonwettable sample exceeds that of the Shale sample, but the 1-naphthol K_{oc} value is drastically lower. The same contradiction between the chemical and sorption data exists for the Solonetz and Brown samples. The CPMAS ^{13}C NMR spectra indicate that the Solonetz, Brown and Black samples contain similar amounts of aromatic carbon, yet the measured 1-naphthol K_{oc} values significantly differ. The low organic carbon and high mineral contents of the Brown and Solonetzic samples may have interfered in accurate NMR spectra acquisition due to a decrease in sensitivity (Schmidt *et al.*, 1997), despite obtaining a sufficient signal to noise ratio. Spinning side bands may have also decreased the accuracy in quantifying aromaticity (Wilson, 1987; Preston, 1996). There is concern about the use of CPMAS ^{13}C NMR as a quantitative method and some suggest it be restricted to determining relative differences between samples (Preston, 1996).

A comparison between the 1-naphthol K_{oc} values with the H/C and percentage of aromaticity (Figures 3-3 and 3-4 respectively) indicates that these values are in poor agreement. Gauthier *et al.* (1987) reported a poor correlation between the pyrene K_{oc} and the H/C values and attributed this to the general description of carbon by the H/C ratio. For instance, -COOH and -HC=CH- will yield the same H/C ratio, however, the manner by which these structural groups react with a molecular probe likely differs. Xing *et al.* (1994b) and Chen *et al.* (1996) suggest a strong relationship between the K_{oc} value and the amount of aromatic carbon in the sample and state that K_{oc} can be predicted solely from sample aromaticity. The data, as presented in Figure 3-4, disagree with these findings. The samples do not signify any relationship between 1-naphthol K_{oc} values and aromatic carbon content. Even though samples with low carbon contents (Brown and Solonetz) that may not produce accurate CPMAS ^{13}C NMR spectra were included, there is still the contradiction between 1-naphthol K_{oc} value and the aromaticity of the nonwettable Black sample. This sample is higher in organic carbon content, hence one can be more confident with the accuracy of the CPMAS ^{13}C NMR spectrum.

There is evidence in the literature that sorption quantity may also be related to the molecular geometry or physical conformation of the sorbent. Humic acids, when in solution, change their "microorganization" depending on pH and ionic strength (Engebretson and von Wandruszka, 1994). Xenobiotic sorption (binding) coefficients have been reported to change depending on the conditions of the humic acid solution (Schlautman and Morgan, 1993; Clapp *et al.*, 1997). Therefore, the sorption coefficient of xenobiotics depends on the chemical and molecular geometry of humic acids. This observation has not been limited to humic acids because Murphy *et al.* (1994) manipulated the orientation of mineral bound humic material by changing the solution conditions during humic binding to the minerals. They reported a variation in the K_{oc} values for several hydrophobic organic contaminants because "coiled" organic matter sorbed less, due to a decrease in hydrophobic domains that were available for sorption than in the "open" configuration. Xing *et al.* (1994c) also found that the sorption of simple hydrocarbons could not be attributed to polarity of the sorbent alone and concluded that with some sorbents, such as collagen, the physical conformation is an important determinant in the extent of xenobiotic uptake.

The chemical methods used in this investigation examine the entire sample. The 1-naphthol sorption method is a surface reaction between 1-naphthol molecules and available organic matter. Measurements with montmorillonite (data not shown) and a report from Burgos *et al.* (1996) indicate that 1-naphthol does not react with the mineral phase, despite the existence of a hydroxyl group in the 1 position on one of the aromatic rings. Therefore, it can be concluded that the measured 1-naphthol K_{oc} values are a result of interaction with surface accessible organic matter domains. The manner in which the organic matter is bound to the mineral phase of soil and geologic samples appears to be a variable in sorption of xenobiotics, however, as this attribute was not tested specifically, it is merely offered as an explanation for the observed contradiction among the sorption and chemical data. Finally, the findings of this study clearly indicate that chemical data are insufficient for predicting the sorption behavior of contaminants, and suggest that the applicability of empirical relationships, as well as the partition theory to a wide range of soil and geologic samples is questionable.

Table 3-1: Ash and selected element contents of samples

Sample	C (g/100g)	H (g/100g)	N (g/100g)	O (g/100g)	H/C	Ash (g/100g)
Black	5.47	0.58	0.46	nd	1.25	87.9
Brown	1.67	0.31	0.16	nd	2.17	94.5
Nonwettable Black	7.42	0.64	0.51	nd	1.03	86.9
Peat	48.35	4.07	3.32	34.16	1.00	13.4
Sand	0.055	nd	nd	nd	nd	99.6
Shale	56.26	3.67	1.32	23.05	0.78	20.1
Solonetz	1.79	0.53	0.18	nd	3.50	92.3

nd = not determined

Table 3-2: Organic carbon character as determined by CPMAS ^{13}C NMR

	Relative distribution of C		
Sample	aliphatic (0-106 ppm)	aromatic (106-165 ppm)	carboxyl + carbonyl (165-230 ppm)
Black	51	37	12
Brown	44	39	17
Nonwettable Black[a]	32	56	12
Peat	65	22	13
Sand	nd	nd	nd
Shale	45	42	13
Solonetz	50	39	11

nd = not determined
a = from Janzen *et al.* (1996)

Table 3-3: 1-naphthol sorption coefficients

Sample	K_d (mL/g)	r^2	K_{oc} (mL/g)
Black	13.7	0.998	250e
Brown	11.0	0.997	657b
Nonwettable Black	16.3[a]	na	219[b]
Peat	146	0.993	301d
Sand	0.600	0.999	nd
Shale	603	0.958	1070a
Solonetz	11.4	0.997	634c

a = from Janzen *et al.* (1996)
b = calculated using carbon value measured in this study
na = not applicable
nd = not determined due to low organic carbon content
letters indicate significant differences at $p<0.01$

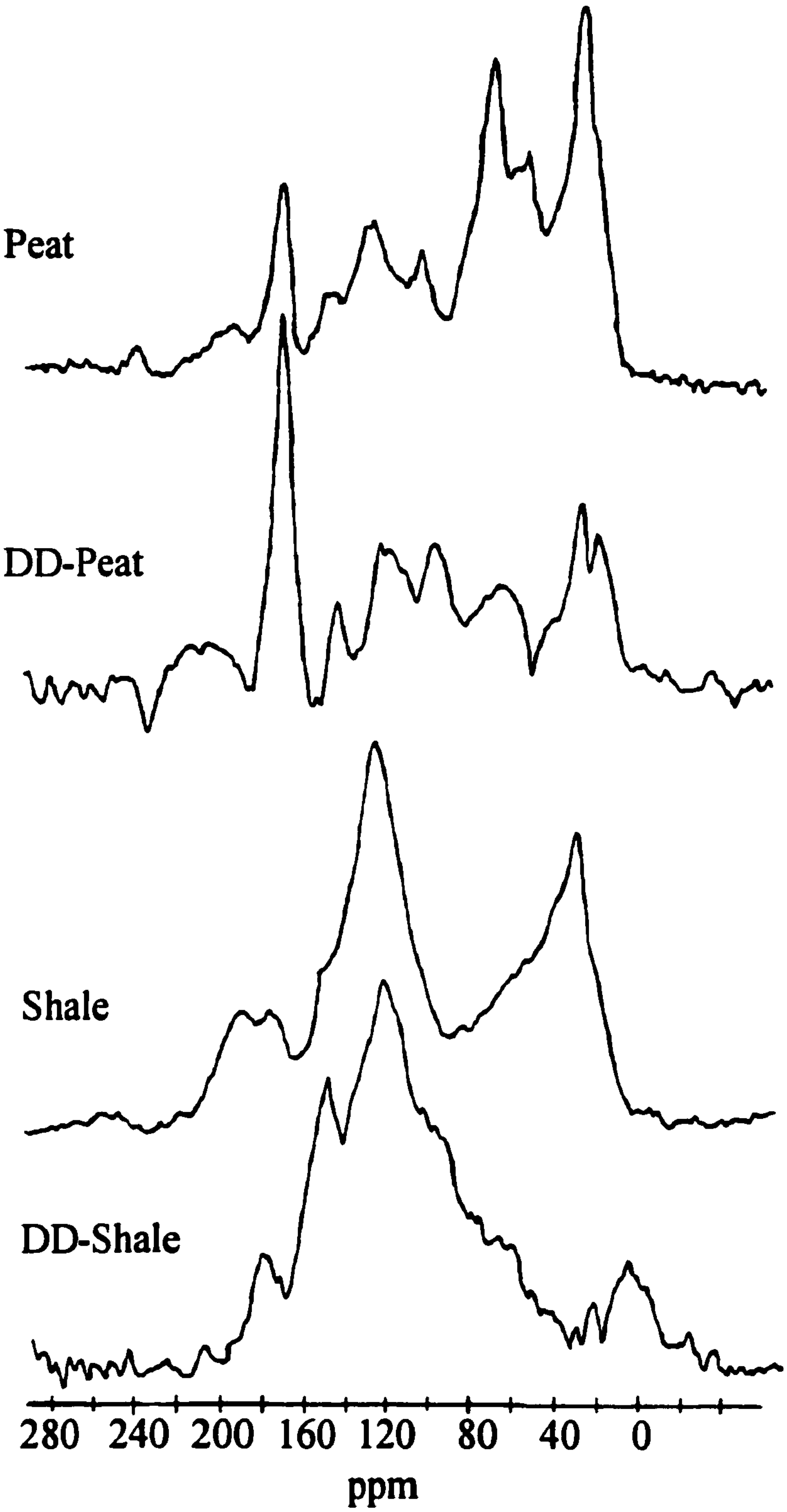

Figure 3-1: Conventional and dipolar dephased (DD) CPMAS ^{13}C NMR spectra of the Peat and Shale samples

