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Studies on the Effect of Natural Organic Matter and Hydration on the Sorption and Desorption of Trifluorinated Pesticides

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**STUDIES ON THE EFFECT OF NATURAL ORGANIC MATTER
AND HYDRATION ON THE SORPTION AND DESORPTION OF
TRIFLUORINATED PESTICIDES**

A Dissertation

**Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
In partial fulfillment of the
requirements for the degree of
Doctor of Philosophy**

in

The Department of Chemistry

**by
Charisma V. Lattao
B. S., University of the Philippines, 1998
December, 2009**

Dedication

This dissertation is dedicated to my family.

To my father, Dominador Lattao

To my mother, Milagros Lattao

To my brother, Dominic Lattao and his family

And to my sisters, Fritzie Sacramento and her family

And Marjorie Lattao

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Table of Contents

Dedication	ii	
Acknowledgements	iii	
List of Tables	vii	
List of Figures	ix	
List of Abbreviations	xii	
Abstract	xiii	
Chapter 1	Introduction	1
1.1	The Interdependency of Land, Food and Population.....	1
1.2	Land-use Changes	1
1.3	Climate Change	3
1.4	Agricultural Chemical Dependence	5
1.5	Functions of SOM	8
1.6	References	13
Chapter 2	Review of Related Literature	20
2.1	Importance of Sorption – Desorption Studies	20
2.2	The Soil Components	21
2.2.1	Soil Air	21
2.2.2	Soil Water	21
2.2.3	Inorganic Components	22
2.2.4	Soil Organic Matter	24
2.3	The Use of Trifluorinated Aromatic Pesticides as Sorbates	31
2.4	Choice of Sorbents	34
2.5	Important Forces of Attraction for HOC Sorption	35
2.5.1	London Van der Waals Forces.....	35
2.5.2	Hydrogen Bonding.....	36
2.5.3	Quadrupolar Interactions	39
2.5.4	Possible Retention Mechanisms for Pesticides in This Study..	44
2.6	Introducing Freundlich Isotherm	45
2.7	Effect of Hydration on Sorption	46
2.8	References	49
Chapter 3	Effect of Hydration and Solvation on the Nature of Organic Matter Released from SOM	59
3.1	Introduction	59
3.2	Materials and Methods	68
3.2.1	Materials and Reagents	68
3.2.2	Exfoliation Procedure	69
3.2.3	Characterization Methods	70

	3.3	Results and Discussion.....	73
	3.4	References	93
Chapter	4	¹ H- ¹³ C Heteronuclear Correlation Nuclear Magnetic Resonance of a Whole Organic Soil*.....	100
	4.1	Introduction	100
	4.2	Materials and Methods	106
	4.2.1	Soil Collection	106
	4.2.2	Soil Characterization	106
	4.2.3	Sample Preparation for NMR Experiment	107
	4.2.4	Nuclear Magnetic Resonance	107
	4.3	Results and Discussion	108
	4.4	References	122
Chapter	5	Sorption and Desorption	128
	5.1	Introduction	128
	5.2	Materials and Methods	132
	5.2.1	Chemicals	132
	5.2.2	Soil sampling	133
	5.2.3	Soil Moisture and pH	133
	5.2.4	Clay Content and Cation Exchange Capacity	133
	5.2.5	Total Organic Carbon	134
	5.2.6	Molecular Modeling of Pesticide Structure	135
	5.2.7	Determination of Wavelength of Excitation of Pesticides.....	135
	5.2.8	Pesticide Analysis of HPLC	135
	5.2.9	Determination of Soil to Solution Ratio	136
	5.2.10	Sorption Kinetics	138
	5.2.11	Mass Balance by HPLC	140
	5.2.12	Sorption	141
	5.2.13	Desorption	143
	5.2.14	Liquid Chromatography-Mass Spectrometer	144
	5.2.15	Total Carbon of Supernatant from Control	144
	5.2.16	Specific UV Absorbance (SUVA) of Supernatant from Control at 280 nm	145
	5.2.17	Fluorescence Excitation and Emission Matrix of Supernatant from Control	145
	5.3	Results and Discussion.....	145
	5.4	Sorbent and Sorbate Characterization	145
	5.5	Determination of Soil to Solution Ratio	149
	5.6	Sorption Rate	150
	5.7	Sorption Capacity in Relation to the Sorbates	154
	5.8	Sorption Capacity in Relation to Sorbents	162
	5.9	Sorption with Respect to Hydration	169
	5.10	Hysteresis	172
	5.11	References	177
Chapter	6	Sorption Rates	185

6.1	Introduction	185
6.2	Method.....	194
6.2.1	K_{OC} in Pahokee Peat	194
6.2.2	K_{OC} in Mandeville Soil	196
6.2.3	K_{OC} in Elliot Soil	202
6.2.4	Sorption K_{OC} of Acifluorfen	203
6.2.5	Sorption K_{OC} of Norflurazon	205
6.2.6	Sorption K_{OC} of Flutolanil	206
6.2.7	k_2 Values and k_2 - K Relationships	206
6.2.8	Fraction of Instantaneous Sorption, α	208
6.2.9	Comparison of K_{OC} from Sorption Rate and Sorption Isotherm	208
6.3	References	213
Chapter 7	Conclusion	219
7.1	References	227
Appendix: Letters of Permission		228
Vita		231

List of Tables

Table 2.1	Average amount (g in 100 g) of main elements in soil humic substances worldwide^a.....	27
Table 2.2	Some relevant H-bonds for this study^a.....	38
Table 3.2.1	Chemical shift assignments in ¹³C NMR spectra (Leenheer et al., 2004)	72
Table 3.2.2	Functional group assignments in FTIR (Leenheer et al., 2004; Stevenson, 1994)	72
Table 3.3.1	Elemental composition of Pahokee Peat II ^a.....	73
Table 3.3.2	Summary of UV absorbance and HIX for 1-day exfoliation	76
Table 3.3.3	Summary of HIX for 20-day exfoliation	76
Table 3.3.4	Summary of HIX for 45-day exfoliation*	77
Table 3.3.5	Summary of HIX for 45-day exfoliation standardized with respect to SOM concentration*.....	77
Table 3.3.6	Physico-chemical properties of solvents	89
Table 4.1	¹³C Chemical Shift.....	108
Table 4.2	Proton Chemical Shift of NOM^a	108
Table 5.1	Flutolanil sorption (http://www.efsa.europa.eu)	132
Table 5.2	HPLC conditions used in the analysis of pesticides	136
Table 5.3.1	Properties of sorbents	146
Table 5.3.2	Metal content of Mandeville soil	146
Table 5.3.3	Physico-chemical properties of the sorbates	147
Table 5.6.1	Sorption capacity of Pahokee Peat	156
Table 5.6.2	Sorption capacity of Mandeville Soil	157
Table 5.6.3	Sorption capacity of Elliot Soil	158
Table 5.7.1	Equation of the line for Figure 5.7.2.....	169

Table 5.9.1	Freundlich N parameter and hysteresis index (HI)	176
Table 6.2.1	Sorption kinetics parameters in Pahokee Peat soil	209
Table 6.2.2	Sorption kinetics parameters in Mandeville soil	209
Table 6.2.3	Sorption kinetics parameters in Elliot soil	209
Table 6.2.4	Comparison of K_{OC} from sorption isotherm and sorption kinetics	212

List of Figures

Figure 1.1	Importance of SOM.....	8
Figure 2.1	Chemical structures of acifluorfen, flutolanil and norflurazon (top to bottom).....	33
Figure 2.2	Quadrupolar moment of benzene (a) and hexafluorobenzene (b).....	40
Figure 3.3.1	Supernatant from exfoliation samples using different solvents.....	74
Figure 3.3.2	Fluorescence at 254 nm excitation wavelength for 24 hr exfoliation.....	78
Figure 3.3.3	Fluorescence at 370 nm excitation wavelength for 24 hr exfoliation.....	79
Figure 3.3.4	Fluorescence at 465 nm excitation wavelength for 24 hr exfoliation.....	79
Figure 3.3.5	Synchronous fluorescence at 18 nm $\Delta\lambda$ for 24 hr exfoliation.....	80
Figure 3.3.6	Emission spectra at 254 nm excitation wavelength of 20-d Supernatant.....	80
Figure 3.3.7	Emission spectra at 370 nm excitation wavelength of 20-day Supernatant.....	81
Figure 3.3.8	Emission spectra at 465 nm excitation wavelength of 20-day Supernatant.....	81
Figure 3.3.9	Synchronous fluorescence of 20-day supernatant.....	82
Figure 3.3.10	Synchronous fluorescence at 18 nm offset of a) 4/50 b) 2/50 c) 0.5/50 (v/v) supernatant: total volume of solution	82
Figure 3.3.11	¹³C CPMAS spectra of freeze-dried soil from one month and 15-day exfoliation	85
Figure 3.3.12	FTIR-ATR spectra of freeze-dried soils from 45-day exfoliation	85
Figure 3.3.13	Figure 3.3.13 Summary of UV absorbance at 280 nm.....	87
Figure 3.3.14	Summary of normalized HIX and UV absorbance for 20-day Exfoliation	87
Figure 3.3.15	Electrostatic potential surface of solvents modeled using Spartan version'02 (Wavefunction Inc., CA) (Top: water, dimethyl sulfoxide Bottom: methanol, acetonitrile)	90

Figure 4.1	Standard cross-polarization pulse sequence	104
Figure 4.2	Ramp cross-polarization pulse sequence.....	105
Figure 4.3.1	^1H-^{13}C 2-D HETCOR spectra of the whole soil collected using Lee-Goldberg cross-polarization pulse sequence and a contact time of 0.5 msec.....	109
Figure 4.3.2	^1H-^{13}C 2-D HETCOR spectra of the whole soil collected using Ramp-CP with a contact time of 0.5 msec.....	110
Figure 4.3.3	^1H-^{13}C 2-D HETCOR spectra of the whole soil collected using Ramp-CP with a contact time of 1.0 msec.....	111
Figure 4.3.4	^1H-^{13}C 2-D HETCOR spectra of the whole soil collected using Ramp-CP with a contact time of 2.0 msec.	113
Figure 4.3.5	1-D ^{13}C spectra extracted from the 7.0 ppm ^1H chemical shift of the 2-D ^1H-^{13}C HETCOR spectra (Scaling of y-axis was set to 1 for all, and offsets were done for visual aid only)	114
Figure 4.3.6	1-D ^{13}C spectra extracted from 4 ppm ^1H shift in 2-D HETCOR data (Scaling of y-axis was set to 1 for all, and offsets were done for visual aid only)	115
Figure 4.3.7	1-D ^{13}C spectra extracted from 0.5 ppm ^1H shift in 2-D HETCOR data (Scaling of y-axis was set to 1 for all, and offsets were done for visual aid only).	116
Figure 4.3.8	Structure of lignin monomeric unit	118
Figure 4.3.9	Typical monomer unit of nonhydrolysable tannins	118
Figure 4.3.10	Conceptual model of how SOM molecular assemblage at different hydration levels affect uptake and release of hydrophobic organic compound.....	121
Figure 5.3.1	Soils used in the study (from left to right: Pahokee, Mandeville and Elliot)	147
Figure 5.3.2	Chemical structure and Electrostatic potential surface of Acifluorfen.....	147
Figure 5.3.3	Chemical structure and Electrostatic potential surface of Norflurazon.....	148
Figure 5.3.4	Electrostatic potential surface of flutolanil	148

Figure 5.4.1	Soil to solution ratio of acifluorfen in Pahokee Peat (red) and Mandeville soil (cyan)	140
Figure 5.4.2	Soil to solution ratio of norflurazon in Pahokee Peat (red) and Elliot soil (green)	150
Figure 5.4.3	Soil to solution ratio of flutolanil in Pahokee Peat	150
Figure 5.5.1	Kinetics of sorption of norflurazon in Pahokee Peat soil	152
Figure 5.5.2	TOC of soil controls normalized with soil weight (red: Pahokee, cyan: Mandeville, green: Elliot)	153
Figure 5.5.3	Difference spectra of fluorescence excitation emission matrix between a 6hr and 4day Pahokee Peat (left) control solution (green: 6hr-4day, red: 4day-6hr); and between a 6hr and 10day Elliot soil (right) control solution (green: 6hr-10day, red: 10day-6hr).	154
Figure 5.6.1	Sorption (left) and desorption (right) in Pahokee Peat	159
Figure 5.6.2	Sorption (left) and desorption (right) in Mandeville soil	159
Figure 5.6.3	Sorption (left) and desorption (right) in Elliot soil	159
Figure 5.7.1	Mineral composition of Mandeville soil	165
Figure 5.7.2	Figure 5.7.2 Sorption-desorption distribution coefficients at 0.5 ppm equilibrium concentration of the different pesticides to the different sorbents.....	169
Figure 6.2.1	Sorption kinetics of acifluorfen in dry (green), 1 day prewetted (blue), and 5 day prewetted (red) Pahokee Peat (a), Mandeville (b) and Elliot (c) soils.	197
Figure 6.2.2	Sorption kinetics of norflurazon in dry (green), 1 day prewetted (blue), and 5 day prewetted (red) Pahokee Peat (a), Mandeville (b) and Elliot (c) soils.	198
Figure 6.2.3	Sorption kinetics of flutolanil in dry (green), 1 day prewetted (blue), and 5 day prewetted (red) Pahokee Peat (a), Mandeville (b) and Elliot (c) soils.	199
Figure 6.2.4	K_{OC} in Pahokee Peat	200
Figure 6.2.5	K_{OC} in Mandeville	201
Figure 6.2.6	K_{OC} in Elliot Soil	204

List of Abbreviations

1-D	one-dimensional
2-D	two-dimensional
HETCOR	heteronuclear correlation
NMR	nuclear magnetic resonance
CP	cross polarization
CPMAS	cross-polarization magic angle spinning
FA	fulvic acid
FTIR	Fourier Transform Infrared Spectroscopy
GHG	green house gases
HA	humic acid
H-bond	hydrogen-bond
HIX	humification index
HOC	hydrophobic organic contaminants
HPLC	high performance liquid chromatography
IHSS	International Humic Substance Society
LG-CP	Lee-Goldberg cross polarization
NOM	Natural Organic Matter
Ramp-CP	Ramped-Amplitude cross polarization
SOM	Soil Organic Matter
SUVA	Specific Ultra Violet Absorbance
TOC	total organic carbon
TSNE	two-site non-equilibrium
UV	Ultra Violet

Abstract

This work was done in order to deepen our molecular level understanding of how soil organic matter (SOM) is assembled in a whole soil and to provide further insight on the effect of SOM assembly on the uptake and release of hydrophobic organic compounds. Various techniques, including ultraviolet absorbance, fluorescence, and total carbon analysis, demonstrate that hydration/solvation of SOM is kinetically controlled. Initial wetting of a soil releases the hydrophobic moieties that are located at the outer surface of SOM, and longer wetting times exfoliate more hydrophobic quinone type moieties that are present in the middle layer, which in turn exposes the previously protected hydrophilic moieties.

The results of 2-Dimensional ^1H - ^{13}C Heteronuclear (HETCOR) NMR affords for the *first time* direct molecular level insight into the molecular assembly of SOM in a *whole soil*. The application of Lee-Goldberg and Ramped CP techniques in the ^1H - ^{13}C HETCOR NMR experiments enabled the observation of intramolecular and intermolecular connectivities within the SOM. As a result, a model of SOM assemblage in its native matrix is forwarded: the first domain consists of alkyl moieties that are spatially isolated; and the second domain consists of aromatic moieties that are strongly associated with O-alkyl moieties over 0.4 nm and up to 0.8 nm distances, probed in this study. It is envisioned that this SOM assembly affects the uptake and release of HOCs.

Sorption of HOCs to a soil also show at least two stages: a region of fast uptake and a second region where sorption is generally slow. Flutolanil showed the highest sorption, followed by norflurazon and then acifluorfen in all soils investigated. The sorption of norflurazon, described in terms of organic carbon-normalized Freundlich sorption capacity (K_{FOC}), indicates that it is predominantly sorbed to organic matter. On the other hand, K_{FOC} of flutolanil or acifluorfen not only is due to organic matter, but is also affected by sand and clay content,

because K_{FOC} was greatest in Mandeville soil, followed by Pahokee Peat and then Elliot soil. Finally, it was demonstrated that sorption K_{FOCS} were generally higher on a dry soil compared to a wet soil, with few exceptions, especially on the less organic-rich, high silt containing Elliot soil.

Chapter 1

Introduction

1.1 The Interdependency of Land, Food and Population

In a span of five decades, the global population has more than doubled, from ~3 billion in 1959 to ~6.7 billion in 2007 (UNEP, 2007). As a result, there has been a continual shrinkage of land area per person, which on a global scale, decreased from 7.91 to 5.15 and then to 2.02 hectares per capita from year 1900 to 1950 and 2005, respectively (UNEP, 2007). This relentless increase in human population is accompanied by an ever-escalating demand of food, water, materials, and energy, which have more than doubled. These demands are met by an alarming amount of pressures applied to Earth's ecosystems, which at present are overdrafted by 30%, relative to its biocapacity (WWF, 2008). Among the Earth's ecosystems, soil is under the greatest amount of pressure (section 1.2 to 1.4), resulting from efforts to increase food production from a decreased amount of land per capita. To understand why this exists, one must appreciate the significance of soil in sustaining life. A healthy soil ecosystem in providing vital services to humanity, a) supports primary productivity and cycling of nutrients such as C, N, S, P; b) provides food, freshwater, raw materials, and fuel; c) regulates water purification, flood and climate; d) stores genetic pools; e) functions as habitat; and f) offers cultural heritages (aesthetic, recreational, educational) (MA, 2005; WWF, 2008; Sposito, 2008; Cook, 2009). Thus, it is appropriate to regard soil as an "elixir" of life. In 2050, the population is predicted to be ~9 billion; by then, two planet Earths will be needed to sustain our needs if current demands, trends and practices are continued (WWF, 2008). Thus, there is urgency in safeguarding our existing resources and starting to use them in a sustainable manner.

1.2 Land-use Changes

Much of our food supply is drawn from soil. At present, humanity relies heavily on soil

for protein production and will continue to be so, since overfishing has resulted in a limited supply of commercial fish stocks worldwide for the foreseeable future (U.S. Commission on Ocean Policy, 2004; WWF, 2008). Thus, land-use changes are apparent. A large proportion of our planet's land surface has been converted into agricultural lands. It has been reported that about 24% of our planet's land mass is currently utilized for croplands (MA, 2005), and as much as ~40% for combined cultivation and grazing, which is also now comparable to the area occupied by forests (Foley et al., 2005; UNEP, 2007). The result of less land being available for cultivation also results from industrial as well as urban development (e.g., land for housing, industrial, and commercial buildings, roads). Moreover, recent land-use changes include such destructive practices as clearing tropical forests for biofuel cultivation (Verwer et al., 2008).

Recently, agricultural lands are used more intensively than in the past. Over the last 20 years, yields per hectare of cultivated land have increased from 1.8 to 2.5 tonnes (FAOSTAT, 2006; WWF, 2008). Excessive farming leads to a faster depletion rate of soil carbon from soil surface. For example, in a simulation study by Donigian et al. (1994), about 47% of soil organic carbon was depleted in the top 20 cm of soil depth of central U.S. soils having been subjected to 40 years of cultivation. Since carbon makes up ~50% of soil organic matter (SOM); this alarming percentage implies that SOM is being used much faster than it is being produced (SOM may take centuries to form). Only upon minimization of tillage operations and application of good soil management practices will a soil's carbon content be replenished, at which time the soil can recover from the damaging effects of minimal SOM content (Donigian et al., 1994; Clapp et al., 2005).

SOM and its associations with inorganic soil phases (i.e., clays, minerals) promote aggregation, which creates a good soil structure, which in turn permits water infiltration, aeration, and stabilization of soil structure (Stevenson, 1994). A good soil structure is essential in

minimizing carbon loss from erosion and runoff. It is not surprising, therefore, that on a global land map showing the intensity of soil degradation, the soils experiencing the most severe deterioration are also most highly cultivated (MA, 2005). The domino effect of land degradation results in nutrient depletion, soil erosion, salinity, and diminishing soil water content, which ultimately leads to desertification. The consequences of land degradation can be severe; a decline in soil productivity leads to food insecurity, pollution, both of which are exacerbated due to climate change.

1.3 Climate Change

The relationship between soil and particularly SOM and climate change has received increasing global attention. Although not fully understood, SOM plays an important role in climate change, because it serves both as a carbon source and carbon sink. In addition, SOM mitigates the effects of climate change, such as flooding and droughts due to extreme rainfall patterns. SOM has the ability to retain water up to twenty times its weight (Stevenson, 1994).

The Earth's soil surface ranks second to oceans as the largest repository of carbon, storing about $2-3 \times 10^{15}$ kg of carbon in dead and living biomass, about half of which is accounted for by humic acids (Trumper et al., 2009; Clapp et al., 2005; Tabatabai and Sparks, 2005). Soil is, however, the largest dynamic repository of carbon and affects carbon cycling processes, such as production and emission of carbon dioxide (CO₂) and methane (CH₄) greenhouse gases (GHG).

The composition of the atmosphere influences the Earth's climate. Since GHG absorb infrared radiation, an increased concentration of GHG in the Earth's atmosphere is linked to a global increase in temperature, which consequently affects rainfall patterns (Schwedt, 2001; IPCC, 2007). Among the primary GHG (CO₂, CH₄, N₂O, O₃, H₂O, and chlorofluorocarbons, carbon dioxide and methane rank first and second with respect to the heavy concentration in the

Earth's atmosphere. In addition, methane is 21 times more potent GHG than carbon dioxide. Thus, human activities and or processes that lead to exceedingly high emissions of these two main GHG are of great concern. Annual GHG emissions are estimated to be 10 billion tonnes (10 GT), 15% of which comes from land-use changes, while the majority is attributed to fossil fuel use and production (Trumper et al., 2009; Canadell et al., 2007). Land use conversion often entails a lowering of carbon from soils and increased GHG emissions to the atmosphere, especially CO₂ and CH₄, as a result of forest clearing of and soil mechanical tillage (Jenkinson, 1990; Mann, 1986; Houghton, 1995). In addition, grazing animals greatly increase GHG emissions through belching of CH₄ gas (Trumper et al., 2009).

At the beginning of the industrial revolution (1750s), the atmospheric CO₂ concentration was approximately 250 ppm (Schwedt, 2001). Since then, levels have risen to ~330 ppm and ~350 ppm in 1975 and 1990, respectively (IPCC, 2007). This increase in CO₂ content in the atmosphere has led to about 0.3 - 0.6 °C increase in global temperature in recent years (Schwedt, 2001). At present, GHG are estimated to be at the level of 430 ppm carbon dioxide equivalent (CO_{2e}) (IPPC, 2007; Cowie et al., 2007). It is predicted that in the year 2050, the global temperature rise may be as high as to 7.5 °C, if current trends and practices are continued (Schwedt, 2001). In order to limit a global increase in temperature to a conservative 2 - 2.4 °C, in order to keep the planet from the most detrimental effects of climate change, the GHG in the atmosphere should not exceed 490 ppm CO_{2e} (IPPC, 2007; Trumper et al., 2009).

With the urgency of this problem, a concerted effort is warranted from the people and the government in order to stabilize or even reduce GHG concentration in the atmosphere. Initial efforts in this regard were presented under the terms of the Kyoto Protocol to the United Nations Framework Convention on Climate Change (Conference of the Parties, 1997). The need to manage, safeguard, and restore carbon in terrestrial biomes such as forests, agricultural soils, and

drylands through land management systems, has also been widely been recognized (Conference of the Parties, 1997; Nabuurs et al., 1999; WWF, 2008; Trumper et al., 2009). Agricultural soils and drylands offer the largest potential for restoring high amounts of carbon lost from soils, because it is less likely to have reached its carbon saturation (Tabatabai and Sparks 2005; Trumper et al., 2009; Johnson, 1995; Johnson and Kern; 1991). Therefore, a better understanding of soil SOM chemical make-up and its associations with the soil mineral phase, as well as the effects of interplay between these two phases in regard to soil aggregate properties such as carbon stabilization in soils, is of crucial importance.

1.4 Agricultural Chemical Dependence

The widespread use of agricultural chemicals, such as fertilizers and pesticides, was necessitated by the need to feed the growing population. The application of such chemicals significantly contributed to increases in yield per hectare of land, as the land area available for cultivation dwindled. Mineral forms of nitrogen and phosphorus fertilizers were extensively applied to supplement the soil nutrient content. This form of fertilizer easily find the way to surface waters, due to agricultural runoffs, in turn causing eutrophication or algal blooms that often result in fish kills in surface waters (i.e., streams, rivers, lakes, fishponds) (Connell and Miller, 1984).

A pesticide, on the other hand, is a chemical substance that controls, mitigates or eradicates pests. Conventional pesticides are classified, based on the types of organism on which they act, such as herbicides (weeds), insecticides (insects), fungicides (fungae), and other pesticides. Aside from impacting target organisms and non-target organisms via direct or indirect routes, pesticides also carry the potential to pollute aquatic systems, such as surface waters, through agricultural erosion and runoff, as well as seepage into groundwater. Once the groundwater is contaminated with persistent pollutants, its natural recovery will be hindered by

its extremely slow movement and a long residence time of ~200 - 1000 years or even longer (Dunnivant and Anders, 2006). Moreover, clean-up efforts may be limited by accessibility, the difficulty of which increases with groundwater depth. Contamination of water with agricultural chemicals, such as pesticides, has been shown to cause adverse effects on aquatic organisms, which may be manifested by the decreased motility and fertility, and increased mortality of such organisms (Cagauan, 1995; Berenzen et al., 2005; Matthews, 2006). Wildlife may also be affected, when feeding on a contaminated food source or drinking from contaminated water systems (Douthwaite and Tingle, 1994; Carson, 1962; Elliot et al., 2001; Newton, 1998). In addition, pesticides may not only reach the target species, but may also affect non-target organisms, which ultimately affects biodiversity. Humans are also at risk from the detrimental effects of pesticides, mainly through intake of contaminated water and food. Also of concern is the emerging potential of some pesticides to act as endocrine disrupters (e.g., dichlorodiphenyl trichloroethane, atrazine, 2,4-D, trifluralin) (Bridges and Bridges, 2004). Furthermore, other health effects related to exposure of humans to pesticides include: developmental toxicity, teratogenicity, pregnancy loss, neurologic effects, and disorders on cognitive abilities (Boxall et al., 2009; Dolk and Vrijheid, 2003; Donald et al., 2007; Fawell and Nieuwenhuijsen, 2003; Goldman and Koduru, 2000; Joffe, 2003; Stillerman et al., 2008).

The use of chlorinated pesticides started in the 1940s. Initially, dichlorodiphenyl trichloroethane was primarily introduced to control disease-carrying and disease-transmitting insects such as mosquitoes. The use of dichlorodiphenyl trichloroethane and other chlorinated pesticides intensified in the 1950s and 1960s as these pesticides were further used agriculturally (Gilliom et al., 2006). In the period of 1965 to 1980, the use of pesticides increased nearly linearly. In 1980 to 1995, however, there was a decline in pesticide use, mainly due to the banning of polychlorinated pesticides such as dichlorodiphenyl trichloroethane (Gilliom et al.,

2006). In fact, the book *Silent Spring*, written by Rachel Carson, raised public concern regarding the adverse effects of pesticides such as dichlorodiphenyl trichloroethane in the environment, especially in wildlife (Carson, 1962). Dichlorodiphenyl trichloroethane and some other organochlorine pesticides are highly stable, which means they are not easily degraded by photochemical processes and/or by microorganisms in the soil. They also exhibit very high persistence in soils, and sediment, for decades and even longer periods of time. In addition, these compounds have a high potential for bioaccumulation, which indicates that the levels of these compounds are higher at the top of the food chain (Connell and Miller, 1984; Newton, 1998; Matthews, 2006; Guo et al., 2007). In a pesticide residue analysis of dichlorodiphenyl trichloroethane concentrations along the food chain located in a Long Island salt marsh, Woodwell et al. (1967) reported the following levels: a) water: 5×10^{-5} ppm; b) plankton: 4.02×10^{-2} ppm; c) silverside minnow: 2.3×10^{-1} ppm; d) pickerel: 1.33 ppm; and e) fish eating duck: 22.5 ppm. Bioaccumulation has also been reported in Lake Michigan (www.pollutionissues.com/Re-Sy/Soil-Pollution.html). Indeed, dichlorodiphenyl trichloroethane and other pesticides were found to be persistent in the environment with a strong tendency to bioaccumulate and thus become toxic to aquatic and wildlife (Gilliom et al., 2006; Schwedt, 2001).

Between 1992 to 2001, active ingredients of conventional pesticides of about 1 billion lbs were used annually in the United States, while worldwide use was estimated at 5 billion lbs in 2001 (Gilliom, et al., 2006; Donaldson et al., 2002; Kiely et al., 2004). Recent reports by the USGS show that the pesticides widely used in the U.S. for agricultural and non-agricultural purposes are also those that are frequently detected in streams and groundwater. In 2001, 76% of the total pesticides used nationwide were for agricultural purposes; of this percentage, herbicides accounted for greater than 50% (Kiely et al., 2004). In addition, more than half of the agricultural

pesticides were used for three major crops: corn, soybean, and cotton. In a 1991–2001 study, the herbicides norflurazon, trifluralin, and atrazine were detected, totaling about 5%, 12%, and 80% in U.S. streams (Gilliom et al., 2006). Moreover in 1992, a six year monitoring study on 90 pesticides in twenty U.S. “major hydrologic basins” evidenced contamination with one or more of those pesticides at 48.4% of the 2485 groundwater sites analyzed, with concentrations generally not exceeding $1\mu\text{g L}^{-1}$ (Barbash et al., 1999).

1.5 Functions of SOM

In relation to food production in order to meet the escalating demands of an ever growing human population, it is apparent that soil/SOM plays a major, centralized role as summarized in Figure 1.1 (Trumper et al., 2009; Lal, 2004).

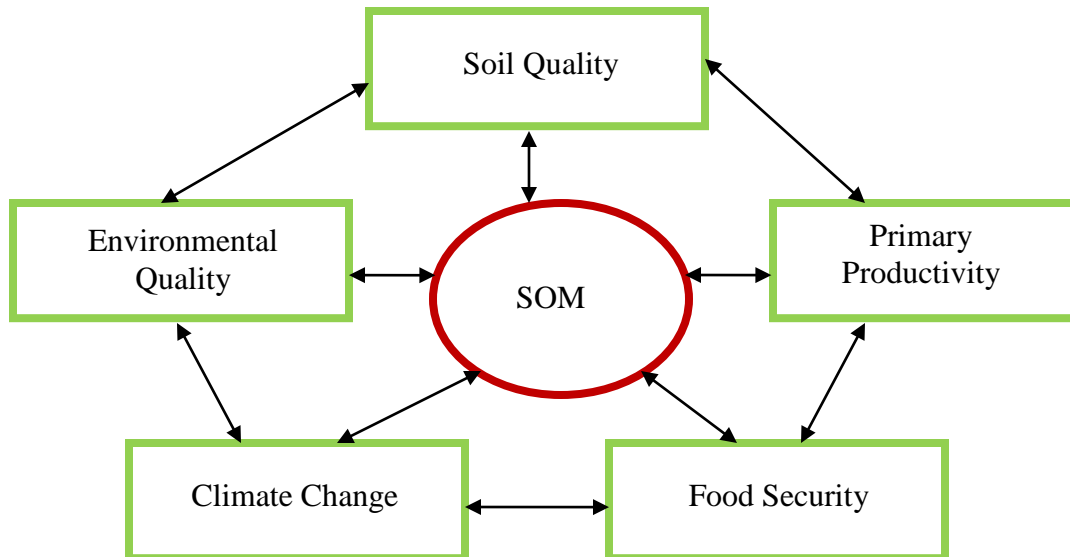


Figure 1.1 Importance of SOM

The potential of soil components (clay/minerals, SOM) to sequester pollutants such as pesticides represents one of the many benefits of soil, which reduces contamination of aquatic systems. In other words, soil-pollutant interaction influences contaminant bioavailability, which

in turn dictates fate and persistence of these contaminants in the environment. The consequences of climate change, such as change in rainfall patterns, ultimately causes flooding or drought in some areas, thus causing a compounding effect on pollutant re-distribution (Boxall et al., 2009). Increasing the frequency and intensity of precipitation has been known to exacerbate surface water pollution by run-off and soil erosion. On the other hand, soils exposed to very dry conditions over longer periods will result in increased migration of hydrophobic moieties at the soil surface (Boxall et al., 2009). However, there is a lack of studies on the effect of such soil hydration conditions in the sorption and desorption of pesticides in soils.

This void in knowledge lays the foundations for the work presented in this thesis. Chapters 3 and 4 of this thesis elucidate SOM chemical make-up and molecular assemblage, while Chapters 5 and 6 provide an understanding of how the SOM chemical makeup and assemblage influences subsequent functions, especially in regard to sorption and desorption of pesticides at different soil hydration levels.

Soil organic matter characterizations do not provide definite chemical structures for its chemical make-up due to its inherent complexity and polydisperse nature. In a whole soil, SOM can also be adsorbed or associated with the minerals, further complicating meaningful characterizations. However, due to the crucial role of SOM, further studies aimed at understanding its structure and properties are needed. Of particular interest in this study, is the role of SOM in sorption of hydrophobic organic compounds. The functional group composition of soil organic matter, as well as the nature and dynamics of SOM as a function of interactions with the mineral and aqueous interface in a soil is of concern, as it affects the wetting behavior of soil and the uptake and release of pollutants.

The recent view of natural organic matter, including that of SOM, is the assembly of heterogeneous molecules, held together by weak molecular forces, also known as

“supermolecular assemblage” (Conte and Piccolo, 1999; Piccolo, 2002; Simpson et al., 2001; Sutton and Sposito, 2005). Studies in this regard made use of NOM isolated fractions of aquatic origin, as well as soil humic and fulvic acids (Rausa et al., 1991; Conte and Piccolo, 1999; Piccolo et al., 2001; Piccolo, 2002; Piccolo et al., 2002). However, this may not represent true SOM assemblage in a whole soil because of the nature of isolation and fractionation process of SOM, which includes removal of metals/cations and very small associated molecules, such as protein-like materials (<http://ihss.gatech.edu/ihss2/>), that are otherwise important in SOM assembly. Thus, the results from SOM isolated parts may not be translated directly to the behavior of a whole SOM in the soil matrix. The ramifications of the aforementioned difference have been indicated as it was found that the sorption hydrophobic organic compounds varied between whole soils and humic fractions (Salloum et al., 2002; Wang and Xing, 2005; Cook, 2009).

Because organic matter in soil consists of both hydrophilic and hydrophobic moieties, it is also envisioned that hydration will affect conformational changes in the three-dimensional structure of these assemblies, as dictated by energy minimization principles (Wershaw, 1993; Engebretson and von Wandruszka, 1994; Wershaw, 2004). Chapter 2 presents a more comprehensive review of the fundamental principles underlying SOM assemblage and its association with and sorption of organic pollutants, especially pesticides. In the presence of water, it is envisioned that hydrophilic moieties would wish to situate near water, while the hydrophobic moieties would favor to be located farther away from water, forming micelle-like structures (Maurice and Namjesnik-Dejanovic, 1999; Kerner et al., 2003; von Wandruszka and Engebretson, 2001; Engebretson and von Wandruszka, 1999; Martin-Neto et al., 2001; Ferreira et al., 2001; Wershaw, 1993). Thus, in addition to affecting soil organic matter assembly, hydration and solvation will consequently affect association of pollutants with SOM. A couple of

studies have strongly indicated such effects, for example, the wetting kinetics of a whole soil demonstrated at least two components, a fast and slow component (Todoruk et al., 2003), and the use of water and dimethyl sulfoxide show differences in the mobilities of SOM moieties (Simpson et al., 2001). Moreover, the uptake of hydrophobic organic compound has been shown to be influenced by soil hydration and/or solvation (Belliveau et al., 2000; Gamble et al., 2000; Borisover et al., 2001; Borisover and Graber, 2002; Altfelder et al., 1999).

Hence, this study focuses on the role of SOM on the uptake and release of hydrophobic organic compounds, to augment what has been known in the literature, and to decrease knowledge gaps. There are two main objectives of this study. The first objective is to gain molecular level insight of SOM assembly in a whole soil, rather than a fractionated SOM. This involved two parts of the study. In the first part of the study (Chapter 3), our hypothesis was that hydration and/or solvation of a whole organic soil will give insights on how SOM is assembled in its native matrix. The approach was the use of whole organic soil, contacted with water or aqueous mobile phase with mM concentration of solvents that are capable of disrupting weak intermolecular forces. The released (exfoliated) SOM in the supernatant were characterized by ultraviolet absorbance, fluorescence, total organic carbon, and attenuated total reflectance Fourier-transform infrared spectroscopy. Whole exfoliated soil was analyzed by solid ^{13}C cross polarization magic angle spinning NMR. The use of a suite of spectroscopic techniques was necessitated by the complexity of the SOM both in solution and in its native matrix. In addition, the use of different techniques was expected to complement each other to provide a better understanding of the results. The findings showed that weak molecular interactions were involved in SOM and its assemblage within a whole soil, but a molecular level understanding was still missing. The second part of the study (Chapter 4) was aimed to further elucidate SOM assemblage down to a molecular level with the use of advanced two-dimensional NMR

technique. Our hypothesis to this effect was that advanced 2D- ^1H - ^{13}C heteronuclear NMR spectroscopy would allow the interrogation of molecular assemblage within an *in situ* soil organic matter. The approach used Lee-Goldberg and Hartmann Hahn cross polarization in combination with different cross polarization contact times. The use of LG as cross polarization method is due to the fact that it suppresses ^1H - ^1H homonuclear dipolar coupling, which in turn does not allow spin diffusion to occur. This enables one to see through bond correlations; hence intramolecular connectivities only (Brus et al, 2002). On the other hand, Hartmann Hahn Ramp-cross polarization method allows spin diffusion. This means that through bond and through space (or intra- and intermolecular), connectivities can be detected (Brus et al., 2002; Hartmann Hahn, 1962).

Based on the results from the two-dimensional heteronuclear NMR study, a model has been proposed that soil hydration affects the assembly of SOM, as well as the uptake and subsequent release of SOM. Hence, the second objective in this body of work is to investigate this effect, and so the hypothesis was that soil solvation would affect the uptake of HOC. This was studied using both sorption-desorption experiments on three different soils (Pahokee Peat, Mandeville and Elliot) of varying organic carbon and mineral content, three different aromatic pesticides (Acifluorfen, Norflurazon and Flutolanil) of varying hydrophobicities, and three different hydration conditions that included dry, 1 day prewetted, and 5 day prewetted soils. On a whole, the sorption findings were in very good agreement with the model derived from the NMR data, however, there were some deviations.

In order to further investigate why deviations were shown in the sorption behavior of Elliot soil in regards to the proposed SOM-hydration assembly model, kinetics data, which have been predetermined prior to sorption-desorption studies, were used. The hypothesis was that sorption kinetics of hydrophobic compounds had at least two rate components as soil wetting

occurs in at least two stages. The approach taken involved fitting the sorption kinetics data, using two-site non-equilibrium model and derived kinetic parameters, such as rate of kinetic desorption from the slow sites, sorption distribution coefficients and fraction of instantaneous sorption.

On aggregate, the work presented here is the *first* systematic study of the assemblage of SOM within a whole soil, followed by providing a link between this assemblage insight and the role of hydration on pesticide sorption within a whole soil. By taking a systematic approach, this study shows that molecular level data obtained from advanced solid state methods, can be linked to macroscopic observables, and hence, provide the promise of future molecular level characterization of “in situ” SOM.

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Chapter 2

Review of Related Literature

2.1 Importance of Sorption – Desorption Studies

Sorption is a general term used to describe adsorption, absorption, and association of a sorbate to a sorbent. It involves a chemical (i.e., sorbate) exchange between the fluid phase and the sorption site (i.e., sorbent) of the solid phase (Pignatello, 2009). When sorption occurs at the outer layer of solids, it is called adsorption, whereas when association occurs inside a three dimensional matrix of the sorbent, it is referred to as absorption (Schwarzenbach et al., 2003). The open and dynamic nature of soil allows continual fluxes of chemicals; hence, sorption is extremely important as a constant process in soils.

One of the many benefits of soil is the ability of its components (i.e., clay/minerals, soil organic matter) to sorb pollutants such as metals, radionuclides, and organic compounds. It has been widely recognized that soil organic matter is the dominant component for sorption of unionized hydrophobic organic contaminants (HOCs), such as polyaromatic hydrocarbons, pesticides, nitroaromatic explosives, and recently to pharmaceutical compounds (Kile et al., 1995). This in turn, influences the bioavailability, fate, and transport. With pesticides, sorption process also affects the bioefficacy. Thus, sorption-desorption studies are integral in estimating or modeling soil and water systems contamination, pollutant risk assessment, and remediation designs. Once contaminated, a soil is more difficult to remediate as compared to air and water (Van-Camp et al., 2004). Hence, retention mechanisms in soils must be elucidated in order to carry out efficient remediation strategies. Moreover, as part of integrated efforts to pursue sustainability, inevitably including soil management and recovery, a better understanding of sorption processes is an urgent need, even down to the molecular level.

2.2 The Soil Components

Soil is a mixture of inorganic materials, dissolved gases, water solution, and organic components (i.e., living and dead biomass), exhibiting both macroscopic and microscopic heterogeneity. The solid portion represents ~50% of the whole soil, which consists of ~45% inorganic and ~5% organic components, respectively (Schwedt, 2001; Brady, 1996). Exceptions are highly organic soils, wherein an organic content accounts for greater than 50% of the solid phase such as peat lands, as well as wetland areas such as swamps, bogs, and marshes (Sposito, 2008; Brady, 1996). The liquid and gaseous phases contribute ~20–30% each of soil composition (Schwedt, 2001). Overall soil composition also varies by geographic location, age, and depth (Elsas et al., 2007).

2.2.1 Soil Air

Soil air is a mixture of gases, similar to that found in the atmosphere, but its composition in soil is variable, due to biological activity and diffusion processes in soil (Ehrlich, 2002). For example, the atmosphere contains about 20.9% O₂ and 0.03% CO₂ in 1 L dry air, while aerobic soils consists of ~18–20.5% O₂ and ~0.3–3% CO₂ in the same volume of dry air (Sposito, 2008; McRae, 1988).

2.2.2 Soil Water

Soil water is regarded as a dynamic solution because it contains dissolved solids (e.g., ions, nutrients) and dissolved gases. Thus, water is essential in the existence of soil life as it transports and translocates nutrients to plants and soil microflora and microfauna (Elsas et al., 2007). In addition, the aqueous soil phase is mainly responsible for pollutant mobility within a soil column.

The unique properties of water, due to a hydrogen-bonding capability, greatly influence water retention and redistribution within soils. For instance, water molecules adhere to soil solid

surfaces, such as minerals and SOM. The edges of minerals and surface of organic matter bear negative charges; thus, water molecules are attracted to these surfaces through ion-dipole interaction (Sposito, 2008; Dunnivant and Anders, 2006). This rather strong interaction holds water molecules rigidly on the surfaces, thereby creating a thin film of water molecules ($\sim 1.7 \times 10^{-3}$ % of particle diameter) referred to as hygroscopic water (Ehrlich, 2002). This type of water does not solidify and is never labile as a liquid; hence this water is unavailable for plant use (Ehrlich, 2002). In a water saturated soil atmosphere, hygroscopic water is surrounded by another layer of water molecules, held cohesively by intermolecular forces of attraction. This water, called capillary water, moves from one particle to another and is a readily available water resource in soils (Ehrlich, 2002). When water is in excess of the optimum capacity of soil, gravitational water surrounds capillary water. This type of water usually fills the bigger soil pore spaces and moves downward by gravity or hydrostatic pressure (Erlich, 2002; Elsas, 2007). This physico-chemical distribution of water in soil serves as a hydration buffer such that it mitigates consequences of severely dry or flooded soil conditions. When water drains or dries from the soil, the order descends from bigger pores to smaller pores. However, during wetting, that order may not be the case. Hence, drying and wetting processes may be irreversible or slowly reversible and will have a varying effect on pollutant sorption at different hydration conditions.

2.2.3 Inorganic Component

The inorganic solid matter in soil mainly comes from weathered parent rock material and partly from soil deposition processes. They are classified, based on their particle size, as: 1) sand grains 50–2000 μm ; 2) silt 2–50 μm ; and clay fraction $< 2\mu\text{m}$ (Elsas et al., 2007; Brady, 1996). These minerals are mainly composed of silicon and oxygen bond, thus forming silicates, with mostly a definite chemical composition and structure (Dixon and Schulze, 2002). Sand grains and silt consist of primary silicate minerals (e.g., mica, silica, quartz) while clay fraction in soils

mostly represent advanced stages of primary silicate weathering (Sposito, 2008).

Primary minerals, such as metal oxides and oxyhydroxide type minerals (e.g., quartz (SiO_2), gibbsite ($\text{Al}(\text{OH})_3$), goethite ($\alpha\text{-FeOOH}$)), possess charges on the surface, resulting from pH dependent proton transfer reactions of surface O^{2-} and OH^- sites in aqueous solutions (Schwarzenbach et al., 2003). Furthermore, clays exhibit permanent, as well as variable, negative charges that confer sites of interaction for ionic molecules. The edges of clays (e.g., aluminum oxides) possess negative charges that vary with respect to pH and ionic strength as in aforementioned primary minerals (Gillman, 1984; Talibudeen, 1981). Clay minerals are alternating layers of tetrahedral sheet (i.e., silicon is covalently bonded with four oxygens) and octahedral sheet (i.e., Al^{3+} is bonded to O^{2-} or OH^- ions in octahedral arrangement) (Dunnivant and Anders, 2006; Sposito, 2008). As an example, montmorillonite is a 2:1 type clay mineral containing two tetrahedral sheets and one octahedral sheet, with a chemical structure of $\text{MO}-7\text{Al}_2\text{O}_3-22\text{SiO}_2-n\text{H}_2\text{O}$, where M is either sodium or calcium (Dunnivant and Anders, 2006). Kaolinite, on the other hand, is a simple 1:1 combination with a structure of $\text{Al}_2\text{O}_3-2\text{SiO}_2-n\text{H}_2\text{O}$ (where $n=0$ or 2) (Evangelou and Phillips, 2005). The permanent negative charge in clays rises from “isomorphic substitution”, whereby lower charge cations (e.g., Mg^{2+} , Al^{3+}) replace higher charge cations (e.g., Al^{3+} and Si^{4+} , respectively) during clay formation (Sposito, 2008). Kaolinite does not undergo this type of isomorphic substitution, unlike other clay minerals. The amount of these negative charges in minerals/clays is related to the cation exchange capacity (Sposito 1984; McBride, 1989). The presence of permanent negative charges can therefore promote adsorption of cationic pollutants through complexation and cation exchange (Dunnivant and Anders, 2006). On the other hand, anionic organic pollutants are less likely to be sorbed on mineral surfaces, due to charge repulsion and therefore may complex with surrounding cations. As a result, possible HOC sorption mechanisms in mineral surface may include the following: 1) complexation,

especially of organocations; 2) H-bonding, whereby a lone pair in oxygen acts as proton acceptor; 3) $n-\pi$ where n refers to the nonbonding electrons in oxygen, as electron donors to electron deficient aromatic π systems; and 4) cation- π where aromatic π serve as electron donors. These interactions will further be discussed under section 2.5.

The crystal packing of clay minerals may also confer a varying degree of clay swelling or expandability. Kaolinite is a non-expandable type of clay (Sposito, 2008). Montmorillonite is a common example of a swelling type of clay, whereby individual layers are rigidly held, but adjacent 2:1 layers may be loosely held together, depending on the chemicals or ions that are present in the interstitial area (i.e., the space between adjacent 2:1 layers). Water also serves to expand this interstitial area, as it commonly hydrates the ions in this space. Illite exhibits medium expandability, but swelling type clays provide a greater surface area for diffusion and binding of HOCs (Dunnivant and Anders, 2006).

2.2.4 Soil Organic Matter

The dead biomass in soil, of which ~ 99% comes from plant litter, is subjected into biotic and abiotic decomposition mainly by the microorganisms in soil (Stevenson, 1994). The resulting material is called soil organic matter (SOM), which consists of low molecular weight compounds and loosely held biomolecules (Sposito, 2008). SOM can be classified into non-humic substances and humic substances. Humic substances are dark-colored, highly recalcitrant mixture of organic compounds; these are further defined operationally, based on their separation into components by pH governed aqueous solubilities. Humic acids are insoluble in $\text{pH} < 2$, and soluble at all other pH, but fulvic acids are soluble at all pH. Humin is the aqueous, insoluble fraction. The traditional approach to isolation of humic substances from aquatic or terrestrial samples based on their solubilities in acidic or basic pH, is provided by IHSS (<http://ihss.gatech.edu/ihss2/>) and the overall procedure is subsequently presented here. A pre-

weighed, air-dried soil, which was previously freed from plant materials and sieved to a 2.0 mm mesh sieve, is added with 1 M HCl to achieve a pH value of about 1–2 at room temperature. Then the solution volume is adjusted with 0.1 M HCl to reach a desired solution to soil ratio of 10 mL solution per 1 g of dry soil sample. The mixture is then shaken at 1 hr, after which, the supernatant is separated from the solids through centrifugation or decantation. The supernatant contains the acid-soluble humic fraction, known as fulvic acids (FA). This FA extract 1 is saved for subsequent XAD-8 treatment.

Next, the soil residue remaining after centrifugation is added with 1 M NaOH until a neutral pH (pH=7.0) is reached. Addition of 0.1 M NaOH is necessary, until a 10 mL : 1 g solution to soil is attained. This step and the subsequent base extraction must be done in an inert atmosphere, through the use of an inert gas such as N₂, so that any chemical reactions of mainly ester hydrolysis may be prevented. The extraction is carried for a minimum of 4 hrs in the presence of N₂, as previously mentioned. After the sample suspension is allowed to settle overnight, supernatant is separated through a centrifugation step. Subsequent to this step, the supernatant is acidified to pH=1.0 with the addition of 6 M HCl, and then allowed to settle overnight (12–16 hrs). The precipitate that settles from the supernatant is humic acid, and the supernatant contains the FA extract 2. After centrifugation, the FA is saved for XAD-8 treatment, and the HA is collected for further purification processes.

The humic acid is redissolved in a minimum amount of 0.1 M KOH, in the presence of N₂ gas. Solid KCl is added to achieve a final concentration of 0.3 M [K⁺]. After centrifugation to eliminate undissolved solids, the resulting clear supernatant is added with 6 M HCl, then allowed to settle overnight to reprecipitate the humic acid. The precipitate collected after centrifugation is suspended with 0.1 M HCl/0.3 M HF solution in a plastic container, in order to keep the metal ions dissolved into the solution. The suspension is shaken overnight. This HCl/HF treatment is

repeated until the ash content in HA is $< 1\%$. The HA is then dialyzed against distilled water in order to remove most of the Cl^- ions from the HCl treatment. The resulting HA is then freeze dried. The FA supernatants 1 and 2 are each passed separately through an XAD-8 resin, composed of methyl methacrylate ester, followed by distilled H_2O rinses (0.65 column volume) and back-elution of adsorbed FA with 1 column volume of 0.1 M NaOH, and followed by distilled water rinses using 2–3 column volumes. The eluate is acidified to pH 1.0 with 6 M HCl, and added with HF solution to attain a 0.3 M HF in solution. Eluates 1 (from FA extract 1) and Eluate 2 (from FA extract 2) are then combined, and passed once again in an XAD-8 resin (resin volume in the glass column should be $\sim 1/5$ of sample volume). Subsequent steps of water rinse and NaOH back elution are repeated as indicated above for FA. However this time, after rinsing the column with 2 column volumes of distilled water, the eluate is passed through a H^+ saturated (the concentration of H^+ is 3x the mole of Na^+ in solution) cation exchange resin. The H^+ saturated FA is then freeze dried (<http://ihss.gatech.edu/ihss2/>).

After fractionation based on solubility differences, the chemical properties of natural organic matter, including soil organic matter, are often characterized by a suite of spectroscopic methods. The first and one of the most necessary measurements is elemental analysis, especially the determination of carbon, hydrogen, and nitrogen. The amount of carbon is often reported as total organic carbon, which is the fraction remaining after inorganic carbon (i.e., carbonates) was subtracted from the total carbon. Rice and MacCarthy (1991) compiled and subsequently evaluated statistically the elemental analysis data of worldwide humic substances from aquatic or terrestrial origins. Given below is the mean (\bar{x}) elemental values (in g per 100 g humic substance sample) and their corresponding relative standard deviation shown in parentheses.

It was further shown by detailed, statistical analysis results that humic acids had more carbon and nitrogen than fulvic acids. Fulvic acids exhibits more oxygen content; thus, humic

acids demonstrate lower H/C and O/C molar ratios, which suggests that these acids have less polar and more aromatic characteristics (Rice and MacCarthy, 1991; Sposito, 2008). From such elemental results, total organic matter content has been approximated as ~2 times (1.72–2) the total organic carbon content.

Table 2.1 Average amount (g in 100 g) of main elements in soil humic substances worldwide^a

Humic substance	C		H		N		O	
	\bar{x}	RSD	\bar{x}	RSD	\bar{x}	RSD	\bar{x}	RSD
Humic acid	55.4	(6.97)	4.8	(20.8)	3.6	(36.1)	36.0	(10.3)
Fulvic acid	45.3	(11.9)	5.0	(20.0)	2.6	(50.0)	46.2	(11.3)

^a (Rice and MacCarthy, 1991)

The UV analysis of humic substances typically exhibit a broad and featureless spectra, owing to the presence of multiple types of chromophores in the structure. Absorbance at 254 nm is commonly used to approximate dissolved NOM concentration. Furthermore, specific UV absorbance (SUVA) at 254 or 280 nm, utilized to roughly estimate aromatic content of humic substances, shows that SUVA 254/280 correlates well with aromatic carbon content, based on ¹³C NMR, ¹H NMR and FTIR data (Kalbitz et al., 1999; Chin et al., 1994; McKnight et al., 1997; Weishaar et al., 2003). SUVA is defined as absorbance at a specific wavelength, divided by dissolved organic carbon concentration.

