University of Alberta

Sorption of Naphthenic Acids to Soil Minerals

by

William Patrick Marsh ©

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Abstract

The sorption of naphthenic acids on clays, soils and oil sands coke was examined using a batch sorption partitioning method. The influence of different clay minerals, exchangeable cation, salt content, organic content in the soil samples, and the pH of the solution on the sorption of naphthenic acids was determined. Experiments were conducted using both commercial naphthenic acids (Merichem) and extracted naphthenic acids originating from tailings pond water. The pH was determined to have the greatest influence with partitioning coefficients (K_D) for clays ranging from 18 to 57 mL g^{-1} for pH 6, and 0 to 10 mL g^{-1} for pH 8. These results indicate high mobility of naphthenic acids in soil-water systems.

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List of Abbreviations and Nomenclature

2,4-D	2,4-dichlorophenoxylacetic acid
4MCHA	4-methylcyclohexaneacetic acid
4MCHC	4-methylcyclohexanecarboxylic acid
Al	Aluminum
BCV	Beaver Creek Valley
C_a	Mass of chemical sorbed per gram of solid
Ca	Calcium
$CaCl_2$	Calcium chloride
$CaSO_4$	Calcium sulfate
CEC	Cation exchange capacity
DCM	Dichloromethane
EDC	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride
ETB	East Toe Berm
f_{OC}	Fraction of organic carbon
FTIR	Fourier transform infrared spectroscopy
GC-DCM	High resolution gas chromatography dichloromethane
GC-MS	Gas chromatography – mass spectrometry

HCl	Hydrochloric acid
HPLC	High performance liquid chromatography
K	Potassium
Ka	Acid dissociation constant
K_D	Partitioning coefficient
K_{OC}	Partitioning coefficient to organic carbon content
K_{OW}	Octanol – water partitioning coefficient
$KHCO_3$	Potassium bicarbonate
KOH	Potassium hydroxide
MFT	Mature fine tailings
Mg	Magnesium
$MgSO_4$	Magnesium sulfate
MSTFA	N-methyl-N-(trimethylsilyl) trifluoracetamide
Na	Sodium
NaCl	Sodium chloride
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
NPH	Nitrophenylhydrazine
NPH-HCl	Nitrophenylhydrazine hydrochloride

OH^-	Hydroxide
PSA	Particle size analysis
R_D	Retardation factor
Si	Silicon
SOM	Soil organic matter
TOC	Total organic carbon
WIP	West-In Pit tailings pond

Chapter 1 Introduction

One of the largest deposits of bitumen is located in the Athabasca Basin in northern Alberta. The basin is speculated to be the largest accumulation of biodegraded oil in the world (Hunt 1979). The Alberta Energy and Utilities Board, in Alberta's Ministry of Energy (AME) 2004-2005 report, stated that the average bitumen production in 2003 was 964,000 barrels d^{-1} and Alberta's remaining reserve of bitumen, which is recoverable with current technology, was 174.5 billion barrels (AME 2005).

Water resulting from the oil-sands extraction activities (also termed process-affected waters) contains a multitude of different compounds including naphthenic acids, salts, hydrocarbons and trace metals (Leung et al. 2003; MacKinnon 1989; Madill et al. 1999). The compounds present in these waters may be transported through soils, surface waters and groundwaters into the surrounding environment. It is therefore necessary to understand the movement and fate of these compounds in order to determine the impact they may have on the surrounding environment. Naphthenic acids (described in Section 1.2) are of particular interest, because they have been found to contribute to the toxicity of the process-affected waters (Schramm et al. 2000). An important process affecting the fate of these compounds is sorption (adsorption and absorption) to soils.

A discussion report from the CONRAD Environmental Aquatic Technical Advisory Group (CONRAD 1998) was prepared to provide background information on naphthenic acids. The report highlighted the interest in the environmental fate and persistence of naphthenic acids. CONRAD (1998) indicated that there was a lack of information about the sorption characteristics of naphthenic acids to soil materials. CONRAD (1998) suggested that further research be conducted to provide the information on this sorption behavior, which would allow an assessment of the dispersive and distributive potential of naphthenic acids if a process-affected water release was to occur.

Studies conducted by MacKinnon et al. (2004) and Oiffer (2004) have shown that process-affected waters are being released into surface water and groundwater systems. The study conducted by MacKinnon et al. (2004) centered on the release of process-affected waters from the East Toe Berm (ETB). ETB is a tailings sand deposit constructed in the late 1990s on the eastern dyke of the Mildred Lake Settling Basin (MLSB) on the Syncrude site. Important findings from MacKinnon et al. (2004) indicated that process-affected waters from the ETB are affecting the surface water in the Beaver Creek Valley and that there is some selective attenuation of naphthenic acids compounds as the surface water progresses further away from the ETB. This selective attenuation could be influenced by either sorption or biodegradation (MacKinnon et al. 2004).

A report by Oiffer (2004) at the University of Waterloo delineated the extent of several contaminant plumes at Syncrude Canada Mildred Lake site. Figure 1.1 shows the naphthenic acids plume. The cross-sectional area represented extends from the MLSB to about 800 m to the East of the basin on the Mildred Lake site. As shown in Figure 1.1, the naphthenic acids plume front has traveled approximately 500 m. The groundwater velocity is estimated by Oiffer (2005) to be approximately 19 m y^{-1}. Comparing the

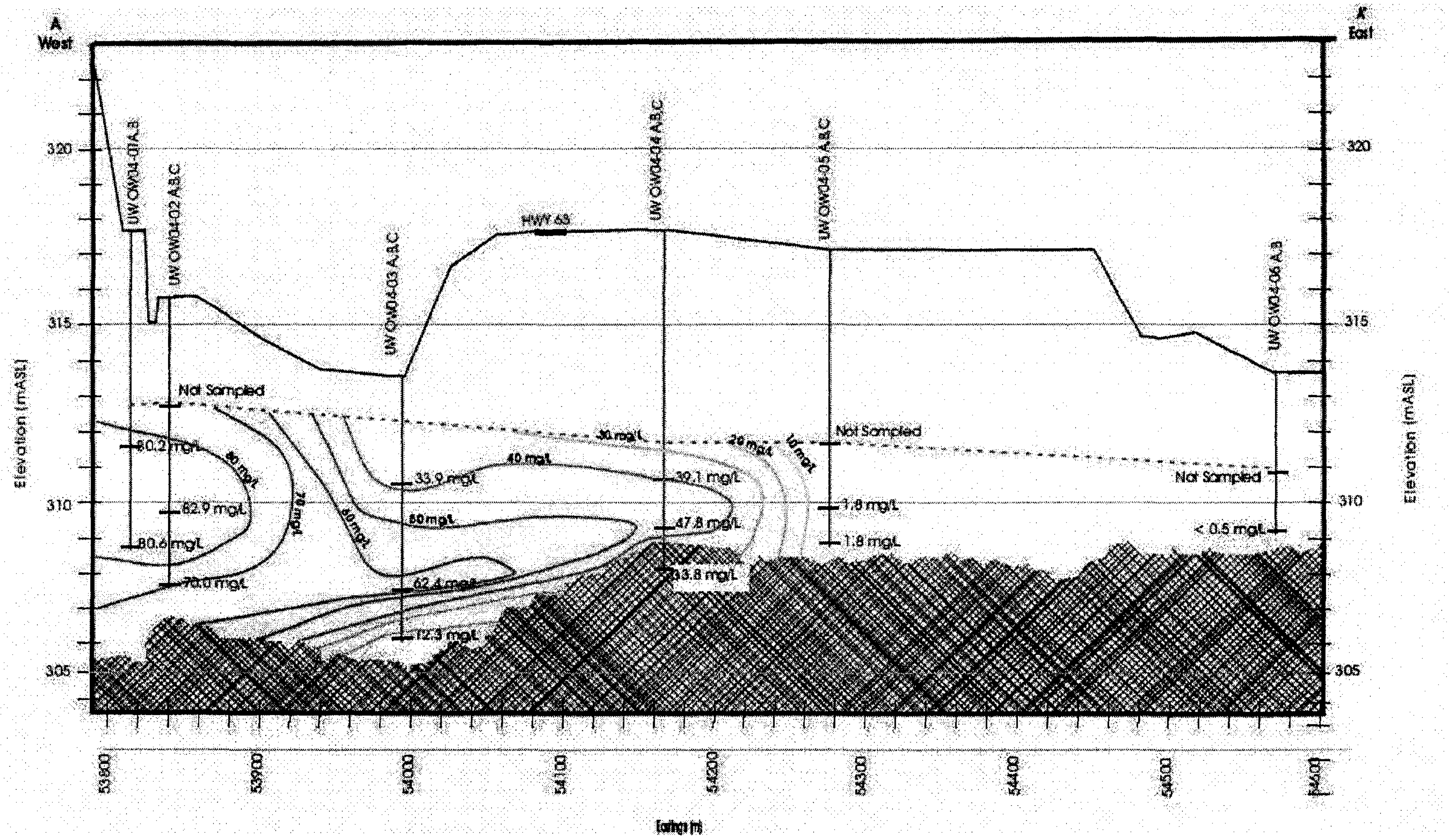

Figure 1.1: Naphthenic acids plume (contour lines at intervals of 10 mg L^{-1}). The left-hand side of the graph begins at the dyke of the MLSB. The dotted line in the subsurface represents the water table and the hatched marks on bottom represents aquitard material. Other significant land marks include Highway 63 at about 300 m from MLSB. (Oiffer 2004)

groundwater velocity to the distance traveled by the naphthenic acids plume suggests that very little retardation is occurring. Any retardation that might be occurring may be due to sorption or biodegradation of the naphthenic acids. These data suggest that there is high mobility of the naphthenic acids in groundwater.

Biodegradation of naphthenic acids has been thoroughly studied and a review conducted by Clemente and Fedorak (2005) highlights the important findings. Since that review was published, data provided by Scott et al. (2005) indicate that indigenous bacteria are able to degrade commercially available naphthenic acids much more readily than they can degrade naphthenic acids found in the process-affected tailings water.

The biodegradation studies conducted to date therefore suggest that naphthenic acids present in oil-sands process-affected water are resistant to biodegradation by indigenous bacteria, indicating that sorption may be the main potential mechanism of attenuation of these acids in groundwater systems. Very few, if any, studies have investigated sorption of naphthenic acids to soils, especially to clay minerals. The focus of this research was to study the sorption of naphthenic acids to soil components, with an emphasis to the sorption of naphthenic acids to clay minerals.

1.1 The Oil Sands

There are three major oil sands deposits in Alberta, delineated in Figure 1.2, which are estimated to contain 1.75 to 2.5 trillion barrels of oil (Chastko 2004). The Canadian

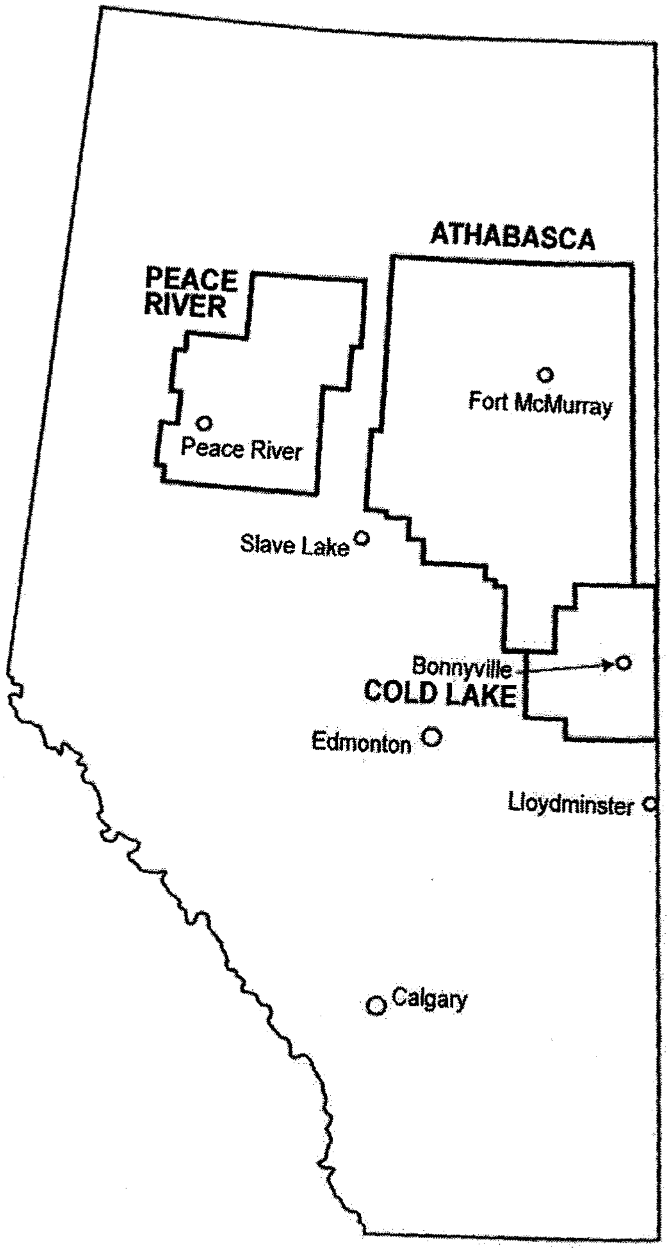

Figure 1.2: The Alberta oil sands areas. Adapted from Chastko (2004)

Centre for Energy (CCE) cited 174.5 billion barrels of oil in reserve which is considered to be recoverable with current technologies (CCE 2005). To put this into perspective, this amount could supply Canada alone for 475 years or all of North America for 47 years at current consumption rates (Chastko 2004).

The oil sands are composed of sand, bitumen, clay and water. The bitumen has the consistency of molasses and has the appearance of a black asphalt-like material. The oil sands ore is typically mined from open-pits and the bitumen is typically extracted from oil sands using the Clark hot water extraction process. The extracted bitumen requires upgrading to produce a synthetic crude to facilitate pipeline transportation to conventional refineries (Ashcroft 2000).

1.1.1 Clark Hot-Water Extraction Process

The Clark hot-water extraction process was developed in 1920 and is currently used to extract bitumen from open-pit mined oil sands. The original concept was developed by Sydney Ells and was modified by Dr. Karl Clark (Clark and Pasternack 1932). This process has been widely used in conjunction with conventional oil sands open-pit mining. Figure 1.3 shows a typical commercial application of the extraction process.

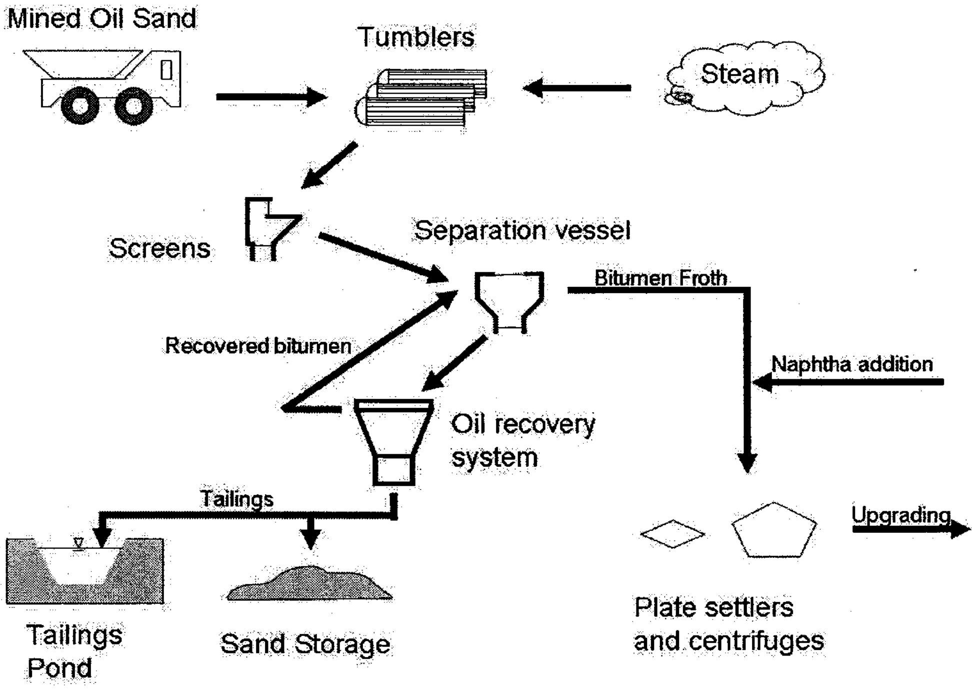

Figure 1.3: Generic diagram of the Clark extraction process used in industry. Adapted from Ashcroft (2000)

Mined oil sands are typically mixed in a tumbler with steam, warm water and sodium hydroxide as a conditioning agent. Approximately 0.7 to 1.0 m^3 of water is required per tonne of ore processed (MacKinnon et al. 2005) and at Syncrude more than 95% of this water is currently recycled from the settling basins, with the balance coming from the Athabasca River (MacKinnon et al. 2005). The resulting oil sands-water slurry is passed on to vibrating screens to eliminate any large objects such as rocks and clay agglomerates (Figure 1.3). The slurry is then fed to the separation vessels where it separates into layers. The top froth layer consists of bitumen. The layers below the froth layer consist of process-affected water, sand, clay and unrecovered bitumen. The layers below the bitumen layer are sent to an oil recovery system in an attempt to recover any remaining bitumen. Recovered bitumen is delivered back to the separation vessels and the balance is sent to tailings ponds (Figure 1.3). The combined froth from the separation vessel and the oil recovery system is treated with naphtha and sent to a combination of centrifuges with or without plate settlers to remove water and solids which are disposed of as tailings. The treated froth is then sent to upgrading (Ashcroft 2000).

Oil sands slurries in warm water are hydrotransported at Syncrude's Aurora site (Agecoutay 2003). As the slurry travels the 3 to 5 km, it is conditioned for extraction at Aurora. After the bitumen is separated, it travels 35 km to Mildred Lake site for froth treatment and upgrading (Agecoutay 2003).

The tailings from the separation vessel and froth treatment areas are typically deposited in large settling basins or tailings ponds. Examples of such settling basins are the MLSB or West-In Pit (WIP) found on the Syncrude site as shown in the aerial photograph presented as Figure 1.4. The tailings are composed of sand, water, silt, clay, dissolved inorganic and organic compounds (including naphthenic acids), and unrecovered bitumen. The sand, silt and clays will settle in these ponds releasing a layer of process-affected water on the upper most portions of the basins. Companies such as Syncrude Canada Ltd. have a zero discharge policy, so the settling basins have a net fluid and solids intake due to the current inability to discharge its process-affected waters off site. Earlier studies showed that the settling basins grew at a rate of 0.25 m^3 per tonne of oil sands processed (MacKinnon 1989), but currently the rate < 0.05 m^3 per tonne of ore processed (MacKinnon 2005).

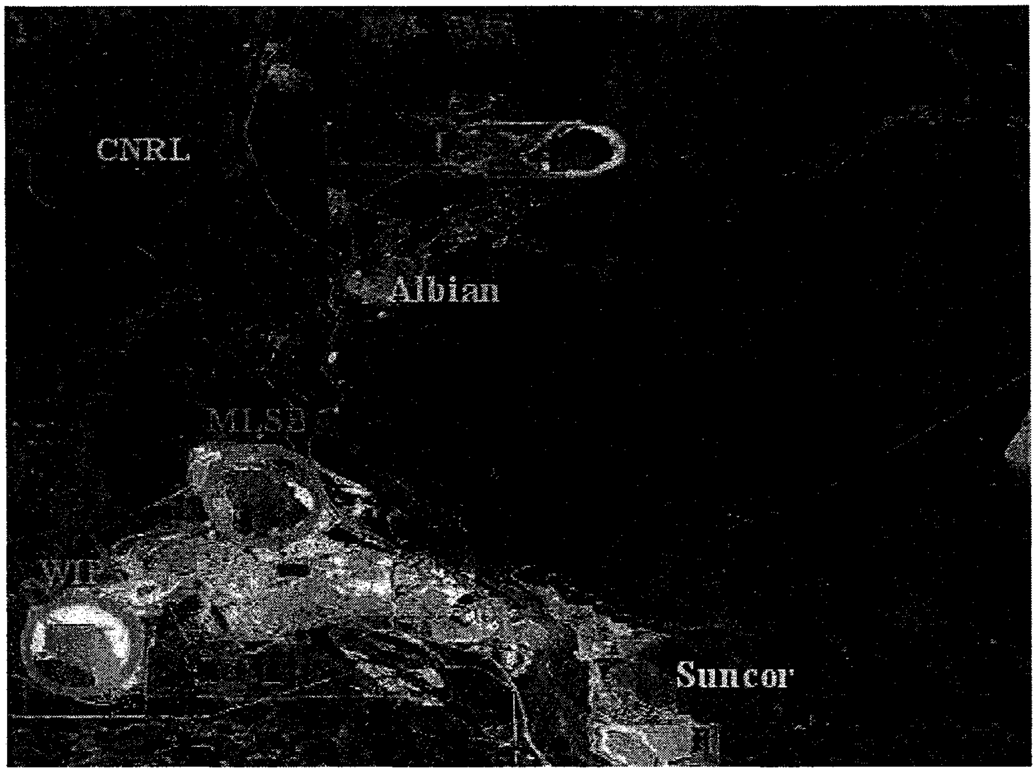

Figure 1.4: Major oil sands operators in the Athabasca region

1.2 Naphthenic Acids

A common problem with process-affected waters is its toxicity. It has been found that the toxicity of the oil sands tailings water is attributed to a specific portion of the dissolved organics termed naphthenic acids (Schramm et al. 2000). Naphthenic acids have been found to be toxic to aquatic life, some terrestrial animals and plant life (Clemente and Fedorak 2005).

The term naphthenic acids is used to collectively describe the naturally occurring carboxylic acid containing compounds found in conventional crude oils and oil sands bitumen. Naphthenic acids are a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids with the general formula, $C_nH_{2n+Z}O_2$, where n and Z represent the carbon number and homologous series, respectively. Examples of naphthenic acid structures can be seen in Figure 1.5. The Z variable is an even negative integer between 0 and –12 that indicates the loss of covalently bonded hydrogen due to the presence of ring structures. For example, each multiple of -2 indicates the presence of another 5- or 6-membered ring structure. Additionally, there are minor components of aromatic, olefinic, hydroxy and dibasic acids (Brient et al. 1995; Gabryelski and Froese 2003; Hsu et al. 2000).

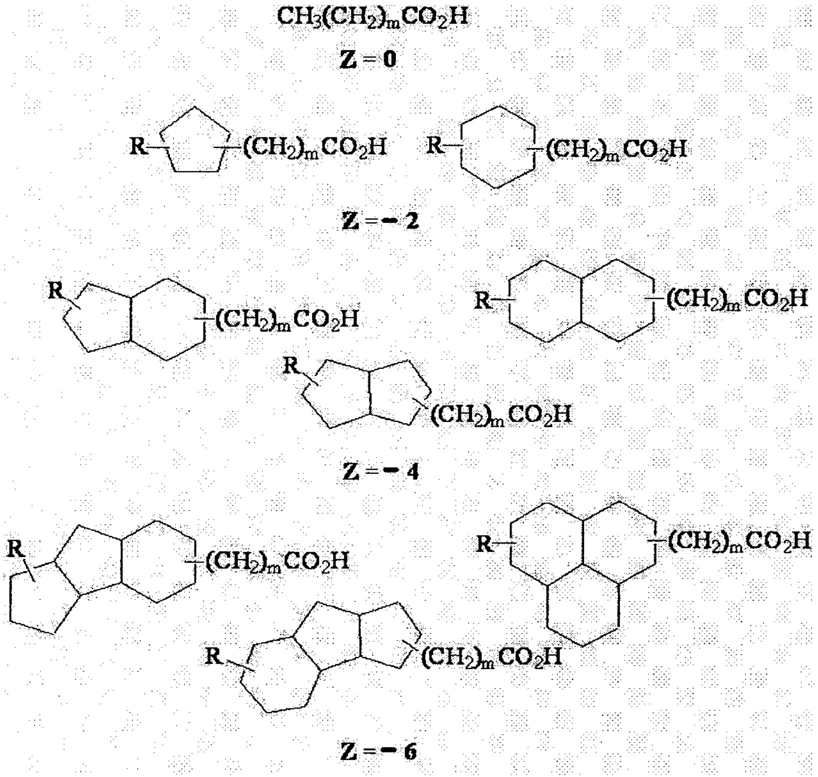

Figure 1.5: Typical structures of naphthenic acids in the Z = 0 to -6 families. Alkyl group substitutions on the ring structures are represented by R. The number of chained carbons attached to the carboxylic acid is represented by m, where m ≥ 0.

Naphthenic acids are found in petroleum because either a deposit is immature and has not undergone sufficient catagenesis or a mature petroleum has been biodegraded by bacteria (Tissot and Welte 1978). Carboxylic acids have been found in deposits of naturally biodegraded oil (Meredith et al. 2000; Nascimento et al. 1999) and in crude oil that was biodegraded in laboratory experiments (Roques et al. 1994; Watson et al. 2002). Naphthenic acids in the Athabasca oil sands in Canada were produced by biodegradation of mature petroleum (Tissot and Welte 1978). The alkaline, aqueous extraction methods used to recover bitumen from the oil sands also extracts naphthenic acids (as naphthenates) into the aqueous phase, and this accounts for the elevated concentrations of these compounds in the process-affected waters.

Naphthenic acids have some commercial uses that include use as wood preservatives (Barnes et al. 2005); plasticizers and lubricants (Mustafaev and Shikhalizade 1980); and as a solvent for the extraction of rare-earth metals (Dupreez and Preston 1992). In many commercial applications, the metal salts of naphthenic acids are used (Brient et al. 1995; CONRAD 1998). Commercial preparations of naphthenic acids originate from caustic washing of refinery distillates of kerosene and diesel fractions between 200 and 370°C (Brient et al. 1995). There are no processes being used at the oil sands plants to recover naphthenic acids for commercial use.

Commercial naphthenic acids are viscous liquids that range from a pale yellow to dark amber color. These preparations have a characteristic odor which is due to the phenolic and sulfur impurities. Naphthenic acids are completely soluble in organic solvents and oils but there solubility in aqueous solutions depends on pH. Naphthenic acids behave like typical carboxylic acids and have acid dissociation constants (Ka) that range between about 10^{-5} and 10^{-6} (Brient et al. 1995; CONRAD 1998).

1.2.1 Analytical Challenges

Because of their complexity, characterization and quantification of naphthenic acids pose a real analytical challenge. To illustrate the complexity, Clemente and Fedorak (2005) calculated that there are 37 isomers with the formula $C_{10}H_{18}O_2$, assuming the compounds contained a six-member ring. Currently, there is no method that can identify or quantify any of the individual acids in a naphthenic acids preparation. Typically, samples are analyzed as groups or sub-groups and appear as unresolved humps when chromatographic methods are used. A recent review was completed by Clemente and Fedorak (2005) which, in part, discusses the challenges of quantifying these acids. Gas chromatography coupled with a mass spectrometer (GC-MS) and high performance liquid chromatography (HPLC) are two commonly used methods to qualify and quantify naphthenic acids. Fourier transform infrared spectroscopy (FTIR) is the most common method used by industry to quantify naphthenic acids (CONRAD 1998) and is discussed in detail in Clemente and Fedorak (2005), Yen et al. (2004) and Jivraj et al. (1995).

A GC-MS method (St John et al. 1998) has been used to characterize the tert-butyldimethylsilyl derivatives of naphthenic acids. The derivatized naphthenic acids elute from the GC column as an unresolved hump as shown in Figure 1.6a. This hump is analyzed for ions at a 1% minimum occurrence over the range of the retention time of 10 to 40 min to produce an average ion abundance spectrum illustrated in Figure 1.6b (Holowenko et al. 2002). Data in this format is difficult to analyze, so a three-dimensional plot was developed with filters to remove ions that do not fit the naphthenic

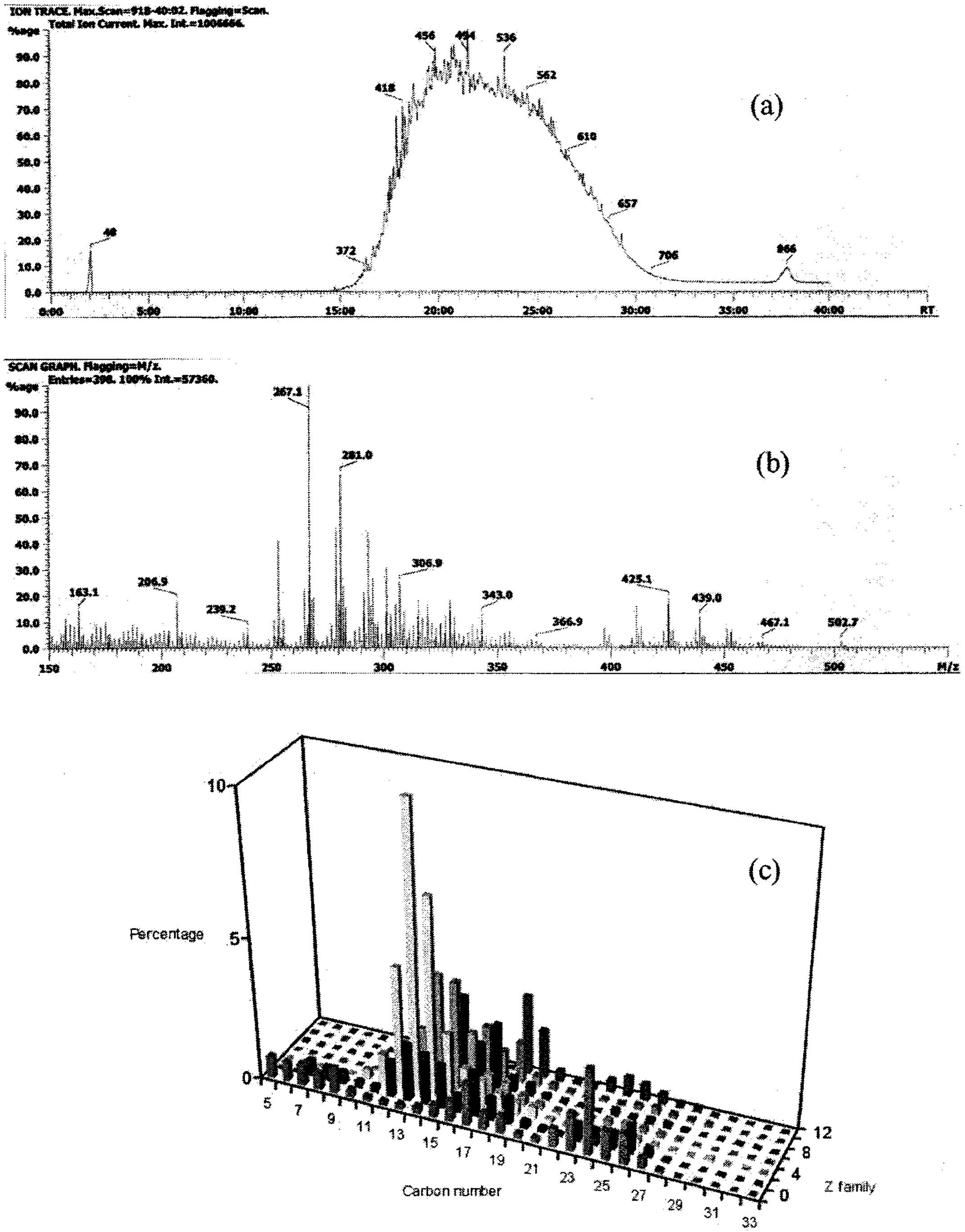

Figure 1.6: GC-MS analysis of an environmental naphthenic acids sample. The total ion current is represented in (a) which shows the start GC elution of the naphthenic acids at about 15 min. The total ion scan is averaged from 15 to 40 min with 1% minimum occurrence is shown as (b). A 3-D plot of the averaged ion scan, (c), shows the relative distribution of the naphthenic acids in regards to carbon number and Z family.

acid general formula of $C_nH_{2n+Z}O_2$ (Holowenko et al. 2002). Figure 1.6c shows an example of a three-dimensional plot which separates the ions into their homologous series (Z) and carbon number (n). Of course, each column in the three-dimensional plot represents a number of different structural isomers. Limitations of this GC-MS method are discussed in detail in Clemente and Fedorak (2004).

A variety of other MS methods have been used to characterize naphthenic acids, and these have been reviewed by Clemente and Fedroak (2005). These methods analyze underivatized naphthenic acids and include fluoride ion chemical ionization (Dzidic et al. 1988), fast atom bombardment (Fan 1991), atmospheric pressure ionization (Hsu et al. 2000), electrospray ionization (Hsu et al. 2000; Lo et al. 2003) and electrospray ionization high-field asymmetric waveform ion mobility spectrometry coupled with MS (Gabryelski and Froese 2003).

Quantitative methods for naphthenic acids have been reviewed by Clemente and Fedorak (2005). These include GC analysis of methyl esters of naphthenic acids that elute as an unresolved hump (Jones et al. 2001) and negative ion electrospray ionization-MS (Headley et al. 2002; Lo et al. 2003). The oil sands industry standard method for measuring naphthenic acids concentration is a FTIR method (Jivraj et al. 1995). For this method, aqueous samples are acidified and extracted with dichloromethane, and the organic extract is analyzed by FTIR at wavelengths of 1743 and 1706 cm^{-1}, which are characteristic of carboxylic acids.

A HPLC method has been developed to quantify naphthenic acids derivatized with 2-nitrophenylhydrazine in aqueous solutions (Yen et al. 2004). The HPLC chromatogram of a naphthenic acids sample, Figure 1.7, is integrated from 2.9 to 6.0 min and the area is compared to a standard curve prepared from a commercially available naphthenic acids. The integrated area has been shown to only include naphthenic acids that have carbon numbers greater than 9 (Yen et al. 2004). The excluded area is a minor component of the total naphthenic acids in most commercially available standards and those found in the oil sands. Yen et al. (2004) demonstrated good agreement between results obtained with the HPLC and FTIR method. However, the detection limit of the HPLC method is about 5 mg L^{-1} (Yen et al. 2004), whereas the FTIR method can detect much lower concentrations because the naphthenic acids from a large volume of water can be extracted and concentrated in dichloromethane prior to FTIR analysis.

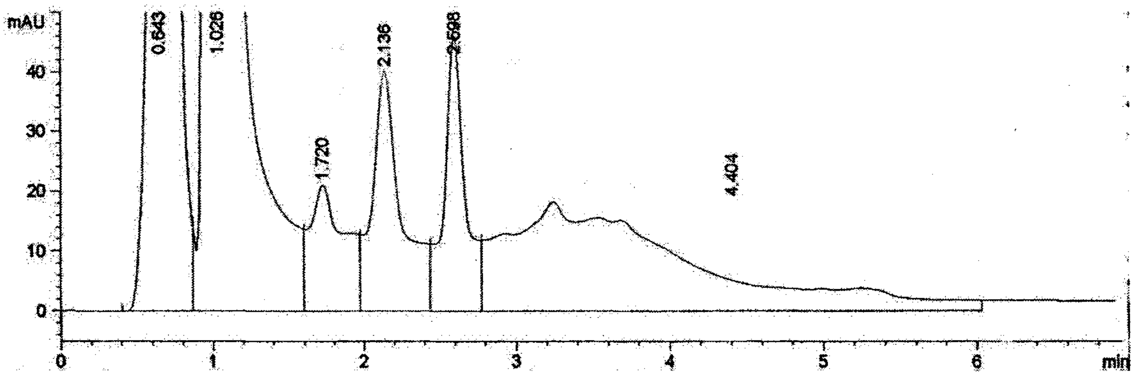

Figure 1.7: HPLC chromatogram obtained from the injection of a solution of 50 mg Merichem naphthenic acids L^{-1}. The naphthenic acids hump is integrated after the last impurity peak elutes which is typically from 2.9 to 6.0 min. In the case above, the last impurity peak eluted by 2.8 min.