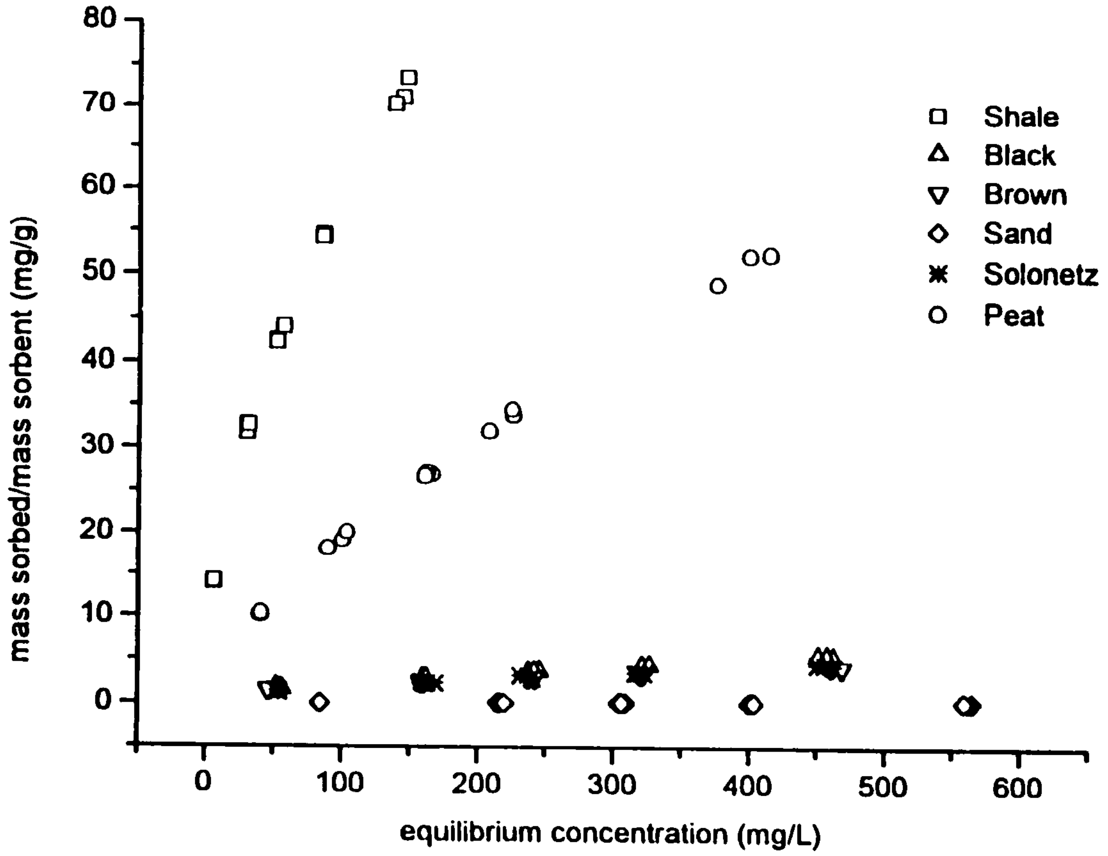

Figure 3-2: Isotherms for sorption of 1-naphthol on soil and geologic samples

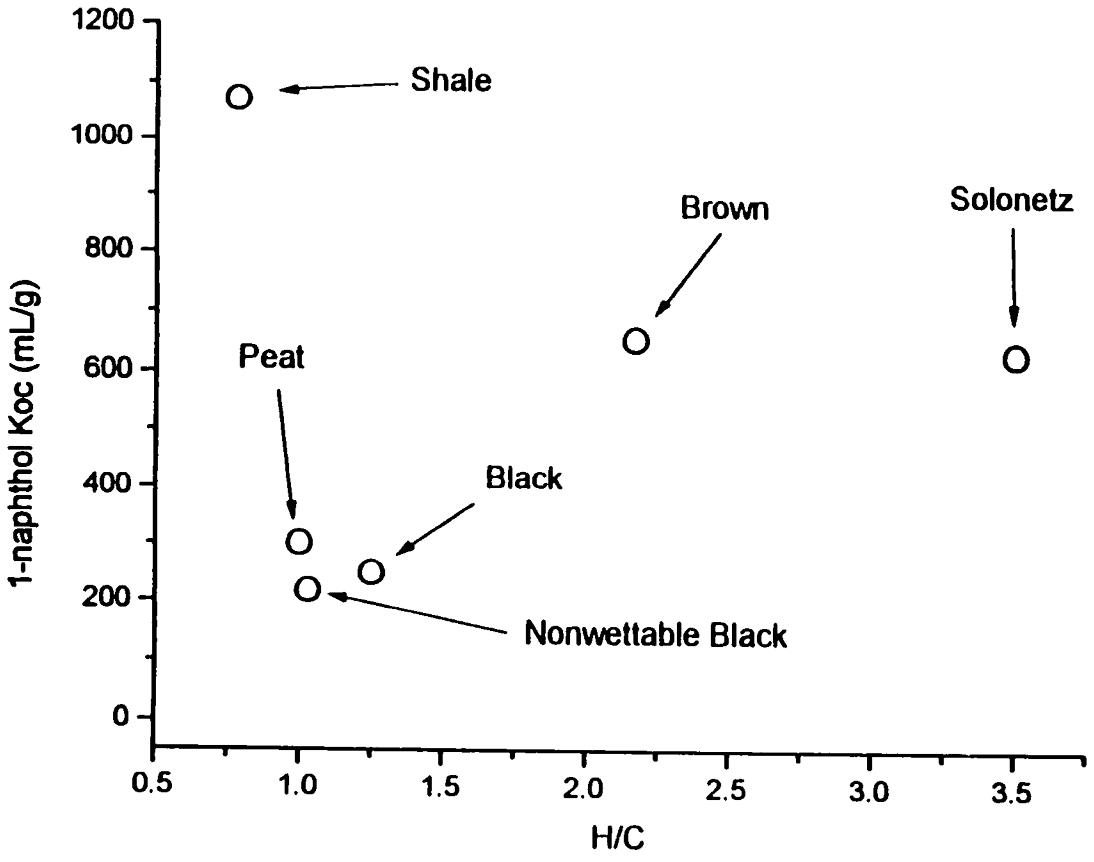

Figure 3-3: Comparison of 1-naphthol sorption coefficients and sample H/C ratios

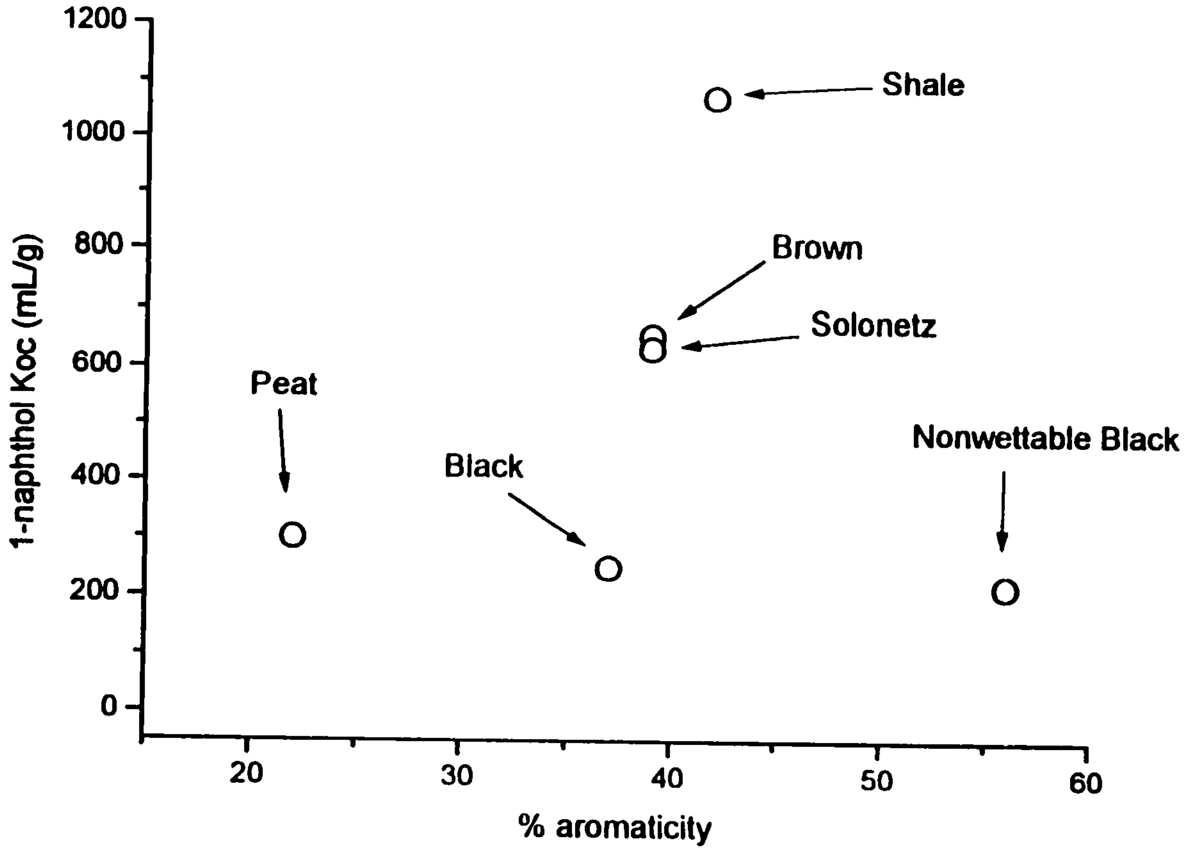

Figure 3-4: Comparison of 1-naphthol sorption coefficients and sample aromaticity as determined by CPMAS ^{13}C NMR

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CHAPTER 4[1]

ORGANIC MATTER MOLECULAR GEOMETRY GOVERNS 1-NAPHTHOL SORPTION IN HUMIC ACID AND HUMIN SAMPLES

INTRODUCTION

Previously, I reported that the elemental and cross polarization magic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance (NMR) spectroscopy data did not agree with that obtained from 1-naphthol sorption. Based on this, it was concluded that organic matter molecular geometry or physical conformation was responsible for the contradiction amongst the data. There are concurring reports in the literature (Garbarini and Lion, 1986; Murphy *et al.*, 1994; Xing *et al.*, 1994b, Jones and Tiller, 1999), however, this concept has not been explored as thoroughly as others, such as sorbent quality, in the consideration of xenobiotic uptake in soils and geologic materials. Past studies have used partitioning to describe the behavior of xenobiotic sorption, and only recently have sorbent characteristics attracted closer attention (Luthy *et al.*, 1997; Huang and Weber, Jr. 1997; Xing, 1997).

The mineral phase is considered to be inert with respect to sorption of nonionic hydrophobic organic chemicals as these chemicals solely react with the organic matter component of soil material (Chiou *et al.*, 1985). Consequently, sorption studies mainly focus on ideal sorbents, such as organic polymers and organic matter fractions, that have well defined chemical characteristics (Chen *et al.*, 1992; Xing *et al.*, 1994a; Xing *et al.*, 1996; Ragle *et al.*, 1997). The exclusion or removal of the mineral phase in sorption studies is not uncommon, however, doing so may cause factors or other considerations in sorption, such as organic matter molecular geometry, to be missed. The division of soil science disciplines has resulted in mineralogists studying organic matter free minerals, and organic matter researchers to focus on ash-free organic fractions (McKeague *et al.*, 1985).

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M. J. Salloum, M. J. Dudas, and W. B. McGill

Hence, little is known about the role of organo-mineral complexes, and even less regarding their interactions with xenobiotics.

To augment and test the contribution of organic matter molecular geometry in sorption, the organic matter of the soil and geologic samples previously examined were fractionated, and the study continued using humic acids (HAs) and humin. The HA and humin fractions were chosen because they contain the majority of organic carbon. The objectives were to : 1) determine the 1-naphthol soprtion coefficients for the organic matter fractions, 2) measure the chemical characteristics and correlate them to the sorption data, 3) compare the sorption behavior of the fractions with that of the source sample.

MATERIALS AND METHODS

Humic acid and humin fractionation

The soil and geologic samples described in Chapter 3, with the exception of the Sand sample, were fractionated into fulvic acid (FA), HA and humin isolates. A modified version of the method reported by Swift (1996) was used. This entailed mixing the soil sample with 0.1M NaOH at a soil to solution ratio of 1:10, under nitrogen, for approximately 20 hours. The solution was separated from the remaining solids by centrifugation (4000 x g for 20 minutes) and to precipitate the HAs, the supernatant was acidified to a pH of 1 with 6M HCl and left to stand overnight. The precipitated HAs were separated from the FAs by centrifugation (9000 x g for 20 minutes) and de-ashed by three cycles of mixing with 0.1M HCl/0.3M HF. Excess chlorides were removed by repeated rinsing with deionized water until chlorides were no longer detected by the addition of silver nitrate to the supernatant. The HAs were freeze-dried and stored for further use.

The addition of 0.1M NaOH was repeated until the extraction ceased to remove any coloured material from the solids. The solids were saturated with 0.1M $CaCl_2$, rinsed with deionized water repeatedly until excess salts were removed, and then freeze-dried. These solids are referred to as humin, defined it as the material remaining after exhaustive 0.1M NaOH extractions. Hence, the organic matter left in the humin fraction was not extractable by 0.1 M NaOH.

C, H, O, and N analysis and Ash Content

C, H, O, and N content was measured using an EA 1108 elemental analyzer (Carlo Erba Instruments) in the Department of Chemistry, University of Alberta. O for the humin samples was not measured due to the high amount of mineral material in these samples. Prior to elemental analysis, the samples were freeze dried for 48 hours to remove water. Ash content was determined from mass lost after heating at 750°C, until a constant mass was obtained.

CPMAS ^{13}C NMR Spectra

The CPMAS ^{13}C NMR spectra for the HA samples were obtained on a Bruker AM 300 instrument in the Department of Chemistry, University of Alberta. The parameters used to obtain spectra were as reported in Chapter 3 except that the cross polarization time was reduced from 2s to 1s. It was observed that a cross polarization time of 2s was too long for HAs and resulted in an increased signal in the aromatic carbon region (data not shown). The number of scans varied between 1003 and 2172, depending on the signal to noise ratio. Dipolar dephasing (DD) experiments entailed the inclusion of a dephasing delay of 70 μs prior to data acquisition. The relative distribution of carbon character was assigned as described in Chapter 3. The alkyl chemical shift regions was divided into the following: 0-50 ppm alkyl carbon, 50-60 ppm methoxyl carbon, and 60-93 ppm O-alkyl carbon (Preston *et al.*, 1997).

Sorption Experiments

The 1-naphthol sorption reactions were carried out as outlined in Chapter 3. The background solution was maintained at a pH of 4 and 6.5 for sorption reactions with HAs and humin respectively. A pH of 4 was used to limit the amount of HA dissolution during the 1-naphthol sorption reaction (Chen *et al.*, 1996). A supporting experiment with a soil sample (Black Chernozem) indicated that the amount of 1-naphthol uptake did not change when the pH of the electrolyte was dropped from 6.5 to 4 (data not shown).

Partition Coefficients and Statistical Analysis

The soil-water sorption coefficient (K_d) and the organic carbon normalized sorption coefficient (K_{oc}) were calculated using the linear equation described in Chapter 3. Statistical analysis were performed as in Chapter 3 at α=0.05, unless otherwise stated.

Delta K_{oc} (ΔK_{oc})

The change in 1-naphthol K_{oc} values between the source sample and the fractions can indirectly detect changes in the surface organization of organic matter and merely be used to monitor any deviation in 1-naphthol sorption. ΔK_{oc} is defined as:

$$\Delta K_{oc} = K_{oc}(fraction) - K_{oc}(source) \qquad (4\text{-}1)$$

where K_{oc} (fraction) refers to the 1-naphthol K_{oc} value of the fraction and K_{oc} (source) represents the 1-naphthol K_{oc} value of the soil or geologic sample from which the HA or humin was isolated. For instance, the ΔK_{oc} for the HAs would be the difference between the 1-naphthol K_{oc} values of the HA and whole soil respectively. Likewise, the ΔK_{oc} calculation for the humin samples would entail a comparison with the quantity of 1-naphthol sorbed by the whole soil versus that of humin. The value of ΔK_{oc} can be used as an indication of how closely the fraction behaves to its source material. A positive ΔK_{oc} demonstrates an increased affinity of 1-naphthol for the fractionated portion of the sample. Conversely, a negative ΔK_{oc} reveals a decrease in the amount of 1-naphthol sorbed in comparison to that sorbed by the source sample.

RESULTS

Sorbent properties

Table 4-1 lists the HA and humin properties. Oxygen was not determined for the humin samples due to the inability to delineate between mineral and organic oxygen. The H/C ratios of the HAs increase in the following order: Shale<Peat<Nonwettable Black<Black<Brown<Solonetz. The order for the humin samples is identical, however, the humin samples generally have higher H/C ratios. The H/C ratio of the HA samples are all lower than the source sample and in contrast, the H/C ratios for the humin samples are all higher. The Brown and Solonetz Humin samples, as with their respective source materials, have distinct H/C ratios that are not representative of soil or geologic samples. Both of these soil samples have low carbon values and high mineral contents, as indicated by their ash values. Hydroxyl groups on the edges of broken minerals may have resulted in high hydrogen values, and due to the low carbon content, this inclusion would manifest itself more than in the other samples, such as those that are rich in organic carbon.

CPMAS ^{13}C NMR Spectra of HAs

The generic carbon distribution of the HAs is listed in Table 4-2. The Shale and Solonetz HAs have the highest and lowest aromatic carbon content respectively. The Black HA, Brown HA, nonwettable Black HA, and the Peat HA all have similar aromatic carbon contents. However, these samples do exhibit differences in the aliphatic carbon region (Figures 4-1a, 4-1b, and 4-1c). The Black, Brown, and Solonetz HAs have prominent peaks in the O-alkyl region (71-73 ppm). These samples, to a lesser extent, contain methoxyl and alkyl carbon. The nonwettable Black and Peat HAs aliphatic region is dominated by alkyl carbon (30-32 ppm), such as in fatty acids, waxes and resins (Baldock *et al.*, 1992). These samples also contain methoxyl and O-alkyl carbon, although the resonance is slightly weaker than that in the alkyl region. The DD spectra for the Brown and Solonetz HAs are nearly devoid of signal, except for carboxylic carbon (170-173 ppm) and some methyl carbon (30 ppm). The signal of the Black, nonwettable Black, and Peat HAs diminished remarkably indicating that most of the carbon in these samples is protonated. In contrast, the Shale HA DD spectrum is similar to the conventional spectrum, except in the late aliphatic region (around 70 ppm). Like the source material, the Shale HA is high in condensed, nonprotonated carbon.

Sorption Coefficients

The isotherms for 1-naphthol sorption to the HAs and Humin are displayed in Figures 4-2 and 4-3 respectively. The samples produced a wide range of K_d values as evident from Tables 4-3 and 4-4. The Shale HA and humin sorbed the most 1-naphthol and the Solonetz fractions sorbed the least. This is in accordance with their source materials (Chapter 3). The humin fractions sorbed much more than the HA fractions. The K_{oc} values for the Black, Brown, and Peat HAs were found to not statistically differ. The 1-naphthol K_{oc} values significantly differ for all the humin samples. With the exception of the Brown and Solonetz HAs, the ΔK_{oc} values are all positive, indicating that they sorbed more 1-naphthol than their source material. Some of the humin samples have ΔK_{oc} values that are considerably higher than the source materials, as evident from the large positive value for the Black, Brown, nonwettable Black and Solonetz humin samples.

DISCUSSION

The 1-naphthol K_{oc} values for the HA and humin samples differ from their associated source material. Similar observations have been made with HAs (Garbarini and Lion, 1986; Rutherford *et al.*, 1992; Qualizza, 1994; Chen et al, 1996) and humin (Nearpass, 1976; Garbarini and Lion, 1986; Qualizza, 1994). The ΔK_{oc} values were positive except for the Brown and Solonetz HAs. Amongst the HAs, these two samples have the highest H/C ratios and their CPMAS ^{13}C NMR spectra indicate that these samples are predominantly composed of aliphatic carbon. Consequently, the 1-naphthol values are lower than the source material, and agree with the chemical characteristics. In contrast, the Brown and Solonetz humin samples have the largest ΔK_{oc} values, indicating the largest deviation in behavior from their source soil sample.

