Wastewater Contaminant Sorption and Dissolved Organic Matter Characterization

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
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Irrigation using reclaimed wastewater can introduce organic contaminants and dissolved organic matter (DOM) to soils. Sorption of three common organic wastewater contaminants to five soils of diverse organic matter composition was studied both before and after the removal of soil carbohydrate and peptide components using acid hydrolysis. Results suggest that these polar components may block organic contaminants from accessing higher affinity sorption sites in soil organic matter. The sorptive fractionation of DOM by three mineral soils was studied to assess the terrestrial fate of this complex environmental matrix. Carboxyl- and aromatic-containing moieties appear to preferentially and reversibly sorb to mineral soils. Conversely, carbohydrate and peptide components of DOM preferentially remain in the aqueous phase while aliphatic moieties were selectively retained only by a soil with high surface area. This thesis illustrates that reclaimed wastewater should be applied to soils cautiously as it may degrade soil and groundwater quality.
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Chapter 1: Introduction

1.1 Overview

The central focus of this thesis is an examination of the terrestrial fate of model components of reclaimed wastewater, namely organic contaminants and dissolved organic matter (DOM). Organic contaminants have been reported to sorb strongly to soil organic matter (OM) through several types of interactions and the quantification of contaminant sorption to soils can be achieved using several established mathematical relationships to provide insight into sorption mechanisms. Several properties of soil OM have been proposed to regulate the extent of contaminant sorption, including the amount and structure of soil organic carbon (OC) in addition to the physical conformation and accessibility of high affinity sorption sites in soil OM. The principal site of DOM sorption in soil is the exposed and reactive surfaces of clay minerals which may interact with several types of functional groups in DOM. Multiple analytical techniques can be used to characterize soil and DOM samples, including nuclear magnetic resonance (NMR) spectroscopy which provides structural information about both solid and soluble components in these samples. As a result of their potential to lower soil and water quality, the sorption behaviour of organic contaminants and DOM in soils requires closer examination to further elucidate their terrestrial fate.

1.2 Reclaimed Wastewater

Reclaimed wastewater is defined as water that has undergone primary wastewater treatment but is still non-potable for human consumption due to the potential presence of high concentrations of nitrogen and phosphorus, organic contaminants such as pharmaceuticals and pesticides as well as DOM.\(^1\)\(^-\)\(^4\) The use of reclaimed wastewater for agricultural irrigation purposes reduces the demand for potable water\(^1\) and is a common practice in countries where
water shortages arise regularly, including Japan, China, Spain, Israel and the United States. However, organic contaminants and DOM within reclaimed wastewater can alter soil chemistry. For example, organic contaminants can bind strongly or irreversibly to soil OM, resulting in long-term soil contamination. Consequently, organic contaminants such as pharmaceuticals have been detected in fields after irrigation with reclaimed wastewater. DOM components of wastewater have been reported to bind strongly to clay minerals in soils in addition to sorbing and potentially transporting organic contaminants. Therefore, understanding soil-contaminant and soil-DOM interactions is critical to understanding the environmental fate of wastewater components and for guiding wastewater management practices.

1.3 Soil Organic Matter

Soil OM is a complex and heterogeneous mixture of transformed and decomposing molecules from plant and microbial sources in addition to anthropogenic inputs such as organic pollutants and biochar. Soil OM contains the largest pool of carbon on Earth and therefore plays a key role in global carbon cycling. Several different classes of compounds comprise soil OM including carbohydrates, peptides, fatty acids, plant waxes and hydrocarbons. As such, soil OM is composed of numerous types of functionalized carbon including alkyl, O-alkyl, anomeric, phenolic, aromatic, carboxyl and carbonyl groups. The abundance of organic functional groups in OM which can favourably interact with organic compounds has resulted in soil OM serving as the primary sorption domain for organic contaminants in soils when the soil OC content is greater than 0.1%. Consequently, strong or irreversible binding of organic contaminants to soil OM may hinder contaminant degradation and remediation processes, resulting in prolonged soil contamination. As such, the affinity of organic contaminant sorption to soils with varying OM
properties requires close examination to determine both the extent and mechanisms of contaminant binding.

1.4 Sorption of Organic Contaminants to Soils

1.4.1 Sorption Mechanisms

Sorption is a general term that describes the movement of a molecule from an aqueous phase to a solid phase. In the context of this thesis, sorption refers to the binding of organic molecules to OM and minerals within soil.\textsuperscript{18} As shown in Figure 1-1,\textsuperscript{19} sorption of organic compounds to soil can occur via several types of binding interactions. Physical phase partitioning involves the transfer or sequestration of a compound from the aqueous phase to the interior of soil OM and is based on hydrophobicity rather than a specific interaction. Chemical sorption includes mechanisms such as surface adsorption and covalent bonds between organic functional groups as well as electrostatic interactions between charged species. Given the diverse range of functional groups that may be present both within organic compounds and on the surface of soil OM, organic contaminant sorption to soil may involve multiple mechanisms occurring simultaneously.\textsuperscript{18,19}

1.4.2 Sorption Isotherm Models

The affinity of organic contaminant sorption to soil is commonly measured using batch equilibration sorption experiments.\textsuperscript{20-25} This technique involves the controlled mixing of soils and aqueous solutions of contaminants for a pre-determined period of time after which the analyte concentrations in the aqueous phase in the presence and absence of soil are quantified. The difference between these values is the solid phase contaminant concentration and is used to infer the extent of binding.\textsuperscript{26} Sorption data are presented in graphs called isotherms where the
solid-phase contaminant concentration is plotted against the aqueous-phase contaminant concentration and the resulting data points are then fitted to established mathematical models. Commonly used isotherm models for organic contaminant sorption to soil OM include the Freundlich, linear and Langmuir models.\textsuperscript{18} The Freundlich and linear isotherm models do not predict a maximum sorption value whereas the Langmuir model assumes monolayer coverage and thus a maximal amount of sorbate that can be bound.\textsuperscript{18} Since the isotherm models will be applied to organic contaminant sorption to soil OM, which has a high sorption capacity for organic contaminants,\textsuperscript{20,26,27} only the Freundlich and linear isotherm models are discussed herein. The Freundlich isotherm model is a nonlinear model of the form: \( \frac{x}{m} = K_F C_e^n \) where \( \frac{x}{m} \) is the equilibrium solid-phase contaminant concentration (in mg/g), \( K_F \) is the Freundlich distribution coefficient (in (mg/g)/(mg/mL)\(^n\)), \( C_e \) is the aqueous-phase contaminant concentration at equilibrium (in mg/mL) and \( n \) is a unitless nonlinearity coefficient which measures deviations from linear sorption behaviour.\textsuperscript{18,26} Freundlich distribution coefficients provide an indication of the extent of contaminant binding. However, comparisons of \( K_F \) values are not valid for soil-contaminant systems with non-identical \( n \) values. Therefore, sorption data are often fitted to the linear isotherm model in which an \( n \) value of unity is assumed. The simpler linear model takes the following form: \( \frac{x}{m} = K_d C_e \) where \( K_d \) is the linear distribution coefficient (in mL/g). This isotherm model assumes a direct linear relationship between the solid and aqueous phase contaminant concentrations which are related by a constant distribution coefficient.\textsuperscript{18} If the OC content of the soil is known, inter-soil comparisons can be achieved by normalizing the linear distribution coefficient to the fraction of soil OC (\( f_{OC} \), where: \( f_{OC} = \% \text{ OC}/100\% \)). This generates an organic carbon-normalized distribution coefficient (\( K_{OC} \), in mL/g, where: \( K_{OC} = K_d/f_{OC} \)).
1.5 Organic Matter Properties Governing Organic Contaminant Sorption

1.5.1 Quantity of Organic Carbon

Several soil OM properties may govern the sorption behaviour of organic contaminants in soil. First, the affinity of contaminant sorption may be directly controlled by the quantity of soil OC. For example, a study that examined naphthalene sorption to five soils reported that sorption generally increased with increasing soil OC content. This is consistent with observations that soil OM has a high sorption capacity for organic compounds that is often modelled well by the linear isotherm model, especially for OM-rich soils. In this model, sorption affinity increases with increasing aqueous contaminant concentration, suggesting that there is no saturation limit or maximum concentration of contaminant that can sorb. For example, peat soils often have very high OC content and therefore many favourable binding sites for organic contaminants. However, other qualitative OM properties such as the OM structure and physical conformation of sorption domains may also play a role in organic contaminant sorption.

1.5.2 Soil Organic Carbon Structure

The structure of OC in soils refers to the relative abundances of major classes of carbon such as alkyl, O-alkyl, aromatic, carboxyl and carbonyl carbon. Studies have examined correlations between $K_{OC}$ values and the relative abundances of the major types of OC in soils as determined by solid-state $^{13}$C NMR spectroscopy. These correlations were constructed to establish whether specific soil OC properties can predict the sorption behaviour of an organic compound in soil. However, correlations have only been examined for a few selected contaminants, in particular model organic contaminants such as polycyclic aromatic hydrocarbons. For example, Chefetz and Xing correlated phenanthrene $K_{OC}$ values with
sorbent aliphaticity and aromaticity using data from multiple published reports. As shown in Figure 1-2, weak correlations were observed between these variables, suggesting that soil OC structure alone cannot fully account for variations in phenanthrene sorption behaviour. However, other studies have found moderate correlations between organic contaminant sorption affinity and soil aromatic and O-alkyl carbon content using small data sets. Since limited published data is available for many common organic contaminants, the generation of similar experimental data sets is necessary to create accurate predictive models of the sorptive fate of organic contaminants in soil.

1.5.3 Organic Matter Physical Conformation and Binding Site Accessibility

The physical conformation of OM refers to the spatial arrangement and accessibility of domains which may change depending on environmental conditions. For example, Murphy et al. reported that the physical conformation of peat humic acid changed from a coiled to an elongated structure after the solution ionic strength and dominant cation were altered. Several studies have reported that the physical conformation of OM plays a key role in organic contaminant sorption since alterations to the spatial arrangement of OM domains via chemical fractionation resulted in changes in soil sorption capacity for organic contaminants. For example, Bonin and Simpson reported that phenanthrene sorbed more strongly to humin and humic acid fractions of whole soils than the original sample. The increase in sorption affinity was attributed to a reorganization of the OM in the samples which may have opened up more favourable phenanthrene sorption sites. Similarly, Salloum et al. observed higher 1-naphthol sorption to humic acid and humin compared to source soil samples and this was attributed to changes in binding site accessibility upon OM physical conformational changes. Furthermore,
Pan et al.\textsuperscript{35} observed different degrees of phenanthrene sorption to dissolved humic acids compared to the solid humic acid samples from which the dissolved samples were derived.

The physical conformation of OM domains may directly govern the accessibility of OM sorption sites through both organo-mineral and OM-OM interactions.\textsuperscript{21} For example, the selective removal of soil lipids has been shown to increase the sorption capacity of soils for polycyclic aromatic hydrocarbons.\textsuperscript{32,39} These studies suggest that lipids physically block higher affinity sorption sites in OM which are opened up after lipid extraction. In addition, two studies demonstrated that the removal of clay minerals from soils and soil fractions via hydrofluoric acid treatment resulted in higher phenanthrene sorption affinity.\textsuperscript{20,21} Furthermore, Ahangar et al.\textsuperscript{20} reported large increases in $K_{OC}$ values when both lipid extraction and hydrofluoric acid treatments were applied to soil samples (see Figure 1-3\textsuperscript{20}). These studies suggest that organo-mineral and OM-OM interactions result in the physical blocking of preferential binding sites in OM which were inaccessible to contaminants until the OM conformation was altered. Furthermore, Simpson et al.\textsuperscript{23} showed that phenanthrene $K_{OC}$ values increased when $O$-alkyl components of humic acids such as carbohydrates and peptides were removed by strong acid hydrolysis. This suggests that polar $O$-alkyl components at the soil-aqueous interface\textsuperscript{40} may also block contaminants from accessing high affinity sorption sites in soil OM. However, the specific role of $O$-alkyl components in sorption blocking has not been assessed for contaminant sorption to whole soils.

1.6 Dissolved Organic Matter

1.6.1 Structural Complexity and Characterization

DOM is a complex mixture of water-soluble organic compounds from decaying plants, microbes and anthropogenic sources that is found throughout terrestrial and aquatic
environments as well as in rainwater. DOM is a major source of OC in aquatic ecosystems and its mineralization provides a source of atmospheric carbon dioxide in the global carbon cycle. Due to its inherent structural complexity, DOM is operationally defined as soluble organic molecules of varying structure which pass through a 0.22 or 0.45 μm filter. Although DOM and soil OM are both heterogeneous environmental organic matrices, they are distinct in that DOM components are fully soluble whereas soil OM is composed of both insoluble and soluble material. Therefore, DOM is generally more mobile than soil OM and may percolate downward through soil horizons with the flow of water.

Despite the fact that DOM likely contains a myriad of different compounds, several analytical techniques can be used to characterize DOM components. For example, fluorescence spectroscopy can provide structural information about DOM such as inputs from protein-, microbial- and humic-like constituents, while Fourier-transform ion cyclotron resonance can be used to calculate molar masses of possible DOM components. Detailed structural information about functional groups that are present in DOM samples can be obtained using infrared spectroscopy and it has been established that DOM contains abundant carboxyl, aromatic and phenolic moieties.

### 1.6.2 Interactions with Organic Contaminants and Soils

Organic contaminants in aqueous solution sorb to DOM and could therefore be transported into soil along with DOM when reclaimed wastewater is applied. For example, Huang and Lee reported that the herbicide chlorpyrifos sorbed strongly to DOM and reduced its sorption affinity for soil thus increasing the potential mobility of this contaminant in soil. In addition, Wu et al. reported enhanced phenanthrene sorption to montmorillonite in the presence of DOM via the formation of organo-clay complexes. Furthermore, DOM sorption to clay
minerals in soils with low OC content may increase the soil sorption capacity by increasing the total soil OC content. As such, DOM may play a key role in organic contaminant sorption and transport in soil systems.

Previous studies have established that the primary sorption domain for DOM in soil is the reactive surfaces of secondary clay minerals. For example, several studies have reported strong sorption of DOM to amorphous clay minerals such as iron and aluminum oxides as well as crystalline clay minerals such as kaolinite and montmorillonite. However, many clay surfaces in upper soil horizons are already coated with OM and thus are not accessible for DOM binding. Therefore, DOM may leach into deeper subsoil horizons which have a greater abundance of exposed clay mineral surfaces that are available for DOM sorption. Lower mineral soil horizons may therefore serve as the primary sorption domain for DOM in terrestrial environments. Indeed, several studies have reported the strong sorption of DOM from different environments to mineral soil surfaces by utilizing a number of advanced analytical methods. However, techniques that are commonly used to characterize DOM are biased toward specific functional groups. For example, fluorescence spectroscopy selectively detects only chromophoric aromatic and phenolic DOM components. In addition, infrared spectroscopy provides information about dipolar functionalities in DOM such as phenolic and carboxylic moieties. Both of these analytical techniques provide limited information about the structure of aliphatic DOM constituents. Consequently, sorptive interactions between DOM components and mineral soils require investigation using a non-selective approach to gain additional information about the selectivity and reversibility of DOM binding to these soils.
1.7 Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy is an analytical technique based on the alignment of the nuclear spin of atoms within a strong magnetic field and the subsequent perturbation of this alignment via the application of a radiofrequency pulse.\textsuperscript{71} NMR spectroscopy is a powerful, non-destructive and non-selective tool for elucidating the chemical structures of organic molecules and is an emerging technique in environmental analytical chemistry.\textsuperscript{72} Solid-state $^{13}$C and solution-state NMR spectroscopy experiments can provide insight into the structure of soil and DOM samples, thus they are the two types of NMR spectroscopy techniques which are discussed herein.