Commercially available naphthenic acids are often used as surrogates in experimentation. The use of surrogates assumes that they have the same structure as those found in environmental samples. Figure 1.8 provides GC-MS three-dimensional plots of

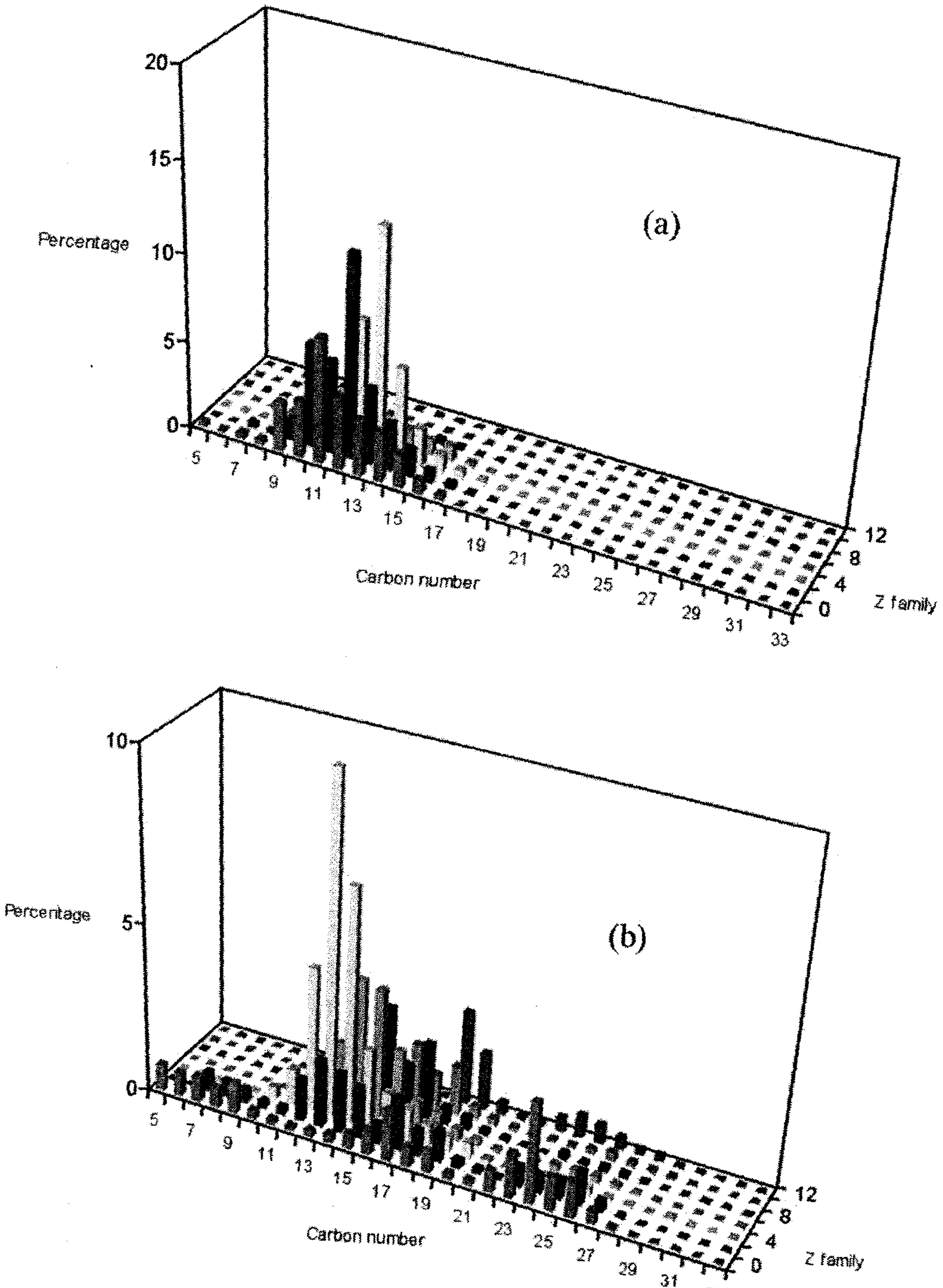

Figure 1.8: GC-MS three-dimensional plots of (a) commercially available Merichem naphthenic acids and (b) naphthenic acids extracted from an environmental water sample.

commercially available naphthenic acids and naphthenic acids extracted from an environmental sample. The plots show that there is a difference in the molecular weight distribution between the commercially available naphthenic acids and the environmental sample, especially in the larger molecular weights (C21 to C27). This different molecular weight distribution may lead to higher or lower apparent concentration in HPLC quantification because there is an overall assumption that the commercial standards and environmental samples are structurally similar (Yen et al. 2004). Recently Scott et al. (2005) demonstrated that the slopes of calibration curves prepared by HPLC analysis differed when different commercial naphthenic acids preparations were used. In summary, no perfect method for the quantification of naphthenic acids has been developed.

HPLC and FTIR methods provide a quantification of naphthenic acids, however they provide little information about the molecular weight distribution of the naphthenic acids. Thus, data from HPLC and from a method such as GC-MS (Holowenko et al. 2002) are important to help characterize the amounts and molecular weight distribution of naphthenic acids in a sample.

1.3 Soil Material

Soil material is composed of both organic and inorganic components. The inorganic portion of soil is created by the weathering of igneous, metamorphic and sedimentary rocks (Bohn et al. 1985). This weathered geologic material can then remain in place or be transported by a variety of processes, which include glacial activity, wind and water (Yong 2001).

The inorganic portion of the soil material is composed of gravels (>2 mm), sands (0.5-2 mm), silts (0.002-0.5 mm) and clays (<0.002 mm). The sand and silts are considered primary minerals that are derived from the weathering of igneous and metamorphic rocks. Some of this material can be found in the clay-sized fraction (<2 µm) but are considered a minor constituent. The clay-sized fraction is mostly secondary mineral that is derived from the weathering of sedimentary rock (Yong 2001). Common minerals found in the clay-sized fraction include carbonates, sulfur minerals, phyllosilicates and various oxides (Bohn et al. 1985).

The phyllosilicates or layer silicates (commonly termed clay minerals) are considered to be the most important portion of the clay-sized fraction. Not all clay minerals are found in the clay-sized fraction, so it is important to know the distinction between the two terms (Bohn et al. 1985).

The organic portion of the soil includes plant material, animal residues, soil organisms, and a complex mixture of compounds synthesized by the soil population. The chemically active components (plant material, animal residues, and synthesized compounds) of the organic portion of soil material are collectively termed soil organic matter (SOM). SOM has a large reservoir of carbon and has a large capacity to exchange cations. SOM combined with clay minerals are the most important components of a soil and tend to be responsible for many soil properties (for example cation exchange and sorption properties) (Bohn et al. 1985).

1.3.1 Clay Minerals

Clay minerals are typically a combination of a two-dimensional array of oxygen atoms in tetrahedral coordination around silicon atoms and a two-dimensional array of oxygen or hydroxyl anions in octahedral coordination around certain cations. Most common cations found in the octahedral layer are aluminum (Al^{3+}), magnesium (Mg^{2+}) and iron (Fe^{2+} and Fe^{3+}). The tetrahedral and octahedral layers are bound together through a common layer of oxygen. Sheets of these combined layers will interact with one another through either hydrogen bonding or through ion bridging. The space in which sheets interact with one another is called the basal plane (Bohn et al. 1985).

Some common clay minerals found in the oil sands area and their respective tetrahedral to octahedral ratio include the non-swelling clays, kaolinite (1:1) and illite (2:1), and the swelling clay, montmorillonite (2:1).

Kaolinite, illustrated in Figure 1.9, is a 1:1 mineral that has a unit cell structure represented by the unit formula $Al_2Si_2O_5(OH)_4$. Kaolinite is composed of the typical silicon-oxygen tetrahedral with aluminum in octahedral coordination with oxygen and hydroxyl groups. Sheets of kaolinite form through the basal plane via hydrogen bonding from the hydroxyl groups of the octahedral to the oxygen surface on the tetrahedral. The hydrogen bonding along the basal plane prevents swelling from occurring when kaolinite is immersed in water. The lack of swelling limits its surface area to its external surfaces (Bohn et al. 1985).

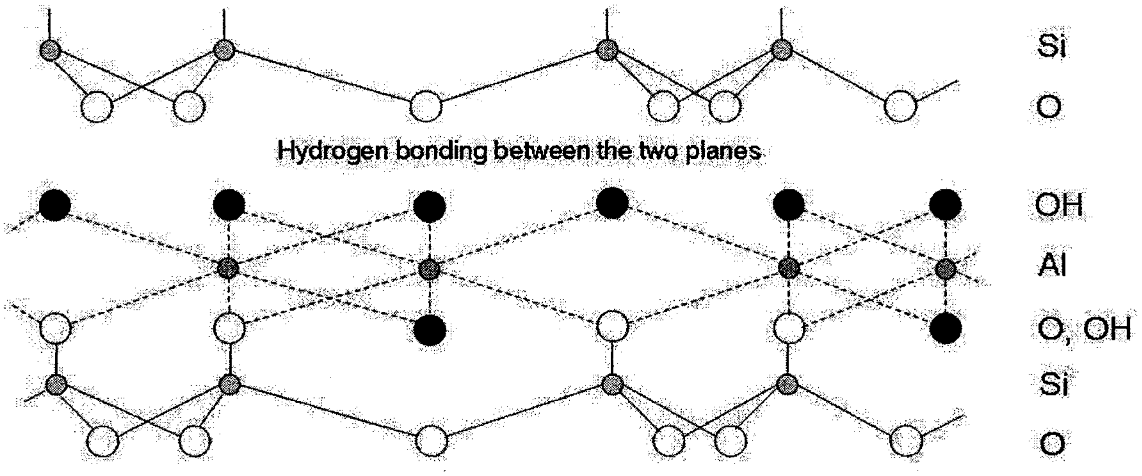

Figure 1.9: Structural composition of kaolinite.

Montmorillonite, illustrated in Figure 1.10, is a 2:1 mineral that has a unit cell structure by the formula $Na_x[(Al_{2-x}Mg_x)Si_4O_{10}(OH)_2]$. Montmorillonite is composed of an octahedral layer of aluminum, oxygen and hydroxyl groups sandwiched between two layers of the silicon-oxygen tetrahedrals. The x in the formula represents the number of Al^{3+} that are being substituted in the octahedral layer by Mg^{2+}. This substitution is termed isomorphic substitution and for each substitution, a net negative charge is produced that is then balanced typically by exchangeable cations in the interlayer region. Sheets will stack upon each other, using the common sodium atoms in the basal layer as a bridge. A negative charge of about 0.25 to 0.6 is formed on average per structural unit. The combination of the developed charge and the sodium cations are not able to produce an association that is strong enough to prevent water from entering the basal layer. The basal layers expand in the presence of water causing this clay mineral to swell. This swelling property increases the surface area to include internal surfaces (Bohn et al. 1985).

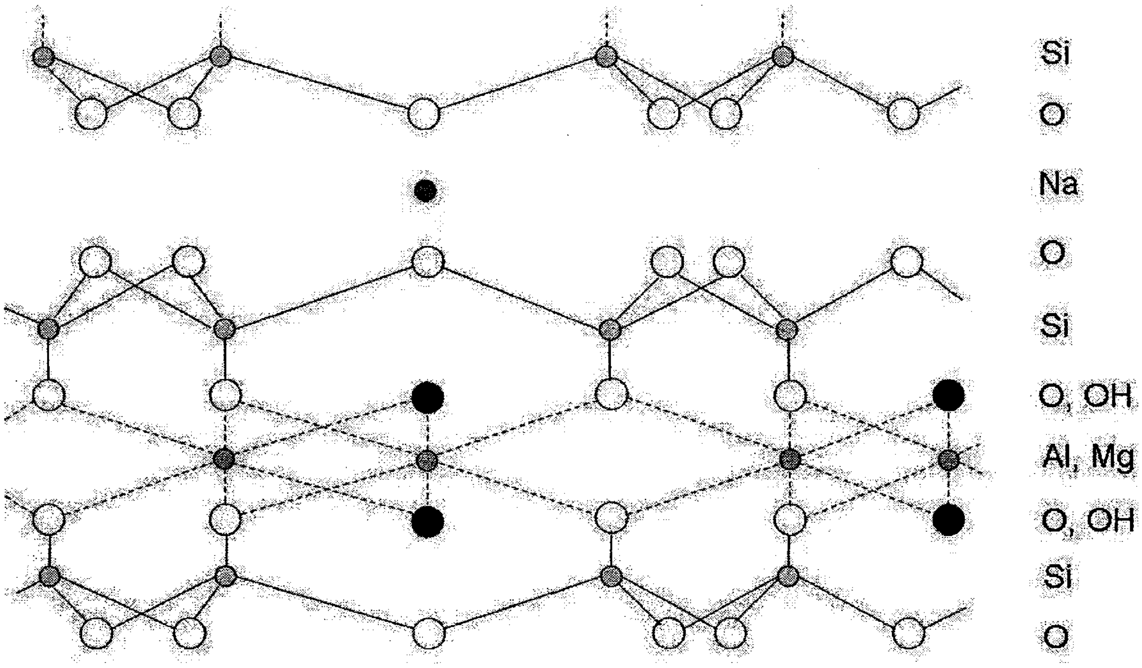

Figure 1.10: Structural composition of montmorillonite

Illite is part of the mica family, which is a group of 2:1 minerals, illustrated in Figure 1.11, generally represented by the formula $K_x[Al_2(Si_{4-x}Al_x)O_{10}(OH)_2]$. Micas are very similar to montmorillonite in that they are composed of an octahedral layer of aluminum, oxygen and hydroxyl groups sandwiched between two layers of silicon-oxygen tetrahedrals. The main difference being that the basic mica structure has aluminum substitution in the tetrahedral layer instead of in the octahedral layer. Illite is however distinct from the well-ordered micas depicted in Figure 1.10 in that there are less potassium cations in the interlayer. As with montmorillonite, a net negative charge is formed due to substitution. Substitution tends to occur more frequently in illite than in montmorillonite and this substitution produces a net negative charge of about 1.0 per structural unit in illite. Potassium cations are found in the basal layer and they balance this charge and to bridge the next layer of illite. This association is strong enough to keep water from entering into the basal plane, so swelling in this mineral does not occur. As with kaolinite, the surface area tends to be lower since the internal surface area is not available (Bohn et al. 1985).

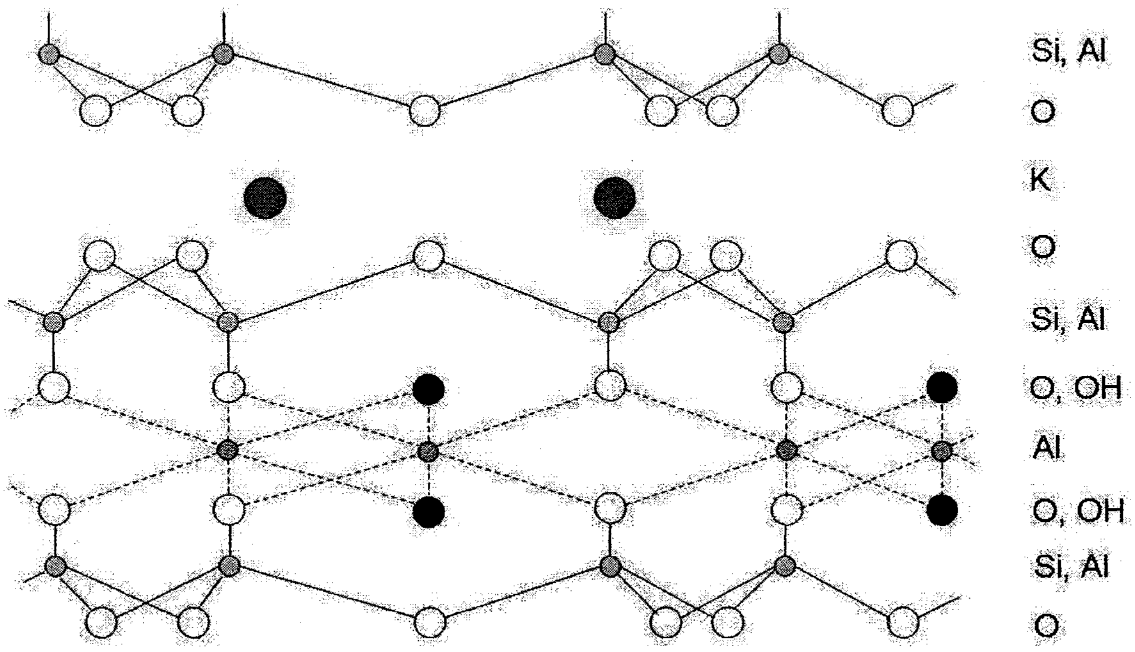

Figure 1.11: General structural composition of mica family of minerals

1.3.2 Cation Exchange Capacity and Surface Area

The cation exchange capacity (CEC) describes the capability of a soil material to exchange positively charged atoms. CEC is also a measure of the negative charge on a soil. For example, the higher the CEC of a soil, the higher the negative charge. The cations that are typically involved in cation exchange are calcium (Ca^{2+}), Mg^{2+}, potassium (K^+), sodium (Na^+) and Al^{3+} (Bohn et al. 1985).

There are two sources that collectively form the CEC in a material. The first source comes from permanent charge present in the soil. Permanent charge is mostly derived from those clay minerals that develop charge through isomorphic substitution, such as montmorillonite and illite, and therefore is not pH dependent (Bohn et al. 1985).

The second source of charge comes from variable charges that are developed as a function of pH. Some clays (such as kaolinite) and SOM develop charges that are pH dependent. These charges are developed through the protonation or deprotonation of carboxylic acid and hydroxyl functional groups in SOM and of the clay materials that contain surface hydroxyl groups. At very low pH, net positive charges are developed and conversely at high pH, net negative charge is developed (Bohn et al. 1985).

Typical CEC values for various soil materials are presented in Table 1.1. The CEC of the clays range from low values for kaolinite of 10 mmol of charge kg^{-1} to high values for montmorillonite of 1200 mmol of charge kg^{-1}. The CEC of SOM ranges from about 1500 to 3000 x 10^3 mmol of charge kg^{-1} (Bohn et al. 1985).

Included in Table 1.1 are the surface area values which correlate well with the CEC values. For example, surface area for kaolinite ranges from 10 to 20 x10^3 m^2 kg^{-1} whereas montmorillonite ranges from 600 to 800 x10^3 m^2 kg^{-1} (Bohn et al. 1985).

Table 1.1: Typical surface area and CEC values compiled from Bohn et al. (1985)

Soil Mineral	Surface Area ($\times 10^3$ m^2 kg^{-1})	CEC (mmol of charge kg^{-1})
Kaolinite	10-20	10-100
Montmorillonite	600-800	800-1200
Micas (Illite)	70-120	200-400
SOM	900	1500-3000

A common method of determining surface area is the use of methylene blue (Bujdák et al. 2003). Methylene blue, shown in Figure 1.12, is a cationic organic dye that associates with the negative charge on the clay mineral surface. The positive charge of the methylene blue associates with the charge on the clay surface and interacts with the mineral surface so that the hydrophobic tail points away from the mineral. The amount of methylene blue remaining in solution is measured to determine the amount of methylene blue coordinated with the clay mineral.

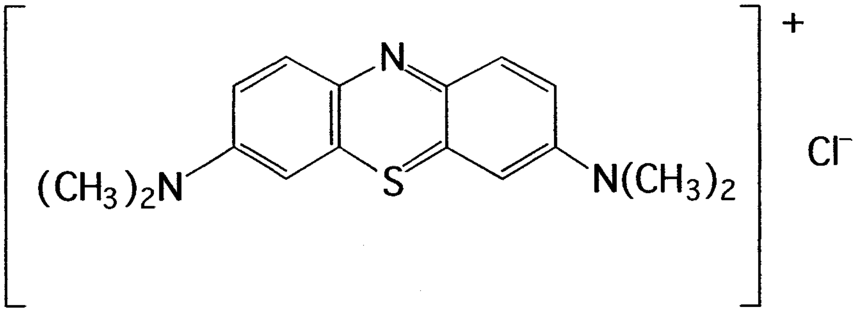

Figure 1.12: Structure of methylene blue.

1.3.3 Sorption Properties

Soil, through its mineral structure and organic content, can sorb or interact with organic and inorganic compounds. The extent of this interaction is often measured using sorption isotherms. Several isotherm models exist and these include the linear (Figure 1.13), Freundlich (Figure 1.14) and Langmuir (Figure 1.15) isotherm models. For the concentrations of contaminants that are normally found in groundwater systems (i.e. for contaminants at low concentrations), the linear isotherm provides an adequate representation of the sorption behavior (Bohn et al. 1985). The Freundlich isotherm is used most frequently to describe sorption over a variety of concentrations in cases where continuous sorption is indicated, such as the sorption of organic compounds to SOM containing soils (Yong 2001). The Langmuir isotherm is used in cases where a fixed number of sorption sites is predicted, such as the sorption of cations to clay mineral surfaces (Dragun 1998). The concentrations of naphthenic acids found in the environment are relatively small, so the linear isotherm model will be used to predict the sorption characteristics of naphthenic acids to the materials used in experimentation.

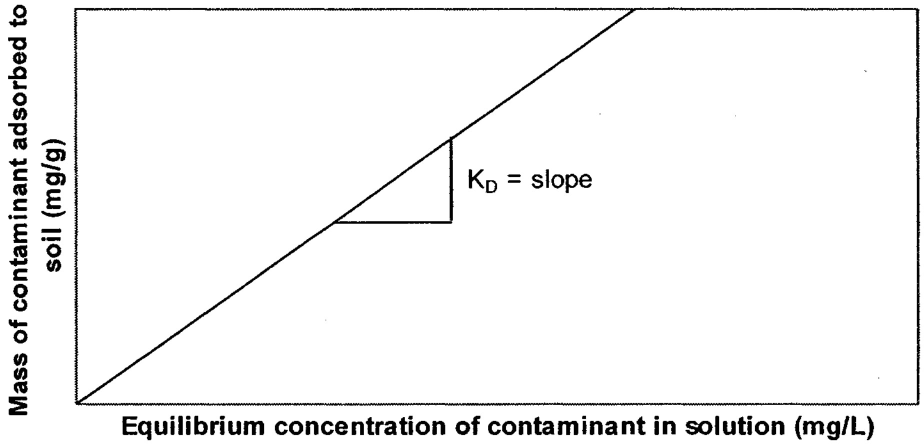

Figure 1.13: An ideal linear isotherm. The ideal linear isotherm has a x and y intercept of zero with slope equivalent to the partition coefficient (K_D). The y-axis represents the mass of the contaminant that has adsorbed to the soil mineral surfaces. The x-axis represents the equilibrium concentration in solution.

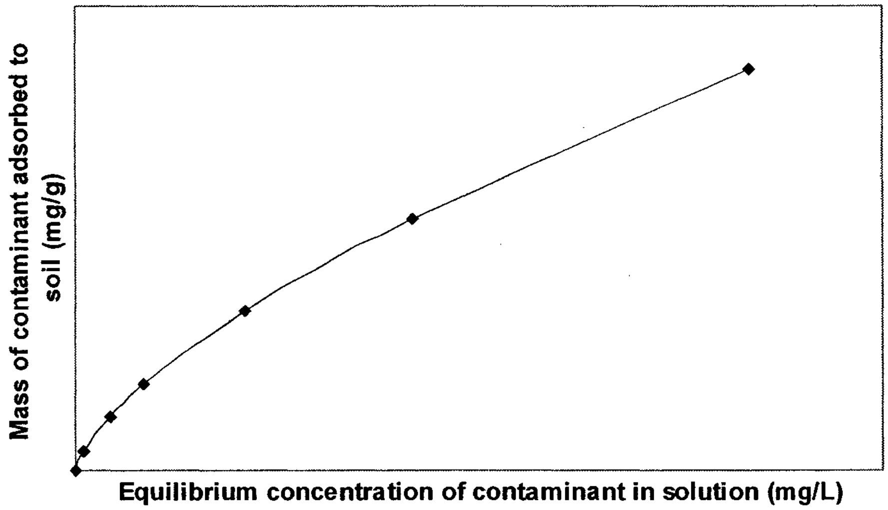

Figure 1.14: Freundlich isotherm model.

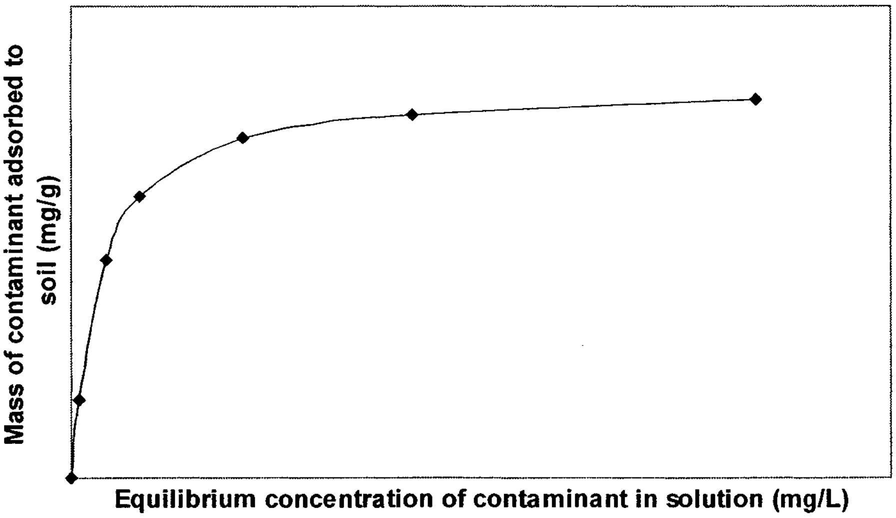

Figure 1.15: Langmuir isotherm model.

The linear isotherm model (Figure 1.13), which is also known as the constant partitioning isotherm model, is a linear plot of the concentration of the contaminant sorbed into the solid soil phase (mg contaminant g^{-1} soil) as a function of the equilibrium concentration of the contaminant found in solution (mg L^{-1}). The slope of this plot is known as the partition coefficient, or K_D (L g^{-1}). The K_D value is an indicator of the relative affinity of the contaminant for the soil phase versus the solution phase. For example, the higher the value of the K_D, the more affinity the contaminant will have for the soil phase (Bohn et al. 1985). K_D values can range as low as 0.01 mL g^{-1} for the sorption of phenol onto kaolinite (Delle Site 2001) or 0.9 mL g^{-1} for the sorption of naphthalene to kaolinite (Lee and Kim 2002), to values as high as 150,000 mL g^{-1} for the sorption of chromium (III) to soils and clays (Dragun 1998).

The K_D value is often used to estimate the rate of travel of a contaminant plume (V_c) relative to the groundwater velocity (V). To determine V_c, V is divided by the retardation factor (R_D). R_D is determined by the following equation: $R_D = 1 + [K_D (b/P_T)]$ where b is the soil bulk density (g cm^{-3}) and P_T is the soil porosity (Dragun 1998).

If the linear isotherm is representing sorption of a contaminant primarily to the SOM, it is often useful to correct the partition coefficient, K_D, to reflect its adsorption to the organic carbon content in the SOM. The corrected value (K_{OC}) is determined by dividing the K_D by the fraction of organic carbon (f_{OC}). Normalizing the K_D value for the organic carbon content allows the comparison of sorption data for different soils, provided the f_{OC} is known (Bohn et al. 1985).

It is possible to estimate the K_{OC} for a given contaminant by determining the octanol-water partition coefficient, K_{OW}. It has been found that octanol seems to replicate the physical-chemical interactions that occur between a contaminant and the organic carbon content of soil. A common empirical relationship for determining the K_{OC} of a polyaromatic hydrocarbons from a K_{OW}, is by the Karickhoff equation: Log K_{OC} = Log K_{OW} – 0.2 (Yong 2001). Other empirical relationships have been determined for a variety of compounds, and many of them are listed in Dragun (1998) and Delle Site (2001).

There have been some studies on the K_{OW} values of individual carboxylic acid compounds such as those listed in Table 1.2. The table lists the log K_{OW} values compiled from Pfannkoch (2003) and shows an increasing trend in preference to octanol as the chain length increases. Table 1.2 clearly shows the distinction between the behavior of the carboxylic acid in its undissociated form and its anionic form. There is almost a four order of magnitude difference between the K_{OW} values of the two forms for a given organic acid.

Table 1.2: List of carboxylic acids and their associated K_{OW} values. (Compiled from Pfannkoch (2003))

Organic Acid	Log K_{OW}	
	Neutral Acid	Sodium Carboxylate
Hexanoic acid	2.05	-1.76
Octanoic acid	3.03	-0.78
Decanoic acid	4.0	0.2
Tetradecanoic acid	5.98	2.17
Octadecanoic acid	7.94	4.13

CONRAD (1998) summarized the log K_{OW} values at different pH values for a naphthenic acids standard liquid from Baker Chemical. These were 4.3 at pH 1.07, 2.38 at pH 7.1, and 2.08 at pH 10. As with the pure organic acids (Table 1.2), the log K_{OW} of naphthenic acids decreases as pH increases.

1.4 Sorption of Naphthenic Acids to Soil Minerals

Very few studies have examined the sorption of naphthenic acids to soil material. Gervais (2004) and Peng et al. (2002) studied the sorption of model naphthenic acids to soils while Zou et al. (1997) studied the sorption of naphthenic acids to clays in a toluene solution.

Based on the studies mentioned above, it appears that the carboxylic acid group of the naphthenic acids is responsible for sorption of these compounds to soil. Any sorption that occurs is dependent upon whether or not the carboxylic acid group is neutral or anionic. The sorption of other carboxylic acids to soil material has been discussed in the literature. Pesticides (Dubus et al. 2001; Tunega et al. 2004), fatty acids (Khalil and Abdelhakim 2002; Meyers and Quinn 1973), and carboxylic acids that fit the $C_nH_{2n+Z}O_2$ general formula (Peng et al. 2002; Zou et al. 1997) have all shown dependency on the state of the carboxylic acid functional group.

1.4.1 Bonding Mechanisms

Carboxylic acids rarely exhibit any significant sorption with clays and SOM (Dubus et al. 2001). If carboxylic acids do exhibit sorption, this sorption is dependent on the protonation of the carboxylic acid functional group. The protonation of the carboxylic acid group is dependent on the solution pH and the pKa of the organic acid. At pH values greater than the pKa of the organic acid, the carboxylic acid functional group deprotonates causing the formation of an anionic carboxylic acid, known as a carboxylate. A resultant K_D for an organic acid at a given pH then represents a weighted distribution of the neutral and anionic form (Dubus et al. 2001).

In acidic conditions, carboxylic acids are protonated producing a neutral compound which is capable of hydrogen bonding, electrostatic-dipole interactions, and Van der Waals forces. The hydrogen bond can form by either interacting with oxygen that is present on clay mineral and SOM surfaces or by hydrogen bonding with water that is coordinated around interlayer cations and clay mineral surfaces (Dubus et al. 2001). The hydrogen bond is considered the most important of these interactions (Dubus et al. 2001; Khalil and Abdelhakim 2002; Zou et al. 1997).

The electrostatic-dipole is considered to be the next most important source of bonding in acidic conditions. A dipole is created due to the nonsymmetrical sharing of electrons in the double bond of the carboxylic acid group. This dipole produces a partial positive charge on the carbon which can interact with negative charges present in the SOM or on the clay mineral surface. (Dubus et al. 2001)

Van der Waals forces do not play a significant role in the sorption of carboxylic acids to clay minerals. The lack of sorption is especially the case when in the presence of a polar solvent such as water. Water will compete with the organic acid for the mineral surface. However, Van der Waals forces do play an important role in sorption of organic acids to organic acids already present on the clay mineral surface (Zou et al. 1997) or in the sorption of organic acids to SOM (Dubus et al. 2001).

In basic conditions, the carboxylic acid looses its hydrogen ion and forms a negative charge. This charge causes repulsion of the organic acid from the SOM and from the negatively charged clay mineral surfaces. However, there are a few limited sorption sites such as limited positive charges that may exist on clay mineral edges and SOM. In addition cationic bridging by divalent or higher charged cations may allow for negatively charged organic acids to interact with the negatively charged clay mineral surface (Dubus et al. 2001).

1.4.2 Sorption Studies

There is limited information on the sorption of naphthenic acids. Peng et al. (2002) studied the sorption of two model single-ring naphthenic acids, 4-methylcyclohexaneacetic acid (4MCHA) and 4-methylcyclohexanecarboxylic acid (4MCHC) to soils under a variety of conditions. A summary of experiments conducted by Peng et al. (2002) is listed in Table 1.3. Aqueous solutions of 4MCHA and 4MCHC were analyzed under the same conditions (pH 6.0, 23°C, 10 mM $CaCl_2$) and gave a linear isotherm with K_D values of 0.18 ± 0.03 and 0.11 ± 0.02 mL g^{-1} respectively.

Table 1.3: Summary of experiments conducted by Peng et al. (2002).

Compound	Temperature (°C)	pH	$CaCl_2$ Content (mmol)	Organic Carbon Content (f_{OC})	K_D ($mL\ g^{-1}$)
4-methylcyclohexaneacetic acid (4MCHA)	23	6	10	0.016	0.18 ± 0.03
	23	6	10	0.027	0.22 ± 0.03
	23	6	30	0.016	0.22 ± 0.03
	4	6	10	0.016	0.21 ± 0.03
	23	2.9	10	0.016	0.20
	23	6.8	10	0.016	0.18
	23	10	10	0.016	0.11
4-methylcyclohexanecarboxylic acid (4MCHC)	23	6	10	0.016	0.11 ± 0.02

Further studies were conducted with 4MCHA alone with various organic carbon content, temperature, pH and $CaCl_2$ concentration. Organic carbon contents were tested at 1.6% and 2.7% and gave K_D values of 0.18 ± 0.04 and 0.22 ± 0.03 mL g^{-1}, respectively. Temperature effects were tested at 4°C and 23°C and gave K_D values of 0.21 ± 0.03 and 0.18 ± 0.03 mL g^{-1}, respectively. An increase in sorption was detected with the increase in $CaCl_2$ concentration of 10 to 30 mM $CaCl_2$ to give K_D values of 0.18 ± 0.03 and 0.22 ± 0.03 mL g^{-1}. Finally, pH was tested at 2.9, 6.8 and 10.0 and provided K_D values 0.20, 0.18 and 0.11 mL g^{-1}, respectively (Peng et al. 2002). Peng et al. (2002) concluded that molecular structure, pH and $CaCl_2$ significantly influenced the sorption of model naphthenic acids to soils; whereas temperature and organic carbon content had negligible effects. The low K_D values observed by Peng et al. (2002) suggest high mobility of the naphthenic acids in aquatic environments.

Gervais (2004) studied the interaction of several model naphthenic acids with soil samples containing various organic carbon contents. A summary of select results are presented in Table 1.4, including K_D values for experiments conducted at conditions of ionic strength of 37 mM, f_{OC} of 0.004 and 0.015, and pH of 7 and 8.

Table 1.4: Summary of selected sorption experiments from Gervais (2004)

Chemical	Molecular Mass ($g\ mol^{-1}$)	f_{OC}	K_D Values ($mL\ g^{-1}$)	
			pH 7	pH 8
Octadecanoic acid	284	0.004	17.21	1.93
		0.015	64.55	7.35
Heptanoic acid	130	0.004	0.01	0.00
		0.015	0.04	0.02
1-Methyl-1-cyclohexanecarboxylic acid	142	0.004	0.02	0.00
		0.015	0.06	0.02
Cycloheptanecarboxylic acid	142	0.004	0.01	0.00
		0.015	0.04	0.02
4-Methylcyclohexaneacetic acid	156	0.004	0.02	0.00
		0.015	0.06	0.02
3-Methyl-octahydropentalene-1-carboxylic acid	168	0.004	0.02	0.00
		0.015	0.07	0.02
3-Methyl-1-adamantanecarboxylic acid	194	0.004	0.03	0.00
		0.015	0.13	0.02
4-Pentylbicyclo[2.2.2]octane-1-carboxylic acid	224	0.004	0.49	0.05
		0.015	1.82	0.19

Gervais (2004) showed that sorption is low for several model naphthenic acids. At a f_{OC} of 0.004, six of the eight tested compounds showed no sorption at pH 8 ($K_D = 0.00$, Table 1.4). The only two compounds to show significant sorption at all conditions were 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid and octadecanoic acid. Sorption of these compounds is most likely related to their higher molecular weight, which tends to cause these compounds to behave as hydrophobic compounds which interact with SOM. In all cases summarized in Table 1.4, the K_D values increased when the sorption study was done at pH 7, rather than 8; and when the f_{OC} increased from 0.004 to 0.015. The results from Gervais (2004) illustrate that sorption of model naphthenic acids is dependent on molecular weight, f_{OC} and pH.

Tunega et al. (2004) studied the sorption of 2,4-dichlorophenoxylacetic acid (2,4-D) onto montmorillonite and kaolinite. Although K_D values were not reported, Tunega et al. (2004) concluded that the pH affected the sorption of 2,4-D to the clay minerals and that sorption was related to the carboxylic acid functional group and to the pH of the solution. Tunega et al. (2004) showed that minimal sorption occurred when the anionic form of the carboxylic acid was predominant. For the case of 2,4-D, the pKa is relatively small at 2.8 and sorption became minimal when pH values were greater than 4.

Meyers and Quinn (1973) conducted an extensive study of the sorption of organic acids ranging from C14 to C18 to minerals found in the sea. They investigated the effects of salinity, pH, and clay mineral type on sorption. Table 1.5 summarizes some of the key results of this study. As shown in Table 1.5, it appears that the amount of organic acids adsorbed increases with fatty acid chain length. As the pH was changed from 6.5 to 8.5 (30 g NaCl kg^{-1} distilled water, 25°C, bentonite clay, C17), Meyers and Quinn (1973) found that the adsorption decreased approximately 6 to 9 % per increase in pH unit. Finally, they observed an increase in adsorption of nearly three times as salinity was increased from 0 to 35 g NaCl kg^{-1} distilled water.