Previous studies aimed at estimating the molecular weight distributions of humic substances were performed using high performance size exclusion chromatography. With size exclusion chromatography, larger molecules elute first, hence exhibiting a faster retention time (Leenheer and Croué, 2003). A soil humic acid and a coal-derived humic acid were demonstrated to have apparent weight-average molecular weight (Mw) of ~79 kDa and ~130 kDa respectively (Rausa et al., 1991). Much lower Mw of approximately 17–57 kDa were reported for humic acids, and ~10 kDa for fulvic acids, which further resulted in decreased Mw, after μ M to mM addition of compounds, known to disrupt hydrophobic/hydrogen-bonding forces (Piccolo et al.,

2001; Piccolo, 2002; Piccolo et al., 2002; Conte and Piccolo, 1999). The latter investigation contended for the polymeric view of NOM and postulated that NOM are made of weak associations of low molecular weight ($\leq 2\text{kDa}$) molecules.

Fluorescence, a nondestructive technique, is also widely used to characterize NOM being more sensitive than UV analysis. Humification index based methods (HIXs) were utilized to estimate the degree of humification of NOM. Humification is defined as the process whereby small organic molecules are transformed into a higher molecular weight organic matter, having a higher proportion of conjugated π systems and aromatic compounds (Ohno, 2002; Miano and Senesi, 1992). HIX is often calculated as a ratio of emission in longer wavelengths to shorter wavelengths; and a higher HIX implies a more humified material (Schaumann et al., 2000; Cory and McKnight, 2005; Del Vecchio and Blough, 2004; Kalbitz et al., 1999; Miano and Senesi, 1992). Emission scan, synchronous, and excitation-emission matrix fluorescence techniques yield very similar insights with respect to the fluorophores present in NOM. Two major fluorophores are often found in NOM and are attributed to protein-like and humic-like molecules (Cook et al., 2009; Leenheer and Croué, 2003; Coble et al., 1990; Coble, 1996; Chen et al., 2003; Stedmon et al., 2003; Ariese et al., 2004). From these studies, amino acid (tyrosine/tryptophan), similar to fluorescence, exhibits characteristic excitation and emission wavelengths at approximately 240 to 325 nm and 300 to 400 nm, respectively. Humic-like fluorescence may arise from quinone-like moieties, based on their degree of conjugation: 1) quinone A moieties contain less conjugated humic materials and show emission at ~ 375 to 475 nm upon excitation at ~ 240 – 325 nm; and 2) quinone B moieties consist of more conjugated humic materials, having an emission at ~ 450 to 550 nm and an excitation wavelength at ~ 250 to 370 nm (Cook et al., 2009). Significant amounts of quinone-like fluorescence features, especially the quinone B type, indicates a more humified NOM, and is consistent with ^{13}C NMR data (Cook et al., 2009).

The Fourier Transform Infrared Spectroscopy (FTIR) provides mainly a qualitative functional group characterization of NOM in solution or solid form. The IR spectra of SOM typically exhibit a broad profile with main absorption features in the following regions (cm^{-1}): 1) 3400–3300: OH stretch arising from hydrogen-bonded groups; 2) 2940–2900: CH stretch in aliphatics (CH_2 , CH_3); 3) ~ 1720 : C=O stretch in carboxyls and ketones; 4) ~ 1610 : C=C vibration in aromatics and hydrogen-bonded C=O stretch; and 5) 1280–1200: C–O stretch and OH in bend carboxyl group (Stevenson, 1994; Stevenson and Goh, 1971). A quantitative FTIR determination of humic substances was reported by Davis et al. (1999), via the use of an internal standard KSCN. Organic matter composition of a whole soil has also been derived by measuring separately the IR spectra of a whole, unmodified soil that has been subjected to pyrolysis to remove all organic components (Cox et al., 1999).

Mass spectrometry has also been applied in the determination of apparent molecular weight distributions and in the elucidation of the structural composition of NOM. The electron spray ionization Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry analysis of FA has been shown to produce an extremely complex spectra, having broad fragmentation peaks in the range of m/z ~ 500 – 3000 , as well as number-average molecular weights of 1.7–1.9 KDa, which increase in the following order: aquatic < soil < peat < lignite (Brown and Rice, 2000). Proceeding studies demonstrated highly resolved spectra, especially at molecular weight less than 1 KDa, supporting previous finds that NOM contains significant amounts of lignocellulosic materials, with increased amounts of larger molecular weight and with more reduced, as well as more condensed forms of these materials upon diagenetic alteration (Kujawinski et al., 2002; Stenson et al., 2002). However, this technique is limited, especially in the analysis of high molecular weights (>1 KDa) compounds due to the following: 1) insufficient ionization; and 2) fragmentation to low molecular weight compounds during the electron spray ionization process,

which renders an mass spectrometry analysis of these high molecular weights compounds rather difficult (Reemtsma and These, 2003).

NMRs have been extensively used to characterize the molecular group distribution of NOM. An ^1H NMR analysis of NOM often yields poorly resolved spectra, due to the polydisperse nature of NOM and to small spread of ^1H chemical shift, while the use of liquid state ^{13}C NMR involves long acquisition times, coupled with a difficulty in obtaining accurate quantitation (Cook and Langford, 1998; Cook et al., 1996). A solid state ^{13}C NMR is the preferred method, which usually involves the use of a cross-polarization (CP) technique, because of advantages this method has; 1) virtually no sample preparation, except for homogenization and the use of a dry sample; 2) is non-invasive; 3) has a faster acquisition time compared to the liquid state ^{13}C NMR; and 4) accurate quantitation is possible (Cook and Langford, 1998; 1999; Cook et al., 1996; Cook, 2004). Specifically, ^{13}C Ramp-CP at high magnetic fields, together with a fast sample rotation process was implemented in the analysis of humic substances, due to great enhancement in the signal-to-noise ratio and resolution (Dria et al., 2002; Cook and Langford, 1998; 1999; Cook et al., 1996). Ramp-CP analyses demonstrated that FA consists of the following: 1) a high amount of polar moieties that are attributed to carbohydrates; 2) a significant amount of unsubstituted aromatics; and 3) large aliphatic moieties (Cook and Langford, 1998; Cook et al., 1996). In contrast, HA is comprised of a high proportion of large aliphatic groups and substituted aromatic moieties, consistent with the literature finding that FA contains more polar functionalities, while HA is more reduced and more aromatic in nature (Cook and Langford, 1998; 1999; Cook et al., 1996). In addition, two-dimensional solid state ^1H - ^{13}C HETCOR NMRs were employed in the analysis of peat humic acid, yielding the following insights: 1) the presence of nonpolar alkyl moieties; 2) a great proportion of aromatic groups containing covalently-bonded methoxyl groups, indicative of lignin materials; and 3) a close

proximity between O-alkyl moieties (possibly carbohydrates) and aromatic groups (Mao et al., 2001).

In contrast with inorganic components of soil which are easily identifiable due to its definite composition, SOM characterizations do not provide definite chemical structures for its chemical make-up, due to an inherent complexity. In a whole soil, SOM can also be adsorbed or associated with the minerals, further compounding an already complex molecular characterization (Cook, 2009). However, due to the vast importance of SOM, as discussed in Chapter 1, further understanding of its structure and properties are warranted. Elucidation of chemical make-up, as well as an assemblage of SOM in whole soils, explored further in Chapters 3 and 4 tends to suggest an influence on sorption of pollutants. Whole soils were used in this study, because physico-chemical properties of isolated fractions of soil SOM may not equal that of a native soil state. This reflects significant implications to pollutant sorption studies, found to vary when humic fractions are used in comparison to whole soils (Salloum et al., 2001; Wang and Xing, 2005; Cook, 2009).

2.3 The Use of Trifluorinated Aromatic Pesticides as Sorbates

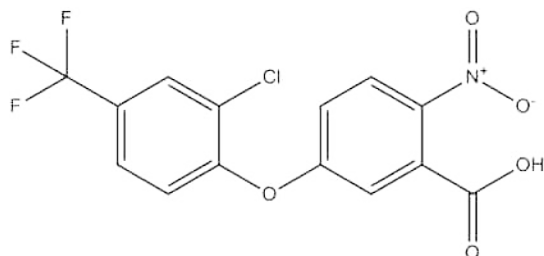
The banning of the dichlorodiphenyl trichloroethane use and some other polychlorinated compounds in early 1970s due to toxicity, persistence, and bioaccumulation tendencies, led to a plethora of sorption research, centered on hydrophobic chlorinated and brominated compounds. Subsequently, efforts to produce agricultural chemicals, as well as compounds of commercial importance that are less toxic than polychlorinated ones, have been on the rise. One outcome is the increase in use and production of synthetic fluorinated organic compounds. Fluorine atoms have unique properties that impart biological effectivity to its organic forms. The Van der Waals size of fluorine is 1.47 Å, which is smallest among halogens, but of similar size to that of oxygen (i.e., 1.52 Å), thus it can satisfy steric requirements on biological activity sites (Smart,

1994; Leroux et al., 2008). Having the highest electronegativity among the halogens, its carbon-fluorine bond has also the strongest polarity and highest bond energy compared to other carbon-halogen bonds (Key et al., 1997; McMillen, 1982; Solomons, 1980). This minimizes its oxidative metabolism, imparting greater stability and lipophilicity, especially in the CF₃ form (Leroux et al., 2008).

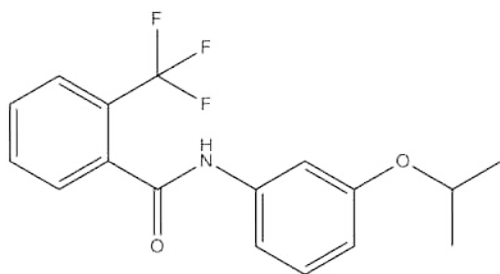
Aromatic fluorinated compounds are used in a wide array of applications, such as pesticides and pharmaceuticals (Elliot, 1994; Mazzola et al., 1984; Rao, 1994). Mixtures of aromatic fluorinated compounds also enter the environment as industrial waste products. Hence, organofluorine compounds have become ubiquitous xenobiotics in the environment. In 1980–1994, the number of organofluorine agricultural chemicals has reached ~9% of all agricultural chemicals (ACs), and its rate of production exceeded that of non-fluorinated agricultural chemicals (Cartwright, 1994). Although single and multiple fluorine groups attached to aromatics are prevalent, trifluorinated pesticides were used in this study for the following reasons: 1) the heavily used ACs are trifluoromethyl substituted aromatics (i.e., Ar–CF₃ where Ar is aromatic); and 2) the CF₃ group is better suited for future solid ¹⁹F NMR studies.

In 2002 alone, herbicides trifluralin, norflurazon, and acifluorfen were used at a rate of 9.0, 1.2, and 0.4 million lbs active ingredient (Tomlin, 1997; Gianessi and Reigner, 2002). Further, about half of these organofluorine chemicals are used as herbicides. It is known that the CF₃ group is highly resistant to defluorination. For example, trifluralin, the most commonly applied herbicide found in corn, cotton, soybean, and wheat crops, was reported to have transformation products that do not involve degradation of the Ar–CF₃ group. Due to wide use and persistence, it is thus not surprising that occurrence of CF₃ substituted aromatics (e.g., trifluralin, norflurazon) have been detected in U.S. streams and groundwaters (Gilliom et al., 2006; Senseman et al., 1997a; Senseman et al., 1997b). Hence, this work focuses on sorption of

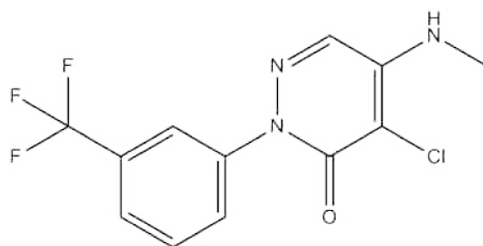
three pesticides containing aromatic $-CF_3$ group and other functionalities (Figure 2.1). These fluorinated pesticides differ in molecular size, solubility and polarity. One of the goals of this study will be to understand how these properties affect their sorption.



5-(2-chloro-a,a,a-trifluoro-p-tolyloxy)-2-nitrobenzoic acid



a,a,a-trifluoro-3'-isopropoxy-o-toluanilide



4-chloro-5-methylamino-2-(a,a,a-trifluoro-m-tolyl)pyridazin-3(2H)-one

Figure 2.1 Chemical structures of acifluorfen, flutolanil and norflurazon (top to bottom)

Norflurazon is a pre-emergence herbicide, applied primarily on orchards and cotton farms. Its mode of action on weeds is through inhibition of carotenoid biosynthesis (Ahrens, 1994; Morillo, et al., 2004). Acifluorfen on the other hand, is a post-emergence herbicide

(Ahrens, 1994; USEPA, 1989). Both pesticides are likely carcinogens: persistent, mobile, and slightly toxic to aquatic organisms. Acifluorfen is also a suspected endocrine disruptor (Tomlin, 1997; Gianessi and Reigner, 2002). The first application of flutolanil was as a fungicide in Japan to eradicate rice sheath blight, caused by *Rhizoctonia solani* (Araki and Yabutani, 1993). Later uses included bulb farming and turf in golf courses (Okamura et al., 1999). In the U.S., flutolanil has recently been approved for use in peanuts, rice and potato farms (www.dec.state.ny.us). It is also persistent and mobile, but exhibits a low toxicity to aquatic organisms, compared to norflurazon and acifluorfen (Okamura et al., 1999).

2.4 Choice of Sorbents

The physico-chemical properties of the sorbate (e.g., size, K_{OW} , solubility, structure) and of the sorbent (e.g., SOM, mineral composition) as well as other environmental factors (e.g., microbiological components, rainfall patterns, soil hydration condition) are well known factors affecting the sorption-desorption behavior of hydrophobic organic chemicals. The sorbents or soils used here are Pahokee Peat, which has the highest organic matter content, followed by Mandeville (Bayou Castine) and Elliot soils. Mandeville and Elliot soils have appreciable organic and mineral contents, which make them suitable representations of agricultural soils. Pahokee Peat and Elliot soil are both standards from International Humic Substances Society (IHSS); the availability of these reference soils allows reproduction and/or continuation of this type of studies by other investigators. Pahokee Peat was also chosen because of the following reasons: 1) it has a similar organic carbon content to the soil used in the SOM molecular assemblage study; and 2) because it is almost purely organic matter (~90%), allowing us to evaluate the contribution of SOM to sorption. Mandeville soil was obtained locally from a wetland. At present, this type of soil is converted to cultivated land. More importantly, in Louisiana, wetlands are used in the final stages of waste water treatment facilities, in order to

further reduce nutrient and pollutant concentrations into allowable limits, prior to effluent discharge into nearby surface waters (Verhoeven and Meuleman, 1999). Thus, this type of soils plays an important role in HOC contaminant sorption and transport. Elliot soil is a typical agricultural soil, because of its organic matter content. Yet Elliot soil cannot be fully representative of mineral content, since it contains no montmorillonite.

2.5 Important Forces of Attraction for HOC Sorption

Pollutants containing aromatic structures are ubiquitous in the environment (e.g., polyaromatic hydrocarbons, Agricultural chemicals). The pesticides acifluorfen, flutolanil, and norflurazon in this sorption-desorption study contain two, six-membered, aromatic rings. A molecular level of understanding in how these aromatic rings influence mechanism of sorption to soils and sediments becomes crucially important since it affects both fate and transport in soil sorption. Sorption of HOCs in soil predominantly comes by physisorption. Physisorption of sorbates to soils are primarily non-covalent in nature. This includes Van der Waals forces, hydrogen-bonding, and quadrupolar interactions. Termed intermolecular forces of attraction, these are generally weaker in strength, compared to covalent attractions (Pignatello, 2009; Schwarzenbach et al., 2003).

2.5.1 London Van der Waals Forces

Nonpolar molecules (e.g., CO₂, benzene) can have a slightly non-uniform distribution of charges at any instant, due to the continuous movement of electrons (Solomons, 1980). This creates “temporary” or induced dipoles. In comparison, when there is an unequal sharing of bonding electrons within an organic molecule due to electronegativity differences, charge separation occurs, thus creating “permanent” dipoles (Brown, 1975).

The intermolecular forces of attraction between two permanent dipoles (“Keesom”), between two induced dipoles (London dispersion), and between temporary and permanent

dipoles (Debye), are collectively called London Van der Waals forces (Pignatello, 2009; Israelachvili, 1992). The magnitude of London Van der Waals forces are related to the separation distance, geometry, and molecular properties of involved structures (i.e., dipole moment, polarizability, electrostatic potential, and planarity) (Pignatello, 2009; Schwarzenbach et al., 2003). When either the sorbate (organic molecule) or the sorbent (clay, mineral, SOM) bear a charge, these intermolecular forces of attraction are called either a “charge-dipole” or a “charge-induced” dipole. The strength of this type of intermolecular forces of attraction is once again affected by separation distance to the fourth power, as well as to the magnitude of the charge (Pignatello, 2009; Israelachvili, 1992). The strength of this type of intermolecular forces of attraction is typically less than 6 kcal mol^{-1} . When both the sorbate and sorbent are attracted due to opposite charges (i.e., charge-charge), coulombic forces significantly contribute to the strength. However, London Van der Waals forces may also act simultaneously and possibly, in various combinations with other types of intermolecular forces of attraction.

2.5.2 Hydrogen Bonding

Hydrogen-bond (H-bond) intermolecular forces of attraction is characterized by a strong dipole-dipole attraction between a proton donor (D) and proton acceptor (:A), as represented below (Solomons, 1980; Gilli et al., 2009; Brown, 1975).



Examples of proton donors are highly electronegative atoms F, N, O, S as well as carbon. Proton acceptors are those that carry lone pairs or nonbonding electron pairs such as N, P, O, S, and Se, or those having multiple π -bonds (Vinogradov and Linnel, 1971; Gilli et al., 2009).

Gilli et al. (2009) classified H-bonding into six types called “chemical Leitmotifs” as follows: ordinary hydrogen-bond, double charge assisted hydrogen-bond, negative or positive

charge assisted hydrogen-bond, resonance assisted hydrogen-bond and polarization assisted hydrogen-bond. Aforementioned hydrogen-bonds have dissociation energies that may range from very weak to strong. For example, homonuclear hydrogen-bonds (i.e., D=A), were reported to have $\sim 2\text{--}42$ kcalmol⁻¹ energies (Brown, 1975; Schwarzenbach et al., 2003). Polarization assisted hydrogen-bond is commonly manifested by multiple H-bonds in hydroxyl groups contained in water, alcohol, and phenol molecules, the strength of which is higher than that of ordinary hydrogen-bond. Resonance assisted hydrogen bond involves proton acceptors and proton donors that have “short and polarizable” conjugated π -systems (Gilli and Gilli, 2000; Gilli, et al., 2000). A few examples are carboxylic acid dimers and diketone enols.

Gilli et al. (2009) devised an accepted method called the “pka slide rule” to determine the relative strength of H-bonds. It is essentially a chart that arranges the proton donors on one side and proton acceptors on the other side, with their corresponding pka values in water. The strengths of the H-bond between donor and acceptor is maximum when their pkas match (i.e., $\Delta pka = 0$). Stated another way, the strength of the H-bond increases as the Δpka between donor-acceptor pair decreases (Gilli et al., 2009). The hypothesized reliability of H-bond energy approximation, based on this pka slide rule, was verified by crystallographic structural database (CSD) searches on the geometry of $\sim 10,000$ H-bonds as well as searches of enthalpic energy, associated with gas phase dissociation, from the NIST database (Gilli et al., 2009). Only ordinary hydrogen-bonds and charge assisted hydrogen-bonds may be described by proton transfer equilibria to a varying extent. Hence, availability of their pka's becomes useful in predicting H-bond strengths. Ordinary hydrogen-bonds represent the weakest form of H-bonds, while double charge assisted hydrogen-bonds usually range from strong to very strong in magnitude. Although weak H-bonds are electrostatic in nature, stronger H-bonds may have both electrostatic and covalent characters (Gilli and Gilli, 2000; Gilli, et al., 2000).

SOM contains a mix of different moieties such as aliphatic acids, carbohydrates, amino acids, and tannin and lignin types, as well as other forms of heterocyclic and polyaromatic functionalities (Hayes and Clapp, 2001; Schnitzer, 1991). It is thus expected that sorption of pollutants due to H-bonding would involve mainly N, O, and S donor and acceptor types (Pignatello, 2009). The acidity of N, O containing organic compounds is given as: carboxylic acids > phenols > alcohols, amides > aniline > amine. In addition, the presence of a nitro group or halogen in a molecule increases its acidity. Maximum H-bond interaction provided by this type of organic donors and acceptors is situated at pka interval $0 \leq pka \leq 14$ due to pka matching at this interval (Gilli et al., 2009). Moreover, H-bonds involving O and N donor-acceptor groups may have energies from $\sim 1.4\text{--}16 \text{ kcal mol}^{-1}$, due to highly ordered geometries (Gilli et al., 2009). Table 2.2 summarizes the H-bond and their expected strengths, relevant to the interactions of pesticides used in this research and the SOM.

Table 2.2 Some relevant H-bonds for this study^a

H acceptor /H donor	Aniline	Azines	Azoles	Amines, Diamines
Phenol	medium	very strong	strong	Strong
Carboxylic acid	medium	very strong	strong to very strong	strong to very strong

^aGilli et al., 2009

In addition, amide donor groups may have a medium strength H-bond with amide acceptor groups. An example of strong double charge assisted hydrogen-bond was suggested between pyridine and pentachlorophenol (Gilli et al., 2009). The presence of amino groups in SOM may help explain the persistence of chlorophenol in contaminated sites in the U.S. that contain chlorinated wastes. Therefore, understanding the contribution of possible retention mechanisms, such as H-bond, would be beneficial in designing effective remediation strategies.

The $\pi\text{--H}$ type H-bonds, where π is pi bonds in alkenes or aromatics will be introduced under aromatic or π -type interactions. H-bonds are also exhibited by acidic proton donors O, N, S, and halogen containing alkyl compounds. The latter is usually weaker in strength, compared

to H-bond between water molecules (Silverstein et al., 2000; Pignatello, 2009).

2.5.3 Quadrupolar interactions

Aromatic ring structures may be nonpolar, polar, or may have both polar and non polar characters due to the type of aromatic heterocycles and the effect of substituent groups. This implies that these aromatic ring structures exhibit different degrees of hydrophobicity; so one possible mechanism of sorption is through weak London Van der Waals forces. In addition, stronger forces of interaction to sorption sites have long been implicated in regard to aromatic-containing organic compounds, including various types of π -aromatic interactions.

As with any other organic molecules, aromatic compounds have molecular quadrupole moments. The dipole moment with a unit of measurement expressed in Debye or Cm in SI units describes the degree of polarization of the organic molecule as a separation of charges by a unit distance (Williams, 1993). In comparison, the molecular electric quadrupole moment is regarded as a better depiction of the charge distribution per unit area of a molecule, with an SI unit of Cm^2 . To illustrate the difference between the two, CO_2 molecules are traditionally thought to have a dipole moment equal to zero debye, whereas its quadrupolar moment was measured to be $-15 \times 10^{-40} \text{ Cm}^2$ (Williams, 1993). The classical approach to quantify a quadrupole moment in molecules is similar to that used for dipole measurements, is accomplished by passing an electric field through the molecule, whereby the resulting orientation of charges is measured with respect to a particular axis in a molecule (Buckingham, 1970; Williams, 1993).

The quadrupole moments of benzene and hexafluorobenzene are $\sim(-)30 \times 10^{-40} \text{ Cm}^2$ and $\sim(+)30 \times 10^{-40} \text{ Cm}^2$, with respect to the C_6 rotational axis (Williams, 1993; Vrbancich and Ritchie, 1980). This means that polarized π electrons are located above and below of the benzene ring, while the positive end is oriented perpendicular to it (i.e. C–H sigma bond), thus making benzene a potential π electron donor or simply called π donor (Figure 2.2a). On the

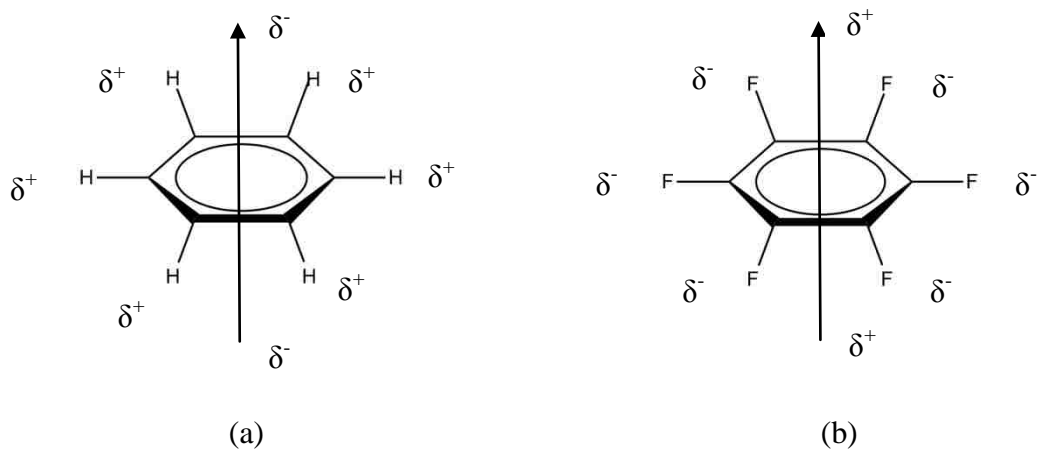


Figure 2.2 Quadrupolar moment of benzene (a) and hexafluorobenzene (b)

contrary, the presence of strongly electronegative fluorine atoms in hexafluorobenzene results in a quadrupole moment that is similar in magnitude, but opposite in sign to that of benzene (Figure 2.2b). This is due to the electron withdrawing capability of fluorine, thereby making the face of the ring more positive; hence, hexafluorobenzene is a π acceptor. This electric quadrupole in aromatic molecules contributes to their π -donor and π -acceptor properties, which have been suggested to be largely responsible for important aromatic interactions as follows: 1) base pair stacking in DNA helix; 2) binding of drugs into DNA; 3) crystal structures of aromatics 4) protein conformation; 5) host guest interactions; 6) porphyrin stacking and 7) chromatographic separations (Hunter and Sanders, 1990; Hunter et al., 2001; Janiak, 2000, Meyer et al., 2003).

The above examples of aromatic π interactions do not involve transfer of electrons, hence they are called π - π electron donor acceptor interactions, rather than π - π^* or charge transfer interactions (Williams, 1993; Hunter and Sanders, 1990). These aromatic intermolecular forces of attraction results in a conformation that allows maximum electrostatic overlap, while minimizing the repulsive component. Examples of these are face to face or “stacked”, offset stacked, and “herringbone” or T-shaped as shown in Figure 2.4 (Hunter and Sanders, 1990). The

offset stacked orientation is implicated for the twist in the DNA helix.

Over the past decade, the importance of this π -electron donor acceptor was increasingly utilized to explain various behaviors in sorption of aromatic and π systems in the terrestrial environment (Zhu et al., 2004). Keiluweit and Kleber (2009) summarized the different types of π interactions that affect not only molecular sorption behavior of aromatic pollutant or SOM in minerals, but also SOM as well as black carbon components in soils and sediments. This may account for adsorption of SOM with minerals including associations within itself. This will be important in efforts to elucidate mechanisms of preservation and recalcitrance of SOM in soil and sediments, eventually helping in the mitigation measures of climate change.

The ^{13}C NMR spectra of SOM has been shown to contain appreciable aromatic moieties from 20–60% of total carbon (Schnitzer, 1991; Mao et al., 2000, Simpson et al., 2001). This is due to aromatic containing moieties in SOM, such as lignins, tannins, and black carbon, as well as their degradation products. Therefore, π - π electron donor acceptor interactions are perceived to be relevant for the sorption of polar and or nonpolar aromatic compounds with π donor and π acceptor systems. For such π - π interactions, the strength are mainly dominated by quadrupolar and dispersion (i.e. Van der Waals forces) energy contributions as given below:

$$E_{total} = E_{quadrupolar} + E_{dispersion}$$

Dispersion energy would once again depend on the extent of π -overlap to the sixth power (i.e., $E_{vdw} \propto 1/r_{ij}^6$), where r_{ij} is the separation distance between atoms i and j , located in two different molecules (Hunter and Sanders, 1990).

It should be noted that the observed lowest energy arrangement of aromatic π interactions, allows the quadrupolar interaction to be a π - σ type of electrostatic interaction, rather than π - π attractive forces. Van der Waals forces, mainly dispersion as well as solvophobic effects add to the strengths of the interaction. Aromatic quadrupolar π systems can have sorption

energies from $\sim 1\text{--}40\text{ kcal mol}^{-1}$, which may be comparable in strengths with H-bond, and sometimes stronger (Keiluweit and Kleber, 2009). The presence of polar or nonpolar substituents in aromatic rings influence the magnitude and sign of their quadrupole moments through inductive and resonance effect (Pignatello, 2009). Electron withdrawing substituents (i.e., halogens, $-\text{NO}_2$, and $-\text{COO}$) draw the electron density toward itself and away from the face of the ring thus increasing the π -acceptor potential of the aromatic ring (Solomons, 1980). Electron donating atoms or moieties (i.e., alkyl, alkoxy, hydroxyl, oxy, phenyl, amino) shifts electron density toward the plane of the ring, thereby increasing its π -donor capability (Brown, 1975).

Aside from π - π interactions, aromatic molecules with π donor and/or π acceptor capabilities can also exhibit other type of binding mechanisms such as: a) cation- π ; b) n- π ; c) H- π ; and d) polar π . The non-covalent attraction between the face of the ring of the electron rich aromatic π system (donor) and positively charged metallic or organic ions (acceptors), is referred to as cation- π (Wijnja et al., 2004; Pignatello, 2009; Keiluweit and Kleber, 2009). In soils, cation acceptors can be found on the mineral phase, recalling that minerals contain different types of coordinating cations (e.g., Si^{4+} , Al^{3+} , Mg^{2+}). The magnitude of cation- π binding is enhanced by the presence of electron-donating groups on the ring, as well as the size of aromatic systems (Keiluweit and Kleber, 2009; Pignatello, 2009). In addition, cation type and hydration also affects its strength, whereby higher binding energies would be expected for weakly hydrated cations (e.g., K^+ , Na^+ , NH_4^+), more so than corresponding strongly hydrated cations (e.g., Ca^{2+} , Al^{3+} , Mg^{2+}). Xu et al. (2005) reported that up to $\sim 8\text{ kcal mol}^{-1}$ can result from cation- π interaction, even when the cation is hydrated by three water molecules. Hence, it is expected that the dry conditions favor cation- π interactions more than water-saturated conditions. Indeed, Qu et al. (2008) showed that sorption affinity of polyaromatic hydrocarbon is higher on minerals with weakly hydrated cations.

The interaction of lone pairs to aromatic π acceptors is called $n-\pi$. Siloxane surfaces in minerals are therefore suggested to have a potential for $n-\pi$ interactions, due to nonbonding electrons in oxygen. This type of π interactions was hypothesized as one with probable sorption mechanisms of nitroaromatic explosives to mineral surfaces, aside from cation- π and hydrophobic forces (Gorb et al., 2000). Similar to cation- π interactions, the strength is also affected by the type of exchangeable cations and hydration. The presence of hydrophobic nanosites in clays can also enhance the magnitude of such π forces on these mineral surfaces. The hydrogen on free silanol groups on silica surfaces of minerals may also interact with aromatic π donors especially in dry conditions. The associated binding strength may be as high as the energy involved in a benzene-water complex, which is $\sim 1.8 \text{ kcal mol}^{-1}$ (Keiluweit and Kleber, 2009).

The presence of amino, as well as ionized weakly acidic groups such as carboxylic and phenolic in SOM (Cook et al., 2003), may also allow specific interactions with aromatic π donors and acceptors. The binding of the positive end of organocation with a π donor is categorized as cation- π . Qu et al. (2008) suggested that cation- π interactions contribute to sorption of polyaromatic hydrocarbon on alkylammonium modified montmorillonite, rather than H-bonding. Modeling studies of complexation energies between ammonium and tetraalkylammonium with π donor benzene, yielded to ~ 10 and 18 kcal mol^{-1} , respectively (Lee et al., 1995; Aschi et al., 2002). Similar to $n-\pi$ interactions in mineral phases, the nonbonding electrons in oxygen from ionized carboxylic, phenolic, and hydroxyl groups in SOM (Talibuden, 1981; Tabatabai and Sparks, 2005), offer a potential attraction with π acceptors such as nitroaromatic carbon pollutants (Qu et al., 2008; Keiluweit and Kleber, 2009). In addition, H- π interactions are also plausible for aromatic π donors and hydrogen in SOM moieties such as amino, amide, and thiols (Keiluweit and Kleber, 2009), and are considered to be weak H-bonds. The strengths of amino

H- π and amide H- π interactions have been reported to be $\sim 1.5 \text{ kcal mol}^{-1}$ and 4 kcal mol^{-1} , respectively (Tsuzuki et al., 2000).

Since anthropogenic aromatic contaminants are widespread, plus the fact that SOM contains appreciable amounts of aromatic moieties, it is important to consider and/or evaluate contributions of aromatic- π interactions in relation to their sorption affinities. The pesticides in this study contain functionalities with a potential for the abovementioned intermolecular forces of attraction, including Van der Waals forces, H-bonding, and aromatic π interactions. These intermolecular forces of attraction act simultaneously, yet some forces may be predominant, based on the overall molecular properties, as well as the properties of sorption sites. Thus, this sorption-desorption study will determine the effect of molecular properties such as size, hydrophobicity, and electrostatic potential (generated from modeling studies), as well as the effect of different functionalities in sorption affinities.

2.5.4 Possible Retention Mechanisms for Pesticides in This Study

All three pesticides used in this study are capable of H-bonding. Norflurazon has azine ($-\text{N}=\text{N}-$) and amino functionalities that may H-bond with phenolic and carboxylic moieties of SOM, with strong to very strong binding energies expected. Furthermore, the carbonyl group will have very weak to weak H-bond tendencies with N-H type moieties in SOM. Acifluorfen contains a nitro (NO_2) group and a pH dependent ionizable carboxylic (COOH) substituent. The nitro group can form a very weak H-bond with N-H groups of SOM. On the other hand, the nitro group enhances the acidity of the Ar- COOH group. The unionized form of this carboxylic group may exhibit a strong to very strong H-bond with azine, azole, and amine moieties in SOM. However, the pK_a of COOH is ~ 3.5 ; thus, at soil pH values, it exists mainly in the unprotonated form, which is less likely to be sorbed on negative surfaces of minerals. Further, the pK_a of COOH also has an ether group, where two aromatic rings are joined to oxygen. The latter confers

a very weak to weak H-bonding with proton donor nitrogen moieties in the SOM. Flutolanil contains amide or ether functional groups. The amide group is suggested to have medium H-bonding with other amide moieties. However, the ether will be expected to have a very weak to weak H-bond contribution with amino groups of SOM. It is also expected that the trifluorinated and chlorine groups in all of these pesticides will exhibit some form of H-bonding.

As each of these pesticides contain two 6-membered aromatic rings, quadrupolar interactions also are highly probable. Taking into account the effect of substituents, flutolanil has π -donor ring in which the π -donor strength is enhanced by the presence of –OR and –NH groups. The rest of the pesticide aromatic rings are potential π -acceptors. The hydrophobicity of the molecule also contributes to its retention, and the expected contribution to Van der Waals forces would be Flutolanil>Norflurazon>Acifluorfen.

2.6 Introducing Freundlich Isotherm

Sorption-desorption studies are performed by equilibrating a fixed amount of sorbent with varying concentrations of sorbate. Appropriate sorption isotherms are then used to model the amount of pollutant sorbed in the sorbent as a function of equilibrium concentration in solution (for aqueous sorption). The Freundlich Equation 2.1 given below, is widely used to describe sorption-desorption in soils.

$$S = K_F C_e^N \quad (2.1)$$

where: S = amount sorbed in a soil (mg kg^{-1})

C_e = equilibrium concentration (mg L^{-1})

K_F = Freundlich sorption coefficient ($\text{mg kg}^{-1}/(\text{mg L}^{-1})^N$)

N = nonlinearity of the isotherm

The log transformation of Equation 2.1 yields Equation 2.2 below, which is a linear equation of the type $y = mx + b$ where m is the slope (N), b is the intercept ($\log K_F$), and $\log C$ is the

independent variable x .

$$\log S = \log K_F + N \log C \quad (2.2)$$

Two main reasons for this use are based on the assumptions using Freundlich, which are: 1) a presence of heterogeneous surface (i.e., different energies) as sorption sites; and 2) it does not assume monolayer coverage only, valid assumptions for soils (Adamson, 1982). Neither of which can be assumed for more classic treatment, such as the Langmuir isotherm.

SOM has been widely recognized as the most important component in hydrophobic contaminant sorption (Chiou et al., 1983; 1998). Here, hydrophobic means low solubility in water. It has also been suggested that HOCs are less likely to sorb on minerals because water strongly competes with HOC on these sites (Chiou and Shoup, 1985; Chefetz et al., 2000). Thus, the sorption coefficient K is often normalized with respect to organic carbon or organic matter content, yielding a relatively constant distribution coefficient (K_{OC} , K_{OM}). However, this is not always the case. Variation in K_{OC} values are often attributed to the following: 1) a type of carbon that composes the SOM; 2) the extent of diagenetic alteration; 3) the presence of different sorption domains; 4) the presence of black carbon; and 5) a hydration condition. All of these will be discussed below in relation to deviations from the partitioning type of sorption (i.e., nonlinearity, hysteresis).

2.7 Effect of Hydration on Sorption

Water is known to be capable of hydrogen-bonding and ion-dipole interactions with mineral surfaces (Sposito, 2008; Schwarzenbach et al., 2003). The presence of positive and negative charges on a mineral surface is highly attractive to ion-dipole interactions with water. In addition, free $-OH$ groups on metal hydroxy minerals will hydrogen-bond with water. Hence, water strongly competes for these sites, resulting in a great reduction regarding sorption of organic pollutants to mineral surfaces (Chiou and Shoup, 1985; Chefetz et al., 2000). With

respect to expandable type of clays, water swells the interstitial layers, possibly allowing greater room for pollutants as a result.

Hydration also affects SOM sorption properties since SOM has a high water holding capacity and can retain water up to four times its weight (Sposito, 2008). Nonpolar compounds benzene and trichloroethylene displayed a sorption suppression of ~50% in water-saturated peat soil, when compared with its dry state (Rutherford and Chiou, 1992). In contrast, polar organic compounds (e.g., phenol, nitrophenol, benzyl alcohol) that are capable of specific interactions with SOM such as hydrogen-bonding, experienced enhanced sorption from an aqueous solution when compared with a hexadecane amended (i.e., dry) Pahokee Peat (Graber et al., 2007; Borisover and Graber, 2002a; Borisover and Graber, 2002b). However, sorption of other polar compounds, such as nitrobenzene and acetophenone, are unaffected (Borisover and Graber, 2002b). The significant increases in sorption were observed at intermediate water activities, peaking at 0.7-0.8 water activities (Graber et al., 2007). A similar behavior was exhibited by pyridine sorption in the presence of acetonitrile. When the effect of hydration on sorption was evaluated on a whole peat soil with isolated fractions, some differences were presented. Nitrophenol had a more enhanced sorption on Peat soil than its humin fraction, while the reverse is true for benzyl alcohol. In addition, greater nonlinearity was shown for Peat soil sorption isotherm (Borisover and Graber, 2004).

A recent study on the sorption properties of an extensive number and a diverse set of anionic organic compounds to a dry versus up to a 98% relative humidic state humic acid showed differences dependent on the polarity of the organic compound. Non-polar compounds show reduction in sorption when the HA hydration condition is greater than its subsaturation level, whereas bipolar compounds (i.e., compounds with electron donor and electron acceptor properties) such as polar aromatic compounds displayed assisted sorption in water saturated

levels (Niederer et al., 2006; Niederer and Goss, 2007). These findings are in keeping with previous studies.

One explanation for the abovementioned phenomenon is that the hydration state of SOM tends to influence its flexibility and conformation arrangement. It is proposed that an initially dry SOM is capable of noncovalent forces, such as hydrogen-bonding with its polar moieties (e.g., –COOH, phenolic), metal-ion complexation, and conformational rearrangements; this results in an intimate and highly cross-linked polar contacts (Rutherford and Chiou, 1992; Graber et al., 2007; Schaumann and LeBoeuf, 2005). In the dry state, it is then envisioned that SOM structure is more rigid, with a high probability of reduced sizes of internal voids or pores. Subsequent opening of these pores will require a high energy and kinetically-controlled disruption of abovementioned cohesive forces that hold the crosslinks together (Schaumann and LeBoeuf, 2005; Todoruk et al., 2003). Hence, diffusion of sorbates to sorption sites is restricted. Hydration of SOM to greater than 12% moisture content can effect SOM conformational rearrangement. As water penetrates and solvates these polar links, mainly by hydrogen bonding, this will result in a more open and flexible or “swelled” SOM (Schaumann and LeBoeuf, 2005). This in turn, creates new sorption sites. However, nonpolar organic solutes still experience a decrease in sorption in hydrated conditions, because water is thought to effectively compete for sorption sites. In contrast, bipolar compounds experience enhanced sorption, because they are also capable of strong noncovalent interactions with the hydrated SOM (Rutherford and Chiou, 1992). However, when water content is much greater than its saturation level, water molecules once again show competition for sorption sites, even for bipolar compounds (Graber et al., 2007).

Few studies have been carried out in regard to the effect of hydration on pesticide sorption. Sorption isotherm of chlortoluron is higher in an initially dry soil of ~1% organic carbon content, compared to a field moist soil; however, sorption has been suggested to be

reversible when the air-dried soil is rewetted at or near its equilibrium (Altfelder et al., 1999). Desorption of diuron and terbuthylazine (after subsequent drying of up to three times) resulted in a factor of 2.7 and 3.5 increase in sorption respectively, which was attributed to reduced pesticide diffusivity, because SOM converts to a more shrunken state upon successive drying cycles (Lennartz and Louchart, 2007).

The implications of soil hydration are significant from the standpoint of agricultural chemical activity, climate change effects, and environmental pollution. A reduced sorption to soil means greater pesticide bioavailability for target organisms. However, as more pesticides become bioavailable, the potential for surface and subsurface contaminant transport to aquatic systems also become high. On the other hand, an enhanced sorption to soil may mean a delayed release of pollutants in the future, corresponding to a greater amount of pesticide that must be applied in order to achieve its target bioefficacy. Climate change may result in changes in rainfall patterns, which in turn may result in droughts or flooding in other areas. Prolonged periods of dry soil conditions facilitate the migration of hydrophobic moieties on the SOM surface, which in turn affects organic pollutant redistribution (Boxall et al., 2009). Thus, it is expected that the soil hydration state will influence sorption and desorption of pollutants.

Thus, this work seeks to decrease knowledge gaps in the following areas: 1) a molecular level understanding of SOM assembly in its native matrix; and 2) the influences of the soil hydration level, sorbate polarity, and structure; as well as soil organic matter content and mineral/clay content on the uptake and release of HOCs.

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Chapter 3

Effect of Hydration and Solvation on the Nature of Organic Matter Released from SOM

3.1 Introduction

Soil is a very complex and heterogeneous system, consisting of three phases, (e.g., solid, solution and gas) and living and non-living component (Sposito, 2008; Filep, 1999). Natural organic matter (NOM) constitutes typically a few percent (i.e., 5–10%) of the total solid phase, while the remaining fraction represents the mineral components. Soil organic matter (SOM), a class of NOM, primarily originates from degradation of plant materials, with some contribution from animal litter (Stevenson, 1994; Steelink, 1999). Since vascular plants are the dominant form of terrestrial plant inputs, degradation products of their components are the major raw material source for SOM. Cellulose is the main form of carbohydrates in these plants. In higher plants, cellulose fibers are also found to be akin to the hemicelluloses (Wershaw, 2004). Other plant components include lignin, plant polyesters such as cutin and suberin, plant lipids, amino acids, proteins and amino sugars (Wershaw, 2004). Lignin in vascular plants consists of phenyl propanoid, guaiacyl, and syringyl propanoid moieties (Douglas, 1996; Saake et al., 1996). Hemicellulosic fragments may also intimately associate with lignin components, forming lignocelluloses through benzyl ester, benzyl ether and phenyl glycosidic linkages (Sun et al., 2000; Donaldson, 2001). Cutins are made up of long chain (e.g., C₁₆, C₁₈) saturated or unsaturated acids (Kolattukudy, 2001), while suberin, found in barks and roots consists of polyaromatic and polyaliphatic domain (Kolattukudy and Espelie, 1989; Bernards, 2002). Cutin and suberin are also commonly associated with soluble plant lipids. Long chain hydrocarbons and long chain aliphatics (>C₁₈) with alcohol, aldehyde, ketone, acid, and ester moieties are also possible via plant lipids (Kolattukudy and Espelie, 1989; Mariani and Wolters-Arts, 2000). In addition, amino acids and proteins from living organisms add to SOM (Martens and

Loeffelmann, 2003). Furthermore, a type of carbons called “pyrolytic carbon” comes from pyrolysis or burning of plant materials. Two types of pyrolytic carbon, referred to as black carbon/charcoal and soot or graphitic carbon are therefore ubiquitous in soils (Karapanagiotti et al., 2000; Schmidt et al., 1999; Skjemstad et al., 1996; 2002; Cambardella and Elliot, 1992). SOM synthesis involves oxidation and/or reduction of the abovementioned compounds inherent in plants. The main degradation pathway is through biotic processes, often facilitated by enzymes present in the soil, primarily from microbes. In comparison, abiotic degradation is thought to have a lesser contribution to the generation of SOM. Another important mechanism of plant decomposition is through pyrolysis, due to occasional occurrence of fires that burn plant materials (Wershaw, 2004).

SOM is one of nature’s major carbon sinks; hence, it plays a key role in CO₂ release and carbon cycling in the environment (Aiken et al., 1985; Jansen, 2004). In addition, SOM influences a large number of soil properties and functions, including: mobility and transport of soil nutrients; pH buffering; metal-binding; water retention; thermal buffering, and aggregate stability, all of which essentially contribute to soil fertility (Wershaw, 2004). Fertile soils are crucial for human survival as the vast majority of human food needs come from soil. Likewise, SOM is also widely recognized in sorption-desorption of hydrophobic organic contaminants as well as binding and release of metallic compounds and other pollutants, including radioisotopes (Perminova et al., 2005; Chin and Weber, 1989). Thus, SOM ultimately affects the bioavailability and distribution of nutrients and xenobiotics in the aquatic and terrestrial environments.

A better chemical understanding of NOM, including SOM, is necessary due to its vital role in ecosystem as mentioned above. There have been numerous studies aimed at elucidating molecular structure of NOM; however, due to its complexity, until now it has been an open and

dynamic field of investigation. According to a classical view, NOM is macromolecular in nature and is made of cross-linked monomers forming higher molecular weight molecules (Stevenson, 1994). These macromolecules exist as long chains or coiled polyelectrolytic molecules in aqueous solution, in which ionizable moieties, mainly carboxyl groups, cause conformational changes in the structure (Rausa et al., 1991; Sutton and Sposito, 2005). Results of most sorption-desorption studies were explained based on this model (Kan et al., 1998; Gunasekara et al., 2003; Chiou et al., 2000; Khalaf et al., 2003). Empirical evidence of the polymeric model is based on ultracentrifugation studies and diffusion measurements which yield mass weighted average of 20–50 kDa (Swift, 1999; Cameron et al., 1972). In another approach, Rausa et al. (1991) determined the molecular weight distribution of four sodium exchanged humic acid (HA) by high performance size exclusion chromatography, using the following conditions: 1) stationary phase: cross-linked sulphonated polystyrene-divinylbenzene copolymer; 2) mobile phase: 0.05M NaNO₃ solution; 3) detector: UV and refractive index; and 4) standards: polysaccharides. Molecular weights were reported as follows: Sub-bituminous coal (130 kDa) > lignite coal (77 kDa) ≈ leonardite HA (~79 kDa) > worm compost (49 kDa).

Spectroscopic based studies raise a number of issues that could not be accommodated by the abovementioned model. High performance size exclusion chromatography were utilized by Conte and Piccolo (1999) and Piccolo (2001) to study the molecular mass of two types of NOM, namely HA and fulvic acid (FA) in aqueous solutions. Average size distribution of HA and FA were determined using a mobile phase of 0.05 M NaNO₃ at neutral pH (mobile phase A) and other solvents made up of mobile phase A amended with micromolar concentration of CH₃OH, HCl or acetic acid. Molecular weights in terms of mass weighted average molecular weights, designated herewith as Mw represent size distribution. The largest Mws were obtained when mobile phase A was used, with initial Mw of 17–57 kDa for HA and ~10 kDa for FA. Mws

gradually decreased as aqueous solutions of CH₃OH, HCl and CH₃COOH were used. CH₃OH showed a ~50% reduction in Mw for HAs with more aromatic and carboxylic character. This finding was explained to have been caused by disruption of noncovalent forces such as Van der Waals forces and hydrogen-bonding thought to be responsible for humic molecule association into larger aggregates. However, for HCl, Mw reduction was hypothesized to have been due to proton transfer reactions to some of the carboxylate groups in humic substances. Subsequent to this, the protonated carboxylate form hydrogen-bonds that lead to the undergoing conformational rearrangement. Of these solvent systems, CH₃COOH exhibited the greatest disaggregation effect, yielding a decreased Mw of up to 90%. This effect was postulated as similar to the effect of (–CH₃) in CH₃OH and H⁺ in HCl, in addition to protonated and unprotonated forms of acetic acid, which may exhibit stronger H-bonding association with humic substances as compared to –OH group in CH₃OH (Sutton and Sposito, 2005; Gilli et al., 2009). Another set of high performance size exclusion chromatography study of HAs using the same mobile phase A and 0.1 mM acetic acid amended mobile phase A yielded Mws of ~49 kDa and ~19 kDa, respectively. These findings were further confirmed by pyrolysis gas chromatography/mass spectrometry (Pyr–GC–MS) analysis of isolated fractions. It was also found that, unsaturated alkyl chains as well as most aromatic moieties exhibit a distribution of large to intermediate Mw whereas carbohydrates displayed the lowest Mw. In this study, almost complete recovery (~98%) of the HA starting material with respect to carbon were noted and was suggested as a validation of the absence of adsorption effects on the stationary phase. In addition, it was also proposed that the used mobile phases do not alter NOM properties, as only very small changes in elemental compositions were observed. These findings add credence to the disruption of hydrophobic and H-bond forces that cause an association of HA into supermolecular assemblies.

Simpson et al. (2001) used 2-D diffusion ordered spectroscopy with ¹H chemical shifts in

one dimension and diffusion coefficient in another dimension to approximate molecular mass at two different concentrations of humic acid. In a 5 ppm solution HA had ~2.5 to 61 kDa molecular mass, while a 100 ppm HA exhibited molecular masses > 66 kDa. Addition of acetic acid resulted in components of varying mobilities and lower molecular masses (0.2–2.5 kDa), but with very similar spectra extracted from the proton dimension. Other mass spectrometric techniques such as Electron Spray Ionization and Laser-assisted Desorption Ionization, have shown number weighted average molecular weights (M_n) of 1–2 kDa and ~0.5 kDa respectively (Leenheer et al., 2001; Piccolo and Spiteller, 2003; Brown and Rice, 2000; Stenson et al., 2002). Differences in M_n or M_w were attributed to possible variation in fragmentation, ionization efficiencies and diminishing resolution of ions representing >1 kDa masses (Brown et al., 1998; Brown and Rice, 2000). In addition, Leenheer and Rostad (2004) observed that methylation of the carboxyl group of FA decreased its average M_w , which was then suggested a likely result of a reduction of the amount of H-bonding.

Consequently, the current view of NOM is that it is made of “loose association of relatively small heterogeneous group of molecules, which are held together by weak hydrophobic forces” (Conte and Piccolo, 1999; Simpson et al., 2001). Wershaw (1993) has long hypothesized a micellar model of humic substances, even when little evidence was available. He speculated that, because SOM is made up of degradation products of mainly plant polymers containing both hydrophobic and hydrophilic (e.g., $-\text{COOH}$) moieties, it is considered as an amphiphile, and so in aqueous solution, it forms aggregates, in which the hydrophilic moieties would wish to situate themselves on the surface layer near the vicinity of water, while the hydrophobic moieties located inside the hydrophobic core remain protected from the water, forming micellar structures similar in behavior to that of surfactants (Wershaw, 1993; Engbretson and von Wandruszka, 1994). It was also thought that the association of SOM to

minerals may be in a form of micellar bilayer, whereby the hydrophilic ends of amphiphiles are oriented towards the mineral phase, while their hydrophobic tails are pointed away from the minerals. These hydrophobic ends, in turn, are layered with the hydrophobic tails of another set of amphiphiles, whose hydrophobic regions are near the vicinity of water (Wershaw, 2004). What served as experimental evidence for this model was that compost leachate organic acids were immobilized on aluminum surfaces through carboxylate groups, as determined by infrared-attenuated total reflectance linear dichroism measurements (Wershaw, 1999). Recent studies based on different spectroscopic techniques support this view. Atomic force microscopy and transmission electron microscopy studies showed no evidence of coiling or uncoiling of humic substances on mineral substances at different pH conditions and ionic strengths, which once again questions the polymer view (Maurice and Namjesnik-Dejanovic, 1999; Plaschke et al., 1999; Namjesnik-Dejanovic and Maurice, 2001). In fact it was observed that aquatic dissolved organic matter fraction that resembles the properties of a soil humic substance, formed “micelle-like colloids” within a few days (Maurice and Namjesnik-Dejanovic, 1999). These aggregates were also relatively unaffected by the removal of multivalent cations through ethylene diamine tetraacetic acid complexation, which is indicative of weak noncovalent forces being the most probable cause of the stabilization of these micelles (Kerner et al., 2003). In another study involving the use of a pyrene probe in a solution of humic substances with a divalent cation added, it was suggested that multivalent cations may enable aggregation of humic substances through cation bridging and charge neutralization, leading to the protection of pyrene within this hydrophobic region and an observed enhancement of fluorescence (von Wandruszka and Engebretson, 2001; Engebretson and von Wandruszka, 1999). However, with time, these cations may ultimately find their most thermodynamically favored associations within the humic material, and may no longer hold these aggregates together.