1.7.1 Solid-state $^{13}$C NMR Spectroscopy

Solid-state $^{13}$C NMR spectroscopy is used to characterize carbon-containing solid materials such as soil OM.\textsuperscript{21,25,33,34,73,74} Functional groups in soil OM are known to resonate in specific regions of the $^{13}$C NMR spectrum (see Figure 1-4\textsuperscript{15}). This includes classes of OC such as alkyl, O-alkyl, anomeric, aromatic, phenolic, carboxyl and carbonyl carbon. The heterogeneity of environmental samples such as soils coupled with the rigidity of atoms in the solid-state results in strong dipolar coupling between adjacent $^{13}$C atoms and thus broad spectral peak shapes. Improved resolution of soil OM components can be achieved by spinning samples at the magic angle of 54.74° with respect to the external magnetic field.\textsuperscript{72} Accurate quantitative analysis of the distribution of types of soil OC in the solid-state can be obtained by direct polarization of the $^{13}$C nucleus using Bloch decay $^{13}$C NMR spectroscopy.\textsuperscript{75-79} However, this technique requires very long experiment times due to the long $T_1$ relaxation time and low natural abundance of the $^{13}$C nucleus (1.13%). As such, a technique known as ramped-amplitude Cross-Polarization Magic Angle Spinning (CP-MAS) $^{13}$C NMR spectroscopy can be used in which magnetization is transferred to $^{13}$C atoms via protons. $^{13}$C CP-MAS NMR depends only on the relaxation time of
the $^1$H nucleus which is much shorter than for the $^{13}$C nucleus. Therefore, $^{13}$C CP-MAS NMR allows for spectral acquisition in less time and with greater sensitivity than direct polarization experiments. In addition, $^{13}$C CP-MAS NMR has been shown to give quantitatively reliable integration values for OM components that are within 5% error of the values obtained by direct polarization of the $^{13}$C nucleus.

1.7.2 Solution-state NMR Spectroscopy

Solution-state NMR spectroscopy techniques can be used to identify specific functional groups and molecules within purely dissolved samples such as soil extracts and DOM. A common issue with solution-state $^1$H NMR techniques is the resonance for water which occurs at ~4.8 ppm when deuterium oxide is used as a solvent or when a sample contains residual water. This signal can dominate the spectrum and prevent the identification of signals from other compounds that resonate within that region, such as carbohydrates. This issue can be overcome via the use of water suppression pulse programs such as Presaturation Utilizing Relaxation Gradients and Echoes (PURGE). Both the high sensitivity of the $^1$H nucleus coupled with water suppression techniques provide the spectral resolution needed to assign functional groups within soil OM and also to identify individual molecules in DOM. In addition, other solution-state NMR experiments can be used to further elucidate the composition of complex environmental samples such as soil OM and DOM. For example, diffusion-edited $^1$H NMR spectroscopy attenuates the signals from small molecules in solution, allowing for the investigation of signals from larger aggregates and macromolecules. Furthermore, compound identification is assisted by two-dimensional NMR techniques such as correlation spectroscopy (COSY) and heteronuclear single quantum coherence (HSQC). COSY provides information about proton-proton coupling on adjacent carbon atoms while HSQC is a powerful structural elucidation
experiment that shows the direct connectivity of protons and carbon atoms.\textsuperscript{72} In addition, advanced software can match NMR peak patterns and chemical shift values with databases of standards in order to identify specific compounds.\textsuperscript{82}

1.8 Thesis Objectives

Soil OM exhibits a diverse array of properties such as carbon structure, polarity and spatial conformation, all of which may govern organic contaminant sorption behaviour.\textsuperscript{21,25,27,29,34,35} In particular, the accessibility of binding sites has emerged as a crucial soil OM quality that may exert great control on contaminant sorption.\textsuperscript{20,34,35} For example, soil $O$-alkyl components are polar and prevalent at the soil surface\textsuperscript{40} and may therefore block contaminant access to high affinity sorption sites below the soil-water interface, possibly via the repulsion of organic contaminants or the preferential sorption of water molecules. Currently, the role of these $O$-alkyl soil components in sorption processes is unclear and warrants closer examination.

Published studies that have correlated organic contaminant sorption affinity data with soil carbon structure have mainly focussed on model contaminants such as polycyclic aromatic hydrocarbons.\textsuperscript{17,22,27,83} Common contaminants that have received less attention include pesticides and herbicides as well as pharmaceuticals, personal care products, and by-products of manufacturing.\textsuperscript{20,25,84-87} As the global population rises, these compounds will be needed in increasingly greater quantities for agricultural and personal uses, likely increasing their presence and concentrations in wastewater and the environment in general. Therefore, additional studies are necessary to generate larger data sets for the sorption of common organic wastewater contaminants to soils, including sorption to soils with diverse OM composition. Such data would assist with the development of predictive models of contaminant sorption affinity across multiple
soil types from a variety of geographic locations. In addition, many studies have concentrated on correlations between contaminant sorption affinity and soil alkyl and aromatic carbon composition as determined using solid-state $^{13}$C NMR spectroscopy.$^{25,27,88}$ However, relationships between organic wastewater contaminant sorption affinity and the $O$-alkyl carbon content of soils$^{6,33}$ should also be examined since these polar components may play a key role in regulating contaminant sorption due to their presence at the soil surface.$^{40}$

In addition to organic contaminants, reclaimed wastewater may also introduce DOM into soil. The structural complexity of DOM has limited its detailed characterization; however, previous studies have demonstrated that advanced analytical techniques can be used to elucidate both the major classes of compounds as well as individual molecules that are present in DOM. For example, Woods et al.$^{52,89}$ illustrated that DOM can be separated into fractions using chromatographic techniques such as size-exclusion and hydrophilic interaction chromatography. Subsequently, the structural complexity of the DOM samples was simplified enough to permit the identification of specific molecules using multidimensional solution-state $^1$H NMR spectroscopy experiments. A previous study has shown that DOM is selectively fractionated via interactions with mineral soils and the extent of fractionation is sufficient to allow for an assessment of the changes in the abundance of specific classes of compounds.$^{56}$ However, the data obtained using infrared spectroscopy in this published study did not provide quantitative information about the relative changes in the distribution of major DOM components and individual molecules could not be detected.$^{56}$ As such, the application of solution-state $^1$H NMR spectroscopy to the study of DOM fractionation may provide a more quantitative measure of the extent and reversibility of DOM sorption to mineral soils.

The application of reclaimed wastewater to soil for agricultural irrigation purposes is an increasingly common practice in arid countries that experience groundwater shortages. However,
this practice may ultimately lower soil quality through the introduction of both organic contaminants and DOM into terrestrial environments. To better understand the terrestrial fate of these two important aspects of wastewater, this thesis examines interactions between organic contaminants and DOM in soils. The first study examines organic wastewater contaminant sorption to untreated and structurally modified soils while the second project involves the characterization of DOM samples after fractionation by sorptive interactions with mineral soils.

The specific objectives of this thesis are as follows:

1. To determine the affinity and mechanism of sorption of the common organic wastewater contaminants atrazine, bisphenol A and diuron to untreated and acid-hydrolyzed soils of varying OM composition using batch equilibration sorption experiments.

2. To characterize five soils before and after acid hydrolysis using solid-state $^{13}$C CP-MAS NMR spectroscopy to examine structural differences in soil OC composition.

3. To examine correlations between organic contaminant sorption affinity and soil carbon structure as a potential method of predicting sorption affinity across multiple soils.

4. To quantitatively assess the role of soil $O$-alkyl components in blocking organic contaminants from accessing high affinity sorption sites in soil OM.

5. To characterize DOM samples before and after sorptive fractionation by mineral soils using one- and two-dimensional solution-state $^1$H NMR spectroscopy experiments.
6. To identify specific compounds and classes of molecules in the DOM samples and to assess the preferential and reversible sorption behaviour of these components.

Objectives 1-4 are discussed in Chapter 2 where data for contaminant sorption to both untreated and acid-hydrolyzed soils with varying OM composition is presented. Solid-state $^{13}\text{C}$ CP-MAS NMR spectra of untreated and structurally modified soils are also presented in this chapter along with correlations between contaminant sorption affinity and soil OC structure. Objectives 5 and 6 are addressed in Chapter 3 which presents one- and two-dimensional solution-state $^1\text{H}$ NMR spectra of bulk and fractionated DOM samples that were derived from biosolids. Subsequently, Chapter 4 provides a summary and synthesis of the results including the overall conclusions and implications of this work as well as recommendations for future experiments.
1.9 References


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1.10 Figures

Figure 1-2. Weak correlations between $K_{OC}$ values and sorbent aromaticity and aliphaticity for phenanthrene sorption to A) untreated soils and B) untreated and structurally modified sorbents. Reprinted with permission from: Chefetz, B.; Xing, B. *Environ. Sci. Technol.* **2009**, *43*, 1680-1688. Copyright 2009 American Chemical Society.
Figure 1-3. Comparing increases in $K_{OC}$ values for diuron and phenanthrene sorption to soils after lipid removal by solvent extraction, clay mineral removal by hydrofluoric (HF) acid treatment, and the sequential application of both treatments. Reprinted with permission from: Ahangar, A. G.; Smernik, R. J.; Kookana, R. S.; Chittleborough, D. J. *Chemosphere* 2009, 74, 1062-1068. Copyright 2009 Elsevier.
Figure I-4. A representative solid-state $^{13}$C CP-MAS NMR spectrum of a grassland soil. The regions of the spectrum where major functional groups are known to resonate are labelled. Reprinted with permission from: Simpson, M. J.; Simpson, A. J. J. Chem. Ecol. **2012, 38,** 768-784. Copyright 2012 Springer.
Chapter 2: High Affinity Sorption Domains in Soil are Blocked by Polar Soil Organic Matter Components

2.1 Abstract

Reported correlations between organic contaminant sorption affinity and soil organic matter (OM) structure vary widely, suggesting the importance of OM physical conformation and accessibility. Batch equilibration experiments were used to examine the sorption affinity of bisphenol A, atrazine, and diuron to five soils of varying OM composition. $^{13}$C cross-polarization magic angle spinning nuclear magnetic resonance (NMR) spectroscopy was used to characterize the organic carbon chemistry of the soil samples. High sorption by a soil low in O-alkyl components suggested that these structures may block high affinity sorption sites in soil OM. As such, soil samples were subjected to acid hydrolysis and NMR results showed a decrease in the O-alkyl carbon signal intensity for all soils. Subsequent sorption experiments revealed that organic carbon-normalized distribution coefficient ($K_{OC}$) values increased for all three contaminants. Before hydrolysis, $K_{OC}$ values correlated positively with soil aromatic carbon content and negatively with polar soil O-alkyl carbon content. While these correlations were weaker after hydrolysis, the correlation between $K_{OC}$ values and soil alkyl carbon content improved. This study suggests that hydrolyzable O-alkyl soil OM components may block high affinity sorption sites and further highlights the importance of OM physical conformation and accessibility with respect to sorption processes.

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$^{1}$This manuscript has been published in *Environmental Science and Technology*. Reprinted with permission from: *Environ. Sci. Technol*. **2013**, *47*, 412-419. Copyright 2013 American Chemical Society. Perry J. Mitchell performed the laboratory experiments and analyzed the data along with Myrna J. Simpson. Perry J. Mitchell and Myrna J. Simpson wrote the manuscript.
2.2 Introduction

A main environmental fate of organic contaminants is sorption to soil organic matter (OM).\textsuperscript{1-3} Sorption is a critical soil process which regulates contaminant concentrations in the soil solution, which in turn controls the rates of processes such as biotic and abiotic degradation, volatilization into the atmosphere and leaching into lower soil horizons and groundwater.\textsuperscript{4} Understanding the sorption behaviour of organic contaminants is therefore crucial to predicting their environmental fate.\textsuperscript{13} $^{13}$C cross-polarization magic angle spinning (CP-MAS) Nuclear Magnetic Resonance (NMR) spectroscopy provides information on the relative distributions of specific classes of organic carbon (OC) in soils and has been used extensively to correlate sorption coefficients to soil OM structure,\textsuperscript{5,6} including various relationships between sorption affinity and either alkyl,\textsuperscript{1,7-9} aromatic\textsuperscript{9-11} and O-alkyl\textsuperscript{10,12} carbon content. However, the variation in the quality of the relationships between contaminant sorption affinity and soil OM structure necessitates the study of additional soil-contaminant systems to further elucidate sorption processes. The physical conformation of soil OM, in addition to soil OM composition, has also been hypothesized to play a key role in contaminant sorption. OM physical conformation has been used to explain observations where correlations between organic carbon-normalized distribution coefficient ($K_{OC}$) values and soil OM composition could not adequately explain sorption data.\textsuperscript{13} Changes in OM conformation have been reported to account for differences in sorption behaviour between soils and their respective extracts such as humic acids and humin.\textsuperscript{13-16} Furthermore, a recent study with various polymers as models for soil OM showed that the spatial conformation of domains is important for the sorption of organic contaminants.\textsuperscript{17}

The accessibility of binding sites in soil OM may also play a role in contaminant sorption.\textsuperscript{18} For example, Ahangar et al.\textsuperscript{12} reported that the removal of clay minerals increased soil sorption capacity for diuron and phenanthrene, suggesting that certain binding sites were
previously inaccessible due to OM-mineral interactions. Several studies have demonstrated that soil lipid removal resulted in increased organic contaminant sorption, suggesting that soil lipid components may block high affinity sorption sites in OM.\textsuperscript{19-21} A second class of OM components which may lower the extent of contaminant sorption are \textit{O}-alkyl components such as carbohydrates, amino acids and peptides since they have been observed to be dominant at the soil-water interface.\textsuperscript{22} Previous studies involving polymers have suggested that oxygen-containing components may reduce the accessibility of high affinity sorption sites thus limiting organic contaminant binding.\textsuperscript{17,23,24} Acid hydrolysis has been previously used to selectively remove carbohydrate and peptide functionalities from soil OM,\textsuperscript{25-28} allowing for investigation of the role of these \textit{O}-alkyl components in contaminant sorption. For example, Simpson et al.\textsuperscript{16} found that the removal of \textit{O}-alkyl components by acid hydrolysis of humic acids resulted in increased phenanthrene sorption. Low sorption affinity \textit{O}-alkyl soil structures may therefore block organic contaminants from accessing higher affinity sorption sites within soil OM. However, the specific role of \textit{O}-alkyl soil components in the physical blocking of organic contaminant sorption sites in whole soils has not been examined in detail.

Three organic contaminants which are found in reclaimed wastewater, groundwater and surface waters were selected for sorption studies with five soils of diverse OM composition. Atrazine and diuron are commonly studied herbicides which are applied worldwide and contaminate water bodies via agricultural runoff.\textsuperscript{29} Bisphenol A is a raw material in plastics manufacturing and is a potential endocrine disruptor which may leach from plastic products over time.\textsuperscript{30} These contaminants may also be introduced to soil when reclaimed wastewater is used for agricultural irrigation, an increasingly common practice in countries that experience water shortages.\textsuperscript{2,31} All three contaminants are capable of interacting with functional groups on the surfaces of soil colloids. Hydrogen bonding through heteroatoms such as nitrogen and
oxygen$^{1,32,33}$ as well as the formation of charge-transfer complexes$^{34}$ may contribute to the net sorption of the contaminants in addition to van der Waals interactions and physical partitioning into soil OM.$^{35}$ However, competition between organic contaminants and water molecules for hydrogen bonding sites may reduce the soil sorption capacity.$^{17}$ Therefore, the sorption behaviour of these three contaminants requires closer examination with soils of diverse composition to elucidate their major sorption mechanisms. While the sorption behaviour of atrazine, bisphenol A and diuron with geosorbents has been previously reported in the form of sorption coefficients, few studies have correlated their sorption affinities with soil OM structure,$^{10,12}$ especially for soils with high organic carbon content. In addition, the role of soil OM physical conformational changes in altering the sorption behaviour of these contaminants has not been assessed. To the best of our knowledge, no published studies have examined changes in the contaminant sorption affinity of whole soils after the targeted removal of carbohydrate and peptide components of OM. Therefore, the objectives of this study were to: (i) quantify and compare the sorption affinities of atrazine, bisphenol A and diuron to five soils that vary in OM composition; (ii) examine correlations between contaminant sorption affinity and soil OC structure; (iii) assess the role of acid hydrolyzable soil O-alkyl components in the potential blocking of high affinity sorption sites.

2.3 Materials and Methods

2.3.1 Soil Samples and Sample Preparation

Five soils with a wide range of OM quantity and quality were selected for comparative sorption of three organic contaminants. Elemental carbon analysis was carried out using the LECO SC444 combustion method (University of Guelph Laboratory Services, Guelph, Ontario). Inorganic carbon was not detected in the samples; therefore the total carbon percentage was
equated to the percentage of organic carbon (% OC) in the soils. Elemental analysis revealed that the % OC values for the soils ranged from 1.7-48.4% (Table 2-1).