Table 1.5: Sorption of various fatty acids onto select clay minerals at pH 8, 25 °C and 30 g NaCl kg^{-1} distilled water (Compiled from Meyers and Quinn (1973)).

Carbon Number	Percent Adsorbed onto Mineral Surface			
	Kaolinite	Bentonite	Illite	Montmorillonite
C14	4.2%	3.1%	6.5%	3.5%
C16	42%	41%	38%	14%
C17	74%	74%	40%	10%
C18	77%	91%	44%	20%

1.5 Objectives

From the literature reviewed, very little data exists on the sorption of naphthenic acids to soils and, in particular, to clay minerals. It appears that all of the studies of naphthenic acids to soils have used model compounds. Because naphthenic acids are important contributors to the toxicity of oil sands process-affected waters, it is important to understand their sorption and potential for migration in groundwater.

The goal of this research was to study the sorption of naphthenic acids to soil minerals. The objectives of this project were therefore to:

1) Determine the sorption of a commercially available naphthenic acids mixture at pH 6 and 8 to clay minerals such as montmorillonite, illite and kaolinite;
2) Determine the sorption of the naphthenic acids extracted from process-affected waters to clay minerals such as montmorillonite, illite, and kaolinite at pH 8;
3) Determine the sorption of extracted naphthenic acids to soil organic matter present in various soil samples; and
4) Examine the extent of sorption of naphthenic acids from extracted process-affected water to coke samples supplied by Syncrude and Suncor.

It is expected that the results of this study will provide an understanding of the sorption potential of naphthenic acids to various soil minerals. The partitioning values determined through this research may then be applied in groundwater modeling work by interested parties to estimate the movement of the naphthenic acids in groundwater systems.

Chapter 2 Methods and Materials

This chapter includes:

(i) Description of clays, soil and coke samples used;

(ii) Procedure outlining the salt interaction studies with naphthenic acids;

(iii) Procedural outline of the batch sorption experiments of the clay, soil and coke samples to the Merichem or WIP-extracted naphthenic acid;

(iv) Procedural outline for the desorption of naphthenic acids from MFT;

(v) and GC-MS and HPLC analytical methodology.

2.1 Clays

Montmorillonite (SAz-1, > 95 %, Appendix A), illite (IMt-1, 85 – 90 %, Appendix A) and kaolinite (KGa-1b, > 95 %, Appendix A) clays used in the experiments were purchased from the Source Clays Repository at Purdue University (West Lafayette, IN). In order to ensure a consistent starting material for all sorption experiments using clay, a pre-treatment procedure was conducted on all three clay minerals. The aim of this procedure was (i) to remove any carbonates that may be present and (ii) to saturate the clay surface charges with calcium or sodium cations. The clay pretreatment was a variation of a procedure outlined by Zhang et al. (1990) and consisted of the following steps:

(1) Approximately 100 g of purchased clay was combined with 500 mL of 0.001 M HCl in a 1-L Erlenmeyer flask. This mixture was placed on a stir plate, heated to 60°C and mixed overnight in a fume hood to remove any carbonates that

may be present. The illite was combined with 500 mL of 0.01 M HCl, instead of 0.001 M, due to the larger amount of carbonate present.

(2) On the following day, the suspension was removed from the stir plate and centrifuged in two 250-mL centrifuge bottles at 17,000 x g for 10 min. The supernatant was discarded and the clay pellet was re-suspended in deionized water and centrifuged again under the same conditions. This washing process was repeated three times. After the third wash, the pellet was re-suspended in 500 mL of deionized water in a 1-L Erlenmeyer flask. Either a 0.5 M calcium chloride or a 1.0 M sodium chloride solution was added depending on the cation selected to saturate the clay surfaces. This suspension was brought up to 60°C on the stir plate and allowed to react overnight.

(3) The following day, the suspension was centrifuged in two 250-mL centrifuge bottles at 17,000 x g for 10 min. As before, the supernatant was discarded and the pellet was washed with distilled water and centrifuged three times. The pellet was once again re-suspended in 500 mL of deionized water and left overnight on a stir plate at 60°C.

(4) On the final day of this procedure, the suspension was centrifuged in two 250-mL centrifuge bottles at 17,000 x g for 10 min. The supernatant was discarded and the pellet was re-suspended in deionized water and centrifuged at 17,000 x g for 10 min. This washing procedure was repeated until the addition of a dilute

solution of silver nitrate to the supernatant did not yield a precipitate of silver chloride. This lack of precipitate indicated a chloride concentration likely lower than 0.001 M. Achieving sufficiently low concentrations of chloride typically required four washings.

(5) Finally the pellet was broken up into two equal portions and placed in 250-mL 24/40 round bottomed flasks. The contents of each flask were frozen in a dry ice and ethanol bath. The flask with the newly frozen contents was attached to a Freezemobile 24 (Virtis) freeze dryer and was left for 48 h to remove any water from the clay. The contents of the flasks were then ground to a powder with a mortar and pestle. The end product was powdery clay which was used in batch sorption experiments.

Thirty grams of each treated and untreated clay were sent to the soils lab at the Department of Renewable Resources, University of Alberta for total organic carbon (TOC) and cation exchange capacity (CEC).

2.2 Ellerslie Soil Sample and Syncrude Site Core Samples

The Ellerslie soil sample was collected on the University of Alberta, Department of Renewable Resources property located south of Edmonton. The soil was collected from a pit on this site at a depth ranging from 10 to 40 cm below the surface.

The Syncrude site core samples were collected at the Syncrude site in Fort McMurray by staff from the University of Waterloo. Portions of these samples were delivered to the University of Alberta. The methods of core extraction and the locations of the core sampling are presented in detail in Oiffer (2004).

Prior to using any of the above core and soil samples, approximately 200 g of each sample were set out on aluminium pans to air-dry for 72 h. After 72 h, samples were ground with a mortar and pestle if necessary. All samples were then sieved through a 2.3-mm sieve. The sieved core samples were split into two 250-mL samples. One sample was sent to the soils lab at the Department of Renewable Resources (University of Alberta) for particle size analysis (PSA), CEC and TOC. The second sample was reserved for batch sorption experiments. PSA was done by a hydrometer method (Sheldric and Wang 1993), CEC was determined by the procedure of Hemdershot et al. (1993), and the TOC was measured using a Shimadzu model 5050A analyzer after inorganic carbon was removed from the soil samples by acidifying them to pH<2 and sparging with CO_2-free air (McGill et al. 1986). The Ellerslie soil sample was not sent for analysis because it was already well characterized by Luther et al. (1998).

2.3 Syncrude and Suncor Coke Sample Preparation

During bitumen upgrading, vast quantities of coke are generated (Scott and Fedorak 2004), and the storage and disposal of this coke is a major challenge. Syncrude has deposited large amounts of coke in MLSB, which retains naphthenic acids-containing process-affected water. Because the sorptive properties of coke have not been well studied, the sorption of naphthenic acids to coke was studied.

Samples of coke were obtained from both the Syncrude and Suncor operations in Fort McMurray. The Syncrude coke was a very fine, homogeneous material and therefore did not require sieving prior to use. The Suncor coke was clumped in large chunks and required sieving through a 2.3-mm sieve prior to use.

2.4 Naphthenic Acids

Two sources of naphthenic acids were used in experiments:

(i) Commercial naphthenic acids

(ii) West-In Pit extracted naphthenic acids

2.4.1 Commercial Naphthenic Acids

The commercial naphthenic acids used in experimentation were donated by Merichem (Houston, TX). Merichem naphthenic acids are amber in color and come as an oil. Stock solutions of Merichem naphthenic acids were prepared by dissolving 0.5 g of Merichem naphthenic acids in a 100-mL volumetric flask with 0.1 M NaOH.

2.4.2 West-In Pit Naphthenic Acids

The West-In Pit (WIP) extracted naphthenic acids were extracted from tailings pond water from the WIP tailings pond located at the Syncrude Canada Ltd. Mildred Lake site. WIP process-affected water was collected by staff at Syncrude in 20-L pails and delivered to the University of Alberta. Once at the University of Alberta, WIP water was stored as received in a 4°C walk-in fridge.

Extracting naphthenic acids from WIP water involved first placing 1 L of water in a 1-L beaker and adjusting the pH to 12.5 or 13 using 10 M NaOH. The contents of the beaker were then transferred to a 2-L separatory funnel and extracted with 50 mL of high resolution gas chromatography grade dicholoromethane (GC-DCM, VWR International). This extraction was conducted as a clean-up step to remove any residual hydrocarbons in the process-affected water while keeping the naphthenic acids in the aqueous phase. After 15 min of equilibration time, the GC-DCM phase (including any emulsion that formed) was discarded and the aqueous phase was transferred back to the 1-L beaker. The aqueous phase was adjusted to pH 2 to 2.5 and transferred to the 2-L separatory funnel and extracted with 50 mL of GC-DCM. The contents of the separatory funnel were shaken for 30 s and the phases were allowed to separate over 15 min. The GC-DCM phase was collected in a 150-mL screw cap bottle and evaporated under industrial grade N_2 (Praxair). The aqueous phase was extracted twice more with 50 mL portions of GC-DCM as described above and collected in the same 150-mL bottle.

The extraction procedure described above was conducted on 10 to 15 L of WIP process-affected water. The GC-DCM phase was collected in a 150-mL screw cap bottle. Once the contents of the bottle were free of GC-DCM, the naphthenic acids residue from the extract was dissolved in 100 mL of 0.1 M NaOH. The concentration of naphthenic acids present in the extract was determined by HPLC and the fingerprint was characterized by

GC-MS. The naphthenic acids extract was stored at 4°C in the 150-mL bottle sealed with Teflon tape until use in the sorption experiments.

2.5 Salt Interaction Experiments

Experiments were conducted using the Merichem naphthenic acids and various salts to determine if there was any precipitation of the naphthenic acids due to the presence of salts. In addition, these experiments would identify if there is any interaction with the HPLC derivatizing agents. Experiments with $CaCl_2$; $NaHCO_3$; NaCl; and a salt mixture of NaCl, $NaHCO_3$, $MgSO_4$ and $CaSO_4$ were conducted.

2.5.1 Salt Mixture

The salt mixture interaction experiment was conducted using the most prominent ions found in the WIP water. The stock salt concentration was prepared at twice the concentration of what was determined to be in the WIP process-affected waters by Syncrude laboratory at the Syncrude Research facility located at the Edmonton Research Park. The concentrations given in Table 2.1, were slightly modified for this experiment to maintain charge balance because the minor ions were omitted. The stock salt solution was prepared in a 1-L volumetric flask to contain 0.03 M $NaHCO_3$, 0.050 M NaCl, 0.001 M $MgSO_4$ and 0.004 M $CaSO_4$.

Table 2.1: Concentrations of major ions in WIP process-affected waters and in the salt mixture used for experiments.

Ion	WIP Concentration (mol L^{-1})	Concentration used in Experiments (mol L^{-1})
Na^+	0.0404	0.04
Cl^-	0.0255	0.025
SO_4^{2-}	0.0023	0.0025
HCO_3^-	0.0144	0.015
Ca^{2+}	0.0003	0.002
Mg^{2+}	0.00035	0.0005

The salt studies were conducted in 40-mL Econo EPA vials (Fisher Scientific) with Teflon-lined cap inserts. Final salt mixture concentrations of 0%, 10%, 20% and 100% were studied with 100 mg Merichem naphthenic acids L^{-1} at pH 8. Stock solutions were pH adjusted using 3.0 M and 0.05 M HCl; and 0.1 M NaOH. Each test condition was established in triplicate. Controls were prepared in absence of naphthenic acids. Contents of the vials were prepared analytically using various amounts of salt stock solution, stock 200 mg Merichem naphthenic acids L^{-1} and reverse osmosis water as make-up to achieve desired concentrations. All vials were placed on a tumbler, set at 20 rpm, in a temperature controlled room set at 20°C for 40 h.

After 40 h, the vials were removed from the tumbler and the contents sampled with a 3-mL Luer-Lok syringe with a 20 Gauge, 1.5-inch needle and passed through an 0.44 μm pore size GS Syringe filter (Millex). Two milliliters of the filtered sample were transferred to a 1-dram vial for HPLC analysis and final pH measurement. Throughout this project, the final pH values were determined using an AR20 Accumet pH meter equipped with an Accumet micro pH probe.

2.5.2 Calcium Chloride with Merichem Naphthenic Acids

The $CaCl_2$ studies were conducted in 40-mL Econo EPA vials (Fisher Scientific) with Teflon-lined cap inserts. $CaCl_2$ concentrations of 0, 0.001, 0.005, 0.01, 0.05, and 0.1 M were studied with a solution of 100 mg naphthenic acids (Merichem) L^{-1} at pH 8. All calcium and naphthenic acid stock solutions were pH adjusted using 3.0 M and 0.05 M HCl, and 0.1 M NaOH. Each test condition was established in triplicate. Controls were prepared in triplicate at the $CaCl_2$ concentrations above in the absence of naphthenic acids. Contents of the vials were prepared analytically using various volumes of 0.2 M $CaCl_2$ stock solution, 200 mg Merichem naphthenic acids L^{-1} and reverse osmosis water as make-up to achieve desired concentrations. All vials were placed on a tumbler, set at 20 rpm, in a temperature controlled room, set at 20°C, for 40 h.

After 40 h, the vials were removed from the tumbler and the contents sampled with a 3-mL Luer-Lok syringe with a 20 Gauge, 1.5-inch needle and passed through an 0.44 μm pore size GS Syringe filter. Two millilitres of the filtered sample was transferred to a 1-dram vial for HPLC analysis and final pH measurement.

2.5.3 Sodium Chloride and Sodium Bicarbonate

The NaCl and $NaHCO_3$ studies were conducted in 2-mL HPLC screw cap vials with PTFE-lined caps. The maximum NaCl and $NaHCO_3$ concentrations were chosen to mimic the salt content of the WIP process-affected water as described in Section 2.5.1. NaCl concentrations of 0, 0.008, 0.016, 0.024 and 0.040 M were studied with a solution of 100 mg Merichem naphthenic acids L^{-1} at pH 10. $NaHCO_3$ concentrations of 0, 0.003, 0.006, 0.009, 0.012 and 0.015 M were studied with 100 mg L^{-1} solution of naphthenic acids at pH 10. Stock solutions were pH adjusted using 3.0 M and 0.05 M HCl; and 0.1 M NaOH. Each test condition was established in triplicate. Controls were prepared in triplicate using the NaCl and $NaHCO_3$ concentrations above in the absence of naphthenic acids. Contents of the vials were prepared analytically with a final concentration of 200 μL using various volumes of the specific stock salt solution, 200 mg Merichem naphthenic acids L^{-1} and reverse osmosis water as make-up to achieve desired concentrations. The 2-mL sample vials were then analyzed on the HPLC.

2.5.4 Calcium Chloride with Extracted West-In Pit Naphthenic Acids

The $CaCl_2$ studies were conducted in 40-mL Econo EPA vials with Teflon-lined cap inserts. $CaCl_2$ concentrations of 0, 0.001, 0.005, 0.01, 0.05, and 0.1 M were studied with a solution of 100 mg WIP-extracted naphthenic acids L^{-1} at pH 8. Stock solutions were pH adjusted using 3.0 M and 0.05 M HCl; and 0.1 M NaOH. Each test condition was established in triplicate. Controls were prepared in triplicate using the $CaCl_2$ concentrations above in the absence of naphthenic acids. Contents of the vials were prepared analytically using various volumes of 0.2 M $CaCl_2$ stock solution, 270 mg WIP-extracted naphthenic acids L^{-1} stock solution and reverse osmosis water as make-up to achieve desired concentrations. All vials were placed on a tumbler, set at 20 rpm, in a temperature controlled room, set at 12°C, overnight.

On the following day, the vials were removed from the tumbler and the contents sampled with a 3-mL Luer-Lok syringe with a 20-Gauge, 1.5-inch needle and passed through a

0.45 μm pore size HA syringe filter. Two milliliters of the filtered sample was transferred to a 1-dram vial for HPLC analysis and final pH measurement. Twenty millilitres of the remaining solution was filtered through a 0.45 μm pore size HA syringe filter using a 10-mL Luer-Lok syringe without tip and transferred to a clean EPA vial for future GC-MS analysis.

2.6 Batch Sorption Experiments

The procedure for batch studies was modified from the American Society for Testing Materials (ASTM 2003). Details of the modified procedure are provided in the following sections. Batch sorption studies were conducted for:

(i) Clay minerals and Merichem naphthenic acids at pH 6 and 8;
(ii) Clay minerals and WIP-extracted naphthenic acids at pH 8;
(iii) Coke samples and WIP-extracted naphthenic acids at pH 8;
(iv) Soil samples and WIP-extracted naphthenic acids at pH 8.

2.6.1 Merichem Naphthenic Acids onto Clay Minerals

Sorption studies with clays were conducted with illite, montmorillonite and kaolinite described in Section 2.1. Additional experiments were conducted using untreated and unmodified 20-30 mesh Ottawa Sand (Fisher Chemicals). The studies were conducted in 40-mL Econo EPA vials (Fisher Scientific) with Teflon-lined cap inserts. Clay to solution ratios were maintained at 1:100 (weight:weight). The sorption experiments with clay were conducted using naphthenic acids (Merichem) solutions with concentrations of 0, 15, 25, 50, 75, 100, 150 and 200 mg L^{-1}. Sand to solution ratios varied from 1:5 to 1:50

(weight:weight). The sorption experiments with sand were conducted using solutions at a constant naphthenic acid concentration of 100 mg L^{-1}. All sorption experiments were conducted with initial pH conditions of pH 6.0 or 8.0. Naphthenic acid stock solutions were pH adjusted using 3.0 M and 0.05 M HCl; and 1.0 M KOH. Additionally, 1 mL of 1.0 M $KHCO_3$ per 500 mL of stock solution was added as a buffer for the pH 8.0 experiments. Two hundred microliter samples of the stock solutions were placed in 2-mL HPLC vials capped with PTFE coated rubber lids for future analysis. A final mass of the contents in the 40-mL vials was maintained at 30 g. The remaining headspace was used to facilitate mixing. Vials were allowed to equilibrate for a minimum of 40 h in a tumbler, set at 20 rpm, located in a temperature controlled room, set at 20 °C. All sorption experiments were conducted in triplicate.

Controls (conducted in triplicate) consisted of 30-g samples of the above solutions of naphthenic acids which were placed individually in 40-mL Econo EPA Vials. No clay or sand was added to the controls. The controls were placed on the tumblers with the clay-containing vials. These controls were used to determine the exact concentration of naphthenic acids using the HPLC method. This concentration was later used in calculations as the maximum mass of naphthenic acids available in each vial.

After 40 h, all vials were removed from the tumbler and centrifuged in 50-mL polypropylene copolymer centrifuge tubes (Nalgene) at 10,000 x g for 10 min. Samples of the supernatant were sampled with a 3-mL Luer-Lok syringe with a 20 Gauge, 1.5-inch needle and passed through an AP 20 glass fiber 2.0 μm pore size prefilter (Millex).

Two milliliters of the filtered sample were transferred to a 1-dram vial for HPLC analysis and final pH measurement. The remaining supernatant in the centrifuge tube was transferred to a clean 40-mL Econo EPA vial for conductivity and GC-MS analysis.

2.6.2 WIP-Extracted Naphthenic Acids onto Clay Minerals

Sorption studies were conducted with the illite, montmorillonite and kaolinite described in Section 2.1. The studies were conducted in 40-mL Econo EPA vials with Teflon-lined cap inserts. Clay to solution ratios were maintained at 1:100 (weight:weight). The sorption experiments with clay were conducted with the extracted naphthenic acids (described in Section 2.4) concentrations of approximately 0, 15, 25, 50, 75 and 100 mg L^{-1}. Sorption experiments were conducted with an initial pH condition of 8.0. Naphthenic acid stock solutions were pH adjusted using 3.0 M and 0.05 M HCl; and 1.0 M KOH. Additionally, 1 mL of 1.0 M $KHCO_3$ per 500 mL of stock solution was added as a buffer. Two hundred microliters samples of the stock solutions were placed in 2-mL HPLC vials capped with PTFE coated rubber lids for future analysis. A final mass of the contents in the 40-mL vials was maintained at 30 g. The remaining headspace was used to facilitate mixing. Vials were allowed to equilibrate for a minimum of 40 h in a tumbler, set at 20 rpm, located in a temperature controlled room, set at 20 °C. All sorption experiments were conducted in triplicate.

Controls (conducted in triplicate) consisted of 30-g samples of the above solutions of naphthenic acids which were placed individually in 40-mL Econo EPA Vials. No clay or sand was added to the controls. The controls were placed on the tumblers with the clay-containing vials. These controls were used to determine the exact concentration of naphthenic acids using the HPLC method. This concentration was later used in calculations as the maximum mass of naphthenic acids available in each vial.

After 40 h, all vials were removed from the tumbler and centrifuged in 50-mL polypropylene copolymer centrifuge tubes (Nalgene) at 10,000 x g for 10 min. Samples of the supernatant were sampled with a 3-mL Luer-Lok syringe with a 20 Gauge, 1.5-inch needle and passed through an AP 20 glass fiber 2.0 μm pore size prefilter. Two milliliters of the filtered sample were transferred to a 1-dram vial for HPLC analysis and final pH measurement. The remaining supernatant in the centrifuge tube was transferred to a clean 40-mL Econo EPA vial for conductivity and GC-MS analysis.

2.6.3 Extracted Naphthenic Acids onto Core, Coke and Soil Samples

Sorption studies were conducted using core samples, coke samples and soil samples. Preparation of each sample is described in Section 2.2. The coke and Ellerslie soil samples used in sorption studies are as described in Section 2.3 and 2.2, respectively. The studies were conducted in 40-mL Econo EPA vials with Teflon-lined cap inserts. Core, coke and soil samples to solution ratios are approximated at 1:30 (weight:weight). About 1 g of material (core, coke or soil sample) and 30 g of solution were transferred per vial. The sorption experiments were conducted with the WIP-extracted naphthenic acids (described in Section 2.4.2) at concentrations of approximately 0, 15, 25, 50, 75 and 100 mg L^{-1}. Sorption experiments were conducted with initial pH condition of 8.0. Naphthenic acid stock solutions were pH adjusted using 3.0 M and 0.05 M HCl; and 1.0

M KOH. Additionally, 1 mL of 1.0 M $KHCO_3$ per 500 mL of stock solution was added as a buffer. Two hundred microliters samples of the stock solutions were placed in 2-mL HPLC vials capped with PTFE coated rubber lids for future analysis. A final mass of the contents in the 40-mL vials was maintained at approximately 31 g (30 g solution and 1 g sample). The remaining headspace was used to facilitate mixing. Vials were allowed to come to equilibrate for a minimum of 40 h in a tumbler, set at 20 rpm, located in a temperature controlled room, set at 20 °C. All sorption experiments were conducted in triplicate.

Controls (conducted in triplicate) consisted of 30-g samples of the above solutions of naphthenic acids which were placed individually in 40-mL Econo EPA Vials. No core, coke or soil was added to the controls. The controls were placed on the tumblers with the core-, coke- or soil-containing vials. These controls were used to determine the exact concentration of naphthenic acids using the HPLC method. This concentration was later used in calculations as the maximum mass of naphthenic acids available in each vial.

After 40 h, all vials were removed from the tumbler and centrifuged in 50-mL polypropylene copolymer centrifuge tubes (Nalgene) at 10,000 x g for 10 min. Samples of the supernatant were sampled with a 3-mL Luer-Lok syringe with a 20 Gauge, 1.5-inch needle and passed through an AP 20 glass fiber 2.0 μm pore size prefilter in combination with a 0.45 μm pore size HA syringe filter. Two milliliters of the filtered sample were transferred to a 1-dram vial for HPLC analysis and final pH measurement.

The remaining supernatant in the centrifuge tube was transferred to a clean 40-mL Econo EPA vial for conductivity and GC-MS analysis.

2.7 Quantification of Naphthenic Acids by HPLC

The derivatization procedure and analytical method are briefly described below. The method described herein is adapted from Yen et al. (2004) with one change; the derivatizing agent 2-nitrophenylhydrazine (NPH, ICN Biomedical Inc., Aurora, OH) replaced with 2-nitrophenylhydrazine hydrochloride (NPH-HCl, TCI America, Portland, OR). This change was made due to a manufacturer claim that NPH-HCl was of higher purity (TCI 2005) and therefore resulted in fewer and less intense impurity peaks during analysis. Merichem naphthenic acids were used to develop the calibration curves throughout this study. The HPLC software method is presented in Appendix B. The detection limit of the HPLC method was 5 mg naphthenic acids L^{-1} (Yen et al. 2004).

2.7.1 HPLC Sample Preparation and Derivatization

The sample contents of the 1-dram vials set aside from the batch experiments were adjusted to pH 10 using approximately 60 µL of 0.1 M NaOH. Two hundred microliters of sample from each 1-dram vial were transferred to 2-mL screw cap HPLC vials equipped with PTFE lined cap inserts and were mixed with 80 µL each of NPH-HCl and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride solutions (EDC). The NPH-HCl solution was prepared by dissolving 18.9 g of NPH-HCl with 3.75 mL of 95% ethanol and 1.25 mL of 0.4 M HCl. The EDC solution was prepared by dissolving 480 mg EDC (Sigma) with 10.0 mL of 95% ethanol and 10.0 mL of a 3% pyridine solution in

95% ethanol. The vials containing the samples and reagents were placed in a 60°C water bath for 20 min. Once removed from the water bath, 40 µL of a KOH solution was added to each vial. The KOH solution was prepared by dissolving 385 mg KOH in 80 mL of HPLC grade methanol and 20 mL double distilled water. The vials were placed in the water bath for an additional 15 min. After 15 min, the vials were cooled in an ice bath for 5 min.

2.7.2 HPLC Method

HPLC analyses were conducted using an Agilent 1100 Series HPLC equipped with an autosampler, a UV-Visible diode array, a degasser, and a temperature controlled column compartment. The HPLC was equipped with an Agilent LiChrospher 100 RP-18 (5 µm particle size, 125 mm x 4 mm) analytical column with a 2 µm RP-18 solid phase guard column. Agilent Technologies Chemstation LC-3D software version A.08.03[847] was used to control the HPLC and analyze the results. The HPLC column was set at 40°C and the sample injection volume was 60 µL. The UV-Visible diode array detector was set at a wavelength of 400 nm (10 nm bandwidth) with a reference wavelength of 510 nm (60 nm bandwidth). The initial mobile phase consisted of 70% HPLC grade methanol and 30% MilliQ water at a flow rate of 1.5 mL min^{-1}. For the first 4 min of the run, the mobile phase changed over a gradient to 100% methanol. The mobile phase was kept at 100% methanol for an additional 3 min for a total run time of 7 min. A post runtime of 4 min was used in between samples to allow the mobile phase time to return to initial conditions. Samples were integrated from the last impurity peak, at approximately 2.9 min, to 6.0 min.

2.8 Calculations and Statistics Used to Generate the Isotherms

For each concentration of naphthenic acids used in the sorption tests, triplicate vials were prepared with sorbent (clay, soil, or coke) and triplicate vials were prepared without sorbents, to serve as controls. Because the amount of sorption was often quite low after 40 h of contact, the average concentration of naphthenic acids in the supernatants from the controls were compared to the average concentration of naphthenic acids in the supernatants from the vials with sorbents and the same initial concentration of naphthenic acids. The t-test at $p < 0.05$ was used for this comparison to determine if there was a statistically significant difference between the two values. If there was no statistical difference between the pairs, it was concluded that sorption could not be detected, and the data from those three vials were excluded from further calculations.

If the average concentrations were significantly different, then sorption was detected and the mass of naphthenic acids (in µg) in aqueous solution (M_a) at equilibrium with the sorbent was calculated as:

$$M_a = [\text{Mass of solution (g)} \times \text{conc. naphthenic acids (mg/L)} \times (1\ \text{mL water}/1\ \text{g water}) \times (1\ \text{L}/1000\ \text{mL}) \times (1000\ \mu\text{g/g})$$

The mass of naphthenic acids (in µg) sorbed to the sorbent was calculated as:

$$M_s = [\text{Mass of solution (g)} \times \text{conc. naphthenic acids (mg/L)} \times (1\ \text{mL water}/1\ \text{g water}) \times (1\text{L}/1000\ \text{mL}) \times (1000\ \mu\text{g/g})] - M_a$$

Finally, the mass of naphthenic acids sorbed per gram of sorbent (C_a) was calculated as:

M_s/g of sorbent added

To determine the K_D value for the sorption of naphthenic acids on a given sorbent, C_a values were plotted against the equilibrium naphthenic acids concentrations, as illustrated in Figure 1.13. A least squares analysis was done to determine the slope of the line, and goodness of fit (R^2). The R value was calculated and used to determine if the slope was significantly different from zero (Triola 1998). If the R value was low, and the slope was not significantly different from zero ($p < 0.05$), the K_D was reported as zero.

In a few cases, the slope was slightly negative, which is theoretically impossible. In these cases the K_D values were also reported as zero. This problem was likely caused by the inaccuracy associated with integrating humps of naphthenic acids that elute from the HPLC column. If the amount of sorption was very small, then it would be difficult to distinguish a small difference between the naphthenic acids concentrations in the controls and in the sorbent-containing vials.

Generally, triplicate vials were prepared with each of six to eight different initial naphthenic acids concentrations. Occasionally, the amounts of sorption were so low, that the t-tests indicated that HPLC analyses could detect sorption in only a few of the vials that contained the highest initial concentrations of naphthenic acids. In these situations, there were insufficient numbers of data points to plot a graph to determine K_D. When this occurred, K_D was estimated by dividing C_a by the equilibrium concentration of naphthenic acids.

The error bars generated on the isotherm plots were calculated using the law of propagation of error as discussed in Wolf and Brinker (1994). In general terms, propagation of error allows for mathematical operations to be conducted on values that have error to produce a combined error. For a function such as Z = f(a,b,c,. . ., *n*), the error in Z would be (Wolf and Brinker 1994):

$$E_z = \pm\sqrt{\left(\frac{\partial f}{\partial a}\right)^2 (E_a)^2 + \left(\frac{\partial f}{\partial b}\right)^2 (E_b)^2 + \left(\frac{\partial f}{\partial c}\right)^2 (E_c)^2 + \cdots + \left(\frac{\partial f}{\partial n}\right)^2 (E_n)^2}$$

For the case of the isotherm presented in Chapter 3, error was first derived through the determination of the standard deviation of the controls. The error in those controls was propagated when the control value or any value that was in part derived from the control value was included in a calculation. The calculations used to produce the isotherms are detailed in Appendix D. Since the largest errors were in the controls, only these errors were considered for the error propagation calculations.

The p-value was generated using the unequal variance t-test in Excel® (Microsoft Corporation, California).

2.9 Characterization of Naphthenic Acids by GC-MS

The derivatization procedure and analytical method are briefly described below. Details are presented in Holowenko and Fedorak (2001).

2.9.1 GC-MS Sample Preparation and Derivatization

Twenty milliliter samples from batch sorption experiments were brought to a pH of 2.0 to 2.5 using concentrated HCl. The pH-adjusted samples were then extracted twice with 5 mL portions of GC-DCM in a 50-mL separatory funnel. Both GC-DCM extracts were filtered through granular anhydrous sodium sulfate (Fisher Chemicals) to remove any water. The extracts were combined and taken to dryness under nitrogen. These samples were then dissolved in sufficient GC-DCM to yield a final concentration of 20 mg mL^{-1}, typically, 100 to 400 µL of GC-DCM. Fifty microliters of the dissolved sample was transferred to a 2-mL screw top HPLC vial. Fifty microliters of N-methyl-N-(trimethylsilyl) trifluoracetamide (MSTFA) was then added to the 2-mL vial and placed into a water bath for 20 min at 60°C. The derivatized sample was then dried under nitrogen. Prior to analysis, 100 µL of GC-DCM was used to redissolve the dried derivatized sample.

2.9.2 GC-MS Analytical Method

Derivatized samples were analyzed by gas chromatography-electron impact mass spectrometry. The gas chromatograph was a Varian Vista 6000 coupled with VG 7070E mass spectrometer operating in electron impact ionization mode, located in the Mass Spectrometry Laboratory in the Department of Chemistry at the University of Alberta. The GC-MS used a 30 m DB-5 capillary column and helium carrier gas. The GC-MS scanned from m/z of 150 to 550. The initial column temperature was set to 100°C and held for 3 min, followed by an 8°C min^{-1} increase until a final temperature of 300°C was reached. The final temperature was held for 12 min. The total analysis time per sample was 40 min.

Data were acquired using the Mass Spec Data System for Windows version 14.0c (Mass Spec Services, England). Ion intensities were averaged by the software from 10 min onward with a minimum required occurrence of 1% of total scans (Holowenko et al. 2002).

Prior to sample analysis, a 2 µL injection of a derivatized naphthenic acid standard (Merichem) was used to determine if the GC-MS was properly calibrated. The indication of proper calibration would show all mass peaks on odd numbered m/z. After proper calibration was ensured, 2-µL injections of the samples were analyzed.

Three-dimensional plots were generated from the spectra as outlined by Holowenko et al. (2002). Pairs of these plots were compared using the statistical method developed by Clemente et al. (2003).

Chapter 3 Results

The following chapter outlines the experimental results for the following:

(i) Salt interaction studies;

(ii) Properties of clay and soil samples;

(iii) Sorption of Merichem naphthenic acids to clays conducted at pH 6 and 8;

(iv) Sorption of WIP-extracted naphthenic acids to clays conducted at pH 8;

(v) Sorption of WIP-extracted naphthenic acids to soil and coke at pH 8; and

(vi) GC-MS analysis of select samples from sorption experiments conducted with WIP-extracted naphthenic acids.

3.1 Salt Interaction Studies

The behavior of Merichem naphthenic acids in the presence of a salt mixture (Table 2.1) was studied at pH 8 and is presented in Figure 3.1. The salt mixture experiment uses a mixture of sodium chloride, sodium bicarbonate, magnesium sulfate and calcium sulfate and attempts to determine the effects between the major ions in tailings ponds on naphthenic acids solubility or detection. The results of this experiment are presented in Figure 3.1. Figure 3.1 shows that there appears to be a linear increase in the amount of naphthenic acids detected despite the fact that the actual naphthenic acids concentration was held constant. This trend indicates that there may be an interaction between the salts in solution and the Merichem naphthenic acids, or an interference of the salt solution with the analytical procedure used to determine naphthenic acids concentration. The two major components of the salt mix are sodium chloride and sodium bicarbonate. In order to assess if either of these salts were causing this apparent trend, separate experiments were run using each salt alone. Figure 3.2 shows that the apparent naphthenic acids concentration did not vary with the sodium chloride concentration over the concentration range studied. Conversely, Figure 3.3 shows the same linear increase of apparent naphthenic acids concentration with increasing sodium bicarbonate concentration as was observed in Figure 3.1.

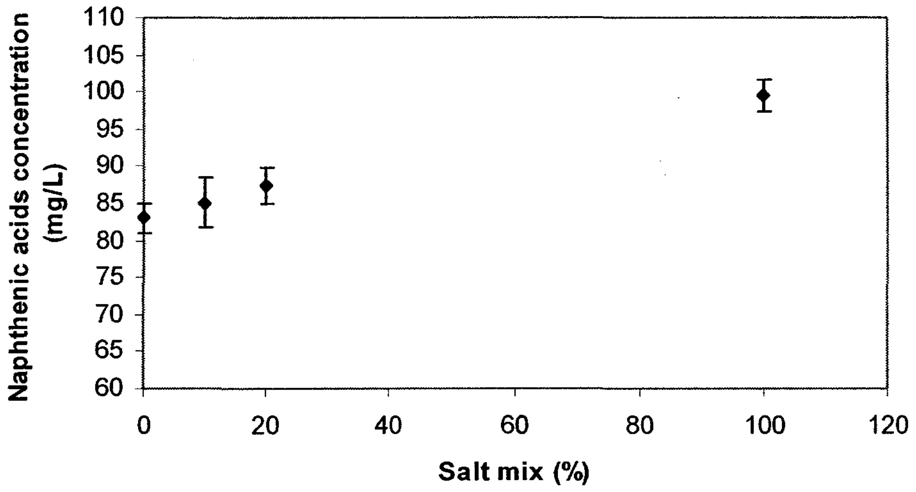

Figure 3.1: Measurements of Merichem naphthenic acids concentration in solutions with different salt concentrations, after 40 h of exposure. The 100% salt mix contained 0.04 M Na^+, 0.025 M Cl^-, 0.0025 M SO_4^{2-}, 0.015 M HCO_3^-, 0.002 M Ca^{2+}, and 0.0005 M Mg^{2+}. The error bars represent 1 standard deviation.