The Peat, Black and Brown HAs have similar generic carbon character, however, their CPMAS ^{13}C NMR spectra indicate some contrasts, especially in the aliphatic region. The Black HA aliphatic region is dominated by O-alkyl carbon and the Peat HA sample has a strong resonance in the alkyl region. These two samples also differ in elemental composition as illustrated by their H/C ratios. Furthermore, the Brown HA sample has a distinct chemical nature as its H/C ratio is much larger than both the Peat and Black HA samples and its CPMAS ^{13}C NMR spectra is considerably different. Despite these notable dissimilarities, the Black, Brown and Peat HAs have statistically similar 1-naphthol K_{oc} values. The nonwettable Black HA has a low H/C value, and comparable aromatic carbon content yet does not fall within the same statistical grouping as the Black, Brown and Peat HAs. The nonwettable Black HA CPMAS ^{13}C NMR spectrum reveals that this sample has more alkyl carbon, but similar amounts of methoxyl and O-alkyl carbon as the Black HA. The 1-naphthol K_{oc} value is larger for this sample, and does not correspond to CPMAS ^{13}C NMR data as the presence of more aliphatic carbon should have been manifested in a lower 1-naphthol K_{oc} value. Overall, there is a poor correlation between the H/C ratio and the sorption values (Figure 4-4) for the HAs. Gauthier *et al.* (1987) reported a linear relationship between pyrene K_{oc} values and the H/C ratios of four HAs. Chen *et al.* (1996) also reported a good correlation between 1-naphthol K_{oc} values with four HA samples (adj $r^2 = 0.85$). The CPMAS ^{13}C NMR and H/C data are in good agreement with each other, however, the contradictions between the chemical and 1-naphthol data imply that another factor, such as organic matter molecular geometry, may dominate in sorption reactions.

The humin samples behaved differently than the HAs, and unlike the HAs, the humin samples produced 1-naphthol values that significantly differed among samples. Humin is historically and operationally defined as the fraction containing mineral-bound organic matter that is base insoluble (Waksman, 1936). Despite that most of the organic matter in mineral soils is associated with the mineral fraction (McKeague *et al.*, 1986), few reports focus on the characteristics of humin and even fewer consider reactions with organic contaminants. Malekani *et al.* (1997) studied the surface properties of humin isolated from mineral soil samples. Surface area and pore size distribution were examined by nitrogen adsorption, surface roughness was measured by small-angle x-ray scattering and fractal geometry, and surface charge was monitored via titration. Based on these analyses, Malekani *et al.* (1997) reported that the removal of smaller organic factions increased the surface area and decreased surface roughness. They further stated that the humin fraction is more porous than the source sample. The investigation of Malekani *et al.* (1997) supports the high 1-naphthol ΔK_{oc} values reported here. The large K_{oc} values are not unique to this sorbate, as similar observations have been reported with: picloram (Nearpass, 1976), toluene and trichloroethylene (Garbarini and Lion, 1986) and anthracene and naphthalene (Qualizza, 1994). The 1-naphthol K_{oc} values do not correlate to the H/C ratios of the humin samples (Figure 4-5), suggesting that these chemical data are insufficient for predicting the extent of sorption.

There are several accounts in the literature that suggest the molecular geometry, also referred to as "physical conformation", "configuration" or "microorganization", is responsible for the variability in K_{oc} values of organic chemicals (Engebretson and von Wandruska, 1994; Murphy *et al.*, 1994; Xing *et al.*, 1994b; Jones and Tiller, 1999). Even early reports identified another factor, other than soil organic matter quantity and quality that determined the degree of xenobiotic uptake in soils. Lambert *et al.* (1965) stated that only the "active fraction" of soil organic matter is available for pesticide binding. Hance (1965) suggested that the surface available groups of soil organic matter were responsible for variations in diuron K_{oc} values. Doherty and Warren (1969) theorized that the correlation between herbicide binding and soil organic matter content may be due to some other physical or chemical factor, to which organic matter itself is correlated.

The data presented in this chapter help unite these two bodies of literature. The Peat and Shale samples are very high in organic carbon, and low in ash content. Presumably, these samples will contain less organo-mineral complexes. The Peat HA and humin have the lowest ΔK_{oc} values, and therefore imply that these fractions behave similarly to their source sample. It is accepted that sorbent aromaticity is a determinant in the sorption of organic contaminants (Luthy *et al.*, 1997) and has been reported to be a factor in 1-naphthol sorption (Xing *et al.*, 1994a). The Peat sample is mostly composed of aliphatic carbon, hence, a reorganization in organic matter may not have been identified as substantially as in the other samples, simply due to the low affinity between aliphatic carbon and 1-naphthol and is a reflection of this samples genesis and morphology. The Shale sample, which is high in condensed aromatic carbon, has larger 1-naphthol ΔK_{oc} values than the Peat, for both its fractions. I speculate, that the removal of the non mineral-bound organic matter fraction exposed more sorption sites or "opened" the mineral-bound organic matter, that had a greater affinity for 1-naphthol than in the Peat sample. The mineral soil fractions displayed the largest deviation from the source sample with respect to 1-naphthol sorption. Again, these changes are attributed to the molecular geometry of the organic matter. Furthermore, the correlation between aromaticity and 1-naphthol K_{oc} values improves in the absence of an abundant mineral phase in the HA samples (Figure 4-6) from that with the source sample, suggesting that the mineral fraction has a bearing on the amount or type of organic matter that is accessible to 1-naphthol. Garbarini and Lion (1986) implicate the mineral fraction as an indirect determinant in the K_{oc} value. This proposition concurs with the data reported here. The ΔK_{oc} values of the humin samples are highest for the mineral soils, and exceedingly large for the Brown and Solonetz samples, and their source material contains the lowest amount of organic carbon, hence, these samples would be more vulnerable to organic matter reorganization at the solid-liquid interface. The inconsistencies between the chemical data (H/C ratios and CPMAS ^{13}C NMR) and the sorption data strongly suggest changes in organic matter molecular geometry. It is unclear, however, if the fractionation process exposed more favorable sorption sites or simply more sorption sites. Nonetheless, it is evident that molecular geometry of organic matter is an important factor in the consideration of organic contaminant sorption in soils and geologic materials.

Table 4-1: Basic element and ash contents of humic acid and humin samples

Sample	C (g/100g)	H (g/100g)	N (g/100g)	O (g/100g)	H/C	Ash (g/100g)
Black HA	43.9	3.70	4.02	33.4	1.00	14.0
Black Humin	3.55	0.463	0.288	nd	1.55	92.9
Brown HA	39.3	4.05	3.91	29.0	1.22	25.7
Brown Humin	1.13	0.311	0.0102	nd	3.28	96.8
Nonwettable Black HA	56.9	4.26	4.49	31.5	0.890	1.36
Nonwettable Black Humin	2.90	0.333	0.180	nd	1.37	92.0
Peat HA	55.4	3.73	3.92	34.6	0.801	0.433
Peat Humin	46.8	4.29	3.22	nd	1.09	15.0
Shale HA	63.2	3.75	1.74	27.1	0.705	0.937
Shale Humin	53.8	3.67	1.24	nd	0.811	20.2
Solonetz HA	45.1	4.82	4.78	32.5	1.26	15.0
Solonetz Humin	1.81	0.729	0.159	nd	4.80	92.9

nd = not determined

Table 4-2: Organic carbon character of humic acids as determined by CPMAS ^{13}C NMR spectra

Sample	Relative distribution of C as		
	aliphatic (0-106 ppm)	aromatic (106-165 ppm)	carboxyl + carbonyl (165-230 ppm)
Black HA	50	31	19
Brown HA	60	29	11
Nonwettable Black HA	55	28	17
Peat HA	52	29	19
Shale HA	39	45	16
Solonetz HA	69	19	12

Table 4-3: 1-naphthol sorption coefficients and ΔK_{oc} for humic acid fractions

Sample	K_d (mL/g)	r^2 (adj)	K_{oc} (mL/g)	ΔK_{oc}^{*} (mL/g)
Black HA	159	0.990	363c	113
Brown HA	137	0.995	348c	-309
Nonwettable Black HA	222	0.995	390b	171
Peat HA	203	0.988	366c	65.0
Shale HA	831	0.976	1310a	240
Solonetz HA	129	0.984	286d	-348

* = $\Delta K_{oc} = K_{oc}$ (HA) - K_{oc} (source)

letters indicate significant differences at $p<0.01$

Table 4-4: 1-naphthol sorption coefficients and ΔK_{oc} for humin fractions

Sample	K_d (mL/g)	r^2 (adj)	K_{oc} (mL/g)	ΔK_{oc}^* (mL/g)
Black Humin	50.8	0.984	1430e	1180
Brown Humin	86.4	0.930	7660a	7000
Nonwettable Black Humin	54.8	0.980	1900c	1680
Peat Humin	181	0.991	387f	85.6
Shale Humin	871	0.957	1620d	550
Solonetz Humin	45.3	0.996	2510b	1880

* = $\Delta K_{oc} = K_{oc}$ (humin) - K_{oc} (source)
letters indicate significant differences at $p<0.01$

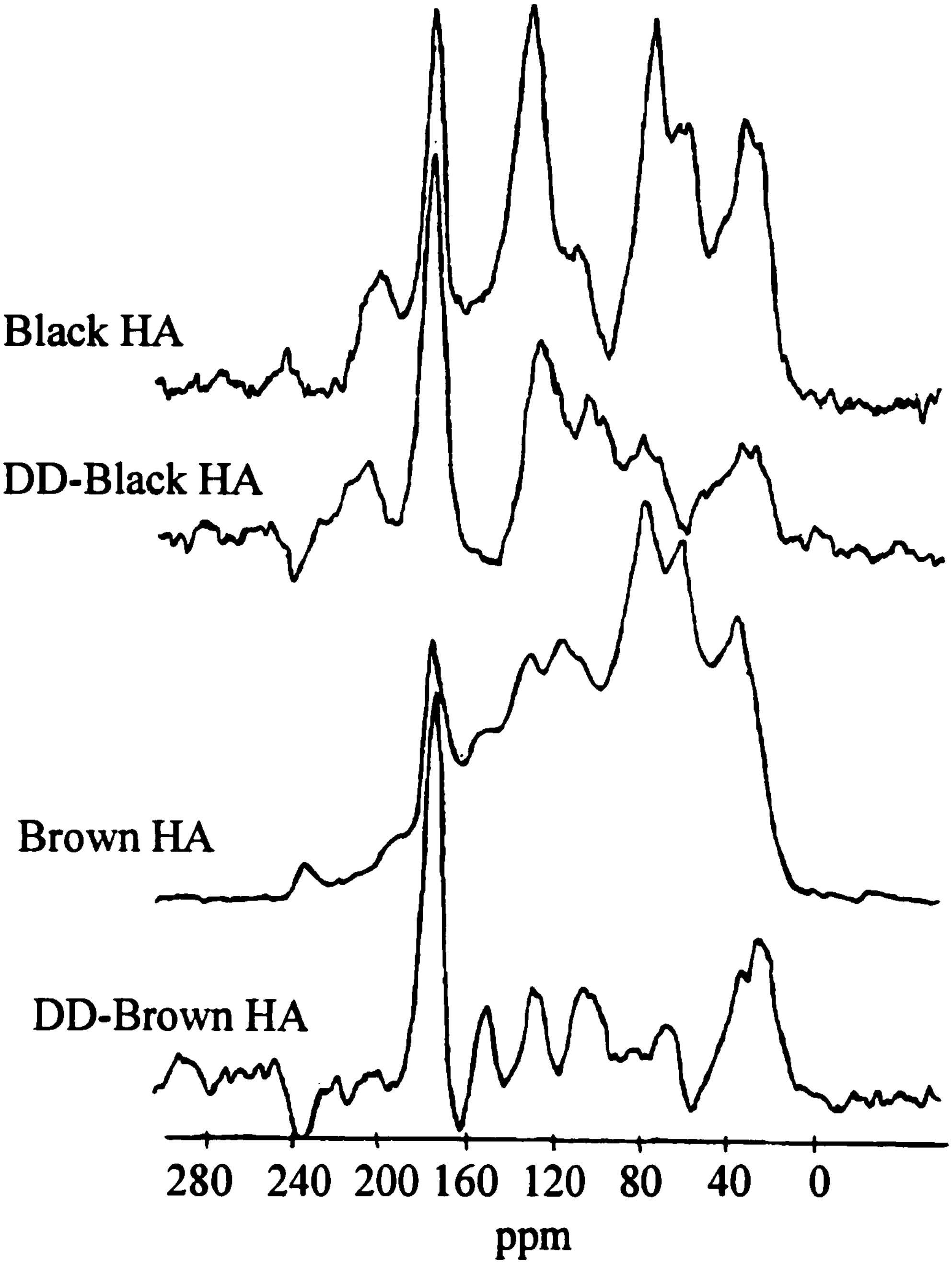

Figure 4-1a: Conventional and dipolar dephased (DD) CPMAS ^{13}C NMR spectra of Black and Brown HA.

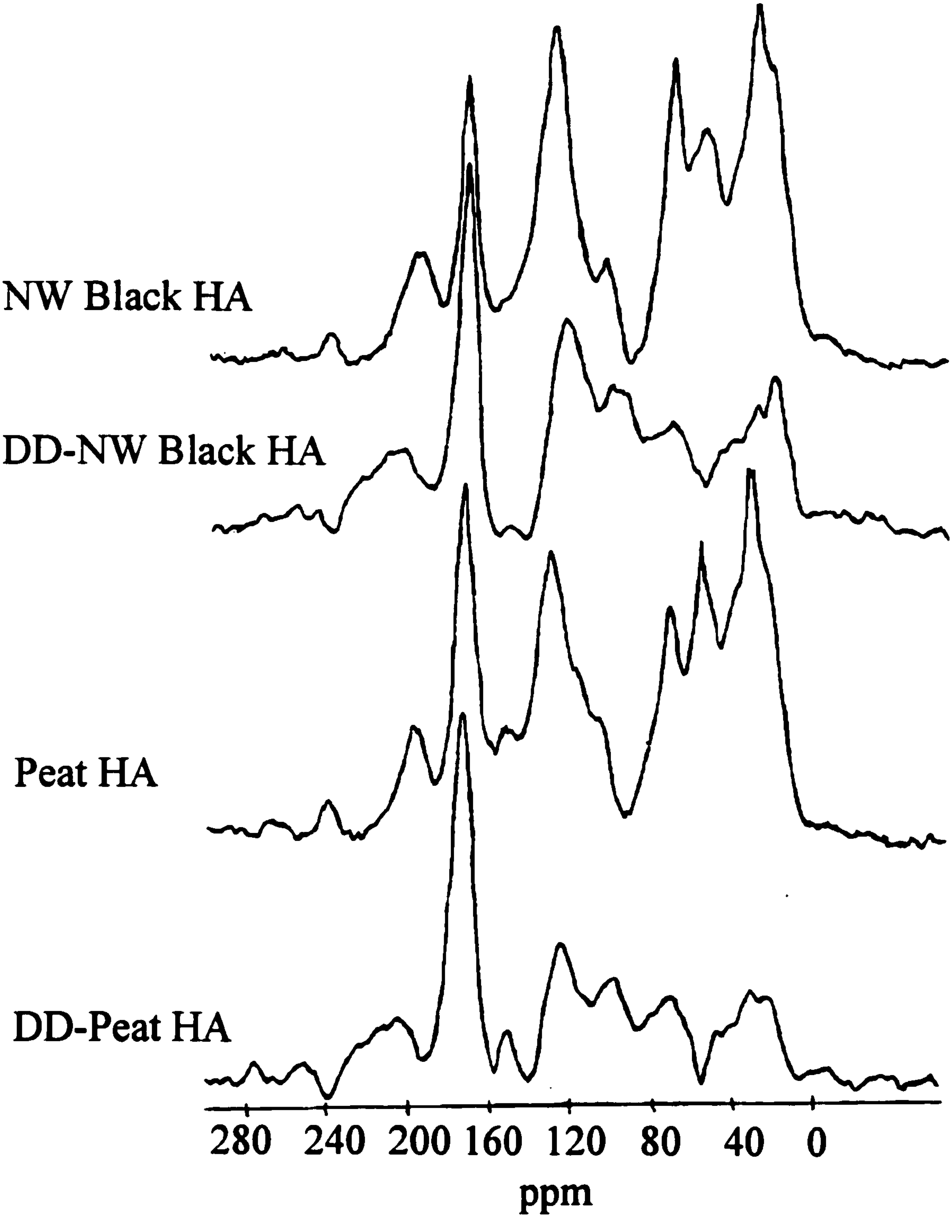

Figure 4-1b: Conventional and dipolar dephased (DD) CPMAS ^{13}C NMR spectra of NW Black and Peat HA.