An Agricultural soil was obtained from Agriculture and Agri-Food Canada’s Central Experimental Farm, Ottawa, Ontario, Canada. Mineralogical studies detected the presence of feldspar, chlorite, vermiculite, illite and other mixed layer minerals. A Grassland soil was obtained from the University of Alberta Ellerslie Research Station near Edmonton, Alberta, Canada. The primary vegetation covering the soil was western wheatgrass (Agropyron smithii). The dominant clay mineral is montmorillonite with lower amounts of illite, chlorite, and kaolinite also present in this grassland soil. A fire-impacted soil (referred to as the Charred soil) was obtained from the surface layer (0-10 cm) at a site in a conifer forest near Nestow, Alberta, Canada in which the dominant species was jack pine (Pinus banksiana). The forest experienced a wildfire in the summer of 2001, resulting in transformations of soil OM structure. Soil from the O horizon of a pristine conifer forest in which the dominant species was Lodgepole pine (Pinus contorta) was collected from a site in Hinton, Alberta, Canada. This soil contains relatively fresh, non-degraded OM and is referred to in this study as the Forest soil. A Peat soil from the Florida Everglades was obtained from the International Humic Substances Society (St. Paul, MN). This soil has high OC and low mineral content. All soil samples were air dried, passed through a 2 mm mesh sieve to remove large soil particles and residual plant matter, and finely ground using a mortar and pestle prior to analysis.

Subsamples of each soil were acid hydrolyzed by mixing each sample with 6 M hydrochloric acid (ACS grade; Caledon Laboratories) at a ratio of 1:25 (w/v) and refluxing for four hours. The soils were then vacuum filtered, rinsed with Millipore-purified deionized water and freeze-dried. Previous studies have shown that hydrochloric acid selectively removes soil carbonate minerals such as limestone. The lack of acid-labile inorganic carbon suggests that
the soil mineralogy did not change during acid hydrolysis. The pH values of the untreated and acid-hydrolyzed soils were measured in duplicate in deionized water\textsuperscript{43} using an Accumet® BASIC (model AB15) pH meter and the results are summarized in Table 2-1.

2.3.2 $^{13}$C CP-MAS NMR Characterization of Soils

Prior to NMR analysis, mineral soil samples were treated repeatedly with 10% hydrofluoric acid (HF; Fisher Scientific) to concentrate the OM and remove paramagnetic minerals. After treatment with HF, samples were rinsed with deionized water, freeze-dried and ground to a fine powder.\textsuperscript{44} Approximately 100 mg of sample was packed into a 4 mm zirconium rotor and sealed with a Kel-F cap (Bruker BioSpin, Rheinstetten, Germany). $^{13}$C CP-MAS NMR spectra were collected using a Bruker BioSpin Avance III 500 MHz NMR spectrometer equipped with a 4 mm H-X MAS probe and using the standard ramp-CP pulse program. Spectral acquisition parameters included a sample spinning speed of 13 kHz, a ramp-CP contact time of 1 ms, and a 1 s recycle delay. Spectra were processed using a zero filling factor of 2 and 50 Hz line broadening. Glycine was used as an external standard to calibrate chemical shift values. The spectra were integrated into four regions using Amix software (v. 3.9.7; Bruker BioSpin): alkyl carbon (0-50 ppm), $O$-alkyl carbon (50-110 ppm), aromatic carbon (110-165 ppm) and carboxyl and carbonyl carbon (165-200 ppm).\textsuperscript{6,36} Relative carbon distributions were calculated based on the total carbon signal between 0-200 ppm.

2.3.3 Batch Equilibration Experiments

Organic contaminants were selected based on their varying degrees of aqueous solubility (see Table 2-2) to test whether altering the physical conformation of OM results in more pronounced changes in the sorption behaviour of less soluble compounds. All compounds were
present in neutral uncharged form at the experimental pH based on their pK_a values (see Table 2-2). Sorption experiments were carried out in triplicate via batch equilibration. A background solution containing 0.01 M CaCl_2·2H_2O (≥99%; Sigma-Aldrich) and a biocide of 1×10^{-4} M HgCl_2 (≥99.5%; Sigma-Aldrich) was prepared in deionized water. The pH of the background solution was adjusted to pH = 6.5 using dilute Ca(OH)_2 solution (≥95.0%; Sigma-Aldrich). Contaminant solutions (2 mg/mL) were prepared in methanol (Optima® grade; Fisher Scientific) and diluted with the background solution to achieve final concentrations with less than 0.5% methanol by volume, to avoid cosolvent interactions. Atrazine (PESTANAL® analytical standard; Fluka Analytical), bisphenol A (≥99%; Sigma-Aldrich) and diuron (≥98%; Sigma-Aldrich) solutions were prepared with concentrations ranging between 2-10 mg/L for batch equilibration experiments. This narrow concentration range was selected since the objective of this study was to examine relative changes in sorption affinity rather than attempting a thorough analysis of contaminant sorption behaviour. Soils and contaminant solutions were mixed in glass test tubes (16 x 100 mm) with PTFE-lined screw caps (Fisher Scientific). Five 6 mm glass beads were added to each culture tube to ensure complete homogenization of the soil-solution mixtures. The mixtures were equilibrated in darkness for 48 hours at room temperature on a mechanical shaker (model no. 6010; Eberbach Corporation). Preliminary experiments indicated that equilibrium was reached within 24 hours. Soils and contaminant solutions were mixed using ratios between 1:5 and 1:2000 to achieve 20-80% sorption of each compound at equilibrium. Lower soil:solution ratios were needed to achieve optimal sorption for acid-hydrolyzed soils. The culture tubes were centrifuged at 1000 rpm for 10 minutes (model HN-S; International Equipment Company) and 2 mL of each supernatant was transferred into amber vials with minimal headspace and sealed with screw cap lids containing PTFE/silicone septa (Agilent Technologies). Control samples containing identical organic contaminant solutions but without
soil were prepared and were subjected to the same experimental conditions. The concentrations of control solutions were compared with the initial contaminant solutions which were analyzed immediately after preparation. Concentration discrepancies of 5% or less were observed and indicated no contaminant sorption to the glass beads or vessel walls during the sorption experiments. Therefore, the solid-phase contaminant concentrations were calculated by difference.³

2.3.4 Quantification of Contaminants

An Agilent 1100 Series High-Performance Liquid Chromatography system (Agilent Technologies, Mississauga, ON, Canada) with an autosampler and diode array and fluorescence detectors was used to quantify all contaminants. Chromatographic separation was achieved using a 5μm C_18 column (4.6 mm x 250 mm; Grace Davison Discovery Sciences). A flow rate of 1 mL/min, a column temperature of 25 °C, isocratic elution and an injection volume of 25 μL were used to analyze all contaminants. Elution solvents for atrazine, bisphenol A and diuron consisted of acetonitrile (Optima® grade; Fisher Scientific) and deionized water containing 0.1% acetic acid (ACS reagent grade; Fisher Scientific; v/v) in ratios of 60:40, 50:50 and 70:30, respectively. Atrazine and diuron were detected using a diode array detector monitoring at 222 and 210 nm, respectively.³,¹⁰ Bisphenol A was detected using a fluorescence detector with excitation and emission wavelengths of 228 and 316 nm, respectively.³⁰

2.3.5 Isotherm Modelling

OriginPro 8 software (OriginLab Corporation, Northampton, MA) was used to construct and fit sorption isotherms and to calculate standard errors. Sorption data were fitted to the Freundlich isotherm model: \( \frac{x}{m} = K_F C_e^n \) where \( \frac{x}{m} \) is the solid-phase or sorbed contaminant
concentration (in mg/g), \( K_F \) is the Freundlich distribution coefficient (in units of \((\text{mg/g})/(\text{mg/mL})^n\)), \( C_e \) is the aqueous contaminant concentration (in mg/mL) and \( n \) is a sorption nonlinearity coefficient (unitless). Organic carbon-normalized Freundlich distribution coefficient (\( K_{FOC} \)) values were calculated by normalizing \( K_F \) to \( f_{OC} \), the fraction of OC in the soils, where \( f_{OC} = \% \text{OC}/100\%^{46} \) (see Tables 2-3 and 2-4). However, \( K_{FOC} \) values cannot be directly compared across soils due to the inherent differences in Freundlich \( n \) values. Therefore, sorption data were also fitted to the linear isotherm model: \( x/m = K_d C_e \) where \( K_d \) is the linear distribution coefficient. \( K_{OC} \) values were calculated by normalizing \( K_d \) to \( f_{OC} \). This isotherm model assumes a nonlinearity coefficient of unity thus allowing for direct comparisons between soils. Reduced concentrations were calculated by normalizing the equilibrium contaminant concentrations to the contaminant solubilities (\( C_e/S_w \)). The sorption isotherms were then re-plotted using reduced concentrations as the x-axis variable to obtain additional \( K_{OC} \) and \( K_{FOC} \) values which are summarized in Tables 2-5 and 2-6. To better illustrate increases in \( K_{OC} \) values for contaminant sorption after acid hydrolysis, \( \Delta K_{OC} \) values were calculated as follows: \( \Delta K_{OC} = K_{OC \text{acid-hydrolyzed}} - K_{OC \text{untreated}} \).

### 2.3.6 Soil Organic Carbon Content

Repeated attempts to remove excess chloride ions from acid-hydrolyzed soils with high OC content (Charred, Forest and Peat soil samples) were unsuccessful and the presence of residual chloride ions interfered with total carbon analysis (data not shown). Extensive washing of the samples removed too much nonhydrolyzable soil OM while dialysis experiments did not adequately remove residual chloride ions (data not shown). It has been demonstrated previously that integration values from \(^{13}\text{C} \) ramp-CP-MAS NMR spectra are quantitatively reliable to within 5% error of the results obtained by Direct-Polarization (Bloch decay) \(^{13}\text{C} \) NMR spectroscopy,\(^{47}\) a
reliable quantification technique for soil OC components. In addition, the integration of $^{13}$C CP-MAS NMR spectra has been used previously to quantify the relative concentrations of various soil OM components. Therefore, the % OC values for the acid-hydrolyzed Charred, Forest and Peat soil samples were estimated based on the percentage of NMR signal change after acid hydrolysis using: $\% \text{OC}_{\text{acid-hydrolyzed}} = (\% \text{OC}_{\text{untreated}})(100 - \% \text{O-alkyl}_{\text{untreated}})/100$. The estimated % OC values for these three soils are shown in Table 2-1 with 5% estimated error. The % OC values for the Agricultural and Grassland soils which did not contain excess chloride ions were also estimated using this method (0.9% and 3.6%, respectively) and the resulting values closely matched those obtained by elemental analysis (0.8% and 3.6%, respectively; see Table 2-1).

2.4 Results and Discussion

2.4.1 Solid-state $^{13}$C NMR Characterization and Contaminant Sorption to Soils

Figure 2-1 shows the $^{13}$C CP-MAS NMR spectra of the five soils and Table 2-1 summarizes the relative signal of the four classes of soil OM expressed as a percentage of the total $^{13}$C NMR signal. The Forest and Agricultural soils contained the largest amounts of $O$-alkyl carbon (50% and 44%, respectively) while the Charred soil exhibited the least (20%). The Charred soil had the highest amount of aromatic carbon (52%) which is likely the result of high concentrations of black carbon formed from plant biomass during burning. The Peat soil displayed the highest relative amount of alkyl carbon (40%) which includes polymethylene-based functionalities.

The linear and Freundlich isotherm distribution coefficients ($K_d$ and $K_F$) increased in the order: Agricultural < Grassland < Forest soils for atrazine, bisphenol A and diuron. However, different trends were observed for the Charred and Peat soil samples with the three contaminants.
For example, bisphenol A sorption was observed to be highest to the Peat soil but atrazine and diuron sorption was highest for the Charred soil. The Peat soil has three times more OC than the Charred soil (48.4% vs. 14.3%) but still exhibited a lower sorption capacity for atrazine and diuron. \( K_{OC} \) values were calculated to further examine sorption trends and in general, the \( K_{OC} \) values for the sorption of all three contaminants to untreated soils increased in the order: Forest < Agricultural < Grassland < Peat < Charred (see Table 2-3). Experimental \( K_{OC} \) values for the sorption of all three compounds to the Agricultural and Peat soils were within the range reported by several studies (see Table 2-7). Comparisons could not be made for the three remaining soils due to the lack of published reports involving the sorption of atrazine, bisphenol A and diuron to soils with high OC content, especially soils with high aromaticity. Despite having intermediate % OC content, the considerably higher \( K_{OC} \) values for the Charred soil suggest that other factors such as OM structure, conformation and accessibility may also play a key role in contaminant sorption processes.

Isotherms for the sorption of atrazine, bisphenol A and diuron to the five soils are shown in Figure 2-2. Atrazine, bisphenol A and diuron sorption results were modelled well by the linear isotherm model \( (R^2 > 0.96; \text{Table 2-3}) \), indicating a strong linear relationship between sorbed and aqueous contaminant concentrations. Sorption data were also modelled well by the Freundlich isotherm model \( (R^2 > 0.99) \). Freundlich \( n \) values generally increased in the order bisphenol A < diuron < atrazine which closely matched the aqueous solubility of the contaminants. Bisphenol A may have exhibited the greatest nonlinearity due to its order of magnitude greater aqueous solubility and potentially lower affinity for the OM phase than atrazine and diuron.

Since OC content and isotherm parameters could not explain the observed trends with \( K_{OC} \) values, we also investigated potential relationships with OM structure as measured by solid-
state $^{13}$C NMR spectroscopy. Very weak correlations were observed between $K_{OC}$ values and the percentage of carbonyl and carboxyl carbon (data not shown). Figures 2-3 to 2-5 show correlation plots of $K_{OC}$ vs. % alkyl, % aromatic and % $O$-alkyl carbon for atrazine, bisphenol A and diuron sorption to the five soils. No clear trend was seen between $K_{OC}$ values and % alkyl carbon for the three contaminants ($R^2 = 0.01-0.03$). Feng et al.$^{45}$ showed that alkyl polymethylene components of OM sorb strongly to clay minerals, especially kaolinite. As such, these alkyl components may be tightly bound to minerals or buried under other OM components and therefore not accessible at the surface for contaminant binding which may explain the weak correlation observed in this study. $K_{OC}$ values for atrazine, bisphenol A and diuron exhibited moderate, positive correlations with soil aromaticity ($R^2 = 0.79-0.84$; Figures 2-3 to 2-5). Wang et al.$^1$ reported a similar positive correlation ($R^2 = 0.70$) between atrazine $K_{OC}$ values and the aromatic carbon content of humic acid and humin fractions of a soil. Similarly, Ahangar et al.$^{10,12}$ reported positive correlations ($R^2 = 0.59$ and 0.62) between soil aromatic carbon content and $K_{OC}$ values for diuron sorption to twelve soils. Therefore, compound-specific correlations with soil aromatic carbon content may serve as modest sorption predictors for these three contaminants. The Charred soil uniquely exhibited very high sorption for all three contaminants. The data points for the Charred soil were therefore excluded from the $O$-alkyl correlation plot in order to obtain a trend line that did not extend into the negative y-axis region. Various degrees of negative correlations were observed between the individual contaminant $K_{OC}$ values and soil % $O$-alkyl carbon content for the remaining four soils ($R^2 = 0.56-0.91$; Figures 2-3 to 2-5). In two studies, Ahangar et al.$^{10,12}$ observed similar negative correlations ($R^2 = 0.84$ and 0.89) between $K_{OC}$ and % $O$-alkyl carbon for the sorption of diuron to twelve soils collected over a small sampling area. Other studies have reported similar negative correlations between $K_{OC}$ values of both polar and nonpolar contaminants to geosorbents.$^{18,50}$ Negative correlations may result from
organic contaminant repulsion by polar soil $O$-alkyl components such as carbohydrates, amino acids and peptides, which are present at the soil-water interface.\textsuperscript{22} Due to the limited number of data points used in this study to construct correlations between sorption affinity and soil carbon structure, future research should examine the sorption behaviour of atrazine, bisphenol A and diuron to a greater number of soils to allow for a more accurate statistical analysis.

