

**A LABORATORY EVALUATION OF THE SORPTION OF OIL SANDS  
NAPHTHENIC ACIDS ON SOILS**

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## ABSTRACT

The adsorption characteristics of an oil sands tailings water (OSTW) mixture of naphthenic acids were determined using a batch partitioning method for two soils from the Alberta oil sands region. The soils were mineral peat mixtures produced during salvage operations, with Soil 1 having a higher organic carbon fraction ( $f_{oc}$ ) than Soil 2. Naphthenic acids are a significant toxic byproduct of bitumen extraction, and are acutely toxic to aquatic organisms. The sorption of naphthenic acids as affected by a high ionic strength solution was examined using a synthetic groundwater (SGW) mixture.

The adsorption isotherms were found to be linear in all cases. All tests were conducted at 4°C, and at a pH of  $8.0 \pm 0.4$ , reflective of the conditions in a tailings settling facility near Fort McMurray, AB.

The adsorption characteristics of the naphthenic acids in the SGW solution were compared to that of the mixture in Milli-Q water for the two soils. In the presence of SGW, the adsorption coefficient ( $K_d$ ) for the mixture of naphthenic acids on Soil 1 was an order of magnitude higher than that observed with the same soil and the Milli-Q water mixture, increasing from  $1.9 \pm 0.2$  mL/g to  $17.8 \pm 1.5$  mL/g. The adsorption coefficient for the mixture of naphthenic acids on Soil 2 was also observably higher in the SGW mixture, increasing from  $1.3 \pm 0.15$  mL/g to  $3.7 \pm 0.2$  mL/g.

In order to determine whether preferential sorption is exhibited by a particular species within the mixture, the relative fractional abundance of the individual naphthenic acids was plotted as a 3-dimensional histogram for carbon numbers 5 to 37. It was found that for all  $Z$  families (where  $Z$  is a measure of the number of carbon ring structures), naphthenic acids within the middle range of carbon numbers showed preferential sorption. A two sample  $t$ -test confirmed that the naphthenic acids in the carbon number groupings 15 to 24 and 25 to 37 sorbed significantly in the SGW mixture when compared to those in the carbon number grouping of 5 to 14. It was concluded that select constituents of oil sands naphthenic acids mixtures sorb strongly to soil under

conditions of elevated salinity and therefore adsorption could be an important attenuating mechanism in groundwater transport. Furthermore, preferential sorption of the individual naphthenic acids is important with respect to toxicity since lower molecular weight naphthenic acids are believed to have a more pronounced toxic effect. Overall, the measured adsorption coefficients indicate that there can be significant sorption of OSTW derived naphthenic acids to soils

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# TABLE OF CONTENTS

ABSTRACT .....	ii
ACKNOWLEDGEMENTS .....	iv
TABLE OF CONTENTS .....	v
LIST OF TABLES .....	viii
LIST OF FIGURES.....	ix
APPENDICES.....	xii
LIST OF ABBREVIATIONS .....	xii
1 INTRODUCTION.....	1
1.1 Oil Sands Processing.....	1
1.2 Naphthenic Acids .....	2
1.2.1 Naphthenic Acids and the Environment .....	4
1.3 Naphthenic Acid Effects in Oil Sands Industry .....	5
1.4 Geology of Oil Sands Region .....	5
1.5 Transport of Naphthenic Acids in Groundwater .....	6
2 LITERATURE REVIEW.....	7
2.1 Introduction .....	7
2.2 Transport and Sorption Theory .....	7
2.3 Equilibrium Sorption Models.....	8
2.3.1 Langmuir Sorption Isotherm .....	9
2.3.2 Freundlich Sorption Isotherms .....	13
2.3.3 Linear Sorption Isotherm .....	14
2.4 Kinetic Adsorption Models .....	15

2.5	Sorption Mechanisms and Affecting Factors .....	16
2.6	Prediction Methods for Sorption Coefficients .....	18
2.7	Experimental Determination of Sorption Coefficients .....	22
2.7.1	Column and Diffusion-Cell Techniques .....	22
2.7.2	Batch Testing .....	25
2.8	Previous Work on Naphthenic Acid Adsorption .....	26
2.9	Summary .....	29
3	MATERIALS AND METHODS .....	30
3.1	Introduction .....	30
3.2	Soils .....	30
	NOTE: CEC, cation exchange capacity; SAR, sodium adsorption ratio. ....	31
3.3	Naphthenic acid extract .....	31
3.4	Batch test setup .....	34
3.5	Preliminary testing .....	35
3.6	Testing of Partitioning coefficient .....	36
3.6.1	Control Tests .....	36
3.7	Solid Phase Extraction Sample Cleanup .....	37
3.8	Analytical Methods .....	39
4	RESULTS AND DISCUSSION .....	43
4.1	Extracted Naphthenic Acids .....	43
4.2	Solid Phase Extraction Results .....	45
4.3	Preliminary Test Results .....	48
4.4	SGW batch test results .....	51

4.4.1	Control Tests .....	52
4.4.2	$K_d$ Values .....	52
4.4.3	Selective sorption .....	56
4.5	Discussion .....	59
CONCLUSIONS AND RECOMMENDATIONS .....		66
4.6	Conclusions .....	66
4.7	Recommendations .....	68
REFERENCES .....		71
APPENDICES .....		80
Appendix A. Derivation of de-protonation factor (Q) and Koc based on pH and pKa. .....		81
Appendix B. Analytical methods for determining the chemical properties of soils (after Enviro-Test Laboratories) .....		83
Appendix C. Statistical Analyses .....		85
Appendix D. Histograms of fractional abundance for pre and post sorption samples at 200 mg/L initial concentration .....		94



## LIST OF TABLES

Table 3.1 Properties of tested soil.....	31
Table 3.2 Synthetic groundwater chemistry.....	36
Table C.1 Carbon number groupings for –Z family.....	87
Table C.2 Group two fractional abundance values.....	90

## LIST OF FIGURES

Figure 1.1	Structures of naphthenic acids (after Rogers et al. 2002b). X equals one or more; R, a small aliphatic group .....	3
Figure 2.1	Typical Langmuir Isotherm.....	10
Figure 2.2	Typical Freundlich isotherm .....	13
Figure 2.3	Typical linear isotherm .....	14
Figure 2.4	Diffusion cell, plan view schematic (adapted from Donahue 1994).....	24
Figure 2.5	Column test, plan view schematic (adapted from Donahue 1994) .....	25
Figure 3.1	Schematic depiction of procedure for extraction of naphthenic acids for OSTW.....	32
Figure 3.2	Typical solid phase extraction apparatus .....	39
Figure 3.3	Fractional abundance matrix .....	42
Figure 4.1	OSTW Naphthenic acid ion chromatogram diluted in Milli-Q water.....	43
Figure 4.2	Comparison of the ion chromatogram of naphthenic acids in SGW a) before SPE procedure, b) after SPE procedure. Concentration of solution tested was 200mg/L.....	46
Figure 4.3	Naphthenic acid fingerprint in Milli-Q, 20 mg/L a) initial solution, b) following extraction by dilution. Concentration of solution tested was 200mg/L. ....	48
Figure 4.4	Total ion count (TIC) values in the reactor vials for a 200 mg/L naphthenic acid solution sampled with time. (0=0 hrs, 1=24 hrs, 2=48 hrs, 3=96 hrs, 4=144hrs, 5=288 hrs. NOTE: Samplings at 192 and 240 hrs were omitted as outliers with concentrations greater than adjacent days.) Error bars represent the relative standard deviation of the triplicates reactor vials..	49
Figure 4.5	Total ion count (TIC) values in the control vials for a 200 mg/L naphthenic acid solution sampled with time. (1=0 hrs, 2=24 hrs, 3=48 hrs, 4=96 hrs, 5=144hrs, 6= 192 hrs, 7=288 hrs. NOTE: Sampling at 192 hrs was omitted as an outlier with a concentration greater than adjacent days.) Error bars represent the relative standard deviation of the triplicates reactor vials..	50

Figure 4.6	Adsorption isotherm of naphthenic acid mixture at $23\pm 1^{\circ}\text{C}$ , pH 8 with Soil 1 in Milli-Q water. The dashed lines represent the 95% confidence intervals.....	51
Figure 4.7	Sorption isotherms for naphthenic acids Soil 1 and 2 in Milli-Q water. The dashed lines represent the 95% confidence intervals.....	53
Figure 4.8	Sorption isotherms for naphthenic acids Soil 1 and 2 in SGW. The dashed lines represent the 95% confidence intervals.....	54
Figure 4.9	a) $Z=-2$ family change in fractional abundance of individual species with time, Soil 1 in Milli-Q water b) $Z=-2$ family change in fractional abundance of individual species with time, Soil 2 in Milli-Q water.....	58
Figure 4.10	a) $Z=-2$ family change in fractional abundance of individual species with time, Soil 1 in SGW b) $Z=-2$ family change in fractional abundance of individual species with time, Soil 2 in SGW.....	59
Figure 4.11	The theoretical relationship of $K_d$ and molecular connectivity index ( $^1\chi$ ).....	62
Figure D.2	$Z=-2$ family change in fractional abundance of individual species with time, Soil 1 Milli-Q water.....	95
Figure D.3	$Z=-4$ family change in fractional abundance of individual species with time, Soil 1 Milli-Q water.....	96
Figure D.4	$Z=-6$ family change in fractional abundance of individual species with time, Soil 1 Milli-Q water.....	97
Figure D.5	$Z=-8$ family change in fractional abundance of individual species with time, Soil 1 Milli-Q water.....	98
Figure D.6	$Z=-10$ family change in fractional abundance of individual species with time, Soil 1 Milli-Q water.....	99
Figure D.7	$Z=-12$ family change in fractional abundance of individual species with time, Soil 1 Milli-Q water.....	100
Figure D.8	$Z=0$ family change in fractional abundance of individual species with time, Soil 2 Milli-Q water.....	101
Figure D.9	$Z=-2$ family change in fractional abundance of individual species with time, Soil 2 Milli-Q water.....	102

Figure D.10	Z= -4 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water .....	103
Figure D.11	Z= -6 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water .....	104
Figure D.12	Z = -8 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water .....	105
Figure D.13	Z= -10 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water .....	106
Figure D.14	Z= -12 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water .....	107
Figure D.15	Z = 0 family change in fractional abundance of individual species with time, Soil 1 SGW .....	108
Figure D.16	Z= -2 family change in fractional abundance of individual species with time, Soil 1 SGW .....	109
Figure D.17	Z= -4 family change in fractional abundance of individual species with time, Soil 1 SGW .....	110
Figure D.18	Z= -6 family change in fractional abundance of individual species with time, Soil 1 SGW .....	111
Figure D.19	Z= -8 family change in fractional abundance of individual species with time, Soil 1 SGW .....	112
Figure D.20	Z= -10 family change in fractional abundance of individual species with time, Soil 1 SGW .....	113
Figure D.21	Z= -12 family change in fractional abundance of individual species with time, Soil 1 SGW .....	114
Figure D.22	Z= 0 family change in fractional abundance of individual species with time, Soil 2 SGW .....	115
Figure D.23	Z= -2 family change in fractional abundance of individual species with time, Soil 2 SGW .....	116
Figure D.24	Z= - 4 family change in fractional abundance of individual species with time, Soil 2 SGW .....	117

Figure D.25 Z= -6 family change in fractional abundance of individual species with time, Soil 2 SGW .....	118
Figure D.26 Z= -8 family change in fractional abundance of individual species with time, Soil 2 SGW .....	119
Figure D.27 Z= -10 family change in fractional abundance of individual species with time, Soil 2 SGW .....	120
Figure D.28 Z= -12 family change in fractional abundance of individual species with time, Soil 2 SGW .....	121

## APPENDICES

Appendix A: Derivation of de-protonation factor ( $Q$ ) and  $K_{oc}$  based on pH and pKa.

Appendix B: Analytical methods for determining the chemical properties of soils

Appendix C: Statistical Analyses

Appendix D: Histograms of fractional abundance for pre and post sorption samples at 200 mg/L initial concentration

## LIST OF ABBREVIATIONS

Adsorption coefficient ( $K_d$ )

Amount of solute sorbed per unit soil ( $S$ )

Athabasca Oil Sands (AOS)

Average linear velocity ( $v_x$ )

Canadian Institute of Mining Metallurgy and Petroleum (CIM)

Concentration of the solute in liquid phase ( $C$ )

Dalton (Da)

Dichloromethane (DCM)

Diffusion coefficient ( $D^*$ )

Hydrodynamic dispersion coefficient ( $D_h$ )

Hydrophobic ionizable organic compounds (HIOC)

Ionization or dissociation constant ( $K_a$ )

Langmuir sorption capacity ( $\beta$ )

Molecular connectivity index ( $^1\chi$ )

Number of hydrogens bonded to a given atom ( $\delta$ )

Octanol/water partition coefficient ( $K_{ow}$ )

Oil sands tailings water (OSTW)

Organic carbon fraction ( $f_{oc}$ )

Organic carbon partition coefficient ( $K_{oc}$ )

Organic matter partition coefficient ( $K_{om}$ )

Porosity of the porous media ( $n$ )

Primary Separation Vessel (PSV)

Relative Standard Deviation (RSD)

Retardation coefficient ( $R_d$ )

Soil Organic Matter (SOM)

Synthetic groundwater (SGW)

The bulk density of soil ( $\rho_d$ )

Time ( $t$ )

# **1 INTRODUCTION**

Canada's oil sands are estimated to contain 177 billion barrels of recoverable oil. Oil sand deposits are concentrated in the northern half of the province of Alberta with the deposits in the Athabasca region being the largest, covering approximately 400,000 square kilometers, and having the most concentrated oil sands production. It is projected that by the year 2010, Alberta's oil sands will generate well over half of Canada's total expected crude oil production (CIM 2005a).

## **1.1 Oil Sands Processing**

Oil sand is natural sand deposit which contains a heavy oil called bitumen. Oil sand is composed of approximately 70% sand and clay, 10% water, and anywhere from 0% to 18% oil. The sand is a silica quartz and is extremely abrasive. The Athabasca Oil Sands are hydrophilic or water wet. Each grain of sand is surrounded by a film of water, which is then surrounded by the raw bitumen (Söderbergh, 2004). The bitumen is a viscous mixture of hydrocarbons with a consistency of approximately 83.2% carbon, 10.4% hydrogen, 0.94% oxygen, 0.36% nitrogen, and 4.8% sulphur. The molasses like substance will not flow unless heated or diluted with lighter hydrocarbons (Government of Canada 2005).

In the process of separating the bitumen from the sand, the oil sand is mixed with air and water, and piped to a Primary Separation Vessel (PSV) where it is allowed to settle into

three layers with the alkaline hot water assisting the process. Sand particles sink to the bottom while the middle stream (Middlings) a combination of bitumen, sand, clay and water are removed for a secondary extraction. Air entrained bitumen froth floats to the top and is drawn off, while the sand and wastewater from the process is pumped into tailings ponds. During this extraction process, naphthenic acids are solublized and removed as dissolved naphthenates and stored along with the other waste products in oil sands tailings water (OSTW) which is stored in tailings ponds (CIM 2005b; CEATAG 1998; Hsu *et al.* 1998; Lai *et al.*, 1996; Brient *et al.*, 1995).

## 1.2 Naphthenic Acids

Naphthenic acids are complex mixtures of alkyl-substituted acyclic and cycloaliphatic carboxylic acids and have the general formula  $C_nH_{2n+Z}O_2$ , where  $n$  is the number of carbons, and  $Z$  is the number which represents the number of hydrogen atoms that are lost as the structure becomes more compact. The  $Z$  number can vary from zero for those with linear hydrocarbon chains where  $Z$  equals zero, to those with cyclic chains where  $Z$  is 2 times the number of fused rings (CEATAG 1998, Rogers *et al.* 2002a). Figure 1.2 illustrates some example naphthenic molecular structures.



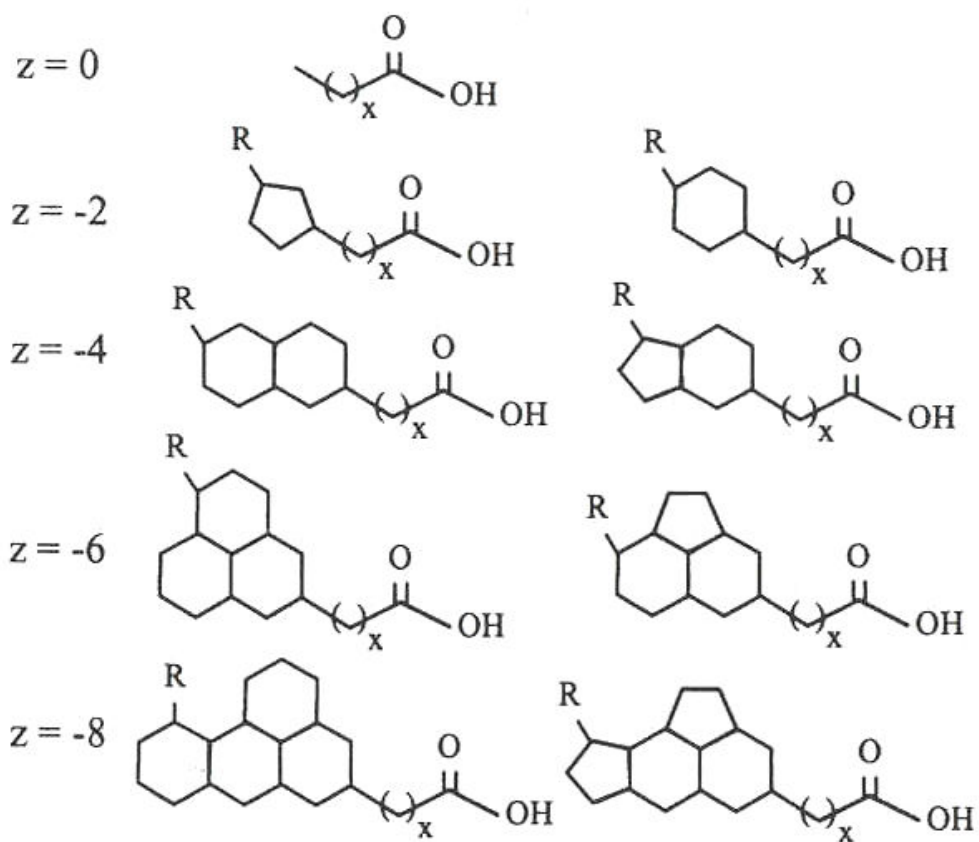


Figure 1.1 Structures of naphthenic acids (after Rogers et al. 2002b). X equals one or more; R, a small aliphatic group

The hydrophobicity and non-volatility of naphthenic acids increases with molecular weight and therefore, each species is unique in physical and chemical properties.

Naphthenic acids are well known agents of acute toxicity to aquatic species and pose a variety of health risk to terrestrial mammals (CEATAG, 1998). The toxicity of an OSTW mixture of naphthenic acids varies with the particular naphthenic acid species contained in the mixture, as well as the concentrations of those species, since each of the individual naphthenic acids has its own toxicological properties. In addition, their solubility in water is more dominantly effected by pH than temperature, and is greatest

at pHs above neutral (eg. 5.04 g/L at pH=9.16; Holowenko et al. 2001; CEATAG 1998; Brient et al. 1995 ).

### *1.2.1 Naphthenic Acids and the Environment*

Naphthenic acids as found in the Athabasca Oil Sands tailings near Fort McMurray AB, Canada, form a significant part of the toxicological characteristics of OSTW (Rogers et al. 2002a, *ibid* 2002b). Naturally occurring naphthenic acid concentrations in this region range from <1 mg/L in surface water sources, to 2 to 5 mg/L in near-surface aquifers which reflect natural contact with oil sands (CEATAG, 1998). In tailings ponds near Fort McMurray, AB, Canada, naphthenic acids can be found at concentrations ranging from 40 to 120 mg/L, which is two orders of magnitude higher than their naturally occurring concentrations (Holowenko et al. 2002, CEATAG 1998). Few studies have been done to date on the transport properties of oil sands derived aqueous mixtures of naphthenic acids as compared to extensive studies conducted to investigate the adsorption characteristics of other natural petroleum hydrocarbons such as benzene, toluene, and naphthalene (Liu et al. 1991; Barone et al. 1992; Donahue 1994; Morrissey and Grismer 1999). CEATAG identifies transport mechanisms, dispersion from point sources, and adsorption of naphthenic acids as areas that require further study (1998).

### **1.3 Naphthenic Acid Effects in Oil Sands Industry**

In addition to the environmental considerations associated with naphthenic acids, they are responsible for a substantial loss of revenue to the oil sands industry by way of the corrosion they cause to crude oil upgrading and refining equipment (Barrow et al. 2003; Gutzeit 1976). The literature indicates that the effects of corrosion become a problem at temperatures exceeding 200°C (Wu et al. 2004).

### **1.4 Geology of Oil Sands Region**

The evaluation of transport parameters for naphthenic acids under field conditions is complicated by the large variations in geochemistry and geostatigraphy of the Athabasca oil sands region. Parameters such as soil texture, minerology and groundwater chemistry vary considerably. With respect to stratigraphy, the McMurray and Grandrapids aquifer/aquitard systems tend to be complex with interwoven beds of sands, shale, and silt (Bachu and Underschultz 1993). Furthermore, the salinity of porewater in the various lithological layers can vary both spatially and temporally in the area and may be orders of magnitude higher than the levels used in this study (Hackbarth 1977; Bachu and Underschultz 1993).

## **1.5 Transport of Naphthenic Acids in Groundwater**

Understanding the transport properties of organic contaminants is a necessary step towards evaluating the potential release rates (concentration and loading) to natural ecosystems and in developing effective remediation strategies for affected groundwater. In turn, transport properties are dependant upon the chemical characteristics of the solute (or contaminant) and the physical and geochemical characteristics of the porous media facilitating transport. The ionizable nature of naphthenic acids along with the complex geology and geochemistry of the Athabasca region pose additional challenges to characterizing the transport properties of naphthenic acids in the laboratory.

This study seeks to develop an analytical method for evaluating the adsorption characteristics of OSTW naphthenic acids. The method will be applied to an illustrative test case using soils from the Athabasca Oil Sands region, naphthenic acids extracted from an oil sands tailings settling basin near Fort MacMurray, and a synthetic groundwater mixture with elevated salinity. In addition, the study will conduct a preliminary evaluation of the impacts of sorption and selective sorption of individual naphthenic acids under the specified test conditions.

The objectives of the study were to determine whether measurable sorption exists in a mixture of OSTW, naphthenic acids, and de-ionized (Milli-Q) water, to evaluate the affect of elevated salinity on the sorption characteristics of the naphthenic acids mixture, and to determine if selected naphthenic acid species exhibit preferential sorption to the soils tested. Sorption experiments were conducted using batch reactors.

## 2 LITERATURE REVIEW

### 2.1 Introduction

Background information pertaining to adsorption and transport theory is presented in this chapter. Mechanisms of sorption and chemical factors effecting sorption are discussed, along with a review of the empirical and experimental methods of determining sorption and retardation coefficients. In addition, a brief review of previous investigations on sorption characteristics of naphthenic acids is presented.

### 2.2 Transport and Sorption Theory

Adsorption differs from absorption in that the former refers to the association of molecules at the solid-fluid interface such as the external surface of a sorbent particle in the presence of the bulk fluid. Absorption occurs when molecules penetrate the solid surface and intermingle with its three-dimensional molecular or atomic matrix (Pignatello 2000). In this study, the term *solute* will be used to refer to the free naphthenic acids in solution. *Sorbent* refers to the solid phase or phases unto which the solute can sorb. The solute that has sorbed onto the sorbent surfaces is referred to as *sorbate*.

In some studies, the distribution of the solute between the dissolved phase and organic fraction of the sorbent is designated by the term “partition” while adsorption is used in reference to the binding of the solute with the sorbent mineral fraction (Chiou et al. 1983). In this study, no such distinction in terminology was made, and both adsorption

and partitioning are used to describe the totality of the processes of binding of solute with the organic and mineral fraction of the sorbent.

### 2.3 Equilibrium Sorption Models

Sorption is a potentially significant attenuating mechanism in transport of groundwater contaminants in groundwater (Fetter 1999; Freeze and Cherry 1979). The following is the governing equation for one-dimensional, advective dispersive transport in porous media, including the effects of advection, dispersion, and adsorption:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{\rho_d}{n} \frac{\partial S}{\partial t} \pm \left( \frac{\partial C}{\partial t} \right)_{\text{rxn}} \quad (2.1)$$

where,  $C$  is the concentration of the solute in liquid phase ( $M/L^3$ ),  $t$  is time,  $D_h$  is the hydrodynamic dispersion coefficient ( $L^2/T$ ),  $v_x$  is the average linear groundwater velocity ( $L/T$ ),  $\rho_d$  is the bulk density of soil ( $M/L^3$ ),  $n$  is the porosity of the porous media,  $S$  is the amount of solute sorbed per unit soil ( $M/M$ ), and  $r_{\text{xn}}$  is a subscript indicating a biological or chemical reaction of the solute (Freeze and Cherry 1979).

Equation 2.1 is derived for a small element in the porous media and assumes that the medium is homogenous and isotropic and that the flow velocity does not vary through space or time. The terms in Equation 2.1, from left to right respectively, represent the time rate of change of mass of solute within the element, the flux of the solute out of the

element by hydrodynamic dispersion, the flux of solute into the element by advection, the loss of solute due to sorption, and the gain/loss of solute due to chemical reactions.

The fourth term in Equation 2.1 is related to sorption of the solute and is of importance since it quantifies the degree of retardation of solute transport. Several models have been proposed to quantify the degree of retardation for solutes. In each case, a relationship for  $S$  as a function of  $C$  is determined by correlating experimental data to the best fit model. While both equilibrium and first-order kinetic models exist for the quantification of sorption, an equilibrium approach is often used since the rate of sorption is often significantly greater than the rate of change in concentration of solute in soil solution due to any other mechanisms (Travis and Etnier 1981). Three of the more common models for quantification of sorption are the Linear, the Freundlich, and Langmuir models.

### *2.3.1 Langmuir Sorption Isotherm*

Langmuir takes into consideration that a solid surface possesses a limited number of sorption sites such that when all sorption sites are filled the solid cannot sorb further solute from the surrounding solution (Fetter 1999). The general shape of the Langmuir isotherm is illustrated in Figure 2.1.

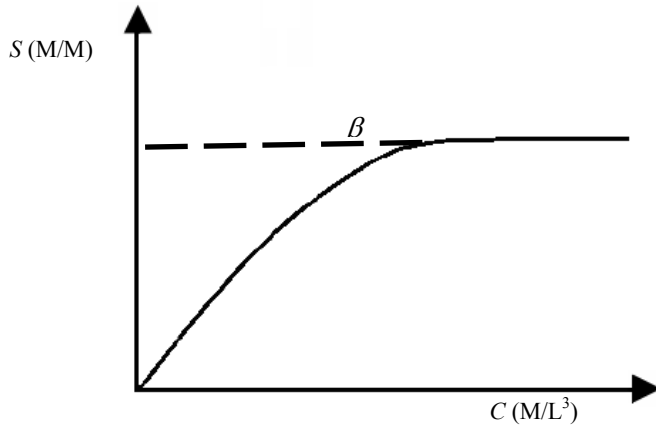


Figure 2.1 Typical Langmuir Isotherm

A sorbent will have a sorption capacity  $\beta$ , defined as the ratio of the mass of sorbate to the unit mass of sorbent.  $S$  represents the concentration of the sorbate in the solid phase, and  $C$  is the concentration of dissolved solute in equilibrium with the mass of solute sorbed onto the solid phase. Therefore the total sorption capacity is described as  $\beta m$ , where  $m$  equals the mass of the sorbent. In developing the associated governing equation, it is assumed that the rate of sorption is proportional to the dissolved concentration of the chemical ( $C$ ) and to the difference between the total sorption capacity ( $\beta m$ ) and amount sorbed ( $S m$ ) (Delle Site 2000). The result is the following equation:

$$\frac{\partial C}{\partial t} = K_2 S m - K_1 C (\beta m - S m) \quad (2.2)$$

Where  $K_1$ , and  $K_2$  are rate constants related to sorption and desorption respectively (Delle Site 2000). At steady-state or equilibrium the concentration at any point in the



medium is constant and the differential equation can be simplified and solved for  $S$  yielding the Langmuir isotherm in Equation 2.3

$$S = \frac{bC\beta}{1 + bC} \quad (2.3)$$

where  $b$  is equal to  $K_1/K_2$ . Sorption data conforming to the Langmuir relationship will reach a maximum sorption value when plotted as  $S$  versus  $C$ . Langmuir parameters  $b$  and  $\beta$  can subsequently be determined by plotting  $C/S$  versus  $C$  where the y-intercept yields  $1/b\beta$  and the slope of the plotted line is  $1/\beta$ . This will result in a linear relationship described by the following equation

$$\frac{C}{S} = \frac{1}{b\beta} + \frac{C}{\beta} \quad (2.4)$$

In the absence of other geochemical reactions, Equation 2.1 can be written in terms of a retardation coefficient ( $R_d$ ) as follows:

$$\frac{\partial C}{\partial t} R_d = D_h \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \quad (2.5)$$

where  $R_d$  is

$$R_d = 1 + \frac{\rho_d}{n} \left( \frac{\partial S}{\partial C} \right) \quad (2.6)$$

Therefore, for compounds whose sorption behavior is described by the Langmuir isotherm, the differentiation of Equation 2.3 and substitution into 2.6 yields a retardation coefficient as follows:

$$R_d = 1 + \frac{\rho_d}{n} \left( \frac{b\beta}{(1 + bC)^2} \right) \quad (2.7)$$

### 2.3.2 Freundlich Sorption Isotherms

The Freundlich model was initially proposed as an empirical model (Freundlich 1926).