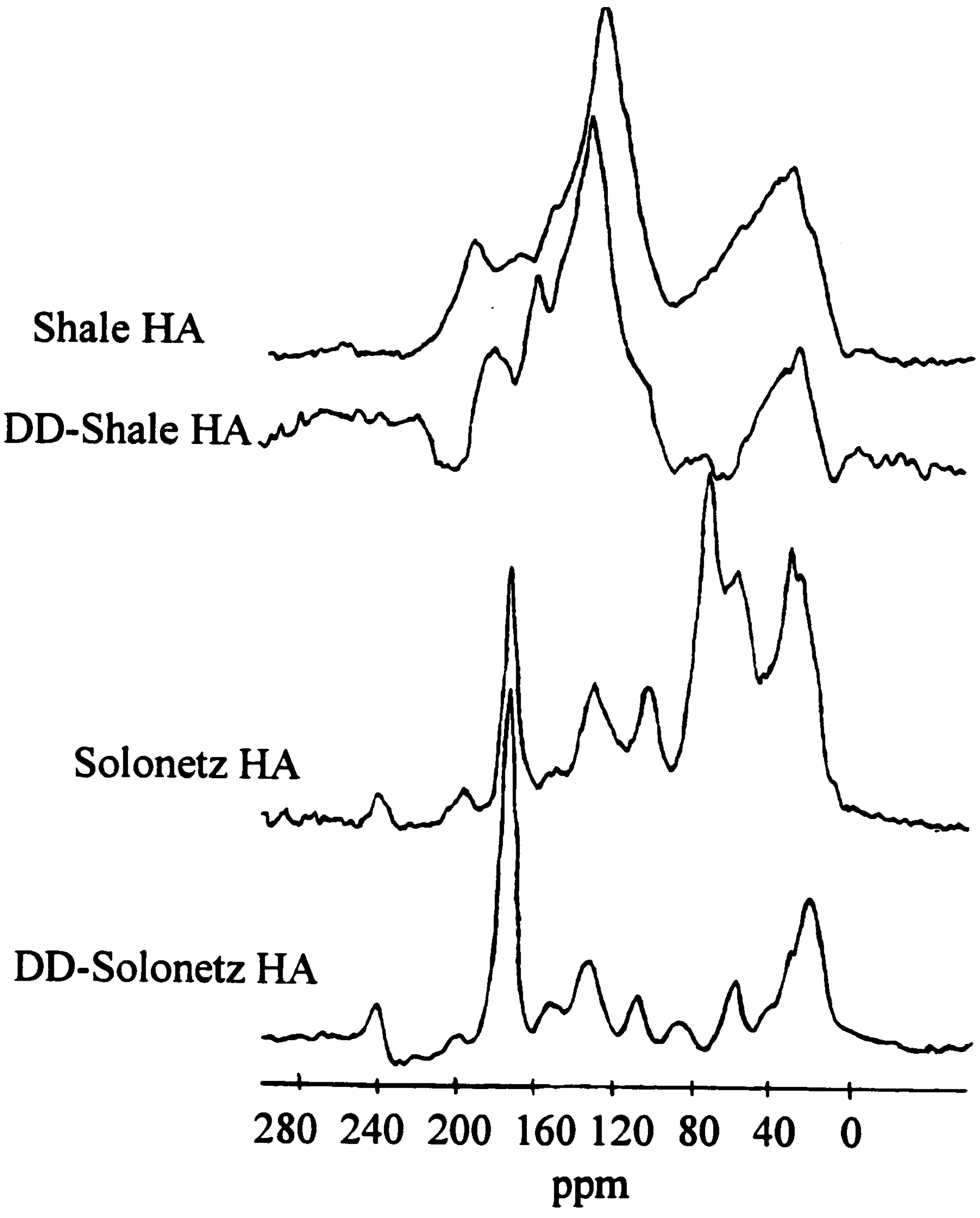

Figure 4-1c: Conventional and dipolar dephased (DD) CPMAS ^{13}C NMR spectra of Shale and Solonetz HA.

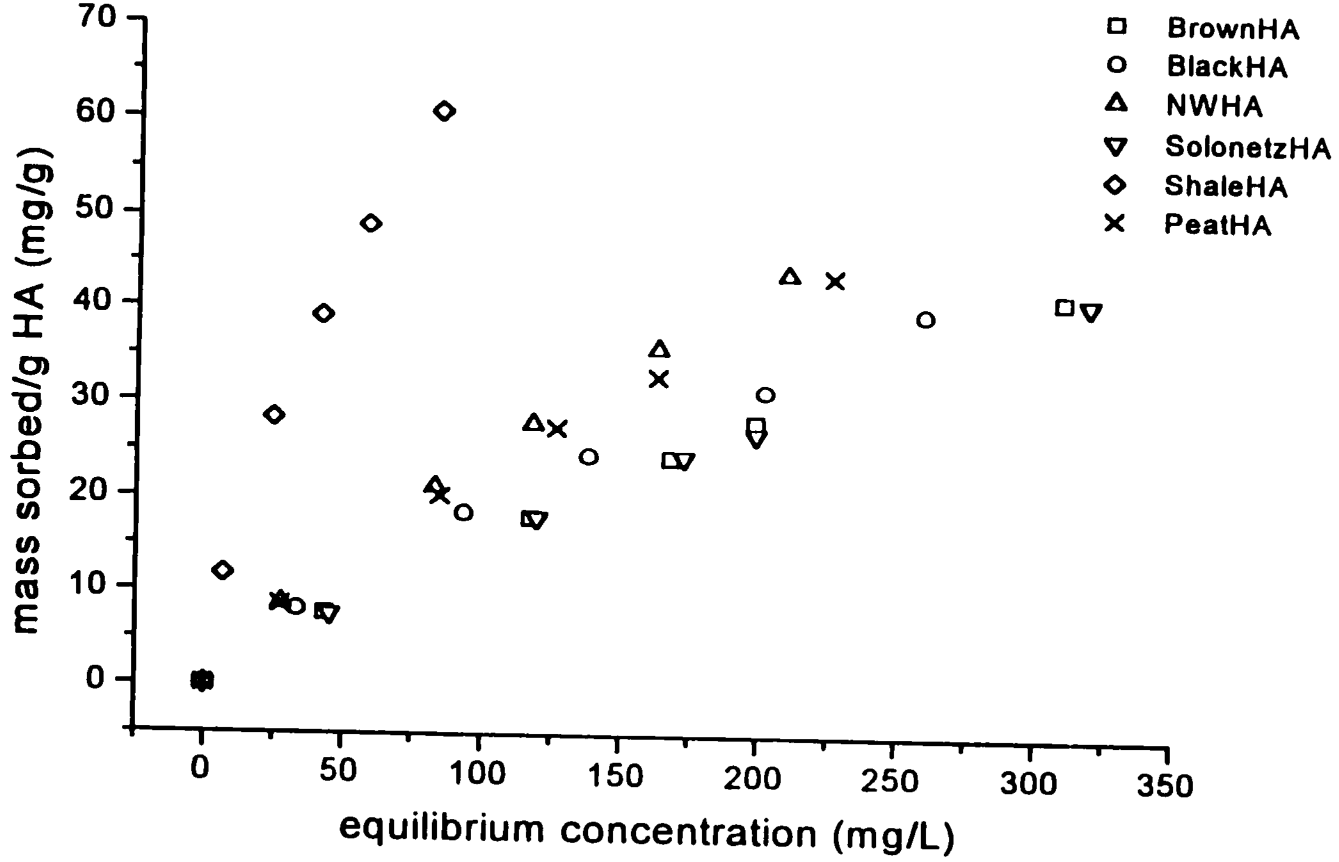

Figure 4-2: 1-naphthol sorption to humic acids

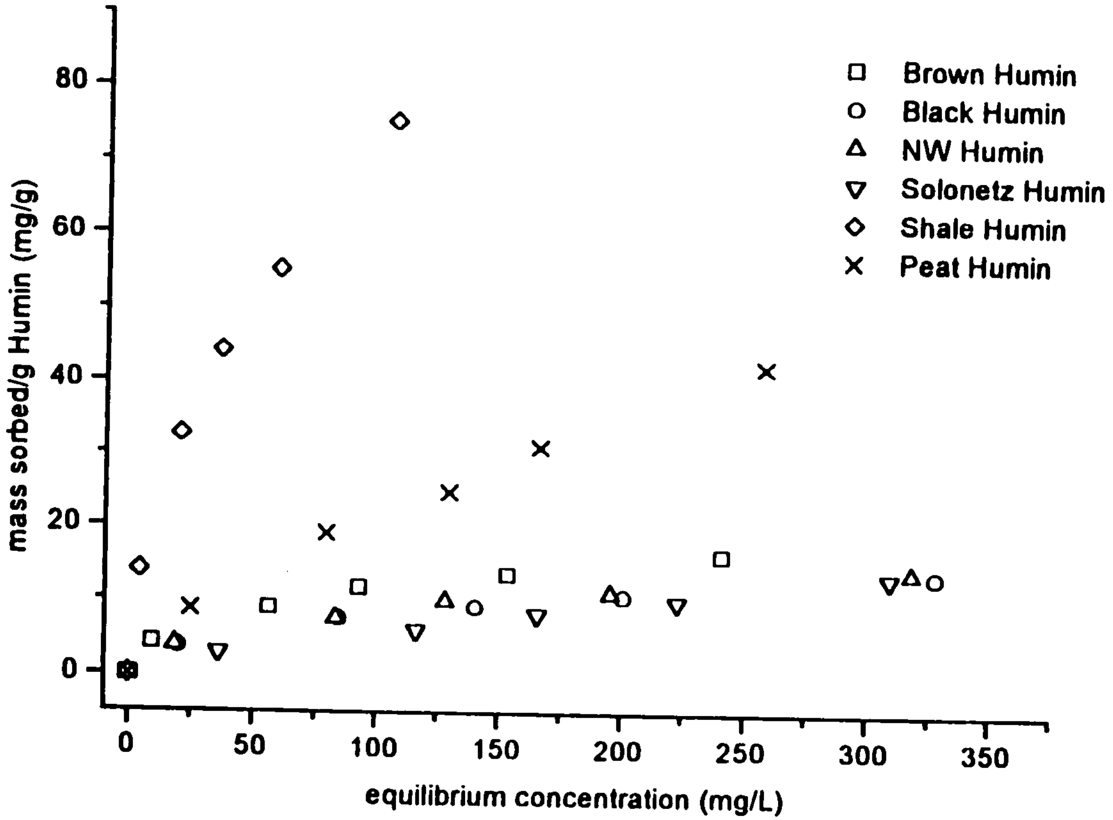

Figure 4-3: 1-naphthol sorption to humin

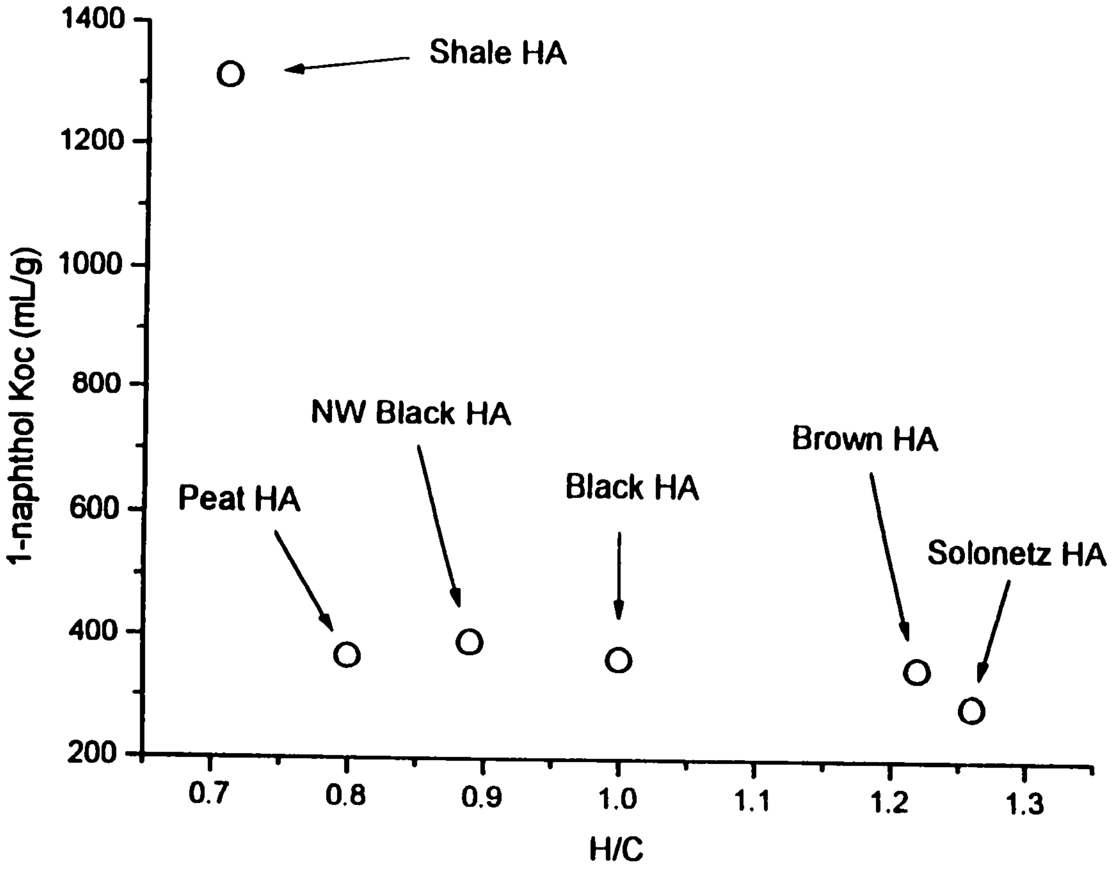

Figure 4-4: Comparison of 1-naphthol sorption coefficients to humic acid H/C ratios