The Charred soil exhibited substantially high $K_{OC}$ values for the sorption of all three contaminants. The high aromaticity of this soil (see Figure 2-1 and Table 2-1) suggests the presence of porous black carbon that likely formed as a result of burning during a wildfire event. Black carbon has been reported to strongly sorb organic contaminants including atrazine, bisphenol A and diuron\textsuperscript{51-54} and contains glassy, rigid sorption domains which give rise to primarily nonlinear sorption.\textsuperscript{9} However, the $^{13}$C CP-MAS NMR results also revealed that the Charred soil contained the lowest concentrations of $O$-alkyl carbon (see Table 2-1) which includes low sorption affinity carbohydrate and peptide functionalities which were removed as a result of burning. $O$-alkyl carbon is prevalent at the soil surface\textsuperscript{22} and may physically block organic contaminants from accessing higher affinity alkyl and aromatic bindings sites buried within soil OM. This is consistent with previous reports that the spatial and conformational arrangement of OM domains may regulate organic contaminant sorption.\textsuperscript{13-15} Therefore, the absence of $O$-alkyl components in the Charred soil may have liberated contaminant sorption sites that were previously inaccessible due to blocking. To test this hypothesis, each of the five soils was subjected to acid hydrolysis to remove $O$-alkyl components and the soil sorption affinities for the three contaminants were re-measured using additional batch equilibration experiments. The $^{13}$C CP-MAS NMR spectra of the acid-hydrolyzed soils were also collected to examine the relative changes in the distribution of OC after acid treatment.
2.4.2 Solid-state $^{13}$C NMR Characterization and Contaminant Sorption to Acid-hydrolyzed Soils

The $^{13}$C CP-MAS NMR spectra of the five acid-hydrolyzed soils are shown in Figure 2-1 and the corresponding integration results are summarized in Table 2-1. Signal intensities for the $O$-alkyl region decreased in comparison with untreated soils in all cases. Integration values of the $O$-alkyl region for acid-hydrolyzed soils (11-24%) also decreased compared to untreated soils (20-50%; Table 2-1). The residual $O$-alkyl region signal was attributed to the methoxy group resonance of lignin (56 ppm$^{36}$) as well as carbohydrates and/or peptides which may be physically protected from hydrolysis by minerals or other OM.$^{55}$ The Charred soil exhibited the lowest decrease in $O$-alkyl carbon content after acid hydrolysis which was expected because this sample has the lowest soil $O$-alkyl carbon concentration, likely due to oxidation of carbohydrates and peptides by a wildfire event.$^{39}$ The removal of $O$-alkyl carbon from all five soils using acid hydrolysis resulted in a redistribution of the total $^{13}$C NMR signal among the other three regions of the NMR spectrum. Aromatic carbon integration values increased in all cases whereas alkyl carbon integration values increased for the Agricultural, Forest and Peat soils. The lower relative integration values for the alkyl region of the acid-hydrolyzed Grassland and Charred soils may have resulted from the hydrolysis of amino acids with alkyl side chains.

Freundlich and linear isotherms and isotherm fitting parameters for acid-hydrolyzed soils are shown in Figure 2-6 and Table 2-4, respectively. $K_d$ and $K_F$ values for acid-hydrolyzed soils were higher for all soil-contaminant systems in comparison with untreated soils. Figure 2-7 shows $\Delta K_{OC}$ values for atrazine, bisphenol A and diuron sorption to the untreated and acid-hydrolyzed soils. All $\Delta K_{OC}$ values were positive, indicating an increased sorption affinity for the acid-hydrolyzed soils in comparison with the corresponding untreated soils. Similar relative differences in $K_{OC}$ values were obtained for isotherms plotted using reduced concentrations (see
Figure 2-8). As was the case for untreated soils, atrazine exhibited the highest Freundlich $n$ values of the three contaminants but no consistent trend was observed between the $n$ values of bisphenol A and diuron. Compared to untreated soils, Freundlich $n$ values for atrazine decreased across all five soils. However, $n$ values for bisphenol A and diuron decreased for the Agricultural, Grassland and Charred soils but increased for the Forest and Peat soils. The removal of $O$-alkyl components by acid hydrolysis may have increased the accessibility of both rigid, crystalline and rubbery, amorphous sorption domains, which give rise to primarily nonlinear and linear sorption, respectively. The preferential sorption of contaminants to these two distinct types of OM domains after acid hydrolysis may account for changes in sorption linearity. Acid hydrolysis may have also removed dissolved OM from the soils and increased the accessibility of high affinity sorption sites. However, given the high soil OM content in these soil samples and the hypothesis that soil OM is the dominant sorption domain for many non-polar organic contaminants, the observed increase in sorption coefficients is likely due to improved access to high affinity alkyl and aromatic sorption domains that have been previously reported to sorb appreciable amounts of various organic contaminants.

The pH values of the acid-hydrolyzed soils (Table 2-1) are within the range in which the three organic contaminants are neutral and uncharged. This suggested that interactions between the soils and the compounds were primarily non-ionic. Hydrogen bonding interactions may be reduced after acid hydrolysis due to the removal of $O$-alkyl components that contain heteroatoms. In addition, sorption mechanisms such as $\pi-\pi$ and cation-$\pi$ interactions may increase in prevalence due to the increased availability of aromatic structures that were previously blocked by $O$-alkyl components.

Correlations between sorption data and NMR integration results for acid-hydrolyzed soils are shown in Figures 2-3 to 2-5. Compared to untreated soils, the observed correlations between
KOC values and soil aromatic content were weaker ($R^2 = 0.10-0.69$), possibly due to the hydrolysis of amino acids with aromatic side chains such as phenylalanine. Weaker correlations were also found between KOC values and soil O-alkyl carbon content ($R^2 = 0.01-0.45$), which may be due to the low concentrations of O-alkyl carbon remaining in the acid-hydrolyzed soils. In contrast, correlation coefficients for KOC values plotted against soil alkyl carbon content were higher for acid-hydrolyzed soils than untreated soils ($R^2 = 0.14-0.47$). This suggests that alkyl binding sites may become more available for contaminant binding after acid hydrolysis of O-alkyl components. Furthermore, soils exhibited different affinities for contaminants after the OM physical conformation was altered by removal of acid hydrolyzable components. This is consistent with observed increases in phenanthrene KOC values after humic acid samples were acid hydrolyzed.\textsuperscript{16}

Other sorption studies have shown that the removal of OM components with low sorption affinity, such as small lipids, as well as the removal of minerals may also result in increases in contaminant sorption coefficients.\textsuperscript{13,19,20} For example, Kohl and Rice\textsuperscript{20} reported that soil lipids may block sorption domains that can sorb high amounts of organic contaminants. Ahangar et al.\textsuperscript{19} reported that diuron and phenanthrene KOC values increased by 31\% and 29\%, respectively after the removal of soil lipids. These results suggest that lipids may block high affinity sorption sites in soils. Bonin and Simpson\textsuperscript{13} showed that OM fractionation in addition to mineral removal increased phenanthrene KOC values. Similarly, Ahangar et al.\textsuperscript{19} observed that the removal of minerals increased both diuron and phenanthrene sorption coefficients and this increase was greater when coupled with lipid removal. Several studies have indicated that cutin-derived plant waxes may act as high affinity sorption domains for organic contaminants such as phenanthrene.\textsuperscript{7,9,57} However, other studies have showed that these components may be buried within the soil matrix because they bind strongly to silicate clay minerals.\textsuperscript{58,59} Aromatic
structures in soil OM have also been shown to sorb appreciable amounts of contaminants.\textsuperscript{56,60-62} Hence, removal of small lipids and minerals likely exposes these high affinity sorption domains and results in higher $K_{OC}$ values. Overall, these observations demonstrate the importance of OM chemistry of specific sorption domains, their varying affinity for organic contaminants, as well as contaminant access to these domains.

Our results are consistent with the hypothesis that both OM chemistry and conformation play a role in sorption processes. We focussed specifically on the role of $O$-alkyl components, namely carbohydrates and peptides, which are a major constituent of OM in most soil samples. Phenanthrene sorption to cellulose, a major component of plant biomass,\textsuperscript{63} has been reported to be an order of magnitude lower than other types of contemporary OM\textsuperscript{7} and may block high affinity sorption sites such as those that arise from aromatic or polymethylene OM components.\textsuperscript{9} The sorption of three contaminants (atrazine, bisphenol A, and diuron) to five soils increased by a factor of two or greater after the removal of acid hydrolyzable $O$-alkyl soil components, which are prevalent at the soil-water interface.\textsuperscript{22} This suggests that lower affinity $O$-alkyl moieties block contaminants from reaching higher affinity sorption sites within soil OM as has been previously reported for soil lipids.\textsuperscript{19} Soil aromatic and $O$-alkyl carbon contents were moderately correlated with sorption affinity, while $K_{OC}$ values correlated more strongly with soil alkyl carbon content after $O$-alkyl components were removed. This suggests that in the absence of $O$-alkyl components, specific high affinity OM structures become more accessible for contaminant binding. In addition, the results support the hypothesis that OM physical conformational changes alter OM sorption properties.\textsuperscript{13-15} Recently, Wang et al.\textsuperscript{1} highlighted the importance of surface accessibility for contaminant sorption in addition to OM polarity, aromaticity and aliphaticity. Furthermore, Guo et al.\textsuperscript{17} showed that the spatial arrangement of sorption domains is a key factor in organic contaminant sorption. Consequently, models of sorption affinity based only on OM
structure may not reliably predict the extent of soil sorption of organic contaminants. Future research should couple investigations of OM chemistry with surface accessibility of OM components in addition to a wider range of contaminant concentrations to further delineate contaminant sorption behaviour of organic contaminants.
2.5 References


(27) Schnitzer, M.; Preston, C. M. Effects of acid hydrolysis on the $^{13}$C NMR spectra of humic substances. *Plant Soil* 1983, 75, 201-211.


2.6 Tables

Table 2-1. Total organic carbon content (% OC) as determined by elemental analysis, pH values and $^{13}$C NMR integration values for alkyl, O-alkyl, aromatic and carboxyl and carbonyl carbon as a percentage of the total $^{13}$C NMR signal (0-200 ppm) for untreated and acid-hydrolyzed soils.

<table>
<thead>
<tr>
<th>Soil</th>
<th>% OC</th>
<th>pH (± SD)$^a$</th>
<th>Alkyl (0-50 ppm)</th>
<th>O-alkyl (50-110 ppm)</th>
<th>Aromatic (110-165 ppm)</th>
<th>Carboxyl &amp; Carbonyl (165-200 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>1.7</td>
<td>5.55 ± 0.01</td>
<td>29</td>
<td>44</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>Grassland</td>
<td>5.4</td>
<td>6.22 ± 0.04</td>
<td>27</td>
<td>33</td>
<td>33</td>
<td>7</td>
</tr>
<tr>
<td>Charred</td>
<td>14.3</td>
<td>4.14 ± 0.08</td>
<td>27</td>
<td>20</td>
<td>52</td>
<td>1</td>
</tr>
<tr>
<td>Forest</td>
<td>23.1</td>
<td>7.02 ± 0.08</td>
<td>26</td>
<td>50</td>
<td>17</td>
<td>7</td>
</tr>
<tr>
<td>Peat</td>
<td>48.4</td>
<td>4.60 ± 0.06</td>
<td>40</td>
<td>37</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>Acid-hydrolyzed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>0.8</td>
<td>2.81 ± 0.04</td>
<td>37</td>
<td>18</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>Grassland</td>
<td>3.6</td>
<td>2.57 ± 0.05</td>
<td>26</td>
<td>13</td>
<td>53</td>
<td>8</td>
</tr>
<tr>
<td>Charred</td>
<td>11.4 ± 0.6$^b$</td>
<td>2.25 ± 0.02</td>
<td>23</td>
<td>11</td>
<td>61</td>
<td>5</td>
</tr>
<tr>
<td>Forest</td>
<td>11.6 ± 0.6$^b$</td>
<td>2.59 ± 0.07</td>
<td>33</td>
<td>24</td>
<td>36</td>
<td>7</td>
</tr>
<tr>
<td>Peat</td>
<td>30.5 ± 1.5$^b$</td>
<td>2.39 ± 0.07</td>
<td>42</td>
<td>15</td>
<td>37</td>
<td>6</td>
</tr>
</tbody>
</table>

$^a$Standard deviation (n=2)

$^b$Estimated from $^{13}$C CP-MAS NMR data based on the signal loss for the O-alkyl region after acid hydrolysis. Values are shown with 5% estimated error based on Dria et al.$^{47}$

Table 2-2. Selected chemical properties of atrazine,$^{1,64}$ bisphenol A$^{54,65}$ and diuron.$^{51,66}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aqueous Solubility (mg/L)</th>
<th>pK$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>33</td>
<td>1.7</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>380</td>
<td>10.1</td>
</tr>
<tr>
<td>Diuron</td>
<td>42</td>
<td>&lt;0</td>
</tr>
</tbody>
</table>
Table 2-3. Linear and Freundlich isotherm fitting parameters for the sorption of atrazine, bisphenol A and diuron to five soils of varying organic matter composition. Parameters include linear distribution coefficients ($K_d$), organic carbon-normalized distribution coefficients ($K_{OC}$), Freundlich distribution coefficients ($K_F$), Freundlich nonlinearity coefficients ($n$) and organic carbon-normalized Freundlich coefficients ($K_{FOC}$). Values are averages and standard errors (SE) of triplicate analyses.

<table>
<thead>
<tr>
<th>Soil-Contaminant System</th>
<th>$K_d$ ± SE (mL/g)</th>
<th>$K_{OC}$ ± SE (mL/g)</th>
<th>$R^2$</th>
<th>$K_F$ ± SE (mg/g)/(mg/mL)$^n$</th>
<th>$n$ ± SE (unitless)</th>
<th>$K_{FOC}$ ± SE (mg/g)/(mg/mL)$^n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atrazine</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>1.5 ± 0.1</td>
<td>87.4 ± 0.7</td>
<td>0.99</td>
<td>1.4 ± 0.1</td>
<td>1.01 ± 0.03</td>
<td>86.1 ± 4.7</td>
<td>0.99</td>
</tr>
<tr>
<td>Grassland</td>
<td>6.1 ± 1.8</td>
<td>112.6 ± 32.4</td>
<td>0.99</td>
<td>8.0 ± 0.2</td>
<td>0.84 ± 0.01</td>
<td>148.2 ± 2.9</td>
<td>0.99</td>
</tr>
<tr>
<td>Charred</td>
<td>150.0 ± 6.6</td>
<td>1049.0 ± 46.0</td>
<td>0.99</td>
<td>219.3 ± 16.5</td>
<td>0.77 ± 0.05</td>
<td>1533.6 ± 115.5</td>
<td>0.99</td>
</tr>
<tr>
<td>Forest</td>
<td>10.0 ± 0.2</td>
<td>43.3 ± 0.6</td>
<td>0.99</td>
<td>11.4 ± 2.9</td>
<td>0.92 ± 0.02</td>
<td>49.1 ± 12.4</td>
<td>0.99</td>
</tr>
<tr>
<td>Peat</td>
<td>79.7 ± 1.0</td>
<td>164.9 ± 2.1</td>
<td>0.99</td>
<td>79.1 ± 5.9</td>
<td>1.01 ± 0.05</td>
<td>163.5 ± 12.2</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>Bisphenol A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>8.2 ± 0.2</td>
<td>495.8 ± 17.1</td>
<td>0.99</td>
<td>11.2 ± 0.7</td>
<td>0.82 ± 0.04</td>
<td>673.5 ± 41.6</td>
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<tr>
<td>Grassland</td>
<td>26.6 ± 2.3</td>
<td>493.7 ± 43.2</td>
<td>0.96</td>
<td>50.6 ± 1.4</td>
<td>0.58 ± 0.02</td>
<td>939.2 ± 26.7</td>
<td>0.99</td>
</tr>
<tr>
<td>Charred</td>
<td>235.8 ± 13.8</td>
<td>1648.6 ± 96.6</td>
<td>0.98</td>
<td>414.8 ± 21.0</td>
<td>0.69 ± 0.03</td>
<td>2900.8 ± 147.1</td>
<td>0.99</td>
</tr>
<tr>
<td>Forest</td>
<td>60.0 ± 3.4</td>
<td>259.9 ± 14.6</td>
<td>0.99</td>
<td>91.3 ± 3.9</td>
<td>0.72 ± 0.03</td>
<td>395.4 ± 17.0</td>
<td>0.99</td>
</tr>
<tr>
<td>Peat</td>
<td>297.3 ± 13.2</td>
<td>614.8 ± 27.3</td>
<td>0.99</td>
<td>403.4 ± 17.6</td>
<td>0.77 ± 0.03</td>
<td>834.3 ± 36.4</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>Diuron</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>4.9 ± 0.1</td>
<td>295.2 ± 5.1</td>
<td>0.99</td>
<td>5.6 ± 0.4</td>
<td>0.92 ± 0.04</td>
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<td>Grassland</td>
<td>31.6 ± 2.2</td>
<td>585.5 ± 37.5</td>
<td>0.98</td>
<td>50.5 ± 1.4</td>
<td>0.68 ± 0.02</td>
<td>937.1 ± 26.5</td>
<td>0.99</td>
</tr>
<tr>
<td>Charred</td>
<td>585.2 ± 50.5</td>
<td>4092.0 ± 353.1</td>
<td>0.96</td>
<td>1022.0 ± 54.8</td>
<td>0.59 ± 0.04</td>
<td>7146.9 ± 382.9</td>
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<tr>
<td>Forest</td>
<td>44.9 ± 1.6</td>
<td>194.4 ± 6.8</td>
<td>0.99</td>
<td>61.1 ± 0.9</td>
<td>0.81 ± 0.01</td>
<td>264.6 ± 3.7</td>
<td>0.99</td>
</tr>
<tr>
<td>Peat</td>
<td>296.2 ± 11.6</td>
<td>612.7 ± 23.9</td>
<td>0.99</td>
<td>414.9 ± 7.2</td>
<td>0.78 ± 0.01</td>
<td>858.1 ± 14.8</td>
<td>0.99</td>
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</tbody>
</table>
Table 2-4. Linear and Freundlich isotherm fitting parameters for the sorption of atrazine, bisphenol A and diuron to five acid-hydrolyzed soils of varying organic matter composition. Parameters include linear distribution coefficients ($K_d$), organic-carbon normalized distribution coefficients ($K_{OC}$), Freundlich distribution coefficients ($K_F$), Freundlich nonlinearity coefficients ($n$) and organic carbon-normalized Freundlich coefficients ($K_{FOC}$). Values are averages and standard errors (SE) of triplicate analyses.