The isotherm is depicted in Figure 2.2, and is described by the non-linear relationship in Equation 2.8.

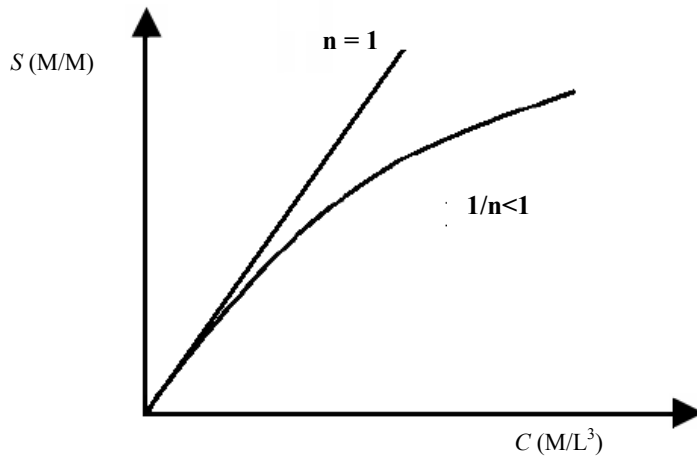


Figure 2.2 Typical Freundlich isotherm

$$S = KC^N \quad (2.8)$$

The values  $K$  and  $N$  are constants. Empirical data fitting to the Freundlich function will be curvilinear when plotted on arithmetic graph paper (Fetter 1999). Plotting  $\log C$  against  $\log S$  will allow for the  $K$  and  $N$  to be determined according to:

$$\log S = \log K + N \log C \quad (2.9)$$

Differentiation of Equation 2.9 with respect to  $C$  and substitution of the result into Equation 2.6 yields the following retardation coefficient:

$$R_d = 1 + \frac{\rho_d KNC^{N-1}}{n} \quad (2.10)$$

### 2.3.3 Linear Sorption Isotherm

Where a direct linear relationship exists between the amount of solute sorbed onto the solid surfaces ( $S$ ) and the concentration of the solute in solution ( $C$ ), the sorption isotherm will be represented as a straight line. A typical linear isotherm is depicted in Figure 2.3.

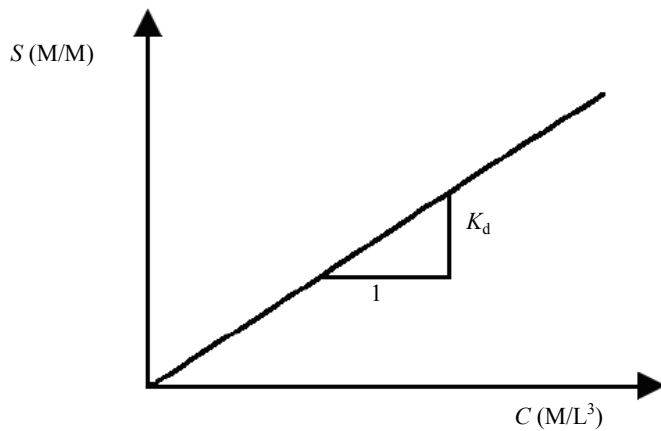


Figure 2.3 Typical linear isotherm

The linear isotherm is described by the following relationship

$$S = K_d C \quad (2.11)$$

with the retardation coefficient being

$$R_d = 1 + \frac{\rho_d}{n} K_d \quad (2.12)$$

In natural systems and at low solute concentrations, all the models approach the linear model (Delle Site 2001; Pignatello 2000).

## 2.4 Kinetic Adsorption Models

Some organic compounds have been known to exhibit sorption which cannot be described by the equilibrium model, that is, the rate of sorption is less than the rate of change of solute concentration due to other factors (Pignatello, 2000). Several models have been developed to describe sorption kinetics. The models can be generally classified into three types; one-box model, two-box model, and diffusion controlled model (Travis and Etnier, 1981; Pignatello, 2000; Wu and Gschwend, 1986).

The least complex of the three proposed models is the one-box system. Here the sorbent is assumed to be a homogenous mixture and adsorption is controlled by one reversible process. Travis and Etnier (1981) present several forms of this model including a reversible linear and a reversible non-linear where the latter proposes a forward sorption reaction that is non-linear and a backwards desorption step that is linear. Other forms include the kinetic product model which is purely empirical in its derivation with no

mathematical foundation, and the bilinear model which holds the same mathematical form as that of the Langmuir adsorption isotherm (Equation 2.3).

The two-box or two-site kinetic model involves the division of the sorbent into two distinct groups of sorption sites. The reasoning behind the division is that a solute in contact with soil may react at different rates with different components of the soil matrix (Travis and Etnier, 1981). That is, the sorbent may have two classes of sorption sites, one being more accessible resulting in a rapid and almost instantaneous sorption reaction (type I), and one less accessible for sorption by the solute resulting in sorption which can best be described by kinetics (type II; Travis and Etnier, 1981). The governing equation for this model takes into account the fraction of sorption sites which are occupied by the type I reaction and relates this value to the fraction of sites available for the type II reactions.

The third model type describing kinetic sorption is known as a diffusion model which can be further subdivided into fixed-pore diffusion models, soil organic matter (SOM) models, and combined fixed-pore and soil organic matter diffusion models (Pignatello, 2000). Here adsorption kinetics results in penetration of the solute into the macropores, mesopores, and micropores of the associated soil aggregates, and dissolution of the solute into a “rubbery” SOM matrix analogous to a highly viscous fluid.

## **2.5 Sorption Mechanisms and Affecting Factors**

The sorption of organic molecules onto soil complexes can be categorized into three

broad mechanisms of *chemisorption*, *physiosorption*, and *ion-pair formation* or ion exchange (Pignatello 2000). *Chemisorption* involves significant molecular interaction via orbital overlap of chemical functional groups in solute and solids phases. Such interactions can have a covalent or ionic character, and the formation of a covalent bond is usually irreversible (Pignatello 2000, Delle Site 2001). *Physiosorption* involves weak intermolecular forces and consists of van der Waals forces, charge transfer, and hydrogen bonding where dipole-dipole type forces are available to all molecules, and H-bonding typically involves organics acids and bases (Pignatello 2000). *Ion-pair formation* can be an important sorption mechanism for hydrophobic ionizable organic compounds (HIOC) such as naphthenic acids, and involves electrostatic attraction between an organic anion or cation and a charged site on the sorbent (Pignatello 2000; Travis and Etnier 1981).

Hydrophobic ionizable organic compounds can also readily adsorb onto ion exchangers. However, ion exchange selectivity is affected by the size of the non-polar group (Li and SenGupta 2004). For this reason the chemical characteristics of the sorbent also strongly effect the sorption behavior. The scenario is further complicated by the fact that solution chemical characteristics such as pH can affect the availability of soil mineral-surface exchange sites which are known to attract HIOC compounds (Delle Site 2001). HIOC sorption behavior is governed by a number of other factors such as moisture content in the sorbing system, the presence of the exchangeable cations, ionic strength of the solution, and water solubility and dissociation constant of the solute ( $K_a$ ) (Martins and Mermoud 1998; Delle Site 2001). Delle Site (2001) reports other

carboxylic acids whose sorption is dependant upon soil organic matter (SOM) content, as well as soil clay species at critically low values of organic mater. Other factors specifically affecting the sorption of HIOCs are discussed in the following section.

## 2.6 Prediction Methods for Sorption Coefficients

There is a small amount of adsorption of neutral organic compounds onto the mineral surfaces of soils, for electrically neutral or non-polar compounds; however, the primary sorbing surface is the fraction of organic matter in the soil containing carbon denoted by  $f_{oc}$  (Fetter 1999; Delle Site 2001, Pignatello 2000).  $K_d$ , which represents the partitioning coefficient for a linear sorption isotherm, can therefore be expressed in terms of the adsorption coefficient with respect to the organic fraction ( $K_{oc}$ ) forming the relationship:

$$K_d = K_{oc} f_{oc} \quad (2.13)$$

This illustrates that the adsorption coefficient can also be directly correlated to aquifer organic matter. Approximately 50% of the organic matter ( $f_{om}$ ) within a soil contains organic carbon (Fetter 1999; Delle Site 2001). Therefore,  $K_{oc}$  relates to the partitioning coefficient of organic matter ( $K_{om}$ ) with the following approximation:

$$K_{oc} = 1.724 K_{om} \quad (2.14)$$



There are numerous empirical relationships developed for estimating  $K_{oc}$  of organic solutes in groundwater. The three most common involve determining  $K_{oc}$  in relation to the octanol/water partitioning coefficient, correlations with water solubility, and correlations with molecular descriptors (Delle Site 2001; Fetter 1999).

Octanol water correlations have been developed for several different classes of compounds and the various equations developed yield similar results for many compounds. The inherent assumptions made by these relationships include the following: sorption is primarily hydrophobic not involving polar groups or ionic interactions; sorption is primarily related to the organic carbon fraction of the soil's organic matter; and that the relationship between sorption and the solute concentration is a linear one (Delle Site 2001; Fetter 1999).

The use of solubility data in determining the adsorption coefficient is complicated by the effects of temperature and ionic strength on solubility of solutes. Solubility data is currently unavailable in the literature for naphthenic acids in OSTW and approximations are reported with wide variability in literature (Fetter 1999). Furthermore, for compounds whose solubility is below 1 ppm, correlations derived from measured octanol/water partition coefficient ( $K_{ow}$ ) and organic carbon partition coefficient ( $K_{oc}$ ) are typically inaccurate since the error in measurement may be larger than the solubility (Delle Site, 2001).

Sorption is also affected by the presence of ions in solution, a phenomenon referred to as the salting-effect or salting-out effect which reduces the solubility of organic compounds in solution. Due to the large number of intermolecular interactions which exist between the solvent and dissolved ions and non-electrolytes in solution, the effect of adding salts is thermodynamically complex. Several different qualitative and quantitative theories have been put forward to explain salting-out, each of which emphasizes different intermolecular interactions (Grover and Ryall, 2005).

The simplest and most concise of these is the hydration theory which postulates that ions in solution attract a layer of solvent molecules (Grover and Ryall, 2005). The ions bond tightly to water molecules forming what is referred to as a hydration shell. This results in an increase in the polarity of the water molecules. The result is that it becomes more difficult for less polar molecules to remain in solution. The more ions that are added to the water, the higher the effective polarity of the solution becomes, ultimately decreasing the affinity of the solution for less polar molecules such as hydrocarbons. Because the charge and degree of hydration experienced by water molecules varies according to which ions are present in solution, salting-effects on the dissolved hydrocarbons also vary with the types of ions present in solution. It is difficult to distinguish the effect of cations from anions on the solubility of hydrocarbons, since any electrolyte in solution is in a state of balanced electrical charge (Gong 1997).

Molecular topology relates the shape of the organic molecule to  $K_{om}$ . The specific parameter that is correlated to  $K_{om}$  is called the first order molecular connectivity index,

${}^1\chi$ . Molecular connectivity index is calculated on the basis of a parameter denoted as  $\delta$  which represents the number of non-hydrogen atoms to which the atom of interest is bonded (Kier and Hall 2002).

Estimating  $K_d$  from molecular topology has some advantage over solubility and octanol water estimation methods since the method can be extended to polar and HIOCs (Sabljic 1987). In relation to naphthenic acids, the molecular topology method does not account for the effect of pH on the degree of ionization of compounds in solution. Furthermore, the exact molecular structure of the compounds in an OSTW mixture of naphthenic acids is unknown making it difficult to calculate  $\delta$  and  ${}^1\chi$ .

For ionizable organic acids such as naphthenic acids, the majority of the molecules will be in their ionized form when the pH of the solution is greater than two plus the  $\text{pK}_a$  (Delle Site 2001), where  $K_a$  is the ionization or dissociation constant for a partially ionized acid, and  $\text{pK}_a$  represents the negative log of the ionization constant. The  $\text{pK}_a$  of naphthenic acids has been cited as being between 4.9 to 6 by various authors (Havre et al. 2003; Headley et al. 2002).

Delle Site (2001) presents an alternate derivation for  $K_{oc}$  based on experiments conducted to study the sorption of nine chlorinated phenols (2001). In determining the total  $K_{oc}$ , Equation 2.15 accounts separately for the fraction of dissociated and undissociated molecules sorbed to the organic carbon fraction of the soil based on the  $\text{pK}_a$  of the solute and the solution pH (2001).

$$K_{oc} = K_{oc,neut} Q + K_{oc,ion} (1 - Q) \quad (2.15)$$

Appendix A outlines the derivation of  $Q$  based on the equilibrium constant ( $K_a$ ). Given an approximate value of  $pK_a$  5.5 and a solution pH of 8,  $Q$  attains a value of 0.00315 which reflects the fact that the majority of the naphthenic acids in OSTW are in their ionized form.

Overall, solubility and  $K_{ow}$  methods were devised strictly for non-polar organic compounds and cannot be extended to polar organic compounds (Fetter 1999).

Furthermore, in relation to the current study, none of the above methods can directly account for elevated ionic strength in the solution, or temperature effects.

## **2.7 Experimental Determination of Sorption Coefficients**

### *2.7.1 Column and Diffusion-Cell Techniques*

The sorption behavior of a compound is typically studied by establishing the sorption isotherm from experimental data in which the equilibrium concentration of the compound in contact with the sorbent is plotted as a function of its equilibrium concentration remaining in solution at a specified temperature. Methods of measuring equilibrium sorption fall into two general categories; steady-state and transient methods, where each method has its own associated apparatus and analysis.

The time-lag method is a steady-state method using a diffusion cell (Figure 2.4). In this case the soil is initially at zero concentration, and the concentration of the solute in the collection reservoir is maintained close to zero throughout the test. The solute concentration in the source reservoir is kept constant and the total amount of diffusing solute per cross-sectional area ( $Q_t$ ) is plotted against time throughout the test (Shackelford 1991). If  $Q_t$  is evaluated as the integral of Fick's first law for diffusion in saturated soil ( $J_D$ ), the resulting expression for  $Q_t$  is:

$$Q_t = \left( \frac{nD^* C_1}{L} \right) \left( t - \frac{R_d L^2}{6D^*} \right) \quad (2.16)$$

where;  $D^*$  is the diffusion coefficient and  $R_d$  can be calculated by reading the value of the time intercept ( $T_L$ ) from the graph of  $Q_t$  versus  $t$  which is:

$$T_L = \frac{R_d L^2}{6D^*} \quad (2.17)$$

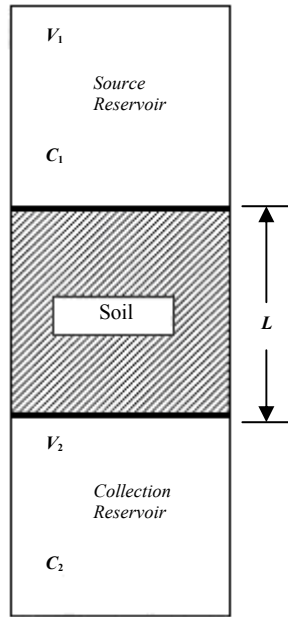


Figure 2.4 Diffusion cell, plan view schematic (adapted from Donahue 1994)

The adsorption coefficient ( $K_d$ ) can then be calculated from  $R_d$  knowing the bulk density ( $\rho_d$ ) and porosity ( $n$ ) of the soil system.

Transient diffusion cell techniques, such as half cell and reservoir methods, are also used (Shackelford 1991). A common transient method is the column test. Here a steady-state fluid flow is established through the soil packed column. The fluid in the influent reservoir (Figure 2.5) is then changed to a solution with a known constant concentration ( $C_o$ ) of the chemical species under analysis. The concentration,  $C$ , of the chemical species appearing in the effluent reservoir is measured with time and the results are plotted as a relative concentration of  $C/C_o$  versus pore volumes of flow in the form of a solute break-through curve. If a non-reactive tracer is added to the influent solution and its concentration monitored with time, the ratio of pore volumes of flow for

the reactive solute to the pore volumes of flow of the non-reactive solute at a relative concentration of 0.5 is typically taken as  $R_d$  (Freeze and Cherry 1979; Shackelford 1991). Both diffusion cell methods and column methods make the assumption that  $K_d$  is described by a linear function (Pignatello 2000).

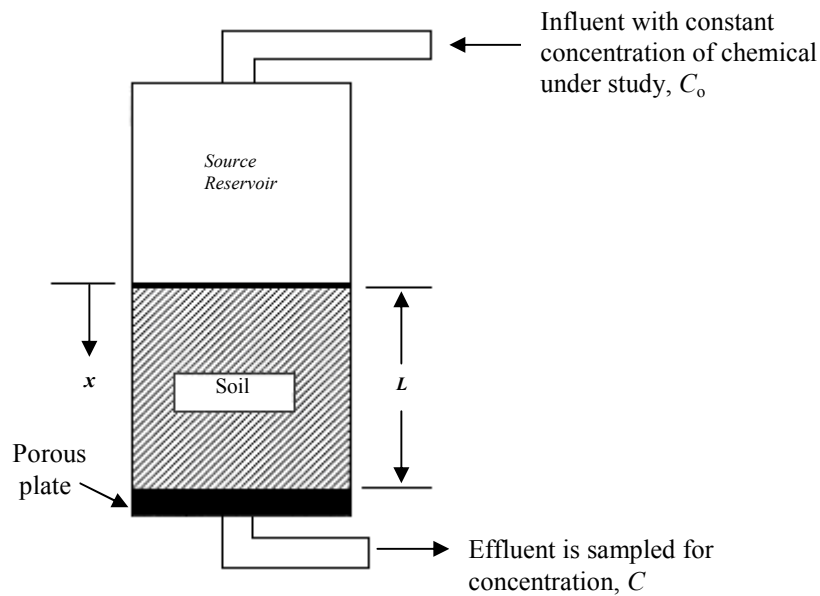


Figure 2.5 Column test, plan view schematic (adapted from Donahue 1994)

### 2.7.2 Batch Testing

In batch experiments, solutions spiked with the solute under study over a range of concentrations are each mixed with the sorbent or geological material in a reactor vessel. The reactor vessel is agitated throughout the course of the experiment in order to achieve uniform conditions. Standards such as the ASTM standard method D-4319 and D-4646 outline batch test procedures in detail (ASTM 2003; Freeze and Cherry 1979; Pignatello 2000). After adequate time has been allowed for the sorption reaction to

reach steady-state, a sufficient aliquot of supernatant can be drawn from each reactor vial and analyzed for the solute concentration. A plot of sorbate concentration ( $S$ ) versus steady-state solute concentration ( $C$ ) can then be developed and sorption parameters quantified using one of the models discussed previously. A set of control tests is often run in order to monitor potential loss of solute onto reactor vessel walls. Batch testing is a convenient and relatively quick method for the study of the sorption characteristics of a solute species.

For compounds whose sorption characteristics are relatively unknown, batch testing provides a simple method for direct determination of the adsorption coefficient or other relevant sorption parameters. Other advantages include the relative ease with which soil blanks can be ran simultaneously with the batch reactors to determine the background concentration of solute that may be present in the soil. Other methods such as the time lag method require that the concentration of the solute in soil be zero at the outset of the test. This may be difficult to achieve particularly in cases where soils investigated are from the same geographical area that the solute is naturally found, such as is the case with naphthenic acids.

## **2.8 Previous Work on Naphthenic Acid Adsorption**

Peng et al. (2002) studied the adsorption of single-ring ( $Z = -2$ ) surrogate naphthenic acids on soils using a batch partitioning method. This study examined the influence of the molecular structure of the sorbate, the organic carbon content of the sorbent, the



temperature, ionic strength (calcium chloride), and the pH of the solution on the adsorption isotherms. The effects of molecular structure of the surrogate acids were also studied by examining the sorption behavior of two related model naphthenic acids, 4-methylcyclohexaneacetic acid (4MACH) and 4-methylcyclohexanecarboxylic acid (4MCCH).

Peng et al. (2002) reported linear sorption isotherms for both model naphthenic acids. The molecular structure of the isomers was not found to have a significant impact on sorption. Similarly the two temperatures studied (23° and 4°) yielded no significant difference in  $K_d$ . Inorganic salt concentration had a significant effect on adsorption causing  $K_d$  to increase with increased ionic strength. Organic carbon content also had significant effects on sorption as sorption increased with increasing organic carbon content. Changing pH also affected sorption where  $K_d$  decreased with increases in pH from acidic to alkali conditions. Overall, low  $K_d$  values were reported, ranging from 0.10 mL/g for 4-MACH in Milli-Q water, to 0.22mL/g for 4-MACH in a 30 mM calcium chloride solution, suggesting that these model naphthenic acids will partition preferentially to the water column in aquatic environments. The soils used in the current program are the same as those used by Peng et al.

Gervais (2004) evaluated the theoretical retardation of naphthenic acids in glacio-fluvial sands using soil-water adsorption coefficients ( $K_d$ ). The  $K_d$  values were determined by batch equilibration experiments for a mixture of OSTW naphthenic acids as well as nine surrogates. The soil tested with the tailings naphthenic acids solution had a low organic

carbon content of 0.6%. The pH of the test solutions ranged from 7 to 8. Gervais found low sorption for the tailings derived naphthenic acids on the soils tested with  $K_d$  values of 0.092, 0.12 and 0.16 mL/g for solutions with initial concentrations 10, 30 and 130 mg/L respectively. This is equivalent to retardation coefficients (porosity of 0.3, bulk density of 1.5 g/mL) ranging from 1.2 to 2.6. However, no measurable sorption was found in the monitoring of an actual plume. Ionic strength in samples tested varied due to variation in the amount of NaOH and HCL required to adjust pH levels but were generally low ranging between 5mM to 7.5mM for most solutions. Gervais found that three of the surrogate naphthenic acids that were tested demonstrated Freundlich sorption isotherms with  $n > 1$ . The OSTW derived naphthenic acids (stock naphthenic acids) tested were found to have Freundlich sorption isotherms ( $n > 1$ ), while the sorption isotherms for three other surrogate acids were found to be linear. Gervais hypothesized that the latter three surrogate acids were not representatives of petroleum derived mixtures and are likely not present in the OSTW mixture of naphthenic acids. The OSTW mixture of naphthenic acids tested were found to be poor in low molecular weight compounds. A statistical  $t$ -test was conducted to determine differences in initial and final sorption samples; however, it is unclear whether the statistical analysis compared all carbon numbers simultaneously from corresponding samples, or whether molecular composition was organized by  $Z$  family, with statistical comparison made between  $Z$  families of corresponding samples. The later approach was adopted in the current study and will be discussed in following sections.

## 2.9 Summary

Both equilibrium and kinetic models are available for the representation of the sorption behavior of organic compounds. When equilibrium isotherms are used to describe the experimental sorption data, the three most common isotherms for describing solid–liquid sorption systems are the Langmuir, the Freundlich, and the linear isotherms. Experimental determination of naphthenic acid sorption parameters requires determination of the best fit to a sorption isotherm model. For naphthenic acids, factors affecting sorption parameters include pH of the liquid-solid sorption system, where pH affects the degree of ionization of the naphthenic acids, as well as the availability of the soil mineral exchange sites.

Prediction methods for determining sorption parameters make a number of assumptions that limit their application to the determination of naphthenic acid sorption parameters (i.e. sorption is hydrophobic; involves primarily the organic carbon fraction of the soil's organic matter; and is described by a linear relationship). Therefore, under both field and laboratory conditions, sorption parameters of naphthenic acids can best be determined experimentally. At the time of this study no additional studies on the sorption behavior of naphthenic acids in liquid-solid sorption systems were available. To the author's knowledge, no studies to-date have evaluated naphthenic acid sorption characteristics under conditions of elevated salinity and investigated selective sorption behavior amongst the individual species in an OSTW mixture of naphthenic acid.

### **3 MATERIALS AND METHODS**

#### **3.1 Introduction**

This laboratory program attempts to determine  $K_d$  values for OSTW naphthenic acids for two soils tested with Milli-Q water or a saline solution as the test solutions. The program will also seek to evaluate whether components of the OSTW naphthenic acids mixture preferentially adsorb. Materials and methods applied in developing an analytical approach for the study of naphthenic acids adsorption are discussed in this chapter. The extraction procedure used to acquire the OSTW naphthenic acid extract is also outlined along with batch reactor test procedures and the solid phase extraction sample cleanup procedure.

#### **3.2 Soils**

Two soils from an oil sands extraction facility located north of Fort McMurray, AB were used as sorbents in this study. The soils were mineral peat mixtures produced during salvage operations, with Soil 1 having a higher organic carbon fraction ( $f_{oc}$ ) than Soil 2. Both samples were air dried and ground to pass a no. 10 sieve. The properties of the soil were tested with standard procedures (Carter, 1993; Tiessen et al., 1983) by Enviro-Test Laboratories, Saskatoon, SK, Canada, and the results are summarized in Table 3.1. Appendix B outlines the analytical methods used by Enviro-Test laboratories to determine the chemical properties of soil samples.

Table 3.1 Properties of tested soil

Properties	Soil No. 1	Soil No. 2
Organic carbon (%)	2.7	1.6
Organic matter (%)	4.7	2.8
Inorganic carbon (%)	0.26	0.23
Na <sup>+</sup> (µg/g)	107	64
Ca <sup>2+</sup> (µg/g)	177	98
Mg <sup>2+</sup> (µg/g)	37	16
K <sup>+</sup> (µg/g)	4	3
CEC (mequiv./100g)	19.4	16.2
pH	7.7	7.7
SAR	1.9	1.6
Moisture (%)	2.3	1.9

**NOTE:** CEC, cation exchange capacity; SAR, sodium adsorption ratio.

### 3.3 Naphthenic acid extract

Figure 3.1 is a schematic illustration of the process of isolating naphthenic acids from OSTW by organic extraction as developed by Rogers et al. (2002b). The procedures as developed by Rogers et al. (2002b) were slightly modified to make the procedure better suited to continuous extraction of a large volume of tailings water.

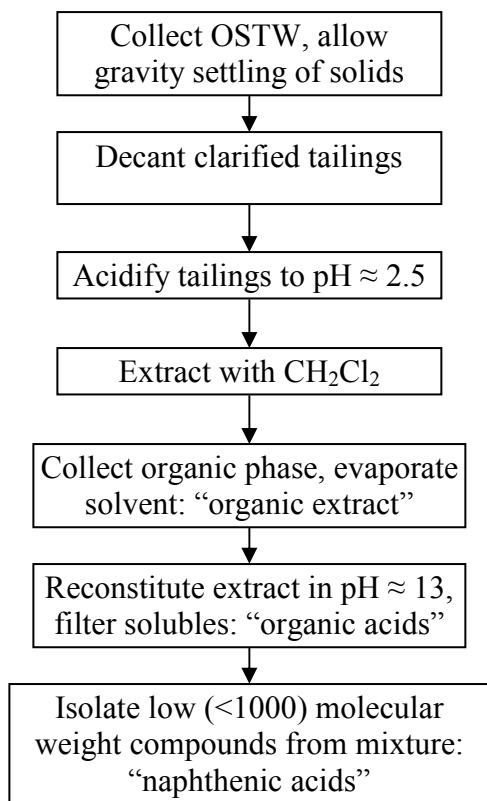


Figure 3.1 Schematic depiction of procedure for extraction of naphthenic acids for OSTW

The OSTW was obtained from an oil sands settling basin at an oil sands mine site north of Fort McMurray Alberta, Canada. The extraction procedure allowed for six liters of OSTW to be extracted simultaneously using three 2 liter separatory funnels. The process calls for acidification of the OSTW by the addition of approximately 0.4ml of 18.76M Sulfuric acid ( $H_2SO_4$ ) for every two liters of OSTW, or enough acid to achieve a pH of 2.5 (Rogers et al., 2002b). This step was accomplished directly in the 20 liter carboys in which the OSTW was originally transported. It was observed that after acidification of the carboy, the majority of the suspended solids settled to the bottom.

Since the solid fraction contains the majority of naphthenic acids in their neutral form, the carboys were vigorously shaken before the transfer of any water to the separatory funnels for extraction.

Two liters of acidified OSTW was transferred to each separatory funnel, and subsequently 400 mL of dichloromethane (DCM) was added to each funnel. In higher turbidity samples, it was found that more DCM was required in order to decrease the emulsification of the organic and aqueous fractions forming in the separatory funnels. The mixture of OSTW and DCM was then alternately shaken and vented for approximately 2 minutes to allow separation of the naphthenic acids to the organic (DCM) phase.

A thick emulsion generally formed in each of the separatory funnels as a result of the mixing of the solutions. This emulsion was allowed to break up for several minutes and the breakup was facilitated by gentle rotation and agitation of the separatory funnels. Particulate solids were mostly confined to the aqueous phase. The solvent phase was drained into a 1 L separatory funnel up to the emulsion interface. At this point, a substantial volume of emulsion still remaining and was transferred to another 1 L separatory funnel. This latter transfer facilitated the breakup of the emulsion, allowing for separation of the solvent phase from the remaining aqueous phase.

The solvent phase was then decanted from each of the separatory funnels into 1 L round-bottom flasks. The solvent was then concentrated by evaporation on a rotary

evaporator at 60°C to a volume of approximately 20 mL and transferred to a 600 mL beaker and allowed to evaporate at room temperature leaving a tar like concentrate. After approximately 100 L of OSTW were extracted, the organic fraction was then reconstituted in 600 mL of water, and was brought to a pH of 13 using 1.0 N sodium hydroxide solution to facilitate dissolution of the organic extract. Upon dissolution, the pH was reduced to below a pH of 10 using sulfuric acid and the mixture was filtered through 0.45 µm and 0.1 µm glass fiber microfilter respectively. The filtrate was then subjected to a 1000 molecular weight cutoff filter with an ultrafiltration procedure in order to isolate the naphthenic acids, producing a naphthenic acid concentrate which was used as a spike for sorption testing.