The effects of calcium chloride on the solubility or detection of naphthenic acids were studied at pH 8 with both the Merichem and WIP-extracted naphthenic acids. The results are presented in Figures 3.4 and 3.5, respectively. The figures illustrate different behavior for the Merichem and WIP-extracted naphthenic acids. The Merichem naphthenic acids show a decrease in the apparent concentration as the concentration of calcium chloride increases. The apparent concentration of the WIP-extracted naphthenic acids did not change with the concentration of calcium chloride.

Data used to produce Figures 3.1 to 3.5 are provided in Appendix C. Error bars in Figures 3.1 to 3.5 are standard deviations of triplicate analysis and calculations are detailed in Appendix C.

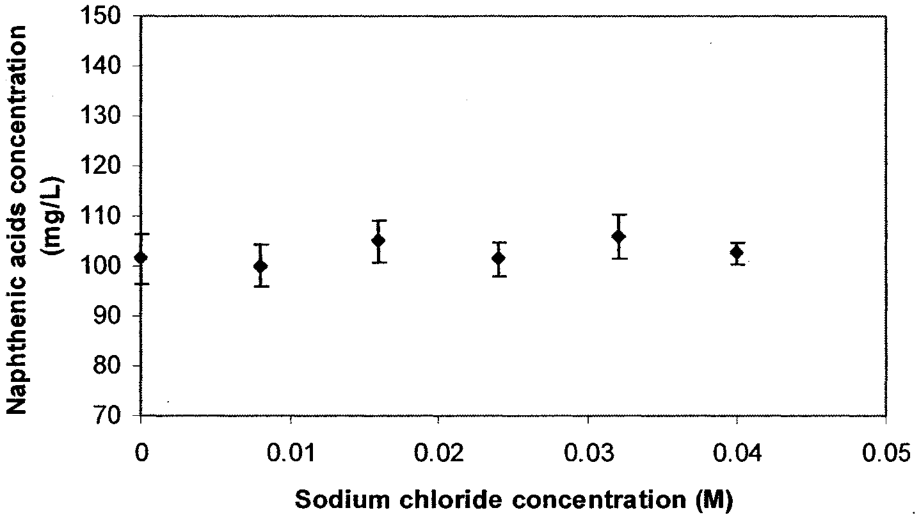

Figure 3.2: Measurements of Merichem naphthenic acids concentrations in solution with different concentrations of sodium chloride. The error bars represent 1 standard deviation.

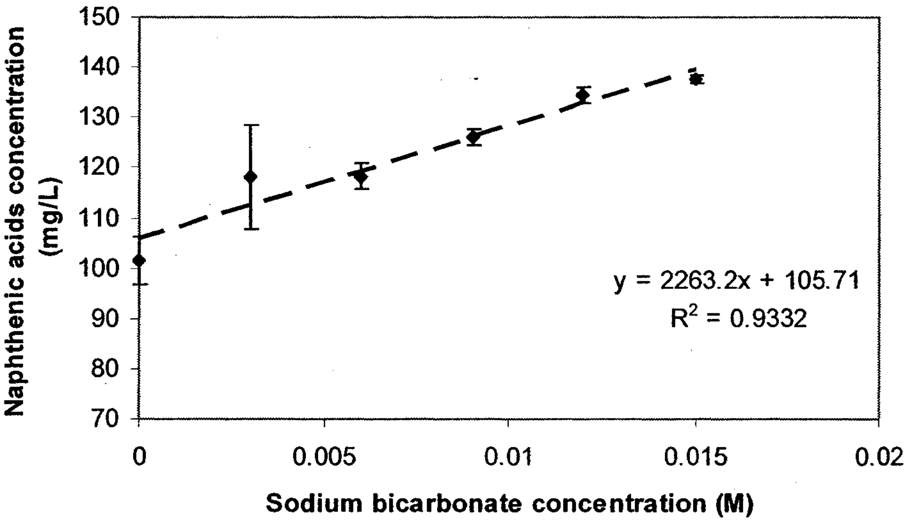

Figure 3.3: Measurements of Merichem naphthenic acids concentrations in solution with different concentrations of sodium bicarbonate. The error bars represent 1 standard deviation.

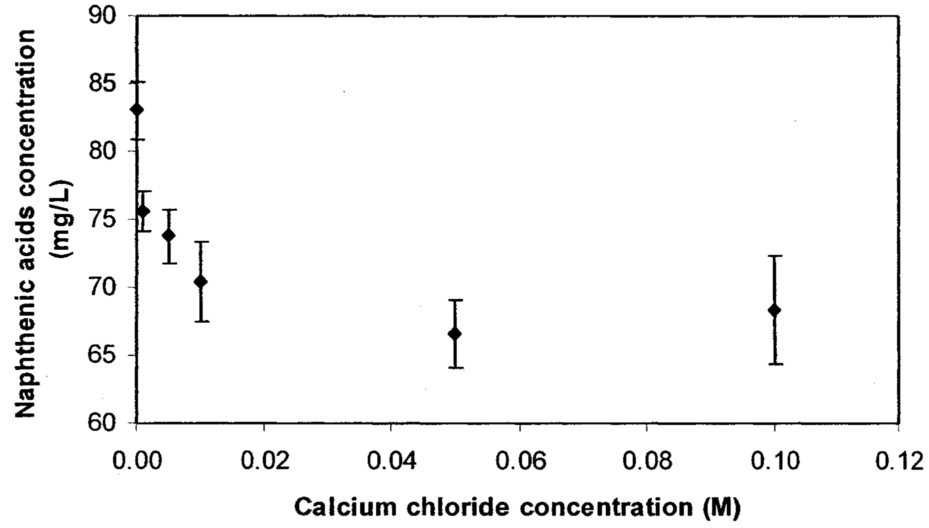

Figure 3.4: Measurement of Merichem naphthenic acids concentrations in solution with different concentrations of calcium chloride, after 40 h of exposure. The error bars represent 1 standard deviation.

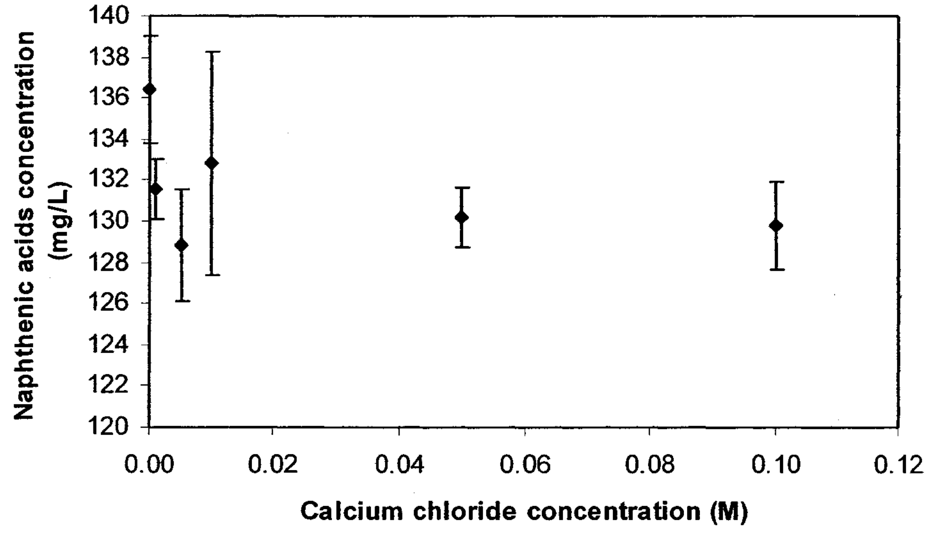

Figure 3.5: Measurement of WIP-extracted naphthenic acids concentration in solution with different concentrations of calcium chloride, after 18 h of exposure. The error bars represent 1 standard deviation.

3.2 Soil Sample Properties

The following sections describe the properties of the core, clay and sand samples used in experimentation.

3.2.1 Properties of Core Samples

Table 3.1 summarizes the PSA, TOC and CEC for core samples collected from the Syncrude Mildred Lake site by University of Waterloo staff. Core samples from core OW04-06 at depths of 4.5 – 5 m, 5.5 – 6 m and 7 – 7.5 m could not be analyzed for PSA or CEC due to their hydrophobicity. According to personnel at the soils laboratory, this hydrophobicity was most likely due to the high bitumen content of these particular samples.

Table 3.1: Syncrude site core sample properties.

Core Sample ID*	Depth (m)	PSA (%)			CEC	TOC (%)
		Clay (<2 μm)	Silt (2-50 μm)	Sand (>50 μm)	[meq (100 g)$^{-1}$]	
OW04-02	3-3.5	1.7	0.4	97.9	0.65	0.05
	3.5-4	1.6	0.2	98.1	0.61	0.09
	4-5	1.6	0.2	98.2	0.54	0.06
	5-6	1.4	0.1	98.5	0.37	0.06
	6-7	1.9	1.4	96.7	0.64	0.09
	7-8	1.8	0.6	97.7	0.49	0.11
	8-8.7	1.7	0.1	98.2	0.36	0.09
OW04-04	4-5	2.2	1.4	96.4	0.84	0.09
	5-5.5	1.4	0.1	98.4	0.67	0.06
	5.5-6	1.3	0.2	98.5	0.61	0.07
	6-6.5	1.3	0.6	98.1	0.85	0.06
	6.5-7	1.1	0.5	98.3	0.95	0.05
	7-8	1.2	0.4	98.4	0.81	0.05
	8-9	1.4	0.2	98.4	17.92	0.05
	9.3-9.7	7.5	19.1	73.3	3.19	0.37
OW04-06	3-4	2.5	1.0	96.6	0.67	0.11
	4-4.5	8.5	11.6	79.8	2.83	0.53
	4.5-5	Hydrophobic				1.41
	5.5-6	Hydrophobic				2.12
	7-7.5	Hydrophobic				2.39

*Core sample ID corresponds to the locations shown in Figure 1.1

The PSA for core samples OW04-02 and OW04-04 indicate that the soil type of these cores is mainly sand. One exception was with core OW04-04 at the depth of 9.3 – 9.7 m where the sand composition dropped to about 73%, indicating a sandy loam textured material (Dragun 1998). Samples from core OW04-06 were primarily hydrophobic except for depths 3 – 4 m and 4 – 4.5 m. The composition of depth 3 – 4 m was very similar to that from the previous two cores with a sand content of approximately 97%. The sample from depth 4 – 4.5 m had a higher silt and clay content which dropped the sand content to about 80%, indicating a loamy sand textured material (Dragun 1998).

As with the PSA, CEC showed very similar results among the soil samples. CECs values ranged from 0.4 to 1 meq (100 g)$^{-1}$. Soil samples with higher clay and silt content showed slightly higher CEC values of about 3 meq (100 g)$^{-1}$. Core OW04-04 from depth 8 – 9 m showed an exceptionally high CEC value of 18 meq (100 g)$^{-1}$.

TOC values for all core samples were quite low, and ranged from 0.05 to 0.11 %. Core samples with higher clay and silt contents (OW04-04 at depth 9.3 – 9.7 m, OW04-06 at depth 4 – 4.5 m) showed slightly larger TOC values ranging from 0.37 to 0.53 %. All hydrophobic samples showed elevated TOC values ranging from 1.4 to 2.4 %. The higher TOC values in the hydrophobic samples could be attributed to the presence of bitumen as mentioned earlier.

3.2.2 Properties of Clay Minerals and Ottawa Sand

Ottawa sand, clay minerals, and sodium- and calcium-modified clay minerals were sent to the Department of Renewable Resources, University of Alberta for CEC and TOC analysis. The results of these analyses are present in Table 3.2. In most cases, the modified forms of a given clay mineral had a similar CEC and TOC values as the parent or unmodified clay mineral. However, the sodium modified montmorillonite and calcium modified kaolinite did show increases in the CEC values with respect to the parent material. This slight increase of 8 – 10 meq (100 g)$^{-1}$ could possibly indicate that there may be some excess salt precipitated in these two particular clay preparations. TOC values for all samples were all low, with values ranging from 0.01 to 0.08 %.

Table 3.2: CEC and TOC for clay minerals and Ottawa sand.

Soil mineral	CEC [meq (100 g)$^{-1}$]	TOC (%)
Illite (IMt-1)*	12.5	0.058
Sodium Modified Illite	10.8	0.068
Calcium Modified Illite	14.5	0.083
Kaolinite (KGa-1b)*	2.0	0.015
Sodium Modified Kaolinite	2.9	0.054
Calcium Modified Kaolinite	10.5	0.031
Montmorillonite (SAz-1)*	25.9	0.014
Sodium Modified Montmorillonite	36.6	0.022
Calcium Modified Montmorillonite	25.5	0.020
Ottawa Sand*	0.2	0.008

*Unmodified, as received from supplier.

The modified clay minerals were used in experimentation rather than the original parent clay mineral. Preliminary experimentation indicated that the clay minerals purchased from the Clay Repository at Purdue University contained various amounts of carbonates. For example, experiments that involved placing the illite, montmorillonite and kaolinite parent material in an aqueous solution originally at pH 6 and mixing for 30 min; yielded a final solution pH as tabulated in Table 3.3. Only kaolinite (KGa-1b) appeared to have little effect on the pH; however, it was decided to pretreat the kaolinite prior to use to ensure a consistent starting material for all experiments. In addition, it was expected that sodium and calcium could play a large role in the experimental results. The clay modification procedure (Section 2.1) therefore ensured a well characterized clay mineral in terms of calcium and sodium content.

Table 3.3: pH variation during preliminary experimentation with unmodified kaolinite, montmorillonite and illite.

Clay Mineral	Initial pH	Final pH
Illite (IMt-1)	6.2	8.74
Kaolinite (KGa-1b)	6.2	6.21
Montmorillonite (SAz-1)	6.2	7.41
Water (Reverse Osmosis)	6.2	6.25

3.3 Batch Experiments with Merichem Naphthenic Acids

This section contains the results of the batch sorption experiments of Merichem naphthenic acids to clay minerals conducted at pH 6 and 8. Results consist of linear sorption isotherms as well as tabulated K_D values.

3.3.1 Batch Sorption Studies with Clay Minerals at pH 6

Batch sorption studies using Merichem naphthenic acids at initial pH of 6 were conducted for sodium and calcium modified kaolinite; and sodium and calcium modified illite. The sorption isotherms are presented as Figures 3.6 to 3.9. The x-axis represents the equilibrium concentration (mg L^{-1}) of naphthenic acids in solution. The y-axis represents the amount of naphthenic acids sorbed per g of clay (denoted as C_a). Calculations used to produce the isotherms are detailed in Appendix D. A summary of the K_D values determined from these isotherms, as well as the final solution pH values is summarized in Table 3.4.

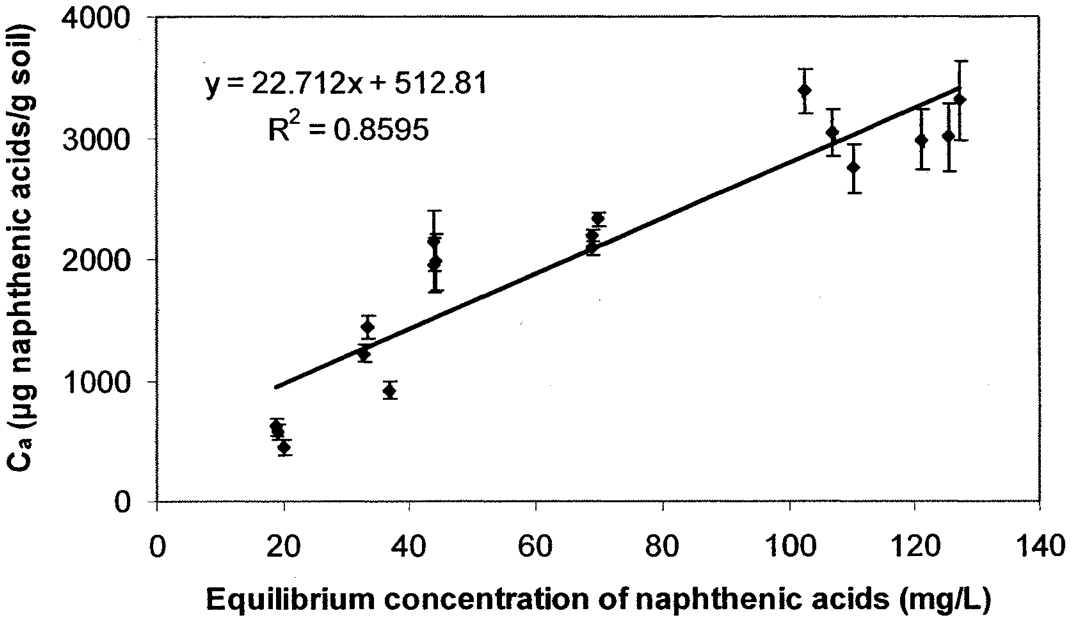

Figure 3.6: Linear isotherm of sodium modified kaolinite and Merichem naphthenic acids conducted at pH 6.

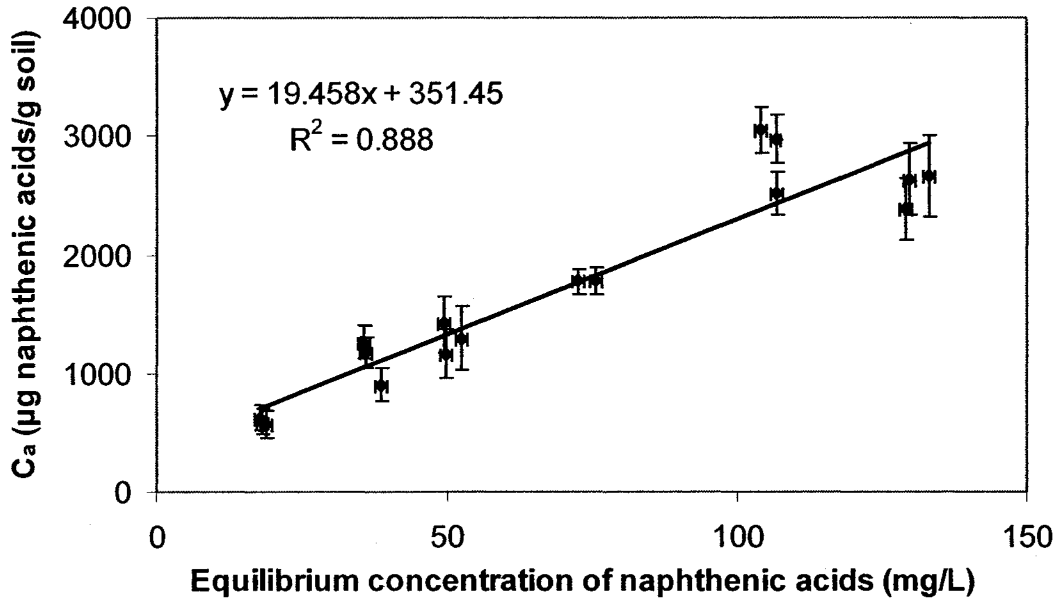

Figure 3.7: Linear isotherm of calcium modified kaolinite and Merichem naphthenic acids conducted at pH 6.

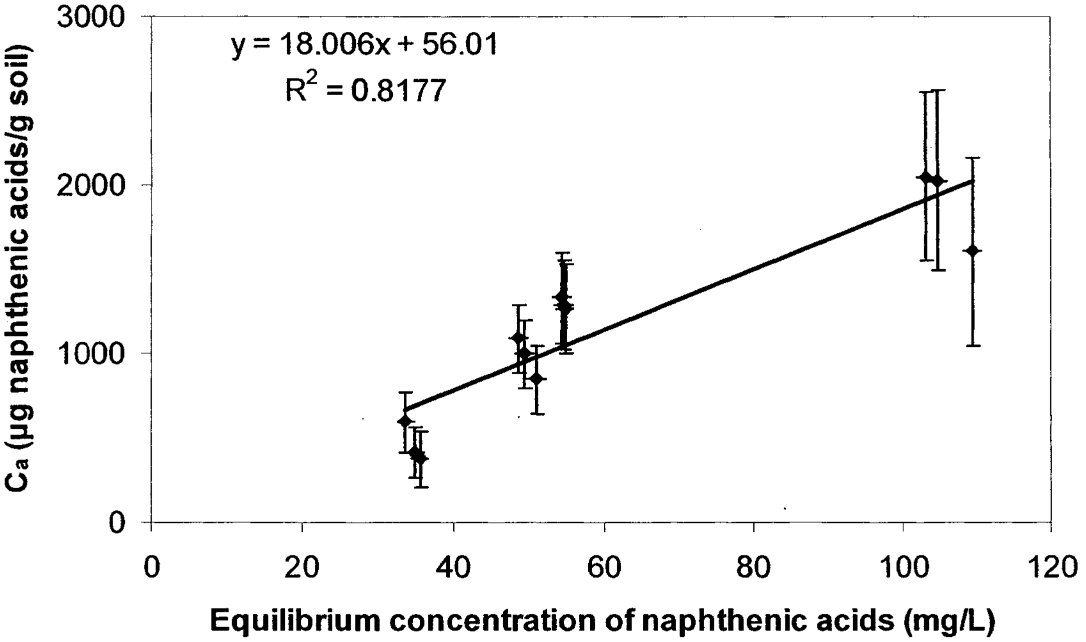

Figure 3.8: Linear isotherm of sodium modified illite and Merichem naphthenic acids conducted at pH 6.

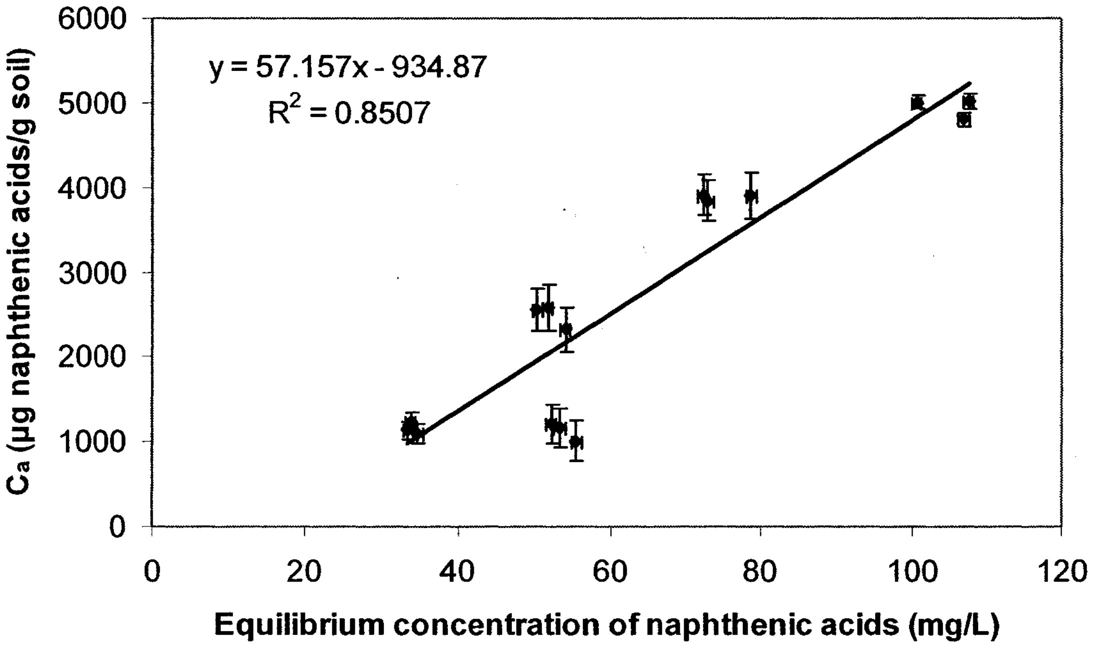

Figure 3.9: Linear isotherm of calcium modified illite and Merichem naphthenic acids conducted at pH 6.

Table 3.4: K_D and final pH values for sorption experiments conducted at pH 6 with Merichem naphthenic acids.

Soil Mineral	K_D (mL g^{-1})	pH at 40 h (± Std. Dev.)
Sodium Modified Kaolinite	23	5.98 ± 0.15
Calcium Modified Kaolinite	19	5.86 ± 0.28
Kaolinte Controls		5.86 ± 0.18
Sodium Modified Illite	18	6.13 ± 0.17
Calcium Modified Illite	57	6.08 ± 0.23
Illite Controls		6.20 ± 0.45

Experiments conducted using the sodium and calcium modified montmorillonite are not shown because the final solution pH during these experiments was approximately 7. The pH of the controls, however, remained at 6. The cause of the pH shift from 6 to 7 in the montmorillonite experiments may be due to the exchange of sodium and calcium cations on the clay surface with the hydrogen ions in solution.

Both the sodium and calcium modified kaolinite experiments resulted in similar K_D values of approximately 20 mL g^{-1}. Calcium and sodium modified illite experiments showed different results depending on which cation was originally present on the clay mineral surface. The calcium modified illite yielded a K_D value of 57 mL g^{-1} whereas the sodium modified illite yielded a K_D of 18 mL g^{-1}. The calcium modified illite yielded the highest K_D of all experiments conducted.

3.3.2 Batch Sorption Studies with Clay Minerals and Ottawa Sand at pH 8

Batch sorption studies with Merichem naphthenic acids with initial pH 8 were conducted for sodium and calcium modified kaolinite; sodium and calcium modified illite; sodium and calcium modified montmorillonite; and Ottawa sand. A summary of the K_D and final pH values is provided in Table 3.5.

Table 3.5: K_D and final pH values for sorption experiments conducted at pH 8 with Merichem naphthenic acids.

Soil Mineral	K_D (mL g^{-1})	pH at 40 h (± Std. Dev.)
Sodium Modified Kaolinite	0	8.06 ± 0.07
Calcium Modified Kaolinite	0	8.18 ± 0.06
Kaolinte Controls		8.40 ± 0.03
Sodium Modified Illite	0	7.98 ± 0.08
Calcium Modified Illite	10*	8.02 ± 0.08
Illite Controls		8.32 ± 0.10
Sodium Modified Montmorillonite	0	8.70 ± 0.05
Calcium Modified Montmorillonite	9*	8.33 ± 0.09
Montmorillonite Controls		8.37 ± 0.11
Ottawa Sand	0	7.02 ± 0.20
Ottawa Sand Controls		7.03 ± 0.28

*Average K_D as described in Section 2.8

Sodium and calcium modified kaolinite; sodium modified illite; sodium modified montmorillonite; and Ottawa sand produced K_D values of zero. The equilibrium naphthenic acids concentrations in supernatant samples from the sodium modified illite and the two kaolinites (sodium and calcium modified) were not significantly different from the respective controls, therefore the K_D values were reported as zero. No sorption was evident with the sodium modified montmorillonite. Data and statistical analyses can be referenced in Appendix D (Tables D 5, D 6, D 7, D 9 and D 11).

The calcium modified illite and the calcium modified montmorillonite both showed significant sorption in some data points; however a sorption isotherm is not shown for either calcium modified illite nor calcium modified montmorillonite. Significant sorption was detected in only two sets of data points, thus there were insufficient data to produce an isotherm plot. The K_D values for the calcium modified illite and calcium modified montmorillonite presented in Table 3.5 is the average K_D determined from the individual data points that were deemed to be significant. Data and statistical analyses can be referenced in Appendix D (Tables D 8 and D 10).

3.4 Batch Experiments with WIP-Extracted Naphthenic Acids

Batch sorption studies reported in this section were conducted using WIP-extracted naphthenic acids. Initially, experiments were to be conducted using WIP process-affected water containing naphthenic acids rather than using WIP-extracted naphthenic acids. The results presented in Section 3.1 however indicated that the presence of ions in the WIP water (bicarbonate and calcium in particular) may affect the results. Naphthenic acids were therefore initially extracted from the WIP water and these were used for batch sorption studies.

The following section presents the results of the batch sorption studies conducted with WIP-extracted naphthenic acids, clay minerals, soil and coke at pH 8.

3.4.1 Batch Sorption Studies with Clay Minerals at pH 8

Batch sorption studies with WIP-extracted naphthenic acids at an initial pH of 8 were conducted for sodium and calcium modified kaolinite; sodium and calcium modified illite; and sodium and calcium modified montmorillonite. A summary of the K_D and final pH values is provided in Table 3.6.

Table 3.6: K_D and final pH values for sorption experiments conducted at pH 8 with WIP-extracted naphthenic acids.

Clay Mineral	K_D (mL g^{-1})	pH at 40 h (± Std. Dev.)
Sodium Modified Kaolinite	0	8.42 ± 0.07
Calcium Modified Kaolinite	0	8.45 ± 0.11
Kaolinte Controls		8.28 ± 0.20
Sodium Modified Illite	0	8.07 ± 0.07
Calcium Modified Illite	0	7.92 ± 0.05
Illite Controls		8.44 ± 0.10
Sodium Modified Montmorillonite	0	8.79 ± 0.07
Calcium Modified Montmorillonite	10*	8.43 ± 0.05
Montmorillonite Controls		8.63 ± 0.08

*Average K_D as described in Section 2.8

Sodium and calcium modified kaolinite; sodium and calcium modified illite; and sodium modified montmorillonite produced K_D values of zero. The equilibrium naphthenic acids concentrations in supernatant samples from the calcium modified kaolinite and the two illites (sodium and calcium modified) gave sorption data that were not significantly different from the respective controls, therefore the K_D values were reported as zero. No sorption was evident with the sodium modified kaolinite nor the sodium modified montmorillonite. Data and statistical analyses can be referenced in Appendix D (Tables D 12, D 13, D 14, D 15 and D 16).

The calcium modified montmorillonite showed significant sorption in some data points; however a sorption isotherm is not shown. Significant sorption was detected in only two sets of data points, thus there were insufficient data to produce an isotherm plot. The K_D value for the calcium modified montmorillonite presented in Table 3.6 is the average K_D

determined from the individual data points that were deemed to be significant. Data and statistical analyses can be referenced in Appendix D (Table D 17).

3.4.2 Batch Sorption Studies with Soil Samples at pH 8

Batch sorption studies with WIP-extracted naphthenic acids at an initial pH of 8 were conducted for two samples originating from cores OW04-02 (depth 6-7 m) and OW04-06 (depth 4-4.5 m); and a sample of Ellerslie soil. OW04-02 (depth 6-7 m) and OW04-06 (depth 4-4.5 m) were chosen as the representative samples of all the core samples. A summary of the partition coefficients (K_D) and final pH values is provided in Table 3.7.

Table 3.7: K_D and final pH values for sorption experiments conducted with various soil samples at pH 8 with WIP-extracted naphthenic acids.

Soil Sample	K_D (mL g^{-1})	pH at 40 h (± Std. Dev.)
Core OW04-02	0	8.80 ± 0.08
Core OW04-06	0	8.66 ± 0.05
Core Controls		8.39 ± 0.10
Ellerslie Soil	0	7.65 ± 0.22
Ellerslie Control		8.18 ± 0.24

Experiments conducted with core samples OW04-02 (depth 6-7 m), OW04-06 (depth 4-4.5 m) and Ellerslie soil sample produced K_D values of zero. The equilibrium naphthenic acids concentrations in supernatant samples from the core OW04-06 and Ellerslie soil were not significantly different from the respective controls, therefore the K_D values were reported as zero. No sorption was evident with the samples from core sample OW04-02. Data and statistical analyses can be referenced in Appendix D (Tables D 18, D 19 and D 20).

3.4.3 Batch Sorption Studies with Suncor and Syncrude Coke Samples

Batch sorption studies with WIP-extracted naphthenic acids at an initial pH of 8 were conducted for two coke samples originating from Suncor and Syncrude. The Syncrude sorption isotherm is presented in Figure 3.10. Calculations conducted to produce the isotherm can be found in Appendix D (Table D21). A summary of the K_D and final pH values is provided in Table 3.8.

The experiment conducted on the Suncor coke sample produced a K_D value of zero. The Suncor coke sample gave sorption data that was not significantly different from the controls, therefore the K_D value was assumed as zero. Data and statistical analyses can be referenced in Appendix D (Table D 22).

Applying the t-test (Section 2.8) to the Syncrude coke sorption data showed that the equilibrium concentrations of naphthenic acids in the supernatant in four of the sets of vials were significantly less than the naphthenic acids concentrations in the corresponding controls (Table D 22). Thus, an isotherm plot was prepared as shown in Figure 3.10. However, linear regression of the data gave an R^2 value lower than 0.264 ($n = 15$; 95% confidence) which indicates no statistical correlation to a linear sorption model (Triola 1998). The K_D value is therefore reported as zero.

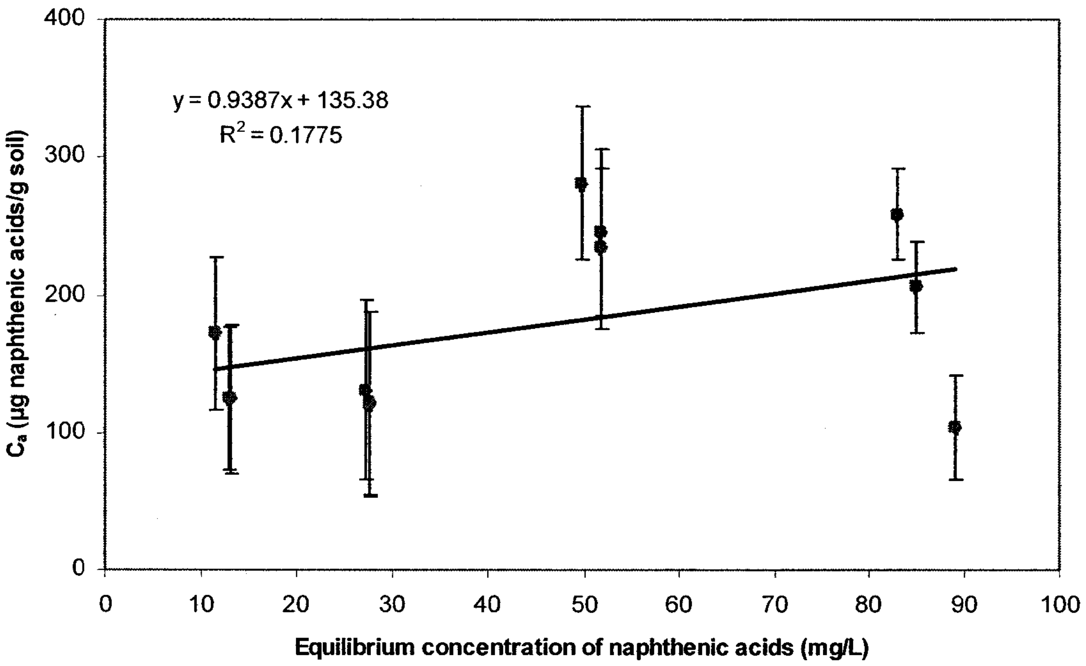

Figure 3.10: Linear isotherm of a coke sample obtained from Syncrude and WIP-extracted naphthenic acids conducted at pH 8.

Table 3.8: K_D and final pH values for sorption experiments conducted with coke samples at pH 8 with WIP-extracted naphthenic acids.

Coke Sample	K_D (mL g^{-1})	pH at 40 h (± Std. Dev.)
Suncor	0	8.62 ± 0.08
Syncrude	0	8.20 ± 0.09
Coke Controls		8.18 ± 0.24

3.5 GC-MS Analyses of Select Naphthenic Acids Samples

The objective of this work was to determine if any preferential sorption of naphthenic acids to various clay and soil samples could be detected.

The GC-MS data are categorized into two sections:

(i) GC-MS analyses of Merichem and WIP-extracted naphthenic acids; and

(ii) GC-MS analyses of naphthenic acids from aqueous solutions obtained following WIP-extracted naphthenic acids sorption studies.

3.5.1 GC-MS Analyses of Merichem and WIP-Extracted Naphthenic Acids

Three-dimensional plots of the GC-MS analyses of the Merichem naphthenic acids and of two samples of WIP-extracted naphthenic acids are presented in Figures 3.11 to 3.13, respectively. The plots show the relative distribution of the naphthenic acids found in each of the source materials used in experimentation. The x-axis describes the number of carbon atoms; y-axis describes the Z series; and the z-axis describes the relative abundance. The three-dimensional plots only show data that follow the general formula of $C_nH_{2n+Z}O_2$.