<table>
<thead>
<tr>
<th>Soil-Contaminant System</th>
<th>$K_d \pm SE$ (mL/g)</th>
<th>$K_{OC} \pm SE$ (mL/g)</th>
<th>$R^2$</th>
<th>$K_F \pm SE$ (mg/g)/(mg/mL)$^a$</th>
<th>$n \pm SE$ (unitless)</th>
<th>$K_{FOC} \pm SE$ (mg/g)/(mg/mL)$^a$</th>
<th>$R^2$</th>
</tr>
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<tbody>
<tr>
<td><strong>Atrazine</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>10.8 ± 0.4</td>
<td>1433.3 ± 50.7</td>
<td>0.99</td>
<td>13.1 ± 0.9</td>
<td>0.83 ± 0.05</td>
<td>1744.0 ± 113.3</td>
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<tr>
<td>Grassland</td>
<td>26.9 ± 1.2</td>
<td>748.2 ± 34.0</td>
<td>0.99</td>
<td>38.6 ± 3.9</td>
<td>0.79 ± 0.06</td>
<td>1073.8 ± 108.9</td>
<td>0.99</td>
</tr>
<tr>
<td>Charred</td>
<td>402.1 ± 22.1</td>
<td>3514.7 ± 192.9</td>
<td>0.99</td>
<td>588.3 ± 24.6</td>
<td>0.71 ± 0.03</td>
<td>5142.5 ± 215.4</td>
<td>0.99</td>
</tr>
<tr>
<td>Forest</td>
<td>295.5 ± 13.1</td>
<td>2558.4 ± 113.6</td>
<td>0.99</td>
<td>335.3 ± 26.2</td>
<td>0.83 ± 0.10</td>
<td>2902.9 ± 227.1</td>
<td>0.97</td>
</tr>
<tr>
<td>Peat</td>
<td>602.3 ± 10.8</td>
<td>1977.3 ± 35.5</td>
<td>0.99</td>
<td>675.6 ± 26.5</td>
<td>0.91 ± 0.03</td>
<td>2218.0 ± 87.0</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>Bisphenol A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>8.6 ± 0.5</td>
<td>1152.0 ± 64.1</td>
<td>0.99</td>
<td>13.7 ± 1.1</td>
<td>0.73 ± 0.05</td>
<td>1826.7 ± 148.0</td>
<td>0.99</td>
</tr>
<tr>
<td>Grassland</td>
<td>34.4 ± 2.0</td>
<td>957.1 ± 56.0</td>
<td>0.98</td>
<td>52.1 ± 2.2</td>
<td>0.71 ± 0.03</td>
<td>1450.7 ± 60.7</td>
<td>0.99</td>
</tr>
<tr>
<td>Charred</td>
<td>302.5 ± 26.9</td>
<td>2644.6 ± 235.2</td>
<td>0.96</td>
<td>604.5 ± 66.4</td>
<td>0.60 ± 0.07</td>
<td>5284.4 ± 580.6</td>
<td>0.97</td>
</tr>
<tr>
<td>Forest</td>
<td>172.0 ± 7.4</td>
<td>1489.3 ± 63.6</td>
<td>0.99</td>
<td>218.4 ± 11.5</td>
<td>0.79 ± 0.05</td>
<td>1890.5 ± 99.7</td>
<td>0.99</td>
</tr>
<tr>
<td>Peat</td>
<td>482.2 ± 14.3</td>
<td>1583.1 ± 46.9</td>
<td>0.99</td>
<td>574.5 ± 32.8</td>
<td>0.86 ± 0.05</td>
<td>1886.2 ± 107.6</td>
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</tr>
<tr>
<td><strong>Diuron</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>Agricultural</td>
<td>12.7 ± 0.6</td>
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<td>0.76 ± 0.04</td>
<td>2508.0 ± 181.3</td>
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<td>Grassland</td>
<td>59.7 ± 3.5</td>
<td>1662.4 ± 97.8</td>
<td>0.98</td>
<td>94.4 ± 5.6</td>
<td>0.70 ± 0.04</td>
<td>2628.7 ± 157.1</td>
<td>0.99</td>
</tr>
<tr>
<td>Charred</td>
<td>1159.6 ± 102.4</td>
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<td>16707.3 ± 773.6</td>
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</tr>
<tr>
<td>Forest</td>
<td>328.8 ± 11.0</td>
<td>2847.0 ± 95.0</td>
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<td>406.3 ± 13.7</td>
<td>0.82 ± 0.03</td>
<td>3517.7 ± 118.2</td>
<td>0.99</td>
</tr>
<tr>
<td>Peat</td>
<td>995.6 ± 30.3</td>
<td>3268.4 ± 99.5</td>
<td>0.99</td>
<td>1189.3 ± 18.1</td>
<td>0.83 ± 0.01</td>
<td>3904.4 ± 59.3</td>
<td>0.99</td>
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</tbody>
</table>
Table 2-5. Linear and Freundlich isotherm fitting parameters for the sorption of atrazine, bisphenol A and diuron to five soils of varying organic matter composition. Parameters include linear distribution coefficients (K_d), organic-carbon normalized distribution coefficients (K_OC), Freundlich distribution coefficients (K_F), Freundlich nonlinearity coefficients (n) and organic carbon-normalized Freundlich coefficients (K_FOC). Values are averages and standard errors (SE) of triplicate analyses and were calculated using reduced concentrations.

<table>
<thead>
<tr>
<th>Soil-Contaminant System</th>
<th>K_d ± SE (mg/g)</th>
<th>K_OC ± SE (mg/g)</th>
<th>R^2</th>
<th>K_F ± SE (mg/g)</th>
<th>n ± SE (unitless)</th>
<th>K_FOC ± SE (mg/g)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atrazine</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Agricultural</td>
<td>47.8 ± 0.4</td>
<td>2878.9 ± 23.9</td>
<td>0.99</td>
<td>48.2 ± 2.4</td>
<td>1.01 ± 0.03</td>
<td>2906.0 ± 145.2</td>
<td>0.99</td>
</tr>
<tr>
<td>Grassland</td>
<td>200.2 ± 5.8</td>
<td>3714.5 ± 107.1</td>
<td>0.99</td>
<td>149.5 ± 3.3</td>
<td>0.84 ± 0.01</td>
<td>2772.7 ± 60.3</td>
<td>0.99</td>
</tr>
<tr>
<td>Charred</td>
<td>4950.2 ± 217.3</td>
<td>34616.9 ± 1519.3</td>
<td>0.99</td>
<td>3189.8 ± 290.4</td>
<td>0.77 ± 0.05</td>
<td>22306.6 ± 2031.0</td>
<td>0.99</td>
</tr>
<tr>
<td>Forest</td>
<td>329.6 ± 4.8</td>
<td>1426.9 ± 21.0</td>
<td>0.99</td>
<td>281.7 ± 8.8</td>
<td>0.92 ± 0.02</td>
<td>1219.4 ± 38.1</td>
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</tr>
<tr>
<td>Peat</td>
<td>2631.3 ± 33.4</td>
<td>5442.2 ± 69.1</td>
<td>0.99</td>
<td>2657.6 ± 228.0</td>
<td>1.01 ± 0.05</td>
<td>5496.5 ± 471.6</td>
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<tr>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Agricultural</td>
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<td>1455.8 ± 226.2</td>
<td>0.82 ± 0.04</td>
<td>87695.8 ± 13623.5</td>
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<tr>
<td>Grassland</td>
<td>10112.4 ± 885.3</td>
<td>187613.9 ± 16424.1</td>
<td>0.96</td>
<td>1613.1 ± 138.9</td>
<td>0.58 ± 0.02</td>
<td>29927.8 ± 2577.2</td>
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<tr>
<td>Charred</td>
<td>89585.5 ± 5253.0</td>
<td>626472.0 ± 36734.5</td>
<td>0.98</td>
<td>24640.5 ± 2945.4</td>
<td>0.69 ± 0.03</td>
<td>172310.8 ± 20597.3</td>
<td>0.99</td>
</tr>
<tr>
<td>Forest</td>
<td>22810.7 ± 1278.1</td>
<td>98747.6 ± 5532.9</td>
<td>0.99</td>
<td>6454.3 ± 866.7</td>
<td>0.72 ± 0.03</td>
<td>27940.8 ± 3751.9</td>
<td>0.99</td>
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<tr>
<td>Peat</td>
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<td>233628.7 ± 10364.5</td>
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<td>39617.5 ± 5968.8</td>
<td>0.77 ± 0.03</td>
<td>81938.9 ± 12344.9</td>
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</tr>
<tr>
<td><strong>Diuron</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
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<td>177.1 ± 13.4</td>
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<td>10666.9 ± 807.8</td>
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<tr>
<td>Grassland</td>
<td>1325.4 ± 84.7</td>
<td>24589.4 ± 1570.7</td>
<td>0.98</td>
<td>634.8 ± 29.7</td>
<td>0.68 ± 0.02</td>
<td>11776.4 ± 551.4</td>
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<tr>
<td>Charred</td>
<td>24576.8 ± 2120.7</td>
<td>171865.7 ± 14829.8</td>
<td>0.96</td>
<td>9090.7 ± 940.1</td>
<td>0.59 ± 0.04</td>
<td>63571.1 ± 6573.8</td>
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</tr>
<tr>
<td>Forest</td>
<td>1886.1 ± 65.5</td>
<td>8164.7 ± 283.3</td>
<td>0.99</td>
<td>1246.6 ± 23.8</td>
<td>0.81 ± 0.01</td>
<td>5396.6 ± 103.0</td>
<td>0.99</td>
</tr>
<tr>
<td>Peat</td>
<td>12441.9 ± 485.3</td>
<td>25732.9 ± 1003.8</td>
<td>0.99</td>
<td>7689.2 ± 195.1</td>
<td>0.78 ± 0.01</td>
<td>15903.2 ± 403.5</td>
<td>0.99</td>
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</tbody>
</table>
Table 2-6. Linear and Freundlich isotherm fitting parameters for the sorption of atrazine, bisphenol A and diuron to five acid-hydrolyzed soils of varying organic matter composition. Parameters include linear distribution coefficients (K_d), organic-carbon normalized distribution coefficients (K_OC), Freundlich distribution coefficients (K_F), Freundlich nonlinearity coefficients (n) and organic carbon-normalized Freundlich coefficients (K_FOC). Values are averages and standard errors (SE) of triplicate analyses and were calculated using reduced concentrations.

<table>
<thead>
<tr>
<th>Soil-Contaminant System</th>
<th>K_d ± SE (mg/g)</th>
<th>K_OC ± SE (mg/g)</th>
<th>R²</th>
<th>K_F ± SE (mg/g)</th>
<th>n ± SE (unitless)</th>
<th>K_FOC ± SE (mg/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>354.8 ± 12.7</td>
<td>47300.0 ± 1690.7</td>
<td>0.99</td>
<td>241.5 ± 31.0</td>
<td>0.83 ± 0.05</td>
<td>32201.3 ± 4130.7</td>
<td>0.99</td>
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<tr>
<td>Grassland</td>
<td>886.5 ± 40.3</td>
<td>24693.3 ± 1122.0</td>
<td>0.99</td>
<td>599.0 ± 69.0</td>
<td>0.79 ± 0.06</td>
<td>16685.8 ± 1920.1</td>
<td>0.99</td>
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<tr>
<td>Charred</td>
<td>13268.5 ± 728.2</td>
<td>115983.7 ± 6365.6</td>
<td>0.99</td>
<td>7079.1 ± 511.0</td>
<td>0.71 ± 0.03</td>
<td>61880.6 ± 4466.6</td>
<td>0.99</td>
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<tr>
<td>Forest</td>
<td>9751.6 ± 433.1</td>
<td>84429.4 ± 3749.9</td>
<td>0.99</td>
<td>6197.7 ± 1646.8</td>
<td>0.83 ± 0.10</td>
<td>53660.1 ± 14258.3</td>
<td>0.97</td>
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<tr>
<td>Peat</td>
<td>19875.3 ± 356.8</td>
<td>65250.4 ± 1171.5</td>
<td>0.99</td>
<td>16391.6 ± 1074.1</td>
<td>0.91 ± 0.03</td>
<td>53813.6 ± 3526.3</td>
<td>0.97</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>3284.7 ± 182.8</td>
<td>437961.3 ± 24376.0</td>
<td>0.99</td>
<td>1017.4 ± 216.0</td>
<td>0.73 ± 0.05</td>
<td>135658.7 ± 28792.0</td>
<td>0.99</td>
</tr>
<tr>
<td>Grassland</td>
<td>13055.4 ± 763.6</td>
<td>363659.9 ± 21271.3</td>
<td>0.98</td>
<td>3469.6 ± 473.4</td>
<td>0.71 ± 0.03</td>
<td>96645.1 ± 13187.2</td>
<td>0.99</td>
</tr>
<tr>
<td>Charred</td>
<td>114965.2 ± 10227.3</td>
<td>1004940.7 ± 89399.7</td>
<td>0.96</td>
<td>20687.2 ± 5953.7</td>
<td>0.60 ± 0.07</td>
<td>180832.2 ± 52043.1</td>
<td>0.97</td>
</tr>
<tr>
<td>Forest</td>
<td>65365.6 ± 2793.1</td>
<td>565936.0 ± 24182.7</td>
<td>0.99</td>
<td>23784.6 ± 5267.6</td>
<td>0.79 ± 0.05</td>
<td>205927.4 ± 45607.0</td>
<td>0.99</td>
</tr>
<tr>
<td>Peat</td>
<td>183241.0 ± 5424.8</td>
<td>601579.0 ± 17809.5</td>
<td>0.99</td>
<td>92472.1 ± 20298.9</td>
<td>0.86 ± 0.05</td>
<td>303585.3 ± 66641.2</td>
<td>0.99</td>
</tr>
<tr>
<td>Diuron</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Agricultural</td>
<td>531.1 ± 25.5</td>
<td>70817.3 ± 3402.7</td>
<td>0.99</td>
<td>320.5 ± 30.7</td>
<td>0.76 ± 0.04</td>
<td>42734.7 ± 4097.3</td>
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<tr>
<td>Grassland</td>
<td>2506.6 ± 147.2</td>
<td>69822.6 ± 4101.4</td>
<td>0.98</td>
<td>1271.2 ± 118.5</td>
<td>0.70 ± 0.04</td>
<td>35408.4 ± 3301.1</td>
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<tr>
<td>Charred</td>
<td>48703.5 ± 4298.6</td>
<td>425730.0 ± 37575.2</td>
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<td>15692.9 ± 1752.0</td>
<td>0.56 ± 0.04</td>
<td>137175.3 ± 15314.3</td>
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</tr>
<tr>
<td>Forest</td>
<td>13810.9 ± 460.7</td>
<td>119575.0 ± 3989.1</td>
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<td>8650.5 ± 644.0</td>
<td>0.82 ± 0.03</td>
<td>74896.3 ± 5575.7</td>
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<tr>
<td>Peat</td>
<td>41813.3 ± 1272.9</td>
<td>137272.8 ± 4178.9</td>
<td>0.99</td>
<td>26587.1 ± 1017.3</td>
<td>0.83 ± 0.01</td>
<td>87285.2 ± 3339.9</td>
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</tbody>
</table>
Table 2-7. Literature $K_{OC}$ values for the sorption of atrazine, bisphenol A and diuron to soils similar to those used in this study.