### **3.4 Batch test setup**

Batch tests were conducted according to ASTM D4646, with the soil to solution ratio adjusted to 1:3 instead of 1:20 in order to minimize the impact of colloidal suspensions. A typical batch reactor consisted of a 20 mL glass vial capped with aluminum and a Teflon-coated septum. In preparing the reactor for the adsorption experiment, a known mass of air-dried soil sample was weighed into each vial and then a series of prepared naphthenic acid solutions at five specified concentrations were added to the vials. All samples were prepared in triplicate. The batch reactors were agitated on a wrist shaker for the duration of the testing. Test duration was two weeks for the preliminary batch experiments, and 24 hours for the sorption batch experiments.



### 3.5 Preliminary testing

The procedures of Peng et al. (2002) were initially repeated to gain familiarity with the batch testing procedure. Subsequently, preliminary batch tests were conducted using Soil 1 and Milli-Q water as background solution for the extracted mixture of OSTW naphthenic acids. The preliminary tests were conducted to determine the time required for adsorption to reach steady-state, and to determine if the extracted naphthenic acids exhibit measurable sorption.

Batch tests in the preliminary trial were conducted for two weeks using a 200 mg/L naphthenic acid concentration, with samples taken before the initiation of the test, every two hours in the first 24 hours, and once in 24 hours for the remainder of the two weeks. In this way, the kinetics of adsorption was evaluated since slow sorption has been exhibited by other aliphatic hydrocarbons (Pignatello 2000; Huang 1998; Pignatello 1996). Preliminary tests were conducted at room temperature  $23 \pm 1^\circ\text{C}$  with pH values adjusted to  $8.0 \pm 0.4$ . pH values were determined using an ISFET mini-lab pH meter (Canadawide, Ottawa, ON).

A second preliminary trial was then conducted testing five different concentrations of naphthenic acids in order to establish a sorption isotherm for Soil 1. The concentrations as tested were 80, 120, 160, 180, and 200 mg/L. The batch tests were conducted at room temperature  $23 \pm 1^\circ\text{C}$  with pH values adjusted to  $8.0 \pm 0.4$ . The batch tests were continuously sampled every six hours for 24 hours, every 12 hours for the following 24 hours, and every 48 hours thereafter for a total of two weeks.

### 3.6 Testing of Partitioning coefficient

Testing of the adsorption characteristics and distribution coefficient of the naphthenic acid mixture was conducted with appropriate concentrations of the mixture prepared in both Milli-Q water as well as synthetic groundwater (SGW). SGW was prepared according to Donahue et al. (1994) as summarized in Table (3.2). Sodium Azide (BDH Chemicals, Toronto, ON) at a concentration of 525 ppm was added to both solutions as a microbial inhibitor. Subsequently, five concentrations (80, 120, 160, 180, and 200 mg/L) were used in order to establish an adsorption isotherm. All samples were run in triplicate.

Table 3.2 Synthetic groundwater chemistry

Composition	Concentration (mg/L)
CaSO <sub>4</sub> (BDH Chemicals, Poole, UK)	1013
MgSO <sub>4</sub> (BDH Chemicals, Toronto, ON)	938
NaN <sub>3</sub> (BDH Chemicals, Toronto, ON)	525

#### 3.6.1 Control Tests

Two types of control tests were run simultaneously with the batch reactors. The first was a set of soil blanks which contained water and soil but no naphthenic acids. The purpose of these was to measure the presence of background naphthenic acids or

compounds that would emulate naphthenic acids in the mass spectrometric analysis. A second set of controls were run which contained the naphthenic acid solutions at the same concentration as the batch tests, but contained no soil. The purpose of these was to detect any measurable loss of naphthenic acids by plating out on the glass surfaces. All testing was conducted in a temperature controlled cooler at 4°C and pH of all solutions was adjusted to  $8.0 \pm 0.4$ .

### **3.7 Solid Phase Extraction Sample Cleanup**

A Solid Phase Extraction procedure (SPE) was implemented for the purpose of eliminating matrix effects resulting from the ions present in the SGW solution. Matrix effects can be described as the combined effect of all components of the sample other than the analyte on the measurement of the quantity. If a specific component can be identified as causing an effect then this is referred to as interference. (IUPAC, 1997). In this case, the interference was a result of inorganic ions in the SGW solution, as discussed in the following results and discussion sections. The SPE procedure was carried out as follows:

After the reactors were removed from the wrist shakers, each reactor was centrifuged for approximately 15 minutes to settle suspended solids. 10 mL of supernatant was drawn from each reactor vial and decanted into a new 20 mL vial to be centrifuged again. The supernatant samples were then acidified with approximately 200  $\mu$ L bringing the pH to approximately 2. Isolute ENV+ cartridges (Biotage, Charlottesville, Virginia) were

used in all extractions. Previous work with the extraction of naphthenic acids used the Isolute ENV+ successfully (Headley et al., 2002), and further testing in this study verified their efficiency in naphthenic acids extraction. The cartridges were conditioned by rinsing with 6-10 mL of acidified Milli-Q water, the same volume of acetonitrile, and a final rinse with Milli-Q water. 5 mL of the naphthenic acid solution under investigation was diluted ten times in an acidified solution (pH 2) and following dilution, the sample was allowed to percolate through the SPE column. The sample was then allowed to decant slowly through the column with an initial vacuum pressure of 660 mmHg applied as a siphon. With the naphthenic acids retained on the column bed material, the columns were rinsed with Milli-Q water and vacuum suctioned to remove excess water. Approximately 10 mL of acetonitrile (ACN) was pipette into each column and the ACN was allowed to slowly percolate through the column, rinsing the naphthenic acids through to storage test tubes. The procedure was then repeated with another 5 mL of ACN. The samples were then dried on a nitrogen evaporator and brought up to the initial volume of 5 mL by pipette, making the samples ready for analysis. This procedure was performed with both the initial ( $t=0$ ) and sorbed samples, as well as the Milli-Q water and control samples in order to ensure all samples were exposed to the same analytical conditions. Figure 3.2 depicts a typical solid phase extraction apparatus.

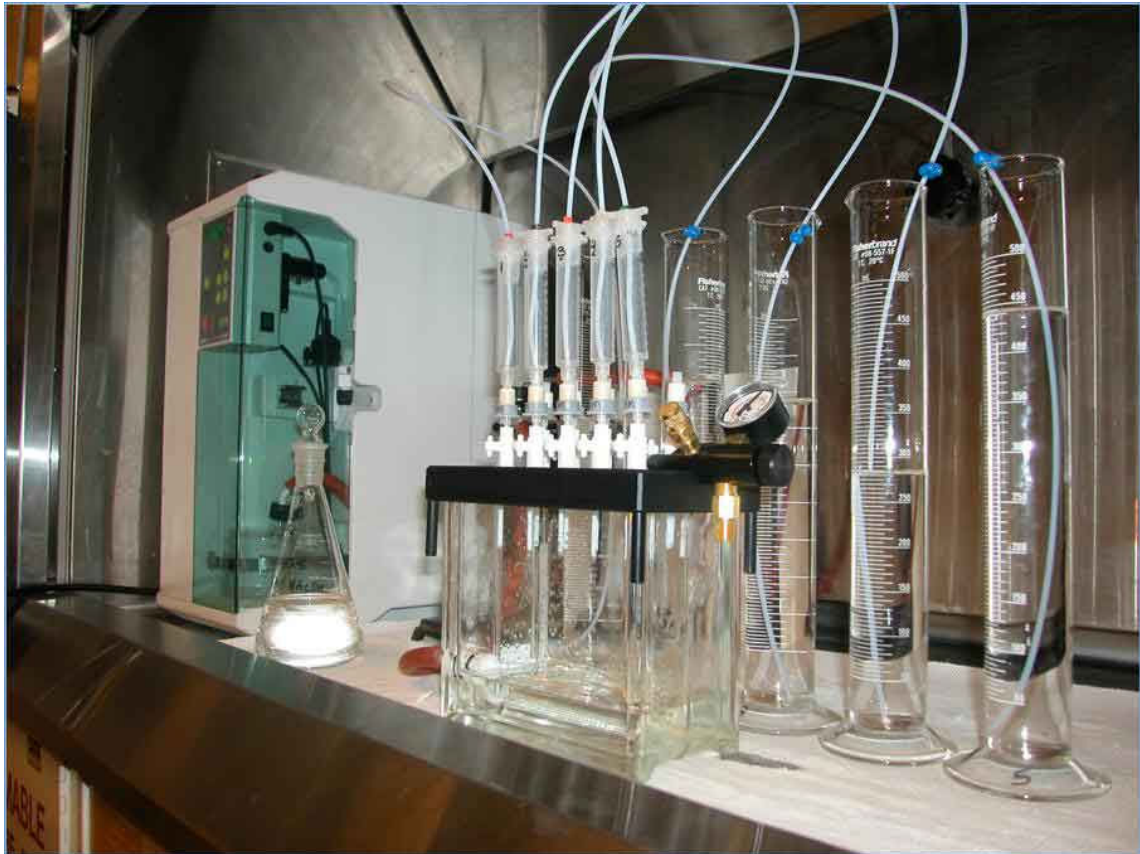


Figure 3.2 Typical solid phase extraction apparatus

### 3.8 Analytical Methods

After each sampling, appropriate aliquots of the supernatant solution were extracted as described in section 3.7 and placed in Autosampler vials. Analysis was conducted using loop injection with an Ultima triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with an electrospray ionization (ESI) interface operating in the negative ion mode (Headley and Peru 2002).

Samples are introduced to the electrospray ion source using loop injection with no chromatographic separation. During the electrospray ionization process, ions are desolvated using a curtain gas and mass analyzed in the quadrupole mass spectrometer. The intensities of all the ions in each spectrum can be summed, and this sum plotted as a function of time to give a total ion chromatogram (TIC). In this case the x-axis represents the retention time of the analyte in the instrument, and the y-axis represents signal intensity or percent relative intensity compared to the intensity of the most intense chromatographic peak. The extracted ion chromatogram can then be derived from the TIC. In this case, the intensity at a single mass-to-charge ratio ( $m/z$ ) (resolution of 1 Da) over the course of a chromatographic run can be displayed to yield a selected ion current profile or ion chromatogram, where the y-axis represents signal intensity in percent, and the x-axis is the value of  $m/z$ . Mass ( $m$ ) refers to the mass of a naphthenic acid molecule ( $M$ ) minus a proton which is lost during the electrospray ionization process, and the charge ( $z$ ) is the number of protons lost or gained during electrospray ionization giving the molecule either a single or multiple charge. It should be noted that  $z$  which represents the value of charge as a result of the electrospray process is not the same as the value of  $Z$  in the general formula of naphthenic acids. In the case of naphthenic acids,  $m = M-1$ , and the value of  $z$  is 1. The relative abundance of naphthenic acid ions is determined by comparison of the area under each  $m/z$  peak which is derived from the ion chromatograms.

Due to the complex nature of the OSTW naphthenic acids mixture, sorption was evaluated on the basis of the collective decrease in naphthenic acid ion count observed in the mixture, rather than attempting to quantify the sorption of individual compounds. It was assumed that the sorption of the naphthenic acids is largely affected by their carboxylic functional group and that sorption mechanisms for the various species of acids are the same.

To determine whether some species of naphthenic acids adsorbed preferentially in comparison to others, the relative abundance of the naphthenic acids in the mixture were summarized as matrices of fractional abundance of specific  $m/z$  mass peak corresponding to the naphthenic acids according to the theoretical formula  $C_nH_{2n+Z}O_2$ , as depicted on Figure 3.3. Fractional abundance was calculated for each naphthenic acid based on the associated  $Z$  family, and was defined as the ratio of the ion count for a given naphthenic acid, to the total ion count for the associated  $Z$  family.

Peak Values (M-1)								TIC areas									
		Z (No. of hydrogen loss due to ring structures)								Z (No. of hydrogen loss due to ring structures)							
Carbon No. (n)		0	-2	-4	-6	-8	-10	-12	Carbon No. (n)		0	-2	-4	-6	-8	-10	-12
5	101								5	6526							
6	115								6	17409							
7	129	127							7	38906	31985						
8	143	141							8	55777	4825						
9	157	155							9	116479	50741						
10	171	169	167						10	285719	346625	433195					
11	185	183	181						11	530841	1082329	1352439					
12	199	197	195	193					12	1067455	2187463	4965039	3255211				
13	213	211	209	207					13	1544358	3579504	13693113	9329485				
14	227	225	223	221	219				14	3142922	6882652	20691880	15896615	2859835			
15	241	239	237	235	233				15	5434935	9581160	18102796	17208374	4410138			
16	255	253	251	249	247	245			16	7070733	11114380	13811427	12909250	5595038	4875486		
17	269	267	265	263	261	259			17	8110469	10978605	9358420	7173906	5003503	6184314		
18	283	281	279	277	275	273	271		18	8055473	8492080	6893817	4555485	4092826	6018667	10448135	
19	297	295	293	291	289	287	285		19	6298343	5915424	4935947	3319593	3511232	4817656	7975968	
20	311	309	307	305	303	301	299		20	4077645	3793291	3474257	2523323	2707566	3695495	6023300	
21	325	323	321	319	317	315	313		21	2466870	2506671	2176165	1750658	1908239	2576259	3603011	
22	339	337	335	333	331	329	327		22	1448278	1471140	1418676	1220673	1285657	1550288	1831501	
23	353	351	349	347	345	343	341		23	994528	1027543	935471	748554	996222	1095127	1210195	
24	367	365	363	361	359	357	355		24	709894	782193	767110	624128	668952	707835	860516	
25	381	379	377	375	373	371	369		25	610517	635978	565596	465400	509646	577913	611363	
26	395	393	391	389	387	385	383		26	526862	482231	483869	469368	479539	503254	499383	
27	409	407	405	403	401	399	397		27	392335	396320	399839	392080	420192	432324	416167	
28	423	421	419	417	415	413	411		28	280323	314626	314445	313569	307444	335981	358812	
29	437	435	433	431	429	427	425		29	253986	292481	270863	286376	262381	269506	265162	
30	451	449	447	445	443	441	439		30	218345	205654	272946	290820	270863	197177	234626	
31	465	463	461	459	457	455	453		31	212803	188392	222549	276882	253252	203102	226212	
32	479	477	475	473	471	469	467		32	147819	184784	236994	279388	218903	166656	154650	
33	493	491	489	487	485	483	481		33	153528	169501	194184	221620	218426	179168	176461	
34	507	505	503	501	499	497	495		34	154121	145019	173602	207717	172036	167049	149893	
35	521	519	517	515	513	511	509		35	156658	196901	161091	179230	164112	156509	157036	
36	535	533	531	529	527	525	523		36	153714	128690	145031	193637	142913	170590	135135	
37	549	547	545	543	541	539	537		37	158520	155215	164200	133954	164546	135791	142004	

Figure 3.3 Fractional abundance matrix

The fractional abundance data was used to construct three-dimensional plots divided into three groups for each Z family (group one having n=5 to n=14, group two having n=15 to 24, and group three having n=25 to n=37). The groupings were chosen based on the naphthenic acids in the approximate carbon number range of n=15 to n=24 exhibiting preferential sorption, as initially verified by visual inspection. A *t*-test was applied to compare corresponding groups in the initial samples to the extracted samples where the plotted data was arcsine-transformed to fit a normal distribution (Clemente et al. 2003). A similar statistical analysis was conducted to determine whether the SPE process changed the composition of the naphthenic acid mixtures. An explanation and example calculation of this procedure is recorded in Appendix C.



## 4 RESULTS AND DISCUSSION

### 4.1 Extracted Naphthenic Acids.

Representations of naphthenic acids such as ion chromatograms, where the fractional or percent abundance of individual compounds is depicted, are often referred to as naphthenic acid fingerprints. The naphthenic acids extracted from the OSTW exhibited a fingerprint similar to that of other studies (Holowenko et al. 2002). The ion chromatogram for the OSTW naphthenic acids is shown on Figure 4.1 below:

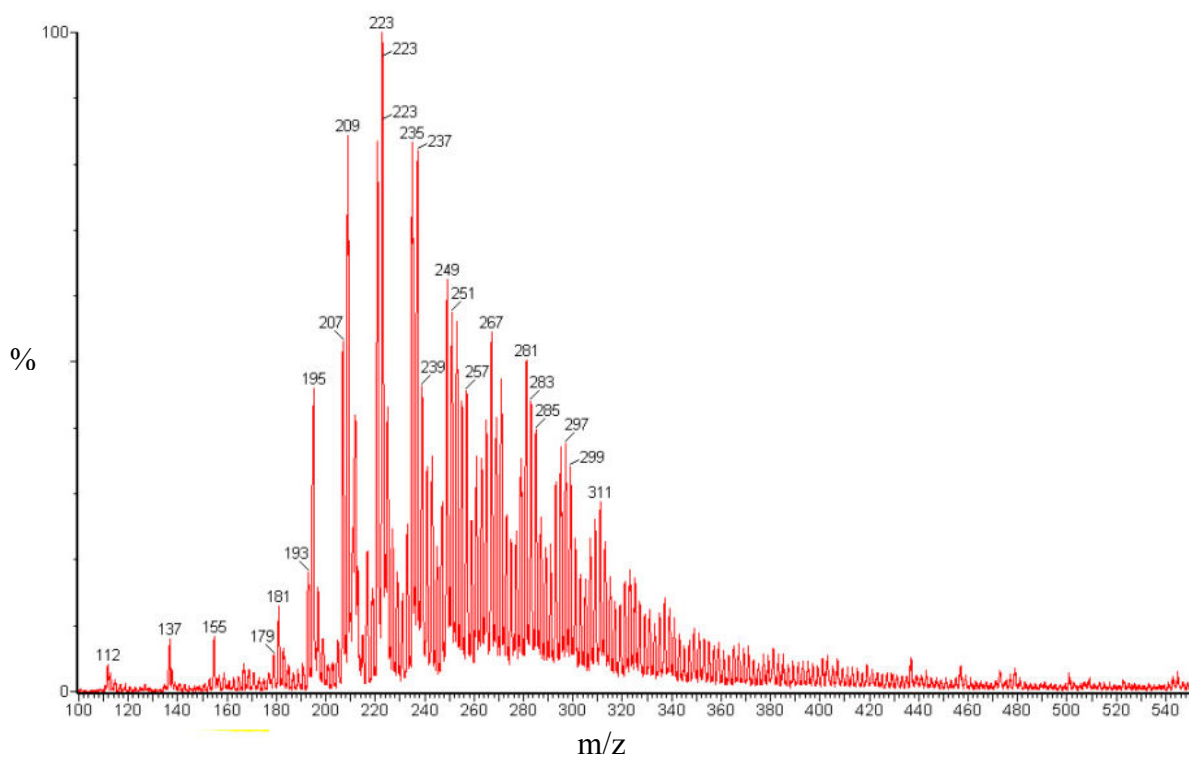


Figure 4.1 OSTW Naphthenic acid ion chromatogram diluted in Milli-Q water.

Figure 4.1 depicts the percentage of ions present with respect to the most abundant ion (y-axis) plotted against the mass to charge ratio ( $m/z$ ) of ions (x-axis). The solution resulting from the extraction of 200 L of tailings pond water had a total naphthenic acid concentration of 3190 mg/L. The solution was then used in appropriate amounts to spike the samples used in the batch tests.

Considering the inherent variations in ionic composition and relative abundance of naphthenic acids from different sources, the naphthenic acid fingerprint observed in the current work was similar to those from several other studies. In this study, naphthenic acids were detected in the molecular carbon number range between  $n=5$  and  $n=37$ . Scott et al. (2005) reported a molecular weight range of  $n=7$  to  $n=28$  for naphthenic acids in tailings water. Holowenko et al. (2002) reported a carbon number range of  $n=5$  to  $n=33$  for Z families of 0 to -12. Similar fingerprints were also found by Chang et al. (2000). In general there is a high degree of variation in species content in various stocks of naphthenic acids (Holowenko et al. 2002; Gervais, 2003). The naphthenic acid fingerprint found was very similar to that found in other stocks analyzed at NWRI laboratories (Roges et al., 2002a).

Naphthenic acid concentrations in the batch reactor supernatant solutions were determined by constructing calibration curves using standard naphthenic acid solutions with known concentrations of 10, 25, 50, 75 and 100 ppm. Standard solutions were prepared using the OSTW extracted naphthenic acid concentrate solution. Calibrations curves were derived by plotting the TIC peak area of standard solutions, versus

concentration using weighted linear regression. The calibration curves were subsequently used to determine the unknown concentrations of naphthenic acid solutions using the method of regression through the origin (Eisenhauer, 2003).

## **4.2 Solid Phase Extraction Results**

Interference from ions in the SWG solution was evident from an initial mass spectrometric analysis of the aqueous naphthenic acids solutions. The SPE procedure as outlined in section 3.7 was used to eliminate the matrix effects resulting from the dissolved ions.

Figure 4.2 (a) shows the ion chromatogram of the naphthenic acids in the SGW solution before the SPE procedure was implemented to eliminate interference of dissolved ions in the SGW mixture. In comparison, Figure 4.2 (b) is the mass spectrum of the naphthenic acids solution after the SPE procedure and resembles the ion chromatogram of the naphthenic acid solution in Milli-Q water.

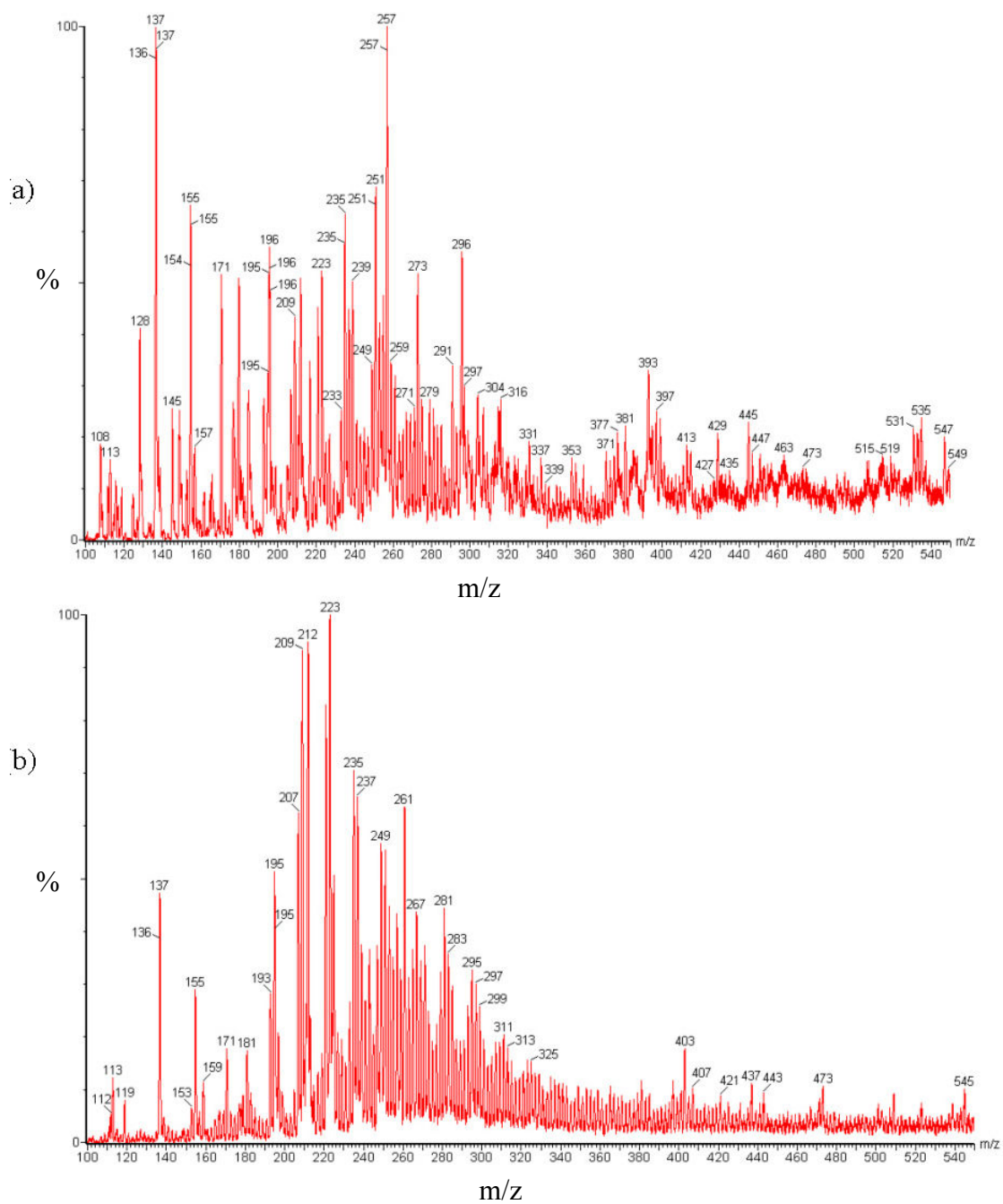


Figure 4.2 Comparison of the ion chromatogram of naphthenic acids in SGW a) before SPE procedure, b) after SPE procedure. Concentration of solution tested was 200mg/L.

In general, the SPE procedure used was similar in principle to the method described in Headley et al. (2002). The method was verified for its applicability to naphthenic acid extraction through a series of tests which compared the relative standard deviation (RSD) of samples that were extracted using the SPE method. Naphthenic acid samples at different concentrations in the range of 20 to 120 mg/L were tested in batches of 7 samples at each concentration. The SPE procedure produced RSD values ranging from 1 mg/L to 1.2 mg/L at each concentration; values which are relatively low for environmental samples.

In order to verify that the SPE procedure imposed no change on the fingerprint of the naphthenic acid solution by removing select naphthenic acids from the mixture, statistical analysis was implemented to compare the naphthenic acid fingerprint before and after extraction. The analysis was a *t*-test similar in its application to that used to compare the results of pre and post sorption batch reactor samples. The analysis showed the extraction procedure imposed no significant change in the naphthenic acid fingerprint for all samples tested. Figure 4.3 depicts the 3-dimensional plots of the fractional abundance of the naphthenic acids for all *Z* families of the 200 mg/L in Milli-Q water in the initial sample (a) and an extracted sample (b).

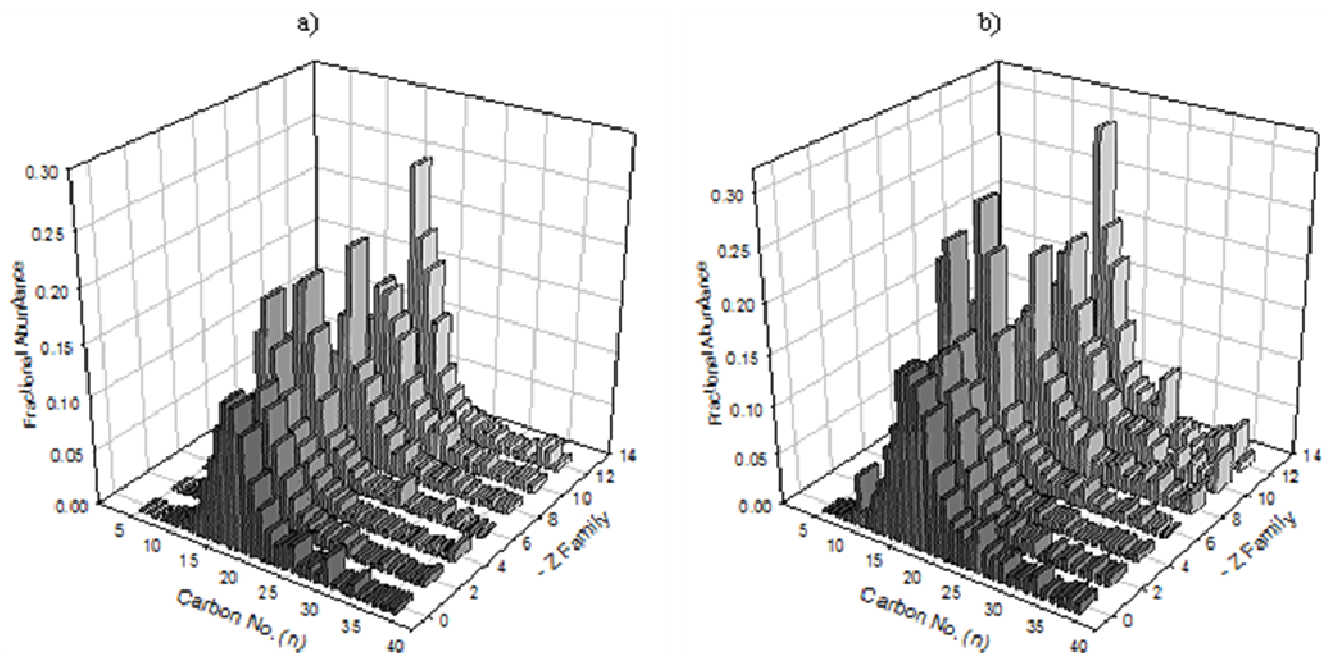


Figure 4.3 Naphthenic acid fingerprint in Milli-Q, 20 mg/L a) initial solution, b) following extraction. Concentration of solution tested was 200mg/L.