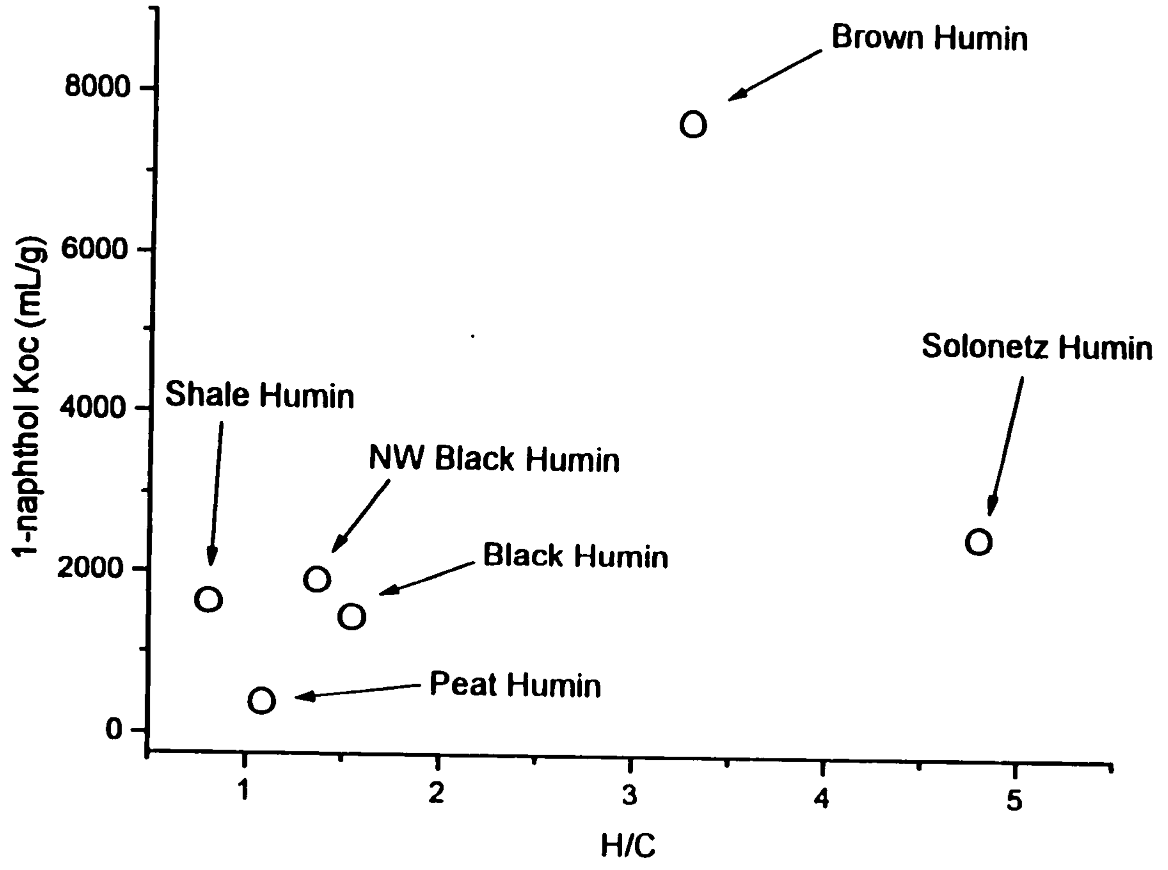

Figure 4-5: Comparison of 1-naphthol sorption coefficients to humin H/C ratios

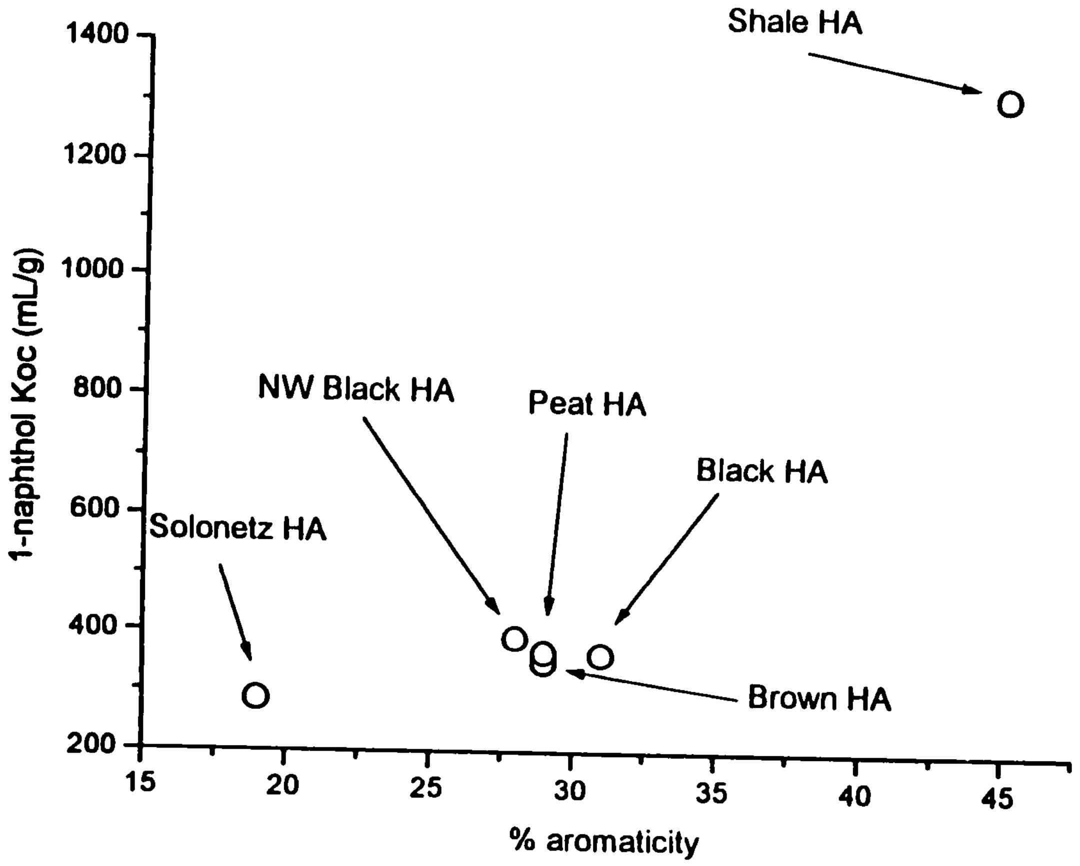

Figure 4-6: Correlation between 1-naphthol K_{oc} values and aromaticity defined by CPMAS ^{13}C NMR

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CHAPTER 5[1]

1-NAPHTHOL SORPTION TO MINERAL-BOUND ORGANIC MATTER AND REEVALUATION OF TOTAL ORGANIC CARBON NORMALIZED SORPTION

INTRODUCTION

Sorption of hydrophobic organic chemicals in soils and geologic materials is of growing concern due to the strong affinity of these compounds to soil colloids, and the potential risks associated with their long term persistence in the environment. The contaminant-soil interaction hinders different forms of remediation or combinations of physical, chemical and biological remedial technologies. Hence, understanding contaminant sorption is vital in the improvement of our ability to remedy areas contaminated with organic chemicals. It is accepted that sorbent characteristics are key in advancing our current understanding of the contaminant-soil interaction. Our comprehension has grown from relating sorption to carbon quantity (Karickhoff *et al.*, 1979) to the realization that carbon quality, as determined by organic matter diagenesis, are important considerations (Xing *et al.* 1994; Luthy *et al.*, 1997; Kleineidam, *et al.*, 1999). Recent studies (Jones and Tiller, 1999; Chapters 3 and 4) have suggested that the physical conformation or molecular geometry of mineral-bound organic matter also contributes to the extent of contaminant sorption.

The sole association of hydrophobic organic contaminants with organic matter in the environment has placed significant emphasis on understanding humic material structure and function. It is well documented that solution conditions such as ionic strength, pH and electrolyte cation valence can manipulate the organization of humic material in solution (Ghosh, and Schnitzer, 1980; Schlautman and Morgan, 1993; Murphy *et al.*, 1994). At high ionic strength and low pH values, humic materials adopt a "coiled" configuration because the negative charge of the humic functional groups are neutralized by the cations. Alternatively, an "open" structure is the result of charge repulsion from

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M. J. Salloum, M. J. Dudas, and W. B. McGill

conditions of low solution ionic strength, and high pH. Depending on the solution conditions, humic materials appear to accept an "open" or closed" geometry on the surface of the mineral, as suggested by the variation in contaminant sorption values (Murphy *et al.*, 1994; Jones and Tiller, 1999).

Previously, it has been hypothesized that fractionation of organic matter into fulvic acid, humic acid and humin fractions causes changes in organic matter molecular geometry because in most instances, the 1-naphthol K_{oc} values were greater for the fractions than the whole soil (Chapters 3 and 4). These findings suggest that the fractionation procedure exposed more favorable, or simply more sorption sites and hence the degree of surface accessible carbon, rather than total carbon, is an important consideration in contaminant sorption. To further explore this concept, the 1-naphthol data from prior investigations were analyzed in a mass balance approach. This calculation is based on the carbon distribution of the whole sample amongst its fractions and the amount of 1-naphthol sorbed by each fraction. Furthermore, using different solution conditions, I attempted to alter the organic matter molecular geometry of two sets of colloids. The objectives were: 1) determine if 1-naphthol sorption of the whole sample could be calculated from the sorption values of the fractions and 2) determine if mineral-bound organic matter molecular geometry can be manipulated by different electrolyte cations and ionic strength values.

MATERIALS AND METHODS

Mass Balance Approach

The studies reported in Chapters 3 and 4 concluded that organic matter molecular geometry contributes to 1-naphthol sorption in soil and geologic samples. In this examination, the uptake of 1-naphthol by whole samples and constituents thereof was measured. It is accepted that nonionic organic chemical sorption is directly proportional to the amount of organic carbon in the sample (Luthy *et al.*, 1997) and the main mechanism of sorption is proposed to be through partitioning (Chiou, 1989). Therefore, based on the relative carbon distribution amongst the fractions, the sorption coefficient for the whole sample can be predicted based on the amount of 1-naphthol sorbed to each of the fractions. Hence, the 1-naphthol organic carbon normalized sorption coefficient (K_{oc}) for the whole sample can be predicted from:

$$K_{oc,sample} = K_{oc,humin} X_{humin} + K_{oc,HA} X_{HA} + K_{oc,FA} X_{FA} \qquad (5\text{-}1)$$

where X represents the fraction of carbon in that isolate. I do not have the 1-naphthol K_{oc} data for the fulvic acid fraction, which constitutes a minor portion of the total organic carbon content, therefore, this term was excluded in this calculation.

Sorbents

Previous reports have concluded, using constructed organo-mineral complexes, that physical conformation of the mineral bound organic matter is a determinant in contaminant sorption (Murphy *et al.* 1994; Jones and Tiller, 1999). In this study, I chose to use organo-mineral complexes isolated from soil samples rather than fabricate some from humic materials and clay minerals. The organic-mineral complexes were fractionated from a young, organic matter rich surface soil sample (Black Chernozemic) whose characteristics are reported in Chapter 3. The soil sample was air dried, and passed through a 2mm sieve prior to the procedure. The fine fraction was isolated by dispersing the whole sample by sonification (de Kimpe, 1993), and fractionating the different particle sizes, using Stokes Law and gravity sedimentation techniques (Genrich and Bremner, 1972). The fine fraction (< 2 μm in size) was collected, then saturated with 0.1M $CaCl_2$ and centrifuged (15 000 x g). The colloids were then rinsed repeatedly with deionized water until excess salts could no longer be detected with silver nitrate. The sample was freeze-dried, and ground to pass a 106 μm sieve for sorption experiments. The Black Chernozemic fine fraction is abbreviated as BCFF.

The second sorbent used was a Shale humin sample. The weathered, Cretaceous age black Shale sample properties are reported in Chapter 3 and the humin fraction was obtained as described in Chapter 4. The Shale sample was mixed with 0.1M NaOH under a nitrogen atmosphere for approximately 20 hours. The solids and liquids were separated by centrifugation (4000 x g), the supernatant was acid treated to separate the humic and fulvic acids, and the remaining solids were subjected to the extraction procedure. This cycle was repeated until the supernatant was colorless. The remaining material contained mineral-bound organic matter that was not 0.1M NaOH extractable and is defined as the humin fraction. The humin fraction was then saturated with 0.1M $CaCl_2$, rinsed repeatedly with deionized water until excess salts were no longer detected with silver nitrate. The humin was then freeze-dried and ground to pass a 106 µm sieve for sorption experiments.

C, H, N, and ash content

C, H, and N content was measured using an EA 1108 elemental analyzer (Carlo Erba Instruments) in the Department of Chemistry, University of Alberta for the Shale humin sample. The Shale humin and BCFF samples were freeze-dried for 48 hours prior to elemental analysis. Ash content was determined from mass lost after heating at 750°C, until a constant mass was obtained.

Sorption Experiments

Prior to the addition of 1-naphthol, the sorbents were equilibrated with different electrolyte cations and ionic strength conditions. The four background electrolyte solutions included: NaCl at ionic strengths of 0.01M (Na low) and 0.1M (Na high) and $CaCl_2$ at ionic strengths of 0.01M (Ca low) and 0.1M (Ca high). In addition, the solutions contained 10^{-4} M $HgCl_2$ to inhibit microbial activity. The sorbents were weighed into 16 x 100 mm KIMAX® test tubes along with 5 glass beads (6mm in diameter) to facilitate mixing. The soil to solution ratio was such that 20-80% of the 1-naphthol was taken up by the sorbent (on a mass to volume basis: 1 to 150 for Shale humin and 1 to 40 for BCFF). The test tubes were filled to minimum headspace with the respective electrolytes and the samples were mixed on a rotating shaker (20 rpm) for 24 hours. The tubes were then centrifuged at 1000 x g for 30 minutes and the supernatant removed. This procedure was repeated two more times prior to the addition of 1-naphthol solutions.

1-naphthol (99%+) and 1-naphthol-1-^{14}C (7.7mCi/mmol) were purchased from Sigma Chemical Co. and used as received. Analysis of the 1-naphthol by Gas Chromatography with Flame Ionization Detection did not reveal the presence of impurities. 1-naphthol and 1-naphthol-1-^{14}C were prepared in the different electrolyte solutions (0.01 M NaCl, 0.1 M NaCl, 0.01 M $CaCl_2$, 0.1 M $CaCl_2$) that included 10^{-4} M of $HgCl_2$ to prevent biological degradation of the sorbate. For the Shale humin, solutions contained total 1-naphthol concentrations of 100 to 600 mg/L labeled with an activity of 100 Bq mL^{-1} (~6000 dpm). For the BCFF, a one point equilibration was performed and the initial 1-naphthol concentration was 275 ppm. The 1-naphthol solutions were added to the test tubes previously equilibrated with the same background electrolyte and were then sealed with a PTFE lined screw cap. The samples were placed on a rotating shaker (20 rpm) and mixed for 48 hours at room temperature (22°C ± 1°C). The samples were then removed from the shaker, and centrifuged at 1000 x g for 30 minutes. A 1 or 2 mL aliquot was removed from the supernatant and placed in a 20 mL glass scintillation vial containing 10 mL of Optiphase 'Hisafe3' Scintillation cocktail (Fisher Scientific) and counted on a Packard Tricarb® 2000CA Liquid Scintillation Analyzer. Reports from the literature (Xing *et al.*, 1994 and Chen *et al.*, 1996) and preliminary tests confirmed that 1-naphthol did not sorb to the test tubes. Hence, all sorbate losses from solution were attributed to 1-naphthol sorption to the sample, and sorption was therefore calculated from the change in solution ^{14}C activity.