<table>
<thead>
<tr>
<th>Sorbent Type</th>
<th>%OC</th>
<th>Compound sorbed</th>
<th>$K_{OC}$ (mL/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat humic acid</td>
<td>48.5(^a)</td>
<td>Atrazine</td>
<td>394</td>
<td>1</td>
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<tr>
<td>Peat humic acid</td>
<td>53.5(^a)</td>
<td>Atrazine</td>
<td>271</td>
<td>1</td>
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<tr>
<td>Peat humic acid</td>
<td>58.4(^a)</td>
<td>Atrazine</td>
<td>277</td>
<td>1</td>
</tr>
<tr>
<td>Peat humin</td>
<td>45.6(^a)</td>
<td>Atrazine</td>
<td>141</td>
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<tr>
<td>Agricultural soil</td>
<td>0.76</td>
<td>Atrazine</td>
<td>70.7</td>
<td>2</td>
</tr>
<tr>
<td>Agricultural soil</td>
<td>1.11</td>
<td>Atrazine</td>
<td>29.9</td>
<td>2</td>
</tr>
<tr>
<td>Agricultural soil</td>
<td>1.51</td>
<td>Atrazine</td>
<td>49(^b)</td>
<td>29</td>
</tr>
<tr>
<td>Agricultural soil</td>
<td>1.50</td>
<td>Atrazine</td>
<td>66(^b)</td>
<td>29</td>
</tr>
<tr>
<td>Agricultural soil</td>
<td>1.52</td>
<td>Atrazine</td>
<td>80(^b)</td>
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<tr>
<td>Clayey Soil</td>
<td>1.37</td>
<td>Atrazine</td>
<td>66(^b)</td>
<td>29</td>
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<td>Agricultural soil</td>
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<td>Atrazine</td>
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<td>1.14</td>
<td>Atrazine</td>
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<td>67</td>
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<tr>
<td>Agricultural soil</td>
<td>1.81</td>
<td>Atrazine</td>
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<td>67</td>
</tr>
<tr>
<td>Sphagnum peat</td>
<td>n/r(^c)</td>
<td>Atrazine</td>
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<tr>
<td>Agricultural soil</td>
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<td>Bisphenol A</td>
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<td>Diuron</td>
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<td>Diuron</td>
<td>390-760</td>
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<td>Diuron</td>
<td>245</td>
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<tr>
<td>Agricultural soil</td>
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<td>Diuron</td>
<td>284</td>
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<tr>
<td>Agricultural soil</td>
<td>1.52</td>
<td>Diuron</td>
<td>339</td>
<td>29</td>
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<tr>
<td>Clayey Soil</td>
<td>1.37</td>
<td>Diuron</td>
<td>221</td>
<td>29</td>
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</tbody>
</table>

\(^a\)Total carbon
\(^b\)Calculated from the Freundlich coefficient, $K_F$ rather than $K_d$
\(^c\)Not reported
\(^d\)Calculated based on reported $K_d$ and $K_{OC}$ values
\(^e\)Average of 36 samples from a small sampling area
\(^f\)Range of $K_{OC}$ values reported for twelve soils
2.7 Figures

Figure 2-1. Comparison of solid-state $^{13}$C cross-polarization magic angle spinning nuclear magnetic resonance spectra of the five untreated and acid-hydrolyzed soils.
Figure 2-2. Sorption isotherms for atrazine, bisphenol A and diuron sorption to five soils. Data points for the Charred and Peat soils are plotted separately for scaling purposes. Data are averages and standard errors of triplicate analyses.
Figure 2-3. Correlations between organic carbon-normalized distribution coefficient ($K_{OC}$) values and the percentages of soil alkyl, aromatic and $O$-alkyl carbon for atrazine sorption to five soils. A data point for the Charred soil was excluded from the correlation between $K_{OC}$ and untreated soil $O$-alkyl carbon content to ensure that the trend line did not extend into the negative y-axis region.

**Atrazine**

**Untreated Soils**

![Graph showing correlation between $K_{OC}$ and % Alkyl Carbon](image)

- $R^2 = 0.03$
- $p = 0.79$

![Graph showing correlation between $K_{OC}$ and % Aromatic Carbon](image)

- $R^2 = 0.81$
- $p = 0.04$

![Graph showing correlation between $K_{OC}$ and % $O$-alkyl Carbon](image)

- $R^2 = 0.61$
- $p = 0.22$

**Acid Hydrolyzed Soils**

![Graph showing correlation between $K_{OC}$ and % Alkyl Carbon](image)

- $R^2 = 0.14$
- $p = 0.54$

![Graph showing correlation between $K_{OC}$ and % Aromatic Carbon](image)

- $R^2 = 0.10$
- $p = 0.61$

![Graph showing correlation between $K_{OC}$ and % $O$-alkyl Carbon](image)

- $R^2 = 0.01$
- $p = 0.89$
Figure 2-4. Correlations between organic carbon-normalized distribution coefficient ($K_{OC}$) values and the percentages of soil alkyl, aromatic and $O$-alkyl carbon for bisphenol A sorption to five soils. A data point for the Charred soil was excluded from the correlation between $K_{OC}$ and untreated soil $O$-alkyl carbon content to ensure that the trend line did not extend into the negative y-axis region.

**Bisphenol A**

**Untreated Soils**

**Acid Hydrolyzed Soils**
Figure 2-5. Correlations between organic carbon-normalized distribution coefficient ($K_{OC}$) values and the percentages of soil alkyl, aromatic and $O$-alkyl carbon for diuron sorption to five soils. A data point for the Charred soil was excluded from the correlation between $K_{OC}$ and untreated soil $O$-alkyl carbon content to ensure that the trend line did not extend into the negative y-axis region.
Figure 2-6. Sorption isotherms for atrazine, bisphenol A and diuron sorption to five acid-hydrolyzed soils. Data points for the Charred and Peat soils are plotted separately for scaling purposes. Data are averages and standard errors of triplicate analyses.

Atrazine – Acid Hydrolyzed Soils

Bisphenol A – Acid Hydrolyzed Soils

Diuron – Acid Hydrolyzed Soils
Figure 2-7. Comparing the difference in organic carbon-normalized distribution coefficient ($\Delta K_{OC}$) values for the sorption of atrazine, bisphenol A and diuron to five untreated and acid-hydrolyzed soils.
Figure 2-8. $\Delta K_{OC}$ values for atrazine, bisphenol A and diuron sorption to five untreated and acid-hydrolyzed soils. Values were obtained by plotting sorption isotherms using reduced concentrations.
Chapter 3: Dissolved Organic Matter is Fractionated by Interactions with Mineral Soils

3.1 Abstract

The fate of dissolved organic matter (DOM) in terrestrial environments may involve sorption to the reactive surfaces of clay minerals in soil. Previous studies have shown that DOM is selectively fractionated by interactions with both pure clay minerals and mineral soils. However, the specific functional groups within DOM that are preferentially sorbed to the mineral surface require examination with a non-selective analytical technique to further elucidate sorption interactions. DOM derived from biosolids was characterized using solution-state nuclear magnetic resonance (NMR) spectroscopy before and after sorptive fractionation by three mineral soils. Multidimensional NMR experiments and pattern matching software identified several short-chain carboxylic acids which are indicative of microbial DOM inputs. Carboxylic and phenolic DOM components were observed to preferentially and reversibly sorb to the soils, likely due to cation bridging and ligand exchange mechanisms. Aliphatic constituents were selectively retained only by a soil with high clay content which suggests possible sequestration of long-chain aliphatic compounds by mechanisms such as van der Waals interactions with clay mineral surfaces. Polar carbohydrate and peptide components of DOM did not exhibit preferential sorption and may therefore accumulate in solution and potentially stimulate microbial activity. The results suggest that DOM sorption to mineral soils may lower soil and groundwater quality.

3.2 Introduction

DOM is a heterogeneous mixture of soluble organic compounds derived predominantly from decaying plants and microbes as well as anthropogenic sources which is found ubiquitously
throughout terrestrial and aquatic environments as well as rainwater.\textsuperscript{1-4} DOM is believed to play a key role in global carbon cycling since DOM mineralization may be a direct source of atmospheric carbon dioxide.\textsuperscript{5} In addition, DOM has been shown to sorb organic contaminants and may facilitate the transport of these pollutants in the environment.\textsuperscript{6,7} As such, understanding the structural composition and fate of DOM is crucial to assessing global environmental issues such as climate change and contaminant mobility. However, the structural complexity and compositional variability of DOM limit its detailed characterization.\textsuperscript{1}

Several studies have examined the terrestrial fate of DOM through investigations of DOM-soil interactions.\textsuperscript{8-20} Evidence from numerous studies suggests that reactive clay mineral surfaces serve as the primary binding site for DOM in soils.\textsuperscript{9,11-16,21} For example, crystalline clay minerals such as kaolinite, montmorillonite and vermiculite have been shown to sorb dissolved soil organic matter (OM) components such as humic and fulvic acids.\textsuperscript{8,10,17,19,20} With respect to amorphous clay minerals, several types of iron oxides including hematite, goethite and ferrihydrite have been shown to selectively sorb carboxylic and phenolic constituents of DOM.\textsuperscript{9,11,12,14-16} These same components have also been reported to preferentially sorb to aluminum and manganese oxide minerals.\textsuperscript{9,15,16} DOM sorption to soil minerals may occur through several mechanisms and specific functional groups have been implicated in the selective binding of DOM components to mineral surfaces.\textsuperscript{9,11-16,18} For example, deprotonated carboxyl and hydroxyl groups of DOM constituents may participate in cation bridging interactions with negatively charged functional groups on clay mineral surfaces.\textsuperscript{20,22,23} These components may also sorb via ligand exchange reactions with surface functional groups such as metal ions and metal hydroxides.\textsuperscript{11,12,24} Soluble aliphatic components of DOM do not appear to bind to amorphous clay minerals\textsuperscript{15} but have been reported to preferentially sorb to kaolinite and montmorillonite.\textsuperscript{10,19} For example, Oren and Chefetz\textsuperscript{23} observed greater sorption of aliphatic
DOM components with increasing proportions of crystalline clay minerals in soils with low OM content. Carbohydrate and peptide components of DOM have been found to accumulate in solution during sorption experiments between DOM and soil minerals\textsuperscript{18,23,25,26} with the exception of some iron oxides for which preferential sorption of these constituents was observed.\textsuperscript{15} These studies suggest that polar carbohydrate and peptide moieties in DOM are not attracted to functional groups on clay mineral surfaces and thus may preferentially bind to water molecules through hydrogen bonding interactions.

Sorptive interactions between DOM components and soil minerals may be reversible depending on experimental conditions such as pH and ionic strength.\textsuperscript{12} For example, Thimsen and Keil\textsuperscript{27} reported that sorption of sedimentary DOM to both montmorillonite and iron oxide was reversible. However, other studies have reported primarily irreversible sorption of DOM components to soil minerals. For example, Gu et al.\textsuperscript{12} investigated the reversibility of wetland-derived DOM sorption to iron oxide and reported strong sorption-desorption hysteresis, suggesting that the majority of sorbed components were irreversibly bound. Similarly, Oren and Chefetz\textsuperscript{23} observed that 83% of total biosolids-derived DOM that sorbed to mineral soil surfaces was irreversibly bound and resisted desorption. Thus, the reversibility of DOM sorption to soil particles may be dependent on the source of the DOM in addition to experimental conditions and soil mineralogy. In upper soil horizons, the majority of clay minerals are coated in OM.\textsuperscript{28} Therefore, reactive mineral surface functional groups in topsoils may not be available for DOM binding.\textsuperscript{29,30} As such, DOM may leach downward through the soil profile via the percolation of water until it encounters low OM-containing mineral soil horizons with an abundance of exposed and reactive clay mineral surfaces.\textsuperscript{25} Thus, the eventual fate of DOM that migrates into subsoil horizons may involve preferential sorption to mineral soils as reported by several studies.\textsuperscript{15,23,29,31-33}
A number of advanced analytical techniques can be used to investigate the structure of DOM that has been isolated from natural environments and each provides complementary structural information. For example, chromophoric aromatic components of DOM can be analyzed using fluorescence spectroscopy coupled to parallel factor analysis to assess the source of DOM, such as inputs from protein-, microbial- and humic-like sources. High-resolution mass spectrometry using Fourier-transform ion cyclotron resonance has been used to calculate molecular formulae of DOM components which can assist with structural elucidation. Other studies have used Fourier-transform infrared spectroscopy (FTIR) to characterize functional groups in DOM components from a variety of environments. Furthermore, several studies have applied solution-state NMR spectroscopy techniques to examine both major classes of compounds and individual small molecules in DOM. Oren and Chefetz used FTIR to characterize the functional groups in biosolids-derived DOM both before and after fractionation by sorptive interactions with mineral soils. While FTIR is a useful technique for identifying and monitoring changes in the relative abundance of functional groups in fractionated DOM samples, it selectively examines only components with a dipole and cannot easily differentiate between aliphatic DOM components which comprise a large portion of DOM samples. In addition, FTIR cannot be used to identify individual molecules in complex environmental mixtures such as DOM. However, solution-state $^1$H NMR spectroscopy has been used successfully to characterize and identify specific molecules in DOM samples following chromatographic separation. In addition, one- and two-dimensional solution-state $^1$H NMR spectroscopy techniques provide a complete, non-selective overview of all molecules in DOM samples and can be used to distinguish between the three major types of aliphatic compounds in DOM. Examining changes in the distribution of DOM components after fractionation by mineral soils will allow for a greater understanding of the sorption behaviour and fate of DOM in
terrestrial environments. Therefore, the objectives of this study were: (i) to examine structural differences between DOM samples before and after sorption to mineral soils using one- and two-dimensional solution-state $^1$H NMR experiments; (ii) to assess the preferential and reversible sorption behaviour of DOM in the presence of mineral soils.

3.3 Materials and Methods

3.3.1 Soil and Dissolved Organic Matter Samples

Soil samples were collected and DOM samples were isolated as described in detail by Oren and Chefetz.$^{23,37}$ Briefly, mineral soil cores (90-120 cm) were collected at three separate sites in Akko, Basra and Nir-Oz, Israel which are used for intensive agriculture. Selected properties of the three soils are shown in Table 3-1. DOM samples were derived from composted biosolids prepared from a 1:1 mixture of composted sewage sludge and tree clippings. The biosolids were mixed with distilled water in a ratio of 1:10 and shaken for 12 hours, after which the samples were pressure filtered through a 0.45 µm filter and then freeze-dried to isolate solid bulk DOM. For sorption experiments, the DOM was re-dissolved in a background solution containing $3.7\times10^{-3}$ M CaCl$_2$ and $1.5\times10^{-3}$ M NaN$_3$ (as a biocide) and then sorbed onto the three mineral soils over a four day period after which a portion of the supernatant was removed and freeze-dried to isolate unbound DOM. Fresh aliquots of water were then added and the mixture was shaken for an additional four days to desorb DOM from the soils, which was isolated by freeze-drying the resulting supernatant.
3.3.2 Nuclear Magnetic Resonance Analysis

3.3.2.1 Sample Preparation

20 mg of each freeze-dried DOM sample was mixed with 60 μL of deuterium oxide (D$_2$O; 99.96% D; Cambridge Isotope Laboratories, Inc.) to which 5 μL of sodium deuteroxide (30% in D$_2$O, Cambridge Isotope Laboratories, Inc.) was added to achieve pH = 12. This mixture was then vortexed for several minutes, centrifuged at 1000 rpm for 5 minutes and 30 μL of the supernatant was transferred to a 1.7 mm NMR microtube (Bruker BioSpin).