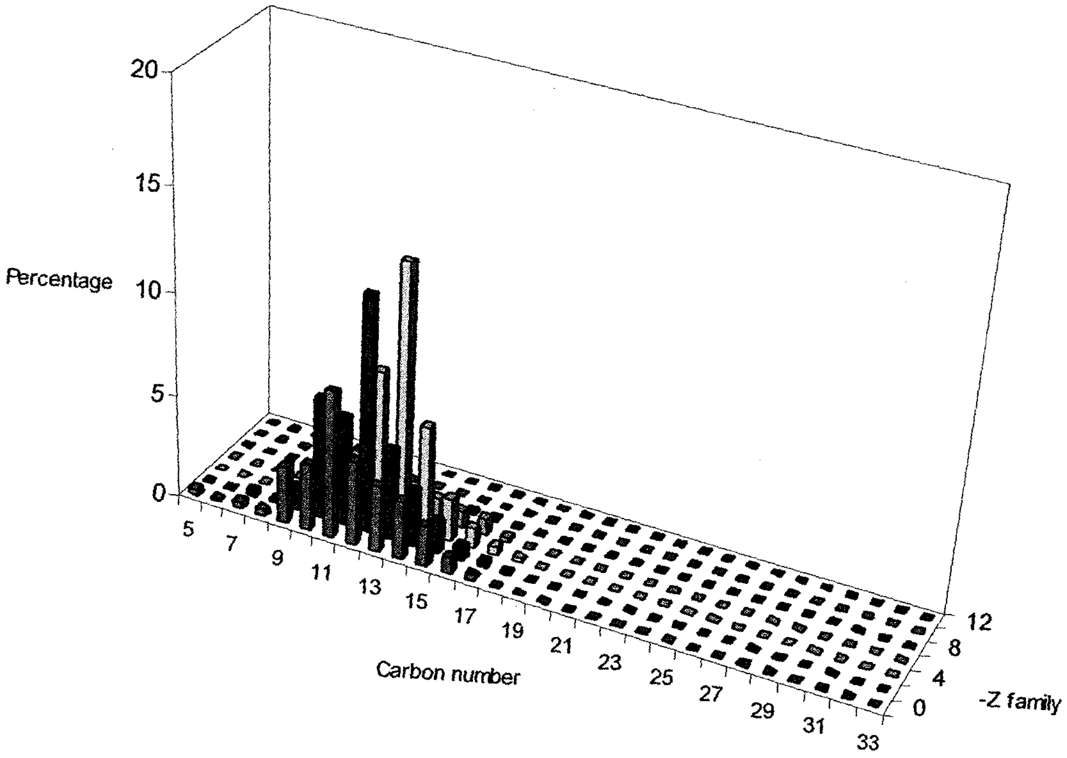

Figure 3.11: Three-dimensional plot from the GC-MS analysis of Merichem naphthenic acids.

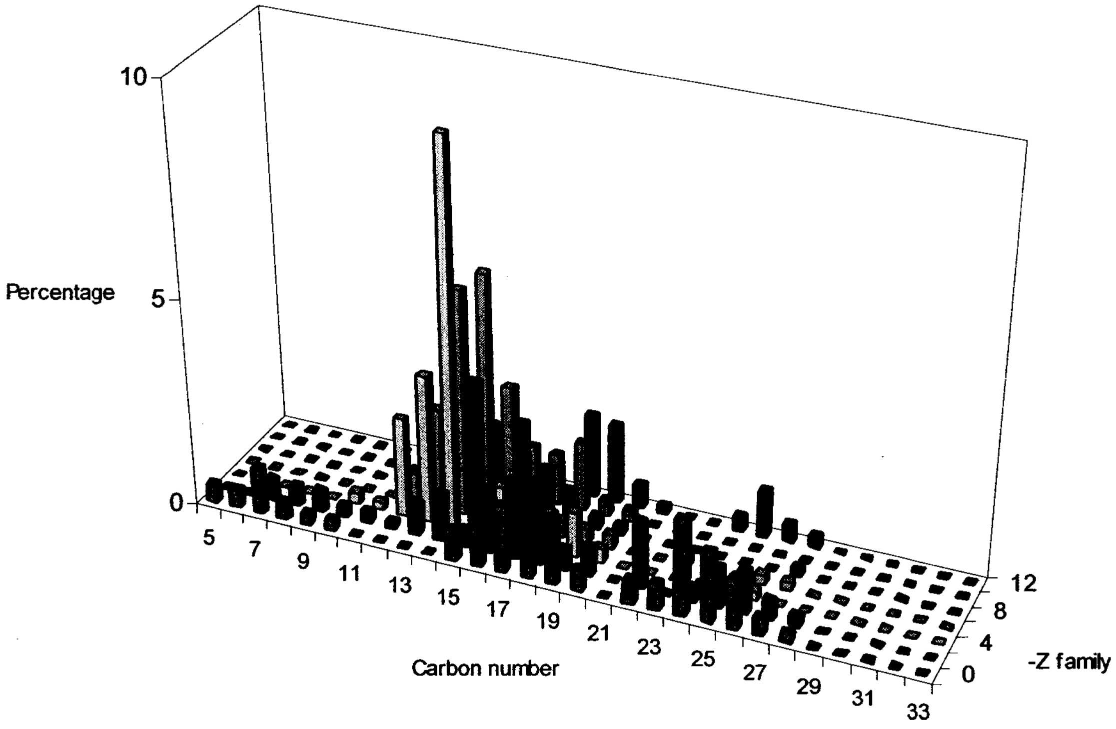

Figure 3.12: Three-dimensional plot from the GC-MS analysis of naphthenic acids found in WIP extract 1.

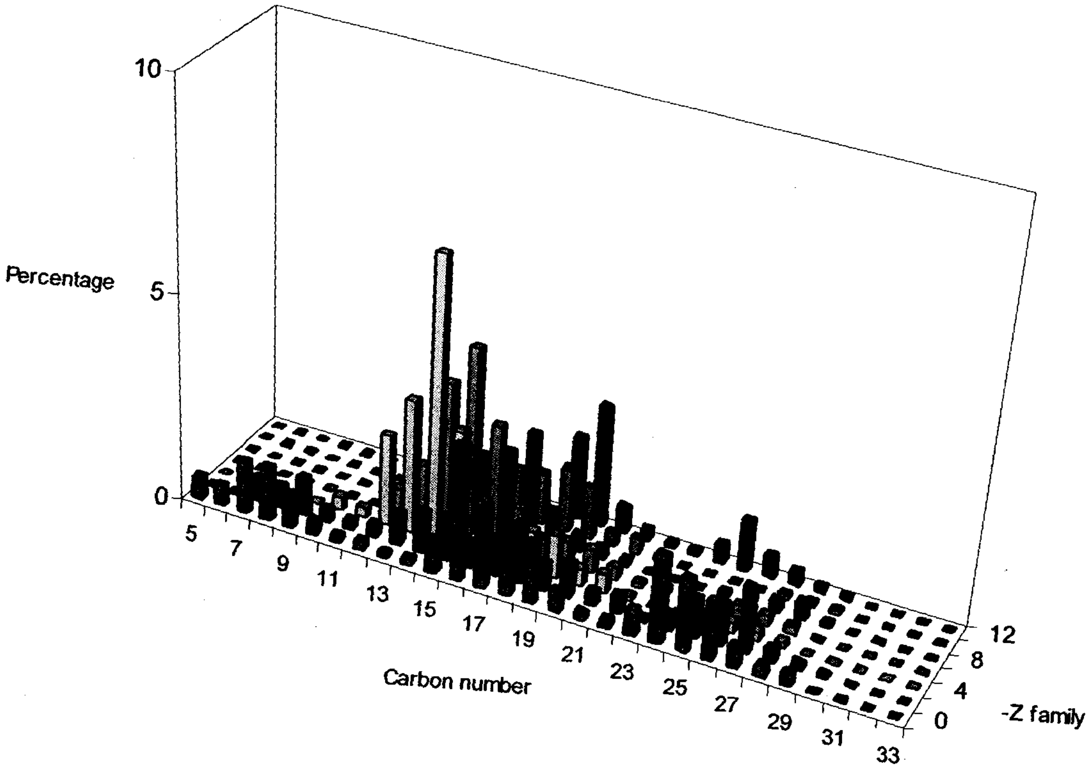

Figure 3.13: Three-dimensional plot from the GC-MS analysis of naphthenic acids found in WIP extract 2.

Data for two samples of WIP-extracted naphthenic acids are presented. Two preparations (herein referred to as WIP extract 1 and 2) were made to ensure sufficient naphthenic acids were available for the experiments. WIP extract 1 was used as the source naphthenic acids for the pH 8 experiments conducted with the clay minerals. WIP extract 2 was used as the source material for the core samples, coke samples and Ellerslie soil sample.

The main difference between the Merichem naphthenic acids (Figure 3.11) and the WIP extracts (Figures 3.12 and 3.13) is the abundance of heavier molecular weight naphthenic acids found in the WIP extracts. The Merichem naphthenic acids have carbon numbers up to C17, whereas the WIP extracts have naphthenic acids with carbon numbers up to C28.

3.5.2 GC-MS Analyses of Naphthenic Acids Solution from Sorption Studies

GC-MS analyses were performed on naphthenic acids solutions following all WIP-extracted naphthenic acid sorption experiments. The GC-MS three-dimensional plots of naphthenic acids present in solution after calcium montmorillonite and Ellerslie soil sorption experiments are presented in Figures 3.14 and 3.15, respectively. Three dimensional plots for the remaining samples are presented in Appendix E.

For statistical purposes, the naphthenic acids are classified into groups first by carbon number then by Z series. Carbon numbers are grouped in three groupings which consist of the low range (C5 to C13), medium range (C14 to C21) and the high range (C22 to C28) (Clemente et al. 2003). Naphthenic acids and naphthenic acids solutions (obtained following a sorption experiment) were then compared by looking at the predominance of each of these groupings. Results of the statistical (t-test) analysis are presented in Table 3.9 and 3.10. Any comparison that yielded a p-value below 0.05 is considered to be statistically different (95 % confidence).

According to the statistics presented in Table 3.9 and 3.10, there was no significant difference in the composition of the WIP-extracted naphthenic acids and that of the WIP-extracted naphthenic acids exposed to the soil minerals tested. The fact that there was no significant difference indicates that there was no detectable, preferential sorption of the naphthenic acids when exposed to the soil materials studied. There was one anomaly found in Table 3.10, where the OW04-02 core produced a significantly different result in the C22 to C28 grouping. This anomaly was due to a GC-MS method detection limit, where the overall concentration of naphthenic acids was too low to detect all the compounds that may be present.

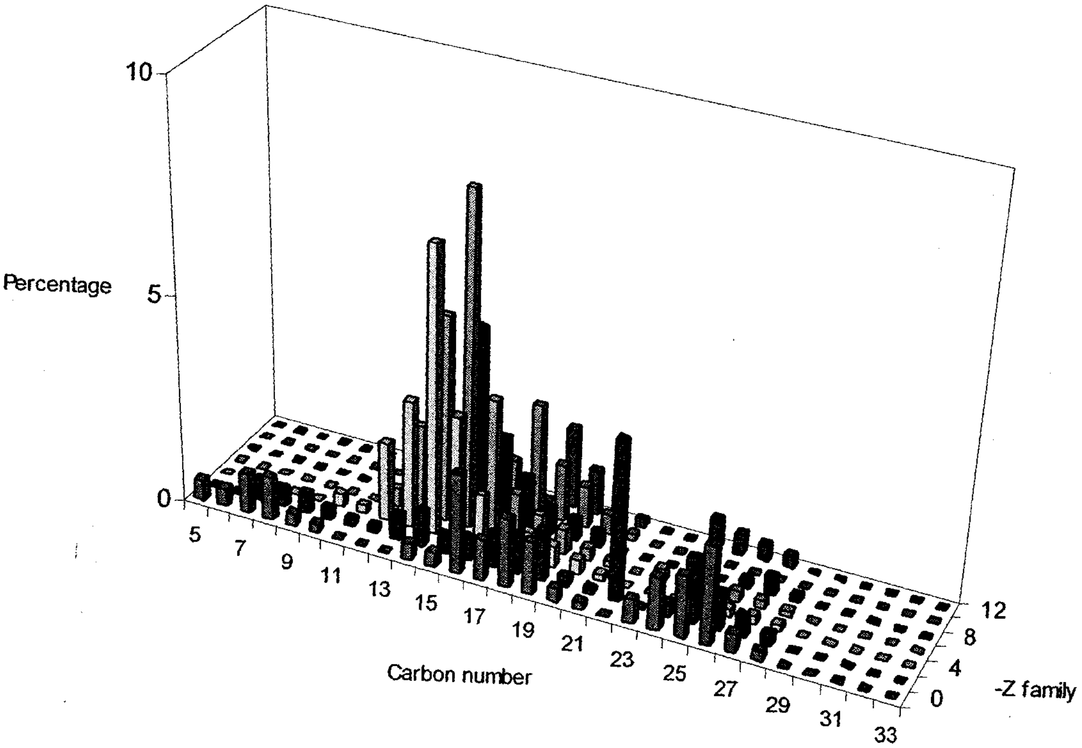

Figure 3.14: Three-dimensional plot from the GC-MS analysis of WIP-extract 1 naphthenic acids with exposure to calcium modified montmorillonite.

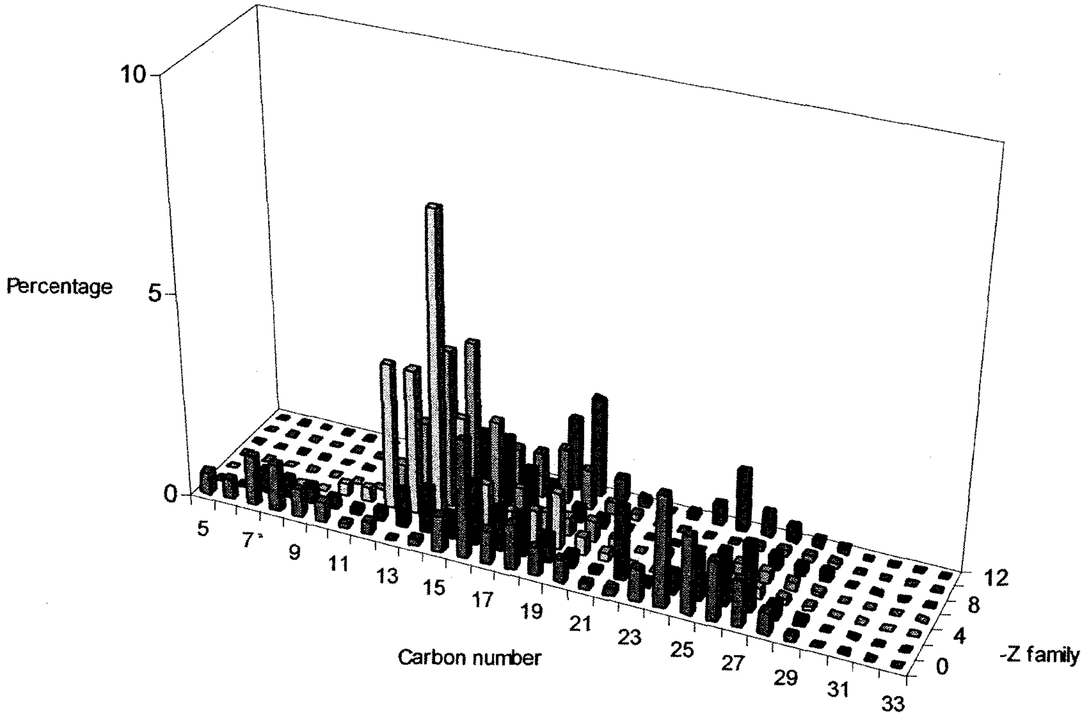

Figure 3.15: Three-dimensional plot from the GC-MS analysis of WIP-extract 2 naphthenic acids with exposure to the Ellerslie soil sample.

Table 3.9: Statistical comparison of the results from GC-MS analyses of naphthenic acids from WIP extract 1 to those of WIP-extract 1 in equilibrium with various clays.

Clay Mineral	p-value									
	Carbon Number			Z Series						
	C5-C13	C14-C21	C22-C23	0	-2	-4	-6	-8	-10	-12
Sodium Illite	0.73	0.8585	0.3884	0.7912	0.229	0.9602	0.6017	0.9602	0.9436	0.6726
Calcium Illite	0.4004	0.7542	0.8881	0.8415	0.7879	0.9649	0.9344	0.9409	0.7945	0.8247
Sodium Montmorillonite	0.8775	0.5632	0.2937	0.6738	0.9326	0.8663	0.8722	0.6561	0.6772	0.9268
Calcium Montmorillonite	0.7995	0.8875	0.6406	0.6459	0.9585	0.7676	0.8687	0.5622	0.606	0.962
Sodium Kaolinite	0.8716	0.8781	0.6738	0.6748	0.9937	0.9763	0.9035	0.6514	0.8006	0.8714
Calcium Kaolinite	0.9993	0.6943	0.3807	0.5748	0.857	0.8205	0.8736	0.579	0.8048	0.6929

Table 3.10: Statistical comparison of the results from GC-MS analyses of naphthenic acids from WIP extract 2 to those of WIP-extract 2 in equilibrium with Ellerslie soil, core soils, or coke samples.

Sample	p-value									
	Carbon Number			Z Series						
	C5-C13	C14-C21	C22-C23	0	-2	-4	-6	-8	-10	-12
Ellerslie	0.7512	0.5308	0.4099	0.9518	0.7264	0.8533	0.9983	0.6861	0.7647	0.9309
OW04-02 6-7 m	0.5842	0.6578	0.0358	0.2556	0.2936	0.638	0.3614	0.568	0.8367	0.2286
OW04-06 4-4.5 m	0.8512	0.8388	0.7889	0.7532	0.9307	0.9955	0.7125	0.5227	0.5632	0.6907
Suncor	0.5587	0.7331	0.9361	0.4236	0.5189	0.8549	0.5158	0.3478	0.5666	0.3253
Syncrude	0.913	0.926	0.9172	0.6106	0.8914	0.8916	0.6667	0.6954	0.9221	0.6543

Chapter 4 Discussion

The discussion in Chapter 4 is presented in the following order:

(i) Salt interaction studies on the concentration of naphthenic acids;
(ii) Summary of clay minerals used in experimentation;
(iii) Sorption of Merichem naphthenic acids to clay minerals;
(iv) Sorption of WIP-extracted naphthenic acids to clay minerals;
(v) Sorption of WIP-extracted naphthenic acids to organic content in soils;
(vi) Sorption of naphthenic acids to Suncor and Syncrude coke; and
(vii) HPLC method sensitivity to bicarbonates;

4.1 Salt Interaction Studies on Concentration of Naphthenic Acids

Several experiments were conducted to determine the effects of various salts found in process-affected waters, on the concentrations of naphthenic acids in solution. Experiments included looking at the effects of sodium chloride, sodium bicarbonate and calcium chloride on Merichem naphthenic acids and the effects of calcium chloride on WIP-extracted naphthenic acids.

For the Merichem naphthenic acids, the salt mixture appeared to cause a higher apparent concentration (Figure 3.1), therefore additional experiments were conducted to identify the compounds of the salt mixture responsible for this trend. The experiment with the sodium chloride component of the salt mixture did not indicate any increase in concentration of Merichem naphthenic acids (Figure 3.2). Experiments with sodium bicarbonate, however showed a higher than expected apparent concentration than the actual concentration (Figure 3.3). This apparent change in concentration of Merichem naphthenic acids increased linearly as the concentration of sodium bicarbonate increased. It was postulated that this could be due to the interference with the derivatization procedure used for the HPLC analysis. This interference may be due to interactions with EDC and NPH-HCl derivatizing agents; however, if this was the case, this interaction would have been observed in samples with bicarbonate alone. This trend was not observed in samples containing only bicarbonate. The derivatization reaction is pH sensitive and has to be kept in acidic conditions for the reaction to take place. It is possible that the bicarbonate content could be buffering the reaction mixture. However, more research would need to be conducted on this issue to determine the actual mechanism of the greater apparent concentration of naphthenic acids in the presence of bicarbonate.

Although the observation that increasing concentrations of bicarbonate yields apparent increases in naphthenic acids concentrations is interesting, this phenomenon would have little or no affect on the results of the sorption studies reported here. The only source of bicarbonate was potassium bicarbonate which was used to buffer the naphthenic acids solutions at pH 8. The buffered naphthenic acids solution contained 1 mL of 1.0 M $KHCO_3$ per 500 mL of stock solution (Section 2.6.1). This gave a final bicarbonate concentration of 0.002 M, which is lower than the first bicarbonate concentration shown in Figure 3.3. Thus, if the HPLC method yielded an increase in the apparent concentration of naphthenic acids, it would be a very small increase.

In addition, the same concentration of bicarbonate was used in vials with sorbent and in the control vials without sorbent, so any apparent increase in concentration caused by the HPLC method would affect both solutions to the same extent. Finally, the affect of the potential increase in apparent naphthenic acids concentrations would be minimal because the difference between the equilibrium concentrations of naphthenic acids in the supernatants from the vials with sorbent and vials without sorbents was used to calculate the amount of naphthenic acids sorbed to the sorbents.

Experiments were conducted with both Merichem naphthenic acids and WIP-extracted naphthenic acids at pH 8 to determine if calcium chloride had any effect on the measured naphthenic acids concentration. Although no apparent trend of the measured naphthenic acids concentration was observed with the WIP-extracted naphthenic acids with calcium chloride was observed (Figure 3.5), the measured concentrations of Merichem naphthenic acids appeared to decrease with increasing calcium chloride concentration (Figure 3.4). The fact that no trend was observed with the WIP-extracted naphthenic acids suggests that this trend is not a result of the derivatization process but rather some other interaction with the naphthenic acids.

The actual structure of naphthenic acids is unknown and it could be postulated that the carboxylic acid functional group could by located anywhere in the structure. It is possible that the higher molecular weight naphthenic acid compounds have carboxylic acid groups that are hindered sterically, or in other words blocked by adjacent R groups. This can lead to an explanation that calcium can more easily bind to two lower molecular weight naphthenic acid groups which would neutralize the charge and lead to precipitation. The heavier molecular weight naphthenic acids, found in the WIP-extract, may have too many interfering R groups causing calcium to bond to one naphthenic acid in its carboxylate form and producing a net positive charge and remaining soluble in solution. This preferential association with calcium is indicated in later sections (Sections 4.2 to 4.4) as this trend seems to also occur when comparing the sorption of the Merichem and WIP-extracted naphthenic acids to clay minerals. However, more work is needed to determine the effects of calcium chloride on naphthenic acids solubility.

4.2 Summary of Clay Minerals used in Experimentation

The clay minerals used in experimentation were purchased from the Clay Repository at Purdue University. Kaolinite (KGa-1b), illite (IMt-1) and montmorillonite (SAz-1) were treated with a dilute solution of hydrochloric acid followed by a treatment of calcium or sodium salt to produce a calcium or sodium clay of each parent clay. The reason for treating these clays was two-fold: (i) to remove carbonates that appeared to be present in early experimentation (Table 3.3); (ii) to saturate the exchangeable cations on the clay surface with a known cation (i.e. calcium or sodium).

The different parent materials were used to determine the effects of clay structure on the sorption of naphthenic acids. The clay mineral structures are discussed in detail in Section 1.3.1. The main differences observed among clay minerals include outside surface structure and CEC.

The available outside surface structure of illite and montmorillonite is primarily composed of tetrahedral SiO_2 subunits which are akin to the surface of sand (Bohn et al. 1985). Kaolinite is slightly different with one side exposing a tetrahedral surface layer of SiO_2 with the opposite side exposing a layer of hydroxyl groups. The SiO_2 surface layers are relatively inert and depend greatly upon the internal octahedral layer to determine the clay mineral properties of illite and montmorillonite. The octahedral layer is typically negatively charged due to isomorphic substitution and this charge is satisfied on the clay mineral surface by cations. The accumulated charge formed in the clay is known as the CEC. For kaolinite, the properties are determined by the surface hydroxyl layers. Surface hydroxyl groups can also be found along the edges of montmorillonite and illite. Hydroxyl groups are pH sensitive and produce charges based on the solution pH (Bohn et al. 1985).

The cation used to satisfy the magnitude of the CEC of the clay mineral can affect the mineral properties which include its capability to sorb organic compounds such as naphthenic acids. Divalent and higher charged cations found on the clay mineral surfaces are known to act as “bridges” between the clay mineral surfaces and anionic compounds (Dubus et al. 2001), such as naphthenic acids in the carboxylate form.

At pH 6, both kaolinite and illite showed some sorption of naphthenic acids. In particular, the calcium modified illite showed the greatest sorption (Table 3.4). The important factor dictating the clay’s capability to sorb these organic acids is its charge. At pH 6, these clays are negatively charged and therefore can be expected that very little, if any, sorption will occur because the carboxylic acid group of the naphthenic acids is mostly dissociated into its carboxylate form under these conditions (Dubus et al. 2001; Khalil and Abdelhakim 2002; Meyers and Quinn 1973; Peng et al. 2002; Tunega et al. 2004; Zou et al. 1997). Low sorption was observed in these experiments.

4.3 Sorption of Merichem naphthenic acids to clay minerals

Figures 3.6 to 3.9 illustrate the sorption isotherms for clay minerals with Merichem naphthenic acids at initial pH of 6 and Table 3.4 summarizes the K_D values derived from these isotherms. Comparing the K_D values at pH 6 (Table 3.4) and at pH 8 (Table 3.5), there seems to be an effect of pH of the solution on the sorption of naphthenic acids to some of the studied clay minerals. The pH 6 experiments with the Merichem naphthenic acids exhibited sorption to the clay minerals, with K_D values ranging from 18 to 57 mL g^{-1} (Table 3.4); whereas the pH 8 experiments showed little sorption, with values ranging from 0 to 10 mL g^{-1} (Table 3.5). The only pH 8 experiments to show any indication of sorption were the calcium modified illite and montmorillonite clays (Table 3.5). This pH dependency can be attributed to the state of the carboxylic acid functional group on the naphthenic acids as indicated by several researchers (Dubus et al. 2001; Khalil and Abdelhakim 2002; Meyers and Quinn 1973; Peng et al. 2002; Tunega et al. 2004; Zou et al. 1997). This loss of sorption capability as pH increases is related to the acid dissociation constant (Ka) of naphthenic acids ranges from 10^{-5} to 10^{-6} (Brient et al. 1995). In light of the literature and the Merichem experiments conducted, the primary form of sorption occurs as hydrogen bonding of the hydroxyl portion of the carboxylic acid functional group to the clay mineral surface or to the water molecules coordinated around the clay mineral surfaces. The pH dependency supports this type of bonding mechanism.

The higher K_D values at pH 6 may also be the result of the precipitation of naphthenic acids at lower pH. To demonstrate that the solubility of naphthenic acids decreases with pH, a solution of Merichem acids (150 mg L^{-1}) was prepared at pH 10 and titrated with 0.05 M HCl (Scott 2005). The results are shown as Figure 4.1. As the pH decreased, naphthenic acids began to precipitate, and the turbidity of the preparation increased (as measured at 600 nm). For example, when pH decreased from 8 to 6, there was a 5-fold increase in the turbidity.

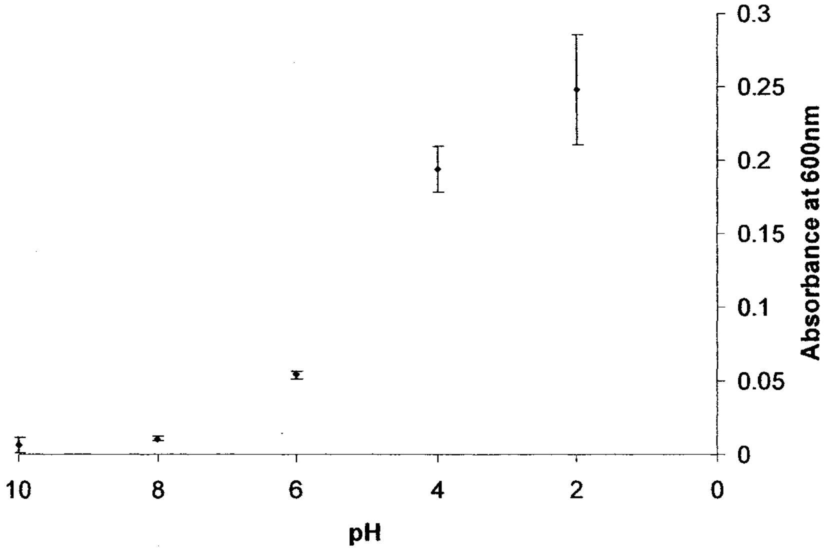

Figure 4.1: Absorbance of Merichem naphthenic acids as a function of pH. Adapted from Scott (2005).

Once the pH of the solution rises beyond the pKa of naphthenic acids (approximately 5 to 6), the capability of the naphthenic acids to sorb to the clay mineral diminishes as seen in the pH 8 Merichem naphthenic acid experiments. The formation of the negative charge on the carboxylic acid functional group on the naphthenic acids will cause repulsion between the naphthenates and the negatively charged clay mineral surface. This repulsion would therefore lead to no sorption of naphthenates by the clay surface. However, the calcium modified illite and montmorillonite (Table 3.5) in the pH 8 experiments with the Merichem naphthenic acids indicated some sorption ($K_D \neq 0$). The sorption may be due to the presence of calcium ions in solution and associated with the clay surface. Divalent or higher charged cations are known to act as a bridge between clay mineral surfaces and anionic compounds (Dubus et al. 2001). The presence of Ca^{2+} at the surface of both the calcium modified illite and the calcium modified montmorillonite could therefore act as a bridge between the negatively charged clay mineral surface and the negatively charged naphthenic acids. This calcium bridging would allow naphthenates to sorb to the negative surface, and hence a small, but statistically significant K_D (10 mg L^{-1}) was measured (Table 3.5).

Meyers and Quinn (1973) studied the sorption of straight chain fatty acids containing 14 to 18 carbons to kaolinite, bentonite, illite and montmorillonite in conditions akin to sea water. They observed sorption that ranged from 3.1 to 6.5 % for myristic acid (C_{14}) and 20 to 91 % for stearic acid (C_{18}) at pH 8 and in a solution of 30 g NaCl kg^{-1} water. The low sorption of myristic acid supports the lack of sorption observed with the Merichem naphthenic acids at pH 8 because the majority (about 75%) of Merichem naphthenic acids are below 14 carbons in size (Figure 3.11). Of note in the study by Meyers and Quinn (1973) is the high concentration of salt used in the sorption experiments. Meyers and Quinn (1973) indicate that the salt concentration has the effect of increasing the amount of fatty acids adsorbed to clay minerals on average by a factor of three. There was no discussion on whether there was any significant precipitation of the fatty acids due to the high salt concentrations. Precipitation of the fatty acids would result in an apparent removal of the fatty acids from solution, which could be incorrectly viewed as sorption. Nevertheless, the data of Meyers and Quinn (1973) show that the sorption of fatty acids to clay minerals is low and is highly dependent on the salt concentration of the fatty acid solution.

4.4 Sorption of WIP-Extracted Naphthenic Acids to Clay Minerals

The K_D values for WIP-extracted naphthenic acids in the presence of clay minerals at pH 8 are presented in Table 3.6. Comparing the K_D values of the WIP-extracted naphthenic acids to those for Merichem naphthenic acids at pH 8, both sets of data showed similar trends (i.e. very little to no sorption). The only difference between the two sets of data was that the WIP-extracted naphthenic acids showed no significant sorption to calcium modified illite (Table 3.6). The lower response to calcium of the WIP-extracted naphthenic acids when compared to the Merichem naphthenic acids could be due to the molecular weight and hence size of the naphthenic acids. It is possible the higher molecular weight naphthenic acids in the WIP-extracted naphthenic acids have difficulty binding through the calcium to the clay surface. Steric hinderances may limit the availability of the carboxylate functional group to interact with calcium which allows sorption to the clay mineral surface.

GC-MS analyses were conducted on all the WIP-extracted naphthenic acids experiments (Figures 3.14, 3.15, and Appendix E) to determine if any preferential sorption of different molecular weight groupings of naphthenic acids would occur. The results of the GC-MS analysis were compared to GC-MS analysis of the original WIP-extracted naphthenic acids (Figures 3.12 and 3.13). The results of this comparison indicate that no detectable preferential sorption occurred because none of the experiments produced significantly different results (Table 3.9). The experiments of the WIP-extract with calcium montmorillonite (Table 3.6) indicated some sorption in batch experiments; however the GC-MS analyses these extracted naphthenic acids showed no preferential sorption of naphthenic acids when compared to the GC-MS analyses of the original WIP-extracted naphthenic acids (Table 3.9). There was some expectation that the calcium montmorillonite would show some preferential sorption because some capability to sorb the WIP-extracted naphthenic acids was evident in the batch experiments. However, it is possible that the GC-MS method may not be sensitive enough to detect any preferential sorption that may occur when sorption is limited.

Meyers and Quinn (1973) suggest that, as the chain length of a fatty acid increases, that the capability of sorption to clay minerals would also increase. The GC-MS data from the analysis of the WIP extract experiments does not support that there is any preferential sorption. As discussed in the previous section, Meyers and Quinn (1973) conducted their experiments in a saline environment (30 g NaCl kg^{-1} water). It is possible that all that the increased sorption capability observed by Meyers and Quinn (1973) may be the result of the precipitation of the fatty acids and may not indicate actual increased sorption to the clay minerals.

4.5 Sorption of WIP-Extracted Naphthenic Acids to Organic Content in Soil

Because little or no sorption of naphthenic acids to clay minerals was found based on previous experiments, additional experiments were conducted at pH 8 to determine if naphthenic acids would sorb to soils or minerals containing some organic matter. Core samples OW04-02 (depth 6-7 m) and OW04-06 (depth 4-4.5 m) were chosen as the samples for experimentation to represent a range of organic content (Table 3.1). In comparison to other soils, these samples contained relatively low organic carbon content of 0.09 and 0.53 %, respectively. Therefore the Ellerslie soil sample was chosen as a higher organic containing soil (3.6 %, Luther et al. 1998). None of the tested samples showed any statistically significant sorption (Table 3.7). The GC-MS analysis did not indicate any preferential sorption either (Figure 3.15, Table 3.10). A K_D of 0 mL g^{-1} also translates to a K_{OC} of 0 mL g^{-1}.

Peng et al. (2002) showed similarly low K_{OC} results when studying single-ring model naphthenic acids sorption to soil samples. Sorption of the single ring compound, MCHA, yielded K_{OC} values ranging from 8 to 11 mL g^{-1}. Typically, increases in fatty acid chain length shows an increasing trend in sorption to organic content (Pfannkoch et al. 2003). It would be expected that the WIP-extracted naphthenic acids should show more sorption than the model single ring MCHA because the average naphthenic acid structure in the extracts ($Z = -4$, $C = 17$) is much larger than MCHA.

Since K_{OC} values for naphthenic acids mixtures were not available in the literature, an attempt was made to estimate K_{OC} from empirical relationships published in the literature. Delle Site (2001) and Dragun (1998) present a review of several empirical relationships commonly used to estimate K_{OC} from K_{OW}, the octanol-water partition coefficient. These relationships typically take the form of a linear relationship between log K_{OC} and log K_{OW}, that is:

$$\log K_{OC} = a \log K_{OW} + b$$

where a and b are constants. Using a log K_{OW} of 2.38 (pH = 7.1) for naphthenic acids published in CONRAD (1998), five relationships available in Delle Site (2001) were used to estimate K_{OC}. The estimated K_{OC} values ranged from 40 (using the relationship proposed by Schwarzenbach and Westall (1981), as cited in Delle Site (2001)) to 150 mL g^{-1} (using the relationship proposed by Karickhoff et al. (1979), as cited in Delle Site (2001)).

Both the experimentally determined K_{OC} and the estimated K_{OC} values suggest that the K_{OC} value for naphthenic acids in soil systems ranges from 0 to approximately 150 mL g^{-1}, if a log K_{OW} of 2.38 is used. K_{OC} values in this range are considered low and imply that little to no naphthenic acids are sorbed to soils. McCall et al. (1980) suggest that compounds with K_{OC} values ranging from 0 to 150 mL g^{-1} will have very high to high mobility in soils.

4.6 Sorption of Naphthenic Acids to Suncor and Syncrude Coke

Based on the tabulated values presented in Table 3.8, the Suncor and Syncrude coke samples showed no sorption of the naphthenic acids. A recent review conducted by Scott and Fedorak (2004) indicate that little is known about the properties of coke. They did indicate however, that activated coke has had some success as a replacement for activated charcoal.

Coke is a carbonaceous solid containing mostly carbon. The Suncor and Syncrude coke samples contain 82 to 84 % and 81 to 84 % carbon; and 4% and 2% hydrogen by weight respectively (Chakravorty 1992; Chung et al. 1996). It was theorized that coke resembles a asphaltene molecule of structure $C_{420}H_{496}N_6S_{14}O_4V$ (Strausz et al. 1992). This asphaltene structure has nearly 10 % hydrogen content by weight whereas the Suncor and Syncrude coke samples used in this work have much lower hydrogen content. The lack of hydrogen present supports a more graphite-like material.

Sorption to graphite is highly dependent on the dispersion interactions between the π - orbitals delocalized along the basal plane of graphite and π - bonds in organic compounds (Coughlin and Ezra 1968; Pimenta and Kilduff 2005). This interaction is what gives activated carbon and graphite the capability to interact with phenolic and aromatic compounds. However, compounds that are primarily saturated hydrocarbons or contain saturated hydrophobic tails may not be able to interact since there is a lack of π – bonds to disperse the delocalized π – orbitals in graphite (Coughlin and Ezra 1968). This supports the lack of sorptive capability of naphthenic acids observed because there is a lack of π – bonds in the hydrophobic region.