### 4.3 Preliminary Test Results

The repetition of the procedures of Peng et al. (2002) confirmed that the single ring model compounds 4-methylcyclohexaneacetic acid (4MACH) and 4-methylcyclohexanecarboxylic acid (4MCCH) have low adsorption coefficients. From the first trial where a 200 mg/L solution of naphthenic acids was used with Soil 1, it was determined that there was significant sorption of the OSTW naphthenic acids with Milli-Q water as a background solution. The results are depicted on Figure 4.4. The error bars represent the relative standard deviation of the triplicates in the reactor vials. It was found that sorption reached equilibrium within the first 6 hours of testing, making

a 48  $K_d$  measurement (as recommended by ASTM D4646) representative of steady-state conditions.

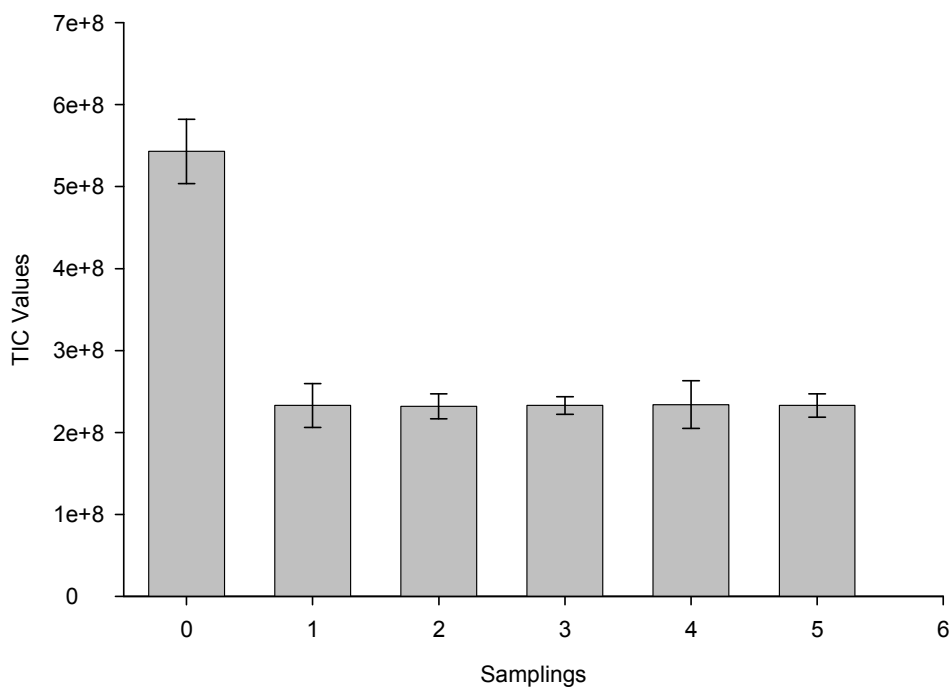


Figure 4.4 Total ion count (TIC) values in the reactor vials for a 200 mg/L naphthenic acid solution sampled with time. (0=0 hrs, 1=24 hrs, 2=48 hrs, 3=96 hrs, 4=144hrs, 5=288 hrs. NOTE: Samplings at 192 and 240 hrs were omitted as outliers with concentrations greater than adjacent days.) Error bars represent the relative standard deviation of the triplicates reactor vials.

Furthermore, it was found that the control samples remained constant for the duration of the 288 hour experiment. This indicates that within experimental error, there is no significant sorption to the glass surfaces of the reactors vials. The results obtained from the control reactors are depicted on Figure 4.5.

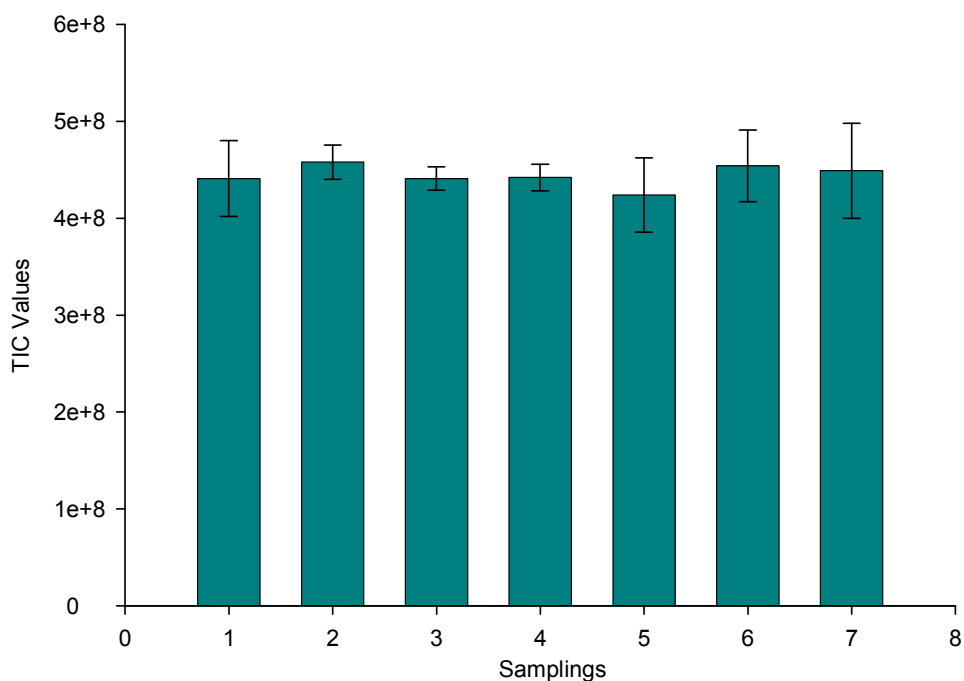


Figure 4.5 Total ion count (TIC) values in the control vials for a 200 mg/L naphthenic acid solution sampled with time. (1=0 hrs, 2=24 hrs, 3=48 hrs, 4=96 hrs, 5=144hrs, 6= 192 hrs, 7=288 hrs. NOTE: Sampling at 192 hrs was omitted as an outlier with a concentration greater than adjacent days.) Error bars represent the relative standard deviation of the triplicates reactor vials.

Figure 4.6 shows the 56 hour sorption isotherm values. The partitioning coefficient was found to be  $5.9 \pm 0.7$  mL/g; a reasonable value given the high organic carbon and organic matter content of the test soil (Pignatello 2000; Fetter 1999). Steady-state solution concentrations (mg/L) are average values from the triplicate reactor vials. The differences in concentration between the triplicates were generally very small after the SPE cleanup procedure was implemented, and therefore error bars reflecting these



concentration differences are not visible on Figure 4.6 due to the scale of the ordinate axis.

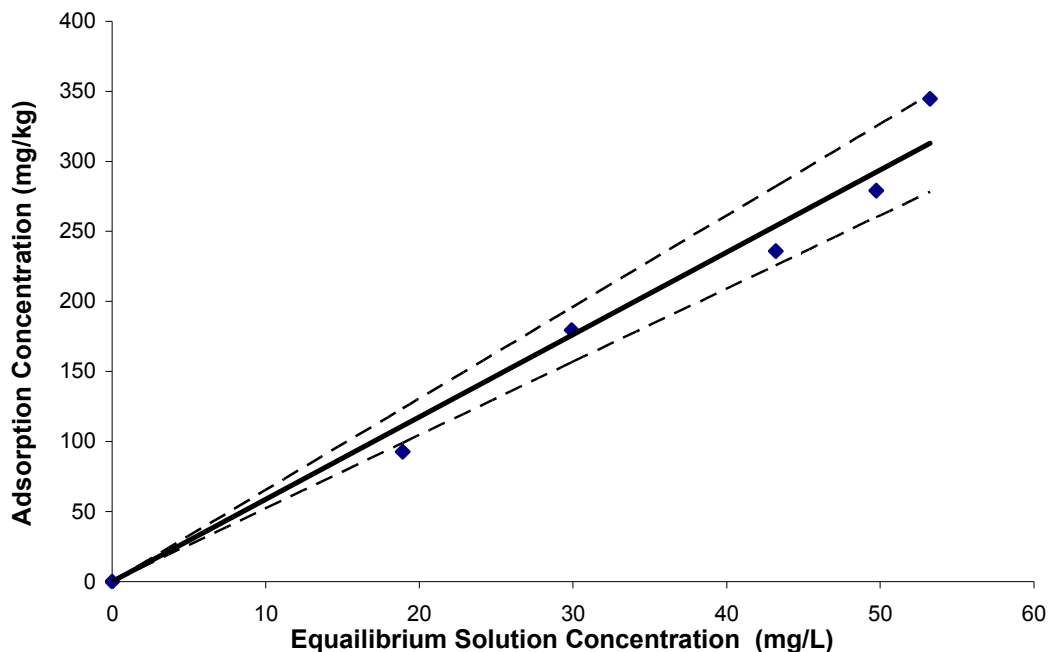


Figure 4.6 Adsorption isotherm of naphthenic acid mixture at  $23\pm 1^{\circ}\text{C}$ , pH 8 with Soil 1 in Milli-Q water. The dashed lines represent the 95% confidence intervals.

#### 4.4 SGW batch test results

The adsorption isotherms for the naphthenic acids mixtures were best described by a linear regression through the origin in each case (Eisenhauer, 2003). A key finding of this investigation was that the measured adsorption coefficients were generally high in comparison to those of previous studies (Peng et al., 2002), indicating that there was considerable sorption of the naphthenic acids by the soils investigated. This would

imply a lower partitioning to the water column in aquatic environments than that previously reported for model naphthenic acid compounds (Peng et al. 2002). Relevant aspects of the results supporting this finding are discussed in turn below.

#### 4.4.1 *Control Tests*

The control tests conducted to determine non-soil related losses of the mixture of naphthenic acids showed no significant decrease between the initial concentrations ( $t=0$ ) and the final concentrations at the conclusion of the test. For this reason, the concentration values used to calculate the amount of naphthenic acids adsorbed on the soils required no adjustment for non-soil-related losses of naphthenic acids. The sorbed concentration was calculated as the difference between the concentration in the initial solution and the supernatant concentration of the batch tests at the conclusion of the test. Controls containing soil and Milli-Q water were used to determine background concentrations of naphthenic acids (or similar compounds) in the test soils. Concentrations of such compounds were detected in the soils, and these concentration values were subtracted from naphthenic acids concentrations in the supernatant as a correction.

#### 4.4.2 *$K_d$ Values*

Equation 2.14 relates the  $K_d$  value to the organic carbon adsorption coefficient ( $K_{oc}$ ), and the organic carbon fraction of the sorbent ( $f_{oc}$ ). The relationship can be rearranged to

equate the ratio of adsorption coefficient to the ratio of organic carbon fraction in two different sorbents as follows:

$$\frac{K_{d1}}{K_{d2}} = \frac{f_{oc1}}{f_{oc2}} \quad (4.1)$$

According to this method, the  $K_d$  value of naphthenic acids in Soil 1 is thus expected to be 1.7 times that of Soil 2.

The adsorption coefficients for the mixture of naphthenic acids in Milli-Q water were determined to be  $1.9 \pm 0.2$  mL/g and  $1.3 \pm 0.15$  mL/g for Soils 1 and 2 respectively.

The isotherms for the mixture of naphthenic acids on both Soils 1 and 2 are depicted in Figure 4.7. All tests were conducted at  $4 \pm 1^\circ\text{C}$  and solution pH of  $8.0 \pm 0.4$ .

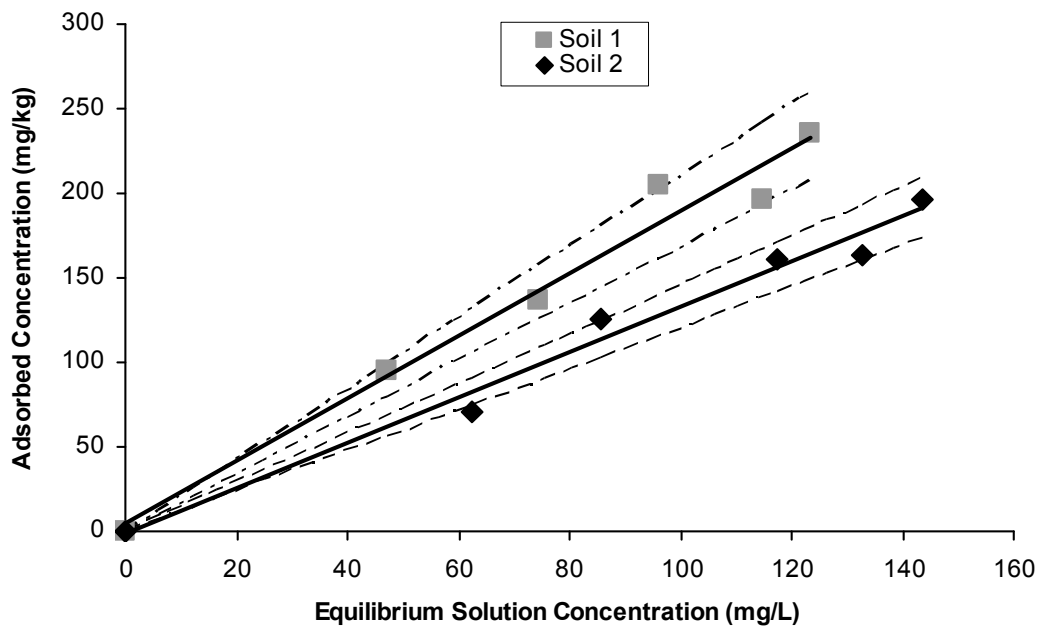


Figure 4.7 Sorption isotherms for naphthenic acids Soil 1 and 2 in Milli-Q water. The dashed lines represent the 95% confidence intervals

The values for the two soils are significantly different, a result which is likely attributable to Soil 1 having a higher  $f_{oc}$  than Soil 2 (Fetter 1999; Pignatello 2000).

In this study the effect of ionic strength was also examined by comparison of the adsorption coefficients of the naphthenic acids mixture in Milli-Q water to that of mixtures in synthetic groundwater. It is well established that the presence of inorganic salts can enhance the adsorption capacity of organic compounds such as hydrophobic ionizable organic compounds, by reducing their solubility (Li and Sengupta 2004; Martins and Mermoud 1998). The measured isotherm of the naphthenic acid mixture in SGW is depicted on Figure 4.8.

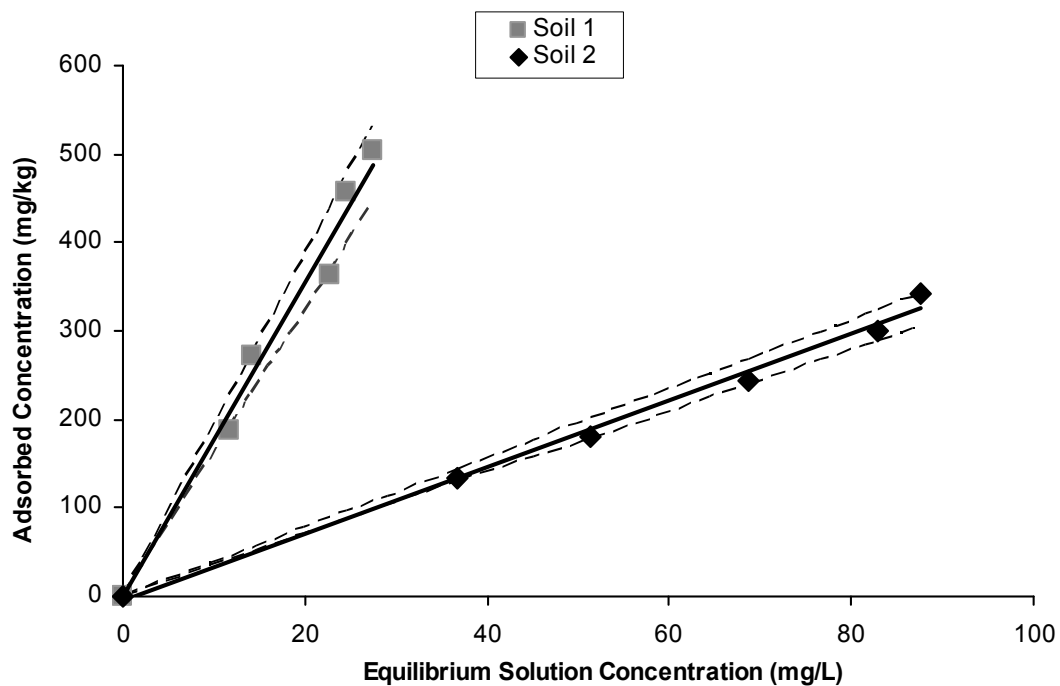


Figure 4.8 Sorption isotherms for naphthenic acids Soil 1 and 2 in SGW. The dashed lines represent the 95% confidence intervals

In the presence of SGW, the adsorption coefficient of the mixture of naphthenic acids on Soil 1 was an order of magnitude higher than that observed with the same soil and the Milli-Q water mixture, increasing from  $1.9 \pm 0.2$  mL/g to  $17.8 \pm 1.5$  mL/g. The adsorption coefficient of the mixture on Soil 2 was also observably higher in the SGW mixture, increasing from  $1.3 \pm 0.15$  mL/g to  $3.7 \pm 0.2$  mL/g.

Salting out is a possible mechanism for the dramatic increase of adsorption coefficient in the presence of SGW. It has been demonstrated that carboxylic acids of varying carbon chain lengths, in their ionized and neutral forms, undergo a decrease in solubility in the presence of inorganic salts, where some salts impose a greater salting out effect than others (Martins and Mermoud 1998; Govindarajan and Sabarathinam 1995; Shah and Tiwari 1981; Eisen and Joffe 1966).

In general, the sorption of organic compounds is inversely proportional to their water solubility. The Setschenow equation describes the solubility of organic compounds in saline aqueous solutions (Xie et al., 1990):

$$\log\left(\frac{S^w}{S^s}\right) = k_s C_s \quad (4.2)$$

where;  $S^w$  is the solubility of the organic substance in water,  $S^s$  is the solubility of the substance in salt water,  $C_s$  is the molar concentration of the salt solution and  $k_s$  is the Setchenow parameter. The value of  $k_s$  is specific to a given electrolyte-organic solvent

system and can be determined experimentally or by the use of predictive models (Ni and Yalkosky, 2002; Schlautman et al. 2004). Although values of  $k_s$ ,  $S^w$  and  $S^s$  are not available in literature for naphthenic acids, for comparison, the Setschenow equation can be used to calculate a solubility ratio to evaluate the relative difference in solubility with the addition of salts to the mixture.

$$\frac{S^w}{S^s} = 10^{k_s C_s} \quad (4.3)$$

Several studies have found the value of  $k_s$  to be higher for sulphate salts such as those used in the SGW mixture (Xie et al., 1990; Ni and Yalkosky, 2002; Schlautman et al. 2004). Assuming a nominal value of 1.5 for  $k_s$ , and using the ionic strength in the SGW solution (0.069 mol/L), the value of the solubility ratio becomes 1.26. The value of  $\log(S^w/S^s)$  therefore becomes approximately 0.1, which implies an approximate reduction in solubility by a factor of 10. The lower solubility likely promotes increased sorption to soil resulting in higher adsorption coefficients.

#### 4.4.3 Selective sorption

The 3-dimensional histograms depicting the fractional abundance of the individual naphthenic acids allow the fractional abundance of the initial and final sorption samples to be compared by Z family. Figure 4.9 depicts the three dimensional fractional abundance histograms for Soil 1 and 2 for naphthenic acids of Z=-2 at 200 mg/L in Milli-Q water. The evidence of selective sorption occurring for naphthenic acids in

carbon number range of approximately  $n=13$  to  $n=17$  was further investigated by statistical analysis.

A two sample *t*-test statistical analysis was conducted to confirm whether significant differences exist in sorption between different naphthenic acid compounds as grouped by carbon number. For each *Z* family fractional abundance was statistically subjected to a *t*-test, where the fractional abundances were grouped by carbon numbers (group one having  $n=5$  to  $n=14$ , group two having  $n=15$  to  $n=24$ , and group three having  $n=25$  to  $n=37$ ). A 95% confidence interval was used for determining significant difference between the sample means. For all concentrations tested, comparisons of fractional abundance from  $t = 0$  to  $t = 48$  hours showed that no particular grouping of carbon numbers sorbed more than others in the Milli-Q water solution; that is, no group statistically exhibited preferential sorption.

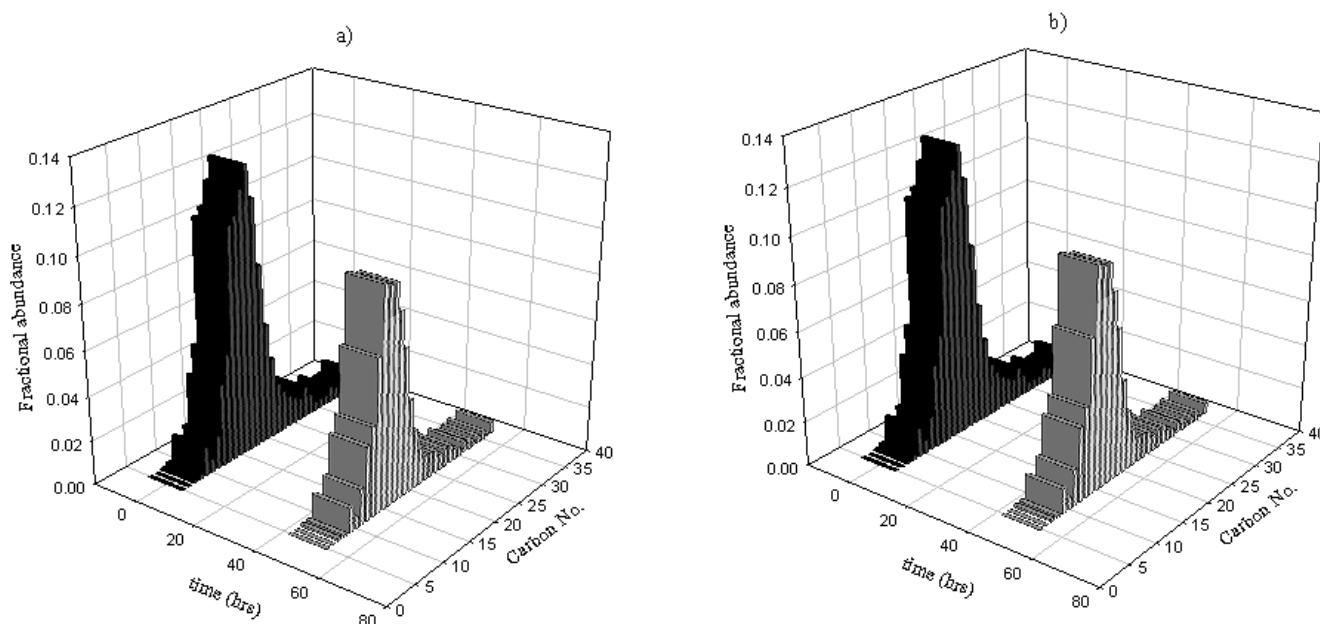


Figure 4.9 a) Z=-2 family change in fractional abundance of individual species with time, Soil 1 in Milli-Q water b) Z=-2 family change in fractional abundance of individual species with time, Soil 2 in Milli-Q water

However, for the samples in SGW, the grouping of carbon numbers  $n=5$  to  $n=14$  did not show a significant difference between the  $t = 0$  and  $t = 48$  hour samples, indicating a greater tendency to partition to the aqueous phase, while adjacent carbon number groupings  $n=15$  to  $n=24$ , and  $n=25$  to  $n=37$  had reduced fractional abundances from  $t = 0$  to  $t = 48$  hours, indicating significant sorption had taken place.

Figure 4.10 depicts the 3-dimensional fractional abundance histograms for Soil 1 and 2 of Z family = -2 at 200 mg/L in SGW. Appendix D shows the comparative histograms by Z families (0 to -12) for the 200 mg/L samples in Milli-Q water and SGW.



Quantification of selective sorption beyond the *t*-test was inhibited by the resolution in the data set.

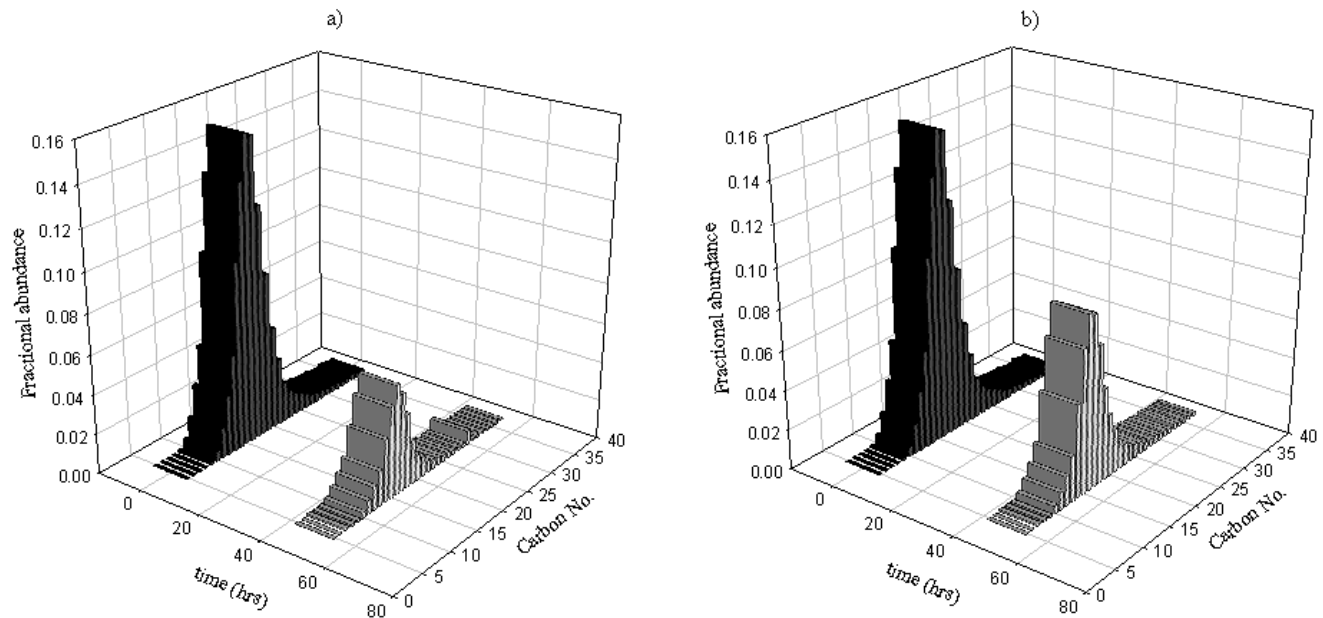


Figure 4.10 a) Z=-2 family change in fractional abundance of individual species with time, Soil 1 in SGW b) Z=-2 family change in fractional abundance of individual species with time, Soil 2 in SGW

## 4.5 Discussion

In general, naphthenic acids show a greater tendency to remain in aqueous solution under conditions of low ionic strength. This implies that naphthenic acids would have a greater affinity for the aqueous phase in fresh water or shallow groundwater relative to waters from regional aquifers in the Athabasca area, which are typically higher in salinity. Thus their toxic effects could be more pronounced since by transport in shallow groundwater which is relatively low in salinity, naphthenic acids can migrate

more easily to waters bearing aquatic life. Furthermore, the sorption behavior of naphthenic acids observed in this study suggests two fractions of naphthenic acids from the standpoint of bioavailability, with one fraction (carbon number  $n=5$  to  $n=14$ ) being more available than the other because of its higher tendency to remain in aqueous solution under conditions of high ionic strength.

The concept of bioavailability must be well understood for the purpose of developing risk-assessment and remediation strategies, as well as a regulatory framework.

Numerous laboratory studies have shown that receptors, such as organisms that are susceptible to toxic contaminants in groundwater, are mainly affected by the freely available aqueous fraction of the contaminants (Ehlers and Loibner, 2006).

Rockne et al. (1999) defined bioavailability as the rate at which a chemical compound can be transported to a specific biological population to induce toxic effects. This suggests that bioavailability of an organic contaminant should be considered with respect to specific biological receptors. Furthermore, the fraction of a substance which is available to microorganisms for degradation is also available to other organisms that are susceptible to its toxic effects. Therefore, controlled interaction of degrading microorganisms with a contaminant such as is done in land farming of contaminated soils for example, is a means of controlling the exposure of susceptible organisms to a contaminant source, while maximizing degradation of the contaminant by metabolizing organisms. In the case of naphthenic acids however, the sheer volume of the oil sand tailings makes containment challenging.

In the case of naphthenic acids, the species exhibiting a preference for the aqueous phase under the conditions tested were the lower molecular weight compounds. The molecular topology method for estimating sorption lends credence to these observations. The relationship between molecular connectivity and  $K_{om}$  was derived on the basis of non-polar compounds; however, Sabljíć provided a correction factor ( $P_f$ ) for polar organic compounds such as organic acids. The relationship including the correction factor is as follows:

$$\log K_{om} = 0.53^1\chi + 0.54 - P_f \quad (4.4)$$

where molecular connectivity ( $^1\chi$ ) is related to the number of non-hydrogen bonds ( $\delta$ ) as follows:

$$^1\chi = \sum(\delta_i\delta_j)^{-0.5} \quad (4.5)$$

Equation 4.4 can be combined with Equations 2.13 and 2.14 to provide an estimate of  $K_d$  on the basis of molecular connectivity as follows:

$$K_d = 1.724 f_{oc} 10^{(0.53^1\chi + 0.54 - P_f)} \quad (4.6)$$

The correction factor which applies to organic acids is 2.39. Molecular connectivity ( ${}^1\chi$ ) values for naphthenic acids in the  $Z = -2$  range from 4.70 to 8.69 for naphthenic acids in the carbon number range of  $n=9$  to  $n=17$ .