Sorption Coefficients

Linear sorption coefficients were calculated using the slope of the initial concentration versus equilibrium concentration curve as described in Chapter 3. The sorption coefficient (K_d) obtained from this method, was then used to calculate the K_{oc} from $K_{oc} = K_d/f_{oc}$ (Karickhoff *et al.*, 1979).

Regression Analyses and Isotherm Model Fitting

Linear regression analysis ($p \leq 0.05$) for the K_d determination was performed using Origin™ version 4.1. The 1-naphthol sorption isotherms are non linear, therefore we elected to determine the most suitable isotherm model for the sorption data. We applied: 1) the linear model ($x/m = K_{Linear}\, C_e$) where x/m represents the quantity of 1-naphthol sorbed per mass sorbent (mg/g), C_e is the 1-naphthol concentration at apparent equilibrium (mg/L), and K_{Linear} (L/g) is a constant whose value depends on the sorbate-sorbent affinity; 2) the Freundlich model ($x/m = K_{Freundlich}\, C_e^{1/n}$) where x/m and Ce are the same as the linear model and $K_{Freundlich}$ (L/g) and 1/n (dimensionless) are constants; and 3) the Langmuir equation ($x/m = K_{Langmuir}\, b\, C_e / (1 + K_{Langmuir}\, C_e)$) where x/m and C_e are the same as in 1), $K_{Langmuir}$ is a constant related to binding energy (L/g) and, b is the maximum sorption quantity (mg/g). All isotherm curve fitting was accomplished using Origin™ version 4.1 ($p \leq 0.05$). A model discrimination test was used to select the model that best justifies the data (Robinson, 1985). This entailed calculating an F statistic from the difference of the residual sum of squares (RSS) between the two models divided by the residual mean square (RMS) of the model with the lowest RMS (Robinson, 1985). The calculated F values were compared to tabular F values at $p \leq 0.01$ with 1 and n-p degrees of freedom, where n is the number of observations and p is the number of parameters in the nonlinear model. If the difference between the calculated F value and the tabulated F value is negative, then the use of the nonlinear model is not justified by the data (Robinson, 1985).

RESULTS

Mass Balance Approach

The distribution of the total carbon for a number of soil/geologic samples amongst its fractions is listed in Table 5-1 The majority of the carbon resided in the humin fraction, especially in the older samples such as the Shale. The Solonetz soil sample also has the majority of its carbon in the humin fraction. These soils develop over saline parent materials, thus, are subjected to large inputs of naturally occurring salts (Agriculture

Canada Expert Committee on Soil Survey, 1987). Consequently, the pH values are in the alkaline range and much of the organic matter is translocated into the horizons below. In the Black, Brown, Nonwettable Black and Peat samples, the majority of carbon is localized in the humin fraction, but to a much lesser extent than in the Shale and Solonetz samples.

Using equation 5-1, 1-naphthol K_{oc} values for the whole sample were generated from the relative carbon distribution and the 1-naphthol K_{oc} values from the humic acid and humin. Table 5-2 lists the 1-naphthol K_{oc} values for: the fractions, that produced by equation 5-1, and that measured for the whole, unfractionated sample. With the exception of the Peat sample, there is a large difference between the 1-naphthol K_{oc} values calculated and with that measured. With some samples, such as the Brown and Solonetz soil samples, the predicted value is several fold higher than that measured. The Black and Nonwettable Black soil samples also have predicted values that well surpass those measured directly.

Sorbent Properties

The properties of the BCFF and Shale Humin are listed in Table 5-3 The BCFF is directly isolated from a mineral soil sample and the Shale humin is a fraction from a geologic material that is rich in condensed, aged, organic matter (Chapter 3). These two samples represent two extremes with respect to organo-mineral complex content. The Shale humin sample has a low ash content and is predominantly organic in composition. Alternatively, the BCFF sample is higher in ash content than the Shale humin, hence the mineral phase is more abundant in this sample.

Sorption Coefficients

The 1-naphthol K_{oc} values for the BCFF and Shale humin samples are presented in Table 5-4. The BCFF K_{oc} values are based on a one point isotherm ($n = 3$), hence, the absence of a linear regression correlation coefficient. Complete isotherms were obtained for the Shale humin samples ($n = 15$). The Shale humin 1-naphthol K_{oc} value is much higher than the BCFF and is likely due to the different diagenic properties of these samples

(Grathwohl 1990; Kleineidam *et al.*, 1999; Chapter 3). More noteworthy are the meager differences between the 1-naphthol K_{oc} values among the different electrolyte cations and ionic strength values. On a log basis, these differences are barely discernible (Table 5-4).

Sorption Isotherms

The linear sorption model as described in Chapter 3 was used because this is a simple model that facilitates comparisons among sorbents. However, the linear regression correlation coefficients were lower than unity, therefore, other isotherm models were employed to better interpret the data. The linear, Freundlich, and Langmuir models were used to fit the data, and all are popular methods of describing xenobiotic and soil/geologic material interactions. Using the model discrimination test, the difference in F statistic values (calculated F and tabular F) calculated for the Langmuir model were all negative (data not shown), an indication that the use of this model would not be justified by the data. Alternatively, the difference in F statistic values for the Freundlich model were positive (Table 5-5), supporting the use of this equation for the sorption data. The linear and Freundlich isotherm parameters are listed in Table 5-5 and for comparison, data from Chapter 3 that examined 1-naphthol sorption to Shale humin that did not involved any electrolyte/ionic strength pre-equilibration are included.

The Freundlich parameters are similar for 1-naphthol sorption to Shale Humin despite equilibration with electrolyte cations at different ionic strengths. These conditions did not result in different isotherm parameters for Ca low, Ca high, Na low and Na high variations. In previous studies, changes in surface accessible carbon were monitored using 1-naphthol sorption (Chapters 3 and 4). Hence, changes in the colloidal surface properties were indirectly monitored by the difference of 1-naphthol sorbed by the fractionated organic material relative to that of the whole sample. Consequently, the similarity between the 1-naphthol sorption isotherm parameters imply that mineral-bound organic matter was not manipulated by solution chemistry. Furthermore, the isotherm parameters from the sorption experiment with the shale humin that did not include any electrolyte/ionic strength pre-equilibration are different than those obtained with a pre-equilibration. As apparent in Figure 5-1, the Ca low, Ca high, Na low and Na high pre-equilibration resulted in a decrease in 1-naphthol sorption compared to the sample that was not pre-equilibrated with any solution.

DISCUSSION

Earlier work (Chapters 3 and 4) suggested that chemical data are insufficient for explaining the observed 1-naphthol K_{oc} values for a variety of soil and geologic materials and suggested that the organic matter molecular geometry contributed to 1-naphthol sorption behavior. The calculated values, based on the 1-naphthol uptake of the fractions, were greater than the measured 1-naphthol uptake values of the whole sample and supports the molecular geometry hypothesis. The sum of the parts exceeded that of the whole implying that accessible carbon, rather than total carbon governs the extent of sorption. Laor *et al.* (1998) observed that humic acid phenanthrene K_{oc} values decreased when that humic acid was associated with a mineral phase. Increases in contaminant K_{oc} for organic matter fractions have been noted elsewhere in the literature (Nearpass, 1976; Garbarini and Lion, 1985; Chen *et al.* 1996) and indicate that contaminant accessibility, in cooperation with chemical data are important considerations in contaminant sorption.

Only the Peat sample yielded satisfactory agreement between the calculated and measured 1-naphthol values. This sample is low in organo-mineral content as indicated by an ash content of 13.4%. The presence of a predominant organic matter phase along with the good agreement between the calculated and measured values, suggest that carbon based sorption was the sole mechanism of 1-naphthol uptake in this sample. The other samples included in this computation increase in ash content in the following order: Shale < Nonwettable Black < Black < Solonetz < Brown. The difference between the calculated and measured values increases in a similar manner as the disagreement is greatest for the two soil samples that contain the most minerals and least in organic carbon. These trends suggest that the mineral phase plays an important, indirect role in 1-naphthol sorption as the mineral phase will dictate the concentration and microscale architecture of surface accessible organic matter. Organic matter can bond to minerals in various forms resulting in many distinct organo-mineral complexes (Garbarini and Lion, 1986). It has also been suggested that the number of organic matter attachment sites on the mineral surface will dictate the configuration of the humic material on the mineral surface (Murphy *et al.*, 1990).

Solution induced changes in humic material organization, and subsequent changes of contaminant K_{oc} values have been reported (Schlautman and Morgan, 1993; Engebretson and von Wandruszka, 1994). Ionic strength, electrolyte cation valence and pH have been reported to manifest the conformation of humic materials during binding to clay minerals, consequently producing a variation in contaminant K_{oc} values (Murphy *et al.*, 1994; Laor *et al.*, 1998; Jones and Tiller, 1999). Jones and Tiller (1999) reported that the phenanthrene K_{oc} for humic acid increased as electrolyte cation valence decreased. They suggested that polyvalent cations could behave as a bridge and condense the humic acid structure. Yet, the manipulation of mineral-bound organic matter using different ionic strength and electrolyte cations, as measured by 1-naphthol sorption, did not produce a change in molecular geometry. The variation in solution conditions did not produce prevalent changes in 1-naphthol sorption values. This suggests that mineral-bound organic matter is inflexible, at least through changes in solution conditions.

These data are consistent with studies involving enzyme and polymer binding to minerals. Once sorbed to the surface of a mineral, enzymes often become inactive. The inactivity is believed to be due to "microenvironmental effects" on the enzyme (Boyd and Mortland, 1990). Bound enzyme inactivity is presumed to occur due to the steric hindrance of the active site, imposed through mineral binding. Some suggest that long, multi-segmented polymers that are normally flexible in solution, become attached to minerals via numerous segment-surface bonds (Theng, 1982). Organic matter macromolecules adsorbing from solution uncoil (Collins *et al.*, 1995) as this conformational change is a net interaction energy gain and results in a highly stable organo-mineral complex (Shevchenko and Bailey, 1998). Adsorption of organic matter is described to be competitive and selective as sorption of large molecular weight polymers is favored (Podoll *et al.*, 1987). Each segment individually interacts with the mineral surface and the other adsorbed segments to form a contiguous series of "tails" and "loops" (Theng, 1982; Collins *et al.*, 1995). Larger polymers will have more of their segments in "loops" and consequently, a greater adsorbed mass than smaller sorbed polymers (Podoll *et al.*, 1987). This process is illustrated in Figure 5-2. Some suggest that the "world" of adsorbed organic matter to be strictly two dimensional (Collins, *et al.*, 1995). Hence, there is evidence that mineral-bound organic matter is inflexible and is consistent with the inability to alter the molecular geometry of mineral-bound organic matter through solution conditions reported here.

The comparison of the 1-naphthol sorption data from Chapter 4 and those reported here reveal that 1-naphthol sorption decreased when the Shale humin was subjected to rinses with different electrolyte cations and ionic strength conditions. This decrease in sorption was similar for all the electrolyte cation/ionic strength variations. The non linearity of the isotherms imply a competitive sorption process (Xing *et al.*, 1996). The discrete differences amongst the Freundlich isotherm parameters imply that water is the likely competitor for 1-naphthol in this system, for the different cations/ionic strength combinations did not produce major differences in the Freundlich sorption parameters. Therefore, the pre-equilibration failed to promote detectable changes in organic matter molecular geometry and subsequently induce a more competitive sorption environment for 1-naphthol.

Solution conditions were unable to manipulate mineral-bound organic matter molecular geometry, however, the mass balance results agree with the suggestion that accessible carbon, rather than total carbon, governs sorption. Evidently, one must go beyond chemical characterization as more emphasis must be placed on the physical arrangement as it is the combination of the chemical and physical properties that appear to govern sorption. The same solution conditions used by Murphy *et al.* (1994) and Jones and Tiller (1999) were employed here, yet a difference in 1-naphthol K_{oc} values was not observed. Nonetheless, there is ample evidence to support the molecular geometry hypothesis, however, it is unclear as to what factor, or combination of factors governs organic matter molecular geometry in soil and geologic samples. Hence, more emphasis should be placed on organo-mineral complexes for chemical data alone can not sufficiently predict sorption behavior.

Table 5-1: Carbon distribution among the FA, HA and Humin fractions

Soil/Geologic Sample	Relative distribution of carbon as		
	fulvic acid	humic acid	Humin
Black	11	34	55
Brown	19	17	64
Nonwettable Black	10	37	53
Peat	12	30	58
Shale	4	4	92
Solonetz	3	3	94

Table 5-2 Comparison of measured 1-naphthol K_{oc} values and those predicted from 1-naphthol uptake by the fractions for a variety of soil and geologic samples

Sample	HA K_{oc} [a]	Humin K_{oc} [a]	measured K_{oc} [b]	Predicted K_{oc} from eqn (5-1)
Black	363	1430	250	910
Brown	348	7660	656	4960
Nonwettable Black	390	1895	219	1150
Peat	366	387	301	334
Shale	1310	1620	1070	1540
Solonetz	286	2510	634	2370

a = from Chapter 4
b = from Chapter 3

Table 5-3: BCFF and Shale humin properties

Sample	C (g/100g)	H (g/100g)	N (g/100g)	Ash (g/100g)
BCFF	6.79	1.25	0.70	82.9
Shale humin	53.8[a]	3.67[a]	1.24[a]	20.2[a]

a = from Chapter 4
BCFF = Black Chernozemic Fine Fraction

Table 5-4: 1-naphthol K_{oc} values for BCFF and Shale humin under different electrolyte conditions

	1-naphthol K_{oc} value (mL/g)			log 1-naphthol K_{oc}	
	BCFF	Shale humin	Shale humin r^2	BCFF	Shale humin
Ca low (0.01M)	449	1090	0.957	2.65	3.04
Ca high (0.1M)	411	1190	0.966	2.61	3.08
Na low (0.01M)	430	1030	0.961	2.63	3.01
Na high (0.1M)	448	1240	0.957	2.65	3.09

note: Black Chernozemic Fine Fraction (BCFF) K_{oc} values are calculated from a single sample analyzed in triplicate

Table 5-5: Isotherm parameters for 1-naphthol sorption to Shale humin

	K_{Linear} (mL/g)	linear r^2	$K_{Freundlich}$ (mL/g)	1/n	Freundlich r^2	(F calc - F table)[b]
no pre-equilibration[a]	818[a]	0.927	6950	0.510	0.999	5970
Ca low	560	0.925	5320	0.553	0.996	1430
Ca high	614	0.936	4950	0.551	0.995	746
Na low	533	0.929	4830	0.536	0.996	1250
Na high	648	0.944	5050	0.553	0.999	5280

a = data from Chapter 4

b = a positive difference between calculated F and tabular F that the Freundlich model is justified by the data