Another explanation for the low ability for coke to sorb is the low coke surface area. The low surface area will affect sorption due to the limited amount of exposed sorption sites that can exist on a surface. Surface areas for Suncor and Syncrude coke samples were reported by Fedorak and Coy (2006) as 11 and 2.9 $m^2\ g^{-1}$ respectively. Surface area of activated carbon was reported by Coughlin and Ezra (1968) to be approximately 1200 $m^2\ g^{-1}$.

The oil sand companies are looking for a use for the vast amounts of coke being generated in the bitumen upgrading process. The findings of the batch sorption tests indicate that these cokes cannot be used to retard the movement of naphthenic acids.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

Illite, kaolinite and montmorillonite showed very little difference in sorption of Merichem and WIP-extracted naphthenic acids. At pH 6, all the minerals tested indicated some sorption. The sodium and calcium modified kaolinite and sodium modified illite showed sorption of approximately 20 mL g^{-1} of Merichem naphthenic acids at pH 6. The calcium modified illite showed sorption of approximately 57 mL g^{-1} of Merichem naphthenic acids at pH 6. At pH 8, only the calcium modified illite and montmorillonite indicated any significant sorption with the Merichem naphthenic acids. These results indicate that the calcium cations present on the clay mineral surfaces are playing an important role in the sorption of naphthenic acids and that the type of the clay mineral has little, if any, importance.

The Merichem naphthenic acids results clearly showed the dependency on pH for the capability of naphthenic acids to sorb to clay minerals. At pH values near or more acidic than the pKa of the Merichem naphthenic acids, the Merichem naphthenic acids were capable of sorption to clay minerals. When the naphthenic acids were in an environment with a more alkaline pH (i.e. pH 8), sorption was either minimal or non-existent. Only the calcium modified illite and montmorillonite clay minerals indicated any sorption at pH 8.

The extracted naphthenic acids from the WIP tailings pond indicated very little difference in the sorption when compared to the Merichem naphthenic acids at pH 8. The WIP-extracted naphthenic acids did show a lower capability to sorb to the calcium modified clay minerals. This decrease in sorption capacity of the WIP-extracted naphthenic acids may be attributed to sterically hindered carboxylic acids functional groups in the larger naphthenic acids compounds found in WIP.

Naphthenic acids did not show statistically significant sorption to soils containing organic matter at pH 8. Because naphthenic acids show little to no sorption to clay minerals and organic containing soils in alkaline conditions, neither clay minerals nor organic containing soils are important factors and contributors to the sorption of naphthenic acids at these conditions.

Samples of coke obtained from Syncrude and Suncor did not show any significant sorption of naphthenic acids. This lack of sorption can be attributed to the low affinity of naphthenic acids for the coke or to a lack of binding locations of coke due to the low surface area.

5.2 Recommendations

It is recommended that future studies be conducted to determine the effect of bicarbonate on the HPLC method. The bicarbonate content seems to improve the sensitivity of the method but studies to confirm the mechanisms must be conducted.

The solubility of naphthenic acids in the environment is not well known and further experimentation needs to be conducted to determine the extent of the role of pH and salts on its solubility.

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Appendix A: Clay Elemental Analysis

Table A 1: Elemental analysis of the major elements in montmorillonite, SAz-1. Compiled from USGS Spectroscopy Lab (USGS 2006)

Composition	Amount (wt%)
SiO_2	60.40
TiO_2	0.24
Al_2O_3	17.60
Fe_2O_3	1.42
FeO	0.08
MnO	0.10
MgO	6.46
CaO	2.82
Na_2O	0.06
K_2O	0.19
F	0.29
Ignition Loss	9.91
Total	99.30

Table A 2: Elemental analysis of the major elements in illite, IMt-1. Compiled from USGS Spectroscopy Lab (USGS 2006)

Composition	Amount (wt%)
SiO_2	52.10
TiO_2	0.79
Al_2O_3	21.90
Fe_2O_3	6.44
MnO	< 0.02
MgO	2.39
CaO	1.07
Na_2O	0.30
K_2O	7.84
P_2O_5	0.10
Ignition Loss	6.91
Total	99.56

Table A 3: Elemental analysis of the major elements in kaolinite, KGa-1. Compiled from USGS Spectroscopy Lab (USGS 2006)

Composition	Amount (wt%)
SiO_2	45.00
TiO_2	1.58
Al_2O_3	38.00
Fe_2O_3	0.26
FeO	0.02
MnO	0.00
MgO	0.02
CaO	0.02
Na_2O	0.01
K_2O	0.04
P_2O_5	0.05
F	0.01
Ignition Loss	14.31
Total	99.38

Appendix B: Agilent 1100 Chemstation HPLC Method

Run Time Checklist

Pre-Run Cmd/Macro : off

Data Acquisition : on

Standard Data Analysis : on

Customized Data Analysis : off

Save GLP Data : off

Post-Run Cmd/Macro : off

Save Method with Data: skipped - no ACQ running

1100 Quaternary Pump 1

Control
- Column Flow : 1.500 ml/min
- Stoptime : 7.00 min
- Posttime : 4.50 min

Solvents
- Solvent A : 30.0 % (MQH2O)
- Solvent B : Off
- Solvent C : Off
- Solvent D : 70.0 % (MEOH)

PressureLimits
- Minimum Pressure : 0 bar
- Maximum Pressure : 300 bar

Auxiliary
- Maximal Flow Ramp : 100.00 ml/min^2
- Primary Channel : Auto
- Compressibility : 100*10^-6/bar
- Minimal Stroke : Auto

Store Parameters
- Store Ratio A : Yes
- Store Ratio B : Yes
- Store Ratio C : Yes

```
    Store Ratio D               : Yes
    Store Flow                  : Yes
    Store Pressure              : Yes

Agilent 1100 Contacts Option
============================

    Contact 1                   : Open
    Contact 2                   : Open
    Contact 3                   : Open
    Contact 4                   : Open

Timetable

    Time   Solv.B Solv.C  Solv.D Flow  Pressure
    |--------|-------|---------|--------|----------|-------|
      0.00   0.0    0.0     70.0    1.500   300
      4.00   0.0    0.0    100.0    1.500   300

Agilent 1100 Contacts Option Timetable
======================================

Timetable is empty


==============================================================
              Agilent 1100 Diode Array Detector 1
==============================================================

Signals

    Signal       Store   Signal,Bw     Reference,Bw        [nm]
      A:         Yes     400  10       510  60
      B:         No      400  10       500  60
      C:         No      400  10       525  60
      D:         No      230   8       320  10
      E:         No      400  10       520  20

Spectrum
    Store Spectra                 : All
    Range from                    : 190 nm
    Range to                      : 700 nm
    Range step                    : 2.00 nm
```

```
    Threshold                        : 1.00 mAU

Time
    Stoptime                         : As pump
    Posttime                         : Off

Required Lamps
    UV lamp required                 : Yes
    Vis lamp required                : Yes

Autobalance
    Prerun balancing                 : Yes
    Postrun balancing                : No
    Margin for negative Absorbance   : 100 mAU

Peakwidth                            : >  0.2 min
Slit                                 : 4 nm

Analog Outputs
    Zero offset ana. out. 1          : 5 %
    Zero offset ana. out. 2          : 5 %
    Attenuation ana. out. 1          : 1000 mAU
    Attenuation ana. out. 2          : 1000 mAU


Agilent 1100 Contacts Option
============================

    Contact 1               : Open
    Contact 2               : Open
    Contact 3               : Open
    Contact 4               : Open


Timetable is empty


Agilent 1100 Contacts Option Timetable
======================================

Timetable is empty
```

```
==========================================================================
           Agilent 1100 Autosampler 1
==========================================================================

Injection
  Injection Mode           : Needle Wash
  Injector volume          : 60.0 µl
  Wash Vial                : 1

Auxiliary
  Drawspeed                : 200 µl/min
  Ejectspeed               : 200 µl/min
  Draw position            : -2.0 mm

Time
  Stoptime                 : As Pump
  Posttime                 : Off


==========================================================================
           Agilent 1100 Column Thermostat 1
==========================================================================

Temperature settings
  Left temperature         : 40.0°C
  Right temperature        : Same as left
  Enable analysis          : When Temp. is within setpoint +/-  0.8°C
  Store left temperature   : Yes
  Store right temperature  : No

Time
  Stoptime                 : As pump
  Posttime                 : Off

Column Switching Valve     : Column 1

Timetable is empty


==========================================================================
             Integration Events
==========================================================================

Results will be produced with the enhanced integrator.
```

```
-----------------------------------------------------------------
        Default Integration Event Table "Event"
-----------------------------------------------------------------
           Event                          Value   Time
|-------------------------------------------|------------|-------|
Initial Slope Sensitivity                  1.000  Initial
Initial Peak Width                         0.040  Initial
Initial Area Reject                        1.000  Initial
Initial Height Reject                      1.700  Initial
Initial Shoulders                          OFF    Initial

-----------------------------------------------------------------
    Detector Default Integration Event Table "Event_ADC"
-----------------------------------------------------------------
           Event                          Value   Time
|-------------------------------------------|------------|-------|
Initial Slope Sensitivity                  1.000  Initial
Initial Peak Width                         0.040  Initial
Initial Area Reject                        1.000  Initial
Initial Height Reject                      1.700  Initial
Initial Shoulders                          OFF    Initial

-----------------------------------------------------------------
    Detector Default Integration Event Table "Event_FLD"
-----------------------------------------------------------------
           Event                          Value   Time
|-------------------------------------------|------------|-------|
Initial Slope Sensitivity                  1.000  Initial
Initial Peak Width                         0.040  Initial
Initial Area Reject                        1.000  Initial
Initial Height Reject                      1.700  Initial
Initial Shoulders                          OFF    Initial

-----------------------------------------------------------------
    Detector Default Integration Event Table "Event_VWD"
-----------------------------------------------------------------

           Event                          Value   Time
|-------------------------------------------|------------|-------|
Initial Slope Sensitivity                  1.000  Initial
Initial Peak Width                         0.040  Initial
Initial Area Reject                        1.000  Initial
Initial Height Reject                      1.700  Initial
Initial Shoulders                          OFF    Initial
```

```
-------------------------------------------------------------------
      Detector Default Integration Event Table "Event_ECD"
-------------------------------------------------------------------
           Event                             Value    Time
|--------------------------------------------|-------------|-------|
 Initial Slope Sensitivity                    1.000  Initial
 Initial Peak Width                           0.040  Initial
 Initial Area Reject                          1.000  Initial
 Initial Height Reject                        1.700  Initial
 Initial Shoulders                             OFF   Initial

-------------------------------------------------------------------
      Detector Default Integration Event Table "Event_MWD"
-------------------------------------------------------------------
           Event                             Value    Time
|--------------------------------------------|-------------|-------|
 Initial Slope Sensitivity                    1.000  Initial
 Initial Peak Width                           0.040  Initial
 Initial Area Reject                          1.000  Initial
 Initial Height Reject                        1.700  Initial
 Initial Shoulders                             OFF   Initial

-------------------------------------------------------------------
      Detector Default Integration Event Table "Event_DAD"
-------------------------------------------------------------------
           Event                                 Value  Time
|--------------------------------------------|-------------|---------|
 Initial Slope Sensitivity                    0.100  Initial
 Initial Peak Width                           0.400  Initial
 Initial Area Reject                          0.010  Initial
 Initial Height Reject                        0.010  Initial
 Initial Shoulders                             OFF   Initial
 Baseline Hold ON                             0.100
 Integration ON                               2.900
 Area Sum ON                                  2.900
 Area Sum OFF                                 6.020
 Integration OFF                              6.030
 Baseline Now                                 6.230

Apply Manual Integration Events     : No

Advanced Baseline                   : No

Peak Top Type                       : parabolic interpolation
```

```
=====================================================================
                    Specify Report
=====================================================================

Destination:                          Printer
Quantitative Results sorted by:       Signal
Report Style:                         Short
Sample info on each page:             No
Add Chromatogram Output:              Yes
Chromatogram Output:                  Portrait
Size in Time direction:               100 % of Page
Size in Response direction:           25 % of Page

=====================================================================
                    Signal Options
=====================================================================

Include: Axes, Retention Times, Baselines, Tick Marks
Font    : Arial, Size: 8

Ranges: Use Ranges          | Min Value | Max Value |
                   ---------+-----------+-----------+
                    Time    |   0.000   |   7.000   |
                   Response |  -5.000   |  50.000   |

Multi Chromatograms: Separated, All the same Scale

=====================================================================
                    Calibration Table
=====================================================================


Calib. Data Modified  :

Calculate                  : Area Percent

Rel. Reference Window      : 5.000 %
Abs. Reference Window      : 0.000 min
Rel. Non-ref. Window       : 5.000 %
Abs. Non-ref. Window       : 0.000 min
Uncalibrated Peaks         : not reported
Partial Calibration        : Yes, identified peaks are recalibrated
Correct All Ret. Times     : No, only for identified peaks
```

```
Curve Type                 : Linear
Origin                     : Included
Weight                     : Equal

Recalibration Settings:
Average Response           : Average all calibrations
Average Retention Time     : Floating Average New 75%

Calibration Report Options:
  Printout of recalibrations within a sequence:
    Calibration Table after Recalibration
    Normal Report after Recalibration
  If the sequence is done with bracketing:
    Results of first cycle (ending previous bracket)


=====================================================================
                Peak Sum Table
=====================================================================

***No Entries in table***
=====================================================================
```

Appendix C: Salt Studies

Table C 1: HPLC data from the salt mix experiment used to produce Figure 3.1.

Sample Name	Salt Percent (%)	Naphthenic Acids	
		Concentation (mg L^{-1})	Standard Deviation (mg L^{-1})
Salt Mix	0	83.0	2.1
	10	85.1	3.4
	20	87.4	2.4
	100	99.5	2.2

Table C 2: HPLC data for the sodium chloride experiment used to produce Figure 3.2.

Sample Name	Salt Concentration (mol L^{-1})	Naphthenic Acids	
		Concentation (mg L^{-1})	Standard Deviation (mg L^{-1})
Sodium Chloride	0.000	101.4	4.9
	0.008	100.2	4.1
	0.016	105.2	4.2
	0.024	101.5	3.3
	0.032	105.9	4.4
	0.040	102.8	2.2

Table C 3: HPLC data for the sodium bicarbonate experiment used to produce Figure 3.3.

Sample Name	Salt Concentration (mol L^{-1})	Naphthenic Acids	
		Concentation (mg L^{-1})	Standard Deviation (mg L^{-1})
Sodium Bicarbonate	0	101.4	4.9
	0.003	118.1	10.4
	0.006	118.3	2.6
	0.009	126.2	1.5
	0.012	134.4	1.5
	0.015	137.6	0.7

Table C 4: HPLC data for the calcium chloride experiment used to produce Figure 3.4.

Sample Name	Salt Concentration (mol L^{-1})	Naphthenic Acids	
		Concentation (mg L^{-1})	Standard Deviation (mg L^{-1})
Calcium Chloride	0	83.0	2.1
	0.001	75.6	1.5
	0.005	73.8	2.0
	0.01	70.5	3.0
	0.05	66.6	2.5
	0.1	68.4	4.0

Table C 5: HPLC data for the calcium chloride experiment used to produce Figure 3.5.

Sample Name	Salt Concentration (mol L^{-1})	Naphthenic Acids	
		Concentation (mg L^{-1})	Standard Deviation (mg L^{-1})
Calcium Chloride	0	136.4	2.6
	0.001	131.6	1.5
	0.005	128.8	2.7
	0.01	132.8	5.4
	0.05	130.2	1.5
	0.1	129.8	2.1

Appendix D: Isotherm Data and Calculation

Guide to Tables D 1 to D 22

Column 1: Column 1 is the sample label. The labels that contain water in the label or naphthenic acids alone are sample controls; the remaining labels indicate samples. Controls do not have values in the tables past Column 5.

Column 2: The mass of the clay, sand, soil or coke sample (g) transferred to the vial.

Column 3: The mass of the solution (g) transferred to the vial. The type of solution transferred is indicated in the sample label (Column 1).

Column 4: The value indicated in this column refers to the concentration of naphthenic acids (mg L^{-1}) in the stock solution (determined by HPLC) prior to pH modification, buffer addition, and delivery to sample vials. The difference between this column and Column 5 will show the cumulative affects of dilution by pH modification, buffer addition, sorption to vial walls and precipitation. This column may not exist in all experiments.

Column 5: The value indicated in this column refers to the equilibrium concentration (mg L^{-1}) of naphthenic acids controls or samples determined by HPLC after 40 hours of contact time.

Column 6: This value indicates the result of the unequal variance t-test between the sample naphthenic acids concentrations in the current row and the respective naphthenic acids concentrations in the control. Any $p\text{-value} < 0.05$ is considered significant (95% confidence). If a p-value is < 0.05, the columns that follow (7 to 9) are calculated. If a p-value is > 0.05, Columns 7 to 9 are left blank.

Column 7: Mass of naphthenic acids in the sample solution at equilibrium conditions [Calculation: (Column 3)*(Column 5)*1mL water/1g water*1L/1000mL*1000μg/1mg] (μg).

Column 8: Mass of naphthenic acids expected to be sorbed into the clay. [Calculation: [(Sample Column 3)*(Control Column 5)*1mL water/1g water*1L/1000mL* 1000μg/1mg] – (Sample Column 7)] (μg).

Column 9: C_a, which is the amount of naphthenic acids sorbed per gram of clay, sand, soil or coke. **Y-axis on the isotherm diagrams**. [Calculation: (Column 8) / (Column 2)] (μg naphthenic acids / g clay, sand, soil or coke). If a value of 0* is placed in this column, a significant value of sorption was indicated by the t-test; however, the amount calculated as sorbed was negative and was therefore assumed as zero.

Column 10: The K_D value reported in this column only in cases where the K_D can not be determined through a linear isotherm plot as per Section 2.8. This column only exists in Tables D 8, D 9, D 10 and D 17.

Table D 1: Data and calculations used to create the isotherm for sodium kaolinite and Merichem naphthenic acids at pH 6, Figure 3.6.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)	t-Test (6) (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g soil) (9)
			T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	29.8858	2.1				
Sodium Kaolinite + Water	0.2819	29.8687	2.1				
	0.2984	29.8839	2.1				
	0.2745	29.6979	2.2				
15 mg/L Merichem Naphthenic Acids	0	29.8373	15.1				
	0	29.8655	15.2				
	0	29.9197	14.9				
25 mg/L Merichem Naphthenic Acids	0	29.8158	24.0				
	0	29.8208	25.0				
	0	29.8957	25.2				
50 mg/L Merichem Naphthenic Acids	0	29.7953	48.0				
	0	29.8679	46.3				
	0	29.8233	47.3				
75 mg/L Merichem Naphthenic Acids	0	29.8695	62.0				
	0	29.7908	66.6				
	0	29.7567	64.0				
100 mg/L Merichem Naphthenic Acids	0	29.7925	92.7				
	0	29.7891	93.0				
	0	29.8009	91.9				
150 mg/L Merichem Naphthenic Acids	0	29.785	134.4				
	0	29.8127	137.1				
	0	29.8932	137.9				
200 mg/L Merichem Naphthenic Acids	0	29.8001	155.2				
	0	29.798	161.2				
	0	29.8463	156.9				
Sodium Kaolinite and 15 mg/L Merichem Naphthenic Acids	0.2898	29.8834	14.9	0.212			
	0.2792	29.8106	13.5				
	0.3175	29.8397	14.5				
Sodium Kaolinite and 25 mg/L Merichem Naphthenic Acids	0.2842	29.9328	18.9	<0.001	565	175	617
	0.2900	29.9335	19.2		575	166	572
	0.3016	29.8843	20.2		603	137	453
Sodium Kaolinite and 50 mg/L Merichem Naphthenic Acids	0.3560	29.8698	32.6	0.005	975	435	1223
	0.2848	29.7664	33.4		995	410	1440
	0.3349	29.8479	36.9		1101	308	920
Sodium Kaolinite and 75 mg/L Merichem Naphthenic Acids	0.3100	29.8465	43.9	0.004	1310	607	1958
	0.3002	29.8174	44.3		1321	594	1979
	0.2821	29.7567	43.8		1305	606	2148
Sodium Kaolinite and 100 mg/L Merichem Naphthenic Acids	0.2894	29.8760	69.9	<0.001	2090	674	2330
	0.3195	29.7972	69.0		2056	700	2191
	0.3371	29.8686	68.9		2059	704	2089
Sodium Kaolinite and 150 mg/L Merichem Naphthenic Acids	0.2992	29.8087	102.5	0.002	3055	1013	3385
	0.2827	29.8044	110.4		3291	776	2744
	0.2887	29.8557	107.1		3196	878	3041
Sodium Kaolinite and 200 mg/L Merichem Naphthenic Acids	0.2751	29.9401	127.4	<0.001	3814	910	3309
	0.3205	29.8258	125.5		3744	962	3000
	0.3652	29.8311	121.3		3618	1089	2981

Table D 2: Data and calculations used to create the isotherm for calcium kaolinite and Merichem naphthenic acids at pH 6, Figure 3.7.

Experiment Label with Target Naphthenic Acids Concentration[1]	Clay Mass [2] (g)	Solution Mass [3] (g)	Naphthenic Acids Concentrations (mg/L)	t-Test [6] (*p-value*)	Mass Balance (μg)		C_a (μg naphthenic acids/g soil) [9]
			T = 40 h [5]		Mass of Naphthenic Acids in Solution [7]	Mass of Naphthenic Acids Sorbed [8]	
Water	0	29.8858	2.1				
Calcium Kaolinite + Water	0.2803	29.9162	1.4				
	0.2732	29.8765	3.2				
	0.2538	29.8936	1.7				
15 mg/L Merichem Naphthenic Acids	0	29.8373	15.1				
	0	29.8655	15.2				
	0	29.9197	14.9				
25 mg/L Merichem Naphthenic Acids	0	29.8158	24.0				
	0	29.8208	25.0				
	0	29.8957	25.2				
50 mg/L Merichem Naphthenic Acids	0	29.7953	48.0				
	0	29.8679	46.3				
	0	29.8233	47.3				
75 mg/L Merichem Naphthenic Acids	0	29.8695	62.0				
	0	29.7908	66.6				
	0	29.7567	64.0				
100 mg/L Merichem Naphthenic Acids	0	29.7925	92.7				
	0	29.7891	93.0				
	0	29.8009	91.9				
150 mg/L Merichem Naphthenic Acids	0	29.785	134.4				
	0	29.8127	137.1				
	0	29.8932	137.9				
200 mg/L Merichem Naphthenic Acids	0	29.8001	155.2				
	0	29.798	161.2				
	0	29.8463	156.9				
Calcium Kaolinite and 15 mg/L Merichem Naphthenic Acids	0.3320	29.8361	16.3	0.424			
	0.3370	29.7805	12.6				
	0.2880	29.8453	12.6				
Calcium Kaolinite and 25 mg/L Merichem Naphthenic Acids	0.3186	29.9386	18.7	<0.001	560	181	568
	0.3354	29.9016	18.1		541	199	594
	0.3333	29.8696	17.7		530	209	628
Calcium Kaolinite and 50 mg/L Merichem Naphthenic Acids	0.2771	29.8248	35.5	0.002	1059	349	1260
	0.2881	29.7915	35.8		1067	340	1179
	0.2881	29.8556	38.5		1149	260	904
Calcium Kaolinite and 75 mg/L Merichem Naphthenic Acids	0.2761	29.7911	52.2	0.002	1555	358	1295
	0.3715	29.7676	49.7		1478	433	1166
	0.3130	29.8854	49.4		1476	443	1416
Calcium Kaolinite and 100 mg/L Merichem Naphthenic Acids	0.3345	29.7989	72.6	0.041	2164	593	1773
	0.2846	29.7935	75.5		2249	507	1781
Calcium Kaolinite and 150 mg/L Merichem Naphthenic Acids	0.3523	29.8013	106.7	<0.001	3180	887	2518
	0.3147	29.6875	104.1		3092	960	3049
	0.2997	29.8583	106.6		3182	893	2979
Calcium Kaolinite and 200 mg/L Merichem Naphthenic Acids	0.3186	29.8356	129.7	<0.001	3868	839	2634
	0.3612	29.8329	128.9		3847	860	2382
	0.2804	29.8379	132.8		3961	747	2663

Table D 3: Data and calculations used to create the isotherm for sodium illite and Merichem naphthenic acids at pH 6, Figure 3.8.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)		t-Test (6) (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g soil) (9)
			T = 0 h (4)	T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	29.8430		5.4				
Sodium Illite + Water	0.2939	29.9337		6.8				
	0.2770	29.8683		4.4				
	0.3066	29.8919		5.1				
15 mg/L Merichem Naphthenic Acids	0	29.9227		15.6				
	0	29.9244		15.6				
	0	29.9366		15.7				
25 mg/L Merichem Naphthenic Acids	0	29.9727		21.8				
	0	29.9242		23.3				
	0	29.9243		22.7				
50 mg/L Merichem Naphthenic Acids	0	29.9483		38.2				
	0	29.9327		40.4				
	0	29.8854		39.1				
75 mg/L Merichem Naphthenic Acids	0	29.9450	68.1	57.6				
	0	29.9373	74.3	58.7				
	0	29.9362	67.7	60.5				
100 mg/L Merichem Naphthenic Acids	0	29.9717	90.7	69.4				
	0	29.9621	90.0	64.9				
	0	29.9470	90.5	67.7				
150 mg/L Merichem Naphthenic Acids	0	29.9491	136.7	114.8				
	0	29.9466	138.9	92.0				
	0	29.9419	138.6	88.3				
200 mg/L Merichem Naphthenic Acids	0	29.9286	181.5	129.4				
	0	29.9646	195.8	119.2				
	0	29.9597	180.3	125.4				
Sodium Illite and 15 mg/L Merichem Naphthenic Acids	0.3005	29.8462		10.4	0.228			
	0.2978	29.9311		9.0				
	0.2900	29.9198		9.0				
Sodium Illite and 25 mg/L Merichem Naphthenic Acids	0.2972	29.9373		15.9	0.365			
	0.3055	29.9309		17.7				
	0.2864	29.9694		15.6				
Sodium Illite and 50 mg/L Merichem Naphthenic Acids	0.3001	29.9286		30.1	0.006	1061	112	374
	0.2820	29.9466		28.2		1007	168	595
	0.3222	29.9649		29.4		1041	134	415
Sodium Illite and 75 mg/L Merichem Naphthenic Acids	0.2868	29.9274	68.1	43.2	0.001	1453	312	1087
	0.2842	29.9474	74.3	45.5		1525	240	845
	0.2890	29.9257	67.7	43.9		1476	288	997
Sodium Illite and 100 mg/L Merichem Naphthenic Acids	0.2994	29.9622	90.7	49.3	0.010	1639	378	1264
	0.2942	29.9643	90.0	48.9		1627	391	1328
	0.2980	29.9353	90.5	49.1		1632	384	1288
Sodium Illite and 150 mg/L Merichem Naphthenic Acids	0.2987	29.9631	136.7	76.6	0.141			
	0.3233	29.9594	138.9	71.5				
	0.2960	29.9327	138.6	73.0				
Sodium Illite and 200 mg/L Merichem Naphthenic Acids	0.2846	29.9497	181.5	104.0	0.009	3277	457	1606
	0.3145	29.9400	195.8	97.7		3088	645	2051
	0.2956	29.9320	180.3	99.3		3132	599	2027

Table D 4: Data and calculations used to create the isotherm for calcium illite and Merichem naphthenic acids at pH 6, Figure 3.9.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)		t-Test (6) (*p-value*)	Mass Balance (μg)		C_s (μg naphthenic acids/g soil) (9)
			T = 0 h (4)	T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	29.8430		2.9				
Calcium Illite + Water	0.3116	29.9265		2.4				
	0.3112	29.9240		3.3				
15 mg/L Merichem Naphthenic Acids	0	29.9227		15.6				
	0	29.9244		16.4				
	0	29.9366		17.0				
25 mg/L Merichem Naphthenic Acids	0	29.9727		25.3				
	0	29.9242		25.8				
	0	29.9243		25.6				
50 mg/L Merichem Naphthenic Acids	0	29.9483		44.7				
	0	29.9327		46.5				
	0	29.8854		46.1				
75 mg/L Merichem Naphthenic Acids	0	29.9450	68.1	64.5				
	0	29.9373	74.3	68.4				
	0	29.9362	67.7	64.2				
100 mg/L Merichem Naphthenic Acids	0	29.9717	90.7	78.0				
	0	29.9621	90.0	81.4				
	0	29.9470	90.5	76.1				
150 mg/L Merichem Naphthenic Acids	0	29.9491	136.7	114.6				
	0	29.9466	138.9	114.1				
	0	29.9419	138.6	118.8				
200 mg/L Merichem Naphthenic Acids	0	29.9286	181.5	154.3				
	0	29.9646	195.8	155.3				
	0	29.9597	180.3	154.7				
Calcium Illite and 15 mg/L Merichem Naphthenic Acids	0.3035	29.9501		9.4	0.131			
	0.3093	29.8993		10.0				
	0.3089	29.9166		9.5				
Calcium Illite and 25 mg/L Merichem Naphthenic Acids	0.3100	29.9248		14.1	0.075			
	0.2786	29.9716		16.8				
	0.3036	29.9219		17.7				
Calcium Illite and 50 mg/L Merichem Naphthenic Acids	0.2999	29.9414		31.9	<0.001	1042	328	1095
	0.2903	29.9503		31.0		1013	358	1233
	0.3247	29.9103		30.6		1002	367	1132
Calcium Illite and 75 mg/L Merichem Naphthenic Acids	0.3007	29.9456	68.1	52.7	0.007	1663	305	1013
	0.3161	29.9349	74.3	50.6		1599	368	1163
	0.3297	29.9353	67.7	49.5		1568	399	1210
Calcium Illite and 100 mg/L Merichem Naphthenic Acids	0.3094	29.9211	90.7	48.9	<0.001	1550	799	2582
	0.3150	29.9825	90.0	51.3		1623	731	2320
	0.3292	29.9421	90.5	47.5		1509	842	2556
Calcium Illite and 150 mg/L Merichem Naphthenic Acids	0.3332	29.9527	136.7	69.5	<0.001	2168	1302	3908
	0.2851	29.9284	138.9	75.8		2355	1113	3903
	0.3331	29.9104	138.6	70.2		2186	1279	3840
Calcium Illite and 200 mg/L Merichem Naphthenic Acids	0.3237	29.9381	181.5	97.8	0.002	3014	1619	5002
	0.2811	29.9347	195.8	104.7		3220	1413	5025
	0.2979	29.9331	180.3	104.0		3199	1433	4811

Table D 5: Data and calculations used to calculate the K_D value for sodium kaolinite and Merichem naphthenic acids at pH 8, Table 3.5.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)		t-Test (6) (*p-value*)	Mass Balance (μg)		C_a (μg naphthenic acids/g soil) (9)
			T = 0 h (4)	T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	30.0145		2.5				
	0	29.9947		2.2				
	0	29.9779		1.9				
Sodium Kaolinite + Water	0.2937	30.0097		1.3				
	0.3117	30.0145		2.6				
	0.2955	29.9945		2.8				
15 mg/L Merichem Naphthenic Acids	0	29.9980		15.7				
	0	30.0027		16.5				
	0	29.9943		16.7				
25 mg/L Merichem Naphthenic Acids	0	29.9558		25.0				
	0	29.9792		27.0				
	0	29.9663		26.7				
50 mg/L Merichem Naphthenic Acids	0	29.9641		48.2				
	0	29.9791		46.3				
	0	29.9644		51.2				
75 mg/L Merichem Naphthenic Acids	0	29.9704	71.1	70.6				
	0	29.9726	71.4	71.4				
	0	29.9826	72.0	72.1				
100 mg/L Merichem Naphthenic Acids	0	29.9969	91.2	96.3				
	0	29.9752	95.5	92.8				
	0	30.0101	93.7	88.9				
150 mg/L Merichem Naphthenic Acids	0	30.0115	142.2	153.2				
	0	30.0260	142.3	140.5				
	0	30.0145	138.3	156.9				
200 mg/L Merichem Naphthenic Acids	0	30.0130	185.4	170.5				
	0	30.0039	184.0	186.2				
	0	30.0179	162.4	184.9				
Sodium Kaolinite and 15 mg/L Merichem Naphthenic Acids	0.2922	30.0030		15.8	0.621			
	0.2852	29.9843		16.5				
	0.2977	29.9928		17.5				
Sodium Kaolinite and 25 mg/L Merichem Naphthenic Acids	0.2957	29.9370		21.6	0.237			
	0.2856	29.9649		24.0				
	0.3217	29.9949		26.3				
Sodium Kaolinite and 50 mg/L Merichem Naphthenic Acids	0.3195	29.9629		48.4	0.795			
	0.3221	29.9678		48.0				
	0.3022	29.9613		48.1				
Sodium Kaolinite and 75 mg/L Merichem Naphthenic Acids	0.2707	29.9908	71.1	67.8	0.529			
	0.2959	29.9548	71.4	70.3				
	0.2810	30.0018	72.0	72.7				
Sodium Kaolinite and 100 mg/L Merichem Naphthenic Acids	0.2778	30.0068	91.2	90.6	0.788			
	0.2955	29.9976	95.5	94.6				
	0.3233	29.9846	93.7	95.1				
Sodium Kaolinite and 150 mg/L Merichem Naphthenic Acids	0.3236	30.0030	142.3	132.2	0.171			
	0.3215	30.0212	138.3	135.7				
Sodium Kaolinite and 200 mg/L Merichem Naphthenic Acids	0.3278	30.0010	185.4	176.2	0.706			
	0.3035	30.0143	184.0	183.8				
	0.3544	29.9888	162.4	189.2				

Table D 6: Data and calculations used to calculate the K_D value for calcium kaolinite and Merichem naphthenic acids at pH 8, Table 3.5.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)		t-Test (6) (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g soil) (9)
			T = 0 h (4)	T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	30.0145		0.2				
	0	29.9947		1.6				
	0	29.9779		-1.4				
Calcium Kaolinite + Water	0.3271	30.0004		0.3				
	0.2939	29.9875		-0.5				
	0.3406	30.0050		0.5				
15 mg/L Merichem Naphthenic Acids	0	29.9980		16.26				
	0	30.0027		15.87				
	0	29.9943		17.08				
25 mg/L Merichem Naphthenic Acids	0	29.9558		23.92				
	0	29.9792		25.81				
	0	29.9663		26.29				
50 mg/L Merichem Naphthenic Acids	0	29.9641		48.78				
	0	29.9791		51.21				
	0	29.9644		45.16				
75 mg/L Merichem Naphthenic Acids	0	29.9704	71.1	71.70				
	0	29.9726	71.4	75.20				
	0	29.9826	72.0	73.41				
100 mg/L Merichem Naphthenic Acids	0	29.9969	91.2	90.72				
	0	29.9752	95.5	90.21				
	0	30.0101	93.7	95.40				
150 mg/L Merichem Naphthenic Acids	0	30.0115	142.2	142.77				
	0	30.0260	142.3	136.70				
	0	30.0145	138.3	159.11				
200 mg/L Merichem Naphthenic Acids	0	30.0130	185.4	184.12				
	0	30.0039	184.0	201.37				
	0	30.0179	162.4	207.74				
Calcium Kaolinite and 15 mg/L Merichem Naphthenic Acids	0.2874	29.9480		16.59	0.283			
	0.2906	29.9674		15.13				
	0.3374	29.9707		15.30				
Calcium Kaolinite and 25 mg/L Merichem Naphthenic Acids	0.2872	29.9700		23.74	0.629			
	0.3494	29.9804		25.93				
	0.3655	29.9720		24.85				
Calcium Kaolinite and 50 mg/L Merichem Naphthenic Acids	0.3555	29.9807		45.70	0.880			
	0.3330	29.9804		48.18				
	0.2839	29.9760		50.20				
Calcium Kaolinite and 75 mg/L Merichem Naphthenic Acids	0.2873	29.9961	71.1	68.34	0.189			
	0.3601	29.9895	71.4	73.47				
	0.3583	29.9868	72.0	69.26				
Calcium Kaolinite and 100 mg/L Merichem Naphthenic Acids	0.3428	29.9887	91.2	94.27	0.443			
	0.2802	29.9942	95.5	95.66				
	0.3466	29.9908	93.7	91.63				
Calcium Kaolinite and 150 mg/L Merichem Naphthenic Acids	0.3298	29.9951	142.2	145.79	0.983			
	0.3722	30.0171	142.3	144.71				
	0.2846	30.0081	138.3	147.59				
Calcium Kaolinite and 200 mg/L Merichem Naphthenic Acids	0.3040	29.9960	185.4	185.11	0.388			
	0.3053	29.9849	184.0	194.33				
	0.3469	30.0170	162.4	190.37				

Table D 7: Data and calculations used to calculate the K_D value for sodium illite and Merichem naphthenic acids at pH 8, Table 3.5.