A separate fluorescence study utilizing a polarity sensitive probe 6-propionyl-2-dimethyl aminonaphthalene (prodan) reveal that at lower pH, this probe is within the hydrophobic region, and is protected from the water molecules, which once again supports the micelle formation in acidic solutions and disaggregation in basic solution (Nanny and Kontas, 2002). Changes in line width of electron spin resonance as a function of relaxation time of aromatic or aliphatic chain free radical probes were investigated in the presence of humic substances. It was shown that the initially observed fine structure diminished in the presence of humic substances at $\text{pH} < 5$ (Martin-Neto et al., 2001; Ferreira et al., 2001). These findings were attributed to sequestration of free radical probes within the hydrophobic region of humic substances, resulting in broader linewidths. It was also suggested that an acidic pH favors the aggregation of hydrophobic moieties, while the reverse is true under basic conditions, corroborating the former findings.

The micellar view of SOM is consistent with the supramolecular assembly. However, it does not take into account some of the important components of NOM. The supermolecular assemblage model, therefore, is an extension of the micellar model as it explicitly includes strongly associated bimolecules within humic substances in its context. For example, phenol-containing hydrolysable and non-hydrolysable tannins are usually intimately associated with carbohydrates and proteins and are therefore important in SOM aggregation, as phenol-type moieties can exhibit electron donor acceptor type interactions, including aromatic- π forces (Wershaw, 2004; Cubberley and Iverson, 2001; Gelema, 1998).

The models discussed above are a result of studies involving isolated fractions of terrestrial or aquatic NOM. The isolation of humic substances involves the use of strong acid and base (i.e., 0.1 M HCl and 0.1 M NaOH) plus further purification methods, such as hydrofluoric acid treatment to remove metals and passing through cation exchange resins, which may result in the loss of some of the strongly associated biomolecules and multivalent cations that may

otherwise have contributed to aggregation (Wershaw, 2004; Burdon, 2001). Thus, in our study, the concept of supermolecular assemblage was extended to the use of unfractionated soil. This study involves the use of an unadulterated soil to address fundamental questions of how NOM is associated and stabilized in soil. If humic materials are indeed supermolecularly assembled, their characterization should exploit intermolecular forces that hold them together. Soil is polyelectrolytic in nature. Aside from ion-ion and cation- π interactions, intermolecular attractions in SOM can be mainly ascribed to H-bonding because the electrostatic potential of a molecular surface is largely positive on a hydrogen atom and negative on electron-rich atoms (Hunter, 2004; Zhu et al., 2003). In addition, the presence of aromatic groups in SOM may cause aromatic electron donor acceptor associations, π - π aromatic stacking, as well as weak hydrogen-bonding (H- π) (Keiluweit and Kleber, 2009; Meyer et al., 2003; Hunter et al., 2001). These forces may contribute to the aggregation into larger molecular weight molecules. A change in hydration and solvation of soil is expected to affect these intermolecular forces. As a consequence, changes in SOM conformation (such as swelling), mobility, and aggregation in soil and soil-solution interfaces will be apparent (Schaumann et al., 2004; Graber and Borisover, 2004), and consequently, sorption and desorption of organic contaminants will be greatly affected (Graber and Borisover, 1998; Borisover et al., 2001).

The inherent fluorescent properties of SOM have been taken advantage of in this study by the choice of a range of fluorescence protocols to characterize humic substances. In addition, this spectroscopic technique is non-destructive. Hence, fluorescence measurements were chosen as one of our analysis methods in order to elucidate SOM assembly in soils. Emission and synchronous fluorescence are the most widely used methods for determining humification indexes (HIXs). Humification is a process whereby small organic molecules are transformed into more conjugated, highly condensed and higher molecular weight matter (Ohno, 2002; Miano and

Senesi, 1992). Hence, fluorescence at longer wavelengths in humic substances may be related to presence of high proportions of (poly)aromatics, conjugated π systems and donor acceptor complexes (Schaumann et al., 2000; Cory and McKnight, 2005; Del Vecchio and Blough, 2004; Kalbitz et al., 1999; Miano and Senesi, 1992). A higher HIX in humic materials will therefore be correlated to an increase in abovementioned components. A commonly used emission based HIX utilizes 254 nm as the excitation wavelength and records emission spectra at 280-500 nm. The HIX_{254} is then calculated as the ratio between the upper quarter in the emission peak and the lower quarter of the same peak, avoiding the part containing Raleigh peaks (Cannavo et al., 2004; Sierra et al., 1994). A slight variation in excitation wavelength of 370 nm (HIX_{370}) was recently introduced by Hood and co-workers (Hood et al., 2005). In yet another variation the excitation wavelength is 465 nm. The excitation energy at the latter wavelength is more resonant of humified groups because it excites only a select portion of the humic material. The total area under the emission peak represents the HIX_{465} (Milori et al., 2002). Alternatively, HIX may be determined by synchronous fluorescence. Synchronous fluorescence is accomplished by simultaneously scanning the excitation and emission wavelengths while keeping a constant wavelength offset, $\Delta\lambda$ ($\Delta\lambda = \lambda_{em} - \lambda_{exc}$) between them (Miano and Senesi, 1992; Senesi, 1990).

The fluorescence intensity in synchronous fluorescence is presented by Lloyd (1971) as:

$$I_s = KCD E_x (\lambda_{em}-\Delta\lambda) E_m (\lambda_{em}) \quad (3.1)$$

where:

I_s = synchronous fluorescence intensity

C = fluorophore concentration

D = sample thickness

$E_x (\lambda_{em} - \Delta\lambda)$ = intensity distribution patterns of excitation spectrum

$E_m (\lambda_{em})$ = intensity distribution of emission spectrum

As can be seen in Equation 3.1, synchronous fluorescence is simultaneously influenced by two wavelengths, rather than only one as in conventional fluorescence. This feature increases selectivity. Empirical evidence suggests that selectivity is optimal when the $\Delta\lambda$ matches the difference between the emission and excitation peaks. This selectivity offers the possibility of differentiating between mixtures of fluorescent compounds (Lloyd, 1971). Based on empirical evidence on selectivity optimization, for humic and fulvic acids, $\Delta\lambda$ is commonly equal to 18 nm. Hence, this is the $\Delta\lambda$ used in this study for the fluorescence-based HIX₁₈.

The attenuated total reflectance-fourier transform infrared was utilized in the analysis of freeze-dried exfoliation supernatant and freeze dried exfoliated soils as it allows: a) functional group characterization based on their characteristic vibrational-rotational energy transitions during absorption of IR radiation; b) direct analysis of samples without the need to use solvents; and c) it is a non-destructive technique. ¹³C Solid Cross Polarization Magic Angle Spinning (CPMAS) NMR was also utilized in this study as it offers the following advantages in humic substances characterization: 1) molecular level elucidation is possible; 2) no solvent is needed in sample preparation; 3) it is a highly non-destructive technique; and 4) semi-quantitative.

The objectives of this study are as follows: 1) to use solvents of different polarity and hydrogen-bonding capability to determine the nature of organic matter released from soil and 2) to use solvent effects as a probe to gain further insight into SOM supermolecular assemblage.

3.2 Materials and Methods

3.2.1 Materials and Reagents

The model soil used throughout was Pahokee Peat II, an IHSS standard. Pre-cleaned, teflon-lined vials with 20 mL and 40 mL capacities were purchased from Quality Environmental Containers (QEC). 125 mL bottles were obtained from Acros. 18 M Ω de-ionized water used in all experiments was sourced from Modulab Water Systems, U.S. Filter purification system.

HPLC grade solvents (>99.9%) acetonitrile, acetone and methanol and water were obtained from Acros. Extra dry dimethyl sulfoxide, glacial acetic acid, hydrochloric acid and sodium nitrate were also acquired from Acros.

3.2.2 Exfoliation Procedure

Aqueous solutions of $4.6 \times 10^{-3}M$ acetonitrile, methanol and dimethyl sulfoxide were prepared using neutral sodium nitrate ($0.05M$) as the diluent. The soil to solution ratio used was 0.005 (w/v). Samples were placed in foil-wrapped 20 mL teflon-lined QEC vials, which were then shaken at 40 rpm (0.67 Hz) for 24 hours at room temperature using a horizontal shaker. Four replicates were prepared for all solution types. In addition, blanks containing the aqueous solutions (without soil) were also prepared and were later used as blanks for UV and fluorescence analyses. Subsequently, the samples were allowed to sit for ~1hr for the floating particulates to settle. Clear supernatants were then extracted from the soil samples. In the event of particles still being present, the supernatants were centrifuged at 2500 rpm for 25 minutes. Supernatants were then subjected to TOC, UV and fluorescence analyses. The 20-day samples were colorimetrically inspected on a daily basis. After 18 days, it was observed that the sample containing the water-acetonitrile binary solution developed red brownish color whereas the other samples had yellow color with subtle differences.

One large batch of $4.6 \times 10^{-3}M$ aqueous solution of each of the following: dimethyl sulfoxide (PD), acetonitrile (PA), methanol (PM), acetone (PA), acetic acid (AA) and hydrochloric acid (HCl) were introduced into a 125 mL glass solution bottle with liner to achieve a 0.005 (w/v) soil to solution ratio, in order to determine the effect of longer incubation period. Subsequent sample treatment was the same as above. Samples were then allowed to settle in the dark for 45-day to allow more contact between the soil and the mobile phase. For all 1-day and 20-day sample exfoliation supernatant, 1 mL aliquots were extracted and diluted to 50 mL with

HPLC water. For the 45-day, accurate volumes of 4 mL, 2 mL, 1 mL and 0.5 mL of each supernatant were diluted to 50 mL to check for inner filter effects.

3.2.3 Characterization Methods

Total organic carbon (TOC) was determined using a Shimadzu TOC-5050A with an ASI-5000A auto sampler. Potassium acid phthalate, was employed as the total carbon standard, while sodium carbonate-sodium bicarbonate was used as an inorganic carbon standard. A new set of calibration curves was prepared for each set of analysis.

UV absorbance at 280 nm was used in order to estimate the aromatic character of exfoliated SOM. Previous studies demonstrate positive correlation of UV absorbance at 280 nm with the amount of aromatics based on ^{13}C NMR, ^1H NMR and FTIR data (Kalbitz et al., 1999; Chen and Bada, 1994). UV-VIS analyses were performed on either an Agilent 8453 spectroscopy system or a Cary Ultraviolet-visible using a 1.0 cm quartz cuvette as a sample container. All readings were blank subtracted.

Emission and synchronous fluorescence spectra were acquired using a Spex 3 Fluorolog Jobin Yvon spectrofluorometer. Lamp emission peak and intensity and the Raman water peak and intensity were recorded prior to analysis. Samples were placed in a 1-cm quartz cuvette during analysis. For the lamp excitation scan, λ_{em} is set at 650 nm and λ_{ex} is collected at 220–600 nm. The Xe arc lamp used should display maximum peak at 467 ± 0.5 nm. The water Raman emission is collected at $\lambda_{\text{ex}}=350$ nm and $\lambda_{\text{em}}=365\text{--}450$ nm. Water Raman peak must be positioned at 397 ± 1 nm. Emission scans were recorded for each sample using the following sets: a) excitation wavelength (λ_{ex}) of 254 nm, emission range (λ_{em}) of 280-500 nm, b) $\lambda_{\text{ex}}=370$ nm, $\lambda_{\text{em}}=380\text{--}600$ nm and c) $\lambda_{\text{ex}}=465$ nm, $\lambda_{\text{em}}=475\text{--}650$ nm. Additional emission measurement parameters are as follows: 1 scan, 0.2 s integration time, 1 nm increment, and slits were set to 4 nm for both emission and excitation. Synchronous fluorescence were collected using $\lambda_{\text{ex}}=290\text{--}$

550 nm and $\lambda_{em}=308-568$ respectively, thereby maintaining a constant $\Delta\lambda$ of 18 nm. Slits were set to 5 nm for both the excitation and emission monochromators while the integration time was 0.1s. A humification index was obtained by ratioing the peaks 461 and 392, and is designated as HIX_{18} . Detection was signal divided by the reference (S/R). All spectra were blank corrected with the corresponding aqueous solution used for exfoliation.

Freeze-dried samples of untreated Pahokee Peat, and 45-day water and acetonitrile exfoliated Pahokee Peat were analyzed by ^{13}C cross polarization magic angle spinning NMR. A 400 MHz spectrometer operating at 400.15 MHz on the proton frequency was used. During cross-polarization, the 1H and ^{13}C fields were set to 67.5 kHz and 62.5 kHz respectively while 100 kHz was used in the decoupling step. The sample spinning frequency was 13 kHz and a recycle delay of 1s was used. The Ramp-CP pulse sequence with two-pulse phase modulated decoupling was used with a contact time of 2 msec. A total of 80k scans were collected and spectra were processed using 30 Hz line broadening. Spectra were analyzed based on ^{13}C chemical shifts given in Table 3.2.1. In addition, attenuated total reflectance-fourier transform infrared spectra on the freeze dried exfoliation supernatants were collected on a Bruker Tensor 27 equipped with a pike single bounce attenuated total reflectance cell with ZnSe crystal as sample container. The parameters used in the analysis were as follows: 96 sample scans; 96 background scans; 4 cm^{-1} resolution; 32 phase resolution; and a zero filling factor of 8. IR absorption band assignments were based from Table 3.2.2.

Spartan calculations (Version '02, Wavefunction Inc., CA) of the solvents used were performed from previously energy minimized solvent molecule (using Tripos force field). The method for electrostatic surface potential calculation is semi-empirical PM3 using single point energy.

Table 3.2.1 Chemical shift assignments in ^{13}C NMR spectra (Leenheer et al., 2004).

Chemical shift (ppm)	Chemical linkage	Compound type
0-55	C-H	Aliphatic hydrocarbon
40-55	C-N	Amines, amides, proteins
55-60	O-CH ₃	Methoxy groups in tannins and lignins
60-90	C-O	Aliphatic alcohols, ethers and esters
90-110	O-C-O	Anomeric carbon in carbohydrates, lactols
110-165		Aromatic carbon (110-137 ppm for C-C and C-H)
135-165	Ar-O	Aromatic esters, ethers and phenols (C-O and C-N)
140-145	Ar-SO ₃ H	Aromatic sulfonic acids
160-190	O=C, O=C-N	Carboxylic acids, esters, amides
170-200	O=C-C=C	Flavones, quinines
190-220	O=C-C	Aliphatic and aromatic ketones

Table 3.2.2 Functional group assignments in FTIR (Leenheer et al., 2004; Stevenson, 1994)

Compound class	Frequencies (cm ⁻¹) and chemical linkage
Carbohydrates	3400-3300 (O-H), 1100-1000 (C-O)
Fulvic acid	3400-3300 (O-H), 2700-2500 (COOH), 1760 (COOR) 1660-1630 (Ar-C=O), 1280-1150 (Ar-O, COOH)
Aliphatic hydrocarbons	2960 (CH ₃), 2940 (CH ₂), 1460 (CH ₂), 1380 (CH ₃)
Aromatic hydrocarbons	1500-1650 (C=C), 700-900 (Ar-H)
Proteins	1660 (amide 1 band, N-C=O), 1540 (amide 2 band, N=C-O)
N-acetyl amino sugars	1660 (amide 1 band, N-C=O), 1550 (amide 2 band, N=C-O), 1380 (CH ₃)
Lipids	1760 (COOR), 1720 (COOH), 2960 (CH ₃), 2940 (CH ₂), 1460 (CH ₂), 1380 (CH ₃)

3.3 Results and Discussion

Pahokee Peat, a well characterized bulk soil from International Humic Substances Society (IHSS), was chosen initially because of its high organic matter content (Table 3.3.1) making it amenable to solid NMR and attenuated total reflectance-fourier transform infrared analyses. More importantly, the use of a whole soil is more meaningful in translating the results to the natural soil environment.

Table 3.3.1 Elemental composition of Pahokee Peat II ^a

%C	%H	%O	%N	%S	%P	H₂O	Ash
46.90	3.90	30.3	3.42	0.58	nd	6.2	12.7

^a IHSS

Methanol, acetic acid and HCl were chosen based on Conte and Piccolo's work (1999) that showed that very dilute (μM to mM) aqueous solutions of these solvents had a disruptive effect on humic acid and fulvic acid aggregation. In sorption-desorption experiments done by Graber and Borisover (2004), acetonitrile was reported to increase sorption of certain pollutants, hence its inclusion as one of the solvents. In addition, the solvents were chosen based on their polarity differences and their 100% miscibility in water.

Visual colorimetric inspection of supernatants from the 24 hr (1-day) samples exhibited a light yellow color in all solutions. 20-day and 45-day exfoliation gave a differentiating color from transparent yellow, which was more intense than that for 1-day exfoliation, to clear brownish-red with acetonitrile (Figure 3.3.1). Interestingly, using acetonitrile as a mobile phase showed the most intense color, implying a greater amount of exfoliated (poly)aromatics and π -conjugated systems. These colorimetric results are also suggestive of kinetically controlled exfoliation process. This is supported by the fact that the 1-day samples had the lowest UV absorbance at 280nm, which increased with longer incubation times (Figure 3.3.1, Table 3.3.2 to Table 3.3.4) consistent with swelling and solvation studies, which may take up to a few days.



Figure 3.3.1 Supernatant from exfoliation samples using different solvents.

Altfelder et al. (1999) showed that soil wetting may take 14–21 days. Schaumann et al., (2000) also indicated the presence of a slow component during hydration kinetics of a whole soil. Todoruk et al. (2003) showed through low-field NMR transverse relaxation time (T_2) studies that wetting of an air-dried soil has at least 2 stages; the first stage shows a fast kinetic uptake of water, which occurs at ≤ 24 hr, and then the subsequent water uptake is a slow process, which may take up to 22 days to reach equilibrium.

The kinetically controlled wetting stage was mainly attributed to diffusion in micropores. In this work, for the 45-day supernatants, serial dilutions were used to eliminate the possibility of polarity altering the optical properties of the exfoliated organic matter (Table 3.3.5). As expected, all fluorescence-based HIX methods were linearly related to UV absorbance at 280 nm and to concentration, ($R^2=0.94-1.0$) except for HIX_{254} , which revealed a logarithmic relationship with $R^2=0.99$. Hence, a 0.02 (v/v) dilution was used in the analysis of 20-d exfoliation to minimize supernatants primary inner filter effects.

At $\lambda_{ex}=254$ nm, all of the different water and water-organic solvent extracts showed a

strong, broad emission profile with a maximum at about 450 nm (Figure 3.3.2; Figure 3.3.6). Emission spectra at λ_{ex} of 370 nm exhibit maximum emission at ~450–500 nm (Figure 3.3.3; Figure 3.3.7). Similarity in emission profiles for the excitation wavelengths of 254 nm and 370 nm suggest that the same type of fluorophores are being excited at both wavelengths. On the other hand, at λ_{ex} of 465 nm the λ_{max} is shifted towards longer wavelengths, with the maxima centered between 500–550 nm (Figure 3.3.4; Figure 3.3.11) where even more condensed and conjugated aromatics are efficient absorbers. The two aforementioned fluorescence features are associated with quinone-like moieties (Hood et al., 2005; Klapper et al., 2002) in fluvic acids. The first emission profile (Figure 3.3.2; Figure 3.3.6) represent quinone A moieties, which have characteristics wavelength of excitation, λ_{ex} , at approximately 240–352 nm and emission wavelengths, λ_{em} , at about 375–475 nm (Cook et al., 2009). Quinone A moieties were suggested to have less functionalized and less conjugated structures, whose fluorescence may arise from quinone-like donor-acceptor complexes with energy transitions of $n-\pi^*$ and $\pi-\pi^*$ during excitation (Cook et al., 2009). The second emission profile (Figure 3.3.3; Figure 3.3.7) corresponds to a more functionalized and more conjugated quinone-like structures, ascribed to a quinone B moieties. Quinone B moieties have longer excitation wavelengths, at ~250–450 nm and thus, also exhibit longer emission wavelengths at ~450–550 nm, likely arising from $n-\pi^*$ energy transitions upon excitation. On the other hand, at λ_{ex} of 465 nm, the emission λ_{max} is shifted towards longer wavelength, at ~500–550 nm (Figure 3.3.4; 3.3.8), where highly conjugated and humidified aromatics are efficient absorbers.

Synchronous fluorescence with 18 nm offset was used as this offset was empirically proven in the past (Kalbitz et al., 1999; Miano and Senesi, 1992) to provide the best spectral resolution compared with other offsets. Such synchronous scan yielded two medium broad peaks; one at around 392 nm and another at about 460 nm (Figures 3.3.5, 3.3.9, and 3.3.10).

Table 3.3.2 Summary of UV absorbance and HIX for 1-day exfoliation

Sample	UV absorbance at 280 nm	HIX Method			
		HIX ₂₅₄	HIX ₃₇₀	HIX ₄₆₅	HIX ₁₈
PW	0.028±0.000	7.58±0.03	0.74±0.00	6.87 x 10 ⁶ ±1.23 x 10 ⁵	1.07±0.02
PD	0.027±0.000	7.54±0.04	0.74±0.01	6.62 x 10 ⁶ ±9.75 x 10 ⁴	1.05±0.01
PA	0.028±0.000	7.88±0.04	0.75±0.01	6.68 x 10 ⁶ ±1.19 x 10 ⁵	1.05±0.01
PM	0.030±0.000	7.73±0.08	0.74±0.00	7.27 x 10 ⁶ ±8.40 x 10 ⁴	1.06±0.01

Table 3.3.3 Summary of HIX for 20-day exfoliation

Sample	UV absorbance at 280 nm	HIX Method			
		HIX ₂₅₄	HIX ₃₇₀	HIX ₄₆₅	HIX ₁₈
PW	0.05±0.00 (0.42±0.00)	8.40±0.08 (0.96±0.01)	0.77±0.00 (0.69±0.00)	1.19 x 10 ⁷ ±3.68 x 10 ⁴ (0.46±0.00)	1.10±0.01 (0.82±0.01)
PD	0.05±0.00 (0.42±0.00)	8.01±0.07 (0.92±0.01)	0.76±0.00 (0.68±0.00)	1.17 x 10 ⁷ ± 3.04 x 10 ⁴ (0.46±0.00)	1.12±0.00 (0.84±0.00)
PA	0.12±0.00 (1.00±0.00)	8.74±0.17 (1.00±0.02)	1.12±0.00 (1.00±0.00)	2.57 x 10 ⁷ ±1.33 x 10 ⁵ (1.00±0.01)	1.34±0.01 (1.00±0.01)
PM	0.07±0.00 (0.58±0.00)	8.46±0.10 (0.97±0.01)	0.78±0.00 (0.70±0.00)	1.42 x 10 ⁷ ±1.42x 10 ⁵ (0.56±0.01)	1.17±0.01 (0.87±0.00)

Note: ± values are mean standard error; values in parentheses are the results of normalization with respect to acetonitrile

Table 3.3.4 Summary of HIX for 45-day exfoliation*

Sample	UV absorbance at 280 nm	HIX Method			
		HIX ₂₅₄	HIX ₃₇₀	HIX ₄₆₅	HIX ₁₈
PW	0.072	7.04	0.71	1.16 x 10 ⁷	0.84
PD	0.074	6.66	0.71	1.25 x 10 ⁷	0.82
PA	0.136	7.63	0.79	2.69 x 10 ⁷	1.08
PM	0.078	6.60	0.71	1.20 x 10 ⁷	0.81
AA	0.071	6.72	0.71	1.16 x 10 ⁷	0.81
HCl	0.070	6.82	0.71	HIX ₄₆₅	0.83

*one trial only

Table 3.3.5 Summary of HIX for 45-day exfoliation standardized with respect to SOM concentration*

Sample	HIX Method			
	HIX ₁₈ ^a	HIX ₂₅₄ ^a	HIX ₃₇₀ ^a	HIX ₄₆₅ ^a
PW	0.74	7.85	0.74	4.09 x 10 ⁵
PD	0.79	7.62	0.74	7.16 x 10 ⁵
PA	0.95	8.46	0.81	3.00 x 10 ⁶
PM	0.72	7.47	0.73	2.55 x 10 ⁵
AA	0.83	7.90	0.75	3.44 x 10 ⁵
HCl	0.75	7.65	0.74	3.50 x 10 ⁵

^acalculated by plotting the different dilutions namely: 0.01, 0.02, 0.04 and 0.08 (v/v) on the x-axis and HIX on the y-axis; the y-intercept in the linear regression is the reported standardized HIX value)

*one trial only

Synchronous scans yielded the following spectral features: a) strong shoulder at ~392 nm; b) a weak shoulder at ~440 nm; and c) intense peak centered at ~460 nm. Feature a represent quinone A like moieties, while feature b and c represent quinone B like moieties. Thus, synchronous spectra essentially showed similar spectral features when compared to collecting spectra at individual excitation wavelength. These peaks are consistent with previously reported fulvic and humic acid peaks by the abovementioned authors. Peaks with longer emission wavelength represent more highly conjugated aliphatic systems and highly substituted aromatics, while peaks at the shorter emission wavelength are representative of low molecular weight and less unsaturated materials.

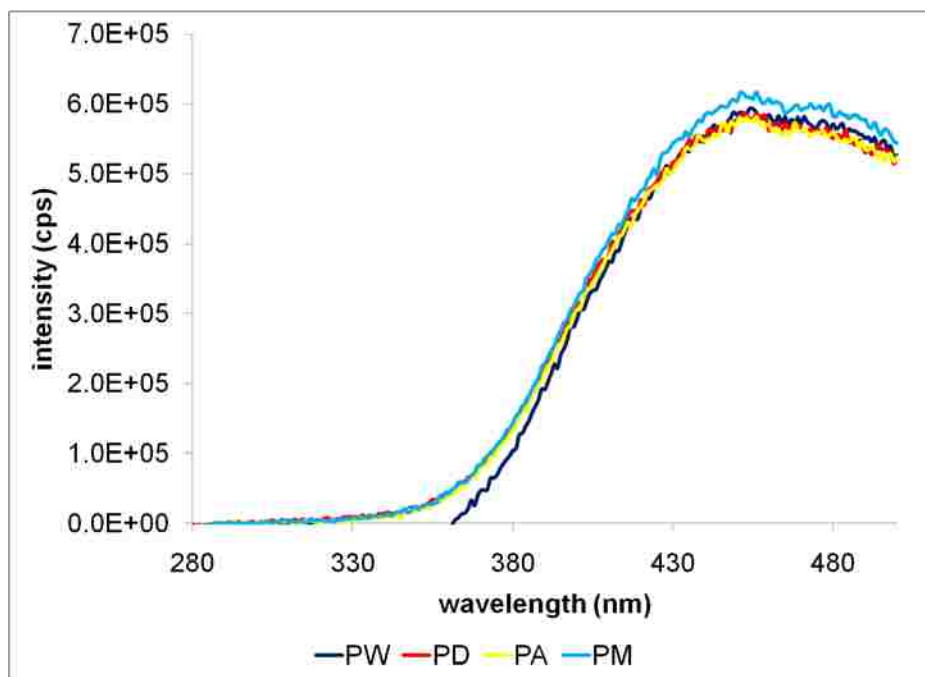


Figure 3.3.2 Fluorescence at 254 nm excitation wavelength for 24 hr exfoliation

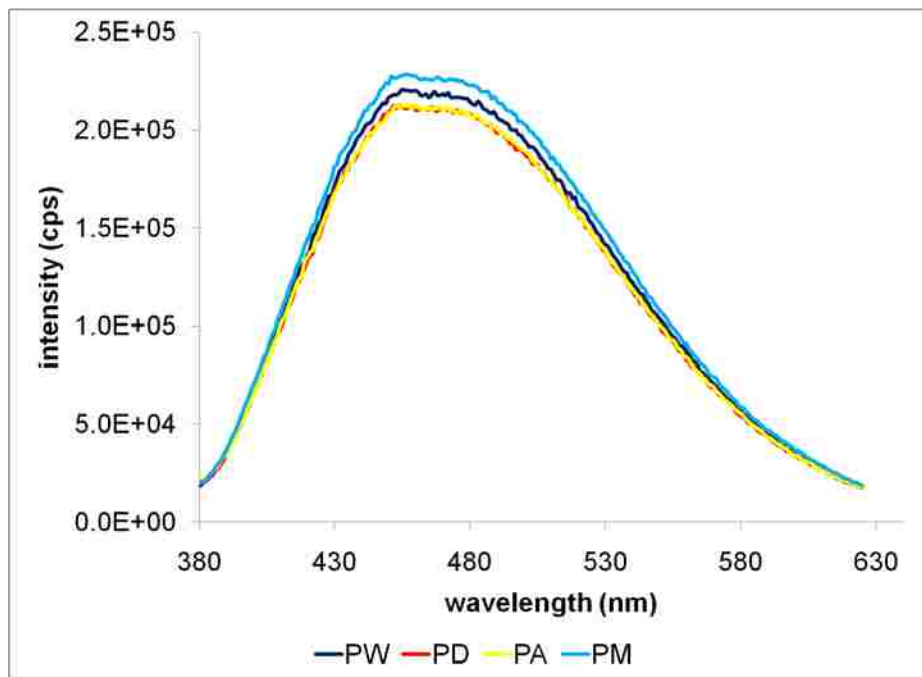


Figure 3.3.3 Fluorescence at 370 nm excitation wavelength for 24 hr exfoliation

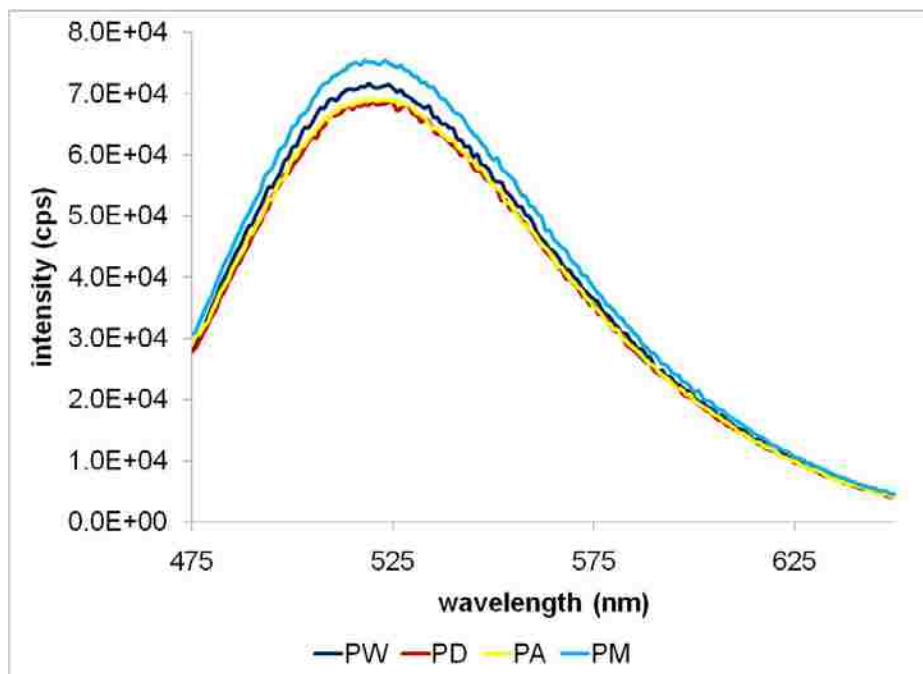


Figure 3.3.4 Fluorescence at 465 nm excitation wavelength for 24 hr exfoliation

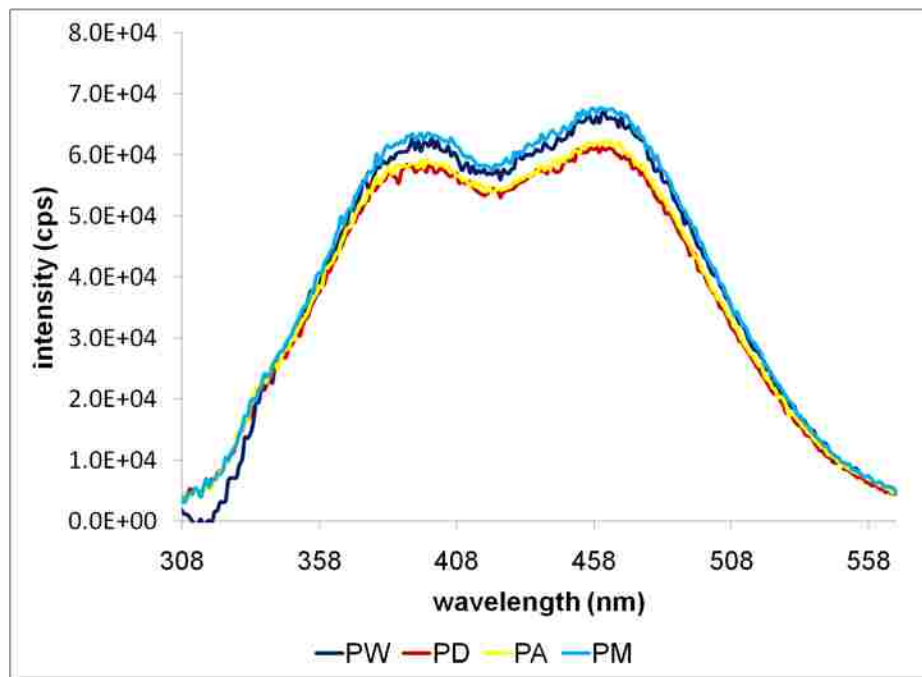


Figure 3.3.5 Synchronous fluorescence at 18 nm $\Delta\lambda$ for 24 hr exfoliation

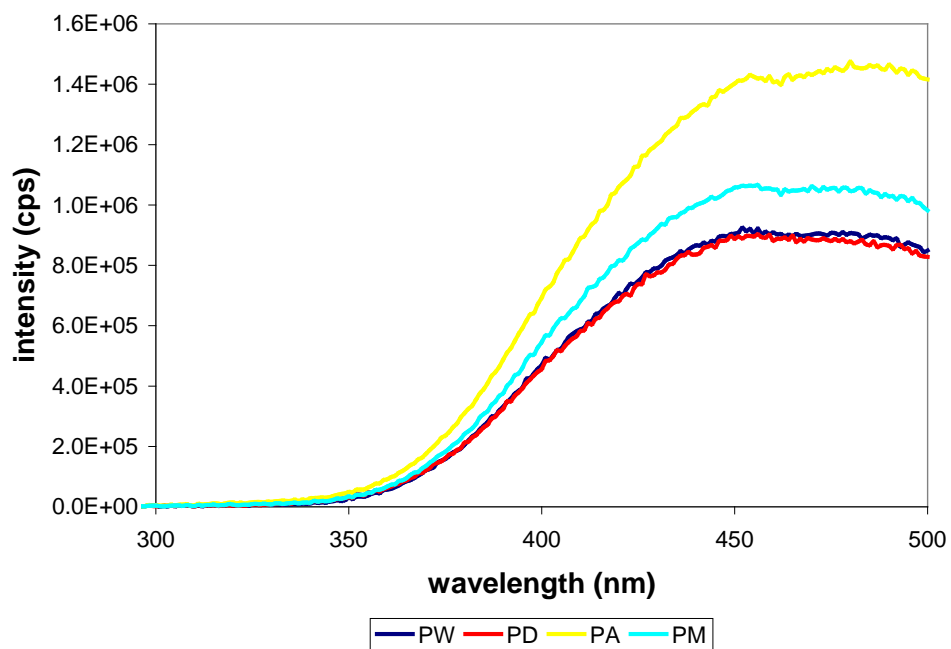


Figure 3.3.6 Emission spectra at 254 nm excitation wavelength of 20-day supernatant

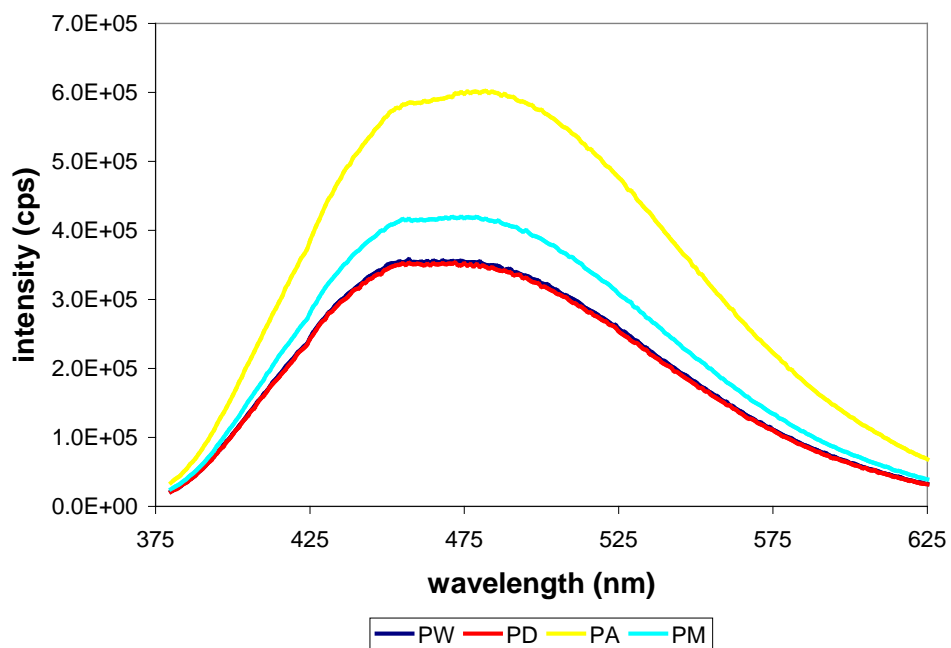


Figure 3.3.7 Emission spectra at 370 nm excitation wavelength of 20-day supernatant

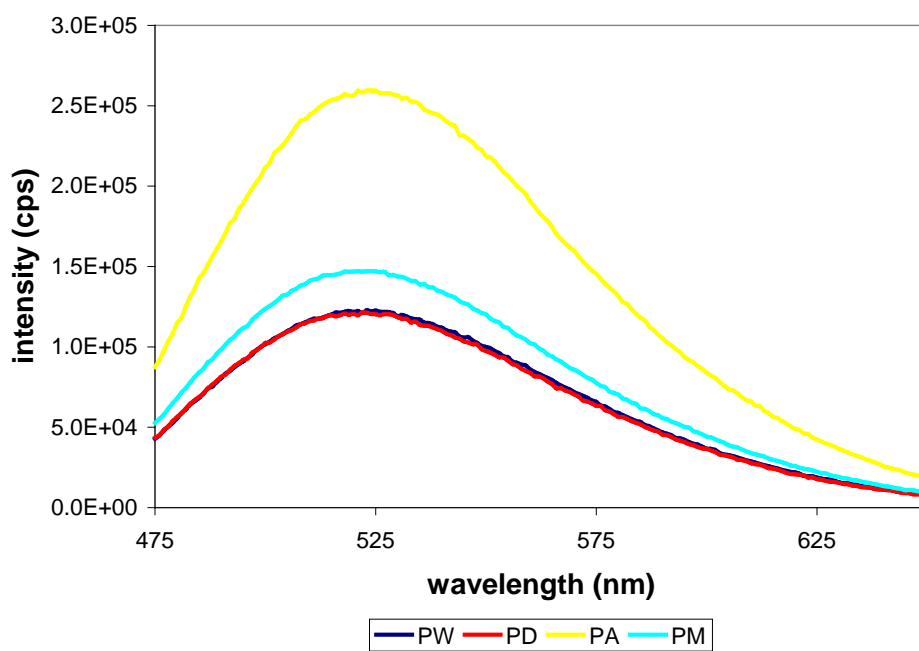


Figure 3.3.8 Emission spectra at 465 nm excitation wavelength of 20-day supernatant

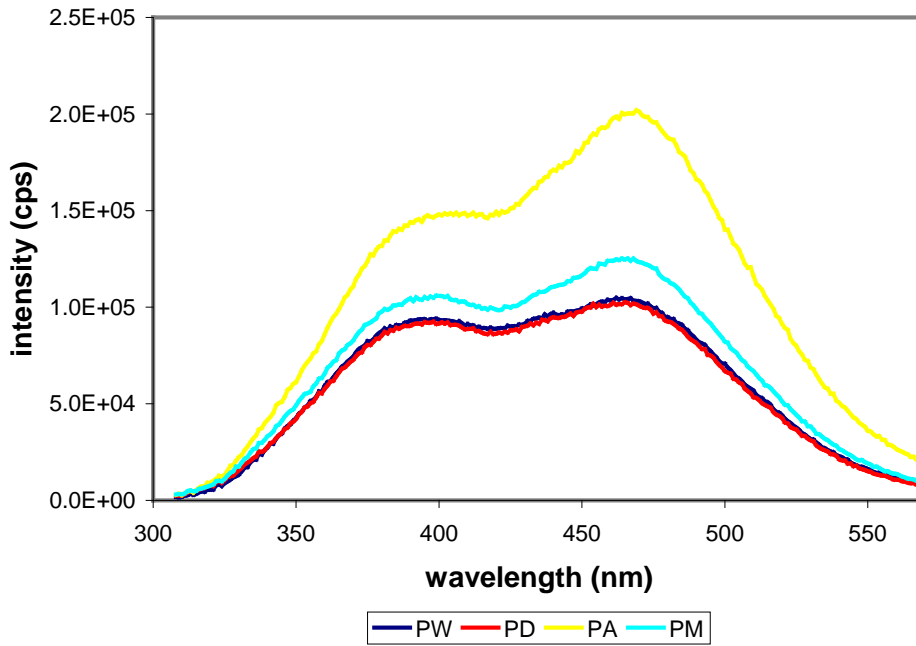
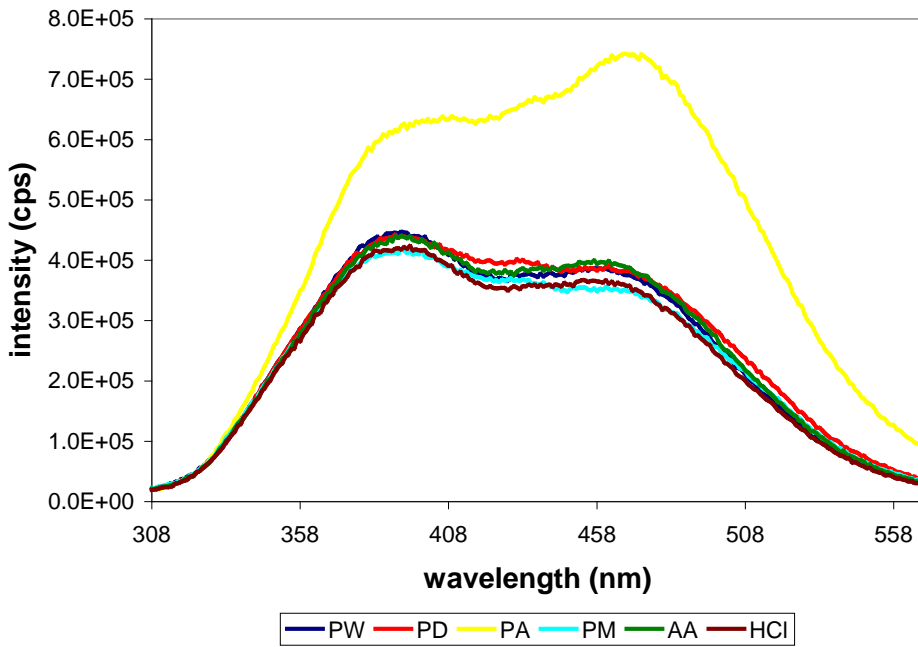


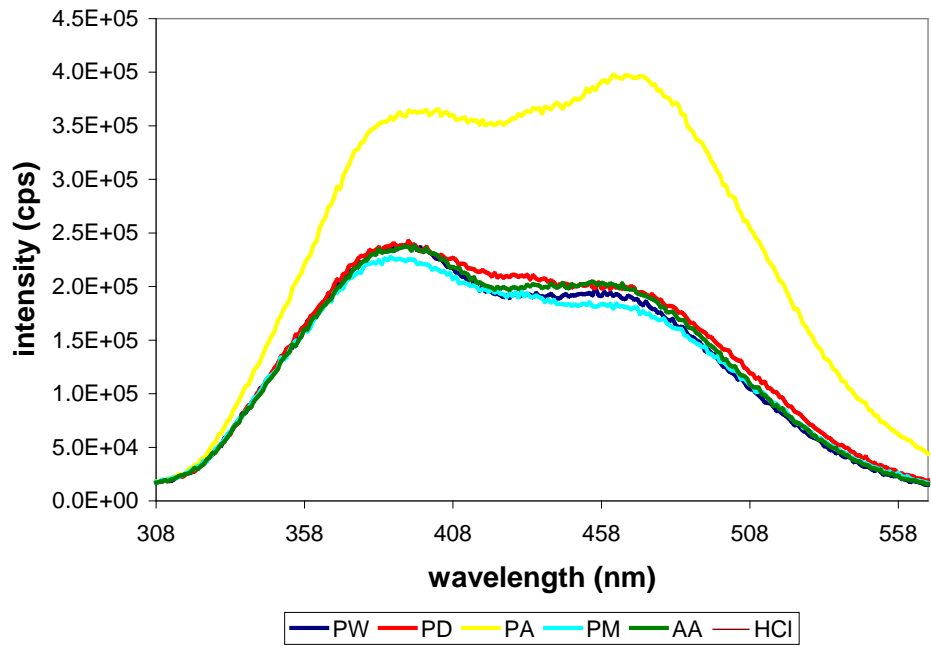
Figure 3.3.9 Synchronous fluorescence of 20-day supernatant



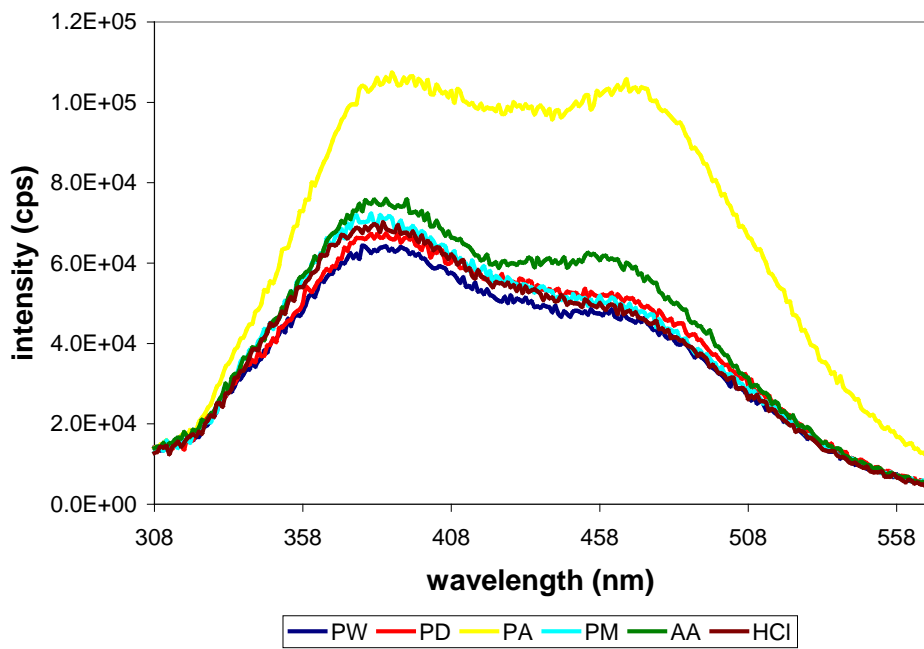
a)

Figure 3.3.10 Synchronous fluorescence at 18 nm offset of a) 4/50 b) 2/50 c) 0.5/50 (v/v) supernatant: total volume of solution

(Figure 3.3.10 continued)



b)



c)

Only PW and PA exfoliated soils were chosen for NMR and FTIR analysis because, among all the solvents, acetonitrile showed a distinctly higher fluorescence while the rest were similar. With regards to the ^{13}C CPMAS spectra analysis, acetonitrile and water-exfoliated Pahokee Peat showed similar decrease in carbon functionalities. It can be seen that hydrophilic moieties including alkyl and aromatic types were preferentially extracted. This is not surprising as the aqueous solutions used were polar in nature. The extraction of both alkyl and aromatic moieties are also due to the fact that these moieties are often strongly associated with hydrophilic moieties such as the case of plant polyesters and plant lipids, and lignocellulosic materials. If the ACN and water exfoliated Pahokee Peat ^{13}C spectra are compared, it can be seen that acetonitrile exfoliated more aliphatic (C–H, 0–55 ppm) and for O-alkyl (60–90 ppm) moieties, such as aliphatic alcohols, ethers and esters (Figure 3.3.11). It can also be seen that for the ACN exfoliated Pahokee Peat there is a decrease in intensity in the region 90–105 ppm for dialkyl-O moieties in carbohydrates and around 125–140 ppm, which are attributed to aromatic C–C and C–H resonance. In addition, the ACN exfoliated Pahokee Peat exhibited a slight decrease in the 135–150 ppm chemical shifts, corresponding to C–O in aromatic esters, ethers and phenols as well as to C–N. FTIR-ATR spectra (Figure 3.3.12) of exfoliation supernatants reveal the following important features: a) 1000–1100 cm^{-1} for C–O stretch in carbohydrates; b) 1150–1300 cm^{-1} for C–O stretch in Ar–O and COOH, which occurs at ~ 1280 – 1150 cm^{-1} ; c) 1300–1500 cm^{-1} for C–H in aliphatics at ~ 1460 – 1450 cm^{-1} (CH_2) and 1380 (CH_3); d) 1500–1800 cm^{-1} , which can be broken down to C=N stretching at 1590–1517 cm^{-1} , C=C stretch in aromatics at ~ 1620 – 1600 cm^{-1} , C=O stretching in amide bonds and quinone at ~ 1600 – 1630 cm^{-1} , C=O stretching in COOH and, to a lesser extent also between 1725 to 1720 cm^{-1} ; e) 2900–3000 cm^{-1} for aliphatics C–H stretch, specifically CH_2 (2940 cm^{-1}) and CH_3 (2960 cm^{-1}); f) 3000–3600 cm^{-1} for OH stretch in carbohydrates and phenols at 3400–3300 cm^{-1} , and N–H stretch to a lesser extent

(Stevenson, 1994, Leenheer et al., 2004). Thus, ^{13}C CPMAS and FTIR reveal similar results that hydrophilic aliphatic and aromatic-type moieties are being released the most easily.

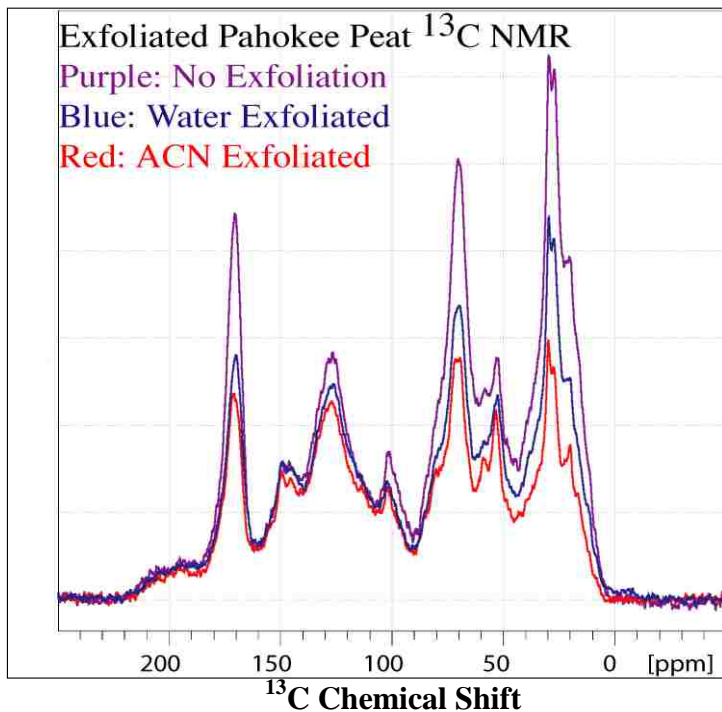


Figure 3.3.11 ^{13}C CPMAS spectra of freeze-dried soil from one month and 15-day exfoliation

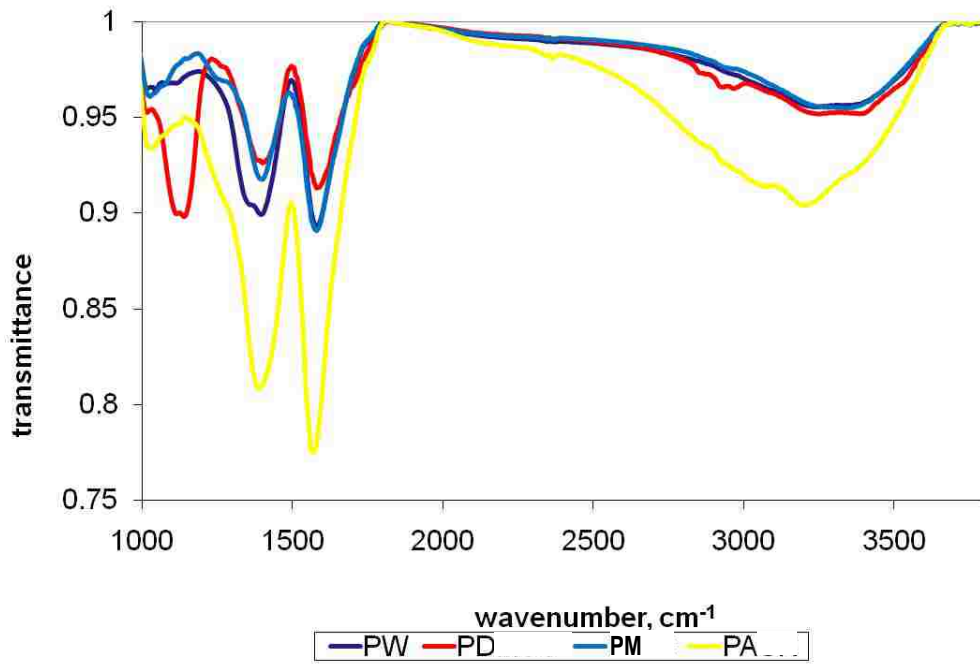


Figure 3.3.12 FTIR-ATR spectra of freeze-dried soils from 45-day exfoliation

From all the 20-day fluorescence spectra one can see that quadruplicate trials of PA consistently showed the highest fluorescence, followed by PM. Thus, acetonitrile as a solvent extracted the largest amount of fluorescent material. The fluorescence spectra are also consistent with more conjugated and condensed aromatic system being exfoliated by the acetonitrile solution (Senesi, 1990). It should be noted that recently, it has been shown that the fluorescence of humic substances arises from intramolecular charge transfer interactions between electron donor-acceptor species, such as hydroxyl-aromatic donors and quinoid acceptors (Del Vecchio and Blough, 2004) and virtually all the fluorescence is due to aromatics (Valeur, 2002). It should be noted that these findings are for dissolved organic materials. In any case, the fluorescence results above show that the acetonitrile solution exfoliates more and different organic matter than any of the other solutions investigated.