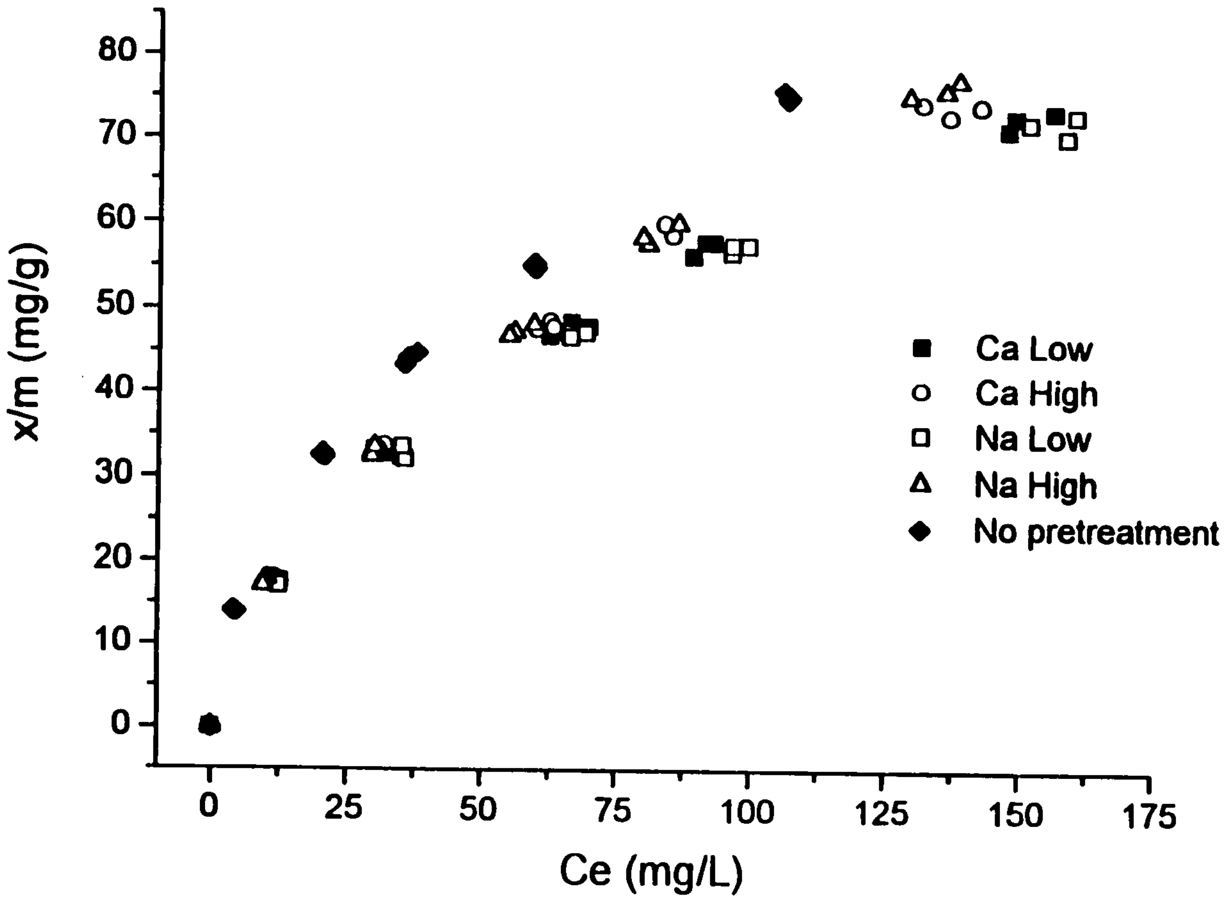

Figure 5-1: 1-naphthol sorption to shale humin under varying electrolyte types and ionic strength values, as well as without any pretreatment

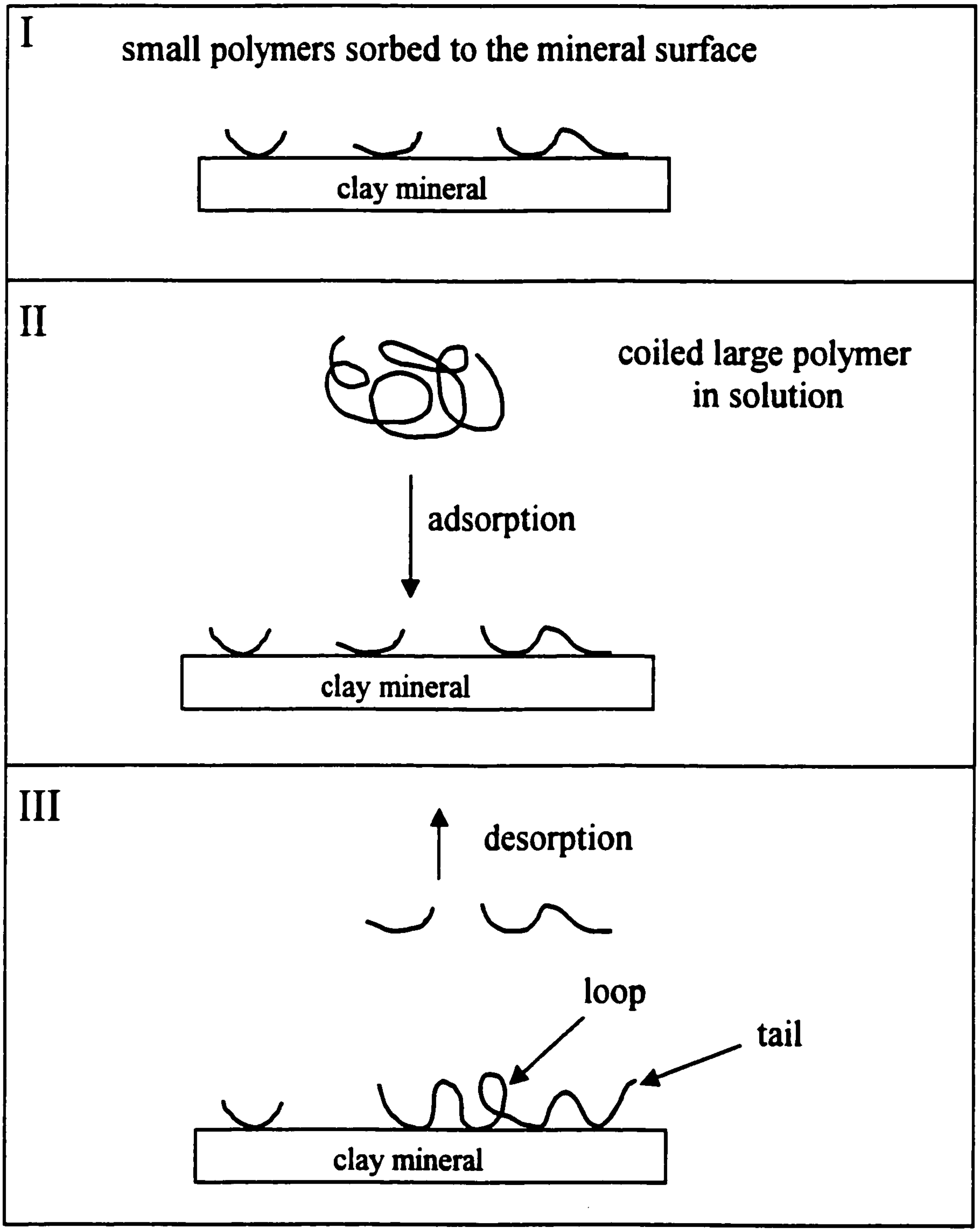

Figure 5-2: Illustration of large polymer coatings on clay minerals. Large polymers are selectively adsorbed by clay minerals, displacing smaller polymers. Large polymers uncoil to form "loops" and "tails" on the surface of the mineral. Adapted from: Theng, (1982) and Collins *et al.* (1995)

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CHAPTER 6
CONCLUSIONS AND SYNTHESIS

Throughout my dissertation, I focused on sorption of organic compounds to soil and geologic samples. This entailed the inclusion of several sorbents, ranging from pure montmorillonite to humin; as well as sorbates such as Triton X-100 and 1-naphthol. The main objective throughout this work was to identify and investigate soil components, such as clay or organic matter content, that could be used as a predictive tool for the extent of sorption. This endeavor led to the use of many sophisticated techniques, such as X-Ray Diffraction and CPMAS ^{13}C NMR but despite the use of these methods, I could not correlate the amount of sorption to a single soil characteristic. I have however, suggested a "new" soil characteristic, organic matter molecular geometry, that encompasses both clay and organic matter as an integral unit, rather than separate entities. This is how they exist in the soil environment, therefore, this is how we should recognize them during scientific research.

SUMMARY

Surfactant and soil interactions

The interest in using surfactant soil washing as a remedial method led to the fundamental investigation of surfactant sorption to soil and soil constituents. The soil samples selected included those with different diagenic properties, as well as, variations in mineralogical and organic matter content. This set of samples proved to represent a large range of soil properties and consequently, was used throughout my dissertation research. The surfactants included in the study had the ability to enhance the aqueous solubility of hydrophobic organic contaminants (Edwards *et al.*, 1991; Rouse *et al.*, 1993). Dowfax 8390, did not react with any of the soil/geologic samples, suggesting that it may be an ideal surfactant for use in larger scale studies. The initial results with Triton X-100 guided the inclusion of two clay minerals as the high uptake of Triton X-100 by the Solonetzic sample suggested a strong interaction between this surfactant and smectite minerals. Further support for including pure minerals in this study was due to an increase in Triton

X-100 sorption when the organic matter of the Black Chernozemic sample was removed. The subset of experiments with the surfactants and pure minerals reinforced the conclusion that Triton X-100 was intercalating with montmorillonite. This aided in the interpretation with the mineral soils, however, the strong sorptive affinity of Triton X-100 for the Shale sample was the first suggestion that this interaction went beyond the straightforward, clay-ethoxylate tail interaction. By definition, surfactants contain both hydrophobic and hydrophilic groups, thus contributing to their success in many applications (Attwood and Florence, 1983). Their nature put forward another sorption interaction, namely one between the organic matter component and the hydrophobic group of the surfactant. Prior to this experiment, there had been two views in the literature: one that correlated ethoxylate surfactant sorption to organic matter content (Urano *et al.*, 1984, Liu *et al.*, 1992) and another that suggested the clay fraction was a better variable for correlation of ethoxylate surfactant sorption to soil samples (Cano and Dorn, 1996a; 1996b). The conclusions from Chapter 2 state that neither soil attribute alone is sufficient for determining the extent of ethoxylate surfactant sorption to soil and geologic samples.

1-naphthol sorption to soil and geologic samples and organic matter fractions thereof

Work described in Chapter 3 was initiated to characterize the soil and geologic samples and to expand upon the work of Xing *et al.* (1994a) and Chen *et al.* (1996). The poor correlation between the chemical and sorption data promoted a focus on this topic for the remainder of my dissertation research. The objective was to chemically define the organic matter of an independent set of soil and geologic samples for future desorption studies. The poor relationship between the 1-naphthol K_{oc} values and the % aromaticity disagreed with the findings of my predecessors. There was concern regarding the use of chemical techniques on mineral soils, hence, the subsequent examination of the organic matter fractions in Chapter 4. The conclusions from Chapter 3 were that another factor, proposed to be organic matter molecular geometry, was governing 1-naphthol sorption.

There is evidence to support the organic matter molecular geometry hypothesis in the literature for model organic sorbents (Xing *et al.*, 1994b; Murphy *et al.*, 1994; Jones and

Tiller, 1999) however, to my knowledge, it has not been discussed with regards to soil or geologic samples. The continuation of this experiment (Chapter 4) reaffirmed the conclusions made in Chapter 3. I had more confidence in the chemical data for the humic acids because of the removal of the majority of the mineral phase during the extraction procedure. Despite the improvement of sample conditions, there was still poor agreement between the H/C, CPMAS ^{13}C NMR and 1-naphthol sorption data. The similar 1-naphthol values of the Peat HA, Black HA, and Brown HA contradicted the obvious differences in their H/C ratios and carbon character as revealed by CPMAS ^{13}C NMR. Furthermore, the H/C values and CPMAS ^{13}C NMR spectra for the Shale and Shale HA are very similar, however, their 1-naphthol values are notably different. The large ΔK_{oc} values for the humin samples also suggested a reorganization of surface accessible carbon.

The elemental and CPMAS ^{13}C NMR measure the total sample. Alternatively, 1-naphthol is a surface reaction, therefore, the likely explanation for the contradiction of the results obtained from the methods employed is that the chemical data examine whole carbon and the sorption data is dependent on accessible carbon. The combined data from Chapters 3 and 4 imply that organic matter molecular geometry, the physical arrangement of organic matter at the solid-liquid interface, governs 1-naphthol sorption.

The mass balance calculation in Chapter 5 undeniably supports this hypothesis as the "sum of the parts" exceeded the "whole". If organic carbon based partitioning is the true mechanism for sorption, then there should have been good agreement between the measured values and those calculated. This was not the case. These results further promote the organic matter molecular geometry hypothesis and suggest that accessible carbon, rather than total carbon is a better indicator for contaminant sorption.

1-naphthol sorption to mineral-bound organic matter

The molecular geometry of humic materials in solution is reported to be manipulated through solution conditions (Schlautman and Morgan, 1993; Ragle *et al.*, 1997 ;Clapp *et al.*, 1997). Furthermore, Murphy *et al.* (1994) and Jones and Tiller (1999) reported that solution conditions can determine the physical conformation of humic material during sorption to mineral surfaces, and is manifested in contaminant K_{oc} values. To investigate if mineral-bound organic matter molecular geometry could be modified, I subjected two different types of colloids to different electrolyte cations and ionic strength conditions, followed by the same 1-naphthol sorption procedure previously used.

The results indicate that mineral-bound organic matter was inflexible, as the 1-naphthol K_{oc} values within a group of sorbents, did not differ. Furthermore, the non linearity of the isotherms suggested that the sorptive process was competitive, and a comparison with the 1-naphthol sorption data from Chapter 4 confirmed that the sorbent pre-equilibration resulted in a decrease in 1-naphthol sorption, thus supporting the notion of a competitive sorption process. From these data, I speculate that water was competing with 1-naphthol, as this was the only major difference between the sorption experiments in Chapters 4 and 5. If the cations were competing with 1-naphthol, then there would have been greater differences between the sorption values. The conclusions from this chapter provided an important "negative" result as this type of investigation is unique and suggests that mineral-bound humic materials are inflexible.

ADVANCEMENT OF KNOWLEDGE

The growing need to understand contaminant sorption and the application of new remedial methods in the soil environment has motivated many scientists to elucidate the underlying mechanisms that are occurring. This usually entails the suggestion of a predictive or correlative empirical relationship based on a single or combination of soil and/or sorbent properties. Throughout my dissertation, I tested the concepts put forth by others and reevaluated some correlations that have been suggested in the literature.