3.3.2.2 One-dimensional NMR Spectroscopy Experiments

NMR spectra were collected using a Bruker Avance III 500 MHz NMR spectrometer using a $^1$H-$^{13}$C-$^{15}$N 1.7 mm microprobe fitted with an actively shielded Z-gradient operating at 298 K (Bruker BioSpin). One-dimensional $^1$H NMR spectra were collected using Presaturation Utilizing Relaxation Gradients and Echoes (PURGE) to suppress the water signal at ~4.7 ppm. Spectra were collected using 4K scans, a recycle delay of 2 s and 24K time domain points. Spectra were processed using TopSpin 3.0 software (Bruker BioSpin) using a zero filling factor of 2 and were apodized by multiplication with an exponential decay corresponding to 1 Hz line broadening. The $^1$H NMR spectra were calibrated to the resonance of acetic acid at 1.903 ppm. Diffusion-edited $^1$H NMR spectra were collected using a bipolar pulse longitudinal encode-decode sequence. A total of 12K scans were collected using a 2.5 ms, 53.5 gauss/cm, sine-shaped gradient pulse, a diffusion time of 180 ms, 16K time domain points and 10 Hz line broadening. Diffusion-edited $^1$H NMR spectra were calibrated to the resonance of the methyl group of N-acetylglucosamine in peptidoglycan at 2.03 ppm.
3.3.2.3 Two-dimensional NMR Spectroscopy Experiments

Two-dimensional NMR spectra were obtained for bulk and fractionated DOM samples. Correlation spectroscopy (COSY) data were acquired using digital quadrature detection with 512 scans, a 6K Hz spectral width and 2K and 256 time domain increments in the F2 and F1 dimensions, respectively. Spectra were processed using a QSINE function and magnitude mode in the F1 dimension, a zero-filling factor of 2 and 1 Hz line broadening. Heteronuclear single quantum coherence (HSQC) data were obtained using digital quadrature detection with echo-antiecho gradient selection. A total of 4096 scans were collected with 2K and 128 time domain increments in the F2 and F1 dimensions, respectively. The $^1J_{^1H-^{13}C}$ value was set to 145 Hz.\textsuperscript{40}

3.3.2.4 Structural Assignments and Spectral Integration

Compound identification was achieved by pattern matching to the Bruker Biofluid Reference Compound Database (version 2.0.3, Bruker BioSpin) and to literature reports.\textsuperscript{40,46} Structural assignments were based on consistency in peak multiplicity and chemical shift in the one-dimensional $^1H$ NMR spectra and were confirmed using two-dimensional NMR experiments. Four general classes of molecules within DOM have been identified based on their chemical shift values in $^1H$ NMR spectroscopy.\textsuperscript{35,40,41,51} To assess the relative abundance of these four components in each DOM sample, the $^1H$ NMR spectra were integrated into four regions using Amix software (version 3.9.7; Bruker BioSpin): material derived from linear terpenoids (MDLT), 0.6-1.6 ppm; carboxyl-rich alicyclic molecules (CRAM), 1.6-3.2 ppm; carbohydrates and peptides, 3.2-4.5 ppm and aromatics, 6.5-8.4 ppm.\textsuperscript{40,41} The region containing residual signal from water (4.5-6.5 ppm) did not contain any peaks of interest and was therefore excluded from integration calculations.
An examination of the relative distribution of the four classes of molecules in the bulk, unbound and desorbed DOM sample $^1$H NMR spectra provides insight for both preferential sorption of DOM constituents and the potential reversibility of these sorption processes. For example, the lower abundance of a DOM component in an unbound DOM sample compared to the bulk DOM may indicate preferential sorption of that component onto the mineral soil surface. In addition, a lower relative integration value for a DOM component in the desorbed vs. unbound DOM sample may suggest an irreversible sorption interaction. Conversely, similar or greater relative amounts of a DOM component in the desorbed fraction compared to the unbound fraction may suggest that a sorption process was reversible. However, the release of native DOM from the mineral soils (% organic carbon = 0.08-0.15%) during sorption experiments$^{32}$ may also contribute to the relative integration values of the unbound and desorbed DOM samples.$^{23}$

### 3.4 Results and Discussion

#### 3.4.1 DOM Source and Structure Identification

Figure 3-1 shows the one-dimensional $^1$H NMR spectrum of the bulk DOM sample which was composed mainly of large, broad peaks due to extensive peak overlap. This observation was consistent with other literature reports which examined DOM from natural environments by $^1$H NMR spectroscopy.$^{40,43,46,47}$ Only four small molecules could be identified based on their chemical shifts in this spectrum due to severe peak overlap. The molecules are presented here in their acidic forms but were likely deprotonated due to the basic pH of the DOM solution. Identified compounds included: acetic acid (1.90 ppm), succinic acid (2.38 ppm), methanol (3.33 ppm) and formic acid (8.44 ppm). These four compounds have been previously identified in DOM$^{40}$ and may result from microbial metabolism.$^{52,53}$ This is consistent with the
origin of the DOM samples which were derived from sewage sludge and compost which contain high microbial populations.\textsuperscript{54,55}

Figure 3-2 shows a $^{1}$H NMR spectrum that is representative of the unbound and desorbed DOM samples which exhibited better resolution than the bulk DOM sample (Figure 3-1). This enhanced resolution was attributed to lower structural complexity and signal overlap in the unbound and desorbed samples compared to the bulk DOM spectrum. This suggests that the bulk DOM may have been selectively fractionated by interactions with the mineral soils. Several small molecules that have been previously reported in DOM were identified in the unbound and desorbed DOM spectra.\textsuperscript{38,40,44,46} Detailed structural assignments are shown in Figures 3-3 and 3-4 for an expanded view of the region between 0.8-4.5 ppm. The DOM samples and the confirmed compounds within each sample are listed in Table 3-2. The compounds included lactic acid (singlet – 1.35 ppm; quartet – 4.25 ppm), acetic acid (1.90 ppm), succinic acid (2.38 ppm), methanol (3.33 ppm), glycolic acid (4.05 ppm), water (4.71 ppm), fumaric acid (6.52 ppm) and formic acid (8.44 ppm). In addition, peaks that were consistent with the chemical shift of multiple short-chain carboxylic acids were also present in the $^{1}$H NMR spectra. As with the bulk DOM sample, several identified molecules are likely microbial-derived and are known to participate in key biochemical processes, such as the Krebs cycle in the case of acetate, succinate and fumarate.\textsuperscript{56} Low concentrations and strong peak overlap prevented the identification of specific compounds which resonate in the aromatic region of the DOM samples. Although a number of distinguishable peaks appeared in the aromatic region of the unbound and desorbed DOM samples, the only aromatic compound that was positively identified was benzoic acid, which may also result from microbial metabolism.\textsuperscript{57} Some peaks in the aromatic region of the DOM spectra were also consistent with the chemical shift of the amino acid phenylalanine but this compound could not be definitively assigned.
Diffusion-edited $^1$H NMR spectra were collected to further assess the composition of the DOM samples as well as to investigate the abundance of large aggregates and macromolecules. Similar spectra were obtained for all DOM samples. Figure 3-5 shows a representative diffusion-edited $^1$H NMR spectrum of a fractionated DOM sample. A shoulder at 0.9 ppm and a peak at 1.25 ppm were attributed to the methyl and methylene group resonances of aggregated aliphatic DOM components such as lipids and phospholipids, respectively (see Figure 3-5). These components may have resulted from the degradation of microbial-derived fatty acids in the biosolids. The microbial origin of the DOM was further supported by a peak at 2.03 ppm in the diffusion-edited $^1$H NMR spectrum which was attributed to the methyl group resonance of N-acetylglucosamine in peptidoglycan from the cell walls of gram-positive bacteria as reported previously in DOM samples. Signals in the diffusion-edited spectrum between 3-4.5 ppm were assigned to carbohydrate and amino acid-containing macromolecules such as polysaccharides, peptides and proteins.

Two-dimensional $^1$H NMR techniques were used to confirm the identity of proposed structural assignments. A COSY spectrum of a fractionated DOM sample can be seen in Figure 3-6 in which the resonances for confirmed compounds are labelled. To further assist with structural elucidation, an HSQC experiment was performed using the Akko unbound DOM sample and the resulting spectrum is shown in Figure 3-7. Positively identified compounds are indicated by increased density of contours and are labelled using arrows while resonances for major classes of molecules are indicated using braces. As a result of severe overlap, only eight individual molecules could be positively identified in the DOM samples, limiting the degree to which the fractionation of individual molecules in DOM by mineral soils could be assessed.
3.4.2 Sorptive Fractionation of DOM Components by Mineral Soils

3.4.2.1 Material Derived from Linear Terpenoids (MDLT)

The $^1$H NMR spectra of the DOM samples were integrated into four major regions based on previous reports (see Figure 3-8) to determine the relative abundances of each class of molecules and the integration results are shown in Table 3-3. The relative amounts of each type of DOM component decreased in the order CRAM > MDLT > carbohydrates and peptides > aromatics for all samples. MDLT is composed primarily of aliphatic molecules which likely derive from extensively conjugated terpenoid molecules such as carotenoids that are found in terrestrial and aquatic biomass.$^{51}$ Similar relative amounts of MDLT were observed across all DOM samples (29-36% of the total $^1$H NMR signal). The relative integration values for MDLT in the unbound DOM samples were very similar to the bulk DOM, suggesting that MDLT components do not preferentially sorb to mineral soil surfaces. For the Basra and Nir-Oz soils, paired unbound and desorbed DOM samples had similar integration values. However, a 7% difference was observed between the integration values of the unbound and desorbed DOM samples after interaction with the Akko soil. The Akko soil has much higher clay mineral content as well as a greater surface area than the Basra and Nir-Oz soils (see Table 3-1). This is consistent with the presence of higher surface area minerals such as montmorillonite and kaolinite in soils from this region of Israel.$^{60}$ The higher clay mineral content and corresponding high surface area may have resulted in a greater abundance of binding sites for aliphatic components in the Akko soil in comparison with the Basra and Nir-Oz soils. Consequently, this may have resulted in the preferential retention of aliphatic-rich MDLT molecules on mineral surfaces in the Akko soil. This is supported by the findings of Oren and Chefetz$^{23}$ who observed that the sorption of aliphatic components in the same samples increased with increasing soil clay content and suggested that weak van der Waals forces were responsible for this type of
interaction. In addition, Feng et al.\textsuperscript{10} reported the preferential sorption of aliphatic components of peat humic acid on kaolinite which was also a dominant clay mineral in the Akko soil. Some studies did not detect sorption of aliphatic DOM components to amorphous clay minerals or mineral soils with low clay content.\textsuperscript{15,16} However, the abundance of high surface area clay minerals such as smectites in the Akko soil may account for the preferential retention of aliphatic DOM structures by this specific mineral soil.

3.4.2.2 Carboxyl-rich Alicyclic Molecules (CRAM)

Previous studies\textsuperscript{35,46,51} have reported the abundance of CRAM in marine and freshwater DOM which likely originate from the degradation and oxidation of sterols and hopanoids, two classes of polycyclic biomolecules. CRAM consistently displayed the greatest relative contribution to all DOM samples (37-46\% of the total $^1$H NMR signal), suggesting an abundance of molecules that contain carboxyl functionalities within the DOM samples. This is consistent with the work of Oren and Chefetz\textsuperscript{23} who observed strong infrared spectroscopy bands for carbonyl groups in all three types of DOM samples. The bulk DOM sample had a higher relative amount of CRAM than all unbound DOM samples (see Table 3-3), suggesting that CRAM preferentially sorbed onto the surfaces of all three mineral soils. The difference between the bulk and unbound DOM integration values was more pronounced for the Nir-Oz soil than the Akko and Basra soils (10\% vs. 5\%, respectively). Although the Nir-Oz soil had the lowest amounts of clay and iron and aluminum oxides, it was the most basic soil (see Table 3-1). Therefore, the iron and aluminum oxides on the surface of the Nir-Oz soil may have been deprotonated to a greater extent, resulting in stronger cation bridging interactions between CRAM and the clay minerals at the soil surface thus leading to greater sorption. Paired unbound and desorbed DOM samples were found to have essentially identical integration values for CRAM after sorptive interactions.
with the three soils. This suggested that the unbound and desorbed DOM samples contained similar relative amounts of CRAM and implied that the sorption of CRAM to the mineral soils was highly reversible.

The finding that carboxyl-rich molecules in DOM preferentially sorb to mineral soils is consistent with previous literature reports. For example, Oren and Chefetz found that the abundance of carboxylic functionalities was highest in the fraction of DOM that was bound to mineral soils, likely due to cation bridging interactions involving carboxylic groups and clay mineral surfaces. The same authors also reported the reversible sorption of some carboxylic DOM components to the soils but that other carboxylic moieties may have been irreversibly bound. Furthermore, Gu et al. demonstrated that ligand exchange-surface complexation mechanisms also result in the sorption of carboxylic DOM components on hematite. Other studies have also reported that DOM sorbs to soil minerals through similar mechanisms in which carboxylic components play a key role.

3.4.2.3 Carbohydrates and Peptides

A third major group of compounds in DOM are carbohydrates and peptides which are derived from decaying terrestrial and aquatic organisms. This group is mainly composed of large aggregates of carbohydrates such as polysaccharides as well as proteins and peptides. Small carbohydrate molecules comprise only a small portion of total DOM, likely due to their highly labile nature and potential for degradation. The relative integration value for the carbohydrate and peptide region of the bulk DOM sample was much lower than the corresponding values for the unbound DOM samples (see Table 3-3). This indicated that there were greater relative concentrations of carbohydrates and peptides in the unbound DOM samples compared to the bulk DOM samples and suggests that components of this class of molecules preferentially
remain in the aqueous phase rather than sorbing to the solid mineral phase. This is consistent with the findings of Kaiser et al.\textsuperscript{26} who observed that these labile components accumulate in deeper mineral soil horizons. This observation could be related to the inherent polarity of these molecules, which have heteroatom-containing functionalities such as alcohol, amino, carbonyl and carboxyl groups\textsuperscript{63} that could interact more favourably with water molecules in solution through hydrogen bonding rather than with functional groups on the mineral surface. The relative integration values of the carbohydrate and peptide region in the unbound and desorbed DOM samples after interaction with the Basra and Nir-Oz soils were similar, suggesting no change in the relative amount of carbohydrates and peptides in each sample. The relative integration value for the desorbed DOM after interaction with the Akko soil was 7\% higher than the corresponding value for the unbound DOM sample. The release of native DOM from the soils may have resulted in an overestimation of carbohydrate and peptide DOM components in this case.

The limited sorption of carbohydrate and peptide components of DOM to the mineral soils is consistent with previous reports.\textsuperscript{15,18,23,26} For example, Oren and Chefetz\textsuperscript{23} observed low sorption of polysaccharide DOM components to the same soil samples using FTIR. A similar observation was noted by Polubesova et al.\textsuperscript{18} for DOM sorption onto Fe\textsuperscript{3+}-saturated montmorillonite. Kaiser et al.\textsuperscript{15} observed preferential sorption of carbohydrate components of DOM to ferrihydrite and hematite, possibly due to hydrogen bonding interactions between heteroatoms in DOM and surface hydroxyl groups of clay minerals\textsuperscript{22} or carbohydrate and peptide components at the soil-aqueous interface.\textsuperscript{64} However, the authors did not observe the binding of carbohydrate components to other types of iron and aluminum oxides.\textsuperscript{15}
3.4.2.4 Aromatic Components

Aromatic molecules are also present in DOM, although usually in low abundance compared to aliphatic components.\textsuperscript{40,46} This class of molecules includes phenolic compounds such as lignin monomers in addition to aromatic amino acids such as phenylalanine and tyrosine\textsuperscript{38,51} and likely excludes strongly hydrophobic aromatic molecules due to the soluble nature of DOM. The aromatic region of the $^1$H NMR spectra of the DOM samples exhibited the lowest relative integration values of the four classes of molecules. This is consistent with other reports that have observed low signal intensity for the aromatic region of DOM samples relative to aliphatic components using solution-state $^1$H NMR spectroscopy.\textsuperscript{38,40,41,44,46,47} The lower relative integration values for the aromatic region of the unbound DOM samples compared to the bulk DOM suggests that aromatic functionalities may preferentially sorb to the mineral soils. Relative integration values for the aromatic region of the desorbed DOM samples were identical to or higher than the corresponding values for the unbound DOM samples in all cases. This implies that the preferential sorption of aromatic components onto mineral soil surfaces may be reversible. As was the case for carbohydrates and peptides, the release of native phenolic DOM components from the three mineral soils may have erroneously increased the relative integration values for the unbound and desorbed DOM samples. This is especially concerning for the aromatic DOM components because the overall integration values for the aromatic regions of all DOM samples were quite low ($\leq$6\% of the total NMR signal in each spectrum) and differences in relative integration values between spectra were small (4\% or less). As such, the reversibility of aromatic DOM component sorption to the mineral soils cannot be positively confirmed.