Figures 3.3.13 clearly shows that Pahokee Peat amended with dilute solution of acetonitrile as a mobile phase consistently demonstrates the highest HIX values (relative standard error = 0.03 to 1.99 % for all mobile phases). Moreover, UV absorbance at 280 nm is directly related to HIX, which strongly indicates aromatic groups that are responsible for the higher HIXs. HIX₂₅₄ showed the lowest correlation because almost all molecules are excited at this very short excitation wavelength. In contrast, excitation at 465 nm showed the highest slope, meaning that there is a strong positive correlation between aromatic content (UV absorbance at 280 nm) and HIX₄₆₅. Figure 3.3.14 is transparent of PA's clear separation from other solvent systems in all HIX methods employed as well as in UV measurements.

TOC measurements after long term incubation periods (20-day and 45-day) were not found to be useful due to negative TOC values after blank subtraction, especially in the case of acetonitrile and methanol. This is an indication that some of the organic solvent molecules penetrated and become sorbed to the SOM moieties (i.e., associated with the solid phase). This

sorption appears to be essential step in the exfoliation step, especially for ACN.

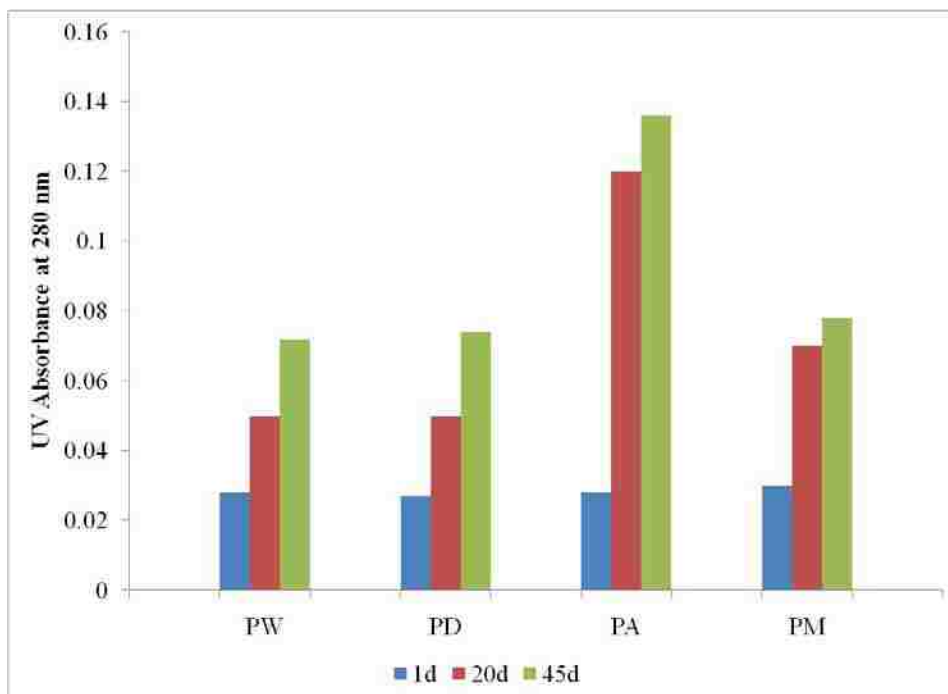


Figure 3.3.13 Summary of UV absorbance at 280 nm

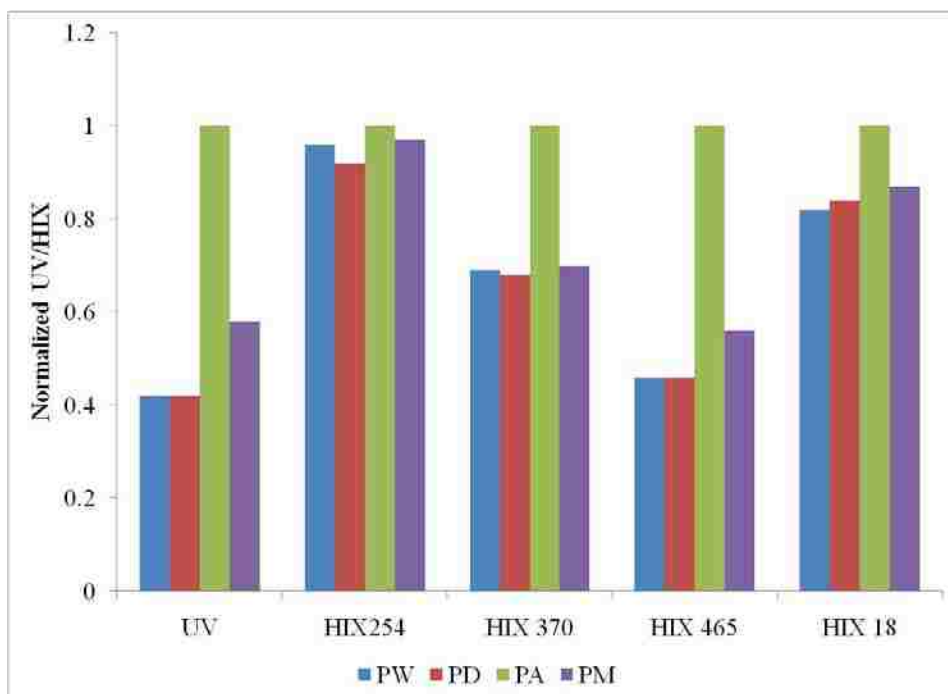


Figure 3.3.14 Summary of normalized HIX and UV absorbance for 20-day exfoliation

Solutions of H₂O–CH₃OH and H₂O–CH₃CN containing the same component ratios have a similar change in the solvent polarity-polarizability (Table 3.3.6). The difference between the two aqueous mixtures is that the H-bond donor acidity (α) of water and acetonitrile are quite different, whereas H₂O–CH₃OH has similar α values. Hence, at the dilute CH₃OH concentration used here, there is less H₂O–CH₃CN solvent interaction and acetonitrile is more available for SOM interaction/solvation. Moreover, as can be seen in Figure 3.3.15, there is a very large separation of charges between the hydrogen atom (highly positive - blue) and nitrogen atom in acetonitrile (highly negative - red). This means that the nitrogen in acetonitrile can be an efficient H-bond acceptor for SOM containing acidic protons, such as carboxylics and phenolics, and N:H-C _{π} weak H-bonding with the aromatics. In addition, the hydrogen atoms in acetonitrile are known to be capable of weak hydrogen-bonding with aromatics. This does raise the question as to why H₂O–(CH₃)₂SO and H₂O–CH₃CN having similar polarities, yield so different results (Table 3.3.3 and 3.3.4). In fact, dimethyl sulfoxide, as a solvent is capable of favorable interactions with a wide variety of functional groups (Hunter et al., 2001). Furthermore, both solvent systems have almost the same solubility parameter scale δ , which suggests fewer interactions among these solvent molecules, and hence, making them more available for solvating less polar solutes in SOM. However, the acetonitrile molecule is linear and has a lower surface volume compared to that of dimethyl sulfoxide, thus enjoys an easier access to the SOM moieties as well as access to larger number of voids within the SOM assembly. In so doing, acetonitrile causes the greatest disruptive effect on the intermolecular forces within the SOM through hydrophobic forces and hydrogen-bonding, where the lone pair in nitrogen acts as a hydrogen acceptor. Complexes of phenol and acetonitrile were calculated to be 5–7 kcal mol⁻¹ from DFT and MP₂ calculation. Also, based on the pK_a slide rule of Gilli et al. (2009), nitriles have potential for weak H-bonding with aliphatic and aromatic alcohols and carboxylic acids

with energies of 2.5 to 4.1 kcal mol⁻¹. In addition, a 1:1 complex of acetonitrile and water with dissociation energy 3.75 kcal mol⁻¹ based on computational studies (Chaban, 2004; Alia and Edwards, 2005) was also reported, which suggests that water may also play a cooperative effect with acetonitrile in the dissociation of SOM weak forces. In the presence of water, acetonitrile was also shown to display H-bonding with the phenolic –OH group in a cyclic fashion that includes n number of water molecules (n is between 1 to 3), acetonitrile and phenol, based on a computational study (Ahn et al., 2004). It was also suggested that a relatively stable clusters were formed in solution with binding energies of 8.7 to 26.5 kcal mol⁻¹ with higher energies observed at n=3. In said results, both the lone pair on nitrogen and the hydrogen atom in the methyl group of acetonitrile were involved in the H-bonding. Thus, water may have a greater cooperative effect with acetonitrile in the disruption of SOM aggregates through this mechanism, and may explain the enhanced fluorescence in H₂O–CH₃CN solutions, as compared with the other aqueous solutions. This is consistent with our NMR results that H₂O–CH₃CN exfoliated soil had a lower intensity in the vicinity of 135-150 ¹³C chemical shift compared to H₂O exfoliation only, which is due to the resonance of aromatic esters, aromatic ethers and phenols.

Table 3.3.6 Physico-chemical properties of solvents

Solvent	¹ BP (°C)	² μ (debye)	³ δ	⁴ α	⁵ β	⁶ V (Å ³)
Water	100	1.85	23.4	2.8	4.5	19
Dimethyl sulfoxide	189	3.96	12.0	0.8	8.9	78
Acetonitrile	81.6	3.92	11.9	1.7	4.7	53
Methanol	65	1.70	14.5	2.7	5.8	41

¹Boiling point (Weast, 1984); ²dipole moment (Weast, 1984); ³solubility parameter scale (Giddings, 1990; Hildebrand, 1936.); ⁴hydrogen donor acidity (Hunter, 2004); ⁵hydrogen donor acceptor (Hunter, 2004); ⁶electrostatic surface potential volume from Spartan calculations

In contrast, the high electrostatic potential surface volume of dimethyl sulfoxide causes steric hindrance in its interactions with SOM. Furthermore, the methyl groups of methanol and

dimethyl sulfoxide most likely participate in hydrophobic forces instead of H-bonding because the localization of positive charges in their methyl group is not as high as compared to acetonitrile (Figure 3.3.15).

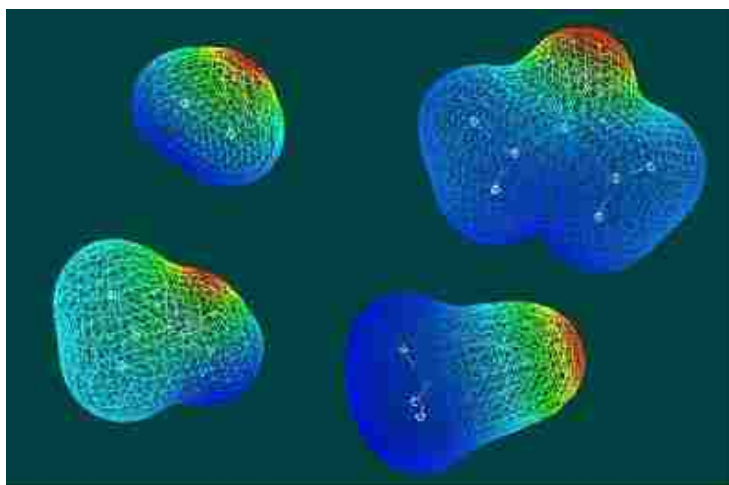


Figure 3.3.15 Electrostatic potential surface of solvents modeled using Spartan version '02 (Wavefunction Inc., CA) (Top: water, dimethyl sulfoxide Bottom: methanol, acetonitrile)

Finally, water displayed much lower HIX values compared to aqueous acetonitrile. In the presence of only water as a mobile phase, hydrophilic groups in SOM would tend to orient themselves towards water molecules, while nonpolar moieties, such as aromatics, would wish to situate themselves away from water. In addition, there is a strong cohesive force between water molecules, thus more energy is needed to solvate SOM molecules, resulting in less exfoliation of aromatic, and hence fluorescent, moieties.

The results from these experiments (carried out at $\ll 1\%$ water-miscible organic solvents) will allow us to better understand solvent assisted sorption-desorption of these nonpolar organic compounds and systems in which they are involved. In sorption-desorption studies, completely water-miscible organic solvents are often used to facilitate the dissolution of organic pollutants in aqueous solutions. A range of $<1\%$ to 2% v/v have been reportedly used in the literature (Kan et al., 1998; Gunasekara et al., 2003; Kleinedam et al., 2002) and is believed to have no effect

on the sorption of sparingly soluble organic pollutants (Schwarzenbach et al., 2003). However, there has been contrasting evidence suggesting that up to 0.72% (v/v) of acetonitrile had a cooperative effect on the sorption of pyridine (Graber et al., 2004). An explanation to this finding can be derived from the above experimental results and discussion. It is probable that acetonitrile is co-sorbed in SOM and its increased contact with the moieties of SOM causes changes in the aggregation leading to the creation of new sorption domains, and thus, strongly questions Graber's assumption that at levels less than 2% (v/v) completely water-miscible organic solvents do not affect the sorption behavior of hydrophobic pollutants within SOM. Beyond laboratory studies, a large range of organic pollutants, such as agricultural chemicals (pesticides, fertilizers and antibiotics) are introduced in the environment by humans. More often than not, these are in the form of mixtures of different chemicals. Moreover, these nonpolar chemicals are dissolved in solvents to aid in their dissolution in water prior to application. Thus, accurate predictive modeling of results from sorption and desorption studies should include solvent and mixed contaminant (bi-solute) effects.

Our fluorescence results showed that dilute aqueous solution of acetonitrile exfoliated significantly more fluorescent (conjugated and condensed aromatic) moieties than any other solvent systems used. This implies that acetonitrile had the greatest disruptive effect on the SOM supermolecular assembly. Indeed, solvents of different polarity affect the nature and amount of exfoliated organic matter, depending on their polarity and H-bonding capability.

A 1-day hydration/solvation period exfoliated the least amount of aromatic moieties, while longer incubation periods extracted more based on UV measurements at 280 nm. A 20-day period exfoliated more humified humic materials, as shown by the higher humification indices across the board, except for HIX₄₆₅, where exfoliation solutions containing dimethyl sulfide or acetonitrile gave higher intensities for the 45-day exfoliation. It is also apparent that

the 45-day solvation period extracted more of less humidified materials because it yielded the lowest HIX values. Furthermore, acetonitrile consistently showed the highest HIX values for 20-day and 45-day contact period, which implies that, among all exfoliation solutions, it extracted the most conjugated and humified (poly)aromatics.

The above observations may be explained analogous to drying and wetting processes in soil. The soil used in this study, primarily an SOM which came from IHSS was subjected to freeze drying. A freeze-dried soil has a much lesser moisture content than an air dried soil. A freeze-dried soil can be envisioned to have hydrophobic SOM moieties on an outer surface, and hydrophilic SOM moieties in the core, the latter being in a more “collapsed” state due to intra and intermolecular H-bonding interactions. When this soil is equilibrated in the air at ambient relative humidity, its moisture content is comparable to an air-dried state. Hence, some of the hydrophilic moieties start to migrate on the outer surface (outershell), although it can be envisioned that an inner shell still exists, and consists of a hydrophobic layer, surrounding the hydrophilic moieties inside this shell. When this air-dried soil is subjected to wetting at complete or more than its saturation level, these hydrophilic moieties at the outer layer are then hydrated and, subsequently, solubilized in the aqueous solution first.

As the soil is subjected to a longer period of wetting (e.g., 20-day), water penetrates into micropores or voids within SOM, where it interacts with SOM moieties through H-bonding. This results in disruption of some of the inter- and intramolecular H-bonding forces within hydrophilic moieties of SOM, as water effectively competes with these forces. The latter processes have been as akin to SOM conformational rearrangement that “reopens” or “reforms” the pores that have been previously collapsed from drying (Schaumann and LeBoeuf, 2005). Thus, hydrophilic moieties, such as fulvic acids, are then hydrated and subsequently exfoliated. In addition, more humidified hydrophobic entities are also slowly extracted due to a more

“expanded or swelled” SOM configuration, as water diffuses into the hydrophobic middle layer. Still longer incubation periods (45-day) will then exfoliate the hydrophilic moieties, which were previously protected by the hydrophobic middle layer.

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Chapter 4

¹H-¹³C Heteronuclear Correlation Nuclear Magnetic Resonance of a Whole Organic Soil*

4.1 Introduction

Soil is a very complex and heterogeneous system consisting of inorganic materials (e.g., quartz, clay), dissolved gases, water solution, living biomass, and dead biomass or soil organic matter (SOM) (Stevenson, 1994; Bohn et al., 2001). The living components in soil are easily identifiable, due to their systematic order. Characterization of inorganic components are readily accomplished due to their definite compositions, while SOM characterizations such as humin, humic acids, and fulvic acids have not yet provided definite molecular structures due to the inherent complexity and polydisperse natures. Detailed molecular characterizations of a whole soil becomes even more challenging due, to intricacies involved in the association/adsorption of SOM with the mineral phase.

SOM is the second largest repository of active carbon on the surface of the earth; hence it is important in biogeochemical cycling of carbon, as well as other elements. SOM also influences soil properties, inclusive of functions such as color, thermal buffering, pH buffering, metal complexation, cation-exchange, water solubility, water retention, and soil particle aggregate formation and stability, which are all important controlling factors of soil fertility (Linn et al., 1993; Stevenson, 1994; Tipping, 2002; Bohn et al., 2001; Wershaw, 2004). Furthermore, SOM plays a major role in sorption of xenobiotics, especially hydrophobic organic pollutants, and in turn affect the fate, transport, and bioavailability of these HOCs (Stevenson, 1994; Bohn et al., 2001). Due to the vast importance of SOM, a plethora of characterizations was attributed in order to gain further insight of its structure, as well as a better understanding of how the structure affects its properties. Due to the complex nature of SOM, most characterizations have been carried on isolated fractions, namely humin, humic acid, and fulvic acid. These

isolated fractions, more often than not, have also undergone further purification processes, including cation exchange and hydrofluoric acid treatment to remove metals (Stevenson, 1994; Tipping, 2002); hence, these isolated fractions may not echo SOM associations as a whole.

The most recent view of natural organic matter (NOM), including SOM, is that it represents an assembly of heterogeneous groups of NOM molecular components, held together by weak forces (Conte and Piccolo, 1999). Investigations leading to the concept of supermolecular assembly of SOM were based on isolated fractions of humic substances (Piccolo et al., 2001; 2002; Piccolo, 2002; Simpson et al., 2001), which may have undergone major perturbations in terms of the associations/assembly, not to mention chemistry during the isolation procedure. Thus, the properties/behavior of these isolated parts and the whole SOM in an unadulterated soil may not parallel one another, hence correlating results from SOM parts to the native matrix may be limited. Evidences of the differences in behavior between a whole soil and its fractions are clearly demonstrated in the literature. Wetting kinetics of a whole soil exhibits a unique slow component that was not observed from its fractions (Todoruk et al., 2003). Sorption of organic compounds on a hydrated humin or humic acid, do not correspond to sorption on a hydrated NOM (Borisover and Graber, 2004). SOM assemblage was also suggested to influence its bulk properties. For example, SOM hydration/solvation may increase or decrease the sorption of organic compounds, depending on the strength of the solvent-NOM interaction and the potential of solvent to penetrate and disrupt SOM associations (Borisover and Graber, 2002a; Borisover et al., 2001; Borisover and Graber, 2002b; Graber and Borisover, 1998; Gamble et al., 2000; Belliveau et al., 2000). In yet another study, solvent dependent differences in the mobility of major SOM components, including aromatics and aliphatic fractions, were demonstrated with the use of water and dimethyl sulfoxide as a swelling agent (Simpson et al., 2001). It was also demonstrated that organic acids from root exudates release organic matter through the disruption

of hydrophobic forces (Nardi et al., 2000; Yang et al., 2001).

The above findings underlie the significance of probing the *in situ* molecular assemblage of SOM. In this context, *in situ* SOM means that SOM is still in its native matrix (i.e., whole unmodified soil). In this study, Ramped-Amplitude cross-polarization (Ramp-CP) and Lee-Goldberg cross-polarization (LG-CP) techniques were utilized to obtain two dimensional ^1H - ^{13}C Heteronuclear Correlation (HETCOR) Nuclear Magnetic Resonance (NMR) spectra of a whole organic soil. Cross-polarization techniques were applied in the solid state analysis of biomolecules, as well as natural organic matter (Cook, 2004; Cook et al., 1996), since these are very useful in detecting low sensitivity nuclei, such as ^{13}C and ^{15}N through sensitivity enhancement. The pulse sequence in a standard CP is shown in Figure 4.1. A $\pi/2$ (i.e., 90°) pulse is applied to the abundant spins (e.g., ^1H) creating magnetization on these spins. During the “spin-lock” condition or cross-polarization, magnetization from the abundant spins are transferred to the rare spins (e.g., ^{13}C). This CP is achieved when Hartmann Hahn match (Equation 4.1) is met.

$$\gamma_H \omega_H = \gamma_C \omega_C \quad (4.1)$$

where:

γ_H, γ_C = gyromagnetic ratio of the abundant nuclei ^1H and rare nuclei ^{13}C respectively

ω_H, ω_C = applied radio frequency field on the ^1H and ^{13}C respectively

The last step involves the removal of ^1H - ^{13}C heteronuclear coupling during acquisition by irradiating the proton resonance frequency with a strong radio frequency field. The use of CP in a solid state ^{13}C NMR offers the following advantages: 1) signal enhancement to $\sim 4x$, because $\frac{\gamma_H}{\gamma_C} = 4$; and 2) faster acquisition times, because the recycling delay (i.e., the delay between the pulses) is dependent upon spin-lattice T_1 , relaxation of the abundant ^1H spins, which are much shorter than T_1 of ^{13}C (Cook, 2004). In addition, rapid spinning at the magic angle ($\theta = 54.7^\circ$)

reduces line-broadening effects that are primarily caused by a chemical shift anisotropy (Cook et al., 1996; Cook, 2004). The chemical shift anisotropy in solid state is due to different molecular orientations with respect to the static magnetic field and is present in aromatic, carbonyls, and alkene carbons, having rather large chemical shift anisotropy compared to other carbon types (Brown and Emsley, 2004; Cook et al., 1996).

In the cross-polarization step, dipole-dipole interactions occur between the same nuclei (i.e., homonuclear) and different nuclei (i.e., heteronuclei). The presence of homonuclear dipolar couplings depends on the natural abundances of the nuclei and their internuclear separation. In this case, the homonuclear dipolar coupling of the abundant spins, between ^1H is expected to be significant, while homonuclear coupling for the rare spins, such as ^{13}C , can be neglected (Rovnyak, 2008). This implies that the ^1H - ^1H “spin-exchange” occurs during the application of the $\pi/2$ pulse as well as in the spin-locked condition (Hartmann Hahn, 1962). In a static CP experiment, dipolar coupling would imply a broadening of the Hartmann Hahn match; however, chemical shift anisotropies are also significant and would result in much greater line broadening. When a sample is rapidly spun at the magic angle (54.7°), chemical shift anisotropy effects, as well as homonuclear and heteronuclear dipolar coupling, are greatly suppressed because they contain a $(1 - 3 \cos^2 \theta)$ term which tends to zero at the magic angle as long as the sample is spun rapidly. Under a spin-lock field and at fast spinning speed, dipolar coupling is reduced by 50%, hence spin exchange is also reduced by 50% (Brus et al., 2002).

It should be noted that during the CP process, proton magnetization is transferred to the carbon spins, and that the proton causing the polarization may come either from the same molecule or from a different molecule. Hence, ^{13}C signals may depict intramolecular and intermolecular connectivities. In the study of molecular assemblage, there is a need to distinguish between the two associations. In order to obtain mainly intramolecular correlations, ^1H - ^1H

dipolar interactions, resulting in spin diffusion, must be greatly reduced. Two possible ways of achieving this are by use of a very short CP time, or by implementing the LG-CP technique. The use of the first technique has the disadvantage of a limited polarization transfer to the distant, unprotonated carbons present in NOM samples, such as unprotonated aromatic or carboxyl carbons. LG-CP was used in this study, as it was proven to greatly alleviate ^1H - ^1H dipolar coupling, which in turn strongly suppresses spin diffusion, thereby allowing the observation of only intramolecular associations.

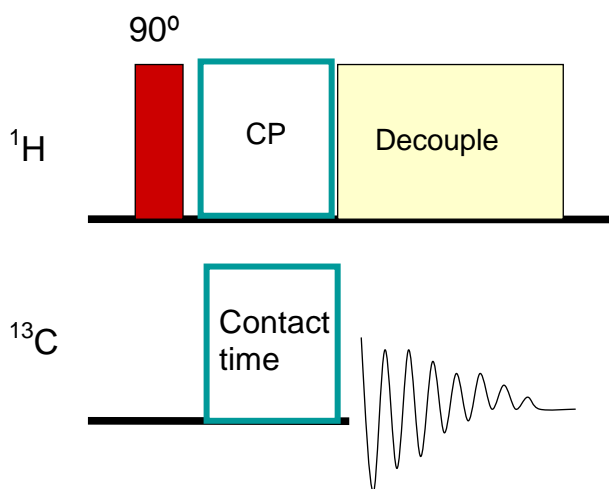


Figure 4.1 Standard cross-polarization pulse sequence

In a Ramp-CP, either one of the channels is “varied” or ramped at the spin-lock (Figure 4.2), thus offering the following advantages: 1) an exact Hartmann Hahn match is achieved, even with highly complex samples such as NOM; 2) this improves resolution, because it allows Hartmann Hahn for the different carbon types; present 3) this overcomes the slowing of spin exchange during fast sample spinning (Cook et al., 1996; Cook, 2004). Furthermore, Ramp-CP was also implemented because it yields both intramolecular and intermolecular correlations. The use of both LG-CP and Ramp-CP techniques is expected to provide direct insight into the molecular assembly of SOM in a whole soil; for the first time these dual techniques, will represent direct molecular level assembly characterization in an *in situ* and unmodified (except

for drying) SOM sample, rather than the isolated components.

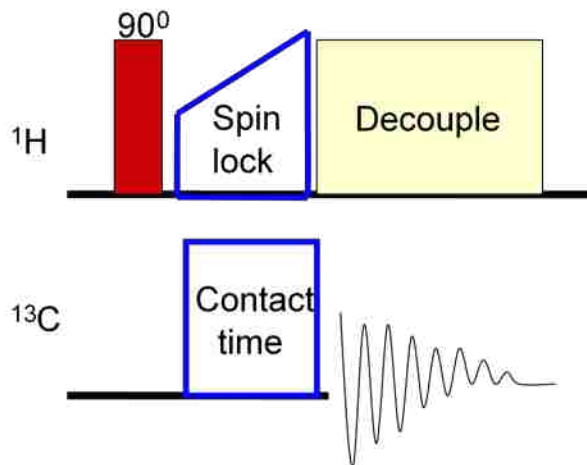


Figure 4.2 Ramp cross-polarization pulse sequence

Soil and SOM fractions for NMR analysis are commonly pre-treated with hydrofluoric acid, in order to remove paramagnetic components, primarily Fe and Mn oxides (Keeler and Maciel, 2003; Skjemstad et al., 1994; Schmidt et al., 1997). These paramagnetic (i.e., containing unpaired electrons) centers can serve as a rapid relaxation pathway for magnetized nuclei, especially in the abundant spins. A shorter relaxation time for ^1H leads to: 1) line broadening of ^{13}C resonances; and 2) less efficient magnetization transfer during the spin lock field. This can result in lower signal intensities of certain fractions of the carbon pool, especially those in close proximity to paramagnetic centers (Cook, 2004; Keeler and Maciel, 2003). Although hydrofluoric acid treatment yields a more quantitative depiction of the carbons in the SOM, the treatment has also been shown to perturb the chemical make-up of the SOM (Dai and Johnson, 1999; Engbretson and von Wandruszka, 1999; Keeler and Maciel, 2003; Schilling and Cooper, 2004; Schmidt and Gleixner, 2005). Removal of these metals by hydrofluoric acid treatment also affects the molecular assembly of SOM within the soil by perturbing certain SOM associations,

including hydrogen-bonds, cation bridging, and mineral-SOM associations. Therefore, the hydrofluoric acid treatment was deemed inappropriate for this molecular assemblage study. Since the sample used in this study is a highly organic soil, it is assumed that most of the ^{13}C pool in the soil organic matter will be observed. Finally, the sample was freeze dried to remove most of its water content. This treatment was necessitated by the nature of the cross-polarization based technique (i.e., transfer of proton magnetization to carbon) used in this analysis. Thus, results for this analysis are for a non-hydrated soil. Furthermore, the sample is organic soil, and it is possible that the molecular assemblage information obtained in this type of soil will not fully represent those of mineral soils.

4.2 Materials and Methods

4.2.1 Soil Collection

The soil was collected from a brackish marsh in southeastern Louisiana (90.275120 °W, 29.552470 °N). It is under soil taxonomy euic, hyperthermic typic haplosaprists. A total of twenty soil samples were obtained from 0 to 75 cm of the topsoil, with the use of a McCaully peat auger. Plant materials were removed and then the soil was air dried. Air dried samples were manually broken and passed through a 2 mm mesh sieve.

4.2.2 Soil Characterization

A composite of these air-dried soil samples was then obtained for soil characterization. The soil bulk density, defined as the mass of air-dried soil per unit volume, was found to be 0.08 g/cm³. The clay mineral fraction is predominantly 2:1 expandable type smectite, $M_x[\text{Si}_8]\text{Al}_{3.2}\text{Fe}_{0.2}\text{Mg}_{0.6}\text{O}_{20}(\text{OH})_4$, where M_x is a monovalent (Li^+ , Na^+ , K^+) interlayer cation (Sposito, 2008). It contains 40.35% carbon and 2.27% nitrogen (Flash EA 1112 elemental analyzer, Thermo Quest Italia S.p.A Italy), while its inorganic carbon content is negligible.

4.2.3 Sample Preparation for NMR Experiment

A composite, air-dried soil was freeze-dried, passed through a 125 μm size sieve, and further ground with a mortar and pestle to ensure a homogeneous sample. The sample was tightly packed in the center of a 50 μL high resolution magic angle spinning rotor (Bruker) in order to achieve a homogeneous radio frequency field during the NMR analysis. It should be noted that the soil did not undergo any chemical treatment prior to NMR analysis, in order to preserve the integrity of the SOM and mineral-SOM assemblage in a whole soil.

4.2.4 Nuclear Magnetic Resonance

A 400 MHz spectrometer, operating at 400.15 MHz on the proton frequency, was used for all NMR experiments. During the cross-polarization step, the ^1H and ^{13}C fields were set to 67.5 kHz and 62.5 kHz, respectively, while a 100 kHz ^1H field was later implemented in the decoupling step. The sample spinning frequency was 13 kHz. Two types of cross-polarization methods were employed; namely, Ramp-CP and LG-CP, using different contact times (0.5, 1 and 2 msec) and decoupling was achieved via the SPINAL64 pulse sequence (Cook et al., 1996; Cook and Langford, 1998; Fung et al., 2000; Khitrin and Fung, 2000). A total of 64 slices constituted the 2-D ^1H - ^{13}C HETCOR spectra, whereby each slice was collected using 4096 scans and 512 data points. A frequency-switched Lee-Goldberg homonuclear decoupling pulse sequence was used to control the evolution of a proton signal. The resulting ^{13}C spectra were processed, using 60 Hz line broadening and a zero filling factor of 2048 points. On the other hand, the ^1H spectra processing utilized 5 Hz line broadening and 128 points zero fill. Prior to application for spectral collection of the soil sample, the performance of the pulse sequences were validated using tyrosine-HCl crystals. Chemical shift assignments for functional groups in the ^{13}C and ^1H dimensions are given in Table 4.1 and 4.2, respectively (Kögel-Knabner, 1997; Almendros et al., 2000; Lorenz et al., 2000; Keeler et al., 2006).

Table 4.1 ^{13}C Chemical Shift

Chemical Shift (ppm)	Functional Group
190 – 220	Aldehyde and ketonic carbons
160 – 190	Carboxyl, amide and ester
160 – 110	Aromatic (137–160 ppm C–O and C–N; 110–137 C–C and C–H)
90 – 110	di-O-alkyl (anomeric carbons in carbohydrates; C ₂ carbons in guaiacyl and syringyl lignin structures; C ₆ carbon in syringyl)
50 – 90	O -alkyl (~54 ppm methoxy; ~72 ppm with 20 ppm spread for C ₂ –C ₆ carbons for cellulose, hemi-cellulose and similar polymeric carbohydrate structures)
0 – 50	Alkyl (~20 ppm for methyl; ~30 ppm for polymethylene)

Table 4.2 Proton Chemical Shift of NOM^a

Chemical Shift (ppm)	Functional Group
0.5 – 2.3	Alkyl
3.3 – 5.5	Primary O-alkyl (HCO in carbohydrates, methoxyl in lignin) and to a lesser extent to protons attached to other heteroatoms
6.5 – 8.1	Aromatic

^aPiccolo et al., 2002; Malcolm, 1990

4.3 Results and Discussion

Figure 4.3.1 shows the ^1H – ^{13}C 2-D HETCOR spectra of the whole soil when LG-CP was used. A contact time of 0.5 msec was employed, therefore this data reveals intramolecular connectivities up to three bonds only (Mao et al., 2003). Further analysis of the spectra suggests that the alkyl (0-50), O-alkyl (50–110), and aromatic (110–160) moieties show no significant correlations with one another (i). This can be explained by the fact that the ^{13}C chemical shifts on the x-axis, assigned to the alkyl, aromatic, and O-alkyl chemical groups, correlate to the same moieties on the ^1H dimension. For example, the alkyl groups with a chemical shift of 0–50 ppm in the ^{13}C dimension (x-axis), has a correlation at ~1ppm in the ^1H dimension, which is also due to protons from alkyl groups. Hence, during cross-polarization, the protons from these alkyl groups polarize the carbons in the same chemical group, leading to the carbon signals in alkyl moieties.

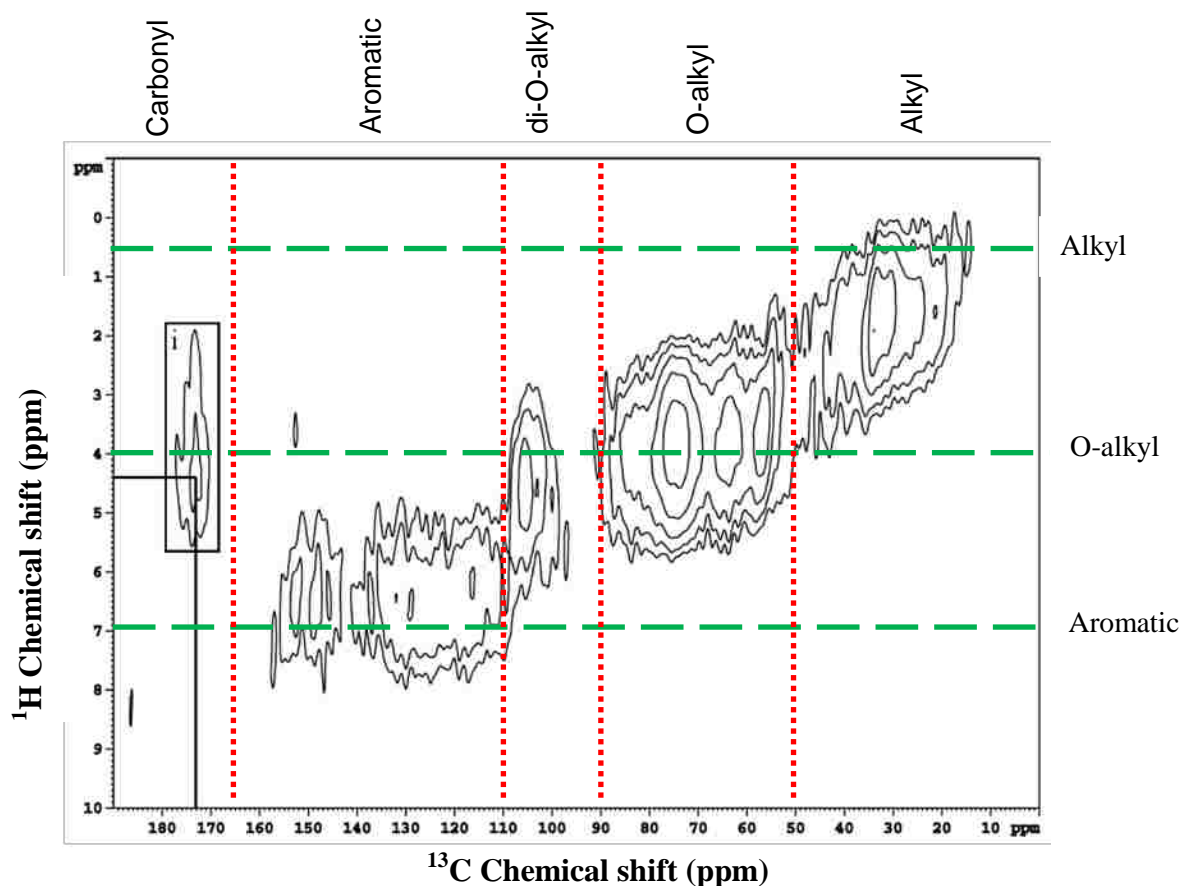


Figure 4.3.1 ^1H - ^{13}C 2-D HETCOR spectra of the whole soil collected using Lee-Goldberg cross-polarization pulse sequence and a contact time of 0.5 msec.

On the other hand, the ^{13}C chemical shift at ~ 173 ppm, assigned to carbonyl groups, has a corresponding ^1H spectral feature on the ^1H dimension, centered at ~ 4.3 ppm, which is due to O-alkyl moieties (i). This implies that the protons from O-alkyl moieties polarize the carbons from the carbonyl groups, rendering them observable. The above observations indicate that there is no significant intramolecular connectivities/covalent bonding between alkyl, O-alkyl, and aromatic moieties, while carbonyl moieties are strongly associated with O-alkyl moieties through covalent bonding. These observations are consistent with the view that natural organic matter (NOM), including SOM, comprises an association of low molecular weight organic compounds, held together by weak forces. This view is a shift from that of the traditional one, where NOM is perceived as a long chain of polymeric molecules, consisting of various types of chemically

distinct moieties and exhibiting high molecular weights (Sutton and Sposito, 2005).

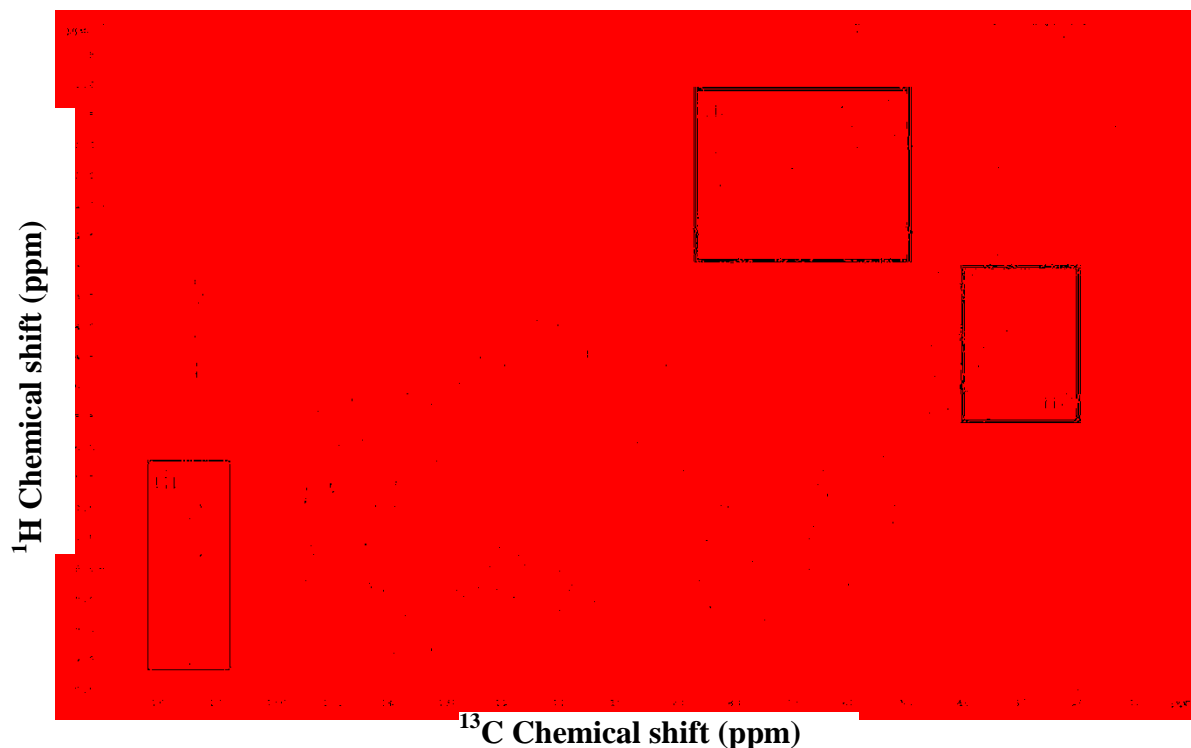


Figure 4.3.2 ^1H - ^{13}C 2-D HETCOR spectra of the whole soil collected using Ramp-CP with a contact time of 0.5 msec.

Figure 4.3.2 represents the ^1H - ^{13}C 2-D HETCOR spectra acquired by using a Ramp-CP. The contact time was set to 0.5 msec, which allowed proton spin diffusion to occur up to ~ 0.4 nm. As a result, the spectral features on the proton dimension show a wider range with respect to ^1H chemical shifts for the different chemical groups. Figure 4.3.2 exhibits similarities with LG-CP spectra in Figure 4.3.1, but some differences are apparent as well. One difference is that there is a hint of connectivity between alkyl and O-alkyl moieties as shown by boxed spectral features denoted as (iia) and (iib), respectively. This connectivity was later confirmed in the 1-D spectra slices derived from 2-D data as discussed below. This pair of spectral features is necessary, because proton spin diffusion occurs from alkyl to O-alkyl and takes place in a reverse direction, as well. Another apparent difference is the presence of ^1H spectral feature at ~ 7.5 ppm (iii); that is associated with carbonyl in the ^{13}C dimension. This is a strong indication of connectivities

between carbonyl and aromatic moieties. The presence of an unpaired box means that proton spin diffusion originates from the protonated moieties and is directed towards the unprotonated moieties. Because of the relatively short distance (~0.4 nm) associated with this proton diffusion, it is plausible that this connectivity is due to H-bonding between carbonyls and phenols.

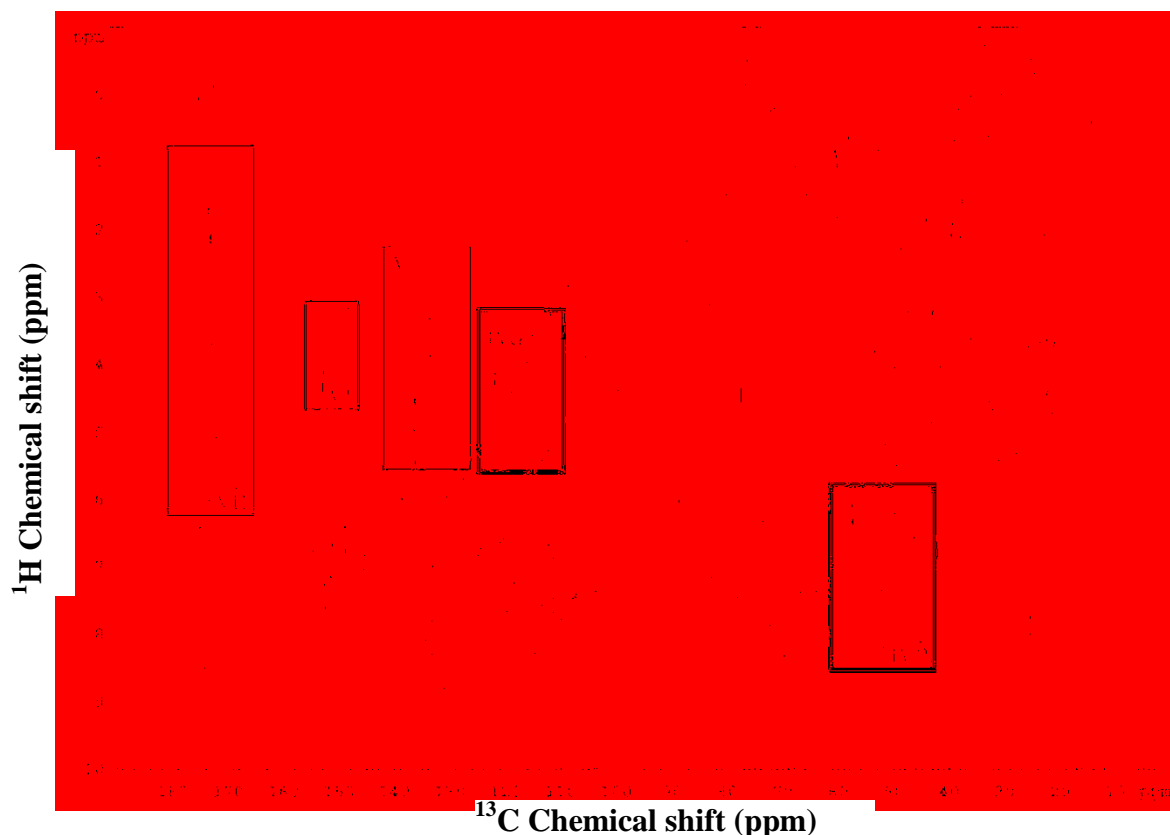


Figure 4.3.3 ^1H - ^{13}C 2-D HETCOR spectra of the whole soil collected using Ramp-CP with a contact time of 1.0 msec.

Figure 4.3.3 illustrates the 2-D HETCOR data obtained with Ramp-CP at a 1 msec contact time. It is more information-rich, compared to Figure 4.3.2, with respect to connectivities between moieties, because it encompasses spin diffusion up to ~0.6 nm. The greater extent of spin diffusion revealed the following connectivities: 1) protonated aromatic and O-alkyl moieties (pair i va and iv b); 2) non-protonated aromatic and O-alkyl (v); 3) O-alkyl carbons and phenolics (vi); 4) carbonyls and alkyls (vii); and 5) carbonyls and O-alkyls (vii). Once again, the presence of a box pair (iva and ivb) signifies that spin diffusion takes place in both directions between

aromatic and O-alkyl moieties. The emergence of a cross peak at $^1\text{H}/^{13}\text{C}$ chemical shift 7/56 ppm corresponds to connectivities between the aromatics and the methoxy groups, and can be attributed to lignin (Salloum et al., 2002) structures, because lignin contains aromatic methoxy moieties. Box vi shows a less intense peak between O-alkyl and phenolics with $^1\text{H}/^{13}\text{C}$ shifts of 3.5/153 ppm, as compared with correlations of O-alkyl with other types of aromatics (iva, ivb, v). This suggests that the connectivities of O-alkyl carbons with phenolics are present at a lesser extent, in contrast with greater connectivities between protonated O-alkyls and protonated aromatic moieties, as well as protonated O-alkyls and non-protonated aromatic moieties. All of the features in box iva to vi indicates connectivities involving lignin structures within the SOM, and to some extent, tannin structures. Furthermore, the carbonyl region in the ^{13}C dimension shows much more developed correlations with alkyls and O-alkyl pools, with clear cross peaks at 1.6/175, 1.9/173, 2.9/175, 4.1/173, and 4.7/175 ppm (vii). These signals can be assigned to connectivities within fatty acid structures.

With a Ramp-CP at a contact time of 2 msec, proton spin diffusion spans a longer distance, this time up to ~ 0.8 nm (Figure 4.3.4). This data displays connectivity between aromatic and carbonyl moieties centered at 7/173 ppm. In addition, a more intense correlation between an alkyl group and a specific subset of nonprotonated aromatic moieties, centered at ~ 130 ppm, has developed. Overall, a greater number of correlations become available at longer contact times (e.g., 1 msec, 2 msec), due to a longer distanced proton spin diffusion. A 2 msec contact time yields a very similar, yet more extensive, amount of connectivities as seen for a contact time of 1 msec, and shows more intense correlations. This means that at 2 msec contact time, the magnetization of the system is at or near equilibrium, except possibly for aliphatic structures.

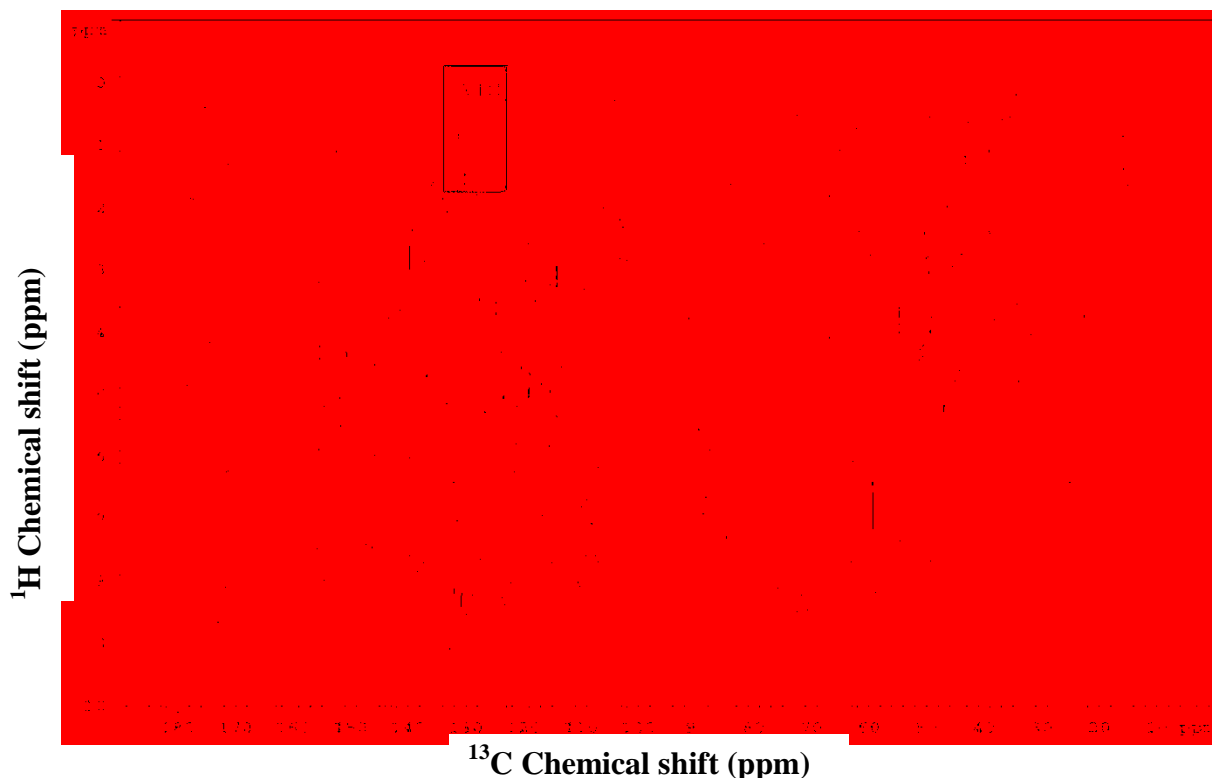


Figure 4.3.4 ^1H - ^{13}C 2-D HETCOR spectra of the whole soil collected using Ramp-CP with a contact time of 2.0 msec.

Figures 4.3.5 to 4.3.7 are 1-D ^{13}C slices, taken from the proton dimension of the 2-D ^1H - ^{13}C HETCOR spectra. Each set or slice from the ^1H shift coordinate represents a specific moiety, and the resulting spectra can essentially be viewed as 1-D ^{13}C spectra. This was done in order to simplify and further elucidate the 2-D data presented earlier (Figure 4.3.1 to 4.3.4). The stacked 1-D ^{13}C plots contained in Figure 4.3.5 represent the slices coming from the 7.0 ppm ^1H chemical shift. From top to bottom, the first three spectra are assigned to 0.5 msec, 1 msec and 2 msec Ramp-CP contact times, because they were extracted from the proton dimension of 2-D HETCOR, obtained using Ramp-CP with contact times of 0.5 msec (Figure 4.3.2), 1 msec (Figure 4.3.3), and 2 msec (Figure 4.3.4) contact times, respectively. The fourth spectra in this figure came from 2-D HETCOR LG-CP (Figure 4.3.1) with a contact time of 0.5 msec, hence it is designated as LG-CP 0.5 msec. The same assignments were followed for the 1-D ^{13}C plots of the succeeding four-stack spectra in Figures 4.3.6 and 4.3.7. Figure 4.3.5 reveals that increasing

the contact times during Ramp-CP acquisition results in an increase in methoxy peak intensity. This further corroborates our hypothesis that the connectivities between methoxy and aromatic moieties are due to lignin structures. In addition, the use of spin diffusion in Ramp-CP allows the observation of O-alkyl signals which are absent in LG-CP. It was also evident that longer spin diffusion generally increases the intensity of these O-alkyl peaks, which implies that the proton magnetization that diffuses into ^{13}C during polarization, may originate from protons farther from ^{13}C (Mao et al., 2001). This observation reveals that there is a close-through-space association between O-alkyl and aromatic moieties in the distance probed here, from ~ 0.4 nm to 0.8 nm, suggestive of H-bonding between functional groups of these two distinct moieties. In the Ramp-CP spectra with a contact time of 2 msec, a weak correlation also develops between the aromatics and a specific group of alkyl moieties, with a chemical shift at ~ 22 ppm.