According to this approximation,  $K_d$  grows exponentially as a function of  ${}^1\chi$ . Therefore  $K_d$  increases with increasing molecular size. According to this model, the  $K_d$  for a molecule of  $n=16$  is two orders of magnitude larger than for a molecule of  $n=9$ , with the  $K_d$  values being 0.203 mL/g and 14.56 mL/g respectively.  $K_d$  values for naphthenic acids become very large for values of  $n>17$ . Figure 4.11 shows the plot of  ${}^1\chi$  and  $K_d$  versus carbon number for naphthenic acids in the  $Z = -2$  family according to the theoretical formula  $C_nH_{2n+Z}O_2$ .

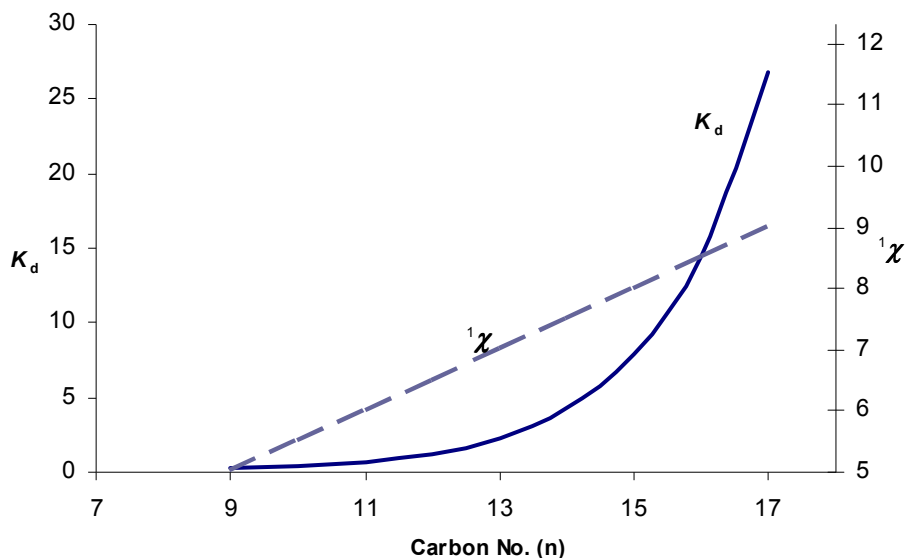


Figure 4.11 The theoretical relationship of  $K_d$  and molecular connectivity index ( ${}^1\chi$ ).

The tendency for larger molecules to sorb more readily combined with the salting out effect could account for the increased sorption observed in the SGW solution. Since dissolved ions form a hydration shell, and increase the polarity of water making it more difficult for non-polar molecules to remain in solution, it is plausible that a molecule with a larger non-polar component, such as a higher molecular weight naphthenic acid, would experience a greater decrease in solubility and increased sorption.

A comparison of  $K_{oc}$  values for naphthenic acids can be made to other organic compounds for which  $K_{oc}$  values have been derived. The average value of  $K_d$  in Soil 1 and the Milli-Q water mixtures was approximately 1.6 mL/g. With a  $f_{oc}$  of 0.027 for Soil 1, an average  $K_{oc}$  value for naphthenic acids can be calculated using equation 2.13, which yields an estimate of 59 mL/g, resulting in a log  $K_{oc}$  value of 1.77. This value is similar in range to the log  $K_{oc}$  values of dichloroethane and benzene (Fetter 1999).

The work of Holowenko et al. (2002) is the only study to date which illustrated that the toxicity of a naphthenic acids mixture is affected by its composition. Although their findings suggest that the lower molecular weight acids contribute most to the toxicity, this has not been demonstrated conclusively. The tendency of the lower molecular weight acids to remain in the aqueous phase means that they are also more available for degradation by microorganisms; however they are also more bioavailable to biota that may be susceptible to their ecotoxic effects.

In a laboratory study, Herman et al. found that microbial breakdown of an OSTW naphthenic acid mixture reduced the acute toxicity by approximately 50% of the original level (Herman et al., 1994). In an *in situ* study of naphthenic acids in groundwater, Gervais (2005) concluded that in field experiments, apparent attenuation of naphthenic acids with carbon numbers less than or equal to  $n=14$  was greater than that for conservative chemicals, suggesting that some attenuation beyond dispersive dilution may have been occurring. However, biodegradation was assessed as having limited attenuating effects. With apparently minor attenuating influence in groundwater, biodegradation may not be a sufficient mechanism to reduce toxicity of naphthenic acids unless optimal circumstances prevail.

The adsorption behavior of naphthenic acids as observed in this study may have implications for their transport in groundwater. The effective velocity of contaminants in soil is  $v_x/R_d$ . As a plume moves along a salinity gradient and becomes more dilute,  $K_d$  will decrease, in turn decreasing  $R_d$ . The decreasing partitioning to the soil results in an increase in the rate of transport of the naphthenic acids in groundwater.

Another effect may arise from the selective sorption of naphthenic acids in the presence of dissolved salts. Under conditions of elevated salinity, the larger molecular weight acids ( $n>14$ ) will partition to the soil leaving the more mobile lower molecular weight acids. The result is a more dilute plume, but one where the constituents are the more toxic fraction of naphthenic acids.

The sorbed fraction of naphthenic acids may also pose challenges to remediation of groundwater systems. In remediation operations, retardation by sorption produces the undesirable effect of gradual release of the contaminant species from soils. The stronger the sorption (the higher retardation factor), the more time is required to accomplish complete recovery of the contaminants from effected soils (Rebhun et al., 1996). Thus it becomes possible for a sorbed contaminant to subsequently become available by slow release through desorption, exposing the contaminant to susceptible organisms. Organic pollutants typically undergo a two phase desorption process whereby a rapid desorption stage is succeeded by a period of slower release (Huang and Weber, 1997; Pignatello and Xing, 1996). For organic chemicals, quantification of the extent to which slow sorption affects remediation efficiency is difficult and requires investigation of how the specific contaminant interacts with the structural and molecular properties of the soil matrix, as well as an understanding of the sorption mechanisms involved in the binding processes (Ehlers and Loibner, 2006). For naphthenic acids, better understanding of the sorption mechanisms and desorption behavior is required for design of effective remediation systems for contaminated soil and groundwater.

## CONCLUSIONS AND RECOMMENDATIONS

### 4.6 Conclusions

The purpose of this study was to develop an analytical method for an OSTW extracted naphthenic acids solution in fresh water and under conditions of elevated salinity, and to determine the sorption characteristics of these naphthenic acids for typical reclamation soils. The conclusions as derived from the objectives of the study are as follows:

- 1) In the preliminary analysis, an overall decrease in concentration of the OSTW naphthenic acids mixture was seen within the first 48 hours of testing indicating that some components of the complex mixture sorbed to soils under the conditions tested. The preliminary testing was conducted using Soil 1 with a relatively high organic carbon content, and Milli-Q water, and at a temperature and pH of  $23 \pm 1$  °C and 8 respectively.
- 2) Subsequently, an analytical method for the OSTW naphthenic acids was developed based on a modified solid phase extraction (SPE) procedure to remove matrix effects and interference from the saline batch reactor supernatant. Analysis for chemical concentration and naphthenic acid fingerprint was subsequently conducted by loop injection with an Ultima triple quadrupole mass spectrometer equipped with an electrospray ionization (ESI) interface operating in the negative ion mode. With the solid phase extraction procedure as a cleanup



method, the naphthenic acid fingerprint is retained in the post extraction analysis.

- 3) The adsorption characteristics of the naphthenic acids in a synthetic groundwater (SGW) solution were compared to that of the mixture in Milli-Q water. Naphthenic acids exhibited measurable sorption coefficients in both solutions, and sorption was best characterized by linear isotherms. In the presence of SGW, the adsorption coefficient ( $K_d$ ) of the mixture of naphthenic acids on Soil 1, having a higher organic carbon fraction ( $f_{oc}$ ), was an order of magnitude higher than that observed with the same soil and the Milli-Q water naphthenic acids mixture. This is likely attributable to a reduction in solubility as a result of the presence of dissolved salts and is consistent with the Setschenow theory of solubility. From the control reactors it was determined that sorption onto glass surfaces was negligible within the experimental error.
  
- 4) The relative fractional abundance of the individual naphthenic acids was plotted in order to determine the presence of preferential sorption between individual species within the mixture. It was found that for all  $Z$  families, naphthenic acids within a specific carbon number range showed preferential sorption. This result was confirmed using a two sample  $t$ -test. It was found that for samples in SGW, the grouping of carbon numbers  $n=5$  to  $n=14$  did not show significant sorption, indicating a greater tendency to partition to the aqueous phase, while adjacent carbon number groupings  $n=15$  to  $n=24$ , and  $n=25$  to  $n=37$  had reduced

fractional abundances from  $t = 0$  to  $t = 48$  hours, indicating significant sorption had taken place. The results are supported by the molecular connectivity theory which indicates that sorption should increase with increased molecular size. The findings observed in this study suggest that mixtures of naphthenic acids sorb to soils with a preference for soils with a higher carbon fraction and under conditions of elevated salinity. This means that in predominantly clay soils, especially those with a higher organic carbon content, sorption can be a significant attenuating mechanism in groundwater transport, and is a process which will likely leave a chemical signature as evidenced by a statistically significant difference in the fractional abundances of specific carbon number groupings in the initial and post-sorption samples.

- 5) Preferential sorption of the individual naphthenic acids is important from a toxicity stand point since there is evidence that lower molecular weight acids contribute most to the toxicity of naphthenic acids solutions. In general, bioavailability is largely affected by sorption, but biodegradation seems to play a minor role in diminishing naphthenic acids concentrations in groundwater.

#### **4.7 Recommendations**

Based on the findings of this study, the following recommendations can be considered for future studies:

- 1) In situ partitioning coefficients of OSTW naphthenic acids should be determined by comparing naphthenic acid concentrations in tailings ponds water with that of extracted pore water from the sediment at the base of the pond or soils adjacent to the pond.
  
- 2) Undisturbed soil cores should be used in column or diffusion tests to determine OSTW naphthenic acids partitioning coefficients which are more representative of field conditions.
  
- 3) Limitations of lab study should be considered in follow-up programs.  
Limitations of batch reactors arise from the fact that the soil is necessarily disturbed in the agitation process in using batch reactors. Therefore, the soil is not necessarily representative of field conditions.
  
- 4) The solubility of naphthenic acids under various solution chemistries should be measured. Solubility characteristics can be used to obtain better estimates of partition coefficients.
  
- 5) Since significant sorption is exhibited by the naphthenic acid mixtures, and particular species of naphthenic acids exhibit preferential sorption, desorption process of naphthenic acids should be studied under various physical and chemical conditions.

- 6) A more definitive quantitation of the selective sorption of OSTW naphthenic acids should be developed.
- 7) Sorption of naphthenic acids should be studied at solution concentrations higher than 200 mg/L in order to determine whether sorption behavior of naphthenic acids changes with increased solution concentrations.

## REFERENCES

ASTM, 2003. ASTM standard method D-4319 and D-4646, 2003 Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA, USA.

Bachu, S. and Underschultz, J.R. 1993. Hydrogeology of formation waters, northeastern Alberta basin. *The American Association of Petroleum Geologists Bulletin*, **77**:1745-1768.

Barone, F.S., Rowe, R.K. and Quigley, R.M. 1992. A laboratory estimation of diffusion and adsorption coefficients for several volatile organics in a natural clayey soil. *Journal of Contaminant Hydrology*, **10**: 225–250.

Barrow, Mark P., McDonnell, Liam A., Feng, Xidong, Walker, Jeremie and Derrick, Peter J. 2003. Determination of the nature of naphthenic acids present in crude oils using nanospray Fourier transform ion cyclotron resonance mass spectrometry: The continued battle against corrosion. *Analytical Chemistry* **75**: 860-866

Cater, M.R.1993. *Soil Sampling and Methods of Analysis*. Lewis Publishers.

Caulcutt, R. and Boddy, R.1983. *Statistics for Analytical Chemists*, Chapman and Hall Publishers.

Chiou, C., Porter, P. and Schmedding, D. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. *Environmental Science and Technology*, **17**: 227—231.

CIM (a) 2005. Fact Sheet – Canada’s Oil Sands [online]. Available from [http://www.oilsands.ca/publications/fact\\_sheets.asp](http://www.oilsands.ca/publications/fact_sheets.asp) [cited January 19, 2006].

CIM (b) 2005. Fact Sheet – Surface Mining: Extraction [online]. Available from [http://www.oilsandsdiscovery.com/oil\\_sands\\_story/pdfs/extraction.pdf](http://www.oilsandsdiscovery.com/oil_sands_story/pdfs/extraction.pdf) [cited January 19, 2006].

Clemente, J.S, Prasad, N.G.N, Mackinnon, M.D. and Fedorak, P.M. 2003. A statistical comparison of naphthenic acids characterised by gas chromatography-mass spectrometry. *Chemosphere*. **50**: 1265-1274.

Delle Site, A. 2001. Factors affecting sorption of organic compounds in natural Sorbent/Water systems and sorption coefficients for selected pollutants, a review. *Journal of Physical and Chemical Reference Data*, **30**: 187 – 439.

Donahue, Robert B. 1994. Diffusion of benzene through Regina Clay. M.Sc. Thesis, University of Saskatchewan, Saskatoon, SK, Canada.

Ehlers, George A.C. and Loibner., A. P. 2006. Linking organic pollutant (bio)availability with geosorbent properties and biomimetic methodology: A review of geosorbent characterisation and (bio)availability prediction. *Environmental Pollution*, **141**: 494-512

Eisen, Edwin and Joffe, Joseph. 1966. Salt Effects in Liquid-Liquid Equilibria. *Journal of Chemistry and Engineering data*, 1966, 11:480-484.

Eisenhauer, Joseph G. 2003. Regression through the origin. *Teaching Statistics*, 25: 76 – 80.

Fetter, C. W. 1999. *Contaminant Hydrology*. MaxWell Macmillon.

Freeze and Cherry. 1979. *Groundwater*. Prentice Hall.

Freundlich, H. 1926. *Colloid and Capillary Chemistry*. Methuen, London, England.

Gervais, F.J. 2004. Fate and transport of naphthenic acids in a glacial aquifer. Thesis, University of Waterloo, Waterloo, ON, Canada.

Govindarajan, M. and Sabarathinam, P. 1995. Salt effect on liquid-liquid equilibrium of the methyl isobutyl ketone-acetic acid-water system at 35 °C. *Fluid Phase Equilibria*, **108**: 269 – 292

Grover, Phulwinder K. and Ryall, Rosemary L. 2005. Critical appraisal of salting-out and its implications for chemical and biological sciences. *Chemical Reviews*, **105**: 1-10.

Gutzeit, J. 1976. Studies shed light on naphthenic acid corrosion. *Oil and Gas Journal*, **74**:156-158.

Hackbarth, D.A. 1977. Regional hydrogeology of the Athabasca oil sands area, Alberta. AGARD Conference Proceedings. pg. 87-102

Havre, T.E., Sjoblom, T. and Vindstad, J.E. 2003. Oil/water-partitioning and interfacial behavior of naphthenic acids. *Journal of Dispersion Science and Technology*, **24**: 789-801.

Headley, J.V., Peru, K.M, McMartin, D.W. and Winkler, M. 2002. Determination of dissolved naphthenic acids in natural waters by using negative-ion electrospray mass spectrometry. *Journal of AOAC International*, **85**: 182 – 187.

Herman, D. C., Fedorak, P. M., MacKinnon, M. and Costerton, J.W. 1994. Biodegradation of naphthenic acids by microbial populations indigenous to oil sands tailings. *Can. J. Microbial.*, **40**: 467-477.



Holowenko, F.M., MacKinnon, M.D. and Fedorak, P.M. 2002. Characterization of naphthenic acids in oil sands wastewaters by gas chromatography-mass spectrometry. *Water Research*. **36**: 2843 - 2855.

Holowenko, F.M., MacKinnon, M.D., and Fedorak, P.M. 2001. Naphthenic acids and surrogate naphthenic acids in methanogenic microcosms. *Water Research*, **35**: 2596 - 2606.

Hsu, C.S., Dechert, G.J. Robbins, W.K. , Fukuda, E. and S.G. Roussis. 1998. Mass spectrometric characterization of acids in crude oils. Proceedings of the 215th National Meeting of the American Chemical Society. March 29-April 3, 1998. Dallas, TX. Pp. 127-130.

Huang, W.L. and Weber, W.J. 1997. A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis and the chemical characteristics of organic domains. *Environmental Science and Technology*, **31**: 2562 - 2569.

Huang, W.L., Yu, H. and Weber, W.J. 1998. Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments - 1. A comparative analysis of experimental protocols. *Journal Of Contaminant Hydrology*, **31**: 129-148.

IUPAC Compendium of Chemical Terminology, 2nd Edition, ed. A. D. McNaught and A. Wilkinson, Blackwell Science, 1997.

Kier, L. and Hall, L. 2002. The meaning of molecular Connectivity: A biomolecular accessibility model. *Croatica Chemica ACTA*, **75**: 371 - 382.

Lai, J.W.S. , Pinto, L.J., Kiehlmann, E., Bendell-Young, L.I., and Moore, M.M. 1996. Factors that affect the degradation of naphthenic acids in oil sands wastewater by indigenous microbial communities. *Environmental Toxicology and Chemistry*, **15**: 1482 - 1491.

Li, P. and SenGupta, A.K. 2004. Sorption of hydrophobic ionizable organic compounds (HIOCs) onto polymeric ion exchangers. *Reactive and Functional Polymers*, **60**: 27-39

Liu, W. P., Zheng, W. and Gan, J. 2002. Competitive Sorption between imidacloprid and imidacloprid-urea on soil clay minerals and humic acids. *Journal of Agricultural and Food Chemistry*, **50**: 6823 – 6825.

Manahan, S. 2000. *Fundamentals of Environmental Chemistry*. CRC Press LLC.

Martins, J. M. and Mermoud, A. 1998. Sorption and degradation of four nitroaromatic herbicides in mono and multi-solute saturated/unsaturated soil batch systems. *Journal of Contaminant Hydrology*, **33**: 187 – 210.

Morrissey, F.A. and Grismer, M.E. 1999. Kinetics of volatile organic compound sorption/desorption on clay minerals. *Journal of Contaminant Hydrology*, **36**: 291–312.

Peng, J., Headley, J.V. and Barbour, S.L., 2002. Adsorption of single-ring model naphthenic acids on soils. *Canadian Geotechnical Journal*. **39**: 1419 - 1426.

Pignatello, J.J. 2000. The measurement and interpretation of sorption and desorption rates for organic compounds in soil media. *Advanced in Agronomy*, **69**: 1 - 73.

Pignatello, J.J. and Baoshan, X. 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology*, **30**: 1 -11.

Rebhun, M., Smedt, D.E. and Rwetabula, F. 1996. Dissolved humic substances for remediation of sites contaminated by organic pollutants. Binding-desorption model predictions. *Water Resource*, **30**: 2077 – 2038.

Riffenburgh, R.H. 1999. *Statistics in Medicine*, Academic Press.

Rockne, K.J., Kosson, D.S., Young, L.Y. and Taghon, G.L. 1999. Sequestration of PAHs in size- and density-fractionated estuarine sediments. *In Situ and On Site Bioremediation*, **5**: 191 - 196.

Rogers, V.V., Wickstrom, M., Liber, K. and MacKinnon, M.D. 2002a. Acute and subchronic mammalian toxicity of naphthenic acids from oil sands tailings. *Toxicol. Sci.* **66**: 347 - 355.

Rogers, V.V, Liber, K. and MacKinnon, M.D. 2002b. Isolation and characterization of naphthenic acids from Athabasca oil sands tailings pond water. *Chemosphere*, **48**: 519-527.

Sabljić, A. 1987. On the prediction of soil sorption coefficients of organic pollutants from molecular structure: Application of molecular topology model. *Environmental Science and Technology*, **21**: 358-65.

Scott, A. C., Mackinnon M.D. and Fedorak, P. M. 2005. Naphthenic acids in Athabasca oil sands tailings water are less biodegradable than commercial naphthenic acids. *Environ. Sci. Technol.*, **39**: 8399 – 8394.

Shackelford, C. D. 1991. Laboratory diffusion testing for waste disposal- a review. *Journal of Contaminant Hydrology*, **7**: 177 -217.

Shah, Dahyabhai J, and Tiwari, Krishna K. 1981. Effect of Salt on the Distribution of Acetic Acid between Water and Organic Solvent. *Journal of Chemical Engineering*, **26**: 375 – 378.

Söderbergh, Bengt. 2004. Canada's oil sands resources and its future impact on global oil supply. M.Sc. Thesis, University of Uppsala, Uppsala, Sweden.

Tiessen, T.H. and Roberts, T.L., Stewart, J.W.B., 1983. Carbonate analysis in soils and minerals by acid digestion and two-endpoint titration. *Communications in Soil Science and Plant Analysis*, **14**: 161 – 166.

Travis, C. C. and Etnier, E. 1981. Survey of sorption relationships for reactive solutes in soil. *Journal of Environmental Quality*, **10**: 8-17

Wu, X. Q., Jing, H. M., Zheng, Y. G., Yao, Z. M. and Ke., W. 2004. Study on high-temperature naphthenic acid corrosion and erosion-corrosion of aluminized carbon steel. *Journal of Materials Science*, **39**, 975– 985.

Wu, S. and Gschwend, P.M. 1986. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environmental Science and Technology*, **20**: 717 – 725.

Yiling Gong 1997. Factors controlling the solubility of condensate hydrocarbons in groundwater at gas plants. Thesis University of Saskatchewan, Saskatoon SK, Canada.

## **APPENDICES**

**Appendix A. Derivation of de-protonation factor (Q) and  $K_{oc}$  based on pH and pKa.**

Assuming that both the ionized form, as well as the neutral, can sorb to a hydrophobic surface by formation of a neutral ion pair or by sorption of the hydrophobic section of the ionizable organic molecule, the overall  $K_{oc}$  can be written as

$$K_{oc} = K_{oc,neut}Q + K_{oc,ion}(1 - Q) \quad (\text{A.1})$$

where  $Q$  represents the fraction of ions remaining in the neutral phase.  $Q$  can be derived on the basis of equilibrium constant as follows

$$K_a = \frac{[A^-][H^+]}{[AH]} \quad \text{and} \quad \frac{[A^-]}{[AH]} = \frac{K_a}{[H^+]} \quad (\text{A.2})$$

where  $\frac{[A^-]}{[AH]}$  represents the ratio of dissociated to neutral compounds in aqueous

solution. Therefore

$$Q = \frac{[AH]}{[AH] + [A^-]} \quad \text{which can be written as}$$

$$Q = \left[ 1 + \frac{[A^-]}{[AH]} \right]^{-1} \quad (\text{A.3})$$

substituting Equation A.2 into Equation A.3 yields

$$Q = \left[ 1 + \frac{K_a}{[H^+]} \right]^{-1} \quad (\text{A.4})$$

and since  $[H^+] = 10^{(-\text{pH})}$  and  $K_a = 10^{(-\text{pKa})}$   $Q$  becomes

$$Q = \left[ 1 + \frac{10^{(-\text{pH})}}{10^{(-\text{pKa})}} \right]^{-1} = \left( 1 + 10^{(\text{pH} - \text{pKa})} \right)^{-1} \quad (\text{A.5})$$

By substitution of A.1 for  $Q$ , Equation A.1 becomes

$$K_{oc} = K_{oc, \text{neut}} \left( 1 + 10^{(\text{pH} - \text{pKa})} \right) + K_{oc, \text{ion}} \left[ 1 - \left( 1 + 10^{(\text{pH} - \text{pKa})} \right) \right] \quad (\text{A.6})$$

Equation A.6 demonstrates the relative contribution of the neutral and ionized HIOCs to total  $K_{oc}$ . (Delle Site, 2001)



## **Appendix B. Analytical methods for determining the chemical properties of soils (after Enviro-Test Laboratories)**

### **Organic carbon and organic matter**

This is a modified version of the Walkley-Black method. The soil sample is treated with potassium dichromate and sulphuric acid. Oxidized organic carbon can be determined by back titrating the remaining dichromate with ferrous ammonium sulphate. Organic matter is estimated assuming that organic matter contains 58% carbon (Van Bemmelen factor).

### **Inorganic carbon**

The distillation/titration method consists of the digestion of a sample in 6N HCL followed by the determination of the evolved carbon dioxide in a sodium hydroxide trap. The carbon dioxide is titrated directly as carbonic acid in a titration between pH 8.3 and 3.7

### **Saturation paste soil pH**

Deionized water is added to the soil until the soil is saturated, but not over saturated.

The paste is allowed to stand overnight or a minimum of four hours. pH of the soil paste is measured using a pH meter.

### **Saturation paste soil cations (Ca, Mg, Na, K)**

Deionized water is added to the soil until the soil is saturated, but not over saturated.

The paste is allowed to stand overnight or a minimum of four hours. After equilibrium, an extract is obtained by vacuum filtration. Individual cations in the extract are determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

### **Cation Exchange Capacity (CEC)**

This method involves saturation of the soil cation exchange sites with ammonium.

Excess ammonium is removed from the soil with alcohol. Ammonium on the cation exchange site is then removed by leaching with NaCl and determined by autoanalyzer.

This value is then used to estimate CEC.

## Appendix C. Statistical Analyses

### 1) Calculation of confidence intervals for sorption isotherms (Caulcutt and Boddy 1983)

Two series of data are acquired from the batch tests, the concentration of adsorbed naphthenic acids ( $x$ ) and concentration of equilibrium naphthenic acids in the batch test supernatant ( $y$ ).

$x$  = equilibrium naphthenic acid concentration

$y$  = adsorbed naphthenic acid concentration on soil

the upper and lower values of the confidence interval is described by the following equation

$$L = b \pm \frac{t(RSD)}{\sqrt{\sum x^2}}$$

where,

$t$  = two tailed value obtained from  $t$ -test table at 95% confidence; degrees of

freedom of  $\nu = n-2$

$L$  = is the upper or lower slope of the confidence limits

$$b = \frac{\sum xy}{\sum x^2}$$

*RSD* = Relative standard deviation

*RSD* can be estimated from the Residual Sum of Squares (*RSS*)

$$RSS = S_{yy} - b^2(S_{xx})$$

where,

$$S_{yy} = \sum(x - \bar{x})^2$$

$$S_{xx} = \sum(y - \bar{y})^2$$

2) *t*-test for the comparison in fractional abundance of carbon number groupings  
before and after sorption by batch testing

Table C.1 Carbon number groupings for -Z family 2

		<u>-Z Family 2</u>	
Carbon No. (n)		t=0	t=56
<b>Group 1</b>	5	0.000	0.000
	6	0.000	0.000
	7	0.000	0.001
	8	0.000	0.001
	9	0.001	0.001
	10	0.005	0.003
	11	0.015	0.007
	12	0.030	0.012
	13	0.049	0.018
	14	0.094	0.032
<b>Group 2</b>	15	0.131	0.046
	16	0.152	0.055
	17	0.150	0.049
	18	0.116	0.037
	19	0.081	0.022
	20	0.052	0.013
	21	0.034	0.010
	22	0.020	0.006
	23	0.014	0.005
	24	0.011	0.004
<b>Group 3</b>	25	0.009	0.003
	26	0.007	0.003
	27	0.005	0.002
	28	0.004	0.002
	29	0.004	0.002
	30	0.003	0.007
	31	0.003	0.001
	32	0.003	0.001
	33	0.002	0.001
	34	0.002	0.001
	35	0.003	0.001
	36	0.002	0.001
	37	0.002	0.001

Table C.1 represents the relative fractional abundance values for each theoretical naphthenic acid molecule in the  $Z = -2$  family of acids between carbon number 5 to 37. Sample calculations for a two-sample two-tailed  $t$ -test for statistical difference of mean with confidence limits of  $P = 0.05$  (Zar, 1984) are shown below. Theoretical explanation for the test is as follows.

$n_i$  = number of samples in each corresponding group

$\nu_i$  = degrees of freedom associated with each sample where,

$$\nu_i = n_i - 1$$

$\bar{X}_i$  = sample mean or sample average

$X_i$  = individual measurements in the sample

$SS_i$  = the sum of square of the deviations from the mean where,

$$SS_i = \sum (X_i - \bar{X}_i)^2$$

$S_p^2$  = pooled variance between the two samples tested where,

$$S_p^2 = \frac{SS_1 + SS_2}{\nu_1 + \nu_2}$$

$S_{\bar{X}_1 - \bar{X}_2}$  = the variance of the difference between the means where,

$$S_{\bar{X}_1 - \bar{X}_2} = \sqrt{\frac{S_p^2}{\nu_1} + \frac{S_p^2}{\nu_2}}$$

Test assumes Gaussian distribution and with test data a transformation may be required to normalize the data. In the case of naphthenic acids, an arcsine-transformation is applied (Clemente et al. 2003).