The observation of preferential sorption of aromatic DOM components to mineral soils is in agreement with previous reports.\textsuperscript{16,18,21,65} For example, Kothawala et al.\textsuperscript{32} reported the selective sorption of aromatic components of forest soil DOM to various mineral soils collected
throughout Canada. In addition, this study highlighted that carboxylic DOM components sorbed more strongly to mineral soils than aromatic components. This was consistent with the greater change in relative integration values of CRAM components between bulk and unbound DOM samples compared to aromatic components. Other studies have reported the retention of aromatic components of DOM on clay mineral surfaces. For example, Feng et al.\textsuperscript{10} observed preferential retention of aromatic components of dissolved humic acids by montmorillonite. In addition, Chorover and Amistadi\textsuperscript{9} reported the sorption of aromatic DOM to the iron oxide goethite. Preferential sorption of aromatic functionalities in DOM to clay minerals may occur through mechanisms such as ligand-exchange surface complexation and van der Waals interactions\textsuperscript{16,18} in addition to favourable interactions between aromatic moieties and uncharged kaolinite surfaces.\textsuperscript{22}

\textbf{3.5 Conclusions}

Carboxylic and aromatic DOM components may preferentially sorb to mineral soil surfaces, in agreement with previous literature reports.\textsuperscript{15,23,32} If these DOM constituents sorb organic contaminants from wastewater, the preferential sorptive interactions between these carboxylic and phenolic moieties and mineral soil surfaces may result in desorption of transported organic contaminants in subsoil horizons. Since mineral soils contain less organic carbon than upper soil horizons, the organic contaminants may remain dissolved in the deeper soil solution rather than binding to OM. The percolation of water downward through the soil profile may result in the leaching of unbound contaminants into aquifers, resulting in potential contamination of groundwater resources. Aliphatic MDLT components of DOM were preferentially retained by a soil with high clay mineral content and a high corresponding surface area. This may result in the sequestration of recalcitrant long-chain aliphatic molecules on soil
minerals and is consistent with a previous study which reported the preferential sorption of dissolved aliphatic molecules to kaolinite.\textsuperscript{10} Polar carbohydrate and peptide components of DOM did not exhibit preferential binding to the mineral soils and therefore may accumulate in the soil solution.\textsuperscript{25} These labile organic molecules may serve as an energy source that stimulates microbial activity,\textsuperscript{26} resulting in greater degradation of other $O$-alkyl soil components. This may ultimately lower soil fertility while also increasing soil carbon dioxide emissions. Overall the results of this study suggest that DOM components of wastewater may play a direct role in altering soil solution chemistry when applied to mineral soils with low organic carbon content.
3.6 References


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<th>Basra</th>
<th>Nir-Oz</th>
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<td>0.08 ± 0.01</td>
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<td>quartz, iron and aluminum oxides</td>
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Table 3-2. Specific compounds that were identified in the $^1$H NMR spectra of the DOM samples. “+” indicates a positive identification whereas “–” indicates a negative identification.

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<th>Molecule</th>
<th>Akko Unbound</th>
<th>Akko Desorbed</th>
<th>Basra Unbound</th>
<th>Basra Desorbed</th>
<th>Nir-Oz Unbound</th>
<th>Nir-Oz Desorbed</th>
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<td>+</td>
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<td>+</td>
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<td>+</td>
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<td>–</td>
</tr>
<tr>
<td>Succinic acid</td>
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<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Methanol</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Formic acid</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
Table 3-3. $^1$H NMR integration values for the MDLT, CRAM, carbohydrate and peptide and aromatic regions of each DOM sample as a percentage of the total $^1$H NMR signal for those four regions. Note that the region between 4.5-6.5 ppm containing water and no diagnostic signals was excluded from the integration calculations.

<table>
<thead>
<tr>
<th>DOM Sample</th>
<th>MDLT (0.6-1.6 ppm)</th>
<th>CRAM (1.6-3.2 ppm)</th>
<th>Carbohydrate and Peptide (3.2-4.5 ppm)</th>
<th>Aromatic (6.5-8.4 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Akko Unbound</td>
<td>36</td>
<td>42</td>
<td>19</td>
<td>2</td>
</tr>
<tr>
<td>Akko Desorbed</td>
<td>29</td>
<td>41</td>
<td>26</td>
<td>4</td>
</tr>
<tr>
<td>Basra Unbound</td>
<td>36</td>
<td>42</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Basra Desorbed</td>
<td>33</td>
<td>41</td>
<td>22</td>
<td>4</td>
</tr>
<tr>
<td>Nir-Oz Unbound</td>
<td>33</td>
<td>37</td>
<td>26</td>
<td>4</td>
</tr>
<tr>
<td>Nir-Oz Desorbed</td>
<td>35</td>
<td>36</td>
<td>25</td>
<td>4</td>
</tr>
<tr>
<td>Bulk DOM</td>
<td>36</td>
<td>47</td>
<td>12</td>
<td>6</td>
</tr>
</tbody>
</table>
3.8 Figures

Figure 3-1. $^1$H NMR spectrum of a bulk, unfractionated DOM sample.
Figure 3-2. $^1$H NMR spectrum of a representative fractionated DOM sample.
Figure 3-3. Expanded view of the region between 0.8-2.5 ppm in the $^1$H NMR spectrum of a fractionated DOM sample with peaks for identifiable compounds labelled. SCA denotes a mixture of short-chain carboxylic acids that resonate at similar chemical shift values.
Figure 3-4. Expanded view of the region between 2.5-4.5 ppm in the $^1$H NMR spectrum of a fractionated DOM sample with peaks for identifiable compounds labelled. SCA denotes a mixture of short-chain carboxylic acids that resonate at similar chemical shift values.
Figure 3-5. A representative diffusion-edited $^1$H NMR spectrum of a fractionated DOM sample with identifiable peaks for polysaccharides, peptidoglycan and aliphatic components labelled.
Figure 3-6. Two-dimensional correlation spectroscopy (COSY) data for a fractionated DOM sample. Identified compounds are labelled as follows: 1 – lactic acid; 2 – short-chain carboxylic acids; 3 – acetic acid; 4 – succinic acid; 5 – glycolic acid.
Figure 3-7. Two-dimensional heteronuclear single quantum coherence (HSQC) data for a fractionated DOM sample. Identified molecules and classes of compounds are indicated with arrows and braces. PG indicates the methyl group resonance of $N$-acetylglucosamine in peptidoglycan.
Figure 3-8. Representative $^1$H NMR spectrum of a fractionated DOM sample with the four major classes of molecules labelled.
Chapter 4: Summary and Synthesis

4.1 Overview

The research presented within this thesis focussed on understanding the environmental fate of two important components of reclaimed wastewater. First, the sorptive interactions between three common organic wastewater contaminants and five soils that exhibit a diverse range of organic matter (OM) composition was studied using batch equilibration sorption experiments and solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. Subsequently, the sorptive fractionation of dissolved organic matter (DOM) components by three mineral soils was examined using a suite of $^1$H NMR spectroscopy experiments. The goal of these studies was to further elucidate the environmental fate of these wastewater components in soils.

4.2 Wastewater Contaminant Interactions with Soil Organic Matter

4.2.1 Summary

The sorption affinity of atrazine, bisphenol A and diuron generally increased with increasing soil organic carbon content, with the exception of the fire-impacted Charred soil. This soil exhibited the greatest sorption affinity for each contaminant but only contained intermediate organic carbon content relative to the other four soils. As such, the soil organic carbon concentrations alone did not accurately predict the contaminant sorption affinities. This suggested that other soil OM properties may govern the sorption behaviour of organic contaminants, including the OM structure, the physical conformation and spatial arrangement of sorption domains as well as the accessibility of high affinity sorption sites. The Charred soil has a low concentration of carbohydrate and peptide components which were previously removed by burning during a forest fire. In addition, this soil had a very high aromaticity including contributions from black carbon that formed during burning which may have increased the soil
sorption capacity. However, the high sorption affinity of the Charred soil coupled with its low concentration of \( \text{O-alkyl} \) components suggested that these structures may physically block organic contaminants from accessing high affinity sorption sites within soil OM. To further investigate this hypothesis, the five soils were treated with strong acid to remove their \( \text{O-alkyl} \) components and the sorption experiments were repeated. Subsequently, the sorption affinities of the three compounds were observed to increase by a factor of two or greater. This suggested that \( \text{O-alkyl} \) components which are prevalent at the soil-aqueous interface physically inhibit organic contaminants from accessing alkyl and aromatic sorption domains that are buried deeper with soil OM. These observations were supported by a stronger correlation between contaminant sorption affinity and soil alkyl carbon content after acid treatment. The results suggest that \( \text{O-alkyl} \) soil components likely play a crucial role in regulating the accessibility of organic contaminant binding sites in soils and should therefore be taken into account when predictive models of sorption affinity are constructed. For example, soil \( \text{O-alkyl} \) carbon content was found to correlate negatively with contaminant sorption affinity. This implies that soils with a greater concentration of \( \text{O-alkyl} \) components may sorb lower amounts of contaminants than soils with greater proportions of alkyl and aromatic carbon. Therefore, in a situation where wastewater that is known to contain organic contaminants is used for irrigation, the extent of sorption could potentially be estimated beforehand if the soil organic carbon structural composition has been quantified. However, the total carbon concentration and physical conformation of OM in the soil may also dictate the extent of sorption in addition to the polarity of sorption domains at the soil surface.\(^{1-4}\) As such, multiple factors should be considered before a decision is made to irrigate soils with reclaimed wastewater that is known to contain organic contaminants to better predict the potential for strong and potentially irreversible contaminant sorption.
4.2.2 Limitations and Future Work

This work examined the sorption behaviour of the common wastewater contaminants atrazine, bisphenol A and diuron with five soils of diverse OM composition. While moderate correlations were observed between contaminant sorption affinity and soil carbon structure, these correlations were limited to only four or five data points. In order to construct more accurate and representative correlations, the sorption behaviour of these contaminants should be examined in the presence of a greater number of soils sampled from different environments. This would allow for the compilation of a larger data set which would produce more accurate statistical analyses.

In addition, this study focussed only on the sorption of three specific organic wastewater contaminants to soils. However, wastewater samples may contain numerous other contaminants with a wide range of structures and solubilities. Therefore, the sorption behaviour of other organic contaminants should be studied in a similar manner to observe how changing the accessibility of sorption domains alters the contaminant sorption behaviour. This includes compounds that are very hydrophobic and insoluble such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls as well as compounds with sparing to moderate solubility. In addition, sorption experiments using mixtures of common wastewater contaminants could be conducted to assess their competitive sorption behaviour. This sorption data could then be compiled and used in predictive models of organic contaminant sorption affinity to better understand the environmental fate of wastewater pollutants in soils.

A further limitation of this study was that a narrow range of contaminant concentrations was used to perform batch equilibration experiments and to construct sorption isotherms (2-10 ppm). Additional sorption experiments should be conducted to examine sorption over a wide range of concentrations up to ~80% of the solubility of each compound. This is especially true for bisphenol A which had an order of magnitude greater solubility than atrazine and diuron and
was only analyzed over a small range of its total solubility. The detection limits of the UV and fluorescence detectors dictated the lower limit of contaminant concentrations which could be quantified in this study. In future experiments, lower concentrations of contaminants could be detected using a different quantification method such as mass spectrometry coupled to gas or liquid chromatography which has a lower detection limit for these compounds. 7-10

4.3 Wastewater Dissolved Organic Matter Fractionation

4.3.1 Summary

DOM is ubiquitous in aquatic environments and comprises a large portion of actively cycling organic carbon on Earth. 11 However, the fate of DOM when transported into soils is unclear and may involve sorption to mineral soils with low OM concentrations and with exposed mineral surfaces. 12 To investigate the terrestrial fate of this important environmental matrix, DOM that was isolated from biosolids was sequentially sorbed onto and desorbed from three mineral soils with varying mineralogical properties. Initial 1H NMR results showed that DOM was selectively fractionated by interactions with mineral soils as evidenced by greater peak resolution in the fractionated DOM samples. However, detailed structural analysis resulted in the identification of only eight specific compounds in the samples due to inherent structural complexity. Additional analyses were undertaken to examine the sorptive fractionation of four major classes of molecules in DOM. Carboxylic- and aromatic-containing DOM components were observed to preferentially sorb onto the mineral soil surfaces, whereas aliphatic DOM components were preferentially retained only by a soil with high clay content and a corresponding high surface area. In contrast, carbohydrate and peptide components of DOM did not exhibit preferential sorption to mineral soils, possibly due to the polarity of these components which may dictate their preference for the aqueous phase.
Strong interactions between DOM components and mineral soils may have implications for organic contaminant transport in soils. Common organic contaminants such as polycyclic aromatic hydrocarbons, pharmaceuticals and herbicides have been shown to preferentially sorb to DOM.\textsuperscript{13-16} Therefore, contaminants may be transported into soils by DOM and desorbed when DOM binds to reactive mineral surfaces in lower soil horizons. Although soil OM is the primary sorption domain for organic contaminants in soils,\textsuperscript{17-19} the low OM content of deeper soils\textsuperscript{20} may not strongly retain organic contaminants which could leach downward through the soil profile and eventually into aquifers. Therefore, the introduction of DOM into subsoil horizons may potentially lead to contamination of groundwater resources.

The results suggest that specific DOM components may interact strongly with mineral surfaces. Since DOM has been shown to sorb several types of organic contaminants,\textsuperscript{13-16} sorption of DOM onto clay minerals may result in desorption of transported organic contaminants in subsoils. These contaminants may be weakly retained by subsoils with low OM content\textsuperscript{20} and may therefore leach into lower soil horizons and eventually into groundwater. In addition, the labile carbohydrate and peptide components of DOM that do not preferentially sorb to minerals can accumulate in the soil solution where they may be bioavailable for microbial degradation. Enhanced microbial activity may in turn stimulate the degradation of additional labile soil OM, resulting in increased carbon dioxide emissions and a decline in soil productivity.\textsuperscript{21,22} As such, policy decisions to irrigate soils with reclaimed wastewater should consider the potential for both organic contaminant transport and the degradation of soil quality which may be attributed to the presence of DOM in wastewater.
4.3.2 Limitations and Future Work

Several limitations restrict the applicability of this research to natural environments. One of the major goals of this work was to elucidate how sorptive interactions with mineral soils result in the selective fractionation of DOM. Although the sorptive fractionation of classes of DOM components was studied, individual molecules could not be assessed in the same manner due to the structural complexity and lack of adequate peak resolution. To further elucidate the relative changes in the fractionation of individual molecules, the DOM samples could be separated using methods such as high-performance size-exclusion chromatography or hydrophobic interaction chromatography, both of which have been applied to the analysis of DOM from natural environments prior to analysis by $^1$H NMR spectroscopy.$^{23,24}$ These separation methods may provide enhanced resolution of DOM components and allow for the identification of additional individual molecules which could not be achieved in this project by sorptive and desorptive fractionation by mineral soils alone.

The mineral soils used in sorption experiments with DOM in this study contained low but not negligible organic carbon content.$^{25}$ Therefore, the release of native DOM from the mineral soils could have increased the concentration of each component in the unbound and desorbed DOM samples and resulted in erroneous relative integration values which would suggest a greater degree of preferential sorption and sorption reversibility than actually occurred. In addition, OM in the mineral soils may have discouraged added DOM from sorbing.$^{25,26}$ To correct for the presence of native DOM, the mineral soils could be sequentially shaken in water to extract the native DOM and the sorption experiments could then be repeated to determine the degree to which native DOM changes the DOM sorption capacity of the mineral soils. A similar experiment was performed by Oren and Chefetz$^{25}$ to assess the relative contribution of native OM to successive DOM sorption-desorption cycles. The sorption capacity of individual
components of the mineral soils could also be examined by performing sorption experiments with the pure clay minerals in the soils and comparing the results to the overall sorption capacity of the unaltered soil. However, these proposed experiments may not have great environmental relevance since soils contain both OM and clay minerals which are strongly interdependent and cannot truly be treated separately.

Aliphatic MDLT components were preferentially retained by the Akko soil which was attributed to the high clay content and corresponding high surface area of this soil. To better assess the role of clay minerals in the sorption of aliphatic components, additional experiments could examine the sorptive fractionation of DOM by soils with a more diverse array of clay content ranging from trace quantities to clay-rich soils. Correlations between soil clay content and the fraction of MDLT components sorbed to the soils may provide additional evidence for the role of higher surface area crystalline clay minerals in the preferential sorption of aliphatic MDLT components on mineral soil surfaces. For example, the threshold of soil clay content that is required for preferential sorption of aliphatic components could be investigated.

The DOM samples used for sorption experiments in this study was primarily derived from microbial sources. As such, future studies could investigate the sorptive and desorptive fractionation of DOM from other sources such as marine and fluvial DOM. This may clarify whether the nature of the input source (e.g. terrestrial vs. aquatic) changes both the composition of DOM and its sorption behaviour in the presence of mineral soils.

4.4 Conclusions

The results of this thesis suggest that both organic contaminants and DOM in wastewater may interact strongly with soils. In surface soils, the fate of organic wastewater contaminants appears to be governed more strongly by the spatial arrangement and accessibility of high
affinity sorption sites than soil organic carbon composition alone. In subsoils, specific DOM components may preferentially and reversibly sorb to clay minerals while other components can potentially accumulate in the soil solution. Overall, both organic contaminants and DOM in wastewater have the potential to degrade soil quality and therefore reclaimed wastewater should be applied to soils cautiously after considering the fate of these components.
4.5 References