Experiment Label with Target Naphthenic Acids Concentration[1]	Clay Mass[2] (g)	Solution Mass[3] (g)	Naphthenic Acids Concentrations (mg/L)		t-Test[6] (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g soil)[9]
			T = 0 h[4]	T = 40 h[5]		Mass of Naphthenic Acids in Solution[7]	Mass of Naphthenic Acids Sorbed[8]	
Water	0	30.0017		-0.3				
	0	29.9917		-0.2				
	0	29.9973		-0.3				
Sodium Illite + Water	0.3029	29.9826		-0.2				
	0.2898	30.0385		-0.3				
	0.3015	30.0036		-0.3				
15 mg/L Merichem Naphthenic Acids	0	30.0188		14.33				
	0	30.0148		14.98				
	0	30.0136		12.93				
25 mg/L Merichem Naphthenic Acids	0	30.0031		27.46				
	0	30.0258		22.53				
	0	29.9969		22.32				
50 mg/L Merichem Naphthenic Acids	0	29.9682		47.36				
	0	29.9942		48.98				
	0	29.9609		47.90				
75 mg/L Merichem Naphthenic Acids	0	29.9770	76.0	70.19				
	0	29.9755	77.2	68.18				
	0	29.9906		71.84				
100 mg/L Merichem Naphthenic Acids	0	30.0071	100.9	92.65				
	0	30.0411	103.7	92.14				
	0	29.9905	100.9	97.51				
150 mg/L Merichem Naphthenic Acids	0	29.9687	151.4	138.06				
	0	30.0122	154.0	143.54				
	0	30.0031	149.6	153.84				
200 mg/L Merichem Naphthenic Acids	0	30.0174	207.9	182.30				
	0	29.9919	206.6	183.43				
	0	30.0067	207.5	188.64				
Sodium Illite and 15 mg/L Merichem Naphthenic Acids	0.2953	30.0099		14.63	0.110			
	0.3389	30.0194		17.03				
	0.3288	30.0027		16.41				
Sodium Illite and 25 mg/L Merichem Naphthenic Acids	0.3337	29.9972		25.38	0.403			
	0.3101	30.0017		28.07				
	0.3245	30.0126		24.56				
Sodium Illite and 50 mg/L Merichem Naphthenic Acids	0.2935	29.9402		47.84	0.884			
	0.3382	29.9485		45.35				
	0.3465	29.9754		52.03				
Sodium Illite and 75 mg/L Merichem Naphthenic Acids	0.3210	29.9891	76.0	67.18	0.733			
	0.2958	29.9613	77.2	72.02				
	0.3154	29.9477		73.45				
Sodium Illite and 100 mg/L Merichem Naphthenic Acids	0.3496	29.9887	100.9	101.43	0.217			
	0.3289	29.9633	103.7	101.47				
	0.3116	30.0122	100.9	93.58				
Sodium Illite and 150 mg/L Merichem Naphthenic Acids	0.3539	29.9941	151.4	139.07	0.626			
	0.3433	29.9546	154.0	145.52				
	0.3473	29.9316	149.6	142.63				
Sodium Illite and 200 mg/L Merichem Naphthenic Acids	0.2874	29.9961	207.9	177.23	0.538			
	0.2813	30.0128	206.6	200.17				
	0.3178	29.9915	207.5	192.05				

Table D 8: Data and calculations used calculate the K_D value for calcium illite and Merichem naphthenic acids at pH 8, Table 3.5.

Experiment Label with Target Naphthenic Acids Concentration$^{(1)}$	Clay Mass $^{(2)}$ (g)	Solution Mass $^{(3)}$ (g)	Naphthenic Acids Concentrations (mg/L)		t-Test $^{(6)}$ (*p-value*)	Mass Balance (μg)		C_s (μg naphthenic acids/g soil) $^{(9)}$	K_D $^{(10)}$ (mL g^{-1})
			T = 0 h $^{(4)}$	T = 40 h $^{(5)}$		Mass of Naphthenic Acids in Solution $^{(7)}$	Mass of Naphthenic Acids Sorbed $^{(8)}$		
Water	0	30.0017		0.5					
	0	29.9917		0.9					
	0	29.9973		0.6					
Calcium Illite + Water	0.2966	30.0089		0.6					
	0.3494	30.0075		1.1					
	0.3101	30.0048		0.4					
15 mg/L Merichem Naphthenic Acids	0	30.0188		16.1					
	0	30.0148		16.4					
	0	30.0136		15.3					
25 mg/L Merichem Naphthenic Acids	0	30.0031		24.7					
	0	30.0258		24.3					
	0	29.9969		26.3					
50 mg/L Merichem Naphthenic Acids	0	29.9682		49.0					
	0	29.9942		50.0					
	0	29.9609		51.4					
75 mg/L Merichem Naphthenic Acids	0	29.9770	76.0	70.7					
	0	29.9755	77.2	70.6					
	0	29.9906		77.2					
100 mg/L Merichem Naphthenic Acids	0	30.0071	100.9	97.5					
	0	30.0411	103.7	103.7					
	0	29.9905	100.9	94.0					
150 mg/L Merichem Naphthenic Acids	0	29.9687	151.4	145.8					
	0	30.0122	154.0	140.4					
	0	30.0031	149.6	150.0					
200 mg/L Merichem Naphthenic Acids	0	30.0174	207.9	186.5					
	0	29.9919	206.6	190.5					
	0	30.0067	207.5	200.0					
Calcium Illite and 15 mg/L Merichem Naphthenic Acids	0.2822	30.0370		17.22	0.610				
	0.3434	29.9826		14.75					
	0.2876	29.9921		17.47					
Calcium Illite and 25 mg/L Merichem Naphthenic Acids	0.3427	29.9627		25.39	0.183				
	0.3256	29.9691		31.12					
	0.3164	29.9876		28.39					
Calcium Illite and 50 mg/L Merichem Naphthenic Acids	0.2862	29.9705		46.74	0.969				
	0.2949	29.9698		47.78					
	0.3316	29.9661		56.24					
Calcium Illite and 75 mg/L Merichem Naphthenic Acids	0.3321	29.9755	76.0	64.48	0.645				
	0.3267	29.9712	77.2	77.01					
	0.3245	29.9805		70.66					
Calcium Illite and 100 mg/L Merichem Naphthenic Acids	0.2973	29.9471	100.9	102.69	0.618				
	0.2856	29.9856	103.7	93.89					
	0.2934	29.9681	100.9	106.06					
Calcium Illite and 150 mg/L Merichem Naphthenic Acids	0.2926	29.9843	151.4	131.87	0.035	3953	405	1183	9.0
	0.3426	29.9783	154.0	134.88		4042	315	935	6.9
	0.3369	29.9674	149.6						
Calcium Illite and 200 mg/L Merichem Naphthenic Acids	0.2906	29.9719	207.9	174.11	0.035	5218	546	1879	10.8
	0.2879	30.0006	206.6	171.34		5140	629	2186	12.8
	0.3339	30.0015	207.5	174.73		5242	528	1580	9.0

Average K_D = 9.7

Table D 9: Data and calculations used to calculate the K_D value for sodium montmorillonite and Merichem naphthenic acids at pH 8, Table 3.5.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)		t-Test (6) (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g soil) (9)
			T = 0 h (4)	T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	30.0049		-2.2				
	0	29.9934		-1.9				
	0	29.9925		-2.4				
Sodium Montmorillonite + Water	0.2770	30.0060		-0.5				
	0.2811	29.9899		0.1				
	0.2923	30.0069		-0.8				
15 mg/L Merichem Naphthenic Acids	0	30.0017		12.1				
	0	29.9775		12.2				
	0	29.9966		12.9				
25 mg/L Merichem Naphthenic Acids	0	29.9734		22.7				
	0	29.9720		23.0				
	0	29.9794		20.9				
50 mg/L Merichem Naphthenic Acids	0	29.9500		47.5				
	0	29.9682		45.4				
	0	29.9841		46.5				
75 mg/L Merichem Naphthenic Acids	0	29.9584	74.5	63.8				
	0	29.9660	77.2	65.8				
	0	29.9553	71.9	66.8				
100 mg/L Merichem Naphthenic Acids	0	29.9648	107.9	90.5				
	0	29.9670	98.4	92.8				
	0	29.9487	99.2	98.0				
150 mg/L Merichem Naphthenic Acids	0	29.9819	156.3	135.9				
	0	29.9977	155.4	138.6				
	0	29.9449	155.4	142.9				
200 mg/L Merichem Naphthenic Acids	0	29.9995	200.4	186.5				
	0	30.0003	203.5	200.5				
	0	29.9991	204.1	198.4				
Sodium Montmorillonite and 15 mg/L Merichem Naphthenic Acids	0.3009	29.9879		13.9	0.032	416	0	0*
	0.3197	29.9702		13.5		403	0	0*
	0.3476	29.9930		13.3		397	0	0*
Sodium Montmorillonite and 25 mg/L Merichem Naphthenic Acids	0.2954	29.9918		22.7	0.585			
	0.2752	29.9697		22.5				
	0.2808	29.9867		18.8				
Sodium Montmorillonite and 50 mg/L Merichem Naphthenic Acids	0.2750	29.9762		49.5	0.013	1485	0	0*
	0.3252	29.9699		49.7		1490	0	0*
	0.3022	29.9541		51.7		1548	0	0*
Sodium Montmorillonite and 75 mg/L Merichem Naphthenic Acids	0.2899	29.9710	74.5	76.1	0.002	2281	0	0*
	0.2926	29.9605	77.2	80.1		2400	0	0*
	0.2836	29.9497	71.9	77.3		2316	0	0*
Sodium Montmorillonite and 100 mg/L Merichem Naphthenic Acids	0.2829	29.9513	107.9	100.4	0.061			
	0.3084	29.9517	98.4	98.8				
	0.2953	29.9565	99.2	103.8				
Sodium Montmorillonite and 150 mg/L Merichem Naphthenic Acids	0.2952	29.9762	156.3	150.4	0.028	4508	0	0*
	0.2985	29.9630	155.4	145.1		4347	0	0*
	0.3061	29.9727	155.4	148.9		4463	0	0*
Sodium Montmorillonite and 200 mg/L Merichem Naphthenic Acids	0.3130	29.9934	200.4	201.6	0.325			
	0.3114	29.9888	203.5	199.7				
	0.3171	30.0093	204.1	200.9				

Table D 10: Data and calculations used to calculate the K_D value for calcium montmorillonite and Merichem naphthenic acids at pH 8, Table 3.5.

Experiment Label [1]	Clay Mass [2] (g)	Solution Mass [3] (g)	Naphthenic Acids Concentrations (mg/L)		t-Test [6] (*p-value*)	Mass Balance (μg)		C_a (μg naphthenic acids/g soil) [9]	K_D [10] (mL g^{-1})
			T = 0 h [4]	T = 40 h [5]		Mass of Naphthenic Acids in Solution [7]	Mass of Naphthenic Acids Sorbed [8]		
Water	0	30.0049		-0.6					
	0	29.9934		-1.1					
	0	29.9925		-0.6					
Calcium Montmorillonite + Water	0.3608	29.9821		-0.6					
	0.3474	29.9846		-1.0					
	0.2783	30.0021		-0.6					
15 mg/L Merichem Naphthenic Acids	0	30.0017		14.1					
	0	29.9775		14.9					
	0	29.9966		14.4					
25 mg/L Merichem Naphthenic Acids	0	29.9734		25.8					
	0	29.9720		23.8					
	0	29.9794		24.2					
50 mg/L Merichem Naphthenic Acids	0	29.9500		45.7					
	0	29.9682		48.0					
	0	29.9841		47.2					
75 mg/L Merichem Naphthenic Acids	0	29.9584	74.5	74.9					
	0	29.9660	77.2	74.4					
	0	29.9553	71.9	75.3					
100 mg/L Merichem Naphthenic Acids	0	29.9648	107.9	96.6					
	0	29.9670	98.4	96.4					
	0	29.9487	99.2	108.4					
150 mg/L Merichem Naphthenic Acids	0	29.9819	156.3	142.8					
	0	29.9977	155.4	144.6					
	0	29.9449	155.4	149.0					
200 mg/L Merichem Naphthenic Acids	0	29.9995	200.4	194.9					
	0	30.0003	203.5	198.1					
Calcium Montmorillonite and 15 mg/L Merichem Naphthenic Acids	0.3377	29.9717		14.6	0.858				
	0.3326	29.9750		14.6					
	0.3399	29.9779		14.0					
Calcium Montmorillonite and 25 mg/L Merichem Naphthenic Acids	0.3032	29.9690		22.4	0.815				
	0.3522	29.9852		25.1					
	0.3030	29.9539		25.4					
Calcium Montmorillonite and 50 mg/L Merichem Naphthenic Acids	0.3246	29.9866		44.5	0.520				
	0.2798	29.9672		46.2					
	0.3510	29.9488		47.7					
Calcium Montmorillonite and 75 mg/L Merichem Naphthenic Acids	0.2789	29.9709	74.5	65.0	0.694				
	0.3285	29.9378	77.2	79.7					
	0.2858	29.9531	71.9	74.1					
Calcium Montmorillonite and 100 mg/L Merichem Naphthenic Acids	0.2883	29.9453	107.9	92.5	0.182				
	0.2947	29.9488	98.4	84.7					
	0.2781	29.9678	99.2	97.6					
Calcium Montmorillonite and 150 mg/L Merichem Naphthenic Acids	0.2995	29.9587	156.3	133.1	0.014	3988	369	1233	9.3
	0.2785	29.9707	155.4	132.7		3978	381	1368	10.3
	0.2908	29.9448	155.4	138.2		4139	216	743	5.4
Calcium Montmorillonite and 200 mg/L Merichem Naphthenic Acids	0.2847	29.9953	200.4	173.6	0.031	5207	686	2411	13.9
	0.2948	29.9667	203.5	179.0		5363	525	1780	9.9
	0.2929	29.9771	204.1	186.2		5583	307	1050	5.6

Average K_D = 9.1

Table D 11: Data and calculations used to calculate the K_D value for Ottawa sand and Merichem naphthenic acids at pH 8, Table 3.5.

Experiment Label with Target Naphthenic Acids Concentration(1)	Sand Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)	t-Test (6) (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g soil) (9)
			T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	30.0002	4.2				
	0	30.0003	4.1				
	0	29.9897	3.8				
5 g Ottawa Sand + Water	5.0505	25.0074	5.9				
	4.9866	25.0119	6.2				
	5.0294	25.0034	6.4				
1 g Ottawa Sand + Water	1.162	28.8231	5.3				
	1.1328	28.8263	4.7				
	1.1699	28.8305	5.4				
0.6 g Ottawa Sand + Water	0.6149	29.4093	5.3				
	0.6102	29.4278	4.7				
	0.5958	29.3968	5.8				
100 mg/L Merichem Naphthenic Acids	0	29.9495	88.3				
	0	29.9175	89.4				
	0	29.9284	90.0				
5 g Ottawa Sand and 100 mg/L Merichem Naphthenic Acids	5.0209	25.0011	91.69	0.175			
	5.0038	25.0129	90.85				
	5.0169	25.0047	97.21				
1 g Ottawa Sand and 100 mg/L Merichem Naphthenic Acids	1.1686	28.8005	89.22	0.428			
	1.1448	28.7927	85.08				
	1.1706	28.8065	89.23				
0.6 g Ottawa Sand and 100 mg/L Merichem Naphthenic Acids	0.5964	29.3548	89.08	0.815			
	0.6171	29.3694	96.94				
	0.6087	29.3723	84.56				

Table D 12: Data and calculations used to calculate the K_D value for sodium kaolinite and WIP-extracted naphthenic acids at pH 8, Table 3.6.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)		t-Test (6) (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g soil) (9)
			T = 0 h (4)	T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	30.0		2.9				
	0	30.0		1.5				
	0	30.0		2.8				
Sodium Kaolinite + Water	0.3507	30.0107		2.4				
	0.2991	29.9880		2.5				
	0.3200	30.0181		2.2				
15 mg/L WIP-Extracted Naphthenic Acids	0	30.0		11.8				
	0	30.0		9.9				
	0	30.0		11.4				
25 mg/L WIP-Extracted Naphthenic Acids	0	30.0	23.1	20.9				
	0	30.0	23.3	22.3				
	0	30.0	24.2	21.0				
50 mg/L WIP-Extracted Naphthenic Acids	0	30.0	54.8	49.7				
	0	30.0	56.5	50.1				
	0	30.0	54.6	51.0				
75 mg/L WIP-Extracted Naphthenic Acids	0	30.0	76.2	71.3				
	0	30.0	74.3	73.5				
	0	30.0	76.9	72.7				
100 mg/L WIP-Extracted Naphthenic Acids	0	30.0	97.7	92.7				
	0	30.0	97.1	90.1				
	0	30.0	99.2	91.5				
Sodium Kaolinite and 15 mg/L WIP-Extracted Naphthenic Acids	0.3323	30.0182		13.3	0.067			
	0.3549	30.0002		13.1				
	0.3068	30.0018		13.1				
Sodium Kaolinite and 25 mg/L WIP-Extracted Naphthenic Acids	0.3287	30.0015	23.1	22.1	0.074			
	0.3060	30.0056	23.3	24.2				
	0.3442	29.9947	24.2	23.7				
Sodium Kaolinite and 50 mg/L WIP-Extracted Naphthenic Acids	0.3399	29.9889	54.8	59.8	0.024	1794	0	0*
	0.3333	29.9595	56.5	55.4		1661	0	0*
	0.3582	29.9864	54.6	57.0		1709	0	0*
Sodium Kaolinite and 75 mg/L WIP-Extracted Naphthenic Acids	0.3645	29.9560	76.2	75.9	0.034	2272	0	0*
	0.3189	29.9793	74.3	80.5		2413	0	0*
	0.3041	29.9779	76.9	79.5		2384	0	0*
Sodium Kaolinite and 100 mg/L WIP-Extracted Naphthenic Acids	0.2980	30.0000	97.7	97.6	0.006	2929	0	0*
	0.3479	29.9852	97.1	98.4		2951	0	0*
	0.3231	29.9737	99.2	98.6		2956	0	0*

Table D 13: Data and calculations used to calculate the K_D value for calcium kaolinite and WIP-extracted naphthenic acids at pH 8, Table 3.6.

Experiment Label with Target Naphthenic Acids Concentration[1]	Clay Mass [2] (g)	Solution Mass [3] (g)	Naphthenic Acids Concentrations (mg/L)		t-Test[6] (*p-value*)	Mass Balance (μg)		C_a (μg naphthenic acids/g soil) [9]
			T = 0 h [4]	T = 40 h [5]		Mass of Naphthenic Acids in Solution [7]	Mass of Naphthenic Acids Sorbed [8]	
Water	0	30		2.9				
	0	30		1.5				
	0	30		2.8				
Calcium Kaolinite + Water	0.3035	29.9905		2.3				
	0.3029	29.9997		1.8				
	0.3056	29.9845		3.0				
15 mg/L WIP-Extracted Naphthenic Acids	0	30		11.8				
	0	30		9.9				
	0	30		11.4				
25 mg/L WIP-Extracted Naphthenic Acids	0	30	23.1	20.9				
	0	30	23.3	22.3				
	0	30	24.2	21.0				
50 mg/L WIP-Extracted Naphthenic Acids	0	30	54.8	49.7				
	0	30	56.5	50.1				
	0	30	54.6	51.0				
75 mg/L WIP-Extracted Naphthenic Acids	0	30	76.2	71.3				
	0	30	74.3	73.5				
	0	30	76.9	72.7				
100 mg/L WIP-Extracted Naphthenic Acids	0	30	97.7	92.7				
	0	30	97.1	90.1				
	0	30	99.2	91.5				
Calcium Kaolinite and 15 mg/L WIP-Extracted Naphthenic Acids	0.3144	29.9885		11.71	0.208			
	0.3485	29.9680		13.97				
	0.3317	29.9795		11.79				
Calcium Kaolinite and 25 mg/L WIP-Extracted Naphthenic Acids	0.2961	29.9831	23.1	22.03	0.174			
	0.3027	29.9938	23.3	22.30				
	0.3768	29.9672	24.2	24.47				
Calcium Kaolinite and 50 mg/L WIP-Extracted Naphthenic Acids	0.3059	29.9716	54.8	53.83	0.148			
	0.3009	29.9730	56.5	55.32				
	0.3127	29.9932	54.6	50.70				
Calcium Kaolinite and 75 mg/L WIP-Extracted Naphthenic Acids	0.3357	29.9567	76.2	73.67	0.169			
	0.3462	30.0063	74.3	78.48				
	0.3506	29.9815	76.9	74.44				
Calcium Kaolinite and 100 mg/L WIP-Extracted Naphthenic Acids	0.3551	29.9858	97.7	95.58	0.073			
	0.3509	29.9855	97.1	92.98				
	0.3326	29.9896	99.2	97.40				

Table D 14: Data and calculations used to calculate the K_D value for sodium illite and WIP-extracted naphthenic acids at pH 8, Table 3.6.

Experiment Label with Target Naphthenic Acids Concentration$^{(1)}$	Clay Mass $^{(2)}$ (g)	Solution Mass $^{(3)}$ (g)	Naphthenic Acids Concentrations (mg/L)		t-Test $^{(6)}$ (*p-value*)	Mass Balance (µg)		C_s (µg naphthenic acids/g soil) $^{(9)}$
			T = 0 h $^{(4)}$	T = 40 h $^{(5)}$		Mass of Naphthenic Acids in Solution $^{(7)}$	Mass of Naphthenic Acids Sorbed $^{(8)}$	
Water	0	30.0		-0.2				
	0	30.0		0.1				
	0	30.0		0.2				
				3.6				
				5.1				
				4.4				
Sodium Illite + Water	0.2913	30.0014		2.2				
	0.3787	30.0050		2.6				
	0.3109	30.0072		1.8				
15 mg/L WIP-Extracted Naphthenic Acids	0	30.0		19.4				
	0	30.0		11.4				
	0	30.0		8.7				
				17.2				
				23.0				
				15.7				
25 mg/L WIP-Extracted Naphthenic Acids	0	30.0	21.0	18.6				
	0	30.0	21.7	19.2				
	0	30.0	20.9	18.5				
				27.8				
				33.1				
				27.6				
50 mg/L WIP-Extracted Naphthenic Acids	0	30.0	55.0	50.1				
	0	30.0	54.3	49.8				
	0	30.0	55.0	50.2				
				62.4				
				59.5				
				61.5				
75 mg/L WIP-Extracted Naphthenic Acids	0	30.0	76.7	70.6				
	0	30.0	77.4	73.3				
	0	30.0	76.3	82.5				
				81.4				
				83.3				
				96.2				
100 mg/L WIP-Extracted Naphthenic Acids	0	30.0	97.3	94.7				
	0	30.0	99.1	93.7				
	0	30.0	100.9	90.4				
				106.5				
				102.4				
				100.0				
Sodium Illite and 15 mg/L WIP-Extracted Naphthenic Acids	0.2876	29.9902		13.9	0.427			
	0.3518	29.9979		13.9				
	0.3032	30.0144		14.4				
Sodium Illite and 25 mg/L WIP-Extracted Naphthenic Acids	0.3118	29.9733	21.0	25.1	0.635			
	0.3081	29.9832	21.7	25.6				
	0.3084	29.9872	20.9	25.5				
Sodium Illite and 50 mg/L WIP-Extracted Naphthenic Acids	0.3000	29.9771	55.0	58.6	0.215			
	0.3380	29.9702	54.3	58.2				
	0.3201	29.9641	55.0	60.9				
Sodium Illite and 75 mg/L WIP-Extracted Naphthenic Acids	0.2900	29.9639	76.7	79.8	0.818			
	0.3285	29.9869	77.4	82.6				
	0.3009	29.9556	76.3	78.4				
Sodium Illite and 100 mg/L WIP-Extracted Naphthenic Acids	0.3430	29.9649	97.3	98.0	0.443			
	0.3073	30.0033	99.1	103.2				
	0.3057	29.9732	100.9	99.7				

Table D 15: Data and calculations used to calculate the K_D value for calcium illite and WIP-extracted naphthenic acids at pH 8, Table 3.6.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)		t-Test (6) (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g soil) (9)
			T = 0 h (4)	T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	30.0		-0.2				
	0	30.0		0.1				
	0	30.0		0.2				
				3.6				
				5.1				
				4.4				
Calcium Illite + Water	0.3312	29.9861		1.9				
	0.3266	30.0086		2.2				
	0.3140	30.0165		2.5				
15 mg/L WIP-Extracted Naphthenic Acids	0	30.0		19.4				
	0	30.0		11.4				
	0	30.0		8.7				
				17.2				
				23.0				
				15.7				
25 mg/L WIP-Extracted Naphthenic Acids	0	30.0	21.0	18.6				
	0	30.0	21.7	19.2				
	0	30.0	20.9	18.5				
				27.8				
				33.1				
				27.6				
50 mg/L WIP-Extracted Naphthenic Acids	0	30.0	55.0	50.1				
	0	30.0	54.3	49.8				
	0	30.0	55.0	50.2				
				62.4				
				59.5				
				61.5				
75 mg/L WIP-Extracted Naphthenic Acids	0	30.0	76.7	70.6				
	0	30.0	77.4	73.3				
	0	30.0	76.3	82.5				
				81.4				
				83.3				
				96.2				
100 mg/L WIP-Extracted Naphthenic Acids	0	30.0	97.3	94.7				
	0	30.0	99.1	93.7				
	0	30.0	100.9	90.4				
				106.5				
				102.4				
				100.0				
Calcium Illite and 15 mg/L WIP-Extracted Naphthenic Acids	0.3513	29.9969		13.7	0.387			
	0.3157	29.9716		12.8				
	0.3430	29.9810		15.0				
Calcium Illite and 25 mg/L WIP-Extracted Naphthenic Acids	0.3681	29.9760	21.0	26.1	0.725			
	0.3319	29.9800	21.7	24.6				
	0.2991	29.9685	20.9	24.5				
Calcium Illite and 50 mg/L WIP-Extracted Naphthenic Acids	0.3784	29.9807	55.0	58.4	0.246			
	0.3170	29.9471	54.3	62.7				
	0.3541	29.9605	55.0	57.2				
Calcium Illite and 75 mg/L WIP-Extracted Naphthenic Acids	0.3706	29.9606	76.7	77.6	0.332			
	0.3600	29.9744	77.4	79.3				
	0.3362	29.9403	76.3	74.3				
Calcium Illite and 100 mg/L WIP-Extracted Naphthenic Acids	0.3097	29.9852	97.3	100.9	0.818			
	0.3045	29.9429	99.1	94.9				
	0.3541	29.9648	100.9	95.9				

Table D 16: Data and calculations used to calculate the K_D value for sodium montmorillonite and WIP-extracted naphthenic acids at pH 8, Table 3.6.

Experiment Label with Target Naphthenic Acids Concentration[1]	Clay Mass [2] (g)	Solution Mass [3] (g)	Naphthenic Acids Concentrations (mg/L)		t-Test [6] (*p-value*)	Mass Balance (μg)		C_a (μg naphthenic acids/g soil) [9]
			T = 0 h [4]	T = 40 h [5]		Mass of Naphthenic Acids in Solution [7]	Mass of Naphthenic Acids Sorbed [8]	
Water	0	30.0		-0.3				
	0	30.0		-1.2				
	0	30.0		-1.3				
	0	30.0		2.2				
	0	30.0		1.0				
	0	30.0		0.7				
Sodium Montmorillonite + Water	0.2836	29.9823		1.1				
	0.2917	29.9768		-0.2				
	0.3068	29.9676		-0.4				
15 mg/L WIP-Extracted Naphthenic Acids	0	30.0		8.6				
	0	30.0		7.9				
	0	30.0		8.0				
	0	30.0		11.6				
	0	30.0		11.0				
	0	30.0		11.1				
25 mg/L WIP-Extracted Naphthenic Acids	0	30.0	18.0	19.8				
	0	30.0	21.0	20.8				
	0	30.0	15.7	18.9				
	0	30.0		24.5				
	0	30.0		23.5				
	0	30.0		23.9				
50 mg/L WIP-Extracted Naphthenic Acids	0	30.0	52.5	48.7				
	0	30.0	58.7	51.9				
	0	30.0	51.6	51.9				
	0	30.0		51.8				
	0	30.0		56.6				
	0	30.0		60.4				
75 mg/L WIP-Extracted Naphthenic Acids	0	30.0	77.0	76.6				
	0	30.0	79.6	71.4				
	0	30.0	76.2	70.3				
	0	30.0		82.8				
	0	30.0		77.4				
	0	30.0		75.1				
100 mg/L WIP-Extracted Naphthenic Acids	0	30.0	96.8	99.0				
	0	30.0	97.2	95.6				
	0	30.0	103.9	92.1				
	0	30.0		93.2				
	0	30.0		101.9				
	0	30.0		98.6				
Sodium Montmorillonite and 15 mg/L WIP-Extracted Naphthenic	0.2806	29.9794		10.9	0.190			
	0.2837	29.9810		10.4				
	0.3248	29.9954		11.1				
Sodium Montmorillonite and 25 mg/L WIP-Extracted Naphthenic	0.3505	29.9859	18.0	20.6	0.281			
	0.3293	29.9774	21.0	20.5				
	0.3745	29.9861	15.7	21.1				
Sodium Montmorillonite and 50 mg/L WIP-Extracted Naphthenic	0.3331	29.9946	52.5	54.3	0.579			
	0.3596	29.9810	58.7	54.2				
	0.3176	29.9599	51.6	55.3				
Sodium Montmorillonite and 75 mg/L WIP-Extracted Naphthenic	0.3188	29.9663	77.0	77.1	0.239			
	0.2989	29.9693	79.6	77.9				
	0.3171	29.9744	76.2	79.5				
Sodium Montmorillonite and 100 mg/L WIP-Extracted Naphthenic	0.3034	29.9658	96.8	99.7	0.039	2987	0	0*
	0.3180	29.9635	97.2	101.3		3035	0	0*
	0.2985	29.9677	103.9	103.1		3091	0	0*

Table D 17: Data and calculations used to calculate the K_D value for calcium montmorillonite and WIP-extracted naphthenic acids at pH 8, Table 3.6.

Experiment Label with Target Naphthenic Acids Concentration(1)	Clay Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)		t-Test (6) (*p-value*)	Mass Balance (µg)		C_s (µg naphthenic acids/g soil) (9)	K_D (10) (mL g^{-1})
			T = 0 h (4)	T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)		
Water	0	30.0		-0.3					
	0	30.0		-1.2					
	0	30.0		-1.3					
	0	30.0		2.2					
	0	30.0		1.0					
	0	30.0		0.7					
Calcium Montmorillonite + Water	0.3685	30.0005		0.8					
	0.2948	30.0153		0.1					
	0.3163	29.9694		-0.4					
15 mg/L WIP-Extracted Naphthenic Acids	0	30.0		8.6					
	0	30.0		7.9					
	0	30.0		8.0					
	0	30.0		11.6					
	0	30.0		11.0					
	0	30.0		11.1					
25 mg/L WIP-Extracted Naphthenic Acids	0	30.0	18.0	19.8					
	0	30.0	21.0	20.8					
	0	30.0	15.7	18.9					
	0	30.0		24.5					
	0	30.0		23.5					
	0	30.0		23.9					
50 mg/L WIP-Extracted Naphthenic Acids	0	30.0	52.5	48.7					
	0	30.0	58.7	51.9					
	0	30.0	51.6	51.9					
	0	30.0		51.8					
	0	30.0		56.6					
	0	30.0		60.4					
75 mg/L WIP-Extracted Naphthenic Acids	0	30.0	77.0	76.6					
	0	30.0	79.6	71.4					
	0	30.0	76.2	70.3					
	0	30.0		82.8					
	0	30.0		77.4					
	0	30.0		75.1					
100 mg/L WIP-Extracted Naphthenic Acids	0	30.0	96.8	99.0					
	0	30.0	97.2	95.6					
	0	30.0	103.9	92.1					
	0	30.0		93.2					
	0	30.0		101.9					
	0	30.0		98.6					
Calcium Montmorillonite and 15 mg/L WIP-Extracted Naphthenic	0.3840	30.0199		9.78	0.783				
	0.3094	29.9970		9.41					
	0.3419	29.9967		9.31					
Calcium Montmorillonite and 25 mg/L WIP-Extracted Naphthenic	0.2882	29.9539	18.0	19.01	0.039	569	87	300	15.8
	0.2992	29.9767	21.0	18.96		568	88	294	15.5
	0.3272	29.9588	15.7	19.67		589	67	204	10.4
Calcium Montmorillonite and 50 mg/L WIP-Extracted Naphthenic	0.3150	29.9710	52.5	48.90	0.122				
	0.3309	29.9644	58.7	51.11					
	0.3446	29.9392	51.6	50.77					
Calcium Montmorillonite and 75 mg/L WIP-Extracted Naphthenic	0.3813	29.9833	77.0	70.48	0.067				
	0.3487	29.9655	79.6	72.72					
	0.3005	29.9761	76.2	70.37					
Calcium Montmorillonite and 100 mg/L WIP-Extracted Naphthenic	0.3042	29.9671	96.8	90.72	0.008	2719	180	592	6.5
	0.3135	29.9840	97.2	90.15		2703	197	629	7.0
	0.3486	29.9627	103.9	89.94		2695	203	583	6.5
								Average K_D =	10.3

Table D 18: Data and calculations used to calculate the K_D value for core OW04-02, depth 6 - 7 m, and WIP-extracted naphthenic acids at pH 8, Table 3.7.

Experiment Label with Target Naphthenic Acids Concentration$^{(1)}$	Soil Mass $^{(2)}$ (g)	Solution Mass $^{(3)}$ (g)	Naphthenic Acids Concentrations (mg/L)	t-Test $^{(6)}$ (*p-value*)	Mass Balance (μg)		C_a (μg naphthenic acids/g soil) $^{(9)}$
			T = 40 h $^{(5)}$		Mass of Naphthenic Acids in Solution $^{(7)}$	Mass of Naphthenic Acids Sorbed $^{(8)}$	
Water	0	30.0	2.5				
	0	30.0	-0.1				
	0	30.0	-1.4				
	0	30.0	9.6				
	0	30.0	9.5				
	0	30.0	6.2				
Core OW04-02 at 6-7 m depth + Water	1.2902	30.0086	4.3				
	0.9950	30.0055	3.9				
	1.0968	30.0157	4.9				
15 mg/L WIP-Extracted Naphthenic Acids	0	30.0	13.9				
	0	30.0	11.5				
	0	30.0	13.9				
	0	30.0	24.3				
	0	30.0	21.1				
	0	30.0	24.3				
25 mg/L WIP-Extracted Naphthenic Acids	0	30.0	29.0				
	0	30.0	28.7				
	0	30.0	27.1				
	0	30.0	39.0				
	0	30.0	39.0				
	0	30.0	33.7				
50 mg/L WIP-Extracted Naphthenic Acids	0	30.0	50.0				
	0	30.0	52.8				
	0	30.0	52.7				
	0	30.0	58.0				
	0	30.0	61.6				
	0	30.0	64.6				
75 mg/L WIP-Extracted Naphthenic Acids	0	30.0	83.6				
	0	30.0	82.8				
	0	30.0	81.5				
	0	30.0	96.4				
	0	30.0	92.6				
	0	30.0	94.4				
100 mg/L WIP-Extracted Naphthenic Acids	0	30.0	107.9				
	0	30.0	110.1				
	0	30.0	107.5				
	0	30.0	114.8				
	0	30.0	113.8				
	0	30.0	111.7				
Core OW04-02 at 6-7 m Depth and 15 mg/L WIP-Extracted Naphthenic Acids	1.0061	29.9739	19.3	0.460			
	1.1708	29.9821	20.6				
	1.1066	29.9656	20.4				
Core OW04-02 at 6-7 m Depth and 25 mg/L WIP-Extracted Naphthenic Acids	1.0671	29.9960	35.7	0.296			
	1.0347	29.9791	34.4				
	1.0260	29.9931	35.9				
Core OW04-02 at 6-7 m Depth and 50 mg/L WIP-Extracted Naphthenic Acids	1.0097	29.9751	58.2	0.252			
	0.9782	30.0265	59.6				
	1.1144	29.9787	61.6				
Core OW04-02 at 6-7 m Depth and 75 mg/L WIP-Extracted Naphthenic Acids	1.3442	29.9951	92.9	0.110			
	1.1891	29.9717	95.5				
	0.9513	29.9669	93.2				
Core OW04-02 at 6-7 m Depth and 100 mg/L WIP-Extracted Naphthenic Acids	1.0714	29.9893	119.2	0.004	3336	0	0*
	1.0223	30.0210	115.9		3362	0	0*
	1.1753	30.0047	117.5		3564	0	0*

Table D 19: Data and calculations used to calculate the K_D value for core OW04-06, depth 4 - 4.5 m, and WIP-extracted naphthenic acids at pH 8, Table 3.7.