The analysis is a two-tailed test of the hypotheses that two sample means are equal. Formally, the null hypotheses is

$$H_o = \mu_1 - \mu_2 = 0$$

and the alternate hypotheses is

$$H_A = \mu_1 - \mu_2 \neq 0$$

For sample groups of the initial (t=0) and post sorption (t=56) naphthenic acids for Z = - 2 family, example calculations are as follows:

Table C.2 Group two fractional abundance values

		Carbon		
		No. (n)		
Group 2		t=0	t=56	
		15	0.131	0.046
		16	0.152	0.055
		17	0.150	0.049
		18	0.116	0.037
		19	0.081	0.022
		20	0.052	0.013
		21	0.034	0.010
		22	0.020	0.006
		23	0.014	0.005
	24	0.011	0.004	

$$n_1 = 10$$

$$n_2 = 10$$

$$\nu_1 = 9$$

$$\nu_2 = 9$$

$$\bar{X}_1 = 0.075913$$

$$\bar{X}_2 = 0.02$$

$$SS_1 = 0.0293$$

$$SS_2 = 0.0036$$

$$S_p^2 = \frac{SS_1 + SS_2}{\nu_1 + \nu_2} = \frac{0.029 + 0.0036}{9 + 9} = 0.0018$$

$$S_{\bar{X}_1 - \bar{X}_2} = \sqrt{\frac{S_p^2}{\nu_1} + \frac{S_p^2}{\nu_2}} = \sqrt{\frac{0.0018}{9} + \frac{0.0018}{9}} = 0.0191$$



In the two-tailed test,  $H_0$  will be rejected if  $t_{calc} \geq t_{0.05(2),v}$ . The calculated value of  $t$  is obtained as follows:

$$t_{calc} = \frac{\bar{X}_1 - \bar{X}_2}{S_{\bar{X}_1 - \bar{X}_2}} = \frac{0.075913 - 0.02}{0.0191} = 2.684$$

from  $t$ -test tables,

$$t_{0.05(2),v} = t_{0.05(2),18} = 2.101$$

where  $v$  is the pooled degrees of freedom, the sum of  $v_1$  and  $v_2$ . In this case therefore,  $H_0$  is rejected, i.e. the two samples are significantly different or have significantly different means.

3) *Significance test for sorption coefficients* (Riffenburgh, R.H. 1999)

The procedure to test whether two sorption coefficients are significantly different is as follows:

- a) establish null hypothesis ( $H_0$ ) and alternative hypothesis ( $H_a$ ) i.e. that  $K_{d1} = K_{d2}$ , and  $K_{d1} \neq K_{d2}$  respectively.
- b) Calculate the combined residual mean square value as follows:

$$S_{yx}^2 = \frac{\sum(y_1 - \bar{y}_1)^2 + \sum(y_2 - \bar{y}_2)^2}{(n_1 - 2) + (n_2 - 2)}$$

- c) Calculate standard error as follows:

$$S_{1-2} = \sqrt{S_{yx}^2 \left( \frac{1}{S_{xx,1}} + \frac{1}{S_{xx,1}} \right)}$$

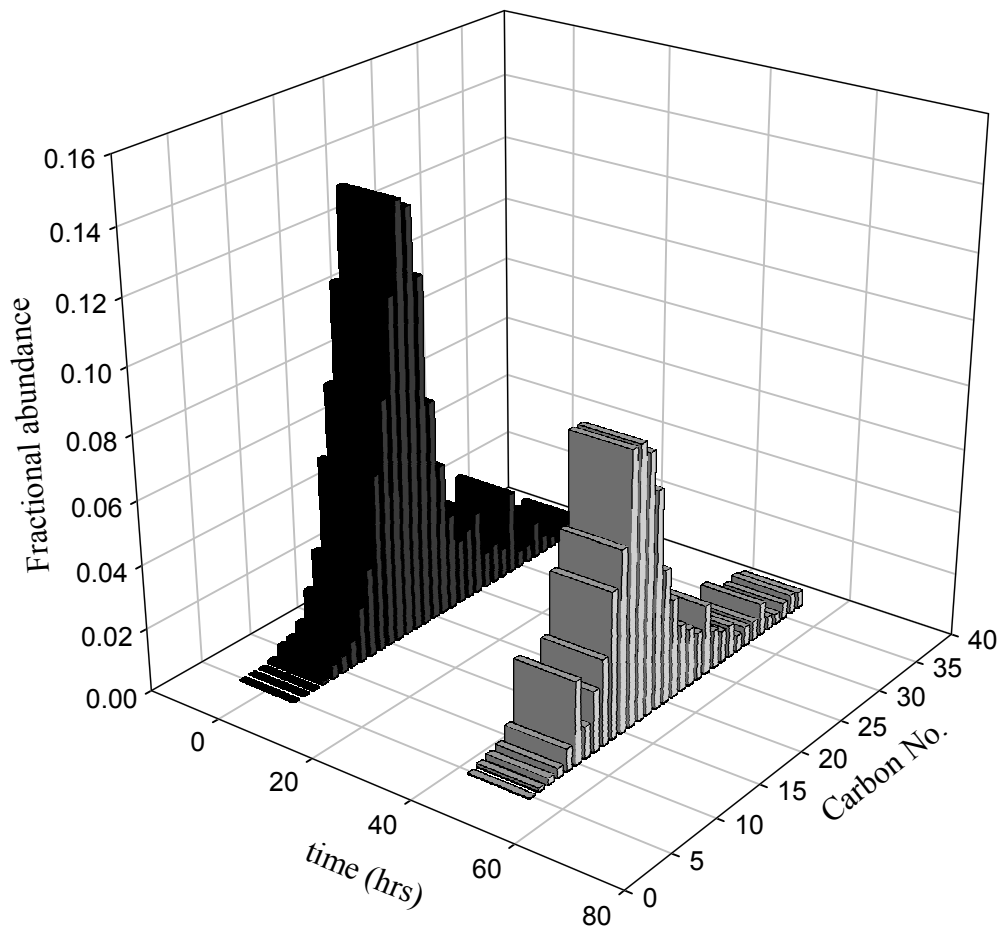
- d) To Calculate a t value

$$t_{calc} = \frac{|K_{d1} - K_{d2}|}{S_{1-2}}$$

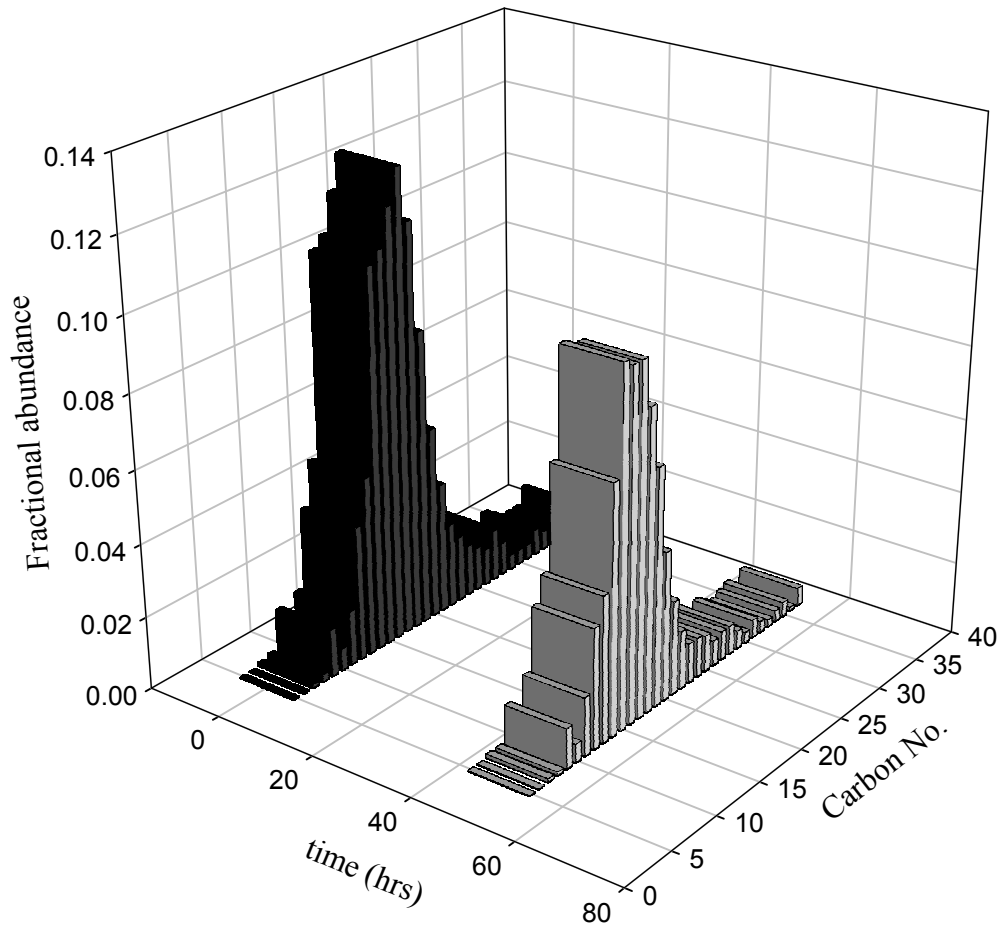
- e) Find the critical value for comparison from the  $t$ -test tables with the degrees of freedom being  $\nu = (n_1 - 2) + (n_2 - 2)$
- f) decide by comparison of the calculated  $t$  value to that derived from the tables to determine whether the null hypothesis is to be rejected or accepted.

**Appendix D. Histograms of fractional abundance for pre and post sorption samples at 200 mg/L initial concentration**

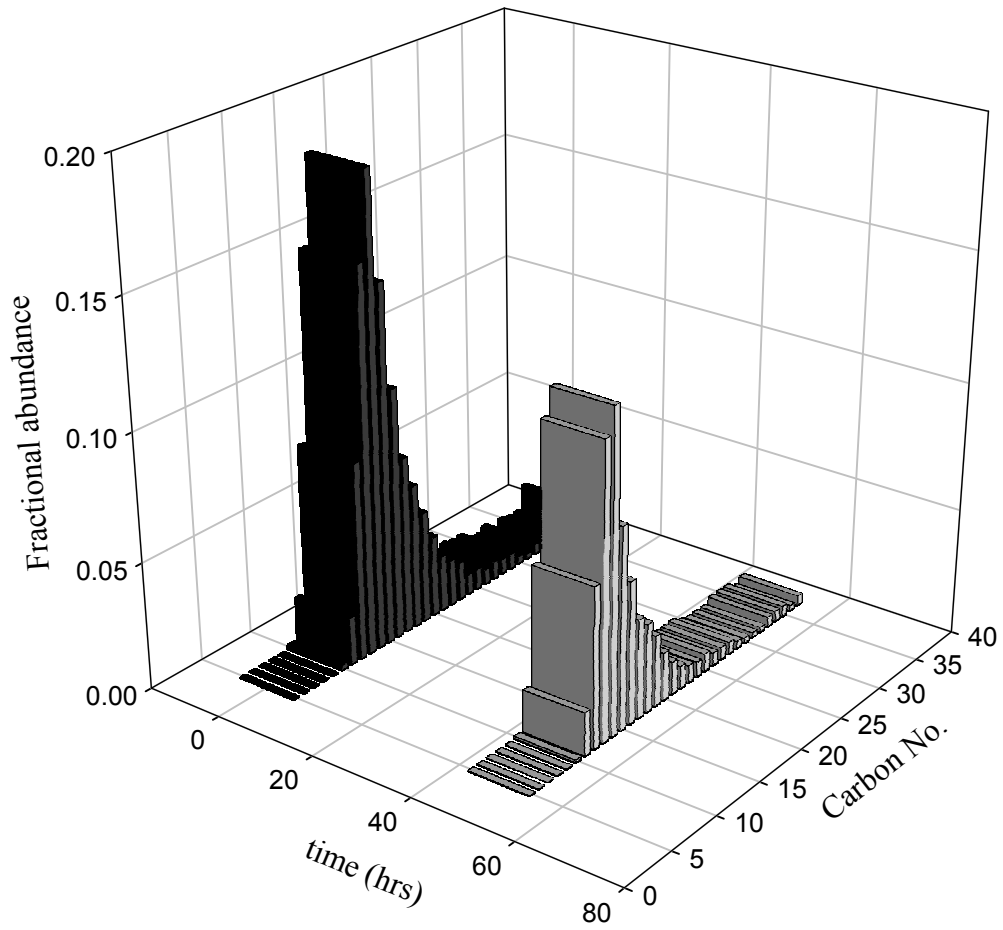
**Milli-Q Water - Soil 1**



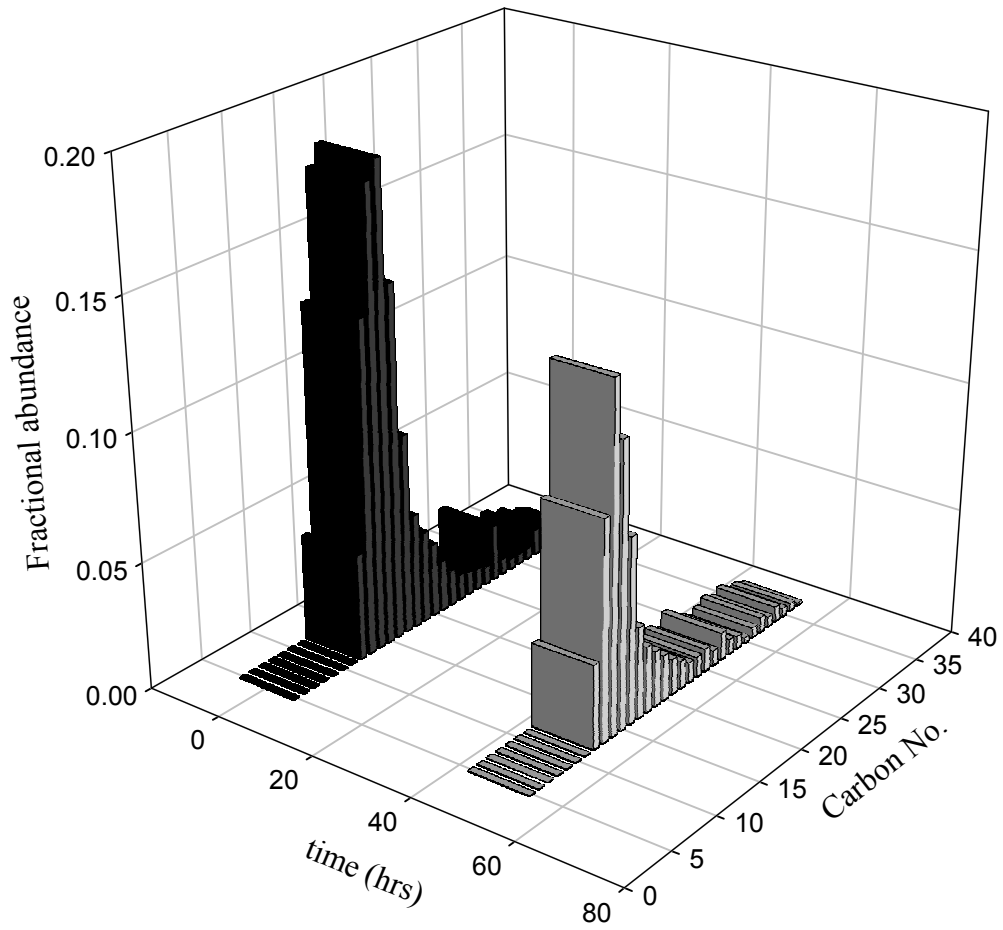
**Figure D.1 Z=0 family change in fractional abundance of individual species with time, Soil 1 Milli-Q water**



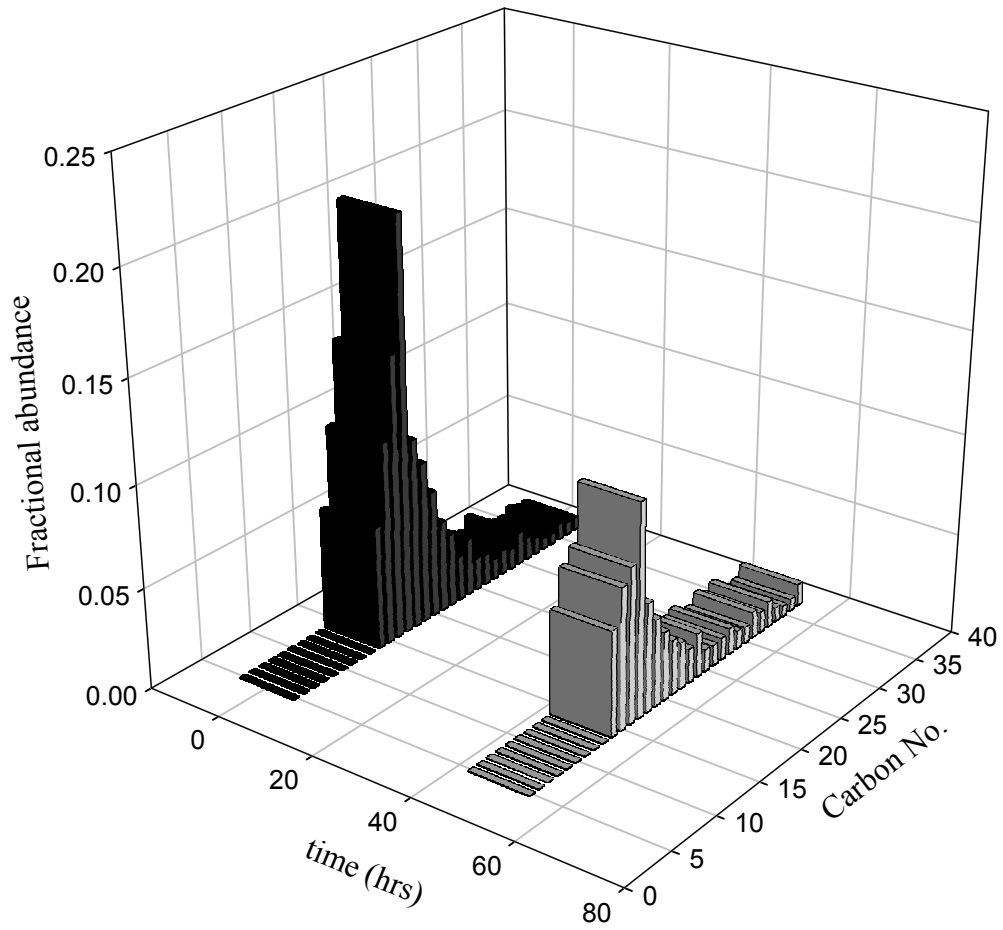
**Figure D.2 Z=-2 family change in fractional abundance of individual species with time, Soil 1 Milli-Q water**