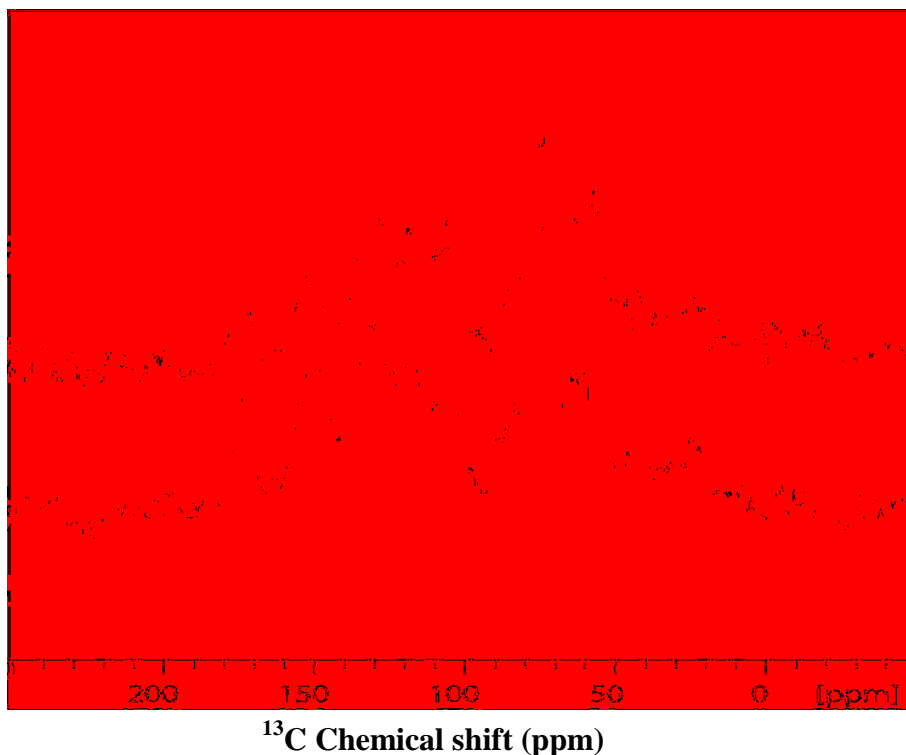


Figure 4.3.5 1-D ^{13}C spectra extracted from the 7.0 ppm ^1H chemical shift of the 2-D HETCOR spectra (Scaling of y-axis was set to 1 for all, and offsets were done for visual aid only).

Figure 4.3.6 shows 1-D ^{13}C plots extracted from a 4.0 ppm ^1H shift, which further illustrates connectivities of O-alkyl moieties. This data displays a close spatial association of O-alkyl with aromatic moieties, which supports previous finds in Figure 4.3.5, and is most likely due to presence of lignocellulosic materials. Strong associations (i.e., covalent) between hemicellulosic fragments and lignin structures are present in plant materials (Sun et al., 2000; Donaldson, 2001). In addition, the presence of lignin-carbohydrate complexes in wood were suggested earlier (Gerasimowicz et al., 1984; Tenkanen et al., 1999) and then were shown by Liitia et al. (2000) to exist in wood fiber extracts through 2-D ^1H - ^{13}C HETCOR NMR with dipolar dephasing. The Ramp-CP spectra also display close associations between O-alkyl and alkyl moieties, although to a lesser extent. A weak intramolecular connectivity (≤ 3 bonds) is observed between O-alkyl and functionalized aromatics (130–160 ppm), as well as phenolic carbons from LG-CP spectrum. This may originate from methoxy carbons in lignin structures,

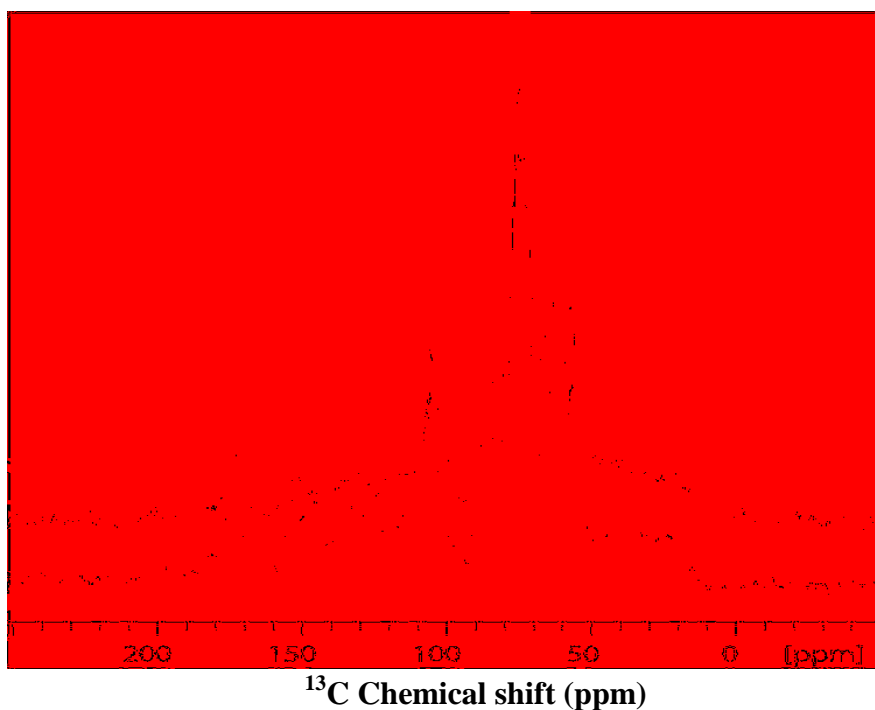


Figure 4.3.6 1-D ^{13}C spectra extracted from 4 ppm ^1H shift in 2-D HETCOR data (Scaling of y-axis was set to 1 for all, and offsets were done for visual aid only).

but this is unlikely as it would require the transfer of ^1H magnetization across three bonds, to then pass through an oxygen atom or lignin-carbohydrates linkages (Guerra et al., 2006). A more plausible explanation is leakage of the above discussed lignin-carbohydrates through space linkages, due to an imperfect proton spin diffusion by the LG-CP pulse sequence.

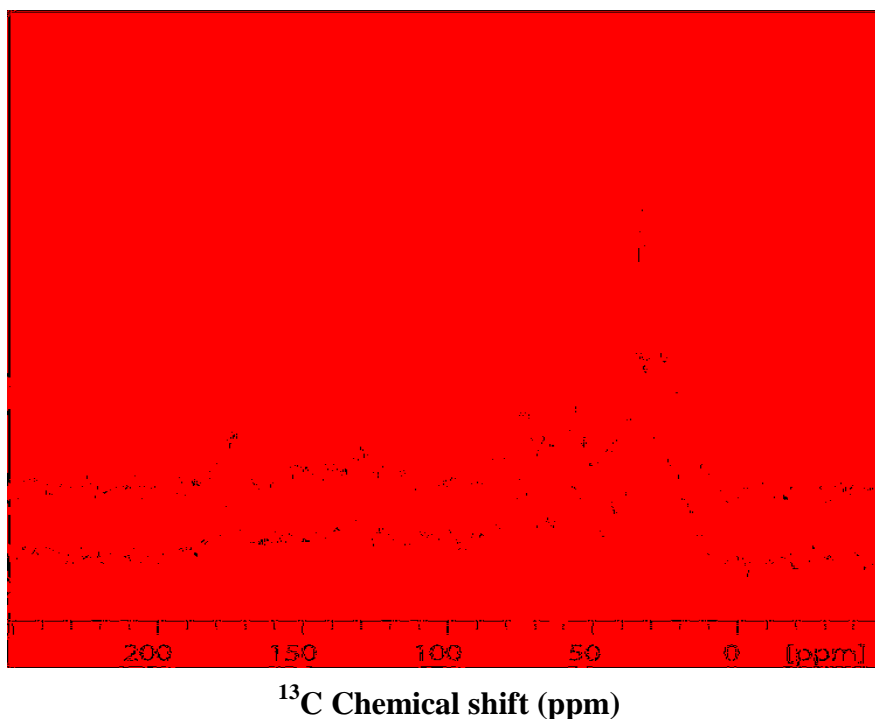


Figure 4.3.7 1-D ^{13}C spectra extracted from 0.5 ppm ^1H shift in 2-D HETCOR data (Scaling of y-axis was set to 1 for all, and offsets were done for visual aid only).

Figure 4.3.7 demonstrates further the spatial associations of alkyl moieties, since these ^{13}C slices were taken from a 0.5 ppm ^1H shift. Alkyl moieties are in spatial proximity to O-alkyl moieties; however, these associations are weaker as compared to the strong associations between O-alkyl and aromatic moieties, as suggested from and discussed in Figures 4.3.5 and 4.3.6. It is also apparent that alkyl moieties are associated through space with carbonyls, especially the carbonyl type (~175 ppm). Alkyl carbons in SOM, most probably come from cuticular materials such as cutin, which consist of long chain saturated or unsaturated acids (Kolattukudy, 2001; Stimler et al., 2006). In addition, cuticular materials are often associated with soluble plant lipids (Kolattukudy and Espelie, 1989; Mariani and Wollers-Arts, 2000), and may explain the

connectivities which are due to fatty acid-like moieties. There is also an evolution of a very weak signal intensity at 130 ppm (C-C, C-H) in Ramp-CP with a contact time of 2 msec, indicating a weak association between alkyl and specific fractions of aromatic moieties. This is consistent with the results in Figure 4.3.5, where the aromatic moieties show a weak spatial association with alkyl groups with a chemical shift of ~22 ppm, and was also indicated in 2-D HETCOR (Figure 4.3.4, viii). Hence, associations between specific fractions of alkyl and aromatic moieties are hinted, which are likely, due to hydrophobic forces. It can be postulated that this is similar to that of suberized materials, which is another type of cuticular material found in barks and roots consisting of aliphatic and aromatic domains (Kolattukudy and Espelie, 1989; Bernards, 2002). However, the exact associations of aromatic and aliphatic groups in a suberized tissue are still unclear (Bernards and Lewis, 1998). Overall, Figure 4.3.7 indicates that alkyl moieties show very little association with other moieties at the spatial distance probed here, and possibly suggests that these are more distant from other major SOM structures. These alkyl moieties show similarities to cuticular and lipid fractions of plant origin.

2-D ^1H - ^{13}C HETCOR NMR provides better resolution due to the wider spread of ^1H and ^{13}C resonances, compared to the use of 1-D ^1H or ^{13}C solid state NMR. Thus, 2-D ^1H - ^{13}C HETCOR NMR has the advantage of revealing information about intramolecular and intermolecular associations, which cannot be provided by 1-D solid-state NMR. From the results presented, it appears that the molecular assembly of SOM in this whole, highly organic, young soil consists of two main domains. One domain is comprised of O-alkyl moieties that are in close proximity with aromatic moieties (Figure 4.3.5 and 4.3.6). In most probability, the existence of these groups takes precedence from primarily lignin materials (Figure 4.3.8), with some contribution from tannins. Lignins in plants are often found covalently linked to carbohydrate structures such as cellulose and hemicelluloses through benzyl-ester, benzyl-ether, and phenyl-

glycosidic bonds (Guerra et al., 2006; Sun et al., 2000; Donaldson, 2001), and the presence of lignin-carbohydrate complexes in wood has also been indicated by ^1H - ^{13}C HETCOR NMR (Liitia et al., 2000). The close association of O-alkyl and functionalized aromatics and phenolic carbons may also be attributed to the presence of tannins (e.g., Figure 4.3.9). This parallels the work presented by Lorenz et al. (2000), that tannins can significantly contribute to forest SOM.

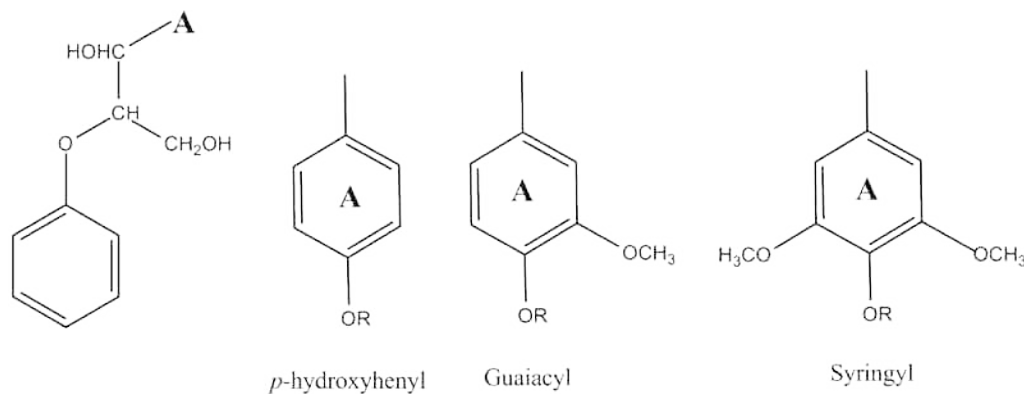


Figure 4.3.8 Structure of lignin monomeric unit (Wershaw, 2004)

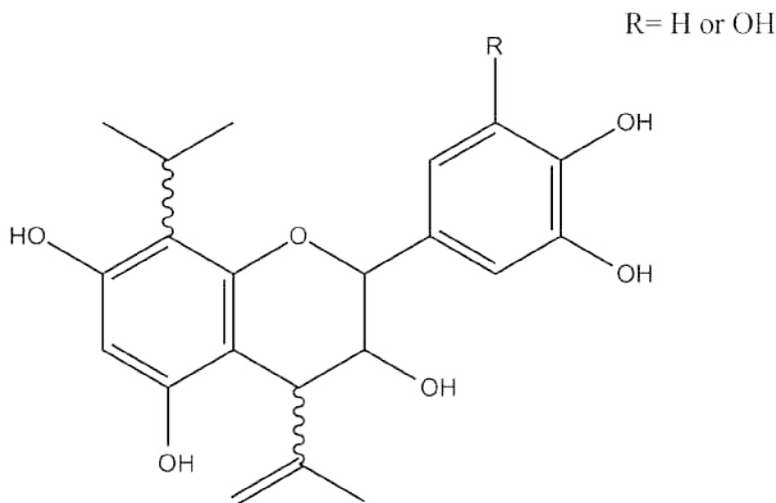


Figure 4.3.9 Typical monomer unit of nonhydrolysable tannins (Wershaw, 2004; Lorenz et al., 2000)

The other domain consists of alkyl moieties, which appear to be spatially isolated with the O-alkyl/aromatic domain discussed above. These isolated alkyl moieties are most likely derived from cuticular components and are supported by the similarity in alkyl moieties such as

^{13}C spectra, presented in Figure 4.3.7 and those reported for cuticular materials (Chen et al., 2005; Shechter et al., 2006; Stimler et al., 2006). These results are consistent with the literature that cuticular materials constitute a significant portion of SOM and are highly recalcitrant (Almendros et al., 1996; Hu et al., 2000).

This finding is in agreement with the previous studies that demonstrate: 1) two distinct peaks at the 30–33 ppm in the ^{13}C NMR spectra; 2) the existence of crystalline and amorphous aliphatic domains in humic materials; 3) the transition between the condensed and amorphous domains as defined by a glass transition temperature and are reversible, giving clear evidence of purely alkyl domains; and 4) the thickness of the crystalline alkyl moieties are at least 4 nm (Hu et al., 2000; Chilom and Rice, 2005; Lehman et al., 2007).

These data were acquired on a freeze-dried soil sample; hence, these represent an assembly of SOM in a dry sample. However, this concept of the existence of O-alkyl moieties that are intimately associated with aromatics, and the alkyl moieties situated at a farther distance from the said domain yet within the length being probed here, may be extended to an SOM arrangement in a hydrated soil. Simpson et al. (2001) applied ^1H high resolution magic angle spinning (HR-MAS) on mineral soil, in order to determine what moieties become mobile when the soil contacted with D_2O or DMSO-d_6 . With D_2O as the swelling solvent, alkyl moieties in the form of fatty acids, aliphatic esters, and ethers/alcohols emerge as the dominant components in the solid-aqueous interface. Furthermore, the use of the more hydrophobic solvent DMSO-d_6 rendered the aromatic moieties observable, in addition to similar signals of alkyl moieties that were present in D_2O swelling. These aromatic moieties were not water-accessible during the short period of hydration utilized in their study, which suggested that it may be located in a hydrophobic core, similar to that of micellar structures.

The micellar model of humic substances in soils was first conceptualized by Wershaw

(1999, 1993) suggesting that in an aqueous solution, the SOM arrange themselves to orient hydrophilic moieties near the vicinal water, while the hydrophobic moieties are located inside the hydrophobic core and away from the aqueous interface, thereby forming aggregates called micellar structures (Wershaw, 1993; Engebretson et al., 1999). The concept of a supramolecular assembly of SOM also recognizes the importance of hydrophobic and hydrophilic associations in dissolved humic substances (von Wandruszka, 2000; Piccolo, 2001). Thus, a conceptual model emerges such that as a soil wets, the hydrophilic O-alkyl moieties would prefer to migrate on the outer layer of the intraparticle air/water soil interface, while the more hydrophobic lignin and tannin structures are protected from water in an inner hydrophobic core. This indicates that for a moist soil, aromatic moieties rather than be highly accessible as sorption sites for HOCs, would rather sorb to the alkyl domain as shown in Step 1 in Figure 4.3.10. As the soil dries, SOM once again undergoes conformational rearrangement; this time, the more hydrophobic moieties in the O-alkyl and aromatic domain are exposed on the surface, while protecting the O-alkyl moieties from the lack of water as demonstrated in Step 2. These hydrophobic aromatic moieties are expected to serve as more thermodynamically favorable sorption sites for HOCs when compared to the alkyl domain, especially for aromatic HOCs through π - π complexes and π - π electron donor acceptor associations (Keiluweit and Kleber, 2009; Wijnja et al., 2004; Zhu et al., 2004). It is therefore probable that the HOC migrates to the exposed aromatic moieties (Step 3); this preferential sorption of HOCs to the aromatic moieties would be influenced by steric hindrance, as well as the governing of kinetic and thermodynamic effects. As the soil undergoes another wetting cycle, it can be envisioned that the hydrophobic aromatic moieties would migrate back to reside once again in the inner core, surrounded by a hydrophilic layer of O-alkyl moieties (Step 4). This hydrated outer layer would render the hydrophobic core inaccessible for further HOC sorption, and also would prevent the release of HOCs associated with the aromatic moieties;

hence these HOCs would remain bound with the moieties. This reveals an important environmental implication in regard to attainment of HOC sorption equilibrium and soil-pesticide interactions at different soil hydration levels, since soils and sediments are exposed to wetting and drying cycles.

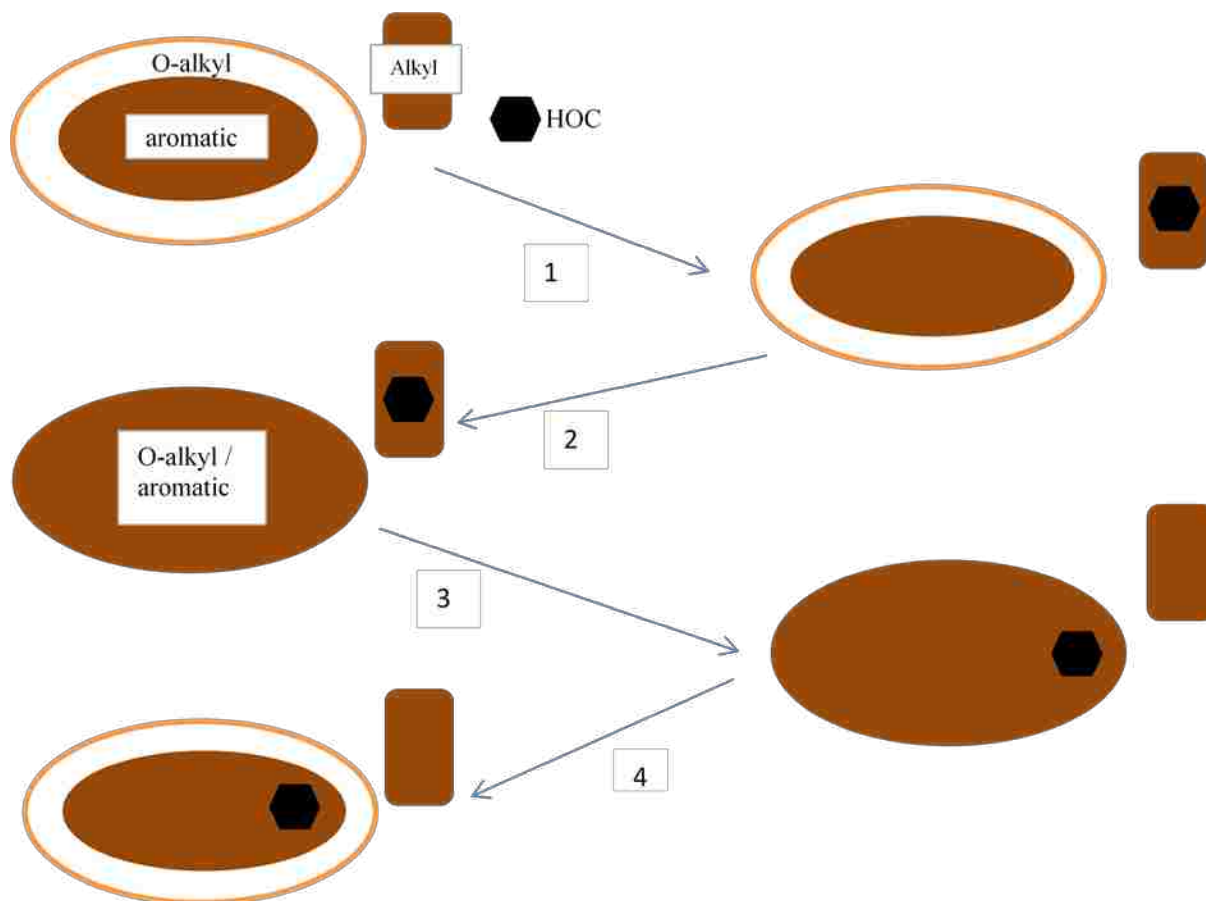


Figure 4.3.10 Conceptual model of how SOM molecular assemblage at different hydration levels affect uptake and release of hydrophobic organic compound

The soil used in this study is a highly organic soil, and the result presented above may not be fully applicable to mineral soils. However, this is in agreement with the results of Simpson et al. (2001), that aliphatic and O-alkyl moieties become mobile upon D_2O swelling, while aromatic moieties are observable upon $DMSO-d_6$ swelling of a mineral soil. Furthermore, the proposed model can explain the initially fast uptake (i.e., labile sorption) within 24 hrs of adding an aqueous solution containing aromatic HOC chlorothalonil, resulting in a decrease in sorption

beyond 24 hrs on a mineral soil. The rapid sorption would be attributed to sorption to aromatic moieties that were initially positioned on the outer surface of the O-alkyl/aromatic SOM domain, while decreased sorption upon longer wetting would be due to the unavailability of aromatic moieties as sorption sites, as the soil migrates back inside the core (Gamble et al., 2000).

The presented model can also explain the increased sorption and thermodynamic favorability of sorption of polyaromatic hydrocarbons to a mineral and organic soil, and sediments, following solvent extraction of lipid (i.e., alkyl moieties) fractions from the sorbents (Chilom et al., 2005). The use of an organic solvent upon lipid fraction removal might have rendered the aromatic moieties more accessible.

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Chapter 5

Sorption and Desorption

5.1 Introduction

Most sorption investigations in the literature have been conducted in order to elucidate the mechanisms involved in the retention and release of xenobiotics in environmental sorbents, such as soil and its components, sediments, and aquifer materials. Xenobiotics may include metals, radioactive materials, and biological toxins, as well as polar and non-polar organic compounds. This study, however, focuses on the hydrophobic organic compounds (HOCs). The sorptive behavior of HOCs in the terrestrial environment greatly influences 1) mobility and transport; 2) persistence; and 3) bioavailability and chemical reactivity.

Sorbate-sorbent interactions are often described by a sorption capacity or distribution coefficient, K , obtained from experiments. Higher K values correspond to stronger affinities of sorbate to sorbent. The implications of sorption capacities are vast from the standpoint of environmental pollution and agricultural concerns. A highly retained HOC is desirable for maintaining groundwater, as well as surface water quality (Lennartz and Louchart, 2007) due to decreased downward movement and surface runoff. In addition, bound HOCs are less bioavailable, thus less susceptible to degradation (Sparks, 1989; Tabatabai and Sparks, 2005; Ogram et al., 1985). For HOCs such as pesticides, reduced bioavailability in the soil solution may mean less bioefficacy on target species. Furthermore, distribution coefficients are an integral part of modeling and thereby predicting the fate of contaminants in the environment. As an illustration, the sorption coefficient K , in combination with two other physical properties of aquifer materials, are required in calculating the retardation factor, R

$$R = 1 + \frac{\rho_b K}{n}$$

where n is porosity and ρ_b is the bulk density of the aquifer materials. Finally, R is part of a series of mathematical equations needed to model the groundwater transport of pollutants (Dunnivant and Anders, 2006).

Herbicides norflurazon and acifluorfen were used at a rate of 1.2 and 0.4 million lbs as an active ingredient in the U.S., in 2002 (Tomlin, 1997; Gianessi and Reigner, 2002) as pre-emergence and post-emergence herbicides, respectively; the herbicides were implemented in soybean and nut crops, nut trees, citrus, orchards and cotton farms (Locke et al., 1997; Sopeña et al., 2007). Flutolanil, on the other hand, is a fungicide used for potatoes, nuts, and rice (www.dec.state.ny.us). Consequently, trifluoromethyl ($-\text{CF}_3$) substituted aromatics such as norflurazon have been detected in U.S. streams and groundwaters (Gilliom et al., 2006; Senseman, et al., 1997a; Senseman, et al., 1997b), which has been attributed to use, mobility, and persistent application in the environment. Hence, this work focuses on sorption of three aromatic pesticides with $-\text{CF}_3$ substituent and other functionalities. These fluorinated pesticides differ in molecular size, solubility, and polarity; hence there is a need to understand how these properties affect their sorption. The abovementioned agricultural applications indicate that these chemicals may be applied in either a dry or a wet soil; hence, the effect of hydration state of the soil in sorption capacities will be evaluated. Based on the model developed in Chapter 5, our hypothesis is that an initially dry soil will sorb a larger amount of a hydrophobic aromatic pesticide than a wet soil. In addition, the effect of organic matter content and mineral/clay composition on sorption will be investigated.

Freundlich Equations 5.1 and 5.2 are widely implemented to describe sorption-desorption in soils, because these assumes the presence of a limited amount of sorption sites of varying energies (Tabatabai and Sparks, 2005).

$$S = K_F C_e^N \quad (5.1)$$

$$\log S = \log K_F + N \log C_e \quad (5.2)$$

where: S = amount sorbed in a soil (mg kg^{-1})

C_e = equilibrium concentration (mg L^{-1})

K_F = Freundlich sorption coefficient ($\text{mg kg}^{-1}/(\text{mg L}^{-1})^N$)

N = nonlinearity of the isotherm

It is rather difficult to compare sorption affinities of sorbates for various sorbents if the N values for the isotherms are different. As a result, this study applies reduced concentrations (Cr) in the Freundlich equation (Carmo et al., 2000). The modified Freundlich equation, hereto referred as reduced Freundlich equation is given below:

$$S = K_{rF} Cr^N \quad (5.3)$$

where: K_{rF} = reduced Freundlich coefficient

Cr = equilibrium concentration normalized to the aqueous solubility (S_W) of the sorbate

The isotherm is therefore plotted with $Cr = C_e/S_W$ in the x-axis and the amount sorbed on the y-axis. It should be noted that the use of Cr does not affect the value of N . Finally, the relationship between Freundlich coefficient and its reduced form is given as:

$$K_{rF} = K_F S_W^N \quad (5.4)$$

Thus, K_{rF} reflects the sorption coefficient when the equilibrium concentration is near saturation only (Carmo et al., 2000; Chiou et al., 2000; 1998). The use of K_{rF} also simplifies the final units into the mass of sorbate sorbed in a given mass of sorbent (Ding et al., 2002; Chen et al., 1999). Soil organic matter (SOM) has been widely recognized as the most important component in hydrophobic contaminant sorption (Chiou et al., 1983; 1998; Chiou, 1989). It has also been suggested that HOCs are less likely to sorb on minerals, because water strongly competes with HOC for these sites (Chiou and Shoup, 1985; Chefetz et al., 2000). Thus, the sorption coefficient K is often normalized with respect to organic carbon or organic matter

content, yielding a relatively constant distribution coefficient (K_{OC} , K_{OM}); however, this is not always the case. Variation in K_{OC} values are often attributed to 1) the type of carbon that makes up the SOM; 2) the extent of diagenetic alteration; 3) the presence of different sorption domains; 4) the presence of black carbon; and 5) the hydration condition. A relatively constant K_{OC} reflects hydrophobic forces as mostly responsible for sorption. Sorption of norflurazon in soils has been mainly attributed to soil organic matter content (Suba and Essington, 1999; Carringer et al., 1994; William et al., 1997). For example, K_{OC} values for norflurazon were reported to be 456–551 L kg⁻¹ (Suba and Essington, 1999).

Previous studies hinted that aside from SOM, other soil properties may influence norflurazon sorption, such as pH and cation exchange capacity (Reddy et al., 1992), although the authors showed a relatively low correlation with $r^2 = 0.57$ and 0.58 for pH and cation exchange capacity respectively, in seven different soils with K_{OC} values of 116 – 229 L kg⁻¹. Clay content also increased sorption of norflurazon (Hubbs and Lavy, 1990), but the type of clay was found to be more significant with respect to norflurazon herbicidal activity, rather than the amount of clay present (Lo and Merkle, 1984; Schroeder and Banks, 1986). In a study utilizing three soils, the presence of expandable clays such as montmorillonite and vermiculite (in addition to organic matter) required a higher amount of norflurazon to effectively control the weeds (Lo and Merkle, 1984). On the other hand, results from Carringer et al. (1975) showed no affinity of norflurazon to Ca-montmorillonite.

In another study, Morillo et al. (2002) showed that soil with a high amount of Fe₂O₃ and Al₂O₃ showed K_{OC} of 691 L kg⁻¹, which was attributed to additional sorption sites afforded by the high surface area amorphous oxides. The most recent and thorough investigation of norflurazon sorption was on 17 different soils. This study indicated that a soil organic matter

content significantly affects sorption with a linear equation: $K_d = -0.91 + 2.14 OM(\%)$, $r^2 = 0.85$ (Morillo et al., 2004).

Currently, the only available K_F and K_{FOC} values for flutolanil are: 1) $K_{OC} = 418 \text{ L kg}^{-1}$ for a turf grass soil with the following characteristics: soil depth: 0–10 cm; pH: 6.8; organic carbon: 4.7 %C; cation exchange capacity (meq per 100g): 9.9; (Suzuki et al., 1998) and 2) K_{OC} values from different soils and sediment, given in Table 5.1 below.

Table 5.1 Flutolanil sorption (<http://www.efsa.europa.eu>)

Soil type	Organic Matter (%)	Soil pH	% sand	% silt	% clay	Cation exchange capacity meq (100g) ⁻¹	K_F	K_{FOC}	N
Sand	0.2	6.5	93	3	4	3.8	1.34	1340	1.16
Clay	2.4	6.7	8	34	58	26	10.6	883	0.91
Mississippi sediment	3.9	7.5	28	38	34	21	10.3	528	0.94
Clay loam	4.9	7.8	26	46	28	25	16.0	653	0.94
Sandy loam	6.2	6.1	76	16	8	11	35.5	1150	0.98

Finally, the sorption of acifluorfen is suggested to be affected by organic matter content, soil pH, and cation exchange capacity (Locke et al., 1997). Previous sorption studies concerning these three pesticides lack an indepth evaluation of sorption mechanism from a perspective of the sorbate structure, sorbent composition (organic matter and mineral/clay) and soil hydration condition; hence, this study will attempt to gain better understanding of these points.

5.2 Materials and Methods

5.2.1 Chemicals

The following chemicals were purchased from Acros: 85% phosphoric acid, HPLC grade methanol, and 99% sodium azide. Anhydrous calcium chloride (96.0%) and sodium phosphate monobasic (99%) were obtained from Sigma-Aldrich, while HPLC grade acetonitrile was purchased from Mallinckrodt Chemicals. Standards used for TOC analysis involving potassium

hydrogen phthalate, glucose, and sodium carbonate were purchased from Acros. All the pesticides, i.e., norflurazon (98.6%–98.7%), acifluorfen (98.8%) and flutolanil (99.5%), were obtained from ChemService (West Chester, PA). A filtering device in the laboratory (Modulab Water Systems, United States Filter Corporation), provided 18 M Ω -cm resistivity water for all solution preparations.

5.2.2 Soil Sampling

The author of this study collected a local wetland soil from Bayou Casbtine, Mandeville, Louisiana (15R784949 °E, 3361530 °N) with samples of topsoil gathered from a depth of 0–10 cm and placed in a pre-washed plastic container. In preparation, the process removed root and plant materials and manually broke bigger soil aggregates, allowing a portion of the soil to air dry, and storing the rest of the soil at 4°C until use. After air drying, soil passed through a 2 mm mesh sieve for homogenation. The International Humic Substance Society (IHSS) provided Pahokee Peat and Elliot soils for purchase.

5.2.3 Soil Moisture and pH

The study determined moisture content (fresh basis, air dry basis, and oven dry basis) for Mandeville soil, allowing a pre-weighed fresh sample to dry in the air, and recording the weights until we obtained a constant, air-dried weight which was subsequently, was weighed as air-dried soil in a pre-tared evaporating dish. It was then placed in oven (Isotemp oven, Fisher Scientific) at 105°C for 12 hours (Black et al., 1982). Soil pH was measured in 18 M Ω water using a pH meter (Accumet AB15, Fisher Scientific) pre-calibrated using buffers (Acros) of pH 4, 7, and 10.

5.2.4 Clay Content and Cation Exchange Capacity

The total percentage of clay as well as mineral components of Mandeville soil, was determined by X-ray diffraction (Bruker/Siemens D5000 automated powder X-ray diffractometer with Rietveld analysis software). Cation exchange capacities were measured for

Elliot and Mandeville soils using a protocol from Methods of Soil Analysis (Sumner and Miller, 1996). Briefly, 5g of soil were placed in a pre-weighed 50 mL centrifuge tube, followed by an addition of 30 mL of 0.2 M NH_4Cl . The mixture was shaken for five minutes, and the mixture was then centrifuged at 6000 rpm for five minutes. The supernatant was decanted into a 250 mL volumetric flask. The addition of 30 mL of 0.2 M NH_4Cl , followed by shaking and centrifugation was repeated four more times. All supernatant solutions recovered after centrifugation were placed in the same 250 mL volumetric flask, and then filled to the mark with 0.2 M NH_4Cl . This solution was then filtered in a Whatman filter paper and analyzed for exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Al^{3+}). The soil was re-suspended with 30 mL of 0.04 M NH_4Cl , from the previous step, followed again by shaking and centrifugation of the re-suspended soil. This process was repeated twice. All supernatants from this step were discarded. After the supernatant from the last centrifugation step was discarded, the centrifuge tube was weighed to determine the volume of solution remaining. Then 30 mL of 0.2 M KNO_3 was used to re-suspend the soil, followed by shaking, centrifugation, and supernatant collection into a 250 mL volumetric flask. This last step was repeated five times. Once again, all supernatants were combined and then diluted to the 250 mL mark with 0.2 M KNO_3 . The solution was filtered using Whatman filter paper and analyzed for NH_4^+ , using Seal AQ2 Discrete Analyzer (Mequion, WI).

5.2.5 Total Organic Carbon

The amount of total organic carbon in the Mandeville soil was determined with a solid state Shimadzu total organic carbon (TOC) analyzer (SSM-5000A), connected to a liquid Shimadzu TOC Analyzer (5050A). The external standards used for total carbon and inorganic carbon analysis were glucose and sodium carbonate, respectively.

The TOC was calculated by subtracting inorganic carbon from total carbon. Reference soil samples with established total organic carbon content, such as Pahokee Peat and Elliot soil

(IHSS), were used to check the solid state total carbon instrument performance.

5.2.6 Molecular Modeling of Pesticide Structure

Each of the pesticides (norflurazon, acifluorfen, and flutolanil) were drawn using Sybyl 8.0 (Tripos International, St. Louis, MO), after which its geometry was minimized using the Tripos force field with Gasteiger-Huckel charges. The resulting structure was then used as the starting molecule in conducting other types of conformational searches. To determine whether the conformations found in each type of search were equivalent, there was an overlay of two molecules from different searches each time to determine the root mean square value. The root mean square value indicated the closeness of the structures. A root mean square value of 0.00 implied that two conformations were exactly the same. A root mean square value of <0.02 is considered a good fit. The pesticide conformations that gave the best fit were the ones used as starting molecules in semi-empirical PM3 Spartan calculations (version '02, Wavefunction Inc., CA), as well as in mapping the electrostatic potential on the molecular surface.

5.2.7 Determination of Wavelength of Excitation of Pesticides

Scanning from 200–600 nm on Ultraviolet-visible Cary 50Bio, determined the maximum absorbance wavelength of the pesticide solutions. A 1-cm pathlength quartz UV cells were used in all analyses. All UV spectra then were blank subtracted.

5.2.8 Pesticide Analysis by HPLC

The optimum excitation wavelengths obtained from UV analysis were used as excitation wavelengths for Ultraviolet-Diode Array Detector detection. An 1100 series Agilent HPLC (Santa Clara, CA) with a quaternary pump was used to quantify the pesticides in solution throughout the study. A reverse phase C18 column (Zorbax Eclipse XDB, 5 μm x 4.6 mm x 150 mm) was employed for method development and sample analysis. The optimum conditions used for the analysis are provided in Table 5.2.

The methods were validated for accuracy, precision, linearity, and sensitivity, prior to their extensive use. Accuracy was determined by spiking a known amount of pesticide into the soil solution matrix, and then calculating the % recovery after HPLC analysis (Snyder et al., 1997).

Table 5.2 HPLC conditions used in the analysis of pesticides

HPLC Parameters	Acifluorfen	Norflurazon	Flutolanil
Mobile phase: (% v/v)	70:30 acetonitrile /pH =2.5 phosphate buffer	70:30 acetonitrile /H ₂ O	70:30 acetonitrile /H ₂ O
Flow rate: (mL/min)	0.6	0.6	1.0
Sample volume: (μL)	20	20	20
Temperature (°C)	35	25	25
DAD detection	288/296	235	210
Retention time (min)	3.91±0.05	3.65±0.05	3.42±0.02
LOQ (ug L ⁻¹)	80	23	24
% Recovery from soil matrix solution (accuracy)	100.23±0.00	100.09±0.20	99.96±0.14

Precision was assessed by repetitive injections of different concentrations of standards, as well as samples, and by determining the % coefficient of variation. Measurements were considered precise when the coefficient of variation was $\leq 2\%$ for all injections. Linearity was determined by measuring the peak area absorbance of different concentration of pesticides. The slope, y-intercept and R² values were obtained using linear least squares regression. A limit of detection was quantified based on S/N equal to 3, while the limit of quantification was determined at S/N equal to 10.

5.2.9 Determination of Soil to Solution Ratio

The soil to solution ratio must be pre-selected before proceeding with sorption kinetics and sorption isotherm studies. This is usually determined by weighing different amounts of sorbent and then adding the same volume of fixed sorbate concentration. Sorbate is the chemical substance (pesticide) to be sorbed on a solid support called sorbent (soil). In this study, five

different weights of soil were contacted with 20 mL pesticide solution in 20 mL scintillation vials. The concentration of pesticide chosen was the highest concentration expected to be used in the sorption kinetics and sorption isotherms experiment. Samples were prepared in quadruplicate. The heterogeneous mixtures were then shaken in the dark, using a C24KC refrigerated incubator shaker (New Brunswick Scientific, Edison, NJ) at 150 rpm and $25\pm 1^\circ\text{C}$ for 10 days. After incubation, the samples were centrifuged (Sorvall Biofuge Stratos, Asheville, NC) at 3000 rpm and 25°C for 15 minutes to separate the soil from the solution. Supernatant was pipetted into HPLC vial and analyzed by direct injection.

The amount sorbed was then calculated as follows:

$$A = \frac{m_s}{m_0} \times 100 \quad (5.5)$$

where:

A = amount sorbed (% w/w)

m_s = mass of pesticide sorbed to the soil (mg)

m_0 = initial mass of pesticide (mg)

The above equation reduces to:

$$A = \frac{C_0 - C_{eq}}{C_0} \times 100 \quad (5.6)$$

where:

C_0 = initial concentration (mg/L)

C_{eq} = concentration in the aqueous phase at the end of incubation (mg/L)

A graph was then plotted that relates the percentage of the pesticide sorbed to the amount of soil used. The choice of soil to solution ratio depends on the percentage sorption desired, in addition to the analytical methodology employed to accurately and precisely measure the concentration of the analyte in solution. The weight of soil used at the highest pesticide concentration was chosen for approximately 20-30% sorption, because at lower pesticide concentration, the % sorption is expected to be higher. With the HPLC methods employed, the accuracy and precision in the analysis of changes in solution concentration at this sorption range

proved to be successful. Although a 20 mg/L initial concentration was used to test the sorption of acifluorfen in all three sorbents, additional concentration points of 40 mg/L and 80 mg/L were later used in the sorption isotherm study to widen the concentration range, in order to investigate its effect on sorption. Thus an 80 mg/L of initial concentration was used in the kinetic study. However, the Elliot soil weight was not increased because of the limitation on the amount of Elliot soil that can be ordered from IHSS. Use of 80 mg/L in the kinetics experiments allowed < 20% sorption of initial concentration for Elliot soil. It was suggested that precision problems might arise when sorption is less than 20% of initial concentration (McCall et al., 1981). However in this study, even with slight changes in solution concentrations, the HPLC method employed proved to be adequate in terms of both precision and accuracy.

Soil-to-solution ratio determination was conducted out for at least one soil per pesticide type. The amount of soil needed for the other soils was then predicted, based on the Total Organic Carbon content. At least two blanks, two controls, and four trials were set for each soil amount.

5.2.10 Sorption Kinetics

All norflurazon pesticide solutions were prepared in the presence of 0.005 M CaCl₂. The use of CaCl₂ served to simulate groundwater (Xia and Pignatello, 2001; Braida et al., 2003). The above sorption kinetics were also performed in the presence of 100 ppm biocide sodium azide (NaN₃) to determine the effect on sorption. A 20 mL of 16 mg/L of norflurazon solution was added to a pre-weighed soil sample in 20 mL scintillation vials. Accurately weighed amounts (± 0.0030 mg) of soil used were as follows: 60 mg Pahokee Peat, 500 mg Mandeville soil and 1500 mg Elliot soil.

For the 5 day and 1 day prewet samples, the soil was initially contacted with 4 mL of electrolyte solution, consisting of 0.005 M CaCl₂ in 18 M Ω -cm of water. Four replicates were

prepared for each soil hydration condition. Controls containing only soil and electrolyte solutions were also prepared in the same manner, using the same number of replicates. The soil mixture was shaken for 5 days or 1 day at 150 rpm and $25\pm 1^\circ\text{C}$. After pre-hydration incubation, the samples were re-weighed in order to check for evaporation losses. A 16 mL of 20 mg/L norflurazon was then added, such that the final concentration in the pre-hydrated samples was also 16 mg/L. For the prewet controls, a 16 mL of electrolyte solution was added. Two blanks (pesticide solutions without soil) were included for each incubation period.

Dry and prewet samples were then shaken in the dark at 25°C and 150 rpm. Samples as well as blanks and controls, were removed after incubation periods of about 6, 9, 12, 15, 18, 24, 48, 72, 120, and 240 hrs respectively. Exact incubation periods were recorded. For norflurazon, an incubation period of ≥ 720 hrs was included in order to assess the effects of longer contact time on the attainment of sorption equilibrium. After the required incubation time, the soil mixture was centrifuged at 3000 rpm and 25°C for 15 minutes. Supernatant solutions were pipetted into 2mL HPLC vials for analysis. Control supernatant samples were also analyzed using Ultraviolet-visible, TOC, and fluorescence excitation emission matrix.

All acifluorfen pesticide solutions were prepared in the presence of 0.005 M CaCl_2 and 100 ppm NaN_3 biocide (Huang and Weber, 1998; Huang et al., 1998), as preliminary kinetics data show a degradation product after 10 days of incubation. The concentration of pesticide used for acifluorfen kinetics was 80 mg/L. Soil weights used were as follows: 400 mg Pahokee Peat, 800 mg Mandeville soil, and 1500 mg Elliot soil.

A 1000 mg/L stock solution of flutolanil was prepared in methanol (CH_3OH). A 6 mg/L of flutolanil solution was subsequently prepared from stock solution in $< 0.1\%$ CH_3OH , 0.005 M CaCl_2 , and 100 ppm NaN_3 . The use of $< 0.1\%$ CH_3OH was necessary to dissolve the sparingly soluble pesticide. In the past, this concentration of CH_3OH was reported to have a negligible

effect on sorption behavior of HOCs (Weber and Huang, 1996). Soil weights were as follows: 100 mg Pahokee Peat, 200 mg Mandeville soil, and 500 mg Elliot soil. All sorption kinetics samples and controls were prepared in quadruplicate and with at least two blanks.

5.2.11 Mass Balance by HPLC

Norflurazon and flutolanil mass balances were determined in the absence and presence of sodium azide, in order to determine the percentage recovery after sorption pseudo-equilibrium, as well as evaluating the extent of pesticide stability. The samples were incubated as in sorption isotherms. After 5 days, supernatant samples were pipetted into HPLC vials for analysis, in order to determine the total amount of pesticide sorbed to the soil. A total of 17 mL of supernatant was removed and replaced with extracting solvent (30/70 water: acetonitrile). Exact masses from an analytical balance were also recorded. The samples added with extracting solvent were sonicated for 10 minutes and then allowed to stand overnight in the dark. It was then centrifuged at 3000 rpm and $25 \pm 1^\circ\text{C}$ for 15 minutes. This time, the supernatant was once again sampled for HPLC, to analyze the amount desorbed or extracted. A second extraction was also accomplished by removing ~17 mL of the first desorption supernatant and then replacing that same amount with extracting solvent.

The formula used for mass balance recovery is given below (OECD, 2000):

$$MB = \frac{m_r}{m_0} \times 100 \quad (5.7)$$

The above equation can be evaluated as:

$$MB = \frac{(V_r \cdot C_{eq} + m_E)}{C_0 V_0} \times 100 \quad (5.8)$$

where:

MB = mass balance (% w/w)

m_r = amount of pesticide recovered (μg)

m_0 =initial amount of pesticide (ug)

V_r =volume of supernatant recovered (mL)

C_{eq} = amount of pesticide in the aqueous phase at sorption equilibrium (ug/mL)

m_E =total amount of pesticide extracted from the soil and sample container (ug)

C_0 = initial pesticide concentration (ug/mL)

V_0 = sorption volume (mL)

Kinetic studies showed that acifluorfen significantly degrades in the absence of sodium azide, especially in Elliot soil. Thus, all subsequent studies were performed in the presence of sodium azide. A 30/70 phosphate buffer pH=3: acetonitrile extraction solution was also used. Other than these two modifications, the same procedure as that for norflurazon and flutolanil was used. Mass balance recoveries in the presence of sodium azide were as follows: acifluorfen (94.53 ± 1.31), norflurazon (91.34 ± 0.10), and flutolanil (96.27 ± 1.22). Thus, our sorption method is valid in the OECD method (OECD, 2000) which specifies that mass balance recoveries should be at least 90% in order to eliminate the possibility of degradation affecting the sorption results.

5.2.12 Sorption

Sorption-desorption experiments were conducted according to the batch equilibrium technique using the parallel method (OECD, 2000). Data set in both sorption and desorption isotherms consisted of 7-10 concentration points, whereby each concentration point consisted of four replicates and two blanks. Equilibrium concentrations spanned a range of 1 to 2 orders of magnitude.

Sorption was initiated by adding different pesticide concentrations of the same volume (20 mL) to a constant amount of soil that was pre-determined in a soil-to-solution ratio. All pesticide concentrations employed were < 70% of pesticide solubility limit in water. Initial concentrations of 1, 2, 4, 6, 8, 10, 12, and 16 mg/L were used for norflurazon, while 1, 4, 8, 12,

16, 20, 40, and 80 mg/L were utilized for acifluorfen; flutolanil concentrations were 0.5, 1, 2, 3, 4, 5, and 6 mg/L, as dictated by their aqueous solubility. All pesticide solutions were made in 0.005 M CaCl₂ and 100 ppm NaN₃; <0.1% CH₃OH was also added in flutolanil pesticide solution preparation.

After pesticide addition, sorption incubation (25°C, 150 rpm) was implemented for all pesticide and soil sample combinations. Based on the sorption kinetics, an incubation time of 5 days was chosen for both sorption and desorption isotherms, because kinetics data revealed that a pseudo-equilibrium is reached at that time. At the end of the sorption step, samples were centrifuged in order to separate the soil from the aqueous solution. An aliquot of this solution was carefully pipetted into 2 mL HPLC vials. All sorption samples were prepared in quadruplicate with at least two blanks. Each sorption/desorption isotherm experiment included 8-12 external calibration standards, encompassing the concentration range used in the study. Possible losses due to headspace volatilization and or sorption to the container were assessed by percentage recovery calculations from blank samples (samples without soil, but using spiked soil matrix solution) and were found to be negligible (<<1%).

The amount of pesticide sorbed in the soil may be represented by the equation below:

$$S = \frac{m_s}{m_{soil}} \quad (5.9)$$

where m_s = mass of pesticide sorbed to soil at equilibrium and

m_{soil} = mass of soil (kg)

In our study, the amount of pesticide sorbed was determined by the difference between the concentration in solution after equilibration and initial concentration as indicated below:

$$S = \frac{(C_0 - C_{eq})V_0}{m_{soil}} \quad (5.10)$$

where: S = amount of pesticide sorbed (mg/kg)

C_0 = initial concentration (mg/L)

C_{eq} = equilibrium concentration in solution (mg/L)

V_0 = initial volume of solution (L)

m_{soil} = mass of soil (kg)

The latter equation was modeled using the Freundlich equation:

$$S = K_F C_{eq}^N$$

Log transformation of the above equation yields a linear form:

$$\log S = \log K_F + N \log C_{eq}$$

where:

K_F = Freundlich sorption capacity coefficient

N = sorption nonlinearity

The best fit line and the parameters, as well as their corresponding standard errors for this linear regression, were obtained via the use of the Marquardt-Levenberg algorithm, as implemented in Sigma Plot version 10 (Systat Software, Inc., CA). The Marquardt-Levenberg algorithm returns the values of the parameters by minimization of the least squares error between the actual values and predicted values of the dependent variable. Yield results were within the 95% confidence limit.

5.2.13 Desorption

The desorption incubation period implemented was identical to the sorption. A volume of about 17 mL of sorption supernatant was removed and replaced with 0.005 M $CaCl_2$ and 100 ppm NaN_3 electrolyte solution. Samples were then shaken in the dark for 5 days, using the same incubation conditions as discussed above for the sorption isotherm. Supernatant removal protocol was then followed to obtain a desorption supernatant for HPLC analysis.

In the desorption step, most of the supernatant was pipetted using a disposable glass pipet. The removal of supernatant was carefully performed to avoid disturbing the solids. Samples were also weighed using an analytical balance, in addition to applying accurate solution volume measurements during initial sorption and after the following steps: sorption equilibrium, removal of supernatant, addition of electrolyte solution to initiate desorption step, and desorption equilibrium, in order to account for any possible liquid/solid phase losses.

The amount sorbed after desorption was evaluated using the formula:

$$S_{des} = \frac{m_s - m_{des}}{m_{soil}} \quad (5.11)$$

where:

S_{des} = amount of pesticide sorbed to soil at desorption equilibrium (mg/kg)

m_s = mass of pesticide sorbed to soil at sorption equilibrium (mg)

m_{des} = mass of pesticide desorbed from soil (mg)

m_{soil} = mass of soil (kg)

5.2.14 Liquid Chromatography-Mass Spectrometer

An Agilent 1200 series 6210 time of flight Liquid Chromatography-Mass Spectrometer was used to identify and confirm the presence of a degradation product of acifluorfen. The same LC parameters utilized in the analysis of acifluorfen samples were used for UV detection, while detection by mass spectrometer used time of flight with the following parameters: electron spray ionization as the ion source, positive scan type, 900 V charging voltage, nebulizer operating at 15 psig, drying gas flow rate at 7.0 L/min, gas temperature at 300 °C, and a 4200 V capillary.

5.2.15 Total Carbon of Supernatant from Control

Supernatant from the sorption kinetic controls experiment of initially dry soil samples were analyzed using a Shimadzu TOC Analyzer (Model 5050A with associated ASI-5000A auto sampler). The amount of total carbon released from the soil samples were calculated, based on

the potassium acid phthalate external standard consisting of a four-point calibration. A methanol standard was used as an additional check for instrument performance, and 18 M Ω water was used as a blank sample. Each sample was injected three times with a coefficient of variation \leq 2% accepted as a measurement precision.

5.2.16 Specific UV Absorbance (SUVA) of Supernatant from Control at 280 nm

Ultraviolet-visible data were collected on a Cary 50Bio with a xenon flash lamp on 10 ppm TOC sorption kinetic control samples from 200 nm–600 nm. In all analyses, 1-cm pathlength quartz UV cells were used. All UV spectra were blank corrected with an electrolyte solution used to prepare samples.