Experiment Label with Target Naphthenic Acids Concentration(1)	Soil Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)	t-Test(6) (*p-value*)	Mass Balance (µg)		C_s (µg naphthenic acids/g soil) (9)
			T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
	0	30.0	2.5				
Water	0	30.0	-0.1				
	0	30.0	-1.4				
	0	30.0	9.6				
	0	30.0	9.5				
	0	30.0	6.2				
Core OW04-06 at 4-4.5 m depth + Water	1.0598	30.0264	4.1				
	0.9761	30.0014	4.1				
	1.0466	29.9948	4.9				
15 mg/L WIP-Extracted Naphthenic Acids	0	30.0	13.9				
	0	30.0	11.5				
	0	30.0	13.9				
	0	30.0	24.3				
	0	30.0	21.1				
	0	30.0	24.3				
25 mg/L WIP-Extracted Naphthenic Acids	0	30.0	29.0				
	0	30.0	28.7				
	0	30.0	27.1				
	0	30.0	39.0				
	0	30.0	39.0				
	0	30.0	33.7				
50 mg/L WIP-Extracted Naphthenic Acids	0	30.0	50.0				
	0	30.0	52.8				
	0	30.0	52.7				
	0	30.0	58.0				
	0	30.0	61.6				
	0	30.0	64.6				
75 mg/L WIP-Extracted Naphthenic Acids	0	30.0	83.6				
	0	30.0	82.8				
	0	30.0	81.5				
	0	30.0	96.4				
	0	30.0	92.6				
	0	30.0	94.4				
100 mg/L WIP-Extracted Naphthenic Acids	0	30.0	107.9				
	0	30.0	110.1				
	0	30.0	107.5				
	0	30.0	114.8				
	0	30.0	113.8				
	0	30.0	111.7				
Core OW04-06 at 4-4.5 m Depth and 15 mg/L WIP-Extracted Naphthenic Acids	1.0803	29.9706	18.4	0.705			
	1.0575	29.9756	20.3				
	1.1558	29.9661	18.7				
Core OW04-06 at 4-4.5 m Depth and 25 mg/L WIP-Extracted Naphthenic Acids	1.1472	30.0014	34.7	0.619			
	1.0360	29.9775	33.1				
	1.2162	29.9786	33.9				
Core OW04-06 at 4-4.5 m Depth and 50 mg/L WIP-Extracted Naphthenic Acids	1.1361	29.9793	57.3	0.723			
	0.9939	29.9822	60.0				
	1.1881	29.9827	55.5				
Core OW04-06 at 4-4.5 m Depth and 75 mg/L WIP-Extracted Naphthenic Acids	0.9875	30.0108	91.9	0.613			
	0.9643	29.9632	87.6				
	1.1827	29.9995	91.0				
Core OW04-06 at 4-4.5 m Depth and 100 mg/L WIP-Extracted Naphthenic Acids	1.1539	30.0031	111.2	0.337			
	1.0962	29.9925	112.0				
	1.0167	29.9945	118.8				

Table D 20: Data and calculations used to calculate the K_D value for Ellerslie soil and WIP-extracted naphthenic acids at pH 8, Table 3.7.

Experiment Label with Target Naphthenic Acids Concentration$^{(1)}$	Soil Mass $^{(2)}$ (g)	Solution Mass $^{(3)}$ (g)	Naphthenic Acids Concentrations (mg/L)	t-Test $^{(6)}$ (*p-value*)	Mass Balance (μg)		C_s (μg naphthenic acids/g soil) $^{(9)}$
			T = 40 h $^{(5)}$		Mass of Naphthenic Acids in Solution $^{(7)}$	Mass of Naphthenic Acids Sorbed $^{(8)}$	
Water	0	30	3.1				
	0	30	0.6				
	0	30	0.5				
	0	30	1.9				
	0	30	0.5				
	0	30	6.5				
Ellerslie Soil + Water	1.1493	30.0076	2.9				
	1.0194	30.0009	1.6				
	1.0461	30.0159	2.0				
15 mg/L WIP-Extracted Naphthenic Acids	0	30	16.9				
	0	30	17.9				
	0	30	14.0				
	0	30	20.9				
	0	30	18.1				
	0	30	16.7				
25 mg/L WIP-Extracted Naphthenic Acids	0	30	32.4				
	0	30	30.6				
	0	30	29.0				
	0	30	35.7				
	0	30	31.7				
	0	30	29.9				
50 mg/L WIP-Extracted Naphthenic Acids	0	30	59.7				
	0	30	60.4				
	0	30	56.4				
	0	30	62.5				
	0	30	59.1				
75 mg/L WIP-Extracted Naphthenic Acids	0	30	89.8				
	0	30	91.4				
	0	30	91.3				
	0	30	94.8				
	0	30	94.5				
	0	30	93.7				
100 mg/L WIP-Extracted Naphthenic Acids	0	30	122.0				
	0	30	116.2				
	0	30	120.9				
	0	30	122.2				
	0	30	118.3				
	0	30	120.7				
Ellerslie Soil and 15 mg/L WIP-Extracted Naphthenic Acids	0.9974	30.0096	15.5	0.185			
	1.0903	29.9703	15.6				
	1.0209	29.9757	16.7				
Ellerslie Soil and 25 mg/L WIP-Extracted Naphthenic Acids	1.1208	29.9754	29.8	0.106			
	1.0086	29.9720	28.9				
	1.1067	29.9682	30.1				
Ellerslie Soil and 50 mg/L WIP-Extracted Naphthenic Acids	1.1239	29.9787	57.85	0.425			
	1.1694	29.9507	59.23				
Ellerslie Soil and 75 mg/L WIP-Extracted Naphthenic Acids	1.0798	29.9521	83.34	0.093			
	1.0133	29.9543	71.57				
	1.0766	30.0048	85.18				
Ellerslie Soil and 100 mg/L WIP-Extracted Naphthenic Acids	1.0477	29.9834	113.32	0.097			
	1.0651	29.9725	116.25				

Table D 21: Data and calculations used to calculate the K_D value for Suncor coke and WIP-extracted naphthenic acids at pH 8, Table 3.8.

Experiment Label with Target Naphthenic Acids Concentration[1]	Coke Mass [2] (g)	Solution Mass [3] (g)	Naphthenic Acids Concentrations (mg/L)	t-Test [6] (*p-value*)	Mass Balance (μg)		C_a (μg naphthenic acids/g coke) [9]
			T = 40 h [5]		Mass of Naphthenic Acids in Solution [7]	Mass of Naphthenic Acids Sorbed [8]	
Water	0	30	3.1				
	0	30	0.6				
	0	30	0.5				
	0	30	1.9				
	0	30	0.5				
	0	30	6.5				
Suncor Coke + Water	1.0542	29.9806	2.9				
	0.9996	30.0104	1.6				
	1.0162	30.0127	2.1				
15 mg/L WIP-Extracted Naphthenic Acids	0	30	16.9				
	0	30	17.9				
	0	30	14.0				
	0	30	20.9				
	0	30	18.1				
	0	30	16.7				
25 mg/L WIP-Extracted Naphthenic Acids	0	30	32.4				
	0	30	30.6				
	0	30	29.0				
	0	30	35.7				
	0	30	31.7				
	0	30	29.9				
50 mg/L WIP-Extracted Naphthenic Acids	0	30	59.7				
	0	30	60.4				
	0	30	56.4				
	0	30	62.5				
	0	30	59.1				
75 mg/L WIP-Extracted Naphthenic Acids	0	30	89.8				
	0	30	91.4				
	0	30	91.3				
	0	30	94.8				
	0	30	94.5				
	0	30	93.7				
100 mg/L WIP-Extracted Naphthenic Acids	0	30	122.0				
	0	30	116.2				
	0	30	120.9				
	0	30	122.2				
	0	30	118.3				
	0	30	120.7				
Suncor Coke and 15 mg/L WIP-Extracted Naphthenic Acids	0.9778	30.0000	17.8	0.791			
	1.0304	29.9850	17.8				
	1.0295	30.0366	17.5				
Suncor Coke and 25 mg/L WIP-Extracted Naphthenic Acids	0.9888	29.9847	33.6	0.047	1009	0	0*
	1.0110	30.0019	34.4		1032	0	0*
	0.9943	29.9940	34.3		1027	0	0*
Suncor Coke and 50 mg/L WIP-Extracted Naphthenic Acids	1.0633	29.9495	57.7	0.316			
	0.9872	30.0091	57.9				
	0.9749	30.0101	59.5				
Suncor Coke and 75 mg/L WIP-Extracted Naphthenic Acids	1.0191	29.9910	97.7	0.374			
	1.0562	29.9959	93.4				
	1.0628	29.9830	92.4				
Suncor Coke and 100 mg/L WIP-Extracted Naphthenic Acids	0.9943	30.0237	124.3	0.706			
	0.9793	30.0096	121.2				
	1.0665	30.0025	117.4				

Table D 22: Data and calculations used to calculate the K_D value for Syncrude coke and WIP-extracted naphthenic acids at pH 8, Table 3.8.

Experiment Label with Target Naphthenic Acids Concentration(1)	Coke Mass (2) (g)	Solution Mass (3) (g)	Naphthenic Acids Concentrations (mg/L)	t-Test (6) (*p-value*)	Mass Balance (µg)		C_a (µg naphthenic acids/g coke) (9)
			T = 40 h (5)		Mass of Naphthenic Acids in Solution (7)	Mass of Naphthenic Acids Sorbed (8)	
Water	0	30	3.1				
	0	30	0.6				
	0	30	0.5				
	0	30	1.9				
	0	30	0.5				
	0	30	6.5				
Syncrude Coke + Water	0.9953	30.0055	2.0				
	1.1307	30.0069	2.3				
	0.9816	29.9893	2.3				
15 mg/L WIP-Extracted Naphthenic Acids	0	30	16.9				
	0	30	17.9				
	0	30	14.0				
	0	30	20.9				
	0	30	18.1				
	0	30	16.7				
25 mg/L WIP-Extracted Naphthenic Acids	0	30	32.4				
	0	30	30.6				
	0	30	29.0				
	0	30	35.7				
	0	30	31.7				
	0	30	29.9				
50 mg/L WIP-Extracted Naphthenic Acids	0	30	59.7				
	0	30	60.4				
	0	30	56.4				
	0	30	62.5				
	0	30	59.1				
75 mg/L WIP-Extracted Naphthenic Acids	0	30	89.8				
	0	30	91.4				
	0	30	91.3				
	0	30	94.8				
	0	30	94.5				
	0	30	93.7				
100 mg/L WIP-Extracted Naphthenic Acids	0	30	122.0				
	0	30	116.2				
	0	30	120.9				
	0	30	122.2				
	0	30	118.3				
	0	30	120.7				
Syncrude Coke and 15 mg/L WIP-Extracted Naphthenic Acids	1.0584	29.8623	13.0	0.002	389	131	124
	1.0942	30.0090	12.9		387	136	125
	1.0323	30.0094	11.5		346	178	172
Syncrude Coke and 25 mg/L WIP-Extracted Naphthenic Acids	0.9776	29.9702	27.6	0.008	827	119	121
	0.9733	29.9981	27.7		830	117	120
	0.9965	29.9791	27.2		815	131	131
Syncrude Coke and 50 mg/L WIP-Extracted Naphthenic Acids	1.0201	29.9810	51.7	0.000	1549	238	234
	1.0592	29.9825	49.7		1489	298	281
	0.9727	29.9678	51.6		1548	239	245
Syncrude Coke and 75 mg/L WIP-Extracted Naphthenic Acids	1.1189	29.9944	82.9	0.045	2488	290	259
	0.9897	29.9968	89.2		2675	102	104
	1.1144	29.9861	85.0		2547	229	206
Syncrude Coke and 100 mg/L WIP-Extracted Naphthenic Acids	1.0163	29.9998	117.7	0.054			
	1.0722	29.9809	117.6				

Appendix E: GC-MS Three-Dimensional Plots

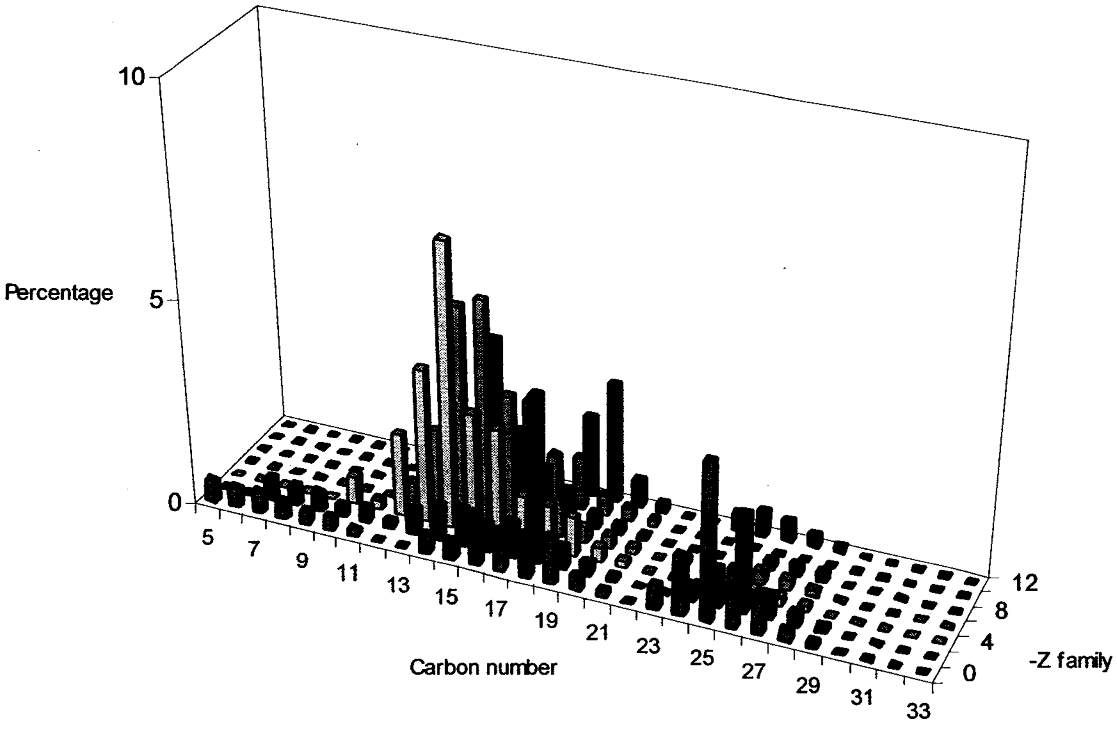

Figure E 1: Three-dimensional plot of the GC-MS analysis of WIP-extract 1 naphthenic acids with exposure to sodium modified kaolinite.

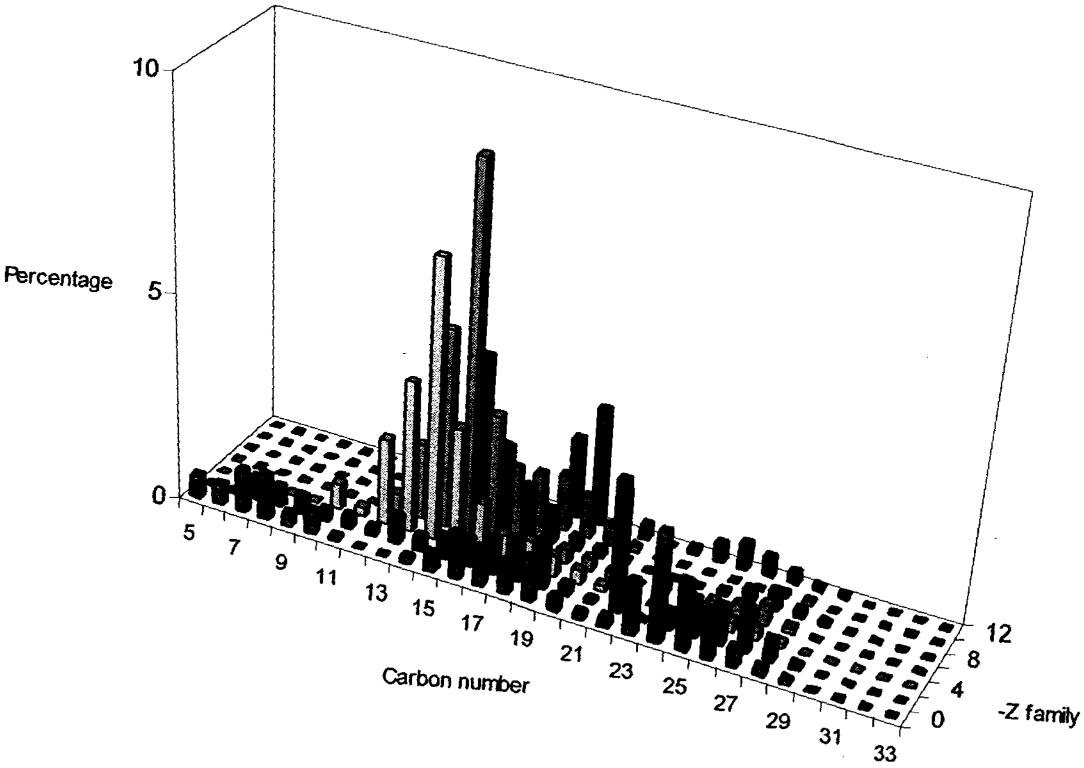

Figure E 2: Three-dimensional plot of the GC-MS analysis of WIP-extract 1 naphthenic acids with exposure to calcium modified kaolinite.

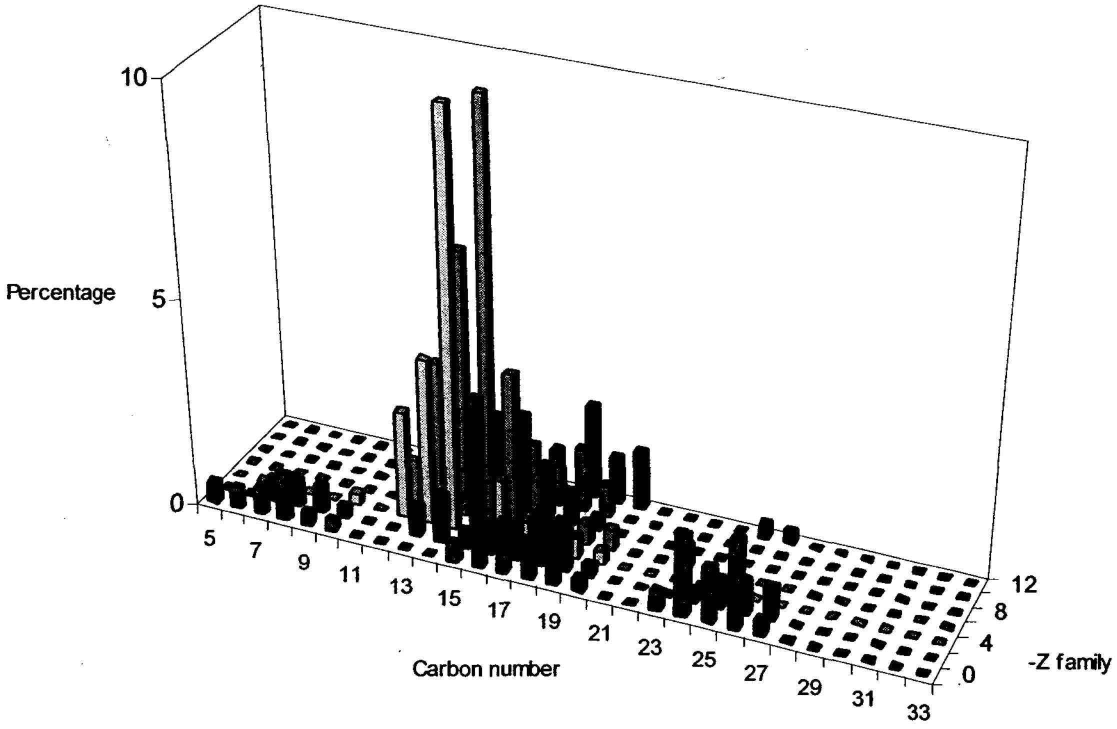

Figure E 3: Three-dimensional plot of the GC-MS analysis of WIP-extract 1 naphthenic acids with exposure to sodium modified illite.

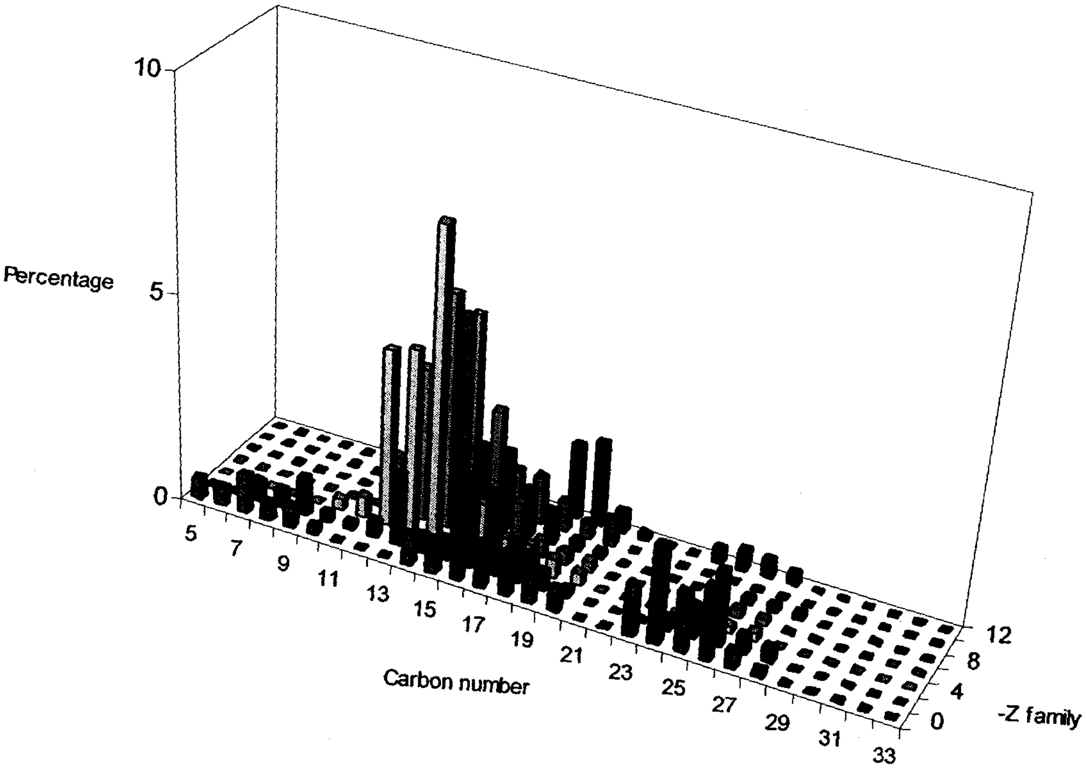

Figure E 4: Three-dimensional plot of the GC-MS analysis of WIP-extract 1 naphthenic acids with exposure to calcium modified illite.

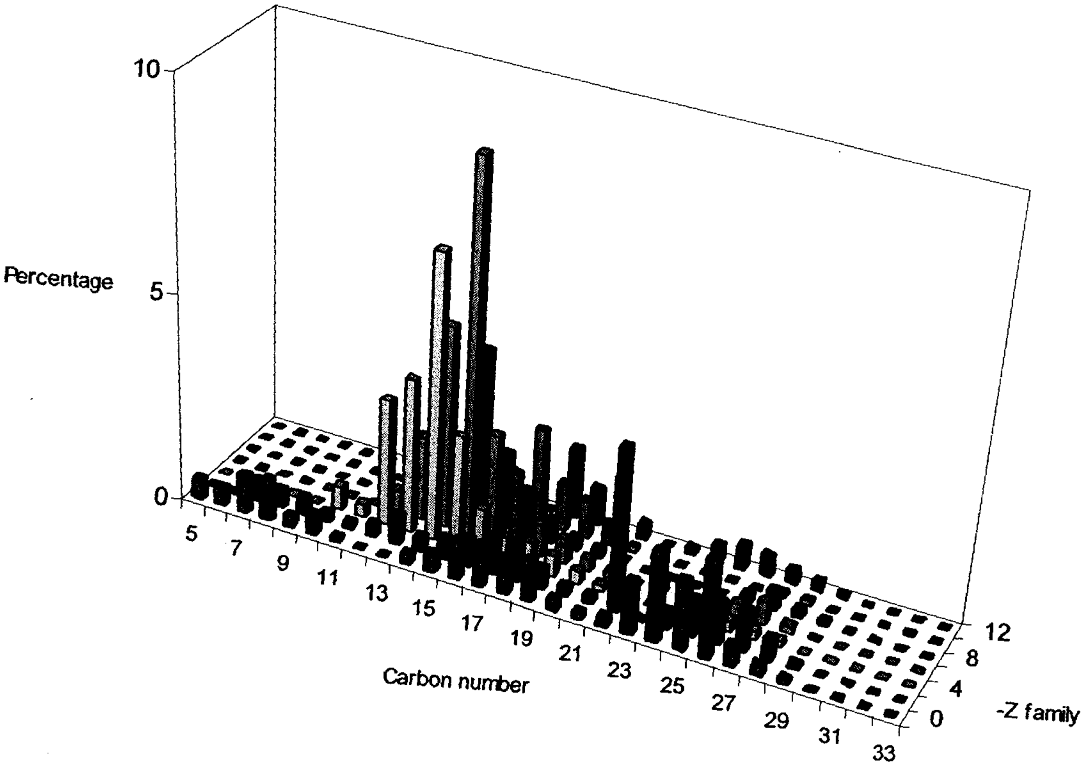

Figure E 5: Three-dimensional plot of the GC-MS analysis of WIP-extract 1 naphthenic acids with exposure to sodium modified montmorillonite.

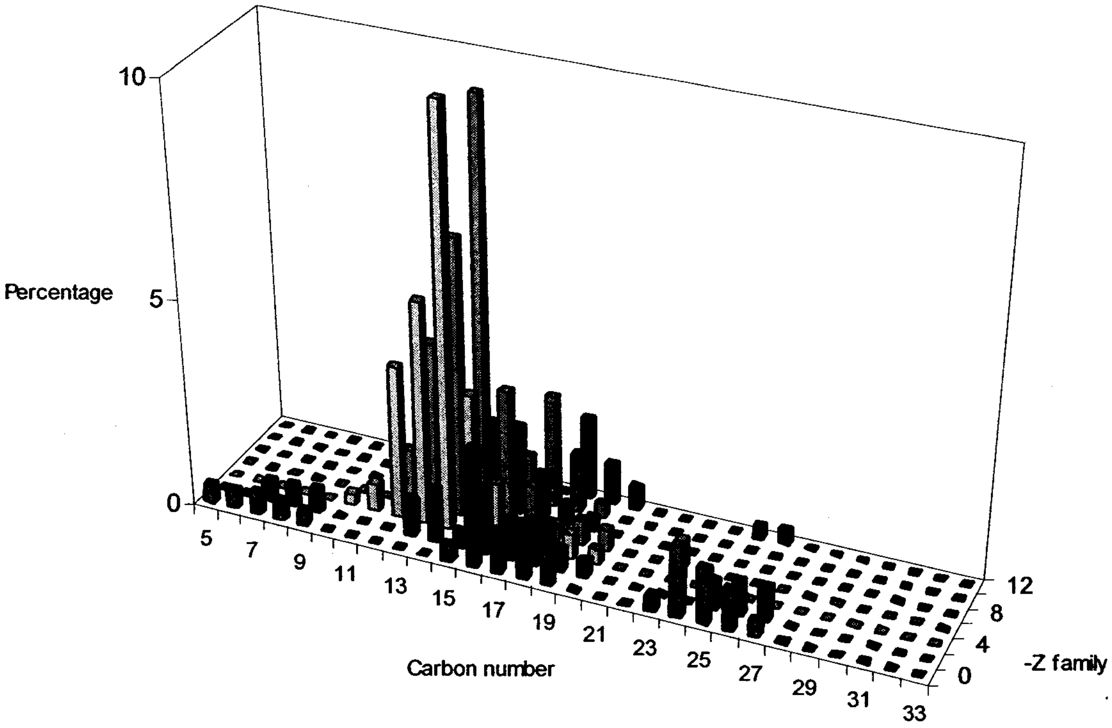

Figure E 6: Three-dimensional plot of the GC-MS analysis of WIP-extract 2 naphthenic acids with exposure to core sample OW04-02.

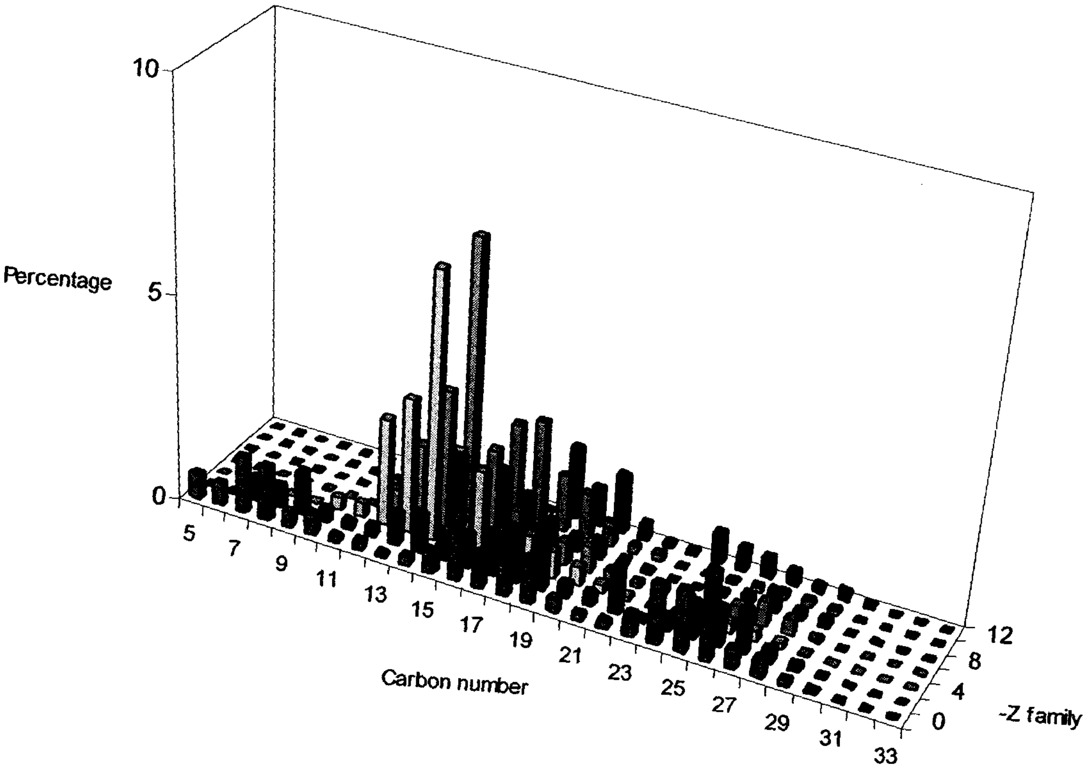

Figure E 7: Three-dimensional plot of the GC-MS analysis of WIP-extract 2 naphthenic acids with exposure to core sample OW04-06.

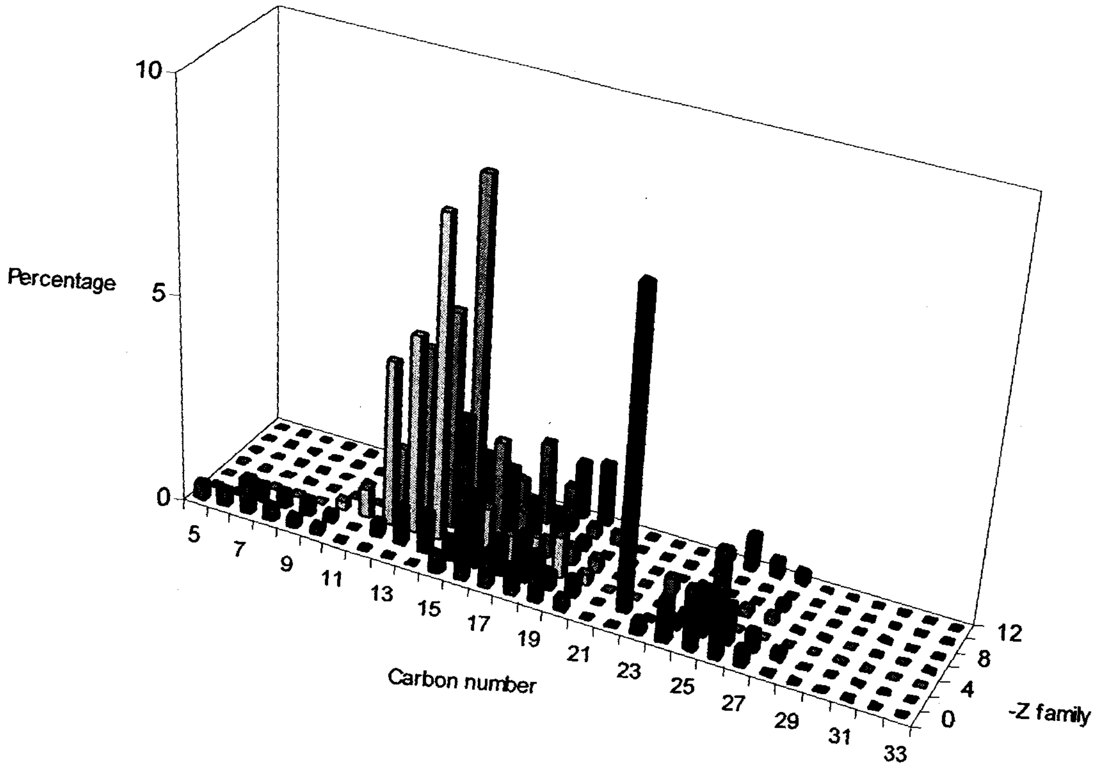

Figure E 8: Three-dimensional plot of the GC-MS analysis of WIP-extract 2 naphthenic acids with exposure to the Suncor coke sample.

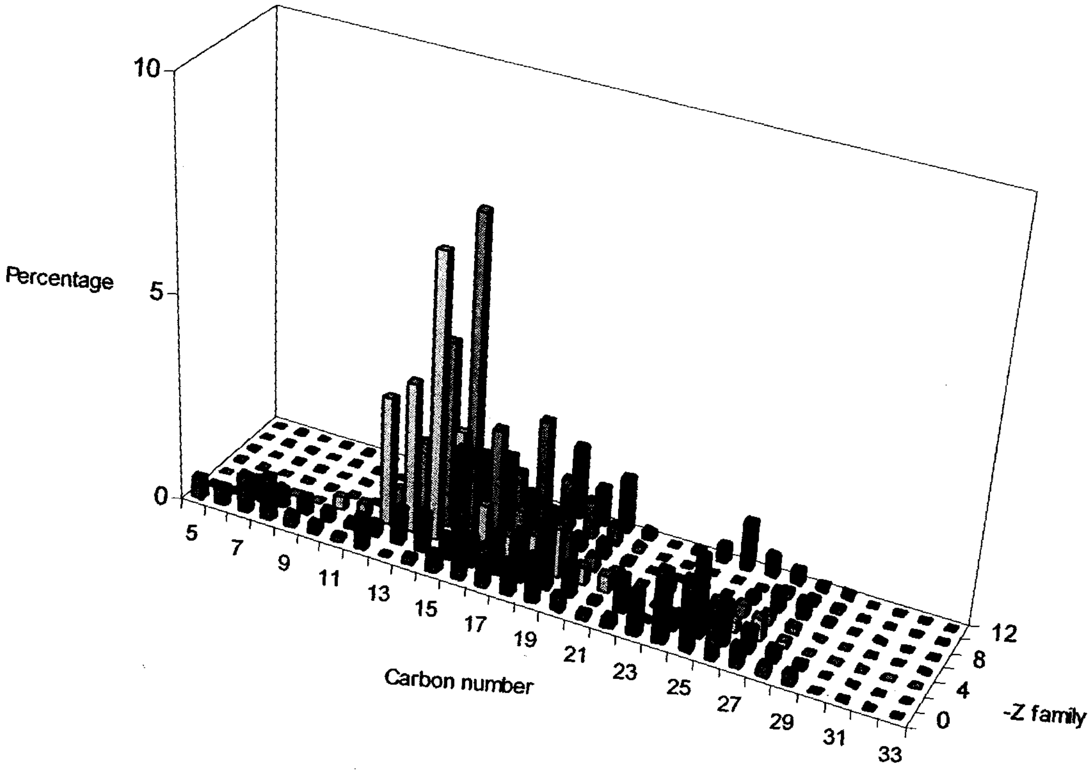

Figure E 9: Three-dimensional plot of the GC-MS analysis of WIP-extract 2 naphthenic acids with exposure to the Syncrude coke sample.