**Figure D.3**  $Z = -4$  family change in fractional abundance of individual species with time, Soil 1 Milli-Q water

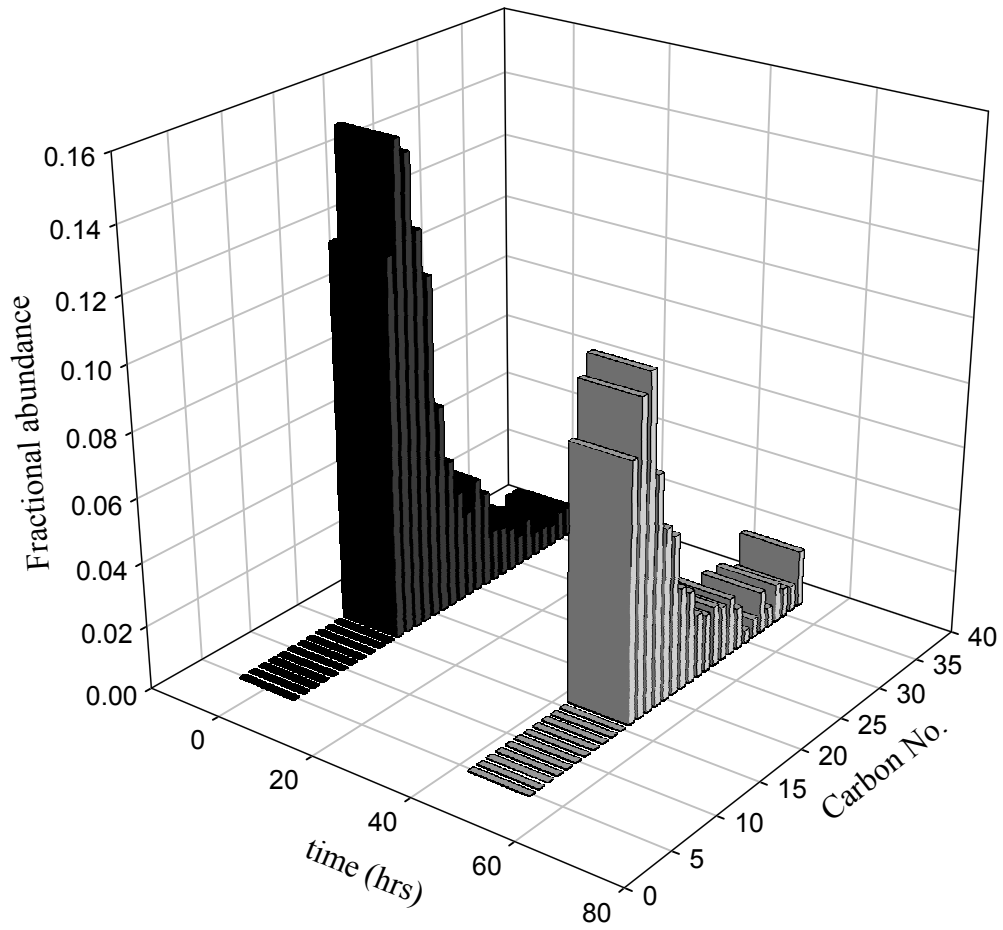


**Figure D.4 Z = -6 family change in fractional abundance of individual species with time, Soil 1 Milli-Q water**

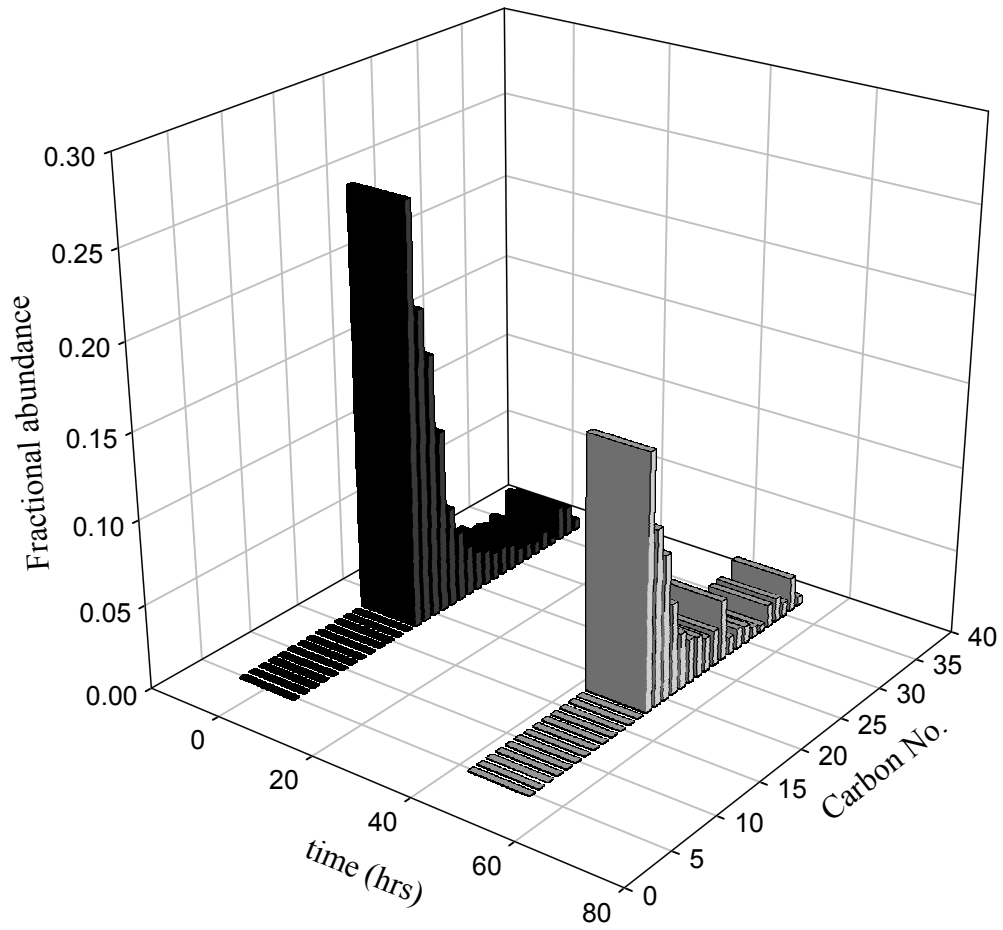


**Figure D.5 Z= -8 family change in fractional abundance of individual species with time, Soil 1 Milli- Q water**



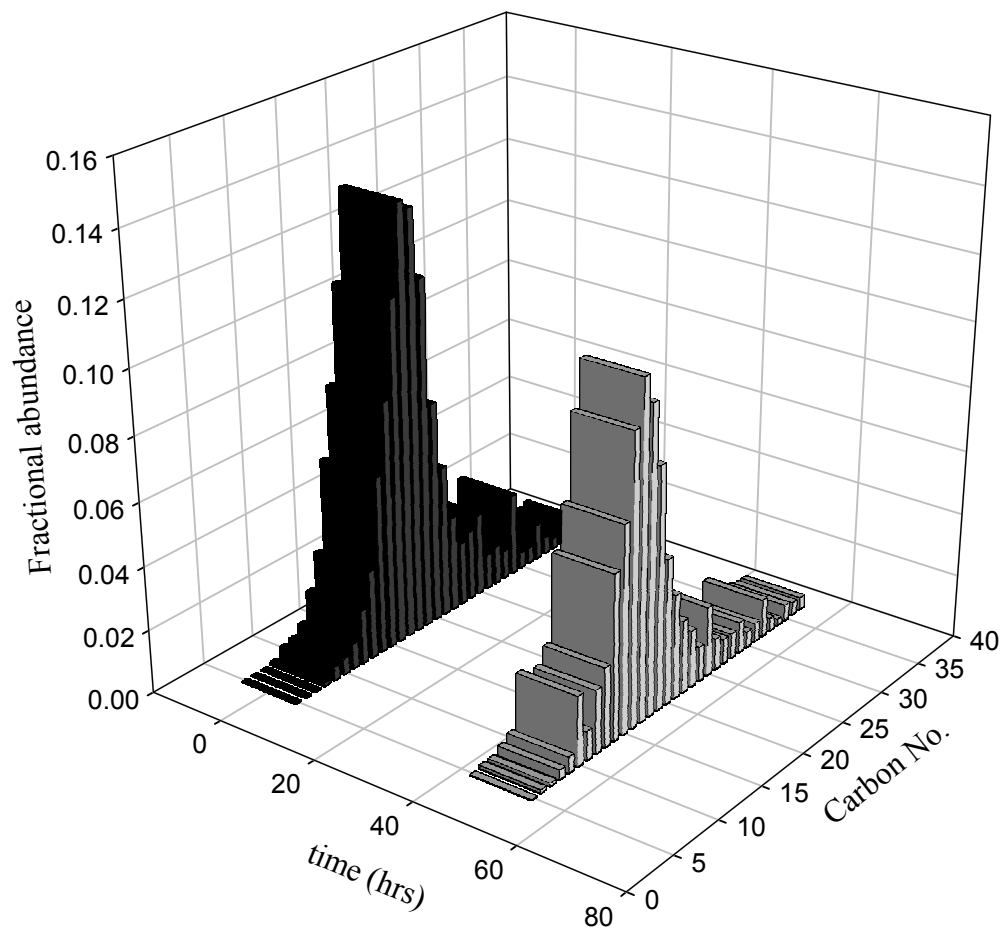


**Figure D.6 Z= -10 family change in fractional abundance of individual species with time, Soil 1 Milli-Q water**

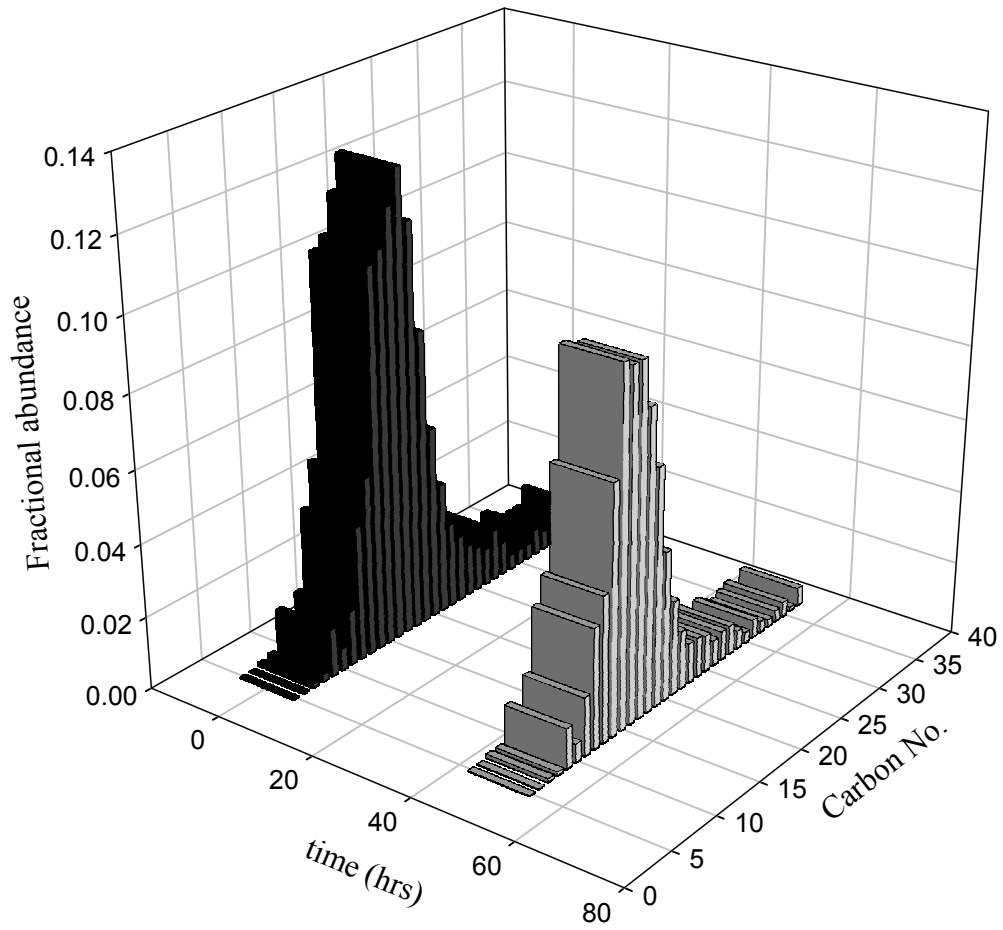


**Figure D.7 Z= -12 family change in fractional abundance of individual species with time, Soil 1 Milli-Q water**

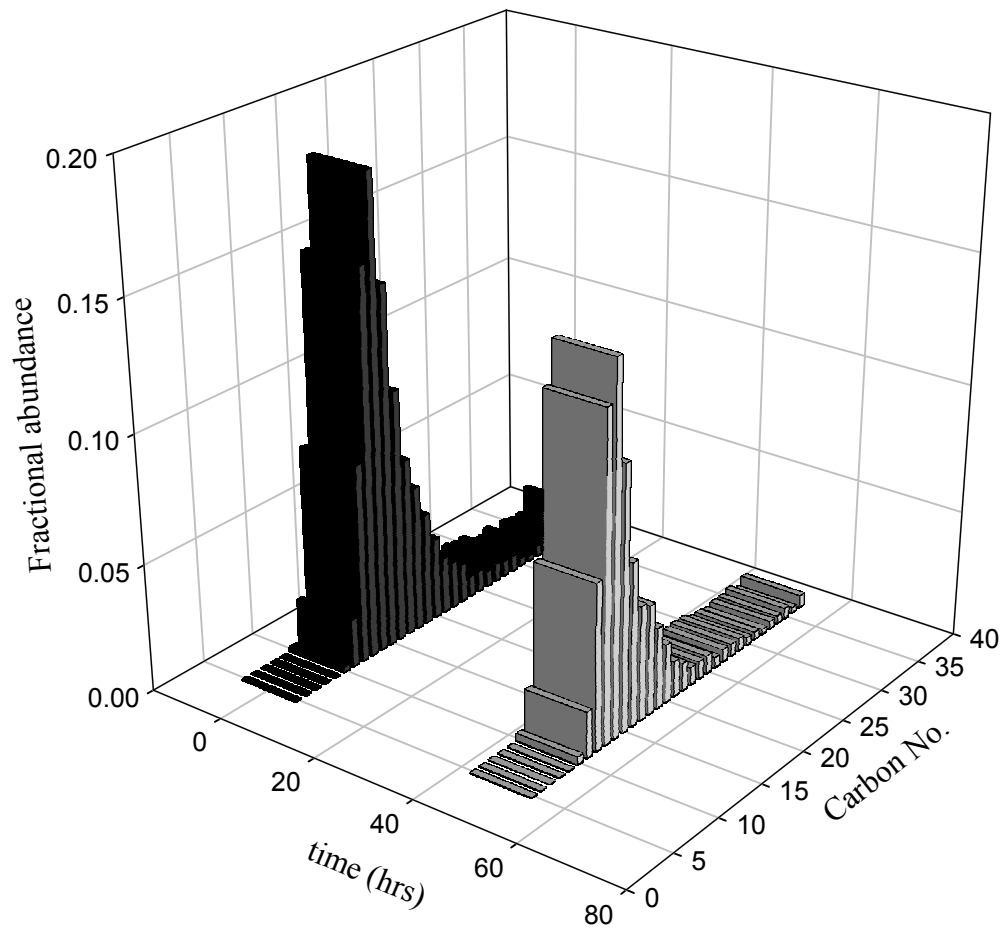
Milli-Q Water - Soil 2



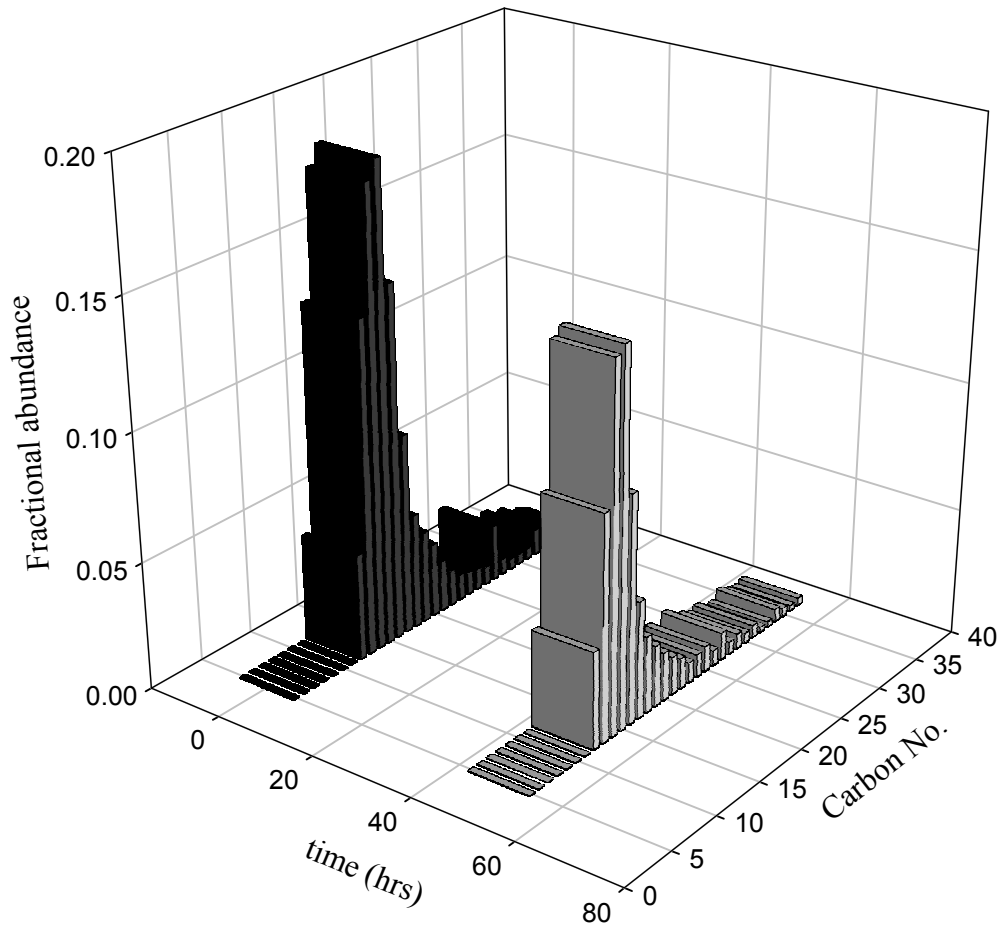
**Figure D.8 Z = 0 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water**



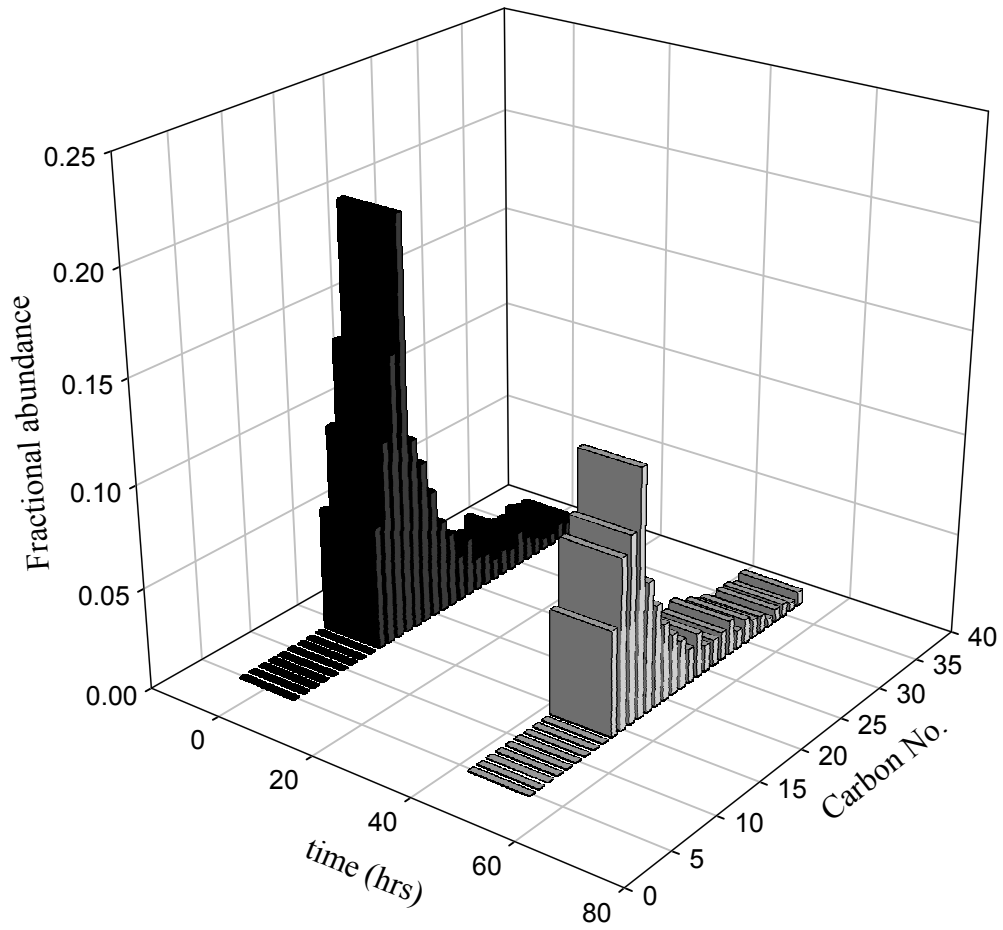
**Figure D.9**  $Z = -2$  family change in fractional abundance of individual species with time, Soil 2 Milli-Q water



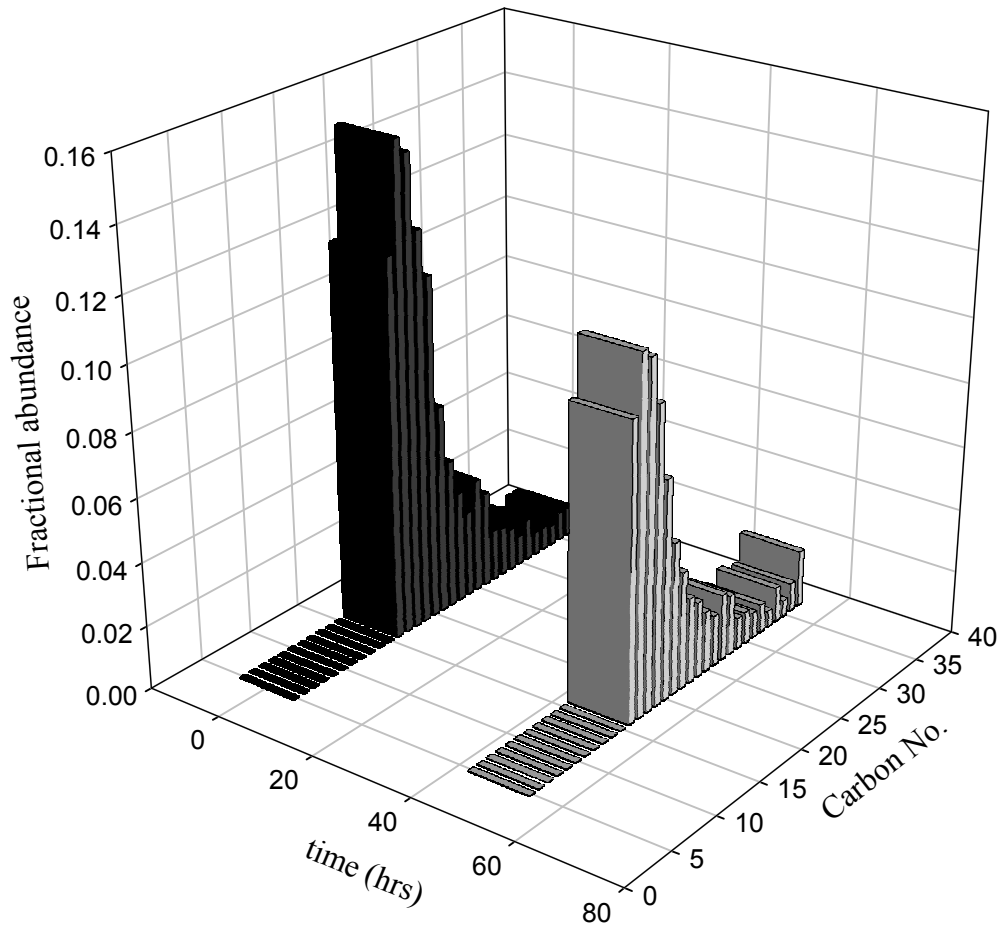
**Figure D.10** Z= -4 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water



**Figure D.11** Z= -6 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water

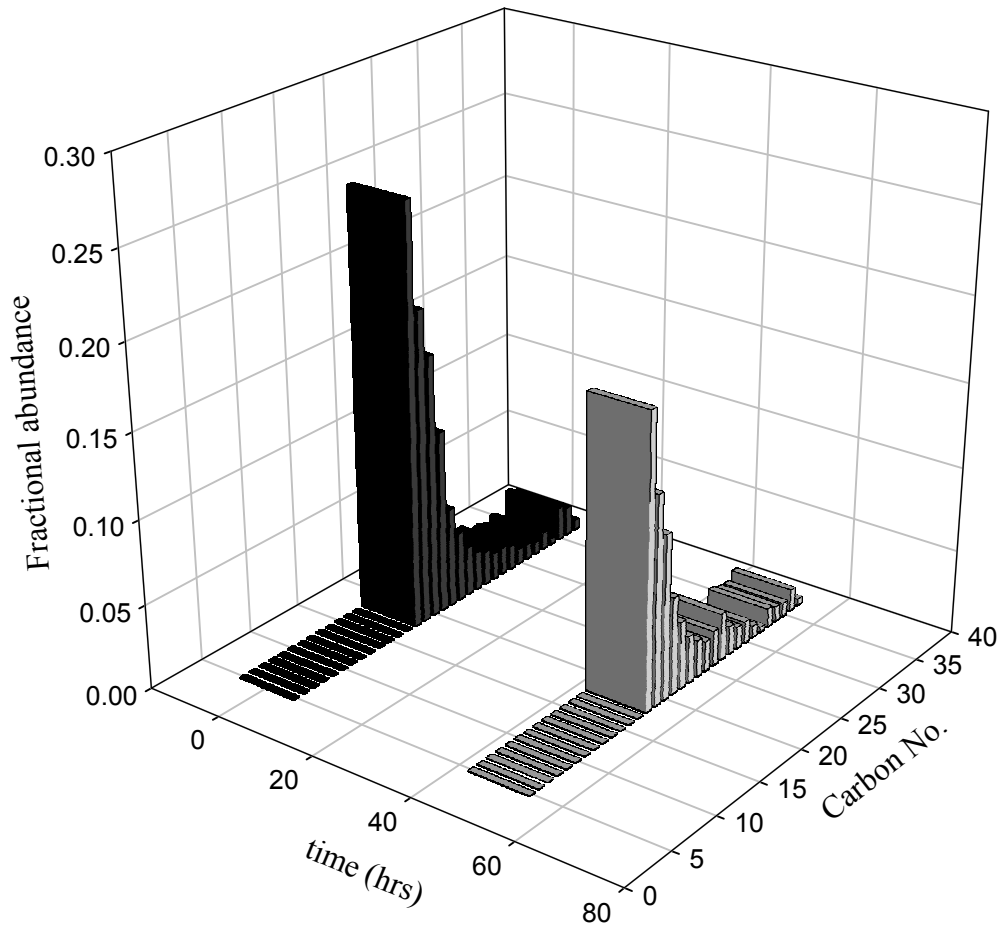


**Figure D.12**  $Z = -8$  family change in fractional abundance of individual species with time, Soil 2 Milli-Q water



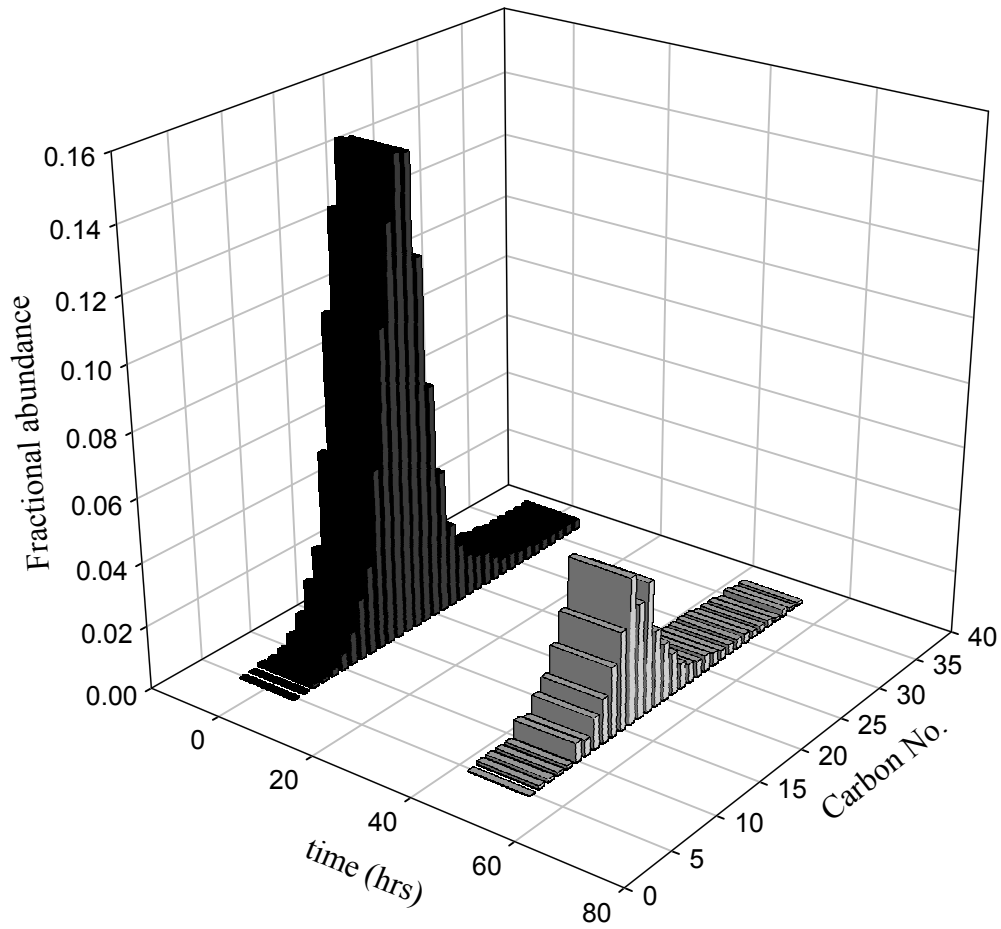
**Figure D.13** Z= -10 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water



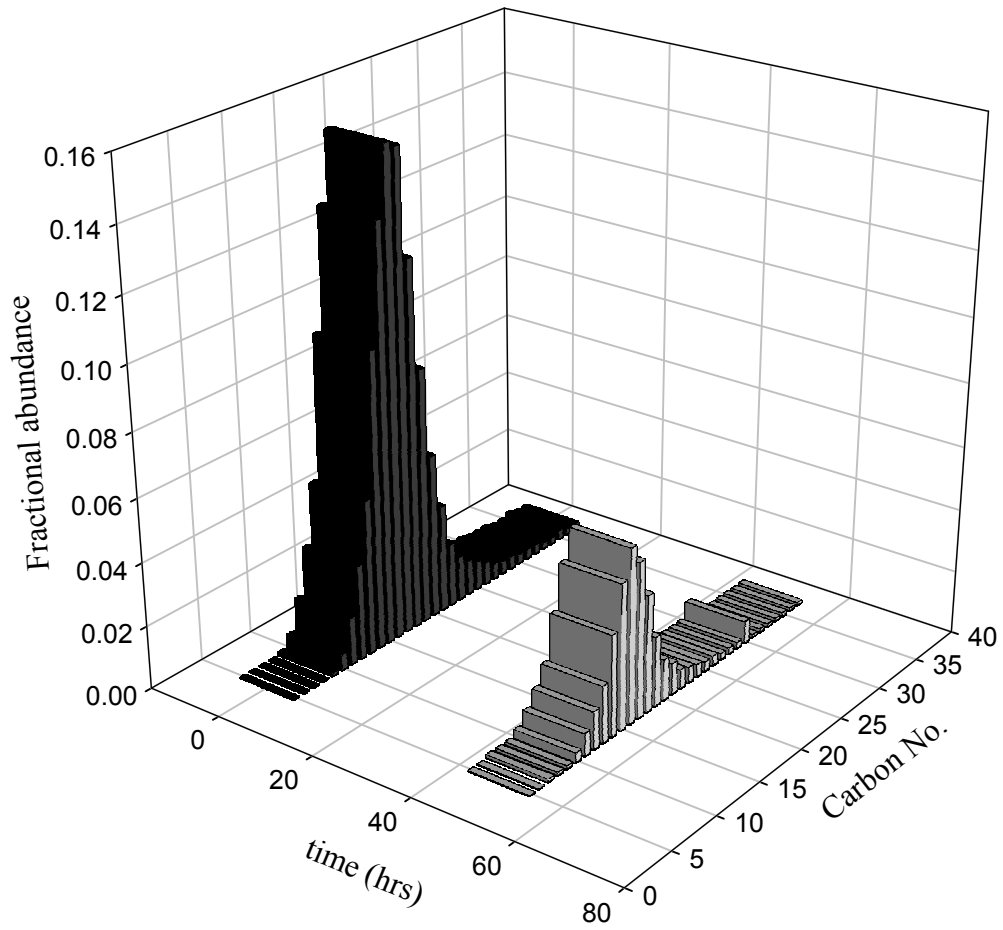


**Figure D.14** Z= -12 family change in fractional abundance of individual species with time, Soil 2 Milli-Q water

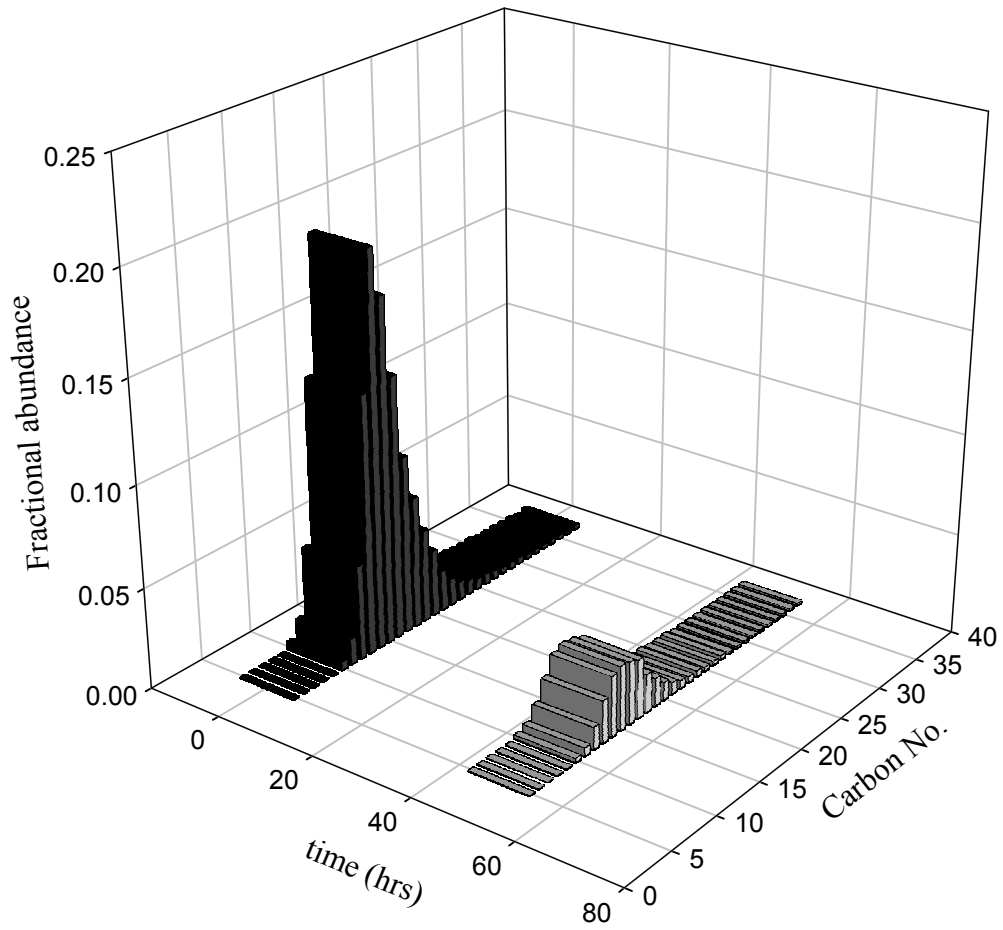
**SGW - Soil 1**



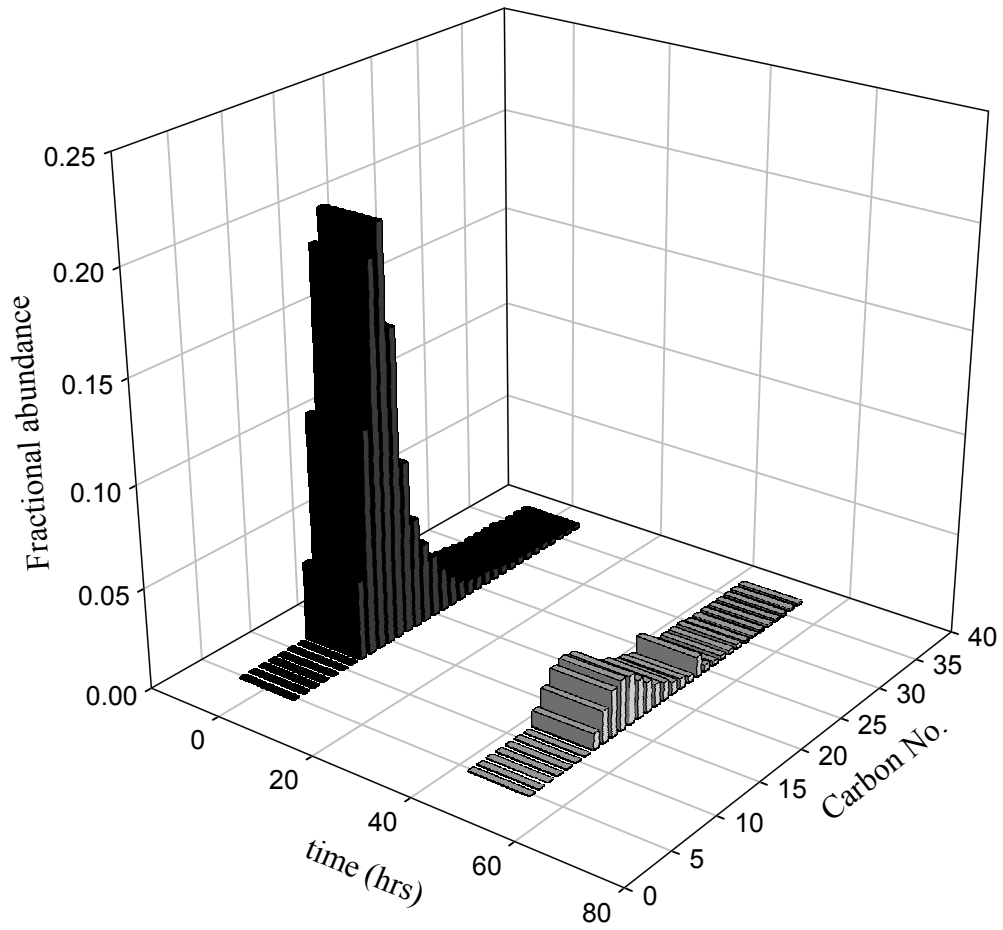
**Figure D.15 Z = 0 family change in fractional abundance of individual species with time, Soil 1 SGW**