5.2.17 Fluorescence Excitation and Emission Matrix of Supernatant from Control

Fluorescence excitation and emission matrices were also obtained on the 10 ppm TOC sorption kinetic control samples, utilizing a Horiba Jobin Yvon spectrofluorometer equipped with a Xe arc lamp. The parameters were: 1-cm pathlength quartz fluorescence cell, excitation from 250–450nm wavelength with 5nm increment, emission from 280–550nm wavelength with 2.5nm increment, slits of 5nm for both excitation and emission, and a detection signal divided by the reference (S/R). Lamp scan and water Raman emissions were always performed prior to the analysis of the sample, in order to check instrument performance.

5.3 Results and Discussion

5.4 Sorbent and Sorbate Characterization

The sorbents were selected based on their organic matter and clay content. Pahokee Peat had the highest % organic carbon, followed by Mandeville soil (Table 5.3.1). Elliot soil had the lowest % organic carbon. Mandeville soil was obtained from a wetland in Louisiana and is similar to the samples used in our 2-D NMR analysis, while Pahokee Peat and Elliot soils are reference standard soils from IHSS, allowing other researchers to reproduce this type of sorption

work. The pesticides chosen for this study have varying solubilities and octanol water partition coefficient K_{OW} ; hence, they have different polarities. In addition, they have carbonyl, amine/amido groups capable of H-bonding.

Table 5.3.1 Properties of sorbents

Parameter	Pahokee Peat	Mandeville Soil	Elliot Soil
Soil taxonomic class	euic, hyperthermic, lithic, Medisaprists ¹	thermic, typic hydraquent ²	mesic, Aquic Argiudoll ³
Soil pedon	muck ¹	silty clay loam ²	Silt loam ³
Moisture content (%)	6.2 ^a	3.96±0.02	1.52 ^a
pH	4.20±0.02	4.62±0.02	6.1 ^a
Total organic carbon, OC (%)	46.90 ^a	10.84±0.17	2.9 ^a
Organic matter, OM (%) OM = 2x(%OC)	93.8	21.68	5.8
Mineral content (%)	nd	clay 31.31, sand 66.40, 1.16% K feldspar, 1.13% plagioclase (23% clay, 49.38% sand in a whole soil)	clay 30.8, silt 62.3, sand 6.9 (28.55% clay, 57.74% silt and 6.39% sand in a whole soil)
Cation Exchange Capacity (c _{molc} kg ⁻¹)	nd	19.83 ± 0.79 ^b	11.58±0.19

nd not determined due to very high organic matter content

¹(<http://www.ihss.gatech.edu/sources.html>) ²Trahan et al., 1990

³(<http://ssldata.ncrs.usda.gov>)

^a IHSS (no standard error is given)

^bConkle et al., 2009

Table 5.3.2 Metal content of Mandeville soil

Metals	Mandeville Soil	
	Total ^a	Exchangeable ^a
Al	29284.3 ± 478.6	11.6 ± 8.2
Ca	1830.9 ± 19.5	1765.4 ± 20.6
Fe	11072.9 ± 158.2	170.9 ± 78.4
K	1527.5 ± 53.4	202.6 ± 20.1
Mg	2155.2 ± 31.2	1117.1 ± 18
Na	502.8 ± 8.8	499.6 ± 17.9

^amg kg⁻¹

Table 5.3.3 Physico-chemical properties of the sorbates

Properties	Acifluorfen	Norflurazon	Flutolanil
^a MW (g/mol)	361.66	303.69	323.31
^a solubility in H ₂ O (mg/L)	120	32	9
log k _{ow}	2.31, 1.54, and 1.25 at pH=4, 5, and 6 respectively ^b	2.45 ^c	3.54±0.17 ^d
^e Surface area (Å ²)	336	277	317
^f Surface volume (Å ³)	326	254	308
^g dipole (debye)	7.00	5.91	3.55

^a Ahrens, 1994 ^{b,c} Advanced Chemistry Development (ACD/Labs), copyright ACS, 2008
^d Nakamura et al., 2001 ^{e,f,g} values are from molecular modeling



Figure 5.3.1 Soils used in the study (from left to right: Pahokee Peat, Mandeville and Elliot)

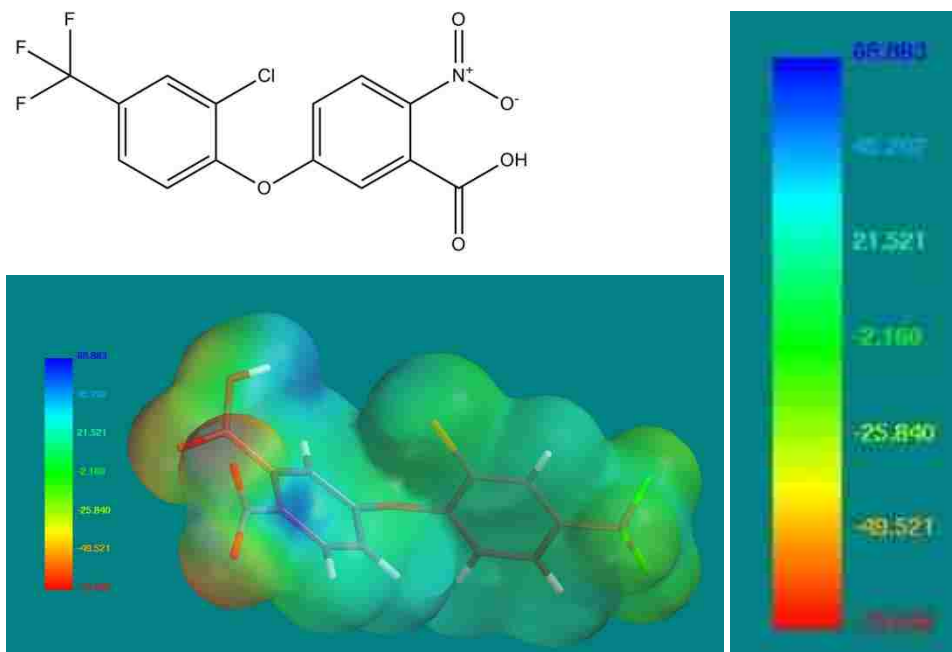


Figure 5.3.2 Chemical structure and Electrostatic potential surface of acifluorfen modeled using Spartan version '02 (Wavefunction Inc., CA)

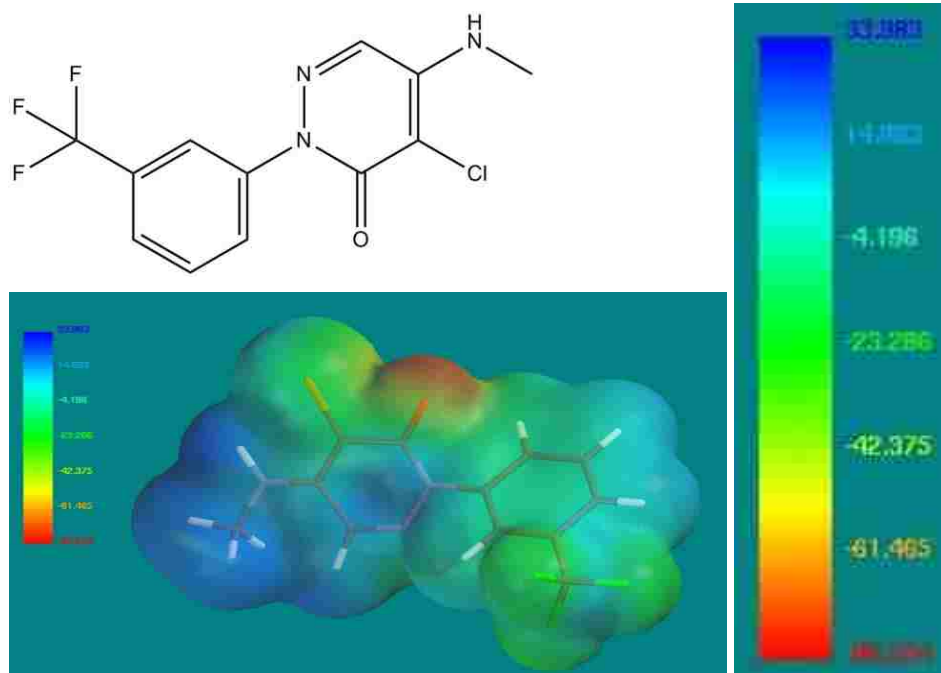


Figure 5.3.3 Chemical structure and Electrostatic potential surface of norflurazon modeled using Spartan version '02 (Wavefunction Inc., CA)

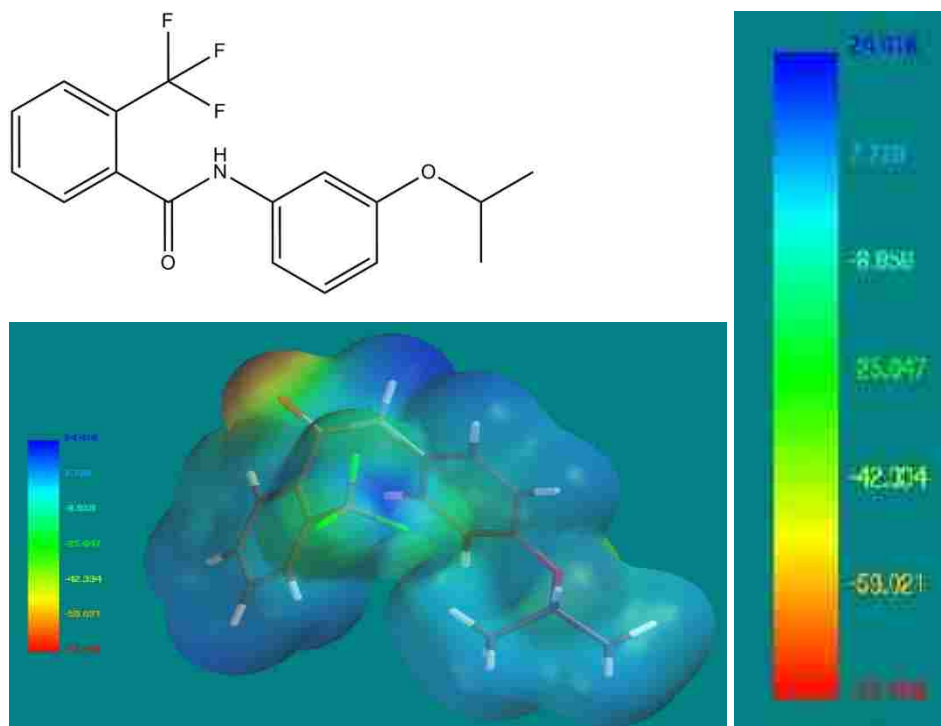


Figure 5.3.4 Electrostatic potential surface of flutolanil modeled using Spartan version '02 (Wavefunction Inc., CA)

5.5 Determination of Soil to Solution Ratio

Soil to solution ratio was investigated for at least one soil per pesticide type (Figures 5.4.1-5.4.3). The amount needed for the other soils was then predicted, based on the total organic carbon content of these soils. The basis of the aforementioned estimation is that organic matter content is well known to correlate with sorption of HOCs (Morillo et al., 2004, Locke et al., 1997; Daly, 1987). In addition, the sensitivity of the methods developed for pesticide analysis also influenced the selection of soil to solution ratios. It is generally recommended that % sorption should be chosen within the range of 20-80%, because a higher concentration will lower % sorption as a result, whereas at lower pesticide concentration, it is expected that % sorption will be higher (OECD, 2000).

For all pesticides, the log amount (in mg) of Pahokee Peat is positively correlated with the amount sorbed in percent ($R^2 = 0.97 - 0.997$). Mandeville soil also exhibited similar behavior with the pesticide tested, which is acifluorfen ($R^2 = 0.96$). In Elliot, the amount of soil is linearly correlated with the amount of norflurazon ($R^2 = 0.995$). Thus, for soils with high organic carbon content, it may be inferred that for a constant amount of sorbate solution, increasing the amount of soil results in an increase in the amount of HOC sorbed.

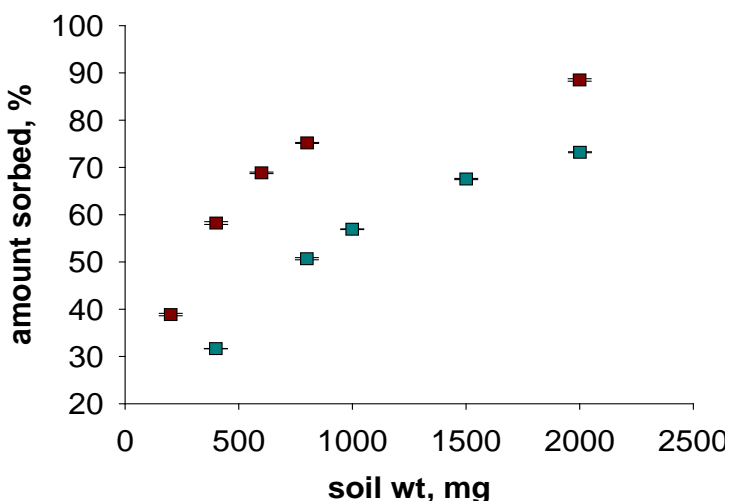


Figure 5.4.1 Soil to solution ratio of acifluorfen in Pahokee Peat (red) and Mandeville soil (cyan)

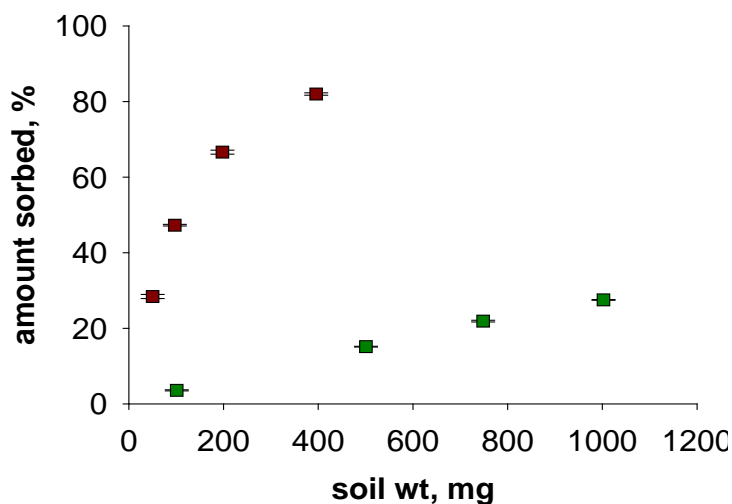


Figure 5.4.2 Soil to solution ratio of norflurazon in Pahokee Peat (red) and Elliot soil (green)

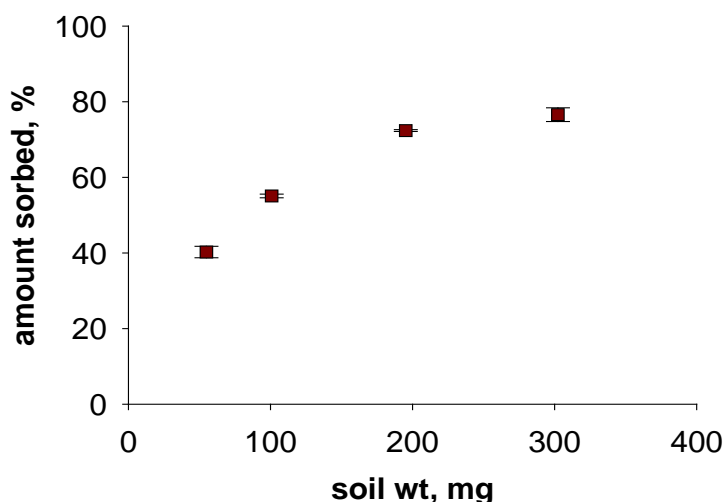


Figure 5.4.3 Soil to solution ratio of flutolanil in Pahokee Peat

5.6 Sorption Rate

Initially, sorption rates for norflurazon were evaluated using incubation times of up to one month (~720 hr), and complete kinetics curve are shown in Chapter 6. Figure 5.5.1 illustrates that apparent pseudo-equilibrium was achieved within five days. Here, pseudo-equilibrium means that the change in relative concentrations was insignificant, compared to longer incubation times (>5 day). Thus, for the other two pesticides, incubation times of up to 10 days were set, later proving to be sufficient in evaluating apparent pseudo-equilibrium. For

flutolanil and norflurazon, apparent pseudo-equilibrium were reached at 5 days (~120 hr), and 2 days (~48 hr) for acifluorfen. Thus, an incubation time of 5 days was used for all.

All sorption kinetic curves are presented and discussed in detail in Chapter 6. Meanwhile, Figure 5.5.1 is a selected kinetics curve for the sorption of norflurazon, one of the pesticides, in Pahokee Peat. Three different hydration conditions were investigated as shown: an initially dry soil, 1 day prewetted soil prior to sorption, and 5 day prewetted soil. The study performed sorption kinetics in Pahokee Peat up to a minimum of 720 hr (30 days), with a constant norflurazon concentration; the region of pseudo-equilibrium is shown in Figure 5.5.1. It appears that an initially dry soil had the fastest kinetics over the initial 72 hr, as well as the highest uptake of norflurazon sorbed, compared to its prewetted counterpart. However, a slight plateau in the region of 12 hr to 20 hr is apparent, which may mean that as the soil wets, there is conformational rearrangement of moieties such that the more hydrophilic moieties (O-alkyl type) would be more available at the outer surface. Prewetted samples demonstrated a slower kinetics and had lower sorption during the early sorption kinetics, as well as on the latter phase of sorption kinetics. However, dry and wet sorption kinetics appears to converge at equilibrium. This implies that within the fast and slow sorption kinetics, norflurazon might be sorbed in different domains and thus, we may not see an effect on sorption isotherms, but we may see differences in desorption kinetics. Similarly in the kinetics profile, fast and slow regions with a plateau at <20 hr were exhibited by Mandeville and Elliot soils.

Total carbon released from initially dry control samples normalized to soil weight (soil samples without pesticide) also reveal fast and slow regions. It is interesting to note that the plateau region demonstrated in the kinetics is seen here, within 10-20 hours of soil incubation as shown by the plots in figure 5.5.2. This further supports previous assumption of possible SOM rearrangement upon wetting. This hypothesis for the presence of fast and slow kinetics during

sorption of these HOC pesticides may be attributed to conformational rearrangement of SOM during its hydration or wetting; therefore this hypothesis will be evaluated further in Chapter 6. The kinetics of pesticide uptake in soils will be fitted to a two-site, non-equilibrium model.

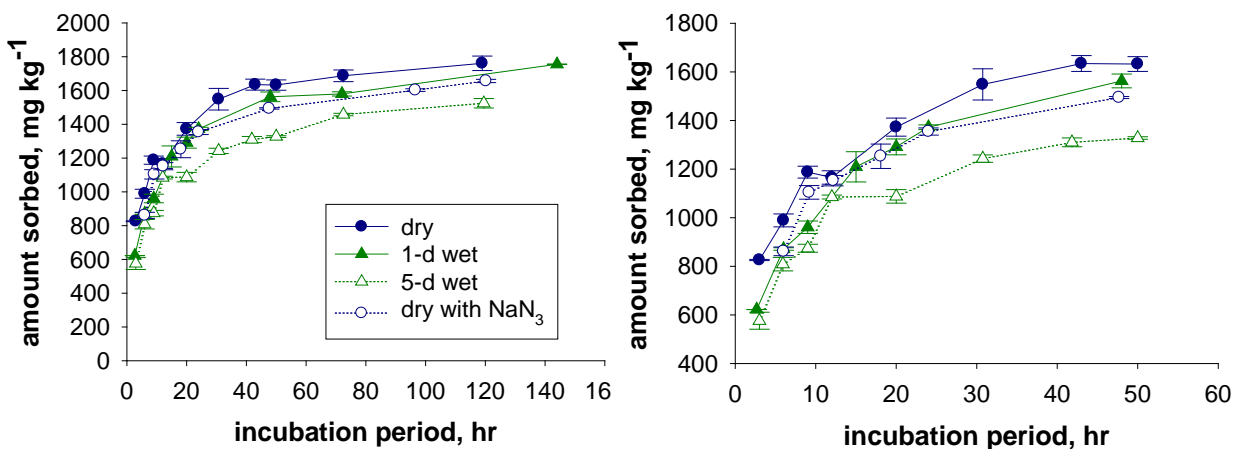


Figure 5.5.1 Kinetics of sorption of norflurazon in Pahokee Peat soil

Figure 5.5.3 shows an excitation and emission matrix difference spectra between a 6 hr and 4 day prewetted Pahokee Peat and 6 hr and 10 day prewetted Elliot soil. The green color corresponds to the subtraction of longer prewetting conditions from that of 6 hr only (e.g., 6 hr–10 day), and the red color corresponds to the reverse (e.g., 10 day–6 hr).

It may be seen that 6 hr pre-hydration time for both Elliot and Pahokee Peat soils extracted more chromophore groups with shorter emission wavelengths, which may correspond to smaller and less condensed SOM. Fluorescence signatures in aquatic or terrestrial natural organic matter (NOM) can be ascribed to quinone-like structures, which may differ in functionalization and conjugation (Cook et al., 2009). Three main chromophore groups are commonly seen with NOM. The first group has an excitation wavelength, $\lambda_{ex} \approx 240\text{--}325$ nm and emission wavelength, λ_{em} at approximately 300–400nm, which are designated in the literature as due to amino acid like moieties (Coble et al., 1990; Coble, 1996; Chen et al., 2003; Stedmon et al., 2003; Ariese et al., 2004; Cory and McKnight, 2005; Holbrook et al., 2006; Ohno and Bro,

2006; Cook et al., 2009). The second group is for quinone A-like moieties which are less functionalized and less conjugated, with $\lambda_{ex} \approx 240 - 325$ nm and $\lambda_{em} \approx 375 - 475$ nm. Lastly, we find quinone-B like moieties with fluorescence properties in the following region: $\lambda_{ex} \approx 250 - 370$ nm and $\lambda_{em} \approx 450 - 550$ nm which are expected to be highly functionalized, and with a high degree of condensation and conjugation (Cook et al., 2009).

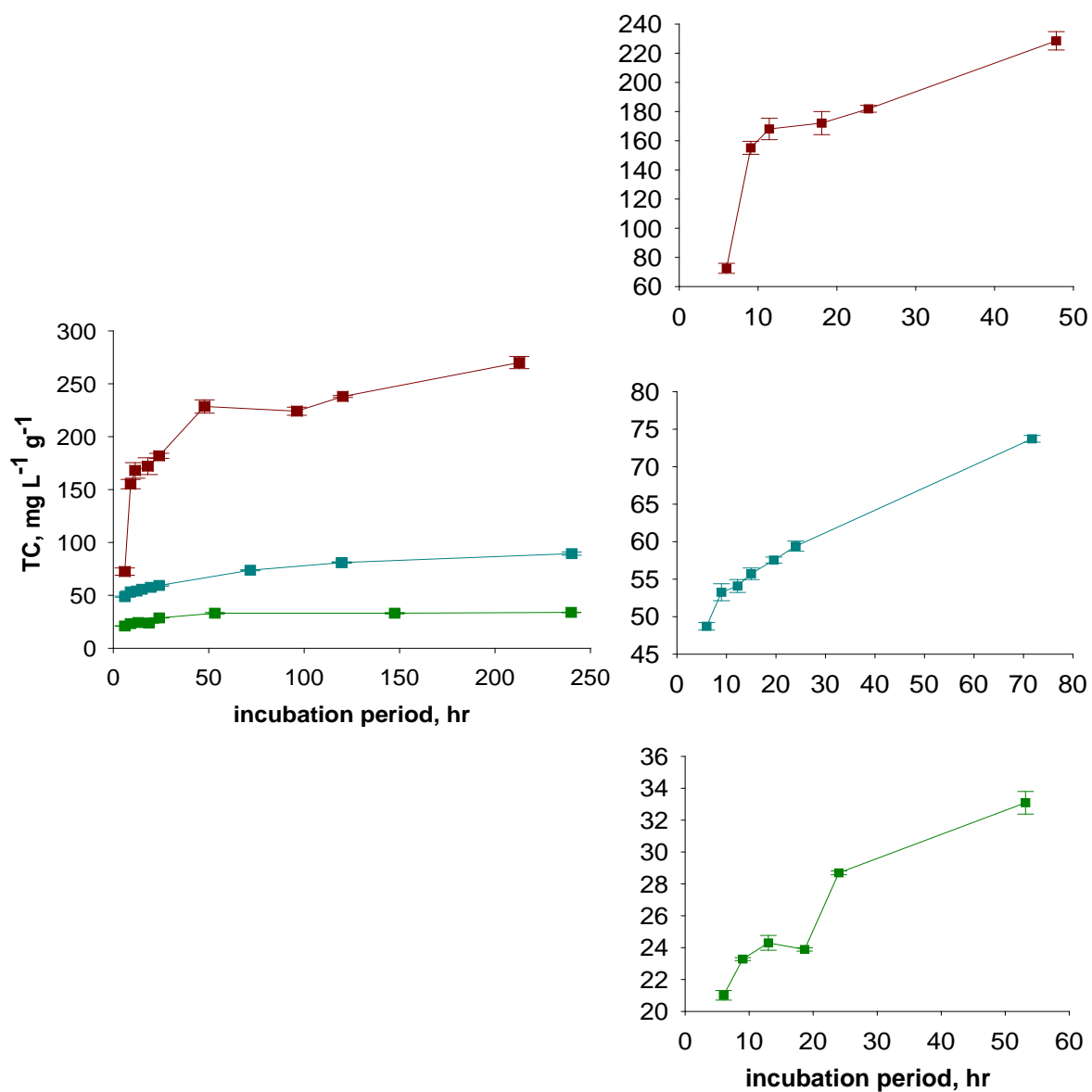


Figure 5.5.2 TOC of soil controls normalized with soil weight (red: Pahokee, cyan: Mandeville, green: Elliot)

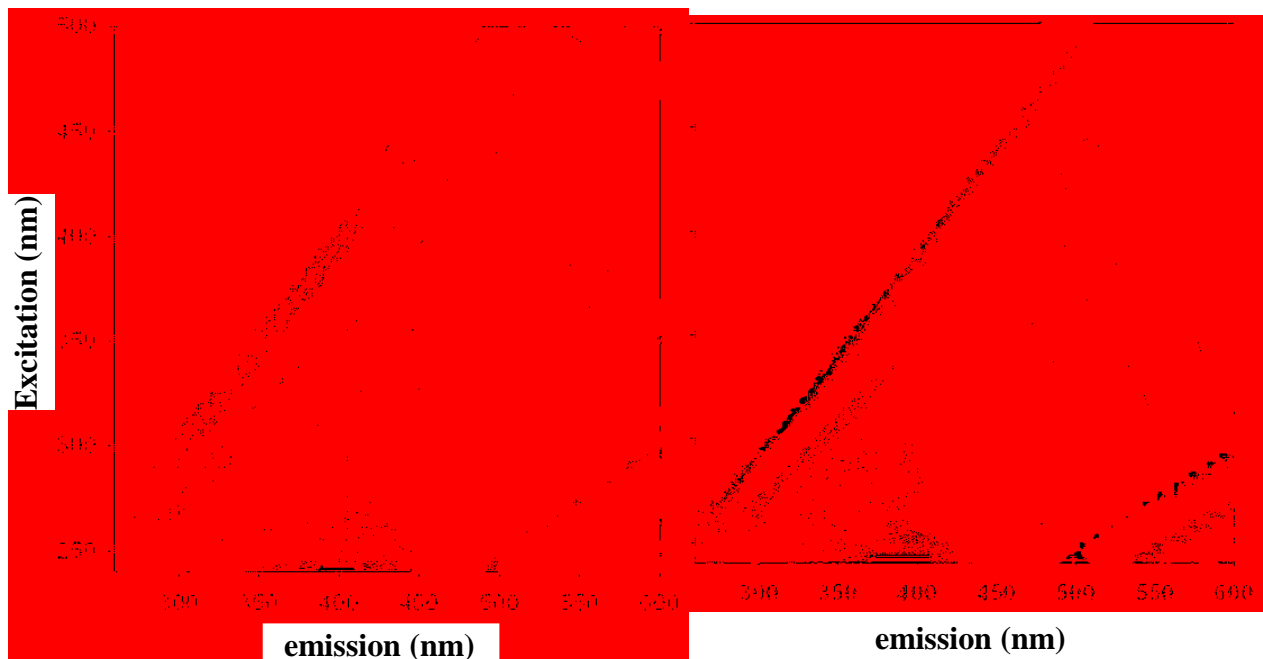


Figure 5.5.3 Difference spectra of fluorescence excitation emission matrix between a 6 hr and 4 day Pahokee Peat (left) control solution (green: 6 hr-4 day, red: 4 day-6 hr); and between a 6 hr and 10 day Elliot soil (right) control solution (green: 6 hr-10 day, red: 10 day-6 hr).

The fluorescence of quinone A and quinone B-like moieties may therefore come from two different energy transitions during excitation: $n-\pi^*$ and $\pi-\pi^*$, occurring at longer and shorter λ s, respectively and are due to quinone-like donor acceptor complexes (Cook et al., 2009; Ariese et al., 2004). Based on the above discussion, a 6 hr pre-moistened soil exfoliates smaller and more hydrophilic type moieties, such as similar quinone A moieties as designated in Figure 5.5.3. At a longer wetting time, quinone B like moieties, which are previously characterized to be more aromatic and hence more hydrophobic in nature (Cook et al., 2009), were exfoliated.

5.7 Sorption Capacity in Relation to the Sorbates

For the three pesticides, organic carbon normalized Freundlich sorption capacity (K_{FOC}) follow the trend Flutolanil > Norflurazon > Acifluorfen in all cases (Table 5.6.1-5.6.3, Figure 5.6.1-5.6.3). For example, in a purely organic dry soil Pahokee Peat, sorption of norflurazon and acifluorfen are only ~63.85% and ~21.17% respectively, of the total K_{FOC} of flutolanil. Possible

reasons for the differences in pesticide sorption in the same organic matter sorbent are pesticide properties such as: a) polarity; b) hydrophobicity; c) structure; d) size; and e) flexibility.

Here, polarity refers to the number of hydrogen bond acceptor and H-bond donor atoms in the molecule. Acifluorfen, norflurazon and flutolanil have 6, 4, and 3 hydrogen bond acceptors respectively, and all of them only have one proton donor group. In terms of hydrophobicity, flutolanil is the most hydrophobic, followed by norflurazon and then acifluorfen, based on their aqueous solubility and octanol water partition coefficients. Each of these pesticides consists of two 6 membered aromatic rings and their molecular sizes decrease in the order, acifluorfen > flutolanil > norflurazon. However, the presence of other substituents may influence electron donor acceptor interactions, as well as imparting differences in the π -donor and acceptor capabilities of these aromatic rings. Lastly, the number of freely rotatable bonds is four for both acifluorfen and flutolanil and two for norflurazon, which influences the molecules' flexibility.

Pollutant solubility, as well as n-octanol water partition coefficient (designated as K_{OW} or P_{OW}), has been used to predict sorption of HOC to sediments and soils (Allen King et al., 2002; Schwarzenbach et al., 2003; Huuskonen, 2003). In a purely organic matter, Pahokee Peat pesticide K_{OW} is highly correlated with pesticide K_{OC} , with $R^2 = 0.998$. In the determination of n-octanol water partition coefficients, the fraction of water in the octanol phase is ~21 mole percent (Pignatello, 2009). Hence, aside from hydrophobic forces, free energy relationship from K_{OW} also includes some polar forces such as hydrogen bonding and dipole-dipole forces (Pignatello, 2009). Free energy relationship, with respect to K_{OW} for diverse polar and nonpolar compounds (n=403), including pesticides (Huuskonen, 2003), provided the relationship: $\log K_{OC} = 0.60 \log P_{OW} + 0.84$ with $r^2 = 0.79$. Another one parameter free energy relationship for polar compounds, as studied by Nguyen et al. (2005), resulted to $\log K_{OC} = 0.73 \log P_{OW} + 0.52$ with $r^2 = 0.83$. If the $\log P_{OW}$ values of flutolanil (3.54), norflurazon (2.45), and acifluorfen (~1.54 at pH

Table 5.6.1 Sorption capacity of Pahokee Peat

	R^2	K_F	K_{FOC}	K_D at 0.5 ppm	K_{DOC} at 0.5 ppm	K_D at 5ppm	K_{DOC} at 5ppm	K_{rF}	K_{rFOC}
Acifluorfen									
sorp dry		71.24±0.35	151.89±0.74	80.81±0.06	172.30±0.06	53.16±0.09	113.34±0.10	3897±40	8310±86
sorp 1d prewet		63.74±0.47	135.91±1.00	71.63±0.08	152.74±0.09	48.61±0.13	103.64±0.14	3740±59	7975±127
sorp 5d prewet		55.15±0.45	117.59±0.96	62.50±0.08	133.27±0.08	41.23±0.11	87.92±0.12	3050±52	6504±110
des dry	0.996	75.09±0.83	160.10±1.77	83.37±0.21	177.75±0.22	69.10±0.40	147.34±0.43	7171±252	15289±538
des 1d prewet	0.988	62.60±1.29	133.48±2.76	68.10±0.33	145.21±0.35	61.06±0.68	130.19±0.73	7273±493	15507±1052
des 5d prewet	0.987	53.75±1.15	114.61±2.46	60.07±0.29	128.08±0.31	53.81±0.61	114.74±0.65	6408±441	13663±941
Norflurazon									
sorp dry		214.91±2.52	458.23±5.37	246.60±1.24	525.80±2.65	156.19±1.83	333.02±3.90	3109±75	6628±161
sorp 1d prewet		211.12±1.96	450.16±4.18	247.72±0.97	528.19±2.07	145.68±1.33	310.61±2.83	2742±52	5847±110
sorp 5d prewet		180.73±1.50	385.35±3.20	212.78±0.73	453.69±1.56	123.72±0.99	263.80±2.10	2309±38	4924±81
des dry	0.997	389.50±1.84	830.49±3.92	450.29±1.77	960.11±3.76	278.18±2.53	593.13±5.40	5433±102	11585±218
des 1d prewet	0.995	350.36±2.17	747.04±4.62	432.58±1.95	922.35±4.16	214.79±2.25	457.97±4.79	3563±77	7597±165
des 5d prewet	0.991	286.24±2.19	610.31±4.67	344.08±2.09	733.66±4.46	186.74±2.63	398.16±5.62	3312±97	7061±206
Flutolanil									
sorp dry		336.54±3.18	717.57±6.78	394.12±2.55	840.35±2.72	233.30±3.50	497.44±3.74	1837±38	3917±80
sorp 1d prewet		320.56±1.77	683.50±3.78	363.95±1.52	776.01±1.62	238.77±2.31	509.10±2.46	1930±25	4115±54
sorp 5d prewet		288.68±1.83	615.52±3.91	334.43±1.80	713.08±1.92	205.19±2.57	437.51±2.74	1630±28	3476±59
des dry	0.981	397.32±7.11	847.16±15.17	533.57±4.26	1137.69±4.54	200.45±3.72	427.41±3.96	1405±36	2997±76
des 1d prewet	0.995	436.36±4.40	930.40±9.39	515.24±2.78	1098.60±2.96	296.74±3.71	632.70±3.96	2320±40	4947±85
des 5d prewet	0.996	373.70±2.56	796.80±5.45	458.46±2.22	977.53±2.37	232.51±2.62	495.77±2.79	1760±27	3752±58

Table 5.6.2 Sorption capacity of Mandeville Soil

	R^2	K_F	K_{FOC}	K_D at 0.5 ppm	K_{DOC} at 0.5 ppm	K_D at 5ppm	K_{DOC} at 5ppm	K_{rF}	K_{rFOC}
Acifluorfen									
sorp dry		18.82±0.11	173.61±1.05	20.60±0.02	190.04±0.08	15.26±0.03	140.74±0.14	1325±16	12227±148
sorp 1d prewet		17.64±0.07	162.70±0.66	19.28±0.01	177.84±0.05	14.34±0.02	132.32±0.09	1251±10	11541±96
sorp 5d prewet		16.18±0.08	149.27±0.73	17.73±0.01	163.55±0.06	13.09±0.02	120.74±0.10	1130±11	10425±101
des dry	0.998	19.89±0.17	183.53±1.52	25.65±0.05	236.59±0.21	22.24±0.09	205.21±0.43	2444±62	22544±576
des 1d prewet	0.995	17.85±0.26	164.69±2.39	23.51±0.07	216.88±0.35	22.09±0.16	203.82±0.75	2761±124	25472±1142
des 5d prewet	0.994	16.20±0.25	149.41±2.31	21.45±0.08	197.84±0.35	20.23±0.16	186.64±0.76	2551±126	23535±1160
Norflurazon									
sorp dry		49.05±0.12	452.45±1.11	54.03±0.07	498.39±0.64	39.18±0.12	361.47±1.07	863±5	7959±49
sorp 1d prewet		44.32±0.12	408.86±1.13	48.71±0.06	449.34±0.59	35.60±0.11	328.38±1.01	788±5	7272±46
sorp 5d prewet		38.44±0.11	354.63±0.98	42.59±0.06	392.94±0.58	30.29±0.10	279.47±0.95	657±5	6064±43
des dry	0.999	55.92±0.19	515.91±1.76	63.16±0.16	582.69±1.51	42.16±0.25	388.91±2.35	872±11	8048±100
des 1d prewet	0.999	54.10±0.20	499.09±1.87	61.14±0.17	564.04±1.58	40.72±0.26	375.69±2.44	841±11	7762±104
des 5d prewet	0.999	47.13±0.17	434.79±1.56	54.23±0.15	500.24±1.40	34.03±0.22	313.97±2.04	673±9	6205±83
Flutolanil									
sorp dry		125.55±0.63	1158.20±5.85	139.65±0.53	1288.24±2.46	98.07±0.87	904.74±4.02	807±10	7441±90
sorp 1d prewet		116.47±0.80	1074.46±7.35	129.57±0.67	1195.28±3.08	90.96±1.09	839.11±5.01	748±12	6901±113
sorp 5d prewet		103.35±0.61	953.42±5.59	116.06±0.50	1070.67±2.31	78.96±0.79	728.44±3.65	644±9	5942±81
des dry	0.991	135.50±1.52	1250.04±14.04	161.73±1.09	1492.00±5.01	89.88±1.40	829.19±6.46	696±15	6425±137
des 1d prewet	0.983	121.36±1.64	1119.57±15.13	144.33±1.41	1331.43±6.49	81.21±1.84	749.20±8.48	631±20	5824±180
des 5d prewet	0.986	108.19±1.46	998.04±13.49	130.40±1.08	1202.95±4.98	70.16±1.35	647.26±6.22	539±14	4974±131

Table 5.6.3 Sorption capacity of Elliot Soil

	R^2	K_F	K_{FOC}	K_D at 0.5 ppm	K_{DOC} at 0.5 ppm	K_D at 5 ppm	K_{DOC} at 5 ppm	K_{rF}	K_{rFOC}
Acifluorfen									
sorp dry		2.73±0.05	94.28±1.63	3.13±0.01	107.86±0.12	2.00±0.01	68.98±0.18	143±5	4939±158
sorp 1d prewet		2.59±0.02	89.19±0.78	3.00±0.00	103.36±0.06	1.84±0.00	63.34±0.08	122±2	4218±68
sorp 5d prewet		4.12±0.11	141.98±3.86	4.90±0.02	168.97±0.31	2.75±0.02	94.79±0.40	166±8	5717±292
des dry	0.920	5.32±0.11	183.44±3.94	7.59±0.06	261.67±0.99	2.33±0.04	80.45±0.71	63±7	2164±229
des 1d prewet	0.920	4.44±0.09	153.03±3.06	6.16±0.05	212.26±0.89	2.08±0.04	71.62±0.70	64±8	2223±261
des 5d prewet	0.934	11.89±0.26	409.83±8.87	17.23±0.11	594.28±1.96	5.02±0.08	172.99±1.32	123±11	4253±393
Norflurazon									
sorp dry		12.21±0.07	421.03±2.54	14.28±0.04	492.54±1.33	8.48±0.05	292.52±1.83	182±4	6273±137
sorp 1d prewet		11.73±0.07	404.31±2.30	13.96±0.03	481.41±1.11	7.82±0.04	269.60±1.44	163±2	5618±62
sorp 5d prewet		10.88±0.06	375.07±2.20	13.00±0.03	448.24±1.14	7.19±0.04	247.99±1.47	135±5	4668±163
des dry	0.997	17.33±0.09	597.47±3.02	20.18±0.08	695.90±2.73	12.16±0.11	419.35±3.82	233±4	8040±152
des 1d prewet	0.986	19.52±0.15	673.02±5.04	24.57±0.19	847.22±6.64	11.44±0.21	394.56±7.18	181±7	6242±235
des 5d prewet	0.994	18.09±0.11	623.91±3.96	22.80±0.11	786.13±3.66	10.58±0.11	364.87±3.94	167±4	5755±129
Flutolanil									
sorp dry		13.55±0.17	467.27±5.86	15.96±0.14	550.21±2.45	9.28±0.19	319.95±3.31	73±2	2508±71
sorp 1d prewet		11.65±0.21	401.64±7.13	13.87±0.16	478.33±2.80	7.77±0.21	267.97±3.64	60±2	2081±77
sorp 5d prewet		11.92±0.15	411.12±5.02	14.45±0.12	498.28±2.01	7.63±0.14	263.21±2.47	58±1	2013±52
des dry	0.899	18.68±0.64	644.18±22.01	26.41±0.44	910.83±7.65	8.38±0.33	288.85±5.63	56±3	1941±103
des 1d prewet	0.923	17.48±0.62	602.91±21.48	22.38±0.41	771.59±7.13	9.89±0.42	340.91±7.30	72±4	2494±146
des 5d prewet	0.951	16.15±0.53	556.88±18.12	21.84±0.36	753.27±6.20	8.03±0.31	276.74±5.29	56±3	1931±101

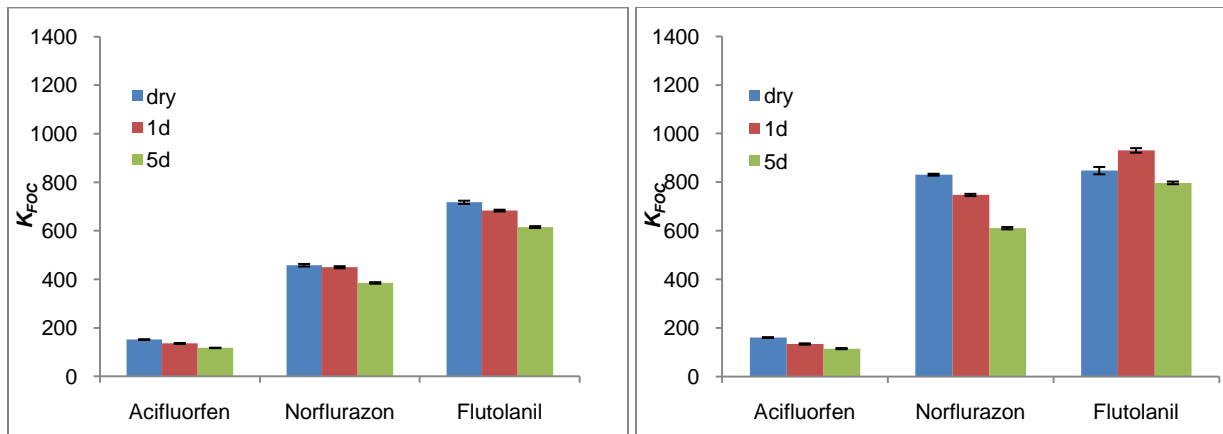


Figure 5.6.1 Sorption (left) and desorption (right) in Pahokee Peat

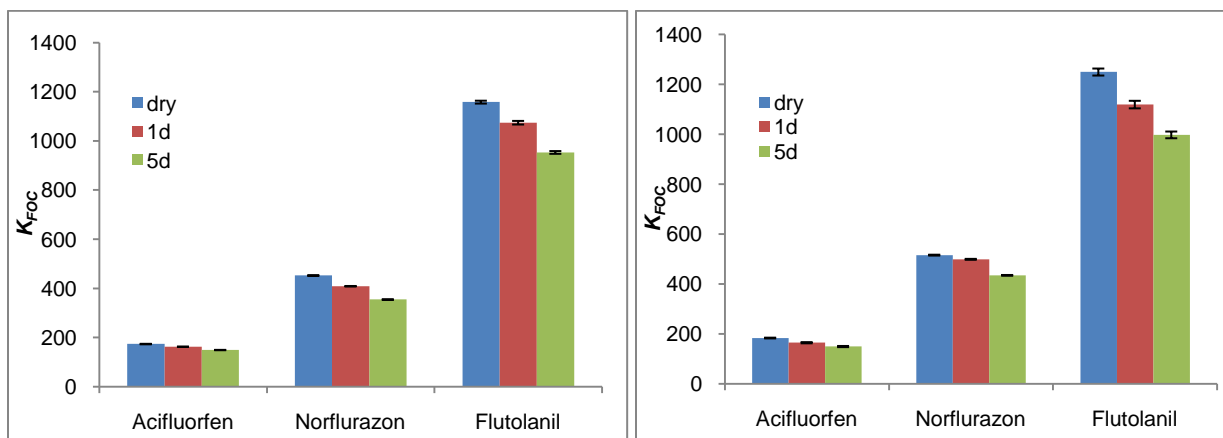


Figure 5.6.2 Sorption (left) and desorption (right) in Mandeville soil

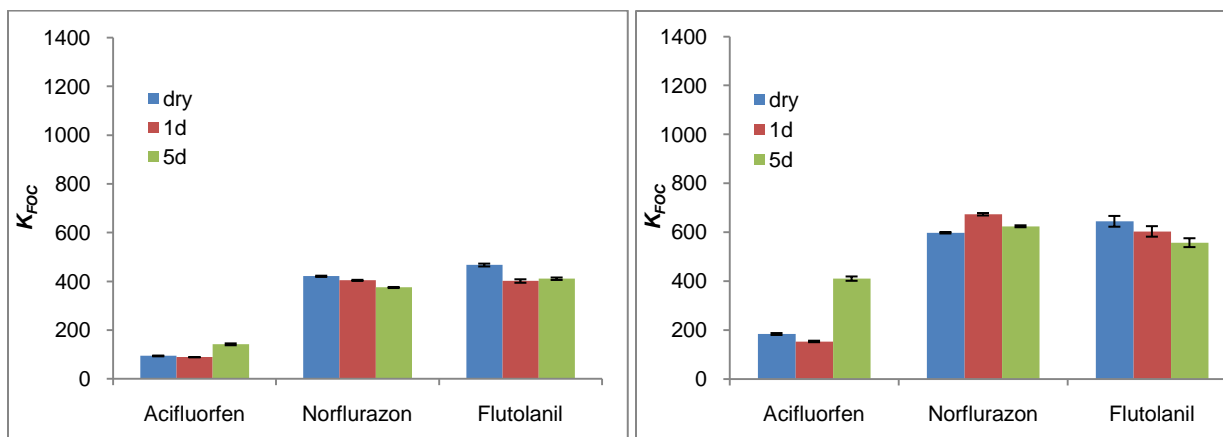


Figure 5.6.3 Sorption (left) and desorption (right) in Elliot soil

= 5), are substituted in the latter equation, yielded K_{OC} values in $L\ kg^{-1}$ are: flutolanil (1271); norflurazon (204); and acifluorfen (44).

Compared to our experimental results on Pahokee Peat (Table 5.6.1), this model overestimates K_{OC} of flutolanil by greater than 40%, while norflurazon and acifluorfen were underestimated by greater than 50% and 70%, respectively. This means that use of P_{OW} alone is insufficient to quantify sorption of these pesticides. Thus, aside from hydrophobic, H-bonding, and Keesom forces, other interactions may contribute to sorption of these pesticides. The multi-free energy relationship by Nguyen et al. (2005) shows that for polar chemicals, hydrophobic forces reflected through cavitation energy (~44%), as well as London and Debye forces (~21%), have the greatest contribution to sorption, followed by dipole-dipole forces (15%) and proton acceptor capability (16%). The least contribution is from proton donor ability (1%) of the molecule.

Zhu and Pignatello (2005) presented another free energy relationship that includes hydrophobic effects, dipolarity and polarizability, H-bonding and π - π electron donor-acceptor interactions. The hydrophobic effect still has the greatest contribution to $\log K_{OC}$, while dipolarity and polarizability (D/P) also carries a significant contribution (i.e., 15–40 %). An increase in dipole moment and polarizability (i.e., molecular size) increases D/P contribution.

Thus flutolanil, having the highest K_{OC} in Pahokee Peat, may be inferred as mainly due to its hydrophobicity. An additional contribution to its sorption is due to the potential for very weak H-bonding with SOM on its ether, CF_3 , Cl groups, and moderate H-bonding energies of benzamide group, with amide moieties in SOM. In addition, the π -donor ability of the aromatic group, is enhanced by the presence of electron donating groups $-OR$ and $-NHR$, may also contribute to π - π electron donor acceptor interactions with SOM; aromatic moieties (typically ~25%) of SOM (in carbon terms) are envisioned to be largely π -acceptor sites due to presence of electron withdrawing groups (Shirzadi et al., 2008a; 2008b; Kellerher and Simpson, 2006). In addition, the presence of four rotational bonds for flutolanil increases its molecular flexibility,

which may increase sorption by being adapting molecular conformation or geometry to the most favored interactions. It can also be noted that the greatest localization of charges from the electrostatic potential surface modeling of pesticides is seen for flutolanil (Figures 5.3.1 to 5.3.4), which may facilitate dipole interactions.

Norflurazon is second in terms of hydrophobicity between the three pesticides, dipolarity, and polarizability (i.e., dipole moment). It is also capable of strong to very strong hydrogen bonding with carboxylic and phenolic groups in SOM through its azine and amino functionalities (Gilli, 2009). The aromatic group containing the CF_3 substituent is also slightly electron rich, thus it can serve as a π -donor to the electron deficient SOM aromatics. The use of K_{OW} to estimate norflurazon's K_{OC} results to 50% underestimation of its K_{OC} , thus the above additional interactions (dipolarity/polarizability, H-bonding, and π - π interactions) also significantly contribute to sorption.

Acifluorfen is the least hydrophobic, based on K_{OW} and solubility, and also has the lowest empirical K_{FOC} . If solely K_{OW} is taken into consideration as influencing K_{OC} , it is greatly underestimated by predictive modeling. Hence other interactions largely contribute to its K_{OC} . In a neutral form, the carboxylic group exhibits strong to very strong H-bonding with nitrogen moieties in SOM such as azine,azole, amine (Gilli, 2009; Gilli and Gilli, 2000). The nitro group in the aromatic ring containing the COOH group enhances its acidity. Acifluorfen also had the highest dipole moment and is the most polarizable among the three pesticides; this finding may also largely influence its sorption (Zhu and Pignatello, 2005). However, it should be noted that only a small proportion of acifluorfen exists in the protonated form at the sorption pH (pH ~ 5), as the pka of COOH in acifluorfen is ~3.5. Hence, the presence of ionized carboxylic and phenolic groups in SOM repels the anion form of acifluorfen, thereby reducing its K_{OC} . In

addition, the aromatic rings of acifluorfen are both π electron acceptors (Figure 5.3.1); hence, π - π electron donor acceptor with SOM moieties would be less probable (Shirzadi, 2008a).

In a high resolution magic angle spinning NMR study of acifluorfen binding at the soil-water interface, the results suggested that interactions with electronegative groups such as the COOH, Cl, and CF₃ groups of the acifluorfen most likely play a dominant role in its sorption at pD values of 5.8 – 5.9 (pD is just like pH, because the solvent used is D₂O). The COOH group may interact through H-bonding and dipole interactions, while F and Cl may also interact through dipole interactions and weak H-bonding. The flexibility of this molecule (number of rotational bonds = 4), can favorably adapt a planar configuration where all the electronegative substituents are on one side of the molecule, thereby facilitating the above interactions.

5.8 Sorption Capacity in Relation to Sorbents

The K_{FOCS} for norflurazon in Pahokee and Mandeville soils are statistically equal in a dry soil, while it is approximately 8% lower in Elliot soil, which implies that sorption of norflurazon is primarily due to organic carbon, especially at organic carbon > 3%. Thus, at the concentrations used in the sorption isotherms, norflurazon did not show affinity to the mineral phase, especially in Mandeville soil, which contains expandable clays. A previous study on sorption/desorption of norflurazon on a Ca-montmorillonite showed similar results (Carringer et al., 1975).

For flutolanil and acifluorfen, the K_{FOC} was highest in Mandeville soil, followed by Pahokee; the lowest sorption was observed in Elliot soil. Three questions arise from these observations, namely:

- 1) Why is K_{FOC} sorption in Mandeville soil > Pahokee Peat?
- 2) Why is K_{FOC} sorption in Mandeville soil >> Elliot?

- 3) Why does norflurazon show a different behavior, compared to the other two pesticides?

The higher K_{FOC} observed for Mandeville soil may be attributed to the presence of an expanding type clay mineral montmorillonite (Figure 5.6.2), as well as presence of an appreciable amount of sand grains (Table 5.3.1). Since all pesticides used have both polar and nonpolar moieties, these have the ability to interact with both polar and nonpolar sites of minerals. We may speculate that the presence of expandable type clay minerals and a high proportion of sand in Mandeville soil, adds to its sorption capacity, when compared with Pahokee Peat. Mandeville soil consists of approximately 23% clay and 49.38% sand. Its mineral fraction consists of quartz, kaolinite, abite, muscovite, and montmorillonite (Figure 5.7.1). Quartz is mainly made of phyllosilicates. Kaolinite is a 1:1 non-expandable clay. Muscovite is a primary mineral that transforms into expandable 2:1 smectite (potassium ion exchanged) clay upon weathering. On the other hand, Na-montmorillonite is a highly expandable 2:1 type clay.