Surfactants have the ability to facilitate remediation of hydrophobic organic compounds. Alkyl ethoxylate surfactants, such as Triton X-100, have received most of the consideration because of their ability to enhance the normally low, aqueous solubility of hydrophobic organic contaminants (Kile and Chiou, 1989; Edwards *et al.*, 1991). Little attention has been given to interactions between soil colloids and surfactants, despite that this interaction may economically prohibit the application of this technique at the pilot or field scale. The conclusions from Chapter 2 indicate that previous correlations made with clay and organic matter content are unacceptable as these two parameters, could not individually account for the surfactant uptake. The strong interaction between montmorillonite and Triton X-100 supported conclusions made by others (Cano and Dorn, 1996a; 1996b). The high sorptive affinity for the Shale sample suggested the prominence of another interaction occurring, namely sorption via hydrophobic groups, rather than the ethoxylate tail - montmorillonite interaction identified earlier. It was concluded that soil properties are not exclusive with respect to ethoxylated surfactant sorption and that it appears to be a combination of these properties that would better suit correlative purposes. This was also the first suggestion that organo-mineral complexes deserved more attention than had been given in the past.

The desire to characterize the organic matter of the samples I had collected led to a continuation of the work started by Xing (1994). He had suggested indirect methods for determining the effective polarity index of soil samples using empirical equations. The inputs for these equations included the percentage of aromaticity as determined from a CPMAS ^{13}C NMR spectrum and the cross-correlation technique using the K_{oc} value of *o*-xylene. Chen *et al.* (1996) expanded on this and provided similar equations for determining polarity index using CPMAS ^{13}C NMR or the K_{oc} value of 1-naphthol. Using these variables (aromaticity and 1-naphthol K_{oc}), I set out to determine the polarity index of an independent set of soil and geologic samples. The initial contradiction between the chemical and sorption methods suggested another contributor to 1-naphthol sorption (Chapter 3). Subsequent studies in Chapter 4 and the mass balance data from Chapter 5 strongly support the organic matter molecular geometry hypothesis, first suggested in Chapter 3. The application of solution conditions reported to change the microorganization of humic materials in solution, did not produce changes in mineral-bound organic matter (Chapter 5).

This dissertation lends a great deal to our current approach in sorption and organic matter studies. During my time as a Ph.D. candidate, I had the opportunity to interact with many scientists from around the world by attending different conferences. Initially, I was astounded at the number of research programs that focused on the extraction, purification and detailed chemical characterization studies of humic materials. The obvious and important question that came to my mind was: how representative are these fractions (fulvic acids, humic acids and humin) to their source material? Many scientists are proceeding in the pursuit of complete characterization of extracted and purified organic materials and it seems to me, that the purpose of all this work has been missed somewhere during the evolution of the humic sciences. I realize that the application of some techniques require pure fractions and components but the mass balance results from Chapter 5 indicate that one can not describe the whole by examining the sum of the parts.

The use of pure and well characterized organic components has spilled over into those in the sorption arena. This pursuit is worthy as some important findings using polymer science techniques have facilitated new hypotheses regarding the overall sorption process. The results from Chapters 3, 4 and 5 suggest that in cooperation with pure organic matter sorbents, we also must examine the role of the organo-mineral complex. The indirect contribution of the mineral fraction lends an entire new way of describing sorption in soils and geologic materials. Furthermore, the inability for chemical data to predict sorption behavior also suggests that the sorption group of scientists must look beyond the chemical data and include some physical investigations. It appears that it is a combination of the chemical and physical properties that are governing sorption in soils and geologic materials, and this is the main contribution that my dissertation research has provided.

FUTURE RESEARCH

The conclusions made in this thesis have contributed new knowledge to my area of research and it also advises new directions to further our understanding as questions often arise from the hypotheses that are supported or negated, as well as the presentation of new theories. The obvious question is what, or what series of factors determine the geometry of mineral-bound organic matter? This is an important consideration as the general conclusion from Chapters 2 through 5 indicate that it is the organo-mineral complex that is the main factor governing sorption processes in soils and geologic materials.

Humic material molecular geometry has been manipulated in laboratory conditions (Murphy *et al.*, 1994; Jones and Tiller, 1999) prior to mineral binding but after this interaction has occurred, the same means could not manipulate the geometry of mineral-bound organic matter (Chapter 5). The major difference between these two studies was in the nature of the colloids used. Murphy *et al.* (1994) and Jones and Tiller (1999) manufactured their organo-mineral complexes and those used in Chapter 5, were isolated from soil/geologic samples. The inflexibility of the isolated colloids suggests that some other environmental factors, such as those involved in soil development, life and weathering, would dictate organic matter molecular geometry. If one can identify these factors, organic matter molecular geometry manipulations may be used to conceal or release contaminants into the environment.

The equilibration time in all of these studies were short (48 hours) and did not address sorption kinetics or reversibility. This reaction time was longer than required for the system to reach apparent equilibrium, however, did not address long term sorption. There may be a correlation between organic matter molecular geometry and the sorptive reversibility of contaminants. Guthrie *et al.* (1999) reported that pyrene was encapsulated by organic matter in laboratory studies that spanned 60 days and was protected from being exhaustively extracted with a series of solvents. Consequently, sorption kinetics and organic matter molecular geometry deserve to be studied in tandem, to enhance current remediation strategies.

I have suggested that organic matter molecular geometry be used as a variable in future studies, but I have neglected to suggest a method for this investigation. Minerals currently interfere with organic matter measurements. Conversely, organic matter intervenes in the detailed measurements performed on soil minerals. There exists two independent groups of scientists: those in clay mineralogy who remove the organic matter and those in the humic sciences that strictly work with ash free, organic materials. Consequently, organo-mineral complexes are usually not studied and one can not directly measure organic matter molecular geometry. These two bodies of scientist must be united as the expertise of both is required to improve the knowledge of organo-mineral complexes and the sorption of components to these minerals. In 1936, S. A. Waksman stated "the various chemical formulae suggested at different times for the "humic acids" were, for the most part, hypothetical in nature". I would contend that chemical structure of humic materials to be "hypothetical", as they consist of well defined functional groups, but the manner by which that humic material coats a mineral should be the focus of research to come.

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APPENDIX A - EXAMPLE CALCULATIONS

1. normalized ΔCMC (mole surfactant/g sorbent)

ΔCMC values were converted to units of mole surfactant/g sorbent to facilitate comparison among samples. For instance, the ΔCMC of the Black Chernozemic soil sample is 4.31×10^{-4} mol/L. This batch equilibration used 45 mL of surfactant and 0.44 g of soil sample (oven-dry basis). Therefore:

$$\Delta\text{CMC} = (4.31 \times 10^{-4}\ \text{mol/L})(0.045\ \text{L})(0.44\ \text{g})^{-1} = 4.4 \times 10^{-5}\ \text{mol surf/g sorbent}$$

2. Ash content

Ash content was calculated using the following equation:

$$\text{ash (\%)} = \frac{100\% \times \text{sample weight after heating at 750°C}}{\text{sample weight after heating at 105°C for 24 hours}} \qquad \text{(A-1)}$$

3. Relative distribution of carbon character as determined by CPMAS ^{13}C NMR

The following chemical shift ranges were used: 0-106 ppm (aliphatic-C), 106-165 ppm (aromatic-C), and 165-230 ppm (carboxyl-C and carbonyl-C). The area of these chemical shift ranges was measured on the spectrum. The relative percent distribution was determined from:

$$\text{\% aromatic-C} = \frac{100\% \times \text{area of 106-165 ppm region}}{\text{total area of the 0-230 ppm region}} \qquad \text{(A-2)}$$

4. x/m

x = (mass of solute taken up by the sorbent)

x = (C_o - C_e)(volume added in the batch equilibration)

m = oven dry mass (g) of the sorbent

12 mL of a 100 mg/L 1-naphthol solution was added to 0.35 g of air-dried soil. After 48 hours, C_e was 60 mg/L. Oven dry weight was measured to be: 4.5% by mass.

$$x = (100\ \text{mg/L} - 60\ \text{mg/L})(12\ \text{mL})(1\ \text{L}/1000\ \text{mL}) = 0.48\ \text{mg}$$

$$m = (0.35\ \text{g}) - (0.35\ \text{g})(4.5\%/100\%) = 0.334\ \text{g}$$

$$x/m = 0.48\ \text{mg}/0.334\ \text{g} = 1.44\ \text{mg/g}$$

5. K_d and K_{oc}

Equation 3-4 from Chapter 3 was used to calculate K_d. The slope of the C_o versus C_e curve yielded the value of K_d.

For example, the plot of C_o versus C_e for 1-naphthol that had been reacted with the Black Chernozemic soil sample, provided a slope of 0.728. Equation 3-4 states:

$$C_e = \frac{C_o}{K_d(mass/volume)+1} \qquad (3\text{-}4)$$

Rearranging yields: $$K_d = \left(slope^{-1} - 1\right)\left(\frac{volume}{mass}\right) \qquad (A\text{-}3)$$

The volume used in the batch equilibration was 12 mL, the oven dry soil mass was 0.328 g. K_d was calculated to be: 13.66 mL/g

Percentage of organic carbon was measured to be 5.47. Therefore, $f_{oc} = 0.0547$. K_{oc} is calculated using equation 3-5 (Chapter 3). For this example:

$$K_{oc} = (13.66\ \text{mL/g})/0.0547 = 249.73\ \text{mL/g} = 250\ \text{mL/g}$$

6. Calculation of ΔK_{oc}

Equation 4-1 (Chapter 4) states:

$$\Delta K_{oc} = K_{oc}(fraction) - K_{oc}(source) \tag{4-1}$$

For the Black Chernozemic sample: K_{oc} (source) = 250 mL/g

K_{oc} (humin) = 1430 mL/g

K_{oc} (HA) = 363 mL/g

Applying equation 4-1 yields: ΔK_{oc} (humin) = (1430-250) mL/g = 1180 mL/g

ΔK_{oc} (HA) = (363-250) mL/g = 113 mL/g

APPENDIX B – CPMAS ^{13}C NMR SPECTRA OF WHOLE SOIL SAMPLES

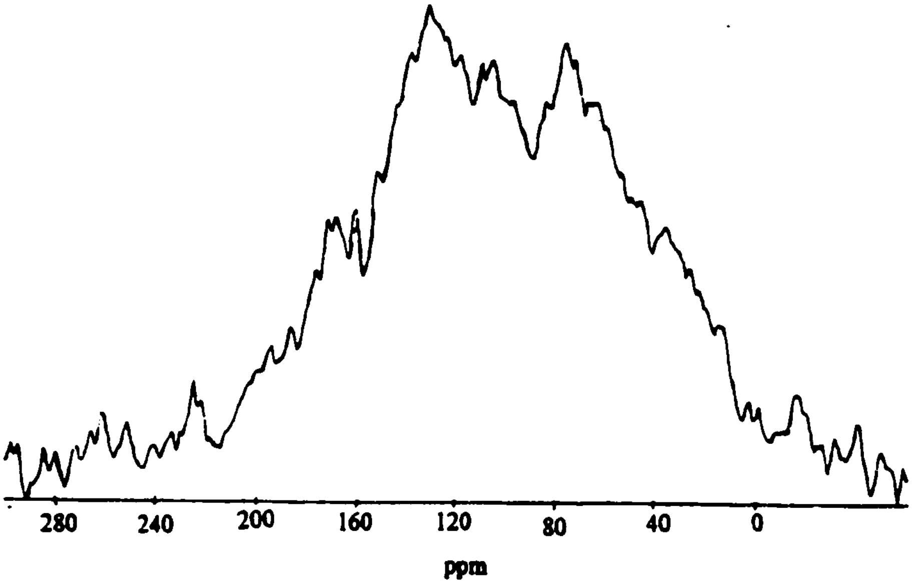

Figure B-1: CPMAS ^{13}C NMR spectrum of the Black Chernozemic Soil Sample

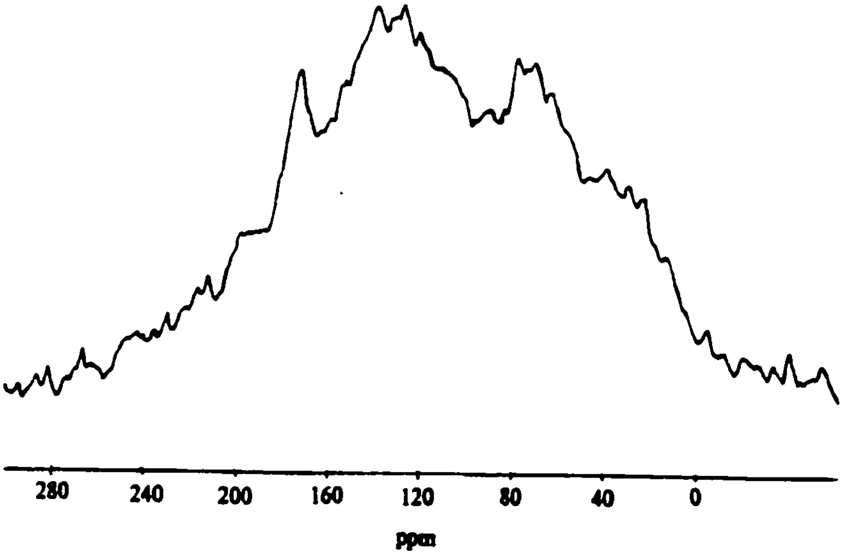

Figure B-2: CPMAS ^{13}C NMR spectrum of the Brown Chernozemic Soil Sample

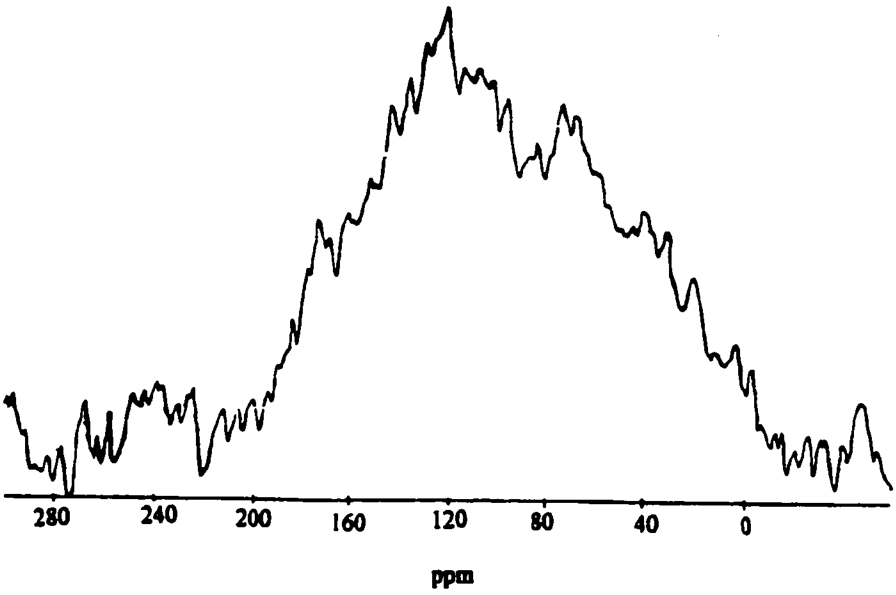

Figure B-3: CPMAS ^{13}C NMR spectrum of the Black Solonetzic Soil Sample