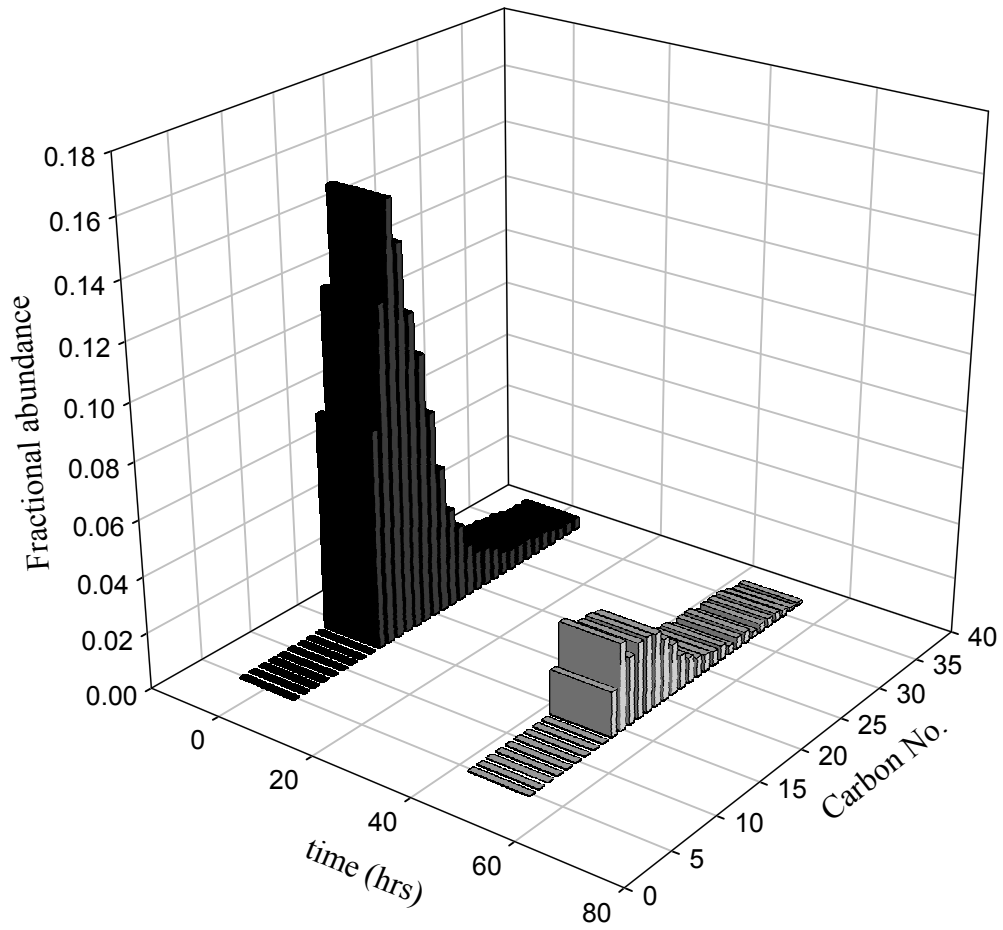
**Figure D.16**  $Z = -2$  family change in fractional abundance of individual species with time, Soil 1 SGW



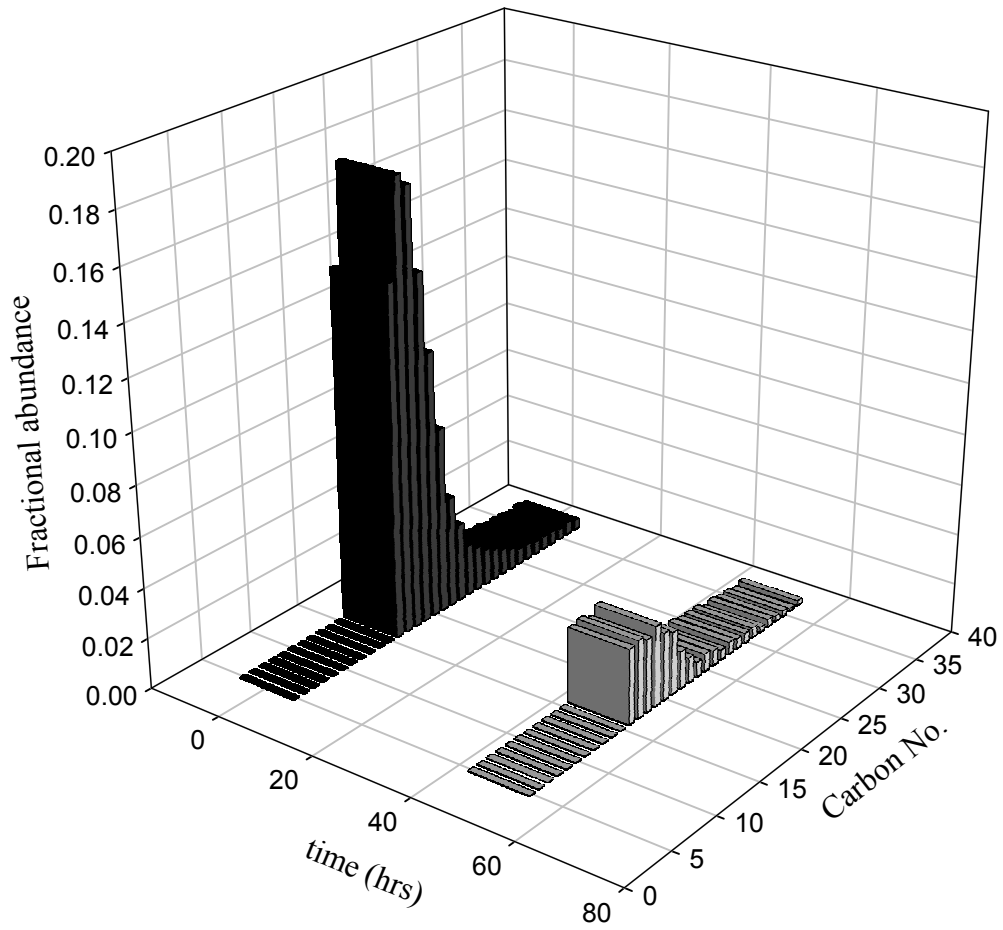
**Figure D.17  $Z = -4$  family change in fractional abundance of individual species with time, Soil 1 SGW**



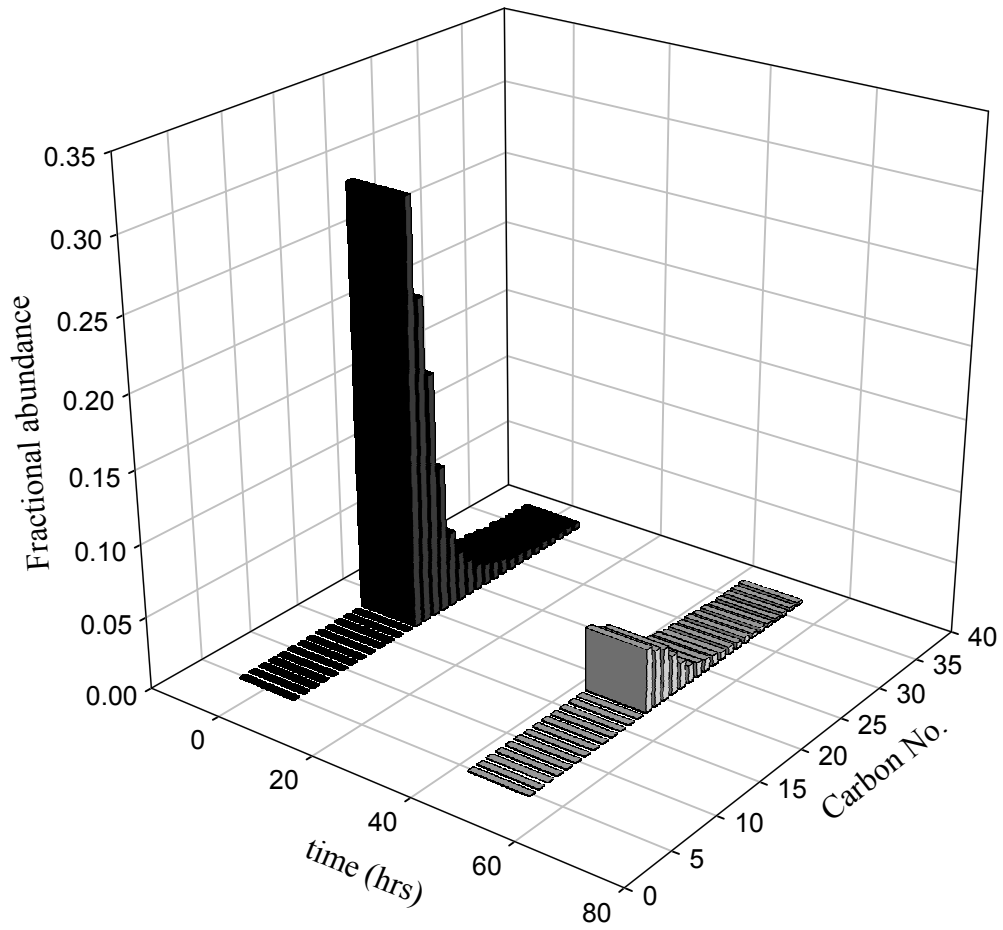
**Figure D.18** Z= -6 family change in fractional abundance of individual species with time, Soil 1 SGW



**Figure D.19** Z= -8 family change in fractional abundance of individual species with time, Soil 1 SGW



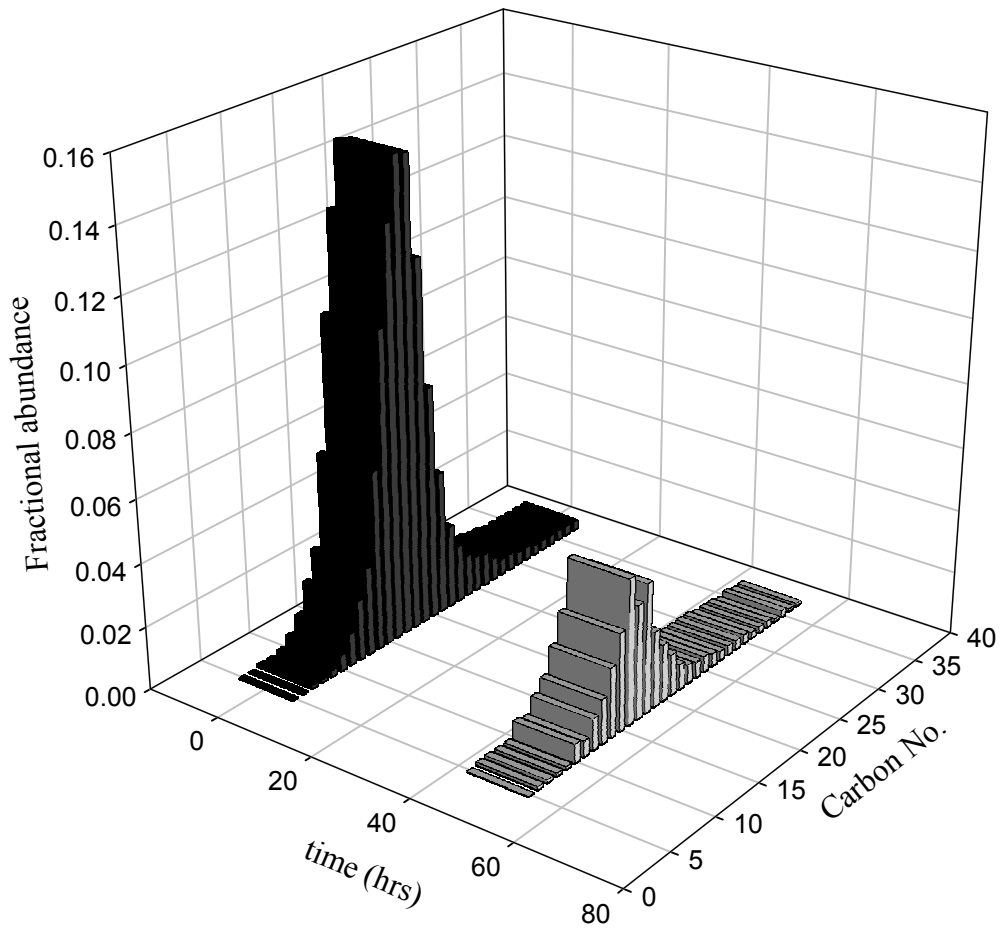
**Figure D.20 Z= -10 family change in fractional abundance of individual species with time, Soil 1 SGW**



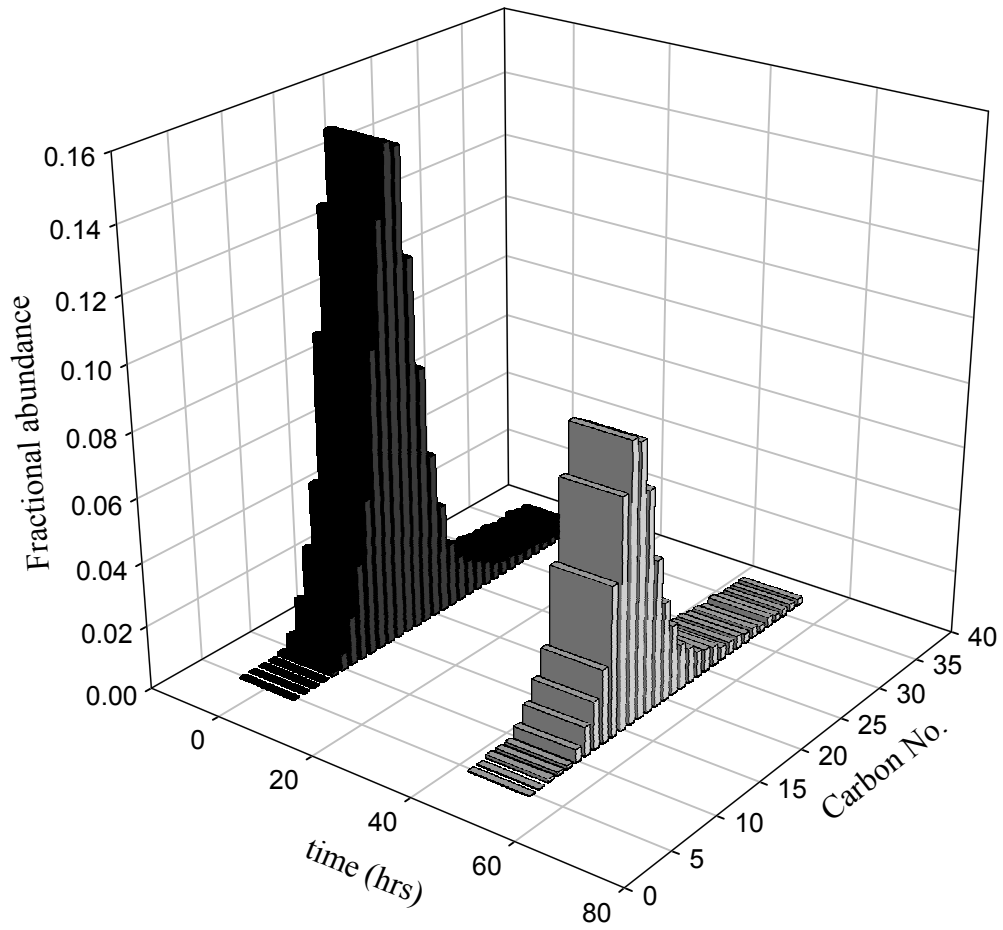
**Figure D.21** Z= -12 family change in fractional abundance of individual species with time, Soil 1 SGW



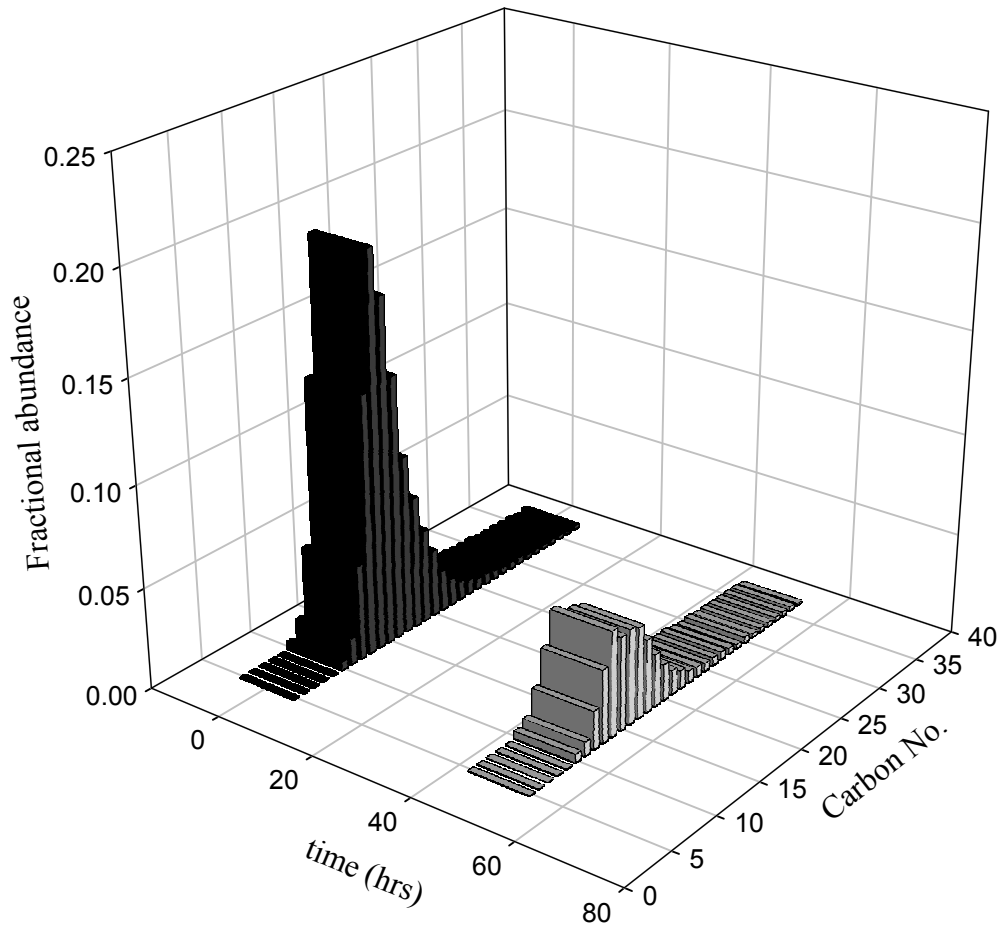
**SGW - Soil 2**



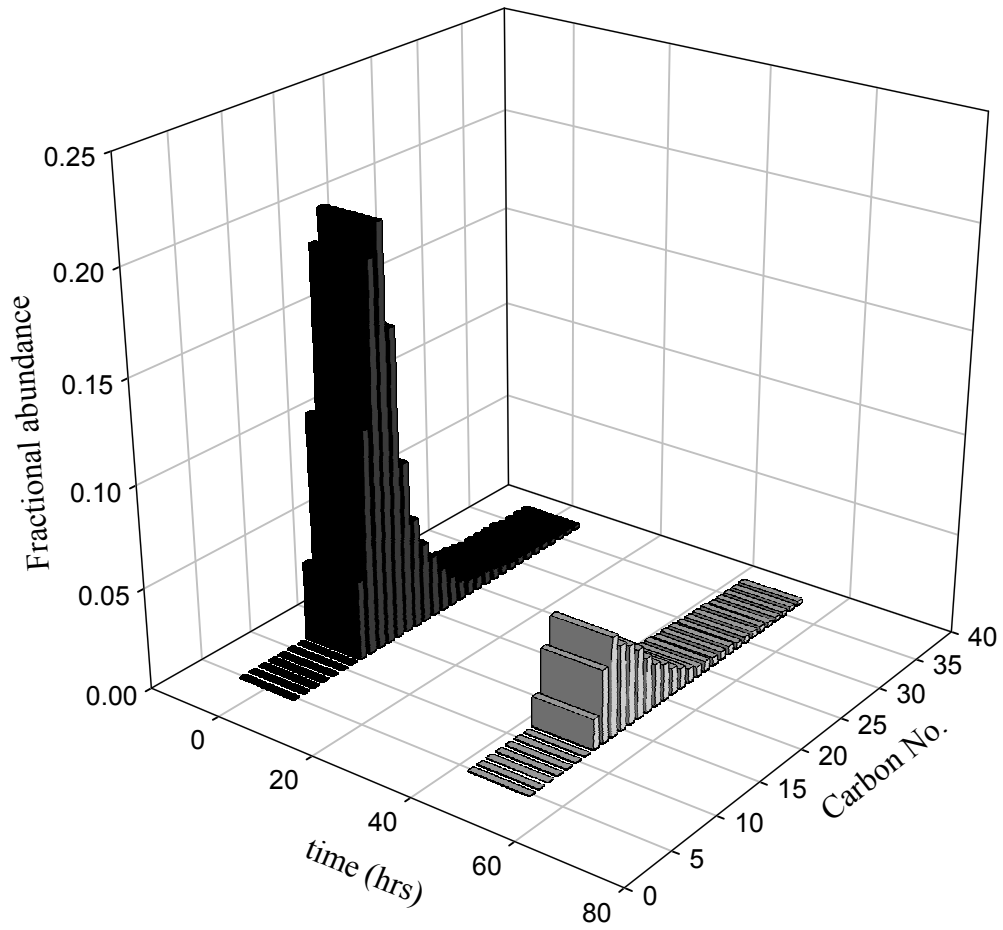
**Figure D.22 Z= 0 family change in fractional abundance of individual species with time, Soil 2 SGW**



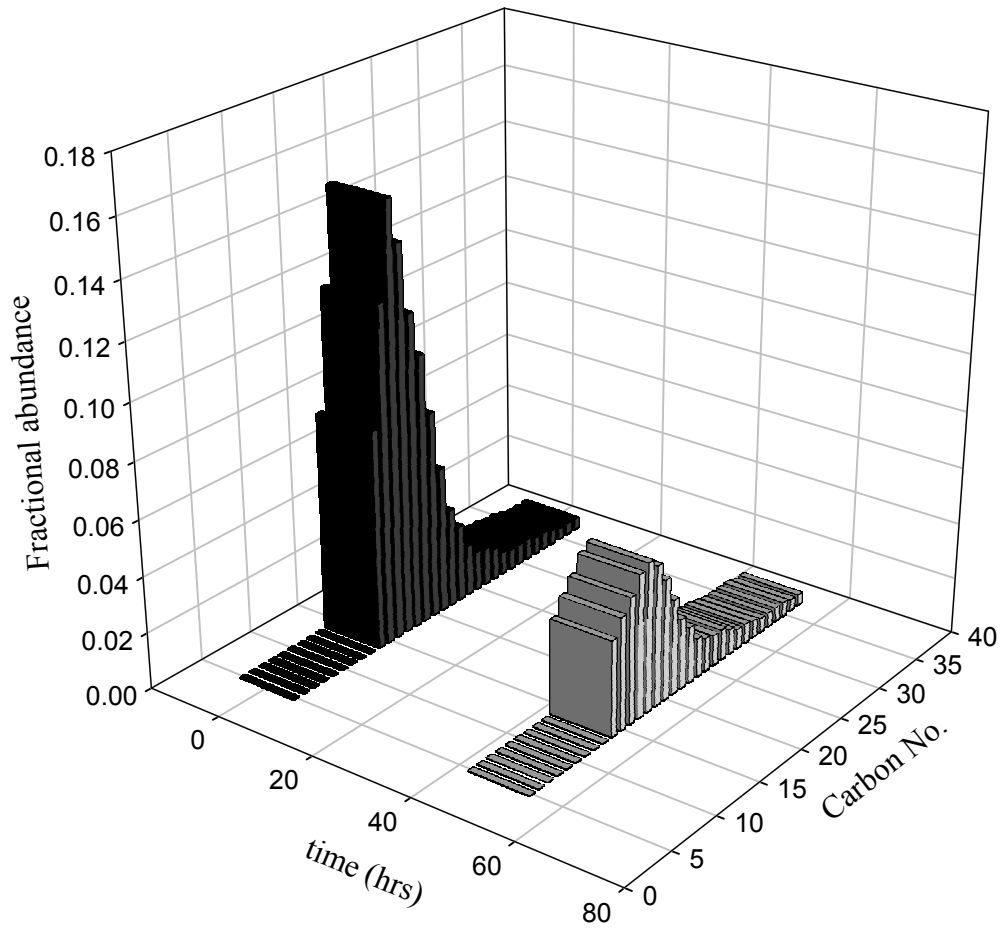
**Figure D.23**  $Z = -2$  family change in fractional abundance of individual species with time, Soil 2 SGW



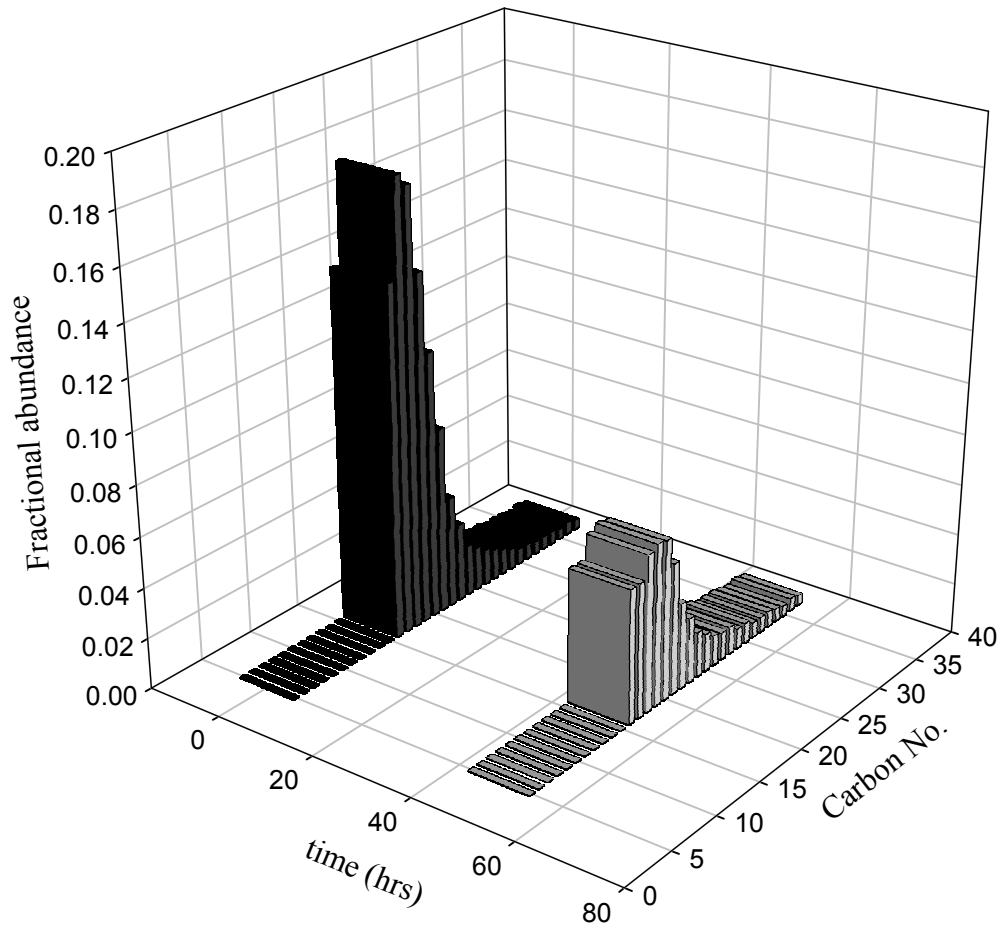
**Figure D.24 Z= - 4 family change in fractional abundance of individual species with time, Soil 2 SGW**



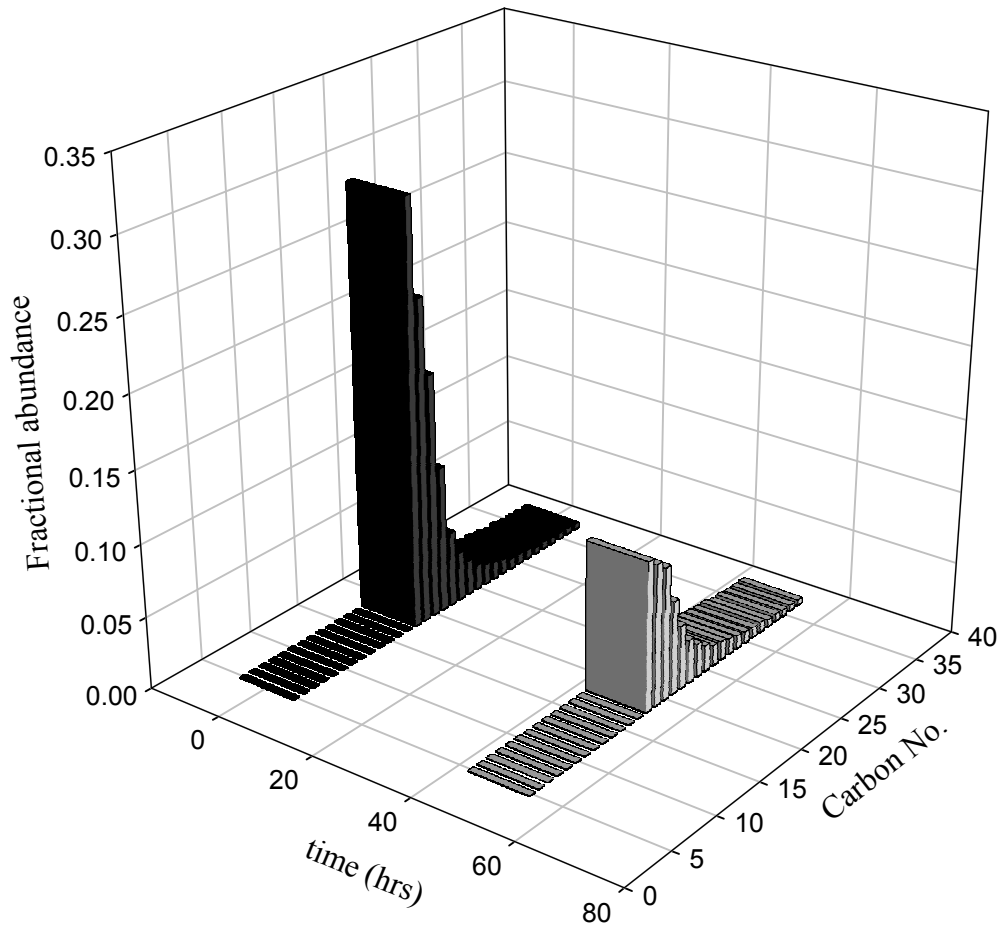
**Figure D.25** Z= -6 family change in fractional abundance of individual species with time, Soil 2 SGW



**Figure D.26** Z=-8 family change in fractional abundance of individual species with time, Soil 2 SGW



**Figure D.27** Z= -10 family change in fractional abundance of individual species with time, Soil 2 SGW



**Figure D.28** Z= -12 family change in fractional abundance of individual species with time, Soil 2 SGW