When 2:1 clays such as montmorillonite and smectite are dispersed in an aqueous solution, water molecules can diffuse in the interstitial layer resulting in hydration of the cations that hold the two layers together and/or diffusion of some of the exchangeable cations in solution (Dunnivant and Anders, 2006; Sposito, 1984; Quirk and Murray, 1999). This will then result to an increase in the interlayer spacing, commonly referred to as clay expansion. This expansion or swelling of clay increases the surface area of contact for HOC, by diffusion into these interstices. In addition, polar interactions with water molecules that hydrate these cations in the interlayer of montmorillonite surfaces are plausible (Hundal et al., 2001; Laird et al., 1992). When favorable interactions between the clay surface and HOC are present, sorption to these sites is then facilitated. For example, cation- π interactions are plausible for the negative quadrupolar aromatic ring in flutolanil (i.e., the ring that contains electron donating groups (-OR and -NHR)

and the exchangeable cations. This favourable interaction and flexibility of flutolanil molecule (i.e., number of rotational bonds = 4), can lead research to envision that: 1) the aromatic π interacts with the cations; and 2) the localized positive surface potential in the amide, propyl, and benzene ring may facilitate n–H bond interactions (where n = nonbonding electrons) in mineral surfaces, such as oxygen in siloxane.

Another plausible mechanism for the enhanced sorption of flutolanil to soils with sand grains is aromatic π –H bonding with free silanol groups. Flutolanil has a π -donor ring, and this π donor capacity is enhanced by the presence of electron donating substituents –NHC=O and –OR. For example, it has been suggested that π cloud of benzene above and below the plane of its ring can form weak H-bonding with water (Gotch and Zwier, 1992), with bonding energy of approximately 1.78 kcal mol⁻¹ (Suzuki et al., 1992). Evidence of the existence of π –H bonding of benzene and toluene with free silanols on a silica surface has been shown through FTIR and Raman spectroscopy (Ringwald and Pemberton, 2000).

In addition, sorption to hydrophobic sites in mineral grains, including clay minerals, may enhance sorption of hydrophobic pesticides (Hundal et al., 2001; Quirk and Murray, 1999; Chiou and Rutherford, 1997). For example, sand grains may be coated with NOM; several of these individual grains with NOM may be intimately associated, thereby forming hydrophobic pores of different sizes (Lehmann et al., 2007). Up to now, there is no absolute definition of these hydrophobic nanopores in terms of pore diameter. The IUPAC classifies pores based in diameters as macropores (>50 nm), mesopores (2–50 nm), and micropores (<2 nm) (IUPAC, 1972; Nam and Alexander, 1998) whereas soil scientist categorizes micropores as having diameters of 5–30 μ m (SSSA, 1997). Hassink et al. (1993) suggested the presence of <100 nm pore sizes in soils. The pesticides in this study range in molecular sizes of ~254 Å³ to 326 Å³ and would therefore require approximately a minimum of 30–40 nm pore

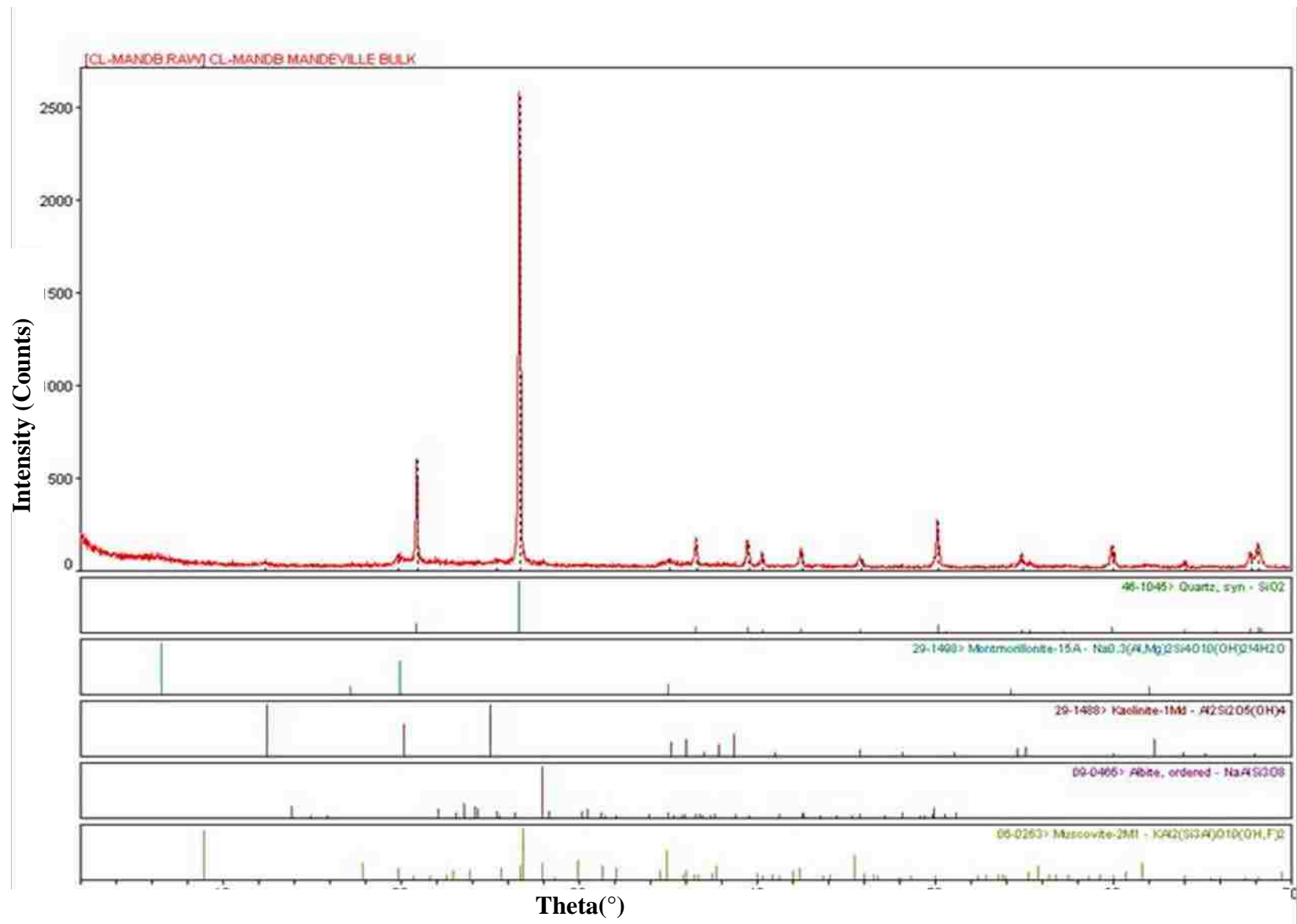


Figure 5.7.1 Mineral composition of Mandeville soil

sizes. It is apparent from Table 5.1 that sandy and sandy loam soils exhibited the highest K_{OC} values. Our results are congruent with aforementioned data, that the presence of an appreciable amount of sand in Mandeville soil may increase flutolanil sorption, by means of sorption by π -H bonding and sorption to hydrophobic nanopores (Daly, 1987; <http://www.efsa.europa.eu>). That norflurazon did not show the same effect in Mandeville soils indicates that hydrophobicity of the HOC is the single most important factor in sorption to these hydrophobic sites. It must be noted, however, that sorption of these three pesticides should still occur predominantly in the SOM, due to the high organic carbon contents of these sorbents.

On the other hand, Elliot soil consists of illite clay, which exhibits medium swelling properties only, and may not enhance sorption of flutolanil and acifluorfen to the above discussed sorbent sites. The soil used by Suzuki et al., (1998) has similarity with Elliot soil in this study, in terms of soil use (turf soil), pedon (both belonging to a loam type of soil), as well as pH and cation exchange capacity values. Their K_{OC} values are 418 L kg⁻¹ and 467 L kg⁻¹, respectively.

At Mandeville soil pH, which is 4.62, a greater proportion of acifluorfen is in ionized form. Acifluorfen anion, therefore, experiences initial repulsion on the negatively charged clay surfaces. However, its carboxylate group may also complex with exchangeable cations in mineral oxides, similar to that suggested for fluoroquinolones (antibiotics having an ionizable carboxylic group attached to an aromatic ring) (Carrasquillo et al., 2008; Mackay and Seremet, 2008; Gu and Karthikeyan, 2005). Since sorption of acifluorfen is much lower, compared to flutolanil in Mandeville soil, it may be speculated that its sorption in this soil is mainly by hydrophobic forces, especially of the unionized form.

Using reduced Freundlich coefficients (K_{rF}), it is possible to compare sorption affinities of HOCs for different sorbents. A plot of the reduced Freundlich coefficient K_{rF} and soil organic

carbon content shows r^2 values of 0.97, 0.99, and 0.99 for flutolanil, norflurazon, and acifluorfen, respectively in dry soils. Thus, for these pesticides found to be at equilibrium concentrations approaching saturation, it may be predicted that sorption to SOM will dominate. Normalization of K_{rF} with organic carbon content yields the reduced organic carbon Freundlich coefficient, K_{rFOC} . If sorption is solely due to dissolution or partitioning in the SOM, then K_{rFOC} should be constant. However, this is not always the case. Differences in K_{rFOC} may be due to the following factors: a) the type of organic carbon moieties that make-up the organic matter and the resulting SOM structure; b) age of soil; c) mineralogy; and d) sorbate structure and polarity (Ding et al. 2002; Chefetz et al. 2000). Both sorption and desorption isotherms generally show that K_{rFOC} decreases in this order: Mandeville > Pahokee > Elliot for all pesticides, except for norflurazon in Pahokee Peat and Elliot soils which shows a near constant K_{rFOC} in sorption isotherms (with only 4–5% difference). This implies that at reduced concentrations, norflurazon sorbs mainly to SOM. It can also be argued that the type of organic carbon moieties that make up these soils are very similar, resulting in a near constant K_{rFOC} . Indeed, similar elemental composition and functional group characterization (by NMR) of Pahokee Peat and Elliot bulk soils, as well as their humic materials, are presented by IHSS. The slightly higher sorption K_{rFOC} of Mandeville soil, when compared to Pahokee Peat soil (17–20% difference), may be due to the differences in: 1) organic carbon make-up and 2) soil mineralogy. This hints at possible sorption to mineral/clay surfaces of norflurazon at concentrations approaching saturation, because other high energy sites (i.e., SOM) are exhausted.

Since K_{rF} is more representative of equilibrium concentrations (C_e), approaching water solubility limit (Carmo et al., 2000), sorption at certain C_e were also evaluated and compared with the original isotherm, in order to have a complete picture irrespective of dimensional analysis. Sorption K_F at a particular C_e (0.5, 5mg/L) reveals a decreasing order, such that

Pahokee Peat > Mandeville > Elliot for all three pesticides investigated as well as in different soil wetting conditions. The organic carbon normalized distribution coefficient (K_{DOC}) results provide the order Mandeville > Pahokee Peat > Elliot for acifluorfen and flutolanil for all C_e evaluated, with the exception of acifluorfen in 5-day prewet Elliot soil. Again, equilibrium concentrations 0.5 mg/L and 5 mg/L of norflurazon, derived from the sorption isotherm, show the slightest K_{DOC} variation among the three sorbent in their dry state, with differences of $\leq 12\%$ only, when K_{DOC} is compared with Pahokee Peat. This implies that for norflurazon, soil organic matter is where the major sorption occurs. A plot of K_D versus organic carbon content of sorbents at $C_e=0.5$ mg/L demonstrate that its slope in the desorption part is greater than its corresponding sorption (Table 5.7.1 and Figure 5.7.2). This is apparent for norflurazon and flutolanil, which suggest that organic matter swelling occurred during sorption. This form of matrix rearrangement may not be fully reversible during desorption, hence it accommodates more sorbate as surface area for sorption is increased. In addition, K_D versus organic carbon desorption slopes at $C_e=0.5$ ppm are quite similar for norflurazon and flutolanil, which suggest that at lower concentrations, both pesticides have a nearly equal affinity for SOM sorption sites. It is also shown that sorption K_D in organic carbon is greater at lower concentration (i.e., 0.5 ppm), than at high concentration (i.e., 5 ppm). High energy sorption sites are filled first at lower sorbate concentrations.

If the organic matter contents of the sorbent used in this study are substituted in the linear equation given by Morillo et al. (2004), norflurazon K_{OC} in $L\ kg^{-1}$ are as follows: Pahokee (426), Mandeville (420), and Elliot (397). These results are similar with empirical data: Pahokee (458), Mandeville (452), and Elliot (421); thus supporting that for norflurazon, sorption to organic matter may be the single most important reason.

Table 5.7.1 Equation of the line for Figure 5.7.2

Pesticide		R ²	Equation of the line
Sorption	Acifluorfen	0.9979	$y = 1.74x - 0.24$
	Norflurazon	0.9999	$y = 5.30x - 2.13$
	Flutolanil	0.9757	$y = 8.12x + 19.07$
Desorption	Acifluorfen	0.9964	$y = 1.68x + 4.81$
	Norflurazon	0.9937	$y = 10.07x - 25.68$
	Flutolanil	0.9918	$y = 11.15x + 15.13$

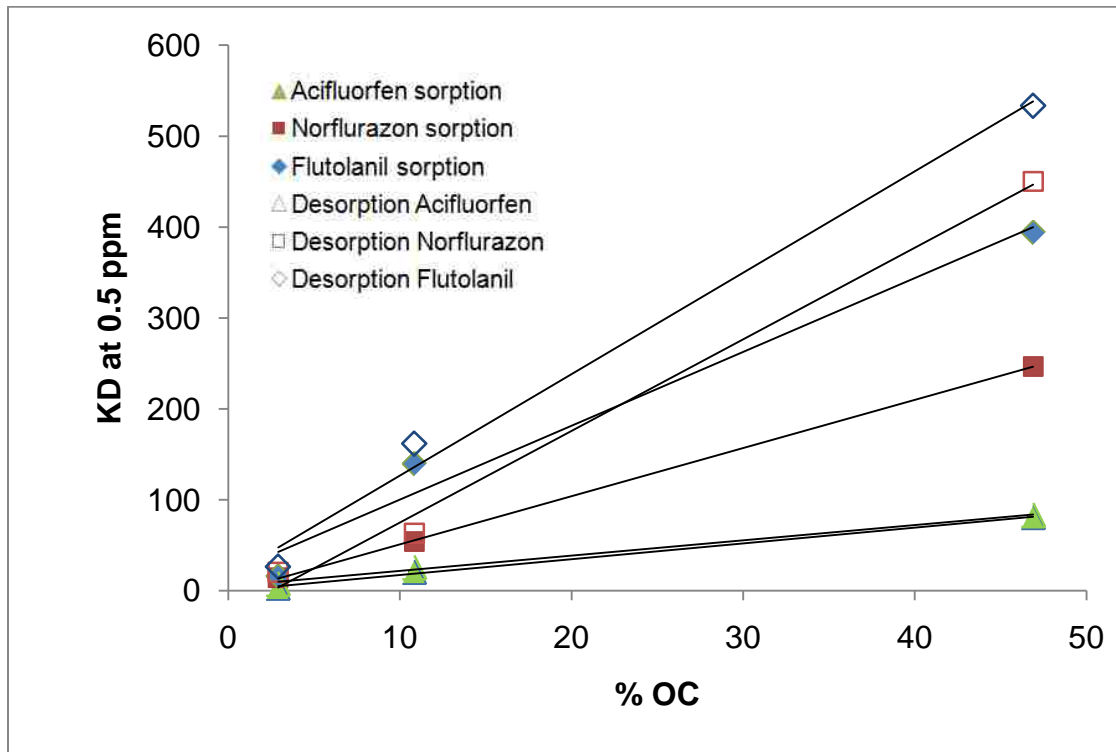


Figure 5.7.2 Sorption-desorption distribution coefficients at 0.5 ppm equilibrium concentration of the different pesticides to the different sorbents

5.9 Sorption with Respect to Hydration

Tables 5.6.1 to 5.6.3 and Figures 5.6.1 to 5.6.3 show that in general, Freundlich sorption capacities or the organic carbon normalized Freundlich sorption coefficient decreases in the order of dry, 1-day prewet, and 5-day prewet respectively for all soil and pesticide combination except for:

- a) norflurazon in Pahokee Peat, where sorption to dry is statistically equal to that of 1-day

- prewet;
- b) flutolanil in Pahokee Peat, where after desorption, K_{FOC} follows the trend 1 day > dry > 5 day prewet;
 - c) acifluorfen in Elliot soil, where K_{FOC} in both sorption and desorption isotherm provide the trend 5 day prewet > dry > 1 day prewet;
 - d) flutolanil in Elliot where dry > 1 day prewet \approx 5 day prewet; and
 - e) norflurazon in Elliot soil where after desorption, sorption capacity was shown to be 1 day > 5 day > dry

The above observation that a dry soil sorbs more of HOC than wet soil is in agreement with our domain model of a whole soil. It was presented in Chapter 4 that the molecular assemblage in a whole soil consists of a domain of carbohydrate-like moieties, which are in close association with aromatic moieties (i.e., lignocellulosic like moieties) and another isolated domain, containing aliphatic-like moieties (Lattao et al., 2008).

In a dry soil, it may be envisioned that the hydrophobic moieties favor residing on the surface of the soil aggregates, while its hydrophilic parts prefer to migrate to the inside of the domain. Both the aromatic and aliphatic moieties are then available as sorption sites. Thus, when an aromatic HOC is exposed to an initially dry soil, sorption to these hydrophobic moieties is favorable through hydrophobic forces. However, sorption to aromatic moieties is thought to be more thermodynamically favorable, due to simultaneous π - π electron donor acceptor interactions, in addition to hydrophobic forces. On the other hand, in an initially wet soil, the hydrophilic moieties prefer to migrate on the surface, while the aromatic moieties reside in the core of the domain. The aliphatic domain, then, is available as sorption sites due to isolation from the second domain. Therefore, a lower sorption capacity for aromatic HOC, observed in 1-day and 5-day prewet soils, therefore is due to availability of mostly aliphatic domains as

sorption sites. These findings are also supported by kinetic studies of HOC uptake, such that a dry soil had a higher amount sorbed in the fast region (i.e., < 20 hrs), even up to 5-day of the slow region, but eventually coincided at longer incubation periods. A 5-day prewet soil had a lower sorption capacity compared to a 1-day prewet soils; this result may be explained by the kinetics involved in wetting of soils, which includes a fast region up to maximum of 24 hrs, and a slow process, which may take several days (Todoruk et al., 2003; Belliveau et al., 2000). In the work of Todoruk et al. (2003) and Belliveau et al. (2000), kinetically controlled wetting is attributed to the diffusion of water into soil micropores, where the redistribution of water in the micropores enables soil conformational rearrangement, resulting in an “expanded” or “swelled state”. In addition, for sorption from aqueous systems, entry or diffusion of contaminants to soil micropore sorption sites would require diffusion of water into these sites (Belliveau et al., 2000; Gamble et al., 2000). Hence, it is not surprising that the kinetic uptake of these HOC on sorption studies in slurried systems tend to follow that of kinetics of soil wetting. For a purely organic matter, soil micropores may be defined as voids that result from the three dimensional conformational geometry of SOM.

For whole soils with organic matter and mineral/clay components, wetting is thought to involve diffusion of water into SOM micropores, mineral micropores, and clay interlayers, as well as micropores that result from interassociations between SOM and mineral particles. In the presence of both soil organic matter and mineral components in soils, wetting will thus affect both components simultaneously, resulting in conformational rearrangements within SOM; these are primarily due to H-bonding forces with water (Todoruk et al., 2003); diffusion of water to mineral surfaces, including clay, will also affect its sorption properties. Sorption of HOC to mineral/clay surfaces may be suppressed by hydration of the exchangeable cations, as well as formation of films of water on mineral/clay surface through ion-dipole interaction. In prewetted

soils, water diffuses into the interlayer spacing of expandable clays, thus forming more layers of water films in comparison to a thinner water film in its air-dried state. Although this swelling of clay by water increases surface area for sorption, the HOC must compete with water for these sorption sites. Sorption of atrazine to a soil containing smectite type of clays, such as montmorillonite, show that atrazine sorption decreases in the order of rehydration time: 24 hrs > 109 hrs > 240 hrs (Chappell et al., 2005). In the same study, molecular simulation of sorption of atrazine to a smectite clay with potassium interlayer cations was provided, which shows that the presence of more hydration layers (e.g., three water layers) results in a greater interaction of atrazine with water molecules than with the interlayer cation; this may explain the reduced sorption at a longer wetting period. Water may also H-bond in order to free silanol groups in silica surfaces, thereby reducing π -H bonding between π donor site in a contaminant and hydrogen of silanols. In summary, regarding a whole soil containing SOM and minerals where both serve as sorption domains, a reduction of sorption capacities of prewetted soils is influenced by the wetting of organic matter/mineral phases.

5.10 Hysteresis

Sorption and desorption distribution coefficients (K_{DS}) were compared at $C_e = 0.5$ mg/L, because this equilibrium concentration is common in both isotherms for all pesticides. The highest initial concentration in the sorption isotherm used for flutolanil was 6 mg L^{-1} ; thus, the equilibrium concentration after desorption was less than 5 mgL^{-1} . Moreover, K_F desorption is always greater than the corresponding K_F sorption in all sorbate-sorbent hydration conditions, except for acifluorfen in 1 and 5 day prewet Pahokee Peat and Mandeville soils. In general, Pahokee Peat and Elliot soils exhibit a larger difference between desorption and sorption K_{FOC} values for norflurazon and flutolanil. This signifies that organic matter of sorbent is where major sorption occurs, if not solely for Pahokee Peat and Elliot. This non-ideal behavior also suggests

that: a) other forms of retention mechanism occur, aside from simple dissolution of these HOCs in the SOM (Carmo et al., 2000), and b) varying sorption energy sites between sorption and desorption are available (Tabatabai and Sparks, 2005).

In Mandeville soil, the difference between desorption and sorption K_F is less compared with Pahokee Peat and Elliot soils. A plausible explanation is that Mandeville soil is younger relative to the other two sorbents. This inference is based on the observation that Mandeville top soil consists of a great deal of plant materials at different stages of biological degradation which are then manually separated during and after soil collections. Hence, its SOM may be assumed as less diagenetically altered. This would imply that it contains more “soft” type organic carbon moieties (i.e., aliphatic) and less condensed organic carbon functionalities, thus lesser deviation to ideal behavior. In addition, HOCs sorbed to the outer rim of inorganic particles in Mandeville soil may easily be desorbed.

All sorption isotherms deviate from linearity, because N values were all less than 1 (Table 5.9.1). These N values are as follows: acifluorfen 0.74–0.87, norflurazon 0.74–0.86, and flutolanil 0.71–0.84. Desorption isotherms showed lesser N values when compared to their corresponding sorption isotherms, as given by acifluorfen 0.45–0.51, norflurazon 0.65–0.82, and flutolanil 0.47–0.75. These findings indicate the presence of different adsorption sites of varying energies (Tabatabai and Sparks, 2005). Only acifluorfen desorption isotherms in Mandeville and Pahokee Peat showed a higher N value, which is actually close to linear (0.91–0.97). N values for sorption-desorption isotherms also showed the following trend: Elliot < Pahokee Peat < Mandeville. Elliot and Pahokee Peat soils, which may consist of older SOM; hence, it is expected to have a harder type carbon fractions (aromatics) as well as a more condensed SOM, resulting in more non-linear sorption isotherms (Ju and Young, 2005; Young and Weber, 1995).

The hysteresis index value is lowest for flutolanil in all three sorbents, followed by

norflurazon, and then acifluorfen. The only deviation is acifluorfen in Elliot soil, where it had the lowest hysteresis index observed. Except for norflurazon in dry Elliot soil, we observe that hysteresis is greatest for Elliot soil, followed by Pahokee Peat, and then Mandeville soil for flutolanil and norflurazon. This indicates that Elliot soil has the oldest SOM with more reduced/more diagenetically altered organic carbon, and Elliot soil also is more hysteretic, compared to Pahokee Peat and the rather young Mandeville soil. For instance, diagenetically-altered SOM may contain some form of graphitic carbon, such as charcoal. This may cause additional sorption sites by diffusion into fixed micropores.

A greater N value and less hysteresis observed for Mandeville soil may be related once again to a large fraction of soft domain (alkyl type moieties) in its organic matter make-up when compared to Pahokee Peat and Elliot soil (Huang and Weber, 1997).

Hysteresis index may be a function of sorbate polarity and structure. The flutolanil molecule has a larger surface area of nonpolarity. This enables greater polarizability, thus allowing more Van der Waals interactions. True hysteresis for this compound may be related to the creation of more pores as a result of macromolecular swelling during interactions with SOM. The penetration of a sorbate to the 3-dimensional macromolecular network of SOM leads to some form of conformational change in the SOM, in order to achieve a more energetically favored association with the sorbate (maximum interactions). This form of molecular rearrangement may induce the formation of new voids for sorption, thereby accommodating more sorbate. Thus during desorption, a greater surface area for sorption is available at lower concentrations. These deformations in the rigid SOM may relax very slowly or may be irreversible. In addition, rearrangement of SOM during desorption may cause entrapment of molecules, which will then be more difficult to desorb (Sander et al., 2005; Beinum et al., 2006; Ding et al., 2002). This explains an increased affinity for sorbate during desorption, rather than

during the sorption process.

Norflurazon hysteresis index values are close to or equal to 1 (0.96–1) for dry sorbents. This implies that the same factors govern its retention at both high and low tested concentrations. In contrast with flutolanil, the lowest hysteresis index values for norflurazon were in prewetted sorbents and are most pronounced in Elliot soil.

For acifluorfen, hysteresis is greatest in Elliot soil. The hysteresis index of pesticides in Elliot soil is seen to decrease in the following order: norflurazon > flutolanil > acifluorfen. It may be hypothesized that the norflurazon sorption in Elliot is mainly due to organic matter, whereas flutolanil and acifluorfen have additional sorption site heterogeneity. Since flutolanil and acifluorfen present molecules bigger than norflurazon, an additional cause of hysteresis may be due to diffusion hindrance in microporous sorption sites. A slightly lower hysteresis index of acifluorfen in Elliot soil when compared with flutolanil, may be attributed to a solute concentration-induced hysteresis. The acifluorfen sorption concentration is almost 2 orders in magnitude with 1–80 ppm. A high concentration may induce SOM swelling (Huang and Weber, 1997; LeBoeuf and Weber 1997, 2000; Lu and Pignatello, 2002; Weber et al., 2002).

The hysteresis observed here can be considered true, and may not be due to colloids effect. Artifacts due to colloids effect may be minimized by adding a pesticide-free background that has some matrix from pre-equilibration of sorbent. However, Huang et al. (1998) revealed that there is no significant difference between this and the use of an electrolyte solution for one-step desorption procedures. Moreover, loss of solids due to supernatant decanting was calculated in all samples; results indicate that the solid loss is insignificant, and therefore had a negligible effect on sorption. Furthermore, the hysteresis observed in the sorption of these three pesticides is not primarily due to slow diffusion of sorbates during the sorption and desorption steps. In order to check whether hysteresis observed in isotherms are true and not mainly due to non-

Table 5.9.1 Freundlich *N* parameter and hysteresis index (HI)

	Acifluorfen			Norflurazon			Flutolanil		
	Nsorp	Ndes	HI	Nsorp	Ndes	HI	Nsorp	Ndes	HI
Pahokee									
dry	0.820±0.003	0.924±0.010	1.127±0.008	0.802±0.010	0.791±0.008	0.987±0.003	0.772±0.013	0.575±0.016	0.744±0.008
1d prewet	0.834±0.005	0.962±0.020	1.154±0.017	0.769±0.008	0.696±0.009	0.904±0.003	0.817±0.009	0.760±0.011	0.931±0.004
5d prewet	0.822±0.005	0.962±0.020	1.171±0.017	0.765±0.007	0.735±0.012	0.961±0.007	0.788±0.011	0.705±0.010	0.895±0.000
Mandeville									
dry	0.871±0.004	0.942±0.007	1.081±0.004	0.861±0.003	0.824±0.005	0.958±0.003	0.847±0.008	0.745±0.014	0.880±0.008
1d prewet	0.873±0.002	0.980±0.013	1.122±0.012	0.864±0.003	0.824±0.006	0.953±0.004	0.846±0.011	0.750±0.020	0.886±0.013
5d prewet	0.870±0.003	0.982±0.014	1.129±0.013	0.852±0.003	0.798±0.006	0.936±0.003	0.833±0.009	0.731±0.017	0.877±0.011
Elliot									
dry	0.811±0.009	0.503±0.031	0.620±0.031	0.774±0.006	0.780±0.008	1.008±0.003	0.764±0.018	0.501±0.034	0.654±0.029
1d prewet	0.790±0.005	0.545±0.034	0.690±0.039	0.748±0.005	0.668±0.016	0.893±0.016	0.748±0.024	0.645±0.038	0.861±0.023
5d prewet	0.756±0.015	0.477±0.027	0.631±0.023	0.743±0.005	0.667±0.010	0.897±0.007	0.723±0.017	0.565±0.034	0.781±0.029

attainment of diffusive equilibrium, additional sorption isotherms were tested and selected for Pahokee Peat and Elliot soils. An increase in K_F was seen at longer incubation times, which was expected (Beinum et al., 2006). However, N values in sorption desorption isotherm are still much less than 1 for norflurazon in 10 day or 15 day time, compared with 5 day contact time. In fact, hysteresis index values are lower. The N value should approach 1 with a longer incubation time; sorption reversibility might be more possible were the hysteresis observed be mainly due to diffusion non-equilibrium processes (Xia and Pignatello, 2001). On aggregate, the results strongly suggest that the physico-chemical properties of both sorbate and sorbent contribute to sorption irreversibility, as suggested by Chen et al. (2000).

In summary, our major findings suggest that a) sorption kinetics in soils of varying organic matter content show that an initially dry soil sorbs a higher amount of pesticide and a faster uptake in the early kinetics stage; b) organic matter is the major domain for sorption, however, the presence of expandable clays, together with an appreciable amount of sand, may also result in additional pesticide retention; and c) the investigated polarity and structure of pesticides and SOM causes nonlinearity and hysteresis in sorption.

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Chapter 6

Sorption Rates

6.1 Introduction

Due to growing concerns about surface and groundwater contamination, soil and water remediation, and waste disposal, it is increasingly essential to elucidate the uptake kinetics and the mechanism involved in the interaction of HOCs with environmental sorbents (Sparks, 1989). Studies on the uptake rates of HOCs are needed to assess the equilibrium time required for sorption isotherm experiments. Although experimental conditions in the laboratory may differ from that of real environmental systems, results of such studies are still relevant in modeling the mobility of contaminants in terrestrial and aquatic systems. In effect, it allows for prediction of surface water pollution and/or groundwater contamination over time. Moreover, sorption as well as desorption kinetics greatly aids in remediation efforts (Farrell and Reinhard, 1994; Sparks, 1989; NKedi – Kizza et al., 2006).

The kinetic approach to equilibrium in laboratory studies varies from days to weeks or even several months in length. In the field it takes much longer to attain equilibrium, which may never reach true equilibrium, as the conditions in the environment are more heterogeneous and dynamic. Various models have been put forward in order to better evaluate sorption kinetics, experimental data, and to identify sources of non-equilibrium.

Non-equilibrium processes are also known as rate-limiting, or processes that proceed slowly. Two major classifications have been suggested: transport related non-equilibrium and sorption related non-equilibrium. The former phenomenon is attributed to a presence of macroscopic heterogeneities in the sorbent that affects the flow of liquids (Brusseau and Rao, 1991). This effect is generally less significant in laboratory studies, since sorbents are often sampled homogeneously in terms of size. In the environment, the presence of different sizes of

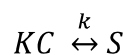
soil and aquifer aggregates, as well as variable porosities and tortuosities, are apparent and may have a pronounced effect on transport related non-equilibrium.

Sorption related non-equilibrium are primarily credited to rate-limited mass transfers across a boundary, or diffusion processes within the sorbent (Wu and Gschwend, 1986). Three probable diffusion mechanisms leading to sorption related non-equilibrium are film, restricted intraparticle, and intrasorbent diffusion. Film diffusion is considered negligible, compared to the other two diffusion processes in the retention and release of HOCs (Brusseau and Rao, 1989). Restricted intraparticle diffusion is associated with the existence of micropores in sorbent particles, such as in silica and quartz or sand. Basic assumptions of restricted intraparticle include 1) micropores are rigid; and 2) since organic matter predominates the uptake organic matter must reside inside the micropore walls in the case of HOCs (Wu and Gschwend, 1986; Ball and Roberts, 1991).

The rate-limited transport of sorbate within the matrices of the sorbent is ascribed to intrasorbent diffusion (Brusseau et al., 1991). Once again, the premise for an uptake of HOCs is that the diffusive mass transfer mainly occurs within the matrices of organic matter. Thus, intrasorbent diffusion also is known as intraorganic matter diffusion (Brusseau and Rao, 1989). Another important assumption of intraorganic matter diffusion is that organic matter is polymeric and its interstices are dynamic in nature. From this polymeric view of SOM, in general, the conformation of organic matter, as well as the hydration state changes as a result of pH and ionic strength. For example, at very acidic pH values ($\text{pH} < 3$), most of the carboxylic and phenolic moieties in SOM reside in their protonated or unionized form, thereby intra- and intermolecular H-bonding between these moieties is facilitated. This leads to a collapsed, more condensed form of SOM, where micropores or voids are expected to diminish in size and number (Stevenson, 1994; Rausa et al., 1991; Sutton and Sposito, 2005). At environmental pH ranges ($\text{pH} \sim 4\text{-}8$), the

aforementioned moieties most likely exist in ionized forms; this would pertain to especially carboxylic groups in humic materials, because their pK_a are ~4-6 (Schwarzenbach et al., 2003) and to a lesser degree, the phenolic groups. The presence of negative charges due to carboxylate and phenolate groups will result in repulsion between these moieties; hence, SOM adapts a more open conformational structure. Conformational rearrangement also occurs as a result of the hydration level/state of SOM. Drying of the soil removes water from the surface of SOM, as well as the assembly view of SOM; this once again will result in a collapsed form of SOM, as explained earlier. As the soil wets, water diffuses into SOM micropore and H-bonds with electronegative moieties of SOM. At lower moisture content (<12%) water acts as a crosslinker, thereby SOM retains a rigid form (Schaumann and LeBoeuf, 2005). At a moisture content >12% and at a longer period of time, more water molecules will surround these electronegative moieties, hence less intra- and intermolecular SOM bonding will be present. The result becomes an “expanded/swelled” or more flexible form of SOM, similar to the transition in polymers from glassy to rubbery states (Schaumann and LeBoeuf, 2005; Pignatello, 2009).

One particular site mass transfer model, represented below, describes sorption kinetics as a first order reaction (Wu and Gschwend, 1986, Nzungung et al., 1997).



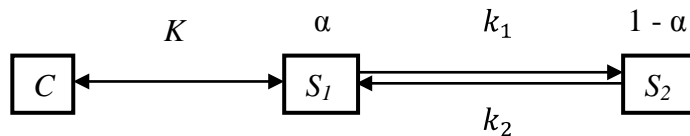
where k is the mass transfer coefficient, modeling a function of various sorbate physico-chemical properties, as well as sorbent characteristics (Nzungung et al., 1997). Furthermore, the model is hypothesized as having only one type of sorption site; the sorption to this site is generally slow. Rapid binding sites are thus considered to be nil (Nzungung et al., 1997). As a whole, it has been found that one-site models, is a typical means of representing experimental data, may yield less than accurate results.

Two-site models may be evaluated by applying diffusion equations or first-order mass

transfer equations (Selim et al., 1976; Cameron and Klute, 1977). Mathematical solutions to diffusion-based models require that the rate-limited mechanism involved must be fully elucidated (Brusseau et al., 1989). In addition, detailed information regarding sorbate and sorbent properties that affect diffusion of HOCs must be known (Brusseau et al., 1989). These requirements may make the use of diffusion-based models daunting in application. Although the first order mass transfer models are a simplification of the former, these may provide results that are comparable to diffusion models (Hance, 1967; Wu and Gschwend, 1986; Brusseau and Rao, 1991; Selim et al., 1976; Cameron and Klute, 1977). For these reasons, mass transfer models may be preferred in representing various non-equilibrium processes.

Two-site models are more common, as most sorption kinetics data depict an initial fast uptake, followed by a segment of slow sorption to equilibrium (Wu and Gschwend, 1986). This conceptualizes the presence of two classes of sorption sites. Moreover, it may correspond to a sorbent with a characteristic geometry involving an outer layer which is easily accessible by sorbate and an inner layer where sorbate interaction is expected to be rate-limited (Wu and Gschwend, 1986; Streck et al., 1995).

In this study, the two site non-equilibrium (TSNE) approach was used to fit our sorption kinetic data. The TSNE sorption model assumes the presence of two possible sorption domains (S_1 and S_2). Sorption in S_1 is usually rapid, while in S_2 it is slow, and may be solved by first order kinetics (Brusseau, 1991, Nkedi-Kizza et al., 2006).



Mathematical treatment of the system was adopted from Nkedi-Kizza (2006), which yields to the following solution:

$$\frac{C}{C_0} \equiv \frac{1}{R} + \left[\frac{1}{FR} - \frac{1}{R} \right] \exp \left[- \left(\frac{k_2}{F} \right) t \right]$$

where:

C = sorbate concentration in solution at a certain time

C_o = initial sorbate concentration

R = retardation factor

F = fraction of retardation in the fast uptake region

k_2 = rate constant for desorption from S_2 domain

t = time

α = fraction sorbed in S_1 domain

K = sorption partition coefficient

From the above equation, the three parameters α (from F), k_2 , and K can be and were obtained from the non-linear fitting procedure of C/C_o versus time using Sigma Plot Software version 10 (Systat Software Inc., 2006). The proceeding equations describe the derivation of TSNE. At equilibrium (time $=\infty$), sorption occurs in two domains (S_1 , S_2)

$$S_1^{[\infty]} = \alpha KC^{[\infty]} \quad (1)$$

$$S_2^{[\infty]} = (1 - \alpha)KC^{[\infty]} \quad (2)$$

Thus, the total amount of sorption at equilibrium is given by:

$$S_T^{[\infty]} = S_1^{[\infty]} + S_2^{[\infty]} \quad (3)$$

It is also assumed that part of the sorbate in site 1 will eventually sorb to site 2:

$$\frac{\partial S_2}{\partial t} = k_1 S_1 - k_2 S_2 \quad (4)$$

At equilibrium, $\left(\frac{\partial S_2}{\partial t}\right)_{t=\infty} = 0$

and thus Equation 4 can be written as:

$$k_1 S_1 = k_2 S_2 \quad (5)$$

By substituting Equations 1 and 2, Equation 5 reduces to:

$$\frac{k_1}{k_2} = \left(\frac{1-\alpha}{\alpha} \right) \quad (6)$$

The total amount of pesticide sorbed to the soil is given by:

$$A = VC + mS_1 + m S_2 \quad (7)$$

where A = total mass of sorbate, V = volume of solution, and m = mass of soil

If S_1 in Equation 1 is substituted into Equation 7:

$$A = VC + m\alpha KC + m S_2$$

$$A = (V + m\alpha K)C + m S_2 \quad (8)$$

$$\text{At } t=0, A = (V + m\alpha K)C^{[0]} + m S_2^{[0]} \quad (9)$$

At any given time:

$$m S_2 = A - (V + m\alpha K)C \quad (10)$$

At equilibrium ($t = \infty$), $S_2 = (1 - \alpha) KC$, the equilibrium solution concentration can be solved by:

$$C^{[\infty]} = \frac{A}{(V+mK)} \quad (11)$$

$$(V + m\alpha K) \frac{\partial C}{\partial t} = k_2 m S_2 - k_1 m\alpha KC \quad (12)$$

Substituting k_1 ($k_1 = \left(\frac{1-\alpha}{\alpha} \right) k_2$) from Equation 6 and S_2 from Equation 9, we get:

$$(V + m\alpha K) \frac{\partial C}{\partial t} = k_2 A - k_2 (V + m K)C \quad (13)$$

Equation 13 may be represented as a linear equation (Perry and Green, 1997):

$$\frac{\partial y}{\partial x} + P(x)y = Q(x)$$

A solution to this differential as applied to Equation 13 yields Equation 14

$$C(V + m K) - A = [(V + m K)C - A]e^{-\left(\frac{k_2}{F}\right)t} \quad (14)$$

where $F = \frac{V+m\alpha K}{V+m K}$

By substituting Equation 11 ($C^{[\infty]} = \frac{A}{(V+mK)}$), Equation 14 is reduced to:

$$C = C^{[\infty]} + (C^{[0]} - C^{[\infty]})e^{-\left(\frac{k_2}{F}\right)t} \quad (15)$$

which in turn can be represented by the equation below:

$$\frac{C}{C_0} = \frac{1}{R} + \left(\frac{1}{FR} - \frac{1}{R}\right) + \exp\left[-\left(\frac{k_2}{F}\right)t\right] \quad (16)$$

where the initial conditions upon adding a pesticide solution of certain concentration can be described below (Nkedi-Kizza et al., 2006):

$$A = V C_0 \quad S_1 = \alpha C_0 \quad S_2 = 0$$

$$C^{[0]} = \frac{VC_0}{V+m\alpha K} \equiv \frac{C_0}{FR}$$

$$R = 1 + MV^{-1}K$$

$$C^{[\infty]} = \frac{VC_0}{V+mK} \equiv \frac{C_0}{R}$$

$$F = \left(\frac{1 + \alpha MV^{-1}K}{R}\right)$$

Most studies on non-equilibrium processes carried out on air-dried soils become slurried upon addition of sorbate solutions. However, it is shown in the literature that fully saturated soils may behave differently. Neutral nonpolar sorbates such as benzene were observed to have a greatly reduced partitioning when sorption was initiated from water solution, or from pre-water soaked sorbent, compared to a dry sorbent containing high organic matter content (Rutherford and Chiou, 1992a; 1992b). In one study, chlortoruron uptake over time with field-moist soil and sand was lower than when using the same sorbents, air-dried (Altfelder et al., 1999). Other investigations have shown that sorption increased when the soil was subjected to drying and rewetting cycles after pesticide application (Shelton et al., 1995; Gamble et al., 2000; Lennartz and Louchart, 2007).

Different postulates, offered in an attempt to explain the above observations, are

discussed below. Structural and chemical reorganization of organic matter particles occur when soil is subjected to drying or wetting, which affects the uptake of HOCs (Lennartz and Louchart, 2007). A change in activation energies in the interactions between HOCs and NOM interfaces may result when the solid interface is subjected to changes in soil water content (Calderbank, 1989; Li et al., 1996; Belliveau et al., 2000). In yet another case, it has been hypothesized that hydration increases the polarity of SOM, thereby decreasing the partitioning of nonpolar compounds to SOM (Rutherford and Chiou, 1992b). Previous explanations mainly point to the influence of wetting on sorbent properties and subsequently on sorbate-sorbent equilibrium interactions.

Belliveau et al. (2000) kinetically monitored the water uptake of an air-dried soil through magnetic resonance imaging (MRI); the soil was pre-soaked overnight. Results show that longer time spans from days to months, were needed to achieve a water-soil equilibrium, suggesting that air-dried soil may recover very slowly from pore structure deformation. Low-field NMR relaxation studies on fractionated soil components, artificial soils, and whole soils show differences in wetting behavior (Todoruk et al., 2003). It was found that the wetting of initially oven-dried montmorillonite is instantaneous with short T_2 s (spin-spin relaxation time), found to be a characteristic of micropore-bound water. In comparison, silica particles took approximately two days to reach equilibrium state. On the other hand, humin wetting is also rapid, with short T_2 values approximating the presence of mesopores and micropores. Humic acid has a slightly longer wetting time of three hours, with all of these representing water migration into micropores. In contrast, wetting of whole soils demonstrates a minimum of three possible water compartments designated as macropores, mesopores, and micropores. It should be noted that this classification is not to be confused with the IUPAC definition of pore sizes in consolidated media. At least two rates were observed: a fast process occurring within 24 hours, and a slow

process that may last for several days. In addition, shorter T_2 peaks, attributed to micropores, develop and dominate over time. From the above observations, it has been concluded that wetting allows swelling, which can be attributed to pore reopening and pore reformation (Belliveau et al., 2000; Todoruk et al., 2003; Schaumann and LeBoeuf, 2005; Borisover, 2001). The implication of the findings above, with respect to HOC uptake may be emphasized with a two step-sorption model. The first step is adsorption of HOC at the surface, followed by a rate-limited diffusion into the sorbent matrix (Belliveau et al., 2000; Kan et al., 1998; Borisover, 2001; Schaumann and LeBoeuf, 2005).

In summary, previous studies demonstrated that the wetting behavior of separate soil components differs from whole soils. It is thus recommended that further investigations be done to elucidate the effect of wetting on solid surfaces and organic matter-mineral interassociations, and on the mechanisms of HOC uptake. Furthermore, experiments to this effect must include presoaking of sorbent with water, taking into account that wetting of soils may take several days (Gamble et al., 2000; Li et al., 1996; Belliveau et al., 2000; Schaumann and LeBoeuf, 2005).

Keeping these suggestions in mind, this study involves the use of pesticides of different polarities and sorbents of different organic matter and mineral contents, as well as three different hydration conditions (dry, 1 day, and 5 day prewet) in the study of sorption kinetics and sorption-desorption isotherms. Our hypothesis is that soil hydration will affect the rate of uptake of HOC based on our model, which was developed from 2-D ^1H - ^{13}C HETCOR NMR, presented in Chapter 4. The specific objectives are as follows: 1) to determine the influence of NOM and mineral content on sorption, as well as the kinetics of the uptake of HOCs in dry and wet soils; 2) to investigate how pesticide polarity and structure affect sorption phenomena; 3) to evaluate possible sources of non-equilibrium sorption rates; and 4) to compare the K_{OC} obtained from sorption kinetics with that of the K_{OC} derived from isotherms.

6.2 Method

Samples of appropriate soil to solution ratio, as previously determined, were incubated for various time intervals. The goals of this step were 1) to determine the time needed to reach sorption equilibrium; 2) to measure the amount of analyte sorbed over the duration of the study; and 3) to evaluate sorption kinetic parameters. The sample analysis was conducted using the parallel method, wherein a different set of samples were prepared for each time period needed to complete sorption kinetics studies (OECD, 2000). At the end of the study, a graph was drawn relating incubation time (hours) to the amount of pesticide sorbed in soil, in the form of relative pesticide concentrations (C/C_0) (Figures 6.2.1 - 6.2.3). The sorption coefficient at equilibrium (K) is then calculated from the curve fitting of Equation 16. It is a nonlinear equation with the form: $y = y_0 + ae^{-bx}$ where y is the relative pesticide concentration and x is incubation period in hours. K is defined as the ratio of the concentration of pesticide adsorbed in soil at equilibrium (mg/kg), and the concentration in aqueous solution phase (mg/L), as described below

$$K = \frac{C_{soil}}{C_{aq}}$$

The parameters α , k_2 and F were also obtained from model fitting.

The best fit line and the parameters, as well as their corresponding standard errors for this non-linear regression, were obtained via the use of the Marquardt-Levenberg algorithm, as implemented in Sigma Plot version 10 (Systat Software, Inc., CA). The Marquardt-Levenberg algorithm returns the values of the parameters by minimization of the least squares error between the actual values and predicted values of the dependent variable. Yield results were within the 95% confidence limit. R^2 is the coefficient of determination, showing how well it fits the model.

6.2.1 K_{OC} in Pahokee Peat

Pahokee Peat is classified as an agricultural peat soil of the Florida Everglades, wherein freshwater marshes contribute to highly organic matter make-up (<http://ihss.gatech.edu>). In

addition, it is a soil type of very poor drainage with an elemental composition of 46.90% C, 3.90% H, 30.30% O and 3.42% N. For additional information, the reader is referred to Table 5.3.1.

It can be seen by the fitted curves in Figures 6.2.1 through 6.2.3, as well as by the values of R^2 (0.92-0.97), reported in Table 6.2.1 through Table 6.2.3, demonstrating that the TSNE model fits the experimental data well. The observed minimal to zero differences in K_{OC} between a dry and one day prewetted soil implies that the time needed for water-soil equilibration may take longer than 24 hours. This is supported in the literature, wherein the wetting process of a whole soil has a fast component that may take up to a maximum of 24 hrs, coupled with a slow component that is longer and may reach up to 5 days, 22 days, or even longer (Todoruk et al., 2003; Belliveau et al., 2000; Gamble et al., 2000; Schaumann and LeBoeuf, 2005). In addition, normalized TOC data (Figure 5.5.2), as well as excitation and emission matrix studies (Figure 5.5.3) on soil controls from kinetic studies, demonstrate a minimum of two-rate components in the wetting process, with the fast step occurring at less than 20 hours.

Flutolanil exhibited the highest difference (14.70%) in K_{OC} between a dry and 5 day prewetted condition (Figure 6.2.4). In addition, the K_{OC} trend in relation to the pesticide type is clearly shown to be flutolanil > norflurazon > acifluorfen, which strongly correlates with hydrophobicity in terms of water solubility ($R^2 = 0.91$) with an octanol water partition coefficient ($R^2 = 0.999$).

The results for Pahokee Peat are not surprising. Pahokee Peat is a highly organic soil (93.8% organic matter, assuming % organic matter = $2 \times$ % organic carbon). Thus, uptake is attributed primarily to a diffusive mass transfer within the organic matter matrix (Madhunet et al., 1986; Nkedi-Kizza et al., 2006; Brusseau et al., 1991; Schwarzenbach and Westfall, 1981). For HOC sorption in aqueous systems, diffusion of water in SOM is necessary (Gamble et al.,

2000; Belliveau et al., 2000). The polymeric model point of view, as SOM is hydrated, it forms a more open and flexible form (i.e., gel-like or rubbery phase). The more hydrophobic the contaminant, the more it partitions to this phase. The lower sorption affinity of an HOC on a 5 day prewetted SOM suggests that the water competes with HOC for sorption sites.

From our domain perspective of SOM, discussed earlier in Chapter 4, hydrophobic moieties are readily available as sorption sites in a dry soil. This includes the isolated alkyl type domain and those aromatic moieties which have migrated to the surface of the second domain during the air drying process. Thus, a more hydrophobic aromatic contaminant will show high sorption in a dry soil. In contrast, in a wet soil, the alkyl moieties will still be available as sorption sites, while the second domain would experience a conformational rearrangement, such that the hydrophilic moieties would be more available on the outer layer. Hence, sorption of aromatic HOCs is reduced.

In comparison with flutolanil, sorption of norflurazon in Pahokee Peat exhibited no statistical difference between a one day prewet and a five day prewet. This can be explained by the preference of norflurazon for polar forces, such as strong hydrogen bonding with -COOH , and -OH containing hydrophilic moieties in SOM due to azine and amino groups in norflurazon structure. It also means that in a wet soil, this preference effectively competes with water for sorption in hydrophilic SOM moieties. Thus, the effects of drying and wetting cycles on sorption of contaminants, is found to be more pronounced in hydrophobic HOCs.

6.2.2 K_{OC} in Mandeville Soil

The Mandeville soil comes from a wetland in Louisiana. It contains a medium amount of organic matter (21.68% organic matter), compared with the other two soils (Table 5.3.1), and a relatively high amount of sand (49.38%) relative to the other soils. Additional information on this soil is provided in Table 5.3.1.

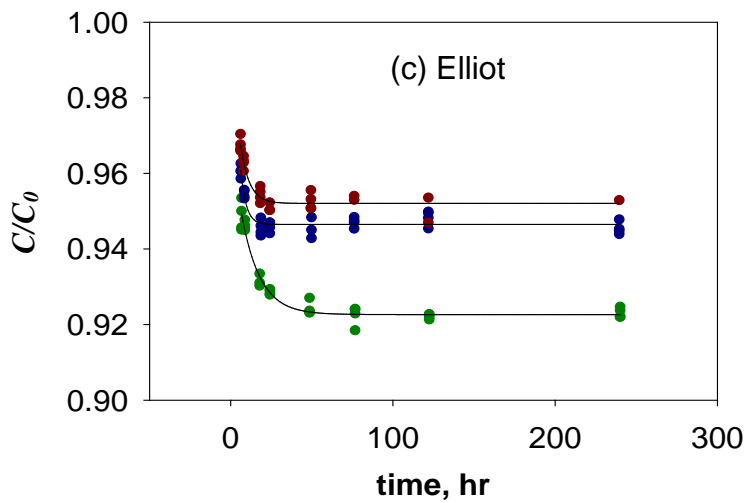
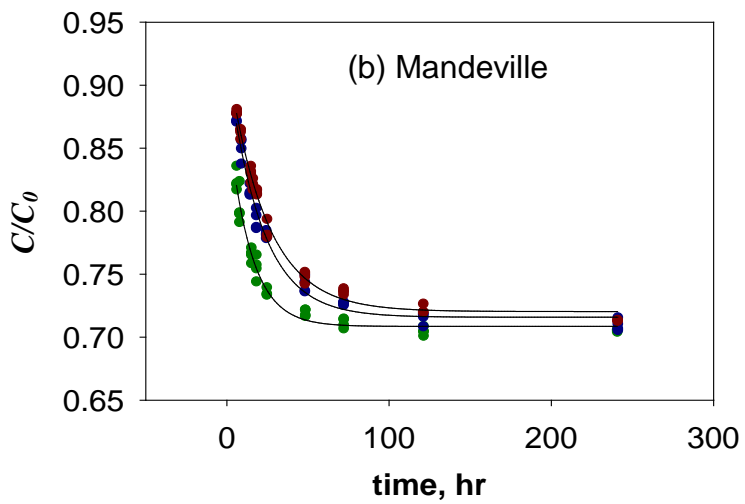
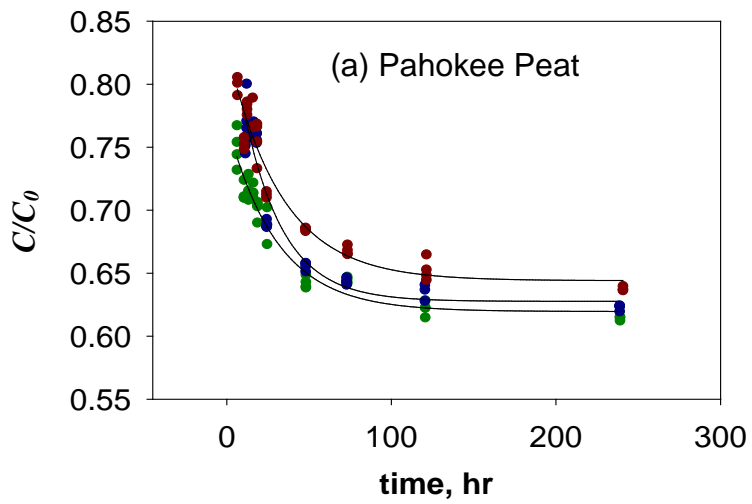


Figure 6.2.1 Sorption kinetics of acifluorfen in dry (green), 1 day prewetted (blue), and 5 day prewetted (red) Pahokee Peat (a), Mandeville (b) and Elliot (c) soils.

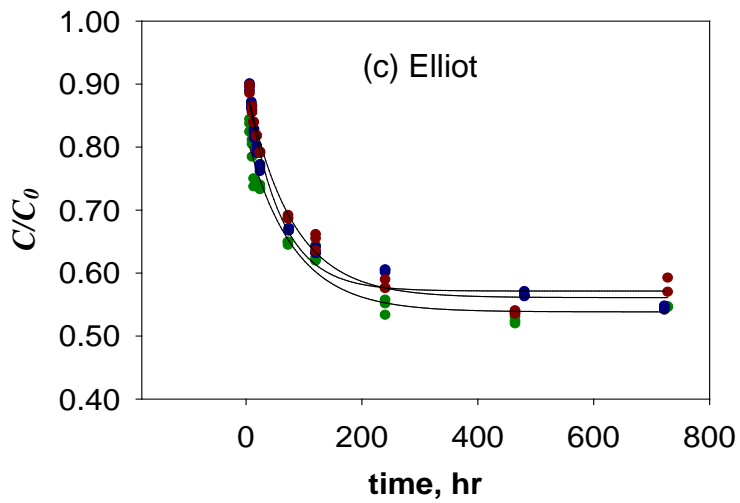
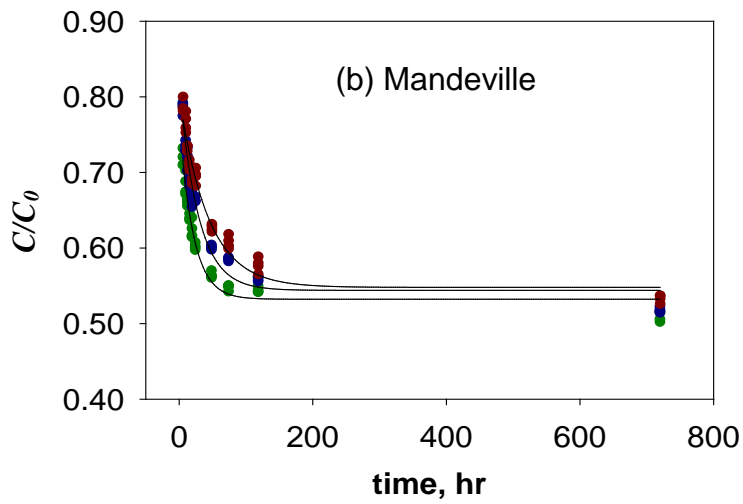
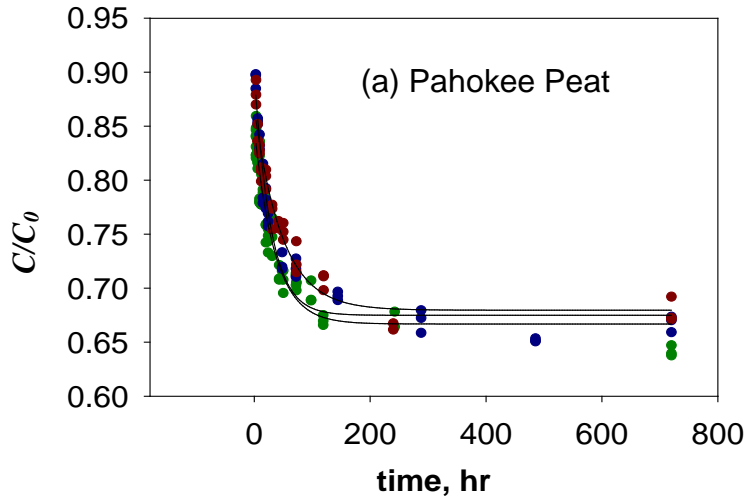


Figure 6.2.2 Sorption kinetics of norflurazon in dry (green), 1 day prewetted (blue), and 5 day prewetted (red) Pahokee Peat (a), Mandeville (b) and Elliot (c) soils.

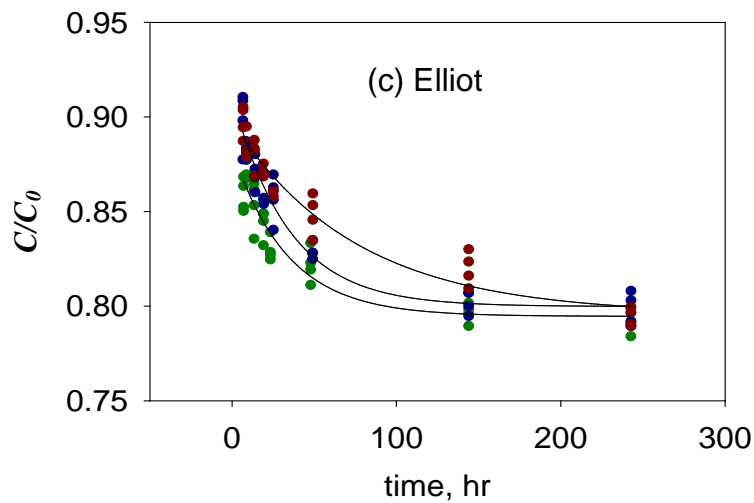
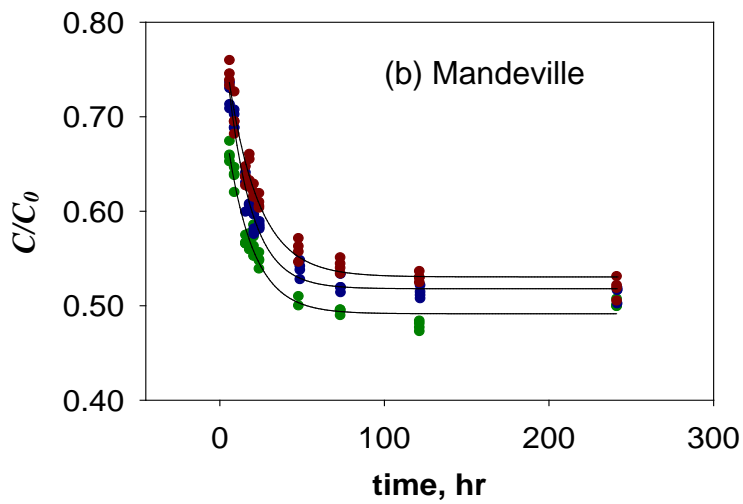
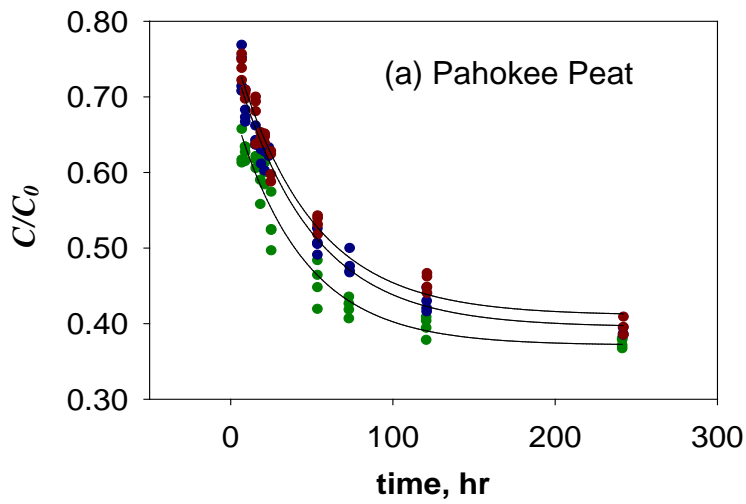


Figure 6.2.3 Sorption kinetics of flutolanil in dry (green), 1 day prewetted (blue), and 5 day prewetted (red) Pahokee Peat (a), Mandeville (b) and Elliot (c) soils.

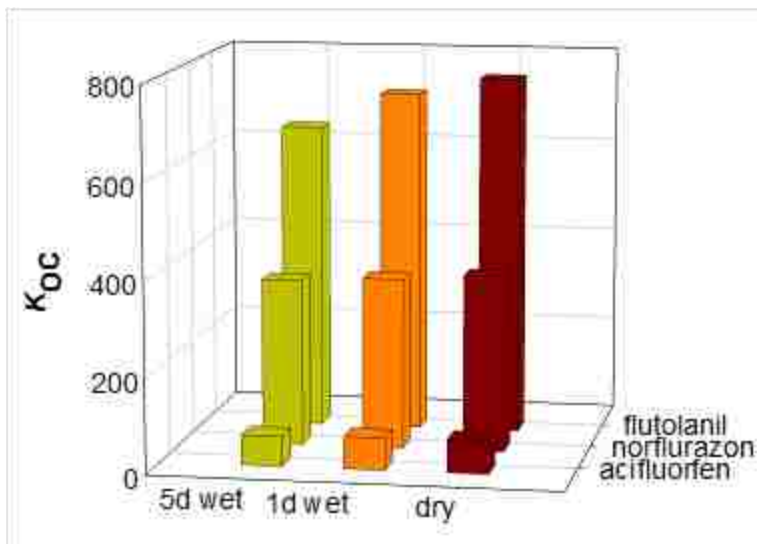


Figure 6.2.4 K_{OC} in Pahokee Peat

Experimental sorption kinetics data in Mandeville soil exhibited the best TSNE model fits for the soils studied, with R^2 values of 0.96-0.99 for the three pesticides: acifluorfen, norflurazon, and flutolanil. This may also be seen from Figure 6.2.5 and the data in Table 6.2.2. The K_{OC} of each pesticide in an initially dry Mandeville soil is higher than those of pre-hydrated soils. This difference is once again more pronounced in the most hydrophobic pollutant flutolanil, with a percent difference of 14.33% between dry and five day prewet. K_{OC} values of the three pesticides in Mandeville reflects that flutolanil > norflurazon > acifluorfen, relating to the hydrophobicity of the molecules ($R^2 = 0.82$, with respect to K_{OC} correlation with water solubility, and $R^2 = 0.96$ with respect to octanol-water partition coefficient). However, the correlation coefficient is lower than that of Pahokee Peat, suggesting that sorption of these compounds is not only due to the amount of organic matter, but possibly the type and nature of organic matter present may be the cause or part of the cause.

Flutolanil and acifluorfen exhibited the highest Koc in Mandeville soil, compared to Pahokee Peat and Elliot soils. Increased sorption capacity of flutolanil and acifluorfen in Mandeville may be due to its additional mineral components, especially the sand component. The presence of an appreciable amount of sand in the Mandeville soil may provide additional

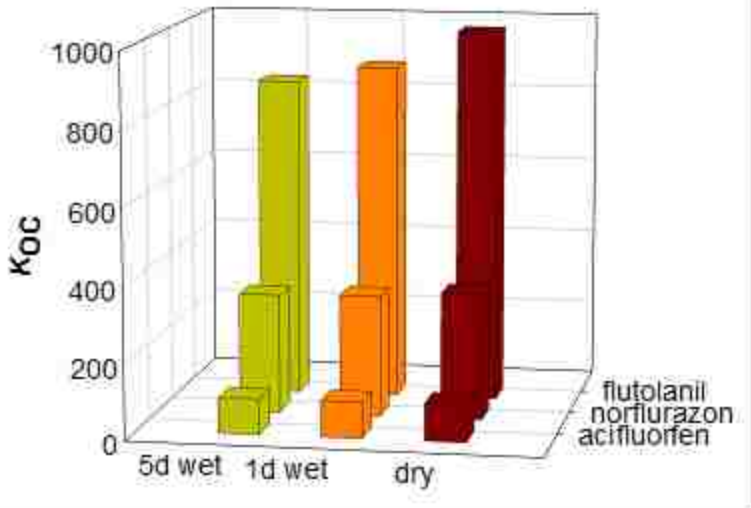


Figure 6.2.5 K_{OC} in Mandeville

binding sites by diffusion into micropores (Sparks, 1989; Brusseau et al., 1991; Brusseau and Rao, 1991; Todoruk et al., 2003). However, the TSNE model may not account for these sorption sites (Farrell and Reinhard, 1994). Mineral grains such as sand may be coated with NOM, and such individual sand grains may aggregate to form pores of varying sizes, such as “hydrophobic nanopores” as explained in Chapter 5. The presence of these hydrophobic nanopores, would then allow certain hydrophobic pollutants to diffuse inside, providing the size of the pollutant is smaller than the critical diameter of the nanopore (Pignatello, 2000). Sorption of flutolanil in soils with high sand content has been shown to be higher (Daly, 1987). Additional sorption of flutolanil to the sand surface would be through aromatic π -H binding with silanol groups. The negative quadrupole moment located above and below the aromatic ring of flutolanil that contains the amide and ether substituent can exhibit H-bonding with free silanol, as explained in Chapter 5.

The presence of Na-montmorillonite clay, by which diffusion within the clay is likely to occur upon clay swelling may also cause an increase in sorption. The presence of Na-montmorillonite and smectite (from muscovite) clay types in Mandeville soil may also add to increased sorption of flutolanil and acifluorfen in this soil, compared to Pahokee Peat. Na-

montmorillonite is a highly swelling 2:1 type of clay. Diffusion of water into the interlayer spacing (swelling) of this clay increases the distance between the interlayer spacing, as water hydrates the interlayer cation (i.e., Na^+). In addition, water also forms layers, or films, on the surface, of these negatively-charged interlayers. Clay swelling enlarges the surface area for sorption of contaminants. However, only sorbates, capable of favorable interactions with the clay interlayer surfaces, may exhibit sorption to these sites. Flutolanil and acifluorfen can sorb to these sites, based on their structures and electrostatic surface potential, as discussed in Chapter 5.

The above K_{OC} results for Pahokee Peat and Mandeville soil corroborates our previous model that an initially dry soil will sorb more HOC. The more hydrophilic molecules will tend to reside inside the NOM domain. The more hydrophobic molecules, on the hand, will migrate on the outer surface of the NOM as a soil dries.

6.2.3 K_{OC} in Elliot Soil

Elliot soil comes from the grasslands of Illinois and is classified as fine, illitic, mesic Aquic Arguidoll (<http://ihss.gatech.edu>; <http://ssldata.nrcs.usda.gov>). Among the three soils, this soil has the least amount of organic matter, 5.8% (Table 5.3.1). The mineral fraction consists of 28.55% clay, 57.74% silt, and 6.39% sand. Additional soil properties are given in Table 5.3.1.

Figure 6.2.6 and Table 6.2.3 reveal that fitting the TSNE model to kinetics experimental data results in higher K_{OC} in dry, compared to wet, Elliot soil for norflurazon only ($R^2 = 0.96-0.97$). Sorption of acifluorfen and flutolanil are lowest in Elliot soil among the soils of this study and are concentration-dependent. The lower uptake of acifluorfen in Elliot soil can be explained by the pH of Elliot soil, further explained under the discussion of acifluorfen sorption. Elliot soil also has lesser sand content, which might partly explain the lower observed K_{OC} in Elliot soil than in Mandeville soil. Lesser porosity corresponds to a lower contribution from intraparticle mass transfer.

Elliot soils also contain illite clay (also known as hydrous micas), which is characterized by low to medium swelling only, in contrast with high swelling montmorillonite clay in Mandeville soil. This difference between the type of clay in Mandeville and Elliot soils can have a significant impact on sorption. The swelling of illite clays may not provide enough surface area to allow diffusion into its interstices of the HOCs used in this study. The effect of clay composition, especially of highly expandable clays, was discussed under section 6.2.2. In addition, the nature of organic matter in Elliot soil, as well as the interplay between its organic matter and mineral components, may influence its sorption capacity.

The sorption of norflurazon to Elliot soil and Pahokee Peat are comparable in both kinetics and isotherm results. This leads us to conclude that norflurazon binding is almost solely influenced by organic carbon content. This is in agreement with a previous report that norflurazon binding to soil is primarily a function of organic matter content (Morillo et al., 2002; 2004). Therefore, sorption of HOCs in soils with little or no expandable clay content and less sand content, are the result of organic matter.

The TSNE model is not applicable to sorption of acifluorfen in one day and five day prewet Elliot soil, as it provides a fraction of instantaneous sorption value, α , equal to 0. This implies that sorption in Elliot soils can be better described by a one-site non-equilibrium model, where the kinetics of uptake is generally slow at all times.

6.2.4 Sorption K_{OC} of Acifluorfen

The sorption capacities (K_s) of acifluorfen in dry soil, obtained from a TSNE curve fitting, follow the trend that Pahokee Peat > Mandeville > Elliot. Of the three studied pesticides, acifluorfen exhibited the lowest K_{OC} . Acifluorfen is a slightly-ionized, nonpolar, organic compound with a pK_a of ~ 3.5 (Roy et al., 1983), while Pahokee Peat, Mandeville, and Elliot soils

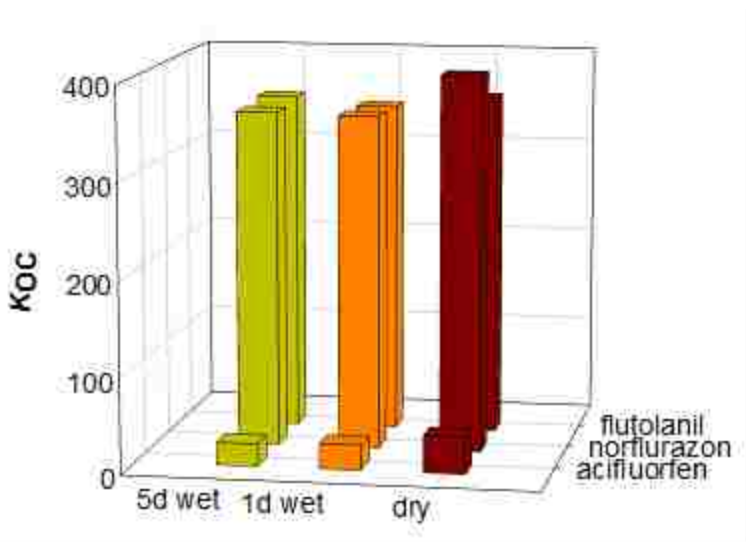


Figure 6.2.6 K_{OC} in Elliot Soil

have pH values of 4.20, 4.62, and 6.1 respectively, in water (Table 5.3.1). At these soil pH values (4-6), acifluorfen exists mainly in its anion form. The carboxylic groups in SOM are also ionized at this pH and to a lesser extent, the phenolic groups (Stevenson, 1994; Schwarzenbach et al., 2003). Therefore, the anion form of acifluorfen will most likely be repelled by these negative charges, except for the amino groups, which are likely to be protonated/positively charged at acidic pHs. Thus, the soil pH affects, in part, the sorption of acidic pesticides (Saltzman and Yaron, 1986). The lower pH in both Pahokee and Mandeville explains the higher sorption of acifluorfen to these soils, because more of acifluorfen exists in nonionic form. In its neutral state, aside from Van der Waals interactions with SOM, the COOH groups in acifluorfen will most likely form strong hydrogen-bonds with the nitrogen-containing moieties in SOM, especially the amino groups and azines, while the NO₂ group may form very weak hydrogen-bonds with amino and amide groups within SOM (Gilli, 2009).

The slightly higher K_{OC} for Mandeville soil, compared to Pahokee Peat, may also be explained by the difference in the nature of organic matter between these two soils. However, as stated earlier, the presence of an appreciable amount of sand grains may have increased sorption into Mandeville soil. In addition, the presence of the montmorillonite type of clay in Mandeville

soil has been identified by X-ray data (Figure 5.7.1). It has been suggested that in montmorillonite clays, acifluorfen has the possibility of complexing with divalent and trivalent cations (Pusino et al., 1991; Pusino et al., 1993). Mandeville soil has a high cation exchange capacity (Table 5.3.1), with high amounts of Al^{3+} and Ca^{2+} (Table 5.3.2), which in turn adds to the effect of increased sorption in Mandeville soils. This can be attributed to the presence of a more ionized form of soil solution pHs, greater than acifluorfen's pK_a (Locke et al., 1997), since an acifluorfen carboxylate group may form complexes with these and other metal cations (Kozłowski et al., 1990; Pusino et al., 1991). This view is supported by Spartan calculations (Figure 5.3.2), where a negative electrostatic potential density is located in the vicinity of the $\text{NO}_2\text{-COOH}$ functional groups.

6.2.5 Sorption K_{OC} of Norflurazon

K_{OC} values of norflurazon for initially dry soils show the trend of Elliot > Pahokee Peat > Mandeville. Norflurazon is a neutral nonpolar compound, yet is less hydrophobic than flutolanil. It has a surface volume of 254\AA^3 and a surface area of 277\AA^2 (Table 5.3.3). The modeled electrostatic potential surface of norflurazon reveals the following: a concentrated, but highly negative, potential in the vicinity of its carbonyl; an area of highly positive potential centered on two nitrogens in its aromatic ring and amine side chain; a slightly negative potential on the aromatic ring that contains the CF_3 group; and a negative electrostatic potential around its CF_3 substituent. Based from its structure and electrostatic potential surface, binding of norflurazon is mainly due to H-bonding, induced dipole, and Van der Waals interaction (Saltzman and Yaron, 1986). If norflurazon sorption is solely due to organic matter content, then the K_{OC} should be constant in all soils.

The higher K_{OC} value of norflurazon sorption to Elliot, compared to the Mandeville soil, can be explained by the higher concentration of silt, coupled with the lower sand content in Elliot

soil. Silt is composed of smaller particles than sand, and requires a higher surface area for sorption, as the latter is often inversely correlated with the square of the particle radius (Pignatello, 2009; Ball and Roberts, 1991; Kleineidam et al., 1999; Wu and Gschwend, 1986; Pignatello, 1990; Steinberg et al., 1987). In addition, norflurazon's K_{OC} values for Elliot and Pahokee Peat soils are higher than in Mandeville soil. It may be postulated that the former soils have older, and therefore more condensed/humified organic matter, while Mandeville soil may be postulated as a younger soil. The researcher observed during soil collection that its topsoil consists of plant debris at various stages of decomposition; hence the presence of a more rubbery phase of NOM is expected.

6.2.6 Sorption K_{OC} of Flutolanil

Flutolanil is the most hydrophobic of all the pesticides used. Its molecular surface area depicts a larger area of positive, electrostatic potential and a small, but dense, highly negative electron density, centered on the carbonyl of the amido group.

The K_{OC} values based upon sorption kinetics reveal the following trend: Mandeville > Pahokee Peat > Elliot soil, regardless of hydration condition. Additional sorption to sand grains once again is the probable explanation for the observed trend. Furthermore, the above observation may also imply that the nature and type of the NOM present also affects sorption. The lower flutolanil sorption in Elliot soils, as compared with Pahokee Peat, may mean that intimate mineral and NOM associations in Elliot soil may restrict diffusion of this hydrophobic contaminant into hydrophobic NOM sites.

6.2.7 k_2 Values and k_2 - K Relationships

Sorption desorption rates are governed by diffusion processes of sorbate into sorbent and thereby greatly influence transport and bioavailability of contaminants (Pignatello, 2009). Diffusion is defined as the tendency of molecules to move about and redistribute as a function of

concentration gradients (Pignatello, 2009). The diffusion of a molecule in a sorbent is affected by the molecular size and structure of the sorbate, the nature and geometry of the sorbent, chemical potential, interfacial boundary conditions, and temperature (Pignatello, 2000; Brusseau et al., 1991; Haws et al., 2006; Karger and Ruthven, 1992). Since neutral hydrophobic organic compounds mainly sorb to organic matter components in soils, the kinetic uptake or release is limited by intraorganic matter diffusion (Nkedi-Kizza, 2006). All pesticides have a lower k_2 value and a higher K value in Pahokee Peat than in Mandeville soil, because Pahokee Peat has a higher organic matter content. As organic matter content increases, the path to be traversed by the diffusing molecule becomes longer; hence, the k_2 value is low, which implies a slower diffusion. It has also been shown from this study by both sorption isotherm and sorption kinetics, that the derived K value is highly and positively correlated to organic matter content.

Acifluorfen has a lower k_2 value and higher K value in Mandeville soil than in Elliot soil. This is expected, because Mandeville soil carries a higher organic matter content. In addition, the lower k_2 in Mandeville soil may be attributed to diffusion in mineral grains (i.e., sand and clay). In Pahokee Peat, flutolanil also showed the smallest k_2 value; this finding supports the idea that more nonpolar HOCs will exchange more slowly into the SOM binding sites, due to the restricted diffusivity of bigger nonpolar molecules. The TSNE fit of flutolanil is lowest in Elliot soil ($R^2 = 0.88$), hence it is rather difficult to compare its kinetic parameters with that of flutolanil sorption in Pahokee Peat and Mandeville. In Mandeville and Elliot soils, k_2 values follow norflurazon < flutolanil < acifluorfen. The slower desorption of norflurazon in these soils may be attributed to a greater amount of varying interactions of norflurazon with the SOM of these soils, illustrated once again by the electrostatic potential. In addition, this molecule has a total of 5 proton acceptor/donor sites, and has the greatest amount and strength of hydrogen-bonding forces with SOM moieties, compared to the other two pesticides.

6.2.8 Fraction of Instantaneous Sorption, α

The variable α is defined as the fraction of pesticide partitioning in S_1 sites at equilibrium. The TSNE model described well the sorption kinetics in Pahokee Peat and Mandeville soils, showing that correlation fit, r^2 equal to 0.92 to 0.99. These soils contain high to intermediate organic matter content; hence the assumption of the TSNE model that intraorganic matter diffusion is the primary cause of slow sorption holds true. The fraction of instantaneous sorption α can only be compared between these two sorbents. In a dry Pahokee Peat soil, α is given to be acifluorfen > norflurazon > flutolanil, while α values in Mandeville soil are similar and within the experimental error. The results of α from Pahokee Peat support further the assumption in the TSNE model that for highly organic soils, diffusion into the organic matter interstices is the main reason for chemical non-equilibrium sorption.

It can also be deduced from the results that an initially dry Pahokee Peat or Mandeville soil has a higher α than prewetted counterparts, for all pesticides and soil combinations. This finding is in agreement with our domain-based SOM model described in Chapter 4. In a dry soil, hydrophobic moieties (alkyl and aromatic types) are both available for sorption, leading to an increased sorption of HOCs. The same α value for norflurazon found in a dry Pahokee Peat and Mandeville soil, is once again a strong indication that sorption of norflurazon is mainly, if not solely, due to organic matter.

6.2.9 Comparison of K_{OC} from Sorption Rate and Sorption Isotherm

K_{OC} values derived from sorption isotherm were compared to a kinetics model using the same starting initial concentration; the results were presented in Table 6.2.4 and will be represented here as K_{OCi} and K_{OCr} , respectively. For acifluorfen, K_{OCi} values are generally higher than from K_{OCr} values, except for five day prewet Mandeville and Pahokee Peat soils. The differences were statistically significant at a 95% confidence level, using the T-test.

Table 6.2.1 Sorption kinetics parameters in Pahokee Peat soil

Hydration Condition	k_2 (hr ⁻¹)	α	K	K_{oc} (L kg ⁻¹)	R^2
Flutolanil					
Dry	0.013(0.001)	0.245(0.013)	356.96(12.07)	761.12(25.75)	0.94
1d wet	0.010(0.001)	0.200(0.010)	339.72(10.34)	724.35(22.05)	0.97
5d wet	0.01(0.001)	0.203(0.011)	304.49(8.27)	649.23(17.63)	0.97
Norflurazon					
Dry	0.024(0.001)	0.359(0.014)	174.82(2.46)	372.76(5.25)	0.94
1d wet	0.026(0.002)	0.233(0.020)	169.09(2.45)	360.52(5.23)	0.96
5d wet	0.016(0.001)	0.326(0.020)	165.04(3.00)	351.89(6.40)	0.95
Acifluorfen					
Dry	0.026(0.002)	0.487(0.015)	32.57(0.37)	69.46(0.79)	0.95
1d wet	0.030(0.003)	0.269(0.037)	31.50(0.56)	67.17(1.20)	0.92
5d wet	0.024(0.002)	0.372(0.020)	29.44(0.49)	62.78(1.05)	0.94

Table 6.2.2 Sorption kinetics parameters in Mandeville soil

Hydration Condition	k_2 (hr ⁻¹)	α	K	K_{oc} (L kg ⁻¹)	R^2
Flutolanil					
Dry	0.042(0.002)	0.35(0.01)	107.19(0.94)	988.88(8.67)	0.97
1d wet	0.043(0.001)	0.22(0.01)	96.47(0.85)	889.94(7.81)	0.98
5d wet	0.035(0.001)	0.26(0.01)	91.84(0.99)	847.19(9.14)	0.97
Norflurazon					
dry	0.033(0.002)	0.34(0.01)	36.23(0.39)	334.23(3.61)	0.96
1d wet	0.023(0.001)	0.27(0.02)	34.67(0.58)	319.82(5.38)	0.96
5d wet	0.016(0.001)	0.30(0.01)	34.17(0.68)	315.18(6.30)	0.96
Acifluorfen					
dry	0.058(0.003)	0.33(0.02)	10.63(0.08)	98.10(0.71)	0.97
1d wet	0.038(0.001)	0.22(0.02)	10.27(0.08)	94.74(0.72)	0.98
5d wet	0.033(0.001)	0.21(0.01)	10.07(0.06)	92.86(0.59)	0.99

Table 6.2.3 Sorption kinetics parameters in Elliot soil

Hydration Condition	k_2 (hr ⁻¹)	α	K	K_{oc} (L kg ⁻¹)	R^2
Flutolanil					
dry	0.027(0.003)	0.51(0.03)	10.45(0.17)	360.52(5.93)	0.88
1d wet	0.026(0.002)	0.39(0.03)	10.12(0.16)	349.12(5.40)	0.94
5d wet	0.012(0.002)	0.44(0.03)	10.38(0.28)	357.95(9.65)	0.93
Norflurazon					
dry	0.008(0.001)	0.26(0.02)	11.49(0.25)	396.32(8.58)	0.96
1d wet	0.011(0.001)	0.14(0.01)	10.21(0.18)	351.96(6.09)	0.97
5d wet	0.009(0.000)	0.15(0.01)	10.27(0.17)	354.02(5.91)	0.97
Acifluorfen					
dry	0.083(0.006)	0.37(0.03)	1.114(0.007)	38.76(0.23)	0.96
1d wet	0.271(0.036)	0	0.763(0.004)	26.37(0.15)	0.88
5d wet	0.164(0.032)	0	0.675(0.006)	23.47(0.22)	0.90

The K_{OCi} of flutolanil and norflurazon in Mandeville soil corresponds to the result of K_{OCr} for sorption rates in dry soil only. A disparity is seen for K_{OCi} of flutolanil and norflurazon in Pahokee Peat and Elliot, compared to its sorption rate counterpart, where K_{OCi} is much lower than K_{OCr} (Table 6.2.4). Norflurazon also exhibited larger differences than flutolanil in Pahokee Peat and Elliot soils. Possible causes of the lower K_{OCi} values of norflurazon and flutolanil are as follows: a) K_{OCi} values include a slow diffusion to sorption sites, and b) the use of linear regression to determine K_F at a particular concentration may not be steadfastly accurate. It is often difficult to reach true equilibrium, because sorption continues to increase with more contact time between sorbate and soil (Beinum et al., 2006). The TSNE kinetic model explicitly includes a time-dependent mass transfer to micropores, whereas the Freundlich sorption model assumes sorption sites have a distribution of energies (Tabatabai and Sparks, 2005; Xia and Pignatello, 2001). Although the use of a linearized form of the Freundlich equation to determine K_{Fs} at a particular aqueous concentration proved to be adequate most of the time, deviations to the Freundlich equation may occur at high and low concentrations (Chen et al., 1999; Carmo et al., 2000) and thus may have contributed to the discrepancies observed between the K_{OCi} and K_{OCr} values.

Based on our kinetic results, an initially dry soil sorbs more pesticide than a wet soil, and also demonstrates a fast uptake in the initial rate of kinetics. However, a prewetting incubation of five days or longer may be needed to observe this effect, because soil-wetting equilibrium may take longer than one day. This finding serves as evidence to our assemblage model from 2-D NMR results that SOM consists of two isolated domains. The first domain contains alkyl type moieties and the second domain consists of O-alkyl and aromatic moieties. When the soil is dry, alkyl moieties as well as aromatic moieties will be more available for sorption sites, resulting in

a fast and increased sorption of HOCs. Contrary to this, when the soil is wet, the O-alkyl type moieties migrate toward the surface of the second domain, while the aromatic moieties reside in the inner part of the second domain. This will most likely result in a decrease in sorption of HOCs, especially of aromatic types, similar to the case in this study (Latta et al., 2008). An explanation has been provided in the literature, that wetting of the organic matrix in soil increases the availability of soft or amorphous domains and hence the organic contaminant becomes more “labile” (Huang and Weber, 1997). Here, soft domains may refer to alkyl-type moieties.

The above findings also show that the TSNE model fits very well for the sorption of HOC in highly organic soils, while it fails to predict the sorption kinetic parameters in a less organic-rich Elliot soil. Most agricultural types of soils and aquifer materials have organic carbon content less than or equal to that of Elliot soils. Thus, with such type of sorbents, there is a need to use kinetic models that better describe transport behaviors of HOC. However, the TSNE model results are useful as it helps elucidate the assumptions in the soil molecular assemblage model. Moreover, our results corroborate previous reports that wetting induces SOM conformational changes, thereby affecting HOC uptake. It was also found that sorption rates of HOCs in different soils generally have fast and slow components. The presence of rate-limited processes may serve to explain the observed irreversibility of sorption and desorption isotherms.

Our results also support the hypothesis that the presence of minerals and its association with organic matter impacts sorption rates, as suggested by Sparks (1989). Another important generalization is that in samples of high organic carbon content, it is imperative to have an idea of the type and nature of organic matter in order to adequately explain how this will affect non-equilibrium sorption.

Table 6.2.4 Comparison of K_{OC} from sorption isotherm and sorption kinetics

Soil type/Wetting conditions	K_{FOC} from sorption, L kg ⁻¹ (K_{OCi})			K_{OC} from sorption kinetics, L kg ⁻¹ (K_{OCr})		
	Acifluorfen	Norflurazon	Flutolanil	Acifluorfen	Norflurazon	Flutolanil
Pahokee Peat dry	75.33±0.18	288.83±1.69	599.60±2.83	69.46±0.79	372.76±5.25	761.12±25.75
Pahokee Peat 1d prewet	71.25±0.26	263.26±1.22	591.62±1.64	67.17±0.71	360.52±5.23	724.35±22.05
Pahokee Peat 5d prewet	58.81±0.24	222.81±0.93	520.69±1.65	62.78±0.23	351.89±6.40	649.23±17.63
Mandeville dry	103.42±0.32	338.53±0.41	978.46±2.47	98.10±1.20	334.23±3.61	988.88±8.67
Mandeville 1d prewet	97.50±0.20	308.02±0.43	907.52±3.10	94.74±0.72	319.82±5.38	889.94±7.81
Mandeville 5d prewet	88.31±0.22	260.69±0.36	793.35±2.33	92.86±0.15	315.18±6.30	847.19±9.14
Elliot dry	41.75±0.36	258.45±0.78	322.90±2.02	38.76±1.05	396.32±8.58	360.51±5.93
Elliot 1d prewet	35.88±0.16	234.91±0.67	270.54±2.40	26.37±0.59	351.96±6.09	349.12±9.65
Elliot 5d prewet	49.42±0.67	215.45±0.63	266.11±1.62	23.47±0.22	354.02±5.91	357.95±5.40

From an environmental and agricultural point of view, the application of HOCs such as pesticides under a dry soil condition would prove more beneficial since it would reduce losses due to leaching and degradation. Furthermore, less pesticidal active ingredient should be applied to sustain biological activity on target organisms. Conversely, wet soil would have an initially slower uptake with less sorption of an HOC, compared to a dry soil. Thus, a downward transport and losses due to metabolites would become more imminent. This may suggest a higher dose of HOC pesticides, in order to meet the required pesticide reactivity. For example, norflurazon is used as a post-emergent herbicide in rice fields. Rice plantations are constantly irrigated, hence applied HOC pesticides are expected to show the greatest amount of loss, and most likely would be found in groundwater and surface waters. Evidence of this result is summarized in the literature (Gilliom et al., 2006, Senseman 1997a). In agricultural fields, the area of pesticide mixing is usually located near a groundwater well. Hence, these areas are mostly exposed to wetting. It is therefore expected that groundwater contamination on these sites will be more prevalent. In fact this was found to be the case (Senseman et al., 1997b). Therefore, it is not surprising that efforts have been undertaken to develop slow release formulations of mobile pesticides such as norflurazon (Undabeytia et al., 2000; Sopena et al., 2007; Villaverde et al., 2006).

To date, this study offers a more extensive and systematic investigation of the effect of wetting on HOC sorption, encompassing the use of a) sorbates of different polarities, b) soils of different organic matter and mineral content, and c) three different hydration conditions on the evaluation of sorption kinetics, sorption isotherms, and desorption isotherms.

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Chapter 7

Conclusion

The main objectives of this study were as follows: 1) to determine the effect of hydration/solvation on the nature of organic matter released from the soil; 2) to gain further insight into *in situ* soil organic matter (SOM) molecular assemblage in a whole soil and to relate its interactions with hydrophobic organic compounds; and 3) to investigate how hydration, natural organic matter, and mineral/clay content affect kinetics of uptake, sorption capacity, and release of hydrophobic organic compounds (HOCs).

Chapter 3 of this thesis discusses our work involving the use of a hydration/solvation effect as a probe to better understand SOM supermolecular assemblage. An aqueous solution (aqueous phase) and an aqueous phase amended with either acetonitrile, methanol, dimethyl sulfoxide, acetic acid, or hydrochloric acid to a final concentration of 4.6×10^{-3} M of the said solvents (viewed as mobile phases) were contacted with a whole organic soil Pahokee Peat at different time intervals of 1, 20, and 45 day, respectively. Colorimetric inspection of the samples revealed a change in color of the supernatants from light to darker yellow at longer contact times for all exfoliating solvents used, with the exception of a water-acetonitrile mobile phase, which gave a differentiating color of light yellow at one day contact time and a distinct brownish red supernatant at 20 and 45 day periods. The UV absorbance at 280 nm also increased in the order: 1 > 20 > 45 day. Since absorbance is mainly due to presence of conjugated and/or aromatic systems, and UV absorbance at 280 nm of SOM was previously shown to correlate to the amount of aromatic moieties, this imply that the acetonitrile mobile phase extracted a greater amount of poly(aromatics) and conjugated π systems. Emission scans utilizing a single excitation wavelength of either 254, 375 or 465 nm and synchronous fluorescence indicated the presence of at least two types of fluorophores. Furthermore, a fluorescence-based humification index (HIX),

defined as the ratio between the fluorescence intensities at the longer wavelengths to that of the lower wavelength intensities, were calculated as a means of comparing the degree of humification of the released SOM. Humification is defined as the process whereby small organic molecules are transformed into larger organic molecules, and these larger molecules are characteristically more conjugated, more condensed and more aromatic in nature.

Higher HIX values are indicative of the presence of more humified materials. The acetonitrile mobile phase consistently showed the highest HIX values, which corroborated the colorimetric and UV results of an exfoliation of the highest amount of aromatic and conjugated systems. Fluorescence analysis also demonstrated a kinetic effect on the hydration/solvation of SOM. At the 20-day incubation period, there was a general increase in the amount of fluorophores at the longer emission wavelength, characterized by the peak, centered at ~462 nm and a shoulder at ~440 nm in the synchronous spectra. In contrast, at the 45-day period, a greater amount of lower wavelength fluorescence features centered at ~392 nm, were exfoliated. The fluorophores released may be ascribed to quinone-like moieties in NOM, more specifically to less conjugated quinone A moieties and to more conjugated, more functionalized quinone B moieties, as described in our recent work (Cook et al., 2009). Thus, more quinone B type moieties and a greater amount of quinone A type moieties, were exfoliated from 20 and 45-day incubation periods, respectively. The ^{13}C CPMAS spectra of freeze-dried exfoliated soil, as well as FTIR analyses of freeze-dried exfoliation supernatants from 45-day water and water-acetonitrile exfoliation samples, were in agreement with UV and fluorescence analyses, that hydrophilic moieties, including aromatic types were preferentially extracted, and that across the board, water-acetonitrile extracted more alkyl, O-alkyl, aromatic and carbonyl type moieties than by water alone. The extraction of both alkyl and aromatic moieties, in the aqueous mobile phases occurred due to frequent associations with hydrophilic moieties, as in the case of plant polyesters,

plant lipids, and lignocellulosic materials. Interestingly, the water-acetonitrile mobile phase exfoliated the greatest amount of SOM, including a greater amount of quinone-B type moieties, which implied that it had the greatest disruptive effect on the intermolecular forces that held the SOM moieties into assemblies. The result may be attributed to the following: 1) differences in H-bond donor acidity (α) of methanol and acetonitrile, suggesting that there are less water-acetonitrile associations; hence, acetonitrile is more available to solvate SOM; 2) smaller volume and linearity of acetonitrile allowed easier penetration and access to molecular voids, compared to methanol and dimethyl sulfoxide; and 3) the ability of acetonitrile to form phenol-water-acetonitrile complexes, due to hydrogen bonding.

The exfoliation of SOM using aqueous solutions was kinetically controlled and may be explained in a similar manner to a soil-wetting process. When an air-dried soil was wetted for a short period (e.g., one day), some hydrophilic moieties, initially present at the outer layer, were hydrated/solvated and subsequently dissolved in the solution. At longer wetting times, for example a 20-day period, more hydrophilic moieties migrated to the outer surface; thus more of these moieties were solubilized, compared to the one day wetting. Furthermore, solvent molecules also penetrated into SOM voids and interacted with SOM moieties through hydrogen bonding (hydrophobic forces in the presence of acetonitrile, methanol, and dimethyl sulfoxide), thereby disrupting the inter- and intramolecular hydrogen bond contacts within SOM, resulting to a “swelled” state or a more open conformation of SOM. Thus, larger and more hydrophobic moieties located in the middle layer were released into the solution. Beyond the 20-day wetting period, as in the case of a 45-day wetting period, hydrophilic moieties which were previously protected by the hydrophobic middle layer were then exfoliated. Sorption-desorption studies of hydrophobic organic compounds often use small amounts of solvent ranging from < 1% to < 2% in order to dissolve hydrophobic organic compounds (HOCs) in aqueous solution. Our results

raised concerns on the possible effect of these solvent additions to the sorption process. HOCs such as pesticides were usually applied with the aid of solvent systems and might also be applied as bi-solute systems; hence the need to have a more accurate predictive modeling of their sorption.

Chapter 4 is based from our previous work (Lattao et al., 2008) and discusses the use of 2-Dimensional ^1H - ^{13}C Heteronuclear (HETCOR) Nuclear Magnetic Resonance (NMR) for the *first time*, to gain direct molecular insight of the SOM assembly at a molecular level in a *whole soil*. The study implemented LG-CP or Ramp-CP pulse sequences in the generation of the 2-D HETCOR spectra and allowed the observation of intra- and intermolecular connectivities within the *in situ* SOM, which demonstrated the existence of at least two distinct domains. The first domain type consisted of alkyl moieties that are isolated in space; in most probability, these alkyl moieties represented cuticular and lipid materials, including degradation products. The second domain type consisted of aromatic moieties that are in close association with O-alkyl type moieties. The distance probed here was over 0.4 nm and up to 0.8 nm. The sample used in this study was a freeze-dried organic soil; hence, the molecular assemblage information derived from these data represented that of a dried soil, but could also be extended to a wet soil based on the literature available on soil hydration. A model was then put forward in relation to the influence of SOM molecular assembly on the sorption of hydrophobic organic compounds. In a wet soil, it may be envisioned that the isolated alkyl domains were more available as sorption sites for HOCs, because hydrophilic O-alkyl moieties would have migrated to the outer layer of the O-alkyl/aromatic domains. The more hydrophobic aromatic moieties were protected in the inner layer and therefore were less available as sorption sites. As the soil dried, the SOM underwent a conformational rearrangement, such that O-alkyl moieties migrated back to the inner core, while aromatic moieties were exposed on the outer surface of the second domain type. These aromatic

moieties were then expected to serve as thermodynamically more favorable sorption sites, especially for aromatic HOCs, through formation of π - π complexes and π - π electron donor-acceptor interactions.

It is therefore plausible that HOCs initially sorbed to the alkyl domains migrated to the aromatic domains, and this step would be controlled by steric, kinetic and thermodynamic effects. When the soil experienced another wetting period, the reverse SOM conformational arrangement was expected, such that the aromatic moieties once again were located in the inner layer, coated by a layer of hydrophilic O-alkyl moieties on the surface. This arrangement hindered the exit of HOCs that were sorbed to the aromatic moieties and restricted further entry of HOCs, as long as the aqueous solution and the HOCs were unable to compete with and/or disrupt the intermolecular forces that held these SOM moieties into supramolecular assemblies. Thus, it may be envisioned that sorption-desorption processes in the environment, including the approach to equilibrium, are influenced by drying/wetting cycles to which soil is subjected.

Chapter 5 involves the sorption and desorption studies on three trifluorinated aromatic pesticides of varying polarities, namely: acifluorfen, norflurazon, and flutolanil. The sorbents were Pahokee Peat, Mandeville and Elliot soils, which have characteristic high, intermediate, and low organic contents, respectively. In addition, Mandeville soil contained a high proportion of sand and an appreciable amount of expandable type clay. On the other hand, Elliot soil has high silt content and also a significant amount of medium expandability type clay. The objectives of this study were as follows: 1) to determine the effect of sorbent's organic matter content and sorbate's polarity on the sorption-desorption of HOCs; 2) to investigate the effect of sorbent's mineral/clay content on sorption-desorption of these HOCs; and 3) to test our hypothesis that the hydration condition of the soil affects the uptake and release of HOCs, based from our molecular assembly model.

The highest sorption to soils was observed for flutolanil, followed by norflurazon, and then lowest sorption was viewed for acifluorfen. This trend correlates well with the hydrophobicity of the sorbates, since flutolanil was the most hydrophobic, while acifluorfen was the least hydrophobic. Aside from London Van der Waals hydrophobic forces, H-bonding and π - π electron-donor acceptor reactions potentially increased the sorption of flutolanil. Flutolanil is capable of very weak to moderate H-bonding with SOM moieties due to its ether, CF_3 and Cl substituents, and amide groups respectively. The presence of negative quadrupolar moments above and below the plane of its aromatic rings made it a suitable π -donor, which also favored sorption to SOM moieties, especially aromatic moieties with π -acceptor abilities. Additional norflurazon sorption could be attributed from strong to very strong hydrogen bonding capabilities, with carboxylic and phenolic groups in SOM through azine and amino functionalities. The ionization of acifluorfen at the sorption pH (~ 5), decreased its sorption potential, since some ionizable functionalities in SOM (i.e., carboxylic and phenolic groups) were also ionized at this pH, causing anion-anion repulsion. The pesticides acifluorfen, norflurazon, and flutolanil inherently have $-\text{CF}_3$ in their structures, making them highly amenable to ^{19}F NMR studies. It is therefore recommended that ^{19}F MAS and high resolution magic angle spin experiments be conducted in order to gain further molecular insight into their associations with SOM moieties.

The organic carbon normalized Freundlich sorption capabilities (K_{FOC}) of Pahokee Peat and Mandeville soils for norflurazon were statistically equal, while a slight difference ($\sim 7\%$) was demonstrated by Elliot soil, implying that norflurazon sorbs primarily to organic matter. Sorption capacities for flutolanil and acifluorfen showed the following trend: Mandeville soil > Pahokee Peat > Elliot soil. The presence of a high proportion of sand and clay in Mandeville soil serves as additional sorption sites, which may be attributed to: 1) presence of hydrophobic sorption sites

in mineral grains (i.e., sand and clay); 2) H-bonding with free silanol groups; and 3) increased surface area for sorption, due to the presence of highly expandable 2:1 type sodium montmorillonite clay. It may be postulated that the presence of medium-swelling clays in Elliot soil has a negligible effect on sorption of these pesticides, possibly due to steric effects on the interstitial layer. Furthermore, Elliot soil carries a high proportion of silt content, and it is possible that the nature and molecular arrangement of SOM in such soil components affects its interactions with HOCs.

The amount of pesticides sorbed during sorption and after desorption, decreased in this order: dry > 1 day prewet > 5 day prewet for all pesticides in Mandeville soil and Pahokee Peat, except for the following: 1) sorption of norflurazon in Pahokee Peat in dry soil is statistically equivalent to that of 1 day prewetted soil; and 2) after desorption, K_{FOC} of flutolanil in Pahokee Peat was shown to be 1 day prewet > dry > 5 day prewet. Thus, in general our results showed that a dry soil sorbs more HOC than prewetted soil, which was in agreement with the molecular assemblage model from Chapter 4. The following deviations to this general trend were observed for Elliot soil: 1) sorption and desorption K_{FOC} of acifluorfen in Elliot soil showed the trend 5 day prewet > dry > 1 day prewet; 2) sorption K_{FOC} of flutolanil in Elliot soil was greatest in a dry soil and is statistically equal for 1 day and 5 day prewet soils; and 3) desorption K_{FOC} of norflurazon in Elliot soil was found to be: 1 day > 5 day prewet > dry. The above deviations for Elliot soil once again raised an interesting question as to the nature of SOM-mineral associations in silty soils, especially at the molecular level. The most agricultural type of soils have an SOM content equal to or less than that of Elliot soils, and typically contain expandable type clay minerals. It is therefore recommended that the type of study carried out in this work be extended to such soil types. It has been suggested in the literature that SOM may exist as coatings or as patches in silt and mineral grains (Schwarzenbach et al., 2003; Pignatello, 2009); which leads to

an interesting question of the associations of SOM with mineral surfaces. Thus, further studies are needed to elucidate this matter, as SOM-mineral associations play a role in 1) sorption of HOCs, 2) stabilization of SOM, hence recalcitrance of carbon pools in SOM; and 3) soil aggregate formation.

Kinetic results indicated that an initially dry soil (Pahokee Peat, Madeville, or Elliot soils), sorbs more (acifluorfen, norflurazon, or flutolanil) and demonstrated a faster uptake of pesticide than a wet soil at the early stage (<24 hr) of the kinetic curve. This difference was more observable between a dry and 5 day prewetted soils; it was suggested in the past that times longer than 24 hours are needed to attain equilibrium wetting of soil. This finding was consistent with the molecular assemblage model, derived from our 2-D ^1H - ^{13}C HETCOR NMR experiments and the implications in relation to HOC sorption and desorption to dry or wet soils. In addition, the pseudo-equilibrium was approached in approximately five days for all soil-pesticide combinations. Furthermore, at 5 days, sorption of dry and prewetted soils tend to converge, which supported the finding once again that wetting of a dry soil may take place within approximately five days or longer.

In Chapter 6, experimental kinetic data were fitted with a two-site non-equilibrium model, yielding a very good fit. Almost all soil-pesticide combinations yielded R^2 values of 0.92 – 0.99 except for slightly lower correlation fits for flutolanil in dry Pahokee Peat, and acifluorfen in 1 day and 5 day wet Elliot soil. Thus, sorption rates of HOCs in different soils generally have fast and slow components, the only deviation is acifluorfen in Elliot soil, with the fraction of instantaneous (fast) sorption ≈ 0 , possibly suggesting a one-site non-equilibrium model, which means that its sorption is slow throughout the sorption process.

The above findings have environmental and agricultural implications. It is envisioned that the application of hydrophobic agricultural chemicals, including pesticides in a dry soil, would

be more beneficial in leading to a greater amount sorbed and an initial fast uptake; hence it would reduce losses due to horizontal (i.e., runoff) and downward water movement. In addition, sorbed pesticides are less bioavailable for degradation. This would result to a greater amount of pesticide being sorbed to soil components, and it may be argued that the availability of this sorbed pesticide for uptake by target organisms would depend on the subsequent hydration levels of the soil. Conversely, pesticide application to a wet soil increases the tendency for losses due to runoff, seepage, and degradation. This suggests that greater amounts of pesticide should be applied for bioefficacy. Thus, a higher risk of contamination of surface water and ground water would be expected for pesticides (and HOC across the board) applications in wet soils.

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Appendix: Letters of Permission

Charisma Lattao <clatta1@tigers.lsu.edu>

Thu, Oct 15, 2009 at 5:46 PM

To: semst@agronomy.org

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Thank you and have a wonderful day.

Sincerely yours,

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Charisma Lattao, Justin Birdwell, Jim J. Wang, and Robert L. Cook. 2008. Studying Organic Matter Molecular Assemblage within a Whole Organic Soil by Nuclear Magnetic Resonance. *J. Environ. Qual.* 37: 1501-1509.

Sincerely,

Susan Ernst
Managing Editor
Journal of Environmental Quality

Vita

Charisma Vinarao Lattao was born in Cabagan, Isabela in the northern part of the Philippines, to parents Dominador and Milagros Lattao. She lived her childhood years in Cabagan, Isabela, and Tuguegarao, Cagayan, where she finished high school at St. Louis College of Tuguegarao. She then attended college at the University of the Philippines at Los Baños, Laguna, where she obtained her degree in Bachelor of Science in agricultural chemistry in December, 1998. After graduation, she worked as an Instructor at the Department of Chemistry at the University of the Philippines at Los Baños, Laguna. She then pursued graduate studies at the Department of Chemistry, Louisiana State University, under the direction of Dr. Robert L. Cook. Currently, she is finishing one of the final requirements for the doctoral degree in analytical chemistry.